WavemiX 2021

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Paul Scherrer Institut

Book of Abstracts

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Welcome Day 1

Corresponding Author: majed.chergui@epfl.ch

WavemiX Network

Corresponding Author: cristian.svetina@psi.ch

Perspective on FEL based WM

Author: Claudio Masciovecchio[1]

[1] *Elettra - Sincrotrone Trieste*

Corresponding Author: claudio.masciovecchio@elettra.eu

In this paper, we will discuss how recent advances in the performance of the FELs allowed non-linear experiments at sub-optical wavelengths. In particular Second Harmonic Generation (SHG) [1] and Transient Grating (TG) [2] experiments have finally demonstrated the high potential of VUV/soft X-ray wave mixing techniques. TG experiments at sub-optical wavelength are relevant for the study of nanoscale dynamics in disordered systems as well as in semiconductors. Exciting phonon modes with nanometer wavelength would allow shedding light on a plethora of scientific open problems ranging from the thermal anomalies in glasses to understanding nanoscale thermal transport [3]. Wave mixing in the soft X-ray could be used as well to investigate drug/target intermolecular vibrational dynamics [4], or to measure natural circular dichroism signals [5].

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[2] F. Bencivenga et al., Adv. In Phys., vol. 63, pp. 327, May 2015.
[3] F. Bencivenga et al., Science Adv. vol. 5, pp. 5805, July 2019.
[4] R. Mincigrucci et al., submitted
[5] C. Masciovecchio et al., in preparation

Nanoscale Magnetic Gratings Generated and Probed by Femtosecond EUV Pulses

Author: Jude Deschamps[1]

[1] *MIT*

Corresponding Author: jdesch@mit.edu

The capability to conduct extreme ultraviolet (EUV) transient grating (TG) experiments at the TIMER beamline at FERMI opens multiple avenues for studying ultrafast dynamics of condensed matter on

the nanoscale. In the first EUV TG experiments [1], the signal was dominated by the thermoelastic response of the sample. A very recent study [2] showed that with a probe wavelength tuned to an absorption edge of a transition metal element, TG measurements become sensitive to dynamics of the electronic and spin systems. In particular, Ref. [2] described the first observation of nanoscale transient gratings of magnetization. In this talk, we will discuss further experiments with magnetic transient gratings conducted at the TIMER beamline in summer 2020. Similarly to the initial experiment, we used a probe wavelength of 20.8 nm tuned to the M-edge of Co; the excitation wavelength was either 20.8 or 41.6 nm, yielding TG periods of 44 and 87 nm. By using a polarizing mirror placed behind the sample, we demonstrate that the diffraction signal from the magnetization grating is polarized orthogonally to the incident linearly polarized probe beam. Consequently, the magnetic TG signal can be separated from non-magnetic thermoelastic and electronic responses. Our measurements reveal drastic differences between the magnetic TG responses from Co-Ni and Co-Pt multilayers and those from a CoGd alloy. Furthermore, we observe a highly unusual dependence of the magnetic TG decay dynamics on the TG period and excitation energy. We also observe an unexpected dependence of the "coherent peak" on the magnetic field and the sense of the circular polarization of the excitation pulses, possibly suggesting a spin-sensitive nonlinear optics process.

[1] Bencivenga, F., *et al.* Nanoscale transient gratings excited and probed by extreme ultraviolet femtosecond pulses, Sci. Adv. **5**, *eaaw5805* (2019).
[2] Ksenzov, D., *et al.* Nanoscale Transient Magnetization Gratings Excited and Probed by Femtosecond Extreme Ultraviolet Pulses, arXiv:2009.13330 [cond-mat.mes-hall] (2020).

Nonlinear X-ray Spectroscopy: a novel probe for interfacial dynamics

Author: Michael Zuerch[1]

