

A COLLABORATION OF EUROPEAN FREE ELECTRON LASER FACILITIES

# Whitebook



### on Science with Free Electron Lasers

Editors: Bruce D. Patterson Mirjam van Daalen

> PSI Bericht 16-01 Januar 2016

### **Table of Contents**

- 5 Preface Rafael Abela, Paul Scherrer Institut Josef Feldhaus, DESY
- 8 I. Fundamental atomic physics Michael Meyer, European XFEL
- 20 II. Infrared Spectroscopy of isolated molecular species
   Jos Oomens and Britta Redlich,
   FELIX Laboratory, Radboud University
- 30 III. Photochemistry Tom Penfold, Paul Scherrer Institute
- 40 IV. Surface chemistry Martin Beye, Helmholtz-Zentrum Berlin
- 48 V. XFEL-based serial proteincrystallography Karol Nass, MPIMF Heidelberg
- 60 VI. 2D membrane proteincrystallography Xiao-Dan Li, Paul Scherrer Institute
- 68 VII. Time-resolved diffractionimaging Adrian Mancuso, European XFEL
- 76 VIII. Imaging fluctuations Anders Madsen, European XFEL Christian Gutt, University of Siegen
- 84 IX. Correlation-function analysis of molecular scattering Richard Kirian, Arizona State University

- 96 X. Ultrafast demagnetization Fulvio Parmigiani, University of Trieste Yves Acremann, ETH Zurich Clemens Korff Schmising, TU Berlin
- 106 XI. Excitons and hot carriers in semiconductors Manfred Helm, Helmholtz-Zentrum Dresden-Rossendorf
- 114 XII. Coupled degrees of freedom in quantum materials Tim Huber, ETH Zürich
- 122 XIII. Orbital control of semiconductor dopants Ben Murdin, University of Surrey
- 130 XIV. XFEL Studies of Strongly-Coupled Plasmas Sam Vinko, University of Oxford
- 140 XV. Non-linear X-ray optics in solids Martin Beye, Helmholtz-Zentrum Berlin Filippo Bencivenga, ELETTRA Trieste
- 154 Appendix A. Basics of FEL physics Bruce Patterson, Paul Scherrer Institute
- 166 Appendix B. Overview of European FELs

### Preface

The present Whitebook is a common document of the **FELs** of Europe consortium. It presents a science case for the ensemble of European Free Electron Laser (FEL) facilities as a whole, illustrating by selected examples the scientific progress achieved so far and providing an excellent basis for future developments. The Whitebook also addresses the major challenges that must be met in order to exploit the revolutionary potential of this new technology. Moreover, it proposes concrete steps towards the enhancement and the firm establishment of the collaboration of all FEL facilities in Europe to the benefit of science and innovation.

The Whitebook is intended as a starting point for the development of coordinated and joint strategies of the collaboration partners as well as policy makers with the overall goal to exploit the full potential of free electron lasers and to maintain Europe's leadership in this field. The importance of FELs for science and innovation has been recognized by the strong, competing economies of the US, Europe and the Far East as e.g. documented in the report of the BESAC (Basic Energy Sciences Advisory Committee to the US Department of Energy) Subcommittee on Future X-ray Light Sources 2013. In the past Europe has been playing a leading role due to pioneering contributions to the development of X-ray FELs and the existence of a number of complementary operating FEL facilities in different European countries. In order to make best use of financial and intellectual resources, while pursuing the aim to maintain a leadership in developing new schemes and operating a large number of facilities, the FELs of Europe partners will collaborate tightly and join forces in new and important developments.

Free electron lasers have become routinely available for researchers worldwide – a dream has finally come true 50 years after the invention of the optical laser and 40 years after the first theoretical work on FELs. In contrast to optical lasers, free electron lasers employ relativistic electron beams to amplify light, and the FEL concept works for the entire spectral range from the far infrared (IR) to hard X-rays, i.e. wavelengths from a millimetre to below a tenth of a nanometre, generating (partially) coherent, ultra-short pulses with extremely high peak power. Infrared FELs developed in the early 1980's, are today well established research infrastructures with open access and have produced thousands of publications worldwide. Technological advances in the 1990s enabled in this century the construction and stable operation of high-gain FELs, which extend the photon range to the hard X-ray regime. FELs are bold examples of disruptive technologies: revolutionary instruments that expand the scope of what can be achieved in a field of science.

The tremendous potential of the new X-ray FEL sources for science and innovation released funding for the development and construction of a number of national facilities in the US, Europe and Asia. The European XFEL project was included in the first ESFRI (European Strategy Forum on Research Infrastructures) roadmap 2006. At the same time a consortium of national FEL facilities was included under the name EuroFEL. Currently, a suite of complementary FEL user facilities is in operation (CLIO, FELBE, FELIX, FERMI, FLASH) and under construction (European XFEL, SwissFEL) in Europe supplementing by the TARLA facility being built in Turkey (see Table below). Further projects are in the planning stage (MAX IV, POLFEL). All European FEL activities are now joining forces in the consortium **FELs of Europe** (Table 1).

**FELs of Europe** has been established as a sustainable, longterm collaboration that is not dependent on external funding, e.g. through European programmes. The goal of the collaboration is to make optimal use of resources and know how available in Europe in order:

- to meet the technological and scientific challenges of the fast-developing FEL technologies, providing the experimental conditions needed by a large, multi-disciplinary user community,
- to strive for full exploitation of the potential of FELs for science and innovation, developing, implementing and maintaining scientific and technological infrastructures at a world-class level.

This goal is going to be achieved by jointly coordinated activities including:

- exchange of information in relevant task areas,
- setting of expert groups for consideration and development of new operation schemes and instrumentation,
- organisation of conferences, workshops and schools for young scientists – potential users of the FEL facilities.

Facility	Institution	Location	Electron energy	Wavelength	number of FELs	FEL type	Start user operation	Funding
EU.XFEL*	XFEL GmbH	Hamburg (DE)	17.5 GeV	0.05-4.7 nm	3 (5)	SASE, self-seeding	2017	international
SwissFEL**	PSI	Villigen (CH)	5.8 GeV	0.1-7 nm	1 (2)	SASE, self-seeding	2017	national
FERMI**	Elettra	Trieste (IT)	1.7 GeV	4-100 nm	2	HGHG seeding	2012	national
FLASH**	DESY	Hamburg (DE)	1.25 GeV	4.2-50 nm	2	SASE (seeding in prep.)	2005	national
FELBE	HZDR	Dresden (DE)	12-34 MeV	4-250 μm	2	optical cavity	2005	national
FELIX	Radboud Univ.	Nijmegen (NL)	10-50 MeV	2.7-1500 μm	3	optical cavity	1993	national
CLIO	CNRS	Orsay (FR)	15-50 MeV	3-120 μm	1	optical cavity	1993	national
TARLA	Ankara Univer- sity, Institute of Accelerator Technologies	Gölbasi (Tr)	15-40 MeV	3-250 μm	2	optical cavity	2019	national

Table 1: \*ESFRI Roadmap 2006, \*\*ESFRI Roadmap 2006 as partner of EuroFEL

### Scientific impact

The fifteen science chapters presented in this Whitebook give an impressive cross section of the science currently pursued at free electron lasers by European academic groups. The involvement of a large user community is very dedicated, competent and enthusiastic. More than thousand publications have emerged, many of them in high impact journals. Moreover the developments initiated at FELs have also an impact in developments at synchrotron radiation sources.

The scientific impact of X-ray FELs is increasing very rapidly. One of many scientific areas opened by X-ray FELs is the opportunity to study matter which has so far been inaccessible to high-resolution structural examination. A prominent goal is the study of inherently non-crystalline biological materials, such as cells or biomolecules. These applications were key motivators for the construction of hard X-ray FELs. The development of methods such as serial femtosecond crystallography has now opened new opportunities for the structural determination of biomolecules free of radiation damage. Furthermore, first experiments in time-resolved structural studies have already been performed. Here, the goal is to "film" a chemical reaction, and not just to observe the final product as we do today.

Very intense radiation in the far-infrared region of the electromagnetic spectrum is mainly used for non-linear spectroscopy of matter. This spectral region covers very well the energy levels in molecules and solids that determine their chemical and physical properties, and also their practical functionalities. Of special relevance is the understanding of the relationship between the electronic properties and the structure of nanoscopic and molecular materials, for instance, to manipulate and control the exchange interaction, which is one of the strongest quantum mechanical effects and which is responsible for magnetic order, at ultrashort time and length scales. This knowledge may become the basis for new technologies in data storage exploiting the spin of an electron (spintronics).

### Challenges

The examples presented in this report emphasize the wide range of wavelengths, methodologies and instrumentation needed to understand and eventually control the function of materials in the widest sense. The field is strongly developing and the experiments performed with X-ray FELs up to now are in many cases still proofs-of-principle. Also the X-ray FEL sources themselves will constantly undergo substantial improvements, e.g. developments are currently under way to bring the facilities to "lase" in a controlled manner by using seeding schemes, to enable the production of twocolour pulses with different time delays and to provide ultrashort pulses in the order of femtoseconds.

These technical developments relate not only to the FEL sources themselves but include relevant improvements in electron and photon diagnostics, X-ray optics, optical lasers and their synchronisation as well as experimental methodology and instrumentation. Many of these developments are extremely demanding and at the cutting edge of current technology providing fertile soil for innovation.

Other challenges arise from the fact that one would like to exploit the potential inherent in free electron lasers that is a combination of the exceptionally wide spectral range, coherence, peak power and femtosecond pulse duration in a similarly or even more successful way as it was done for optical lasers and synchrotron radiation sources. Indeed, the potential range of applications is enormous and has immediately attracted scientists from both the traditional laser and synchrotron radiation user communities.

So far FELs have been implemented as facilities delivering beam to one user at a time. This has been limiting their capacity of user experiments, leading to a situation where the until 2017 operational facilities, with their specific portfolio of beam parameters, instrumentation and experimental methods, were only able to accept a fraction of the user research of the international community, including the regional or national user communities. With the upcoming availability of facilities providing beam to several user groups quasi-simultaneously, and the parallel start of operation of two new X-ray facilities (European XFEL and SwissFEL, see Table above) in Europe and the extension of FLASH a new era is entered where significantly more user time will be given for FEL scientific and innovation applications. Furthermore, high repetition rate facilities (FLASH and European XFEL in Europe, LCLS-II in the U.S.) will provide new opportunities for small cross-section experiments and applications requiring the highest average brilliance. Particularly European XFEL will be the first large scale multiuser facility of this kind supplying potentially 5 independent SASE sources with 10-15 instruments that will cover the full breadth of science. Thus, a set of complementary FEL light sources, outfitted with a number of complementary beam lines and a variety of experimental stations, will soon be available to the European scientific community and shall be used in a most efficient way to exploit the enormous potential these facilities offer to a growing multi-disciplinary user community.

The scientific use of X-ray FELs and their contribution to innovation are in an early stage of development. The currently existing facilities, i.e. FLASH and FERMI in Europe, LCLS in the United States and SACLA in Japan, have paved the way, with an impressive number of highly visible exploratory studies and publications in prestigious journals. In order to exploit the full potential of FEL sources, it is very important to include diverse user communities, to develop new methods and to invest in systematic studies in specific strategic areas of science, engineering and medicine.

### Recommendations

 Under the circumstances outlined above it is important that all FEL facilities in Europe work effectively together and also interact closely with the user community and other stakeholders.

The FELs of Europe collaboration was established with this intention in 2012 and provides a suitable frame based on a memorandum of understanding. FELs of Europe should be fostered and enhanced by the partners and should be regarded as an effective instrument for promoting the use of free electron lasers for a wide range of scientific, technological and innovation applications.

• Although FEL facilities compete in their scientific achievements and in other areas, it is fundamental that they collaborate.

----> FELs of Europe should promote a transparent, open and cooperative relationship of independent partners. At the same time, the autonomy and specific interests of the facilities will be considered in the joint working towards their common goal. With the new potentials of FELs it is important to keep track of and analyse the development of the user communities, the beam time capacity and the research areas in the coming years. -----> FELs of Europe should together with the existing and potential new user communities discuss and identify ways how capacities can be enhanced, new applications, methods and instrumentation explored and developed, complementarities enhanced and new users motivated and supported.

- A sustainable solution for transnational access to the FEL facilities is indispensable, not only because most European countries do not have their own FEL facilities, but also because all the science of the national communities cannot be done at a single national facility.
- Efficiency and throughput is a key feature of all FELs.
   FELs of Europe should facilitate the regular exchange of best practices between the facilities and assist by joint efforts in technical improvements and the training of personnel.

Rafael Abela and Josef Feldhaus on behalf of FELs of Europe

## I. Fundamental atomic physics

Michael Meyer, European XFEL

Atoms are the smallest building blocks of matter, and their behavior and their particular arrangement in larger systems such as molecules, clusters, nanoparticles and solids define many properties of these larger entities. The investigation of isolated, multi-electron atoms therefore highlights the fundamental aspects of light-matter interaction.

- Introduction
- Two-photon double ionization
- Multiple ionization in the X-ray regime
- Direct multi-photon ionization at short wavelength
- Photoionization in intense external fields
- Outlook
- Summary

Free-electron laser sources offer unique possibilities to study the interaction of atoms and intense radiation in the VUV, XUV and X-ray wavelength regimes. Due to the high irradiance levels produced by these ultra-bright sources, various non-linear processes, such as multi-photon ionization, above threshold ionization and sequential multiple ionization, can be explored at these photon energies. Moreover, the short pulse duration allows insight into the dynamics of electronic relaxation through the additional interaction with an overlapping synchronized optical laser. Special emphasis is placed on fundamental multi-photon processes as well as on applications of atomic photoionization for the characterization of the temporal properties of free-electron laser pulses.

### Introduction

Photoionization has been extensively explored during the last few decades at synchrotron radiation facilities. The wide range of photon energy tunability and the high spectral resolution of these sources have enabled very detailed studies of resonant and non-resonant processes involving the excitation by one photon. The principal mechanisms and processes are basically well understood, and advanced theoretical approaches are able to properly account for all relevant electronic interactions. Ionization induced by *multi*-photon processes and strong radiation fields has been investigated primarily in the long wavelength (optical) regime, *i.e.* at photon energies far from the atomic ionization thresholds.

With the advent of new accelerator-based free-electron laser (FEL) facilities, such as FLASH in Germany, LCLS in the USA, SCSS and SACLA in Japan, and FERMI in Italy [1-5], the research of light-induced processes in small quantum systems has again stimulated strong interest. These intense photon sources operating in the short-wavelength regime enable for the first time investigations of multi-photon processes at photon energies far above the atomic ionization thresholds (*e.g.* [6]). In contrast to conventional lasers operating in the optical regime, FELs can also access inner valence and core level electrons. Thus, all advantages of core-level spectroscopy, especially its site and element specificities, can now be combined with the benefits of non-linear spectroscopy. New phenomena caused by competing fast processes, *e.g.* single-hole Auger decay and the formation of double core-holes, dominate the experimental spectra and require the development of new theoretical approaches. An outstanding feature in core-level spectroscopy is resonant inner-shell excitation, because it dramatically increases the core-level photoionization cross-section. In addition, it offers a way to obtain chemical contrast in the experimental spectra or to excite, in a complicated multi-atom system, only those atoms at a well-defined site. Finally, atoms, with their well-known properties in the linear photoionization regime, serve as very sensitive probes to characterize many important properties of the ultra-intense x-ray laser pulses.

The investigation of multi-photon multiple ionization, *i.e.*, the ejection of several electrons by a single intense light pulse (Figure I.1a), began at FLASH with the observation of xenon ions in charge states up to 21+, after irradiation with FEL radiation at a photon energy of 93 eV [7]. Numerous subsequent studies have demonstrated the dominance of sequential ionization for the formation of these high charge states. However, the detailed understanding of the underlying dynamics, *e.g.* of the very basic two-photon double-ionization [8], of the role of intermediate resonances [9] and of the influence of direct processes [10], is still debated. Concrete examples will be discussed in the following sections.



Fig. I.1: (a) Schematic representation of a multi-photon multiple ionization process in an isolated atom. (b) Schematic representation of a two-color ionization process induced by spatially and temporally overlapping FEL and optical laser pulses. The short pulse duration of the FEL sources enables not only time-resolved studies in the femtosecond time domain, it also opens the possibility to investigate ionization dynamics in the presence of the strong external field created by a synchronized optical laser (Figure I.1b). The controlled modification of the FEL-induced process by the optical laser, as a function of the optical intensity, wavelength or polarization state, can provide complementary information on the electron dynamics in highly excited atomic states [11] and in the ionization continuum [12]. The rich potential of this type of XUV-optical pump-probe spectroscopy will be emphasized at the end of this chapter.

### Two-photon double ionization

One of the most fundamental multi-photon processes is the interaction of two photons with two electrons, as occurs in the two-photon double ionization of the two-electron system atomic helium. Despite its simplicity, an exact theoretical description of the process is extremely challenging [13], since the interaction between the three charged particles, two electrons and the ion, especially the mutual screening of the ion, has to correctly be taken into account. The photon energy range between 39.5 and 54.4 eV is of particular interest - at these energies sequential ionization, *i.e.* the ionization of the singly-ionized helium, is energetically forbidden (Figure I.2), but the direct double ionization via a quasi-instantaneous absorption of both photons is possible and is enabled by electron-electron correlation [14]. Only the intense VUV pulses of FELs provide sufficiently high photon densities that the observation of the two-photon double ionization becomes feasible.

Experimental observations of this process have been performed by measuring the recoil-ion-momentum distribution using a reaction microscope [8]. At photon energies of 44 eV (Figure I.3a), the momentum distribution of the He<sup>2+</sup> ion shows a maximum near the origin, which is consistent with an equal energy sharing between both electrons and a backto-back electron emission, *i.e.* into opposite directions. At slightly higher photon energies (52 eV, Figure I.3b), but still below the threshold for sequential double ionization, two maxima are observed, indicating an asymmetric energy



sharing. This behavior is in good agreement with a theoretical treatment of the process (Figure I.3, right) [13], but is very different from the patterns recorded at higher photon energies and for double ionization induced by a one-photon process [8].

At higher photon energies (> 54.4 eV), the sequential process dominates, and the emission of the two electrons can be considered as independent processes, each characterized by a dipole-like structure in its momentum distribution. In contrast, double-ionization induced by a single photon requires very strong electron-electron interaction, and as a result, the back-to-back emission along the polarization direction is forbidden by the dipole selection rules.



Fig. I.3: Experimental (left) [8] and theoretical (right) [13] ion momentum distributions for doubly-charged helium upon ionization at photon energies of 44 (top) and 52 eV (bottom).



Fig.I.4: (a) Ion yield spectra of atomic xenon recorded at FLASH for different intensities of the FEL, operating at a photon energy of 93 eV [7]. (b) Ion yield spectra of atomic neon, recorded at LCLS for different photon energies [16], demonstrating the efficient production of high charge states for photon energies above the 1s ionization threshold.

The probability of the two-photon double ionization has been calculated using various theoretical approaches [8], but a consistent interpretation could not be established until now. This demonstrates the extreme difficulty of properly treating the electron-electron interaction in a system of more than two particles.

### Multiple ionization in the soft X-ray regime

In the case of multi-electron atoms, the high number of photons delivered within one FEL pulse induces a cascade of sequential ionization steps and leads to the formation of highly charged atomic ions. In one of the first experiments performed at FLASH [7], xenon atoms were irradiated with short (10-20 fs) and intense (up to  $8 \times 10^{15}$  W/cm<sup>2</sup>) light pulses with 93 eV photon energy. At the highest intensity, ions with a charge state of 21+ were observed (Figure I.4a). The total energy required for extracting 21 electrons from the xenon atom can be calculated to be approximately 5 keV. As a consequence, the total number of photons absorbed by the xenon atom within a single FEL pulse must be greater than 50, in order to satisfy the energy balance. Single-

photon sequential ionization is initially the dominant mechanism, and for higher charge states, where a single photon is not enough to reach the next higher charge state, direct multi-photon processes must be taken into account. The detailed theoretical analysis of the process is quite cumbersome, because all possible ionization pathways for the different ions must be included [15], and cross sections for most of these processes are not precisely known. Particularly challenging for the experiments on xenon is the correct treatment of the 4d giant resonance, which gives rise to a broad and strong absorption structure in the neutral atom at photon energies between 85 and 115 eV. The importance of this resonance for the production of the highest charge states has been discussed extensively.

Although the formation of highly-charged ions can also be observed upon excitation with intense optical lasers, the process of atomic multiple ionization in the soft X-ray regime is governed by a complex interplay between core ionization and Auger decay for each charge state. In the optical field, the outer electrons are stripped off one-by-one through direct multi-photon processes. At shorter wavelengths, the ionization of more tightly bound core electrons and the subsequent Auger decay becomes possible. The final dis-

### Sequential multi-photon ionization

The formation of highly-charged ions after interaction of an atomic target with intense soft X-ray FEL radiation can to a large extend be explained by sequential multi-photon ionization. Depending on the photon energy of the FEL pulses, ionization proceeds via one-photon processes, causing the emission of a valence electron (process "V"). This process is repeated during the pulse until the photon energy is too low to eject one more electron. For the example of atomic neon, ionization of Ne<sup>8+</sup> requires about 1.2 keV and is therefore impossible with 800 eV photons. However, at higher photon energy, ionization of a 1s core electron (process "P") is possible and is the most efficient process. The ejection of an inner electron is followed by Auger decay (process "A"). The subsequent ionization of a 1s electron is possible with photons of 1050 eV up to Ne<sup>6+</sup>, but can proceed at 2000 eV up to 10+, *i.e.* the complete ejection of all electrons.

All processes discussed above increase the charge state by one, and a sequence of processes taking place during the FEL pulse is required to reach the maximal charge state observed in the experiment. The charge state distribution is reproduced by theoretical simulations based on the solution of rate equations for the underlying processes. The main contributions to the experimental ion spectra can be explained by this sequential ionization. Other possible processes, such as direct multi-photon excitation or resonant intermediate states, are identified though differences between calculations and experimental data.



Fig. I.i1: Scheme of sequential ionization processes of atomic neon at incident photon energies, 800, 1050 and 2000 eV (from [16]). The three main processes are indicated: "V" valence ionization of the outer 2s and 2p electronic subshells; "P" photoionization of the inner 1s electronic subshell; "A" Auger decay following 1s ionization.

tribution of charge states now depends critically on the selected wavelength, as has been demonstrated in experiments on atomic neon at the LCLS [16]. At photon energies below the ionization threshold of the neon 1s core electron (800 eV), charge states of up to 6+ are produced with decreasing intensity, consistent with the sequential ionization of the outer 2p electrons (Figure I.4b). When the photon energy is high enough to ionize the 1s electron (1050 eV), the charge state distribution changes strongly and displays a maximum for ions around 7+. This observation is directly related to the higher efficiency for the ionization of Ne 1s electrons and to fast relaxation processes of the core hole with lifetimes on the order of a few femtoseconds. At even higher photon energies (2000 eV), the core hole formation is energetically possible even for higher charge states, thus shifting the maximum of the charge state distribution to larger values and causing the production of fully ionized Ne<sup>10+</sup>.

The general features of the ion spectra produced from multiphoton ionization can to a large extent be interpreted in terms of sequential processes. The detailed dynamics and the importance of excited states, of resonances and of direct two- or multi-photon processes can only be understood via comparison with a theoretical description [17]. Since the detailed understanding of these ionization processes in atoms is an essential prerequisite for many other FEL applications, such as *e.g.* nano-scale imaging and structural dynamics studies, more sophisticated experimental approaches, *e.g.* based on coincidence techniques, will be necessary in order to unravel and characterize the different ionization steps.

### Direct multi-photon ionization at short wavelength

In the optical regime, the instantaneous absorption of many photons from a laser beam is an important and efficient processes for many applications, especially for inducing the ionization of a species. At shorter wavelengths, a single



Fig. I.5: Electron spectrum of atomic xenon, recorded upon excitation with intense FEL radiation at a photon energy of 105 eV. At low kinetic energies (< 105 eV), the one-photon ionization from the 5p, 5s and 4d shells is indicated, as well as the electron lines arising from the decay of the 4d hole via Auger relaxation involving the 5p and the 5s shells. At high kinetic energies (> 105 eV), the signal arising from the direct two-photon process is highlighted (from [10]).

photon may suffice to cause ionization, and, as discussed above, the absorption of several photons from an intense beam often leads to a sequence of ionization steps. The *direct* process, *i.e.* the simultaneous absorption of several photons, generally becomes important only when sequential ionization by a single photon is energetically forbidden. For the analysis of the relative importance of these direct processes at the intensities available at present FEL sources and, more generally, for exploring the potential of non-linear phenomena in the XUV, electron spectroscopy is applied. The electron emitted after the absorption of two photons can be measured at a kinetic energy which is well-separated, *i.e.* by the difference of one quantum of photon energy, from the corresponding single photon events (see Figure I.5).

In a recent experiment, xenon atoms were irradiated with intense FEL pulses from FLASH, operating at a photon energy of 105 eV [10]. The ionization from the 4d shell, induced by the absorption of two photons, is clearly seen at electron kinetic energies of approximately 140 eV. This process is known as above-threshold ionization (ATI), since the emission of a 4d electron is already possible with a single photon, and the subsequent absorption of the second photon can be considered as a transition in the continuum. The probability of this process is quite low, which explains the 5 orders of magnitude smaller signal of the 4d two-photon ATI line compared to the one-photon 4d line at kinetic energies around 35 eV. The ATI signal displays a quadratic dependence on the pulse energy, as expected for a two-photon process, in contrast to the one-photon signal, which increases linearly with increasing photon intensity.

Because the charge state after one-photon ionization and after two-photon ATI is the same, the two processes are indistinguishable in measurements of the ion distribution. However, in the electron spectra, they appear in distinct energy regions, and the observation of both processes in the same spectrum allows a quantitative analysis of the relative probabilities. After normalization to the well-known one-photon signal, an absolute cross section for the twophoton process can be extracted from the experimental spectra, providing valuable data for comparison with theory. In the case of xenon, excellent agreement has been found between experiment and theory, provided strong electronelectron correlations are taken into account [10].

Beside this demonstration of the importance of electronelectron correlations in multi-photon processes, the study of the 4d ATI in xenon has also demonstrated a first application of non-linear studies in the short-wavelength regime. The photon energy dependence of the 4d ATI signal displays a second maximum in the broad 4d giant resonance, which could not be observed in all prior experimental investigations performed in the linear, one-photon regime, but which has already been theoretically predicted a long time ago [18]. The two-photon signal is much more sensitive to this substructure [10]. Again, this structure is only present when electron correlations are properly included in the calculations: the ionization pathways corresponding to the emission of each individual electron by the two-photon processes are no longer independent. As a consequence, the 4d ATI of atomic xenon has to be treated as a collective process, similar to various phenomena in much larger systems.

### Photoionization in intense external fields

In many experiments performed at FEL sources, a two-color pump-probe excitation scheme is applied, using the combination of optical and XUV radiation. Via interaction with the outgoing electron, the synchronized intense optical pulses can be used to change and eventually to control the process of resonant excitation or of direct ionization induced by the XUV pulse. For resonant excitation, the optical field may cause a shift of the resonance position and strongly modify the relaxation dynamics [11]. For ionization, the interaction of the optical field with the outgoing electron strongly affects the kinetic energy distribution of the electrons and may lead to pronounced interference patterns in their angular distributions [19]. Investigations of atomic two-color photoionization can therefore serve to obtain a detailed understanding of the response of an electron to an intense electromagnetic field. The results provide a firm background for other two-color experiments on more complex systems, such as large molecules or solids, for which a clean disentanglement of various processes is more difficult.

The interaction of the electron with the light field can be described as an exchange of optical quanta, *i.e.* by absorp-

tion and emission processes induced by the optical field. As a consequence, one observes in the photoelectron spectrum so-called sidebands on both sides of the main feature (Figure I.6), which are energetically separated from the central line by one optical quantum. The sidebands are only observable when both pulses, optical and XUV, overlap in both space and time. Their signal strength is therefore a very sensitive parameter for use in characterizing the properties of the FEL pulses. Beside the determination of the temporal and spatial stability of the FEL pulses, which was demonstrated in some experiments [20], it is also possible to obtain information on the state of polarization of the XUV beam, in particular on the degree of circular polarization, which is difficult to obtain by other means.

In Figure I.6 (left), the electron emission of atomic helium is shown as a function of the electron kinetic energy and

the emission angle with respect to the beam propagation axis [21]. It was recorded at FERMI, after ionization by an FEL pulse with 48.4 eV photon energy, in the presence of an intense optical field. The pronounced line at a kinetic energy of approximately 24 eV corresponds to the emission of a He 1s electron. The structures on each side of this line are the sidebands caused by the interaction with the optical (784 nm) field.

For these experiments, circularly polarization of both the FEL and the optical radiation was used. The relative intensity of the two sidebands depends on whether the FEL and optical pulses have the same or opposite helicity: The extracted difference is known as circular dichroism (Figure I.6, right). Dichroism is often used to probe asymmetries in, *e.g.*, chiral molecules or magnetic samples. For the initially symmetric atoms, this asymmetry is induced by the first photon



Fig. I.6: (left) Angle-resolved electron spectrum of atomic helium, recorded upon excitation with FEL radiation at a photon energy of 48.4 eV, in the presence of an intense optical laser pulse (794 nm, 0.8 mJ). (right) Circular dichroism in the two-photon ionization of atomic helium. The upper and lower curves represent the experimental and theoretical results, respectively (from [21]).

### Dichroism in atomic two-color photoionization

Dichroism in a photoionization process is defined as the difference between the electron (or ion) signals measured for two different polarization states of the ionizing photon. Investigations of dichroic phenomena are used to gain information about asymmetries of a sample, e.g. the spin system in magnetic substances or the atomic arrangement in chiral molecules. For atomic species, dichroism in photoionization is generally only observed using two polarized photon sources, e.g. the combination between linearly or circularly polarized XUV and optical lasers. For illustration, the two-color above-threshold ionization of atomic helium is discussed. The ionizing FEL photon introduces the asymmetry, *i.e.* the ionization step leads to a non-isotropic population of the magnetic sublevels in the continuum state, which is further excited by the optical photon. For a detailed understanding, basic dipole selection rules have to be applied, *i.e.* absorption of a photon changes the



total angular momentum "J" and the angular momentum of the excited electron "l" by 1. Linearly polarized light does not change the value of the magnetic sublevels,  $\Delta m=0$ , and circularly polarized light induces changes  $\Delta m=+1$  and -1 for right- and left-handed circular polarization, respectively.

Following the selection rules, photoionization of the He  $1s^2$  (J=0) ground state leads to the ejection of an electron with angular momentum "p" and to the formation of the continuum state (ion plus electron) with total angular momentum J=1 and m=+1, for right-handed circularly polarized light. Additional absorption of optical photons changes again the angular momentum according to the number of photons absorbed and to the state of polarization. A two-photon process, *e.g.*, therefore results in the formation of electrons with "d", if both photons have the same helicity, and to a combination of electrons with "s" and "d" symmetry, for opposite helicity. Different cross sections for both transitions explain directly the appearance of the dichroism in the two-photon above-threshold ionization. The given description is valid at low intensities of the optical field, *i.e.* in the validity range of perturbation theory. For stronger optical fields, the coupling between more and more angular momenta has to be taken into account. For these cases, the description using the strong field approximation is possible, but the interpretation of the results can no longer be given within a simple picture.

Fig. I.i2: Scheme of the two-color above-threshold ionization in atomic helium. The angular momenta of the outgoing electrons and the magnetic sublevels m of the final state (ion + electron) are indicated

upon ionization by the circularly-polarized FEL beam and is probed by the circularly-polarized optical field. A theoretical model based on the so-called strong-field approximation is able to describe the underlying electron dynamics in the two-electron system helium [22], and the results are in good agreement with the experimental data (Figure I.6). A comparison of the absolute value for the measured and theoretical dichroism could be used to determine the degree of circular polarization as well as the sign of the helicity of the FEL pulses [21].

### Outlook

During recent years, the multi-photon regime for photoionization processes with free-electron laser sources has been shown to provide exciting new results, mainly related to multiple ionization. This has been explored principally by ion spectroscopy and by theoretical studies, with the goal of identifying and understanding all relevant processes. A more advanced experimental characterization of the complex dynamics requires the application of more specific spectroscopic tools, such as electron or fluorescence spectroscopy, which will enable one to distinguish the individual ionization steps. An increase in repetition rate of the FEL pulses delivered within one second, by approximately 2 orders of magnitude - 27 kHz are envisaged for example at the European XFEL - will certainly favor this type of investigation. Coincidence techniques can then be efficiently applied, and recording charge-resolved electron or fluorescence spectra will become feasible. The advantage of direct multiphoton processes for the investigation of specific research problems has been demonstrated. In the domain of optical laser applications, this non-linear spectroscopy has led to a multitude of new research topics and has provided novel information about processes which are difficult to unravel by linear one-photon spectroscopy.

The combination of FEL and optical laser pulses has proven to be ideally suited for characterizing the temporal characteristics, *i.e.* the arrival time, the pulse duration and the temporal jitter, of the FEL pulses. For scientific applications, the combination with THz pulses is probably one of the most promising methods. Similar to methods developed in the attosecond regime, the electron streaking technique can be applied for femtosecond FEL pulses [23]. THz radiation with optical cycles of 100s of femtoseconds, provides the electrical field used to modify the electron emission. The kinetic energy distribution of the outgoing electron is then changed in a characteristic way depending on the precise time of emission, which is determined by the FEL pulse, with respect to the local electric field of the THz pulse. Temporal resolution in the femtosecond range can be obtained, and the technique can be applied to the study of phenomena which take place on a time scale of a few femtoseconds, *e.g.* for the determination of Auger dynamics in atoms and molecules.

For experiments employing an additional external laser, the influence of the strong optical field applied during ionization and the effects of tuning the optical wavelength can be explored. Resonant processes can be investigated in a new and very versatile way, *i.e.* the electronic relaxation dynamics and relaxation pathways can be modified, *e.g.* by the coupling of resonances of different symmetry and lifetimes. Control of the temporal and spectral stability of the pulses will be a decisive factor for these measurements.

Finally, XUV-XUV pump-probe experiments will be developed, aiming to access ultra-short temporal phenomena in sequential or resonant processes. Possibilities to separate the two pulses in time, with sub-femtosecond resolution, will enable time-resolved investigations of atomic systems. Advanced split-and-delay techniques using two parts of the same FEL pulse, and developments at seeded FELs are expected to provide new possibilities, including the control of the spectral phase between two XUV pulses, thereby opening the area of coherent control, normally applied in the optical regime, also for the XUV wavelength regime.

### Summary

- Atomic physics experiments have been among the first experiments carried out at the new free electron laser sources. The good overall understanding of the basic processes by theory has provided an excellent framework with which to simulate in detail the experimental conditions and to permit using the results to quantitatively characterize pulse parameters of the new sources.
- In addition, new applications and research methods, which make use of the high intensity and the short pulse duration provided by the FELs, are being explored and provide new insight into various fundamental processes governing the atomic photoionization dynamics. The results of these measurements are essential for the development of theoretical models, which describe the complex physical processes in the atomic multi-electron system. Only the detailed comparison with the experimental data has provided a thorough basis for the identification of the relevant interactions, which must be included in the calculations for a precise description of a given process.
- First experiments performed at the FELs in the multiphoton regime have demonstrated the dominance of sequential processes for the proper interpretation of the observed multiple ionization. The characterization of the

underlying dynamics provides relevant information for improving molecular imaging experiments aiming to take a picture of a molecule prior to its Coulomb explosion. Direct processes have much lower probability in the parameter space of present FELs. But exploring new methods based on the direct, i.e. simultaneous absorption of many XUV photons promises to bring out new features and novel information, which are only accessible by non-linear spectroscopy.

Pump-probe experiments combining the FEL pulses with those of an external intense optical laser have a wide range of applications, and the promise of this approach will be systematically explored during the coming years. The intense optical field, when overlapped with the ionizing XUV field, modifies in a very characteristic way the electronic processes, i.e. ionization and resonant excitation. This allows the extraction of very specific information on the photoionization process, more precisely on the symmetry and phase of the outgoing electron wave, on the dynamics of the electronic relaxation of a core hole and on the temporal evolution of the photo-induced processes. Various schemes will be applied in the future, aiming to demonstrate new research possibilities which open up with each improvement of FEL performance.

#### References

- [1] W. Ackermann, et al, Nature Photonics 1, 336 (2007).
- [2] P. Emma, et al, Nature Photonics 4, 641 (2010).
- [3] T. Shintake, et al, Nature Photonics 2, 559 (2008).
- [4] T. Ishikawa, et al, Nature Photonics 6, 540 (2012).
- [5] E. Allaria, et al, Nature Photonics 6, 2012 (2012).
- [6] N. Berrah, et al, J. Mod. Opt. 52, 1015 (2010).
- [7] A. A. Sorokin, et al, Phys. Rev. Lett. 99, 213002 (2007).
- [8] A. Rudenko, et al, J. Phys. B: At. Mol. Opt. Phys. 43, 194004 (2010).
- [9] B. Rudek, et al, Nature Photonics 6, 858 (2012).
- [10] T. Mazza, et al, Nature Comm. 6, 6799 (2015).
- [11] T. Mazza, et al, J. Phys. B: At. Mol. Opt. Phys. 45, 141001 (2012).
- [12] M. Meyer, et al, J. Phys. B: At. Mol. Opt. Phys. 43, 194006 (2010).

- [13] E. Foumouo, et al, J. Phys. B: At. Mol. Opt. Phys. 41, 051001 (2008).
- P. Lambropoulos, L A A Nikolopoulos and M G Makris, Phys. Rev. A 72, 013410 (2005).
- [15] P. Lambropoulos, K G Papamihail and P Decleva, J. Phys.B: At. Mol. Opt. Phys. 44, 175402 (2011).
- [16] L. Young, et al, Nature 466, 56 (2010).
- [17] B. Rudek, et al, Nature Photonics 6, 858 (2012).
- [18] G. Wendin, J. Phys. B: At. Mol. Opt. Phys. 6, 42 (1973).
- [19] M. Meyer, et al, Phys. Rev. Lett. 108, 063007 (2012).
- [20] S. Düsterer, et al, New J. Phys. 13, 093024 (2011).
- [21] T. Mazza, et al, Nature Comm. 5, 4648 (2014).
- [22] A. K. Kazansky, et al, Phys. Rev. Lett. 107, 253002 (2011).
- [23] I. Grguras, et al, Nature Photonics 6, 852 (2012).

# II. Infrared Spectroscopy of isolated molecular species

Jos Oomens and Britta Redlich, FELIX Laboratory, Radboud University

Structure and function are intimately related in molecular and material sciences. Methods to accurately determine molecular structure are therefore under continuous development. Advanced light sources like Free Electron Lasers in frequency regimes ranging from (near) infrared to the THz range have now entered the wide field of molecular structure determination, and here we briefly review applications of Action Spectroscopy driven by current astrochemistry, catalysis, and biomolecular research.

- Introduction
- Molecular spectroscopy in the Infrared and THz regimes
- IR action spectroscopy
  - in ion traps
  - of clusters
  - in a molecular beam
- Outlook and Summary

### Introduction

Chemical and physical systems undergoing change display spectral signatures from the radiofrequency to the X-ray region of the electromagnetic spectrum. This has led to the development of versatile spectroscopic techniques across the entire range. While some of these techniques have been around for many decades, others undergo rapid development as a consequence of the emerging availability of advanced radiation sources. A good example of rapid current progress are the new opportunities [1-3] emerging from the recent development of X-Ray Free Electron Lasers [4,5].

Over the last three decades, Infrared and THz Free Electron Lasers have developed from infancy into mature radiation sources constantly providing new insights into, for example, the nature of molecular vibrations, carrier dynamics in condensed matter (*e.g.* semi-conductors) physics as well as gas-phase processes such as the dissociation, fragmentation and ionization of (bio)molecules, complexes and clusters. This chapter focuses on spectroscopic methods in the infrared and THz range using Free Electron Lasers as radiation source and more specifically on applications to various types of gas-phase systems. Separate chapters (no. 11 and 13) of the Whitebook are devoted to time-resolved applications mainly in condensed matter systems, which are therefore not discussed here.

Infrared absorption spectroscopy is a routine method for the analysis of molecules and materials. However, the standard linear absorption approach is no longer feasible when samples become optically very thin, such as species at low gas-phase densities, including species in a molecular beam, gaseous ionic species, weakly-bound complexes and clusters. In order to overcome this limitation, methods collectively referred to as Action Spectroscopy have been developed. In contrast to linear absorption spectroscopy, it is not the change in intensity of the incident light field, but the effect on the sample induced by the radiation that is recorded and converted into an infrared spectrum. Examples for an action of the sample are a change in molecular mass (fragmentation), a change in charge state (ionization), or a change in quantum state. While such spectroscopic methods are common in the UV/VIS range (think of ionization and fluorescence spectroscopy), the past decade(s) have witnessed a rapid development of a number of variants of action spectroscopy in the infrared, largely benefitting from the high intensities and wide tunabilities provided by Infrared Free Electron Lasers such as CLIO (Orsay, Paris) [6] and FELIX (Nijmegen, The Netherlands) [7] (see Appendix B).

### Molecular Spectroscopy in the Infrared and THz regimes

Optical spectroscopy provides a very sensitive probe of the molecular structure and does not rely on an a priori knowledge of any reaction mechanism or potential energy landscape. Infrared vibrational spectroscopy is an experimental technique that has long been used for the characterization of molecular structures. Over the last decades, the rapidly increasing capabilities of computational chemistry packages that can nowadays be employed routinely have considerably broadened the range of applications of vibrational spectroscopy. Efficient ab initio and DFT routines have been developed that allow one to optimize molecular geometries and reliably compute harmonic vibrational spectra for quite large systems. Comparison of the results of such calculations with experimentally obtained vibrational spectra, preferably under isolated conditions, *i.e.*, in the gas phase, has become a widely used and very effective strategy to determine molecular structures of a variety of systems. Since it remains difficult to unambiguously identify the global minimum energy structure on a complex potential energy surface, generally both experiment and theory are required for a reliable structure assignment. Furthermore, comparison of calculated and experimental values for properties like vibrational frequencies or binding energies can serve as a sensitive benchmark for testing and improving the performance of different computational models. This is a prerequisite for quantifying their accuracy and for enlarging their scope of application, for example to larger, more complex systems or to expanding the wavelength range into the THz regime.

Infrared spectroscopy of (bio)molecules, clusters, molecular ions and complexes in the gas phase is experimentally, however, far from trivial. The extremely low number densities available for these systems in the gas phase preclude the

### Infrared and THz Action spectroscopy

Gas phase (bio)molecules, clusters and complexes

Infrared absorption spectroscopy is a standard tool for the investigation of molecules and matter. However, it is not straightforwardly applicable to species at very low densities in the gas phase, such as (bio)molecules in molecular beam expansions, ionic species, weakly-bound complexes and clusters. Several versions of the so-called action spectroscopy method have been developed to circumvent this problem. These techniques have in common that they measure the effects in the sample induced upon irradiation by the light instead detecting directly the absorption, *i.e.* the change in intensity of the transmitted light beam. Examples for an "action" of a molecule are *e.g.* a change in molecular mass (fragmentation), in charge state (ionization), or in quantum state.

#### Mechanism of Action spectroscopy

Species under study are irradiated with the output of an infrared or THz (free electron) laser. When the laser frequency is in resonance with an allowed IR transition in the sample, photon absorption occurs, leading to an action, *e.g.* dissociation or ionization, which is detected mass spectrometrically. Monitoring the photodissociation yield as a function of the IR frequency provides the IR spectrum of the species. As the dissociation thresholds for covalently-bound species are higher than the IR photon energies, multiple photons need to be absorbed sequentially and call for a powerful light source. Wide frequency coverage is required to provide spectra that can be analysed to determine the structure of the species. This assignment generally requires the comparison with computed IR spectra for a given structure.



Fig. II.11: *Left – The mechanism of IR multiple photon excitation*. Infrared light is resonantly absorbed by the sample, and the energy is redistributed via internal vibrational redistribution (IVR). After this IVR process, the sample is ready to absorb a second photon, and energy redistribution leads to an overall increase in internal energy of the species. This process repeats until *e.g.* the dissociation threshold is reached, and photofragmentation occurs. *Middle – Mass spectrometric detection*. A mass spectrum recorded off-resonance shows the signature of the parent ion only. When the laser is tuned to resonance, a decrease in intensity of the parent ion peak and the appearance of the fragment ion peak are observed. *Right – Recording of the infrared spectrum*. By monitoring the fragmentation yield as a function of the IR wavelength, an IR spectrum can be constructed. Structural information can be inferred from comparison of this experimental spectrum with calculated IR spectra for candidate structures.



Fig. II.1: Overview of an ion trap arrangement. The solvated species is gently brought into the gas phase and ionized by electro-spray ionization. The ions are guided, accumulated, selected and stored in the ICR cell, where they are irradiated by the IR free electron laser. [9]

use of conventional linear absorption techniques. In the last two decades, Infrared and THz Free-Electron Lasers have given a substantial boost to the field by enabling the development of new "Action Spectroscopy" methods, based on the possibility of inducing multiple-photon absorption (see Infobox). The various action spectroscopy schemes rely on the detection of light-induced effects in the samples, such as dissociation, ionization or change of quantum state, instead of the change of intensity of the incident light. In most cases, the detection of this action is done using a mass spectrometric approach, as these techniques inherently give extremely high sensitivity and and have the added advantage of mass discrimination.

The study of gas-phase molecular and cluster systems in the neutral as well as the ionic state is a rapidly growing field. Studies in the gas phase permit one to investigate individual, isolated molecules, clusters and complexes and thereby to eliminate influences from a solvent or other environment. Moreover, interactions can also be added selectively, for example by the addition of individual ligands, such as water molecules or by attaching a metal ion. These techniques offer the possibility to perform studies on conformation-selected systems as well as on systems of different charge states. Since under these conditions, *e.g.*, the conformational dynamics is unaffected by the environment, it is possible to distinguish the intra- from the inter-molecular forces. Mechanisms can be studied in great detail that otherwise are likely hidden by heterogeneities induced by environmental interactions.

In the following sections, three selected cases will be discussed in more detail, showing the strength of the action spectroscopic techniques in the application to ionic systems of astrophysical as well as biochemical relevance, to adsorbate-cluster interactions in the context of catalysis and to neutral molecules in a molecular beam, motivated by questions from biology, biochemistry and biophysics.

### IR action spectroscopy in ion traps

As a consequence of their enhanced reactivity compared to neutral species, molecular ions play a central role in many areas of chemistry. For instance, the role of ions in biochemistry can hardly be overestimated, considering the importance of proton and electron transport, reaction centers in metallo-enzymes, ion channels, etc. One may also think of the importance of carbocations in organic chemistry, the redox chemistry of transition metals in catalytic cycles, and the formation of complex molecular species in low-temperature and low-density astrophysical environments [8].

Fundamental knowledge of reactions involving ions is conveniently obtained by application of mass spectrometry, where the ions and their chemical reactions can be studied in complete isolation in the gas phase. Ion traps present a versatile playground, since the species of interest can be trapped, isolated, and reacted. In addition, they are detected with very high mass resolution and superior sensitivity and can also easily be irradiated with laser light, as shown schematically for the case of an FTICR-MS arrangement in figure II.1.

The number of different ion trap configurations and IR laser sources, as well as the number of systems these combinations have been applied to, is widespread, and a consistent review is far beyond the scope of this section. The success of this type of investigation may be judged from the fact that about 50% of the beam time at the CLIO and FELIX free electron laser facilities are nowadays devoted to studies on ionic species in ion traps and that an increasing number of lab-based ion traps are coupled to table-top infrared laser sources. Moreover, dedicated sections at conferences are regularly devoted to these topics.

An excellent illustration of the potential and versatility of these techniques is the application to the unidentified IRbands in astrophysical observations. Since the early 1980's, Fig. II.2: *Infrared spectroscopy of PAHs*. (a) Emission spectrum of the Unidentified Infrared Bands. (b) IR spectra of different cationic PAHs [10]. (c) IR spectrum of protonated coronene [13]. (d) IR spectrum of the naphthyl cation and calculations for the triplet and singlet state [11]. (e) IR spectrum of deprotonated (anionic) PAHs – the 9-anthracyl anion [12].



polycyclic aromatic hydrocarbon species (PAH) have been suggested as origin for an abundantly observed set of emission features in the mid-IR range of the spectrum. Under astrophysical conditions, these PAHs may occur as neutral but also as ionic species, requiring laboratory IR spectra of ionized PAHs for comparison with astronomical spectra. A large number of studies of various PAH species – *i.e.* cationic [10, 11], anionic [12], protonated [13], substituted [14] etc. – have been performed and compared to astronomical





observations; they give substantial evidence for the PAH hypothesis (see figure II.2).

Another example of important contributions of ion spectroscopy is the understanding of the fundamental reaction chemistry underlying MS-based peptide sequencing [15]. The unraveling of peptide and protein sequences relies on the low-energy fragmentation of protonated peptides in a mass spectrometer and, nowadays, the identification of the fragments is fully automated via database search algorithms (see e.g. [16, 17]). Studies of the underlying reaction mechanisms (see e.g. [18, 19, 20]) aid in a fundamental understanding of the process, which may lead to more reliable peptide identification and reduced false-positives. Such problems have, for instance, been suggested to arise from sequence scrambling as a consequence of cyclization reactions during collisional activation, as schematically depicted in figure II.3. In experiments where peptide fragments are subjected to further dissociation, so called MS<sup>n</sup> experiments, cyclization may take place in between two fragmentation steps. If in a subsequent fragmentation step, the macrocyclic ring opens at a position different from the closing position, the original sequence is permuted, and the sequencing result is incorrect. As another example, the formation of a 5-membered cyclic structure (oxazolone) upon cleavage of the peptide bond had long been suspected, although alternative structures had also been put forward. Ion spectroscopy was used to experimentally establish the oxazolone structure. After fragmentation by collision-induced dissociation (CID), the infrared spectrum of the so-called b<sub>2</sub>-fragment from protonated tri-alanine clearly shows the signature of an oxazolone (see figure II.3). Very detailed mass spectroscopic studies have substantially contributed to the overall understanding of the fragmentation pathways and the respective fragmen-

Fig. II.3: *Peptide fragmentation*. (a) Schematic illustration of peptide fragmentation into b- and y-ions. (b) Schematic overview of a cyclization reaction leading to a macrocyclic structure via the oxazolone fragment and subsequent formation of possible sequence mutations after a ring-opening reaction. (c) Possible nucleophilic attack reactions in a model peptide, leading to oxazolone (green) or diketopiperazine formation. (d) IR spectroscopic identification the oxazolone structure of the b<sub>2</sub> fragment ion of protonated tri-alanine [19].

tation ion structures. However, ion spectroscopy has identified many previously unrevealed structural information by exemplary studies on peptide anions, the special role of proline, side-chain induced rearrangements [21], *etc*.

### IR action spectroscopy of clusters

A prime motivation for performing experiments on isolated clusters lies in the fundamentally driven curiosity in studying this peculiar state of matter. Clusters containing a few up to a few tens of atoms are not simply intermediates between isolated atoms/molecules and macroscopic particles. They tend to exhibit unique properties that lie in the nonscalable regime and that therefore cannot be extrapolated from the properties of larger nanoparticles [22]. Apart from the fundamental interest, it is often found that these unique properties make clusters of metals, metal oxides, *etc.* important ingredients of catalytic processes like the Fischer-Tropsch synthesis, the Steam Reforming process or the Haber-Bosch reaction.

Infrared action spectroscopy can be used to characterize the bare (mixed) clusters or their oxides, carbides, *etc.*, as well as the products of a reaction of the cluster with a gas or gas mixture (for an overview see *e.g.* [2]). The experiments are usually performed in a molecular beam apparatus, where the cluster formation is started by laser ablation from a metal target, as shown in figure II.4. The clusters are formed by cooling in the expansion, interact downstream with the IR radiation (and depending on the detection scheme with an additional UV/VIS laser) and are detected by mass spectrometry.

Two comparably simple examples are selected to demonstrate the strength of this technique (see figure II.5); they show how structure identification can eventually aid in the understanding of the complex and complicated processes and reaction pathways underlying heterogeneous catalytic reactions. The infrared spectrum of a cluster containing 20 gold atoms (Au20) in the far infrared regime is surprisingly simple, with one infrared mode only. This suggests a highly symmetric structure, as confirmed by guantum-chemical calculations that reveal a pyramidal geometry. Removing one of the gold atoms breaks the symmetry of the cluster, lifts the degeneracy and leads to the appearance of an additional infrared band for the Au<sub>19</sub>-cluster [24]. In the second example, the reaction of a methane molecule with two different 5d transition metal atoms is investigated [25]. Even for such a seemingly simple reaction, it becomes evident from the spectroscopic investigations how important small changes are. In this case, the reaction product changes from a carbene structure for platinum, where an intact CH<sub>2</sub> fragment is bound to the metal (M<sup>+</sup>-CH<sub>2</sub>), to a carbyne structure for iridium, with a CH and a hydrogen atom bound to the metal ion separately (H-M<sup>+</sup>-CH).



Fig. II.4: *Molecular beam cluster experiment.* In the Smalley type cluster source, the rotating target rod is irradiated with a laser pulse of 532 nm, creating a plasma. The ablated material is transported downstream by a short gas pulse, and in the course of the expansion, the clusters are formed. Additional cooling channels or gas valves supplying reaction partners can be implemented into the setup. In the extraction region of the time-of-flight mass spectrometer, the clusters are irradiated by the infrared laser, and the products after irradiation are analyzed mass spectrometrically.



### IR action spectroscopy in a molecular beam

Laser spectroscopy in molecular beams is an efficient way to obtain high-resolution spectra on isolated molecules and their clusters, not only in the UV/VIS region, but progressively more also in the infrared and very recently THz spectral range. With the development of laser desorption methods, which allow one to bring labile, involatile (biological) molecules into the gasphase without dissociation, the range of applications has broadened spectacularly. The supersonic expansion, which provides cooling of the molecules down to a few (tens of) Kelvin, not only enhances the spectral resolution considerably, but also makes it possible to study

weakly-bound complexes. Combination of molecular beam techniques with double-resonance laser schemes, such as ion-dip spectroscopy (see figure. II.6), opens novel, fascinating possibilities for conformer-selective IR spectroscopy of biomolecules. It has become possible to distinguish the vibrations originating from the peptide from those of the environmental water contributions by simply removing the water. On the other hand, controlled solvation, where a selected number of individual water molecules are attached, allow one to study the changes upon going from isolation to solution in the finest detail. Conformation selection by UV resonant ionization allows one to handpick a specific conformer out of a mixture of multiple conformers of the same molecule, thereby minimizing conformational heterogeneity, resulting in sharply resolved IR spectra. These spectra can be compared to quantum-chemical calculations, providing detailed conformational structures for the isolated systems.

This technique has proven its capabilities on a large number of systems, including single amino acids, small to mid-size peptides, as well as complexes with water molecules, and metal ions (for a recent overview see [26]). Experiments have been performed in the near- and mid-IR regimes, using advanced laser sources such as IR free electron lasers, but also table top OPO laser sources have been employed, although in a more limited frequency range.

One might suspect that the use of IR spectroscopy on such systems may be limited by molecular size, due to spectral congestion, however recent studies have shown convincingly that this limit has definitely not been reached yet and that especially the extension to longer wavelengths into the THz range will push the size limits even further.

In general, it is appealing to open the far-infrared and THz spectral range to studies of the structure and dynamics of biomolecules. Here one can, for example, probe the global nuclear motions responsible for conformational changes. Intra- and intermolecular hydrogen bonding responsible *e.g.* for the formation of intra  $\beta$ -strand and inter  $\beta$ -sheet hydrogen bonds, may have characteristic vibrations in this spectral range. The detailed interpretation of the THz spectra is one of the challenges for current spectroscopic methods, when studying peptides and proteins in either thin films or protein crystals. This is mainly caused by the fact



Fig. II.6: *Left: Schematic overview of the molecular beam apparatus*. The sample is desorbed from the sample bar by a laser pulse and carried along in a molecular expansion by a gas pulse through a skimmer. The jet-cooled species are interrogated with the IR and UV lasers and detected in a mass spectrometer. *Right: IR/UV-ion dip spectroscopy scheme*. The system under study is resonantly, and therefore conformer-selectively, ionized by two UV photons, creating a constant ion yield. When the IR laser irradiates the molecule resonantly before the UV laser, the ground-state population is depleted, and the UV ion yield decreases, resulting in a dip in the ion current being detected.

that the hydrated as well as the dehydrated spectra are usually broad and lack distinct features. Also, liquid water is a strong THz absorber, masking the peptide or protein contribution. It is likely that the complementary approach of studying isolated species not only delivers results on these systems, but can potentially aid the interpretation of experiments in complex environments.

