Time-resolved studies with FELs

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Abstract

Intense femtosecond VUV and X-ray pulses from free-electron lasers (FELs) enable time-resolved experiments studying ultrafast dynamics in a large variety of systems relevant, e.g., to physics, chemistry, biology, and material sciences. In this paper, we focus on time-resolved studies of gas-phase molecules, which lie at the crossroad between atomic, molecular and optical physics and ultrafast photochemistry. We describe the current status of the field and discuss typical experimental configurations used for pump-probe experiments with FELs. We illustrate them with three recent examples for such experiments performed at the FLASH and LCLS FELs studying charge transfer following XUV and X-ray photoabsorption as well as photoelectron diffraction from aligned molecules. We conclude with a short outlook on future developments and perspectives for femtosecond pump-probe experiments with FELs.

1. Introduction

Molecular structure and its evolution in time play a central role in our understanding of chemistry and biology on the microscopic level. Although a lot of information on both, structure and dynamics of molecules can be obtained from various high-resolution spectroscopic techniques (e.g., absorption, scattering, fluorescence, photoemission), a broad range of intermediate states in molecular reactions can hardly be accessed by such energy or frequency domain measurements performed in a “continuous wave” mode [Zewail2000]. Direct characterization of these “transition states”, i.e., sets of configurations through which the reacting molecules evolve from reagents to products, typically relies on time-domain measurements, where the above-mentioned spectroscopic probes are applied throughout the course of the reaction to obtain a timed sequence of snapshots of the evolving system. As changes of the molecular structure in gas-phase molecules typically occur on a femtosecond time scale, this first became possible in the early 1980s, when rapid evolution of laser technology made lasers with sub-picosecond pulse durations routinely available [Fork81, Valdmanis85]. Since then, the dynamics of numerous reactions ranging from bond-breaking in di-atomic molecules to intramolecular rearrangement in large organic and biological complexes have been studied, forming a new field dubbed *femtochemistry* [Zewail2000].

Even though tremendous progress has been achieved over the last decades in time-resolved imaging of molecular dynamics using femtosecond optical lasers, this approach has some

fundamental limitations related to the wavelength regime. First, the ultimate limit on the time resolution is essentially set by the duration of the optical cycle, which is ~ 1 fs for the ultraviolet (UV) and few femtoseconds for the infrared (IR) light. Second and more importantly, the wavelength of light limits the spatial resolution for direct imaging experiments and restricts the ability to target only a localized area within a larger system. Both of these limitations can be circumvented by using short-wavelength light. XUV pulses shorter than 1 fs have been demonstrated [Hentschel2001, Sansone2006, Chini2014] and applied to study electronic dynamics in atoms [Drescher2002, Schultze2010], molecules [Sansone2010], and solids [Cavalieri2007, Schultze2013]. At the same time, conventional X-ray sources such as synchrotron radiation facilities are routinely used for structure determination with Angstrom spatial resolution [Drenth1999, Rupp2009].

Free-electron lasers (FELs) [Ackermann2007, Shintake2008, Feldhaus2010, Emma2010, Allaria2010, Allaria2012, Ishikawa2012] provide intense coherent radiation at pulse lengths from a few to a few hundreds of femtoseconds and cover an enormous span of wavelengths from the VUV to the X-ray regime, thus combining the high intensities and short pulse durations of lasers with the high spatial resolution and element/site specificity characteristic of short-wavelength sources. Owing to their unique combination of properties, FELs now allow researchers to perform ultrafast time-resolved experiments from the VUV to the X-ray regime. Within the pump-probe scheme typical for time-resolved measurements, both, the pump triggering the dynamics and the probe capturing the evolving structure of the system can benefit from the availability of intense short wavelength, short-pulsed radiation. Using VUV/XUV pump pulses allows one to efficiently excite high-lying molecular states, either in neutral or ionic species, while X-ray pump pulses makes inner-shell (and, thus, element-specific) excitations experimentally accessible. This is difficult or even impossible to achieve in experiments employing optical lasers as a pump. Perhaps even more importantly, FELs provide numerous options for implementing novel probing scheme. In the VUV/XUV domain, the FEL pulses can be used as efficient single-photon ionizing probe, which is more homogeneous over the whole reaction coordinate and much easier to understand (within the perturbative regime) as compared to multi-photon ionization by optical lasers [Ullrich2012]. In the X-ray domain, additional probe schemes of potential breakthrough character include direct X-ray scattering [Küpper2014], inner-shell photoelectron diffraction [Boll2013], or photoelectron holography [Krasniqi2010].

The world's first XUV and soft X-ray FEL, the Free-electron LASer in Hamburg (FLASH), has now been operational for more than a decade and presently covers the photon energy range from ~ 40 eV to ~ 300 eV [Ackermann2007, Feldhaus2010]. It was followed by the Linac Coherent Light Source (LCLS) in Stanford, which extended the photon energy range into the hard X-ray domain [Emma2010]. Another hard X-ray FEL, SACLA [Ishikawa2012], and its precursor, the EUV-FEL at Spring-8 Compact SASE Source (SCSS) [Shintake2008] are currently operational at SPring-8 in Japan. The first seeded XUV FEL, FERMI@Elletra, was recently commissioned in Trieste [Allaria2010, Allaria2012]. A number of other large-scale FEL facilities, including the European XFEL, the SwissFEL, and several projects in China and Korea are currently under construction, promising a bright future for FEL-based science.

