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Ultrafast Structural Dynamics

Scientific program and abstracts



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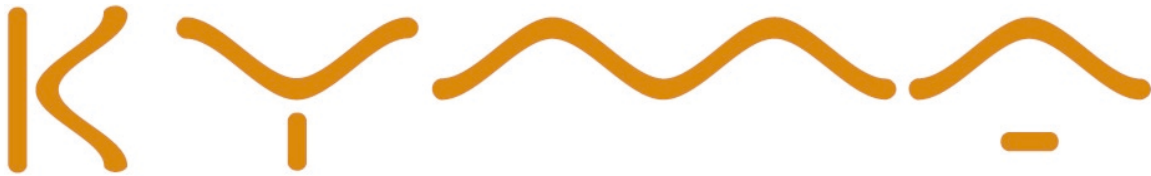
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ICUSD 2017 Scientific Program

Tuesday, 5 December 2017

12:00 Registration

Opening Session

14:00 Welcome (prof. A. Franciosi, C. Masciovecchio)

Session A: Novel photon coherent sources and methods (chair G. De Ninno)

14:30 Giulia F. Mancini - Revolutionary new nano-imaging and coherent scattering: harnessing the power of short wavelength EUV light

15:10 Philippe Jonnard - Stimulated emission in MgO following irradiation by EUV FEL pulses at FERMI

15:40 Primož Rebernik Ribič - Generation of intense femtosecond optical vortices in the extreme-ultraviolet

16:10 coffee break + POSTER SESSION

Session B: Advances in ultrafast electron sources (chair M. Kiskinova)

17:20 Ralph Ernstofer - Accessing microscopic coupling in solids with momentum resolving ultrafast techniques

18:00 Yuya Morimoto - Microscopy and diffraction with attosecond electron pulse trains

18:30 Henrike Müller-Werkmeister - Direct observation of reaction dynamics by femtosecond electron diffraction

19:00 Christoph Hauf - Soft-mode driven ferroelectric switching mapped by ultrafast x-ray diffraction

Wednesday, 6 December 2017

Session C: Ultrafast multidimensional spectroscopies (chair: F. Parmigiani)

8:30 Peter Hamm - 2D-IR spectroscopy at its best: structure and dynamics of molecules immobilized at solid/liquid surfaces

9:10 Hugo Marroux - Combining attosecond EUV pulses and shaped near infrared pulses: Multidimensional 4 wave mixing spectroscopy

9:40 Federico Cilento - Time-resolved XUV photoemission: a new clue for understanding the ultrafast dynamics in copper oxides

10:10 Jonathan Tollerud - Multidimensional spectroscopy with weak-pulses reveals unexpectedly large coherence length of excitons in a quantum well

10:40 coffee break

Session D: Structural dynamics in biomolecular systems (chair F. Capotondi)

11:00 John Spence - Imaging dynamic of radiation-sensitive molecules

11:40 Heinrich Schwoerer - Photo-induction of the insulator to metal transition in the organic mono-crystal Cu(Me,Br - DCNQI)₂ as studied by UED

12:10 Jan Helbing - Ultrafast deep-UV 2D and transient CD-spectroscopy of peptide backbone conformation

12:40 lunch

Session E: Solid state structural dynamics (chair F. Bencivenga)

14:00 Giovanni Vanacore - Unraveling the ultrafast dynamics of spatially confined phonons and plasmons in low-dimensional nanosystems

14:40 Emmanuelle Jal - Structural dynamics during laser-induced ultrafast demagnetization

15:10 Christopher Nicholson - Ultrafast dynamics of bands and bonds during a photo-induced structural phase transition at a surface

15:40 coffee break

Session F: EUV and X-ray nonlinear spectroscopies (chair M. Coreno)

16:00 Filippo Bencivenga - EUV-transient grating experiments at the nanoscale

16:40 Royce Lam - Soft X-ray second harmonic generation as an interfacial probe

17:10 Thomas Northey - Ultrafast X-ray absorption spectroscopy using direct quantum dynamics

17:40 visit to FERMI

20:15 Social Dinner

Thursday, 7 December 2017

Session G: Ab-initio simulations of nonequilibrium condensed matter (chair E. Princi)

9:00 Davide Sangalli - Pump and probe experiments from first principles

9:30 Pietro Tozzi - Confined plasmons at extreme temperatures: theory and possible experiment

ROUND TABLE

10:00 Round Table

10:40 coffee break

Session H: Magnetism and strongly correlated systems (chair: G. Ghiringhelli)

11:00 Michele Buzzi - Pressure tuning of light-induced superconductivity in K₃C₆₀

11:40 Alexandre Marciniak - Vibrational control of d-d transitions in the model cuprate CuGeO₃

12:10 Francesca Giusti - Optical control of the superconducting gap in optimally doped B2212 with mid-infrared pulses

12:40 Ganesh Adhikary - Orbital-dependent ultrafast electron dynamics in Fe-pnictide superconductors

13:00 lunch

Session I: Femtochemistry in biomolecular systems (chair: F. Cilento)

14:20 Albert Stolow - Ultrafast nonadiabatic molecular dynamics via time-resolved valence and inner shell spectroscopies

15:00 Maria Ekimova - Hydrogen bonding structure of aqueous ammonia and ammonium probed with IR and X-ray spectroscopy

15:30 Carino Ferrante - Direct observation of ultrafast processes in conjugated molecules through femtosecond stimulated Raman spectroscopy

16:00 Kyle Wilkin - Photodissociation dynamics of 1,2-diiodotetrafluoroethane captured with femtosecond gas phase electron diffraction

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Invited Talks

EUV-transient grating experiments at the nanoscale

Filippo Bencivenga¹

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Nonlinear optical methodologies at sub-optical wavelengths have waited to be implemented till the recent development of Free Electron Lasers (FELs): light sources providing the necessary intensity brightness and coherence. In this context, the unique properties of the seeded FEL pulse FERMI have been used to demonstrate a time-dependent 3rd order nonlinear response (four-wave-mixing) [1], which is at the basis of most of nonlinear methods presently used in the optical regime.

The aforementioned proof-of-principle experiment has been performed using a dedicated compact setup (mini-TIMER; integrated in the DiProI end-station), which is able to generate extreme ultraviolet (EUV) transient gratings (TG's), whose time evolution can be monitored by transient diffraction from an additional probing pulse. Such a unique instrument has been exploited by users in a range of different experiments and has helped us to optimize the parameters of a larger setup, EIS-TIMER, which has been successfully commissioned and is now exploitable by users [2]. This instrument only uses EUV/soft x-ray FEL pulses and hence overcomes the main limitation of mini-TIMER, namely the impossibility to detect the dynamics stimulated by TG's with spatial periodicity below ≈ 200 nm. Hereby we report on the first EUV-TG data collected at EIS-TIMER, which allowed us to determine the phonon and thermal dynamics in an uncharted length-scale range, extending down to ≈ 20 nm [3]; i.e. well beyond the range accessible by any optical methods. Such a novel experimental capability would permit to probe a large array of dynamical processes, ranging from electronic excitations to magnetic and structural dynamics, at the nanoscale, thus providing a new tool for addressing a range of scientific open problems.

Further extensions of the EUV-TG approach to shorter wavelengths, as well as the implementation of other wave-mixing approaches (also exploiting the multi-pulse/multi-colour operation readily available at FERMI), will be discussed. Overall, the demonstration that time-resolved nonlinear wave-mixing experiments can be extended at sub-optical wavelengths paves the way to a bunch of experiments that, for instance, can exploit core-hole resonances to monitor energy and charge transfer processes at the molecular scale with atomic-site selectivity.

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- [3] F. Bencivenga et al., in preparation

Pressure tuning of light-induced superconductivity in K_3C_{60}

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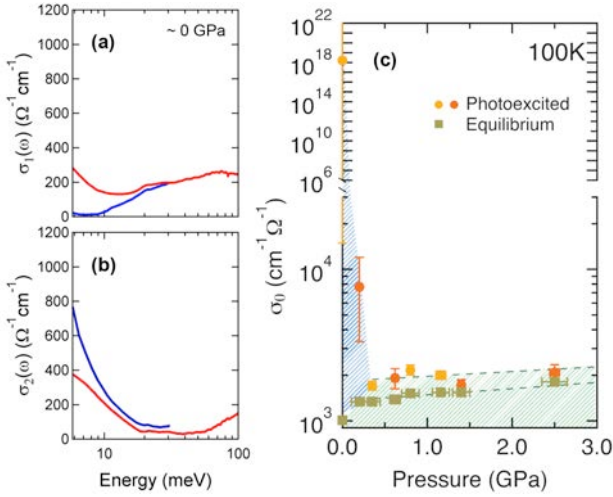


Figure 1: (a,b) Real and imaginary part of the optical conductivity of K_3C_{60} measured at zero applied external pressure, at a temperature $T=100\text{K}$, in equilibrium (red) and upon MIR excitation (blue). (c) Extrapolated low frequency optical conductivity as a function of applied pressure at $T=100\text{K}$. Figures adapted from Ref. [5]

divergence in its imaginary part (Fig. 1b). Strikingly, this effect persists up to a temperature of 100K, five times the equilibrium T_c [3].

Such observations are consistent with a light-induced superconducting state at an unprecedented high temperature. However, without further experimental insights, these data may also be interpreted as an exotic conducting state of normal carriers with giant mobility. To distinguish the nature of the photo-induced state, we studied how it reacts to the application of an external hydrostatic pressure. While the formation of an enhanced mobility metal is expected to be favored at increased external pressure, BCS-like superconductivity is expected to be suppressed [4].

We find that, upon application of an external hydrostatic pressure, the gap in the real part of the optical conductivity is progressively filled and a peak at finite frequency appears in its imaginary part. This indicates the disruption of a superconducting state and the transition to a metallic one [5]. Such transition is best captured by the low-frequency optical conductivity σ_0 , extrapolated from a Drude-Lorentz fit of the measured transient optical properties. Fig. 1c shows the variation of σ_0 as a function of pressure, highlighting the evolution from the blue-shaded area where $d\sigma_0/dP < 0$, as expected for a superconductor, to the green-shaded one where $d\sigma_0/dP > 0$ as for the equilibrium metal. These observations indicate that the light-induced optical properties carry the signature of a non-equilibrium superconductor.

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- [1] W. Hu et al., *Nature Materials* **13**, 705 (2014). [2] R. Mankowsky et al., *Nature* **516**, 71 (2014).
 [3] M. Mitrano et al., *Nature* **530**, 461–464 (2016). [4] O. Gunnarsson, *Review of Modern Physics* **69**, 575 (1997)
 [5] A. Cantaluppi, M. Buzzi et al., arXiv:1705.05939 (2017)

Accessing microscopic coupling in solids with momentum-resolving ultrafast techniques

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Microscopic coupling phenomena in solids, e.g. the coupling of electronic and vibrational degrees of freedom, are typically described on the level of ensemble averages, based on the assumption of thermal distribution functions. In nanoscale materials and heterostructures, however, a refined understanding of electron-phonon interaction is required. Ultimately, a quantum state-resolved picture of microscopic coupling is desired. This is achievable with pump-probe techniques providing momentum-resolved information on ultrafast electron and phonon dynamics. As depicted in Fig. 1, we employ XUV-based time- and angle-resolved photoelectron spectroscopy (trARPES) and femtosecond electron diffraction (FED) to obtain a state-resolved understanding of microscopic coupling beyond ensemble-average descriptions [1,2,4]. Specifically, I will discuss electron and phonon dynamics in the semiconducting transition metal dichalcogenide WSe_2 . TrARPES reveals the distribution and evolution of excited states in the Brillouin zone and their potential spin- and pseudospin-polarization [3]. The complementary momentum-resolved view on phonon dynamics is obtained by FED [4]. By combining this information, a microscopic picture of electron-lattice coupling and energy flow emerges.

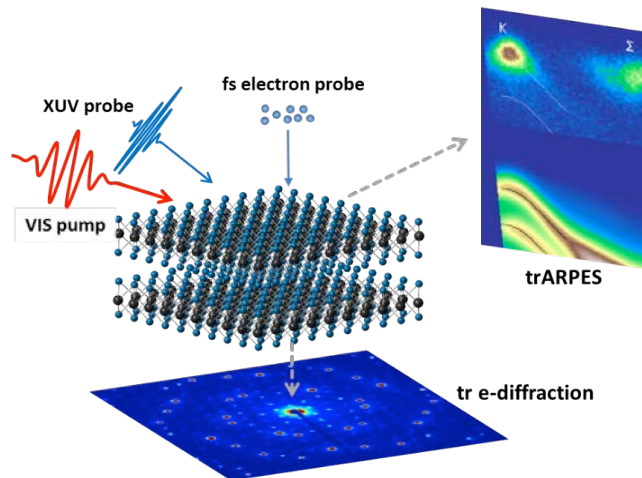


Figure caption: Illustration of the experimental approaches used for obtaining momentum-resolved information on the ultrafast dynamics of electrons and phonons and for revealing electron-phonon coupling.

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2D-IR Spectroscopy at its Best: Structure and Dynamics of Molecules Immobilized at Solid/Liquid Surfaces

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2D-IR spectroscopy can tell us a lot about solvation dynamics, structural dynamics and energy transfer processes of molecular systems in different environments. After a brief introduction into multidimensional spectroscopy, I will illustrate its capability by discussing structure and dynamics of molecules immobilized at solid/liquid surfaces [1], which play an important role in electro- and photocatalysis. I will show that time-dependent cross peaks between two isotopomers of a CO₂-reduction catalyst (Re(4,4-dicarboxyl-2,2-bipyridine)(CO)₃Cl) originate from through-space transition-dipole coupling (Fig. 1) [2]. From the transfer rate, we can estimate that the molecules are bound to the surface with essentially a closest packing. We furthermore studied the vibrational energy transfer rate on different types of surfaces with different levels of plasmonic enhancement, and somewhat surprisingly find that the transfer rate is not affected, an effect that is explained with the help of an image-dipole picture.[3] Finally, I will discuss the 2D IR spectroscopy of the Pt-H bond, a transient species which must appear during electrolysis with Pt still being the only catalyst that is of technological relevance. [4]

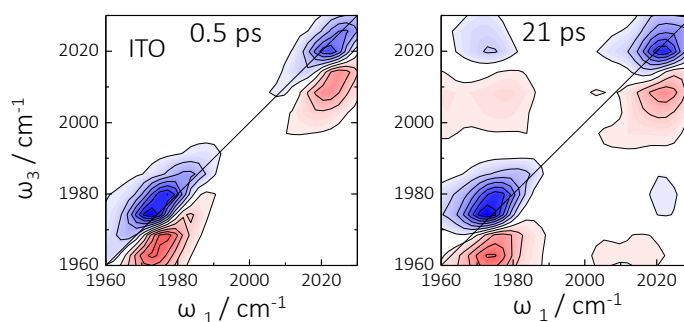


Figure 1: 2D ATR IR spectrum of Re(4,4-dicarboxyl-2,2-bipyridine)(¹³/¹²CO)₃Cl/Br on an ITO surface. Cross-peaks appear as a function of population time.

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Revolutionary new nano-imaging and coherent scattering: harnessing the power of short wavelength EUV light.

Giulia F. Mancini*†, Robert Karl Jr., Dennis Gardner, Elisabeth Shanblatt, Joshua Knobloch, Travis Frazer, Jorge N. Hernandez-Charpak, Begoña Abad Mayor, Michael Tanksalvala, Christina Porter, Charles Bevis, Daniel Adams, Henry Kapteyn and Margaret Murnane

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High-resolution imaging is an essential tool for understanding nanoscale systems. In particular, tabletop extreme ultraviolet (EUV) coherent diffractive imaging (CDI) techniques [1-3] based on high harmonic generation (HHG) [4,5] are ideal for investigating complex nanostructured systems, including their static and dynamic electronic, phononic and magnetic properties. Tabletop EUV-CDI combines elemental and chemical selectivity with spatial resolutions that are comparable to the illuminating wavelength (nm), and pulse durations in the femtosecond (fs)-to-attosecond (as) range. Because no optical elements are needed between the sample and detector, coherent imaging is the most photon efficient form of imaging, and can be non-destructive, with no charging effects or resolution loss with depth. Moreover, the contrast mechanisms in EUV CDI are relatively straightforward and intrinsically high: amplitude images exhibit exquisite sensitivity to material composition, while phase images are sensitive to both material composition and topography.

Recently, revolutionary new nano-imaging capabilities have been enabled by the combination of particularly powerful method of CDI, called Ptychography [6,7], with high spatial coherence tabletop EUV light from HHG sources. In this talk, I will present the power and promise of EUV and X-ray tabletop microscopy, providing examples of applications such as quantitative chemically-specific detection of reactions at buried interfaces [8], sub-wavelength imaging of periodic extended objects [9], structural characterization of opals metalattices by desktop coherent EUV scattering [10] and dynamic imaging of acoustic waves in nanostructures [11].

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- [9] D. Gardner *et al.*, *Nat. Photonics* **11**, 259–263 (2017).
- [10] G. F. Mancini, R. M. Karl Jr., *et al.*, submitted.
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Imaging dynamic of radiation-sensitive molecules.
John Spence
Physics, Arizona State University, Tempe, Az. USA.