A recent example of an investigation of a peptide in the far-IR region by IR/UV-ion dip spectroscopy is shown in figure II.7 and clearly demonstrates the advantages and the potential of this gas-phase technique. [27] The recorded experimental spectrum is characterized by a large number of very sharp absorption bands that can be attributed to a specific structure of one conformer of the gas-phase peptide under study, using advanced calculations like Born-Oppenheimer Molecular Dynamics simulations. With this level of detail, it becomes conceivable to resolve questions related to the structure and function in increasingly complex systems and environments.

### Outlook

The techniques of infrared and THz action spectroscopy of (bio)molecules, complexes and clusters have proven to be versatile tools that decisively aid in the understanding of molecular systems by addressing questions with relevance *e.g.* to the structure-function relationship in biological systems or to reaction chemistry relevant for (heterogeneous) catalysis, but also to (laboratory) astrochemistry. A large number of action spectroscopy schemes have been developed with the goal to ever broaden the range of applications. These action spectroscopy methods are not necessarily restricted to the use of advanced light sources such as Infrared and THz Free Electron Lasers, but can also be used with lab-based, table-top sources.

Current trends in the development of the technique include the application of alternative radiation sources, however, future breakthroughs may also be inspired by developments geared toward (i) larger and more complex (bio)molecular systems, complexes and clusters, (ii) advances in quantumchemical calculations, which increase the range of applications and enhance the reliability, (iii) expanding the usable frequency range to ever longer wavelengths in the infrared and THz regime, (iv) experiments including complementary techniques and information including, for instance, ion mobility, photoelectron spectroscopy, *etc.*, and (v) the development of time-resolved action spectroscopy experiments that may, for instance, permit one to study reaction intermediates or follow the process of protein folding, one of the holy grails of chemistry and biology.



Fig. II.7: Far-IR molecular beam spectrum of individual conformers of a small gaseous peptide. The soft vibrational modes in this range of the spectrum are typically delocalized over the entire molecule and are therefore particularly sensitive to the overall conformational structure. Structural information is deciphered from the experimental spectrum with the use of advanced computational methods, taking implicitly into account the anharmonicity of the shallow vibrational potentials. [27]

### Summary

- *IR action spectroscopy is a mature, versatile technique to elucidate the structure of molecules, complexes and clusters in the gas-phase.*
- *IR-* and *THz-free* electron lasers allow *IR* action spectroscopy of gas-phase species over a large frequency range, enabling studies of both local and collective vibrations.
- The bottom-up approach of increasing complexity, through the study of isolated systems, to which solvent molecules (or other environmental elements) are attached in a stepwise fashion, is applicable to a wide range of systems and gives detailed mechanistic information.
- Studies of isolated as well as complexed species contribute to the general understanding of molecular systems, intermolecular interactions and, in particular, of the structure-function relationship.
- Developments toward larger systems and longer wavelength, as well as the combination with other sophisticated methods, hold great promise for future investigations.

#### References

- "Free-Electron Lasers: New Avenues in Molecular Physics and Photochemistry" J. Ullrich, A. Rudenko, and R. Moshammer, Annu. Rev. Phys. Chem. 63 (2012) 635 -660
- "Coherent science at the SwissFEL x-ray laser" B.D.
   Patterson, R. Abela, H.-H. Braun, U. Flechsig, R. Ganter,
   Y. Kim, E. Kirk, A. Oppelt, M. Pedrozzi, S. Reiche, L. Rivkin,
   Th. Schmidt, B. Schmitt, V.N. Strocov, S. Tsujino, and
   A.F. Wrulich, New Journal of Physic **12** (2010) 035012
- [3] "The big guns: Powerful X-ray lasers are getting to the heart of matter" M.M. Waldrop, Nature 505 (2014) 605-606
- [4] "X-ray free electron lasers present and future capabilities" J.N. Galayda, J. Arthur, D.F. Ratner, and W.E. White, J. Opt. Soc. Am. B 27 (2010) B106-B118
- [5] "X-ray free-electron lasers" B.W.J. McNeill and
   N.R. Thompson, Nature Photonics 4 (2010) 814-821
- [6] www.clio.lcp.u-psud.fr

- [7] www.ru.nl/felix; http://youtu.be/Bed2ZUDvKvc
- [8] "Mass spectrometric studies of organic ion/molecule reactions" S. Gronert, Chem. Rev. 101 (2001) 329-360
- [9] "Free electron laser-Fourier transform ion cyclotron resonance mass spectrometry facility for obtaining infrared multiphoton dissociation spectra of gaseous ions" J.J. Valle, J.R. Eyler, J. Oomens, D.T. Moore, A.F.G. van der Meer, G. von Helden, G. Meijer, C.L. Hendrickson, A.G. Marshall, G.T. Blakney, Rev. Sci. Instrum. **76** (2005) 023103
- [10] "Gas-phase infrared photodissociation spectroscopy of cationic polyaromatic hydrocarbons" J. Oomens, A.J.A. van Roij, G. Meijer and G. von Helden, ApJ 542 (2000) 404, "Gas-phase infrared multiple photon dissociation spectroscopy of mass-selected molecular ions" Jos Oomens, Boris G. Sartakov, Gerard Meijer, Gert von Helden, Int. J. Mass Spectrom. 254 (2006) 1-19

- [11] "Spectroscopic Evidence for a Triplet Ground State in the Naphthyl Cation "Héctor Alvaro Galué and Jos Oomens, Angew. Chem. Int. Ed. **50** (2011) 7004
- "Laboratory Infrared Spectroscopy of Gaseous Negatively Charged Polyaromatic Hydrocarbons" Juehan Gao, Giel Berden, Jos Oomens, ApJ 787 (2014) 170
- [13] "Infrared spectra of protonated polycyclic aromatic hydrocarbon molecules: Azulene" Dawei Zhao, Judith Langer, Jos Oomens, and Otto Dopfer, ApJL **706** (2009) L66
- "Gas-Phase infrared spectra of cationized nitrogensubstituted polycyclic aromatic hydrocarbons" H. Alvaro Galué, O. Pirali, and J. Oomens, A&A 517 (2010) A15
- [15] "Fragmentation pathways of protonated peptides" B. Paizs,
   S. Suhai, Mass Spectrom. Rev. 24 (2004) 508-548; "To b or not to b: the ongoing saga of peptide b ions" A.G. Harrison,
   Mass Spectrom. Rev. 28 (2009) 640-654
- [16] "Mass spectrometry in proteomics" R. Aebersold,D.R. Goodlett, Chem. Rev. **101** (2001) 269-295
- [17] "The ABC's (and XYZ's) of peptide sequencing" H. Steen, M. Mann, Nat. Rev. Mol. Cell Biol. 5 (2004) 699-711
- [18] "Infrared Multiple Photon Dissociation Spectroscopy as Structural Confirmation for GlyGlyGlyH<sup>+</sup> and AlaAlaAlaH<sup>+</sup> in the Gas Phase. Evidence for Amide Oxygen as the Protonation Site" Ronghu Wu and Terry B. McMahon, JACS **129** (2007) 11312; "Structure of Electron-Capture Dissociation Fragments from Charge-Tagged Peptides Probed by Tunable Infrared Multiple Photon Dissociation" Gilles Frison, Guillaume van der Rest, Frantisek Turecek, Thierry Besson, Joel Lemaire, Philippe Maıtre, and Julia Chamot-Rooke, JACS **130** (2008) 14916; "Evidence of Diketopiperazine and Oxazolone Structures for HA b<sub>2</sub><sup>+</sup> Ion" Brittany R. Perkins, Julia Chamot-Rooke, Sung Hwan Yoon, Ashley C. Gucinski, Arpad Somogyi, and Vicki H. Wysocki, JACS **131** (2009) 17528;
- [19] "Spectroscopic evidence for an Oxazolone Structure of the b<sub>2</sub> Fragment Ion from Protonated Tri-Alanine" J. Oomens, S. Young, S. Molesworth and M. van Stipdonk, J. Am. Soc. Mass Spectrom. **20** (2009) 334
- [20] "Infrared spectroscopy and Theoretical Studies on Gas-Phase Protonated Leu-enkephalin and Its Fragments: Direct Experimental Evidence for the Mobile Proton" Nick C. Polfer, Jos Oomens, Sándor Suhai, and Béla Paizs, J. Am. Chem. Soc. 129 (2007) 5887; "Reaction products in mass spectrometry elucidated with infrared spectroscopy" Nick C. Polfer, Jos Oomens, Phys. Chem. Chem. Phys. 9 (2007) 3804; "Oxazolone Versus Macrocycle Structures for Leu-Enkephalin b<sub>2</sub>-b<sub>4</sub>: Insights from Infrared Multiple-Photon Dissociation Spectroscopy and Gas-Phase Hydrogen/ Deuterium Exchange" Xian Chen, Jeffrey D. Steill,

Jos Oomens, and Nick C. Polfer, J. Am. Soc. Mass. Spectrom. **21** (2010) 1313

- [21] "Structure of anionic c-type peptide fragments elucidated by IRMPD spectroscopy" J. Grzetic, J. Oomens, J. Mass Spectrom. **316-318** (2012) 216-226; "Gas-Phase conformations of small polyprolines and their fragment ions by IRMPD spectroscopy" J.K. Martens, J. Grzetic, G. Berden, and J. Oomens, Int. J. Mass Spectrom. **377** (2015) 179-187; "Effect of the ASN side chain on the dissociation of deprotonated peptides elucidated by IRMPD spectroscopy" J. Grzetic and J. Oomens, Int. J. Mass Spectrom. **354-355** (2013) 70-77
- [22] J. Jortner, in Physics and Chemistry of Finite Systems: From Clusters to Crystals, ed. P. Jena, S.N. Khanna and B.K. Rao, World Scientific, Singapore, 1992, pp 1-18
- [23] "Vibrational Spectroscopy of Clusters and Cluster-Adsorbate Complexes in the Gas Phase", K.R. Asmis, A. Fielicke,
  G. Meijer, G. von Helden, Chapter in *Atomic Clusters: From Gas Phase to Deposited*, edited by D.P. Woodruff; Vol. 12 of *The Chemical Physics of Solid Surfaces*, (Elsevier, Amsterdam, The Netherlands, 2007)
- "Structures of Neutral Au<sub>7</sub>, Au<sub>19</sub>, and Au<sub>20</sub> Clusters in the Gas Phase" P. Gruene, D.M. Rayner, B. Redlich, A.F.G. van der Meer, J.T. Lyon, G. Meijer, and A. Fielicke, Science **321** (2008) 674-676
- [25] "Structures of the Dehydrogenation Products of Methane Activation by 5d Transition Metal Cations" V.J.F. Lapoutre, B. Redlich, A.F.G. van der Meer, J. Oomens, J.M. Bakker, A. Sweeney, A. Mookherjee, P.B. Armentrout, J. Phys. Chem. A **117** (2013) 4115
- [26] "IR Spectroscopic Techniques to Study Isolated Biomolecules " Editors: Anouk M. Rijs and Jos Oomens, Top. Curr. Chem, **364** (2015) 1-406
- "Gas-Phase Peptide Structures Unraveled by Far-IR
   "Spectroscopy: Combining IR-UV Ion-Dip Experiments with Born-Oppenheimer Molecular Dynamics Simulations" S.
   Jaeqx, J. Oomens, A. Cimas, M.-P. Gaigeot, A.M. Rijs, Angew.Chem.Int.Ed. 53 (2014) 3663

# III. Photochemistry

Tom Penfold, Paul Scherrer Institute

Understanding chemical reactions on the atomic resolution of both time (femtoseconds) and space (Angström) is the central motivation for Chemistry at X-Ray Free Electron Lasers that holds the promise for an unprecedented level of insight into important chemical processes.

- Introduction
- Photophysics and photochemistry in solution
- Time-resolved X-ray absorption spectroscopy
- The photophysics and applications of transition metal complexes
- Probing the spin crossover phenomenon in iron tris-bipyridine
- Outlook

Probing the preliminary steps of a chemical reaction after perturbation or activation is the principle aim of ultrafast chemistry. This area is particularity pertinent for photochemical and photophysical processes, during which the ultrafast dynamics are epitomized by the breakdown of the Born-Oppenheimer Approximation and ensuing nonadiabatic phenomena, arising from the coupled electronic and nuclear dynamics. Consequently, probing these dynamics with both high temporal (on the femtosecond time scale) and spatial (on the order on tenths of an angström) resolution, as offered by X-FELs, represents a unique opportunity to understand a wide variety of fundamental processes, especially those occurring within electronically excited states.

### Introduction

When addressing the question of chemical reaction mechanisms, the characteristics of the process under study depend largely on the time and length scales in question [1]. For many chemical reactions the relevant time scale for the formation of intermediate and/or product species can be on the order of microseconds, seconds or even longer. This, for the purposes of chemistry, would therefore appear to negate the need for light sources capable of probing nonequilibrium dynamics in the femtosecond  $(10^{-15} s)$  domain. However, electrons move and atoms vibrate on the femtosecond timescale adjusting to the effects of an external perturbation [2]. Indeed, a single dissociation event, structural distortion (such as an isomerization) and/or relaxation of electronically excited states can all occur within some femtoseconds. Consequently, being able to probe, understand and establish the connection of these dynamics to molecular and/or material properties and chemical products is of both fundamental as well as practical importance if one wishes to engineer or improve systems for applications.

This is especially pertinent in the case of photochemistry [3] that aims at understanding the dynamics occurring within an electronically excited state. Indeed, exploiting this understanding to design systems capable of utilizing solar energy to produce chemical fuel, such as hydrogen, represents one of the most promising approaches to satisfy escalating global energy demands. The last two decades has seen significant advances of devices that directly use solar radiation suitable for photocatalysis [4] and photovoltaic [5-7] applications. Besides the direct use of sunlight, electroluminescent materials, which use electric current through a luminphor to make energy efficient lighting devices, such as Organic Light Emitting Devices (OLEDs) [8,9] is another important area of research where the excited state plays a crucial role.

In all of these cases, the focus is upon the system in its electronically excited state, and it is the properties and lifetimes of these excited states that play a crucial role in their suitability for a particular device. This is exemplified by photocatalysis. Until now many photocatalytic devices exhibit limited solar-to-fuel efficiencies because the lifetimes of these photogenerated excited states (fs–ms) are often incommensurate with the prolonged timescales required to facilitate photocatalytic reactions at the semiconductor surface (ms-s) [10]. It is this kinetic discrepancy, arising from loses (such as non-radiative decay) in the excited state that often hinders the realization of efficient photosynthetic devices for solar energy conversion. The decay (radiative or non-radiative) of the excited states begins immediately after photoexcitation and therefore it is the femtosecond timescale that is critically important for understanding advantages or limitations of a particular system for solar energy conversion.

However, despite its importance, the ultrafast time scale for many photochemical and photophysical processes remains poorly understood. Femtosecond linear and non-linear optical spectroscopies [2,11] have had a huge impact, owing to their ability to probe, in real-time, the nuclear motion within these different types of systems. However, for systems of more than two atoms the link between the optical domain spectroscopic observables and the molecular structure is ambiguous. Consequently, from the early days of ultrafast spectroscopy much effort was invested to develop methods that achieve both high temporal (on the femtosecond time scale) and spatial (on the order on tenths of an angström) resolution. Due to the technical and technological developments of the X-ray Free electron lasers (X-FELs) this is now possible and these 4<sup>th</sup> generation light sources promise to provide exciting and important new insight into the nonequilibrium dynamics of complex systems [12,13].

### Photophysics and Photochemistry in Solution

As established in the introduction, understanding photophysical and photochemical processes [1], especially on the ultrafast timescales has important implications for a large range of possible applications. In this context of developing devices for solar energy conversion and optoelectronic applications, processes dominated by the former (photophysical) are often essential, as this permits the device to be reused and continual cycled during operation.

In the following subsections I outline three important concepts for photophysical and photochemical processes in solution. The first, nonadiabatic dynamics, which arises from the breakdown of the Born-Oppenheimer approximation, is applicable to all excited state dynamics. In the second subsection I introduce the concepts and important aspect of intersystem crossing. Indeed, as many devices aimed at solar energy conversion and optoelectronic applications rely on transition metal complexes, the description of the intersystem crossing mechanism plays an important role in determining their efficiency and/or suitability for a particular application. Finally, molecules surrounded by solvent molecules or embedded in a matrix can be strongly altered by electrostatic effects, spatial confinement, or explicit reactions with the solvent. As many applications also require technologies exploiting the systems that are optimized in solution; in the final subsection I discuss the implications of the environment on these processes.

#### Nonadiabatic dynamics

The full time-dependent Schroedinger equation can be expressed:

$$i\hbar\frac{\partial}{\partial t}\Omega_{j}(\boldsymbol{R},t) = \left[-\sum_{\gamma}^{Nn}\frac{\hbar^{2}}{2M_{\gamma}}\nabla_{\gamma}^{2} + E_{j}^{el}(\boldsymbol{R})\right]\Omega_{j}(\boldsymbol{R},t) + \sum_{i}^{\infty}F_{ji}(\boldsymbol{R})\Omega_{i}(\boldsymbol{R},t) \quad (1)$$

Here,  $\Omega_j$  represent the nuclear wavefunction,  $E_j^{el}(\mathbf{R})$  is the total electronic energy. By neglecting the last term on the right hand side we recover the Born-Oppenheimer approximation, which is one of the key concepts in chemistry that invokes a quantum description of matter. This, by virtue of the large difference in their masses, allows us to decouple



the motion of nuclei and electrons and assume that because the motion of the nuclei is slow compared to that of the electrons, the electrons can instantaneously adapt to any changes of the nuclear configuration. This leads to the convenient picture of nuclei as classical particles evolving over a potential energy surface generated by the electrons. Within the Born-Oppenheimer approximation, as depicted in Figure 1, a molecule evolving in the highlighted ground state cannot populate other electronic states and its dynamics is governed by only one electronic state.

However, upon population of an electronically excited state, large potential energy gradients created by the new nonequilibrium electronic configuration drives fast nuclear motions. In such cases, we can no longer neglect the coupling matrix ( $F_{ji}$ ), which is expressed:

$$F_{ji}(\boldsymbol{R}) = \int d\boldsymbol{r} \ \Phi_{j}^{*}(\boldsymbol{r};\boldsymbol{R}) \left[ -\sum_{\gamma}^{Nn} \frac{\hbar^{2}}{2M_{\gamma}} \nabla_{\gamma}^{2} \right] \Phi_{i}(\boldsymbol{r};\boldsymbol{R})$$
(2)  
+ 
$$\sum_{\gamma}^{Nn} \frac{1}{M_{\gamma}} \left\{ \int d\boldsymbol{r} \Phi_{j}^{*}(\boldsymbol{r};\boldsymbol{R}) [i\hbar\nabla_{\gamma}] \Phi_{i}(\boldsymbol{r};\boldsymbol{R}) \right\} [-i\hbar\nabla_{\gamma}]$$

 $F_{ji}$  are the terms that mix the different electronic wavefunctions ( $\Phi_i$  and  $\Phi_j$ ). The motion of the electron and nuclei may now no longer be considered independently and a careful attention to how the dynamics of the nuclei leads to coupling between two or more electronic states must be considered. These so called nonadiabatic (or dynamical) couplings give rise to phenomena such as internal conversion (IC), which leads to population transfer between states of the same spin multiplicity and plays a key role in the decay of photoexcited states (See Figure 2). A particularly striking and important example of the result of this coupling is a conical intersection [15].

Fig. III.1: Schematic representation of the adiabatic electronic energies of a molecular system versus its nuclear configuration R. Note that other electronic states exist and are shown in light grey. However, within the Born-Oppenheimer adiabatic approximation and in a dynamical picture, a molecule evolving in the highlighted ground state cannot "visit" other electronic states, its dynamics is governed by only one electronic state. Figure reproduced from Ref.[14].



These features, arising from a breakdown of the non-crossing rule in systems of two or more nuclear degrees of freedom, act as photochemical funnels providing highly efficient nonradiative pathways between two coupled states. Such topological features are ubiquitous throughout excited state surfaces. Indeed, while the most commonly known way to get rid of the energy gained by light absorption is for the molecule to emit a photon, i.e. fluorescence, the breakdown of the Born-Oppenheimer approximation and the ensuing nonadiabatic effects makes it possible for the molecule to return to its electronic ground state without emitting light, via, for example, a conical intersection. These non-radiative relaxations are common, but especially in terms of applications such as OLEDs, where one wishes to obtain a light (radiative photon) emission, these non-radiative relaxations are highly undesirable and much research effort is focused upon minimizing or removing them.

#### Intersystem Crossing

Besides the nonadiabatic effects associated with the breakdown of the Born-Oppenheimer approximation, for heavier elements, such as transitions metal complexes it is often important to also consider the intersystem crossing (ISC) relaxation processes [16], which can be decisive for understanding both the decay mechanisms and light-harvesting efficiency [17]. In contrary to IC discussed in the previous section, ISC is the radiationless process involving the tran-

Fig. III.2: Schematic representation of excited state dynamics. Up: Upon promotion of a nuclear wavepacket into an electronically excited state the large potential energy gradients created by the new non-equilibrium electronic configuration drives fast nuclear motions. Down: This leads to the breakdown of the Born-Oppenheimer approximation and coupling between different potential energy surface leading to nonadiabatic phenomena. Figure reproduced from Ref. [14].

sition between two electronic states with different spin multiplicity and whose rate is expressed, using Fermi's golden rule as:

$$k_{nm}^{ISC} = \frac{2\pi}{h} \langle S_n | \hat{H}_{SO} | T_m \rangle^2 x \ FCWD \quad (3)$$

including the spin–orbit coupling (SOC) integral between the pure spin states  $S_n$  and  $T_m$ , and the Franck–Condon weighted density of states (FCWD). Assuming the accuracy of the one-electron SOC Hamiltonian commonly adopted for heavy transition metal, we can write the SOC operator as:

$$\widehat{H}_{SO} = \xi \sum_{i} \widehat{l}_{i} \cdot \widehat{s}_{i} \qquad (4)$$

where  $(\hat{l}_i)$  and  $\hat{s}_i$  represent the orbital and the spin angular momentum operator, respectively, for the i<sup>th</sup> electron. ξ is the spin-orbit coupling constant, which is proportional to the atomic number and inversely proportional to the mean cubic radial distribution (r<sup>3</sup>) of the electron. This is therefore responsible for the so-called *heavy atom effect*. However, in order to assess the importance and role of ISC, one must also consider the integral over the two states involved. This integral, sometimes referred to as the *internal effect* [18], depends principally on the character of the states involved, as outlined for organic systems by El-Sayed [19]. For efficient ISC, the change in spin must be compensated for through a change in orbital angular momentum. For the metal to ligand charge transfer (MLCT) states commonly encounter in transition metal complexes, this is most effectively achieved between configurations involving the d-orbitals with a different orientation. Indeed, this is the reason why, despite the heavy atom effect that, Au(I) complexes generally exhibit smaller SOC matrix elements than Cu(I) complexes [20], as due to the larger crystal field splitting in Au(I) complexes, they exhibit a smaller contribution of d-orbitals in the excited state.

The final contributing factor towards the role of ISC in transition metal complexes is the energy gap between the two coupled states. Indeed, it is important to remember that because the first-order mixing coefficient between singlet and triplet states (I) is inversely proportional to the energy gap, efficient ISC can be achieved with small SOC constants [21-23]. This was recently highlight for a Cu(I) transition metal



Fig. III.3: Two selected frames from excited state molecular dynamics simulations of the  $[Ru(bpy)_3]^{2+}$ together with part of the first solvation shell of water molecules. The selected frames (t = 0 fs on the left and t = 46 fs on the right) show the fast rotation of a water molecule (in yellow) occurring during the dynamics. Figure reproduced from Ref. [28].

complex for which it was demonstrated that sub picosecond ISC occurs via a dynamic effect, in the sense that it arises from the system traversing the a region of the excited state potential coordinate where the singlet and triplet states become degenerate, leading to efficient crossing [24].

#### The role of the solvent

The vast majority of chemical processes occur in the condensed phase and, in particular, liquids. Consequently, understanding the properties of a solute and the effect of the surrounding solvent is key to a detailed description of many chemical processes in chemistry. Indeed, molecules surrounded by solvent molecules or embedded in a matrix could be strongly altered by electrostatic effects, spatial confinement, or explicit reactions with the solvent. Furthermore, for excited state dynamics, which are a particular focus of the present chapter, geometric structural changes that are initiated or accompanied by electronic structural changes following excitation by an external field will result in some kind of solvent response [25-27], which can often play a significant role in the reaction.

Broadly speaking the effects of the solvent may be classified into two distinct groups; passive or active. Passive solvents don't change the quantum states of the solute, but alters their relative energies. An interesting example of this can be seen in the effect of the first solvation shell during the ultrafast excited state relaxation of  $[Ru(bpy)_3]^{2+}$ . Using excited state molecular dynamics simulations [29], Tavernelli and co-workers [28] reported that following photoexcitation, the complex solvent-solute interaction (See Figure 3) drives the localization/ delocalization of the unpaired electron in the ligand system, thought to be important for the intersystem crossing. While this shifts the energetics of the states involves, the solvent does not explicitly taken part in the dynamics.

In contrast, active solvent molecules take part in the chemical reaction via explicit interactions with the solute, leading to new molecules. A classic example of this is the photochemistry of  $[Fe(CN)_6]^{4-}$  [30-32]. This complex exhibits two distinct excitation wavelength dependent photoinduced reactions when dissolved in water. Below 313 nm, the quantum yield of photochemical reactions is dominated by the generation of solvated electrons via the photooxidation channel. This occurs through charge-transfer-to-solvent (CTTS) states arising from to the strong interaction between the solute and solvent [33]. In contrast, above 313 nm excitation, the products were assigned to the so-called photoaquation channel. Here population of the metal centered states leads to dissociation of one of the CN<sup>-</sup> ligands, which is replaced by a water molecule. Despite a number of studies the exact mechanism of this active solvent effect on the ultrafast timescale remains unknown.

### Time-resolved X-ray absorption spectroscopy

As noted in the introduction, the importance of ultrafast time scale for many photochemical and photophysical processes has led to entensive studies using linear and non-linear optical spectroscopies [2,11]. However, for systems of more than two atoms the link between the optical domain spectroscopic observables and the molecular structure is ambiguous. Consequently, since the early days of femtochemistry, there has been a strong driving force aimed at extending structurally sensitive techniques into the ultrafast regime.

Among the most popular of these is X-ray absorption spectrum (XAS). An XAS spectrum is characterized by absorption edges that reflect the excitation of core electrons to the ionization threshold. Consequently, it is element specific [34,35]. For a particular edge, an electron is initially excited to unoccupied or partially filled orbitals just below the ionization potential (IP) giving rise to bound-bound transitions, which form the pre-edge features. This region, thus, yields information about the nature of the unoccupied valence orbitals, as the transition probability is governed primarily by the atomic dipole selection rules. Above the IP, resonances show up due to interferences of the photoelectron wave from the absorbing atom with the wave scattered back from the neighboring atoms. Just above the absorption edge (<50 eV), in the X-ray Absorption Near-Edge Structure (XANES) region, the low photoelectron energy (i.e. long de Broglie wavelength) implies that the photoelectron undergoes multiple scattering (MS) events. XANES therefore contains information about the three-dimensional structure around the absorbing atom, including both bond distances and bond angles. At higher energies, in the Extended X-ray Absorption Fine Structure (EXAFS) region, single scattering (SS) events usually dominate, as the scattering cross section of the photoelectron decreases as the energy increases. This region delivers information about coordination numbers and bond distances of the first coordination shell around the absorbing atom.

The simplest and most common method of measuring the X-ray absorption coefficient is X-ray transmission, shown schematically in Fig. 4. Using a tuneable monochromatic X-ray beam both the transmitted (I<sub>T</sub>) and incident (I<sub>0</sub>) X-ray signals are measured as a function of incident photon energy. The X-ray linear absorption coefficient  $\mu(\omega)$ , at a



Fig. III.4: Sketch of a typical time-resolved XAS setup for the study of liquid samples. The continuously-refreshed sample can be a flow capillary, a flow-cell, or a high speed liquid jet.  $\Delta t$  is the time-delay between the laser pump and X-ray probe pulses. Figure reprinted from ref. [12].

particular incident photon energy  $\omega$  is then derived from the Beer-Lambert law:

$$A(\omega) = \mu(\omega) \cdot d = \ln\left(\frac{I_0}{I_T}\right) \qquad (5)$$

where d represents the sample thickness. When extended to the time-domain as shown schematically in Fig. 4, the XAS signal at a particular X-ray energy and pump-probe time delay ( $\Delta$ t) is recorded twice, alternating between the signal from the excited sample (pumped) and that from the unexcited sample (unpumped). The transient spectrum, containing information about the dynamics around the absorbing atom is then expressed as the difference between the pumped (excited) minus the unpumped (ground state) [36,37]:

At present, due to the shot-to-shot fluctuations in the X-ray beams from the X-FEL, this traditional approach is challenging. Consequently, spectra are generally obtained by detecting the fluorescence induced by absorption of the X-ray photon. This is clearly a second order processes and must be described using second-order perturbation theory [38,39]:

$$F(\Omega,\omega) = \sum_{f} \left| \sum_{n} \frac{\langle f | \hat{H}_{int} | n \rangle \langle n | \hat{H}_{int} | i \rangle}{E_i - E_n - \hbar\Omega - i\frac{\Gamma_n}{2}} \right|^2 x \frac{\Gamma_f / 2\pi}{(E_i - E_n + \hbar\Omega - \hbar\omega)^2 + \Gamma_f / 4}$$
(6)

Eq. 6 describes the absorption of a photon, forming an intermediate state n from the ground state *i*, before it decays into a final state *f*. This second-order process can be described as absorption and emission processes that are coherently coupled. One effect of this coupling is that interference between different intermediate states can alter the spectral weights. However, in the case of hard X-rays, these are generally small and the interference terms can be neglected. Under this approximation Eq. 6 becomes:

$$F(\Omega,\omega) = \sum_{f} \sum_{n} \frac{\langle f | \hat{H}_{int} | n \rangle^2 \langle n | \hat{H}_{int} | i \rangle^2}{E_i - E_n - \hbar\Omega - i\frac{\Gamma_n}{2}} x \frac{\Gamma_f / 2\pi}{(E_i - E_n + \hbar\Omega - \hbar\omega)^2 + \Gamma_f / 4}$$
(7)

This describes a non-coherent process in which the absorption matrix elements from initial state *i* to intermediate state *n* are weighted by the emission matrix element. Such secondorder spectroscopies (also called photon-in/photon-out [40]) have spawned a whole range of approaches, and while the yields are much smaller than signals from traditional transmission XAS, they are able to probe both the unoccupied and occupied molecular orbitals, obtain soft X-ray L-edge, M-edge and UV/Vis excitations using hard X-rays, and record high-resolution spectra proportional to the X-ray absorption spectrum [41,42]. Importantly, the low scattering cross sections of these spectroscopies has so far restricted their use in time-resolved studies, however the increased available photon flux of the X-FELs means that time-resolved second-order spectroscopies [43] are emerging as powerful tools in coordination chemistry.

### The photophysics and applications of transition metal complexes

Due to their ability to exist in a variety of oxidation states, strong absorption in the UV-visible region of the spectrum (i.e. the region where the solar spectrum is strong) and long-lived excited states, transition metals are a focus of much research with potential applications in organic lightemitting diodes (OLEDs) [9], light-emitting electro-chemical cells (LEECs) [44], light absorbers in dye-sensitized solar cells [45], chemical photo-catalysts [4], chemo- and biosensors and fluorphors in cell imaging [46]. Indeed, their extensive use for such applications has been the main driving force for a large research effort aimed at understanding their fundamental photophysical and photochemical properties, including resolving the decay mechanisms and the ultimate fate of the initially excited state. These outcomes include radiative and non-radiative decay, intramolecular relaxation processes such as internal conversion (IC), and intramolecular vibrational redistribution (IVR). In most cases these processes are accompanied by structural modifications. All the processes discussed above (IC, IVR and structural changes) occur on ultrashort time scales, often in a competing fashion and consequently a femtosecond temporal resolution is critical is one wishes to fully resolve these dynamics.

To a large extent, the research effort on transition metal complexes has been focussed upon polypyridyl ligands complexed with d<sup>6</sup> metal ions, such as iron and ruthenium.

Here, the archetypal luminescent transition metal complex is tris-(bipyridyl) ruthenium(II), [Ru(bpy)<sub>3</sub>]<sup>2+</sup>[47-49]. The amalgamation of a relatively easily oxidised d<sup>6</sup> metal ion and the electron accepting bipyridine ligands means that the low lying excited states exhibit metal-to-ligand charge transfer (MLCT) character. Once populated (i.e. by photoexcitation), the participation of the metal ion in these excited states not only facilitates large spin-orbit coupling (SOC) and permits ultrafast intersystem crossing (ISC) [28], but also promotes a strong  $T_1 \rightarrow S_0$  radiative transition which has a lifetime of approximately 500 ns and a high quantum vield [50]. A related transition metal complex which has been the focus of much research is [Fe(bpy)<sub>3</sub>]<sup>2+</sup> [51]. Compared to [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, this 1<sup>st</sup> row transition metal coordination complex has a smaller crystal field splitting of the non-bonding and anti-bonding d-orbitals and consequently exhibits low-lying non-emissive metal centred transitions which quench the excited MLCT state emission. In the following section, the photophysics of this complex are described.

### Probing the spin crossover phenomenon in iron tris-bipyridine

As mentioned in the previous section, in comparison to [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, due smaller crystal field splitting of the Fe<sup>2+</sup> d-orbitals, [Fe(bpy)<sub>3</sub>]<sup>2+</sup> exhibits non-emissive metal centered states lie below the MLCT, providing efficient deactivation pathways of the excited state [51]. This is a serious problem if one wishes to enhance the luminescence from such complexes, however these states do give rise to a rich photochemistry which is a classic example of the importance of SOC and has been extensively studied. Indeed it has long been established that 200 fs after photoexcitation, initially excited into a singlet MLCT, the system populates a lowing lying high-spin (quintet) state [51]. This low-high spin transition is called the of spin crossover (SCO) phenomenon and is common in iron(II)-based molecular complexes. When optically triggered by photoirradiation is known as the lightinduced excited spin state trapping (LIESST). However, while the end result is the same as thermal excitation, what is most surprising is the speed at which this transition (from <sup>1</sup>MLCT-<sup>5</sup>T<sub>2g</sub> state) occurs.


As shown in Figure 5, the transition from LS to HS spin in  $[Fe(bpy)_3]^{2+}$  is accompanied by a substantial elongation of the 6 Fe-N bond lengths. This arises due to the promotion of two electrons from the nonbonding orbitals to the antibonding orbitals. This significant structural change has made this complex popular for X-ray techniques, such as time-resolved X-ray absorption spectroscopy, as the transient XANES and EXAFS features give you direct insight into both the structural and electronic changes during the spin cross-over phenomenon, leading to a detailed understanding of the photoexcited state mechanisms.

Indeed, one of the first picosecond time-resolved studies using optical pump X-ray probe spectroscopy was performed on iron(II)-tris-bipyridine by Chergui and co-workers [52,53]. They probed the structural changes induced by ultrashort pulse excitation with 100 ps temporal resolution, the temporal limitation of 3<sup>rd</sup> generation synchrotrons. They observed population of the quintet high spin state and identified the associated 0.2 Å Fe-N structural relaxation. In a later study, they used the X-ray slicing technique [54] to track the same dynamics with a 200 fs temporal resolution [55]. This time they observed that the quintet state is populated in about 150 fs, and proposed that the long-standing question [56] about the relaxation mechanism, was in fact a simple  ${}^{1}MLCT \rightarrow {}^{3}MLCT \rightarrow {}^{5}T$  cascade from the initially excited state. Due to the temporal resolution and similarity between the character of the <sup>1</sup>MLCT and <sup>3</sup>MLCT states, no intermediate species was directly observed.

However, recently, high-level calculations have cast doubt on this interpretation. Using CASPT2, De Graaf and coworkers [57,58] found that the spin-orbit coupling between the <sup>3</sup>MLCT and <sup>5</sup>T states is small ( $\leq 6$  cm<sup>-1</sup>), as this transition requires the simultaneous movement of two electrons into Fig. III.5: Schematic representation of the potential-energy surfaces of the lowest electronic states of  $[Fe(bpy)_3]^{2+}$  as function of the Fe-N distance and the main experimental findings on the deactivation dynamics. The ligand-field states are labeled according to  $O_h$  symmetry. Figure reproduced from Ref. [58].

Fe  $3d(e_g)$  orbitals, one from the ligand  $\pi^*$  orbital and the second from the Fe  $3d(t_{2g})$  orbital. Therefore, even taking into account the large density of MLCT states, it this coupling appear to be too small for ultrafast intersystem crossing. Alternatively, the co-authors proposed as spin cascade which passes through the metal centred triplet states, which due to the large spin-orbital coupling, small nuclear motion required to reach crossing points contribute the ultrafast mechanism of the deactivation. Gaffney and co-workers [59] recently used this mechanism to fit their transient data arising from femtosecond X-ray emission spectroscopy. They reported that a triplet metal centered state, with a lifetime of 50-100 fs. This however has recently been challenged [60,61] and therefore remains somewhat debated in the literature awaiting even higher temporal resolution (>50 fs).

# Outlook

Due to their significant increase in temporal resolution and per-pulse X-ray flux, X-FELs offer many exciting opportunities for probing the ultrafast dynamics within chemical systems, which is highlighted by the recent work of Gaffney and coworkers <sup>59</sup> on the ultrafast dynamics of [Fe(bpy)<sub>3</sub>]<sup>2+</sup>. However, the number of these studies remains small. This is undoubtedly, in part, a consequence of the technical developments required to address the time and intensity fluctuations of the X-FELs pulses. However, one must also bear in mind that the inherently complicated and detailed nature of the timeresolved X-ray spectra means that for achieving a full understanding of an experimental spectrum, theoretical simulations are essential. Simulations that can describe the ultrafast dynamics or provide a quantitative interpretation of the experimental spectra are a challenge that is presently under much research development.

Therefore I conclude by highlighting that while X-FELs offer many exciting opportunities for probing chemical dynamics, the next five years represents a critical juncture in determining their true worth. Consequently, experimentalists and theoreticians must come together and routinely demonstrate that one can indeed achieve a quantitative description of the ultrafast coupled electronic and nuclear dynamics, beyond what is possible with alternative lab-based sources.

# Summary

- Probing chemical reaction dynamics with the atomic resolution of both time (femtoseconds) and space (Angström) is the central motivation for Chemistry at X-Ray Free Electron Lasers
- The femtosecond time-scale is especially relevant in electronic excited states where non-adiabatic effects are important.
- The excited state dynamics of transition metal complexes is a central focus of research owing to their potential application in a wide variety of devices, such as solar cells and OLEDs.
- Interpreting femtosecond X-ray experiments places a great emphasis on the collaboration between experiment and theory to provide an atomistic description of the processes occurring.
- For molecules in solution the role of the solvent is often very important for determining the outcome of the reaction.

#### References

- [1] A. Zewail, Angew. Chem. Int. Ed. Engl. **39**, 2586 (2000).
- [2] A. Zewail, J. Chem. Phys. **104**, 5660 (2000).
- [3] V. Balzani, P. Ceroni, and A. Juris, *Photochemistry and Photophysics: Concepts, Research, Applications* (John Wiley & Sons, 2014).
- [4] A.L. Linsebigler, G. Lu, and J.T. Yates Jr, Chem Rev 95, 735 (1995).
- [5] B. O'Regan and M. Gratzel, Nature **353**, 737 (1991).
- [6] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, Md. Khaja Nazeeruddin, and M. Gratzel, Nat Chem 6, 242 (2014).
- [7] M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, and H.J. Snaith, Science **338**, 643 (2012).
- [8] M. Wallesch, D. Volz, D.M. Zink, U. Schepers, M. Nieger,
   T. Baumann, and S. Bräse, Chem-Eur J 20, 6578 (2014).

- [9] H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials* (John Wiley & Sons, 2008).
- [10] J.S. DuChene, B.C. Sweeny, A.C. Johnston-Peck, D. Su, E.A. Stach, and W.D. Wei, Angew. Chem. Int. Ed. Engl. n (2014).
- [11] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford University Press, USA, (1995).
- [12] C.J. Milne, T.J. Penfold, and M. Chergui, Coord Chem Rev 277, 44 (2014).
- [13] T.J. Penfold, C.J. Milne, and M. Chergui, Adv. Chem. Phys. 153, 1 (2013).
- [14] B. Curchod, A classical and quantum trajectory description of nonadiabatic dynamics within time-dependent density functional theory. PhD Thesis EPFL (2013).
- [15] G. Worth and L. Cederbaum, Annu Rev Phys Chem 55, 127 (2004).

- [16] M. Chergui, Dalton Trans. 41, 13022 (2012).
- [17] S. Fantacci, E. Ronca, and F. De Angelis, J Phys. Chem. Lett.5, 375 (2014).
- [18] E.Y.-T. Li, T.-Y. Jiang, Y. Chi, and P.-T. Chou, PCCP 16, 26184 (2014).
- [19] M.A. El-Sayed, J. Chem. Phys. **38**, 2834 (1963).
- [20] C.-W. Hsu, C.-C. Lin, M.-W. Chung, Y. Chi, G.-H. Lee, P.-T. Chou, C.-H. Chang, and P.-Y. Chen, J Am Chem Soc 133, 12085 (2011).
- [21] R. Minns, D. Parker, T.J. Penfold, G. Worth, and H. Fielding, Pccp 12, 15607 (2010).
- [22] T.J. Penfold, R. Spesyvtsev, O.M. Kirkby, R.S. Minns,
   D. Parker, H.H. Fielding, and G. Worth, J. Chem. Phys. 137, 204310 (2012).
- [23] D. Parker, R. Minns, T.J. Penfold, G. Worth, and H. Fielding, Chem Phys Lett 469, 43 (2009).
- [24] G. Capano, M. Chergui, U. Rothlisberger, I. Tavernelli, and T.J. Penfold, J Phys. Chem. A **118**, 9861 (2014).
- [25] V. Pham, T.J. Penfold, R. van der Veen, F.A. Lima, A. el Nahhas, S.L. Johnson, P. Beaud, R. Abela, C. Bressler, and I. Tavernelli, J Am Chem Soc 133, 12740 (2011).
- [26] T.J. Penfold, C.J. Milne, I. Tavernelli, and M. Chergui, Pure Appl. Chem. 85, 53 (2012).
- [27] T.J. Penfold, I. Tavernelli, M. Doemer, R. Abela, U.Rothlisberger, and M. Chergui, Chem Phys **410**, 25 (2013).
- [28] I. Tavernelli, B. Curchod, and U. Rothlisberger, Chem Phys 391, 101 (2011).
- [29] B. Curchod, U. Rothlisberger, and I. Tavernelli, Chemphyschem 14, 1314 (2013).
- [30] M. Shirom and G. Stein, The Journal of Chemical Physics 55, 3372 (1971).
- [31] M. Shirom and G. Stein, The Journal of Chemical Physics 55, 3379 (1971).
- [32] M. Reinhard, T.J. Penfold, F.A. Lima, J. Rittmann, M.H.
   Rittmann-Frank, R. Abela, I. Tavernelli, U. Rothlisberger, C.J.
   Milne, and M. Chergui, Struct. Dyn. 1, 024901 (2014).
- [33] Journal of Physical Chemistry A, **118**, 9411–9418. (2014).
- [34] J. Stöhr, NEXAFS Spectroscopy, 1st ed. Springer (2003).
- [35] J. Rehr, Rev. Mod. Phys. 72, 621 (2000).
- [36] C. Bressler and M. Chergui, Chem Rev **104**, 1781 (2004).
- [37] C. Bressler and M. Chergui, Annu Rev Phys Chem 61, 263 (2010).
- [38] L.J.P. Ament, M. van Veenendaal, T.P. Devereaux, J.P. Hill, and J. van den Brink, Rev. Mod. Phys. 83, 705 (2011).
- [39] A. Kotani and S. Shin, Rev. Mod. Phys. 73, 203 (2001).
- [40] P. Glatzel and U. Bergmann, Coordin Chem Rev 249, 65 (2005).
- [41] F.M.F. de Groot and A. Kotani, Core Level Spectroscopy of Solids CRC Press (2008).
- [42] F.M.F. de Groot, Chem Rev **101**, 1779 (2001).

- [43] J. Szlachetko, C.J. Milne, J. Hoszowska, J.-C. Dousse,
  W. Błachucki, J. Sa, Y. Kayser, M. Messerschmidt, R. Abela,
  S. Boutet, C. David, G. Williams, M. Pajek, B.D. Patterson,
  G. Smolentsev, J.A. van Bokhoven, and M. Nachtegaal,
  Struct. Dyn. 1, 021101 (2014).
- [44] **130**, 3413 (2008).
- [45] M. Gratzel, Nature **414**, 338 (2001).
- [46] E. Baggaley, J.A. Weinstein, and J.A. Williams, Coordin Chem Rev 256, 1762 (2012).
- [47] N.H. Damrauer, Science **275**, 54 (1997).
- [48] A.T. Yeh, Science **289**, 935 (2000).
- [49] A.C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, J Am Chem Soc **124**, 8398 (2002).
- [50] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.* 84, 85 (1988).
- [51] A. Cannizzo, C.J. Milne, C. Consani, W. Gawelda, C. Bressler, F. van Mourik, and M. Chergui, Coordin Chem Rev 254, 2677 (2010).
- [52] W. Gawelda, V. Pham, M. Benfatto, Y. Zaushitsyn, M. Kaiser,
   D. Grolimund, S. Johnson, R. Abela, A. Hauser, C. Bressler,
   and M. Chergui, Phys Rev Lett **98**, 057401 (2007).
- [53] W. Gawelda, V. Pham, R. van der Veen, D. Grolimund,R. Abela, M. Chergui, and C. Bressler, J. Chem. Phys. **130**, 124520 (2009).
- [54] R.W. Schoenlein, S. Chattopadhyay, H. Chong, T.E. Glover,
   P.A. Heimann, C.V. Shank, A.A. Zholents, and M.S.
   Zolotorev, Science 287, 2237 (2000).
- [55] C. Bressler, C.J. Milne, V. Pham, A. ElNahhas, R. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D. Grolimund, M. Kaiser, C. Borca, G. Ingold, R. Abela, and M. Chergui, Science **323**, 489 (2009).
- [56] A. Hauser, Spin Crossover in Transition Metal Compounds II, Springer (2004).
- [57] C. de Graaf and C. Sousa, Chem-Eur J 16, 4550 (2010).
- [58] C. Sousa, C. de Graaf, A. Rudavskyi, R. Broer, J. Tatchen,M. Etinski, and C.M. Marian, Chem-Eur J 19, 17541 (2013).
- [59] W. Zhang, R. Alonso-Mori, U. Bergmann, C. Bressler,
  M. Chollet, A. Galler, W. Gawelda, R.G. Hadt, R.W. Hartsock,
  T. Kroll, K.S. Kjaer, K. Kubiček, H.T. Lemke, H.W. Liang,
  D.A. Meyer, M.M. Nielsen, C. Purser, J.S. Robinson,
  E. Solomon, Z. Sun, D. Sokaras, T.B. van Driel, G. Vanko,
  T.-C. Weng, D. Zhu, and K.J. Gaffney, Nature **509**, 345 (2014).
- [60] O. Vendrell, J. Küpper, M. Wolf, H.N. Chapman, M. Chergui,
  K. Reid, K. von Haeften, R. Moshammer, G. Williams,
  A. Tehlar, G. Dixit, H.J. Wörner, J. Underwood, J. Marangos,
  M. Woerner, C. Bressler, M. Minitti, A. Kirrander, C. Vozzi,
  and D. Rolles, Faraday Discuss **171**, 145 (2014).
- [61] M. Chergui, Faraday Discuss **171**, 11 (2014).

# IV. Surface chemistry

Martin Beye, Helmholtz-Zentrum Berlin

X-ray free-electron lasers are well-suited to study dynamics in surface chemistry, since they allow one to resonantly address the active atoms and provide sufficient intensity to characterize dilute systems with femtosecond time resolution.

- Introduction
- Heterogeneous catalysis at surfaces
- Time-resolved X-ray emission spectroscopy
- Outlook

Surface chemistry is relevant for the majority of industrial chemical processes, with future applications towards solar energy conversion, renewable fuels and energy storage. A full mechanistic understanding of the underlying processes can be used as input to improve the industrial processes. Such an understanding can be gained through time-resolved spectroscopy studies at free-electron lasers together with a collaborative effort from many disciplines. First results demonstrate the applicability of this approach.

# Introduction

Surface Chemistry asks questions about the evolution of chemical reactions on surfaces and how the reaction parameters can be tuned to optimize the outcome of the reaction. Typically, two different parameters are addressed: Firstly, the required amount of energy and chemicals should be kept as low as possible, thus addressing the *efficiency* of the reaction. And secondly, only the desired products should be produced, rather than other species that either inhibit the reaction or contaminate the product. This addresses the *selectivity* of the reaction. Processes in heterogeneous catalysis are often surface chemical processes, where the surface acts as a passive catalyst, which drives the reaction with improved efficiency and selectivity. In such processes, the big challenge is to identify the best catalyst for a given reaction.

Theoretical approaches nowadays can simulate the relevant electronic structure of the catalyst together with the reactants. From these simulations, the free energies can be extracted for several configurations of the involved atoms and one can thus estimate how the reactants evolve into the product, what energies are needed for the process and what concurrent processes are present. Thus, theory in principle can deliver a complete picture of surface chemical reactions, and often theorists are able to benchmark a whole series of catalysts with appropriately tuned compositions, to find the optimum for reaction efficiency and selectivity. However, typical uncertainties of such calculations can be on the order of 0.3 eV for each of the steps in a reaction. Converted into a temperature, this would amount to errors on the order of 3000 K (although it is hoped that most errors are systematic and thus cancel each other when comparing relative energies). Isolated theoretical estimates are thus often insufficient for a successful design of a catalyst and a full understanding of surface chemical reactions.

The experimental access to surface chemical reactions is not easy. One fundamental reason is that the actual reaction on the surface, the breaking and formation of chemical bonds, is an electronic process and thus proceeds on the femtosecond timescale. Typical distances over which molecules and the surface interact are also limited to the subnanometer scale, thus the molecules can enter and leave



Fig. IV.1: CO desorbs from a surface after laser excitation (from Greg Stewart, SLAC National Accelerator Center).

the reaction site extremely quickly. Furthermore, these fast dynamics happen in the presence of an immense inactive background: the rest of the surface on the one hand and the rest of the molecules (reactants and products) on the other hand. An extremely selective experimental tool is needed to single out solely the reaction centers.

Since such a general tool does not exist, one limits the experimental studies to a set of model reactions under welldefined conditions and uses these to improve the theoretical models that then in turn can be extrapolated to more complex situations. Although attempts are being made to generalize the experimental tools, we will describe here the model system approach. One of the preconditions for the experiment is that one starts with a well-defined and wellprepared surface. Carefully oriented single crystals of pure metals are often used and cleaned such that no contaminant atoms are present. Most experiments are also conducted under ultra-high vacuum conditions to prevent contamination of the surface with undesired atoms or molecules. Although sometimes these conditions prevent the study of the full reaction mechanism (for example, an oxygen partial pressure of several Torr may be needed to activate oxygen for the reaction), the well-controlled conditions allow for a direct comparison with theory. The inability to study reactions under atmospheric pressure is often called the "pressure gap".

Under these well-controlled conditions, many molecules on a variety of surfaces have been prepared and often been fully analyzed with X-ray spectroscopies, to determine the spatial arrangements, the bonding configuration and the electronic structure under static conditions. On the other hand, a set of methods has been developed with ultrafast laser pulses to study surface chemistry on the femtosecond time scale and thus extract reaction mechanisms directly in the time domain. Here, the ultrashort laser pulse triggers the reaction, not through a direct electronic stimulation of the reaction on the surface (photoexcitation), since the absorption of the laser pulse at the surface adsorbed molecules is much too small, but through the accompanying ultrafast rise in the temperature (electronic and phononic) of the surface material [1]. This temperature rise then provides the energy for the adsorbed molecules to overcome reaction barriers and form the products. Since the trigger pulse homogeneously pumps the probed region, all excited molecules in this region proceed synchronously through the reaction steps. With an ultrashort, highly selective probe pulse, the evolution of the electronic structure can then be analyzed in the time domain for each of the reaction steps, and a full experimental reaction mechanism can be extracted.

This probe pulse is nowadays provided by free-electron lasers, thus allowing the combination of the superior analysis quality of X-rays with ultrashort methods to study dynamics in the time domain. Applied to surface chemical dynamics, this combination has been shown to open novel opportunities in the understanding of surface chemistry - a crucial step in the design of optimized catalysts.

#### Catalysis: social and economic importance

Approximately 85% of all industrially relevant chemical processes involve catalysis, according to estimates from 2009. The 2013 market for catalysts exceeded 20 Billion US-\$ per year, and it is estimated that the value generated through catalysts is more than 100-times larger.

While catalysis is certainly highly important for producing specialized chemicals, two application fields are of hallmark importance: On one hand, most fertilizers are produced through catalytic processes based on the Haber-Bosch cycle. Thus catalysis insures that valuable farmland can be optimally used to feed the world's population. On the other hand, every molecule in modern transportation fuels has been in contact with a solid catalyst. The improvement of catalysts and the large-scale application of novel catalysts in artificial photosynthesis for the conversion of

sunlight into fuel is therefore central to a sustainable energy future. [2]



Fig. IV.i1: Use of catalysis in industrial chemical processes [2].



# Heterogeneous catalysis at surfaces

The best-studied example of a catalytic reaction on a surface, and one which is a very illustrative, is the oxidation of carbon monoxide to carbon dioxide on a metal surface. This is the main reaction that happens in the catalytic converter of a car, converting poisonous CO in the exhaust gases to harmless CO<sub>2</sub>. Gerhard Ertl and his co-workers described the fundamental steps of the reaction mechanism, and these findings were one of the reasons that he won the Noble prize in chemistry in 2007 [3].

Ertl studied how the CO oxidation proceeds on platinum and discovered the following general steps:

- First, the reactants, gaseous CO and O<sub>2</sub> impinge on the surface, enabling the subsequent reactions.
- CO becomes chemisorbed on the surface in an upright configuration, where the carbon atom points towards the surface and the oxygen points away.
- The oxygen molecule splits into its constituent atoms, which then move separate from one another on the surface.
- Another CO molecule and the atomic oxygen get into close contact with one another on the surface, triggering the formation of a chemical bond.
- The newly-formed CO<sub>2</sub> molecule leaves the surface, freeing up adsorption sites for further reactants.

The catalytic surface here fulfills several functions: It removes translational energy from the molecules so that they can actually interact without just scattering off of each other, it modifies the electronic structure of CO such that states become available to allow interaction with the oxygen atom and it splits the oxygen molecule into its constituent atoms and separates them spatially. The energetic position of electronic states of the catalytic surface relative to the Fermi level and to molecular levels plays a crucial role in determining the bond strengths of atoms and molecules to the surface. It has been shown that in particular the position of the rather localized band of d-symmetric metal states is largely responsible for the strength of adsorption of molecules to a metal surface [4], and it is this bond strength that determines the catalytic function of the surface. If it is larger than the translational energies of the adsorbates, they will preferentially bind to the surface instead of bouncing off. If it is

Fig. IV.2: Fundamental steps during CO oxidation [3]:

- 1. Molecules from the gas phase encounter the surface.
- 2. CO adsorbs in the upright configuration, oxygen splits into atoms.
- 3. With close contact between oxygen and CO, a chemical bond is formed.
- 4. The product  $CO_2$  desorbs into the gas phase.

large enough, it can sufficiently modify the electronic structure of CO. But, most importantly, it has to be large enough to overcome the internal bond of the oxygen molecule to split the oxygen molecule into atoms. On the other hand, the chemisorption energy (the surface bond strength) has to be small enough such that the bond formed between CO and atomic oxygen is stronger than the binding to the surface. If this is not the case, the bond will not be formed. Furthermore, the chemisorption energy of the product of the reaction has to be weak enough so that the product molecules can readily leave into the gas phase. Otherwise, the product will quickly block all reactive sites on the catalyst surface and the reaction will cease.

This delicate balance of a catalyst-reactant interaction which is strong enough, but not too strong, is what is aimed for when novel catalysts are explored. Different materials will have varying bond strengths, which will in turn also depend on temperature and other parameters. For example, some elements like platinum, rhodium and palladium have been shown to have the right energy balance to catalyze the CO oxidation reaction. Platinum, as the most abundant of those metals, is used in the catalytic converters of cars - another important aspect in the search for industrially relevant catalysts is not only the ability to catalyze the reaction efficiently, they also have to be plentiful and inexpensive. On ruthenium, on the other hand, the CO oxidation reaction does not proceed under equilibrium conditions since the surface bond between ruthenium and oxygen is so strong that no bond can be formed between oxygen and CO. However, it has been shown, that an ultrafast laser pulse can trigger this reaction: through the created temperature rise of the electronic system of the catalyst, the bond to the oxygen is selectively weakened, and oxygen can react with CO before the phononic temperature of the catalyst rises so high that CO desorbs [5].

