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WORKSHOP REPORT

Attosecond to Few-Femtosecond Ultrafast Science at Future FELs

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General Introduction

Ultrafast Science aims at the exploration of the dynamical mechanisms of fundamental processes. It targets the quantum-mechanical origins of motion, such as general light-matter interaction, the transfer of energy between electrons and nuclei in matter, or relaxation processes after exciting atoms, molecules, surfaces, solids or nanostructures, either in electronic, spin, or vibrational/phononic degrees of freedom, to name only a few. Ultrafast motions of electrons in excited states are also at the heart of chemical dynamics and functional materials, thus directly addressing societal challenges such as atmospheric chemistry (e.g. the formation and breakdown of ozone or carbon-containing molecules including CO_2), charge localization and transfer in biomolecules (electron dynamics in amino acids potentially influencing their folding for biological function) as well as energy conversion/harvesting (photosynthesis and light harvesting).

In recent years, technological breakthroughs with optical lasers have enabled first glimpses with **attosecond or few-femtosecond resolution**. With recent breakthroughs in advanced undulator and seeding schemes, first exciting results documented in top-impact publications, free-electron lasers (FELs) are now moving into focus. To fully unleash the power of attosecond and few-femtosecond science (see below sessions and summary) they are excellently positioned to solve a few critical technological bottlenecks:

- High-intensity soft-to-hard x-ray attosecond pulses
  (e.g. for site-selectively pumping, probing, and steering electron migration through molecules/materials)
- **Controlled attosecond pulses from seeded FELs**
  (e.g. for controlling photoionization processes)
- **Merging optical laser and x-ray FEL pulses with attosecond resolution**
  (e.g. by employing angular streaking for clocking electronic relaxation pathways)

Recent proof-of-principle demonstrations at the first attosecond FELs (LCLS@SLAC, USA and FERMI@ELETTRA, Italy) show that this is just the beginning: Interest across many science fields is extreme. These fields would benefit from further development and routine implementations of these techniques for user access. EuXFEL and its future mission provides a substantial opportunity to pioneer and explore these exciting unique opportunities, putting itself and its users as leaders at the international forefront of growing research fields.

This situation motivated an international workshop to bring together leading expert scientists and emerging science leaders/young researchers to push forward and discuss their ideas and technological machine/FEL and endstation requirements to enable their visions.

The workshop "Attosecond to Few-Femtosecond Ultrafast Science at Future FELs" (AsToFewFs@FutureFELs https://indico.desy.de/event/29232/) thus consisted of 9 sessions with short invited presentations (15-20 min.), and joint long (30 min.) open discussion rounds to broadly cover entire science directions. To remain fully open to the diverse and multi-disciplinary community, in the announcement of the workshop we also invited submissions of contributed slides on additional topics that could be presented as part of the discussions, resulting in 10 contributions with stimulating new ideas.

Below, you find reports on the individual sessions and the results of the discussions for each session:

- Technical Capabilities / Developments
- Correlated materials and phase transitions
- Magnetism down to attoseconds
- X-ray–Matter Interactions
- Chemical Dynamics
- Charge transfer and charge migration
- Dynamics and Control down to the Attosecond Timescales
- Time Resolved Imaging from Femtoseconds to Attoseconds
- Emerging FEL-Science Capabilities

The session topics and invited speakers where selected by the Program Committee:

Stefano Bonetti, Francesca Calegari, Hermann Dürr, Gianluca Geloni, Gerhard Grübel, Marc Guetg, Steve Johnson, Alexander Kuleff, Alexander Lichtenstein, Anders Madsen, Fernando Martín, Michael Meyer, Andreas Scherz, Serguei Molodtsov (EuXFEL/Local Chair), Thomas Pfeifer (Chair)

1 Session I: “Technical Capabilities / Developments”

Chair: Gianluca Geloni (European XFEL)

Introduction by G. Geloni and M. Guetg. This session brings together FEL developers and users; it prepares for the following sessions, orders developers efforts (and therefore users applications) within a timeline, see https://confluence.desy.de/display/ FELRD/Short+Pulse+Table : several methods for short-pulse generation require no or little hardware, and are already being pursued at EuXFEL. Other methods require relatively small additions (e.g. eSASE-chirp-taper) and can be pursued within a 5 years horizon. Methods requiring large hardware additions and dedicated beamlines are at the stage of discussion.

What is the best direction for EuXFEL in terms of techniques, serving present science cases? Uniqueness of EuXFEL: what are the implications for short pulse production? What are the best technical developments for applications in 10-20 years from now?

1.1 T. Tanaka (RIKEN Spring-8 Center)

“Generation and Control of Attosecond Pulses”

Optical slippage was discussed as a limiting factor for the production of monocycle pulses. This limit can be overcome by obtaining “chirped” microbunches (with changing period along the electron bunch) emitting in a tapered undulator: necessary condition for the generation of a monocycle is then matching the slippage at the n-th undulator period with the interval at the n-th microbunch.

A way to obtain chirped microbunching is by means of a seeding setup (laser, modulator wiggler and dispersive section) where the seed is chirped, while the matching is obtained by a sequence of sub-radiators and retarders. Parameters were discussed for a low-energy machine in the SXR. Simulations yield 40 as monocycle pulses with several GW power level, with possibilities for pulse control in terms of duration and Cycle/CEP. A double-pulse option was also discussed.