A broad description of current and potential FEL applications in ultrafast and ultra-intense X-ray science in the gas phase can be found in [Ullrich2012, Feldhaus2013, Bostedt2013, Yabashi2013]. The goal of this article is to describe some very recent pump-probe experiments highlighting basic directions for the development of molecular dynamics studies at FELs. We will focus on gas-phase experiments, which lie at the crossroad between atomic, molecular and optical (AMO) physics and ultrafast photochemistry. Numerous time-resolved measurements in the liquid phase, as well as experiments on surfaces and solid-state targets are beyond the scope of this paper and merit their own review(s).

The paper is organized as follows: Chapter 2 introduces FEL-pump FEL-probe experiments and focuses on the example of imaging the charge rearrangement in I_2 molecule after (multiple) inner-shell photoabsorption in the XUV domain. Chapter 3 describes laser-pump FEL-probe measurements and the potential and limitations for this type of pump-probe experiments while discussing a specific example studying charge transfer in laser-dissociated CH_3I molecules. Chapter 4 focuses on three-pulse photoelectron spectroscopy and photoelectron diffraction experiments on laser-aligned molecules. Finally, a brief summary and outlook is given in chapter 5.

2. FEL-Pump FEL-Probe Experiments

Molecules exposed to intense FEL radiation can easily absorb more than one short-wavelength photon. This results in the ejection of two or more electrons and typically leads to further disintegration (dissociation, Coulomb explosion) of the created molecular ions. FEL pulse durations currently ranging from few to few hundred femtoseconds match the characteristic timescale of these fragmentation processes. This leads to very rich dynamics and creates multiple possibilities to study light-induced molecular reactions. In fact, every two- or multi-photon absorption process in the XUV or X-ray domain essentially corresponds to a pump-probe measurement, where the first absorbed photon creates a molecular wave packet (typically in a highly excited or ionic state, bound or dissociating), and the following photoabsorption step probes the wave packet on the timescale of the pulse [Ullrich2012]. Therefore, shortly after the first experimental evidence of two-photon, multi-electron ionization [Sorokin2006, Sato2008], a lot of effort was devoted to disentangling the different multiple ionization pathways [Yiang2009, Fukuzawa2009, Jiang2010a, Yamada2010]. One of the most successful schemes turned out to be splitting of the FEL pulse in two replicas and using them as time-delayed pump and probe pulses. In this manner, the timing of the two (or few-) photon absorption can be efficiently controlled. This technique relies on beam-splitting devices for the XUV [Mitzner2008, Jiang2010b, Sorgenfrei2010] or X-ray light [Roseker2009, Castagna2013] and can be used to characterize FEL pulses via autocorrelation-type measurements [Mitzner2009, Jiang2010b, Moshhammer2011, Senftleben2012]. During the first decade of FEL experiments, two practical reasons made this approach particularly important. First, the timing between the two replicas of the FEL pulse does not depend on its absolute arrival time, and thus is free of the jitter of the latter, which for the SASE FELs was the main limiting factor for time resolution of the experiments involving

synchronization with an external laser [Düsterer2014]. Second, this scheme based on non-linear two-photon absorption represent the most realistic test ground for future pump-probe experiments with attosecond HHG-based pulses, which are not yet intense enough to realize this concept [Krausz2009].

One of the possible experimental arrangements used in the XUV domain at FLASH is illustrated in Fig. 1. The FEL beam is split at the focusing mirror with two halves movable with respect to each other. Combined with coincident ion momentum imaging used to probe the dynamics [Rudenko2010], this setup was successfully applied to study such XUV-induced processes as ro-vibrational wave-packet motion in simple di-atomics [Jiang2010c], prototypical isomerization reactions in simple hydrocarbons [Jiang2010d, Jiang2012, Jiang2013], interatomic Coulombic decay in neon dimers [Schnorr2013], and charge transfer in dissociating iodine molecules [Schnorr2014a]. A conceptually similar technique was recently developed in the X-ray domain at LCLS [Castagna2013, Fang2014] and applied to study acetylene-vinylidene isomerization reaction triggered by inner-shell photoabsorption [Liekhus-Schmaltz2015]. An even more elaborated version, which makes use of a pairs of X-ray pulses with slightly different wavelengths [Lutman13, Marinelli13], was used to study site-specific photoionization dynamics in XeF_2 [Picon15]. The key common feature of these experiments is a coincident ion detection, which allows for unambiguous identification of the reaction final states and considerably facilitates the disentanglement of different pathways leading to those. This is illustrated in Fig. 2, where the time-of-flight (TOF) spectrum of the first detected ionic fragment is plotted as a function of the TOF of the second one for the fragmentation of I_2 molecules by 85 eV FLASH radiation. True coincident events resulting from different Coulomb explosion channels can be clearly identified as hyperbolic (or diagonal) lines reflecting momentum conservation, whereas false coincidences (fragments originating from two different molecules) appear as horizontal or vertical lines. The spectrum provides information on the total charge state of the molecule and the charge sharing between two fragments [Feldhaus13, Schnorr14a].

