

Project template for Wavemix workshop

Project title:

Soft X-ray Second Harmonic Generation of Aqueous Solutions in the bulk and at the surface

The aim of the experiment is to perform bulk and surface specific spectroscopy with element and chemical specificity of liquid systems. This experiment will leverage the recently developed thin flat jet technology and combine it with newer XFELs. The challenges are related to both producing stable jets, and performing spectroscopy at an ultrafast, inherently noisy SASE source while maintaining the high flux required to perform nonlinear experiments. We can perform the experiments in a time-resolved manner by optically pumping a jet, and probing it via XAS and soft X-ray SHG.

Short description / abstract:

The aim of this project is to perform spectroscopy of aqueous solutions. Ideally, we will be able to perform simultaneous measurements of bulk liquid water bulk (by energy resolved transmission XAS) and by reflective soft X-ray second harmonic generation following an optical excitation. This will enable measurements of bulk solvation and surface solvation as a function of time. The high power and repetition rate of newer XFELs will enable us to study the dynamics of aqueous systems. This is seen as a general class of measurements and not a specific measurement that we are aiming to perform. The very rough setup is sketched below.

Descriptive figures:

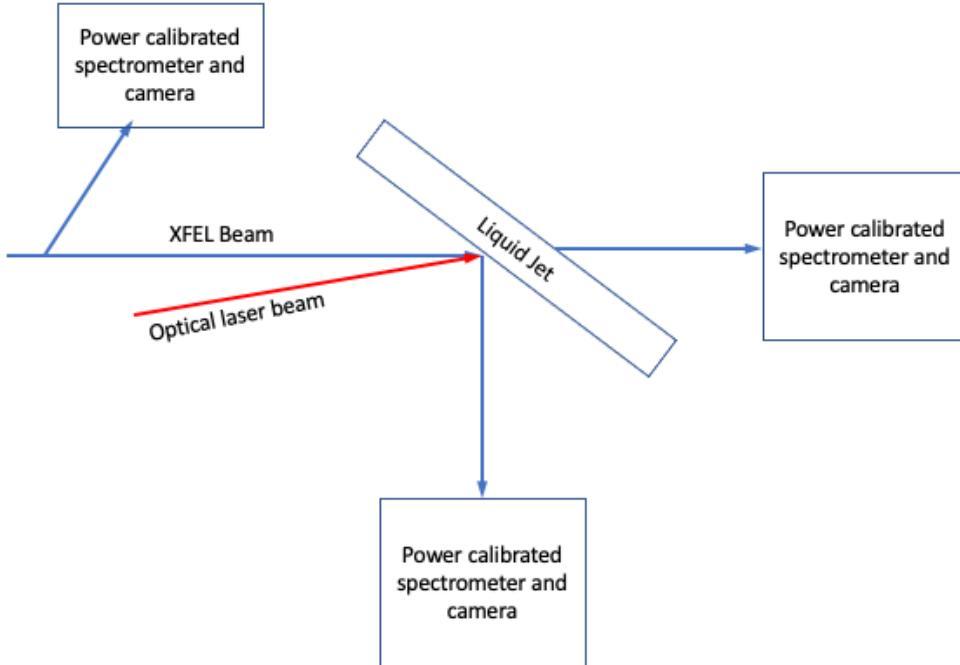


Figure 1: Conceptual schematic for proposed experiment

Requirements:

We will be leveraging the jet technology from Jake Koralek, and we will be combining it with spectroscopy based endstations such as ChemRIGS at LCLS-II or Malorja at SwissFEL. We think these experiments will be feasible in the near future.

Tentative project timeline

We plan to write a proposal on this in the second half of 2021, probably vesting in early 2022.

Preliminary team:

Required skills include – Familiarity with liquid jets, familiarity with spectrometer design, knowledge of X-ray cameras, data analysis (python), familiarity with nonlinear optics

Contact Person:

Michael Zuerch mwz@berkeley.edu & Craig Schwartz CPSchwartz@lbl.gov

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Project title:

Homodyne and heterodyne detection of All X-ray Transient Gratings generated by Talbot effect

The advent of coherent short-wavelength sources such as the X-ray Free Electron Laser allows the development of new spectroscopies relying on nonlinear interactions with multiple pulses. Transient Grating (TG) spectroscopy is a non-collinear four-wave mixing technique, in which two ultrashort pulses cross coincidentally on the sample and generate ultrafast dynamical response (electronic/lattice/spin/thermal excitations) at a wavevector determined by the beam interference pattern. A delayed third pulse is then diffracted by the grating and the TG signal is coherently scattered in the phase matching direction. The time evolution of the signal is a direct signature of the excitation grating dynamical response, including relaxation. TGs are currently being used to study a wide range of phenomena such as the propagation of phonons and phonon-polaritons, thermal transport, molecular diffusion, carrier and spin dynamics in semiconductors, and dynamical behavior of proteins. Recently TG experiments were extended to the extreme UV range [1, 2]. EUV TG measurements permit far higher TG wavevectors than with optical light, and can be conducted with wavelengths that are resonant with some core transitions. Hard X-ray TG could ultimately be conducted with sub-nm TG spatial periods, accessing wavevectors that span the entire Brillouin zones of most crystalline samples, allowing excitation of acoustic and optical phonon modes with correspondingly wide wavevector ranges, and enabling measurement of transport on microscopic length scales. They also permit access to a very wide range of core transitions with which the wavelengths could be resonant, and they provide access to bulk properties because of the deep penetration depth. We intend to conduct All X-ray Transient Grating experiments with homodyne and heterodyne detection. The goal of the experiments will be to extend the XTG – optical probe technique [3] to All X-ray TG (with X-ray probe, AXTG), via the Talbot effect for convergent XFEL Gaussian beams [4], investigating silicon.

[1] Bencivenga, F. et al. *Nature* **520**, 205-208 (2015)

[2] Bengivenga, F. et al. *Sci. Adv.* **5**, 7 (2019)

[3] Svetina, C., Rouxel, J, “Hard X-ray Transient Grating Spectroscopy on Bismuth Germanate”, submitted (2020)

[4] Svetina, C. et al. *Opt. Lett.* **44**, 574-577 (2019)

Short description / abstract:**Descriptive figures:**

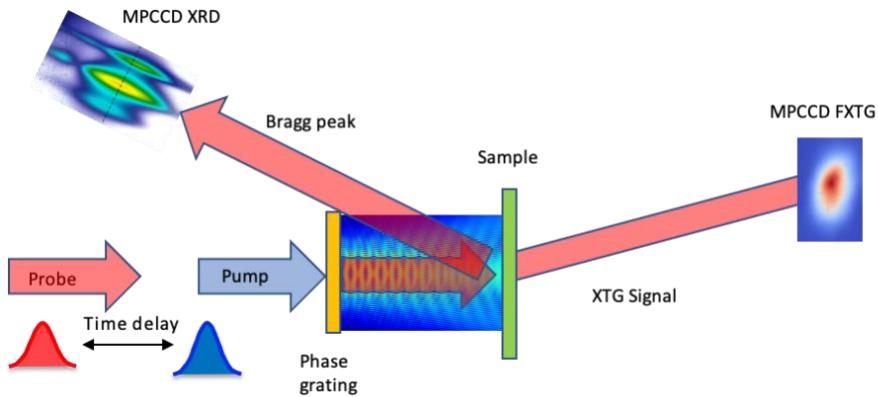


Figure 1 Geometry of the proposed All X-ray Transient Grating experiments. At SACL A we plan to perform AXTG in homodyne detection while measuring the sidebands on a Bragg peak. At LCLS we plan to perform AXTG with heterodyne detection by taking advantage of a X-ray reference beam.

Requirements:

Experience with XFELs and/or data analysis experience and/or condensed matter knowledge and/or transient grating experience

Tentative project timeline

Two proposal currently submitted (LCLS and SACL A). The beamtime at SACL A will focus on homodyne detection of AXTG signal on silicon while detecting a structural Bragg peak in parallel. If granted, the beamtimes should occur in the first half of 2021. The beamtime at LCLS will focus on heterodyne detection of AXTG signal on silicon. If granted, the beamtime should occur in the second half of 2021.

Preliminary team:

SwissFEL, FERMI, LACUS, PULSE, LCLS, SACL A, UC Irvine. More active collaborators are welcome to join

Contact Person:

cristian.svetina@psi.ch

Project template for Wavemix workshop

Project title:

Optical Pump - Soft X-ray Second Harmonic Generation of Liquid Water Surfaces at LCLS-II

The aim of the experiment is to perform surface specific time-resolved spectroscopy with element and chemical specificity of liquid systems. This experiment will leverage the recently developed thin flat jet technology and combine it with LCLS-II. The challenges are related to both producing stable jets, and performing spectroscopy at an ultrafast, inherently noisy SASE source while maintaining the high flux required to perform nonlinear experiments. We will perform the experiments by optically pumping a jet, and probing it via XAS and soft X-ray SHG.