1.2 E. Schneidmiller (DESY)

“Short Pulses at the European XFEL: Present Experiences and Development Possibilities”

Few-fs pulses (with 100 pC and 250 pC charges) were obtained in hard- and soft X-ray with the help of nonlinear compression, with pulse energies > 100 µJ (tapering). Dispersion-based fresh slice is being developed, dechirper will be installed. Attosecond pulses were generated exploiting harmonics (test at SASE3: 1% good events, 10 µJ, 200 as; with several segments entering amplification we expect peak power increase to few-tens GW level).

eSASE/chirp-taper techniques are being studied with in mind the 2024 shutdown for most installations, upgradable, starting with 10 Hz, 100 GW peak power, ~200 as; two colors should be possible (split/delay of laser pulse, dechirper and split undulator).

In the long term, one aims at reaching sub 100-as scale with TW power levels and tuneable photon energy from few hundreds eV to few tens keV, two-colors with tuneable delay, as pulse trains, full use of burst mode (<2030). Beyond that time (>2030) one aims at covering CW, having a dedicated undulator line, and at sub-cycle synchronization with external laser, going towards single-cycle, waveform control, and zeptosecond trains.

1.3 A. Marinelli (SLAC, Stanford Univ.)

“Attosecond Techniques at the LCLS: Present and Future”

XLEAP demonstrated generation of 100 as pulses with 100 GW level peak power using energy modulation induced by coherent emission in the modulator wiggler and in the SXR (the slippage limit now referring to a large current due to non-linear chirp induced by space-charge). Angular streaking is used to diagnose the pulses.

XLEAP II uses new wigglers with λ_w=50 cm and K~44, and showed 10s of µJ with 8 eV FWHM bandwidth at 500 eV (a factor 2 improvement with respect to XLEAP), with pulse duration analysis ongoing.

Solutions beyond the split undulator have been proposed (double chirp-taper method, x-ray delay line, cascaded amplification).

1.4 Discussion / Session conclusions

During the discussion, the following points were considered:

- Generation and control of as pulses down to the mono- or few-cycle level vs wavelength, which is -at the moment- in the soft x-ray range
- CW operation is being considered at EuXFEL as a lower-electron energy addition to the current burst mode
- Possibilities of using the CEP-stable CSR from the electron bunch as pump or for synchronization, and possible addition of (synchronized) optical pump, SXR/HXR pump and probe.
- Usage of xleap based on self-modulation at different machines (can be tricky -but to be studied- for beam dynamics reasons), cathode and laser-heater modulation.
- Possibilities of using HHG sources as alternative or a complement to FEL sources, and synchronization issues.

2 Session II: “Correlated materials and phase transitions”

Chair: Steve Johnson (ETHZ / PSI)

Strongly correlated materials are materials where electronic correlations are essential in understanding key properties. The broader class of materials known as “quantum materials” includes strong correlated materials but also includes other non-generic quantum effects as possible key factors in determining material properties. This session explores the possible unique role of attosecond or few-femtosecond x-ray pulses in exploring new physics in such materials.

2.1 Kai Rossnagel (Univ. of Kiel / DESY)

“Few-Femtosecond Dynamics in Quantum Materials”

In his talk Kai Rossnagel provided an overview of what might be possible to explore using few-femtosecond time resolution for spectroscopy on quantum materials, with a strong emphasis on using ~ 10 fs transform-limited and tunable pulses. For these applications high repetition rates are essential to obtain sufficient statistics. Such experiments can address questions about the ultimate time scale of electronic screening, thermalization, and the dynamics of doublons in strongly correlated materials, as well as new concepts to explore Floquet engineering.

2.2 Martin Eckstein (Univ. of Erlangen)

“Sub-Cycle Resolved Femtosecond Dynamics in Driven Correlated Materials - Theoretical Proposals”

Martin Eckstein presented from a theory perspective some ideas on what kinds of new phenomena might be observed in pump-probe experiments with extremely high time resolution at XFELs. He discussed photo-doping in a charge transfer insulator, where band shifts from dynamic screening and inter-orbital interaction might be visible using x-ray absorption spectroscopy with 10 fs time resolution. He also discussed Floquet engineering, where transient modifications to the Hamiltonian of quantum materials might be visible using angle-resolved photoemission or resonant inelastic x-ray scattering with high time resolution.

2.3 Margaret Murnane (Univ. of Colorado)

“Attosecond Structured Light for Applications in Materials and Nano Science”

Margaret Murnane presented a perspective from high-harmonic based sources on attosecond spectroscopy on solids. She placed a strong emphasis on the need for “customized” pulses, meaning Fourier-transform-limited pulses with variable duration / bandwidth. She also presented numerous applications of these methods to nanostructured materials, where heat transport effects play a major role, and emphasized the need for many complementary methods from both experiment and theory to have a complete understanding.

2.4 Discussion / Session conclusions

The discussion opened with some topics relevant to the specific talks:

- The band shift effects predicted from photodoping of charge-transfer systems in the talk of M. Eckstein are expected to happen on a sub-fs time scale
- There was also some discussion of whether attosecond pulses are useful for photoelectric diffraction experiments. The emerging conclusion was that since this method probes mostly atomic structure, to first order one would not expect such fast dynamics in most systems. There may be some effects from core electron dynamics, but this is usually not relevant for the understanding of quantum materials.

In addition to the talks summarized above, this session had two contributions in the form of single slides:

- **Michael Zuerch (UC Berkeley)** presented ideas on using intense XFEL pulses to study materials using second-harmonic generation in the XUV and soft-x-ray range. This method offers element-specific access to surface states, buried interfaces and structural or electronic inversion-symmetry-breaking. Such methods applied on ultrafast time scales to the study of electronic structure formation, catalysis, and dynamic symmetry-breaking.
  - In the following discussion it was pointed out that high repetition rates are also essential for SHG spectroscopy applications
- **Daria Gorelova (Univ. Hamburg)** described her recent theoretical work on reconstructing complex electronic dynamics on atomic length scales and few-femtosecond time scales. Her group considers different techniques such as resonant inelastic x-ray scattering, time- and angle-resolved photoelectron spectroscopy, and sub-cycle x-ray/optical wave mixing. Current projects include imaging of exciton dynamics and imaging strong-field-driven electron dynamics in solids.