# Time-resolved X-ray emission spectroscopy

Time-resolved X-ray emission spectroscopy is a highly selective spectroscopic tool which provides a wealth of information about the electronic structure of the molecular systems studied. X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS) are two flavors of the same spectroscopic tool: Generally, a specific core level of an element is resonantly addressed by choosing the appropriate photon energy for excitation. Since the core level binding energies for different elements are distinctly different and, furthermore, can be different for the same element in different chemical surroundings, selectivity to a distinct atomic site is built into the process. A photon is absorbed at the selected atom, and the core electron is transferred to an unoccupied state, leaving a core hole behind. In the soft Xray range, typically 1% (the "fluorescence yield") of the excited core holes decay by emitting a photon, when an electron from an occupied state fills the core hole; the energy of the emitted photon encodes the energy of the occupied state.

Such an experiment allows one to extract several types of important information:

- The energies of the emitted photons correspond to the energetic structure of the occupied electronic states.
- From the intensity of the emitted photons at a given emission energy, one can extract information on the density of states.
- The total emitted intensity at a given excitation energy is, under certain conditions, proportional to the creation probability of core holes – the absorption cross-section.

In a typical XES or RIXS experiment, the energy of the incoming photons is scanned across the core level absorption resonance, while a spectrometer detects in parallel a range of emission energies. Then, the emission spectra are sorted according to incoming photon energy and compiled into a "RIXS map". The projections of this map are then related to the occupied density of states (projection on the emission energy axis) and the unoccupied density of states (projection on the incoming photon energy axis). The process involves dipole transitions, and the appropriate selection rule,  $\Delta l =$ 





±1, must be obeyed. Thus, XES is sensitive to *s*- and *d*-symmetric states when observing decays into a *p*-symmetric core hole, while *p*-symmetric states are analyzed when an s-symmetric core hole is excited. Furthermore, a dipole does not radiate in the direction of its oscillation axis. For the example of oxygen *1s* core holes in the upright-oriented CO on a surface, XES will not see emission from the  $\sigma$  orbit-

als (the orbitals that are cylindrically-symmetric about the bonding axis), when the spectrometer is placed along the surface normal. Only  $\pi$ -orbitals are visible. When placing the spectrometer at a grazing angle to the surface, both  $\pi$ - and  $\sigma$ -orbitals contribute equally to the signal. In this way, one can extract the spatial symmetry of orbitals by carefully choosing the experimental geometry [6].

## Entropy and Energy: The precursor state of CO

Even when a catalyst is found that enables a reaction (the reaction pathway is energetically possible, i.e. in each step energy is gained, the pathway is completely "downhill"), there is still a question about how fast the reaction proceeds. The kinetics of a chemical reaction is often determined by how fast the reactants adsorb on the catalyst and are transferred into an active state. Thus, the specifics of adsorption are crucial.

For CO on ruthenium, it has been speculated from kinetic considerations that in addition to the strongly-bound adsorption state with the CO standing upright on the surface, there should be another "precursor state" that is weakly bound. This state was believed to capture the molecule efficiently on the surface while keeping it mobile enough to be transferred to the reactive sites. Most calculations of the binding energy of the molecule to the surface failed to find this state. Only with the inclusion of van-der-Waals forces into advanced density-functional calculations, a small lowering of the potential energy at large surface-molecule distances was found. But this lowering turned out to be sufficient to form the anticipated precursor state.

To fully understand how an ensemble of molecules will evolve on average, it is not sufficient to calculate energies only; entropy, the availability of configurations for a given state, also has to be included. In the CO on ruthenium example, the precursor state allows for all relative orientations of the molecule towards the surface, while the chemisorption geometry is limited to the upright configuration. Therefore, the entropy of the precursor state is high compared to that of the chemisorption state, and it turns



Fig. IV.12: Thermal evolution of the potential of mean force. The "potential of mean force" is similar to a free energy, although one coordinate is excluded from the degrees of freedom in the entropy to display the evolution as a function of distance from the surface. The curves sketch how the potential evolves from OK (blue) via 300 K to around 1500 K (red). The low entropy of the chemisorbed state makes it rise with temperature, while the high entropy precursor state stays constant. In between an entropic barrier evolves [7].

out that at high temperatures, the precursor state actually forms a free energy well which is as deep as that for the chemisorbed state. Therefore, the ensemble of molecules will populate the precursor state with the same probability as the chemisorption state. When the sample is cooled down again, the chemisorption state again becomes favorable. This occurrence of a second bonding state is enabled by the small lowering of the energy, but its occupation becomes probable at higher temperature due to its high entropy [7]. The distinction between RIXS and XES is typically made after the measurements have been completed: if the observed features disperse (change in energy) together with the excitation energy, one speaks of RIXS. This is a signature of a localized system, where energy conservation has to be fulfilled inside the observed system and thus the emission energy of a feature changes with the excitation energy. This is typically not observed for adsorbates on a metal surface. When the observed features instead remain fixed at constant emission energy, one talks about XES. The additional energy is taken up by the continuum of states in the metal, and the core hole is well screened. This is what is observed with strongly coupled adsorbates on a metal surface.

For time-resolved spectroscopies, a pump laser is added. The pump pulse and the probing X-ray pulse have to be short enough to resolve the fast electron dynamics. The relative pump-probe delay is scanned, and for each delay a RIXS map is recorded. RIXS and XES are based on photons and are thus not influenced by the strong electromagnetic fields generated by the pump laser.

RIXS and XES require a lot of photons, since the fluorescence yield is rather low and the decaying photons are generally emitted isotropically, while the angular acceptance of highresolution spectrometers is small. In particular, when applied to the very dilute densities of adsorbates on surfaces, a high photon flux is needed, and only free-electron lasers are currently intense enough for studies with time-resolution. But their high spectroscopic selectivity and information content make them ideal tools for surface chemical problems.

# Outlook

Since the introduction of the X-ray free-electron laser, e.g., the Linac Coherent Light Source (LCLS) at Stanford, which provides high enough photon energies to resonantly address the core levels of the most relevant elements for chemistry (carbon, nitrogen and oxygen), several experiments have addressed the dynamics of surface chemical reactions. An example is the direct experimental observation of the abovementioned precursor state to desorption of CO on ruthenium [7,8]. Although successful, the experimental realization was difficult and required careful consideration of the experimental geometry, pulse repetition rates, and pump and probe fluence levels. One of the big challenges is to drive the reaction efficiently enough to observe large changes in the electronic structure of the majority of the reactants involved while not destroying the surface. Since the signal levels are low, it has to be ensured that the reaction can be driven continuously during many hours of beam time. A chemical reaction is a process that does not reverse itself before the next excitation pulse, so that advanced scanning schemes, in connection with appropriate repetition rates, shutter operation and surface restoration through in-situ preparation, have to be applied.

A full understanding of the high complexity of a chemical reaction on a surface can only be obtained if use is made of all the available tools: During the preparation phase of an FEL experiment, it is important to optimize the continuous operation parameters, usually in a pump-laser only laboratory. A mass-spectrometer is used to check for the optimal reaction conditions. Furthermore, steady-state synchrotron experiments are necessary in order to characterize the expected spectra and the possible changes which can be observed. Such experiments are further used for optimizing the geometry of the setup and the excitation energy ranges. The high-dimensional data sets (2D-RIXS maps as a function of pump-probe delay and possibly other variables) need to be carefully analyzed, and the changes in the electronic structure have to be extracted. By comparison with measurements on model compounds, a first idea of the underlying geometrical changes can be gained, but only through the application of multi-step theoretical modelling. This begins with calculations of potential energy surfaces and the relevant entropies, followed by molecular dynamics simulations, where geometry snapshots are used as input for spectrum calculations that in turn can be compared to the experiment. In this way, the full picture of the dynamics can be extracted and novel insights can be generated.

Only with this concerted effort of various disciplines, can such studies have an impact on our ability to tailor catalysts for industrial processes. Nevertheless, the high relevance of heterogeneous catalysis for modern societies justifies the effort.

# Summary

- Surface chemistry is at the heart of heterogeneous catalysis, the dominant process in modern industrial chemistry.
- Important contributions are expected in the fields of solar energy conversion, renewable fuels for transportation and energy storage.
- Industrial improvements will be triggered through largescale theoretical modeling that has to be developed in close connection with experimental verifications.
- X-ray free-electron lasers are ideal tools to analyze the dynamics of surface chemical reactions, and the first results from fundamental studies are now becoming available.
- A full understanding can only be gained through a concerted effort of experiments in different fields (e.g. surface science, optical lasers, synchrotrons, FELs) and multi-scale theory (e.g. potential energy surfaces, molecular dynamics, spectrum simulations).

## References

- [1] C Frischkorn, & M Wolf, Chem Rev 106, 4207 (2006).
- [2] KP de Jong (ed.), Synthesis of Solid Catalysts, Wiley-VCH (2011).
- [3] G Ertl, Angew Chem Int Edit 47, 3524 (2008).
- [4] B Hammer, & JK Norskov, Adv Catal 45, 71 (2000).
- [5] M Bonn, *et al.*, Science 285, 1042 (1999).
- [6] A Föhlisch, *et al.*, Phys. Rev. B 61, 16229 (2000).
- [7] M Dell'Angela, et al., Science 339, 1302 (2013).
- [8] M Beye, et al., Phys. Rev. Lett. 110, 186101 (2013).

# V. XFEL-based serial protein crystallography

Karol Nass, MPIMF Heidelberg

Intense XFEL pulses allow high-resolution structure determination on micrometer-sized protein crystals, and the short pulse duration permits data collection from undamaged material, prior to the beam-induced disintegration of the sample.

- Introduction
- Serial femtosecond crystallography and ultrafast radiation damage processes
- Sample preparation and delivery
- Data collection and analysis
- Solving the phase problem
- Outlook

The primary method for protein structure determination is X-ray crystallography. To date almost 95,000 protein structures that have been deposited to the PDB data bank were solved using this method. This accounts for almost 90% of all protein structures in PDB, solved by all available methods. However, the X-ray crystallography is limited by the requirement of growing sufficiently large crystals, which can be difficult to obtain, as well as by radiation damage, that causes severe problems during data collection, especially when small crystals are used. Fortunately, the peak brightness of X-ray free-electron lasers (X-FELs) is a billion times larger than the brightest synchrotron beam available today, and XFELs produce femtosecond pulses that outrun most radiation damage processes, allowing the determination of undamaged structures even from microscopic crystals. Typically, micro-crystals are exposed to X-FEL pulses in random orientations in a serial approach at room temperature. Each diffraction image requires a new crystal, since they are destroyed upon a single exposure. New sample delivery techniques that replenish crystals continuously, as well as serial data analysis methods, are described. Time scales of radiation damage processes and proposed new phasing methods using high intensity beams or two color X-ray pulses are also presented.

# Introduction

The emerging technique of serial femtosecond crystallography (SFX) holds the promise to be a revolutionary innovation in structural biology [1]. In SFX diffraction, scattering data from biological macromolecules are collected using very intense, femtosecond X-ray pulses before most damage processes take place [4, 5]. In this 'diffraction-before-destruction' approach, [2, 6-8] protein crystals smaller (microor nano-sized) than those used for conventional macromolecular crystallography (MX) at synchrotrons can be used to record damage-free diffraction data. Typically, at modern synchrotron beamlines, crystals tens of microns in size are used successfully, whereas data collection from smaller crystals is often difficult or impossible due to inherent problems of radiation damage, even at cryogenic temperatures [9, 10]. Unfortunately, many macromolecules fail to form large crystals (e.g., membrane proteins). However, they often form "showers" of micrometer-sized crystals that may be used to obtain useful diffraction signals at X-FEL sources. Several experiments have already demonstrated the potential of this new method for room temperature high-resolution structure determination [10, 12-15].

Any sample irradiated by the ultra-intense X-ray pulse will be ionized, and as a result of ionization, it will be destroyed. The time scale on which this process occurs is important for obtaining interpretable diffraction. The X-ray pulse must be short enough such that the entire pulse passes through the sample before major rearrangements of the atomic positions and electronic damage takes place. As a consequence, a new crystal has to be supplied for the next pulse. Therefore, crystals must be replaced with the X-ray repetition rate (120 Hz at the Linac Coherent Light Source (LCLS) and diffraction patterns need to be recorded in a serial fashion, each pattern from a new crystal. The technology currently used for serial delivery of protein crystals to the X-FEL beam includes various forms of liquid jets, for example, low [17-19] or high [10, 16] viscosity liquid jets, which keep the crystals solvated and at room temperature.

Pulse durations on the order of femtoseconds have implications for the acquisition of diffraction data. It is not possible to rotate crystals during exposures to collect conventional oscillation or rotation data that yields fully integrated reflections. Instead, only partial reflections are recorded from single crystals in random orientations. Therefore a large number of snapshot diffraction patterns must be collected,

## Coherent diffraction features in XFEL crystallography

X-ray pulses from an FEL have a very high degree of transverse coherence. In combination with the finite, small sizes of the crystals used in SFX coherent diffraction, this causes features to appear between Bragg diffraction peaks. Figure V.i1 shows a low-angle diffraction pattern recorded from a photosystem I nanocrystal with inter-Bragg fringes [1]. The scattering between Bragg reflections could be used to aid in the solution of the phase problem by oversampling the continuous molecular transform at half Bragg spacing, which determines the autocorrelation of the molecular density. Then iterative phasing methods [3] could be used to solve the phase problem and recover an image of the molecule [11]. An alternative but related approach to exploiting coherent features in X-FEL crystallography to resolve the phase problem relies on measurements of intensity gradients near the Bragg reflections. Difficulties may arise from surface truncation of the unit cells, in particular for multi-molecule cells, as discussed by [20]. The issue of partial unit cells has also been discussed by [28].



Fig. V.i1: A SFX diffraction snapshot of a nanocrystal of photosystem I, showing coherent fringes between Bragg diffraction peaks [1].

indexed and then merged in order to obtain a data set of fully integrated reflections. The resulting large amounts of data must be efficiently analyzed using specially developed software [21-25].

# Serial femtosecond crystallography and ultrafast damage processes

X-ray free-electron lasers produce very bright and extremely short femtosecond coherent X-ray pulses with adjustable photon energy [26, 27]. The peak brilliance of an X-FEL beam exceeds that of the most advanced 3rd generation synchrotrons by many orders of magnitude. Such unique properties of the X-ray beam create new opportunities for a variety of research fields, ranging from material science to biology and medicine. One of the largest successes of currently operating X-FEL sources is serial femtosecond crystallography (SFX). For many macromolecules and complexes, growing large, well-ordered crystals is very difficult if not impossible. It is here that X-FELs make an impact in crystallography, by allowing the use of crystals which are smaller than those typically used at synchrotron sources for data collection. X-FELs take a step beyond the conventional radiation damage limits in protein crystallography and enable studies of irreversible reactions at previously inaccessible time scales, providing essential information about the mechanisms of protein function.

Although the energy of an X-FEL pulse is so high that it destroys any material with which it interacts, the pulse duration is so brief that it traverses the sample before the appearance of significant radiation damage initiated by photoionization [4, 6, 7]. Therefore, diffraction snapshots can be recorded from undamaged crystals at room temperature. After exposure, the crystal is destroyed, and a new one must be supplied at the repetition rate of the FEL laser. Currently, the highest repetition rate at which the data is being collected is 120 Hz. Such serial data collection scheme is facilitated by the use of liquid jet sample injection methods that rely on a continuous flow of the sample that intersects the X-FEL beam. The sample flows through a capillary ending with a Gas Dynamic Virtual Nozzle (GDVN), which focuses the low viscosity liquid suspension with crystals down to a few microns in diameter [17]. In the case of a high-viscosity sample carrier, such as lipidic cubic phase (LCP) or grease [29], a high viscosity extrusion (HVE) injector is used [10, 16].

A schematic representation of a typical experimental setup for SFX experiments is shown in Fig. V.1. X-FEL pulses intersect the stream of crystals in a jet created by a GDVN or HVE injector. Experiments are typically performed in vacuum. The probability of hitting a crystal is given by the X-FEL repetition rate, the crystal concentration and the diameters of the X-ray beam and sample stream. Snapshot diffraction patterns are recorded on a 2D detector that operates at the frame rate of the X-FEL beam.



Fig. V.1: Schematic of the experimental setup for SFX. X-ray pulses traverse the stream of crystals delivered in the liquid jet. Snapshot diffraction patterns are recorded on the 2D detector located downstream of the interaction region. From [12]. Lipidic Cubic Phase (LCP), see *e.g.* [30] for a recent review, has shown great potential as a crystallization medium for membrane proteins, and possibly also soluble proteins [31]. The LCP crystallization method was used to obtain the first high-resolution structure of bacteriorhodopsin [32]. Since then, simplified protocols have been established, making LCP crystallization a popular method for delivering highresolution structures of membrane proteins [8]. Crystals grown in LCP are very well suited for serial data collection at X-FEL sources, because the entire crystallization setup can be directly transferred to the high viscosity extrusion injector and delivered to the X-FEL beam at very low flow rate, reducing sample consumption to a minimum.

Since the beginning, protein crystallography has suffered from the radiation damage caused by the ionizing X-rays. Cryo-cooling techniques slow down the diffusion of free radicals, but data collection from small crystals is very difficult if not impossible [9]. The femtosecond-duration X-ray pulses used for SFX provide a way to overcome the problem of radiation damage in crystallography, by outrunning the diffusion of free radicals and the disintegration of the crystal after extensive ionization caused by the high-energy pulse [1, 5, 33]. This "diffraction-before-destruction" approach seems to be valid for doses of 30-150 MGy/crystal [12, 14, 34], however, effects of global radiation damage are observed in the case of higher doses and long pulses [6, 7]. Both studies showed a decrease of the high-resolution diffraction signal with increasing pulse lengths.

By using sufficiently short pulses, the effects of disintegration of the crystal due to Coulomb repulsion of ions (global radiation damage) can be outrun. However, the almost instantaneous photoionization and subsequent very fast Auger decay (10 fs for C, 1.3 fs for S and 0.55 fs for Fe atoms) and impact ionization cascades (10 fs) caused by unbound photo- and Auger-electrons that do not leave the sample will cause modifications to the atomic scattering form factor to an extent that depends on the atomic number. Due to differences in absorption cross-sections, heavier elements absorb photons (and are hit by unbound electrons) more efficiently than lighter elements and therefore will be ionized to a higher degree (localized radiation damage). At the higher doses necessary for obtaining reasonable scattering signals in single-molecule imaging experiments, where every

atom in a typical protein molecule will be photoionized at least once [5], electronic radiation damage could cause problems in retrieving an image of the undamaged molecule. Radiation damage is initiated by inner-shell photoabsorption. Because of the differences between scattering and absorption cross-sections, for every scattered photon that contributes to the diffraction pattern, typically many more photons are absorbed and deposit their energy in the sample. The excited atoms quickly relax through non-radiative Auger decay, which is more probable than radiative decay even for Fe. Auger and photoelectrons generate electron cascades through electron impact ionization, leading to the emission of secondary electrons, which further ionize the sample. A recent experiment to investigate the occurrence of localized electronic and structural damage in SFX was performed at the LCLS using ferredoxin micro-crystals as the model system and the highest available X-FEL beam intensity. Plasma code simulations [35] performed under the same conditions as the experiment showed that all atoms in a sample, of protein-like composition and with selected heavier elements to imitate ferredoxin's [4Fe-4S] clusters, rapidly lose electrons within the first 10 fs of the pulse and reach a high ionization state by the end of a 80 fs pulse. Additionally, experimental data and MD simulations revealed not only preferential ionization of Fe atoms but also correlated atomic displacements of the S atoms of the two [4Fe-4S] clusters [36, 37].

# Sample preparation and delivery

Macromolecular crystallography at conventional synchrotron-based X-ray sources requires growing large single crystals. Often many hundreds or thousands of crystallization conditions need to be tested in order to grow sufficiently large and well-diffracting crystals. Frequently, during initial screens intended to identify suitable crystallization conditions for growing large crystals, microcrystalline showers are observed, which form the starting point of an optimization protocol to obtain large single crystals. With the advent of serial femtosecond crystallography, microcrystals have become useful for data collection, thanks to the very intense and ultra-short X-ray pulses generated by X-FELs that outrun



Fig. V.2: A Hamilton syringe containing 60  $\mu$ l of precipitant and 5  $\mu$ l of protein-laden LCP, with microcrystals growing in it, at two zoom levels. The highest-zoom photograph is taken with a stereo microscope equipped with cross-polarizers. Microcrystals are visible as bright dense dots inside a "snakelike" LCP string. Adapted from [38].

most of the radiation damage processes and permit acquisition of data with sufficient signal to noise ratio from such small crystals. In order to understand the necessary conditions to obtain showers of microcrystals for SFX experiments, it is useful to look at a crystallization phase diagram. Nucleation occurs in a supersaturated phase, while crystal growth takes place in the metastable phase. For microcrystal growth, a high degree of supersaturation needs to be achieved. Since sufficient nucleation can be difficult to achieve, it may be useful to use microseeding techniques, which may also increase the likelihood for the growth of isomorphous microcrystals.

When an optimized crystallization condition for growing large crystals already exists, it is very convenient to use the batch method for microcrystallization. With this method, the amount of crystal suspension can be easily scaled from micro- to millilitres, as is usually required for a full data set. Typically, by optimizing the ratio of the initial protein and precipitant concentrations, as well as the temperature and pH, a controlled crystal size distribution can be obtained. Reasonable amounts of microcrystalline material can also be obtained using "sitting drop" setups.

In the case of LCP, crystallization setups can be scaled up by injecting the protein-laden LCP as a thin column into a Hamilton syringe filled with precipitant solution, (see Fig. V.2 and and reference [14]). This has the advantage of providing a convenient means to transfer the microcrystals into the injector sample reservoir.

Protein crystals are very sensitive to mechanical stress, dehydration and changes in the environment such as temperature, pH and concentration of components in the mother

#### Lipidic cubic phase crystal growth and delivery

Lipidic cubic phase (LCP) crystallization has been successfully used for obtaining high-resolution structures of a variety of membrane proteins, including ion channels, transporters and enzymes, as well as G-protein coupled receptors (GPCRs) [2] [8]. This method leads to highly-ordered crystals that are, however, often limited in size. The small crystal size imposes significant challenges at various steps in standard crystallographic protocols, including detecting and harvesting crystals, as well as in collecting high-resolution diffraction data and overcoming radiation damage. SFX offers a relatively easy protocol for data collection from small microcrystals of membrane proteins grown in LCP. The whole LCP crystallization setup can be directly transferred to the high viscosity injector [10] [16] and injected to the X-FEL beam. By adjusting the flow rate of the sample stream to 3-300 nl

min<sup>-1</sup>, a full data set can be obtained from a much smaller sample volume (~30  $\mu$ l of LCP or ~300  $\mu$ g of protein) than is the case when using a low viscosity liquid jet injector (GDVN), whose flow rates are typically on the order of 10-20  $\mu$ l min<sup>-1</sup>. The LCP approach provides a high hit rate, low protein consumption and the prospect of an integrated crystal growth medium. liquor in which they are grown. Thus, sample delivery techniques need to be gentle, and take account of these variables. Further considerations for sample injectors are the scarceness of protein material and the potential need to perform SFX experiments in vacuum to reduce background scattering from air and to accommodate detector needs. While goniometer-based chips, capillaries or loop mounts can be used for data collection from macroscopic crystals at X-FEL sources [39-41], different approaches are required when using microcrystals for data collection.

A convenient method for sample delivery is offered by liquid jets, which allow high throughput exchange of crystals in the interaction region. The GDVN represents a sample delivery device that can be used for this purpose. A GDVN injector consists of a inner capillary for the sample stream (typically 50  $\mu$ m in diameter), and the inner capillary is surrounded by a larger diameter outer capillary. Pressurized helium gas flows through the outer capillary, which serves to focus the liquid stream into a much smaller diameter than the diameter of the inner capillary (typically 1 - 5  $\mu$ m). Thus the GDVN gas focusing reduces the sample flow rate and prevents ice formation in vacuum.

Settling of microcrystals in their storage container during the experiment can be avoided by using a rotating syringe pump as a sample reservoir [42]. GDVN based sample injection setups [18] have been used for many SFX experiments [1, 12, 13, 43, 44]. The GDVN injector runs continuously during data collection, producing a stream of liquid that moves at high velocity (typically 10 m s<sup>-1</sup>). Such a sample injection scheme requires large amounts of sample, because the jet has to be running at relatively high flow rates (10-30 µl min<sup>-1</sup>), a consequence of which is that a large volume of sample is injected between the FEL pulses. Therefore most of the material is wasted, i.e. does not intersect the FEL beam. This may be less of a problem for future FELs with very high repetition rates such as the European XFEL in Hamburg or LCLS-II in Stanford. Several different soluble and membrane protein crystals in their low viscosity (waterlike) mother liquor as well as in a sponge phase (moderate viscosity) [45, 46] have been successfully injected into the X-FEL interaction region.

In order to reduce sample consumption, an elegant solution is to slow down the jet. This can be done by using high



Fig. V.3: High viscosity injector in operation. Viscous LCP is extruded from a 50  $\mu$ m diameter inner capillary, at a flow rate of 0.3  $\mu$ l min<sup>-1</sup>, ambient pressure and room temperature. The inner capillary ends with a cone, which sticks out from the orifice of the outer capillary. Helium gas flows through the outer capillary in order to keep the end of the nozzle clean and to maintain a stable flow of the jet. During data collection in vacuum, the helium sheath gas prevents the LCP stream from evaporative cooling. Decrease of the temperature of the LCP or its dehydration is undesirable for data collection because at lower temperatures the LCP undergoes a phase transition, producing strong background scattering, which may complicate data analysis and damage the detector.

viscosity carrier materials, including LCP or grease [10, 14, 29]. In this case the sample is slowly extruded through a typically 50 or 100  $\mu$ m diameter glass capillary in a high viscosity extrusion injector. The same helium gas sheath approach as for GDVN injectors is used to keep the end of the nozzle clean and to shield the LCP stream from vacuum during data collection, which to some extent prevents drying of the LCP. Fig. V.3 shows the end of the injector extruding high viscosity material at a flow rate of ~300 nL min<sup>-1</sup>. Another low flow rate liquid jet injection method is based on the principle of electrospinning, for focusing the liquid jet [19].

# Data collection and analysis

Typically, SFX data sets consist of a large number of snapshot diffraction patterns, each recorded from a randomly-oriented crystal embedded in a liquid jet at room temperature. The crystals differ in size and quality. This affects the recorded diffraction intensities. The crystal can be hit by the periphery of the X-ray pulse or its center and the X-ray pulse energy will vary by at least few percent. Another source of fluctuation in data collection is the changing spectral distribution of the SASE FEL beam.

Currently, three different programs: CrystFEL [23], cctbx.xfel [24, 47] and nXDS [25] are available for the analysis of serial diffraction data; they differ in approaches and algorithms. CrystFEL identifies Bragg peaks in diffraction patterns and uses MOSFLM [48], DirAx [49] or XDS [50] for indexing and then performs intensity integration and merging of the partial diffraction intensities in a Monte Carlo fashion [51, 52]. In CrystFEL a common resolution limit is determined for all diffraction patterns included in the data set. Hit identification is typically done by programs like Cheetah [22] or CASS [21].

A common resolution limit for all frames used in CrystFEL can result in artificially high Wilson B-factors and relatively low signal/noise ratios, 100% completeness and high multiplicity of observations in the high resolution shells, due to the inclusion of weak reflections or noise from patterns from weakly-diffracting crystals. In contrast, nXDS and cctbx. xfel determine the resolution cut-off for each diffraction pattern individually, which results in lower multiplicities and higher signal/noise ratios of reflections in the highresolution range and in lower Wilson B-factors compared to CrystFEL. While nXDS uses global scaling, profile fitting and post-refinement, neither CrystFEL nor cctbx.xfel does so yet. Indexing of SFX data can be difficult, because the orientation of the crystals intersecting the X-ray pulse is unknown. Another complication in indexing SFX data arises when the symmetry of the Bravais lattice is higher than that of the space group. This results in an indexing ambiguity [53]. If the possibility for an indexing ambiguity exists, a decision between possible indexing modes has to be made for each diffraction pattern that is to be included in the final data set. In the case of SFX data, failure to assign the correct indexing mode results in a data set that appears perfectly twinned (50%).

Three approaches have been developed to resolve the indexing ambiguity of the diffraction patterns in the case of crystals which have a lower point group than the lattice symmetry. nXDS uses correlations with a reference data set, or, in its absence, a selective breeding algorithm. Pairwise correlations of patterns and a clustering of patterns approach [53] have been implemented in CrystFEL and cctbx. xfel. A proposed algorithm based on an expectation maximization algorithm has been tested on simulated data [54].

# Solving the phase problem

Crystallographic structure determination requires the retrieval of phases of diffracted waves, which are lost during the measurement of diffraction intensities. Conventional experimental phasing methods rely on contributions of heavy atom scatterers, as with multiple or single isomorphous replacement approaches and/or multi- or single-



Fig. V.4: Calculated atomic form factors for selected configurations of different charge states of Fe. Reproduced from [60]. wavelength anomalous dispersion (MAD or SAD) measurements, which exploit element-specific scattering close to X-ray absorption edges. As has been recently demonstrated, SFX data are accurate enough for SAD phasing to be feasible [55]. In that study, a high-resolution SFX data set of a lysozyme heavy atom derivative was collected that gives a strong anomalous signal from two gadolinium atoms per asymmetric unit [56].

New approaches for solving the phase problem in crystallography that make use of the unique properties of FEL radiation have been proposed. The fully coherent X-FEL pulses allow measurements of the inter-Bragg intensities in diffraction patterns from nanocrystals [1]. It has been demonstrated theoretically that this approach allows phasing by oversampling techniques, exploiting the shape transform function derived from the diffraction patterns [11] or gradients of the diffraction intensities at the Bragg positions [20], as reviewed by [57].

The high peak brilliance of the FEL can be used for variations of radiation-induced phasing [58, 59]. The high fluence of FELs introduces significant electronic damage to atoms due to multiple ionizations. This changes the electronic configuration of atoms, which modifies their scattering response in a time- and intensity-dependent manner, shifting the absorption edges to higher energies. Fig. V.4 shows calculated atomic form factors for selected configurations of different charge states of Fe. The change in atomic form factors of the heavy atoms can be used for a high-intensity MAD phasing approach, where low- and high-intensity data sets are collected, below and above the modified absorption edge of the heavy atom [60].

Another promising approach for solving the crystallographic phase problem could make use of the self-seeding schemes implemented and used reliably at currently operating X-ray FEL sources [61]. In this scheme, a Bragg reflection from a diamond crystal is used to create the necessary X-ray seed pulse from the initial SASE pulse that is then overlaid with the electron bunch. This scheme produces X-ray pulses with a bandwidth reduced by a factor of 10 to 40, compared with the typical SASE bandwidth. In particular, two-color selfseeding [62] may be used for a new phasing method. In the two-color self-seeding scheme, two X-ray pulses are created that differ in their photon energy by few tens of eV, within

the SASE bandwidth of the initial pulse. When larger spectral separation between the two self-seeded pulses is required, the so-called "pulse-stacked" FEL setup can be used. The energy of the two pulses can be tuned to match energies above and below the absorption edge of the heavy element in the sample. The diffraction patterns originating from both X-ray pulses are then recorded on the same detector frame, from the same crystal, since the temporal separation between the pulses can be short enough so that also the second pulse diffracts from still undamaged crystal. The resulting Bragg spots from the two pulses of different photon energy can be sufficiently separated in the diffraction pattern to enable simultaneous measurement of diffraction intensities at the two wavelengths. Despite the fact that many new possibilities taking advantage of unique properties of the X-ray FEL sources for phasing have been proposed, none of them have been demonstrated experimentally yet.

# Outlook

The rapidly developing method of serial femtosecond crystallography at X-ray free-electron laser sources has proven to be the most successful application of FEL technology in structural biology. Although SFX has not yet reached its full potential, and the experiments are not as easy to perform as for example data collection at synchrotron macromolecular crystallography beamlines, it holds the promise of delivering novel results that cannot be obtained at 3<sup>rd</sup> generation synchrotron sources due to their limitations, in particular with respect to radiation damage issues and insufficient time resolution, which FELs overcome.

With the advancements being made in micro-crystallization techniques, sample delivery, methods and software for data analysis, and machine upgrades, the method of serial femtosecond crystallography will become accessible for a broader community that will explore the opportunities that SFX and FELs offer.

The author would like to thank Ilme Schlichting for support and discussions, and parts of this chapter are based on her recent review article [63]. A detailed review of crystallography at X-FELs has also been published by Bruce Patterson [64].

# Summary

- Serial femtosecond crystallography at X-FEL sources provides high-resolution diffraction data, from very small crystals, without visible radiation damage and with the possibility of ultra-fast time-resolved measurements.
- Novel methods for retrieving the crystallographic phase have been proposed, based on the high intensity and coherent properties of X-FEL pulses.
- High-viscosity lipidic cubic phase (LCP) crystallization and delivery techniques produce showers of microcrystals and reduce the sample consumption to a minimum.
- Constant improvement in data analysis methods reduce the number of indexed patterns required and hence the measurement time and sample volume needed.

#### References

- Chapman, H.N., et al., *Femtosecond X-ray protein* nanocrystallography. Nature, 2011. **470**(7332):
   p. 73-U81.
- [2] Caffrey, M., D. Li, and A. Dukkipati, Membrane Protein Structure Determination Using Crystallography and Lipidic Mesophases: Recent Advances and Successes.
   Biochemistry, 2012. 51(32): p. 6266-6288.
- Fienup, J.R., PHASE RETRIEVAL ALGORITHMS A COMPARISON. Applied Optics, 1982. 21(15): p. 2758-2769.
- [4] Caleman, C., et al., On the Feasibility of Nanocrystal Imaging Using Intense and Ultrashort X-ray Pulses. Acs Nano, 2011. 5(1): p. 139-146.
- [5] Chapman, H.N., C. Caleman, and N. Timneanu, *Diffraction before destruction*. Philosophical Transactions of the Royal Society B-Biological Sciences, 2014. **369**(1647).
- [6] Barty, A., et al., Self-terminating diffraction gates femtosecond X-ray nanocrystallography measurements. Nature Photonics, 2012. 6(1): p. 35-40.
- [7] Lomb, L., et al., *Radiation damage in protein serial femtosecond crystallography using an X-ray free-electron laser*. Physical Review B, 2011. **84**(21).
- [8] Cherezov, V., *Lipidic cubic phase technologies for membrane protein structural studies*. Current Opinion in Structural Biology, 2011. 21(4): p. 559-566.
- [9] Holton, J.M. and K.A. Frankel, *The minimum crystal size* needed for a complete diffraction data set. Acta Crystallographica Section D-Biological Crystallography, 2010. 66: p. 393-408.
- Botha, S., et al., Room temperature serial crystallography at synchrotron X-ray sources. Acta Cryst. D, 2015.
   Accepted.
- [11] Spence, J.C.H., et al., *Phasing of coherent femtosecond X-ray diffraction from size-varying nanocrystals*. Optics Express, 2011. **19**(4): p. 2866-2873.
- [12] Boutet, S., et al., High-Resolution Protein Structure Determination by Serial Femtosecond Crystallography. Science, 2012. 337(6092): p. 362-364.
- [13] Redecke, L., et al., Natively Inhibited Trypanosoma brucei Cathepsin B Structure Determined by Using an X-ray Laser. Science, 2013. **339**: p. 227-230.
- [14] Liu, W., et al., Serial Femtosecond Crystallography of G Protein-Coupled Receptors. Science, 2013. 342(6165): p. 1521-1524.
- [15] Liu, W., et al., Femtosecond crystallography of membrane proteins in the lipidic cubic phase. Philosophical Transactions of the Royal Society B-Biological Sciences, 2014. 369(1647).

- [16] Weierstall, U., et al., *Lipidic cubic phase injector facilitates membrane protein serial femtosecond crystallography*.
   Nature Communications, **2014**. 5.
- [17] DePonte, D.P., et al., Gas dynamic virtual nozzle for generation of microscopic droplet streams. Journal of Physics D-Applied Physics, 2008. 41(19).
- [18] Weierstall, U., J.C.H. Spence, and R.B. Doak, *Injector for scattering measurements on fully solvated biospecies*. Review of Scientific Instruments, 2012. 83(3).
- [19] Sierra, R.G., et al., Nanoflow electrospinning serial femtosecond crystallography. Acta Crystallographica Section D-Biological Crystallography, 2012. 68: p. 1584-1587.
- [20] Elser, V., *Direct phasing of nanocrystal diffraction*. Acta Crystallographica Section A, 2013.**69**: p. 559-569.
- [21] Foucar, L., et al., CASS-CFEL-ASG software suite. Computer Physics Communications, 2012.
  183(10): p. 2207-2213.
- Barty, A., et al., Cheetah: software for high-throughput reduction and analysis of serial femtosecond X-ray diffraction data. Journal of Applied Crystallography, 2014.
   47: p. 1118-1131.
- [23] White, T.A., et al., CrystFEL: a software suite for snapshot serial crystallography. Journal of applied crystallography, 2012. 45: p. 335-341.
- [24] Sauter, N.K., et al., New Python-based methods for data processing. Acta Crystallographica Section D-Biological Crystallography, 2013. 69: p. 1274-1282.
- [25] Kabsch, W., Processing of X-ray snapshots from crystals in random orientations. Acta Crystallographica D, 2014.
   70: p. 2204-2216.
- [26] Emma, P., et al., First lasing and operation of an angstromwavelength free-electron laser. Nature Photonics, 2010.
   4(9): p. 641-647.
- [27] Ishikawa, T., et al., A compact X-ray free-electron laser emitting in the sub-angstrom region. Nature Photonics, 2012. 6(8): p. 540-544.
- [28] Kirian, R.A., et al., Phasing coherently illuminated nanocrystals bounded by partial unit cells. Philosophical Transactions of the Royal Society B-Biological Sciences, 2014. 369(1647).
- [29] Sugahara, M., et al., Grease matrix as a versatile carrier of proteins for serial crystallography. Nature Methods, 2015.
   12(1): p. 61-63.
- [30] Caffrey, M. and V. Cherezov, *Crystallizing membrane* proteins using lipidic mesophases. Nature Protocols, 2009.
   4(5): p. 706-731.

- [31] Aherne, M., J.A. Lyons, and M. Caffrey, A fast, simple and robust protocol for growing crystals in the lipidic cubic phase. Journal of Applied Crystallography, 2012.
   45: p. 1330-1333.
- [32] Pebay-Peyroula, E., et al., X-ray structure of bacteriorhodopsin at 2.5 angstroms from microcrystals grown in lipidic cubic phases. Science, 1997.
   277(5332): p. 1676-1681.
- [33] Neutze, R., et al., Potential for biomolecular imaging with femtosecond X-ray pulses. Nature, 2000. 406(6797): p. 752-757.
- [34] Kern, J., et al., Simultaneous Femtosecond X-ray Spectroscopy and Diffraction of Photosystem II at Room Temperature. Science, 2013. 340(6131): p. 491-495.
- [35] Scott, H.A., Cretin a radiative transfer capability for laboratory plasmas. Journal of Quantitative Spectroscopy & Radiative Transfer, 2001. 71(2-6): p. 689-701.
- [36] Nass, K., et al., Indications of Radiation Damage in Ferredoxin Microcrystals Using High Intensity X-FEL Beams. Journal of Synchrotron Radiation, 2015. Accepted.
- [37] Hau-Riege, S. and B.J. Bennion, *Reproducible radiation damage processes in proteins irradiated by intense X-ray pulses*. Phys. Rev. E, 2015. Accepted.
- [38] Liu, W., A. Ishchenko, and V. Cherezov, Preparation of microcrystals in lipidic cubic phase for serial femtosecond crystallography. Nature Protocols, 2014.
   9(9): p. 2123-2134.
- [39] Cohen, A.E., et al., Goniometer-based femtosecond crystallography with X-ray free electron lasers. Proceedings of the National Academy of Sciences of the United States of America, 2014. 111(48): p. 17122-17127.
- [40] Hirata, K., et al., Determination of damage-free crystal structure of an X-ray-sensitive protein using an XFEL. Nature Methods, 2014. 11(7): p. 734-U174.
- [41] Suga, M., et al., Native structure of photosystem II at 1.95 angstrom resolution viewed by femtosecond X-ray pulses. Nature, 2015. 517(7532): p. 99-U265.
- [42] Lomb, L., et al., *An anti-settling sample delivery instrument for serial femtosecond crystallography*. Journal of applied crystallography, 2012. **45**: p. 674-678.
- [43] Aquila, A., et al., *Time-resolved protein* nanocrystallography using an X-ray free-electron laser.
   Optics Express, 2012. 20(3): p. 2706-2716.
- [44] Kupitz, C., et al., Serial time-resolved crystallography of photosystem II using a femtosecond X-ray laser. Nature, 2014. 513(7517): p. 261-+.
- [45] Johansson, L.C., et al., *Lipidic phase membrane protein* serial femtosecond crystallography. Nature Methods, 2012.
   **9**(3): p. 263-U59.
- [46] Johansson, L.C., et al., *Structure of a photosynthetic*

*reaction centre determined by serial femtosecond crystallography.* Nature Communications, 2013. **4**.

- [47] Hattne, J., et al., Accurate macromolecular structures using minimal measurements from X-ray free-electron lasers. Nature Methods, 2014. 11(5): p. 545-548.
- [48] Powell, H.R., O. Johnson, and A.G.W. Leslie, Autoindexing diffraction images with iMosflm. Acta Crystallographica Section D-Biological Crystallography, 2013.
   69: p. 1195-1203.
- [49] Duisenberg, A.J.M., INDEXING IN SINGLE-CRYSTAL
   DIFFRACTOMETRY WITH AN OBSTINATE LIST OF REFLECTIONS.
   Journal of Applied Crystallography, 1992. 25: p. 92-96.
- [50] Kabsch, W., *XDS*. Acta Crystallographica Section D Biological Crystallography, 2010. **66**: p. 125-132.
- [51] Kirian, R.A., et al., Femtosecond protein nanocrystallography-data analysis methods. Optics Express, 2010. 18(6): p. 5713-5723.
- [52] Kirian, R.A., et al., *Structure-factor analysis of femtosecond micro-diffraction patterns from protein nanocrystals*. Acta Crystallographica Section A, 2011. **67**: p. 131-140.
- [53] Brehm, W. and K. Diederichs, *Breaking the indexing ambiguity in serial crystallography*. Acta Crystallographica Section D-Biological Crystallography, 2014.
   **70**: p. 101-109.
- [54] Liu, H. and J.C.H. Spence, *The indexing ambiguity in serial femtosecond crystallography (SFX) resolved using an expectation maximization algorithm*. IUCrJ, 2014.
   1(Pt 6): p. 393-401.
- [55] Barends, T.R.M., et al., De novo protein crystal structure determination from X-ray free-electron laser data. Nature, 2014. 505(7482): p. 244-+.
- [56] Girard, E., et al., Gd-HPDO3A, a complex to obtain highphasing-power heavy-atom derivatives for SAD and MAD experiments: results with tetragonal hen egg-white lysozyme. Acta Crystallographica Section D-Biological Crystallography, 2002. 58: p. 1-9.
- [57] Millane, R.P. and J.P.J. Chen, Aspects of direct phasing in femtosecond nanocrystallography. Philosophical Transactions of the Royal Society B-Biological Sciences, 2014. 369(1647).
- [58] Banumathi, S., et al., Structural effects of radiation damage and its potential for phasing. Acta Crystallographica Section D Biological Crystallography, 2004.
  6: p. 1085-1093.
- [59] Ravelli, R.B.G., et al., Specific radiation damage can be used to solve macromolecular crystal structures. Structure, 2003. 11: p. 217-224.
- [60] Son, S.-K., H.N. Chapman, and R. Santra, *Multiwavelength* Anomalous Diffraction at High X-Ray Intensity. Physical Review Letters, 2011. 107(21).

- [61] Amann, J., et al., Demonstration of self-seeding in a hard-X-ray free-electron laser. Nature Photonics, 2012.
   6(10): p. 693-698.
- [62] Lutman, A.A., et al., Demonstration of single-crystal selfseeded two-color X-ray free-electron lasers. Physical review letters, 2014. 113(25): p. 254801-254801.
- [63] Schlichting, I., *Serial femtosecond crystallography: the first five years*. IUCrJ, 2015. **2**(2).
- [64] Patterson, B.D., *Crystallography using an X-ray free-electron laser*. Crystallography Reviews, 2014. **20**(4): p. 242-294.

# VI. 2D membrane protein crystallography

Xiao-Dan Li, Paul Scherrer Institute

Important membrane proteins are very difficult to crystallize in three dimensions - intense XFEL pulses may allow high-resolution static and dynamic structure determinations on two-dimensional membrane protein crystals.

- The biological importance of membrane proteins
- Electron and X-ray diffraction by 2D crystals on a solid support
- XFEL data collection and analysis
- Outlook

Membrane proteins facilitate the transport of matter and energy across membrane in all cells from ancient bacteria to human. The structures of membrane proteins in 2D crystals determined using cryo-electron crystallography differ from those found X-ray crystallography in the relatively few examples which crystallize in 3D, due possibly to the differing sample environment. It is not possible to measure micrometer-sized 2D membrane protein crystals at the most advanced synchrotron radiation sources, but it is feasible to measure membrane protein 2D crystals under ambient conditions on a solid support using an XFEL, with a flux of 10<sup>12</sup> photos per pulse. Further developments, particular of high-dynamic range detectors, should make high-resolution data collection of tiltable 2D crystals routine, leading to radiation-damage-free structures. Furthermore, dynamic properties of membrane protein at various time scales can be studied at an XFEL with pump-probe experiments.

# The biological importance of membrane proteins

In the living cell, membrane proteins are situated within the cell membrane, a double lipid layer which separates the cytoplasm from the cell exterior (see Fig. VI.1). In the course of the Human Genome Project, it was discovered that genes encoding membrane proteins make up approximately 30% of the genome. These proteins regulate the cellular homeostasis, act as receptors, transporters and channels, and are responsible for cell development, inter-cell interactions, nerve transmission, muscle contraction, signaling and

programmed cell death. Mutations in membrane proteins cause a large variety of inherited or acquired diseases, including cystic fibrosis, drug resistance, diabetes, Alzheimer's, kidney and digestive diseases, hypertension and heart failure.

It has been predicted that more than 50% of all future drugs will target membrane proteins, yet they represent less than 2% of the protein structures determined using X-ray and electron diffraction/imaging. The XFEL method presented here may allow the routine analysis of membrane proteins which are embedded in the native-like lipid bilayer at ambient temperature.



Fig. VI.1: Left: A schematic view of the membrane protein bacteriorhodopsin, one of the relatively few membrane proteins whose high-resolution structure could to date be determined using X-ray crystallography [1,2]. Right: Bacteriorhodopsin works as a primary proton pump to generate a proton-motive force leading to the phosphorylation of low-energy ADP + phosphate (Pi) to high-energy ATP by ATPase in bacterial photosynthesis [3].

# 3D vs. 2D crystal diffraction

Crystal diffraction, whether of electrons or X-rays, in 3 dimensions yields the familiar Bragg reflections, at positions in the reciprocal lattice determined by selection rules based on the crystal symmetry. Scattering from a strictly 2-dimensional crystal, on the other hand, yields continuous "reciprocal lattice rods" of scattering (see Fig. VI.i1). The region of reciprocal space which is actually sampled in a diffraction experiment is given by the "Ewald construction", shown for 3D and 2D in Fig. VI.i2. Non-zero diffracted intensity only results for scattered vectors k corresponding to intersections of the Ewald sphere and Bragg points or lattice rods.

A 2D protein crystal, in which each crystal lattice point is an extended molecule, will yield reciprocal lattice rods for which the diffracted intensity varies along the rod. This variation, which encodes the three-dimensional protein structure, can be sampled by tilting the 2D crystal in the incident beam.



Fig. VI.i1: Crystal diffraction in 3 and 2 dimensions yields, respectively, Bragg reflections and reciprocal lattice rods in reciprocal space.



Fig. VI.i2: The Ewald construction for 3D and 2D diffraction.



Fig. VI.2: Typical 2D membrane protein crystals, as seen in a transmission electron microscope [5].

# Electron and X-ray diffraction by 2D crystals on a solid support

Well-ordered micrometer-sized 2D membrane crystals are required for collecting high-resolution cryo-EM data (see Fig. VI.2). Besides the crystalline quality, other factors which limit resolution include background scattering from embedding media (cryo-protectants to preserve the structural properties) and the support film upon which the 2D crystals are mounted, the crystal flatness and uncontrolled tilting, and finally, the electron beam-induced radiation damage of the sample. The most time-consuming steps are obtaining well-diffracting, micrometer-size 2D crystals, determining the optimal freezing conditions and the data collection. With ambient 2D crystallography at the XFEL, freezing and cryoprotectants are avoided. Furthermore, 2D crystals can be studied under controlled conditions, perhaps involving a micro-fluid device, and time-resolved pump-probe experiments can be performed. Finally, because of the "diffractbefore-destroy" nature of XFEL serial crystallography, radiation damage is avoided.

Electrons (100-500 keV) are scattered by matter more strongly than are hard X-rays, and the amount of energy deposited by inelastic scattering events per useful elastic scattering event is 1000 times less for electrons than for X-rays [4]. The stronger scattering of electrons generally implies that the simple kinematic approach, which neglects multiple scattering and which is generally valid for X-rays, must be replaced for electrons by the more complex dynamical approach.

# XFEL data collection and analysis

Successful observations have been made at the LCLS of X-ray diffraction features from single-layer 2D crystals of the



Fig. VI.3: A diffraction image from a single 2D crystal of bacteriorhodopsin [13], with colored circles showing the predicted positions of Bragg reflections – clearly identifiable peaks are circled in red. The large dashed red circle corresponds to a resolution of 10 Å.

## Electron crystallography of 2D membrane protein crystals

Henderson and Unwin published in 1975 their landmark work using electron crystallography to determine the 3D structure of 2D bacteriorhodopsin crystals [6,7]. 2D membrane protein crystals with thickness of about 3-4nm are idea samples for cryo-electron microscopy structure determination, using images of the 2D crystals and/or electron diffraction data. Radiation damage is the main problem which prevents high-resolution structure determination using any kind of microscopy [4]. For given amount of radiation damage, electrons give more useful information than X-rays or neutrons; the amount of damage per each useful elastic scattering produced by X-rays is several hundreds time greater than for electrons, at all wavelengths and energies. A typical process to obtain 3D structure using electron microscopy image analysis of 2D membrane protein crystals is illustrated in Fig. VI.i3.

Use of a direct electron detector [9] and automated image processing [10] has tremendously increased the image signal-to-noise ratio and the achievable structural resolution, particularly for highly tilted samples. A major bottleneck in EM structural analysis remains finding the best cryo-conditions to preserve the structural integrity of the sample [11].



Fig. VI.i3: Cryo EM of two-dimensional crystals. (a) Crystals of the water channel aquaporin-0 are large and have sharp edges, attesting to a high degree of order. (b) High-resolution image of the crystal area high-lighted by a *box* in (a). (c) Fourier transform of the image in (b), showing strong and sharp spots to ~6Å resolution. Such an analysis of microscopy data may be augmented by changing the microscope setup to collect electron diffraction data [8].



Fig. VI.4: Processing 2D XFEL diffraction data (8450 eV photon energy) to obtain an electron density projection map for bacteriorhodopsin [12]. (a) Background-subtracted diffraction patterns for 2-D crystals of bacteriorhodopsin. Blue circles correspond to 30.0, 15.0 and 7.5 Å resolutions, and red circles highlight the highest resolution peaks. (b) Experimental 2-D electron density projection map (2 × 2 unit cells) obtained from the observed integrated peak intensities and phases calculated from the known crystal structure of bacteriorhodopsin. (c) Ribbon diagram of bacteriorhodopsin created using the known crystal structure, symmetry and unit cell for comparison with (b).

membrane protein bacteriorhodopsin (bR) [12,13]. In the work of Ref. [13], purple membranes containing 2D bR crystals were isolated from *Halobacterium salinarum*, and 2D crystals were prepared using an established annealing protocol. The final suspension was spread onto 5 nm thick carbon films, supported in arrays of  $100 \times 100 \text{ mm}^2$  windows etched in Si wafers. To prevent dehydration, glucose was mixed with the 2D crystals.

The authors then irradiated bR crystals with 8.8 keV XFEL pulses, of duration 30 fs, focused to 0.1 mm. Each XFEL pulse required repositioning the wafer to present a fresh carbon film window, which limited the data collection rate to 324 images in 6 minutes. Of these images, 15 showed diffraction patterns from a single bR crystal, and of these, 11 could be indexed (see Fig. VI.3).

The diffraction patterns were assumed to be untitled and normal to the X-ray pulse. Initially, the diffraction patterns were overlaid with expected lattice positions calculated from unit-cell parameters (a = b = 63 Å and  $a = \beta = 90^{\circ}$ ,  $\gamma = 120^{\circ}$ ,  $P_3$  symmetry) derived from EM data from similarly prepared samples and from previous publications [1,14,15]. This yielded a good match and served as a marker for subsequent peak searches. Localized peak searches were then performed, and the integrated intensity for each identified peak was calculated by summing over all connected pixels within a given pixel search area. The measured intensities and phases determined by a generalized molecular replacement scheme were Fourier-transformed to yield the 2-D electron density projection map of a 2 × 2 unit cell (see Fig. VI.4).

# Outlook

The major challenges faced by XFEL-based 2D protein crystallography are: to obtain well-ordered 2D crystals in sufficient quantity and quality, to conveniently mount large numbers of environmentally-protected crystals on a lowmass, rapidly-repositionable substrate, and to have available an array detector with unprecedented high-dynamic range and low noise. Solutions to these challenges will make XFEL-based studies of 2D crystals an attractive method of membrane protein structure determination.

The relatively large freedom of movement of protein molecules in 2D crystals, without destruction of the crystal, may allow novel observations with the XFEL of dynamic structural changes. This will require the development of suitable triggers, such as visible, infrared or terahertz pulses, to rapidly and reproducibly initiate such changes.

# Summary

- Single-shot diffraction patterns of 2D membrane protein crystals on a solid support can easily be measured at an XFEL.
- Radiation damage is eliminated in the short-pulse "diffract-before-destroy" mode.
- The diffraction patterns can be indexed, and unit cell dimensions can be calculated.
- Data taken on tilted samples indicate the potential of obtaining 3D structures using molecular replacement.
- Pump-probe experiments will provide dynamic information of membrane proteins in a close-to-physiological environment.

#### References

- Edman, K., et al., *High-resolution X-ray structure of an early intermediate in the bacteriorhodopsin photocycle*. Nature, 1999. 401(6755): p. 822-6.
- [2] Pan, Y., et al., Structural Characterization of an Integral Membrane Protein in Its Natural Lipid Environment by Oxidative Methionine Labeling and Mass Spectrometry. Analytical Chemistry, 2009. 81(1): p. 28-35.
- [3] http://en.wikipedia.org/wiki/Bacteriorhodopsin
- [4] Henderson, R., The potential and limitations of neutrons, electrons and X-rays for atomic resolution microscopy of unstained biological molecules. Q Rev Biophys, 1995.
   28(2): p. 171-93.
- [5] Schertler, G., private communication (2009).
- [6] Henderson, R., The structure of the purple membrane from Halobacterium hallobium: analysis of the X-ray diffraction pattern. J Mol Biol, 1975. 93(2): p. 123-38.
- Henderson, R. and P.N. Unwin, *Three-dimensional model* of purple membrane obtained by electron microscopy. Nature, 1975. 257(5521): p. 28-32.
- [8] Gonen, T., *The collection of high-resolution electron diffraction data*. Methods in molecular biology (Clifton, N J), 2013. **955**: p. 153-69.
- [9] McMullan, G., et al., Comparison of optimal performance at 300keV of three direct electron detectors for use in low dose electron microscopy. Ultramicroscopy, 2014.
   147: p. 156-63.

- [10] Scherer, S., et al., 2dx\_automator: Implementation of a semiautomatic high-throughput high-resolution cryoelectron crystallography pipeline. Journal of Structural Biology, 2014. 186(2): p. 302-307.
- [11] Schmidt-Krey, I. and J.L. Rubinstein, *Electron* cryomicroscopy of membrane proteins: Specimen preparation for two-dimensional crystals and single particles. Micron, 2011. 42(2): p. 107-116.
- [12] Frank, M., et al., Femtosecond X-ray diffraction from twodimensional protein crystals. IUCrJ, 2014.
   1(Pt 2): p. 95-100.
- Pedrini, B., et al., 7 A resolution in protein twodimensional-crystal X-ray diffraction at Linac Coherent Light Source. Philosophical transactions of the Royal Society of London Series B, Biological sciences, 2014.
   369(1647): p. 20130500.
- [14] Henderson, R., et al., Model for the structure of bacteriorhodopsin based on high-resolution electron cryo-microscopy. Journal of molecular biology, 1990.
   213(4): p. 899-929.
- [15] Verclas, S.A.W., et al., X-ray diffraction from a single layer of purple membrane at the air/water interface. Journal of Molecular Biology, 1999. 287(5): p. 837-843.