Figure 1: Schematic of the split-mirror setup for XUV-pump XUV-probe experiments combined with an ion momentum spectroscopy apparatus (from [Jiang2010b]).

As an illustrative example of FEL-pump FEL-probe measurements, we discuss here a recent experiment performed by Schnorr et al. [Schnorr14a], which was designed to image the electron transfer between two iodine ions after dissociation of an I_2 molecule triggered by multiple ionization with a femtosecond 85 eV pump pulse. As sketched in the inset of Fig. 3, the dissociating system is then further ionized by the delayed probe pulse of the same photon energy. Depending on the time delay (or, correspondingly, on the increasing internuclear distance) and on the charge states created by the pump pulse, an electron can be transferred from one constituent to the other. The probability of electron transfer is then deduced from the final state charge distributions of the fragment for different final state channels identified from the coincident data shown in Fig. 2, while the distance between the fragments is calculated from the measured kinetic energy release (KER) for each channel.

Figure 2: Photoion-photoion coincidence spectrum measured for I_2 fragmentation by 85 eV FLASH pulses ($\sim 10^{14} \text{ W cm}^{-2}$). The time of flight (TOF) of the first ion is plotted versus the TOF of the second ion. Inset: enlarged view of the high charge state region (from [Feldhaus2013]).

The key results of the experiment are summarized in Fig. 3, where the measured KER for symmetric (Fig. 3a, $I^{3+} + I^{4+}$) and asymmetric (Fig. 3b, $I^{1+} + I^4$) final charge state distributions is plotted as a function of the pump-probe delay. The results exhibit a series of descending curves reflecting molecular dissociation along different states populated by the pump pulse. The dashed lines depict the classical motion of the center of gravity of the nuclear wave packet calculated under the assumption that all the intermediate states (labelled on the right side of the figure) are purely Coulombic, and that the electrons are removed instantaneously at the equilibrium distance of the neutral molecule. As can be seen in Fig. 3a, the simulations for the lowest charge states fit the experimental data reasonably well, whereas they seem to overestimate the measured KERs for the highest charge states. This is due to the non-negligible nuclear motion during the time

needed to reach these final states, which are produced by sequential photoabsorption, mainly by the iodine 4d shell, followed by one or two Auger decay steps [Erk2013]. The most striking difference between the two plots can be observed around zero pump-probe delay (i.e. overlapping pulses). For the $\text{I}^{3+} + \text{I}^{4+}$ channel, the highest yield and the highest KER are found at zero delay, whereas the $\text{I}^{1+} + \text{I}^{4+}$ channel exhibits a pronounced yield minimum at small delays. This difference reflects the charge rearrangement dynamics at different internuclear separations R . A strong positive charge created at one of the ions by the localized photoabsorption attracts electrons throughout the molecule, and efficient electron transfer thus favors a symmetric breakup equalizing any significant charge asymmetry induced by the probe pulse. This is valid for small delays corresponding to small internuclear distances.

However, at larger R , the probability of electron transfer decreases and becomes negligible beyond a certain critical distance R_{cr} , i.e., the two individual ionic fragments respond as if they were isolated and all charges thus remain localized at the nuclei where they were created. This critical distance for each particular final charge state combination can be determined from the delay-dependent yields of the corresponding asymmetric channels [Schnorr2014a]. It was shown to be in perfect agreement with the predictions of a semi-classical over-the-barrier model developed earlier for ion-atom collision experiments [Ruifuku1980, Niehaus1986].

Figure 3: (a) Measured kinetic energy release (KER) from I_2 fragmentation at 85 eV photon energy for the $\text{I}^{3+} + \text{I}^{4+}$ final state as a function of pump-probe delay. Since the pump and the probe pulses are identical, the spectrum is symmetric with respect to zero delay. (b) Same for the $\text{I}^{1+} + \text{I}^{4+}$ channel. The small arrow indicates nearly zero yield of this strongly asymmetric channel for small delays. The dashed lines in (a) and (b) reflect the calculated nuclear wave packet motion on the Coulomb potential curves corresponding to the pump-pulse excitation to the states indicated on the right. Inset: Illustration of the XUV-pump XUV-probe scheme. The pump pulse triggers the dissociation into $\text{I}^{1+} + \text{I}^{2+}$ by multiple ionization. The delayed probe pulse creates an I^{4+} ion that attracts electrons from the other side of the molecule, resulting in the more symmetric breakup into $\text{I}^{2+} + \text{I}^{3+}$. Figure adapted from [Schnorr2014].