[1] *University of California, Berkeley*

Corresponding Author: mwz@berkeley.edu

Chemistry at interfaces is central to applications spanning energy science, catalysis, energy storage, the water-energy nexus, and solar fuel generation. Understanding this chemistry at the molecular scale remains a grand challenge, due to the complex nature of buried interfaces. This is largely due to the lack of reliable in situ characterization tools with the chemical and interfacial sensitivity needed to track chemical transformations and transport at these interfaces. Recently, soft X-ray Second Harmonic Generation spectroscopy (SXR-SHG) was demonstrated for the first time on carbon films [1]. Aside of surface-specific X-ray spectroscopy, SXR-SHG is highly promising for studying buried interfaces due to the high penetration depth, elemental selectivity, and extremely high interfacial sensitivity (1-3 atomic layers) while providing electronic structure information that is sensitive to chemical bonding, symmetry, and weaker interactions such as hydrogen bonding. In recent experiments we were able to quantify the interfacial bond geometry of an organic-inorganic interface with a precision of 0.1Å [2]. In addition, we studied the second-order phase transition in a polar metal and monitored the displacement of the alkali metal ions within the unit cell of the atomic lattice using SXR-SHG [3] as well as performing SXR-SHG polarimetry for anisotropy analysis [4]. The inherent femtosecond nature of the required highly intense X-ray pulses provides excellent prospects for time-resolved interfacial studies and our most-recent findings show that SXR-SHG can be expanded to wide availability using laboratory sources [5].

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Break

Spectral Shaping at the SwissFEL Soft X-ray Beamline Athos

Author: Sven Reiche[1]

[1] *PSI - Paul Scherrer Institut*

Corresponding Author: sven.reiche@psi.ch

Current developments of Free-electron lasers are going beyond the limited temporal and spectral coherence of Self-amplified Spontaneous Emission (SASE) FELs. The soft X-ray beamline Athos at SwissFEL addresses this by its unique layout and operation modes. This presentation gives an overview on the expected control of the spectral content in the FEL pulse from fully coherent signals with a narrow bandwidth to an ultra-wide bandwidth of the order of 10 percent.

Ultrafast X-ray Stimulated Raman and Diffraction for Probing Molecular Coherences at Conical Intersections

Author: Shaul Mukamel[1]

Co-authors: Keefer Daniel [1]; Cavaletto Stefano [1]

[1] *University of California, Irvine*

Corresponding Author: smukamel@uci.edu

X-ray laser sources provide unprecedented temporal and spectral resolutions, thereby enabling access to ultrafast phenomena during conical intersection dynamics. There, coherences emerge as a unique feature of the non-adiabatic passage. We present several spectroscopy techniques that are sensitive to these molecular coherences and provide different windows into their physics.

The first application is TRUECARS, where a hybrid broadband/narrowband probing scheme records the coherence signature free from the usually dominating population contributions. On the RNA-nucleobase uracil, we present the sensitivity of the TRUECARS signal to the underlying physics [1]. Through its Wigner representation, the signal directly maps the topology of the potential energy surface around the conical intersection explored by the wavepacket coherence and gives the vibronic energy distribution of the latter.
In the second application, time-resolved X-ray diffraction is simulated for the photoisomerization of azobenzene, a textbook photochemical process [2]. Besides monitoring the isomerization reaction via its diffraction patterns, mixed elastic/inelastic scattering from coherences emerges as a weak contribution in the total signal. This can be amplified by employing hard X-rays, realizing high momentum transfer amplitudes, where the coherence contribution is stronger. This signature gives access to the transient real-space molecular charge density, providing a movie of the conical intersection passage.

X-ray free-electron lasers (FELs) relying on the self-amplified spontaneous emission (SASE) mechanism generate stochastic x-ray pulses lacking phase control. This has represented a major bottleneck, since most time-resolved multidimensional nonlinear x-ray spectroscopy schemes are based on sequences of coherent, phase-controlled pulses. We show that suitable correlation signals averaged over independent realizations of stochastic FEL pulses can retrieve the same joint temporal and

spectral resolutions of signals with phase-controlled pulses [3]. This is demonstrated both for Raman spectroscopy and imaging signals described above and can be extended to additional complex multidimensional nonlinear x-ray spectroscopy experiments.

Time-Dependent Quantum Model for Attosecond X-ray Non-Linear Spectroscopy

Authors: Solène Oberli[1]; Antonio Picón[2]; Jordan T. O'Neal[3]; Elio G. Champenois[4]; Andre Al-Haddad[5]; Agostino Marinelli[4]; James P. Cryan[6]

[1] *Ecole Polytechnique Fédérale de Lausanne*

[2] *Departamento de Química, Universidad Autónoma de Madrid, Madrid 28049, Spain*

[3] *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA and Department of Physics, Stanford University, Stanford, California 94305, USA*

[4] *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA*

[5] *Paul-Scherrer Institute, CH-5232, Villigen PSI, Switzerland and Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA*

[6] *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA and Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA*