After these presentations followed a more general discussion on possible new methods enabled by attosecond / few-fs pulses:

- X-ray pump / x-ray probe experiments might be interesting to study but at present the needed theory to understand this is not developed
- Coherence relations between x-ray pulses might be exploited to gain additional insights

3 Session III: “Magnetism down to attoseconds”

Chair: Hermann Dürr (Uppsala University)

The introduction to the session started with an overview of ongoing attempts to control magnetic interactions and probe spin transport phenomena on fs timescales and nm length scales. The availability of attosecond soft x-ray pulses would enable to break the current ~10 fs barrier and open access to a new regime discussed in more detail by the speakers below.

3.1 Alexei Kimel (Radbout University Nijmegen)

“Controling magnetic exchange down to attoseconds”

Alexei Kimel’s talk introduced the relevant energy- and timescales for magnetic (exchange and spin-orbit) interactions in solids. He described how optical laser radiation can interact with spins and ultimately control their orientation by mimicking the actions of a light-induced magnetic field. Discussing preliminary experiments, he concluded that this can lead to a sub-10 fs control of the exchange interaction. Attosecond laser pulses would be the key to understand the ways to manipulate the exchange interaction, to reveal dynamics of the exchange and thus to obtain a control over the interaction, which is ultimately responsible for the magnetic order.

3.2 Oscar Grånäs (Uppsala University)

“Light-matter interaction of strongly correlated electrons”

Oscar Grånäs introduced the idea of coherently manipulating the electronic momenta via the vector potential of a driving optical laser pulse. He showed first-principles calculations for the prototypical correlated insulator NiO that demonstrate a transient O-Ni charge and spin transfer within one optical cycle. Attosecond probing of this response would open up a new regime of theoretical predictions by testing important concepts such as the timescale for electronic screening.

3.3 Martin Schultze (TU Graz)

“Attosecond probe of ultrafast charge & spin dynamics”

Martin Schultze introduced his first experiment with attosecond resolution of the electronic motion driven by the electric field component of optical laser pulses. He stressed the need to extend such experiments beyond current access to 3p core-levels to the 2p absorption edges of transition metal magnets. For this, the synchronization between pump and attosecond probe similar to what he can achieve now with table-top attosecond lasers is imperative. Phase sensitive measurements and theory developments were also identified as being important.

3.4 Discussion / Session conclusions

The science and key experimental parameters of attosecond experiments were discussed as summarized below:

- 100 μJ pulses with 1-10 fs duration would enable an excellent start for first experiments. These will also be important to identify the need and strategy to access faster timescales.
- The x-ray spectroscopy and scattering techniques developed for current XFEL experiments can easily be extended to ~1 fs pulse lengths given the larger available x-ray flux compared to laser-based attosecond experiments.
- Scattering/diffraction would provide access to nanoscale spin transport and to probing of coherent spin-wave excitations in analogy with what is currently done in Fourier transform spectroscopy of phonons.
- Element-specific probing of spin and orbital magnetism with variable (circular and linear) x-ray polarization is imperative to disentangle ferro- and antiferromagnetic dynamics.
- Developing phase sensitive detection of the x-ray probe similar to what can be done with lasers would be advantageous.
- Synchronization to optical few-cycle pump pulses is crucial.
- Two-color x-ray experiments could provide synchronization for initial experiments.
- Measurements should cover the O K-edge and L-edges of 3d and 4d transition metals (approx. 0.5 – 3 keV)
- Further details should be identified during a focused Workshop across the present Instruments at EuXFEL.

4 Session IV: “X-ray–Matter Interactions”

Chair: Thomas Pfeifer (MPIK Heidelberg)

X-ray–matter interaction is a broad area, aiming at the understanding & control of the fastest (typically attosecond) electronically triggered processes at high intensities. Compared to the (r)evolution for visible lasers from perturbative 2nd-harmonic generation to the dawn of strong-field physics, we can also expect novel regimes of non-perturbative processes in the x-ray regime, especially when intense & increasingly controlled (e.g. seeded) XFEL fields couple to resonant transitions. Early examples from the XUV/soft-x-ray FEL FLASH illustrate significant and measurable energy-level shifts.

4.1 Carlo Callegari (FERMI@Elettra)

“Opportunities for Few-Femtoseconds and Sub-Femtosecond AMO Science with a Temporally-Coherent Seeded FEL”

Carlo Callegari's presentation highlighted the technical and scientific state-of-the-art of the seeded FEL facility FERMI and its beamlines, including the new 5-fs superradiant scheme. Some recent key experiments, making use of the outstanding (phase-stable) controllability and synchronization of such seeded sources were presented, including coherent demodulation experiments for nonlinear spectroscopy and coherent control approaches. From such experiments, including the recent attosecond pulse-train control, information on attosecond dynamics, such as Wigner time delays, can be accessed.

4.2 Linda Young (Argonne, Univ. of Chicago)

“Resonant X-ray Propagation Through Strongly Absorbing Media”

Linda Young's talk introduced several historic nonlinear-optical light–matter interaction examples in the optical regime and presented a key experiment aiming at exploring such effects in the x-ray regime. In particular, the spectral and temporal reshaping mechanisms occurring during the propagation of intense x-ray light pulses through matter are of key importance to several experiments aiming at the understanding of fundamental light-matter interaction at high x-ray intensities. Angular photoelectron streaking by cross-correlation of XFEL pulses with visible/infrared fields provides an opportunity to measure such general reshaping effects directly in the time domain.