3. Laser-Pump FEL-Probe Experiments: Imaging Charge Transfer in Laser-Dissociating Molecules

One of the biggest technical challenges for pump-probe experiments combining optical femtosecond lasers with (SASE) FELs is the synchronization of the two independent laser systems on the femtosecond level. Despite considerable efforts that were spent early-on on developing precise locking schemes [Feldhaus2010, Glowonia2010], it turned out that drifts on the level of a few picoseconds per hour as well as an intrinsic jitter of the arrival time of the FEL pulse significantly limited the resolution of the early pump-probe experiments far beyond the pulse lengths of the FEL and the femtosecond laser [Radcliffe2007, Glowonia2010, Petrovic2012, Rouzée2013, Rolles2014]. While the slow drifts on the picosecond level are now under control in most of the current pump-probe arrangements, the arrival time jitter on a level of hundreds of femtoseconds arising from jitters in the electron beam energy in the accelerator combined with the statistical nature of the self-amplified spontaneous emission (SASE) process remains a critical issue that severely limits the temporal resolution of laser-pump FEL-probe experiments if it cannot be corrected for. This can be clearly seen when comparing the outcome of the jitter-free FEL-pump FEL-probe experiment on I_2 discussed above [Schnorr14a] and a similar experiment, where an external 800 nm laser was used as a pump [Schnorr14b]. Because of the uncertainty of the exact pump-probe delay resulting from the arrival time jitter, the R-dependent charge transfer dynamics at small delays and correspondingly small R, which were observed in [Schnorr14a] could not be resolved in the latter.

This jitter problem was addressed first at FLASH [Maltezopoulos2008, Gahl2008, Drescher2010, Grguras2012, Riedel2013] and later at LCLS [Bionta2011, Schorb2012, Beye2012, Harmand2013, Bionta2014, Eckert2015] by developing single-shot cross-correlators for XUV/X-ray and IR laser pulses, which allowed recording and correcting for the jitter by experimentally determining the actual delay value on a shot-by-shot basis. This has now brought the time resolution of state-of-the-art pump-probe experiments down to the limit determined by both laser and FEL pulse durations [Krikunova2009, Krikunova2011, Krikunova2012, Erk2014]. Furthermore, new developments of synchronization tools also resulted in a significant reduction of the relative arrival time jitter [Schulz2014]. At the same time, efficient routines have been developed to establish and optimize spatial and temporal overlap between the IR and the XUV/X-ray pulses [Radcliffe2007, Glowonia2010, Rouzée2013], providing much better experimental control during such pump-probe experiments.

In the following, we will briefly discuss a recent LCLS experiment, which addresses the question of distance-dependent electron transfer after inner-shell ionization in an IR-pump X-ray-probe configuration [Erk2014]. While the physical question considered here is essentially the same as the one discussed in chapter 2, the practical realization of the experiment is quite different. In order to exploit the element specificity of the X-ray absorption, the experiment was performed on CH_3I molecules, which contain only one heavy atom (iodine). At the photon energy of 1500 eV chosen for this measurement, the absorption cross section for an iodine atom is ~ 60 times larger

than for the rest of the molecule, such that the X-rays are almost exclusively absorbed at the iodine site. As sketched in Fig. 4, the 800 nm IR laser dissociates the molecule, and the X-ray pulse arriving after certain time delay multiply ionizes the iodine atom (ion) at different separations from the methyl group. The momentum vectors of the created ionic fragments are measured as discussed in chapter 2. An IR / X-ray cross-correlator was mounted downstream of the interaction region in order to correct the arrival time jitter between the two pulses.

Figure 4: Sketch of the experimental setup. A supersonic beam of CH_3I molecules is overlapped with two collinear femtosecond infrared laser and X-ray FEL beams inside a 3D momentum resolving ion spectrometer. Ions are extracted by a constant electric field onto a position and time-sensitive charged particle detector, while the relative arrival time difference between the IR and FEL pulses is recorded shot-by-shot on a cross-correlator. The inset on the left shows a schematic of the ionization and charge transfer process. Figure adapted from [Erk2014].

Fig. 5a depicts an ion TOF spectrum integrated over all IR – X-ray delays (from -200 to 1400 fs) measured in this two-color pump-probe experiment. Three narrow peaks due to different charge states of the parent molecule can be identified in the spectrum along with numerous broad structures due to the energetic fragments. More insight into the energy and momentum distributions of the different fragments can be obtained from Fig. 5b, where the same TOF spectrum is plotted against the hit position on the detector (the x-coordinate along the direction of the molecular beam propagation, as sketched in Fig. 4). This two-dimensional projection of the three-dimensional momentum distribution reflects both, the energy and angular distributions of each fragment. The low-charge iodine ions (I^+ and partly I^{2+}) are mainly produced by the IR laser alone, whereas the highly charged fragments result from the X-ray absorption, with or without the influence of the IR pulse. A noticeable feature of the spectrum is the appearance of very low energy iodine ions, which appear as narrow dots in the middle of the TOF-vs-position pattern for the corresponding ion (observable for all charge states starting from I^{4+}). It should be noted that these structures are absent in X-ray only spectra and in the pump-probe spectra for which the X-ray pulse precedes the IR pulse.