# VII. Time-resolved diffraction imaging

Adrian Mancuso, European XFEL

The excellent transverse coherence of XFEL radiation allows high-resolution imaging to be performed without lenses. The short-duration XFEL pulses also permit time-resolved measurements using pump-probe techniques. Of particular interest is the study of irreversible dynamic processes, which is made possible by the extreme pulse energy of XFELs.

- Introduction
- Coherent diffraction imaging
- Instrumentation requirements
- Morphology of superfluid helium droplets
- Acoustic waves in gold nanocrystals
- Outlook

Coherent diffractive imaging (CDI) offers a structure determination technique that does not rely on high-resolution X-ray optics. It instead inverts a measurement that only uses the coherence of the incident illumination. The resolution is determined by the quality of the measured diffraction pattern, which depends, among other parameters, on the degree of coherence and the number of photons used to illuminate the sample. This reliance on coherence and brightness makes CDI particularly amenable to X-ray Free Electron Laser application, since even a single XFEL pulse often provides invertible, two-dimensional diffraction data. Alternatively, many frames of data from so-called "reproducible" samples may be combined to produce an invertible data set in two- or three-dimensions. The principal advantages of CDI at an XFEL are the ultra-short duration of the XFEL pulse and the ability to control its arrival-time to within tens of femtoseconds of an external laser trigger. Furthermore, for reproducible samples, irreversible temporal processes can be explored since a new copy of the sample can be used with each XFEL pulse.

# Introduction

This chapter seeks to outline only the very basics of CDI, and to demonstrate its application at XFELs with two short examples, one of which is time-resolved. It does not aim to provide a comprehensive introduction to coherent X-ray diffractive imaging nor to describe all possible applications at XFELs. For excellent primers on the mathematics and methods of coherent imaging see [1,2]. A review of possible biological applications can be found in [3], and a brief overview of the capabilities for biological structure determination at the now under construction European XFEL can be found in [4], which addresses in part the application of CDI. Possibilities for exploring material samples are explored in [5].

Coherent X-ray Diffractive imaging at XFELs has two distinct advantages over synchrotron-based coherent diffractive imaging. One key advantage is the possibility to record images at a resolution better than radiation damage would normally allow. This is due to the milli-Joule pulse energies that are delivered in tens of femtoseconds with a single pulse of XFEL radiation, allowing for measurements that "outrun" radiation damage [6]. Such a pulse, when focused to match the sample size, illuminates the sample with many more photons than could be achieved with a continuous or pseudo-continuous X-ray source without sample damage (which in turn leads to limited image resolution). An early proof-of-principle "diffract-then-destroy" experiment is described in [7].

The second key advantage lies in the femtosecond-scale pulse durations of an XFEL. These can be exploited to explore time-resolved phenomena at these or slower timescales, many orders of magnitude faster than at synchrotron sources. Furthermore, the immense single pulse energy at an XFEL allows individual time-resolved measurements to be interpretable, whereas a weaker source relies on integrating many identical processeses over many measurements. Time-resolved phenomena at XFELs have been explored, not only with coherent imaging [8], but also with crystallography [9], spectroscopy [10] and solution scattering [11]. The geometry of a coherent diffractive imaging experiment is conceptually simple. A beam of coherent X-rays, often focused to a spot size comparable to the sample size, is incident upon a sample. The sample scatters the X-rays, which then are allowed to simply propagate to a two-dimensional (2D) detector, where the diffracted intensity is measured (see Fig. VII.1).

The reconstruction of the measured diffracted intensities is not as conceptually straightforward as the experiment, but nowadays, provided the measurement collects sufficient



Fig. VII.1: Conceptual schematic of a "traditional" coherent diffractive imaging experiment on a two-dimensional (2D) sample. A coherent plane wave is incident on the sample, and the corresponding far-field diffraction pattern is measured at a 2D detector a sufficient distance downstream. The detector is protected from the direct beam, typically by an aperture in the detector (not shown here). Provided that the diffraction pattern is sufficiently well sampled [12] and that low angle diffraction data is also collected [13], the pattern can be reconstructed (see infobox) to provide an image of the sample. Figure originally published in [14].

# The phase problem in diffractive imaging

The "phase problem" in coherent diffractive imaging addresses the issue of how a measurement of a reciprocalspace far-field diffraction pattern is analyzed and reconstructed into a real-space "image" of the sample under



study. A simplified sketch showing the key features of how the phase problem is solved in CDI is shown in figure I1. Miao and others [18] performed the first experimental example of such a reconstruction, using X-rays, in 1999.

Fig. VII.1: Phase retrieval scheme for coherent diffractive imaging. A diffraction pattern  $I_{exp}(q)$  is measured by a detector placed sufficiently far enough from an illuminated sample to satisfy both the far-field condition and the necessary sampling condition [12,15]. This intensity pattern represents the "reciprocal space constraint". Initially, the diffraction phases are set to random values. The Fourier transform of the reciprocal space data yields real space data, which are constrained to yield a positive electron density and to agree with the known physical extent ("support") of the sample. Repeated iterations between real and reciprocal space yield, finally, the unknown diffraction phases, and hence a real-space image of the sample.

low scattering angle data [13] and is correctly sampled [12,15], reconstructions generally proceed to successfully recovered images (electron densities) of the sample under investigation. There are a variety of algorithms used for these reconstructions, though they all follow approximately the same form outlined in [16]. A generic version of this is explained in the infobox. A modern example of such an algorithm is the difference-map algorithm [17], which is a generalization of the earlier, simpler algorithms described in [16].

## Instrumentation requirements

Coherent Diffractive Imaging (CDI), sometimes termed Coherent X-ray Diffractive Imaging (CXDI) in the X-ray context, is a form of indirect imaging, where a typically non-crystalline sample is illuminated with a plane-wave beam and the corresponding far-field diffraction data are collected on a twodimensional detector a sufficient distance from the sample. Far-field diffraction patterns are ideally of high dynamic range (see Fig. VII.2). In practice, the dynamic range is lim-



Fig. VII.2: High dynamic range diffraction data from a (synchrotron) coherent imaging experiment. Note the seven orders of magnitude in the left figure and eight in the right figure. These patterns were collected on an MMPAD detector [21], which was specifically designed for high dynamic range data. Figure originally published in [22]. Fig. VII.3: The basic geometry of a coherent imaging experiment at an XFEL for a weakly scattering sample. Here, the sample is injected with an aerosol jet, which replenishes the sample, ideally from shot-to-shot, since a single focused XFEL pulse will destroy any sample illuminated. Note that such a sample may produce a signal at the detector that, for a single pulse, may contain only a single or even no photons in a number of pixels. This gives rise to the need for 2D detectors which can distinguish single and no photon events with high fidelity. Figure courtesy of Klaus Giewekemeyer, European XFEL.



ited by the measured signal level, by the noise floor of the detector and by the pixel well depth (or "maximum photon level"). For XFELs, the CSPAD detector [19] and the upcoming AGIPD detector [20] are two of the most promising high dynamic range detectors.

For very weakly scattering samples, such as non-crystalline biological samples containing predominantly low Z elements, the scattered intensity may be the limiting factor in the signal quality at the detector. In such cases, single photons may be incident on a detector pixel for an individual exposure (see Fig. VII.3), and the reliable detection of such a photon is essential [23].

Any experiment seeking to exploit individual pulses of XFELs and maximize scattering signal in a "diffract-and-destroy" mode must start by maximizing the number of photons incident on the sample. In practice this means focusing the XFEL beam to a spot that matches the sample size, with a high-transmission, large-acceptance optical system. Typically such systems at XFELs are focusing mirrors [24,25].

To explore time-resolved phenomena in "diffract-and-destroy" mode, one needs to collect data for a number of different pump-probe time delays and to combine multiple measurements for each delay. These requirements imply a definite "start" time of the process under study. Systems typically under study at XFELs often use an ultra-short pulse of optical laser radiation to start or trigger a reaction or process [8-11]. Ideally, these optical lasers have pulse durations significantly shorter than the timescale of the phenomena under study, and they must have sufficient pulse energy to efficiently initiate the reaction or process to be studied. Because some timing jitter is unavoidable, both slow and fast timing tools [26] are required to determine the "time-zero" and the actual pump-probe delay time of a given measurement.

Last, but not least, analysis software to interpret many thousands of frames of data is required to make sense of the data. An example of such an analysis package is presented in [27].

# Morphology of superfluid helium drops

While much interest in exploiting CDI at XFELs has centered on the technique's potential applicability to biological samples, successful examples of CDI applied to non-biological materials have been demonstrated at the Linac Coherent Light Source (LCLS) and elsewhere. The success of these investigations relies, at least in part, on the high scattering cross-section of high-Z material and on the relatively large samples. In this section, we report on work by Gomez et al



Fig. VII.4: Coherent diffraction data from superfluid He droplets with quantum vortices. The droplets are doped with Xe atoms to enhance the contrast of the vortices. Image originally appeared in [28].

[28] on Xenon doped, superfluid Helium droplets, and in the next section we look at the dynamic behavior of gold nanocrystals excited by an optical laser.

Superfluid He nanodroplets represent a model system that allows the exploration of quantum hydrodynamics in a relatively simple case. The no-imaging-optics geometry of CDI provides an ideal environment to explore samples that are not amenable to being physical held in place in the X-ray beam, that require faster replacement than a mechanical stage can provide, or both. Superfluid helium nanodroplets require both conditions, and in the work of Gomez, et al, a great many (of order 600) nanodroplets were probed with the XFEL beam in order to draw statistically meaningful conclusions about their morphology.

The experimental arrangement was broadly similar to the generic setup shown in Fig. VII.3. The experiment was performed at the Coherent X-ray Imaging (CXI) instrument of the LCLS, with nanodroplets of Xe-doped He injected into the LCLS beam. Diffraction data from these droplets demonstrated not only a heterogeneity in shape of the droplets, which could be characterized into a few distinct classes [28], but also showed the presence of regularly arranged quantum vortices (see Fig. VII.4), which become visible upon their "decoration" with Xenon atoms. The presence of such quantum vortices is a consequence of the superfluidity of the nanodroplets, and CDI imaging at an XFEL represents one of the few techniques capable of observing and characterizing them.

# Acoustic waves in gold nanocrystals

An exemplary case of time-resolved CDI is the work of Clark et al [8], where gold nanoparticles were optically stimulated with a laser and their corresponding acoustic oscillations observed as a function of time. This work exploits *Bragg* 

#### Bragg Coherent Diffractive Imaging (Bragg CDI)

In Bragg CDI, coherent diffraction data is measured in the vicinity of a Bragg peak as opposed to around the direct beam, as in plane-wave 'traditional' CDI. This has the advantage of being able to measure the low relative scattering angles readily, as no direct beam is present to saturate or damage a 2D detector, and gives ready access to three-dimensional information by simply 'rocking' the angle of the crystalline sample [30]. The iterative methods as described in box 1 remain largely identical, and additionally the phase information gives access to information about the strain in the crystal [33].



Fig. VII.i2: Bragg Coherent Diffractive Imaging geometry. Image originally appeared in [14]. Note the detector intersects a single Bragg peak, with the direct beam allowed to propagate beside the detector (which alleviates the need for a hole in the detector).


Coherent Diffractive Imaging (BCDI) [29,30], which is possible due to the crystalline nature of the particles under study (see the infobox).

Individual gold nanocrystals were explored in BCDI in a non-destructive (low-fluence) mode, to allow multiple investigations of the same sample. The samples were excited ("pumped") with an optical laser (800 nm wavelength, 50 fs pulse duration, 1 mJ/cm<sup>2</sup>), causing acoustic excitation of the nanocrystals. These samples were then "probed" some time later with LCLS X-rays, and the corresponding coherent Bragg diffraction patterns were recorded as a function of the delay time. One can observe the difference in the diffraction from the unperturbed (Fig. VII.5A) and a "pumped" (Fig. VII.5B) case. Fig. VII.5C and D show the acoustic vibrations, by plotting the deviation of the Bragg peak from its nominal position as a function of delay time. The 3D phase (strain) map of the nanocrystal is also reconstructed as a function of delay time, and is favourably compared to a theoretical model [8].

This experiment very elegantly shows - at relatively long timscales for an XFEL - the value of time-resolved coherent diffractive inaging in exploring the dynamics of nanostructures in 3D. The future hope is to be able to explore a variety of systems, including those exhibiting ultrafast behaviour, such as magnetic systems [31], with this time-resolved CDI technique.

# Outlook

The future of coherent imaging at XFELs, for both static and dynamic structures, indeed looks bright. The combination of an objective-free image forming system that conveniently allows for the interrogation of rapidly-replaced (XFEL destruc-

Fig. VII.5: Diffraction around the Bragg peak of the gold nanocrystal before (A) and after (B) optical excitation. (C,D) Angular deviation of the Bragg spot as a function of delay time for two different gold nanocrystals. Figure originally published in [8].

tion-friendly) samples and a method for structure determination of non-crystalline structures at XFELs promises a highly applicable technique, as indicated by the examples above. A limitation of present XFELs is their relatively low repetition rate, of 120 Hz at LCLS and a little lower at SACLA. As the determination of a structure at one pump-probe delay point may require around 10<sup>5</sup> or more diffraction patterns, and if the "hit-rate" (the "hit-rate" is the proportion of frames that contain data from the samples in question. Depending on the experiment, the hit-rate may vary from less than 1% to close to unity) of an imaging experiment is generously be estimated to be 10%, at least 2.5 hours of beamtime is then required, in a best-case scenario, for each time point to be measured. This means that with the realities of scheduling experiments, only very few time points could be investigated for a given sample system in a realistic duration of an experiment.

The next generation of high repetition-rate XFELs, such as the European XFEL under construction in Germany [32] and the LCLS-II project in California, USA, offer great potential for time-resolved studies, as the orders-of-magnitude higher pulse rates delivered by these sources make it feasible to collect sufficient data at a large number of time delays, in order to explore dynamic phenomena in a reasonable amount of experimental time. Possible investigations include fast dynamics in crystalline and non-crystalline biological systems, fast switching phenomena in magnetic structures, and much, much more.

# Summary

- Coherent diffractive imaging (CDI) allows "objective free" X-ray microscopy.
- The high pulse energy of XFELs yields for images with a high resolution exceeding than that obtained from bright continuous sources.
- The femtosecond pulse duration of the XFEL, permit ultrafast time-resolved CDI studies of dynamic structural changes.
- Time-resolved coherent imaging of acoustic phenomena in nanocrystals has been observed at an XFEL using Bragg CDI.
- The potential to use CDI to investigate weakly scattering samples at faster time scales is on the horizon, with the advent of high repetition-rate XFELs.

#### References

- [1] H. M. Quiney, Journal of Modern Optics **57**, 1109 (2010).
- [2] K. A. Nugent, Advances in Physics **59**, 1 (2010).
- [3] A. P. Mancuso, O. M. Yefanov, and I. A. Vartanyants, Journal of Biotechnology 149, 229 (2010).
- [4] M. Altarelli and A. P. Mancuso, Philos. Trans. R. Soc. Lond.,
   B, Biol. Sci. 369, 20130311 (2014).
- [5] I. A. Vartanyants, I. Robinson, I. Mcnulty, C. David,
   P. Wochner, and T. Tschentscher, J Synchrotron Radiat 14, 453 (2007).
- [6] R. Neutze, R. Wouts, D. van der Spoel, E. Weckert, and J. Hajdu, Nature 406, 752 (2000).
- H. N. Chapman *et al.*, A. Barty, M. Bogan, S. Boutet,
   M. Frank, S. Hau-Riege, S. Marchesini, B. Woods, S. Bajt, and W. Benner, Nature Physics 2, 839 (2006).
- [8] J. N. Clark, L. Beitra, G. Xiong, A. Higginbotham, D. M. Fritz, H. T. Lemke, D. Zhu, M. Chollet, G. J. Williams, M. Messerschmidt, B. Abbey, R. J. Harder, A. M. Korsunsky, J. S. Wark, and I. K. Robinson, Science **341**, 56 (2013).

- [9] A. A. Aquila, *et al.*, Optics Express, **20**, 2706 (2012).
- [10] H. T. Lemke, C. Bressler, L. X. Chen, D. M. Fritz, K. J. Gaffney, A. Galler, W. Gawelda, K. Haldrup, R. W. Hartsock, H. Ihee, J. Kim, K. H. Kim, J. H. Lee, M. M. Nielsen, A. B. Stickrath, W. Zhang, D. Zhu, and M. Cammarata, J. Phys. Chem. A **117**, 735 (2013).
- [11] D. Arnlund, L. C. Johansson, C. Wickstrand, A. Barty,
  G. J. Williams, E. Malmerberg, J. Davidsson, D. Milathianaki,
  D. P. Deponte, R. L. Shoeman, D. Wang, D. James, G. Katona,
  S. Westenhoff, T. A. White, A. Aquila, S. Bari, P. Berntsen,
  M. Bogan, T. B. van Driel, R. B. Doak, K. S. K. A. r, M. Frank,
  R. Fromme, I. Grotjohann, R. Henning, M. S. Hunter,
  R. A. Kirian, I. Kosheleva, C. Kupitz, M. Liang, A. V. Martin,
  M. Nielsen, M. Messerschmidt, M. M. Seibert,
  J. S. O. hamn, F. Stellato, U. Weierstall, N. A. Zatsepin,
  J. C. H. Spence, P. Fromme, I. Schlichting, S. E. B. Boutet,
  G. Groenhof, H. N. Chapman, and R. Neutze, Nature
  Methods 11 (9) 923-926 (2014).

- [12] R. Bates, Computer Vision Graphics and Image Processing, 25, 205-217 (1984).
- P. Thibault, V. Elser, C. Jacobsen, D. Shapiro, and D. Sayre, Acta Crystallographica Section a: Crystal Physics, Diffraction, Theoretical and General Crystallography 62, 248 (2006).
- [14] A. P. Mancuso and G. Williams, Nature Photonics 6 (9), 574-575 (2012).
- [15] J. Miao, J. Kirz, and D. Sayre, Acta Crystallographica Section D: Biological Crystallography 56, 1312 (2000).
- [16] J. Fienup, Appl. Opt **21**, 2758 (1982).
- [17] V. Elser, J. Opt. Soc. Am. A **20**, 40 (2003).
- [18] J. Miao, P. Charalambous, J. Kirz, and D. Sayre, Nature 400, 342 (1999).
- [19] G. A. Carini, S. Boutet, M. Chollet, A. Dragone, G. Haller,
  P. A. Hart, S. C. Herrmann, C. J. Kenney, J. Koglin,
  M. Messerschmidt, S. Nelson, J. Pines, A. Robert, S. Song,
  J. B. Thayer, G. J. Williams, and D. Zhu, J. Phys.: Conf. Ser.
  493, 012011 (2014).
- [20] B. Henrich, J. Becker, R. Dinapoli, P. Goettlicher, H. Graafsma, H. Hirsemann, R. Klanner, H. Krueger, R. Mazzocco, A. Mozzanica, H. Perrey, G. Potdevin, B. Schmitt, X. Shi, A. K. Srivastava, U. Trunk, and C. Youngman, in *Nucl Instrum Meth A* 633, S11–S14 (2011).
- M. W. Tate, D. Chamberlain, K. S. Green, H. T. Philipp,
   P. Purohit, C. Strohman, and S. M. Gruner, J. Phys.: Conf. Ser. 425, 062004 (2013).
- [22] K. Giewekemeyer, H. T. Philipp, R. N. Wilke, A. Aquila,
  M. Osterhoff, M. W. Tate, K. S. Shanks, A. V. Zozulya,
  T. Salditt, S. M. Gruner, and A. P. Mancuso, J. Synchrotron Rad **21**, 1167-1174 (2014).
- [23] N.-T. D. Loh and V. Elser, Phys. Rev. E 80, 026705 (2009).
- [24] S. Boutet and G. J Williams, New J. Phys. **12**, 035024 (2010).
- [25] A. P. Mancuso, A. L. Aquila, G. Borchers, K. Giewekemeyer, and N. Reimers, Technical Design Report: Scientific Instrument Single Particles, Clusters, and Biomolecules (SPB), (2013). doi:10.3204/XFEL.EU/TR-2013-004
- M. Harmand, R. Coffee, M. R. Bionta, M. Chollet, D. French,
   D. Zhu, D. M. Fritz, H. T. Lemke, N. Medvedev, B. Ziaja,
   S. Toleikis, and M. Cammarata, Nature Photonics 7, 215-218 (2013).
- [27] B. C. Heisen et al., Karabo: an integrated software framework combining control, data management and scientific computing tasks, 14<sup>th</sup> International Conference on Accelerator & Large Experimental Physics Control Systems, ICALEPCS 2013, San Francisco, U.S.A..
- [28] L. F. Gomez, K. R. Ferguson, J. P. Cryan, C. Bacellar,R. M. P. Tanyag, C. Jones, S. Schorb, D. Anielski,

A. Belkacem, C. Bernando, R. Boll, J. Bozek, S. Carron,
G. Chen, T. Delmas, L. Englert, S. W. Epp, B. Erk, L. Foucar,
R. Hartmann, A. Hexemer, M. Huth, J. Kwok, S. R. Leone,
J. H. S. Ma, F. R. N. C. Maia, E. Malmerberg, S. Marchesini,
D. M. Neumark, B. Poon, J. Prell, D. Rolles, B. Rudek,
A. Rudenko, M. Seifrid, K. R. Siefermann, F. P. Sturm,
M. Swiggers, J. Ullrich, F. Weise, P. Zwart, C. Bostedt,
O. Gessner, and A. F. Vilesov, Science **345**, 906 (2014).

- [29] M. A. Pfeifer, G. J. Williams, I. A. Vartanyants, R. Harder, and I. K. Robinson, Nature 442, 63 (2006).
- [30] G. J. Williams, M. A. Pfeifer, I. A. Vartanyants, and I. K. Robinson, Phys. Rev. Lett. 90, 175501 (2003).
- [31] C. Gutt, L.-M. Stadler, S. Streit-Nierobisch, A. P. Mancuso, A. Schropp, B. Pfau, C. Günther, R. Könnecke, J. Gulden, and B. Reime, Phys. Rev. B. **79**, 212406 (2009).
- [32] M. Altarelli, et al., European XFEL Technical Design Report (2006). doi:10.3204/DESY\_06-097
- [33] I.A. Vartanyants and I.K. Robinson, J. Phys. Condens. Matter 13, 10593 (2001).

# VIII. Imaging fluctuations

Anders Madsen, European XFEL Christian Gutt, University of Siegen

Disordered matter undergoes fluctuations on a wide range of time and length scales – using the coherence properties of the XFEL and "split-pulse X-ray Photon Correlation Spectroscopy", the aim is to characterize such fluctuations, for example in non-crystalline or glassy materials, at the picosecond and nanometer scales.

- Introduction
- Beam properties and experimental challenges
- Time correlation spectroscopy
- Experimental results
- Outlook

Compared with 3<sup>rd</sup> generation synchrotron sources, X-ray Free-Electron Lasers (XFELs) provide new opportunities to study dynamics in condensed matter by coherent X-ray scattering and photon correlation spectroscopy. We discuss coherent scattering and speckle and give examples of recent results in the study of glass dynamics, as well as directions for future work taking advantage of the XFEL properties.

# Introduction

X-ray free electron lasers (XFELs) have been on-line for a few years now and several new facilities are under construction worldwide. This has revolutionized the application of X-ray based methods and the development will continue as even more powerful XFELs turn on.

In this chapter we describe the new possibilities for timecorrelation analysis offered by X-ray XFELs. The emphasis will be on studies of structure and dynamics of materials in a broad sense. When doing experiments with XFEL radiation the X-ray beam itself may perturb or even destroy the sample, but not necessarily. We will discuss the extreme situations, *i.e.* from experiments where the sample is destroyed by a single shot to measurements using multiple exposures of the same spot. Some experiments will also require pumping the sample by an optical laser, e.g. to excite dynamics or create extreme states of matter.

## Beam properties and experimental challenges

Due to the amplification in the SASE process the peak brilliance of an X-ray free-electron laser is many orders of magnitude higher than for any storage ring source. In turn, the duration of the pulse is short, only about 1-100 fs depending on the machine operation parameters, and the beam is almost fully transversely coherent [1,2]. All in all this makes the coherent peak flux of XFELs up to 13 orders of magnitude larger than for a 3<sup>rd</sup> generation synchrotron source. Typically, XFEL experiments aim to take advantage of one or several of these distinct properties which poses particular challenges to every part of the experiment, e.g. sample environment, detectors, and photon beam diagnostics.

An infobox, "Coherence and Photon Statistics", illustrates the particular usefulness of a coherent beam. The exact structural properties of the sample is encoded into the scattering image when a coherent beam is employed. The image appears speckled, *i.e.* with additional intensity and fine structure around the features originating from average properties, *e.g.* form factor and Bragg peaks. As a consequence, if the scatterers move inside the scattering volume

#### **Coherence and photon statistics**

Scattering images taken with incoherent X-rays give ONLY access to information about quantities averaged over the scattering volume like particle size and interparticle distance. In a region of a 2D detector with constant average intensity, e.g. circles in a small-angle scattering image taken on an isotropic sample of spheres, this leads to Gaussian (Poisson) probability distributions for images with good (poor) statistics. When a coherent beam is employed the situation is completely different. The image appears grainy with so-called "speckles" of intensity. The photon statistics is described by the Gamma distribution  $P_{\Gamma}(I)$  which has a high intensity tail and is markedly different from a Gaussian distribution. The M parameter in the expression for  $P_{\Gamma}(I)$  describes the degree of coherence as 1/M, so for instance M=100 corresponds to 1% coherence. For such low coherence it is difficult to distinguish the scattering image from the completely incoherent case with pure Gaussian statistics. For weak speckle patterns a Poisson-Gamma distribution describes the photon statistics instead of the Gamma distribution.



Fig. VIII.i1: Illustration of the fundamental difference between X-ray scattering images taken with a partially coherent (50%, M=2) or an almost incoherent (1%, M=100) beam. The "speckles" are apparent in the former case which also is reflected in the differences in photon statistics. but the average properties are maintained, the speckle pattern will fluctuate while an incoherent scattering image would remain static. From these properties two of the main applications of coherent X-ray scattering are derived: XPCS (X-ray photon correlation spectroscopy) where dynamics of the sample is inferred from the fluctuations of the speckle pattern, and CXDI (coherent X-ray diffraction imaging) where the phase of the speckle pattern is retrieved (*e.g.* by using an iterative phasing algorithm eventually in combination with ptychography) and a high-resolution real space image is achieved like in microscopy. The latter method, also denoted lensless X-ray diffraction microscopy, is the subject of Chapter 7.

The photon statistics of a speckle pattern obtained by illumination of a disordered sample follows the Gamma distribution:

$$P_{\Gamma}(I) = \frac{M^{M_{I}M-1}}{\Gamma(M) < I > M} exp\left(-\frac{MI}{}\right),$$

where I is the observed intensity in a pixel,  $\langle I \rangle$  is the average intensity of the ensemble, and M is the number of modes characterizing the contrast or graininess of the speckle pattern. For  $M \rightarrow \infty$  the Gamma distribution approaches a Gaussian distribution.

For this reason, speckle patterns are normally easy to identify, except if the photon statistics is poor. In this case the Poisson-Gamma distribution (convolution between Poisson and Gamma distributions), also known as the negative binomial distribution, describes the statistics [3] and it can be difficult to distinguish from a regular Poisson distribution. In the case of 100% speckle contrast (M=1) the speckle intensity follows negative exponential statistics where the maximum probability is found at I=0, i.e. the speckle pattern consist of many dark regions with no intensity. This means that weak incoherent scattering images easily can be mistaken for speckle patterns of very high contrast. To avoid this pitfall a careful analysis of the image has to be performed within the framework of the Poisson-Gamma model paying particular attention to multi photon events [4].

## Time correlation spectroscopy

X-ray free electron lasers will allow performing novel experiments to investigate the static and dynamic properties of matter with a much higher sensitivity than previously possible. This progress is directly linked to the properties of the source. The challenge for experimentalists is to pre-





Fig. VIII.2: Two-times correlation functions  $G(t_1,t_2)$  illustrating equilibrium dynamics (left) and aging dynamics (right). The color scale encodes the value of G where yellow is the highest number. The data were taken on a colloidal suspension under stable temperature conditions (left) and after a temperature quench (right) that triggered a gelation process and a subsequent slow-down of the dynamics. This leads to the contour lines moving away from the diagonal as t increases (right). Details about multi-speckle two-times correlation functions can be found in Ref. [6].





serve the parameters of the beam and transport it to the sample without unwanted perturbations which could lead to wavefront distortions, reduced intensity, or stretching of the pulses. To this end, a careful design of the X-ray transport system that guides the beam to sample is needed. Another big challenge is to develop novel experimental techniques that allow performing the desired measurements. In some cases the techniques will closely resemble those utilized at synchrotrons while in other cases the difference is marked. Speckle patterns will be generated whenever the coherent XFEL beam is scattered from a sample. However, to observe the fine structure a high resolution detector is required. The angular size of a speckle is approximately  $\lambda/d$  where  $\lambda$  is the wavelength and d is the beam size. Hence, to correctly resolve the speckle pattern it is required that the pixel size p of the detector fulfills  $p < L\lambda/d$ ,

where L is the distance from the detector to the sample. In the case of  $\lambda$ =1 Å, L=5 m, and d=10 µm we find that a pixel size of 50 µm, or less, is required in order not to wash out the speckle pattern. While it is not a problem to obtain CCD cameras of this pixel size it is a big challenge to develop fast hybrid pixel detectors with these specifications. This is in particular true if the detector is required to have on-chip memory, i.e. if the images are stored internally in order to enable MHz operation, the characteristic repetition rate of the European XFEL.

If the images from single pulses can be recorded and stored it is possible to make a speckle image movie. The variation of the speckle intensity can be characterized for every pixel by calculating the temporal auto-correlation function as illustrated in figure VIII.1. This is equivalent to X-ray Photon Correlation Spectroscopy (XPCS) performed at a synchrotron source [5,6] but with the advantage of higher average Brilliance and better coherence properties of the free-electron laser.

The fluctuations of the speckle pattern can be characterized by a time correlation function  $g_2$  for every value of the momentum transfer  $Q = \frac{4\pi \sin\theta}{\lambda}$ , where  $\theta$  is the scattering angle. If the system is in equilibrium the correlation function only depends on time via the time difference  $\Delta t$  between two images so

$$g_2(Q,\Delta t) = \frac{\langle I(Q,t)I(Q,t+\Delta t)\rangle}{\langle I\rangle^2}$$

where the averaging is performed over time t. If the dynamics depends explicitly on t (non-equilibrium dynamics) the time averaging must be replaced by an ensemble averaging, for instance over a subset of pixels in a 2D detector which correspond to the same Q (multi-speckle XPCS), and the correlation function

$$G(Q, t_1, t_2) = \frac{\langle I(Q, t_1) I(Q, t_2) \rangle}{\langle I(Q, t_1) \rangle \langle I(Q, t_2) \rangle}$$

is used.  $G(Q,t_1,t_2)$  is calculated directly as a function of the two times  $t_1$  and  $t_2$  at which the speckle images are taken. A visualization of this "two-times" correlation function G for non-equilibrium dynamics is shown in Fig. VIII.2.



Fig. VIII.3: Illustration of a split-delay line for hard X-rays [9]. This instrument allows studying fast dynamics i.e. beyond the repetition rate of X-ray pulses. Moreover, sophisticated pump-probe schemes can be realized by synchronization with an external optical laser.

The pulsed nature of XFELs with many photons arriving during a very short time interval allows in principle to study dynamics in real time down to the pico- and femto-second timescales. However, operating a 2D detector at such repetition rates is not possible and different experimental schemes must be developed. One such idea is presented in figure VIII.3 where an X-ray pulse is divided in two parts by a beam splitter (BS). The beam splitter is a semi-transparent single crystal operating in Bragg geometry and can for instance be realized in Silicon or Diamond. The two beams are sent out on different trajectories with a certain path length difference between them. The two pulses come together again at the beam merger crystal (BM) after which they travel collinearly. However, due to the path-length difference a time delay is introduced. Such a bimodal timestructure of the beam can be useful for many purposes, for instance to study dynamics. The time delay is scanned by moving the crystals of the split-delay line and figure VIII.3 shows an example of a device under commissioning at LCLS [8].

For every 10  $\mu$ m increment in the path length difference the time difference will grow by ~30 fs. After a time delay  $\Delta$ t has been introduced between the two pulses, they are sent towards the sample and generate each a speckle pattern on the detector. However, the detector cannot resolve the two speckle images that arrive within femto- or picoseconds and only the sum image will be registered. If the two images are identical the contrast of the summed image will be identical to that of the individual images, but if the atoms

or molecules move significantly on a length scale L during  $\Delta t$  the contrast will be reduced correspondingly at Q>2 $\pi$ /L. This allows mapping out the dynamics and quantifying the timescales [10]. Importantly, this experimental scheme only requires the sample to be illuminated once by the double pulse and hence it can be combined with a continuous injection of a renewable sample.

# **Experimental results**

The dramatic slowdown of dynamics associated with the transition from a liquid to a glassy state has been the subject of human fascination for centuries. Glass has been fabricated for thousands of years and for instance both the ancient Egyptians and Romans were able to manufacture many sorts of glassware, figurines, ornaments and gemstones. Only much later the term "glass" was used by scientists to designate the particular state of matter where the average structure is liquid-like (e.g. no long range ordering) but the dynamics is arrested. Typically, the transition from a viscous liquid to a glass happens by rapid cooling below T<sub>G</sub>, the glass transition temperature, after which the liquid solidifies. The characteristic timescales of structural dynamics increase by 12 orders of magnitude when the temperature is lowered by about 100 K. Despite the enormous scientific interest in the field a complete understanding of the underlying molecular mechanisms responsible for the glass transition is still lacking.

Fig. VIII.4: Correlation functions taken on a aqueous suspension of Laponite that forms a Wigner glass at certain concentrations. The differences between stretched (a) and compressed (b) exponential correlation functions is readily seen, in this case probably related to the different preparation protocols that in case (b) involves shear rejuvenation [14,15].



Because it allows probing Q-resolved slow dynamics in

tion functions can be studied as a function of Q and age and are typically approximated by an exponential form

$$g_2(Q,t) \sim \exp(-2[t/\tau(Q)]^{\alpha})$$

where  $\alpha$  is an exponent that allows modelling functions that either decay slower ( $\alpha$ <1) or faster ( $\alpha$ >1) than the pure exponential form ( $\alpha$ =1) as known from simple diffusion.

An example is shown in figure VIII.4 where a colloidal glass was investigated by multi-speckle XPCS [15]. Depending on the preparation protocol the correlation functions can assume both stretched ( $\alpha$ <1) and compressed ( $\alpha$ >1) exponential behaviors at a particular age ( $t_w$ ). Whereas  $\alpha$ <1 behavior has been known in glassy systems for a long time and associated for instance with a distribution of relaxation times it is only much more recently that  $\alpha$ >1 was observed. It has been speculated that compressed correlation functions are signatures of stress relaxation dynamics and for instance α>1 has also been seen in systems with short-range attractive interactions when load-bearing structures form, e.g. upon gelation [16].

Today, most dynamics studies by coherent X-ray scattering are limited by the available coherent flux at synchrotron sources. The grand challenge for the future will be to develop the techniques and employ XFELs to access regions of space and time in condensed matter dynamics that currently are out of reach for measurements. In the particular case of



non-equilibrium systems, multi-speckle XPCS has been widely employed to investigate the glass transition using partially coherent synchrotron radiation [11-14]. The correla-

ment at the LCLS.

patterns are re-

delay ∆t. (b) TEM

image of the gold

(5.5 nm diameter)

in a polystyrene

pattern produced

nanoparticles

Fig. VIII.6: (a) Correlation functions at different wave vector transfers with the relaxation times indicated in each plot, (b)  $\alpha$  exponent, and (c) corresponding relaxation time  $\tau$  as a function of q [17].



glasses structural dynamics in the micro- to picosecond range is today often inaccessible by lenghtscale resolved methods, particularly on the important meso-scale between the atomic scale and the macroscopic limit.

The first proof-of-principle XPCS experiment at XFEL sources has been performed at the LCLS recently [17]. By measuring the relaxation dynamics of gold nanoparticles suspended in glassy polymer melts it has been demonstrated that despite of inherently large pulse-to-pulse intensity and position variations of the XFEL beam, XPCS measurements can be realized. It has been found that the X-ray induced damage and heating are less problematic than initially expected for soft matter materials. A sketch of the experimental setup is shown in Fig. VIII.5a together with a TEM image of the gold nanoparticles (5.5 nm diameter) dispersed in a polystyrene matrix. At a temperature of 393 K the polystyrene matrix is not frozen thus enabling the gold particles to move slowly. This particle movement yields a gradual change of the corresponding speckle patterns. A total of 150 frames with 100 pulses per frame have been recorded at each sample position, which allow computing the temporal intensity autocorrelation function  $g_2(t)$  at different Q-positions (Fig. VIII.6a). The functions are modeled by a compressed exponential behavior yielding the characteristic relaxation time  $\tau$  (Fig. VIII.6b) and the compression exponent  $\alpha$  (Fig. VIII.6c). A linear dispersion of  $\tau(q)$  is observed together with an average compression exponent  $\alpha$ =1.28 pointing towards a ballistic type of motion of the gold particles in a highly visco-elastic medium.

One important result from this first XPCS study using XFEL sources is that a window in the X-ray photon density/sample

absorbance regime exists which allows performing such experiments in a quasi-equilibrium state. Under the experimental conditions used here neither the steady state sample heating nor the adiabatic heating by a single pulse are preventing the measurement of thermodynamically driven nanoparticle motion in polymer systems. The shot-to shot SASE fluctuations represent a challenge for data analysis since two consecutive frames may have intensities that differ by orders of magnitude but it can partially be compensated for by proper normalization schemes. While the time scale demonstrated here is still slow, the experiment proves that with the advent of the European XFEL with its high repetition rate and the availability of faster 2D detectors, XPCS experiment on much faster time scales will be possible.

#### Outlook

LCLS has given us the first possibilities to use X-ray beams of unprecedented intensity and coherence for imaging and dynamics experiments. Techniques inveted at synchrotron radiation sources can be further developed to take advantage of the unique properties of FEL radiation. This work has only just begun as we have discussed in this chapter concerning XPCS. In the future, the possibility of seeding the SASE process and operating with a higher source repetition rate will greatly benefit such developments. A state-of-theart experimental station for Materials Imaging and Dynamics (MID) is planned at the forthcoming European XFEL [18] with the aim of pushing these ideas further.

# Summary

- XFELs have a high degree of transverse coherence and are as such ideal machines for the study of dynamics by speckle correlation techniques
- The intrinsic fluctuations of the machine due to the SASE process pose challenges to the experimentalists
- Machine developments like seeding is expected to reduce the fluctuations and enable advanced experimental schemes like split-delay XPCS
- Despite experimental challenges, XPCS was recently demonstrated at the LCLS
- The advent of XFELs with higher repetition rate and highspeed area detectors will push investigations of structural relaxations in condensed matter into the nano- to femtosecond domains at length scales previously inaccessible by other direct methods

#### References

- [1] I. Vartaniants *et al.*, Phys. Rev. Lett. **107**, 144801 (2011)
- [2] C. Gutt *et al.*, Phys. Rev. Lett. **108**, 024801 (2012)
- J. Goodman, Statistical properties of Laser Speckle Patterns
   (Ch. 2) in Laser Speckle and Related Phenomena (J. C. Dainty, Ed). Springer-Verlag (1975)
- [4] S. O. Hruszkewycz *et al.*, Phys. Rev. Lett. **109**, 185502 (2012)
- [5] G. Grübel *et al.*, X-Ray Photon Correlation Spectroscopy (XPCS) in Soft Matter Characterization (R. Borsali and R. Pecora, Eds). Springer-Verlag (2008), p. 953
- [6] A. Madsen *et al.*, New Journal of Physics **12**, 055001 (2010)
- [7] G. Grübel et al., Nucl. Instr. Meth. B 262, 357 (2007)
- [8] W. Roseker et al., J. of Sync. Rad. 18, 481 (2011)
- [9] W. Roseker *et al.*, DESY Photon Science 2009. Highlights and HASYLAB Annual Report, pp. 48-49

- [10] C. Gutt et al., Optics Express, 17(1), 55 (2009)
- [11] C. Caronna et al., Phys. Rev. Lett. 100, 055702 (2008)
- [12] B. Ruta et al., Phys. Rev. Lett. 109, 165701 (2012)
- [13] P. Kwasniewski et al., Soft Matter 10, 8698 (2014)
- [14] R. Angelini et al., Soft Matter 9, 10955 (2013)
- [15] R. Angelini *et al.*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **460**, 118 (2014)
- [16] O. Czakkel and A. Madsen, Europhys. Lett. 95, 28001 (2011)
- [17] J. Carnis et al., Scientific Reports 4:6017 (2014)
- [18] A. Madsen *et al.*, MID Technical Design Report (2013), XFEL.
   EU technical report.
   https://bib-pubdb1.desy.de/record/154260

# IX. Correlation-function analysis of molecular scattering

Richard Kirian, Arizona State University

Ensembles of identical but randomly oriented nano-objects scatter X-rays into characteristic patterns that are usually isotropic about the beam direction. XFEL pulses of femtosecond duration and immense brightness produce non-isotropic scattering from states of matter that are "frozen in time". The analysis of angular intensity correlations from many such scattering patterns can provide detailed structural information.

- Introduction
- Ensembles of non-interacting, identical particles
- Ensembles of interacting particles
- Outlook

A basic description of methods that utilize angular intensity correlations in order to determine structural information, including atomic arrangements in molecules, is presented. The cases of *ab initio* projection imaging and 3D structure determination are considered, along with the more challenging situation in which densely packed amorphous materials are investigated. Illustrations and examples from the literature are provided.

## Introduction

X-ray scattering methods are among the most important tools available for the study of disordered materials and biomolecules. The long penetration lengths of X-rays allow them to peer deep into matter, to yield information about its atomic configuration. In the Born approximation, diffraction patterns can reveal the target's electron pair distance distribution function – essentially a histogram of pair distances between the electrons that scatter X-rays. Much can be revealed from a pair distribution function, such as the coordination number (the number of nearest-neighbor atoms), and, in the case of biomolecules in solution, properties such as molecular volume, surface area, and even three-dimensional molecular envelopes can be determined without prior-known structural information.

In contrast to conventional scattering analysis, in which only the radial intensity function is analyzed, new methods are being developed to exploit the statistical properties of intensity correlation functions. Such analyses are performed on large numbers of "snapshot" diffraction patterns in which different localized regions of a disordered target are exposed. In these snapshot patterns, the target is frozen in time by sufficiently brief illumination – no significant motion occurs during each X-ray exposure. This approach naturally applies to static solid-state targets (where radiation damage and exposure timescales are not problematic), but can also apply to liquid targets, provided that the X-ray diffraction intensities are sufficiently high and the exposure is shorter than the diffusion timescales of the target.

Intensity correlation measurements have been performed using both synchrotron X-ray sources and electron beams in the last decade or two, but synchrotrons are limited in their brightness, while methods based on electrons, which have elastic scattering cross sections that are several orders of magnitude greater than X-rays, are limited to long timescales and thin targets, ranging from a few tens to hundreds of nanometers thickness, depending on the material composition. A surge of interest in intensity correlation approaches has emerged as a result of the recent advent of X-ray free-electron lasers (XFELs). XFELs produce laser-like pulses of coherent radiation, with wavelengths down to about an angstrom (1 Å = 0.1 nanometers), pulse durations down to a few femtoseconds (1 fs =  $10^{-15}$  seconds), pulse energies of a few mJ (about  $10^{12} - 10^{13}$  photons), and pulse repetition rates ranging from about 100 Hz at present sources to about 1 MHz at sources presently in the planning and construction phases. Due to their immense brightness, XFELs allow one to effectively record snapshot diffraction patterns from nearly any target, because the pulse terminates prior to the onset of atomic motion. By outrunning atomic motion, XFELs also overcome the fundamental resolution-limiting problem of X-ray-induced damage to sensitive organic targets.

Intensity correlation measurements may be divided into two realms of application: The first application is disordered ensembles of identical, non-interacting particles. A dilute solution of biomolecules is a good example of this type of system, and it is the sample that was investigated originally by Z. Kam in 1977 [1], as will be discussed in the next section. The other application is to densely packed systems of particles, which was originally considered (for both electrons and X-rays) following Kam's first reports [2,3]. Densely packed systems result in a more complicated interpretation of the intensity correlation measurement, as we will also discuss.

# Ensembles of non-interacting, identical particles

A remarkable paper written by Z. Kam appeared in 1977 [1], in which he suggested that the three-dimensional structures of macromolecules might be determined *ab initio*, and without resolution restrictions, by analyzing the angular diffraction intensity correlations that arise from snapshot solution scattering measurements. Provided that the duration of the illumination is shorter than the time it takes for the molecules to rotate significantly, Kam's approach utilizes angular intensity correlations in order to unscramble the orientational disorder in the target. Subsequently, one seeks to recover the three-dimensional diffraction intensity map, or, ultimately, the electron density of just one molecule (as depicted in Fig. IX.1). This idea might be best understood by first considering a single molecule that rotates only about the axis of the X-ray illumination. Since the diffraction pat-

#### From intensity correlations to real-space projection image

The intensity correlation measurements described in the main text directly provide the products of the angular Fourier expansion coefficients of single-particle diffraction intensities:  $I_m(q_i) I_m^*(q_j)$ . In principle, this information allows the direct determination of the magnitudes  $|I_m(q)|$  along with the phase differences  $\chi_{mi}-\chi_{mj}$  for a given m, where we express the complex coefficients as  $I_m(q_j) = |I_m(q_j)| \exp(im\chi_{jm})$ . The challenge is to determine the individual phases  $\chi_{mi}$  that are needed in order to reconstruct the single-particle diffraction pattern, which requires only one phase for each m, since relative phases for i,j are known.

Unfortunately, intensity *pair* correlations provide no useful coupling between coefficients of different *m*, and hence one must in general utilize additional information, such as the fact that the diffraction intensity arises from a finite object. Pedrini et al. [5] devised an approach in which intensity *triple* correlations (that is, the averaged products at three points in the detector) are extracted from the data, which uniquely determines all phases. Following the determination of all  $\chi_{mi}$ , one can reconstruct a real-space image from the single-particle diffraction intensities using iterative phasing methods.



Fig. IX.i1: Experimental demonstration of two-dimensional projection imaging with intensity correlations. Panel (a) depicts the experiment in which a sample is scanned across the X-ray beam, and a series of diffraction patterns is collected at many points on the sample. Intensity correlations are measured for each pattern and averaged. Panel (b) shows the single-particle diffraction pattern recovered from the intensity correlations, from which the real-space image shown in panel (c) was reconstructed using conventional iterative phase-retrieval methods. Panel (d) shows the sample membrane with many particles. A magnified view of a single particle is shown in panel (e) [5].

tern rotates in correspondence with the molecule, a simple average over the diffraction patterns from many snapshots of randomly oriented molecules would produce a conventional, azimuthally-symmetric, scattering pattern (although one which is restricted to a single axis of rotation). Such an averaged pattern yields only a one-dimensional data set: the radial intensity profile.

The key rationale in Kam's approach is that the angular autocorrelation function is *independent of the molecule's orientation* and does not rotate with the molecule. Hence a greater amount of information (which grows in proportion to the cube of the molecule's size) can be obtained if we instead form the *average angular intensity correlation* of the scattering from the molecule. To place this in concrete terms, let the diffraction intensity from the molecule be  $I(q,\phi)$ , where q is the radial component of the diffraction intensity, and  $\phi$  is the azimuthal angle (see Fig. IX.1). The angular intensity correlation may be written as

$$C(q_i, q_j, \Delta \phi) = \frac{1}{2\pi} \int_0^{2\pi} I(q_i, \phi) I(q_j, \phi + \Delta \phi) d\phi \quad (1)$$

We also refer to this as the "ring cross-correlation function", since it involves two rings of diffraction intensities, as shown in Fig. IX.2.

Remarkably, when we illuminate an ensemble of molecules simultaneously, the resulting angular intensity correlation reduces to that of just one molecule, apart from a term that is featureless with respect to the azimuthal angle  $\phi$ . In the case of a partially coherent beam, with a coherence length sufficient to produce diffraction from each molecule but insufficient to produce interference fringes from neighboring molecules, the *k*<sup>th</sup> diffraction pattern from *N* molecules may be written as the incoherent sum of individual diffraction intensities:

$$I_k(q,\phi) = \sum_{m=1}^{N} I(q,\phi+\omega_{k,m}) \qquad (2)$$

where  $\omega_{k,m}$  is the orientation of the  $m^{\text{th}}$  molecule in the  $k^{\text{th}}$  diffraction pattern. Upon inserting the above equation into Eqn 1, and averaging the angular intensity correlation over many diffraction patterns, we obtain:

$$C_{N}(q_{i},q_{j},\Delta\phi) = \left\langle \frac{1}{2\pi} \int_{0}^{2\pi} I_{k}(q_{i},\phi) I_{k}(q_{j},\phi+\Delta\phi) d\phi \right\rangle_{k}$$
(3)  
=  $NC_{1}(q_{i},q_{j},\Delta\phi) + (N^{2}-N) \left\langle I(q_{i})_{\phi} \right\rangle \left\langle I(q_{j})_{\phi} \right\rangle$ 

where the angle brackets  $\langle f(a) \rangle_a$  indicate the average of the function f(a) with respect to the variable a. The terms on the right-hand side of the above equation may be under-



Fig. IX.1: Illustration of Kam's method. X-rays produce diffraction from multiple ensembles of molecules. The average angular intensity correlation function is then produced from these many frames. An algorithm, perhaps with additional known constraints, then produces an image or structure of a single molecule. stood by noting that the intensity correlation involves a product of two summations, each with N terms. There are  $N^2$ -N products that are uncorrelated (because different molecules are assumed non-interacting, with random and independent orientations), and hence the average product is equal to the product of averages. These  $N^2$ -N terms are just the product of conventional radial intensity profiles.

The remaining *N* terms are perfectly correlated, and correspond to the *single-particle* angular intensity correlation. In the case of a fully coherent beam, which produces "speckle" due to the interference fringes that arise from pairs of molecules, the same result as Eqn. 3 is found, assuming a broad illumination of ensembles of molecules with no particular spatial correlations.

#### Time-resolved three-dimensional structure determination

Methods for determining three-dimensional electron density maps from intensity correlation data can be devised in some cases. Pande *et al.* [14] considered the case of time-resolved studies, and demonstrated a method in which the difference in electron densities can be determined, provided measurements are made from a structure with small perturbations from its known ground state. This approach is based on the fact that a small variation in the reduced intensity correlation data may be expressed too good approximation as

$$\delta B_l(q_i, q_j) = \sum_m \delta I_{lm}(q_i) I_{lm}^*(q_j) + I_{lm}(q_i) \delta I_{lm}^*(q_j)$$

where  $\delta I_{lm}$  (*q*) is the difference in the spherical harmonic expansion coefficients of the object's 3D diffraction intensity map. Similar to the problem in two dimensions, in which the coupling between phases of expansion coefficients cannot be deduced from the intensity correlation data alone, the 3D problem suffers from ambiguities involving unitary transformations of expansion coefficients of a given *m*. Roughly speaking, the known ground state expansion coefficients that appear in the above equation provide the needed coupling amongst expansion coefficients. Quite remarkably, the procedure of Pande *et al.* is *noniterative*.



Fig. IX.i2: A protein solution scattering experiment in which a laser pump, followed by time-delayed X-ray probe, strikes a jet of protein solution (left panel). The difference electron density map, recovered from the simulated intensity correlation data from photoactive yellow protein (right panel) [14].

Another notable feature of angular intensity correlations is that the signal-to-noise ratio (SNR) is essentially independent of the number of molecules illuminated. A Heuristic argument for why this is so can be made as follows: If we take the magnitude of our "signal" to be the root-meansquared (RMS) intensity fluctuation, we note that it grows as  $\sqrt{N}$ . (It is equivalent to a one-dimensional random walk process in which the size of each step is drawn randomly from a bounded pool of single-particle diffraction intensities). The mean signal for a given angular intensity ring grows in proportion to N and thus the RMS Poisson photon counting noise is proportional to  $\sqrt{N}$ . Therefore, both signal and noise grow in proportion to each other, which renders the SNR independent of *N*. Note that the intensity fluctuations do not "vanish" in the limit of infinite *N*; on the contrary, they grow without bound. However, the ratio of fluctuations to the mean intensity does vanish since it scales as  $1/\sqrt{N}$ . The ratio of Poisson noise to the mean intensity also decreases as  $1/\sqrt{N}$ . Since no significant improvement can be expected when the number of illuminated particles is increased, the primary concerns in intensity correlation measurements are the noise due to the solvent scattering (which can be reduced by increasing the particle concentration, to the extent that particle interactions do not complicate the data analysis) and the incident fluence (photons/ area, integrated over the pulse duration). More generally, in the absence of detector errors, the SNR in an intensity correlation grows in proportion to  $J\sqrt{M}\lambda^2$  where J is the fluence (photons/area), *M* is the number of diffraction patterns, and  $\lambda$  is the X-ray wavelength [4]. Clearly, it is best to distribute a given time-averaged X-ray power into relatively few pulses of high intensity, and to use the longest wavelength that is compatible with the experiment.

We now consider how the angular intensity correlation function can be used to produce an *ab initio* real-space projection image of the illuminated identical particles. Firstly, we note that the continuum of diffraction intensities from an isolated object almost always provides sufficient information to form a unique image, provided that the object has a finite size that is smaller than the illumination profile. Since only the diffraction intensities (and not their phases) are recorded, this requires the use of phase-retrieval algorithms, which have been extensively developed in the field of coherent diffractive imaging. The objective here is to recover the single-particle diffraction intensities from the measured correlation function. To do this, we first expand  $I(q,\phi)$  in terms of an angular Fourier series:

$$I(q,\phi) = \sum_{m} I_m(q) e^{im\phi} \quad (4)$$

Next, we take the angular Fourier transform of Eqn. (4) to give:

$$B_m(q_i, q_j) = \frac{1}{2\pi} \int_0^{2\pi} C_1(q_i, q_j, \Delta \phi) e^{-im\Delta \phi} d\Delta \phi$$
  
=  $I_m(q_i) I_m^*(q_j)$  (5)

We can now see that the angular Fourier transform *magni*tudes are immediately accessible from the terms  $B_m$  (q,q), and in addition that we have the phase differences (for a particular *m*) of these *complex-valued* coefficients from the terms  $B_m$  ( $q_i$ , $q_j \neq q_i$ ). In general, the problem of determining a consistent set of phases is over-determined, and a variety of methods of solutions exist [5-9] (See Fig. IX.I1 for an example).

For the problem of determining three-dimensional structures, we must allow the particles to rotate over a wider range of orientations, including axes that are not aligned to the incident beam. In that case we may write the singleparticle diffraction pattern more generally as  $I(q;\omega)$  where q is the scattering vector in the laboratory frame, and  $\omega$ specifies the orientation of the molecule with respect to the laboratory frame (this may represent a set of three Euler angles, for example). If we measure the intensity correlation for a given pair of scattering vectors (two pixels in an area detector), we obtain the quantity:

$$C_{N}(\mathbf{q}_{i},\mathbf{q}_{j}) = NC_{1}(\mathbf{q}_{i},\mathbf{q}_{j}) + (N^{2} - N)\langle I(\mathbf{q}_{i};\omega)\rangle_{\omega}\langle I(\mathbf{q}_{j};\omega)\rangle_{\omega} \quad (6)$$

where we again used the simple fact that the average product of uncorrelated quantities is equal to the product of their individual averages. We write the recovered single-particle pair correlation function as

$$C_{1}(\mathbf{q}_{i},\mathbf{q}_{j}) = \left\langle I(\mathbf{q}_{i};\boldsymbol{\omega})I(\mathbf{q}_{j};\boldsymbol{\omega})\right\rangle_{\boldsymbol{\omega}} \quad (7)$$

One can visualize this single-particle correlation function by first imagining the molecule's diffraction intensities

#### Colloidal systems of densely packed spheres

While the atomic structure of atomic glasses is difficult to study due to signal limitations, X-ray diffraction studies on colloidal glasses have been used to demonstrate the potential of intensity correlation techniques. Wochner *et al.* [17] conducted the first of such studies with X-rays, and showed how angular correlations can reveal pronounced symmetries in systems of apparently disordered spherical PMMA nanoparticles. The authors attributed the observation of 5-fold symmetries in angular autocorrelations to the presence of local icosahedral packing of spheres and near-field effects (which break the inversion symmetry that is often associated with small-angle diffraction). Results reported here demonstrated the great potential of angular intensity correlation analysis, and notably included timeresolved data in which the evolution of angular correlations were observed as colloidal solutions slowly relax.



Fig. IX.i3: Experimental demonstration of intensity correlation measurements from a densely packed colloidal sample. The experimental geometry is shown in panel (a), in which diffraction patterns are collected from a suspension of spherical nanoparticles. Panel (b) shows the conventional scattering profile, with four different regions indicated that correspond to the angular intensity autocorrelations shown in panel (c) [17].