Short description / abstract:

The aim of this project is to perform spectroscopy of aqueous solutions in a time resolved manner. Ideally, we will be able to perform simultaneous measurements of bulk liquid water (by energy resolved transmission XAS) and by reflective soft X-ray second harmonic generation following an optical excitation. This will enable measurements of bulk solvation and surface solvation as a function of time. The high power and repetition rate of LCLS-II will enable us to study the dynamics of liquid water. This is seen as a general class of measurements and not a specific measurement that we are aiming to perform. The very rough setup is sketched below.

Descriptive figures:

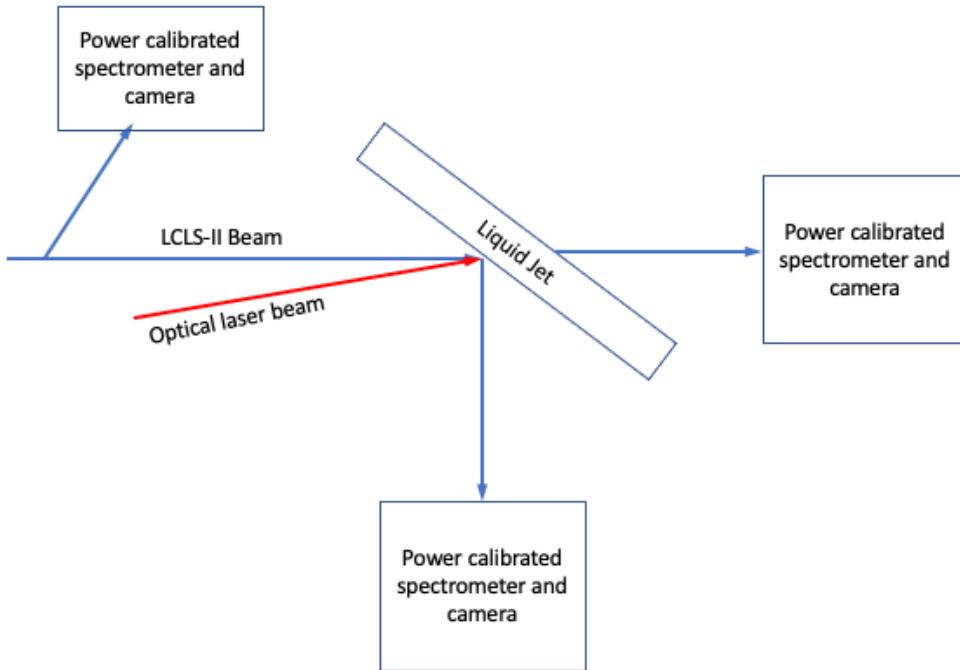


Figure 1: Conceptual schematic for proposed experiment

Requirements:

We are specifically trying to do experiments at LCLS-II with this particular proposal. We will be leveraging the jet technology from Jake Koralek, and we will be combining it with the ChemRixs endstation. The idea is to not have a build a lot to make it doable right when LCLS-II issues its first call.

Tentative project timeline

We plan to write a proposal on this in the first call for LCLS-II in late 2021, probably vesting in early 2022.

Preliminary team:

Required skills include – Familiarity with liquid jets, familiarity with spectrometer design, knowledge of X-ray cameras, data analysis (python), familiarity with nonlinear optics

Contact Person:

Craig Schwartz CPSchwartz@lbl.gov

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Daria Gorelova, I. Institute for Theoretical Physics and Center for Free-Electron Laser Science (CFEL), Universität Hamburg

Project title:

Atomic-scale imaging of laser-driven electron dynamics in solids using subcycle-resolved x-ray-optical wave mixing

We propose to resolve optically-induced charge and current distributions on atomic scale by means of subcycle-resolved x-ray optical wave mixing. In this experiment, an optical pulse and an x-ray pulse with a duration shorter than an optical cycle simultaneously interact with a crystal. The x-ray-optical wave-mixing signal results in side peaks to the Bragg peaks at scattering vectors \mathbf{G} shifted in energy and in momentum [1,2,3]. The spectral positions of the side peaks are at scattered energies $\omega_j \pm n\omega$, where ω_j is the incoming x-ray photon energy, ω is the photon energy of the optical pulse, and n is an integer. The intensity of the n -order side peak is given by the \mathbf{G} -component of the Fourier transform of the n -order optically induced charge distribution. Even when n -order macroscopic optical response is forbidden, corresponding microscopic charge distributions can be considerable and give rise to x-ray-optical wave mixing signal [3,4].

If the duration of the x-ray pulse is shorter than an optical cycle, time-dependent interference terms between side peaks appear in the signal [4]. We propose to choose the x-ray pulse duration such that only nearest-neighbour side peaks interfere. In this case, the delay-dependence of the x-ray-optical wave-mixing signal provides the phases of \mathbf{G} -Fourier components of the n -order optically induced charge distribution. In addition, subcycle-resolved x-ray-optical wave-mixing signal would be different for \mathbf{G} and $-\mathbf{G}$ scattering vectors. This difference reveals time-dependent microscopic electron current.

Subcycle-resolved x-ray optical wave mixing signal is modeled in two steps [3]. In the first step, microscopic optical response of a laser-dressed crystal is calculated using the Floquet-Bloch framework combined with DFT calculations. Fig. 1 shows the second-order charge distribution in GaAs induced by an optical pulse with the photon energy of 1 eV and the intensity $4 \times 10^{11} \text{ W/cm}^2$. In the second step, x-ray scattering signal involving transitions between laser-dressed states is calculated. Fig. 2 shows the x-ray scattering signal from the laser-dressed GaAs. The dotted green lines show the inelastic scattering signal due to x-ray transitions to initially unoccupied laser-dressed states. The gray lines show the relative intensity of the side peaks. The red lines show subcycle-resolved x-ray-optical wave mixing. It follows from our calculations that x-ray optical wave-mixing signal is considerable and not affected by inelastic x-ray scattering at scattered energies $> \omega_j$.

Subcycle-resolved x-ray optical wave mixing will reveal new insights into strong-field excitation of solids.

Short description / abstract:

Descriptive figures:

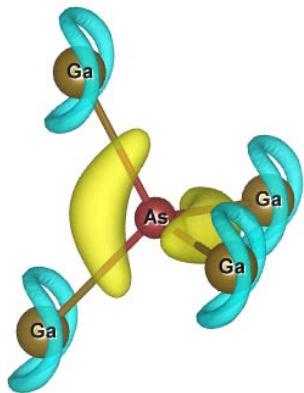
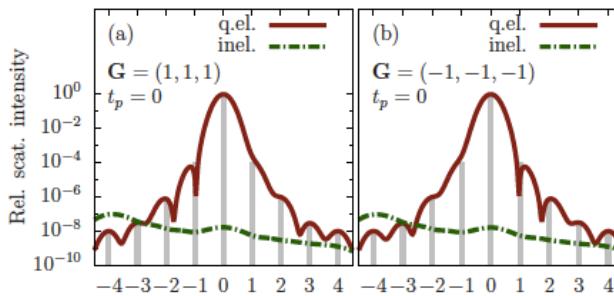


Fig.1 Calculated second-order charge distribution in GaAs induced by an optical pulse with the photon energy of 1 eV and the intensity $4 \times 10^{11} \text{ W/cm}^2$. Blue - positive charge, yellow- negative charge.



Scattered- incoming photon energy, eV

Fig.2 subcycle-resolved x-ray-optical wave mixing signal by an x-ray pulse with 3.5 fs duration.

Literature:

- [1] P. M. Eisenberger and S. L. McCall, Phys. Rev. A 3, 1145 (1971).
- [2] T. E. Glover et al, Nature 488, 603 (2012).
- [3] D. Popova-Gorelova, D. A. Reis, and R. Santra, Phys. Rev. B 98, 224302 (2018).
- [4] Daria Popova-Gorelova, V. Guskov, Robin Santra, arXiv:2009.0752

Requirements:

Technical equipment desired: optical pulses with intensity $\sim 10^{12}$ W/cm², 1eV photon energy, x-ray pulse of 5 keV photon energy and 3.5 fs duration. The ability to control x-ray pulses with sub-femtosecond timing jitter, and to overlap an optical and an x-ray pulse in time and space are required. Bragg signals at various scattering angles must be collected. Energy resolution must be sufficient to resolve side peaks shifted by integer multiples of 1 eV. Momentum resolution must be sufficient to resolve momentum shifts by integer multiples of 1240 nm (optical pulse wavelength).

Tentative project timeline

Including: experimental design, proposal editing and submission, experiment...