The possibility of out-running radiation damage by the "diffract-and-destroy" method, using femtosecond pulses of either electrons or hard X-rays, opens completely new vistas for imaging molecular dynamics at atom resolution and sub-picosecond speeds (1). First, I'll compare high-energy electron beams for this purpose, and compare them in regard to damage mechanisms and time-scales with XFEL radiation. I'll suggest a fast mode of image formation which provides high resolution despite the use of the large incoherent photocathode. I'll then review our work using the hard X-ray pulsed laser at SLAC within our BioXFEL 6-campus NSF consortium (<http://www.bioxfel.org>), aimed at the application of X-ray lasers (XFELs) to Structural Biology. I'll show molecular movies from light-sensitive proteins with 150 fs time resolution and near-atomic spatial , using both crystals and solution scattering obtained from the LCLS XFEL at SLAC, and very recent single-particle virus images (one virus per shot) showing dynamics. I'll discuss work in my lab on methods for hydrated sample delivery for an XFEL, and the compact XFEL under construction on the ASU campus. Finally, I'll review a recent proposal for the use of intensity interferometry to analyse the angular dependence of inner-shell X-ray fluorescence from a molecule. See Google Scholar for references and the many collaborators whom I thank.

1. J.Spence. XFELS for structure and dynamics in biology. IUCrJ 4, 322 (2017).

Ultrafast nonadiabatic molecular dynamics via time-resolved valence and inner shell spectroscopies

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One of the most important yet general dynamics in photo-excited molecules involves the non-adiabatic coupling of electronic charge with nuclear motion, typically involving Conical Intersections. These leads to coupled charge and vibrational energy flow on the molecular frame and is the first step in any ensuing photochemical processes. Using examples from the dynamics of unsaturated hydrocarbons in the gas phase, we will discuss two ultrafast techniques which, when combined with ab initio on-the-fly dynamics simulations, address this important problem. The first is a valence shell approach, Time-resolved Photoelectron Spectroscopy [1]. The second, an inner shell approach, is based on Time Resolved X-ray Absorption Spectroscopy [2].

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Unraveling the ultrafast dynamics of spatially confined phonons and plasmons in low-dimensional nanosystems

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Understanding the ultrafast evolution of low-dimensional materials under non-equilibrium conditions plays a fundamental role in deciphering the mechanism governing chemical and physical functions. With direct visualization, the technological development of new generation nanoscale devices would become feasible. Although an enormous effort has been devoted to the comprehension and improvement of these materials and devices, the capability of investigating their dynamic behavior is hindered by the difficulty of simultaneously studying their evolution in space and time at the appropriate scales. The traditional characterization techniques and the steady-state theoretical models are both not adequate for describing their non-equilibrium behavior. Instead, a novel approach for visualization of matter with high temporal and spatial resolutions, together with momentum and energy selection, is indispensable to fully exploit their potential.

Ultrafast electron microscopy (UEM) has been recently developed with the capability of performing time-resolved imaging, diffraction and electron-spectroscopy [1]. The high scattering cross-section for electron/matter interaction, the high spatial resolution (down to the atomic scale), the ultrafast temporal resolution and the high energy selectivity of UEM represent the key elements that make this technique a unique tool for the dynamic investigation of surfaces, interfaces and nanostructures. In this contribution, we will address several recent applications to the investigation of elementary excitations, such as phonons and plasmons, in low-dimensional nanosystems, highlighting for each case the challenges that had to be overcome and the main scientific contribution. In particular, ultrafast diffraction, which provides atomic-scale resolution at a femtosecond time scale, is used to unveil the effect of the reduced dimensionality on the non-equilibrium dynamics of lattice vibrations (phonons) and their transport regimes [2,3]. Also, using the near-field variant of UEM, called Photon-Induced Near-Field Electron Microscopy (PINEM), it is now possible to visualize and control the dynamics of the plasmonic near-field optically created in the vicinities of single nanostructures or arrays of nanocavities with nanometer spatial and femtosecond temporal resolutions [4,5].

The highly inter- and multi-disciplinary approach presented here will pave the way for an unprecedented insight into the non-equilibrium phenomena of advanced materials, and should play a decisive role in the rational design and engineering of future applications.

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Selected Talks

Orbital-dependent ultrafast electron dynamics in Fe-pnictide superconductors

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The discovery of High- T_c superconductivity in Fe-based compounds has generated high curiosity in the condensed matter community. Although extensive research has already been carried out, many unconventional properties of these compounds still remain unexplained [1]. Here, we use orbital selective time resolved ARPES measurements (trARPES) on EuFe_2As_2 , a parent compound of Fe-pnictide superconductors to probe different excitations and coupling phenomena of the system. We observed different relaxation time-scales for d_{xz}/d_{yz} and d_{xy} electrons, selectively excited by changing the polarization of the pump beam [2]. The relaxation time-constant for d_{xy} electrons is approximately 2 ps, whereas d_{xz}/d_{yz} electron relaxes faster within approximately 800 fs. The time-constant also increases below the spin density wave transition at 190 K due to the opening of gap at the Fermi level. The different time-constants can be explained by taking into account the degree of localization of different orbitals. Previous ARPES results show that d_{xy} orbitals are localized, whereas d_{xz}/d_{yz} electrons have higher degree of itineracy because of their hybridization with As p states [3]. Although electron effective masses for different orbitals show small differences in the parent compound, the differentiation increases with hole-doping. The contrast between the relaxation dynamics of d_{xy} and d_{xz}/d_{yz} orbitals therefore indicates that the photo-induced excited state of EuFe_2As_2 behaves like a hole-doped composition. Our results support orbital-selective Mott behaviour in Fe-pnictide systems, which can explain many exotic properties of these compounds [3].

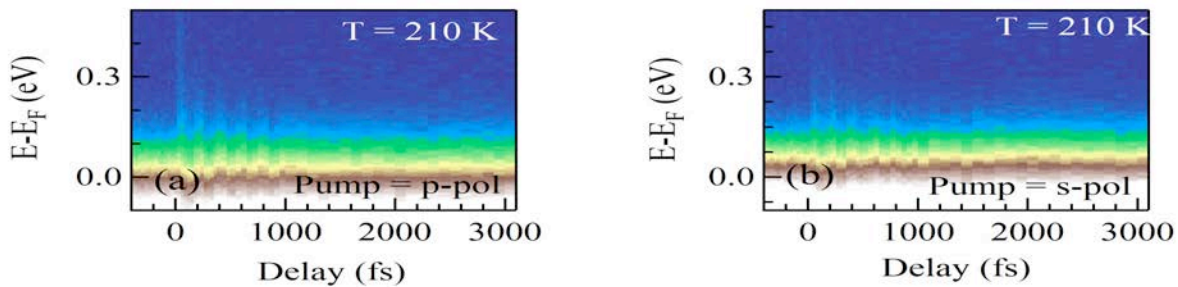


Figure 1: Pump-probe spectra at 210 K for (a) p-polarization and (b) s-polarization of pump, the probe in both cases is s-polarized.

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Time-resolved XUV photoemission: a new clue for understanding the ultrafast dynamics in copper oxides

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The origin of the universal antinodal suppression of quasiparticle states in the normal phase of high- T_c superconducting (HTSC) copper oxides remains a lively debated issue. In this presentation I will report on the first time- and angle-resolved extreme-ultra-violet (EUV) photoemission experiment performed on a prototypical HTSC cuprate to disclose the ultrafast dynamics of the antinodal states. After photoinducing a non-thermal charge redistribution within the Cu and O orbitals, the modification of the antinodal bandstructure via the formation of transient additional states at the Fermi level is observed, which relax back on the ~ 100 fs timescale. These results suggest that the antinodal suppression of states in the normal phase stems from the correlation-driven freezing of the electrons moving along the Cu-O bonds, analogously to the Mott localization mechanism. Finally, the observed ultrafast gaussian broadening of the non-bonding O-2p_z states points to an intrinsic spatial inhomogeneity of the charge-transfer photo-excitation process. On a complementary side, I will discuss the latest developments and the future perspectives of the T-ReX Laboratory, where novel ultrafast photon sources of EUV and XUV coherent radiation are being developed in order to perform TR-ARPES experiments on correlated materials with high statistics, high energy/momentum resolutions, and low space charge. This is made possible by the high repetition rate operation of the driving laser sources, opening the door to the long-sought TR-ARPES investigations of the electron dynamics over the entire Brillouin zone of complex materials.

Spin Polarized Research Instrument in the Nanoscale and Time Laboratory

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Photoemission experiments are at present witnessing a continuous progress towards the increase in resolution and optimization. In such experiments, the modern ability to control with the highest degree of precision the state of the incident photons in terms of momentum, monochromaticity and polarization, can be combined with state-of-the art techniques to evaluate the energy, momentum and spin state of the photoemitted electron. This allows to completely characterize the initial and final states of the probe particles and hence to reconstruct with highest precision the electronic structure of the sample under investigation and its possible excitations. The implementation of pump/probe technique, based on X-rays pulsed sources, allows the analysis of the relaxation processes enabled by the incident light, connecting the nanometric space resolution with the femtoseconds time scales.

We propose a new facility for users, based on high harmonics generation at high repetition rate, covering the extreme ultraviolet regime, and a new endstation, addressed at the study of ultrafast magnetic processes in solid state physics with a vectorial Mott detector upgraded to perform single-shot spin-polarization detection. The new source allows repetition rate up to 1 MHz, guaranteeing the strong statistics required for photoemission. Moreover, the lower energy per pulse avoid the space charge effect, which reduce the application of high intensity laser pulses from Free Electron Lasers to the photoemission experiments.

The characterization of the machine parameters, the first measures of the 3D spin-polarization vector of photoemitted electrons from magnetic materials and all the opportunity for external users will be described in details.

Hydrogen Bonding Structure of Aqueous Ammonia and Ammonium Probed with IR and X-ray Spectroscopy

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In a multi-faceted investigation combining local soft-x-ray and vibrational spectroscopic probes with *ab initio* molecular dynamics simulations, hydrogen-bond interactions of two key principal amine compounds in aqueous solution are quantitatively assessed in terms of electronic structure, solvation structure, and dynamics [1]. Ammonia (NH₃) and ammonium ion (NH₄⁺), model compounds chosen, are crucial constituents in the nitrogen cycle and function as test cases for acid-base chemistry of amino acid compounds (which are themselves one important class of the building blocks of life). From the x-ray measurements, using novel liquid flatjet technology [2] and from the complementary determination of the IR-active hydrogen stretching and bending modes of NH₃ and NH₄⁺ in aqueous solution, the picture emerges of a comparatively strongly hydrogen-bonded NH₄⁺ ion via N-H donating interactions, whereas NH₃ has a strong accepting hydrogen bond with one water molecule at the nitrogen lone pair but only weak N-H donating hydrogen bonds. In contrast to the case of hydrogen bonding amongst solvent water molecules, we find that energy mismatch between occupied orbitals of both the solutes NH₃ and NH₄⁺ and the surrounding water prevents strong mixing between orbitals upon hydrogen bonding, and –thus – inhibits substantial charge transfer between solute and solvent. This is markedly different from hydrogen bonding interaction of liquid water, where a major charge transfer component has been found upon hydrogen bonding between water molecules, with large overlap and associated hybridization of the occupied H₂O(3a₁) orbitals on neighbouring water molecules[3]. Our results provide a benchmark for hydrogen bonding of other nitrogen containing acids and bases, including (protonated) amine groups in protein structures. Possible extensions to time-resolved studies with the novel liquid flatjet will be discussed.

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Direct observation of ultrafast processes in conjugated molecules through Femtosecond Stimulated Raman Spectroscopy

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Femtosecond Stimulated Raman Spectroscopy (FSRS) is a powerful technique to study photoinduced ultrafast dynamics with structural sensitivity. In addition, the detection of stimulated Raman signatures, obtained by the interaction of a narrowband picosecond pulse and a broadband femtosecond continuum, allows achieving a higher spectral and temporal resolution [1] than the traditional Time Resolved Resonance Raman technique. Here we unveil the structural dynamics upon photo-excitation of the model compound 2-methyl-5-phenylthiophene (MPT), an example of conjugated organic polymer relevant for organic optoelectronic devices, such as photochromic molecular switches, solar energy conversion devices and light-emitting diodes. By combining FSRS [1-2] and quantum chemical calculations (time-dependent density functional theory) we provide a detailed mapping of the excited state dynamics [3].

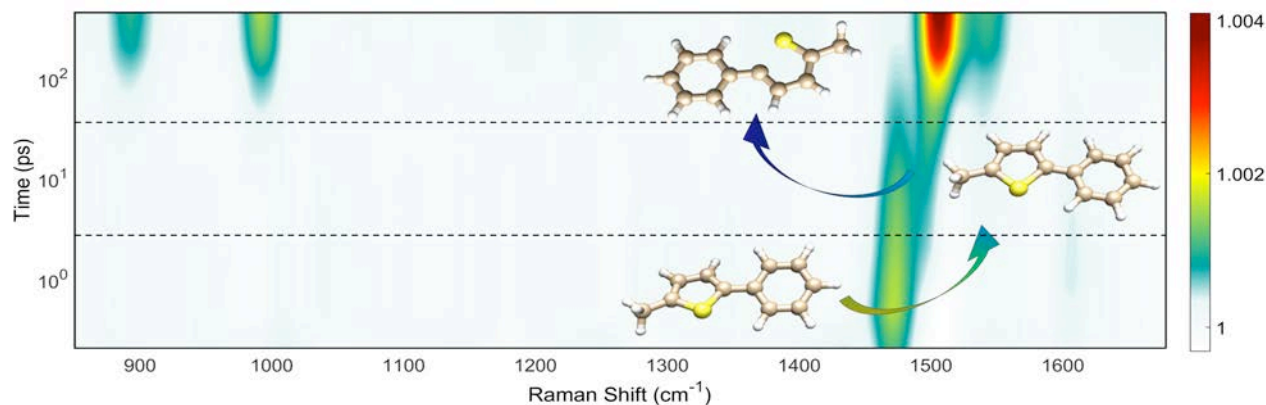


Fig. 1: Femtosecond Stimulated Raman spectrum of 2-methyl-5-phenylthiophene upon 266nm photo-excitation. After an ultrafast planarization and cooling of the system promoted on the excited singlet state, the slow opening of the thiophene ring triggers an intersystem crossing to the triplet state.

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Optical control of the superconducting gap in optimally doped B2212 with mid-infrared pulses

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My contribution will focus on addressing the difference response of superconducting gaps to photoexcitation with large photon energy ($h\nu > 2\Delta$, with Δ superconducting gap) and subgap excitation ($h\nu < 2\Delta$). By studying the ultrafast changes of the reflectivity of optimally doped B2212 to the two kinds of photoexcitation we could on one hand confirm that high photon energy excitations trigger a sudden quench of the superconducting gap [1], but, more intriguingly, I will show how sub gap excitations can dynamically stabilize the superconductor. In particular, by measuring the divergent timescale of the relaxation [2], we could experimentally address the critical behavior at T_c and thereby directly accessing the superconducting transition temperature subsequently to photoexcitation. Our measurements reveal an enhancement of the critical temperature T_c up to 2 K following the excitation with a low photon energy pump ($h\nu < 2D$). The transient stabilization of the superconducting gap is further confirmed by the freezing of the relaxation dynamics for subgap excitation. The evidences are tentatively rationalized in the Eliashberg formalism [3,4], where a transient non-equilibrium depletion of the lowest energy states above the superconducting gap can lead to a transient stabilization of the superconductors. Our results open the way to a bidirectional control of superconducting properties in complex oxides.