4.3 Wolfram Helml (TU Dortmund)

“Dynamics in Matter correlated to the SASE Structure”

Wolfram Helml introduced the concept of angular streaking for shot-to-shot temporal diagnostics of x-ray FEL pulses with a circular time-of-flight electron spectrometer array (the so-called “cookie-box”) detector. It has already been successfully used for measurements at LCLS, where the temporal shape of isolated attosecond pulses could be measured. This or similar devices are of extreme importance for future attosecond-pulse x-ray FEL experiments, not only for temporal diagnostics (which could improve with seeding schemes) but also for timing synchronization/tagging between x-ray and infrared/visible or (vacuum)ultraviolet pulses generated by optical lasers.

4.4 Discussion / Session conclusions

The discussion evolved around future opportunities for this field, with the main directions of shortest controllable pulse duration, the trade-off between high intensity and short pulses, the importance of diagnostics, and the achievable

time-resolution of in-situ (parasitic) pulse-shape reconstructions techniques, which were considered extremely important for future facilities.

- Attosecond pulse generation: The fundamental limits of superradiance schemes are determined by the number of undulators and the number of fresh electrons, which is currently at the limit for FERMI. Also, for shorter wavelengths, it would be harder to reach saturation, so different methods are important, e.g. such as currently explored by XLEAP at LCLS. Phase-shifting methods to achieve attosecond delays attract great interest.
- Aiming at nonlinear processes, it was discussed where the trade-off between short pulses vs. higher pulse energies (intensities) should be placed. Some experiments can be done with intense SASE pulses of longer duration, but for attosecond pulses certainly many effects can be more easily/cleanly observed. Attosecond x-rays could be particularly interesting for nonlinear effects in solids.
- There is interest in chirped x-ray pulses, as they would open novel opportunities for nonlinear x-ray–matter interaction experiments. E.g. chirped optical laser pulses opened new routes for the coherent nonlinear control of matter by light.
- Diagnostics are of crucial importance, even for seeded FELs. E.g. at FERMI, spectral and polarization diagnostics are available, and there is need for future pulse-shape diagnostics, in particular in the light of the new attosecond pulse-train generation capabilities.
- The angular streaking (cookie-box) technique for time-resolving dynamical processes is promising to achieve high temporal resolution (currently on the order of 100 as), even beyond the one directly obtainable by controlling the generation process. Experimental techniques such as time-resolved double core hole or Auger spectroscopy could benefit substantially, in particular also from the angular information that can be extracted.
- The combination of attosecond two-color options with angular-streaking detection is interesting, first experiments are underway, key is to achieve separable streaked electron spectra for both colors simultaneously. A discussion also emerged on optimal wavelengths for streaking, where

certainly long wavelengths, such as 10 micron (e.g. by a CO_2 laser) would be helpful, but need to be sufficiently intense. A synchronization (or timing reconstruction) of x-ray FELs to such intense infrared lasers could also open new opportunities, e.g. in molecular or solid-state physics.

5 Session V: “Chemical Dynamics”

Chair: Fernando Martin (UAM)

In his general introduction, the chair described the advantages of using intense attosecond x-ray pulses to study electron and fast nuclear dynamics in molecules in comparison with the weak pulses available from HHG sources. Then he showed a few examples that have been investigated theoretically by using an attosecond x-ray pump / attosecond x-ray probe scheme in which time-resolved photoelectron spectra are the key observables. Theoretical predictions indicate that the shot-to-shot variation of the XFEL pulses does not seem to affect too much the imaging of such dynamics and that time-resolved polarization-averaged molecular frame photoelectron angular distributions can provide a direct imaging of hydrogen migration without the need for any reconstruction.

5.1 Nora Berrah (Univ. of Connecticut)

“Attosecond Electron Dynamics in Molecules Using Non-Linear Multidimensional Methodologies with FELs”

Berrah’s talk started with the general description of non-adiabatic effects and conical intersections. The idea is to map in real time the evolution of electronic coherences created at conical intersections. To this end, a method has been originally proposed by S. Mukamel that is dubbed TRUECARS (Transient redistribution of ultrafast electronic coherences in attosecond Raman signals). Berrah showed how TRUECARS could be implemented with attosecond x-ray FELs exploiting the stochastic nature of the SASE pulses.

5.2 Daniel Rolles (Kansas State Univ.)

“Probing Ultrafast Charge Dynamics in Atoms and Molecules with Attosecond X-ray Pulses”

Rolles is interested in imaging (using coincidence detection techniques - COLTRIMS), charge migration, and charge transfer mechanisms in molecules. Three examples have been provided: (1) inner-valence attosecond charge migration induced by inner-shell excitation in OCS by using an ω-3ω scheme, (2) ultrafast hole hopping in N_2: charge density oscillations induced in the K-shells of N_2 by an attosecond XFEL pulse, probed by another attosecond XFEL pulse, and (3) femtosecond charge transfer induced by UV excitation in PENNA, probed by an attosecond XFEL pulse. The charge transfer can be mapped by looking at transient chemical shifts in the photoelectron spectrum.

5.3 Martin Wolf (FHI-MPG Berlin)

“Probing Electronic and Nuclear Dynamics of Solids and Surfaces on their Intrinsic Timescales”

Martin’s talk focused on surface femtochemistry. The proposal is to induce ultrafast CO oxidation using an optical fs laser pulse and to probe it with time-resolved XAS. Alternatively, one could probe the electron dynamics at surfaces using time-resolved ARPES: in this case one can map the band structure dynamics and see ultrafast phase transitions at interfaces, e.g., In/Si(111) and $MoTe_2$. All these methods will highly benefit from the availability of few-fs x-ray pulses.