Preliminary team:

Specify skills, expertise, technical equipment desired/needed for this project

Contact Person:

Daria Gorelova, darya.gorelova@uni-hamburg.de

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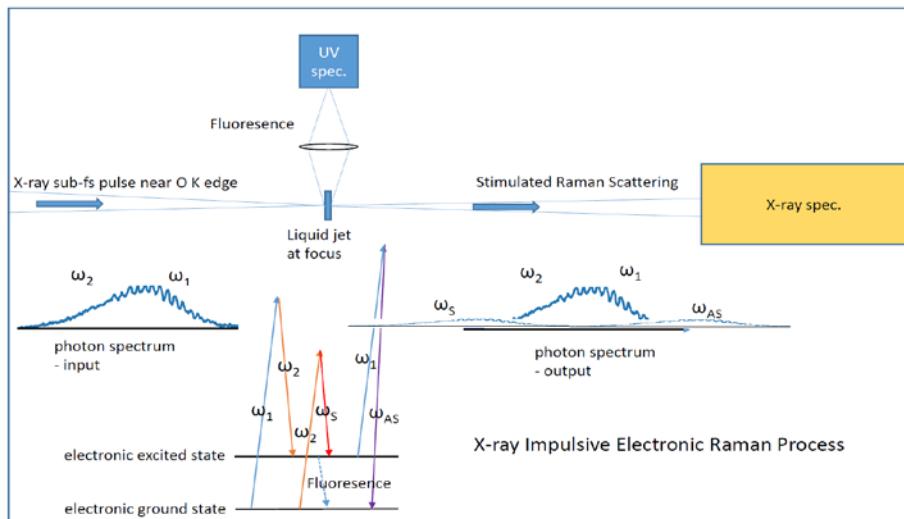
Project title:

Impulsive X-ray Raman: from gas to liquid phase samples

We propose to explore nonlinear X-ray Raman interactions in the impulsive limit for the electronic states of a liquid sample through the modifications to the transmitted XLEAP pulse spectrum. The investigation of X-ray nonlinear interactions is motivated by the future prospects for X-ray nonlinear time-resolved spectroscopy, i.e. a multidimensional spectroscopy anticipated to uncover ultrafast electronic couplings in matter with atomic localisation. To pave the way to that goal for future science, that is well matched to the anticipated capabilities of LCLS II, we propose a proof-of-concept measurement of the stimulated Raman emission in a liquid phase molecular system. This will demonstrate the feasibility of the impulsive X-ray Raman process and the applicability to liquids. We choose to investigate organic liquids, e.g. isopropanol, that have a ~6 eV energy separation between the ground and excited electronic state, which is compatible with demonstrated bandwidth of XLEAP. We have already demonstrated the required stable, in vacuum, micron thick liquid sheets with a low surrounding vapour pressure.

Short description / abstract: as above

Descriptive figures:



Requirements:

Technical equipment desired/needed for this project, applicable energy range, ...

SXR (250 – 1000 eV), < 0.5 fs near transform limited, intensity > 10¹⁷Wcm⁻²

Tentative project timeline

Proposal submitted to LCLS currently but if unsuccessful hope for 1st experiment 2021-22

Preliminary team:

Imperial College (Lead), PULSE Institute Stanford (e.g. Bucksbaum, Cryan), LCLS beamline staff (e.g. Deponte, Dakovski, Marinelli), + groups from U.Connecticut (Berrah), U.Hamburg (Huse), U.California Irvine (Mukamel)

Contact Person:

Jon Marangos, Imperial College London

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Project title:

X-ray Chronoscopy: exploring the time-domain of XFEL pulses

We aim to study the dynamics of nonlinear interactions of X-rays with matter including X-ray-optical wave-mixing experiments. In order to improve the limit resulting from the time resolution of pulse-length we will apply spectroscopy schemes aiming at measuring temporal profiles of X-ray beams transmitted through the sample. The measurements of temporal beam profile before and after the sample are foreseen to be performed with terahertz streaking methodology that may provide down to sub-femtosecond time resolution. In this way the changes in X-ray pulse intensities in the time domain can be explored to capture the very first steps of electron dynamics in matter. The same approach will be evaluated in a linear regime of interactions for pump-probe experiments.

Short description / abstract:

To date, most of X-ray experiments are based on the measurement of energy and intensity of X-ray photons, either transmitted through or emitted from matter. Derivatives of these two physical quantities are main observables used to interpret physical, chemical or biological processes and are studied by means of x-ray diffraction, x-ray imaging, x-ray tomography and x-ray spectroscopy techniques. However, in order to picture the origin of electronic change that drives the transformations in atomic species, femto or sub-femto second observations are necessary. With the advent of XFELs, the ultrashort X-ray pulses are available but still they are too broad in the time domain and do not allow capturing the very first steps of electronic transformations. To overcome this challenge, instead of studying the energy/intesity distribution of X-ray pulses interacting with sample, we aim at analyzing the X-ray pulse in the time domain. Preliminary calculations showed that it should be feasible with down to fs time resolution when exploring 30 – 50 fs-long X-ray pulses.

The project is funded by the National Science Centre in Poland (2017/27/B/ST2/01890) and executed since 2018 in close collaboration with dr. Christopher Arrell from the Paul Scherrer Institute, Switzerland. To date, preliminary calculations and signal estimates were performed together with test experiments using the THz streaking method at the SwissFEL facility.

The general project objectives are following:

a) X-ray Chronoscopy instrumentation: to develop spectroscopy schemes capable of measuring temporal distribution of X-rays, before and after interaction with sample, all working on a shot-to-shot basis.

b) X-ray Chronoscopy application:

- to apply the method to study electron dynamics leading to nonlinear processes (e. g. saturable X-ray absorption) and in two-photon absorption processes via X-ray-optical wave mixing,

- to evaluate and to test the method in the pump-probe scheme for study of charge transfer dynamics following optical excitations.

Descriptive figures:

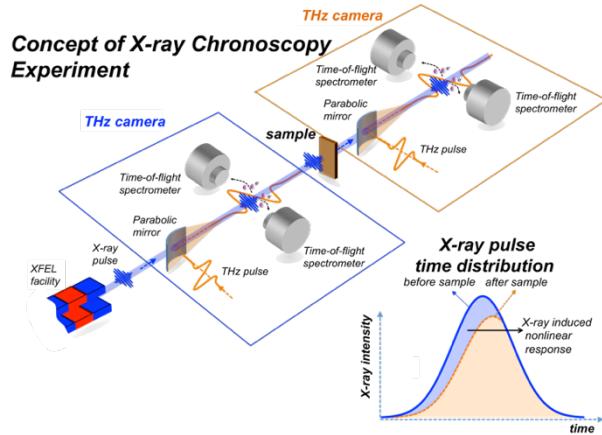


Figure: Schematic presentation of X-ray chronoscopy experiment using two terahertz-streaking units. The first THz setup is used to determine time distribution of incoming pulse ($I_0(t)$) and the second THz setup provides measure of time distribution of X-ray pulse after interaction with sample ($I_1(t)$). Both spectrometers should work in shot-to-shot mode giving the possibility of either single-shot or cumulative/average analysis. Signal analysis will be based on the ratio of measured X-ray pulse time-distributions.

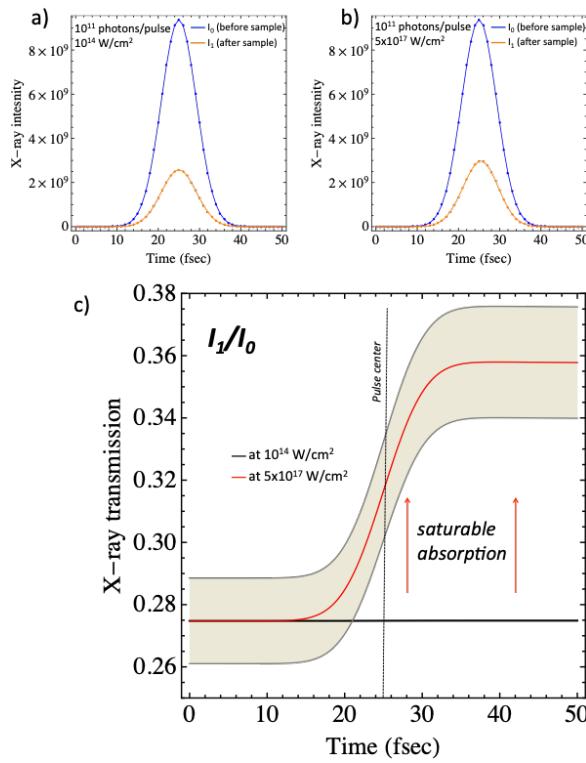


Figure: Time-domain calculations for saturable X-ray absorption process in metallic Fe using rate equations with simplified two-level model. a) Time-distribution of X-ray pulse for low fluency of 10^{14} W/cm^2 . b) Time-distribution of X-ray pulse for high fluency of $5 \times 10^{17} \text{ W/cm}^2$. c) Ratio of I_1 and I_0 signals for low- (black) and high-fluency (red) cases. For low fluency a constant signal is obtained at expected transmission value of 0.275. For high fluency increased transmission through the sample is observed. The calculated effect of increased transparency of about 20 % is similar to recently reported experimental observations. Gray area marks region assuming 10 % uncertainty of the measurement.