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Soft-mode driven ferroelectric switching mapped by ultrafast x-ray diffraction

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Ferroelectricity, the presence of a spontaneous electric polarization in a crystalline solid even in the absence of an external field represents a key topic of current research. However, the macroscopic polarization \mathbf{P} cannot be derived solely from the periodic equilibrium distribution of electronic and nuclear charge in a crystal [1]. Instead, only the change $\Delta\mathbf{P}$ resulting from a variation of the charge density, caused by an external trigger is accessible [1]. Furthermore, the exact nature of the interplay between lattice excitations and charge dynamics in ferroelectric materials on atomic length and time scales is still under debate [2]

In this contribution, we demonstrate that femtosecond x-ray powder diffraction is a method uniquely suited to address these open questions. We determine transient charge density maps in the prototypical ferroelectric ammonium sulfate [(NH₄)₂SO₄, AS] at $T = 200$ K, just below the critical temperature $T_c = 223$ K [Fig. 1 (a,b)]. Upon phonon excitation, we observe a previously undiscovered soft-mode with a 3 ps period and minute sub-picometer displacements of the nuclei, which induce periodic charge relocations over much larger distances of some 100 pm. This is in striking contrast to the behavior of AS in the paraelectric phase or at much lower temperatures [3]. Surprisingly, the soft-mode oscillations result in a transient switching of the full macroscopic electric polarization, as shown in Fig 1 (c). This suggests a prominent role of this mode in the phase transition at $T_c = 223$ K, and establishes the displacive nature of ferroelectricity in ammonium sulfate. These findings will allow for benchmarking ab-initio quantum theory of ferroelectrics, which in turn will be crucial in the understanding and tailoring of ferroelectric materials for a wide range of applications

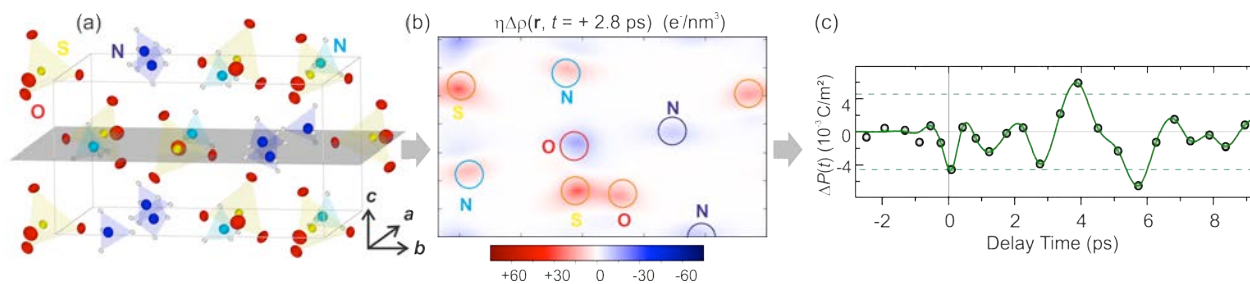


Figure 1: (a) Equilibrium crystal structure of ferroelectric AS. (b) Transient changes in the electron density $\eta\Delta\rho(r, t)$ in the highlighted plane. (c) Resulting time dependent change of the macroscopic electric polarization $\Delta P(t)$.

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Ultrafast Deep-UV 2D and Transient CD-Spectroscopy of Peptide Backbone Conformation

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An important motivation for developing broad-band ultrafast and multidimensional spectroscopies in the deep UV [1][2] is to directly access the transitions of amino-acid residues, nucleotides and backbones of biopolymers. In this context, the very recent extension of ultrafast broad-band time-resolved Circular Dichroism (CD) spectroscopy into the deep-UV [3] provides a powerful additional tool for probing the structural dynamics of biosystems.

In the case of polymer backbones, the challenge is extremely difficult because these absorb only below 220 nm. Here we overcome this difficulty by “UV-labelling” the peptides via a single-atom sulphur substitution of one or two backbone oxygen atoms [4][5]. This creates strongly red-shifted π - π^* absorption bands near 260 nm, which can be used as localized spectroscopic probes of backbone conformation.

We thus measured, for the first time, time-resolved 2D-UV and transient CD spectra of a peptide backbone. As a model system, we investigated a structurally well-defined dipeptide, with two thio-substituted amide bonds. Ultrafast broad-band transient CD spectroscopy should reveal coupling changes during the transient photoisomerization of one of the two peptide bonds, reflecting the reorientation of the C=S moiety. We expect our approach to provide a new and powerful tool for investigating structural dynamics in proteins, for which thio-substitution of selected amino-acids has already been demonstrated [6].

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Structural dynamics during laser-induced ultrafast demagnetization

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The mechanisms underlying femtosecond laser-pulse-induced ultrafast demagnetization dynamics remain elusive despite two decades of intense research. When looking at the literature one notes that

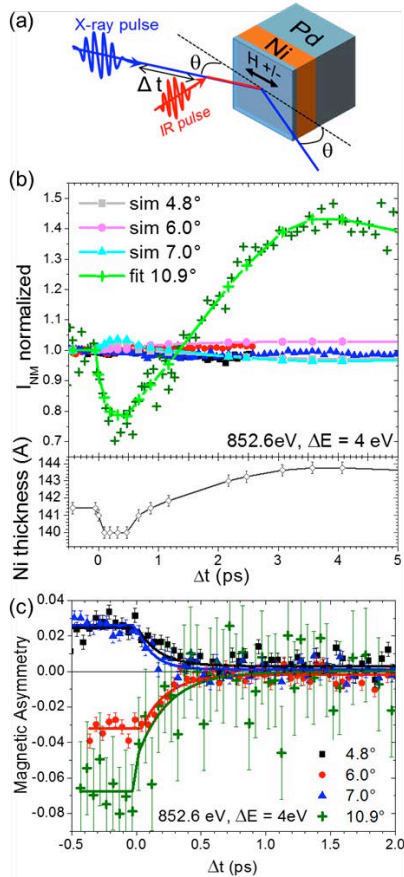


Figure 1: (a) Experimental geometry. (b) Evolution I_{NM} with pump-probe delay (symbols) and their simulated temporal evolution (light symbols and lines). (c) Magnetic asymmetry time (lines are guide to the eyes).

none of the experiments has simultaneously probed structural and magnetic dynamics.

X-ray resonant magnetic Reflectivity (XRMR) is one of the few techniques capable to do so [1]. At magnetically dichroic x-ray absorption edges, the normalized difference (asymmetry) of the reflected intensity for opposite magnetization directions probes the magnetization of the sample whereas their average (I_{NM}) characterizes structural parameters. We performed a time resolved XRMR experiments [2] on a prototype thin Ni film (Fig. 1a) at the FEMTOSPEX beamline of BESSY II. For a series of incidence angles and the two opposite magnetization directions we measured the reflected intensity as a function of the time delay between IR pump and X-ray probe (852.6 eV, Ni L_3). Fig. 1b and c show, respectively, the average non-magnetic reflectivity I_{NM} and the magnetic asymmetry. One notes that I_{NM} exhibits a strong time dependence for the incidence angle of 10.9° with changes of up to 30%. As discussed in detail in Ref. [2] our XRMR simulation can reproduce the ensemble of the time resolved reflectivity traces by varying only the thickness of the Ni film (Fig. 1b).

The magnetic asymmetry curves shown in Fig. 1c exhibit, within the error bars, a monotonous decrease, which indicates the typical global ultrafast demagnetization. Extending our simulations to larger incidence angles and better energy resolution we show that time resolved XRMR can be employed to discriminate experimentally between different models currently discussed as mechanism driving the ultrafast demagnetization process. Our study thus paves the way for future time resolved XRMR experiments at X-ray Free Electron Lasers, which provide photon flux and energy resolution necessary to access the required X-ray incidence angles.

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Stimulated emission in MgO following irradiation by EUV FEL pulses at FERMI

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Stimulated emission is a fundamental process that deserves to be investigated and understood in the extreme ultra-violet (EUV) and x-ray regimes. Today this is possible by using the high energy density free electron laser (FEL) beams. In this context, we demonstrate soft-x-ray stimulated emission from a MgO single crystal pumped by EUV FEL pulses provided by FERMI facility. This emission arises in the regime of travelling-wave amplified spontaneous emission and in backward geometry. Our results combine two effects separately reported in previous works: emission in a privileged direction and existence of a material-dependent threshold for the stimulated emission. We develop a theoretical framework, based on the coupling of rate and transport equations and taking into account the solid-density plasma state of the target. The model accounts for both observed mechanisms that are the privileged direction for the stimulated emission of the Mg L_{2,3} characteristic emission and the pumping threshold.

Soft X-ray Second Harmonic Generation as and Interfacial Probe

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Nonlinear optics has recently been extended from visible and near UV wavelengths to new regimes with the development of X-ray free electron lasers (XFELs) capable of delivering X-ray pulses with high brightness, ultrashort pulse duration, and high coherence. One fundamental nonlinear probe is second harmonic generation (SHG), a second order process which combines two photons of the same energy to generate a single photon with twice the energy. At infrared, visible, and ultraviolet wavelengths, second order nonlinear spectroscopies have become important tools in surface science, as symmetry considerations, within the dipole approximation, constrain signal generation to regions lacking centrosymmetry, such as surfaces and interfaces.¹ In contrast, at hard X-ray wavelengths, second harmonic and sum frequency generation (SFG) have been observed in centrosymmetric materials with a non-uniform electron density and are essentially bulk probes.^{2,3} As soft X-ray wavelengths fall in between the hard X-ray and UV regimes, there has been uncertainty regarding the interface specificity of soft X-ray SHG. Here, by utilizing the soft X-ray free electron laser, FERMI, we report the first observation of soft X-ray second harmonic generation near the carbon K-edge (~284 eV).⁴ Our experimental results and accompanying theoretical analysis indicate that soft X-ray SHG is an interface specific probe with symmetry constraints similar to optical SHG/SFG, and is highly sensitive to resonance effects. This enables a powerful new approach for surface and interface analysis with broad applicability to many scientific fields, as it combines the elemental and chemical specificity of X-ray absorption spectroscopy with the rigorous interfacial specificity of second-order nonlinear spectroscopies, while maintaining a fully coherent signal. With several new coherent free electron lasers under development this new technique offers exciting applications to a wide range of problems.

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Vibrational control of d-d transitions in the model cuprate CuGeO₃

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The interplay between phonon excitation and electronic transitions is at the core of the exotic properties of complex material. Recent development of mid-infrared impulsive sources have enabled the study of ultrafast responses of different electronic degrees of freedom following the resonant excitation of vibrational modes [1,2]. In particular, pioneering experiments have shown that the resonant excitation of low energy vibrational states by THz pulses can trigger the onset of surprising transient states of matter such as superconductivity.

Following the scheme of resonant excitation of low energy modes and spectroscopic probe of the visible transient response, we have developed a setup coupling tunable mid-IR pump pulses (from 4 to 17.5 μm) and tunable visible probe pulses (from 600 to 900 nm) in order to study electron-phonon coupling in copper germanate (CuGeO₃). Thus, by exciting vibrational modes along the b or c axis of CuGeO₃ with mid-IR pulses, we are able to control specific lattice distortion and measure their influence on copper d-d onsite transition. By monitoring the transient transmittivity and birefringence of the probe we have revealed an ultrafast change of the optical properties resonant to the d-d absorption band demonstrating, on a model crystal, that vibrational excitation can be used to control the local crystal field in transition metal oxides.

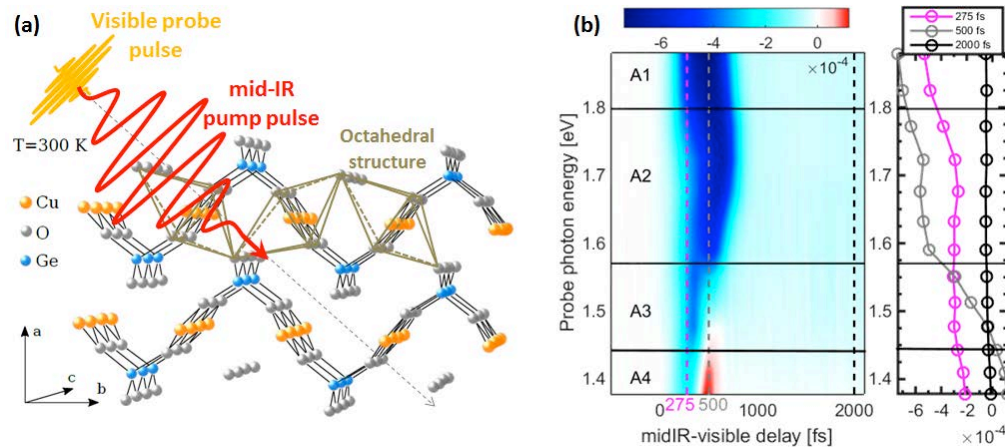


Figure caption: (a) Scheme of the study performed on CuGeO₃. (b) Probe transient transmittivity map around the d-d transition energies. The particular response shows how the crystal field is modified by a low-energy excitation.

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Combining attosecond extreme ultraviolet pulses and shaped near infrared pulses: Multidimensional four wave mixing spectroscopy

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With the emergence of isolated XUV attosecond pulses, bandwidths as large as 40 eV are now commonly used in many laboratories. Dynamics following excitation with those pulses will arise from all accessible excited states, complicating the retrieval of state-specific time evolution. In optical multidimensional spectroscopy, correlations between excitation and probe frequencies are obtained using four wave mixing (FWM) formalism to identify the signal dependence on the incident field spectral phases, amplitudes and k vectors. Our laboratory has recently shown that FWM signal is generated using the combination of an attosecond pulse centered at 15 eV and two 5 fs NIR pulses centered at 750 nm.¹ The goal is to develop a two-dimensional extreme ultraviolet (XUV) technique using the signal field dependence on the NIR pulse phases and amplitudes. To that effect a spatial light modulator based pulse shaper is implemented to control the emitted XUV and gain spectral information on the NIR transition in play. Interactions involved in the FWM scheme are indicated in **figure 1a**). The coincident XUV and NIR pulses create a wavepacket in the 4p Rydberg dark states of Argon via the bright ns/n'd Rydberg states between 14.4 and 15.4 eV. At a later time delay, a noncollinear shaped NIR pulse couples the 4p dark states wavepacket back to the ns/n'd states manifold, which subsequently emit the signal field. The experimental beam geometry is shown in **figure 1b**). The first NIR and the XUV are collinear while the shaped NIR is noncollinear. The emitted field shown in violet is spatially separated from the other beams. The pulse shaper is used to extract the second interaction frequency by modulating the amplitude and phase of a tunable single frequency of the NIR pulse spectrum. The emitted frequency is correlated with the NIR transition frequency and the 2D spectrum obtained, shown in the **figure 1c**).

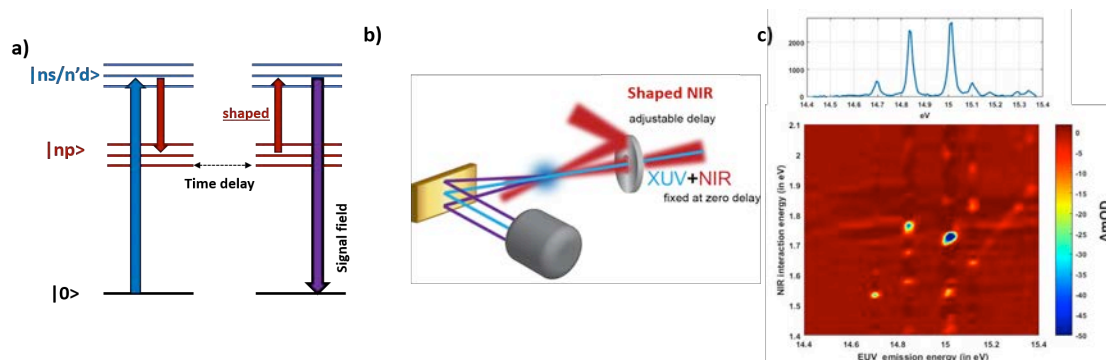


Figure 1: a) Energy level diagram. b) Beam geometry. The blue beam represents the incident EUV pulse and the violet beams the emitted EUV fields. c) XUV emitted field spectrum and 2D NIR-XUV spectrum.

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Microscopy and diffraction with attosecond electron pulse trains

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Generation of attosecond XUV pulses allowed real-time access to light-driven electronic dynamics in atoms, molecules, solids, and nanostructures, but visualizing electronic motion in space and time requires in addition atomic spatial resolution, which is unfortunately ~ 100 times shorter than the wavelength of XUV photons.

In this presentation, we report generation, characterization, and applications of attosecond electron pulse trains for space-time imaging [1]. The concept of our method is presented in Fig. 1(a). A monoenergetic 70 keV electron beam at 4 pm wavelength is temporally modulated by a laser field impinging on a Si_3N_4 membrane. In order to characterize the temporal structure, we use a second membrane with a streaking laser field. We obtain a streaking signal of the electron pulse as shown in Fig. 1(b). Through a fitting procedure, we obtain a pulse duration of 820 as (full width at half maximum).

These attosecond electron pulses are suitable for atomic-scale diffraction and sub-cycle microscopy, as demonstrated by two proof-of-principle experiments. First, we report Bragg diffraction from a Si single crystal with a high enough signal-to-noise ratio to perform diffractive imaging of electronic dynamics in solids [2]. Second, we advance waveform electron microscopy [3] to attosecond resolution and visualize in real space the electromagnetic fields of a travelling light-wave at a nanoscale membrane.

These results [1] mark a first step into unifying the atomic imaging capability of keV electrons with the sub-cycle resolution of attosecond physics, in order to directly visualize the foundations of light-matter interaction in space and time.

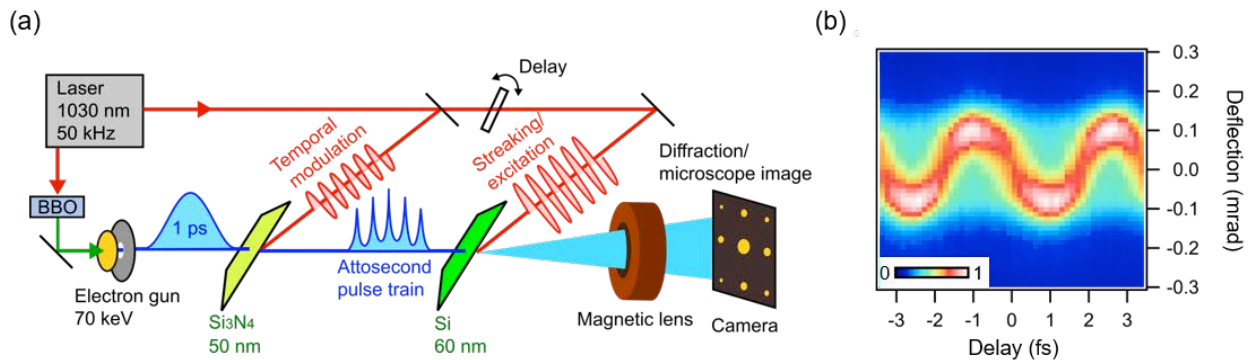


Figure 1: Generation and characterization of attosecond electron pulse trains. (a) Experimental setup. (b) Attosecond streaking of temporally modulated electron pulses.