Corresponding Author: solene.oberli@epfl.ch

The recent capacity of X-ray free-electron lasers (XFELs) to produce ultrashort and intense X-ray pulses gives access to the observation of electron motion in molecules with high temporal (attosecond) and spatial (angström) resolutions. In the present study, we use a promising nonlinear technique called impulsive stimulated X-ray Raman scattering (ISXRS) to produce a coherent superposition of neutral excited electronic states in nitric oxide (NO) [1]. An attosecond X-ray pulse first core-excites the O atom, promoting a core electron to a $2\pi^*$ orbital. Before this short-lived core-excited state decays, a second photon is absorbed from the same X-ray pulse and creates a coherent superposition of neutral valence-excited states. A time-delayed femtosecond UV pulse probes the induced dynamics by ionizing the molecule, and the NO+ yield allows us to quantify the population transfer induced by the ISXRS process.
We developed a sophisticated quantum model to interpret this first experimental demonstration of ISXRS in a molecule. It is based on the time-dependent Schrödinger equation for the electrons, and takes into account the interaction of the X-ray pulse with the molecule, the Auger decay, as well as the strong electron correlation effects in the presence of a core vacancy. With this model, we are able to provide a quantitative and qualitative interpretation of the ISXRS process, as well as to characterize the X-ray pulse parameters. This work
demonstrates the possibility to induce electronic population transfer via ISXRS using a single attosecond X-ray pulse, and sheds light on the role of electronic coherences at the earliest stage of chemical processes. Moreover, this study is relevant for future two color attosecond X-ray pump / X-ray probe set-ups that will also permit to probe site-selectively the induced dynamics at a remote atom in the molecule. This joint experimental and theoretical investigation is thus a stepping stone towards studying electronic dynamics in more complex systems and opens a path for investigation of transient electronic phenomena in matter at XFEL facilities.

[1] J. T. O'Neal et al., Phys. Rev. Lett., 125 073203 (2020)

Resonant X-ray spectroscopy of selenophene with hard-X-ray pulses

Author: Stefano Cavaletto[1]

Co-authors: Daniel Keefer [1]; Shaul Mukamel [1]

[1] *University of California, Irvine*

Corresponding Author: scavalet@uci.edu

Due to their short wavelengths, hard-X-ray FEL pulses are sensitive to spatial variations within the size of the molecule. They can thus monitor the evolution of the molecular charge and current densities. This is shown for the resonant X-ray sum-frequency-generation (XSFG) signal of aligned selenophene molecules [1]. A wavepacket of valence-excited states, initiated by an XUV pump pulse, is monitored by 12-keV X-ray probe pulses resonant to the Se core states for variable time delays. The associated wavelength of the X-ray probe, $\lambda \sim 1$ Å, is comparable to the molecular size. By varying the propagation direction of hard-X-ray pulses, we predict observable changes in the XSFG signal, which can be attributed to the spatial dependence of the transition current densities in the molecule.

We further apply related time- and frequency-resolved X-ray Raman signals to monitor nonadiabatic molecular dynamics. By taking advantage of the correlations between the spectral components of the field, we show that high joint spectral and temporal resolutions can be achieved, without requiring phase control [2]. The approach can thus be applied with existing stochastic SASE FEL pulses.

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[2] S. M. Cavaletto, D. Keefer, and S. Mukamel, manuscript submitted (2020).

Coherent spectroscopy of high wave-vector phonons

Author: David Reis[1]

[1] *Stanford PULSE Institute*

Hard x-ray free-electron lasers have emerged as an invaluable tool for studying materials dynamics near and far from equilibrium. Advanced nonlinear x-ray methods will allow us to greatly expand on our ability to understand and control materials properties at the atomic-scale. In this talk I will present results of all time-domain x-ray scattering-based spectroscopies to study transient lattice dynamics in photo-excited materials spanning the Brillouin zone using both optical and x-ray excitation. Ultrafast optical excitation typically produces broad-band coherences in the mean-square displacements of the ions that we subsequently resolve in time and momentum via femtosecond diffuse scattering [1,2]. I will briefly discuss the mechanism of excitation [3] whereby we can measure the excited state phonon-dispersion [4] and momentum-resolved anharmonic decay channels [5] using photo-excited bismuth as an example. We have also shown that to some extent selective-excitation using optical pulses can be used to control which modes are excited [3,6]. Finally, I will discuss progress towards arbitrary x-ray selective excitation using atomic-scale transient gratings including preliminary results of x-ray pump, x-ray probe experiments on cubic perovskites.
This work was supported by the U.S. Department of Energy.
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Closing Session Day 1