Requirements:

Two THz streaking spectrometers, hard X-ray energy range, few tens of fs-long X-ray pulses, both monochromatic and SASE operation

Tentative project timeline

Project is in its starting phase. We participated in first experiments for THz streaking development (Wojciech Blachucki IFJ PAN, Krakow PL in collaboration with Christopher Arrell PSI, CH). Number of preliminary theoretical calculations is available.

Preliminary team:

Everyone willing to join this project (experimental & theoretical) is welcome.

Contact Person:

jakub.szlachetko@ifj.edu.pl

Project template for Wavemix workshop

Project title:

Studies of the ultrafast dynamics of polarons in transition metal oxides.

The study of the carrier relaxation is crucial to understand the transition metal oxide photocatalytic response. In this project we want to investigate the role of polaron formation in photoexcited TMOs (as Fe_2O_3 , CeO_2 , CoO , $SrTiO_3$ and TiO_2) using EUV transient grating. These studies will be fundamental to understand how TMOs photoconversion efficiency is modified by the presence of polarons.

Short description / abstract:

Understanding the behavior of excited carriers in transition metal oxides (TMOs) is fundamental for their use in photocatalytic applications as photoelectrochemical (Grätzel) solar cells or hydrogen production. Their efficiency is strongly related to the possibility of the free electrons to diffuse to the surface of the catalyst, activating potential reactive sites. Usually, the injection of electrons into the TMOs conduction band - induced by doping or chemical reduction – changes the chemical and physical properties of TMOs and so their functionalities. Despite their very promising nature, TMOs photocatalytic applications are hampered by the quite short recombination lifetimes usually ascribed to surface and mid-gap trap states. The presence of such traps is due to the localization of the excess electrons at 3d orbitals of the metal which induce the relaxation of the surrounding lattice. These quasiparticles, called polarons, are characterized by the strong coupling of the TMOs electronic and atomic structures causing the self-trap of excited charges inducing new states within the bandgap (e.g. TiO_2 as in Figure 1a) and reducing the electronic mobility if compared to band transport in conventional semiconductors. While the phenomenology of the ground-state polarons (generated by defects or doping) is quite well established, only recently the formation of polarons in photoexcited states has been investigated. Indeed, UV pulses can be used to accelerate the carriers' localization into polarons since the optical transitions in almost all the TMOs involve a charge transfer from oxygen to the metal centers. However, the propagation of photoinduced polarons have not been studied by the literature, to the best of our knowledge. In this project we propose a new method to study polaron diffusion, involving the transient grating method with FELs. This type of investigation could involve several difficulties: small polarons (polarons which involve the single unit cell) are extremely confined and their mobility via hopping does not exceed few nanometers. Unlike UV-Vis TG, EUV TG periodicities can match the typical diffusion lengths of polarons allowing the study of the effects of polaron formation and migration on the electronic and thermal relaxation in different TMOs. Thus, the generation and detection locations in the TG method can be spatially separated to study propagation over very long distances or the interaction with nanostructures, interfaces, etc.

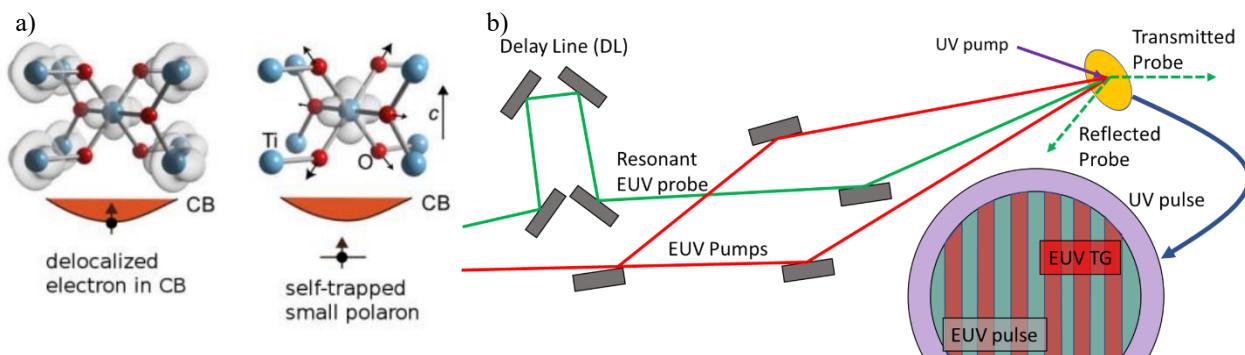


Figure 1 **a.** Representation of electrons in conduction band (CB) in TiO_2 : electrons are shared by all the Ti atoms of the lattice. On right there is a sketch of small polaron formation and the consequent formation of a self-trapped state below the delocalized CB. The electrons are localized on a single Ti site and this generates a strain in the lattice. Taken from Reticcioli et al. Phys. Rev. B 2018, 98 (4), 045306. **b.** Scheme of the four-wave mixing experiment proposed.

Requirements:

We ask for a four-wave scheme setup (as the one presented in Figure 1b). First a UV pump pulse will induce the polaron formation, then EUV TG will generate a thermal transient grating with very short periodicities which can enhance the mobility of polarons. Finally, a EUV probe resonant with an absorption edge of the transition metal will be used. We will detect the modulation of the intensity of the probe generated by the modification of the edge induced by the polaron formation and propagation (e.g. Fe_2O_3 shows an edge shifts of about 2 eV in presence of polarons). Each pulse (UV and EUV) will be synchronized with each other. The evolution of the probe will be studied on different time scale (from the sub-ps to the ps) changing the path of the probe. Then, results obtained with and without the UV pulse will be compared. Since almost all the TMOs have M edges between 10 to 30 nm, the experiments must require particular mirrors for the transport of the EUV pumps and probe (e.g. for Fe $M_{2,3} = 23.5$ nm or for Co $M_{2,3} = 21$ nm).

Tentative project timeline

Thin films of different TMOs will be grown on EUV transparent substrates (e.g. Si_3N_4 thin windows) in well controlled conditions using MBE or magnetron sputtering in the Labs of the University of Bologna and CNR - NANO Modena. The thickness of the samples will not exceed a few tens of nm to guarantee optimal transmission of EUV radiation; in this way the sample can be measured in reflection or transmission. A complete characterization of the morphological properties, optical response and electronic structure will be performed before the EUV TG experiment. The most promising TMO to test this class of experiments is the hematite (Fe_2O_3) because Fe $M_{2,3}$ edges show an intense shift caused by the small polaron formation. Finally, we will focus on others TMOs comparing the results. Moreover, the possibility of reaching FEL high energies will allow accessing to deeper edges of TMOs as the metal L edges (which are more sensitive to oxidation states) or making experiments were probe and pump are resonant respectively with the metal and the oxygen centers.

Preliminary team:

Filippo Bencivenga, Emiliano Principi Elettra-Sincrotrone Trieste, Strada Statale 14 km 163.5 in Area Science Park 34012 Basovizza, Trieste, Italy

Paola Luches CNR-NANO, Centro di Ricerca S3, via G. Campi 213/a, 41125 Modena, Italy.

Federico Boscherini Dipartimento di Fisica e Astronomia, Alma Mater Studiorum – Università di Bologna, Viale C. Berti Pichat 6/2, 40127 Bologna, Italy

Contact Person:

Jacopo Stefano Pelli Cresi Elettra-Sincrotrone Trieste, Strada Statale 14 km 163.5 in Area Science Park, 34012 Basovizza, Trieste, Italy

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Project title:

Exploring optical interference patterns in multi-pulse SASE XUV spectra

The transfer of multidimensional spectroscopy concepts to the XUV and x-ray regime at free-electron lasers can benefit from broadband photon spectra. Existing intense (X)FEL sources are based on self-amplified spontaneous emission (SASE) being a partially coherent light source. In previous measurement campaigns on all-XUV-optical transient-absorption spectroscopy at the SASE free-electron-laser in Hamburg (FLASH) transmitted photon spectra have been acquired (around 50 eV and 60 eV; approx. 0.5 eV - 1 eV SASE bandwidth) after the nonlinear interaction with various atomic and molecular gas-phase targets. A two-pulse split&delay geometry has been employed by means of spatial beam splitting, benefitting from transversely coherent beam modes. In ongoing analysis of single-shot FEL spectra, spectral interference structures have been successfully identified.