(usually proportional to the modulus squared Fourier transform of the electron density) in three-dimensional reciprocal space, with coordinate q, and then averaging the product at two points in that space as the particle rotates according to its orientational freedom. Notably, in the case of isotropic suspensions of particles, we may again use the "ring cross correlation" method described previously, without loss of information, since the diffraction intensities are statistically independent of a global rotation of the target about the beam axis. For off-axis alignment, in which the particles are (partially) aligned about an axis that differs from the incident beam axis, this independence is not valid, and ring cross correlations are not appropriate [8]. The details of the subsequent analysis now depend on the orientational freedom of the particles and the constraints on the particle's electron density.

For isotropic suspensions of particles, one might consider expanding the three-dimensional diffraction volume (which we wish to recover) in a spherical harmonic expansion [1]:

$$I(\mathbf{q}) \equiv I(q,\theta,\varphi) = \sum_{lm} I_{lm}(q) Y_{lm}(\theta,\varphi) \quad (8)$$

A Legendre transform of  $C_1(q_i,q_j)$  can be used to yield the relations:

$$B_l(q_i,q_j) = \sum_{m=-l}^{l} I_{lm}(q_i) I_{lm}^*(q_j) \quad (9)$$

The problem of determining a general 3D structure now lies in the determination of the expansion coefficients  $I_{lm}(q)$ , given the summation of products above. In general, for a molecule with a spherical region of unknown electron densities, it can be shown that this problem is under-constrained [10]. However, there are some cases in which the problem can be solved, for example when additional constraints can be introduced (such as known symmetry [11-13]) or in situations where one seeks only a perturbation of a known ground state of the molecule [14] (see Fig. IX.I2). In other cases, modeling approaches similar to those used in SAXS can be used [15], and it is conceivable that methods associated with crystallography, such as specific labeling with heavy atoms or resonant scattering, might be extended to the problem of structure determination with intensity correlations [1].

#### Ensembles of interacting particles

We now consider the more complex case of densely packed amorphous samples, such as glasses, polymers, colloids, nucleation sites, and paracrystalline materials. In this situation, we cannot neglect the inter-particle interference that arises as a result of the beam coherence spanning neighboring particles with correlated positions and/or orientations. Coherence can only be neglected in cases where there are no interactions between neighboring particles, and in the study of densely packed samples it is precisely these interactions that we wish to study. For example, our goal may be to reveal a short-range ordering corresponding to polyhedral atomic configurations within a glass, along with the longerrange ordering associated with the packing of such polyhedra.

Consider a material formed with a single species of atom or molecule with real-space electron density  $\rho(\mathbf{r})$  and reciprocal-space diffraction *amplitude*  $A(\mathbf{q})$ . A rotated and translated copy of that molecule produces the diffraction amplitudes  $A(\mathbf{q},\omega) e^{i\mathbf{q}\cdot\mathbf{R}}$ , where  $\mathbf{R}$  is its translation vector and  $\omega$  again specifies its orientation. In the following, we will use the shorthand notation  $A_{ki\alpha} = A(\mathbf{q}_{i},\omega_{k,\alpha})e^{i\mathbf{q}\cdot\mathbf{R}_{k,\alpha}}$  to specify the singleparticle diffraction amplitude at the *i*<sup>th</sup> detector pixel arising from the  $\alpha$ <sup>th</sup> particle in the k<sup>th</sup> X-ray exposure. The diffraction intensity of a single particle is equal to  $I_{ki\alpha} = A_{ki\alpha} A_{ki\alpha}^*$ , whereas the diffracted intensity from the k<sup>th</sup> *ensemble* of N such particles is

$$I_k(\boldsymbol{q}) = |\sum_{\alpha}^N A_{ki\alpha}|^2 . \quad (10)$$

The *ensemble* averaged intensity correlation is proportional to

$$C_N(\boldsymbol{q}_i, \boldsymbol{q}_j) = \langle \sum_{\alpha\beta\gamma\delta}^N A_{ki\alpha} A_{ki\beta}^* A_{kj\gamma} A_{kj\delta}^* \rangle_k .$$
(11)

The sum over terms for which  $\alpha = \beta$  and  $\gamma = \delta$  are precisely equal to the intensity correlations already described in Eqn. (6) in the previous section, since the phase factors are  $e^{iq.(R_{k,\alpha}-R_{k,\alpha})}=1$ . The remaining terms contain information about the correlations among the vectorial separations  $R_{k,\alpha}$ and angles  $\omega$  for multitudes of objects in real space (up to four objects in the case of pair correlations). Note that if the positional vectors and corresponding phases  $e^{iq.R_{k,\alpha}}$  are statistically independent (as in the case of non-interacting particles), these additional terms average to zero, and the correlation function reduces to that in Eqn. (6). (The statistical errors, however, might not be independent of N.) To make some sense of the above, one might first consider a hypothetical mixture of atomic dimers, with occasional occurrences of tetrahedral configurations. A dilute gas of such a system would produce the correlation function

$$C(\boldsymbol{q}_i, \boldsymbol{q}_j) = N_a C_1^{(b)}(\boldsymbol{q}_i, \boldsymbol{q}_j) + N_b C_1^{(b)}(\boldsymbol{q}_i, \boldsymbol{q}_j) + G(\boldsymbol{q}_i, \boldsymbol{q}_j) \quad (12)$$

where there are  $N_a$  dimers with single-particle correlation function  $C_1^{(a)}$ ,  $N_b$  tetrahedra with single-particle correlation function  $C_1^{(b)}$ , and, because this dilute system of multiple species is non-interacting, a featureless term G containing products of conventional scattering intensities. We can see that, in this simple case with limited interactions, the intensity correlation function corresponds to a number-weighted average over the types of local configurations. This result can be extended to an arbitrary number of species, including the case of polycrystalline material with domains of varying shape and size. If no dominant local configuration is present, the correlation function might be featureless at large length scales. On the other hand, if only a few dominant species exist in an otherwise random network of particles, and if the relative number densities of each species can be varied (for example with an external applied field, temperature, or pH change) it is in principle possible to isolate the correlation functions corresponding to each species.

For a densely packed system with strongly correlated networks of particles, the term  $G(q_i,q_j)$  is not featureless and contains information about the interrelationships between particles [16]. Unlike a conventional radial intensity function, this term is sensitive to properties such as bond angles and packing relationships, as shown in X-ray diffraction experiments from colloidal systems of particles that indicated the existence of icosahedral packing [17] (see Fig. IX.i3). Unlike the simple cases described so far, the inverse problem of determining structures from this measurement is by no means straightforward and, as with the problem that Kam considered, is information-deficient in the most general case in which no prior knowledge is available. However, such information can be used in conjunction with modeling, since the forward problem of generating  $G(q_i, q_j)$  from a density map is straightforward.

Despite our present inability to directly invert intensity correlation measurements into structural models of amorphous materials, it should be noted that even a modest amount of information, in addition to a pair distribution function, can be used to rule out structural models. This is perhaps best illustrated by results from a closely related technique known as fluctuation electron microscopy (FEM) [18]. FEM essentially consists of measuring only the subset  $C(q_i,q_j=q_i)$  (that is, the intensity variance) and has proven sufficient to rule out long-standing atomic models for amorphous materials in cases where the radial intensity distribution alone proved insufficient [19]. Notably, FEM sometimes utilizes varying illumination profile parameters to generate a greater amount of structural information.

### Outlook

A wealth of literature on angular intensity correlation methods has appeared in recent years. For dilute suspensions of identical particles, one emerging viewpoint focuses on the connections between correlation measurements and the iterative phasing methods associated with coherent diffractive imaging, with the aim of recovering images and structures using only modest constraints. Exquisite experimental results for both 2D and 3D targets have demonstrated the basic principle on non-biological samples, although in 3D only the structures of axially-symmetric particles have been determined so far. The success of ab initio methods based on iterative phase retrieval procedures will likely depend on the ability of experimentalists to measure nearly complete datasets. Some estimates suggest that approximately one order of magnitude improvement beyond present XFEL source intensities will be required for complete datasets at sub-nanometer resolution [4]. However, it is conceivable that such improvements may indeed be achieved at future XFEL sources [20].

Another viewpoint on the problem of solving structures from dilute solutions highlights connections between correlation measurements and the analysis methods associated with SAXS, which utilize constrained models. Notably, conventional SAXS data typically yield only about 15-20 unique measurements, and thus one can expect significant gains even if only a similar number of additional measurements is obtained through intensity correlations. Indeed, experiments and simulations suggest that model-based approaches are a practical and feasible means of determining molecular envelopes (albeit demonstrated only on inorganic samples so far), and that the addition of intensity correlations improves the reliability of resulting structures over conventional SAXS. Since model-based approaches simply seek to maximize agreement between model and data, they may be applied to incomplete datasets.

The investigation of densely packed amorphous samples, such as glasses, polymers, colloids, nucleation sites, and paracrystalline materials, appears at present to be limited mainly to analysis methods based on structural models. Despite this apparent limitation, it has been shown that even a modest gain in information can be sufficient to rule out long-standing structural models, as noted above. Using the basic argument that the signal-to-noise ratio for correlation measurements is largely independent of the number of scattering objects, the study of samples consisting of small and weakly scattering molecules (such as water) would be extremely challenging. However, intensity correlations from systems of particles with high degrees of local symmetry (such as paracrystalline materials) or strongly scattering objects (such as metallic glasses) might be within the reach of experimental observation, particularly if the integrated intensity of few-femtosecond XFEL pulses continues to increase.

Intensity correlation measurement and analysis methods are presently topics of much on-going research; firm experimental limitations have not yet been established, and new analysis methods have been reported with remarkable frequency in recent years. In principle, the above approaches to the analysis of snapshot XFEL diffraction data can clearly reveal a wealth of new information about a rich variety of targets. In cases where intensity correlations are required from weakly scattering particles at high resolution, experimental developments will be strongly dependent on the continued increase in integrated XFEL intensity, and our understanding of ultrafast radiation-induced damage processes.

# Summary

- Snapshotscattering patterns, with exposures of duration shorter than the motion of the target, capture structural details from disordered targets that is not seen in conventional x-ray scattering. This information may be recovered through the measurement of intensity correlations acquired from many statistically identical ensembles of particles.
- For ensembles of identical objects, methods are under development to recover real-space electron density maps without prior structural knowledge. Sufficiently intense x-ray pulses would allow, for example, the determination of biomolecular structures in solution, without crystallization, and at physiological temperature.
- A variety of methods have been developed for recovering two-dimensional images and even three-dimensional structures for cases in which the objects can be strongly aligned about an axis.
- The general problem of solving a 3D structure from randomly aligned particles without prior structural knowledge suffers from a slight information deficiency. However, creative approaches to circumvent this apparent problem are under rapid development, such as model-based approaches, variational approaches (based on similar known structure), and symmetry assistance.

- A wealth of information can also be found from densely packed structural networks, such as glasses and paracrystalline materials. Whereas conventional scattering intensity data only reveals information about the electronic distances, two-point intensity correlations can also uncover information about bond angles. Minimally, such data may be used to rule out structural models.
- For the case of identical, repeating structures (particles), the signal-to-noise ratio reduces to that of a single particle illuminated by the beam in each shot. From a signal-to-noise standpoint, intensity correlation measurements are akin to single-particle diffraction measurements if background scatter is insignificant.

#### References

- [1] Z. Kam. *Macromolecules*, 10(5):927–934 (1977).
- [2] N. Clark, et al. Physical Review Letters, 50(19):1459–1462 (1983).
- [3] A. Howie, et al. Journal de Physique, 46(C-9):59–62 (1985).
- [4] R. A. Kirian, et al. Physical Review E, 84(1):011921 (2011).
- [5] B. Pedrini, et al. Nature Communications, 4:1647 (2013).
- [6] D. K. Saldin, et al. Physical Review E, 81(17):174105 (2010).
- [7] D. K. Saldin, et al. Physical Review Letters, 106(11):115501 (2011).
- [8] V. Elser. New Journal of Physics, 13(12):123014 (2011).
- [9] R. P. Kurta, *et al. New Journal of Physics*, 15(1):013059 (2013).
- [10] V. Elser. Ultramicroscopy, 111:788–792 (2011).
- [11] D. Saldin, et al. Optics Express, 19(18):17318–17335 (2011).

- [12] H. Poon, et al. Physical Review Letters, 110(26):265505 (2013).
- [13] D. Starodub, et al. Nature Communications, 3:1276–7 (2012).
- K. Pande, et al. Phil. Trans. B, 369(1647):20130332– 20130332 (2014).
- [15] H. Liu, et al. Acta Crystallographica Section A, 69(4) (2013).
- [16] M. Altarelli, et al. Physical Review E, 82(10):104207 (2010).
- [17] P. Wochner, et al. PNAS, 106(28):11511–11514 (2009).
- [18] M. Treacy, et al. Reports on Progress in Physics, 68(12):2899–2944 (2005).
- [19] M. M. J. Treacy and K. B. Borisenko. The Local Structure of Amorphous Silicon. Science, 335(6071):950–953 (2012).
- [20] S. Serkez, V., et al. arXiv preprint arXiv:1308.0448 (2013).

# X. Ultrafast demagnetization

Fulvio Parmigiani, University of Trieste Yves Acremann, ETH Zurich Clemens Korff Schmising, TU Berlin

A short pulse of infrared laser light destroys the magnetization in a ferromagnet within 100 fs – what is the microscopic mechanism, how is angular momentum transferred, and what are the implications for ultrafast magnetic switching?

- Introduction
- Models of ultrafast demagnetization
- Superdiffusive spin transport
- Phonon-induced spin flips
- Outlook

Magnetism is responsible for one of the oldest inventions, the magnetic compass, and further applications have revolutionized our world, through, e.g., ferrite core memory to today's high-density magnetic data storage, where of the order of 400 gigabits can be written per square inch at a rate of one bit per two nanoseconds. The fact that many fundamental magnetic processes take place on the nanometer length and picosecond time scales, and the high magnetic sensitivity of resonant, circularly-polarized X-rays and of spin-polarized photoemission, make the XFEL a versatile instrument for state-of-the-art research in magnetism. Of particular current interest is the ultrafast reduction of ferromagnetic order, following laser excitation.

# Introduction

The origin of magnetic phenomena in materials is the electron spin and its associated magnetic moment. A "ferromagnetic" material has a spontaneous net magnetic moment when its constituent atoms with unpaired electron spins (e.g., transition-metal, lanthanide and actinide ions) interact via an "exchange interaction" - an electrostatic interaction arising from the Pauli exclusion principle. Magnetic phenomena in materials show interesting effects on a wide range of characteristic length and time scales (see Fig. X.1), which are important to both fundamental understanding and applications. Although the scattering of X-rays by matter is generally due to their electric interaction with electronic charge, for photon energies at resonance with core transitions, strong magnetic contributions arise from angularmomentum selection rules. An example is the spin-orbit split  $2p \rightarrow 3d$  transitions (L<sub>2</sub> and L<sub>3</sub> edges, in the soft X-ray region) of 3d magnetic ions, near which the absorption and

scattering probabilities for circularly-polarized X-radiation are strong functions of the magnetization (see the Infobox on X-ray Magnetic Circular Diochroism).

In 1996, Beaurepaire et al. published a very remarkable observation [2]: a ferromagnetic Ni film exposed to an intense 60 fs pulse from an optical laser becomes demagnetized in less than a picosecond. Using the magneto-optical Kerr effect as probe, an ultrafast decrease was observed in the magnetization, followed by a slower recovery (see Fig. X.2). This observation, together with later measurements using other methods of detection, raised the fundamental question, as yet unanswered, of where the spin angular momentum of the electrons goes and how it can be transferred so quickly. This problem of "ultrafast demagnetization" has stimulated a large amount of ongoing experimental and theoretical work, with the XFEL playing a major role, and it has direct bearing on applications using ultrafast magnetic manipulation in novel data storage and spintronics.



Fig. X.2: Sub-picosecond demagnetization of a Ni film following an optical laser pulse, observed with the magneto-optic Kerr effect [2]. This observation has stimulated much speculation on the as yet unanswered question of how angular momentum can be transferred so efficiently from the spin system to the lattice.



# X-ray Magnetic Circular Dichroism (XMCD)

# The difference absorption between parallel and antiparallel orientations of the sample magnetization and the incident photon spin is directly proportional to the atomic magnetic moment and is called the XMCD difference intensity (difference between red and green cross section in Fig. X.i1). In a simplified view, one can understand the microscopic origin of the XMCD effect by a two step model: first, during the X-ray absorption process, angular momentum is transferred from the circularly polarized photon $(\pm\hbar)$ to the excited photoelectrons via spin-orbit coupling. The spin polarization of the electrons depends on the absorption edge involved and on the helicity of the X-ray photons.

#### Models of ultrafast demagnetization

The ultrafast loss of magnetic order in a ferromagnet is surprising: It is still not clear how the spin angular momentum can be transferred to the surrounding in order to cause demagnetization. Shortly after the discovery, there was a debate if the magneto-optical Kerr effect (MOKE) used in the first experiments is actually able to reliably detect the magnetization of a laser-excited sample [3]. Since MOKE is dependent on spin-orbit coupling and works with visible light photons, it is conceivable that the hot electron gas created by the laser pulse affects the MOKE effect itself. If the MOKE contrast would be reduced by the laser excitation, one might

In the second step, the final, exchange-split 3d state acts as a spin-resolving detector. For example, in the specific case of a partially filled spin-up 3d valence shell, only spin-up electrons can be excited from the 2p core level, because spin flips are not allowed during excitation. Magnetic contrast at the M-edges of 3d metals allows experiments at lower X-ray energies (40-72 eV).

The XMCD effect therefore requires polarization control of the incoming X-ray beam. This is provided by an APPLE II-type undulator at the FERMI FEL and is planned with a Delta-type undulator at the LCLS. The FLASH FEL will be equipped with an efficient polarizer based on Fresnel reflection by mid-2015.







Fig. X.3: Three-temperature model: The electron gas is initially excited by the pump laser pulse, and the subsequent behavior of the lattice, the electrons and the spin system is determined by phenomenological coupling time constants [1].

misinterpret the observed signal as ultrafast demagnetization. X-ray magnetic circular dichroism (XMCD) also depends on spin-orbit coupling, but is much less sensitive to the electron gas temperature, since all the empty states of the valence band are probed. In [4], XMCD measurements of the ultrafast demagnetization of Ni are presented, demonstrating the ultrafast loss of both the spin and orbital magnetic moments.

A prominent feature of ferromagnetism is the formation of an exchange splitting - the shifting of the minority and the majority electron energies. In Ref [5], a spin-integrated photoemission experiment (see Infobox) was performed which follows the dynamics of the exchange splitting after the pump laser pulse. A further experiment was performed using valence band photoemission with free electron laser pulses [6]: Photoelectrons were emitted from the entire valence band by a vacuum ultraviolet pulse from the free electron laser at Hamburg (FLASH). The spin polarization of the cascade electrons was detected using a Mott spin polarimeter. Because the cascade electrons represent an average spin polarization of the entire valence band, the measurement yields a direct representation of the spin magnetic moment. This pump-probe experiment confirms, that the ulrafast loss of the magnetization is not an artefact of the optical detection methods.

In order to explain ultrafast demagnetization, it is essential to understand both the transfer of energy and of angular momentum. Initially, the laser pulse excites the electron gas. Beaurepaire [2] introduced the 3-temperature model, where a temperature is assigned to all three reservoirs of the solid: the lattice, the electron gas and the spin system (see Fig. X.3). Each reservoir alone is assumed to always be in equilibrium, such that a temperature can be assigned to each of them at any time. The interaction between the reservoirs is modeled by a coupling constant. This way, the changes of the temperatures of the reservoirs are given by:

$$\begin{split} C_{el}\left(T_{el}\right)dT_{el} / dt &= -G_{el-lat}\left(T_{el} - T_{lat}\right) - G_{el-mag}\left(T_{el} - T_{mag}\right) + P(t) \\ C_{mag}\left(T_{mag}\right)dT_{mag} / dt &= -G_{el-mag}\left(T_{mag} - T_{el}\right) - G_{mag-lat}\left(T_{mag} - T_{lat}\right) \\ C_{lat}\left(T_{lat}\right)dT_{lat} / dt &= -G_{el-lat}\left(T_{lat} - T_{el}\right) - G_{mag-lat}\left(T_{lat} - T_{mag}\right) \end{split}$$

The electron gas is heated by the laser pulse represented by the term P(t). The  $C_x$  represent the specific heat for the electron gas, the lattice and the spin system, and the coupling constants  $G_x$  define the couplings between the reservoirs. The three-temperature model (3TM) can describe the ultrafast demagnetization process, and the coupling constants can be determined by fitting the parameters to experimental data. However, the 3TM does not describe how spin angular momentum is transported away from the spin system.

One possible source of angular momentum would be available by the absorption or emission of circularly polarized radiation. Dallalonga, et. al. [8] have investigated this possibility by measuring the demagnetization time as a function of the pump beam polarization. It turns out that there is no effect of the circular polarization on the demagnetization time. Therefore, the direct interaction of the light field with the magnetization is not a dominant effect in ultrafast demagnetization. Remaining possibilities are that the magnetization is either lost in the bulk of the ferromagnet (through spin-orbit coupling) or that spin angular momentum is transported into the substrate, where spin flips can occur on a longer time scale outside of the view of the observer [9]. In the following, we discuss bulk spin flip scattering and transport effects.

### Phonon-induced spin flips

So far the most successful bulk spin flip scattering model [10] uses the Elliot-Yafet scattering mechanism to describe spin flip scattering of electrons on phonons. In this way, the 3TM is extended as described in Figure X.4: The temperature of the phonons causes a change of the coupling between the electron gas and the spin system. At lower temperature, the coupling is weaker than at higher temperatures. In most ferromagnets, the heat capacities of the electron gas and of the lattice greatly exceed the heat capacity of the spin system. Therefore, a two-temperature model can describe the thermodynamics of the lattice and the electron gas. The dynamics of the magnetization is then described by [10]

$$\frac{dm}{dt} = Rm \frac{T_{lat}}{T_c} \left[ 1 - m \coth\left(m \frac{T_c}{T_{el}}\right) \right]$$

Here, m is the magnetization relative to the saturation mangetization at zero temperature,  $T_C$  is the Curie temperature

#### Spin-resolved photoemission

Modern femtosecond light sources allow a direct measurement of the magnetization of a ferromagnet by spin-resolved photoemission. In the present example, the soft free electron laser in Hamburg (FLASH) provides the probe X-ray pulses, but also a state-of-the-art laser-based highharmonic generation (HHG) source could in principle provide the probe pulses.

The photoemitted electrons are collected by an electrostatic lens system and accelerated onto a gold film. Due to spin-orbit coupling, the number of backscattered electrons depends on the spin polarization perpendicular to the scattering plane and on the scattering angle. By using two detectors, as shown in Fig. X.i2, one can determine the spin polarization and therefore the magnetization of the sample.

Depending on the wavelength of the probe photons, different parts of the valence band can be investigated. X-ray and vacuum ultraviolet pulses allow probing of the entire valence band, whereas lower energy photons just probe and *R* is a constant describing the efficiency of the Elliot-Yafet scattering mechanism. Both, the electron gas temperature  $T_{el}$  and the lattice temperature  $T_{lat}$  drive the magnetization dynamics. The first term describes the coupling between the lattice and the spin system, and the coupling between the magnetization and the electron gas temperature is described by a term which is also proportional to the lattice temperature.

Initially, the electron gas, the lattice and the spin system are in thermal equilibrium at room temperature. The laser pulse heats the electron gas to a high temperature. Now, we need to distinguish two cases (see Fig. X.5): a) If the coupling constant R is large enough, the spin temperature directly follows the electron gas temperature ("type I"). Once the electron gas temperature thermalizes with the lattice, the magnetization will start to return to a value corresponding to the common temperature of the lattice and electron gas. This behavior is typical of 3d transition metals, Co, Ni, Fe (see Fig. X.2). b) We can also imagine a situation where

the vicinity of the Fermi surface. The number of photoelectrons per pulse is limited by electron-electron interactions - therefore, sources with a high pulse repetition rate are required.



Fig. X.i2: Experimental setup for a pump-probe, spin-resolved photoemission experiment.



Fig. X.4: Modified three-temperature model: The lattice temperature mediates the coupling of the electron bath with the spin system through Elliot-Yafet spin-flip scattering [10].

the spin system is only loosely coupled to the other reservoirs ("type II"). In this case, *R* is small, and the initial temperature rise of the electron gas does not lead to demagnetization beyond the value reached once the lattice, electron gas and spin system are in equilibrium. In this case, the magnetization initially drops fast. Once the electron gas has cooled and thermalized with the lattice, the magnetization still drops, but at a slower rate, until the spin system has thermalized with the lattice. This two-step demagnetization process has been observed in Gadolinium, where the

5f electrons, which are only loosely coupled to the rest of the world, carry the majority of the spin angular momentum. The model of Koopmans [10] can even describe a crossover from type I to type II behavior, depending on the pump pulse energy. If we pump a Ni film harder, eventually it will show type II behavior: It first shows sub-picosecond demagnetization, and after electron-phonon thermalization, the ferromagnet continues to demagnetize, but at a slower rate, see Fig. X.6.



Fig. X.6: Crossover from type I to type II behavior in Ni, as the pump fluence is increased [10].



Fig. X.5: The demagnetization process for materials with a) a high value of the Elliot-Yafet coupling constant R and b) a small coupling constant R. In a), the magnetization follows the electron gas temperature, overshoots and relaxes back to a common temperature after thermalization with the lattice. In b), the coupling is insufficient to cause full demagnetization while the electron gas is still hotter than the lattice. Therefore, the magnetization further decreases slowly after electron-phonon thermalization [10].

Although the model of Koopmans is very successful in describing ultrafast demagnetizaton dynamics, the exact value of the constant R is still not completely understood: there is an ongoing debate whether a sufficiently large value can be obtained from first-principle calculations.

# Superdiffusive spin transport

Non-local phenomena in femtosecond, optical control of magnetization are based on the spin-polarized transport of laser-excited hot electrons. After early experimental observations [11,12], a semiclassical model for 3d ferromagnets (e.g. Ni, Co, Fe) was introduced, predicting that a considerable contribution to the ultrafast demagnetization process can be provided by spin-dependent superdiffusive transport of non-equilibrium electrons [9]: after optical (spin-conserving) excitation of electrons from quasi-localized d-bands into mobile sp bands, the non-equilibrium electrons begin moving, generating a cascade of further (hot) electrons by inelastic scattering. (Quasi-)elastic scattering with phonons or impurities are considered to be spin-conserving, in contrast to the model of "phonon-induced spin flips" described above. The resulting electron motion is in a superdiffusive regime, characterized by ballistic transport for early times and diffusive transport for later times. Such light-induced superdiffusive transport gives rise to ultrafast magnetization dynamics, because laser-excited majority and minority electrons have different velocities and lifetimes. Majority carriers in typical 3d ferromagnets have both a higher velocity (of the order of the Fermi velocity, 1nm/fs) and a longer mean free path compared to the minority carriers. This leads to a depletion of majority spins in the excited area and hence to an ultrafast spatial redistribution of magnetization on the order of several tens of nanometres. This scenario automatically conserves the spin angular momentum, and the total magnetization of the electronic system remains constant.

Interfaces between different materials constitute a second important contribution to magnetization dynamics, because a sudden change of transport properties leads to regions of spin accumulation. This implies that superdiffusive spin transport is expected to be most important in heterogeneous systems, such as (perpendicular magnetic anisotropy, PMA)



Fig. X.7: Schematic of the experimental setups for small angle X-ray scattering (SAXS) and Fourier Transform Holograpyh (FTH) studies at FEL light sources. While in SAXS, the average spatial information is stored in a scattering pattern in reciprocal space, in FTH, the real-space information is encoded by the interference of radiation from a scattered object and reference wave. Both methods are compatible with single-shot "diffract and destroy" techniques using ultrabright FEL pulses.

multilayers and alloys, exchange-coupled layered structures or magnetically heterogeneous samples with domain wall boundaries. For example, optical excitation of thin magnetic films on a *conducting* substrate will lead to a rapid demagnetization of the magnetic film, accompanied by a flow of majority carriers into the previously non-magnetic substrate. Similarly, in antiferromagnetically coupled layers (e.g. Ni-Ru-Fe), majority spins may be transported from one layer (Ni) to an adjacent layer (Fe), even leading to a local increase of magnetization [13,14].

Hence, experimental methods investigating superdiffusive spin transport for all-optical control of magnetization must combine element specificity with both nanometer spatial and femtosecond temporal resolution. This makes X-ray FEL radiation the preferred experimental tool. Element specificity is achieved by tuning the X-ray energy to the L or M resonance of the element and exploiting the X-ray magnetic circular dichroism (see Infobox). Access to the transient magnetization can be obtained either by resonant absorption experiments or by resonant small-angle X-ray scattering (SAXS) from nano-scale magnetic domain networks [15,16]. Furthermore, the coherent and ultrabright X-ray flux available at FEL sources allows for the first time to record realspace 2d movies of ultrafast magnetization dynamics [17]. In the following, we give two examples of experiments recently performed at FEL light sources that have contributed to field of superdiffusive spin transport (see Fig. X.7).

#### Small-angle scattering by domain structures

Superdiffusive spin currents within a nanometer-scale network of oppositely-magnetized domains of a Co/Pt multilayer system was investigated by resonant small angle X-ray scattering at the FEL facility FLASH [15]. The X-ray energy was tuned to the M-edge of cobalt at 20.8 nm, and the isotropic scattering ring at  $Q = 2\pi/d$  stemming from the labyrinth-like domain pattern with periodicity d ~100 nm was recorded by an area detector. Time-synchronized near-infrared laser pulses were used for excitation, and the scattering intensity and the peak position Q of the scattering ring were recorded for varying time delays between optical pump and X-ray probe. While an ultrafast reduction of the scattering intensity was attributed to ultrafast demagnetization, an observed shift of the scattering vector to lower Q values gave direct

evidence of nanometer-scale spatial changes within the magnetic domain pattern. Excellent agreement with the following simplified microscopic picture could be established: optically-excited mobile majority spins are transported superdiffusively until they reach a domain wall boundary, where they become minority carriers and their transport properties are abruptly changed. Since minority spins have a much smaller free mean path, their further transport is suppressed. The same scenario obviously also holds for the oppositely magnetized domains, resulting in spin accumulation at the domain boundary. The effect therefore results in a broadening of the domain walls on the order of 30 nm, causing the observed ultrafast shift of the small-angle X-ray scattering peak Q. This implies that advances in ferromagnetic domain engineering may in the future allow an enhanced control of spin currents in electronic and spintronic devices.

#### Magnetic Fourier-transform holography

Magnetic Fourier transform holography (FTH) allows one to encode real-space information by interfering the coherent X-ray radiation scattered by a magnetic object with the scattering by a point-like reference hole. The reconstruction is simply achieved by a 2 dimensional Fourier transform and allows robust, high-resolution, lens-less imaging of the magnetization [18]. The XMCD effect again gives the magnetic contrast. The real-space image can even be retrieved with a single X-ray pulse, which makes this technique ideally suited for ultrabright FEL sources [19], where a single X-ray pulse may be so intense that it destroys the sample ("diffract before destroy"). In a recent experiment, ultrashort, coherent X-ray pulses from the FEL facility FERMI were used to holographically image the magnetization dynamics in a magnetic domain pattern. A tailored sample- and excitationgeometry allowed the experimenters to localize the optical excitation, leading to a spatially-confined reduction of magnetization within the field of view. The time-dependent real-space images not only allowed following the light-induced magnetization dynamics on a femtosecond time-scale but also gave evidence of a spatial evolution of the magnetization. These effects could be attributed to ultrafast transport of nonequilbirium spin-polarized electrons at early times and to a fluence-dependent remagnetization rate for later times. Technologically, investigations of the lateral magnetization after a localized optical excitation are of great interest for miniature all-optical magnetic switching applications [20] and for heat-assisted magnetic recording [21]. Here nano-scale plasmonic antennas or near-field transducers will confine the optical excitation [22], however, it has not been determined to what degree the transport of hot electrons or superdiffusion of majority carriers may fundamentally limit the smallest possible bit size. Considering today's storage densities, which exceed 1Tbit/in<sup>2</sup> or 1bit/  $(25 \times 25 \text{ nm}^2)$ , this is an important issue, which can be tackled with the existing and emerging FEL sources of coherent, energy-tuneable, bright and ultrashort X-ray radiation.

#### Outlook

Ultrafast demagnetization is interesting from a fundamental point of view: We still don't understand how the spin angular momentum can be transferred away from the spin system. We know that the effect happens on a femtosecond time scale, and there are two likely contributions: spin-flip scattering and transport. It is unknown which contribution dominates, and there are indications that depends on the geometry and heterogeneity of the sample.

There is no doubt that the demagnetization can lead to a very large spin current pulse. This fact may be used as a spin current source for future experiments in the field of spintonics, the development of electronic devices using the spin degree of freedom to process information. The current density of the laser-generated spin currents can be orders of magnitude larger than is achievable with conventional spin valve structures. In addition, the spin current has the femtosecond time structure of the demagnetization process cite: T. Kampfrath et al., Nature Nanotechnology 8, p256–260 (2013). In this way, ultrafast demagnetization may expand the field of spintronics into the femtosecond time scale.

Besides its scientific interest, ultrafast demagnetization is also of technological relevance: In hard drives, one wants to write a magnetic bit within less than a nanosecond. On the other hand, the bit needs to be stable against thermal fluctuations for many years. The stability is given by the anisotropy energy  $K_u V$ , where  $K_u$  is the crystalline anisotropy per volume V, compared to the thermal energy  $k_B T$ . As the storage density increases, the volume decreases, and the only way to keep the bit stable is to increase  $K_u$ . However, a larger anisotropy implies higher magnetic fields to write the bit. In order to be able to write the bits, the heat assisted magnetic recording (HAMR) technology is being developed. Here, a short laser pulse will be used to heat the magnetic bit in such a way that a smaller magnetic field is needed for switching. Besides the magnetic softening, the magnetization of the bit will also be reduced due to ultrafast demagnetization.

As the size of magnetic devices decreases, spin transport mechanisms, whether by hot electrons or by superdiffusive behavior, also become more important. The demonstrated ability of circularly-polarized pulses from an X-ray FEL to study spin transport at the nanoscale could represent an important technological contribution of XFEL facilities.

# **Summary**

- The time and length scales of a wide variety of phenomena in magnetic materials fit well with the capability of XFELs. X-ray Circular Magnetic Dichroism provides strong magnetic contrast for X-ray absorption and scattering, and spin-resolved photoemission allows the direct measurement of the time-dependent electron spin polarization.
- The observation of laser-induced demagnetization on a sub-ps time scale demonstrates that ultrafast magnetic manipulation is possible. A "three-temperature" model assumes that the spin, charge and lattice degrees of freedom represent coupled thermal reservoirs.
- Existing X-ray experimental studies of ultrafast demagnetization have demonstrated that both the spin and orbital moments are reduced. A major open question regards the fate of the electronic angular momentum – where does it go, and how can the transfer be so rapid?

- One piece of the puzzle may be phonon-induced spin flips ("Elliot-Yafet scattering"), in which the presence of phonons influences the coupling of the charge and spin reservoirs.
- Another piece may be "superdiffusive spin transport", which leads to different propagation velocities of minority and majority electrons. The resulting perturbations of spatial magnetism can be imaged using small-angle X-ray scattering and magnetic Fourier transform holography.

#### References

- B.D. Patterson, SwissFEL Science Case, PSI Report Nr. 09-10 (2009)
- [2] E. Beaurepaire, et al, Phys Rev Lett **76**, 4250 (1996).
- [3] B. Koopmans, et al., Phys. Rev. Lett. **85**, 844 (2000)
- [4] C. Boeglin, et al., Nature **465**, 458 (2010)
- [5] H.S. Rhie, et al., Phys Rev Lett **90**, 247201 (2003)
- [6] A. Fognini, et al., Appl. Phys. Lett. **104**, p032402 (2014)
- [8] F. Dallalonge, et al., Phys Rev B **75**, 224431 (2007)
- [9] M. Battiato et al., Phys Rev Lett **105**, 027203 (2010)
- [10] B. Koopmans et al., Nature Materials 9, p259 (2010)
- [11] Malinowski et al., Nat. Phys., **4**, 855 (2008)
- [12] Melinkov et al., Phys. Rev. Lett., **107**, 076601 (2011)

- [13] Rudolf et al., Nat Commun, **3**, 1037 (2012)
- [14] Turgut et al., Phys. Rev. Lett., **110**, 197201 (2013)
- [15] Pfau et al. Nat. Comun., **3**, (2012)
- [16] Graves et al., Nat. Mater. 12, 293–298 (2013)
- [17] von Korff Schmising et al., Phys. Rev. Lett., **112**, 217203 (2014)
- [18] Eisebitt et al., Nat., **432**, 885 (2004)
- [19] Wang et al., Phys. Rev. Lett., 108,267403 (2012)
- [20] Kirilyuk et al, Rev. Mod. Phys. 82, 2731–2784 (2010)
- [21] Challener et al., Nat. Phot., 3, 220 (2009)
- [22] Liu et al., arXiv:1409.1280v1 (2014)

# XI. Excitons and hot carriers in semiconductors

Manfred Helm, Helmholtz-Zentrum Dresden-Rossendorf

(Quasi)particles such as excitons or hot carriers in semiconductors can be manipulated by the THz radiation from free electron lasers and their low-energy relaxation dynamics can be investigated.

- Low-energy excitations in solids
- Excitons in semiconductors
- Carrier relaxation in semiconductors
- Outlook

Semiconductors are the building blocks of modern micro-and optoelectronics. An understanding of the ultrafast dynamics of charge carriers in these materials is of key importance for device performance. These dynamics, i.e., the relaxation of the carriers, can be investigated using picosecond pulses of infrared or terahertz free-electron lasers. Here we present results obtained for semiconductor quantum dots and the two-dimensional material graphene, which both may play important roles in future (opto)electronics. In addition we discuss more fundamental nonlinear phenomena that occur when high-intensity infrared radiation interacts with electrons, and here in particular with bound electron-hole pairs (excitons).

#### Low-energy excitations in solids

Electromagnetic radiation is a key means to understanding the properties of solids. This is true for UV and X-rays, yielding (besides structural information from diffraction experiments) chemical information due to transitions from and between deeply bound states in the 10 eV to 10 keV range, of course for the spectral range in the vicinity of the visible (1 - 5 eV), where the properties are determined by valence electrons (conduction and valence bands, HOMO and LUMO), but also for the infrared and terahertz range (IR/ THz). For these long wavelengths the photon energies lie in the 1-100 meV range and correspond to a variety of so called low-energy excitations in solids. Examples for such excitations (or quasiparticles) are lattice vibrations (phonons), or charge oscillations (plasmons), shallow impurity states in semiconductors, internal excitations of bound electron-hole pairs (excitons), fundamental excitations in narrow- and zero-gap semiconductors (graphene) or topological insulators, and confined states in low-dimensional semiconductor structures such as quantum wells, wires and dots. In an external magnetic field cyclotron resonance and electron spin resonances are the fundamental low-energy excitations. Furthermore, many collective excitations in correlated-electron materials fall into this range, such as spin waves (magnons) in (anti)ferromagnets, superconducting energy gaps in superconductors, or soft modes and electro-magnons in multiferroic materials.

#### Relevant energy / frequency scales in light-matter interactions

In the interaction of an electromagnetic wave with matter, several fundamental distinct energy or frequency scales play a role. If only two energy levels, which are excited nearly resonantly, are considered, these are:

- (1) the energy level spacing  $\omega_{21}$ ,
- (2) the angular light (THz) frequency  $\omega$ . For resonant interaction, this is usually quite close to the level spacing,  $\omega \cong \omega_{21}$ .
- (3) the Rabi frequency  $\Omega = \mu_{21}F/\hbar$  describing the strength of the light-matter coupling, where  $\mu_{21}$  is the dipole matrix element and F is the electric field amplitude.
- (4) Any realistic system is also dissipative, and relaxation processes do occur. In the simple two-level system one can distinguish two different relaxation constants,  $\gamma_1$ and  $\gamma_2$ . The decay constant  $\gamma_1$  describes population relaxation and  $\gamma_2$  the decay of phase or polarization. Between them, the relation  $\gamma_2 > \gamma_1/2$  holds, *i.e.*  $\gamma_2$  can be orders of magnitude larger than  $\gamma_1$ .

Mathematically this can be described by the so-called optical Bloch equations in a very similar way as nuclear magnetic resonance (NMR) or electron spin resonance (ESR). In the usual model applied in atomic physics, the condition  $\Omega \ll \omega$  is fulfilled to a very high degree, which allows one to use the rotating wave approximation (RWA) by neglecting rapidly oscillating terms. Then the relevant equations for the two-level system can be solved analytically, yielding the Autler-Townes splitting in steady state and Rabi oscillations in the time domain before the coherences have decayed.

(5) For very high electric fields or low frequencies, the energy levels are not important anymore and electrons follow the electric field in a quasi-classical manner. This regime is reached, if the so-called ponderomotive energy,  $U = e^{2F^2/4m\omega^2}$  becomes the largest energy scale in the problem (where e is the elementary charge and m the carrier mass). The ponderomotive energy is the average classical kinetic energy of an electron in an electromagnetic wave of circular frequency  $\omega$ . A quantity often defined to characterize this regime is the so called Keldysh parameter, being the square root of the ratio of ionization energy and twice the ponderomotive used by Nordstrom *et al* [1], the ratio between the ponderomotive energy and  $\hbar\omega$ .

While the spectral range of the visible and its vicinity has acquired an extremely advanced technological status thanks to the development of lasers and detectors over the past decades, this is much less the case for shorter as well as longer wavelengths. For the short-wavelength range the development of synchrotrons and now free-electron lasers has represented a gigantic leap concerning intensity, sensitivity and time resolution. But also in the terahertz range, while the availability of table-top sources is continuously being improved, free-electron lasers and other short-pulse sources (superradiant coherent terahertz sources) still offer properties not equaled otherwise.

#### Excitons in semiconductors

The fundamental optical excitation of an undoped semiconductor is the generation of an electron-hole pair, bound to each other via the Coulomb interaction. Such excitation (quasiparticle) is called exciton and its internal energetic structure resembles the one of a hydrogen atom, i.e. a 1s ground state, 2s, 2p excited states etc. However, in contrast



Fig. XI.1: Schematic of a semiconductor quantum well with near-infrared (NIR) optical excitation (probe) across the band gap (left) and THz FEL pumping of intra-excitonic states (middle), giving rise to the Autler-Townes splitting (right). Reprinted from New J. Phys. **15**, 065007 (2013) [3].



Fig. XI.3: Near-infrared absorption spectrum of the quantum well sample while the 1s-2p intra-exciton transition is pumped with the THz FEL at 1.6 THz. The line splitting (Autler-Townes splitting) evolving for increasing THz electric fields can be clearly observed.

to the H-atom, where the ground-state binding energy amounts to 13.6 eV, in semiconductors this is in the range of 10 meV due to their smaller effective mass and larger permittivity. THz FELs now enable resonant excitation of the intra-excitonic 1s-2p transition. In a two-color experiment combining THz pumping using an FEL and near-infrared probing across the bandgap of (In)GaAs quantum wells, the Autler-Townes or AC Stark splitting of the 1s state has been observed, a quantum optical evidence for mixed lightmatter states (dressed states), well known from atomic physics, but difficult to observe in semiconductors, cf. Fig. XI.1 [2,3]. Pumping non-resonantly at even smaller photon energies, one can observe high-harmonic sideband generation, based on the very same recollision effect which is known from atomic physics to give rise to high-harmonic generation (HHG). Here the electron is separated from the



Fig. XI.2: Schematic of the two-color experiment, where the quantum well sample is pumped by the FEL and probed by near-infrared light. Reprinted from Phys. Rev. Lett. **105**, 167401 (2010) [2].


Fig. XI.4: Two-dimensional contour plot of the near-infrared absorption as a function of near-infrared (NIR) photon energy (horizontal) and delay time between FEL pulse and NIR pulse (vertical). The line splitting can be observed while the FEL pulse pumps the excitons. Reprinted from New J. Phys. **15**, 065007 (2013) [3].

hole due the THz high electric field, but is forced to return when the direction of the electric field has reversed after one half oscillation period [4].

#### Carrier relaxation in semiconductors

The relaxation dynamics of hot charge carriers in semiconductors play a major role in electronic and optoelectronic devices. To thoroughly understand their behavior in relevant materials is thus of key importance. Graphene, an ideal two-dimensional material made from a single layer of hexagonally ordered carbon atoms, is nowadays discussed as being a key player for the post-silicon CMOS electronics. Graphene can be considered as a semiconductor, yet with a zero band gap and a linear energy dispersion, symmetric for the valence and conduction bands that cross each other in the so-called Dirac point. In order to properly study the carrier dynamics in undoped or only slightly doped graphene, one would like to approach the Dirac point as closely as possible. This can only be done using photons with small energies, like in the infrared and THz range. Corresponding

pump-probe experiments have been performed using a

free-electron laser. As can be seen in Fig. XI.5 the relaxation



Fig. XI.5: Single-color pump-probe curves of graphene measured a low temperature for different photon energies. It is clearly seen that the relaxation becomes slower (and non-exponential) for smaller photon energies. Adapted from Phys. Rev. Lett. **107**, 237401 (2011) [5].

occurs more slowly for smaller photon energies, when the excitation gets closer to the Dirac point [5]. This is because the relaxation via higher-energy optical phonons is suppressed in this case.

Graphene in a magnetic field perpendicular to the graphene layer exhibits a non-equidistant Landau level (LL) spectrum. This allows one to directly address individual LL transitions optically. According to the selection rules for dipole radiation, two LL transitions, e.g.  $LL_1 \rightarrow LL_0$  and  $LL_0 \rightarrow LL_1$ , are energetically degenerate, but can be distinguished by applying left or right circularly polarized radiation, respectively. Pump-probe experiments in all four combinations of pumping and probing with left or right circularly polarized radiation, respectively, reveal a surprising effect: pumping the  $LL_{-1} \rightarrow LL_0$  transition results in a depopulation of the zeroth Landau level even though this level is optically pumped at the same time. This depopulation is directly evidenced by a sign change of the pump-probe signal when probing with opposite helicity (positive transmission change, see bottom panel (c,d) in Fig. XI.6). The reason for this is very efficient Auger scattering between the lowest Landau levels [6]. The fact that the sign reversal occurs for pumping the  $LL_1 \rightarrow LL_0$ transition is related to the slight n-type doping of the sample used in Ref. 6. For neutral graphene no sign reversal is

expected while in a p-type sample the sign reversal would occur for pumping the  $LL_0 \rightarrow LL_1$  transition.

Another type of semiconductor nanostructures that may be important for future information technology are quantum dots, grown epitaxially in self-assembled fashion. Since charge carriers are strongly confined in the quantum dots, new energy "sublevels" are formed due to the quantum confinement. This can be viewed as an artificial atom, however interacting with the phonons of the constituting crystal. A theoretical model called "quantum dot polaron" has emerged in this connection. Since the energy separation between ground and excited state in those quantum dots lies between 10 and 60 meV depending on their size and shape, resonant pump-probe experiments can only be performed using free-electron lasers. In a series of measurements performed at all three European infrared FEL facilities, a complete understanding has been obtained [7-11]. Whereas for an energy separation of around 30 meV, near the opticalphonon energy, the relaxation time is only a few picoseconds, it increases dramatically for shallower quantum dots. For energy separations only a factor of two smaller (15 meV) the relaxation time even reaches 1.5 ns, three orders of magnitude larger [10].

In recent four-wave-mixing experiments it has been demonstrated that also the dephasing time becomes very long, which is important for possible applications as qubits in quantum information processing [11]. Using a different semiconductor system as possible solid-state implementation for qubits, namely phosphorus impurities in silicon (Si:P), full qubit operations have been demonstrated using free-electron laser pulses. Full coherent control using photon echoes and Rabi oscillations have been demonstrated (see Ch. 13).



Fig. XI.6: Single-color pump-probe transients for resonant excitation of Landau quantized graphene with circularly polarized radiation. Pump and probe beam feature opposite helicity. The photon energy is 75 meV, B = 4.2 T. While the negative pump-probe signal (i.e. induced absorption) for pumping the LL<sub>0</sub>  $\rightarrow$  LL<sub>1</sub> transition (a and b) is expected directly from single-particle dynamics by pumping and probing with opposite helicity, the positive signal (i.e. induced transmission) for pumping the LL<sub>1</sub>  $\rightarrow$  LL<sub>0</sub> transition (c and d) is unexpected in this framework. It points to a depletion of LL<sub>0</sub> by Auger scattering. Adapted from Nature Physics **11**, 75-81 (2015) [6].

Fig. XI.7: Measured polaron relaxation times in quantum dots as a function of energy level separation. A mere doubling of the energy results in a change of three orders of magnitude in relaxation time. Reprinted from Nature Materials **8**, 803-807 (2009), doi:10.1038/nmat2511 [10].



### Graphene

Graphene is a two-dimensional carbon crystal. It consists of a single layer of sp<sup>2</sup> bonded carbon atoms ordered in a hexagonal crystal lattice. The material is characterized by extraordinary mechanical, electrical and optical properties such as very large tensile strength, high room temperature mobility and constant optical absorption over a large frequency range. The combination of these properties makes graphene particularly interesting for optoelectronic applications on flexible substrates. Graphene is a gapless semiconductor with linear dispersion for low-energy excitation. The linear dispersion implies that graphene electrons have properties of massless Dirac fermions.



Fig. XI.i1: Hexagonal graphene lattice.

GaAs Graphene conduction band Dirac point valence band

Fig. XI.12: Semiconductors, such as GaAs, are characterized by a band gap between valence band and conduction band (left). Typically the dispersion of the bands is parabolic and holes have a larger effective mass (smaller band curvature) than electrons. Graphene, on the other hand, is a gapless material where conduction band and valence band intersect linearly in the Dirac point (right).

### Outlook

Infrared and THz free-electrons lasers can provide radiation for manipulating low-energy excitations is semiconductors and other solids. This is due to their high intensity that provides high electric fields and their narrow spectrum that enables selective excitation. In addition, the short pulse of the FEL radiation allows one to probe the relaxation dynamics of such excitations. The understanding of such relaxation processes will always be an important task for newly developed materials with possible applications ind nano- and optoelectronics.

#### Quantum wells and quantum dots

Quantum wells and quantum dots are semiconductor nanostructures with confinement in one and three directions, respectively. Quantum wells are layers of semiconductor with lower energy gap sandwiched between layers of larger energy gap. The energy spectrum of the two-dimensional system, where electrons can move freely within the quantum well plane, consists of subbands. For quantum dots the three-dimensional confinement results in set of discrete energy sublevels. Since this resembles the situation in an atom, quantum dots are often referred to as artificial atoms. While the energy of optical transitions





Fig. XI.i3: Quantum confined states for electrons (red) and holes (blue) in a semiconductor quantum well heterostructure.



Fig. XI.i4: Schematic depiction of self-organized InAs quantum dots (dark blue) grown on GaAs (grey). The light blue area indicates the InAs wetting layer that is formed in the Stranski-Krastanov growth mode before the three-dimensional growth of the quantum dots sets in.

# Summary

- Resonant pumping of intra-excitonic transitions induces a line splitting due to the AC Stark effect.
- Carrier relaxation phenomena in the zero-gap 2D semiconductor graphene are revealed by pump-probe experiments.
- The relaxation of electronic quasiparticles called polarons in quantum dots varies over three orders of magnitude in a small energy range.

#### References

- K. B. Nordstrom, K. Johnsen, S. J. Allen, A.-P. Jauho,
   B. Birnir, J. Kono, T. Noda, H. Akiyama, and H. Sakaki, *Excitonic dynamical Franz-Keldysh effect* Phys. Rev. Lett. **81**, 457 (1998).
- M. Wagner, H. Schneider, D. Stehr, S. Winnerl,
   A. M. Andrews, S. Schartner, G. Strasser, and M. Helm,
   Observation of the intra-exciton Autler-Townes effect in
   GaAs/AlGaAs semiconductor quantum wells
   Phys. Rev. Lett. 105, 167401 (2010).
- [3] M. Teich, M. Wagner, H. Schneider, and M. Helm, Semiconductor quantum well excitons in strong, narrowband terahertz fields New J. Phys. 15, 065007 (2013).
- B. Zaks, R. B. Liu, and M.S. Sherwin, *Experimental observation of electron-hole recollisions* Nature 483, 580-583 (2012).
- [5] S. Winnerl, M. Orlita, P. Plochocka, P. Kossacki,
  M. Potemski, T. Winzer, E. Malic, A. Knorr, M. Sprinkle,
  C. Berger, W. A. de Heer, H. Schneider, and M. Helm, *Carrier relaxation in epitaxial graphene photoexcited near the Dirac point*Phys. Rev. Lett. **107**, 237401 (2011).
- [6] M. Mittendorff, F. Wendler, E. Malic, A. Knorr, M. Orlita,
  M. Potemski, C. Berger, W. A. de Heer, H. Schneider,
  M. Helm, and S. Winnerl, *Carrier dynamics in Landau-quantized graphene featuring* strong Auger scattering
  Nature Physics 11, 75-81 (2015).
- S. Sauvage, P. Boucaud, R. P. S. M. Lobo, F. Bras, G. Fishman, R. Prazeres, F. Glotin, J. M. Ortega, and J.-M. Gérard, Long polaron lifetime in InAs/GaAs self-assembled quantum dots Phys. Rev. Lett. 88, 177402 (2002).

- [8] E. A. Zibik, L. R. Wilson, R. P. Green, G. Bastard, R. Ferreira, P. J. Phillips, D. A. Carder, J-P. R. Wells, J. W. Cockburn, M. S. Skolnick, M. J. Steer, and M. Hopkinson, *Intraband relaxation via polaron decay in InAs self-assembled quantum dots* Phys. Rev. B **70**, 161305 (2004).
- [9] E. A. Zibik, T. Grange, B. A. Carpenter, R. Ferreira,
  G. Bastard, N. Q. Vinh, P. J. Phillips, M. J. Steer,
  M. Hopkinson, J. W. Cockburn, M. S. Skolnick, and
  L. R. Wilson,
  Intersublevel polaron dephasing in self-assembled
  quantum dots

Phys. Rev. B 77, 041307 (2008).

- [10] E. A. Zibik, T. Grange, B. A. Carpenter, N. E. Porter, R. Ferreira, G. Bastard, D. Stehr, S. Winnerl, M. Helm, H. Y. Liu, M. S. Skolnick, and L. R. Wilson, Long lifetimes of quantum dot intersublevel transitions in the terahertz range Nature Materials 8, 803-807 (2009), doi:10.1038/ nmat2511.
- [11] M. Teich, D. R. Stephan, S. Winnerl, H. Schneider, M. Helm, and L. R. Wilson, Intersublevel dephasing in InAs/GaAs quantum dots below the Reststrahlenband Appl. Phys. Lett. 103, 252110 (2013).

# XII. Coupled degrees of freedom in quantum materials

Tim Huber, ETH Zürich

Strong electron correlations are responsible for phenomena such as metal-insulator transitions, high-temperature superconductivity and colossal magnetoresistance – the phase diagrams of highly correlated materials arise from the interplay of charge, spin, orbital and lattice degrees of freedom.

- Introduction
- Coupled degrees of freedom
- Resonant nonlinear excitation of quantum materials using IR and THz FELs
- Time-resolved X-ray probing of strongly correlated materials
- Outlook

"Electron correlation" is a dominant theme in condensed matter science, manifesting itself in "metal-insulator transitions" (MIT), "high-temperature superconductivity" (HTS) and "colossal magneto-resistance" (CMR). On the microscopic scale, one speaks of the charge (C), spin (S) and orbital (O) degrees of freedom, each of which may show short or long-range order, and each of which may exchange energy with the others and with the crystal lattice (L). Important correlation effects occur in systems with partially-filled electron shells, such as 3d, with anisotropic, quasilocalized character. Vast amounts of experimental and theoretical work have been published on electron correlation, since the advent in 1986 of HTS: phase diagrams of many interesting materials have been investigated in detail, and numerous theories of the microscopic C-S-O-L interactions have been proposed. Much has been achieved, but much is still unclear. There is increasing evidence of the importance of nanoscale inhomogeneities and fast fluctuations in correlated electron materials - indicating the important role that the XFEL will play. Furthermore, it has been suggested that the "chicken-or-egg" problem, of determining the cause and effect relationships among the C, S, O and L subsystems, may best be approached with pump-probe time-resolved spectroscopy: one pumps energy into a particular degree of freedom and measures the time required for a response to appear in another.

## Introduction

Many phenomena in semiconductors can, to a large degree, be understood using a single-particle description of the electronic properties. In so-called strongly correlated-electron materials, however, the Coulomb interaction between electrons is so strong that such band structure concepts fail to describe the underlying physics. Entirely new phases of matter can emerge, difficult to describe by conventional theories and characterized by enormous responses to external stimuli. Metal-to-insulator transitions, colossal magnetoresistance, multiferroicity and high temperature superconductivity are prominent examples of these physics (see Fig. XII.1).