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Direct Observation of Reaction Dynamics by Femtosecond Electron Diffraction

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Femtosecond electron diffraction (FED) is a sensitive tool to directly study molecular dynamics in structural detail. Here, we present recent results from two different experiments, both focused on the direct observation of reaction dynamics on the ultrafast timescale. All experiments have been performed in a 95 keV DC-RF hybrid FED setup [1] to allow for the best temporal and spatial resolution.

The first experiment is a study on the photoinduced phase-transition in the organic salt (EDO-TTF)₂XF₆, an extension on an earlier work where X = P [1]. We have studied another derivative with SbF₆⁻ as counter ion; using SVD analysis (Singular Value Decomposition), we were able to directly determine the number of contributing motions relevant to describe the ultrafast dynamics. The photoinduced insulator-to-metal phase transition in both derivatives varies depending on the counter ion [2]. For X = P, three dominant motions are present and the molecules undergo the transition completely; whereas in the case of X = Sb, only two dominant motions are found and the molecules do not evolve into the metallic state. This different phase-transition behaviour is explained by the influence of the counterion size. SVD of time-resolved electron diffraction data in reciprocal space proves to be a promising data analysis approach to reduce the dimensionality of complex FED data sets.

The second experiment [3] is focused on the study of photoinduced spin crossover (SCO). We have studied by FED the coordination compound [Fe^{II}(PM-AzA)₂](NCS)₂ (or AZA) in single crystalline form to investigate the structural dynamics associated with this spin transition. The unique capability of FED allows us to directly probe atomic motions and to track ultrafast structural changes within the crystal lattice of AZA. By monitoring the time-dependent changes of the Bragg reflections, we observed the formation of a photoinduced structure similar to the thermally induced high spin state. The data and refinement calculations indicate the global structural reorganization within 2.3 ps, as the metal–ligand bond distribution narrows during intramolecular vibrational energy redistribution (IVR), driving the molecular rearrangement. Three independent dynamical groups are identified to model the structural dynamics upon photoinduced SCO.

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Ultrafast dynamics of bands and bonds during a photo-induced structural phase transition at a surface

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In the Born-Oppenheimer picture, nuclear dynamics evolve on a free energy surface determined by the transient occupation of electronic states. Access to the non-equilibrium distribution of excited electronic states therefore allows a determination of the forces that govern the trajectory along the reaction coordinate during a photo-induced ultrafast structural transition. Such a description including the complete electron dynamics goes far beyond that of a “molecular movie” [1]. To address these ideas we investigate a model phase transition system – indium nanowires at the silicon(111) surface – which undergoes an order-order structural transition accompanied by an electronic insulator-to-metal transition [2]. Utilizing femtosecond time and angle resolved photoemission spectroscopy with a novel 500 kHz XUV laser source, we obtain direct access to the transient k -resolved electronic structure during the photo-induced phase transition (PIPT) in In/Si(111). By observing the dynamically changing band structure a detailed reaction pathway is resolved, including temporal separation of the insulator-to-metal (200 fs) and structural (700 fs) phase transitions; the latter in extremely good agreement with recent time-resolved electron diffraction measurements [3]. The reaction pathway is reproduced by ab initio molecular dynamics simulations, which reveal the crucial role played by localized photo-holes in shaping the potential energy landscape of the structural transition. This furthermore allows us to extend the description of ultrafast PIPTs to real space, and chart the ultrafast formation of chemical bonds during the phase transition.

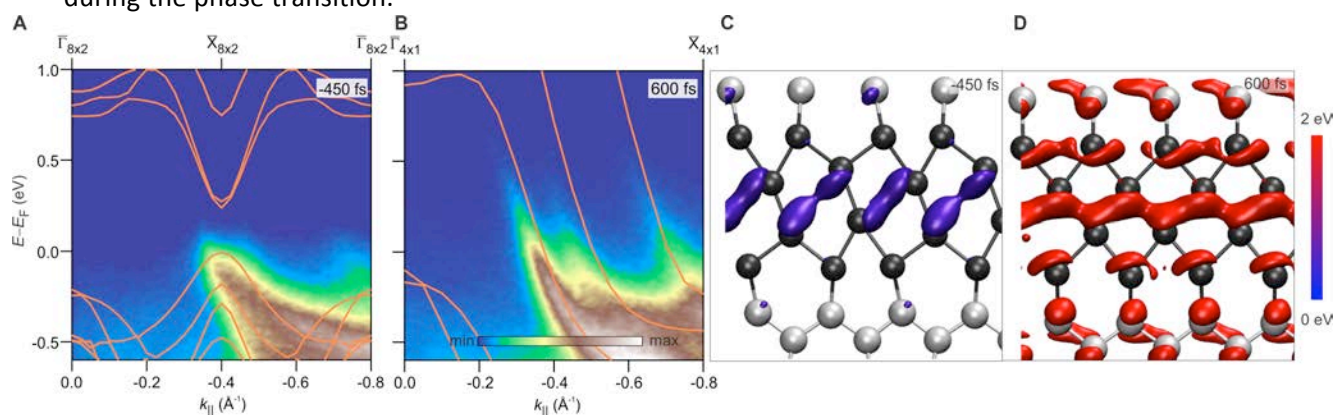


Figure: Measured and calculated electronic band structure in k -space in the 8x2 (A) and, following photoexcitation, the 4x1 phase (B). A real space description (C and D) reveals ultrafast bond formation during the phase transition.

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Ultrafast X-ray absorption spectroscopy using direct quantum dynamics

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New opportunities for probing ultrafast molecular dynamics are available due to the arrival of X-ray free-electron lasers (XFELs) and novel high harmonic generation (HHG) sources. To aid experimental analysis, theory which explicitly treats the nuclear dynamics is important. Quantum dynamics simulations allow mapping between ultrafast spectroscopic data and the complex nuclear dynamics and electronic structure changes that occur during photochemical reactions.

In this work, a direct quantum dynamics method is used in conjunction with X-ray absorption spectroscopy (XAS) calculations. Previous work used a grid-based approach to calculate the Cu K-edge signal from a copper phenanthroline complex [1]. Such a grid approach is limited to two or three dimensions, whereas the approach herein effectively tackles the inherent exponential scaling problem. Comparison is made to the femtosecond XAS of the CF_4^+ and SF_6^+ dissociative reactions in Pertot et al. [2], and an alternate approach is used to the Cu phenanthroline XAS calculations from Capano et al.

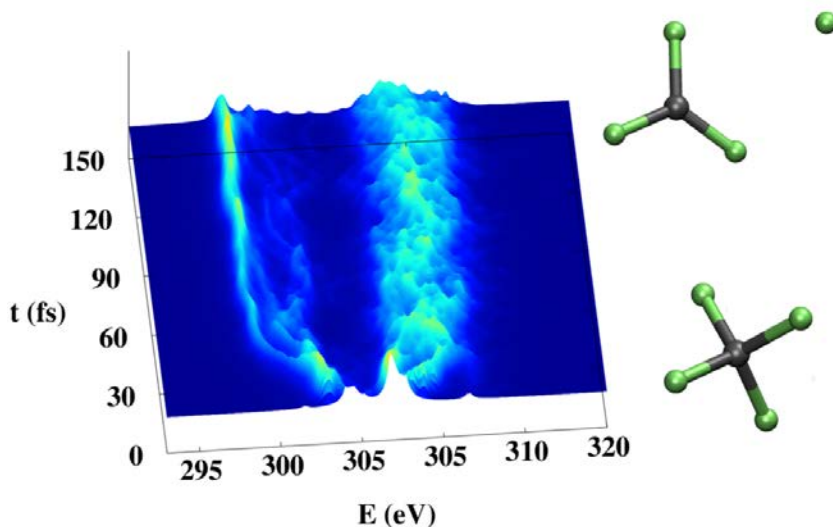


Figure caption: Calculated carbon K-edge signal of CF_4^+ during dissociation to $\text{CF}_3^+ + \text{F}$.

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Generation of intense femtosecond optical vortices in the extreme-ultraviolet

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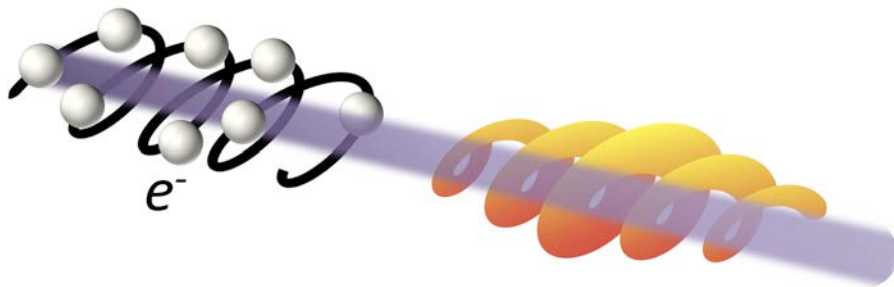
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Optical vortices are helically phased beams with a field dependence of $\exp(i/l\phi)$, where l is the topological charge and ϕ the azimuthal coordinate in the plane perpendicular to the beam propagation [1]. Such beams carry an orbital angular momentum (OAM) of $l\hbar$ per photon. In the extreme-ultraviolet (XUV) spectral region, vortex beams are expected to trigger new phenomena, such as such violation of dipolar selection rules during photoionization, generation of charge current loops in fullerenes with an associated orbital magnetic moment, and the production of skyrmionic defects, which show promise for applications in nanoscale magnetic memory devices. Here, we present three schemes to generate intense, femtosecond, coherent optical vortices in the XUV. At the FERMI free-electron laser we generate optical vortices either by taking advantage of nonlinear harmonic generation in a helical undulator, producing vortex beams at the second harmonic of the fundamental emission, or by using a spiral zone plate, producing intense micron-size optical vortices at the fundamental FEL wavelength [2]. In the third experiment, we employ a two-colour wave-mixing setup to generate XUV vortices with tunable topological charge using high-harmonic generation in gas [3].



Electrons spiraling through a helical undulator in an FEL emit harmonics which carry OAM.

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Pump and probe experiments from first principles.

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The development of ultra-short laser pulses has opened the opportunity to investigate the dynamics of electrons on the fs time-scale (1 fs=1.E-15 seconds). After the photo-excitation with such lasers pulses, electrons are in a regime which is highly out-of-equilibrium. Here we present a novel numerical approach, based on the merging of the out-of-equilibrium Green's function method with the ab initio, Density-Functional-Theory, to describe this regime in semi-conductors. [1-5] Silicon [6-7] is used as reference material to show the physical process involved. The simulations are also compared with recent two photon photo-emission and transient-reflectivity measurements. Moreover we consider MoS2 [8] and WSe2 [9] monolayers and discuss transient absorption and transient Kerr in the system. Also in this case the simulations are also compared with recent transient-absorption and transient-kerr measurements. We show that we capture both the frequency shape of transient absorption and the time decay of both transient absorption and kerr signal.

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Photo-induction of the Insulator to Metal Transition in the Organic Mono-Crystal Cu(Me,Br - DCNQI)₂ as studied by Ultrafast Electron Diffraction

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Organic molecular solids are intriguing substances from a fundamental physics and an applied technology perspective. The strong intramolecular bonds and the spectroscopic character of the isolated molecules predominantly stay intact while intermolecular forces are typically weak. This hierarchy of forces and the interaction of delocalized orbitals of planar, aromatic molecules introduce a wide range of peculiar (macroscopic) electronic, magnetic and structural properties. The radical ion salt Cu(R₁,R₂-DCNQI)₂ is a special case of a coupled molecular π - atomic d- orbital system, responsible for high 1D electrical conductivity. With certain ligands (R₁, R₂) in the molecular anion it undergoes a dramatic first order transition to an insulating phase, associated with a structural Peierls transition and a unit cell trimerisation, and exhibiting a conductivity drop of many orders of magnitude. Here we observe the structural and electronic dynamics during this macroscopic phase transition, in order to determine the driving microscopic molecular motion and its ultimate speed.

We investigate the photo-induced reversed Peierls transition in monocrystalline organic Cu(Me,Br-DCNQI)₂ with ultrafast electron diffraction (UED) in the ps regime. We monitor time-delayed electron diffraction patterns after photo-switching the transition by femtosecond laser excitation, and directly detect the insulator-to-metal transition by lifting of the lattice three-fold periodicity within 1 ps in the entire crystal volume. By converting diffraction data into real space, several distinct collective molecular motions are revealed during this transition such as change of the tetrahedral coordination angle, a local stretching motion and an anisotropic contraction. We observe that certain collective spectator modes occur in an initial ultrafast lattice response, lifting the insulating state transiently. These are necessary for the phase transition, but not sufficient. However, only if a specific mode related to an internal volume change, is activated, the insulator to metal transition is permanently induced.

This work demonstrates the power and potential of Ultrafast Electron Diffraction for the investigation of structural and electronic dynamics of ultrafast macroscopic processes in organic molecular crystals.

Multidimensional spectroscopy with weak-pulses reveals unexpectedly large coherence length of excitons in a quantum well

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The intrinsic coherence-length of excitons in semiconductor quantum wells is not well understood, but may play an important role in macroscopic optical and electronic properties. Transient four-wave mixing (FWM) based experiments can directly measure decoherence dynamics, but typically require high pulse energy – and thus high exciton-density – which leads to interactions between excitons and a many-body response. Indeed, it is generally accepted that such many-body effects dominate the third-order response in FWM measurements, and obscure the intrinsic coherence length of the individual excitons.

We have established an ultra-stable coherent multidimensional spectroscopy experiment based on a pulse-shaper, in which a FWM signal is detected interferometrically. The stability of the setup results from the use of all common optics, and – combined with the sensitivity provided by the interferometric detection – allows us to detect signals using pulses orders of magnitude lower than those typically used in FWM experiments. At these low excitation densities, we observe dynamics that diverge significantly from those typically observed at high excitation densities. At high density, we observe a photon echo typical of excitons localized to well-width fluctuations. However, as the excitation density is decreased, we observe a second contribution to the signal which is a spatially extended exciton state, and which dominates the FWM response at the lowest excitation densities. We also observe a commensurate increase in coupling between excitons in two neighbouring quantum wells, due to the increased coherence length. These results show that the intrinsic coherence length of excitons in quantum wells is much larger than one might expect based on the results of past FWM experiments.

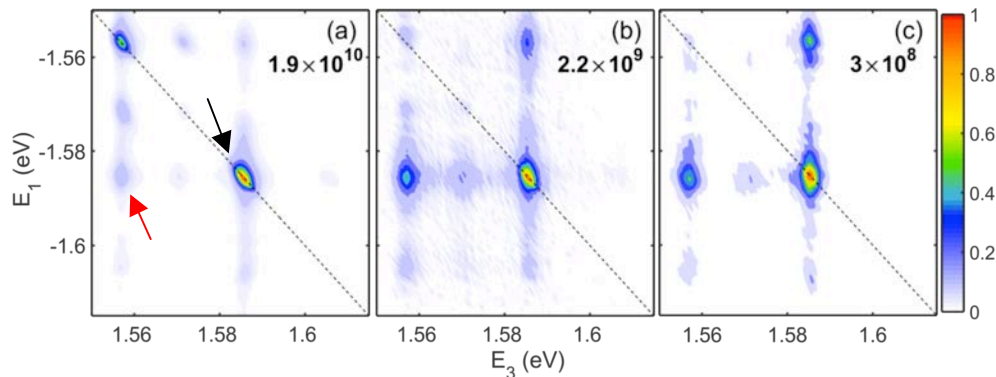


Figure caption: Absolute value 2D spectra of a double quantum well sample for three different photon densities (given in photons/cm²). The change in shape of the diagonal peak (black arrow) and the increasing relative amplitude of the cross-peak (red arrow) as a function of the excitation density indicate the presence of a spatially extended exciton state which also mediates coupling between the two neighboring quantum wells.