It is the goal of this project to explore how such datasets can be utilized for the coherent multi-pulse pumping and probing as it is used in traditional two-dimensional spectroscopy. The project is based on the analysis of previously acquired experimental single-shot datasets and modelling. Within the scope of this project we aim to identify key methods, new data analysis approaches, and concepts that are necessary for the transfer of coherence-based multidimensional methodologies from the visible into the x-ray domain, always guided by original experimental data. In particular we also aim at exploring how these new concepts may even benefit from the partially coherent broadband SASE spectra, also including correlation-based methods.

The measurement concept is depicted in Fig. 1, illustrating how shot-by-shot SASE spectra have been previously obtained in different experimental campaigns at FLASH (see also [T. Ding et al., Faraday Discuss., 2020, Accepted Manuscript, <https://doi.org/10.1039/D0FD00107D>]). Parasitic measurement of the incoming spectra with a separate online VLS-based photon spectrometer, operating in coincidence on a single-shot basis, are also available (see Fig. 2). Thereby sorting for incoming photon flux, or other selections based on spectral content, is possible, and correlation maps can be constructed (Fig. 2c). Datasets typically contain order of 10,000 events, whereby when scanning the delay, order of several 100 single events have been acquired for each delay step. In Fig. 3 we illustrate how single-shot Fourier analysis of FEL spectra reveals pronounced maxima that encode the split-mirror delay setting.

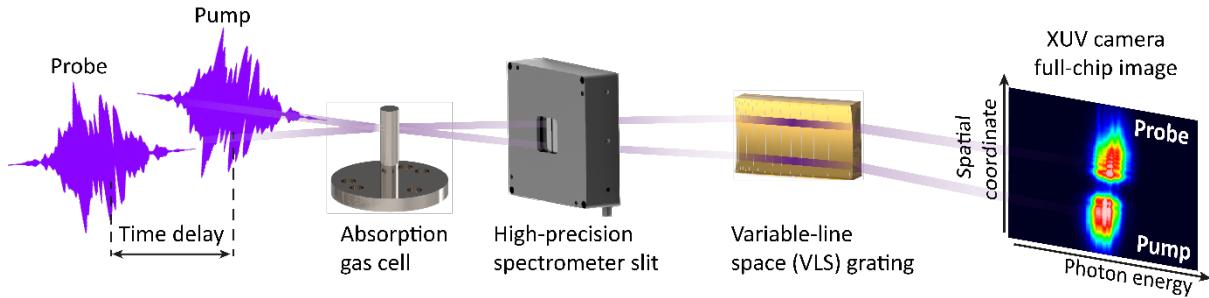


Fig. 1: Measurement principle of split-beam XUV-pump XUV-probe transient absorption spectroscopy. After focusing the pulses into the absorption gas cell filled with a moderately dense gas medium the transmitted pulses are coupled into a grating spectrometer consisting of a high precision slit, a VLS grating, and an XUV-sensitive camera which simultaneously detects the spatially separated pump and probe pulse spectra on a single-shot basis. Note: both due to stray light, but most importantly also due to nonlinear wave-mixing interaction in the target medium, portions of both initially non-collinear beams are emitted in the same direction also in the far field and interfere. Figure reprinted from T. Ding et al., Faraday Discuss. 2020, Accepted Manuscript, doi: 10.1039/D0FD00107D.

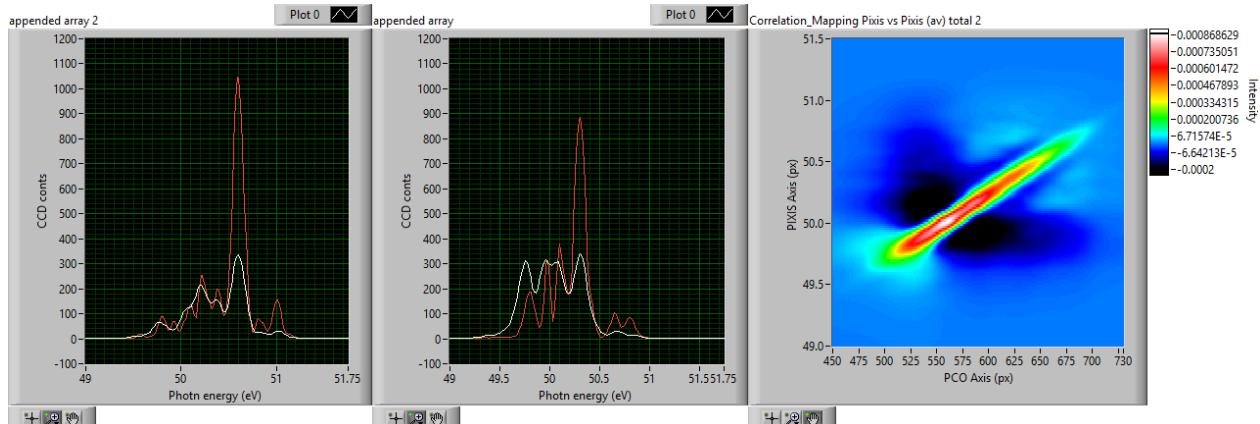


Fig. 2: (a-b) Two exemplary single-shot SASE spectra taken behind the target (red line) and, parasitically, before the target (white line). The peculiarity is: due to different spectrometer resolution and spatio-spectral beam inhomogeneities the spectra may not be perfectly identical, yet strong spectral correlations exist. (c) Covariance map of these spectra over a large ensemble of pulses, demonstrating that the application of spectral correlation methods can be employed within the scope of this project.

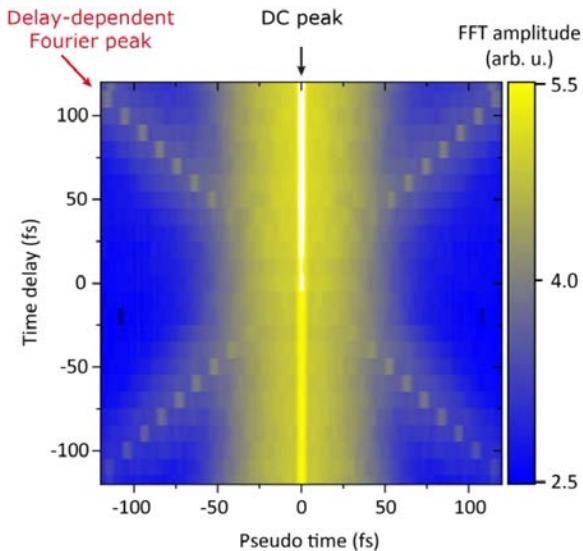


Fig. 3: Single-shot Fourier analysis of experimentally acquired pump-probe transient absorption spectroscopy data at 50 eV on neon. The vertical time-delay axis denotes the split&delay mirror setting while the horizontal axis is obtained after Fourier transform of the ~1-eV-wide SASE spectra. A clear maximum, tracing the time-delay-setting is revealed, which is experimental proof that spectral interference structures are contained in the ensemble of SASE spectra. For each time-delay bin, the amplitude after Fourier transform is averaged for approximately 200 single-shot FEL spectra. Figure reprinted from T. Ding et al., Faraday Discuss. 2020, Accepted Manuscript, doi: 10.1039/D0FD00107D.

Requirements:

Experience with analysis of complex data sets and/or multidimensional methodologies and correlation methods.

Tentative project timeline

Due to offline analysis of already acquired data the timeline is quite flexible. Envisioned monthly Zoom meetings on progress of different collaborators.

Preliminary team:

Christian Ott, MPIK Heidelberg (spokesperson & PI, expert on transient absorption spectroscopy with SASE FELs)

Thomas Ding, MPIK Heidelberg (co-PI, expert on transient absorption spectroscopy with SASE FELs)

Thomas Pfeifer, MPIK Heidelberg (co-PI, expert on transient absorption spectroscopy with SASE FELs)

Shaul Mukamel, UC Irvine (expert on multidimensional methodologies)

Stefano Cavalletto, UC Irvine (expert on quantum modelling with SASE pulses)

Contact Person:

Christian Ott christian.ott@mpi-hd.mpg.de

Thomas Ding thomas.ding@mpi-hd.mpg.de

Thomas Pfeifer tpfeifer@mpi-hd.mpg.de

Project title:

Applications of ultrashort and fully coherent FEL pulses in AMO science

In a series of pilot experiments performed at the FERMI free electron laser, superradiant operation was proven as a viable method, well compatible with the existing infrastructure, to produce sub-10 fs pulses. These can access the core electrons of many important elements while matching their Auger lifetimes. Access to the C, N, and O 1s shells via two-photon excitation is already within the technically accessible photon range. Nonlinear excitations of short-lived doubly-excited valence states is also of extreme interest in the study of electron correlations. This project plans to promote such experiments on atoms and simple molecules.