Corresponding Author: majed.chergui@epfl.ch

Welcome Day 2

Corresponding Author: martin.beye@desy.de

X-ray Transient Grating & 2D Spectroscopy

Author: Keith Nelson[1]

[1] *MIT*

Corresponding Author: kanelson@mit.edu

There are a great many motivations for extending nonlinear wave mixing experiments to the x-ray spectral range. Many are based on high x-ray wavevectors which enable transient grating (TG) measurements with cor-respondingly high wave wavevector magnitude q, i.e. extremely short spatial periods $\Lambda = 2\pi/q$ formed by crossed x-ray beams. We have conducted EUV TG experiments in collaboration with the FERMI team at the TIMER beamline [1,2]. The signals reveal surface and bulk acoustic waves with wavelengths of tens of na-nometers (equal to Λ) and thermal transport from the heated TG peaks toward the unheated nulls across dis-tances given roughly by 1/q. Nanoscale thermal transport in insulators shows highly non-diffusive kinetics since most of the phonons that carry heat have nanometer mean free paths. Thermal transport may approach the ballistic limit at sufficiently short TG periods. We have also conducted experiments in which transient magneti-zation gratings are formed. We anticipate measurements with TG periods at or near those of modulated phases such as a charge-density or spin-density wave systems, allowing excitation of the characteristic modes in those phases.

Hard x-ray TG measurements using Talbot imaging of etched periodic patterns [3] are now possible. We con-ducted preliminary experiments at the SwissFEL BERNINA beamline, led by our conference organizer, with x-ray excitation and optical probing. All-x-ray experiments are anticipated, allowing

TG measurements deep with-in bulk samples. Phase-coherent 2D x-ray spectroscopy will also be possible. Even without reaching the highest wavevectors, measurements on molecular electronic transitions will reveal new information that cannot be ob-tained using optical wavelengths [4]. 2D x-ray spectroscopy of nuclear transitions should also be possible. Angstrom TG periods and coherent excitation of collective modes at zone-boundary wavevectors may become possible.

Hybrid forms of 2D spectroscopy can be conducted using colinear low-frequency pulse pairs or pulse sequenc-es and x-ray probes. This is 2D optical, IR, or THz spectroscopy with signals measured as x-ray diffraction (XRD), absorption, or induced emission which may reveal key information about the structural, electronic, or magnetic effects of phase-related excitation pulses at the lower frequency. Hybrid 2D spectroscopy of quantum phases may reveal the roles played by coupled degrees of freedom in excursions across the multiphase land-scape in particularly incisive ways.

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Research Opportunities with X-Ray Four-Waves Mixing Capability with FELss

Author: Nora Berrah[1]

Co-authors: Stephen Leone [2]; James Gaynor [2]; Daniel Neumark [3]

[1] *University of Connecticut*

[2] *University of CA Berkeley/LBNL*

[3] *University of Ca Berkeley/LBNL*

Four-waves mixing techniques (FWM), based on third-order non-linear photon-matter interaction, have been used as a very powerful methodology in the optical and recently in the XUV domains to uncover dynamics inaccessible by linear (one-dimensional) spectroscopy. The latter provides information about the frequencies absorbed by the molecule, but lacks detail about the individual transitions and their coupling. The coherent and multi-wave nature of the FWM technique has pushed forward basic scientific understanding as well as in the development of new technologies.
X-rays FELs provide an opportunity to extend FWM since they provide atomic specificity as well as temporal and spatial resolution. We will propose possible FWM experiments as well as discuss the experimental requirements.

Monitoring Conical Intersection Signatures with Time-Resolved X-Ray Spectroscopy and Enhancing Them w ith Qu antum Optimal Control

Author: Daniel Keefer[1]

Co-author: Shaul Mukamel [1]

[1] *University of California, Irvine*

Corresponding Author: dkeefer@uci.edu

Conical intersections are ubiquitous features in molecular photophysics that enable ultrafast relaxation channels. Wavepacket bifurcation in these regions gives rise to vibronic coherences, emerging as unique signatures of the non-adiabatic passage. Recently, we put forward several spectroscopy techniques to monitor these signatures on different molecular examples [1-3]. The signals are enabled by X-ray laser sources, available both from free-electron lasers and tabletop setups with different properties. Particularly, high temporal resolution provides access to the necessary timing windows of conical intersection passages, and a high bandwidth enables e.g. stimulated Raman processes between electronic states within a single pulse.