Figure 5: (a) Ion time-of-flight (TOF) spectrum of CH_3I molecules ionized by X-rays with 1500 eV photon energy and by the femtosecond IR laser integrated over all IR – X-ray delays from -200 to 1400 fs. (b) Corresponding hit positions on the position-sensitive ion detector (along the jet propagation / FEL polarization direction) plotted as a function of the ion time-of-flight. The data are integrated over all delays between the two pulses as well as over the second hit position coordinate (along the FEL / NIR beam propagation direction). The NIR laser polarization is along the time of flight axis. Figure adapted from [Erk2014].

Fig. 6a displays the kinetic energy spectrum for one of the fragments (I^{6+}) plotted as a function of IR – X-ray delay. Three major features (marked I, II, and III in Fig. 6a) can be clearly distinguished in the spectrum. I^{6+} fragments in the broad high-energy band I centered at ~ 7 eV originate from molecules that absorb one or several X-ray photons at or close to the equilibrium geometry of the molecule. This feature can also be observed in the X-ray only data and results from the events in which the molecules either did not interact with the NIR pulse, or remained bound after this interaction. The projection of this band on the delay axis is shown as a red line in Fig. 6b and manifests significant enhancement at small delays, reflecting the cross-correlation between the IR and the X-ray pulses. The delay-dependent structure II, which descends from the high energy band I at small time delays to low kinetic energies as the delay increases and

asymptotically approaches 0.54 eV, corresponds to events where the molecule is first dissociated by the IR laser and later Coulomb exploded by the X-ray pulse. The internuclear distance in the dissociating molecule increases with the pump-probe delay, which is reflected in decreasing fragment kinetic energies.

Figure 6: (a) Kinetic energy of iodine 6+ ions as a function of IR – x-ray delay. The lowest energy channel III represents iodine ions which have a neutral fragmentation partner and thus are not influenced by Coulomb repulsion. (b) Delay dependent yields of channel I (blue, energies >6eV) and channel III (red, energies <0.3eV). Channel I shows a pronounced increase when the NIR and the X-ray pulse overlap in time. This cross-correlation signal can be fitted by a Gaussian of ~110fs (FWHM), which provides a measure of the experimental time resolution as well as the nominal “zero” delay. (c) Delay-dependent yields of iodine fragments of this low-energy channel from the iodomethane dissociation into I^{n+} and neutral CH_3 . As the iodine charge increases, the distance up to which charge transfer can occur also increases. The experimentally determined critical distances, where charge transfer can no longer occur, agree well with predictions from a simple classical model that are indicated as colored triangles. Figure adapted from [Erk2014].

Finally, a narrow band III can be observed at very low energies (~ 0.06 eV). These very low-energetic ions correspond to the narrow central dots observed in the momentum distribution patterns of Fig. 5b. As detailed in Fig. 6b, where the projection of this band onto the delay axis is shown in blue, this channel opens only at time delays larger than 100 fs. The only pathway for which the I^{6+} ion can emerge in the continuum with such ultra-low energy implies that the rest of the molecule (i.e., the methyl group) remains neutral after the interaction with both, IR and X-ray

pulses. Otherwise, the Coulomb repulsion between I^{6+} and any charged partner would result in considerably higher energies. Thus, the delay-dependent yield of this channel reflects the probability for the methyl group to remain neutral in the vicinity of the highly charged iodine, i.e., it directly reflects the distance-dependent electron transfer probability. In order to reveal more details of this charge transfer process, the yield of this lowest-energy channel is plotted for four different charge states of iodine in Fig. 6c. Assuming a constant dissociation velocity for the ($I^+ + CH_3$) dissociation channel and using the measured asymptotic value of the kinetic energy, the measured NIR-X-ray delay can be mapped to internuclear distance. Similar to the gap in the asymmetric channels yield for I_2 discussed in chapter 2 (see Fig. 3b), the initial zero yield of this channel indicates that at rather small distances, at least one electron always leaves the methyl group or, in other words, the electron transfer probability is saturated. For larger delays, the transfer rate decreases, and there is a finite probability for the CH_3 fragment to remain neutral, which is reflected in the increasing yield of low-energy iodine fragments. Beyond a certain distance, the charge transfer between iodine and carbon becomes prohibitively improbable. As can be clearly seen from the data, this critical internuclear distance R_{cr} depends on the iodine charge state, which is in good agreement with the predictions of the over-the-barrier model discussed in chapter 2 that are shown as triangles in Fig. 6c. Since the R -dependent experimental yields predicted by the model are smeared out by the limited time resolution, the dashed lines in Fig 6c reflect these expectations taking into account the experimentally determined time resolution. The deviations of these expectations from the experimental data, which are most clearly observed for higher charge states, reflect the exponential distance-dependence of the actual electron transfer probability beyond the classical model. It can be seen from Fig. 6c that for the highest charge states shown, the charge transfer probability remains non-negligible up to internuclear separations of ~ 20 Å.