Short description / abstract:

Superradiance mode is a mode of operation of FELs [1] which provides very short pulses (< 5 fs) with higher peak power than the normal HGHG operational scheme. Recently the FERMI team has demonstrated superradiance [2]; in that occasion, the wavelength was fixed at the third harmonic of the IR laser, which ensured best performance. Meanwhile development has proceeded, and it is now possible to use the OPA as a seed, that is, the FEL wavelength can be chosen and tuned. This greatly enhances the capabilities of this superradiance for experiments. The high intensity of these short pulses opens the door to the observation of non-linear dynamics associated with short-lived states embedded in the background electronic continua. In the last few years, the ultrafast dynamics of atomic autoionizing states has been explored employing attosecond transient absorption spectroscopy, combining an attosecond XUV and a delayed NIR pulse. Helium, the simplest many-electron system, is a favorite target [3—7], indicating that a general understanding of these phenomena has just begun and will only be achieved through a strong and protracted effort. Even ignoring the increase of complexity of the system under study, the intensity increase alone, and the ensuing nonlinear optical regime, strongly alters the XUV-induced dynamics [8,9]. We aim now to investigate this dynamics with photoelectron spectroscopy, while promoting the further development of the light source (and its synchronization with external lasers) on the one side, and of theoretical/computational tools on the other. A seeded FEL such as FERMI, operated in superradiance mode, is ideal in that many good properties inherited from the seed (synchronization; longitudinal coherence; possibly, phase-locking between harmonics) are preserved; furthermore a swap between “standard” (HGHG) and superradiant mode allows the most controlled comparison possible between “short” and “long” pulses.

- [1] L. Giannessi et al, Phys. Rev. Lett. **108**, 164801 (2012); *ibid.* **110**, 044801 (2013).
- [2] N. S. Mirian et al, “Generation and measurement of intense few-femtosecond superradiant soft X-ray free-electron laser pulses”, under review.
- [3] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963)
- [4] M. Domke et al, Phys. Rev. A **53**, 1424 (1996).
- [5] Ch. Ott et al., Science **340**, 716 (2013).
- [6] A. Kaldun, A. Blättermann, V. Stooß, S. Donsa, H. Wei, R. Pazourek, S. Nagele, C. Ott, C. D. Lin, J. Burgdörfer, T. Pfeifer, Science **354**, 738 (2016).
- [7] Ch. Ott et al., Phys Rev. Lett. **123**, 163201 (2019).
- [8] A. N. Artemyev et al., Phys Rev A **96**, 033410 (2017).
- [9] G. Mouloudakis and P. Lambropoulos, Eur. Phys J. D **72**, 226 (2018).

Descriptive figures:

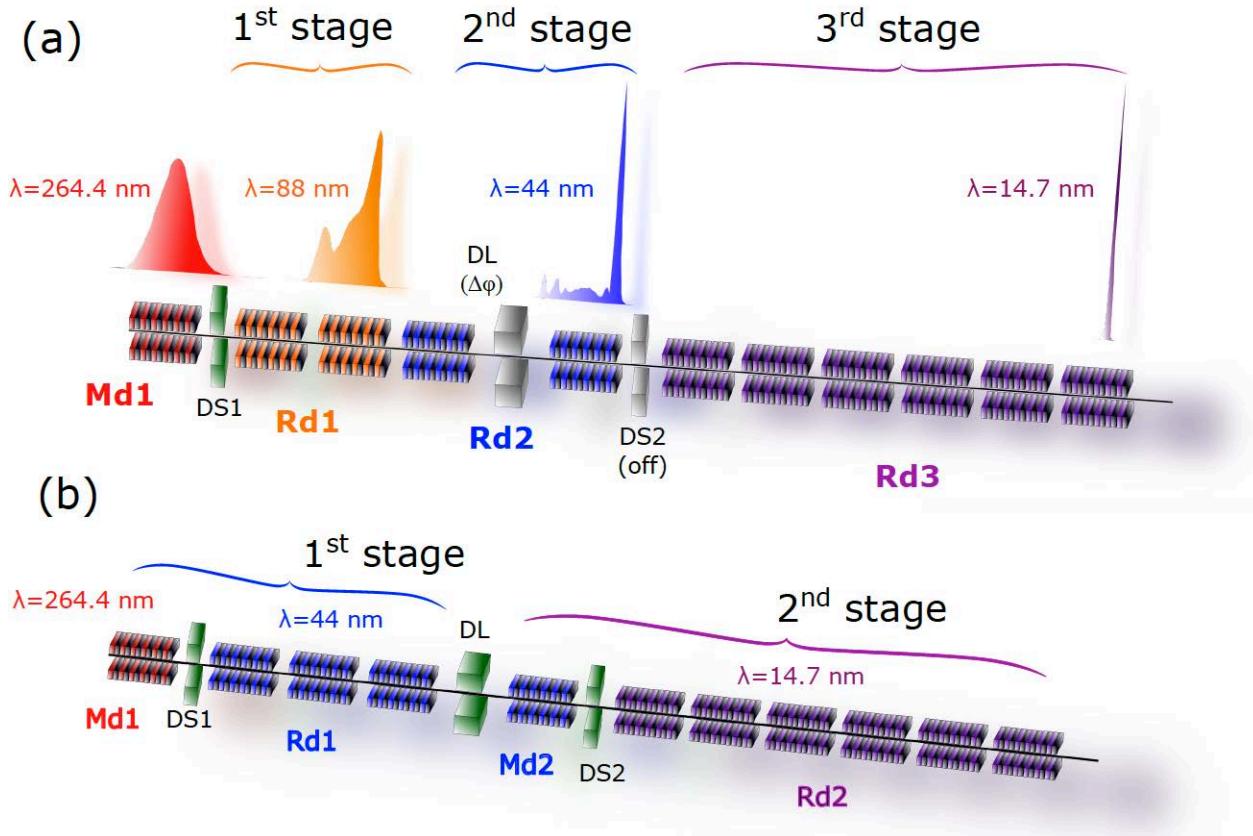


Figure 1: Layout of FERMI in superradiant mode (a), and standard (HGHG) mode (b).

Requirements:

Access to beamtime at the FERMI free electron laser in HGHG and superradiant configuration; full characterization of the PADRES autocorrelation delay line, and focusing mirrors; access to the Low Density Matter endstation at FERMI in its standard “magnetic bottle” configuration; access to computational resources (estimated: 300k CPU hours).

Tentative project timeline

Month 1—4: identification of a target experiment; preliminary calculations; experimental design. Month 5: proposal editing and submission. Month 6—11: technical evaluation and scheduling; offline/parasitic experiments. Month 12: experiment. Month 13—24 data analysis and theoretical/computational simulations.

Preliminary team:

FERMI core team [technical development, and associated simulations; machine operation]. PADRES team [photon transport characterization and operation]. LDM team [experiment planning, setup, and operation]. R. Feifel & R. Squibb [magnetic bottle optimization] G. Sansone; J Marangos, M. Zitnik, T. Pfeifer, M. Meyer & T. Mazza [experiment planning; data analysis]. A Picon, A Palacios, J Feist [theory and simulations].

Contact Person:

carlo.callegari@elettra.eu; kevin.prince@elettra.eu; luca.giannessi@elettra.eu

Project template for WavemiX workshop

This template aims at facilitating synergies between the various members of this growing community. Here, you can build your draft of a project, in a proposal structure, to be shared with the WavemiX community during the workshop. This project will compose the *WavemiX 2021 Book of Projects*. The information requested below might be preliminary and can be seen as a working draft for the project.

Project title:

Hybrid THz/x-ray 2D spectroscopy

2D THz spectroscopy will be conducted with XRD probing. This is a prototype for a broad range of 2D spectroscopies using phase-related THz, IR, or optical pulse pairs (or sequences) and x-ray diffraction, absorption, or induced emission. The resulting 2D spectra will reveal couplings among vibrational, electronic, or magnetic degrees of freedom and, in systems undergoing classical or quantum phase transitions, the roles played by the coupled modes in the phase transition dynamics.