Research with ultrafast optical tools in this area has grown at an extremely rapid pace. Progress has been motivated by the opportunity of understanding strong many body interactions in the time domain, but also by the possibility of using light to switch matter between competing phases. Researchers in this field dream of new functionalities being controlled with light and of new strategies for high-speed device applications. Furthermore, the rich short-range texture of these electronic phases, such as spin, charge and orbital order, may one day be used to encode information at unprecedented densities. For these studies, tabletop laser technology alone is largely viewed as being insufficient, as for excitation and probing of strongly correlated systems pulses of electromagnetic radiation from the THz- to the hard X-ray regime are required.



Fig. XII.1: Examples of the evolution of resistivity with temperature in strongly correlated systems [12].



Fig. XII.2: The coupled degrees of freedom in correlated electron materials. The Chimera is a figure in Greek mythology; here it is used to illustrate the intimate connection of lattice, spin, charge and orbital order [13].

# Coupled degrees of freedom

In correlated systems, broken symmetry ground states with several kinds of long- and short-range order can emerge. The properties of these technologically and scientifically important materials are based on the intricate balance of different kinds of order present in a system. As a simple example, in charge density wave systems the lattice couples to an instability in the electronic subsystem, leading to a periodic modulation of the lattice equilibrium positions. A perturbation of one of the two subsystems will lead to collective excitations involving both electronic and structural order. In more complicated systems, coupling between charge, orbital, spin and lattice degrees of freedom occur – and a complete understanding of all degrees of freedom and their interaction is necessary to fully understand a material (see Figs. XII.2 and XII.3).

Experiments operating in thermal equilibrium often only give limited information on the interaction between different subsystems. By using ultrafast external stimuli that create excited states far from equilibrium, however, it becomes possible to destroy the initial balance of the subsystems and study their coupling in more detail by observing a sys-

#### THz interaction with matter

The THz frequency range is loosely defined as the portion of the electromagnetic spectrum spanning approximately 0.1 THz to 30 THz. It bridges the gap between conventional electronics and optics, posing new conceptual and technological challenges and possiblities [11]. Electromagnetic radiation in this frequency range has been notoriously hard to generate with sufficient field strength, leading researchers to use the term "THz gap" to describe the absence of intense THz frequency electromagnetic radiation for technological and scientifical applications. In recent years however, the advent of new sources, based on non-linear difference-frequency generation and long-wavelength free electron lasers, have allowed us to generate THz radiation with ever-increasing field strength and spectral tunability. THz radiation couples to dipole-active excitations when interacting with matter, allowing one to probe (using THz time domain spectroscopy) and excite a wide array of spectral features lying in this frequency range. While optical laser pulses generally excite all subsystems of a correlated material in an uncontrolled way, THz radiation selectively couples to a particular degree of freedom, without initially perturbing other degrees of freedom or introducing excessive amounts of heat. In correlated electron systems, numerous collective excitations lie in the THz range. Examples include lattice vibration modes (phonons) that are intrinsically associated with a brokensymmetry ground state, the gap of the superconducting ground state, and multiferroic and antiferromagnetic excitations. Resonantly exciting these modes with high-field THz radiation provides a fundamentally new route to manipulating properties of matter on an ultrafast timescale. With sufficiently large field strengths, nonlinear manipulation of matter becomes possible, allowing, for example, the study of anharmonic phonon coupling.



Fig. XII.i1: Time domain view of the electric field of a pulse of THz frequency radiation with a center frequency of around 1.5 THz.



Fig. XII.3: Long-range order may occur in correlated electron materials, with unit cells particular to each degree of freedom. The figure shows the perovskite material La<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub>, with the unit cells corresponding to the color-coding in Fig. XII.2. In a time-resolved experiment, the coupling between different kinds of order can be studied, for example by perturbing the charge order and then probing another subsystem, answering the question how long It takes for another degree of freedom to react to the perturbation - and in what way it reacts [14].



Fig. XII.4: Mid-infrared lattice control. Tabletop sources have been used to directly drive large-amplitude lattice distortion-, inducing insulator-to metal, orbital- and magnetic-melting transitions, as well as to restore superconductivity in frustrated striped cuprates [15].

tem relax back to equilibrium. Excitation with ultrashort laser pulses furthermore allows one to control material properties and to induce phase transitions on sub-picosecond timescales.

# Resonant nonlinear excitation of quantum materials using IR and THz FELs

A new class of experiments has emerged recently, which aims at exploiting strong field terahertz (THz) and mid-infrared sources to drive dipole-active, low-frequency excitations. While it is possible to generate optical laser pulses at almost arbitrary power levels, resonant THz excitation offers crucial advantages for studying and manipulating solid state systems (see infobox *THz interaction with matter*). The first applications have relied on tabletop pump-probe techniques, combining mid-infrared excitations with visible or narrow band THz probes. Among these we mention the demonstration of lattice-driven insulator-metal transitions in bulk solids [1] and heterointerfaces [2] and the melting of orbital order [3]. Furthermore, single-cycle low-frequency THz techniques have been used to drive superconducting interlayer-coupling [4] and antiferromagnetic excitations in NiO [5].

More recently, this class of experiments has been greatly extended by the availability of infrared Free Electron Lasers. The spectral purity of accelerator-based sources has been exploited to study nonlinear excitations with extreme spectral selectivity, such as the excitation of solitonic waves in cuprate superconductors [6] and gap excitations in BCS superconductors [7].

#### **Resonant X-ray diffraction**

With standard X-ray diffraction, the structure of a material can be observed by measuring a certain set of Bragg reflections. If the energy of the X-rays is tuned to an absorption edge of the material, the measurements also become site specific and can contain spectroscopic information. The basic idea behind resonant X-ray scattering is presented in Figure 8. Resonant X-ray scattering can provide additional contrast for valence elctron density, orbital-ordering or spin density. Many relevant transitions in correlated electron systems can be accessed with soft X-ray radiation. In Figure XII.i3, it is shown how a charge difference can change the energy levels of core electrons, ultimately leading to a change of the diffraction intensity for a certain X-ray energy. This provides information on the valence at a specific site and allows the investigation of charge-ordering in a correlated material. By using ultrashort X-ray pulses generated from an FEL, the temporal evolution of charge-order can be monitored.



Fig. XII.i2: The resonant elastic scatterring process, indicating a virtual transition from an occupied state (blue) to an unoccupied intermediate valence state (red) promoted by an incoming X-ray photon. Recombination leads to emission of a photon with the same energy. If the X-ray energy is tuned close to a transition, enhancements in the scattering cross section occur [16].



Fig. XII.i3: A charge-dependent shift in the core-level energy shifts the energy-dependent scatterring profile, providing contrast for charge-ordering [17].



Fig. XII.5: THz control with narrowband THz radiation. Infrared free electron lasers deliver intense pulses at low frequencies with a spectral purity that is not easily achieved on tabletops, enabling high-resolution nonlinear excitation. In the figure, the excitation of a Josephson Plasma Soliton in a cuprate superconductor is depicted, made possible when the excitation is detuned to the red side of a Josephson Plasma Resonance by approximately 1% [6].



Fig. XII.6: Schematic of a typical pump-probe experiment with a laser pump and X-ray probing. In this case, the excited sample is a perovskite-type manganite, an example of a strongly correlated electron system where material properties depend on the balance of different degrees of freedom of the material. The data shown is a real-time view of the structural dynamics during a photoin-duced phase transition [18].

# Time-resolved X-ray probing of strongly correlated materials

All-optical pump-probe spectroscopy has become a widespread tool for time-resolved studies of correlated materials, but results obtained this way contain information that cannot be assigned unambiguously to a specific degree of freedom. Time-resolved X-ray probing methods allow one to gather specific information about the dynamics of a particular subsystem of a correlated material. With timeresolved hard X-ray diffraction, direct views of the structural dynamics can be recorded. X-ray energies on the order of 10 keV provide sufficient spatial resolution to record information on the average position of the atoms, and FELs now provide the possibility to perform experiments with a time resolution on the order of 10 fs. With these techniques, the structural dynamics associated with an ultrafast phase transition in a correlated system can be recorded, for example, the nonthermal melting of a charge density wave [8]. Knowledge of the exact crystal structure often is the starting point for a theoretical treatment of a material, making direct measurements of the atomic positions in states far away from equilibrium crucial for a full understanding of a coupled system.

The unprecedented brightness and time resolution of a FEL also make it possible to conduct time-resolved measurements with the X-ray energy tuned to a resonance of the system under study (see infobox Resonant X-ray diffraction). Since orbital, charge or spin order typically only affect a fraction of the valence electrons, this technique provides a very specific way of probing a certain degree of freedom. Using time-resolved resonant X-ray diffraction, it was possible to separate the dynamics of structural, orbital and charge-order in a manganite perovskite [9] and to follow the coherent dynamics of all the subsystems. In another experiment, THz excitation in tandem with a resonant X-ray probe tuned to the energy of the Mn L<sub>2</sub> edge in TbMnO<sub>3</sub> gave a direct view of the spin dynamics associated with a resonantly excited electromagnon - a coupled excitation in a multiferroic that allows the control of magnetic order via an electric field [10].

#### Outlook

Recent experiments performed at FELs have already demonstrated the tremendous possibilities that FELs offer for the investigation of strongly correlated materials. In the future, the development of new experimental techniques and the increased availability of X-ray FELs will strongly shape research on this class of materials.

# Summary

- Strongly correlated systems are technologically and scientifically important materials that exhibit phenomena such as high-temperature superconductivity, metal-to-insulator transitions, colossal magnetoresistance and multiferroicity.
- Since these phenomena depend on the complicated interaction of structural, spin, orbital and charge-order, a complete understanding of strongly correlated materials requires specific knowledge of all coupled degrees of freedom.
- Selective excitation of collective modes has become possible with sources of intense mid-infrared and THz radiation and presents a new approach to perturbing and modifying properties of strongly correlated systems on an ultrafast timescale.
- Time-resolved X-ray techniques provide very specific probes of certain subsystems and help to disentangle the dynamics of coupled degrees of freedom.

#### References

- [1] M. Rini, et al, Nature **449**, 72 (2007).
- [2] A.D. Caviglia et al., Phys. Rev. Lett. **108**, 136801 (2012)
- [3] R.I. Tobey et al., Phys. Rev. Lett. **101**, 197404 (2008)
- [4] A. Dienst et al., Nat. Photonics 5, 485 (2011)
- [5] T. Kamprath et al., Nat. Photonics **5**, 31 (2011)
- [6] A. Dienst et al., Nat. Materials **12**, 535 (2013)
- [7] M. Beck et al., Phys. Rev. Lett. **110**, 267003 (2013)
- [8] T. Huber et al., Phys. Rev. Lett **113**, 026401 (2014)
- [9] P. Beaud et al., Nat. Materials 13, 923 (2014)
- [10] T. Kubacka et al., Science **343**, 1333 (2014)
- [11] M. Tonouchi, Nat. Photonics 1, 97 (2007)
- [12] Ultrafast Phenomena at the Nanoscale:Science opportunities at the SwissFEL X-ray Laser ed. by B.D. Patterson (2009)
- [13] S. L. Johnson, private communication (2014)
- [14] S. L. Johnson, private communication (2014)
- [15] A. Cavalleri, private communication (2014)
- [16] J. E. Lorenzo, private communication (2014)
- [17] Y. Joly private, communication (2014)
- [18] A time-dependent order parameter for ultrafast photoinduced phase transitions. Beaud et al. 2014. Nature Materials 13, 923–927 (2014); doi:10.1038/nmat4046

# XIII. Orbital control of semiconductor dopants

Ben Murdin, University of Surrey

Hydrogen-like donor states in semiconductors provide a long-lived, addressable medium for THz-based control of coherent quantum states.

- Introduction
- Solid-state quantum technologies
- THz dynamics and control in Si:P
- Outlook

A remarkable fact of physics is that impurities with one more valence electron than the host semiconductor display ground and excited states that are closely analogous to the free hydrogen atom Rydberg series, which was the touchstone for the Bohr formulation of quantum mechanics. This analogy between atoms in vacuum traps and impurities trapped in a crystal has led to exciting work at the cross-over between atomic physics and the solid state. New capabilities for deterministic doping have arisen, providing the opportunity for a new field of "crystal traps", with the aim of coherent control of spin and orbital quantum states of flexible "designer" wave-functions permanently fixed in space. Control of the orbital degree of freedom is in many cases only currently possible using a THz Free Electron Laser.

## Introduction

Atoms and ions trapped in vacuum are attractive for quantum coherence experiments and applications because the interactions of each atom with the environment are weak, providing sharp lines and long lifetimes for experiments. Because coherent manipulation of the quantum states of atoms in traps is possible, this ability has been used to demonstrate quantum computational gates and algorithms. The quantum information is encoded in the states of trapped ions - the qubits. A qubit is simply any two-state quantum system that can be put into a superposition, and a qubit register contains several entangled qubits. Quantum logic is carried out by controlled modification of the probability amplitudes (usually) in pairs of qubits. Successful demonstration of qubit gates requires two contradictory achievements. First, to ensure quantum dynamics of the components, these must be isolated from their environment; second, to control the computation, external intervention is required. However, to preserve the quantum nature of the computation the intervention must also be quantum mechanical. Finally, it must be possible to scale the system up to a large enough size to perform useful computations.

It is of great interest to perform quantum coherence experiments on atoms trapped in crystals such as silicon. There is an enormous wealth of sophisticated electrical contacting and manipulation technologies that can be borrowed from the CMOS industry to enable control and read-out of the potentials around the impurities. The three-dimensional structures that can be constructed have a huge variety compared to the potentials that can be achieved in free space, with far closer connection to the target atoms. The electronics industry is not looking to academia for help with making smaller CMOS, but it is looking for completely new ways of manipulating and storing information, ideally using the same platform. Quantum coherent control of spin and orbit ("spintronics" and "orbitronics") provides the possibility of completely new, very powerful information technology devices.

#### Solid-state quantum technologies

The analogy between free hydrogen atoms and shallow dopants in semiconductors, such as the phosphorus substitutional impurity in silicon, has long been recognized,

	н	Si:P
Dielectric permittivity, $\varepsilon_r$	1	11.4
Electron (effective) mass factor, m*	1	0.19
Rydberg energy, $E_{R} = \frac{1}{2} \left( \frac{e^{2}}{4\pi\hbar\varepsilon_{0}} \right)^{2} \frac{m*m_{e}}{\varepsilon_{r}^{2}}$	13.6 eV	0.020 eV
Bohr radius, $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2} \frac{\varepsilon_r}{m^*m_e}$	0.056 nm	3.2 nm

Table XIII.1: The scaling rules for hydrogenic shallow dopants in silicon relative to free hydrogen. The actual state energies are modified slightly by the periodic lattice (which produces an anisotropy of the effective mass, that lifts some degeneracies e.g splits the  $2p_0$  from the  $2p_{\pm}$  states) and the quantum defect (a.k.a. the central cell correction, that reduces the s-state energies). and they have a single mobile electron orbiting a singly positively charged ion. The Bohr model may be used to explain their binding energy with two simple corrections (Table XIII.1): the electron orbits far from the ion so the many intervening electrons from the host crystal screen the Coulomb force (i.e.  $\varepsilon_0$  is replaced by  $\varepsilon_r \varepsilon_0$ ); and the fact that the host is periodic means that the electron energy-momentum dispersion is modified so the conduction band is characterized by an "effective mass" (i.e.  $m_e$  is replaced by  $m^*m_e$ ). Indeed a solution of the hydrogenic Schrödinger Equation with these two corrections (and allowing  $m^*$  to be anisotropic) works extremely well for the excited states (though the ground state requires more sophistication) [1]. For the case of Si the binding energy is a few 10's of meV, which puts the Lyman series in the THz part of the spectrum, i.e. in the range of the THz Free Electron Laser. For example the Si:P 2p<sub>0</sub> first excited state has a radial extent of 10 nm, and approaches the size of transistors already in commercial use. The 1s-2p<sub>0</sub> transition is at 8.2 THz (=275 cm<sup>-1</sup>, 34 meV, or 36 µm), and states with principal quantum number up to

#### **Deterministic doping**

For the last 60 years, randomly placed group III and V donors have been a key feature of semiconductor technology. The last decade has witnessed the development of deterministic doping, with the associated possibility of creating arbitrary low dimensional solids within the "vacuum" provided by the world's cleanest host, silicon, as well as constructing new devices atom by atom. Our view is that this capability is as significant for condensed matter and device physics as the development of cold atom technologies has been for atomic physics. There will be a wide range of impacts, from the improvement of classical devices for which disorder-based scattering and localization effects will be suppressed, through to integrated quantum gate networks.

As silicon technology is developed, ever more effort is being invested in proof-of-concept research for novel devices. There have been significant advances in deterministic doping, leading to the fabrication of atomically precise wires and single electron transistors (SETs), for electron spin detection. The process of atomic scale engineering consists of patterning a hydrogen resist using current pulses through a Scanning Tunnelling Microscope tip (which can be performed with atomic resolution), exposing the patterned surface to the dopant precursor gas phosphine (PH<sub>3</sub>), annealing to incorporate the dopant atom into the surface layer, and encapsulating the dopant structure in silicon using molecular beam epitaxy.



Fig. XIII.i1: Deterministic doping is performed with atomic reolution in an STM. The image shows a silicon surface where the dangling bonds are passivated with hydrogen atoms (blue features). Two H atoms have been removed by current pulses so the dangling bonds of the silicon (white features) poke through the hydrogen layer, ready for attaching phosphorus-containing molecules. Arbitrary arrangements can be produced and subsequently encapsulated in overgrown silicon. Picture by Steven Schofield

6 (radius ~100 nm) are easily observable in high purity commercial material. The remarkable fact is that in clean crystals, the levels can be extraordinarily sharp, down to 1 GHz.

The binding energy for silicon (Table XIII.1) is about the same as the thermal energy  $k_BT$  at room temperature, so the extra electron thermally ionizes and becomes available for conduction, which is why semiconductors are so highly controllable. However, at temperatures below about 50K, the electron is bound and the impurity resembles atomic hydrogen. Even higher temperatures may be satisfactory for some less commonly used impurities that have much greater binding energies.

Deterministic doping can be used to position some impurities with atomic resolution [2,3], so the solid state environment for these impurities can therefore be seen as the nanoscale analogue of an optical lattice in atomic physics. In terms of single spins, i.e. single electrons bound to a single impurity, read-out may be achieved using atoms near or within a single electron transistor (SET) [4]. Both single electron and single nuclear qubit readout have been demonstrated using randomly implanted phosphorus atoms, and readout of deterministically placed donors seems imminent. The latter possibility has generated great excitement world-wide (evidenced by a number of recent reviews) [5,6]. The classic demonstrations of quantum coherence are Ramsey interference and the spin echo, which allow measurement of inhomogeneous and homogeneous dephasing times, respectively. Even several decades ago Si:P demonstrated the longest electron spin coherence times in the solid state; many seconds. In isotopically pure <sup>28</sup>Si it far exceeds even this, and it can be as much as three hours at low temperature when the donor is ionized. The nuclear spin of a phosphorus donor is 40mins even at room temperature [7]. As mentioned above, the desire for minimal environmental decoherence somewhat contradicts that for easy external control - the small dipole moments of nuclear spins protect them but make them slow to manipulate. Electron spins or electron orbits are successively less protected but allow faster control. This suggests the possibility of very robust quantum memory with the nucleus, with information swapped to the electron using control of the S.I coupling (the hyperfine interaction), which is magnetic field sensitive [8].

#### THz dynamics and control in Si:P

Control over the orbital quantum number provides even faster electric-dipole interaction (with consequently faster decoherence) and a crucial tool in the quantum logic kit because the change of wavefunction extent/shape changes the overlap with neighbours.

To perform dynamics experiments and quantum control a coherent pulsed source is required, and for Si:P it must be in the THz spectrum. Because the transitions are sharp, a tunable source is required, and the bandwidth must be broader than the absorption line (1 GHz) but smaller than the separation between lines (~100 GHz). Finally the intensity must be high to be able to achieve  $\pi$ -pulse excitations (one of the pulses in the echo sequence, required for complete control of superposition states). The precise intensity value required depends on the pulse duration and on the atomic dipole moment, and in the Si:P case for 10ps pulses approximately 1mJ/cm<sup>2</sup> is required. In this case only the r.f.



Fig. XIII.1: A THz photon echo from Si:P using the FEL [12]. Echoes are shown as a function of time relative to the arrival of the  $\pi$ -pulse, for various delays between the  $\pi/2$  and  $\pi$ . The echo amplitude shrinks with exp(- $4\tau/T_2$ ) where  $\tau$  is the delay and  $T_2$  is the homogeneous dephasing time. The factor of 4 arises because the duration of the coherence is  $2\tau$  and the echo strength is proportional to the square of the superposition amplitude.

#### Optical Rabi oscillations, Ramsey interference and Hahn echoes

In a spin coherence experiment a strong electromagnetic field rotates the electron (or nuclear) spin, putting it into a superposition state. The angle of rotation increases with the amplitude and duration of the pulse, so that the probability of occupation of the excited state rises and falls sinusoidally (Rabi oscillations). A second, delayed pulse, can be used to manipulate the quantum coherence. In a Ramsey interference experiment the second pulse is equal in amplitude, and depending on the phase it either increases or decreases the rotation. As the arrival time of the second pulse is increased the macroscopic phase decays e.g. by inhomogeneous broadening, so the fringe amplitude reduces. In the Hahn echo experiment (Fig. XIII. i2) the second pulse reverses the accumulated phase, and after a time equal to the delay between the pump pulses a spin echo is detected. The strength of the echo decays with increasing delay between the pulses as coherence is lost.

There are electric-dipole equivalents of these spin effects, and the mathematical description is exactly equivalent. The natural frequency that defines the evolution of the relative phase of the probability amplitudes in the dark is  $(E_2-E_1)/\hbar$ , just as for spins. The Rabi frequency is  $(1|\mu_{\rm E}|2) \cdot E_1/\hbar$  instead of  $(\uparrow|\mu_{\rm M}|\downarrow) \cdot B_1/\hbar$  where  $\mu_{\rm M,E}$  are magnetic and electric dipole moment operators and B<sub>1</sub> and E<sub>1</sub> are the a.c. magnetic and electric field amplitudes. The evolution can also be represented by a Bloch vector with the same coordinate definition as for spins, though commonly the sign convention is such that the ground state is at the south pole:  $(c_1c_2^*+c_2c_1^*, ic_1c_2^*-ic_2c_1^*, c_2c_2^*-c_1c_1^*)$ where  $c_{1,2}$  are the amplitudes for states 1 & 2. As usual, the z-coordinate equals the probability difference in a two-level superposition state, and the azimuthal angle equals the relative phase of the amplitudes,  $Arg(c_2/c_1)$ . A technical difference is that the wavelength is small enough to use free-space beams with waist smaller than typical samples. This produces an advantage that the echo emission is directed, and spatially separated from the other beams in the phase matching direction  $2k_2 - k_1$  where  $k_{1,2}$  are the directions of the  $\pi/2$  and  $\pi$  pulses. The disadvantage of a free-space beam, i.e. without a cavity, is that the sample experiences a non-uniform field amplitude and Rabi oscillations are unresolved.



Fig. XIII.i2: The Hahn echo sequence, shown in conjunction with a Bloch sphere in the laboratory frame. In this convention the ground state is at the South pole. The Rabi frequency during excitation is  $\Omega_R = ex_{12}E_1/\hbar$ . The first pulse has "area"  $\Omega_R t = \pi/2$  where t is the pulse duration and the 2<sup>nd</sup> has area  $\pi$ . At a time 2 $\tau$  (where  $\tau$  is the delay) the oscillators are back in phase, i.e. there is a macroscopic polarisation and an echo is emitted.

linac pumped FEL is suitable, although it is expected that once the physics is understood and applications are clear, developments in Quantum Cascade Laser diodes or Ti:sapphire-based THz sources will follow.

FELs have been used to make the only measurements of the population decay of orbital excitations for silicon dopants using a degenerate pump-probe experiment [9,10,11]. Here, a strong pump-pulse excites the population to bleach the absorption. A weak probe pulse, incident at a small angle to the pump with controllable arrival time, measures the recovery. This is an incoherent experiment, but still requires short pulses and high intensity of the right frequency. The lifetimes observed are only an order of magnitude shorter than those in atomic hydrogen (the  $2p_0$ -1s relaxation in Si:P is ~200ps compared with 1.6ns for H), although phonon, rather than photon emission implies a much shorter time-scale than might be expected from a THz-frequency transition in atoms.

Coherent control of Si:P was first demonstrated with an orbital photon echo [12]. Those experiments take advantage of the coherence of the THz pulses from the FEL – they are bandwidth limited - to stimulate and observe photon echoes (Fig. XIII.1), the orbital analog of the Hahn spin echo. Rabi oscillations were also observed, although unresolved due to integration over the Gaussian beam profile. The echo experiment showed that the homogeneous dephasing time (also ~200ps) is very similar to the population lifetime, i.e. that the only source of decoherence is the phonon emission responsible for the energy relaxation. This is amazing, since the electron orbits within a volume containing  $10^6$  other charges, all with zero-point fluctuations (motions associated with the uncertainty principle). This coherence lifetime is long enough to be used in certain quantum gates.

A range of coherent manipulation and control effects have been demonstrated with optical detection [14], such as echo detection of  $T_1$  (with a  $\pi$ - $\pi/2$ - $\pi$ -echo sequence), and Ramsey Interference. This latter is a crucial process in gating, which requires the coherent excitation and de-excitation of the control atom that mediates the exchange between the two qubits.

One of the primary reasons for interest in silicon is the opportunity for integration with readout electronics, and electrical detection of single spins has already been mentioned. Electrical readout of ensembles has been developed for orbital excitations too [13,14]. Ramsey interference has been generated in electrical detection, and Fig. XIII.2 shows clear fringes that last for  $T_2^*$ ~30ps, consistent with the inverse linewidth of the spectrum, far longer than the autocorrelation of the light pulses with duration 2 ps measured simultaneously.



Fig. XIII.2: Electrically detected Ramsey interference. The first of a pair of  $\pi/2$  pulses creates a superposition and the second interferes with the coherence left in the sample by the first. The color map shows a "wavelet" transform, i.e. the frequency of the fringes in the interference as a function of time delay, when the laser is tuned to the 1s-2p± transition at 9.75THz. The Ramsey interference (left) lasts many 10's of ps, while the autocorrelation of the pulse (right) is much shorter.

### Outlook

The phosphorus impurity in silicon has shown the longest spin coherence time known in the solid state, and experiments with the FEL have shown long, useful orbital coherence times too. Much is still to be explored, and many other important impurities have yet to be examined. The spin of a single deterministically placed dopant atom has yet to be measured, although small clusters have been detected. The challenge now is to develop the equivalent control and read-out for single orbital excitations. Deterministic doping allows the creation of a host of designer structures, from a simple H<sub>2</sub> molecule analogue to lattices of many donors. So far nothing is known about the electric dipole (or spin) dynamics of such structures, and this will be crucial for exploitation. There are still significant challenges to overcome in deterministically placing multiple species of single atoms for ultimate flexibility. A great variety of potential "molecule" and "lattice" structures could then be made to create designer solids, and there is a bright future for THz FEL experiments.

#### The Stoneham-Fisher-Greenland (SFG) qubit gate scheme

Fig. XIII.i3 shows a particularly simple scheme by which the exchange interactions between ions may be modulated in an impurity molecule trimer [15]. There are two deeper donor impurities (the gubits) with a shallower donor (the control) situated between them. This might be realized in silicon with a pair of bismuth gubits and a phosphorus control. Quantum information is stored in the Bi electron spins, and the gate control is via the P electron orbit, illustrating the utility of coherent manipulation of electricdipole transitions. If the control impurity is in its ground state, the spins of the qubit impurities are uncorrelated. However, when the control impurity is excited by a THz laser to a higher, more extended state, there is a magnetic exchange interaction between all three impurities - even though the qubits remain in their tightly confined ground states, well isolated from interactions with the continuum. The time required for the control is determined by the strength of the magnetic exchange interaction between the qubits, J, and how much rotation of the qubit spins is required. / scales inversely with the distance between the donors  $- J/h \sim 4$ GHz at 10nm separation, and for common gates a rotation of order  $\pi$  is required. At the end of the desired gate period, the control atom must be de-excited, and this can be performed with a second THz pulse with appropriate phase. To achieve a half-cycle rotation at a few GHz requires that the control atom must remain coherent for 100ps or so, and this also sets the time scale for the required laser pulses.





# Summary

- Impurities in silicon and other semiconductors provide sharp transitions with long coherence times and make good candidates for quantum technology platforms
- Transition frequencies are often at small energy due to the dielectric screening of the crystal host, meaning that the THz FEL provides an invaluable tool for studying coherent and incoherent dynamics and control.
- Deterministic doping with atomic precision is about to make a very exciting range of impurity "molecules" and impurity lattices available for study.

#### References

- [1] B.N. Murdin, et al Nature Communications **4**, 1469 (2013)
- [2] S. R. Schofield, et al, Phys Rev Lett **91**, 136104 (2003)
- [3] S. R. Schofield et al, Nature Communications 4, 1649 (2013)
- [4] J.J. Pla et al, Nature **489**, 541 (2012)
- [5] P.M. Koenraad and M Flatte, Nature Mats 10 91 (2011)
- [6] D.D. Awschalom et al, Science **339**, 1174 (2013)
- [7] K. Saeedi, et.al. Science **342**, 830-833 (2013)
- [8] G. W. Morley et al, Nature Materials 12, 103 (2013)
  [9] N.Q. Vinh et al, Proc. Natl. Acad. Sci. USA 105, 10649
- (2008)
- [10] N. Q. Vinh et al, Phys. Rev. X **3**, 011019 (2013)
- [11] H.-W. Hubers et al, Phys Rev **B88**, 035201 (2013)
- [12] P. T. Greenland et al., Nature **465**, 1057 (2010)
- [13] E.T. Bowyer, et al Appl Phys Lett. **105**, 021107 (2014)
- [14] K.L Litvinenko et al Nature Communications, 6, 6549 (2015)
- [15] A.M. Stoneham, A.J. Fisher and P.T. Greenland, J. Phys: Condens Matter. 15, L447 (2003)

# XIV. XFEL Studies of Strongly-Coupled Plasmas

Sam Vinko, University of Oxford

Extreme conditions of temperature and pressure, at constant volume, can be created in matter by irradiation with an ultrafast XFEL pulse. Understanding the resulting "high-energy-density" state is a challenge to existing theory.

- Introduction to Matter under Extreme Conditions
- Isochoric Heating and Saturable Absorption
- Generating Warm Dense Matter
- Generating Hot Dense Matter
- Ionization Potential Depression
- Outlook

The high peak-brightness of X-ray FELs, coupled with X-ray optics enabling the focusing of pulses down to sub-micron spot sizes, provides an attractive route to generate high energy-density systems on femtosecond timescales, via the isochoric heating of solid samples. Once created, the fundamental properties of these plasmas can be studied with unprecedented accuracy and control, providing essential experimental data needed to test and benchmark commonly-used theoretical models and assumptions, but also to develop new predictive capabilities in the study of matter in extreme conditions.

# Introduction to matter under extreme conditions

The study of high energy density physics (HEDP) is of great importance for both fundamental and applied physics. Matter is loosely defined to be in this regime if it has an energy density exceeding about 10<sup>11</sup> Jm<sup>-3</sup>, which corresponds to temperatures above a few eV at a typical density of a solid, or pressures above one Mbar. Such matter is widespread in the universe in a variety of forms, ranging from the interiors of giant planets, such as Saturn and Jupiter, to the constituent matter of all the different types of stars. Importantly, understanding the properties and the dynamics of matter in these extreme conditions, and its interaction with radiation, is essential for inertial confinement fusion investigations.

Within the realm of HEDP, a further practical distinction is often made between warm-dense matter (WDM), describing partially degenerate, dense systems at temperatures around the Fermi energy of a typical metal (5–10 eV), and hot-dense matter (HDM), where the temperatures are sufficiently high so that there is no degeneracy in the free-electron distribution. What these systems have in common is a high density of charged particles, so that their Coulomb energies are non-negligible compared with their kinetic energies. This significantly complicates the theoretical description of such systems, as approaches based on kinetic theory become inadequate, many-body effects become important, and the system exhibits strong correlations between its constituent particles. In this sense, theoretical work on HEDP often lies on the boundary between condensed matter physics and classical plasma physics, borrowing techniques from both, but generalizable to neither. Further, the complexity of these systems, combined with the vast scale of interactions and processes that need to be accounted for, makes the development of simplified, approximate models necessary, and their validation with experimental data is all the more essential.

To date, creating a homogeneous system, which is both very dense and has a high energy density, has proven a remarkable experimental challenge. While such states of matter are produced any time plasmas are created from solid samples, they are highly transient, and also exhibit steep, juxtaposed gradients in density and temperature. As such, creating and isolating well defined WDM and HDM states is an important experimental goal in its own right, in addition to the clear interest in the development of dedicated diagnostic techniques aimed at the study of their properties and dynamics. Importantly, the experimental difficulties in studying these systems impact theoretical developments, as little quantitative data is available to validate and guide calculations and modelling.

#### Warm Dense Matter



#### **Hot Dense Matter**



Fig. XIV.1: High energy density matter in the interior of the planet Jupiter (left) Image credit LLNL, https://www.llnl.gov/str/September03/gifs/Moses12.jpg, and the Sun (right) Image credit NASA, http://www.nasa.gov/mission\_pages/hinode/solar\_020.html.

In this context, X-ray FELs are now starting to prove their potential as a tool to both create and study HED systems. On the one hand, X-rays, characterized by photon energies much larger than the plasma frequency of a typical dense system (10–20 eV), are capable of penetrating deep into samples, depositing energy and probing them volumetrically. On the other, the high peak brightness afforded by FELs, combined with sub-micron focusing X-ray optics, now enables the deposition of milli-joules of energy into volumes of a few cubic microns, and on sub-picosecond time scales, sufficient to generate high energy density systems on inertially confined timescales.

# Isochoric heating and saturable absorption with X-ray FELs

Using intense X-rays to deposit energy in free-standing foils is an attractive route to creating solid-density plasmas, both because of its simplicity in terms of experimental setup, and because the energy deposition of X-rays is volumetric. Provided the thickness of the target foil is comparable to the absorption depth of the X-rays used, this deposition can also be made fairly homogeneous. For these reasons, this route towards the controlled generation of HED matter was seen as very promising and was proposed and extensively investigated theoretically over the past decade, forming a key component in the drive for HEDP to be performed on XFEL facilities [1–6]. With the commissioning and beginning of user operation of XUV and X-ray FELs worldwide, these techniques have now become experimentally feasible, and are starting to justify their promise. Of course, this method is not limited to foils. For example, isochoric (constant volume) heating of cryogenic hydrogen droplets to WDM conditions has been recently demonstrated on the FLASH XUV FEL [7].

While the absorption of X-rays is volumetric in dense matter, in the linear absorption regime the X-ray intensity still decays exponentially within a thin foil following Beer's law. For this reason, targets thicker than about one absorption length are generally not used to create homogeneous HED systems, and even at a single absorption length, gradients of over a factor of two may form between the front and back surfaces of samples. However, the X-ray intensities that can now be achieved at FELs are sufficiently high for non-linear absorption effects, such as saturable absorption, to take place. Besides being of interest to the study of fundamental atomic physics and plasma dynamics, saturable absorption is an important process to consider in the generation of HED systems, because it can reduce the longitudinal gradients in energy density within samples. In fact, it is becoming increasingly clear that at the highest FEL intensities, which are also those often used to create HED samples, photoexcitation and photo-ionization can compete with atomic recombination rates, such as fluorescence and Auger decay, saturating absorption channels. This effect is generally welcomed, as the dense plasmas created tend to be more homogeneous than if the X-ray deposition process were linear. The reason for this is that as a particular absorption channel starts saturating at the surface of the sample, more energy can be transmitted through and deposited deeper, reducing or eliminating the overall exponentially decreasing energy deposition.

The first experimental proof of saturable absorption at FELs was observed in very thin Al samples at the XUV FEL FLASH in Hamburg [8]. Performed at a photon energy of 92 eV, the intense, 15 fs pulse saturated the L-shell absorption channel, leading to a large increase in the transmitted signal and an energy deposition gradient between the front and rear of the target foil that was deduced to be linear rather than exponential. The sample was estimated to have been heated to temperatures of around 20 eV, sufficient to create a warmdense Al plasma [9,10]. Saturable absorption has now been observed in multiple systems irradiated by intense FEL beams over a range of wavelengths, from the XUV [11], to soft and hard X-rays [12–15].

#### Generating Warm Dense Matter

The idea that intense X-rays from an FEL source could produce HED states in well-defined conditions via isochoric heating of thin foils was initially proposed over a decade ago [1-5], and was recently put to the test in an experiment on the Linac Coherent Light Source (LCLS) X-ray FEL [16]. Here, a 0.5 micron thick silver foil was irradiated and heated

by X-rays at a photon energy of 8.9 keV. The target was designed to be much thinner than an absorption length at this wavelength (~6 µm), so as to minimize energy deposition gradients between the front and the backside of the foil. The X-ray pulse was 60 fs long and was focused to a spot size yielding an intensity of about 5 × 10<sup>15</sup> W cm<sup>-2</sup> on target. The energy absorption mechanism of the X-ray pulse in the target was predominantly Ag L-shell photoionization, although some M- and N-shell photoionization also took place. These processes occurred during the ultra-short FEL pulse, creating core-ionized and excited electron configurations, which quickly equilibrated via X-ray fluorescence, and Auger and collisional processes, leading to a heating of the electron sub-system. The ions, in turn, remained cold during the X-ray irradiation, and were subsequently heated by the hot electrons to the equilibrium temperature on the timescales of electron-ion coupling, of the order of 10 ps [17,18]. Because of the difference in equilibration timescales, the X-ray heating mechanism was largely decoupled from any ion density gradient in the sample.

The peak temperature deduced via hydrodynamic calculations was of  $10^{-15}$  eV, while the sample was still at solid density. At later times, because of the high internal pressure, the sample expanded into the surrounding space and cooled, with its evolution dictated by its Equation of State. This expansion was the main observable in the experiment, measured via time-and-space resolved interferometry, simultaneously on both the front and back surfaces of the WDM sample. The expansion was observed to be similar on both sides of the foil, broadly within the margin of experimental error and in agreement with hydrodynamic calculations. This was the first experimental confirmation of isochoric heating by looking directly at the sample explosion on the relevant-picosecond-time scales, and has quantified the temperature uniformity in the longitudinal direction to be within about 10% [16].

#### X-ray driven Emission Spectroscopy

By pumping a hot-dense plasma with intense, narrowbandwidth X-rays, the electronic structure of ions immersed in a strongly coupled plasma can be investigated on ultrashort timescales, via X-ray driven Ka emission spectroscopy. The ions will only emit  $K_{\alpha}$  photons if the X-ray pulse from the FEL can ionize or excite a 1s electron and create a K-shell hole. So for each ion, emission will be observed only if the X-ray photon can drive a transition from the 1s level to some other state, bound or free, allowing the states to be directly mapped in energy, as shown in the figure for an Al plasma [19]. Bound-bound transitions can be observed as islands in the emission spectrum; here these correspond to the resonantly driven 1s-2p transitions [20]. Photo-ionization corresponds to driving the 1s electrons into some state in the continuum. Such transitions will yield broadly flat emission intensities over an extended range of FEL wavelengths, increasingly observed at higher FEL photon energies.



Fig. XIV.11: Spectrally-resolved Ka emission above the K-edge from different ionic charge states in Al, excited with the LCLS XFEL. The emission "islands" at low emission energy are bound-bound K-L transitions [19,20].

### Generating Hot Dense Matter

The first demonstration of generating HDM with an X-ray FEL from thin foils was also recently performed on the LCLS, by irradiating a one-micron thick Al foil (~1 absorption length) at X-ray intensities up to 10<sup>17</sup> Wcm<sup>-2</sup> [19]. The X-ray wavelength of the FEL was tuned around the various K-edges of increasingly ionized Al ions, in the range 1460–1800 eV [19,20].

The dominant absorption mechanism is K-shell photoionization, provided the X-ray photon energy of the FEL is above the ionization threshold of the ions in the system. Below threshold, L-shell and free-free absorption take place, with significantly smaller cross-sections. The various absorption channels transfer energy from the X-ray pulse to the target, heating it and ionizing it further, creating a range of ionic configurations with inner-shell vacancies. These unstable ionic configurations recombine in two ways: radiatively, where an electron fills the core hole and a photon is emitted, or non-radiatively, via Auger processes, which further ionize the ion by emitting electrons. In Al, Auger processes dominate, accounting for over 96% of the recombination events [21]. As the Auger electrons have very high collisional cross sections, very few escape the sample, and most transfer their energy to the remaining electrons and ions in the system via collisional processes on ultra-short time scales, so that the energy deposited by the X-ray beam is efficiently retained in the newly generated plasma. Peak temperatures approaching 200 eV and electron densities exceeding 5×10<sup>23</sup> cm<sup>-3</sup> were reported, deduced from detailed atomic kinetics calculations, and in agreement with the observed spectral emission [19].

The plasma was diagnosed via X-ray spectroscopy of the emission generated from the radiative K-shell recombination process. Despite the relatively small X-ray fluorescence yield, the Ka emission (photons generated by the 2p-1s transition) for the FEL-driven sample was observed to be sufficiently strong to record spectra pumped by a single, sub-100 fs, X-ray pulse. This emission is driven by the FEL pulse, since the intense X-ray beam is the only significant generator of K-shell core holes, making the technique very different from normal X-ray (self)emission spectroscopy (XES). In fact, this diagnostic has several similarities with X-ray absorption spectroscopy (XAS) measurements, since the narrow band-

width of the X-ray pulse (~0.4%) will only be absorbed if a 1s electron can be either excited to some higher-lying bound state, or ionized. However, unlike XAS, which for a single photon energy yields only a transmitted intensity, here the absorption process gives rise to inner-shell radiative recombination in the plasma, providing an entire emission spectrum. The integrated photon yield of this spectrum is, of course, directly related to the absorbed energy fraction via the radiation transport function. This measurement is therefore unique, and by scanning the FEL X-ray photon energies across the various ion energy levels, the authors reported a measurement of the electronic structure of all the ions present in the dense plasma (see Fig. XIV.1). As such, this is an extremely information-rich experimental technique for dense plasmas studies, and shows great potential for future investigations.

#### **Ionization Potential Depression**

The ionization potential depression (IPD) of ions in a plasma due to their interaction with the environment, is a fundamental component of dense plasma studies, as the ionization thresholds are needed to determine all ionic binding energies within the system. This is essential for virtually every property of partially-ionized plasmas, from the ionization balance and absorption cross-sections, to the plasma equation of state, the temperature and the emission spectrum. While it underlies so many plasma properties, extracting accurate IPDs from experimental observations in hotdense plasmas prior to the advent of X-ray FELs had proven extremely challenging, in part because of difficulties in creating well-defined WDM and HDM conditions, and in part because of a lack of experimental techniques capable of tracking ionization thresholds with sufficient accuracy. The IPD energy is highest in conditions of both high density and high ionization (temperature), so it is clearly crucial for the correct description of HDM systems, but it is also essential for WDM, even though the degree of ionization is much lower and absolute IPD energies are small [22,23].

The capability to measure the electronic structure of ions in hot and dense plasmas at known ion density (and structure) has proven of great interest for the investigation of the phys-



Fig. XIV.2: Experimentally measured K-edges for Al charge states 3–7 in a hot-dense plasma, compared with the K-edges for isolated Al ions (no plasma, dashed lines), and two models, the Stewart-Pyatt model (blue) and a modified ver-sion of the Ecker-Kroell model (red). Figure taken from Ref. [24].

ics of IPD in these extreme conditions. As can be seen from Fig. XIV.1, alongside bound-bound resonant features, the data show clear emission thresholds as a function of FEL photon energy, with near-constant emission intensities above them. At least for the first several charge states, Ciricosta and co-workers identified these thresholds as the K-edges of Al ions embedded in the solid-density plasma, and could therefore extract the experimental IPDs in these conditions for the first time [24].

The IPD measurements at the LCLS proved to be particularly interesting not only because they were the first measurement of this kind, but also because the results disagreed by a considerable margin with the predictions of the most commonly used models for dense plasmas, such as the Zimmerman and More ion sphere model [25], or that of Stewart & Pyatt (SP) [26]. Instead, a modified version of a model put forward by Ecker & Kröll (EK) [27] (where the leading constant in the expression was replaced by unity), was found to reproduce both the experimental edges and the full range of emission spectra shown in Fig. XIV.1. A comparison between the experimental edges and the prediction of the models is shown in Fig. XIV.2, reproduced from Ref. [24]. The experimental edges, indicated in pink in the figure, correspond to the observed emission thresholds, and, as can be seen, these are much lower (larger depression) than those predicted by the SP model for all charge states, indicating much larger IPDs are needed to explain the experimental results. Recently, experiments on the Orion laser at AWE, in the United Kingdom, have also attempted measurements from which the IPD could be extracted, on small Al dots buried in plastic or diamond [28,29]. These dots were compressed to several times solid density and heated to temperatures up to 700 eV by both short and long-pulse optical laser beams. The plasma conditions produced by Orion were more weakly coupled compared with those generated on the LCLS, but a comparison of the results is interesting, in part because the IPDs deduced from this experiment were seen to lie about halfway between the predictions of the EK and SP models, agreeing with neither within the quoted experimental error.

In light of the failure of the popular SP model to reproduce the measured results in the conditions of either experiment, and the somewhat enigmatic success of the EK model on the LCLS data, a renewed interest in the topic from the theoretical point of view has emerged, highlighting the need for a much better treatment of density effects in strongly-



Fig. XIV.3: Comparison of five different models for the ionization potential depression with the experimental results from the LCLS [24].

coupled plasmas. Crowley has recently argued that at least two different IPDs must be used in considering a plasma, a thermodynamic IPD to describe equilibrium phenomena (such as the equation of state), and a non-equilibrium, spectroscopic IPD to describe processes such as photoionization, in particular the experimental results from the LCLS described above [30]. This model yields a noticeable improvement over that of Stewart & Pyatt when applied to the conditions of both the LCLS and the Orion experiments. Son and co-workers have developed a two-step Hartree-Fock-Slater model, which they claim also yields a better agreement with both the Orion and LCLS results [31]. Vinko and co-workers have conducted a detailed finite-temperature density functional theory (DFT) study of the electronic structure of ions in a dense plasma with the view of investigating the effect of continuum lowering [32]. In this work, the electronic structure, and in particular the K-edges for the various charge states were seen to agree very well with the LCLS experiments, however, the authors were unable to

# reach the conditions of the Orion experiments due to the difficulty in using DFT methods at high temperatures. The results from these models are shown alongside the LCLS measurements in Fig. XIV.i2.

The disparity of these calculations point to several important deficiencies in the way dense plasmas are currently modelled. In particular, a clear cut-off in the energy of the bound state partition function is, in general, too crude an approach to modelling the depression of the ionization potential due to high density. Worse yet, it entirely ignores the fundamental mechanism by which the continuum forms in dense systems at energies which would otherwise correspond to bound states in isolated ions: the overlapping of valence wave functions giving rise to a non-zero probability of finding a valence electron at some later time far from the ion from which it originated. This is in the zero-temperature limit simply the tight-binding theory of band formation, which is a continuous process, complicating the definition of a free or bound electron, and of the ionization of a dense plasma

#### **DFT Calculations of Hot-dense plasmas**

Density Functional Theory calculations of core-excited Al configurations in plasmas at finite temperatures [32] can provide a theoretical basis to investigate the electronic structure of ions embedded in a dense, strongly-coupled plasma. The calculated structure and position of the con-

tinuum is seen to agree well with charge-state-resolved measurements recently performed at the LCLS; shown in Fig. XIV.i2 for lines IV and VII, corresponding to charge states  $3^+$  and  $6^+$ .



Fig. XIV.i2: The results of density functional theory calculations showing the predicted density of states for ions in a hot plasma, compared with experimental results from the LCLS [32]. in general. Dharma-wardana and Perrot were the first to discuss these effects, and their importance in dense plasmas, via the neutral-pseudoatom model with an ion correlation sphere [33], and several difficulties still persist in commonly used average-atom models [34]. A fully threedimensional DFT calculation of the electronic structure in a dense plasma, accounting for a realistic ion distribution and treating all electrons in the same manner, was instead only performed very recently [32]. Regardless, the problem is unlikely to be solved by theoretical work alone, and further effort, both on X-ray FELs and other facilities, will be crucial in resolving the many outstanding questions on the properties of dense plasmas.

### Outlook

The isochoric heating of foils to WDM and HDM conditions with FEL radiation is now an established technique capable of creating extreme and exotic states of matter in well defined conditions of temperature and density on inertially confined time scales. The high X-ray intensities required to generate the highest energy density systems invariably drive non-linear processes in the samples under investigation. Such processes, as was shown in the case of saturable absorption, can be very beneficial to sample homogeniety, but a detailed knowledge of the interaction dynamics of the intense X-ray pulse with the sample is required to exploit this capability in full.

The first investigations of plasma properties of mid-Z elements have been performed on the LCLS using novel spectroscopic techniques, and have yielded the first measurements of continuum lowering, resolved by charge state, in a 100–200 eV, solid-density Al plasma. Further results on Si, Mg, as well as on compounds of Al and Si, have been recently reported at conferences, and are expected to be published soon [35]. While the interpretation of the experimental results is still being debated (e.g. Refs. [36,37]), as are the methods used to model these effects in codes dedicated to simulating dense plasmas, there now exists for the first time a clear set of comprehensive experimental data from a well-defined hot-dense plasma, with which codes and models can be benchmarked. In this context, further experimental data are much needed and can only be provided by future campaigns on XFEL sources.

Few experimental investigations dedicated to generating high-Z hot-dense plasmas have been conducted so far on XFELs [15]. Such systems, while very important from a physical point of view, may be harder to perform and analyze using the spectroscopic techniques presented above for several reasons: Firstly, atoms with higher atomic number contain many more electrons, and the core states are more strongly bound, so that more energy is required for significant ionization. There are also many more weakly bound electrons, for which very different charge states can produce similar emission spectra. Further, inner shell (K or L) spectroscopic techniques require much higher photon energies to generate core holes, a process which generates higher energy Auger and photoemission electrons that are less likely to thermalize within the small plasma volume. Isochoric heating via core-state photo-absorption with increasingly harder X-rays is also less efficient because of higher energy losses due to radiative recombination (the probability of radiative recombination between two energy levels grows with their energy separation). Some of these issues may be mitigated by using higher X-ray pump intensities. The peak intensities generated so far at XFELs are in the region of 10<sup>20</sup> W/cm<sup>2</sup>, achieved by focusing to spot sizes a few 10s of nm across [38]. Although these intensities are very promising for a range of (non-linear) studies, at some point hot electron losses during the collisional thermalization process, due to the small plasma size, may become important, placing a limit on their usefulness for creating hot-dense plasmas.

Isochoric heating experiments performed with a single X-ray FEL pulse are limited to the study of ion densities of the samples in their ground state. Future work involving X-ray pump-probe configurations, or coupling X-ray FELs with intense optical lasers will be needed to investigate plasma systems at different densities and at temperatures beyond those currently reachable at FEL facilities by X-ray heating. These are perhaps the most promising future developments, and have great potential to further our understanding of matter in extreme conditions, providing insight into its fundamental interaction processes and dynamics, of broad relevance to a range of astrophysical and ICF investigations.

# Summary

- Isochoric (constant volume) heating of systems to warmand hot-dense plasma conditions is now an established procedure for investigating low and mid-Z elements with FEL X-ray energies of a few keV. Plasmas at solid density and temperatures of several hundred eV have been produced on femtosecond timescales, with reasonably well-characterized inhomogeneity.
- High-Z systems can be heated to WDM conditions on inertially-confined timescales with temperature gradients around 10% over micron-scale sizes, and with essentially no density gradients. First results show great promise for investigations in the challenging WDM regime.
- X-ray driven emission spectroscopy on FELs shows promise as a technique to accurately characterize the structure of dense plasmas. Measurements of fundamental plasma properties, such as the ionization potential depression, are already having a significant impact in the field and are providing the much needed experimental data in regimes were none previously existed.
- Key developments in the future will aim at producing higher Z plasmas and in generating plasma conditions that cannot be reached by FEL irradiation alone. High power short and long pulse optical lasers placed alongside XFELs afford the potential to provide this capability and further broaden the range of plasma investigations.

#### References

- R.W. Lee et al., Plasma-based studies with intense X-ray and particle beam sources, Laser and Particle Beams 20, 527-536 (2002).
- [2] R.W. Lee et al., "Finite temperature dense matter studies on next-generation light sources," Journal of the Optical Society of America B 20, 770 (2003).
- [3] A. Ng et al., Idealized slab plasma approach for the study of warm dense matter, Laser and Particle Beams 23, 527–537 (2005).
- [4] T. Tschentscher and S. Toleikis, Investigations of ultrafast phenomena in high-energy density physics using X-ray FEL radiation, The European Physical Journal D 36, 193–197 (2005).
- [5] D. Fisher et al., Core holes, charge disorder, and transition from metallic to plasma properties in ultrashort pulse irradiation of metals, Laser and Particle Beams 24, 81–94 (2006).

- [6] S.J. Rose, The effect of a radiation field on excitation and ionisation in non-LTE high energy density plasmas, HEDP 5, 23–26 (2009).
- [7] U. Zastrau et al., "Resolving ultrafast heating of dense cryogenic hydrogen," Phys. Rev. Lett. 112, 105002 (2014).
- [8] B. Nagler et al., "Turning solid aluminium transparent by intense soft X-ray photoioniza- tion," Nat Physics 5, 693– 696 (2009).
- [9] S.M. Vinko et al., "Electronic Structure of an XUV Photogenerated Solid-Density Aluminum Plasma," Phys. Rev. Lett. 104, 225001 (2010).
- [10] N. Medvedev et al., "Short-Time Electron Dynamics in Aluminum Excited by Femtosecond Extreme Ultraviolet Radiation," Phys. Rev. Lett. 107, 165003 (2011).
- [11] Y. Inubushi et al., "Measurement of saturable absorption by intense vacuum ultraviolet free electron laser using fluorescent material," Rev. Sci. Inst. 81, 036101 (2010).

- [12] L. Young et al., "Femtosecond electronic response of atoms to ultra-intense X-rays," Nature 466, 56–61 (2010).
- [13] M. Hoener et al., "Ultraintense X-ray induced ionization, dissociation, and frustrated absorption in molecular nitrogen," Phys. Rev. Lett. 104, 253002 (2010).
- [14] D.S. Rackstraw et al., "Saturable absorption of a hard X-ray free-electron-laser heated solid-density aluminium plasma," Phys. Rev. Lett., in press (2014).
- [15] H. Yoneda et al., "Saturable absorption of intense hard X-rays in iron," Nat Commun 5, 5080 (2014).
- [16] A. Levy et al., Submitted (2014)
- B.I. Cho et al., "Electronic structure of warm dense copper studied by ultrafast X-ray absorption spectroscopy," Phys. Rev. Lett. 106, 167601 (2011).
- [18] T.G. White et al., "Electron-phonon equilibration in laserheated gold films," Phys. Rev. B 90, 014305 (2014).
- [19] S.M. Vinko et al., "Creation and diagnosis of a solid-density plasma with an X-ray free-electron laser." Nature 482, 59– 62 (2012).
- [20] B.I. Cho et al., "Resonant Kα Spectroscopy of Solid-Density Aluminum Plasmas," Phys. Rev. Lett. 109, 245003 (2012).
- [21] W. Bambynek et al., "X-Ray Fluorescence Yields, Auger, and Coster-Kronig Tran- sition Probabilities," Rev. Mod. Phys. 44, 716–813 (1972).
- [22] L.B. Fletcher et al., "X-ray Thomson scattering measurements of temperature and density from multishocked CH capsules," Physics of Plasmas 20, 056316 (2013).
- [23] L.B. Fletcher et al., "Observations of continuum depression in warm dense matter with X-ray thomson scattering," Phys. Rev. Lett. 112, 145004 (2014).
- [24] O. Ciricosta et al., "Direct Measurements of the Ionization Potential Depression in a Dense Plasma," Physical Review Letters 109, 065002 (2012).
- [25] G. B. Zimmerman and R. M. More, "Pressure ionization in laser-fusion target simulation," J. Quant. Spectrosc. Radiat. Transfer 23, 517–522 (1980).
- [26] J. C. Stewart and K.D. Jr. Pyatt, "Lowering of ionization potentials in plasmas," The Astro- physical Journal 144, 1203–1211 (1966).
- [27] W. Ecker, G.Kröll, "Lowering of the Ionization Energy for a Plasma in Thermodynamic Equilibrium," The Physics of Fluids 6, 62–69 (1963).
- [28] D.J. Hoarty et al., "Observations of the Effect of Ionization-Potential Depression in Hot Dense Plasma," Physical Review Letters 110, 265003 (2013).
- [29] D.J. Hoarty et al., "The first data from the Orion laser; measurements of the spectrum of hot, dense aluminium," High Energy Density Physics 9, 661–671 (2013).
- [30] B.J.B. Crowley, "Continuum lowering a new perspective," High Energy Density Physics 13, 84–102 (2014).