We present several time-resolved X-ray signals that exploit the capabilities of X-ray sources. The molecular examples range from small molecules with interesting photochemistry (uracil [1] and azobenzene [2]) to a large synthetic heterodimer with more than 100 atoms exhibiting photovoltaic properties [3]. Stimulated Raman and time-resolved diffraction signals are used to sensitively monitor vibronic coherences at conical intersections, retrieving different physical aspects.

In addition to this, we explore how quantum optimal control of the UV/Vis pump pulse can be employed to prepare the molecule in favourable states for spectroscopic detection. The coherence signatures are inherently weak and can be masked by the dominant population contributions. By shaping the pump pulse and thereby steering the molecular wavepacket, these signatures can be enhanced, allowing for better spectroscopic detectability.

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Phase cycling and coherent spectroscopy in the XUV domain

Author: Frank Stienkemeier[1]

[1] *University of Freiburg*

Corresponding Author: stienkemeier@uni-freiburg.de

In the visible spectral range, coherent nonlinear spectroscopy is an important concept for the real-time study of ultrafast dynamics in complex quantum systems [1]. Likewise, theorists have suggested numerous applications in the XUV and X-ray domain [2]. However, corresponding experiments have been hindered by severe technical challenges involved with XUV/X-ray optics. These include the demand for sub-cycle phase stability and background-free detection of weak nonlinear signals based on phase matching/phase cycling schemes.
We present a new concept facilitating XUV/soft X-Ray interferometry combined with phase cycling. The method relies on precise manipulation of the timing and phase properties of the fundamental laser field driving harmonic generation. This enables interferometric XUV-pump, XUV-probe experiments with high sensitivity while omitting any modifications of the XUV beamline. The approach is demonstrated for high harmonic generation (HHG) in a gas cell [3] and at a seeded free-electron laser (FEL) [4]. In the tabletop HHG experiment, narrow-bandwidth harmonics around 14 eV in argon and krypton are characterized with high resolution through fringe-resolved linear XUV autocorrelation measurements [3]. At the seeded FEL, XUV wave packet interferometry is performed to probe the coherence decay of an atomic inner-valence excitation (28eV) in real-time [4]. Furthermore, Interatomic Coulombic Decay (ICD) dynamics in the HeNe dimer are studied. The combination of wave packet interferometry and phase cycling opens up a palette of methodologies in a single experiment, ranging from high-resolution absorption spectroscopy to time-resolved photoelectron spectroscopy and multidimensional coherent methods.

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Open Discussions (via REMO

All WavemiX members

Bringing Transient Grating Spectroscopy into the X-ray regime

Authors: Jérémy Rouxel[1]; Cristian Svetina[2]

[1] *Université Jean Monnet*

[2] *PSI - Paul Scherrer Institut*

Corresponding Authors: jeremy.rouxel@univ-st-etienne.fr, cristian.svetina@psi.ch

Transient Grating Spectroscopy (TGS) is a versatile four-wave mixing technique that has been widely used in the optical regime. It notably provides information on transport and acoustic relaxation. We present how TGS can be extended into the X-ray range using the Talbot effect to generate the transient grating. We further explore how full X-ray pump and probe TGS can be implemented and the physical phenomena that we expect to access in that regime.

XUV transient grating spectroscopy of electronic dynamics in spinel cobalt oxide

Author: Hugo Marroux[1]

Co-authors: Camila Bacellar [2]; Gregor Knopp [2]; Oliviero Cannelli [1]; Flavio Capotondi [3]; Romain Geneaux [4]; Rebecca Ingle [5]; Riccardo Mincigrucci [6]; Giulia Mancini ; Filipo bencivenga [6]; Ludmila Leroy [1]; Emanuele Pedersoli [6]; Claudio Masciovecchio [7]; Laura Foglia ; Majed Chergui [8]