5.4 Discussion / Session conclusions

During the discussion, several questions were raised:

- The use of attosecond pulses might be a problem for ARPES due to the loss of energy resolution, but there are cases where one can still find a good compromise between energy and time resolution which are worth exploring. Probably, in many cases, few-fs XFEL pulses could be a better choice.
- Phase transitions at interfaces are usually investigated in the vis-infrared but can also be produced by x-rays (inner shells). For this, one has to find optimal conditions for excitation, which are not yet clear.
- The inner-shell excitation by XFEL pulses is expected to trigger charge migration in molecules due to electron correlation, as predicted by theory several years ago. This is different to charge migration induced in the valence shell by XUV attosecond pulses, which is mainly due to the coherences imprinted by the attosecond pulse in the system and not to electron correlation. Attosecond and few-fs x-ray pulses open the way to explore correlation-driven electron dynamics.
- x-ray spectroscopy is in principle superior to optical spectroscopy to see electron and nuclear dynamics arising from conical intersections because the probing step is clean (one-photon absorption). In any case, accessing conical intersections requires the use of ultrashort UV pump pulses, which must be synchronized with the x-ray probe, ideally with few-fs or sub-fs resolution. This is not yet possible and requires further developments.
- TRUECARS, which takes advantage of the possibility to generate non-linear processes with intense x-ray pulses, also needs short UV pulses to pump the system, as confirmed by theoretical predictions. So, similar limitations apply to this case.

From this discussion, some general conclusions can be extracted

- Attosecond x-ray pulses open the way to more localized excitation and ionization, since they mainly involve the K and inner-valence shells of molecules. They will also allow one to investigate correlation-driven charge migration processes.
- Improving the synchronization of attosecond XFEL pulses with ultrashort UV pulses, i.e., reducing the duration of the UV pulses and improving the time resolution in the pump-probe delay, is a critical issue to access ultrafast electron and nuclear dynamics in the excited states of neutral molecules.
- Attosecond XFEL pulses open the way to implement non-linear schemes (not possible with other light sources) to investigate electronic coherences and non-adiabatic effects in real time.

6 Session VI: “Charge transfer and charge migration”

Chair: Francesca Calegari (DESY)

In this session we learned how attosecond soft-x-ray pulses could pave the way for a complete understanding of ultrafast mechanisms such as charge migration, solely driven by the electron dynamics. There have been also proposals to use ultrafast electronic processes to control the nuclear dynamics and/or other molecular properties such as chirality.

6.1 Jon Marangos (Imperial College London)

“Measurement of Ultrafast Electronic Dynamics with X-rays”

Marangos’ talk focused on two different topics: HHG-based XANES in molecular systems of photovoltaic interest, namely P3HT, and recent soft-x-ray pump / soft-x-ray-probe experiments performed at XFELs on isopropanol, glycine and aminophenol. All these examples showed the capabilities of current ultrashort x-ray pulses (durations few femtoseconds) to initiate and track correlation-driven phenomena such as charge migration. He pointed out the need for high repetition rate (operation in CW) and understanding the effects of the thermal load that will derive from this future operation of FELs.

6.2 Françoise Remacle (University of Liège)

“Exploiting Electronic Coherences for Steering Selectively Ultrafast Reactivity in Molecules”

Remacle’s talk focused on the theoretical modelling of ultrafast charge migration processes induced by ultrashort UV pulses (few fs duration). Two

examples were discussed in detail: UV-induced ring closure in norbornadiene leading to quadricyclane and Jahn-Teller rearrangement of the methane cation and its fully deuterated isotopomer. The importance of the coupling between electronic and nuclear degrees of freedom was highlighted and in particular she discussed how electronic coherences can influence the nuclear dynamics.

6.3 Valérie Blanchet (University of Bordeaux)

“Molecular Chirality on the Short Time-Scale”

Blanchet’s talk focused on time-resolved aspects of molecular chirality. Two general strategies were considered: the use of different combinations of circularly and linearly polarized pump and probe pulses (PECD and PXCD), and the use of “chiral” light pulses. All reported experiments were performed with HHG-based pulses and the limitations derived from their use were highlighted. Proposals for a soft-x ray excitation and probing have been done. In particular, it has been highlighted that not only coherent nuclear dynamics but also electronic beatings are expected to modulate the PECD signal on an ultrafast time scale.

6.4 Discussion / Session conclusions

We heard about “charge migration” or “correlation-driven electron dynamics” several times in the workshop. It is clear that there is still a huge interest in the real-time imaging of these processes and a strong push towards the full control of the electron dynamics, potentially leading to attochemistry. In this context, attosecond XFELs offer new experimental schemes overcoming the current limitations of tabletop sources.

From the above three talks and the general discussion, the following conclusions can be extracted:

- There is the necessity to combine few-fs laser pulses (for instance UV pulses) with soft-X-ray attosecond pulses. The former are needed to excite most molecules in the valence and induce ultrafast electron dynamics (although a similar excitation can be obtained with soft-X ray pulses using non-linear schemes) and the latter to provide a clean probe of that dynamics. So far, the time resolution that can be achieved is not better than few tens of femtoseconds and this must be improved in order to access electron dynamics (bottleneck synchronization).
- The need for higher repetition rates (CW operation) was also mentioned in order to improve the statistics of the measurements, thus facilitating the use of multi-coincidence detection methods as those mentioned in other sessions of the workshop. It was also pointed out that one needs to understand the effects of the thermal load that will derive from this future operation of FELs.
- The possibility to combine ultrashort pulses with electron and ion beams was suggested. This would allow one to obtain temporal information about ultrafast electron dynamics induced by electrons and ions in matter, which is not currently possible. Temporal synchronization between the light pulses and the electron or ion beams is a major issue, but this might be solved by using the same light pulses to produce the electrons or the ions.
- The importance of performing accurate theoretical calculations to interpret attosecond pump-probe measurements and to guide future experimental developments was emphasized.
- The convenience of using ultrashort XFEL pulses with arbitrary polarization to improve our knowledge of time-resolved aspects of molecular chirality was also raised. This would require the use of two XFEL pulses, a pump and a probe, with at least one of them circularly polarized.
- The use of attosecond XFEL pulses in a soft-x-ray pump / soft-x-ray probe scheme was proposed as the best scenario to investigate the dynamics of double-core hole states by performing time resolved measurements of

hypersatellite Auger lines. The short lifetime of these states justifies the attosecond duration of the pulses and the low probability of hypersatellite lines their high intensity.