Confined plasmons at extreme temperatures: theory and possible experiment

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The free electron gas is a reference model for studying interacting electrons, and the effect of extremely high temperature on such system can give important information on the dynamical screening effects. Even more interesting is the case of a free electron gas confined within a nanoscale volume. A real example of this ideal system is represented by the free electrons of a small metal nanoparticle (NP), in which one can monitor the surface plasmon, that is the collective electronic oscillation inside a metal NP, typically lying in the visible spectral range. We have previously calculated the temperature dependence of the surface plasmon resonance in metal NPs using an electron gas model within the Random Phase Approximation [1]. Our approach enables to directly study the effect of finite, high temperatures on relatively large NPs, sized up to 10 nm. We find a possible blue shift of the plasmon resonance position when the temperature is increased while keeping the NP volume fixed. The blue-shift is appreciable only when the electronic temperature is a large fraction of the Fermi energy (see Fig.1a). The experimental observation of the expected plasmon frequency shift seems feasible by pumping an ensemble of Au NPs with a high intensity, short wavelength FEL pulse and probing the optical transmission of the electron system at short delays (up to 2 ps). Given the NP arrangement in a few-layer film and their small size, we expect to deposit our energy uniformly in the system because of the relatively small absorption of gold (see Fig. 1b) at the pump wavelength: we can therefore assume that we are heating the NPs homogeneously. Experimental tests realised at TIMEX beamline at FERMI ($\lambda_{\text{exc}}=37$ nm) on a film of gold NPs deposited on a LiF substrate have allowed to identify the critical parameters of such an experiment and to gain some insights in the behaviour of both the excited NP system and crystalline LiF substrate.

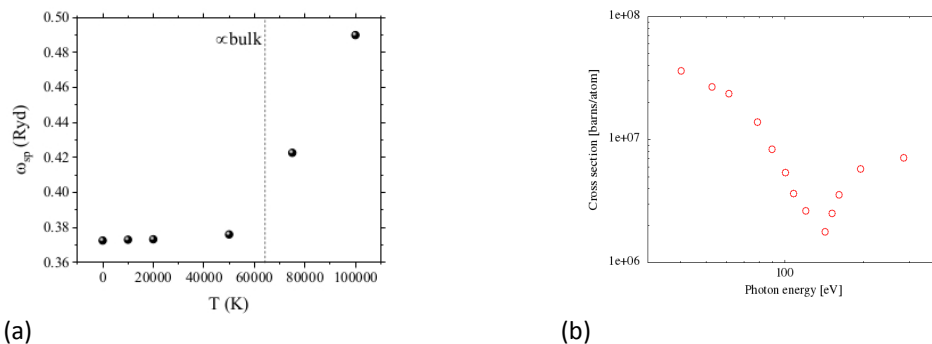


Figure 1: (a) Expected spectral profile of the surface plasmon resonance of a gold NP ($r = 1.34$ nm), as a function of temperature in the range 0-10⁵ K. The dashed line marks the position of the Fermi temperature in bulk Au. (b) Total photon cross-section σ_{tot} in lead as a function of energy [2]; it is very similar to gold one.

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Photodissociation Dynamics of 1,2-Diiodotetrafluoroethane Captured with Femtosecond Gas Phase Electron Diffraction

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We have used ultrafast electron diffraction (UED) to capture the structural dynamics during the UV photodissociation reaction of 1,2-Diiodotetrafluoroethane ($C_2F_4I_2$). The experiment was performed at the SLAC UED facility with a 3.7 MeV electron beam where previous experiments have shown femtosecond resolution [1][2]. Previously, H. Ihee et al. used UED with 5 ps resolution to study the evolution of photo-dissociated $C_2F_4I_2$ and found the structure of the transient state C_2F_4I to be the classical non-bridged structure [3]. No evidence of a bridged structure was found; however, a question remained on whether a bridged structure with a femtosecond lifetime also existed. The Ihee experiment also observed a fraction of the transient C_2F_4I further dissociating to form C_2F_4 with a time constant of 30 ps. We have observed that the non-bridged structure forms within 200 fs of the laser excitation, without the iodine atom ever moving into the bridged position. We have determined this by following the position of the dissociating iodine wavepacket as it moves away from the molecule. After the first iodine dissociates we observe no evidence that the transient further dissociates to C_2F_4 , in contrast with the earlier experiment. After dissociation an oscillation with a 200 fs period is observed in the inter-atomic distances of the transient. This oscillation is likely a fundamental stretch of one of the bonds, a beating between multiple fundamentals, or a rotation of CF_2 with respect to the remaining CF_2I . These findings are in good agreement with numerical simulations of the dissociation trajectories and work is still being done to extract the underlying nature of the periodic motion observed in the C_2F_4I after dissociation.

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Posters

New Approach for the Characterization of Photoluminescence Intensity Created by Soft X-rays in Lithium Fluoride Crystals

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Abstract

Point defects in lithium fluoride (LiF) crystals have permanently attracted wide attention due to both fundamental and application interests because the possibility of detecting images in the extreme ultraviolet (EUV) and soft x-ray spectral range (photon energies $h \approx 20\text{--}8000\text{ eV}$), at a high spatial resolution and on a wide field of view which is considered a topical task nowadays.

The LiF crystal host various aggregate of colour centres, that only F_2 and F_3^+ have practical relevance for imaging applications in addition to our analysis in this study as shown in the read-out stage diagram in Figure (1).

In this work, enhanced procedure of readout stage and new digital processing has been applied to scrutinize and study the behaviour of optically stimulated luminescence of colour centres (CCs) in LiF crystal, that used for high-performance water window soft x-ray imaging.

Besides that, the work will discuss the optical properties of LiF luminescence which is connected with the behaviour of LiF crystal photoluminescence (PL) response to a soft X-ray fluence.

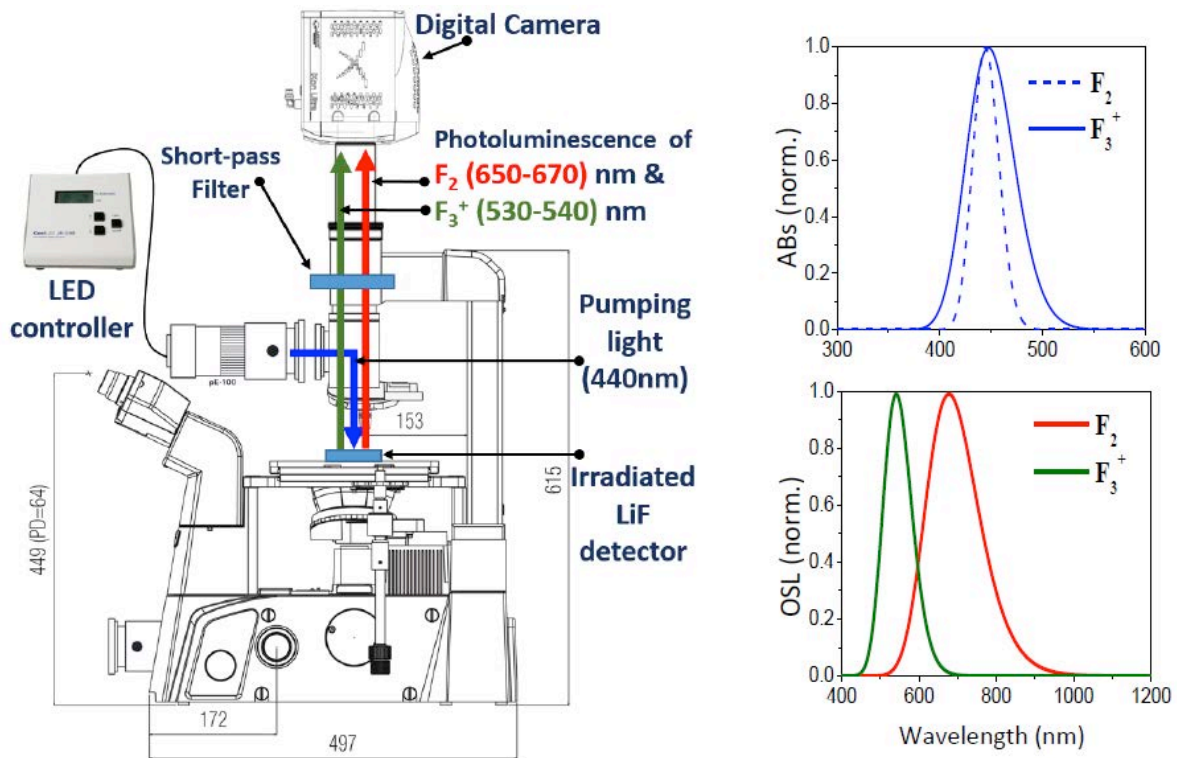


Figure (1)

Step-readout process of the irradiated LiF samples by optical microscope operating in the fluorescence mode (Left), Normalized absorption (top) and emission (bottom) bands of F_2 and F_3^+ colour centres in LiF at RT (right).

The European Cluster of Advanced Laser Light Sources (EUCALL)

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The European Cluster of Advanced Laser Light Sources (EUCALL) generates collaboration and synergy between large scale sources of laser-driven and accelerator-driven X-ray radiation.

The lead project partner is European XFEL, while the other partners are DESY, the Extreme Light Infrastructure (ELI) in Czech Republic, Hungary and Romania; ESRF in Grenoble, Helmholtz Zentrum Dresden-Rossendorf, Lund University, the Paul Scherrer Institute and Elettra Sincrotrone Trieste. The networks Laserlab-Europe and FELs of Europe are also involved, while representatives from the user communities of FELs and Optical Lasers are members of EUCALL's steering committee. EUCALL is the first serious effort to bring together the two scientific communities who have been using X-ray light in parallel to each other, and from different scientific and technological backgrounds.

EUCALL's scientific outcomes are devoted to the development of new software for simulation and processing of advanced radiation experiments, as well as for new hardware for standardised sample delivery and beam diagnostics for ultra-fast laser experiments. This presentation will outline the significant achievements that EUCALL has delivered during the first two years of the project period.

Femtosecond transmission electron microscopy: an apparatus architecture

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Recent developments [1,2] in ultrafast electron microscopy and diffraction indicate that spatial and temporal information can be collected simultaneously [3,4]. In the present work, we push the capability of femtosecond transmission electron microscopy (fs-TEM) towards that of the state of the art in ultrafast lasers and electron microscopes. This is anticipated to facilitate unprecedented elucidation of physical, chemical and biological structural dynamics on electronic time and length scales. The fs-TEM numerically studied employs a nanotip source, electrostatic acceleration to 70 keV, magnetic lens beam transport and focusing, a condenser-objective around the sample and a terahertz temporal compressor [5], including space charge effects during propagation. With electron emission equivalent to a 20 fs laser pulse, we find a spatial resolution below 10 nm and a temporal resolution of below 10 fs, as shown in figure 1, will be feasible for pulses comprised of on average 20 electrons. The influence of a transverse electric field at the sample is modelled, indicating that a field of 1 V/ μm can be resolved.

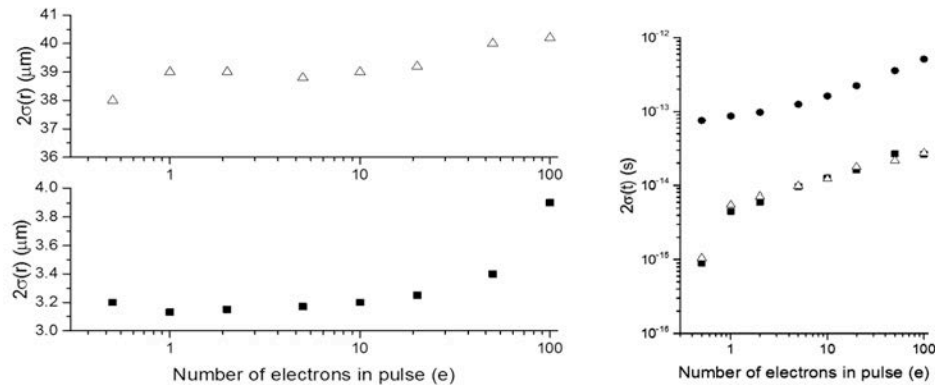


Fig. 1. Performance of the fs-TEM displayed as a function of electrons per pulse for both large ($\approx 40 \mu\text{m}$) and small ($\approx 3 \mu\text{m}$) radius pulses.

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Long-lived nonthermal electron distribution in aluminum excited by femtosecond extreme ultraviolet radiation

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We report a time-resolved study of the relaxation dynamics of Al films excited by ultrashort intense free-electron laser (FEL) extreme ultraviolet pulses. The system response was measured through a pump-probe detection scheme, in which an intense FEL pulse tuned around the Al $L_{2,3}$ edge (72.5 eV) acted as the pump, while a time-delayed ultrafast pulse probed the near-infrared (NIR) reflectivity of the Al film. Remarkably, following the intense FEL excitation, the reflectivity of the film exhibited no detectable variation for hundreds of femtoseconds. Following this latency time, sizable reflectivity changes were observed. Exploiting recent theoretical calculations of the EUV-excited electron dynamics [1], the delayed NIR-reflectivity evolution is interpreted invoking the formation of very-long-living nonthermal hot electron distributions in Al after exposure to intense EUV pulses. Our data represent the first evidence in the time domain of such an intriguing behavior.

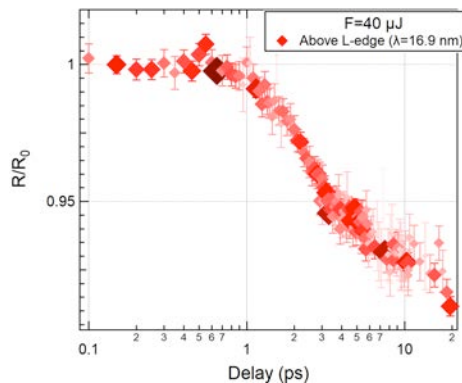


Figure caption: Optical-reflectivity variation vs pump-probe delay time. The FEL fluence was 2 J/cm^2 , the optical wavelength was 780 nm. The optical reflectivity is invariant for 1 ps after absorption of an intense 60 fs FEL pulse.

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Element specific channels in photo excitation of V – doped TiO₂ nanoparticles

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An in - depth understanding of electron photo-dynamics is essential to develop efficient knowledge-based photocatalytic devices. We present a differential illumination HERFD-XAS investigation of charge transfer phenomena in V-doped TiO₂ nanoparticles [1]. We found that light absorption induces the transfer of electrons from the V dopants to the host matrix cations in defective sites. With a steady state model, we estimated the lifetime of the excited state at 1ms, which suggests that dopant-injected electrons can remain trapped near Ti atoms for a very long time. The main result is illustrated in Fig. 1.

In parallel, we are also performing pump and probe ultra fast transient optical absorption. Selected results are reported in Fig. 2. The signal around 400 nm is due to trapped holes while the broad feature around 650 nm is related to trapped and free electrons. It is clear that V doping induces faster evolution of the excitation and relaxation dynamics.

The outlook for FEL measurements on this interesting materials system, which will allow to combine fs time resolution with chemical sensitivity, will be discussed.

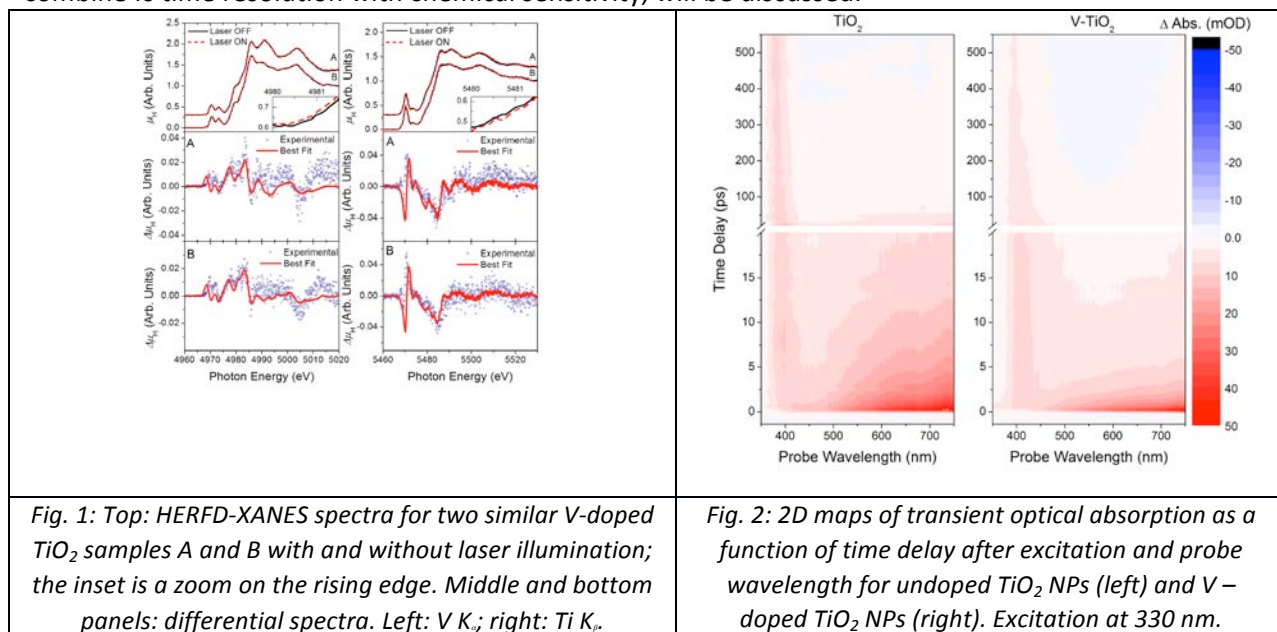


Fig. 1: Top: HERFD-XANES spectra for two similar V-doped TiO₂ samples A and B with and without laser illumination; the inset is a zoom on the rising edge. Middle and bottom panels: differential spectra. Left: V K_α; right: Ti K_α.