[1] *EPFL*

[2] *PSI - Paul Scherrer Institut*

[3] *Elettra Sincrotrone Trieste*

[4] *Université Paris-Saclay*

[5] *Department of Chemistry, University College London,*

[6] *Elettra Sincrotrone Trieste*

[7] *Elettra - Sincrotrone Trieste*

[8] *Ecole Polytechnique Fédérale de Lausanne*

Corresponding Author: hugo.marroux@epfl.ch

Four wave mixing experiments in the extreme ultraviolet were pioneered at the free electron laser FERMI.1 In these experiments two coherent FEL pulses are overlapped on the solid sample creating a transient grating pattern which time evolution is probed by diffracting a delayed visible pulse. On solid samples, the XUV excitation creates a complicated phonons dynamics which dominates the diffracted signal. Observing electronic dynamics using this technique is a challenge and only smalls effects have been observed so far.2
In this presentation we report on the monitoring of electronic dynamics induced by excitation at the cobalt M2,3 edge of a Co3O4 sample in its spinel structure. Excitation of the cobalt core-levels at 63.5 eV is followed by monitoring the first and second orders of a diffracted 400 nm beam. To confirm the core-level excitation the FEL photon energy is tuned bellow and above the cobalt M2,3 edge. The time evolution of the diffracted first order shows very little changes with the excitation energy. On the other hand, the second order of diffraction shows large changes in its time evolution depending if the excitation is performed bellow or above the cobalt edge. These changes are tentatively described in terms of the evolution of the spatial profile of the XUV transient grating. The results demonstrate a new sensitive probe to follow XUV induced electronic dynamics with high spatial and temporal accuracies.

Closing Session Day 2

Corresponding Author: martin.beye@desy.de

Welcome Day 3

Corresponding Author: claudio.masciovecchio@elettra.eu

Coherence effects in gas-phase nonlinear spectroscopy with SASE-FELs

Author: Thomas Pfeifer[1]

[1] *Max-Planck-Institut für Kernphysik*

Corresponding Author: thomas.pfeifer@mpi-hd.mpg.de

Nonlinear spectroscopy approaches have revolutionized entire science areas from physics&chemistry to biology and medicine. Based on the interaction with several mutually coherent fields, these methods now routinely operate throughout a major part of the electromagnetic spectrum from radio to UV with applications from nuclear-magnetic-resonance(NMR) imaging to the study of chemical dynamics in small and large molecules. They rely on the availability of intense light for (at least) interacting twice (two-photon-type) with a system of interest. Intense high-frequency light of FELs thus fulfills this important requirement, fueling the vision of site-specific pumping and probing of electron dynamics in molecules. Another frontier requirement towards unfolding the full potential of such x-ray nonlinear spectroscopy is the exploitation of coherent (or even quantum-)correlated interactions with high-frequency light fields. Impressive progress on this frontier has been achieved in recent years with seeded-FEL schemes, in particular FERMI@ELETTRA.

Here, we will discuss some recent experiments in which SASE FELs, in contrast to common expectation, are used to drive coherent interactions with gas-phase samples.

A first example is the strong-field dressing of Helium atoms in a Fraunhofer-type absorption experiment, where a modification of the absorption line shape was observed as a function of intensity [1]. This demonstrates XUV-driven phase control of an atomic resonance on a time scale shorter than the (17 fs) excited-state lifetime, manifesting in the interference of the driving FEL(sub-)pulses and the emitted light from the coherently excited atoms.

As a second result, a time-resolved transient-absorption experiment in Neon atoms based on a split-and-delay approach revealed a 2-fs coherence spike near time delay zero [2]. This was enabled by mutually coherent pump and probe pulses for each SASE shot, employing the spatial coherence in the FEL beam, enabled by an existing split-and-delay unit [3]. In addition, intensity-dependent Stark shifts on XUV transitions in Ne^{2+} atoms could be observed, indicating strong coupling at high frequencies.

Spectral interference structures were observed in the >1 eV probe spectrum near 50 eV transmitted through the Neon target [4]. Depending directly on the time delay between pump and probe pulses, this result is a proof-of-principle for realizing coherent pump-Stokes excitation scenarios directly with SASE FELs.

We propose a cooperative project within the scope of this workshop to drive the evolution of advanced single-shot based data-analysis methods to extract the key (phase) information from such measurements.