Short description / abstract:**Descriptive figures:**

We will conduct 2D THz spectroscopy using a pair of THz excitation pulses with variable delay τ (and with relative phase controlled) and using measuring XRD with a femtosecond x-ray probe pulse delayed following the THz pulses by time t . The initial experiments (planned for SwissFEL BERNINA beamline, beamtime to be rescheduled) will be conducted on the quantum paraelectric (QPE) phase of strontium titanate (SrTiO_3 , STO) in which THz fields have been shown to drive ions along the soft lattice vibrational coordinate far enough to induce a transient ferroelectric (FE) phase [1]. Variably delaying the two THz excitation pulses will cause different nonlinear THz field interactions (e.g. excitation of vibrational population, driving of 2-quantum or higher-order multiple-quantum coherences, etc.) to be optimized or suppressed, measured through XRD signals from Bragg peaks that are sensitive to motion along the soft mode or along other phonon modes coupled to the soft mode. The results will provide insight into the mechanism through which nonlinear THz field interactions are able to induce the quantum phase transition. Operating at current FEL repetition rates, it will not be realistic to continuously scan both temporal coordinates. Instead, selected inter-pulse delay times τ will be used. Given what we already know about the soft mode and phase transition dynamics, that will allow direct testing of different multiple-field excitation pathways. High repetition-rate XFEL operation will enable full 2D hybrid spectroscopy. Other x-ray observables such as XAS will allow electronic and magnetic responses as well as structural dynamics monitored through XRD to be assessed. Similar experiments will be possible with THz, IR, or optical pulses that drive different collective or molecular modes.

[1] “Terahertz field–induced ferroelectricity in quantum paraelectric SrTiO_3 ,” X. Li, T. Qiu, J. Zhang, E. Baldini, J. Lu, A. M. Rappe, and K. A. Nelson, *Science* **364**, 1079–1082 (2019).
<https://doi.org/10.1126/science.aaw4913>

Requirements:

The crucial requirement is high-field THz excitation compatible with x-ray probing of a sample in a cryostat. We are demonstrating methods through which only optical excitation pulses are needed. These will generate THz fields at the sample, obviating the need for bringing in THz fields from outside the cryostat.

Tentative project timeline

As soon as our beamtime is rescheduled!

Preliminary team:

We look forward to working with SwissFEL and other collaborators.

Contact Person:

Keith Nelson, kanelson@mit.edu

Project template for WavemiX workshop

This template aims at facilitating synergies between the various members of this growing community. Here, you can build your draft of a project, in a proposal structure, to be shared with the WavemiX community during the workshop. This project will compose the *WavemiX 2021 Book of Projects*. The information requested below might be preliminary and can be seen as a working draft for the project.

Project title:

Highly sensitive XUV and X-ray interferometry

Nonlinear spectroscopy demands a detection scheme with high dynamic range in order to measure weak nonlinear signals that are covered by much stronger linear signals and noise contributions. Coherent wave mixing is one approach to solve this issue [1]. However, this concept needs complex XUV/X-ray beamlines and high target densities. In our project, we follow an alternative approach, which is based on phase cycling of XUV/X-ray pulse sequences. Phase-cycling enables selective detection of nonlinear signals and achieves a comparable dynamic range to coherent wave mixing methods [2]. As an advantage, phase cycling can be implemented in a collinear geometry, which simplifies the XUV/X-ray beamlines. Furthermore, it can be applied to samples of very low target densities, in principle down to the single-molecule level [3].

We have recently implemented phase cycling at a XUV free-electron laser and a tabletop XUV high-harmonic source [4-6]. We demonstrated high interferometric stability and performed XUV quantum interference spectroscopy. This opens-up exciting perspectives for coherent multidimensional spectroscopy [7], multi-quantum detection schemes [8] and coherent control applications.

- [1] F. Bencivenga *et al.*, *Nature* **520**, 205 (2015)
- [2] P. Tian *et al.*, *Science* **300**, 1553 (2003)
- [3] D. Brinks *et al.*, *Nature* **465**, 905 (2010)
- [4] A. Wituschek *et al.*, *Nat Commun* **11**, 1 (2020)
- [5] A. Wituschek *et al.*, *Opt. Express*, *OE* **28**, 29976 (2020)
- [6] A. Wituschek *et al.*, *New J. Phys.* **22**, 092001 (2020)
- [7] L. Bruder *et al.*, *Nat Commun* **9**, 4823 (2018)
- [8] L. Bruder *et al.*, *Phys. Chem. Chem. Phys.* **21**, 2276 (2019)

Short description / abstract:

Descriptive figures:

Requirements:

Technical equipment desired/needed for this project, applicable energy range, ...

Tentative project timeline

Including: experimental design, proposal editing and submission, experiment...

Preliminary team:

Specify skills, expertise, technical equipment desired/needed for this project

Contact Person:

Lukas Bruder, University of Freiburg, lukas.bruder@physik.uni-freiburg.de

Project template for Wavemix workshop

Project title:

Development of soft x-ray transient polarization grating spectroscopy

Short description / abstract:

The proposal aims to demonstrate the feasibility of transient polarization grating experiments in the VUV soft x-ray wavelength. This will allow measuring spin dynamics at the nanometer scale and core resonances may be exploited to introduce chemical selectivity. The development of this technique could allow measuring resonant circular dichroism in chiral molecules exploiting the different absorption of CL and CR light. Finally, the possibility to monitor electron diffusion at the nanoscale could shed new light on the mechanism of spin diffusion in quantum wells materials (<https://doi.org/10.1038/nature04206>).

Requirements:

Two pulses with cross polarizations. TIMER beamline or mini-TIMER setup.

Tentative project timeline:

Preliminary measurements performed successfully. Proposal submitted at FERMI

Preliminary team:

Required skills include – Familiarity with spectroscopy, data analysis (python, matlab)

Contact Person:

Claudio Masciovecchio claudio.masciovecchio@elettra.eu

Project template for Wavemix workshop

This template aims at facilitating synergies between the various members of this growing community. Here, you can build your draft of a project, in a proposal structure, to be shared with the Wavemix community during the workshop. This project will compose the *Wavemix 2021 Book of Projects*. The information requested below might be preliminary and can be seen as a working draft for the project.

Project title:

Perspectives for hard X-ray selective cancellation of the effect of target molecules in pathogens.

We have recently studied four-wave mixing processes with FELs pulses around the atomic edges exploiting the random phase characteristics of ω - 3ω pulses and concluded that the anti-Stokes 5ω component can be efficiently generated with high spectral selectivity. In this project, we propose to explore the low-dose regime, using hard X-rays as in medical imaging, to selectively cancel the effect of the active center of specific molecules maybe combined with molecule labellings in pathogens such as viruses, bacteria or cancer cells.

Short description / abstract:

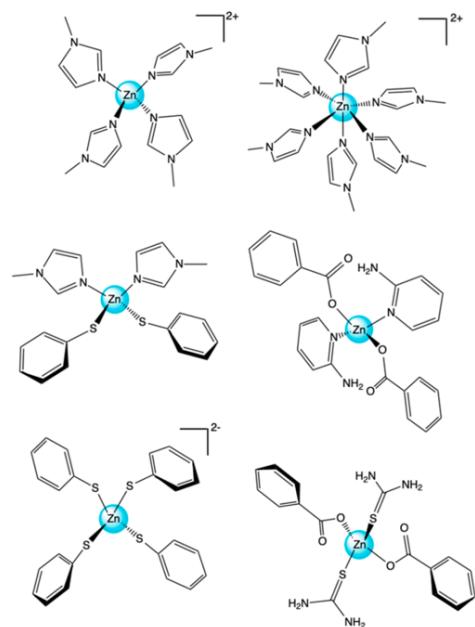
X-ray absorption spectroscopy may provide a unique absorption spectrum that can serve as a fingerprint of the state of a particular atom or molecule. It was reported that exposure to laser-produced X-rays pulses with relatively high peak intensities does not lead to increased harm to mammalian cells exposed in vitro compared with the harm induced from exposure to X-rays with the same dose from conventional medical sources, concluding that the use of high-power laser facilities for medical imaging is justified [1]. We propose to study both through numerical simulations and experimentally the capability of the four-wave mixing (FWM) effect described in [2] at relatively low laser peak pulse intensities in biomolecules maybe also combined with biomolecules labellings. Initially the optimal biomolecules targets and possible labeled molecules have to be identified by characterizing with precision their X-ray absorption spectra. As first tests, we will consider simple zinc complexes that have recently been characterized [3], to later study more realistic metalloproteins active centers and other molecules. We hence expect to be able to effectively produce nonlinear FWM processes locally and selectively in some biologically relevant molecules using ultrashort laser pulses with medical harmless doses (mGy).

[1] C. Tillman et al., "Survival of Mammalian Cells Exposed to Ultrahigh Dose Rates from a Laser-produced Plasma X-ray Source", Radiology 1999, 213, 860–865.

[2] C. Serrat, "Localized Core Four-Wave Mixing Buildup in the X-ray Spectrum of Chemical Species", J. Phys. Chem. Lett. 2021, 12, 1093–1097.

[3] O. M. Stepanic et al., "Probing a silent metal: A Combined X-ray Absorption and Emission Spectroscopic Study of Biologically Relevant Zinc Complexes", Inorg. Chem. 2020, 59, 13551–13560.