7 Session VII: “Dynamics and Control down to the Attosecond Timescales”

Chair: Michael Meyer (European XFEL)

The general scope of the session was outlined in the introduction. Examples of processes, which are governed by ultra-fast electron dynamics, were presented highlighting the essential role of attosecond pulses for the corresponding studies as well as the vital requirement for a precise single-pulse characterization of their spectral, temporal and spatial distribution. Some advanced techniques to access the attosecond regime, such as angular streaking and phase sensitive methods, were briefly described providing thereby a transition to the following presentations.

7.1 Anne L’Huillier (Lund University, Sweden)

“Photoionization Dynamics Measured at the Attosecond Timescale”

Anne L’Huillier presented a recent study on the 4d ionization of atomic Xenon applying the RABBITT excitation scheme. Delays in the attosecond range were measured demonstrating the high sensitivity to threshold dynamics and resonances, especially to the Xe 4d “giant” resonance. Similar experiments addressing stronger-bound core electrons are possible by using attosecond FEL pulses. In a more general sense, Anne L’Huillier pointed out that the efficient use of attosecond pulses requires thinking beyond standard pump-probe experiments, since experiments providing simultaneously spectral and temporal resolution are possible. In addition, coincidence measurements between electron and ions would enable the extraction of more detailed information on the dynamics of individual excitation and relaxation channels in the photoionization process.

7.2 Reinhard Dörner (University of Frankfurt, Germany)

“The Power of Coincidences”

In his talk Reinhard Dörner discussed the exciting achievements of COLTRIMS measurements allowing to correlate the momenta of electrons and ions in a coincidence scheme. Beside the possibility to retrieve the molecular structure from Coulomb explosion imaging, the investigation of the molecular structure “from Within” by photoelectron diffraction was demonstrated via experiments on the time-resolved fragmentation of O_2. Future pump-probe experiments together with the precise characterization of the (attosecond) FEL pulses will enable to monitor the electronic evolution during structural molecular changes site-specifically with sub-femtosecond resolution or to correlate molecular structure and function during their ultrafast evolution at their very origin, close to and entering the attosecond regime.

7.3 Giuseppe Sansone (University of Freiburg, Germany)

“New Opportunities for Attosecond Experiments using FELs”

The presentation of Giuseppe Sansone was mainly related to attosecond metrology at seeded free-electron lasers, with the particular example of the seeded FEL FERMI. A RABBITT scheme enabling attosecond spectroscopy was employed for experiments using FEL pulses, i.e. opening a much broader photon energy range for these experiments. The inherent temporal instabilities (jitter) of FEL sources and the corresponding loss in synchronization can be overcome by using correlation (or covariance) analysis of the recorded single-shot spectra. For future applications at FELs, the use of two- (or multi-) color excitation schemes with variable delays between the pulses and possibilities of amplitude and phase shaping of the attosecond radiation were considered to be the most promising and most exciting developments.

7.4 Discussion / Session conclusions

The final discussion of the session was mainly concentrating on particular aspects of the RABBITT measurements and its application to FELs. In particular, the possibilities and difficulties to use this powerful scheme not only for attosecond experiments with tabletop lasers or at seeded FELs, but also for SASE pulses were pointed out. In addition, the coincidence schemes and their advantages for various experiments on gas-phase samples were again highlighted. The recent examples of successful coincidence studies at FELs using COLTRIMS show clearly that the complete characterization of photo-induced processes, enabled by measuring and correlating all particles produced in the process, opens up a large variety of new investigations, in particular also for time-resolved experiments in the attosecond regime. Addressing ultrafast electron dynamics, including electron correlations during photoionization (of core electrons), charge migration in molecules upon inner-shell excitation as well as resonant processes and subsequent electronic relaxation, is possible by using these techniques. But, as it was also discussed, the precise control and characterization down to the level of the spectral phase of the x-ray pulses is required to ensure that dynamical information on the attosecond time scale can be extracted from the experiments.

All contributors to the discussion came to the common conclusion that there is an extremely exciting and bright future for experiments enabled by the application of attosecond x-ray FEL pulses, which will provide unique inside into electron dynamics of atoms and molecules. Various techniques for controlling the attosecond pulses have already been developed for tabletop laser systems and can almost certainly also be used and adapted for attosecond x-ray FEL pulses.

8 Session VIII: “Time Resolved Imaging (from Femtoseconds to Attoseconds)”

Chair: Anders Madsen (European XFEL)

This session comprised three speakers discussing new ideas for exploiting the unique properties of XFEL radiation in imaging. In addition, two poster clips were presented on imaging of electronic fluxes and ring current in excited symmetric molecules as well as a proposal to combine ultrafast electron diffraction with XFEL imaging in a dedicated end-station. The session was concluded by a Q&A session with the speakers and a round of general discussion.