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Observation of resonant two-photon ionization of He via a doubly excited state using superradiant FEL pulses

Author: Michele Di Fraia[None]

Co-authors: Najmeh Mirian ; Simone Spampinati ; Oksana Plekan ; Filippo Sottocorona ; Enrico Allaria ; Laura Badano ; Miltcho Danailov ; Alexander Demidovich ; Giovanni De Ninno ; Simone Di Mitri ; Giuseppe Penco ; Primoz Rebernik ; Carlo Spezzani ; Giulio Gaio ; Mauro Trovò ; Nicola Mahne ; Michele Manfredda ; Lorenzo Raimondi ; Marco Zangrando ; Michael Meyer ; Tommaso Mazza ; Raimund Feifel ; Richard Squibb ; Xi Yang ; Matteo Bonanomi ; Robert Richter ; Marcello Coreno ; Antonio Picon ; Alicia Palacios ; Johannes Feist ; Matjaz Zitnik ; Giuseppe Sansone ; Jon Marangos ; Kevin Prince ; Luca Giannessi ; Carlo Callegari

Corresponding Author: michele.difraia@elettra.eu

High-brilliance Free Electron Lasers (FELs) greatly increase the range of accessible experimental conditions and physical phenomena for non-linear studies of atoms, molecules and clusters with VUV and soft X-ray radiation. The seeded Free Electron Laser FERMI in Trieste (FEL-1: 100–20 nm. FEL-2: 20–4 nm) [1] provides typical pulse durations from 90 to 20 fs [2]. However in order to track atomic and molecular dynamics occurring on a faster timescale (i.e. proton motion after ionization [3], isomerization in molecules [4], Auger decay processes in atoms [5]) or to exploit the effect of simultaneous absorption of photons by matter (i.e. collective ionization in clusters [6], double core-hole excitation [7]) the scientific community is pushing for even shorter pulses ideally below 10 fs. A recent innovative FEL operational scheme, superradiance [8], has demonstrated the generation of

few-femtosecond pulses at FERMI [9] further increasing the range of multiphoton, non-linear studies.
We will show how the compression of the pulses is achieved in such an operational scheme and how the temporal duration has been experimentally characterized by means of auto-correlation measurements with two-photon, above-threshold ionization of Ar. In addition, we present results of a first experiment on He performed at the Low Density Matter beamline [10] with superradiant pulses.
Two-photon ionization of He, via the resonant 2s2p doubly excited state [11], was investigated by photoelectron spectroscopy. The superradiant pulse duration was less than the lifetime of this intermediate excited state, allowing us to explore the physics of the resonant excitation. The spectra showed that in this system, two-photon ionization led mostly to excited final states, that is, He ions with an electron in a shell higher than 1s. This result is in excellent agreement with detailed calculations.
The experiments also showed that a common problem with two-photon ionization by FEL light, contamination by second harmonic radiation which creates a background for the two-photon signal, was not a significant problem for superradiant operation.
The success of this experimental campaign opens the possibility to implement the superradiant configuration as one of the operational modes of FERMI available for users' proposals.

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XUV-FEL chirp characterization by Transient Absorption Spectroscopy

Authors: Thomas Ding[None]; Christian Ott[None]; Thomas Pfeifer[None]

Corresponding Authors: thomas.ding@mpi-hd.mpg.de, christian.ott@mpi-hd.mpg.de

Having direct access to the spectro-temporal pulse characteristics of FEL pulses is a key ingredient for state-selective multidimensional spectroscopy at high photon energy which now comes into reach with next-generation XUV and x-ray FEL radiation sources. While the characterization of visible and infrared laser pulses is nowadays a matter of routine, a direct transfer of these concepts to XUV/x-ray FELs, which are based on the self-amplified spontaneous emission (SASE) process, remains challenging. One of the major difficulties is the lack in temporal/spectral coherence which complicates their synchronization to external timing references.

Here, we present a new self-referencing method for the spectro-temporal characterization of high-frequency SASE FEL radiation pulses. Without requiring any additional external fields, it is based on the technique of all-XUV split-beam pump-probe transient absorption spectroscopy and provides a combined high temporal and spectral resolution (≤1 fs relative timing stability with spectral resolving power E/ΔE ˜1500) over a 1-2 eV broad spectral bandwidth of probing photon energies. For this XUV-frequency sensitive timing tool we utilize sequential double ionization in neon via two XUV photons derived from the pump pulse and probe the ultrafast ionization dynamics in real time. We employ the near-instantaneous response of the target system due to ionization as an ultrafast temporal gate on the spectrally resolved probe pulse. This allows to extract the group-delay dispersion, that is, the time-delay vs. photon-energy relationship from a measured two-dimensional transient-absorption spectrogram. Thereby, our measurement revealed a pronounced linear chirp of about 30 fs² [**1**], while the method is also sensitive to higher orders of nonlinear chirp.