- [31] S.-K. Son et al., "Quantum- mechanical calculation of ionization-potential lowering in dense plasmas," Phys. Rev. X 4, 031004 (2014).
- [32] S.M. Vinko, O. Ciricosta, and J. S. Wark, "Density functional theory calculations of contin- uum lowering in strongly coupled plasmas," Nature Communications 5 (2014).
- [33] M.W.C. Dharma-wardana and F. Perrot, Level shifts, continuum lowering, and the mobility edge in dense plasmas, Phys. Rev. A 45, 5883–5896 (1992).
- [34] M.S. Murillo et al., Partial ionization in dense plasmas: Comparisons among average-atom density functional models, Phys. Rev. E 87, 063113 (2013).
- [35] O. Ciricosta, private communication
- [36] Carlos A. Iglesias, "A plea for a reexamination of ionization potential depression measure- ments," High Energy Density Physics 12, 5 – 11 (2014).
- [37] Carlos A. Iglesias and Philip A. Sterne, "Fluctuations and the ionization potential in dense plasmas," High Energy Density Physics 9, 103 – 107 (2013).
- [38] H. Mimura et al., "Generation of 10<sup>20</sup> W cm<sup>-2</sup> hard X-ray laser pulses with two-stage reflective focusing system", Nat Commun. 5, 3539 (2014).

# XV. Non-linear X-ray optics in solids

Martin Beye, Helmholtz-Zentrum Berlin Filippo Bencivenga, Elettra – Sincrotrone Trieste

The invention of the visible laser in 1960 was the dawn of the vast field of non-linear optics – it is reasonable to expect, with the advent of the XFEL, that we are now at the threshold of non-linear X-ray optics.

- Introduction
- Light-matter interactions
- FEL-based non-linear experiments
- Amplified spontaneous emission
- Transient-grating spectroscopy
- Outlook

The high brightness and coherence of optical lasers have allowed the development of non-linear optics. Presently non-linear optics is exploited in all fields of physics, chemistry and biology to study a multitude of dynamics and fundamental processes and is the basis of a large number of cutting-edge applications. The availability of XFELs, with brigthness and coherence comparable to those of optical lasers, has stimulated the evaluation of non-linear optics in the X-ray range. The extension of such an approach at sub-optical wavelengths will enable elemental selectivity as well as the capability to study high-energy excitations, such as valence band excitons. This may allow the detection of electronic correlations and charge flows among different atoms in a sample, the probing of structural fluctuations, nuclear motions and relaxation processes, and study of the dynamics of elementary excitations, such as phonons, polaritons and polarons - all of this in real time, with sub-fs and sub-nm resolution and with no limitations due to dipole selection rules. Such promises are bold enough to be considered as the dawn of a new era for X-ray science. In this chapter we briefly outline the basics of X-ray non-linear optics, we review the steps made to date, and we discuss possible future directions.

#### Introduction

The field of non-linear optics dates back to 1961 [1], when P. A. Frenken and co-workers used the unprecedented brightness and coherence of optical lasers (discovered just the previous year [2]) to observe a basic non-linear optical phenomenon, second harmonic generation. From this first step until the present day, the applications of coherent non-linear optics have been widespread across almost all fields of science. These experiments allow one to combine time resolution with energy and wavevector selectivity, and to explore dynamics inaccessible by linear methods [3]. Such features have brought important advances in fundamental science and have been exploited in cutting-edge technologies, ranging from quantum communications and subwavelength microscopy to ultrafast silicon photonics and wavefunction tomography in chemical reactions. Additionally, the coherent nature of non-linear interactions often results in a large signal increase and/or in a "background free" measurement, compared to linear spectroscopic or pump-probe methods. Such a signal-to-noise was exploited, *e.g.*, to study subtle phenomena such as second sound [4] in liquids and dynamics of rarefied vapours [5] or flames. It has even been suggested that the vacuum may produce an appreciable non-linear signal [6] that could provide relevant information on fundamental processes.

An interesting point to mention is that the foundations of non-linear optics (outlined in the following Section) could have been developed by JC Maxwell in 1861, if he had included the power series in Eq. 1 in his celebrated equations, and HA Lorentz in 1878, if he had allowed for anharmonic terms in his oscillator model of the atom. However, neither Maxwell nor Lorentz had the experimental tools that stimulated their fundamental research in this direction. Similarly, excluding some pioneering works on parametric conversion [7-9] and frequency up-conversion [10], until a few years ago non-linear interactions have been essentially ignored in extreme ultraviolet (EUV) and X-ray applications. We now have the right tools to exploit them. FEL sources, in particular those stabilized by seeding processes, are indeed able to provide the key requirements for bringing concepts and methods basic to the most advanced coherent optical methods into the realm of EUV and X-ray radiation.

A few, yet relevant, steps towards this direction have been already made. The theoretical grounds for non-linear X-ray applications, among them Four-Wave-Mixing (FWM) were discussed by, e.q, the group of Shaul Mukamel in several papers (see e.g., Ref. [11]). Practical issues in the experimental design were discussed as well [12]. These works outline some non-trivial desiderata concerning the FEL source, namely: high temporal-spatial coherence and pointing stability, few to sub-fs pulses, multi-color FEL emission with independent wavelength tunability and timing/frequency jitter substantially lower than the pulse duration/ bandwidth. The recent demonstration of multi-color FEL emission at X-ray [13-15] and EUV wavelengths [16-17], the latter with the relevant advantage of laser-seeding, was also motivated by these experimental wishes; ad hoc developments of FEL sources for FWM applications have been proposed as well [12,18].

On the experimental side, a few FEL-based non-linear experiments, discussed later in this Chapter, have already been performed. Substantial additional efforts are required to fully exploit non-linear methods, in particular those based on third-order FWM effects [11], at sub-optical wavelengths. However, the potential is so great that such efforts are definitely warrented. EUV/X-ray non-linear approaches would permit one to probe, in real time, electron dynamics and correlations, structural fluctuations, nuclear motions and relaxation processes with elemental selectivity and (time, space) resolution from the few to the sub-(nm, fs) scale. This enables one to detect, e.q., charge flows among different atoms in a sample and their relationships with molecular vibrations, heat diffusion and other dynamical variables. The long wavelength of optical photons limits the study of dynamics of elementary excitations (phonons, excitons, polarons, etc.) to excitation energies ( $\Omega$ ) and wavevectors (Q) below the eV and 10 µm<sup>-1</sup> range, respectively. The use of EUV and X-ray photons would allow the extension of the  $(\Omega, Q)$ -range up to the 100's of eV and Å<sup>-1</sup> ranges, basically including the entire excitation spectrum, unconstrained by dipole selection rules and with the important advantage of atomic selectivity. Such features are further discussed later in this Chapter, where we describe the X-ray analogue of coherent Raman scattering [11].

## Light-matter interactions

Before the advent of non-linear optics, the interactions of light with matter were accounted for by a linear relation between the applied field (E) and the induced sample polarization (P), i.e.:  $P = \epsilon_0 \chi E$ , where  $\epsilon_0$  and  $\chi$  are the vacuum permittivity and the susceptibility, respectively. Such linear interactions turn into a variety of phenomena, such as absorption, diffraction or inelastic scattering. The first conceptual step towards non-linear light-matter interactions is to generalize the linear relation between P and E, i.e. [3,19]:

$$P = \varepsilon_0[\Sigma_i \chi E_i + \Sigma_{i,j} \chi^{(2)} E_i E_j + \Sigma_{i,j,k} \chi^{(3)} E_i E_j E_k + ...] =$$

$$P^{L} + P^{(2)} + P^{(3)} + ... = P^{L} + P^{NL},$$
(1)

where  $E_i$  and  $P^{(n)}$  (n>2) are the input fields and the n<sup>th</sup>-order non-linear polarizations, respectively, while  $\chi^{(n)}$  (n>2) are tensors of rank n+1 called n<sup>th</sup>-order non-linear susceptibilities. The intensity of the non-linear response (~P<sup>NL</sup>) over the linear one (~P<sup>L</sup>) grows up with the input field strength (|E<sub>i</sub>|), up to become comparable when  $|E_i| ~ E_a = e/(4\pi\epsilon_0 a_0^2) \approx 0.5^{*10^{12}}$ V/m (where  $E_a$ , e and  $a_0$  are the the atomic field strength, the elementary charge and the Bohr radius, respectively), meaning that  $\chi^{(n)} \approx E_a^{1-n}$ . Such a simple order of magnitude estimate is quite correct for most processes and implies that when  $|E_i|$  are comparable or larger than  $E_a$  the power series in Eq.1 does not converge. In this case the non-linear response can be very different from that discussed here. The range of coherent non-linear optics is thus a "not-too-high" field regime  $(|E_i| \ll E_a)$ .

When Eq. 1 is inserted into the Maxwell relations it results into a set of inhomogeneous wave equations:

$$\nabla^2 \mathbf{E}_i \cdot (\mathbf{n}/\mathbf{c})^2 (\partial^2 \mathbf{E}_i/\partial^2 \mathbf{t}) = (1/\varepsilon_0 \mathbf{c}^2) (\partial^2 \mathbf{P}^{\mathsf{NL}}/\partial^2 \mathbf{t}), \tag{2}$$

where n and c are the refraction index and the speed of light in vacuum, respectively. The right hand side of Eq. 2 is a source term, that couples the input fields and leads to the generation of a new (output) field, coupled to the input ones. The output frequency ( $\omega_{out}$ ) is not necessarily equal to any  $\omega_i$ , since  $P_{NL}$  oscillates at sum/difference combinations of the various  $\omega_i$ 's. For instance, when two fields (frequency  $\omega_1$  and  $\omega_2$ ) are coupled into the sample by  $\chi^{(2)}$ , then P<sup>(2)</sup> has oscillatory terms at  $\omega_{\text{out}}{}^{\text{SHG}}{=}2\omega_{1,2}\text{, }\omega_{\text{out}}{}^{\text{SFG}}{=}\omega_{1}{+}\omega_{2}$  and  $\omega_{out}^{DFG} = |\omega_1 - \omega_2|$ , that are related to second-harmonic (SHG), sum (SFG) and difference frequency generation (DFG), respectively. "Footnote1: for sake of completeness we mention that second order processes also include an induced nonoscillatory response ( $\omega$ =0), related to the phenomenon of optical rectification [3]." Such a "mixing" between coupled fields is the reason as n<sup>th</sup>-order processes are also referred to as (n+1)-wave-mixing. In non-linear interactions a key role is played by coherence, as already evident from the first experiment of Frenken. To understand this point, one shall consider an isolate emitter. In this case the non-linear signal (say the SHG one; see Fig. XV.1a) can be radiated in all direc-



Fig. XV.1: (a) SHG field radiated by an isolated emitter:  $\omega$  and k are the frequency and wavevector of the input field, respectively, while  $2\omega$  is the SHG frequency. (b) SHG field radiated by an extended set of emitters:  $L_{coh}$  is the coherence length of the input radiation and  $k_{SHG}$ ~2k is the SHG wavevector. (c) Intensity distribution as a function of  $k_{SHG}$ -2k, here N is the number of emitters within  $L_{coh}$ . Figure adapted from Ref. [19]

tion. On the other hand, if the coherence length of the radiation (L<sub>coh</sub>) extends over N emitters of an extended sample, then the induced polarizations oscillate in phase. The fields radiated by all members a such a phased array of oscillators are hence coherently rebuild along the direction of the input beams (k<sub>i</sub>; see Figs. XV.1b-1c). Along such a "phase matched" direction the intensity (I<sub>out</sub>) increases as ~N<sup>2</sup> and the the non-linear signal may turn into a well defined coherent beam with intensity comparable to that of the input radiation.

In a finite non-linear medium of length L, the total intensity of an n<sup>th</sup> order non-linear process is thus:

$$I_{out} \sim |\chi^{(n)}|^2 \prod_{i=1,n} I_i L^2 sinc^2 (\Delta k L/2),$$
(3)

where  $I_i$  are the intensity of the input fields and  $\Delta k$ =k-( $k_1 \pm k_2$  ...  $\pm k_n$ ) is the wavevector mismatch; here  $k_{out}$ = $k_1 \pm k_2$  ...  $\pm k_n$  is the combination of the wavevectors corresponding to the process of interest, e.g.:  $2k_i$ ,  $k_1$ + $k_2$  and  $|k_1$ - $k_2|$  for SHG (see Fig. XV.1c), SFG and DFG, respectively, or  $k_1$ - $k_2$ + $k_3$  for coherent Raman scattering (CRS) and impulsive stimulated scattering (ISS); see Figs. XV.2, 4 and 5. The latter are third order processes in which  $k_{out}$  is typically different from any  $k_i$  (see Figs. XV.2e and 4b), with a remarkable increase in the signal-to-noise ratio.

In X-ray spectroscopy, people are often more familiar with considering single photon excitations and decays. Crosssections for those transitions, lifetimes of core-excited states (the inverse of the core-decay rate) and the ratio between fluorescence decays and the total decay rate are well-known and tabulated. Those can be used to model non-linear processes as well, substituting the equations for the electric field and intensity coupled through the macroscopic polarization of the medium with rate equations for the involved photons, the ground and the (core-)excited states of the medium. In the medium fluence regime (where non-linear processes are relevant but not dominating), those equations can model the processes equally well, but some care has to be taken: concepts in X-ray spectroscopy only treat the energy conservation but disregard the wavevector matching and coherence in the process. One can formulate rate equations which only consider the coherent, k-matched fraction of the involved photons and get correct results. It has to be

carefully analyzed which photons are considered and if they have the right direction, polarization and coherence. This can lead to several subsets of photons that have to be treated with different rate equations that are coupled. Often, this yields a large set of coupled differential equations that cannot only be solved analytically.

The rate equation approach will break down for example, when the fields get so strong that Rabi oscillations are observed. Here, the population of the ground and excited state of the medium oscillates between both with a frequency depending of the light field intensity. With rate equations, the relevant processes can be included but will only lead to an equal population of ground and excited states without any oscillation. This is a result of considering photons, which inherently neglects the phase of the electric field, i.e. the coherence.

The possibility to use non-linear light matter interactions to establish a controlled coherent population of excited states have allowed the developments of stimulated scattering methods. In order to illustrate how non-linear processes can be used to selectively study excitations, in Fig. XV.2 we compare "spontaneous" Raman scattering (SRS) with its "stimulated" counterpart, i.e. CRS. SRS is a well known photon-in/photon-out method (see Fig. XV.2a). Energy and momentum conservation laws set the energy ( $\Omega = \omega_{out} - \omega_{in}$ ) and momentum ( $Q=k_{out}-k_{in}$ ; see Fig. XV.2b) transfer to the sample excitations (here the subfix in/out refers to the incoming/scattered photons). A SRS spectrum is sketched in Fig. XV.2c; it is typically featured by an elastic/quasi-elastic peak and by symmetric side peaks located at  $\omega = \omega_{out}$ - $\omega_{in} = \Omega_i(Q)$ , where  $\Omega_i(Q)$  are the Q-components of the excitation spectrum (e.g. the eigenfrequencies of ther vibrational field in the case of vibrations). Assuming just one possible excited state, the system can be regarded as the sum of two stationary distributions of ground and excited states, i.e.  $(1-\alpha)\Psi_{GS}+\alpha\Psi_{ES}(\Omega_i,Q)$ , where  $\Psi_{GS/ES}$  is the ground/excited state wavefunction and a<1 quantifies the number of occupied excited states among the available ones at a given temperature (for vibrations this is the Bose occupation factor). Each count in the side peaks of the SRS spectrum is associated to a single creation (Stokes:  $\Psi_{GS} \rightarrow \Psi_{ES}$  transition) or annihilation (anti-Stokes:  $\Psi_{ES} \rightarrow \Psi_{GS}$  transition) process for such excitation (see insets of Fig. XV.2c). "Footnote2: The Fig. XV.2 Sketches of: (a) a SRS (photon-in/photon-out) experiment, (b) the related momentum conservation and (c) a typical spectrum; the insets close to the peaks at  $\pm \Omega$  are levels schemes for the Stokes and anti-Stokes processes. Here GS, ES and VS are the ground, excited and virtual states, respectively, while  $I_{in/out}$  is the intensity of the outcoming/incoming radiation. Sketches of: (d) a CRS (FWM) experiment, (e) the related phase matching diagram and (e) time profile of the signal; the insets are level schemes for the excitation ( $\Delta t$ =0) and probing ( $\Delta t$ >0) processes. Here  $I_{out}$  is the FWM signal intensity while  $I_i$  (i=1-3) is that of the input beams, respectively. The ISS process corresponds to the case in which  $\omega_1=\omega_2$  (and then  $|k_1|=|k_2|$ ), in this situation  $\Omega$  is within the bandwidth of the excitation pulses and, therefore, slower modulation of the FWM are in general observed. Figure adapted from Ref. [19]



intensity asymmetry in the CRS spectrum is hence due to the relative probability, i.e. a/(a-1), for the Stokes and anti-Stokes processes to happen."

These creation and annihilation events randomly occurs while the sample is illuminated by the probing radiation, so that they are uncorrelated among each other and the experimental signal is then simply the sum of such "spontaneous" scattering events. In CRS the input fields (see Fig. XV.2d) are tuned in a way such  $\Omega_i(Q) = \omega_1 - \omega_2$  and  $Q = k_1 - k_2$ [3,5]. The forcing non-linear term resulting from the interference between such coherent fields is modulated in both time and space (as  $\Omega$  and Q) and hence allows to drive the selected mode. Differently from SRS, all such driven modes are in phase and the further interaction between a third coherent beam ( $\omega_3$ ,  $k_3$ ) allows the radiation of a fourth beam at  $\omega_{out}=\omega_3+\Omega$  and  $k_{out}=k_3+Q$  (see Figs. XV.2d-2e) via FWM. Pulsed beams allow to define the time at which the in-phase (i.e. coherent) population of the selected excited states is created and when it is eventually probed. In other words CRS allows to "interrogate" the sample if such a selected excitation is permitted and, eventually, to follow its time evolution in real time by applying a time delay ( $\Delta t$ ) between the excitation and probing pulses. The case in which  $\omega_1 = \omega_2$ (and therefore  $|k_1| = |k_2|$ ) essentially corresponds to ISS processes [20], in this case only modes with energy lower than the bandwidth of the excitation pulses ( $\delta\omega$ ) can be probed and the phase matching condition reduces to Bragg scattering. ISS is thus suited to detect relatively slow dynamics, such as thermal excitations (i.e. low energy Raman modes, acoustic phonons, structural and thermal relaxations, etc.). In the case of vibrations we would then observe oscillations in the CRS and ISS signals as a function of  $\Delta t$  (see Fig. XV.2e), which are related to the back-Fourier transform of the SRS lineshape in Fig. XV.2c (in the case of ISS from low frequency
excitations the time dependent FWM signal may be be also related to the back-Fourier transform of the Rayleigh-Brillouin lineshape [20]). In turns, such oscillations are a manifestation of the coherence of the process, i.e. the indistinguishableness of the driven excitations enables to determine the dynamics of the elementary excitation from the collective coherent response. Such a coherent addition of the sample response may also turn into an increase of the experimental signal with respect to linear methods, a feature routinely exploited in CRS and common to several other wave-mixing applications (for instance it was exploited in the stimulated Rayleigh scattering experiment on second sound quoted in the introduction [4]). Additionally, the possibility to vary the inter-beam angles at fixed  $\omega_{1,2,3}$  also permits to independently set  $\Omega$  and Q, thus allowing for determination of the full Q-dispersion relations, while since  $\omega_{out} \neq \omega_{1,2,3}$  and  $k_{out} \neq k_{1,2,3}$  both spectral and spatial discrimination of the signal is possible, with a large improve in the signal-to-noise. FWM-based methods, as CRS and ISS, are not limited to probe vibrations but can be applied to any kind of dynamical variable coupled to the electromagnetic field. "Footnote3: It is woth mentioning that non-linear methods can also probe dynamics that are uncoupled to the fields in the linear response, such as, e.g., silent Raman modes [21] or spin waves and spin relaxations [22]." FWM processes may also involve electronic transitions, provided that some of the involved frequencies are properly tuned, and provide information on the correlations between electronic and vibrational dynamics. Since the effects of light-matter interactions are not suddenly lost and information on coherent dephasing and rephasing dynamics can be gained by applying an additional time delay ( $\Delta t_{12}$ ) between the two "beating" pulses ( $\omega_1$  and  $\omega_2$ ), an approach also termed photon-echo that consents to determine the coherence properties of excited states [23]. The combined scan of multiple time-delays and/or frequencies (possible only in such kind of multi-wave processes) is at the base of the so-called multi-dimensional spectroscopy [24]. We finally stress that the basic prerequisite for these approaches is the possibility to assume that all photons in a given pulse are in a "single mode", since in this case the intrinsically low non-linear signal (see also Box-1 and Box-2) can be raised up by the coherent addition, up to become dominating in some cases. Therefore, non-linear coherent signals are likely to be more effectively generated at FEL sources based on seeding technologies, while the randomphase relation among the several longitudinal modes emitted by SASE devices could severely hamper the observability of such processes.

## FEL-based non-linear experiments

On the experimental side second-order spontaneous nonlinear X-ray processes were reported even before the advent of FELs. In 1971 Eisenberger and McCall used an X-ray tube to observe the conversion of an X-ray photon (at frequency  $\omega_{X-ray}$ ) into two time-coincident lower frequency photons ( $\omega_1$ and  $\omega_2$ , with  $\omega_1 + \omega_2 = \omega_{X-ray}$ , a process also known as parametric down conversion (PDC) [8]. This is essentially the inverse process of "stimulated" SFG (or SHG if  $\omega_1 = \omega_2$ ), in which the phase matching conditions  $(k_1+k_2=k_{X-ray}+G; where$ G is a reciprocal space vector) allow to determine a discrete Fourier component of the charge density. More recently Xray/EUV PDC has been used to demonstrate Å-scale spatial resolution (typical of X-rays) keeping the probe in the EUV, in order to visualize the optical response of a diamond crystal with sub-wavelength resolution (up to  $\lambda/380$ ) [9]. The extension towards X-ray/visible PDC may allow a new class of spectroscopy able to probe the optical response of chemical bonds and valence electrons at their natural energy-length scales (i.e. eV's and Å's). Spontaneous processes can be considered as stimulated processes driven by the zero-point field (see Box-2). The power density of the latter rapidly increases on decreasing wavelength, so that the power density required for stimulated processes involving X-ray photons is so large to be unforeseeable in the 70's ("Direct observation of sum-frequency mixing of a laser and a source of X-rays is unattractive because of the low spectral brightness of available spontaneous-emission X-ray devices" from Ref. [25]). X-ray FELs have changed this situation, as demonstrated by the fact that sum-frequency mixing of optical and X-ray photons was reported in 2013 by Glover and co-workers [26].

FEL-based non-linear experiments appeared in the litterature in the last few years. A prominent example is the "FELpumped X-ray laser" [27]. In this experiment a population

#### Box 1: Non-linear signals: from the discovery to X-rays

SHG was the first discovered non-linear optical phenomena and contains all the main elements of non linear optics (see Fig. XV.1). In SHG two photons "work together" to drive the polarization of an elementary emitter at twice the photon frequency, thus resulting in the emission of a second harmonic photon. Furthermore, the coherent nature of laser radiation allows for the coherent addition of the SHG signal radiated by the elementary emitters throughout the sample, which may turn into a well defined (macroscopic) coherent beam that propagates downstream the sample, as observed by Frenken (Fig. XV.1a).

After this pioneering experiment, optical SHG has been quickly developed. Today the optimization of the phase matching for many materials and laser wavelengths have allowed for the generation of second harmonic beams with intensity comparable with the incoming one (see Fig. XV.i1d) and routinely used in many optical appplications. SHG at X-ray wavelengths has been recently observed in an experiment carried out at the SACLA XFEL facility [30]. The extremely low count rate of a few X-ray SHG photons per 100 FEL shots (each one with flux >  $10^{16}$  W/cm<sup>2</sup>; see Fig. XV.i1c) is mainly due to the intrinsic decrease of the nonlinear susceptibilities on increasing the photon frequency and to the much lower degree of coherence of the XFEL source, as compared to optical lasers. The former issue belongs to nature while the latter can be tackled by the FEL technology through the implementation of seeding schemes to largely improve the coherence. Furthermore, it is worth noticing that the values of the non-linear susceptibilities are expected to largely increase in correspondence of core resonances, which fall within the EUV/X-ray spectral range. On rough orders of magnitude grounds, in correspondence of an EUV or soft X-ray resonance the nonlinear susceptibilities may compare or be just some orders of magnitude lower than the non-resonant non-linear susceptibilities in the optical spectral range [12,41]. These gross estimates were done using expressions derived from classical non-linear optics, which are not appropriate for X-rays (a more rigorous treatment of second-order X-ray non-linearity can be found in Refs. [7,8,25]), but somehow agrees with results obtained by more solid formalisms [11] and tells us the directions that can be followed to develop the new-born field of non-linear X-ray optics.



Fig. XV.i1: (a) picture of the first laser developed by Maiman in 1960 [2] and the first non-linear signal observed by Frenken in 1961 and due to a SHG process (highlighted by the red circle; the black dot on the right is the direct beam) [1]. (b) SACLA XFEL facility where it has been observed the first X-ray SHG signal (c) [30]. (d) Picture of a common laboratory experiment where an intense SHG beam (blue beam) is generated by two IR pulses (red beams) delivered by a modern ultrafast table-top laser system. The large drop of the SHG conversion efficiency on going from the optical to the X-ray range is mainly due to the intrinsic decrease of the non-linear susceptibilities on increasing the photon frequency. This issue can be mitigated by exploiting the resonant increase of the non-linear susceptibilities close to core-resonances [11,12,41] and by implementing seeding schemes to improve the degree of coherence of XFEL sources, which is presently much lower than that of optical lasers.

inversion of the k<sub>a</sub> transition (849 eV) in gaseous Ne was established by FEL pulses at higher photon energy. This allows for the exponential amplification (through stimulated emission) of X-ray photons resulting from the radiative k<sub>a</sub> decay of core-excited atoms, pretty much the same as in a conventional laser tube. Indeed, in spite of the large photon energy jitter of the pumping FEL source, the X-ray output at 849 eV shows a sharp "laser-like" line, confirming the coherent (i.e. in phase) nature of such an emission. Further investigations provided evidences for stimulated electronic inelastic X-ray scattering [28]. Amplified stimulated emission (ASE) was also observed in solid samples at EUV wavelengths [29] where additional consideration about the geometry become very important due to largely different cross-sections.

These investigations are examples of stimulated non-linear processes, closely related to the first step of the X-ray CRS process shown in Fig. XV.5. The stimulated processes start from spontaneous emission and the coherence builds up in the process itself. Thus, the coherence of the FEL radiation plays a marginal role, the non-linear process is not driven by the combined action of two or more photons, and wavemixing and phase matching arguments do not apply.

FEL-stimulated non-linear wave-mixing processes (i.e.: IR/Xray SFG [26] and X-ray SHG [30]) have been reported. In both these experiments the phase matching involved the exploitation of a reciprocal space vector (G). This had permitted to set the direction of the signal beam different from the one on the input beams, hence increasing the signal-to-noise (this was very relevant in light of the small amount of signal; see Box 1). One may view the optical X-ray SFG carried out by Glover and co-workers as the result of the X-ray scattering from optically induced charge oscillations. X-rays hence probe the optically polarized charge density, in the same way as X-ray diffraction probes the ground-state charge density. In such a picture of optically modulated X-ray diffraction, it is quite evident how optical X-ray SFG would allow to probe the optically induced fields on atomic scales, a quantity not directly accessible by optical methods (here the information are averaged out over the lengthscales of the probing optical fields). Measurements carried out as a function of the time delay between the optical and X-ray pulses would in principle allow to determine the time evolution of the optical-induced microscopic polarization. However, no attemps to do that was done in the discussed experiments.

The first third-order process observed at X-ray wavelength is two-photon absorption in gaseous Ne, which was revealed by a quadratic dependence of the Ne<sup>9+</sup> yield on the FEL fluence below the Ne<sup>8+,152</sup> edge (1196 eV); a nonlinear cross section orders of magnitude higher than the expectations was also reported [31]. Later on, two-photon absorption was observed in solid Ge by measuring the X-ray fluorescence spectrum (K-edge; 11.2 keV) from a sample illuminated by photons at half of such energy (i.e. 5.6 keV) [32]. Similarly to stimulated emission and ASE, such process does not provide evidences for coherent ("phase-matched") signals but indicate that third-order nonlinearities might be appreciated at X-ray wavelengths. More recently, a third-order

## Box 2: Stimulated vs sposntaneous non-linear processes

Spontaneous emission can actually be considered as stimulated emission, where the stimulating photons come from vacuum fluctuations. In second quantization, the electromagnetic field is treated like a set of harmonic oscillators. Each mode of the field (defined through a frequency, wavevector and polarization) forms a separate oscillator and the number of photons in a mode (the field strength) reflects the occupation number of the oscillator. As known from quantum physics, the ground state of a harmonic oscillator contains already a well-defined amount of energy. This is the vacuum energy or, if identified with the electromagnetic field, the so-called zero point field. The energy density of this field can be given and it is the coupling to this field which drives spontaneous decays. In order to observe non-linear processes over the spontaneous linear processes, one has to provide fields that are stronger than the zero point field. Since the zero point field gets larger with the square of the field frequency, the needed field strengths to observe "truly" stimulated non-linear processes strongly increases when going from the optical to the UV, EUV, soft and hard X-ray ranges.

FWM process (i.e. ISS) stimulated by transient EUV gratings and detected by a phase-matched optical pulse has been reported [33]. The observed conversion efficiency of the probe photons into signal ones is as large as that reported for IR/X-ray SFG and several orders of magnitude larger than in X-ray SHG, despite these are lower order processes. This can be partially ascribed to the large drop in the magnitude of the non-linear response at short wavelengths (see Box 1), but also highlights the benefits of the high coherence of seeded FEL source.

## Amplified spontaneous emission

In amplified spontaneous emission (ASE) from core excitations, a high density of core holes needs to be created (not necessarily coherent). If the density is high enough during the lifetime of the core excitations (typically in the femtosecond regime), a spontaneously emitted photon can interact with a core excitation through stimulated emission. In this process, a second photon, identical in energy, polarization and direction is emitted. Those two photons can then further interact with core excitations creating an exponential amplification of the first spontaneously emitted photon. Typically, the cross-section for stimulated emission for an excited atom is similar to the absorption cross-section of an unexcited atom (both describe dipole transitions between a core level and valence states). The inverse absorption (respectively gain) length is then given by the product of the

cross-sections with the number density of the respective

In a gas phase target, where this process has been demonstrated [27], the sample is dilute and the absorption length is much longer than typical focal dimensions (on the order of several µm). Signal gain is only created, where core excitations are present. Here, this is the case in the excited column along the X-ray beam with a length on the order of the absorption length. In order to produce observable gain, the spontaneously emitted photons should interact with the excited medium over about one gain length. Since the length of the excited column is about one absorption length, this yields the condition that the absorption and gain lengths should be of similar size. With similar cross-sections, this means that the ground state density and the excited state density have to be similar. In a more quantitative analysis, this leads to the need of a population inversion in the medium in order to produce substantial gain.

On a dense, solid target, the situation is very different. Here, the absorption length is typically much shorter (tens of nanometers) than the dimensions of the X-ray spot, such that the shape of the excited medium is similar to a thin disk on the sample surface. Now, the spontaneously emitted photons can interact with the core excitations over lengths that are given by the focal size instead of the absorption length and can thus be a hundred times larger. To facilitate the interaction over one gain length, the latter can be hundred times longer than the absorption length. The population inversion is not needed anymore, but an excitation of about 1% of the atoms is sufficient in this simplified example. Nevertheless, all directions within the excited thin disk can now equally amplify spontaneously emitted photons and compete for the available core excitations since each stim-



Fig. XV.3: Left: A typical X-ray spot is round with dimensions much larger than the absorption length of a solid sample, such that a thin disk-shaped volume is excited. Right: Since every direction inside the disk surface is similar, ASE develops with similar amplitudes in all direction grazing to the surface, all directions competing for the available core excitations and limiting the gain in each direction.

atoms.

ulated photon is emitted by deexciting a core excitation. This leads to a substantial lowering of the possible gain although most of the core excitations decay via stimulated emision. It is thus advantageous to shape the excited volume by extending it in one direction. Gain will then preferentially develop in this direction and thus suppress unwanted ASE in other directions.

But it is not only the geometry of the experiment that is important for the observation of gain through ASE, it is also considerations of the temporal evolution. Especially in condensed matter, it has been demonstrated that short pulses are crucial [34]. The core excitations (in the soft X-ray region) mainly decay via the emission of an energetic electron, that in turn scatters multiple times on the sub-femtosecond time scale with other atoms and creates a multitude of valence excitations that change the electronic distribution and structure and can lead to many unwanted effects. It is thus crucial to use ultrashort pulses to create the core excitations, not only to have a high density of core-excited atoms available during the core-hole lifetime, but also to be able to generate ASE before the electronic structure is destroyed through the Auger cascade.

For a full understanding of ASE from dense targets, it is also necessary to explicitly consider the travelling times of the connected photons, since the micrometer dimensions of the focal spot are traversed by ASE photons during a time that is typically longer than the core hole lifetime. Care has to be taken that ASE can develop over a long interaction length with core excitations. This can be achieved by the so-called "travelling wave excitation" where the exciting field travels nearly parallel to the ASE field, when the sample is placed at grazing incidence to the exciting X-ray beam. A last consideration concerns the spectrum of the ASE photons. Since they are generated by spontaneous emission, they will mimick the spontaneous emission spectrum, although it is expected that the gain in strong emission features is larger than in weak ones, since they will preferentially win the competition for available core excitations. However, it remains unclear how much of the spectrum can be restored, when the process os driven into saturation.

A complete modelling of the full process of ASE from a solid target including all these subtleties has not been achieved yet, since it requires a four dimensional tracking of the position and direction of all the around 10<sup>12</sup> photons travelling through the sample. Systematic experimental studies are thus crucial to further our understanding and to get into a situation where simplified models can be developed to make full use of this technique that can amplify signals in emission spectroscopy by orders of magnitude.

## Transient-grating spectroscopy

In the last three years FEL-based experiments have addressed several fundamental properties of non-linear lightmatter interactions at sub-optical wavelengths, ranging from stimulated emission to FWM. The latter are the mostly used processes in the optical domain, since they are not vanishing for any sample simmetry and are able to provide a large amount of information on different kind of dynamics (not necessarily coupled to the field in the linear approximation), occurring at different timescales and with high selectivity in both energy and momentum. FWM in the EUV range was demonstrated at FERMI in an experiment in which two coherent FEL pulses (time duration ~70 fs, photon energy 45 eV) were crossed on a vitreous SiO<sub>2</sub> sample to generate a EUV transient grating (TG) [33]. The time evolution of the sample response driven by such grating was then probed by a phase matched optical pulse (time duration ~100 fs, photon energy 3.1 eV), which originated a clearly observable FWM signal propagating along the phase matching direction (kout=kEUV1k<sub>EUV2</sub>+k<sub>opt</sub>; see Figs. XV.4a-4b), similarly to what usually observed in the optical regime. Such a FWM signal had the form of a well-defined beam (see Fig. XV.4c) that is made out of some 10<sup>5</sup> photons/shot. This is a huge number of photons, as compared to other FEL-based wave-mixing experiments, and permitted to determine the FWM response over a wide time-delay range (0-100 ps), which shows signal modulations compatible with impulsively stimulated modes (i.e. longitudinal acoustic phonons and Raman modes).

This result demonstrates that coherent FEL pulses, similarly to optical lasers, can generate dynamic EUV gratings able to drive coherent excitations, such as molecular vibrations, into the sample via ISS and how the time dependence of the FWM response can be effectively read. The natural development of such EUV/soft X-ray FWM approach is to replace the optical pulse with an EUV/soft X-ray probe (EUV probing of optically stimulated transient gratings has been already reported [35-36]). This will allow to use ISS to detect low energy modes in a Q-range inaccessible by optical TG and matching the characteristic length-scales of heterogeneities in the local structures of many materials (such as block copolymer, relaxor ferroelectrics, glasses, etc.), the characteristic sizes and periodicities of many nanostructures or the incommensurate dimensions of many crystalline phases showing super-lattices of structural, charge or spin density nature. Among these possible applications of EUV/ soft X-ray ISS we may mention the study of phonon-like dynamics in glasses at "mesoscopic" (~10 nm) lengthscales, corresponding to Q~0.1-1 nm<sup>-1</sup> and to acoustic frequencies ( $\Omega_{ac}$ ) in the THz range [37]. The latter corresponds to the temperature (T= $\hbar\Omega_{ac/}/k_B \sim 10$ 's K) where general and debated anomalies in the thermal properties of glasses are observed [38]; such anomalies are expected to be determined by the baheviour of phonon-like modes at THz frequencies, which are the dominant heat carriers in this temperature range. However, the lack of data in such a "mesoscopic" range does not allow to discern among the proposed (often discording) theories able to explain the thermal behaviour of glasses equally well. Additionally, a key role could be played by nm-sized heterogeneities of the

elastic medium, whose effects are average out on macroscopic scales but can drastically perturb the THz acoustic phonons [39].

#### Outlook

Such a rapid development of the FEL-based non-linear approach calls for the development of more sophisticated and comprehensive methods. A possibility offered by the FEL technology is the use of two-color FEL pulses [13-17], with the concrete outlook to move from the two-color to the multicolor option.

The implementation of a two-color FEL excitation pulses into a TG scheme is hence at reach and would be the major step towards the implementation of the soft X-ray CRS (XCRS) approach, proposed by Tanaka and Mukamel [11] and schetched in Figs. 5a-5b. The much larger energy of soft X-ray photons (100's eV) as compared to optical ones (~eV's) would permit to coherently populate excited states with energy largely exceeding that achievale by optical methods. XCRS can be hence used to study the dynamics of valence band excitons ( $\Omega$ ~1-10 eV), out of the range of optical methods, with the unique option to achieve atomic-scale localization of the site at which the selected excitation is created



Fig. XV.4: (a) sketch of a FEL-based FWM experiment and (b) phase matching diagram. (c) FWM signal observed at  $\Delta t=0$  along the phase matched direction ( $k_{out}=k_{FEL1}-k_{FEL2}+k_{opt}$ ). (d)  $\Delta t$ -dependence of the FWM signal (reported in a logarithmic vertical scale), blue and red curves are a Gaussian function, accounting for the peak at  $\Delta t=0$ , and the modulations expectedly due to impulsively stimulated vibrational modes, respectively. Figure adapted from Ref. [33].



Fig. XV.5: sketch (a) and level schemes (b) for a XCRS experiment involving core resonances; VB and CB are the valence and conduction bands, respectively.

and/or probed. This feature is expected to have relevant applications, for instance in the study of charge transfer processes or intramolecular relaxation dynamics [12], and arose from the fact that in XCRS one may tune some of the input field frequencies in correspondence of core resonances of selected atoms of the sample (independently from the values of  $\Omega = \omega_1 - \omega_2$  and  $Q = k_1 - k_2$ ). For instance, if  $\omega_1$  stimulates a core-hole transition at the atomic site A, then the localization of core shells turns into an atomic-scale localization of the induced excitation (e.g. a valence band exciton) with energy  $\Omega = \omega_1 - \omega_2$  and momentum  $Q = k_1 - k_2$ . The excited electronic wave packet can be then detected after a given timedelay ( $\Delta t$ ) by a third pulse (frequency  $\omega_3$ ) tuned at a core resonance of the atomic site B. The FWM signal at frequency  $\omega_{out} = \omega_3 + \Omega$ , propagating along  $k_{out} = k_3 + Q$  hence contains real-time information on the propagation of the selected excitation from atom-A to atom-B, as well as on the possible coherences between the two atomic sites. Such kind of information are intriniscally related to the multi-wave nature of the FWM process and are missing in linear experiments, since in this case the experimental signal arises from an interaction that forcely takes place in a single atomic site. Additionally, the possibility to determine Q-dependence of the XCRS independently on  $\Omega$  and  $\omega_{1,2,3}$  (by simply varying the interbeam angles) can provide information on the involved interatomic distances and symmetries. Moreover, optical CRS has to respect dipole selection rules, while these do not apply to X-rays (here the wavelength compares to the molecular size), thus allowing to probe the entire excitation spectrum. Finally, multi-pulse FEL sources would allow for the application of an additional time delay between  $\omega_1$  and  $\omega_2$ . This is a major step towards X-ray multi-dimensional

spectroscopy and might permit to discriminate between resonant and non-resonant contributions to the FWM signal, hence allowing to deterimine correlations between different quantum states of the system. Again, this is a direct consequence of the multi-wave nature of wave-mixing interactions. We finally stress, once again, the benefits of the "full coherence" (longitudinal and transverse) for this kind of applications. In the frame of FEL technology this "special feature" can be achieved by laser-seeding and self-seeding approaches, which, indeed, are being evaluated with special attention also in light of forthcoming wave-mixing applications [12,18].





## Summary

- The development of non-linear optics has represented a fundamental milestone for experimental science and resulted in relevant technological advances. The implementation of the non-linear approach at suboptical wavelengths might have an even more relevant impact since it would allow to extend the study of dynamical processes, occurring over the more disparate time scales, at molecular length and energy-scales (i.e. nanometers and electronvolts), a range that embodies the very essence of chemistry and material science.
- Non-linear optics was "hidden" in the classical electromagnetic theory and was discovered after the development of the "right tool", i.e. the optical laser. Since a few years ago non-linear light-matter interactions were essentially ignored by X-ray scientists. Nowadays, after the development of the "right tool" (i.e. XFELs), X-ray non-linear optics is starting up with encouraging proof-of-principle experiments.
- The full exploitation of this new-born field requires the sharing of concepts and methods (wave-mixing, coherence, phase-matching, etc.) from the communities working with optical-laser and the development of FEL technologies able to provide X-ray pulses as much similar as possible as that delivered by lasers. Seeding techniques, multi-color FEL emission and full tunability in both photon wavelength and polarization is a must.
- Coupled rate equations for photons and populations of states can mostly describe non-linear processes equally well as the field approach, but care has to be taken to consider the inherently neglected directionality (wavevector matching) and phase (coherence) of the photons.

- To observe non-linear processes on solids in the EUV to X-ray range, it is important to consider that most interaction cross-sections are very different from the optical regime and purely electronic Auger decays are a strong competing channel that annihilate excited states and create distortions in the electronic structure without adding to the photon fields.
- Stimulated wave-mixing processes at sub-optical wavelengths have been observed and, as in the optical regime, critically depend on phase matching conditions, which are inherently related to the coherence properties of the radiation. On the experimental side a coherent and stable source of radiation is required, while on the theoretical side an appropriate description of the process has to go beyond the concept of "one photon at a time", which is at the basis of the classical formalism of X-ray interactions with matter. To date these requirements are met, since seeding technologies can provide a suitable FEL source and the formalism of non-linear optics has already been extended into the EUV/soft X-ray range.
- The set of non-linear EUV/X-ray experiments carried out in the last few years can be considered as the first step towards advanced multi-wave methods, so far only considered on theoretical grounds. The demonstration of time-resolved four-wave-mixing stimulated by EUV transient gratings is a strong indication that the applications envisioned by theoreticians could be put on practice. The next steps in this direction are the combination of the four-wave-mixing approach with multi-color FEL pulses and its extension to soft X-rays.

#### References

- [1] P. A. Frenken *et al.*, Phys. Rev. Lett. 7, 118 (1961).
- [2] T. H. Maiman, Nature 187, 493 (1960).
- [3] R. Boyd, Nonlinear optics (Academic Press, 2008).
- [4] D. W. Pohl, S. E. Schwarz and V. Irniger, Phys. Rev. Lett. 31, 32 (1973).
- [5] M. Schmitt, G. Knopp, A. Materny and W. Kiefer, Chem. Phys. Lett. 270, 9-15(1997).
- [6] F. Moulin and D. Bernard, Opt. Commun. 164, 137-144 (1999).
- [7] I. Freund and B. F. Levine, Phys. Rev. Lett. 23, 854 (1969).
- [8] P. M. Eisenberger and S. L. McCall, Phys. Rev. Lett. 26, 684 (1971).
- [9] K. Tamasaku *et al.*, Nat. Phys. 7, 705 (2011).
- [10] L. Misoguti et al., Phys. Rev. A 72, 063803 (2005).
- [11] S. Tanaka and S. Mukamel Phys. Rev. Lett. 89, 043001 (2002).
- [12] F. Bencivenga et al., New J. Phys. 15, 123023 (2013).
- [13] A. A. Lutman et al., Phys. Rev. Lett. 110, 134801 (2013).
- [14] A. A. Lutman *et al.*, Phys. Rev. Lett. 113, 254801 (2014).
- [15] T. Hara *et al.*, Nat. Commun. 4, 2919 (2013).
- [16] G. De Ninno et al., Phys. Rev. Lett. 110, 064801 (2013).
- [17] E. Allaria et al., Nat. Commun. 4, 2476 (2013).
- [18] G. Marcus, G. Penn and A. A. Zholents, Phys. Rev. Lett. 113, 024801 (2014).
- [19] F. Bencivenga *et al.*, Adv. Phys. 63, 327 (2015)
   DOI: 10.1080/00018732.2014.1029302.
- [20] L. Dhar, J. A. Rogers and K. A. Nelson, Chem. Rev. 94, 157-193 (1994).
- [21] B. Hehlen et al., Phys. Rev. Lett. 84, 5355–5358 (2000).
- [22] C. P. Weber *et al.*, Nature 437, 1330-1333 (2005).
- [23] E. T. J. Nibbering, D. A. Wiersma and K. Duppen, Phys. Rev. Lett., 66 (1991).
- [24] S. T. Cundiff and S. Mukamel, Phys. Today 66, 44-49 (2013).
- [25] I. Freund and B. Levine, Phys. Rev. Lett. 25, 1241 (1970).
- [26] T. E. Glover *et al.*, Nature 488, 603 (2012).
- [27] N. Rohninger et al., Nature 481, 488 (2012).
- [28] C. Weninger et al., Phys. Rev. Lett. 111, 233902 (2013).
- [29] M. Beye et al., Nature 501, 191-194 (2013).
- [30] S. Shwartz et al., Phys. Rev. Lett. 112, 163901 (2014).
- [31] G. Doumy et al., Phys. Rev. Lett. 106, 083002 (2011).
- [32] K. Tamasaku *et al.*, Nat. Phys. 9, 313–316 (2014).
- [33] F. Bencivenga *et al.*, Nature 520, 205 (2015)DOI: 10.1038/nature14341.
- [34] S. Schreck et al., Phys. Rev. Lett. 113, 153002 (2014).
- [35] R. I. Tobey et al., Appl. Phys. Lett. 89, 091108 (2006).
- [36] E. Sistrunk et al., Opt. Express 23, 4340 (2015).

- [37] F. Bencivenga and C. Masciovecchio, NIMA 606, 785-789 (2009).
- [38] R.C. Zeller and R.O. Pohl, Phys. Rev. B 4, 2029-2041 (1971).
- [39] C. Ferrante et al., Nat. Commun. 4, 1793 (2013).
- [40] F. Bencivenga et al., Faraday Discuss. 171, 487 (2014).
- [41] B. D. Patterson, SLAC Technical Note, SLAC-TN-10-026 (2010).

# Appendix A. Basics of FEL physics

Bruce Patterson, Paul Scherrer Institute

In a Free Electron Laser, the active medium consists of bunches of unbound, relativistic electrons flying in vacuum. In periodic magnetic fields these electrons generate radiation - this process can be accurately described using classical physics.

- A graphical description of synchrotron radiation
- The FEL operating principle
- The 1D FEL model and the Pierce parameter
- The IR FEL oscillator

Free electron laser technology is used to produce tunable, high-intensity, shortduration pulses of highly transverse-coherent radiation ranging from the infrared/ THz to the X-ray spectral regions. Laser radiation is generated starting from synchrotron radiation in a periodic magnetic undulator, and amplification occurs via a cooperative interaction with the electron beam due self-organized "microbunching". While the X-ray FEL is a single-pass device, IR radiation is best generated with a multi-pass FEL oscillator, where an optical cavity is used to provide positive feedback.

## A graphical description of synchrotron radiation

In his introductory "Lectures on Physics", Feynman gives an elegant graphical explanation of how synchrotron radiation is generated [1, 2]. The present Section is taken approximately verbatim from Ref. [2]. Feynman considers an electron moving along the path  $\vec{r}(\tau)$ , as seen by an observer at the point (x, y, z), and he distinguishes between  $\tau$ , the time in the frame of the electron (*the emitter time*) and *t*, the time in the observer's frame (the *observer time*);  $\vec{r}(\tau)$  is the *true* path of the electron, and  $\vec{r}'(t)$  is the *apparent* path. Feynman gives a rigorous expression for the electric and magnetic fields of the moving electron:

$$\vec{E}(x, y, z) = \frac{e}{4\pi\varepsilon_0} \left[ \frac{\hat{r}'}{r'^2} + \frac{r'}{c} \frac{d}{dt} \left( \frac{\hat{r}'}{r'^2} \right) + \frac{1}{c^2} \frac{d^2 \hat{r}'}{dt^2} \right]$$
$$\vec{B} = \frac{-1}{c} \hat{r}' \times \vec{E}.$$

The first term in the electric field is the familiar  $1/r^2$  Coulomb law, and the second term is a relativistic correction. Of interest here is the third, radiation term,  $\vec{E}_{rad}$ , which in the farfield decreases more slowly as 1/r. Complications arise from the appearance of the apparent position  $\vec{r}'$  and the observer time *t*, which, for relativistic motion, may differ dramatically from the true position  $\vec{r}'$  and the emitter time *t*. For example, suppose that we observe from the position  $z = R_0$  the motion of an electron following the true trajectory  $\vec{r}(\tau)$  in the vicinity of the origin. In Fig. 1, the positions of the observer and electron are indicated (in two dimensions), along with the apparent position of the electron  $\vec{r}'(x',y')$  and the corre-



Fig. 1: The motion of an electron near the origin is followed by an observer at  $z = R_0$ .



Fig. 2. (a) An electron undergoes circular motion at an orbital 'electron' radius *r*. (b) Its apparent x-position x'(t) is obtained from the true position x(t) by a translation along the time-axis by the light propagation time z/c. This procedure yields a curtate cycloid for x'(t) m which is equivalent to the path traced out by the position of the electron at t = 0 as the diagram in (a) is unrolled along the circle with larger ('light') radius  $R = r / \beta$ . This figure is adapted from Ref. [1].

sponding unit vector  $\hat{r}'$ . Note that  $\hat{r}'$  points from the observer toward the electron. For a distant observer (x' <<  $R_0, z' \approx -R_0$ ) we have

$$\hat{r}' = \frac{x'\hat{x} + z'\hat{z}}{\sqrt{x'^2 + z'^2}} \approx \left(\frac{x'}{R_0}\right)\hat{x} - \hat{z},$$

and the radiation term in the expression for  $\vec{E}$  becomes

$$ec{E}_{
m rad} = rac{e}{4\piarepsilon_0c^2}rac{d^2\hat{r}'}{dt^2} pprox rac{e}{4\piarepsilon_0c^2}rac{d^2}{dt^2}igg(rac{x'}{R_0}igg)\hat{x}$$
 $pprox rac{e}{4\piarepsilon_0c^2R_0}a'_{\perp}(t)\hat{r}_{\perp}.$ 

Note that the radiation field decreases with distance as  $1/R_0$ , is perpendicular to the electron-observer direction and is proportional to the transverse component of the apparent acceleration.

From a distant vantage point at  $z = R_0$ , we consider the motion of an electron that follows the circular trajectory shown in Fig. 2(a). A segment of this trajectory near time zero will correspond to that in a bending magnet, or near a pole of the FEL undulator. Because of the nonzero propagation time of light over the distance  $R_0-z$ , the observer time *t* associated with the emitter time  $\tau$  for an electron with coordinate  $z(\tau)$  is given by

$$t = \tau + \frac{R_0}{c} - \frac{z(\tau)}{c}$$

In what follows, we disregard the constant term  $R_0/c$ .

As shown in Fig. 2(a), the true path  $\vec{r}(\tau)$  of the electron is the dark 'electron' circle. A point moving with the same angular velocity on the slightly larger circle moves with speed c. In Fig. 2(b), we use a graphical method to construct from the true x-coordinate  $x(\tau)$  (points) the apparent position x'(t) (dark curve). Each of the  $x(\tau)$  points is shifted in time to account for the light propagation. Consider, for example, point -4. Because it is more distant from the observer than the origin, the apparent time is later than the true time, and we move the point in Fig. 2(b) to the right by the corresponding line segment in Fig. 2(a). Analogously, point +5 undergoes a shift to earlier time. The result for the apparent particle trajectory x'(t) is a curtate cycloid. Of particular importance for synchrotron radiation is the sharp cusp in x'(t), which occurs at the moment when the electron moves directly toward the observer (t = 0). At this point in the trajectory, the large apparent transverse acceleration causes the emission of an intense burst of synchrotron radiation. For a quantitative discussion of this radiation and an extension of these arguments to the case of a periodic magnetic undulator, see Ref. [2].

## The FEL operating principle

The principle of FEL operation was invented by Madey in the early 1970's [3] and demonstrated with a prototype operating in the infrared spectral region in 1976 [6] at Stanford by Madey and coworkers. The active medium in a FEL consists of highly collimated bunches of relativistic electrons traversing a magnetic undulator (see Fig. 3). The general principle is independent of the wavelength to be generated, but the technical implementation is and results in rather different machines and configurations e.g. oscillator (low gain), SASE or seeded (high gain) FELs. Contrary to the closed orbits of synchrotrons, where stochastic synchrotron radiation degrades the electron beam quality, the FEL uses a linear accelerator (LINAC).

A pulse of relativistic electrons, with relativistic factor  $\gamma = 1/\sqrt{1-\beta^2} = 1/\sqrt{1-v^2/c^2} >> 1$ , moves along an undulator, experiencing the magnetic field  $B_y = B_0 \cos(k_u z)$ , where  $k_u = 2\pi/\lambda_u$ , and  $\lambda_u$  is the undulator period. The Lorentz force on the electron leads to the equations of motion:

#### The undulator equation

The x-oscillation causes emission of undulator radiation, with wavelength  $\lambda$ . Consider in Fig. i1 successive wavefronts, corresponding to points A and B on the electron trajectory.

From the figure, we see that the condition for coherent superposition is  $\frac{\lambda_u}{\beta} = \lambda_u + \lambda$ , where  $\lambda_u$  is the undulator period and the average value of the z-component of the electron velocity is

$$\overline{\beta}c = \left[1 - \frac{1}{2\gamma^2} \left(1 + \frac{K^2}{2}\right)\right]c$$

Here  $\gamma$  is the relativistic energy factor and K is the dimensionless "undulator parameter" defined in the text. We thus arrive at the "undulator equation" for the wavelength of the radiation:

$$\lambda = \frac{\lambda_u}{2\gamma^2} \left( 1 + \frac{K^2}{2} \right)$$

At this resonant condition, the radiation overtakes the electrons by one wavelength per undulator period.