8.1 T. Gorkhover (DESY/Uni Hamburg)

“Transient resonances as a potential optimization parameter in XFEL CDI”

Imaging of small objects in reciprocal space is appealing but the competition from Cryo-EM is fierce concerning single particle imaging (SPI). Here, x-rays offer opportunities for exploiting non-linear effects at resonances. In particular, it was shown that ultrashort x-ray pulses from FELs can take advantage of transient resonances in CDI originating from the overlap of electronic orbitals upon excitation.

8.2 D. Rupp (ETH Zurich)

“Imaging electron dynamics in isolated nanoscale particles”

Resonant imaging is highly photon energy and pulse duration dependent and allows to investigate ultrafast electron dynamics with improved resolution. Spatially heterogeneous systems are for instance of interest where a core-shell structure can be identified in excited Xe clusters. A fully tunable pump-probe setup with a two-color operation mode and coherent control is advantageous for full exploitation of this electron imaging approach based on transient resonances.

8.3 H. Chapman (DESY/Uni Hamburg)

“Imaging with high intensities and short pulses”

The concept of diffraction before destruction with ultrashort pulses has led to significant improvements in XFEL techniques like holography, CDI and SPI but challenges persist, e.g. concerning flux on the sample and unwanted background signals. Full dispersion control in x-ray focusing has the potential of advancing SPI further and new ideas using diffractive optics have been presented, also aiming to compress XFEL pulses further in time by compound x-ray optical devices.

8.4 Discussion / Session conclusions

The session highlighted how transient resonances can be utilized for further advancing ultrafast imaging and progress was suggested towards SPI by development of novel x-ray optics. Questions about applicability of holography techniques and pros/cons with respect to CDI were raised by the attendees and discussed. The importance of a performant pump-probe scheme for full utilization of transient effects in ultrafast electron imaging by CDI were highlighted. The role of theory and simulations prior to experiments,

sometimes as a necessary prerequisite defining the experimental parameters, was also repeated by several attendees and speakers. Finally, the overlap and complementarity of XFEL experiments with respect to ultrafast electron diffraction and cryo-EM was discussed. The chairman pointed out that imaging without a full reconstruction (or any at all) is also sometimes of interest. This relates for instance to time-resolved molecular orbital tomography by ARPES and speckle imaging (XSVS, x-ray speckle visibility spectroscopy) where temporal resolution is crucial and aiming for a few fs. These techniques are related to classical imaging and share many of the technical requirements and challenges but are typically only focusing on a few Fourier components. XSVS images speckles in reciprocal space and can be regarded as an ultrafast extension of x-ray photon correlation spectroscopy (XPCS) which will benefit enormously from control of the pulse duration and the pulse pattern, for instance modified by an x-ray split and delay line.

9 Session IX: “Emerging FEL-Science Capabilities”

Chair: Alexander Kuleff (Heidelberg University)

In his introduction, Alexander Kuleff presented the main scientific questions and the experimental challenges in the study of ultrafast charge- and energy-transfer dynamics in molecular systems. The requirements for implementing the large palette of linear and non-linear x-ray pump-probe spectroscopies and multi-color schemes, as well as the prerequisites for development of electron-dynamics control schemes, involving precise control of pulse characteristics (shape, duration, frequency, phase, etc.), were then briefly discussed.

9.1 Shaul Mukamel (UC Irvine, USA)

“Monitoring Conical Intersection Dynamics in Molecules through Vibronic Coherences in X-ray Stimulated Raman and Diffraction Signal”

Shaul Mukamel introduced two ideas for monitoring transient electronic coherences allowing to directly detect a passage through a conical intersection in molecules – TRUCARS and time-resolved diffraction. Apart from the original TRUECARS, requiring precise timing and phase control of an attosecond x-ray and a femtosecond IR pulses, a new TRUCARS scheme based on a single stochastic (SASE) x-ray pulse was presented. Moreover, it was shown that the time-resolved x-ray diffraction can be a useful technique to follow conical intersection dynamics, producing weak, but very rich signal.

9.2 Kirsten Schnorr (PSI, Switzerland)

“Opportunities for Studying Ultrafast Dynamics at the Maloja Endstation at SwissFEL”.

Kirsten Schnorr gave a progress report on the construction and technical capabilities of the soft X-ray line at the SwissFEL, Athos, and the Maloja end-station. The modular design, allowing easy undulator reconfiguration, and CHIC (Compact, High power, and Improved Coherence) chicane modes offer high operational flexibility and possibilities to generate short, multicolor double pulse sequences suitable for a variety of ultrafast dynamics studies. First test results have been presented (double core hole in neon and XMCD signal from an Al-foil) and proposals to measure Excitation-Transfer Mediated Decay (ETMD) in microsolvated metal ions and to perform single-particle imaging have been briefly discussed.

9.3 Tommaso Mazza (EuXFEL)

“X-ray steering of electron dynamics in small quantum systems”

In his talk Tommaso Mazza discussed several aspects of the interaction of intense x-ray pulses with matter, in particular atoms and small molecules. Recent results from experiments performed at EuXFEL on the creation and decay of double-core holes in the neon atom were presented and the competition between photoionization and electronic decay discussed. Estimations based on rate equations were shown, demonstrating that in the strong-field x-ray regime, depending on the characteristics of the system and the core level, reducing the pulse length when keeping the intensity may lead to a substantial reduction in sample depletion by single-photon ionization, thereby enabling and enhancing the observation of non-linear multi-photon processes.