4. Time-Resolved Photoelectron Spectroscopy and Femtosecond Photoelectron Diffraction

As discussed in the introduction, VUV and X-ray FELs can reach sufficiently high photon energies to ionize the inner-shell and core levels of many atoms and molecules. For example, the photon energy range of FLASH encompasses the $3p$ edges of metals such as iron, the $3p$ and $3d$ edges of krypton and bromine, and the $4d$ and $4p$ edges of xenon, iodine, and many 4th and 5th row metals, as well as the carbon $1s$ edge. At the AMO and SXR beamlines of LCLS, the photon energy ranges covers the C($1s$), N($1s$), O($1s$), F($1s$), and Ne($1s$) ionization thresholds as well as the $2p$ ionization thresholds of all elements up to krypton (and slightly beyond), and the $3p$ and $3d$ edges of many transition metals. The hard X-ray beamlines at LCLS and SACLA even cover the $1s$ thresholds of the 4th row metals.

Taking advantage of the site-specificity of the core-level photoionization process, it is therefore possible to selectively excite or ionize a specific part of a molecule, as already discussed in the previous chapters. When combining this with time-resolved photoelectron spectroscopy, one can, for example, probe chemical changes at a specific site in a large molecule by observing changes of the chemical shift of the core-level binding energies [Hellmann2012, Siefermann2014].

However, for gas-phase studies that often require higher photon fluxes than those available at FEL monochromator beamlines, the broad photon energy bandwidth of SASE FELs poses a serious limitation to the energy resolution that can be achieved in such experiments. They are therefore better suited for seeded FEL sources, which have a much smaller spectral bandwidth [Allaria2012, Lutman2013]. The bandwidth problem can be circumvented in the related time-resolved Auger electron spectroscopy technique, which also offers a site-specific probe and additionally probes the structure of valence electrons that are involved in chemical bonds [McFarland2014].

In contrast to these spectroscopic methods, which yield only indirect information on geometric changes inside a molecule, a number of recent studies have focused on the direct structural information that one can obtain from photoelectrons and, in particular, their angular distribution, via femtosecond photoelectron diffraction [Boll2013, Kazama2013, Rolles2014, Boll2014, Rolles2014a] and photoelectron holography [Krasniqi2010]. The underlying idea is that scattering of the photoelectrons on the molecular environment and the interference between direct and scattered photoelectron waves leads to a diffraction pattern that encodes information on the molecular geometry similar to the way structural information is contained in “standard” electron or X-ray diffraction images. This structural information can be retrieved by comparison of the experimental diffraction patterns to calculations [Boll2013, Rolles2014, Boll2014, Rolles2014a] or via direct holographic reconstruction [Krasniqi2010]. For the case of molecular samples in the gas phase, the main advantages of the femtosecond photoelectron diffraction technique over the related time-resolved X-ray diffraction and ultrafast electron diffraction techniques lie in the considerably higher photoionization and electron scattering cross sections for low-Z elements as compared to the corresponding X-ray scattering cross sections at equivalent wave lengths, and in the improved temporal resolution as compared to ultrafast electron diffraction since there is no velocity mismatch between the pump and probe pulses.

The principle of femtosecond photoelectron diffraction is sketched in Fig. 7. A femtosecond pump pulse, e.g. a NIR, VIS, or UV pulse from a femtosecond laser, initiates a change of the molecular structure, such as a dissociation or isomerization reaction, which is then probed by a femtosecond XUV or X-ray pulse that emits a core-level photoelectron from a specific atom inside the molecule. The interference between the directly emitted photoelectron wave and the secondary waves created by scattering on the neighboring atoms in the *same* molecule produces a diffraction pattern, i.e. an angularly varying intensity distribution, on the photoelectron detector in the far field.

From an experimental point of view, it is important to point out that this diffraction pattern is only visible if the molecules are oriented in space. Otherwise, the typically random orientation of gas-phase molecules averages out most of these intensity variations, and the angular distribution is given by a simple second order Legendre polynomial [Cooper1968], such that all direct structural information is lost.

Figure 7: Principle of time-resolved photoelectron diffraction: A femtosecond pump pulse initiates a change of the molecular structure which is then probed, after a certain time delay Δt , by a femtosecond XUV or X-ray pulse. The emitted inner-shell photoelectron wave (blue), here created from the F(1s) level of a C₈H₅F molecule by linearly polarized X-rays, scatters on neighboring atoms inside the molecule. The superposition of direct and scattered photoelectron waves, the latter drawn only for one of the neighboring carbon atoms, creates an interference pattern in the far field, which is recorded, e.g., on an electron imaging detector. It can be interpreted as a photoelectron diffraction pattern that contains the information on the molecular structure. Figure adapted from [Boll2014].

In order to observe photoelectron diffraction patterns from gas-phase molecules and to extract structural information, e.g. by holographic reconstruction, from the photoelectron angular distributions, one therefore needs to “fix the molecule in space”. This is typically done either by means of angle-resolved photoelectron-ion coincidences [Becker2000, Landers2001, Zimmermann2008, Reid2012], which allows determining the orientation of a suitable molecular axis at the time of the photoionization for each individual molecule from the emission directions of the fragment ions, or by actively aligning the molecules in space, e.g. by laser alignment techniques [Stapelfeldt2003, Küpper2014]. While we are pursuing both experimental approaches for our photoelectron diffraction studies, the following example employed adiabatic laser alignment. The experimental setup is described in detail in previous publications [Boll2013, Rolles2014] and is therefore only briefly summarized here.