The characterization method presented here is not limited to the XUV domain nor to femtosecond time scales; it can be straightforwardly extended even to hard x-ray and attosecond pulses, and only requires an x-ray intensity-induced change of the absorbance properties of a moderately dense target medium, e.g., through nonlinear ionization of rare gas atoms [**2**].

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Resonance-enhanced XUV-NIR four-wave mixing

Authors: Robin Y. Engel[1]; Jan Schunck[1]

Co-authors: Piter S. Miedema [1]; Martin C. Borchert [2]; Siarhei Dziarzhytski [1]; Günter Brenner [1]; Marion Kuhlmann [1]; Naghita Ekanayake[1]; Ulrich Eichmann [2]; Daniel Schick [2]; Clemens von Korff Schmising [2]; Stefan Eisebitt [2]; Martin Beye [1]; Horst Rottke [2]

[1] *DESY*

[2] *Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie*

Corresponding Authors: robin.engel@desy.de, jan.schunck@desy.de

While wave-mixing processes are widely exploited in the IR and optical regime, attempts to mix IR/optical photons and XUV or soft X-ray photons have hitherto been hampered.
A spectroscopy based on sum- and/or difference-frequency generation (SFG/DFG) around soft X-ray or XUV resonances promises, like Resonant Inelastic X-ray Scattering (RIXS), detailed spectroscopic insights on low-energy excitations within the material of interest, while overcoming the critically low signal levels that constitute the core limitation of RIXS.
We show preliminary results of an experiment at the free-electron laser in Hamburg (FLASH) on lithium fluoride (LiF) observing both SFG and DFG involving one XUV photon around the Li+ 1s-2p resonance (62 eV) and two 800 nm NIR photons in reflection from a LiF single crystal ($\omega = \omega_{XUV} \pm 2\omega_{IR}$). Within the experimental sensitivity, the corresponding processes involving the mixing of only one optical photon with an XUV photon ($\omega = \omega_{XUV} \pm \omega_{IR}$) were not observed.
We observe SFG and DFG during temporal overlap of the XUV and IR laser pulses as well as a strong dependence on the XUV photon energy explainable through the presence of the core level excitonic resonance. To develop an understanding of the wave-mixing process involving NIR and XUV photons, we discuss the role of material resonances and phase matching conditions as well as upcoming experimental efforts to explore them further.

Break

Challenging previous findings on x-ray parametric down conversion

Authors: Christina Boemer[1]; Dietrich Krebs[1]

[1] *DESY*

Corresponding Authors: christina.boemer@desy.de, dietrich.krebs@desy.de

We present both theoretical and experimental insights on parametric down-conversion of x-ray photons into (pairs of) x-ray and optical photons. This three-wave mixing process promises to combine the high-resolution capabilities of x-ray diffraction with features of optical-domain spectroscopy. In particular, it offers the prospect of valence-selective probing for solid-state systems.
The detection of x-ray parametric down-conversion is challenging, however, as the nonlinear signal is weak and occurs in close proximity to strong elastic background. In order to clearly distinguish these contributions and thus obtain conclusive evidence of down-conversion, we emphasize the necessity to detect the effect's characteristic phase-matching signature.
Investigating the scattering signal beyond qualitative considerations, we introduce a theoretical description of parametric x-ray optical wave mixing processes, which we apply to the case of down-conversion.
Our simulations confirm the characteristic signature, but conclude very low conversion efficiencies at the same time.
Addressing this challenge, we present the development of an experimental setup that offers a broad acceptance for collecting the down-converted signal while suppressing the elastic background through multiple crystal reflections. Applying our setup ultimately, we do not find measurable evidence of the nonlinear effect, which corroborates the low conversion efficiencies predicted by our theory. On the other hand, our findings challenge previous claims on the effect's observation, which notably abstained from showing the characteristic signature.
For future resolution of the search for parametric down-conversion, we give an outlook to the development of alternative detection schemes.
In addition, we consider the prospect of stimulating the effect, which would amount to x-ray optical difference frequency generation.

Projects short presentation

Corresponding Authors: darya.gorelova@uni-hamburg.de, jacopostefano.pellicresi@elettra.eu, j.marangos@imperial.ac.uk, wojciech.blachucki@ifj.edu.pl

Round Table

All WavemiX members

Closing Session and Remarks Day 3

WavemiX Panel