Fig. 2: 2D maps of transient optical absorption as a function of time delay after excitation and probe wavelength for undoped TiO₂ NPs (left) and V – doped TiO₂ NPs (right). Excitation at 330 nm.

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Structure and electron dynamics at the nanoscale: Metal-Insulator Transition in VO₂

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Transition metal oxides (TMO) are typically correlated systems and vanadium dioxide (VO₂) is one of the most studied system. Because of the interplay between electrons and lattice, it undergoes a hysteretic metal insulator transition (MIT) around room temperature (~340 K) with a change in resistivity of different orders of magnitude [1], paired to a complex structural phase transition (SPT) starting from an insulating monoclinic phase at low temperature to a final stable metallic phase at high temperature with the rutile symmetry.

VO₂ is also extremely sensitive to chemical and physical perturbations such as stress and strain [2] that slightly tune the MIT temperature. Moreover, as other TMOs, it is characterized by a phase separation, intermediate phases at the nanoscale with different micro- and nano-domains having different electrical, structural and optical properties [3-5]. All these phenomena make VO₂ an extremely interesting case-study with a wide range of potential applications in optics, sensors and novel memory devices [6-7].

Actually, the occurrence of an extremely fast reversible electronics and structural transitions is unusual and the nature and the driving mechanism of the VO₂ MIT are still under debate despite decades of efforts since its first observation in 1959 [8-9]. Because of the strong interplay between lattice and electronics properties, to investigate the MIT transition it is mandatory the use of a fast technique, sensitive to both local structural and electronic properties simultaneously. XANES spectroscopy is thus a suitable method to probe local properties and changes induced by the MIT in this complex system.

In addition, the MIT can be photo-induced on ultra-fast time scales in the UV regime. The natural consequence is to use time resolved experiments to shed some light on the very nature of the MIT on the femtosecond timescale. This could bring to new technological application like ultra-fast switching devices. We present here preliminary results from XANES spectra measured with the Auger yield technique and ResPes measurements on thin films of VO₂ from 8 nm to 32 nm, in order to monitor changes induced from the MIT to electronics and structural properties and the possible presence of metastable phases during the transitions in these films. We will discuss the results and experimental perspectives based on the synthesis and characterization of VO₂ nanoclusters of 5-10 nm using a Pulsed Microplasma Cluster Source (PMCS) under installation at Elettra. Finally we discuss future plans for time resolved experiments on clusters and thin films with ultra-fast XUV light sources .

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Optical control and quasiparticle witnessing in strongly correlated electron systems

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The prospect of “forcing” the formation of quantum coherent states in matter, by means of pulsed electromagnetic fields, discloses a new regime of physics where thermodynamic limits can be bridged and quantum effects can, in principle, appear at ambient temperatures. In this presentation I will introduce the field of optical control of correlated electron systems. I will focus on the possibility of coherently driving low-lying excitations of quantum many body systems making light-based control of quantum phases in real materials feasible. I will review the recent results in archetypal strongly correlated cuprate superconductors and introduce our new approach to go beyond mean photon number observables. I will show that quantum features of light can provide a richer statistical information than standard linear and non-linear optical spectroscopies. This will potentially uncover with unprecedented detail the evolution and properties of light-induced transient states of matter.

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Ultrafast dynamics of energy relaxation in CsI measured by TRXEOL with sub-picosecond time resolution

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We report on the first to our knowledge measurements of TRXEOL (time-resolved X-ray excited optical luminescence) with sub-picosecond time resolution. The up-conversion gating technique applied to luminescence in CsI excited by XUV pulses from FLASH allowed monitoring the energy relaxation during thermalization, self-trapping of charge carriers and formation of luminescence centers followed by their de-excitation. Two types of intrinsic luminescence, corresponding to the two components seen in time evolution of 340 nm luminescence after 125 eV excitation (Fig. 1a), have been identified. The rise-on time of the slower component of ~ 6 ps corresponds to the few picoseconds long estimated thermalization time in CsI, and the spectral content of this component is found in the same UV range as steady state luminescence. Although the UV luminescence in CsI is well known and widely used for its high light yield for scintillator applications, there is no common understanding on the origin of this luminescence at room temperature. Based on our investigations of the luminescence development within first tens of picoseconds in pure and doped CsI samples and of the nonlinear flux dependence, the origin of this luminescence is discussed. The first fast peak growing and decaying within the first two picoseconds occurs during a first stage of thermalization. Such behaviour along with other properties as wider spectral range than for steady state luminescence (Fig. 1b, only fast component is seen in visible range) and linear dependence on incoming flux irrespective to flux level and impurities introduced in crystal, allows to attribute this fast contribution to intraband luminescence (IBL) corresponding to electron radiative transitions within conduction band during thermalization. This is the first time that the intraband luminescence has been temporally resolved and unambiguously identified. We would like to emphasize that intrinsically fast intraband luminescence is presently of high interest for improving time resolution of scintillator based detectors down to the ten-picosecond level which is of demand for such applications as time-of-flight positron emission tomography [1], positron annihilation lifetime spectroscopy [2] and high energy physics.

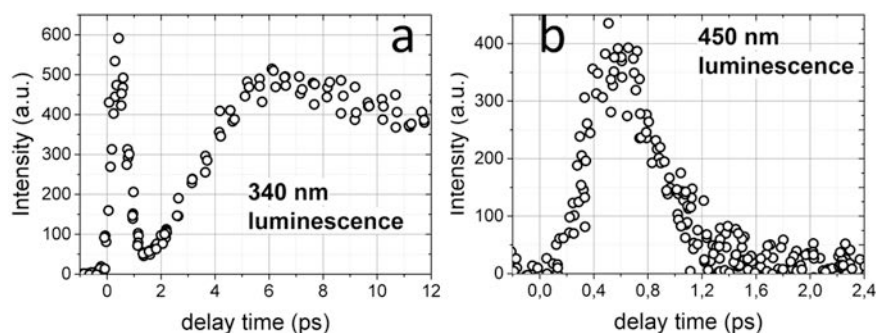


Figure caption: 340 nm (a) and 450 nm (b) luminescence in CsI excited by 125 eV photons.

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Novel sample delivery strategies for single-particle imaging of biomolecules

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One of the primary bottlenecks in realizing single-particle diffractive imaging at XFELs is the efficient delivery of isolated, reproducible target particles into the x-ray beam. We present here novel approaches for the production of cold and controlled samples of both biological molecules (e.g., peptides) and biological nanoparticles (e.g., viruses), designed for use in XFEL experiments.

We have successfully combined a supersonic-expansion laser-desorption source [1] with an electrostatic deflector [2]. This enables us to introduce intact dipeptide molecules into the gas-phase, rapidly cool them to rotational temperatures below 10 K, and spatially separate different structural isomers according to dipole moment. We demonstrate this powerful approach for the dipeptide Ac-Phe-Cys-NH₂ and produce cold and conformerically-pure beams of either main conformer of the dipeptide. The produced beams are well suited for XFEL experiments, such as single-molecule diffractive imaging [3].

For larger samples, such as viruses or nanoparticles, we have recently introduced a buffer-gas cell setup to rapidly cool aerosolized single particles to cryogenic temperatures. The produced nanoparticle beams can be aerodynamically collimated to yield high-density beams, ideal for single-particle diffractive imaging experiments. They are furthermore highly amenable to further control techniques, such as optical manipulation [4].

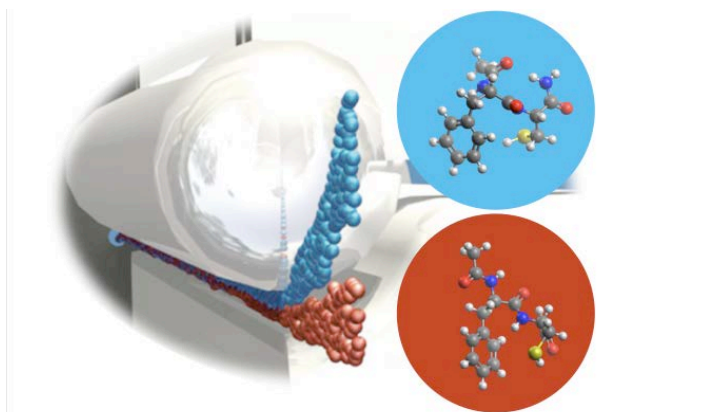


Figure caption: The two main conformers of a dipeptide molecule can be spatially separated using electrostatic deflection, and pure samples of either structure obtained in a molecular beam.

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Exploring the band curvature of low-bandgap semiconductors using few-cycle THz 2D-spectroscopy

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2D spectroscopy has been recently extended to the THz frequency range, from 1 THz to 25 THz, showing the potential of this technique for probing and exciting low-energy excitations, including electronic and lattice coupling [1], 2-phonon coherence [2] magnon nonlinearities [3], with 2D-THz spectroscopy and water molecules polarizability [4] with 2D-Raman-THz spectroscopy.

Here, we present 2D-THz experiments in the range between 1-10 THz in a reflective geometry (see Figure 1) investigating the electronic band-nonlinearities of InSb and InAs, using THz electric fields generated from a 2-colour plasma source (up to 100 kV/cm) and optical rectification in an organic crystal (up to 250 kV/cm). In the very first picoseconds after excitation, coherent motion dominates the nonlinear response. Subsequently, electron-electron scattering effects, i.e. impact ionization and intervalley scattering, start to dominate. Using 2D THz spectroscopy, we show that we can follow the continuous ballistic trajectory of the out-of-equilibrium electron population in the ($\Gamma \rightarrow X, K$)-plane of InSb and InAs. By using cross-polarized beams to separate contributions to the nonlinear response of different parity (see Figure 2), we observe distinct features in the 2D spectra.

To better understand the system response at times when the pulses overlap, we simulate our results using the finite-difference time-domain technique (FDTD). The simulations show that the nonlinear response is dominated by deviations of the conduction band dispersion from the radially symmetric, parabolic bands expected from a simple free electron gas model. These deviations can be categorized by their parity.

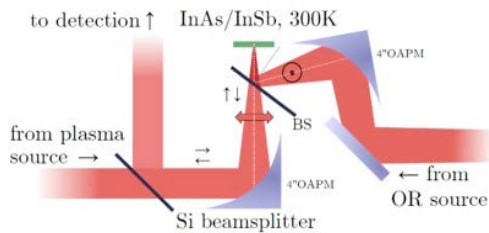


Figure 1: Measurement geometry of reflective 2D-THz spectroscopy on InSb and InAs.

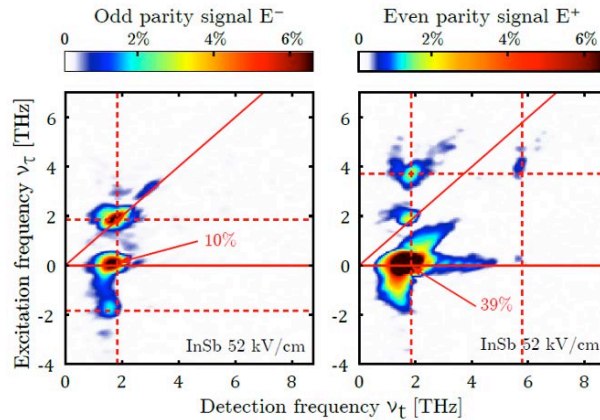


Figure 2: Odd and even parity 2D-spectra of InSb. Broken lines indicate the plasma-edge and phonon features.

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Non-equilibrium electron dynamics in cuprate superconductors by VUV and HHG photoemission spectroscopy

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Since their discovery in 1986, copper-oxide high-temperature superconductors stimulated a wide interest of the scientific community, because of their property to sustain the superconducting state at considerably higher temperature than conventional superconductors. After 30 years of intense studies, both theoretical and experimental, a number of questions remain still elusive. In particular, the dichotomy in the nature of the quasiparticles across the Fermi surface of the material, that has been speculated as being the origin of several unconventional properties of these materials, has never been directly measured.

Here we report on time- and angle-resolved photoelectron spectroscopy (TR-ARPES) studies on the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (Bi2212) compound, performed with a VUV probe. With this approach we are able to overcome the limits of TR-ARPES setups operated with ~ 6 eV photon energy and probe both the nodal and the antinodal states, allowing to characterize the nature of excitations over the entire Brillouin zone of the compound. To this aim we developed a novel source of ultrashort VUV photons, obtained as the sixth harmonics at 8.55 eV of the IR output of a parametric amplifier. This source provides a large flux thanks to the possibility to produce third-harmonic-generation (THG) in Xenon in the negative-dispersion regime. Furthermore, we report on the first characterization of a novel high-harmonic-generation (HHG) setup operating at high repetition-rate (>50 kHz), that will allow us to further widen the range of momenta and kinetic energies that can be probed with TR-ARPES. These preliminary results are compared with numerical simulations on the phase-matching conditions in Argon gas. Thanks to the developments we pursued in advancing the ultrafast sources for TR-ARPES, we have been able to considerably widen the range of accessible energy-momentum space, which is particularly relevant for the case of correlated materials with strongly anisotropic Fermi surfaces, paving the way to the study of the previously inaccessible antinodal state. This novel possibility will provide key information for a deeper understanding of the nature of antinodal quasiparticle in copper oxides.

Numerical Study on the Possibility of Generation of Two Dimensional Top-Hat Beam Using Deformable Mirror

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Photon distribution in the illumination is a crucial parameter in many microscopic and spectroscopic measurements. For instance, a uniform-intensity illumination is preferred to a gaussian-distribution-illumination in microscopic methods such as coherent diffraction imaging [1]. This is largely because they facilitate the straight-forward extraction of the true density of the sample without necessity to decouple the intensity distribution. While generation of such uniform-intensity illumination in a photon loss-less manner is a routine task at the optical wavelengths, they are quite challenging task at the x-ray wavelength. Here, we study, numerically, the feasibility of generation of such uniform-intensity illumination commonly called as top-hat or flat-top illumination using x-ray deformable mirrors. We also present, the numerical study of application of such top-hat beam in the imaging of extended object by using coherent diffraction imaging.

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Opportunities of X-ray resonant reflectivity experiments at FEL sources: superradiance and spin-currents

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Demagnetization of a ferromagnet by an optical excitation pulse is known to proceed on an ultrafast timescale, typically in the femtosecond regime. The prospect of controlling magnetization on ultrafast time scales is of considerable interest since the first observation of laser-induced ultrafast demagnetization by Beaurepaire et al. [1]. The XUV and X-ray free laser sources provide the ultrafast time resolution, the magnetic sensitivity and the short wavelength radiation to probe interface structures and depth profiles in great detail. Using the specular reflectivity of XUV-rays in reflection geometry at FELs allows us to probe the charge / magnetic density profiles and investigate the spatial evolution of these profiles on fs timescales.

In our work [2], we present the results of resonant magnetic XUV reflectivity experiments performed at the X-ray free-electron laser FERMI. The asymmetry exhibits ultrafast changes on 240 fs time scales upon pumping with ultrashort IR laser pulses. Depending on the value of the wavevector transfer Q_z we observe both decreasing and increasing values of the asymmetry parameter, which is attributed to ultrafast changes in the vertical spin-density profile of the trilayer film. By measuring femtosecond scattering dynamics in a surface geometry we demonstrate nanoscale and ultrafast lateral spin-reversal in the surface region of a ferromagnetic thin film [3].

Nonlinear processes are expected to occur in X-ray scattering experiments using an FEL when the X-ray intensities exceed the damage threshold for condensed matter systems. Superradiant resonant effects [4] may reduce the intensity where nonlinear processes such as X-ray induced transparency or stimulated emission can appear by many orders of magnitude, especially for photon energies in the XUV regime. We present the results of ultrafast XUV resonant reflectivity experiments of a permalloy/tantalum/permalloy trilayer system at the FEL FLASH with the FEL photon energy resonantly tuned to the Ni $M_{2,3}$ edge [5]. We measure the specular reflectivities for a large range of XUV fluences and determine a lower bound for the threshold fluence where superradiant non-linear processes play a dominant role in the fluence dependence of XUV reflectivities at the M-edges. The experimental results suggest that incoherent and non-resonant photo-absorption processes are dominant processes for resonant XUV reflectivity experiments.

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Temporal and spatial characteristics of electron cascades triggered by X-ray photons in LiF

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Low-fluence X-ray irradiation of alkali halides may result in a creation of long-living lattice defects called color centers. It is assumed that their spatial distribution reflects the X-ray beam lateral shape and, therefore, may serve as an efficient and precise diagnostic tool for the spatial pulse profile [1]. The color centers may be created via exciton decay mechanism; excitons are created when self-trapped valence holes catch free electrons, both produced by an intense X-ray pulse.

However, X-ray-induced energetic photoelectrons trigger secondary electron cascades, which may strongly influence the final distribution of the valence holes before their self-trapping, and thereby of the color centers. Our in-house classical Monte-Carlo simulation tool XCascade-3D [2] follows the electron cascades in time and space. It provides distributions of the electrons and holes in various X-ray-irradiated materials, including alkali halides. For the study case of LiF, we present the corresponding calculations which enable to establish a connection between the experimentally measured distribution of the X-ray-induced color centers in LiF and the spatial shape of the X-ray beam - with potential experimental application.