9.4 Discussion / Session conclusions

Both the scientific aspects and the technical challenges for monitoring and eventually controlling ultrafast electronic and molecular dynamics have been discussed with the invited speakers and among the participants. The main conclusions of the discussion are summarized below:

- Performing reduced-dimensionality simulations of the passage through a conical intersection can give a good description of the process and should reflect well the measured signal. This is especially important for simulating experiments on large molecules, where full-dimensionality calculations are out of reach.
- For a proper description of the high-intensity regime, it will be desirable to go beyond the rate-equation formalism. Understanding how short and intense pulses interact less with the system compared to longer pulses containing the same number of photons is very important, as it may put natural limits on the target FEL pulse-durations necessary for pump-probe spectroscopies.
- For preparing and then probing charge- and energy-transfer dynamics in molecules, two-color schemes with UV/XUV and soft x-ray pulses are needed. In this respect, the modular undulator design and CHIC chicane modes demonstrated at SwissFEL for producing two-color double-pulse with well controlled delay and high stability appears very attractive.
- Pulses with high temporal coherence and phase control are desirable. Different non-linear spectroscopic techniques with x-ray pulses can be used to trace charge and energy transfer in atomic and molecular systems. These techniques, however, rely on the possibility to generate several x-ray pulses with a precise control of their characteristics. The latter calls for a seeded FEL pulse generation.
- Different schemes based on stochastic (SASE) x-ray pulses can also be implemented and seem promising. For those, however, a good synchronisation (ideally below 1 fs) with a table-top external laser source is necessary.

- On a long run, for being able to control photo-induced chemical processes by manipulating the initially created electron coherence, the paradigm of “attochemistry” discussed several times over the workshop, it will be extremely interesting to think about possibilities to have pulses with spectrally and temporally tailored profiles: Pulse-shaping in the soft x-ray regime.

10 General Conclusions

The broad range of speakers, contributors, and discussions arising at the workshop provided an excellent overview of major parts of the (currently visible) extent of the science area to be illuminated by x-ray FELs with intense pulses on the attosecond and few-femtosecond time scales. Different disciplines ranging from fundamental physics through chemical dynamics, energy and materials science to biomolecular structure and dynamics would leap forward by qualitatively new possibilities to explore, technologically employ, and controllably steer the motion of electrons. Acting as the glue of all ordinary matter, they are at the very core of light-matter interaction and photochemical processes. As such, basic-science insights on their dynamics can be expected to drive an emerging era of new (dynamical) quantum materials. The latter is in timely demand, especially as currently written structures (e.g. for computing) have now entered the few-nm scale with corresponding challenges and opportunities as they converge toward the final (Angstrom) atomic limit.

The following list provides a non-exhaustive selection of science drivers, the corresponding machine parameters, and potential future technologies that could develop towards applications.

10.1 Science Opportunities

- Time-resolved measurement, understanding, and steering of (correlated) electron motion as the origin of any dynamical process in matter
- Tracking electronic and structural coherences during and after passing through conical intersections and chemical transition states
- (Resonant) x-ray imaging of time-dependent electronic fluxes/currents on the atomic level

- Quantifying the couplings between electronic and (internuclear) structural degrees of freedom
- Monitoring and inducing/steering electronic&magnetic phases&transitions by modifying the molecular structure, spin, or crystal-lattice control
- Ultrafast anti-/ferromagnetism, spin transport, and exchange control in solids
- Measurement and control of screening, thermalization, and band-gap dynamics in solids
- Observing and finally employing electron-correlation driven motion to drive structural dynamics in molecules, including isomerization and chiral structures
- Most stringent tests of quantum-dynamical electronic/molecular structure theories
- Imaging of the fastest structural changes, including hydrogen migration
- …

10.2 Source Characteristics

- Attosecond to few-femtosecond pulse duration (best case: controllable and transform limited by seeding)
- Intensity high enough to enable nonlinear interactions with matter (e.g. for pump-probe and multidimensional spectroscopy and imaging), >100 TW level
- CW-operation with repetition rates at 100 kHz and higher
- Two-color time-delay controlled soft x-rays near C, N, O edges for biomolecules, hard x-rays for imaging
- Multi-pulse sequences with relative phase stability for nonlinear/multidimensional spectroscopies, beyond pump-probe
- …

10.3 X-ray pulse Diagnostics

- Single-shot resolved spectral, temporal, spatial, polarization-state properties, and pulse energy (e.g. by x-ray spectroscopy and space-resolved angular streaking)
- Time tagging or synchronization to external (laser) light pulses (from THz to (X)UV) for excitation of chemically or technologically relevant reactions/modes of operation of molecules/materials
- …

10.4 Experimental Techniques

- Multiple observables (Ions, Electrons, Photons)
- Multi-coincidence detection (e.g. COLTRIMS Reaction Microscopes) or covariance techniques, both combined with single-shot x-ray spectro-temporal pulse information
- Multidimensional spectroscopy and transient absorption, time-resolved RIXS, EXAFS, XANES
- angularly resolved photoemission spectroscopy (ARPES) of surfaces
- single-shot x-ray diffractive imaging with few-femtosecond time resolution, also by employing site-selective photoelectron or relativistic-electron diffraction
- time-resolved Coulomb-explosion imaging
- x-ray second-harmonic spectroscopy
- …

10.5 Potential & Emerging Technologies

- Site-specific chemical reaction control (“attochemistry”), from gas-phase molecules to surfaces and tissues
- Multidimensional characterization of materials, similar to current NMR methods, but acting on core electrons rather than nuclear spins, and with temporal resolution allowing to observe structural changes of molecules and their electronic states on their characteristic time scales from few femtoseconds to attoseconds
- Floquet engineering: Dynamical quantum materials
- Atomic length- and time-scale molecular (quantum) computing
- Quantum materials for high-efficiency energy conversion, power transmission, sensing, and catalysis
- X-ray imaging in the absence of electronic damage (beating the core-hole clock)
- …

EuXFEL is currently in a position to become a future driver of this emerging field with major scientific, technological & societal impact on an international scale. To realize this potential, a clear decision towards attosecond pulses needs to be made and followed up by a solid strategy for its realization.

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