Fig. i1: Coherent radiation wavefronts from successive undulator poles at A and B.



$$\gamma m\ddot{z} = -e\dot{x}B$$
  
 $\gamma m\ddot{x} = e\dot{z}B$ 

to  $\frac{dW}{dt}$  averages to zero. A constant energy transfer between electrons and radiation occurs when  $\psi^+ = const$ , *i.e.*, for

We first assume 
$$\dot{z} \approx const \equiv \beta c \gg \dot{x}$$
 and find:

$$\dot{x} = \frac{cK}{\gamma} \sin \omega_u t$$

where  $\omega_u = k_u \overline{\beta}c$ , and the "undulator parameter" is defined as  $K = \frac{eB_0\lambda_u}{2\pi mc}$ . Averaging over many undulator periods, we find:

$$\left\langle \dot{z} \right\rangle = \left\langle \sqrt{\beta^2 c^c - \dot{x}^2} \right\rangle = \left[ 1 - \frac{1}{2\gamma^2} \left( 1 + \frac{K^2}{2} \right) \right] c \equiv \overline{\beta} c \; .$$

The major difference between undulator radiation at a synchrotron and at the FEL is that the radiation field in the FEL undulator becomes sufficiently strong to influence the electron trajectory. The electron energy is  $W = \gamma mc^2$ , which varies under the influence of the radiation field  $E_x(t)$ :

$$\frac{dW}{dt} = -e\dot{x}(t)E_x(t) \ .$$

This interaction is strongest when  $|\dot{x}|$  is at its maximum, *i.e.*, at the zero-crossings of the electron trajectory. Assuming plane-wave radiation,  $E_x(t) = E_0 \cos(kz - \omega t + \psi_0)$ , and using the expression for  $\dot{x}(t)$ , we obtain:

$$\frac{dW}{dt} = \frac{-eKcE_0}{2\gamma} \left( \sin \psi^+ - \sin \psi^- \right) ,$$

where  $\psi^{\pm} = \left[ \left( k \pm k_u \right) \overline{\beta} c - kc \right] + \psi_0 = \psi_0 - ct \left[ k \left( 1 - \overline{\beta} \right) \mp k_u \overline{\beta} \right]$ . Since  $\psi^-$  is always rapidly changing, the  $\sin \psi^-$  contribution

$$k(1 - \overline{\beta}) = k_u \overline{\beta}$$

$$\frac{2\pi}{\lambda} (1 - \overline{\beta}) = \frac{2\pi}{\lambda_u} \overline{\beta} \approx \frac{2\pi}{\lambda_u}$$

$$\lambda = \lambda_u (1 - \overline{\beta}) = \frac{\lambda_u}{2\gamma^2} \left( 1 + \frac{K^2}{2} \right)$$

Thus, a constant energy transfer occurs for a radiation wavelength which satisfies the undulator equation. Consider now the electron motion caused by the radiation field. The quantity  $\psi = \psi^+$  is called the "ponderomotive phase", and its time dependence is given by  $\dot{\psi} = -k(1 - \overline{\beta}) + k_u \overline{\beta} c$ . We define the relative energy 'deviation'  $\eta \equiv (\gamma - \gamma_r)/\gamma_r$  and the relative energy 'detuning'  $\Delta \equiv (\gamma_0 - \gamma_r)/\gamma_r$ , where  $\gamma_r$  is the 'resonant' value for which the undulator equation is satisfied,  $\gamma_0$  is the average value and  $\gamma_r, \gamma_0 <<1$ . After some algebra, we obtain:

$$\dot{\psi} = 2k_{\mu}c(\eta + \Delta)$$

On the other hand, the energy transfer is given by:

$$\frac{dW}{dt} = -e\dot{x}E_x = \frac{-eKcE_0}{2\gamma_0}\sin\psi = mc^2\dot{\gamma} = mc^2\gamma_0\dot{\eta},$$

implying that  $\eta = -\frac{eKE_0}{2mc\gamma_0^2}\sin\psi$ . Taking a second time derivative, we obtain:

$$\ddot{\psi} = -\Omega^2 \sin \psi,$$

which is the equation of motion for a physical pendulum



Fig. 4: Oscillatory (blue) and rotational (red) motion of an electron in phase space is separated by the "separatrix" (black).



Fig. 5: The development of an initially uniform electron distribution in phase space in the FEL undulator (for zero detuning  $(\Delta = 0)$ ). The ponderomotive phase  $\psi$  and its time derivative  $\dot{\psi}$  effectively correspond to the position in a moving reference frame and the particle energy, respectively. At the point where "microbunches" are established (red), the undulator is terminated.



Fig. 6: Schematic comparison of the incoherent radiation of randomly positioned electrons (left) and coherent radiation from microbunches (right).



Fig. 7: Schematic logarithmic plot of the power produced by an electron bunch as a function of distance it has travelled along the magnetic undulator in the case of a SASE FEL. After an initially phase of "lethargic" growth of spontaneous undulator radiation, the initially homogenous electron distribution starts to show a periodic modulation at the scale of the wavelength. These microbunches begin to radiate coherently, causing an exponential power increase and a more pronounced "microbunching". If the undulator is extended beyond the position of optimal microbunching, energy begins to flow back from the photon field to the electron motion, and the X-ray power decreases. with frequency  $\Omega = \sqrt{\frac{ek_w K E_0}{m\gamma_0^2}}$ . The pendulum motion can be represented in a  $(\psi, \psi)$  phase-space plot, where oscillatory and rotational trajectories are separated by a curve called the separatrix.

Interaction in the FEL undulator of a pulse of electrons with its own radiation field causes the initially uniform density distribution along the pulse to become modulated, with a period equal to the radiation wavelength  $\lambda$ . We see how this occurs by plotting electron trajectories in phase-space.

The horizontal axis in Fig. 5, the ponderomotive phase  $\psi$ , is essentially the z-coordinate of an electron in the pulse, in a coordinate system moving with the electrons at their average velocity  $\overline{\beta}c$ . A fraction of the pulse equal in length to the radiated wavelength  $\lambda$  is shown; the plot is repeated to the left and right. The vertical axis gives the deviation  $\eta$  of the electron energy from the resonant condition  $\gamma = \gamma_r$ . Dots show the successive positions of the, initially uniformly distributed (blue), electrons. At the final situation shown (red), the approximate alignment of the dots at zero phase implies the formation of a micro-bunch, and hence a strong density modulation of the pulse with a period equal to  $\lambda$ .

Whereas an electron pulse with randomly-distributed electrons, as in a synchrotron, radiates incoherently, microbunching with periodicity  $\lambda$ , as occurs in the FEL, results in coherent emission.

For incoherent emission, the total radiated power  $P_{incoh} = NP_1$ is the sum of that emitted by each of the *N* electrons in the pulse. For coherent emission, it is the radiated electric field  $E_{coh} = NE_1$  which adds up, implying a total power  $P_{coh} = N^2P_1$ which is amplified by the factor *N*. For a typical pulse charge of 200 pC,  $N \approx 10^9$ !

XFEL operation thus proceeds as follows (see Fig. 7): the initially homogeneous electron pulse enters the undulator and spontaneously emits incoherent radiation. As the radiation field builds up, microbunching begins to develop, implying increasingly coherent emission and hence stronger microbunching and an exponential increase in the radiation power. It is arranged that maximum microbunch modulation occurs in an XFEL at the end of the undulator, after which the electrons are discarded and the radiation is directed to the experiment. This process is called self-amplifying spontaneous emission (SASE). A simple mathematical model for the spectral properties of SASE XFEL pulses is given in [4].

## The 1D FEL model and the Pierce parameter

A more detailed treatment of the XFEL operation principle is provided by the 1-dimensional XFEL model [5]. The existence of of an exponentially growing solution for the FEL equations has been studied by many authors, the first theory of a SASE FEL in the 1-dimensional case including the start from spontaneous radiation and saturation is given in [8]. The description here follows [5]. We begin with the Maxwell wave equation in the Lorentz gauge:

$$\left[\nabla^2 - \frac{\partial^2}{c^2 \partial t^2}\right] \vec{A} = -\mu_0 \vec{J}$$

The relation between the vector potential and the electric field is:  $\vec{r}$ 

$$\vec{E} = -\frac{\partial A}{\partial t} - \nabla \rho \approx -\frac{\partial A}{\partial t}$$
$$\vec{E} = \hat{x} E_0 e^{ik(z-ct) + i\psi_0}$$

where the gradient term is neglected, because it does not contribute significantly to the radiated field. The electron current density represents a source term:

$$\vec{J} = -\hat{x}e\sum_{j} \dot{x}_{j}\delta(\vec{r}_{j} - \vec{r})$$
$$\dot{x}_{j} = \frac{eK}{\gamma_{j}}\sin k_{u}z_{j}$$

where the sum over *j* is over all electrons in the bunch. We make the "slowly-varying envelope" approximation:

$$\frac{\partial E_0}{\partial z} << kE_0$$
$$\frac{\partial E_0}{\partial t} << kcE_0$$

which allows us to write:

$$\left[\nabla^2 - \frac{\partial^2}{c^2 \partial t^2}\right] A_x \approx e^{i(kz-ct)} \left[\nabla_{\perp}^2 + 2ik\left(\frac{\partial}{\partial z} + \frac{\partial}{c\partial t}\right)\right] \frac{E_0}{ick} e^{i\psi_0}$$

yielding the relation:

$$\left[\nabla_{\perp}^{2} + 2ik\left(\frac{\partial}{\partial z} + \frac{\partial}{c\partial t}\right)\right]\frac{E_{0}}{ick} = \mu_{0}ecK \,\mathrm{e}^{-i\psi_{0}}\sum_{j}\frac{\sin k_{u}z_{j}}{\gamma_{j}}\delta\left(\vec{r}_{j} - \vec{r}\right)e^{-i(kz-ct)}$$

#### **XFEL seeding**

Although the X-ray pulses emitted from an XFEL in SASE mode have a high transverse coherence (typically 1.5 lateral modes), their longitudinal coherence is poor (relative bandwidth typically 0.2%). This is due to the fact that the SASE process initiates from noise. The bandwith can, of course, be reduced after the fact by using a grating or crystal monochromator, but this generally entails a large reduction in flux. An attractive alternative is to actively "seed" the XFEL process using a source of narrow-band photons, which initiate coherent amplification at a harmonic of the input pulse.

An external laser pulse is used to seed the soft X-ray XFEL at FERMI (see Fig. i2) [10]. In a further development, this facility has also demonstrated 2-stage seeding [11], which uses the coherently-amplified output of an externallyseeded XFEL to seed harmonic amplification in a second stage. Besides allowing fine tuning of the photon energy, triggering the XFEL with an external laser seed pulse allows highly precise XFEL – laser timing synchronization. And shaping of the seed pulse furthermore permits innovative XFEL pulse shaping (double pulses, multi-color pulses, etc.).

External source seeding becomes difficult at hard X-ray wavelengths, due the absence of a suitable narrow-band photon source. By introducing a wavelength filter at an intermediate position along the XFEL undulator, however, one may use filtered SASE pulses from the upstream sections to seed the XFEL amplification in the downstream sections. Such a filter also introduces an optical delay, which is compensated by the delay introduced in an electron chicane (see Fig. i3). In order to minimize the delay time, and hence the size of the electron chicane, an innovative single crystal "forward Bragg diffraction" technique has been successfully applied at the LCLS [12].



#### Fig. i2: The external laser seeding scheme of the FERMI XFEL [10].



Fig. i3: The "forward Bragg diffraction" single-crystal technique for producing self-seeded X-ray pulses in the hard X-ray regime [13]. We now average the source term over a volume  $\delta V = 1/n$ , where *n* is the electron density, we write the terms as complex exponentials and, as in the previous section, we disregard terms which oscillate with the rapidly changing ponderomotive phase  $\psi^-$ . Finally, we introduce a dimensionless radiation field

$$u \equiv \frac{eE_0}{imc^2k}$$

to obtain:

$$\left[\nabla_{\perp}^{2} + 2ik\left(\frac{\partial}{\partial z} + \frac{\partial}{c\partial t}\right)\right] u = \frac{ine^{2}\mu_{0}K}{2m}\sum_{j}\frac{e^{-i\psi_{j}}}{\gamma_{j}}$$

In our simplified 1-d model, we disregard on the left-handside the first term (describing diffraction) and the third term (describing the time-evolution of the field at a fixed point along the undulator – the so-called "slippage"), and we perform an average over an undulator period:

$$\frac{du}{dz} = \frac{ne^2\mu_0 K}{4km\gamma_0} \left\langle e^{-i\psi_j} \right\rangle$$

From the previous section, we have the two additional equations describing the evolution of the electron phase and energy:

$$\frac{d\psi_j}{dz} = \frac{1}{c}\dot{\psi}_j = 2k_u(\eta_j + \Delta)$$
$$\frac{d\eta_j}{dz} = \frac{1}{c}\dot{\eta}_j = -\frac{eKE_0}{2mc^2\gamma_0^2}\sin\psi_j = -\frac{kK}{4\gamma_0^2}\left(ue^{i\psi_j} + u^*e^{-i\psi_j}\right)$$

It is convenient to rescale the parameters as follows:

$$z' \equiv 2k_{u}\rho z$$
$$\eta' \equiv \eta / \rho$$
$$\Delta' \equiv \Delta / \rho$$
$$A' \equiv \frac{kK}{8\gamma_{0}^{2}k_{u}\rho^{2}}u$$

and to define the so-called "Pierce parameter"

$$\rho \equiv \left[\frac{e^2 \mu_0 n K^2}{64 m \gamma_0^3 k_u^2}\right]^{1/3}$$

with a typical value between  $10^{-4}$  and  $10^{-2}$ .

Using these dimensionless parameters, we obtain the "1-d FEL equations":

$$\begin{aligned} \frac{d\psi_j}{dz'} &= \eta'_j + \Delta' \\ \frac{d\eta'_j}{dz'} &= -\left(A'e^{i\psi_j} + A'^*e^{-i\psi_j}\right) \\ \frac{dA'}{dz'} &= \left\langle e^{-i\psi_j} \right\rangle \end{aligned}$$

These equations describe the evolution of, respectively, the electron position, the electron energy and the radiation field. Using the second and third equations, energy conservation along the XFEL undulator can be demonstrated:

$$|A'|^2 + \langle \eta' \rangle = const$$

A simple solution of these equations can be performed as follows: We take further derivatives to obtain

$$\begin{split} \frac{d^{2}A'}{dz^{\prime2}} &= -i\left\langle \frac{d\psi_{j}}{dz} e^{-i\psi_{j}} \right\rangle = -i\Delta' \left\langle e^{-i\psi_{j}} \right\rangle - i\left\langle \eta'_{j} e^{-i\psi_{j}} \right\rangle \Longrightarrow \frac{d^{2}A'}{dz^{\prime2}} + i\Delta' \frac{dA'}{dz'} = -i\left\langle \eta'_{j} e^{-i\psi_{j}} \right\rangle \\ \frac{d^{3}A'}{dz^{\prime3}} + i\Delta' \frac{d^{2}A'}{dz^{\prime2}} &= -i\left\langle \frac{d\eta'_{j}}{dz'} e^{-i\psi_{j}} \right\rangle - \left\langle \eta'_{j} \frac{d\psi_{j}}{dz'} e^{-i\psi_{j}} \right\rangle \approx iA' + iA'' \left\langle e^{-2i\psi_{j}} \right\rangle \approx iA' \end{split}$$

In the second line, the term involving the deviation energy times the phase derivative can be neglected, since it is a product of two small quantities. In addition the average over  $e^{-2i\psi_j}$  can be neglected, because microbunching at the second harmonic is unimportant. Making the Ansatz that  $A' = A'_0 e^{pz'}$ , we obtain the following relation for the field exponent:

$$p^3 + i\Delta' p^2 = i$$

For the case of zero detuning ( $\Delta' = 0$ ), we find the three solutions

$$p = \left\{-i, \frac{\sqrt{3} \pm i}{2}\right\}$$

one of which is oscillating, one is exponentially decaying and one is exponentially growing. At a sufficiently large distance along the undulator, the last will dominate:

$$P \propto \left|A'\right|^2 \propto \left|\exp\left(\frac{\sqrt{3}+i}{2}z'\right)\right|^2 = e^{\sqrt{3}z^2} = e^{\sqrt{3}2k_w\rho z}$$

implying a "gain length" which is inversely proportional to  $\rho$ :

$$L_g = \frac{\lambda_u}{4\pi\sqrt{3}\rho}$$

Note that since to achieve saturation of the XFEL, the undulator length should be chosen to be approximately 12 times the gain length. This implies:

$$N_u \lambda_u \approx 12L_g$$
$$\rho = \frac{\lambda_u}{4\pi\sqrt{3}L_g} \approx \frac{1}{N_u}$$

where  $N_u$  is the number of undulator periods.

Beginning from an initial state with virtually no radiation field and all electrons close to the resonant energy, transfer of energy from the electron beam to the radiation field proceeds until "saturation", when the microbunching is complete:

$$\frac{dA'}{dz'}\Big|_{sat} = \left\langle e^{-i\psi_j} \right\rangle\Big|_{sat} \sim 1$$
$$\frac{dA'}{dz'} \approx pA' \sim A' \quad \Longrightarrow A'_{sat} \sim 1$$

This implies that

$$\begin{split} \left|A_{0}^{\prime}\right|^{2} + \left\langle\eta'_{j}\right\rangle_{0} &\approx 0 \approx \left|A_{sat}^{\prime}\right|^{2} + \left\langle\eta'_{j}\right\rangle_{sat} \approx 1 + \left\langle\eta'_{j}\right\rangle_{sat} \\ &\left\langle\eta'_{j}\right\rangle_{sat} \approx -1 \\ &\left\langle\gamma_{j}\right\rangle_{sat} - \left\langle\gamma_{j}\right\rangle_{0} \approx -\rho\gamma_{r} \end{split}$$

or that the change in electron beam energy and the final FEL power are given by

$$\Delta \gamma = \rho \gamma$$
$$P_{FEL} \approx \rho P_{beam}$$

*i.e.*, approximately 0.1% of the electron beam energy is converted to X-ray photons.

Finally, we find that the Pierce parameter also determines the XFEL bandwidth: We differentiate the undulator equation

$$\lambda = \frac{\lambda_u}{2\gamma^2} \left( 1 + \frac{K^2}{2} \right)$$

to obtain

$$\omega = \frac{2ck_u}{1+K^2/2}\gamma^2$$

$$\frac{d\omega}{d\gamma} = \frac{2ck_u}{1+K^2/2}2\gamma = \frac{2\omega}{\gamma}$$

$$\Rightarrow \Delta\omega = \frac{2\omega\Delta\gamma}{\gamma}, \quad \Delta\gamma = \rho\gamma$$

$$\frac{\Delta\omega}{\omega} = 2\rho$$

These results imply that: a) for a given wavelength, the electron beam energy can be detuned by  $\Delta \gamma = \rho \gamma$  and still amplify the X-ray field, and b) for a given beam energy, the wavelength can deviate by the bandwidth  $\Delta \omega = 2\rho \omega$  and still be amplified. The relative bandwidth of SASE radiation is thus of order 10<sup>-3</sup>.

## The FEL oscillator

At wavelengths, where the radiation to be produced by a FEL is in a spectral range where mirrors with good reflectivity are available, a FEL may profit from multi-pass amplification. Such an arrangement is termed a "FEL oscillator" (see Fig. 8). This arrangement is implemented for e.g. FELs operating in the infrared and THz regime. The basic FEL physics described in the previous sections applies also to the FEL oscillator.

For the FEL oscillator the length of the undulator can be strongly reduced in comparison with the high gain SASE FEL by placing the undulator inside an optical resonator. The length of the undulator in this case is determined by the requirement that the single-pass gain should be larger than the cavity roundtrip loss due to the finite reflectivity of the mirrors and the diffraction losses. Moreover, in the case that the 'on-time' of the electron beam is limited, the time to reach saturation is only a fraction thereof. Typically, this requires an undulator with a single-pass gain of a few to several tens of percent, i.e. with a length (substantially) less than half a gain length, which is to be compared with the 12 times gain lengths typically required for a single-pass (SASE) FEL (see above).

Recirculation of the electron beam would require a very complex beam transport system rather than the simple mirrors as needed for the light, and has therefore never been implemented.<sup>1</sup> Instead, 'fresh' electrons are injected at the entrance of the undulator at each roundtrip of the optical

<sup>&</sup>lt;sup>1</sup> In case high energy efficiency is an issue, the electron beam can and has been recirculated through the accelerator to extract most of the unspent beam energy.



Fig. 8: An IR FEL oscillator includes two mirrors to provide positive feedback.

pulse.<sup>2</sup> This means that the electrons first need to be microbunched by the circulating light pulse before they will radiate in phase and thereby amplify it.

Also in the infrared, RF accelerators with either normal- or superconducting structures are almost exclusively used to drive the FEL. As these produce bunches that are only a few ps long, the optical pulses will also be very short and the cavity length has to be matched to (a multiple) of the electron bunch separation. In general, the optical output will mimic the electron bunch structure: a few-microseconds long, up to 3 GHz bursts of pulses that are repeated at a tens of Hz repetition rate for normal conducting structures, or a (quasi-) CW optical pulse train at tens of MHz repetition rate when superconducting structures are used.

Slippage, the fact that the optical pulse advances relative to the electron bunch by one optical period for each undulator period travelled, tends to be important for IR FELs as  $n \cdot \lambda$ is often of the same order or even quite a bit larger than the

electron bunch length. One manifestation is the so-called laser lethargy. During start-up, at low light intensity, the process of micro-bunching is slow and the electrons will only radiate coherently towards the end of the undulator, thereby amplifying primarily the trailing part of the optical pulse. To maintain good time overlap with the electron bunches, the cavity length has to be reduced somewhat compared to its synchronous value, when it is exactly equal to (a multiple of) the bunch separation. As the intensity grows, the micro-bunching will speed up and at saturation the cavity length should be close to its synchronous value for optimal time overlap. In fact, the slippage can be used to change the bandwidth of the radiation. At large cavity desynchronism (a few times  $\lambda$ ) the optical pulse will become relatively long with a corresponding decreased bandwidth. On the contrary, when the cavity is close to synchronism, the overlap at saturation is good and, as the leading part of the optical pulse does not suffer from re-absorption by the electrons when these have moved to the absorbing phase of the ponderomotive potential well, the optical pulse can continue to grow while at the same time becoming shorter. Transform-limited pulses with a duration between 6 and 100 optical cycles (FWHM) have been demonstrated this way for a 40-period undulator.

<sup>&</sup>lt;sup>2</sup> So the reduction in undulator length comes at the expense of an increased demand on the number of electrons during the time needed to reach saturation.

## Summary

- Free electrons in a FEL emit synchrotron radiation upon deflection in the magnetic field of the undulator poles. Feynman has presented a simple graphical description of the emission process.
- In a FEL, interaction with the radiation field causes an initially homogeneous electron bunch to form microbunches, which then emit super-radiantly.
- From a FEL physics point of view, the main difference between a single-pass FEL and a FEL that makes use of a resonator, is the fact that in the latter the electron micro-bunching is effectively "erased" after every (fraction of a) gain length.

#### References

- RP Feynman, RB Leighton and M Sands, *The Feynman* Lectures on Physics (Addison-Wesley, New York, 1963), Vol 1, Chap 28.
- [2] BD Patterson, A simplified approach to synchrotron radiation, *Am J Phys* **79**, 1046-1052 (2011).
- [3] JMJ Madey, Stimulated emission of Bremsstrahlung in a periodic magnetic field, *J Appl Phys* **42**, 1906 (1971).
- [4] T Pfeifer, Partial-coherence method to model experimental free-electron laser pulse statistics, *Opt Lett* **35**, 3441-3443 (2010).
- [5] S Reiche and E Prat, private lecture notes (2014).
- [6] L R Elias, J M J Madey, G J Ramian, H A Schwettman, and T I Smith, First Operation of a Free-Electron Laser D. A. G. Deacon, *Phys. Rev. Lett.* **38**, 892
- [7] JMJ Madey, Relationship between mean radiated energy, mean squared radiated energy and spontaneous power spectrum in a power-series expansion of the equations of motion in a free-electron laser, *Il Nuovo Cimen* **50B**, 64-88 (1979).

- [8] New reference: R Bonifacio, C Pellegrini, and L Narducci, *Opt. Commun.* **50**, 373 (1984)
- [9] G Dattoli, A Renieri and A Torre, *Lectures on Free-Electron* Laser Theory and Related Topics (World Scientific, Singapore, 1993).
- [10] E Allaria, et al, Highly coherent and stable pulses from the FERMI seeded free-electron laser in the extreme ultraviolet, *Nature Phot* 6, 699-704 (2012).
- [11] E Allaria, et al, Two-stage seeded soft-X-ray free-electron laser, *Nature Phot* **7**, 913-918 (2013).
- [12] J Amann, et al, Demonstration of self-seeding in a hard-X-ray free-electron laser, *Nature Phot* **6**, 693-698 (2012).
- [13] X Yang and Y Shvyd'ko, Maximizing spectral flux from selfseeding hard X-ray free electron lasers, *Phys Rev ST Accel Beams* 16, 120701 (2013).

# Appendix B: European FEL facilities

The following information on existing and planned IR and X-ray FEL facilities in Europe has been taken verbatim from the FELs of Europe web page: www.fels-of-europe.eu

## ALICE

ALICE (Accelerators and Lasers In Combined Experiments) is an Energy Recovery Linac test accelerator at Daresbury Laboratory. High quality trains of bunches of electrons are produced by a DC photo-injector source. The electron bunches are then accelerated to around 30 MeV through two superconducting linacs. The electron bunches are then each compressed in a magnetic chicane to around 0.6 picoseconds, stimulating the production of intense pulses of coherent THz light. In addition the bunches are used to generate coherent infra-red radiation (typically 6 to 8 micron wavelength) in an oscillator FEL before passing through one of the linacs for a second time on the decelerating phase and so losing energy to the RF field which can then be used to accelerate subsequent bunches.

This unique facility is used to investigate and overcome the challenges presented to scientists in designing and building future generations of accelerators. This research is useful for both future light sources and other advanced accelerator development. The intense light produced from ALICE has been used to carry out pilot experiments to study quantum dot solar cells and to develop new cancer diagnosis techniques. This has led to the award of a major grant from EPSRC in the UK to operate ALICE in a dedicated mode for part of the year for three years just for additional cancer studies using both the infra-red and THz light sources. This work is a major collaboration led by Liverpool University and includes several clinicians from research hospitals.

#### Contact

STFC Daresbury Laboratory Daresbury Science and Innovation Centre Keckwick Lane Daresbury Cheshire WA4 4AD United Kingdom Tel: +44(0)1925603714 Email: yuri.saveliev@stfc.ac.uk. http://www.stfc.ac.uk/1320.aspx/



## CLARA

CLARA (Compact Linear Accelerator for Research and Applications) is a proposed FEL test facility at Daresbury Laboratory, a major upgrade to the existing RF photoinjector test facility, VELA. The CLARA project aims to build on the UK's existing expertise and experimental experience in free electron lasers, to pave the way for a state-of-the-art FEL facility in the UK, whilst simultaneously contributing to international R&D of single pass FELs.

The ultimate aim of CLARA is to develop a normal-conducting test accelerator (delivering approximately 250 MeV electron beam energy), able to generate longitudinally and transversely bright electron bunches, and to use these bunches in the experimental production of stable, synchronized, ultra-short photon pulses of coherent light from a single pass FEL, using techniques directly applicable to the future generation of light source facilities. It is also foreseen that the CLARA beam will be used for testing other advanced concepts such as beam driven wakefield acceleration. CLARA will generate intense pulses of light in the wavelength range 100 nm to 400 nm, and it will generate pulse lengths of only a few cycles in the most extreme ultrashort pulse demonstration – equivalent to sub-attosecond in the X-ray region. CLARA will be located in an existing building previously used for the Synchrotron Radiation Source (SRS), and will utilize the VELA RF photoinjector, as a first stage. The conceptual design of CLARA was published in 2013 and the first accelerating section (up to 50 MeV) will be installed in 2015.

#### Contact

STFC Daresbury Laboratory Daresbury Science and Innovation Centre Keckwick Lane Daresbury Cheshire WA4 4AD United Kingdom Tel: +44(0)1925603267 Email: jim.clarke@stfc.ac.uk http://www.astec.stfc.ac.uk/ASTeC/Programmes/ 38749.aspx

## CLIO

CLIO is a pulsed free-electron laser continuously tunable between 4 and 120  $\mu$ m. It has a double pulsed structure: "macro-pulses" 10  $\mu$ s long (at 1 to 25 Hz) contain "micropulses" of length adjustable from 0.3 to 5 ps (with Fourier transform spectral width). The micropulse interval is 16 ns. CLIO can lase simultaneously at 2 different, independently tunable frequencies, allowing 2-colours pump-probe experiments.

#### **User facility**

Vacuum beamlines transport the optical beam to 8 user rooms. They include various equipment: mirrors, detectors, optical mounts, monochromators, cryostats, etc. The users have computer control of the laser wavelength and spectral scans. In addition, 5 different set-ups are available. 4 of them are operated by permanent scientists:

- A sum frequency generation (SFG) experiment, dedicated to surface studies. This installation includes a short pulse (5 ps) Nd:YAG laser synchronized with CLIO and the computerized control of the experiment. Optical parametric oscillators are pumped by this Nd:YLF laser and are synchronized with CLIO. They cover the visible and near-infrared up to 8-9 µm. This allows to vary both the visible and infrared wavelengths in the SFG set-up as well as multicolor experiment. This permits the studies of surfaces in various conditions: in electrochemical cells, in air and under ultra high vacuum (UHV).
- Mass spectrometers allow ultra-sensitive gas phase spectroscopy by multiphoton dissociation (IRMPD) driven by the infrared FEL. It has been shown that this combination is highly effective in identifying reaction intermediates. Many are available to users. In particular, 2 stations are available : a Paul trap and a 7T ICR spectrometer installed in a newly adapted room of CLIO in



2010. Several ion preparation chambers and electron gun to fragment ions are available. A high power ns-OPO is also coupled to the spectrometer, making this installation a unique set-up in the world.

- A near-field infrared microscope with high spatial resolution capable of local spectroscopy and microscopy ("chemical mapping"). A new technique, called AFMIR, has been developped at CLIO. It allows to overcome the probleme encountered when one wants to perform spectroscopy under the Rayleigh (~λ) limit for spatial resolution. It is based on a photo-thermal method, providing a direct measurement of the infrared absorption, avoiding influence of the real part (topography) of the index of refraction. It is also coupled with an OPO laser, allowing developments in near-infrared complementing CLIO. The lateral resolution is better than 100 nm.
- A pump-probe and photon echo experiment (no permanent scientist) using either 1 or 2 simultaneous colors.

Beam parameters	Value
Spectral range [µm]	4 - 120
Polarization	Linear
Minimum Spectral width D1 [%]	0.2 - 1
Stability in wavelength [%]	0.1
Macropulse length [µs]	1 - 9 (tunable)
Micropulse [ps]	0.3 - 5 (tunable)
Peak power [MW]	10 - 100
Maximum average power [W]	1.5 (25 Hz, 16 ns/
	micro-pulse)
2-coulours FEL [µm]	Tested up to 32
OPOS [µm]	5 – 11

## Contact

LCP - CLIO - Universit. Paris-Sud Bat.201 Porte 2.Universit. Paris-Sud Orsay 91405 Paris, France http://clio.lcp.u-psud.fr SFG: Christophe.Humbert@u-psud.fr IRMPD: Vincent.Steinmetz@u-psud.fr AFMIR: Rui.Prazeres@u-psud.fr Pump-Probe: Jean-Michel.Ortega@u-psud.fr

## ELBE

The superconducting electron accelerator ELBE, operated by the Helmholtz-Zentrum Dresden-Rossendorf (HZDR), feeds two infrared/THz free electron lasers (FELBE) and two coherent low-frequency THz radiation sources (TELBE).

## FELBE

The two free-electron lasers cover the mid- and far-infrared spectral range from 4 – 250  $\mu$ m (75 – 1.2 THz). FELBE can operate in three different modes: continuous pulsing with a repetition rate of 13 MHz, pulsing with 1 kHz by applying a pulse picker, and macrobunch operation with bunch length > 100  $\mu$ s and macrobunch repetition rates  $\leq$  25 Hz. Pulse duration and pulse energy vary with wavelength and lie in the range from 1 – 25 ps and 100 nJ - few  $\mu$ J, respectively. The user labs at FELBE are equipped mainly for time-resolved spectroscopy. Various table-top near-infrared and THz sources can be synchronized to FELBE and setups exist for single-colour and two-colour pump-probe experiments, time-resolved photoluminescence measurements, near-field spectroscopy and Fourier-transform infrared spectroscopy. Samples can be studied in an 8 T split-coil magnet with optical access.

Furthermore FELBE is linked to the Dresden High Magnetic Field Laboratory, which enables infrared spectroscopy in pulsed magnetic fields up to 70 T (150 ms magnetic pulse).

Beam parameters	Value
Photon energy [meV]	5 - 300
Wavelength [µm]	4 – 250
Polarization	Linear; circular possible for some wavelengths
Estimated pulse length [ps]	1 – 25
Repetition rate [MHz]	13 MHz, 1 kHz; also mac- robunch (rate < 25 Hz)
Pulse Energy [µJ]	0.1 – 2
Peak power [MW]	up to 1
Average power [W]	up to 20
FEL mode	TEM_00
FEL bandwidth [%] (FWHM)	0.3 – 1.5

## TELBE

The new superradiant TELBE THz facility provides low-frequency, high-field THz pulses from two different sources, in combination with a variety of table-top light sources based on femtosecond lasers. It shall eventually cover the lower THz range between 0.1 and 3 THz with pulse energies up to 100 µJ. Pulses from TELBE are carrier-envelope-phase stable and can be provided at flexible repetition rates between a few tens of Hz to eventually 13 MHz. The frequency bandwidth can be either 100%, utilizing the diffraction radiator source, or ~20%, utilizing an 8-period undulator. The TELBE laboratory is equipped with various set-ups for multi-colour pump-probe experiments, as well as near-field THz spectroscopy. Samples can be studied in cryogenic conditions and in a 10 T split-coil magnet with optical access. Timing between laser systems and the THz sources on the sub 30 fs level is provided.

Beam parameters	Value	
Design values		
Frequency [THz]	0.1 – 3	
Frequency bandwidth	100% (single-cycle) or 20% (8 cycles)	
Polarization	linear, radial and circular (for selected frequencies)	
Estimated pulse length [ps]	0.3 - 80	
Pulse energy /repetition rate	1 μJ @ 13 MHz, 100 μJ @ 100 kHz	
to date 04/2016		
Frequency [THz]	0.1 – 1.1	
Pulse energy /repetition rate	1 μJ @ 100 kHz	

#### Contact

Helmholtz-Zentrum Dresden-Rossendorf Bautzner Landstr. 400 01328 Dresden, Germany Tel: +49 351 260 2684 Fax: +49 351 260 1 2684 Email: b.schramm@hzdr.de https://www.hzdr.de/elbe

## **European XFEL**

The European X-Ray Free-Electron Laser Facility GmbH is a limited liability company under German law that was officially founded in Hamburg, Germany, on 28 September 2009. The company is in charge of the construction and operation of what will be the world's brightest source of ultrashort X-ray pulses: the European XFEL, a 3.4 km long X-ray freeelectron laser facility extending from Hamburg to the neighbouring town of Schenefeld in the German federal state of Schleswig-Holstein. It is being realized as a joint effort of many partners. To this end, the European XFEL GmbH cooperates closely with the research centre DESY and other organizations worldwide. Civil construction started in early 2009 and the user operation is planned to start in 2017.

With its repetition rate of 27 000 pulses per second and a peak brilliance a billion times higher than that of the best synchrotron X-ray radiation sources, the European XFEL will open up new research opportunities for scientists and industrial users. Thanks to its ultrashort X-ray flashes, the facility will enable scientists to map the atomic details of viruses, decipher the molecular composition of cells, take three-dimensional images of the nanoworld, film chemical reactions, and study processes such as those occurring deep inside planets.

Presently, 11 countries are participating in the European XFEL project: Denmark, France, Germany, Hungary, Italy, Poland, Russia, Slovakia, Spain, Sweden, and Switzerland. The UK has announced is intention to join as well. UK will acces the project in the near future.

Beamlines: (operative and under construction) 3 (6 experiment stations), upgradeable to 5 (10 experiment stations).

Beam parameters	Value
Max. Electron Energy [GeV]	17.5
Wavelength range [nm]	0.05 - 4.7
Photons/pulse	~10 <sup>12</sup>
Peak brilliance	5x10 <sup>33</sup>
Pulses/second	27000

#### Contact

European XFEL GmbH Albert-Einstein-Ring 19 22761 Hamburg, Germany

After June 2016: European XFEL GmbH Holzkoppel 4 22869 Schenefeld, Germany Tel: +49 40 8998-6006 Fax: +49 40 8998-1905 Email: contact@xfel.eu http://www.xfel.eu



## FELIX

The FELIX (Free Electron Lasers for Infrared eXperiments) laboratory at the Radboud University is an international user facility providing the scientific community with tunable radiation of high brightness in the mid- and far-infrared as well as the THz regime. The facility houses two independent accelerators that together drive four free electron lasers (FELs): FELIX-1, FELIX-2, FELICE and FLARE. The total spectral coverage ranges from 3 to 1500 µm. The temporal and transverse beam profiles are close to transform, respectively diffraction limited.

Primary scientific applications are found in areas benefitting either from the high brightness or the high fluence of the light sources. The 12 experimental user stations at FELIX are connected to the IR and THz lasers and equipped with highly advanced auxiliary equipment dedicated to molecular spectroscopy experiments (FTICR mass spectrometers, various types of ion traps, molecular beam machines, a He-droplet machine) as well as time-resolved experiments (pumpprobe, transient grating, photon-echo setups). In several user stations additional tabletop laser sources synchronized to the FELs are located providing nanosecond or femtosecond pulses in UV, VIS and THz regime.

Unique user stations are those connected to FELICE, the free electron laser for intra-cavity experiments. In these two dedicated experiments (a FTICR mass spectrometer and a molecular beam machine) the intensity at the point of the

Beam parameters	Value
Spectral range [cm <sup>-1</sup> ]	6.6 - 3500 cm <sup>-1</sup> (0.2 - 100 THz)
Tunability [%]	200 - 300
Pulse structure:	5 - 10 μs, 10 Hz / 1000
Micropulse/micropulse	or 25 MHz or single pulse
Micropulse energy [µJ]	0.5 - 30
Spectral width [%, rms]	0.2 - several
Micropulse duration	Transform limited, tunable
Peak Power [MW]	up to 100
FEL mode	TEM_00
Polarization	Linear





experiment is up to a factor of 100 higher compared to the conventional outcoupling.

The combination of infrared and THz radiation from the FELs and the high magnetic fields of the neighboring high filed magnet laboratory (HFML) enables infrared and THz spectroscopy in quasi continuous fields up to 33T (45T in 2018).

#### Contact

FELIX Laboratory Radboud University Toernooiveld 7c 6525 ED Nijmegen The Netherlands Tel: +31 24 3653935 Email: felix@science.ru.nl http://www.ru.nl/felix/

## FERMI

FERMI is a state of the art Free Electron Laser (FEL) source, based on a high gain harmonic generation free electron laser. The FEL is seeded in the UV by a tunable solid state laser system. The seed is multiplied in frequency in the FEL cascade extending the operation in the VUV soft X-ray range of the spectrum. Two FEL undulator lines, FERMI FEL-1 and FEL-2, are optimized to deliver radiation in the ranges 100-20 nm and 20-4 nm respectively.

Seeded operation ensures control of the FEL spectrum, pulse duration and synchronization with conventional laser sources for pump and probe applications. Synchronized radiation pulses of duration less than 100 fs, characterized by unprecedented spectral purity and stability for this class of lasers are available.

Nominal parameters of FEL-1 and FEL-2 are shown in the table; both lines have reached the expected performance and are open to external users. In the first 5 calls for proposals at satotal of 265 proposals for experiments were submitted, with an oversubscription rate of about 3.5 in the last call.



Activities with users are characterized by a high degree of interaction and collaboration, which has stimulated the development of several new operational schemes, for example two color experiments based on FEL pump and FEL probe pulses. A portion of the seed laser is transported to the experimental station as a user laser in the IR or UV, with unprecedented time jitter values between the user laser and the FEL, namely less than 6 fs.

Photon Beam Parameters	FEL-1*	FEL-2*
Photon Energy (eV)	12.4 – 65	65 -310
Average pulse energy [µJ]	200 – 25 **	100 – 10 **
Pulse duration [fs] (FWHM)	100 – 50	60 – 20
Peak power [GW]	3 - 0.4	2.5 - 0.4
Repetition rate [Hz]	10 - 50	
FEL mode	SEEDED, TEM	_00
Photon energy fluctuations	1 – 2	4 – 15
[meV][rms]		
FEL bandwidth $\Delta E/E$ [rms]	2.5-5 (x 10-4)	2-7 (x 10-4)
FEL bandwidth fluctuations	3 – 5	3 – 40
[%] [rms]		
Polarization	Linear Horizo	ntal
	Linear Vertica	l
	Circular Left	
	Circular Right	

- \* The value in the range depends on wavelength, polarization and seed pulse settings.
- \*\* Higher values can be obtained at the cost of a longer pulse duration and a broader spectral distribution.

#### Contact

Elettra - Sincrotrone Trieste S.C.p.A. S.S. 14 Km 163,5 in AREA Science Park IT-34149 Basovizza, Trieste, Italy Tel: +39 040 37581 Fax: +39 040 9380902 Email: fpo@elettra.eu http://www.elettra.eu/lightsources/fermi.html

## FLASH

FLASH (Free Electron Laser in Hamburg), is the world's first FEL designed and constructed for the extended ultraviolet and soft X-ray spectral range (XUV) by the Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. Since 2005 this facility has been providing extremely bright, coherent and ultra-short XUV pulses for a broad science programme conducted by scientists from all over the world. FLASH has also served as a pilot facility for the European XFEL which has been under construction in Hamburg since 2009 and is based on the same accelerator technology.

FLASH is a high-gain FEL which achieves laser amplification and saturation in a single pass of a relativistic electron packet through a magnetic structure called undulator. The electron bunches are produced in a short-pulse laser-driven photo injector and accelerated by a superconducting linear accelerator. The superconducting technique allows to accelerate thousands of bunches per second which is not possible with other technologies. The lasing process is initiated by spontaneous radiation in an undulator, and brought to saturation by the self-amplified spontaneous emission (SASE) process. Femtosecond coherent light pulses with 10<sup>11</sup> to 10<sup>14</sup> photons per pulse are produced with tunable wavelengths in a range of approximately 4 - 50 nm.

Between 2011 and 2015 the FLASH facility has been extended with a second free electron laser line, FLASH2, which covers essentially the same spectral range as FLASH1. In spring 2016 the first two beamlines in the new experimental hall have become operational, making it now possible to run two experiments simultaneously on FLASH1 and FLASH2, both delivering intense, ultra-short laser pulses with different user-specific parameters.

Just behind the FLASH1 undulator, an additional planar electromagnetic undulator with ten periods can be used to create strong, coherent THz radiation pulses with pulse energies up to 100  $\mu$ J which are strictly synchronous with the FEL pulses and can be combined with them on a sample with variable time delay. Ultrafast optical laser systems synchronised with the FEL are also available for the experiments.

Beam parameters	Value
Photon energy [eV]	25 - 300
Average FEL pulse energy [µ]	10 - 500
Pulse duration [fs] (FWHM)	<50 - 200
Peak power [GW]	1-3
Spectral width [%] (FWHM)	0.7 – 2
Number of pulses	10 - 6000 (in bunch
per second	trains at 10 Hz)
FEL mode	SASE
Polarisation	Linear (horizontal)

#### Contact

Deutsches Elektronen-Synchrotron DESY Notkestrasse 85 22607 Hamburg, Germany Tel: +49 40 8998 2769 Fax: +49 40 8998-3282 Email: photon-science@desy.de http://flash.desy.de





## LUNEX FELs-of-Europe

LUNEX5 (free electron Laser Using a New accelerator for the Exploitation of X-ray radiation of 5<sup>th</sup> generation) is a project of advanced and compact Free Electron Laser (FEL). It aims at investigating the production of short, intense, coherent Free Electron Laser (FEL) pulses in the 40-4 nm spectral range (on the first, third and fifth harmonics). It is a collaboration of different partners : Synchrotron SOLEIL, LOA (CNRS/Palaiseau), PhLAM (Univ. de Lille-CNRS), LAL (CNRS-IN2P3, Orsay), CEA/IRAMIS and IRFU, LCPMR (Univ. Paris VI/CNRS, Paris) and ESRF.

It comprises two different types of accelerators. A 400 MeV superconducting linac (SC) with 2-3 modified XFEL type cromodules at 1.3 GHz (fed with solid state amplifiers) will enable a CW operation for high repetition rate (10 kHz) and multiple users. The electron bunch is compressed thanks to a dogleg with sextupoles, enabling phase space linearization and cancellation of the second order dispersion. The gun will be either superconducting or APEX type. In addition, using a LWFA for FEL will be explored, requiring a specific beam transfer line to handle the divergence (1 mrad) and energy spread (1%). The superconducting linear accelerator is adapted for studies of advanced FEL schemes. A Laser Wakefield Accelerator (0.4 -1 GeV) is also considered as an advance compact accelerating concept, to be qualified by the FEL application.

The single FEL line with different cryo-ready undulator segments of 15 mm (radiators) and modulators of 30 mm period will allow Echo Enable Harmonic Generation (echo) and HHG seeding to be compared for further handling of the spectral and temporal properties. SC linac based FEL calculations anticipate more than 10<sup>11</sup> photons/pulse and 10<sup>27</sup> peak brightness on the fundamental wavelength. Two pilot user experiments in gas phase and condensed matter will qualify the FEL performance in the different cases.

After the completion of the LUNEX5 Conceptual design Report at the end of 2011, complementary studies and R&D are under way. In the frame of two ERC Advanced Grants COXINEL and X-Five, test experiment for the demonstration of 180 MeV LWFA based FEL amplification at 200 nm is under preparation, thanks to a proper electron beam manipulation enabling to handle the large divergence and energy spread of LWFA beam: electrons are first strongly focused thanks to a variable permanent magnet quadrupole of variable strength. The electrons are sorted in energy thanks to a magnetic chicane, and the focus of the electron bunch slices, where correlation between position and energy has been introduced, is synchronised with the advance of the optical wave.

Specific hardware is also under development such as a cryo-ready 3 m long undulator of 15 mm period and 1.65 T at 3 mm gap (under the frame of the SOLEIL/VR collaboration), the permanent magnet quadrupole of variables strength (200 T / m) which concept was patented (QUAPEVA program-Triangle de la Physique, SOLEIL/Sigmaphi collaboration). The study and test of an elementary RF unit with sc cavity, low level RF and solid state amplifier for CW operation is launched (SESAME Ile de France, partners: SOLEIL, LAL, IFRU, ALSYOM, Thalès, Sigmaphi Electronics).

The photonic time-stretch strategy combined to usual electron bunch length measurement technique based on the spectrally encoded electro-optic sampling detection enables single-shot recordings up to 88 MHz, as tested experimentally with the Coherent Synchrotron Radiation pulses on the AILES beamline at SOLEIL and to be applied for LUNEX5. A new method for characterizing the temporal properties of the radiation emitted by LUNEX5 even in the presence of partial longitudinal coherence has been developed. The measurement scheme relies on laser-dressed XUV photoionization: the evolution of the shot-averaged photoelectron spectrum with the laser/XUV delay provides a two-dimensional spectrogram. The statistical properties of the XUV pulses accumulated during the measurement are then extracted from this spectrogram using a phase-retrieval algorithm.

#### Contact

Synchrotron SSOLEIL L'Orme des Merisiers Saint-Aubin BP 48 91192 GIF-sur-YVETTE CEDEX, France Tel: +33 1 69 35 90 00 Email: webcom@synchrotron-soleil.fr http://www.synchrotron-soleil.fr/

## MAX IV FEL

The MAX IV Laboratory (http://www.maxlab.lu.se) in Lund, Sweden, is currently operating three storage rings for synchrotron radiation. An upgrade of of the laboratory is currently being built containing two low emittance storage rings at 1.5 and 3 GeV and a 3 GeV linear accelerator. The new MAX IV will go into operation in 2016. A free electron laser is planned to become a part of the MAX IV facility and is created in two phases.

In the first phase a Short Pulse Facility (SPF) driven by the 3 GeV linac system is built. Here, short and highly brilliant X-ray pulses will be produced by spontaneous radiation in undulators and fed to the FemtoMAX beamline (https://www. maxlab.lu.se/femtomax). The MAX IV FEL is planned as a second phase, but has not been funded to date. An extension of the linac up to 5-6 GeV is foreseen as driver of the X-ray FEL.

The MAX IV linac system was installed in 2013 and is to a large extent already adapted to be expanded into a driver of an FEL. A low emittance photo cathode gun is used as injector and two bunch compressors reduce the bunch length below 100 fs. Preliminary design of an FEL system targets wavelengths in the Ångström region, pulses shorter than 100 fs, seeding and multi GW peak power. Branch lines will be able to produce soft X-rays in the nanometer range. The envisaged FEL system will be utilizing the main components of electron gun, gun lasers, linac system, bunch compressors already installed in the 300 m MAX IV tunnel. The additional investments should thus be relatively moderate to achieve a full FEL.

For more than 20 years, development of FEL techniques has been performed at MAX-lab (now the MAX IV Laboratory). From coherent harmonic generation at the MAX I storage ring via harmonic generation and seeding at the FEL test facility on a 400 MeV linac system and now the commissioning of the SPF and highly compressed low emittance electron pulses at 3 GeV.

#### Contact

MAX IV Laboratory Ole Römers väg 1 223 63, Lund, Sweden Tel: +46-(0)46-222 98 72 Fax: +46-(0)46-222 00 00 Email: maxlab@maxlab.lu.se https://www.maxlab.lu.se/maxiv



#### POLFEL

The Polish free electron laser (POLFEL), will provide tunable coherent electromagnetic radiation in the range from several nanometers (Soft X rays, SX) to several hundred micrometers (Terahertz radiation, THz). The radiation of free electron lasers (FEL) is emitted in impulses, which last from a few femtoseconds for SX to tens of picoseconds for the THz range, with peak power of the order of 1 GW over the whole range of the frequency spectrum.

As one of the few free electron lasers, the proposed source will be able to switch to the emission of high average power of the order of several tens of watts over its entire operating range. For the most part of this range it will be one of the most powerful sources of coherent radiation. POLFEL will complement the capabilities of conventional lasers by extending the available spectrum and will provide transverse and longitudinal coherent light, which is impossible for synchrotrons. It will also provide higher intensity by several orders of size and magnitude and pulse durations from 10 to 10 000 times faster than existing sources.

POLFEL will consist of three parts: the electron accelerator, an undulator (where the scattered electrons emit radiation), and the experimental stations. POLFEL's linear accelerator will employ the TESLA technology, which was used in the FLASH laser accelerator and is currently being used in the construction of the European X-FEL, and is planned for the future lepton collider for particle physics, ILC. Undulators which can produce light with variable linear polarization plane and direction of the axis of elliptical polarization will be installed in POLFEL. Achieving the planned wavelength range requires the construction of an accelerator which is capable of giving electrons an energy of several hundred mega electron volts, the associated undulators and several experimental systems designed to operate in the appropriate ranges of wavelength will be required to exploit the experimental possibilities fully.

The construction of POLFEL will be divided into two stages. In the first stage, a source will be created, capable of emitting radiation in the range from the infrared to terahertz wavelengths. It will be equipped with an accelerator with a final energy of 50 MeV, two undulators and an experimental line. The first stage of this project will discover new optimizations which will be used in further phases. A possible development will be to perform experiments exploiting the unique capabilities of the NCBJ center in Swierk by creating a laboratory that uses both FEL photon beams and neutrons produced in the MARIA nuclear reactor. POLFEL beamlines will be open to users from both Poland and abroad.

#### Contact

Narodowe Centrum Badań Jądrowych ul. Andrzeja Sołtana 7 05-400 Otwock Tel: +48 22 71 80 001 Fax: +48 22 77 93 481 Email: ncbj@ncbj.gov.pl http://polfel.pl

#### SPARC FEL

SPARC FEL was approved and funded in 2003 by the Italian Ministry of Research in the framework of the national strategic research program (FISR) shared by INFN and ENEA, and got additional support by the EuroFEL project within the 6<sup>th</sup> Framework Programme of the EU. The test facility is now completed, hosting a 150 MeV electron beam linac which feeds a 12-metres-long undulator. More recently (2012) SPARC has been included in the SPARC\_LAB facility.

The SPARC\_LAB facility (Sources for Plasma Accelerators and Radiation Compton with Lasers And Beams) is an interdisciplinary laboratory with unique features in the world. Born from the integration of a last generation photo-injector (SPARC), able to produce electron beams up to 200 MeV energy with high peak current (>1 kA) and low emittance (<2 mm-mrad), and of a high power laser (> 200 TW) (FLAME), able to produce ultra-short pulses (<30 fs), SPARC\_LAB has already enabled the development of innovative radiation sources and the test of new techniques for particle acceleration using lasers.

In particular the following highlight results have been achieved:

 a Free Electron Laser has been commissioned producing coherent radiation tunable from 500 nm down to 40 nm in various regimes of operation like: SASE, Seeding, Single Spike, Harmonic Generation and Two Colors;

- a source of both broad band, narrow band (< 30 %) and high energy (> 10 μJ) THz radiation has been tested, experiments with users have been successfully conducted;
- electrons have been accelerated up to 100 MeV in 4 mm long plasma wave excited by the high power laser FLAME;
- the electrons and photons beams have been synchronized at the scale of hundreds of fs, an essential requirement for the recent successful operation of the X-rays (~ 50 keV) Thomson back-scattering source and for the future investigation of new ultra-compact acceleration techniques (> 1 GV/m) based on external injection of high quality electron beams in a plasma wave driven both by Laser or Electron beams.
- A FEL experiment driven by a plasma accelerator is in preparation.

#### Contact

Massimo Ferrario INFN Frascati, Via E. Fermi, 40, 00044 Frascati, Italy Tel: +39 06 94032216 Email: massimo.ferrario@lnf.infn.it http://www.lnf.infn.it/acceleratori/sparc\_lab/SLmaps.php/

SPARC LAB facility layout: the 1.6 cells S-band RF gun (1) is followed by the three S-band accelerating sections (2), a THz radiation source (3) and a RF-Deflector (4). Four beamlines are downstream the dipole (5), devoted to FEL physics (6a) both in SASE and Seeded configuration (6b), beam diagnostics based on THz radiation (7a) and Electro-Optical Sampling (EOS) (7b), plasma acceleration (8) and X-rays radiation source by Thomson scattering (9) using the FLAME laser (10). The EOS laser is split from the Photocathode laser system (11), and delivered by an optical line (12).



#### SWISSFEL

The new X-ray laser project known as SwissFEL, will extend PSI's unique platform of large interdisciplinary research facilities to serve international research teams from universities and industry. SwissFEL is an essential part of PSI's strategic focus and will establish Switzerland's leading position in scientific research for years to come. It will attract top scientists from all over the world and enhance PSI's acknowledged position as a world-class research institute. Furthermore, the new high-tech facility will provide an incentive for Swiss industry through which existing highly-qualified jobs can be maintained and new ones created.

Based on the SwissFEL science workshop series, input from the PSI departments and international review committees, the science case ("SwissFEL Science Case") was published in 2009.

The SwissFEL project was finally approved by the Swiss Parliament in December 2012 and the building permit acquired in January 2013. In March 2013, construction began, with the official laying of the foundation stone on the 3<sup>rd</sup> July 2013.

The technical design of SwissFEL has to keep a delicate balance between the demand from experimentalists for breathtaking performance in terms of photon beam properties, on the one hand, and essential requirements for a user facility, such as confidence in technical ability, reliable and stable functioning, and economy of installation and operation, on the other hand. The baseline design aims to produce FEL pulses covering the wavelength 1 Å - 70 Å, with a compact and economic design which is affordable on the scale of a national laboratory.

In order to meet both the performance requirements and the cost constraints, substantial technical developments for some key components are underway to push their performance beyond the present state of the art:

- A newly developed 2.5 cell RF gun
- A wavelength-tunable RF Photo-electron-gun laser system
- Development of solid-state power modulators on a large scale for the
- LINAC RF sources.
- Adaptation of the C-band RF technology
- Construction of in-vacuum undulator technology with an unprecedented short magnet period for this kind of applications for the hard X-ray beamline
- Design of new undulators is based on APPLE II technology, with the capability of full polarization control, for the soft X-ray beamline

The construction of the SwissFEL project is progressing very well. The project will be realized in 2 phases: Phase 1, a hard X-ray beamline ("Aramis", wavelength 1 - 7 Å; with 3 experimental stations), will be completed by 2016, with routine user operation in 2017, and Phase 2, a soft X-ray beamline ("Athos", wavelength 7 - 70 Å; with 3 experimental stations), will be completed by 2018.

#### Contact

Paul Scherrer Institut 5232 Villigen PSI Switzerland Tel: +41 56 310 21 11 Fax: +41 56 310 21 99 http://www.psi.ch/swissfel/



## TARLA

TARLA (Turkish Accelerator And Radiation Laboratory at Ankara) is located in the town of Gölbasi, near Ankara. The construction of the laboratory building was finished in May 2011. The site also hosts the Institute of Accelerator Technologies (IAT).

TARLA is based on a 40 MeV super conducting electron beam (using two 20 MeV SRF modules) and the electron source is a 300 keV thermionic electron gun. There will be two buncher cavities (260 MHz and 1.3 GHz) to establish the desired time structure. Two undulators of 90 mm and 25 mm period will be installed to form two optical resonators.

The obtained laser light will be delivered to 5 experimental stations. At the current time, the thermionic electron gun has been manufactured and being tested. Contracts for the SRF modules and a He plant were signed in June 2012 and they will be delivered within 24 months. Work on the rest of the beam line is ongoing.

TARLA's first FEL line (u25) is expected to start commissioning by 2018 and will be ready by 2019, the second line (U90) will be ready by the end of 2020 / beginning of 2021.

Beam parameters	Value
Photon energy [eV]	0.4 - 0.5xE-2
Expected laser pulse length	0.5 - 6 ps (depending on wavelength)
Makropulse repetition	1Hz> CW
Makropulse Duration	40 μs> CW
FEL mode	Oscillator

## Contact

Ankara University Institute of Accelerator Technologies Golbasi Kampusu 06830 Golbasi / Ankara, TURKEY Tel: +90 (312) 485 37 45 Fax: +90 (312) 484 74 56 http://tarla.org.tr/

Coordination Rafael Abela

Layout and printing Paul Scherrer Institut

Available from FELs of Europe www.fels-of-europe.eu

Copying is welcomed, provided the source is acknowledged and an archive copy sent to FELs of Europe.

January 2015