The target molecules, in this case 1-ethynyl-4-fluorobenzene (C₈H₅F, pFAB), are delivered in a rotationally cold supersonic beam and are adiabatically laser aligned by the pulses of an injection-seeded Nd:YAG laser (1064 nm, 10ns, ~500 mJ). A second laser pulse from a femtosecond Ti:Sapphire laser (266/400/800 nm, ~80 fs, < 1 mJ) initiates a photochemical

reaction, e.g. a photodissociation or isomerization, which is subsequently probed, at various time-delays, by photoelectron diffraction using femtosecond X-ray pulses (~ 730 eV, 60 fs, ~ 3 mJ) from the LCLS X-ray Free-Electron Laser. The FEL pulses ionize the aligned molecules by emitting photoelectrons predominantly from a targeted inner-shell level of a specific atom in the molecule, in this case the fluorine $1s$ level. These photoelectrons are then imaged shot-by-shot on one side of a double-sided velocity map imaging (VMI) spectrometer equipped with two MCP detectors with phosphor screens, while the resulting fragment ions are simultaneously imaged on the other side of the spectrometer, such that the degree of molecular alignment can be constantly monitored.

Typical VMI images for F^+ fragment ions and the $F(1s)$ photoelectron angular distributions resulting from the photoionization of laser-aligned pFAB molecules at LCLS are shown in Fig. 8. Assuming that the energetic F^+ ions, which result from a Coulomb explosion of the core-ionized molecule after Auger decay are emitted along the axis of the F-C bond, the angular distribution of these F^+ ions can be used as a quantitative measure for the degree of molecular alignment achieved in the experiment. This is usually done by calculating the expectation value $\langle \cos^2 \theta_{2D} \rangle$, where θ_{2D} is the angle between the momentum vector of the F^+ ion, projected onto the detector plane, and the polarization direction of the YAG laser pulse [Stapelfeldt2003]. For the image shown here, this yields a value of $\langle \cos^2 \theta_{2D} \rangle = 0.89$, indicating that the molecules probed by the FEL pulses are very well aligned.

If the polarization axis of the YAG laser pulse is rotated such that it has a non-zero component along the axis of the VMI spectrometer, the electric extraction field of the VMI together with the field of the YAG laser pulse additionally induces molecular *orientation* [Nevo2009, Holmegaard2009, Boll2014]. In the case of the pFAB molecule, this means that there is a higher probability of the fluorine atom pointing “up” or “down”, i.e. towards or away from the ion detector. This is shown in Fig. 8 (b) and (c), where the polarization direction of the YAG laser is turned by $+45^\circ$ or -45° with respect to the detector plane, and the F^+ ion images show an “up-down” asymmetry.

Using this adiabatic laser alignment and mixed-field orientation technique, we can then obtain the photoelectron diffraction patterns as described above. In order to extract the interference effects from the photoelectron images, we subtracted the electron images recorded without YAG pulses from those recorded with YAG pulses present [Boll2013, Boll2014]. The resulting photoelectron angular distribution differences (Δ PADs) for different photoelectron kinetic energies are shown as polar plots in Fig. 8 (d-f). The experimental data obtained by integrating the difference images over the region of interest around the $F(1s)$ photoelectron line are shown as dots, while the experimental Δ PADs obtained by subtracting the electron images after inversion with the pBasex algorithm [Garcia2004] are shown as shaded areas. Both agree well with each other as well as with the results of DFT calculations that take into account the angular averaging due to the molecular alignment (for further details, please refer to our previous publications [Boll2013, Boll2014]). For the case of oriented molecules, a clear “up-down” asymmetry can be observed in the Δ PADs.

Figure 8: *top row:* F^+ ion images recorded at the LCLS for ionization of pFAB molecules with linearly polarized X-rays at 723 eV photon energy; (a) with the YAG laser pulse linearly polarized parallel to the FEL polarization, and (b) and (c) with the YAG polarization rotated out of the detector plane by $+45^\circ$ and -45° , respectively. The polarization direction of the X-rays is indicated by the arrow in panel (a). *bottom row:* $F(1s)$ photoelectron angular distribution differences (Δ PADs) of pFAB corresponding to aligned and oriented molecules as shown in the row above. Raw data are shown as dots, inverted data (for the case of aligned molecules) as shaded areas, and calculated Δ PADs as lines (blue: negative difference; cyan: positive difference). All distributions are plotted on the same radial axis. Figure adapted from [Boll2014].