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Dissipation of extra energy in the primary hydration shell of DNA for poster abstract at Science@FELs, Trieste 2017

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Hydration dynamics of water is key critical to understand the role water in DNA function and its interaction with proteins. A two-color pump-probe experiment has been carried out on DNA with two hydration levels: 20 and 140 water molecule per base pair. Since the lifetime of the OH stretching mode and The HOH bending mode of water is no more than 200 fs. It will change to extra energy in the intermolecular freedom, i.e. weakening hydrogen bonding and a blue shift of phosphate band. As a result that there is only no more than 5% of the water has been excited by the pump pulse; a dissipation process of the extra energy in the close hydration shell has been discovered.

This dissipation process shows up in the transient spectra as a red shifting process of the blue-shifted band of the phosphate groups. The time behavior of center frequency, FWHM, and the area of this blue shifted band is analysis, by comparing the with previous simulation studies [2][3] on hydrogen bond.

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Ultrafast Vacuum Ultraviolet probe of the photoinduced dynamics of solvated molecules

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Femtoseconds to picoseconds structural dynamics of molecular complexes in solution are probed with transient absorption methods, that limits the access to optically bright states. A more complete picture of the dynamics that occur can be observed by time-resolved photoelectron spectroscopy (tr-PES) which doesn't have those constraints. Thanks to the liquid micro jet technique [1], we carry out PES studies on solvated molecules by means of VUV pulses with energy from 25 eV to 110 eV (Harmonium facility @ LACUS - EPFL) [2]. A recent tr-PES study on Iron hexacyanide successfully observed the ultrafast Ligand-to-Metal charge transfer (LMCT) that occurs in the molecule upon the 400nm-wavelength excitation [3]. The prompt reduction of the iron induces an energy shift of the HOMO electronic orbital, which appears as a new spectral feature among the outer-valence features. We observe the relaxation dynamic which corresponds to the electron transferring back to the ligand in about 0.5 ps (figure 1).

Such a capability of the technique paves the way to study a plethora of photoinduced electronic excitations in molecules and metal complexes in the liquid phase. Moreover, the high-energy harmonics (70-110 eV) allow us to access the first inner-shell electrons of molecules (figure 2), allowing a localized element-selective probing of nuclear motion. The simultaneous measurement of valence and core electrons allows us to observe ultrafast relaxation processes in the molecular complexes as well as the environment effects on the structural dynamics in a complete picture, every excited states being accessible through photoionization with the XUV probe pulse. The observation of the spectroscopic trace of vibrational wave packets in simple molecules such as Iodine will be the benchmark for this kind of structural dynamics studies by means of tr-PES of solutions.

References:

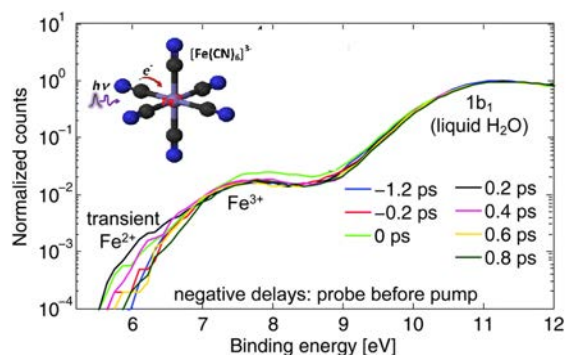


Figure 1: Transient PE spectra of $[\text{Fe}(\text{CN})_6]^{3-}$ in aqueous solution upon 400nm excitation [2]

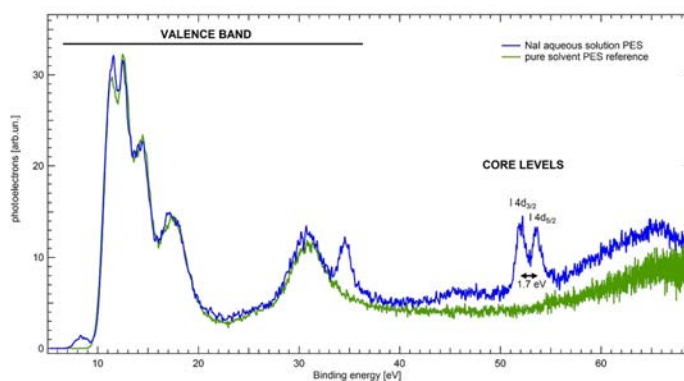


Figure 2: PE spectrum of NaI in water probed at 85eV photon energy. The I 4d inner-shell electrons appear at around 53 eV of binding energy

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Structural phase transitions induced by inverse and ionic Raman scattering

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The structural dynamics associated with the Raman-active amplitude mode of the charge density wave (CDW)-state in $K_{0.3}MoO_3$ were probed with ultrashort x-ray pulses. In a first experiment the system's response to different excitation fluences was investigated [1]. Starting in a regime of coherent oscillations, increasing the excitation fluence leads to a complete melting of the ordered state. Remarkably, a further increment to the fluence results in a short recovery of the CDW on a sub-picosecond time scale. In follow-up measurements, we could create a second recovery by applying another photoexcitation to the first one, which is shown in fig. 1. This recovery control may help to enhance our theoretical understanding of transitions equivalent to the one from a CDW- to a metallic state in $K_{0.3}MoO_3$.

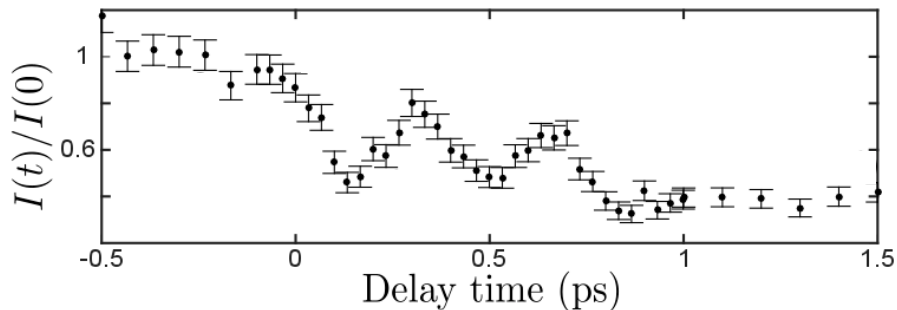


Figure 1: Temporal evolution of the intensity of the CDW superlattice-Bragg peak: A first 800 nm-excitation pulse is applied at 0 delay time and the second one at 0.35 ps. A second recovery is clearly visible.

As a next step in the exploration of photoinduced phase transitions we are currently investigating the possibility of driving simple structural phase transitions in perovskites in the electronic ground state. For this we excite an infrared-active mode at high frequency that according to theoretical predictions couples to a lower frequency Raman-active soft mode. The excitation pulses are created in a difference frequency generation setup, whose performance we are optimizing at present.

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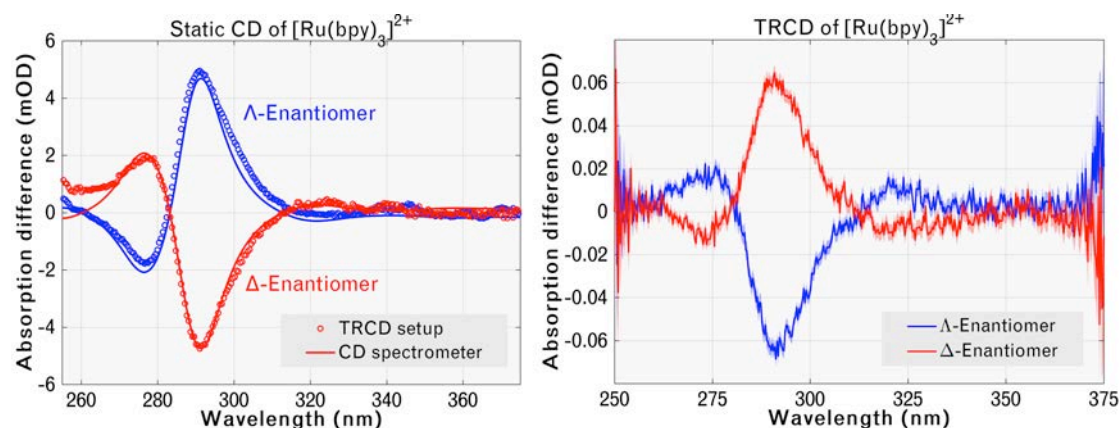
A broadband femtosecond circular dichroism spectrometer in the deep-UV

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Circular dichroism (CD) denotes the difference in absorption of left- and right-handed circularly polarized light and is a well-established tool in analytical biochemistry. In the deep-UV range (< 300 nm), it is sensitive to the coupling and thus spatial arrangement of transition dipoles on amino acid residues, nucleotides and peptides. Time-resolved CD spectroscopy (TRCD) is thus a promising experimental technique that is sensitive to changes in biomolecular configuration as a function of time [1], combining the time-dependent electronic information provided by traditional transient absorption spectroscopy with the structural information encoded in the chirality of molecular systems. Nevertheless, technical challenges have only allowed for slow progress with regards to the experimental implementation of TRCD [2].

We now present the first broadband femtosecond TRCD setup in the deep-UV, which employs exceptionally broadband probe pulses (250–370 nm) with low intensity noise (< 1% rms) at 20 kHz repetition rate. We achieve shot-to-shot data acquisition [3] and polarization state switching via a photoelastic modulator. Through polarization scrambling prior to dispersive detection and the elimination of polarization sensitive optics, we successfully minimize polarization artefacts in both static and transient CD spectra. Here, we demonstrate the capabilities of the setup via its application to enantiomerically pure samples of Λ - and Δ -[Ru(bpy)₃]²⁺, whose ligand-centred transition dipoles couple to give a strong CD signal centred at about 285 nm. The figure below compares the static and TRCD spectra of the two enantiomers, where an excellent symmetry is achieved in both cases. For TRCD, a 395 nm pump pulse induces a metal-to-ligand-charge-transfer, which reduces the probed CD signal.



Static (left) and transient CD (right) of Λ - and Δ -[Ru(bpy)₃]²⁺ in aqueous solution, pumped at 395 nm with a 50 ps delay. For the static CD, the TRCD setup is compared to a commercial CD spectrometer.

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Attosecond charge carrier dynamics in TiS₂ revealed by soft x-ray HHG laser spectroscopy

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We have investigated the time- and spatially-resolved motion of electron charge carriers in the dichalcogenide system TiS₂ using attosecond soft x-ray HHG laser spectroscopy at the Ti L-edges around 460 eV (see Fig. 1). It appears that in this two-dimensional topological insulator system, the motion of the Bloch walls is triggered by the pump pulse-induced inter- and intra-band charge transfer within the electronic band structure. This could be evidenced in a real-time manner by an unexpected modulation of the x-ray absorption coefficient, thus giving evidence for a direct impact onto the absorption process and resulting into a clear alternation of the absorption line shape starting at low pump field strengths. These results should help shading some light onto the complex spatio-temporal coupling of charge carriers in this topological system, and may path the way towards a better understanding of advanced materials relevant for various applications such as, e.g., ultrafast electronics, batteries, and energy converters.

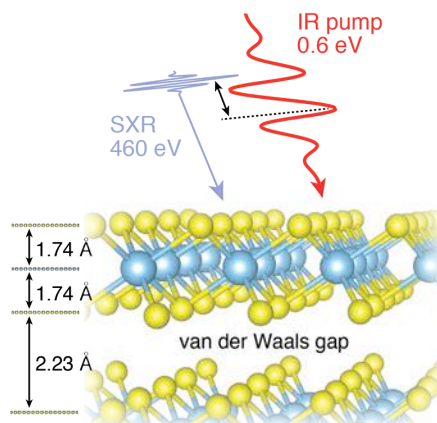


Figure 1: Attosecond transient soft x-ray (SXR) absorption spectroscopy in TiS₂. A sub-2-cycle 1.85- μm pump pulse stimulates carrier dynamics inside a 150-nm-thin TiS₂ crystal (sketched are two layers), which is probed by a 300-as-duration SXR pulse in small-angle non-collinear geometry.

Femtosecond Ho:YAG thin-disk oscillator enabling two-octave 5-20 μm frequency comb generation

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Synchrotron infrared radiation is finding applications in diverse fields ranging from biology to material science due to its broad bandwidth and high coherence [1,2]. The spectral region spanning $500\text{--}5000\text{ cm}^{-1}$ is of particular interests for chemical identification, since most organic molecules exhibit characteristic fundamental vibrational absorptions in this window. Here we present a table-top system that can simultaneously cover a significant part of this 'finger-print' region at $\sim 20\text{ mW}$ -level average power. The system is based on a high power Ho:YAG thin-disk laser providing 220 fs pulses at $2\text{ }\mu\text{m}$ wavelength with 18.7 W average power and 77 MHz repetition rate. The output is then coupled into an endlessly single-mode fiber with a core diameter of $12\text{ }\mu\text{m}$, where soliton self-compression occurs [3].

The resulting 15 fs pulse (see corresponding spectrum in Fig.1a) is subsequently focused into a gallium selenide (GaSe) crystal, where intra-pulse difference frequency generation (DFG) takes place to produce coherent radiation from $500\text{--}2250\text{ cm}^{-1}$ ($5\text{--}20\text{ }\mu\text{m}$) at 24 mW of measured average power (Fig. 1b). The entire system, with a foot print of $1.8\text{ m} \times 0.6\text{ m}$, has been running for over 4 weeks at full power with no damage to the crystal observed. This compact table-top system has the potential to bring broadband high brightness mid-infrared radiation to individual research labs.

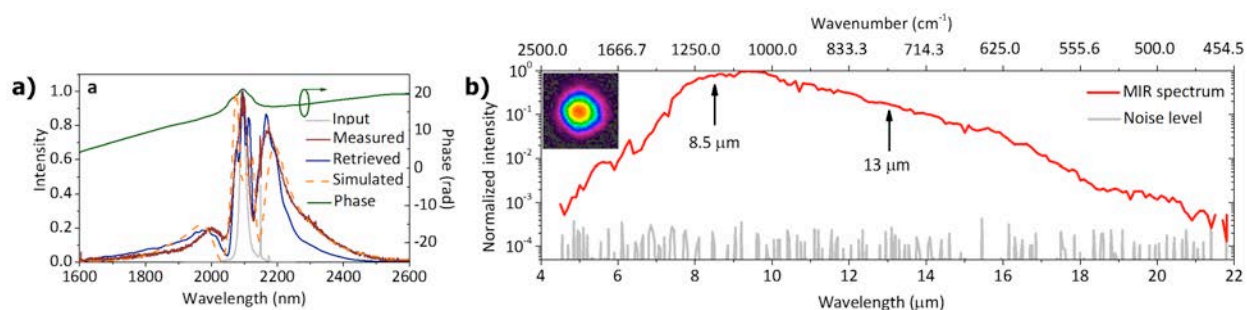


Figure 1. **a)** Measured output spectrum of the 15 fs compressed pulses **b)** Measured mid-infrared spectrum. No spectral corrections for losses in optics and diffraction gratings were performed. Inset: measured beam profile.

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Coherent phonon excitation and ultrafast phase transitions in manganese arsenide

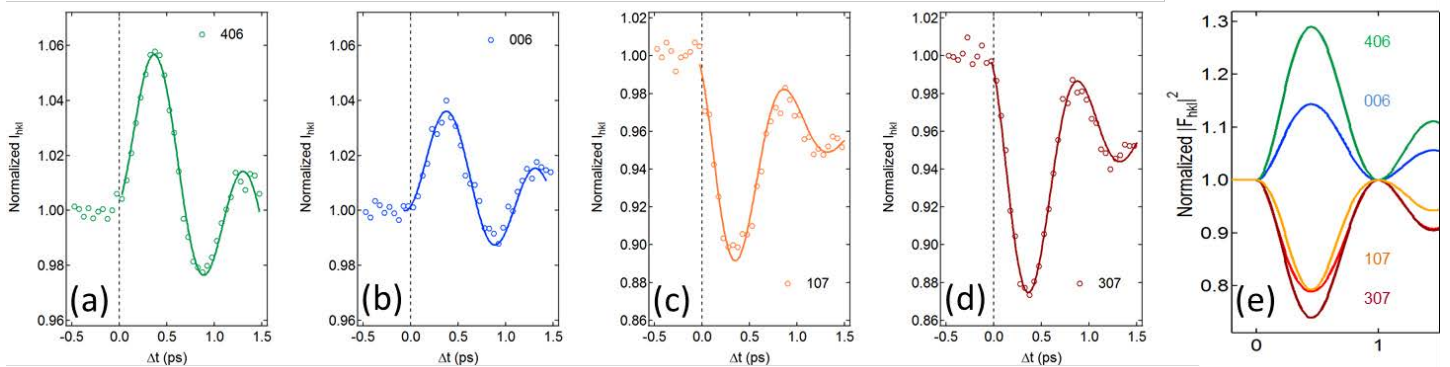
F. Vidal¹, Y. Zheng¹, L. Lounis¹, M. Eddrief¹, E. Ferrari², C. Spezzani², A. Ciavardini², E. Allaria², H. Wang³, J. Zhao³, R. Alonso Mori⁴, M. Seaberg⁴, M. Chollet⁴, H. Popescu⁵, C. Laulhé⁵, M. Sacchi^{1,5}

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We have investigated the laser-induced MnAs structure dynamics in MnAs/GaAs(001) epitaxial films, by measuring time-resolved x-ray diffraction at the XPP station of the LCLS.