Descriptive figures:



Schematic figure of some Zn complexes, borrowed from [3]: $[\text{Zn}(\text{MeIm})_4]^{2+}$ top left, $[\text{Zn}(\text{MeIm})_6]^{2+}$ top right, $[\text{Zn}(\text{MeIm})_2(\text{SPh})_2]$ center left, and $[\text{Zn}(\text{BzO})_2(\text{pyNH}_2)_2]$ center right, $[\text{Zn}(\text{SPh})_4]^{2-}$ bottom left, and $[\text{Zn}(\text{BzO})_2(\text{SC}(\text{NH}_2)_2)]$ bottom right.

Requirements:

For the simulations a supercomputing center is required. A project in Marenostrum (BSC)-Barcelona has recently been applied. For the experiments XUV and hard X-ray energy range, fs-ps pulses, $10^8\text{-}10^{12}\text{ W/cm}^2$, SASE operation with the ability to synchronize $\omega\text{-}3\omega$ pulses.

Tentative project timeline

The project is in its starting phase. We have some funding for 2021 for the theory which will likely be extended to 2024. We need to find funding for PhD and postdoctoral scientists willing to join the project.

Preliminary team:

Computational simulations expertise with NWChem and similar. We look forward to establishing collaborations with experimental groups. Everyone willing to join the project is very welcome!

Contact Person:

Carles Serrat

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Project title:

Second- and Third-order nonlinear X-ray Resonance Applied in Nuclear Transitions

Short description / abstract:

Second- and third-order nonlinear optical effects are widely used to achieve resonance with different transitions ways. In the second-order case, we have the Second-Harmonic Generation (SHG) and the Sum Frequencies Generation (SFG) as effects where the excitonic levels generate an increase in the collected signal [1]. Similarly, in the third-order, we have the Four-Wave Mixing (FWM) and Third-Harmonic Generation (THG) that also amplify in the presence of real excitonic levels, and also the specific case of FWM called Coherent Anti-Stokes Raman Scattering (CARS) where we amplify the resonance with the presence of phonons in the materials [2].

With x-ray beams' appearance, a window opens where we can study the effects of nuclear transitions, such as the Mössbauer effect, applying these nonlinear techniques. By combining a pulsed X-ray beam with a visible spectrum laser in a synchronized way, it may be possible to obtain an enhancement when the energy of the effect generated [3], whether SFG or FWM, is equal to the energy of the nuclear transition, figure 1 show the diagram of the (a) SFG and (b) FWM energy transition off (left-side) and on (right-side) resonance near a nuclear transition state.

In this work, I propose the study of the transitions of the ^{57}Fe isotope, which is a material widely known and studied by Mössbauer spectroscopy, that has a nuclear transition between the fundamental state $1/2$ and excited state $3/2$ with 14,4 keV energy [4], this transition can be studied through the SFG, for the second-order case, and the FWM, for the third-order case, using a beam of X-ray pulsed synchronized to a tunable pulsed laser in the visible spectrum, to compare and confirm the efficiency of the proposed technique.

We could also measure the lifetime of these excited states, applying a delay between the beams as long as that lifetime is less than the pulse duration of the stimulus beams, functioning as a pump-probe when the effect is in resonance with the nuclear transition.

If the result is positive, it would be possible to study nonlinear quantum phenomena of the transitions that occur in the nucleus of atoms of different materials and the lifetime of their excited states, in addition to the use of the technique for measures of Mössbauer effect in matters whose source of emission is not efficient or is unstable to function as a source [5].

The most difficult to carry out this type of experiment would be to develop an efficient detector for the generated wavelength that had the resolution to distinguish the resonant state from the non-resonant state. Besides, it would be necessary to develop a way to focus the beams in the sample since these phenomena depend on a great intensity to occur. Moreover, the beams must be synchronized and have the same focus so that the probability of the effect occurring is greater since they are confocal techniques.

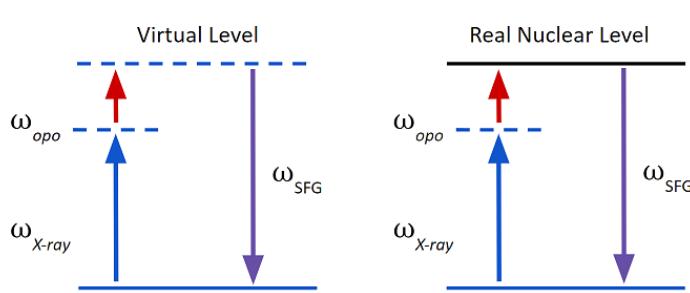
In figure 1(c), I present a possible setup for use an X-ray beam. There is a possibility to use a polycapillary lens to solve the focus problem and solve the phase-matching necessity, like the standard objective in conventional optical measures, however probably without then and using a phase-match between the lasers can be a good result too.

Another possibility is to use only one tunable X-ray pulsed laser, around 7,2 keV for SHG and 4,8 keV for THG measures. Still, it requires a very precise tunable system because the nuclear levels are very narrow in energy.

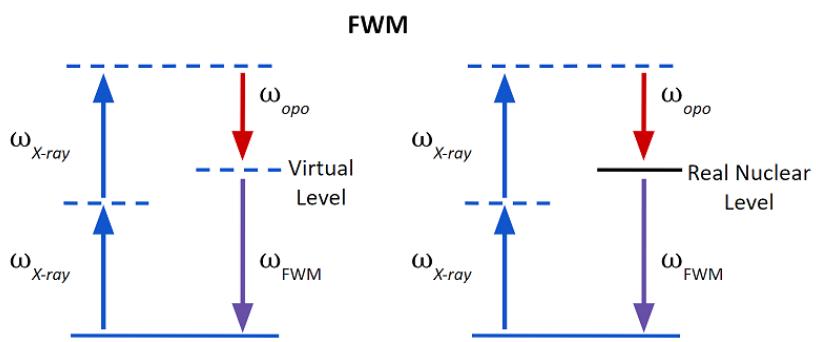
- [1] Malard L M *et al.* Phys. Rev. B **87** 201401 (2013).
- [2] Lafetá L *et al.* Nano Lett. **17** 3447–51 (2017).
- [3] Röhlsberger R *et al.* *Quantum and Nonlinear Optics with Hard X-Rays*, Springer International Publishing, 2ed. pp 1399–431 (2020).
- [4] Heeg K P and Evers J, Phys. Rev. A **88** 043828 (2013).
- [5] Kuznetsova E and Kocharovskaya O, Nat. Photonics **11** 685–6 (2017).

Descriptive figures:

(a)

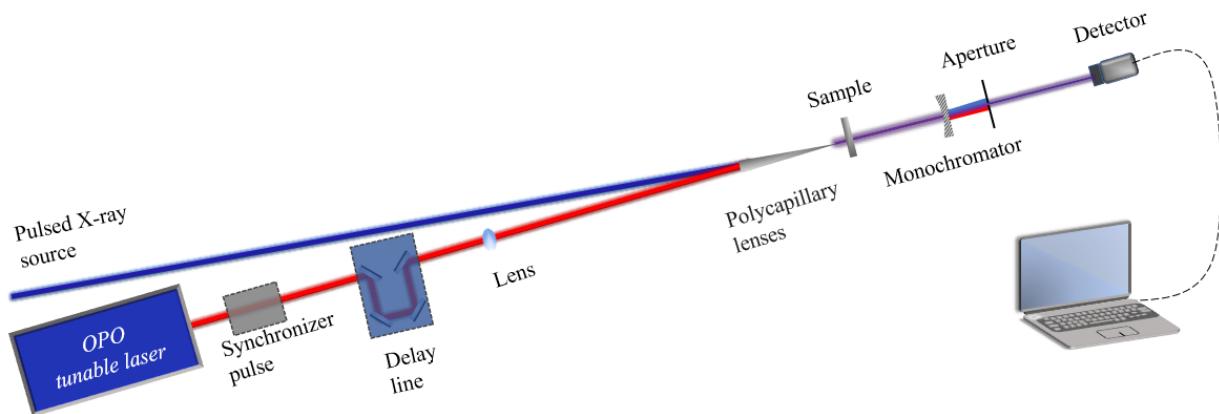


(b)



(c)

Setup for nonlinear X-ray measures



Requirements:

Pulsed X-ray beam with 14398 eV, for SFG, and 7201 eV, for FWM, Tunable optical pulsed laser, probably an optical parametrical oscillator (OPO) tunable between 500 to 800 nm (1.5498 to 2.4797 eV), picosecond pulsed is preferential because we need a narrow energy range in pulse. Equipment to manipulate X-ray and optical beams, and detectors to measure the expected effect precisely.

Tentative project timeline

It's necessary to discuss with more experienced X-ray scientists to determine the viability and how long time it is necessary to apply this technique.

Preliminary team:

It's important to compound this team with engineers, line scientists to operate the X-ray and optics beams, physicists to prepare the experiments, analyze the results, and theoretical physicists to simulate the results previously.

Contact Person:

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