Having established the femtosecond photoelectron diffraction technique for aligned molecules, the next step is to perform a pump-probe experiment to observe a change in the Δ PADs as a function of pump-probe delay, which can then be related to a change in the molecular structure. We have shown the feasibility of such three-color experiments [Rolles2014]. However, the corresponding time-resolved data for the pFAB molecules were not acquired yet due to a lack of machine time. Nevertheless, we have simulated the molecular-frame photoelectron angular distributions that one would obtain for different intermediate structures that are predicted during the UV-photodissociation of pFAB as shown in Fig. 9. All of these molecular geometries results in very distinct angular distributions, which should be clearly distinguishable in a time-resolved experiment.

Figure 9: Calculated fluorine ($1s$) photoelectron angular distributions for pFAB molecules at a photoelectron kinetic energy of 35 eV obtained from DFT calculations for (a) the equilibrium geometry, (b) for a pFAB molecule with twice the equilibrium bond length between fluorine and the benzene ring, and (c), (d) for two proposed transition states TS 3 and TS 4 [Wu2004]. The molecules are one-dimensionally aligned with the F-C axis parallel to the x-ray polarization as indicated by the arrow. The calculations correspond to an experimental kinetic energy of 45 eV. Figure taken, with permission, from Ref. [Boll2013]. Copyright (2013) by the American Physical Society.

5. Summary and Outlook

In the previous sections, we have discussed three recent examples for three different types of pump-probe experiments on gas-phase molecules performed at FELs: an FEL-pump FEL-probe experiment, a laser-pump FEL-probe experiment, and a three-color experiment, where two laser pulses were used to prepare the sample that was then probed by an FEL pulse. We chose these examples not only to show the breadth of time-resolved experiments at FELs but also to demonstrate that in contrast to early FEL pump-probe experiments, which had mostly a proof-of-principle character, the technology has matured enough by now to address actual open questions in physics and chemistry related, e.g., to isomerization and charge transfer processes. Similar progress has been made in pump-probe experiments on surfaces [Dell'Angela2013, Öström 2015], solid-state samples, and in the liquid phase [Wernet2015], for which a more detailed discussion is, however, beyond the scope of the present paper.

Looking ahead into the future, some of the next steps the field has to take and will be taking is to work on achieving an even better temporal resolution that will eventually be pushing into attosecond regime [Emma2004, Rosenzweig2008, Reiche 2008, Hartmann2014] and lead to even more cross-fertilization with “traditional” attosecond experiments performed with laser-based high harmonic generation sources [Krausz2009]. Somewhat related to this is the need to achieve better control over all experimental parameters such as the pulse characteristics (pulse shapes and

pulse lengths, spectral distribution, etc.) of both pump and probe pulses as well as over the processes that are triggered by the pump pulse. This may either be achieved by better single-shot pulse diagnostics, which are currently being developed at FELs worldwide, or by recent advanced in self-seeding [Lutman2013] or laser-seeded FELs such as FERMI@Elletra [Allaria2012], which has now been running in standard user operation for several years. Such laser-seeded FELs can provide more well-defined and more controllable pulse characteristics and, in particular, also a considerably smaller photon energy bandwidth, which will make both core- and valence-level photoelectron spectroscopy a much more powerful tool for time-resolved studies on gas-phase molecules, especially when combined with higher repetition rates that allow reducing the single-shot count rates and thereby potential space charge problems. At the same time, laser-seeding may also significantly reduce the timing jitter in laser-pump FEL-probe experiments.

Given the complexity that many of the pump-probe experiments have now reached, which require long setup times of several weeks before the actual experiments, a more viable option for the future will be to establish dedicated pump-probe end-stations, similar in spirit, e.g., to the XPP instruments at LCLS, also for gas-phase pump-probe experiments, since many of the laser setups and diagnostics required for these experiments are beyond the scope of what can be set up “on the fly” for a few-day experiment. The recently commissioned CAMP instrument at FLASH is envisioned as such a permanently installed, dedicated end-station for pump-probe experiments [Mueller2015, Erk2015], and several permanently installed VUV and X-ray split-and-delay units [Mitzner2008, Sorgenfrei2010, Roseker2009, Castagna2013] are now available for FEL-pump FEL-probe experiments with others currently being under construction.

New possibilities will also arise from exciting technological developments such as the new two-color modes at LCLS [Lutman2013, Marinelli2013, Lutman2014], SACLA [Hara2013], and FERMI [Allaria2013], which allow for new pump-probe schemes for X-ray pump-probe experiments if sufficiently high pulse energies can be reached; or the development of high-repetition rate FELs such as the European XFEL and LCLS-II, which will, among many other things, make time-resolved coincidence experiments, as described in section 2, a lot less time consuming and thereby much more versatile. For FEL-pump FEL-probe experiments, the long pulse trains available at FLASH, which provide a repetition rate of several kHz, are already a first step into this direction, and the planned upgrade of FLASH burst-mode pump-probe laser to higher pulse energies will soon allow using this repetition rate also for laser-pump FEL-probe experiments in the gas-phase. These and other developments will enable an even broader range of pump-probe experiments in the future and guarantee that the field will continue the rapid growth that it is currently experiencing. Complemented with table-top experiments employing infrared, visible, and UV lasers as well as their high-harmonics in the XUV, time-resolved studies at FEL facilities thus promise to become an important experimental tool in ultrafast photochemistry.

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