Bulk MnAs features a first order transition at $\sim 40^\circ\text{C}$ between the hexagonal ferromagnetic α phase and the orthorhombic paramagnetic β phase, whose origin is still the object of debate [1]. In addition, a less studied second order transition to the hexagonal paramagnetic γ phase takes place at $\sim 125^\circ\text{C}$. In MnAs films grown on GaAs(001), epitaxial constraints make the α and β phases coexist over the temperature range $\sim 10\text{--}40^\circ\text{C}$, in the form of a regular set of stripes. In the past, we studied the evolution of the morphological and magnetic properties of MnAs/GaAs(001) by XUV and soft x-ray resonant scattering, probing the MnAs microstructure and the α/β stripes formation [2]. In an optical-pump/XUV-probe scattering experiment performed at the FERMI FEL source, we showed that the magnetization of an Fe layer deposited on top of the MnAs can be reversed locally by a single fs optical laser pulse [3], establishing a clear link between Fe magnetization and MnAs microstructure dynamics. Therefore, understanding the photo-induced structure dynamics of MnAs/GaAs(001) is relevant for applications in laser-driven magnetization switching. Synchrotron based time-resolved x-ray diffraction experiments spanning the μs range of delays allowed us to determine the timescales of the structural changes that are relevant for the laser-driven magnetization reversal [4].

In our diffraction experiments at the XPP station of the LCLS, we have shown that a complete transition to the γ -MnAs phase takes place within ~ 20 ps, regardless of the initial phase being α , β or a mixture of the two, demonstrating that it is the $(\alpha, \beta) \rightarrow \gamma$ transformation that drives the microstructure dynamics. The initial α or β crystalline phases are disrupted within a few ps, supporting previous results that probed the evolution of the α/β stripes [3]. Thanks to the ~ 50 fs overall time resolution, we could address the $\sim\text{ps}$ range of delays with high accuracy (see Figure). We observed the excitation of a $\sim\text{THz}$ coherent phonon mode and analyzed its dependence on the static temperature and on the laser excitation strength. The temperature dependence of the mode frequency provides a direct experimental evidence of a soft-mode at Γ in β -MnAs. Soft phonon modes in MnAs had been invoked often in the theoretical description of the magneto-structural phase transitions [1], but had never been observed experimentally.



(a-d): experimental intensity of four Bragg reflections as a function of pump-probe delay Δt .

(e): calculated structure factors (no DW term included) for a vibration mode along the orthorhombic-hexagonal path.

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Following Structural and Magnetic Dynamics in Antiferromagnetic Dysprosium Thin Films with Strong Magnetostriction

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In ultrafast demagnetization studies, the lattice is often regarded chiefly as a spin sink. In a simplified picture, the photoexcitation of the electrons leads to a heating of the spin system and hence a decrease of magnetic order, while the spin angular momentum is transferred to the lattice by electron-phonon scattering [1]. In reality, the interactions between the spin system and the crystal lattice are much more complex. The lattice spacing and symmetry directly defines the amplitude and sign of the exchange coupling within the spin system. In cases where nearest-neighbor (NN) and next-nearest-neighbor (NNN) couplings of different sign compete this relation between lattice spacing and magnetism is strongly enhanced. In rare earth metals, e.g. dysprosium, this interplay leads to dramatic effects already in the static case like a negative thermal expansion due to magnetostriction and a temperature-driven change of the antiferromagnetic spin helix periodicity which exceeds that of the lattice by two orders of magnitude. In this study, we probe the photo-induced structural and magnetic dynamics of an *in-situ* grown 80 nm dysprosium film in one and the same experiment at the laser-slicing facility at the BESSY II electron storage ring. We use ultrafast resonant soft X-ray scattering at the Dy M_5 absorption edge to follow the dynamics of the antiferromagnetic spin helix, which can be probed as a superstructure Bragg peak at $(0\ 0\ \tau)$ [2]. By tuning the X-ray photon energy just below the Dy M_5 absorption edge we can reduce the sensitivity to magnetic signatures and can scan the layer thickness oscillations at lower q by transient X-ray reflectivity measurements. Our results thus link the recent work on the ultrafast demagnetization [3] and structural dynamics [4] in the rare earth metal dysprosium.

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Materials Imaging and Dynamics Instrument at the European XFEL

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The unique properties of hard X-ray laser beams generated by the European XFEL will enable completely new experiments in materials science. In particular, the Materials Imaging and Dynamics (MID) station will offer extended capabilities for scattering and imaging experiments, *e.g.* coherent X-ray diffractive imaging (CXDI) and X-ray photon correlation spectroscopy (XPCS), compared to present state-of-the-art facilities. Based on the high degree of coherence, the exceptional flux, and the ultra-short pulses of the X-ray laser it will be possible to investigate materials with unprecedented resolution in space and time [1].

The X-ray energy at MID will be in the range of 5 to 25 keV either using the full SASE spectrum ($\Delta E/E \approx 2 \cdot 10^{-3}$), using the seeded beam ($\Delta E/E < 10^{-4}$), or filtered by the use of monochromators (Si(111) & Si(220)). The use of CRL transfocator or a nanofocus setup enables beam sizes down to a few micrometers and 10th of nanometers, respectively.

Allowing a broad variety of different dynamical investigations, MID will be equipped with an optical pump laser system as well as with a pulsed magnet module in order to measure the response of various materials after external excitation. Furthermore, a Split and Delay Line (SDL) can be used to split single FEL pulses into two and delay them with respect to each other. By this, an X-ray pump / X-ray probe scheme as well as dynamical investigations in the sub-ps time range will be possible.

The MID instrument provides a multitude of different detector systems, such as the AGIPD (adaptive gain integrating pixel detector), depending on the experimental requirements. The data acquisition system will collect - beside the recorded X-ray scattering pattern - also the shot-to-shot beam parameter (*e.g.* spectrum, intensity) in a dedicated diagnostic endstation enabling widespread possibilities for an optimal data treatment.

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Time-resolved optical and photoelectronic studies of the semimetallic transition metal dichalcogenide WTe₂

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Tungsten ditelluride (WTe₂) has been receiving increasing attention due to the recent discovery of peculiar properties such as its extremely large magnetoresistance and possible topology features as a type-II Weyl semimetal. To obtain information to possibly control the magnetoresistance using pulsed laser beams, we studied the nonequilibrium behavior of WTe₂. Using time-resolved optical spectroscopy, we investigated its response to a 250 kHz 800 nm laser beam with pulses presenting a ~50 fs duration using a 250 kHz ultrabroad supercontinuum pulsed beam as probe beam. We found a highly anisotropic differential reflectivity with a two-fold symmetry and a ~1 ps relaxation time. Four different A₁ coherent optical phonons effects were resolved with ~9 cm⁻¹, ~80 cm⁻¹, ~134 cm⁻¹ and ~215 cm⁻¹ frequencies. For the two lower energy modes, the amplitude symmetry and temperature dependence were analyzed. Spectral profiles of the reflectivity variations were modelled as the modification of dielectric function parameters. In particular, the effect of the ~9 cm⁻¹, ~80 cm⁻¹ phonon modes is mainly connected to a change of the central frequency of a single dielectric function term. Using time-resolved photoelectronic spectroscopy, the Γ -Y direction was studied. A large non-oscillating negative variation was observed just below the Fermi level with ~1 ps relaxation time, found to be common to all of the resolved band features.

Noise correlation spectroscopy for non-equilibrium measurements of low energy Raman modes of electronic and vibrational origin

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In this contribution I will introduce the idea of performing noise correlation spectroscopy (NCS) experiments with ultrashort light pulses, in order to address the dynamical response of low energy Raman active modes in complex materials.

We are confident that NCS will provide a useful tool to address the low energy Raman modes in real materials. The central idea of this approach is to witness how stimulated Raman processes imprint in the ultrashort light pulses a correlation between different spectral components. In appropriate conditions, stimulated Raman processes can amplify the intrinsic noise which characterizes ultrashort light pulses at frequencies whose difference is resonant to the phonon mode.

By repeated single shot measurements of the noise, after the interaction of ultrashort light pulses with a sample, we will be able to evaluate the induced correlation between different spectral components, thus retrieving the Raman response of the material.

We stress that should NCS become viable, it will provide the possibility of measuring the Raman response in matter on a timescale solely limited by the pulse duration. This would open new perspectives for non-equilibrium studies of electronic and vibrational degrees of freedom in complex materials.

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The FAB10 beamline at ATTOLAB: a versatile facility for attosecond physics

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The recent improvement in terms of reliability and stability of ultrafast high energy lasers based on Ti:Sapphire technology is driving the development of high performance VUV-XUV ultrafast light sources, attracting the attention of a large scientific community interested to the study of femto and sub-femtosecond dynamics in matter. The process of High order Harmonic Generation (HHG) that can take place when focusing intense lasers on gas targets, supplies an XUV spectrum that shows unique specificities as for its high degree of coherence, its low duration, which lies in the attosecond to femtosecond range, and its excellent synchronization to a Visible-IR laser that may be used for pump-probe experiments with interferometric time resolution. Starting from a $\lambda=800$ nm wavelength, typical HHG spectra lie in the 10 eV-120 eV range, which can address a large variety of applications from solid state physics (e.g. spin dynamics, dynamics of Dirac fermions in topological insulators, multi-ferroic materials, to cite few examples) and gas phase chemical physics (e.g. time-resolved photoionization in the core- and valence shell of atoms/molecules, highly non-linear harmonic spectroscopy...).

Based on this scientific landscape, we designed an ultrafast XUV facility which offers free-ports to users from solid state and chemical physics backgrounds. The laser system, which has been developed at Attolab, in collaboration with Amplitude Technologies, is a Ti:Sapphire system which delivers 23 fs CEP stabilized pulses of 2 mJ at a 10kHz repetition rate. The beam is focused in a continuous gas jet to produce HHG spectra. The FAB10 beamline, currently under commissioning, has been designed and constructed by consensus among users partners of the project. The main element is a three stage spectro-temporal selector device that is used to switch between what we call very broadband, broadband, and narrowband operating modes. The spectral band extends over the full 10-100 eV range, with respectively 20 eV, 1 to 5 eV and 100 meV FWHM spectral resolution, corresponding to pulse durations in the 100 as, 1 fs and 10 fs ranges. The user can switch between spectrally resolved to attosecond resolution configuration within 15 minutes. All three configurations are synchronized, down to attosecond precision with IR-UV laser pump beams. In order to meet the needs of the largest scientific community, extreme care has been taken to provide a very stable and reproducible beamline toolset and diagnostics, adopting the synchrotron radiation technological standards and methods adapted to the ultrafast science. The beamline is fully UHV compatible and the two-foci layout allow for the parallel use of a magnetic bottle TOF electron spectrometer that can be used for on-line measurements of the XUV spectral phase or as a diagnostic for the XUV-IR delay.

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Ultrafast Protein Response of a Phytochrome to the Excitation of the Bilin Chromophore

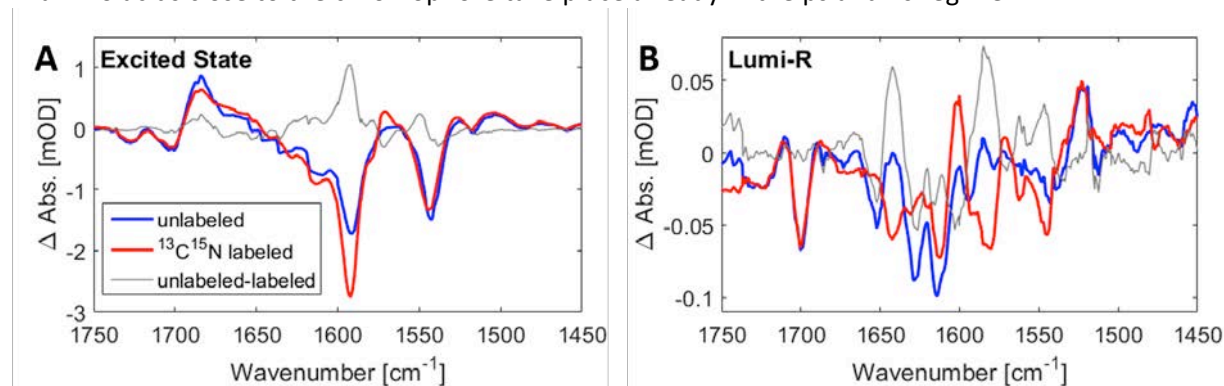
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Phytochromes are photosensory proteins that respond with a structural change to the illumination with red or far red light. The initial photochemical reaction (an isomerization in the associated bilin chromophore) leads to a signal amplification through the protein to the remote active domain [1].

We have studied the bacteriophytochrome from *Deinococcus radiodurans* through pump-probe IR spectroscopy. With this method, we access the responses of the chromophore and the protein in the earliest step of the photocycle, i.e., from the excited state to the first intermediate (the Lumi-R-state). ¹³C¹⁵N isotope labeling revealed that already in the excited state, the protein and not only the chromophore contributes to the IR difference spectrum (Fig. A). This highlights the importance of the direct connections of the chromophore to the protein environment. The Lumi-R spectra (Fig. B) show even more differences between isotope labeled and unlabeled protein. These changes are most likely due to differences in the amide I and amino acid side chain modes. It has been shown that the major structural changes, such as a β -sheet- α -helix transition [2,3] and the opening of the dimer [4], happen at later stages in the photocycle (on a millisecond timescale). However, our data shows that small changes in amino acids close to the chromophore take place already in the ps and ns regime.



Time-resolved IR spectra as a difference to the red absorbing ground state (the Pr state). Comparison between ¹³C¹⁵N labeled and unlabeled protein with biliverdin at natural abundance in both cases. **A)** Excited state (average of data between 0 ps and 1 ps after excitation) **B)** Lumi-R state (2.6 ns to 2.66 ns).

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Nucleation and growth kinetics from Mie scattering in the free molecular regime

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Understanding aerosol formation and growth is fundamental for the development of better weather models, the design of catalysts, nano-electronics and novel nanomaterials with controlled morphology. However, due to the intrinsic speed of aerosol growth, studying its kinetics and mechanism has been limited in the past because it requires instruments with temporal resolution in the sub-millisecond range and the capability to measure aerosols in situ as they grow, with minimal sampling bias and characterization artifacts. Something that most available characterization instruments do not fulfil. An optical detector used for nucleation and condensation studies of newly formed aerosol particles is the so-called constant-angle Mie scattering (CAMS) detector [1]. In principle, this instrument measures scattered light that occurs when particles reach a size comparable to the wavelength of the laser beam. The scattered light intensity is a function of size as predicted by Mie theory. Particle growth measurements have been validated in the past for the continuum regime (diffusion dominated) using a CAMS with a HeNe laser ($\lambda = 632 \text{ nm}$). [2]. Nevertheless, the initial phases of aerosol growth occur in the kinetically dominated free molecular regime. Characterization of this regime require radiation with high intensity at wavelengths below 100 nm. Achieving this is a challenging experimental task but understanding aerosol growth in the kinetically dominated regime represents an important milestone in the field. This research has the potential to open exciting new applications and be the basis for better understanding and controlling material properties and synthesis in the nano-scale.

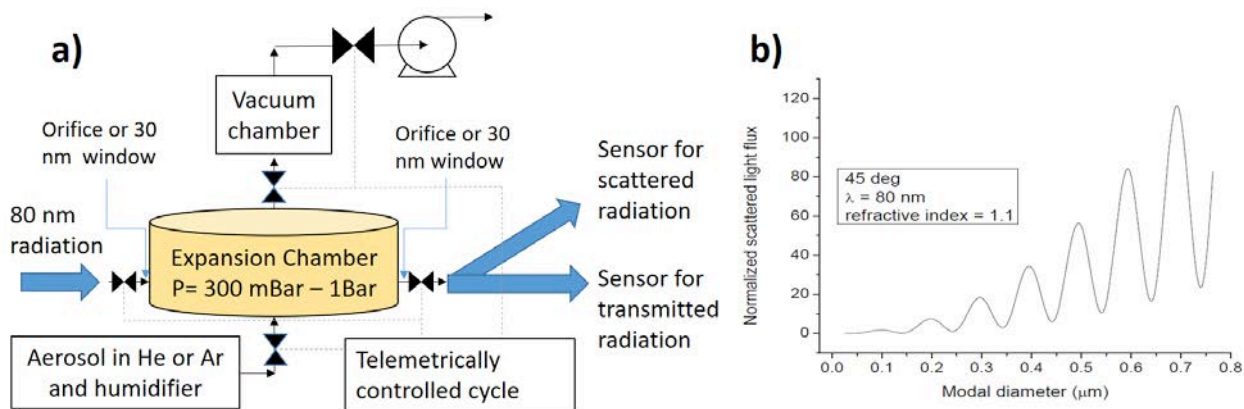


Figure 1. a) Schematic of the experimental setup to measure aerosol growth rate in the free molecular regime in situ. b) Calculated light scattering based on Mie theory for particles growing under a wavelength of 80nm.

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