

X-ray split and delay device for ultrafast x-ray science at the AMO instrument at LCLS

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Abstract. Ultrafast molecular dynamics can be studied using x-rays from both synchrotrons sources and x-ray free electron lasers. Synchrotron studies are limited by the 10-100 ps duration pulses to processes where the Auger lifetime can be used to probe dynamics initiated by excitation of an inner-shell electron to an antibonding orbital. The short pulses produced by x-ray free electron lasers offer the opportunity to study molecular dynamics directly with pump-probe techniques. A two-mirror x-ray split and delay device has been developed for x-ray pump – x-ray probe experiments at the soft x-ray AMO instrument at the LCLS. The device operates over a photon energy range of 250-1800 eV with a variable delay of up to 200 femtoseconds with 0.1 fs resolution.

1. Introduction

X-rays from synchrotron radiation sources are widely used for experimental studies of electronic and nuclear structure of atoms, molecule, clusters and nanoparticles, i.e. isolated species or dilute matter, using techniques such as x-ray absorption, x-ray photoelectron, ion yield and momentum, Auger and x-ray emission spectroscopies and their various coincidence techniques. Improvements in synchrotron sources, high resolution beamlines and spectroscopic techniques and instrumentation have resulted in a continuous increase in the knowledge of the structure of matter. X-rays are also an attractive source for studying molecular dynamics by pump-probe methods. As a pump they have the advantage of having elemental and even chemical sensitivity to create an excitation at an individual atomic site within a molecule. As a probe they have the same elemental and chemical sensitivity but have the further advantage of providing a universal excitation scheme, through photoionization, which does not suffer from unallowed transitions or dark states and uncertainties of the resonance energies like bound-bound transitions. Until the recent development of x-ray free electron lasers (FEL's), however, the temporal resolution of the predominant x-ray source, synchrotron radiation, was not generally sufficient to directly observe ultrafast dynamics on the femtosecond time scale through pump-probe methods.

2. Synchrotron Radiation

In spite of this limitation of inadequate temporal structure, synchrotron radiation has been used to study ultrafast molecular dynamics through the excitation of core-level electrons to empty

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molecular orbitals below the ionization potential of the molecule, as indicated by the blue arrow in Fig. 1, initiating changes in the molecular structure while simultaneously starting a synchronized core hole lifetime clock that results in an electronic decay of the core excited state. During the lifetime of the core-hole, typically on the order of a few to 10 fs, the molecular structure evolves along the potential energy surface of the excited state, which can be either dissociative or have a different equilibrium nuclear geometry than the initial state. The energy spectrum of the electrons emitted in the deexcitation process, indicated by the red arrow in Fig. 1, probes differences between the intermediate (excited) state and the final state at the time the decay occurs providing a stroboscopic view of the state of the molecule.

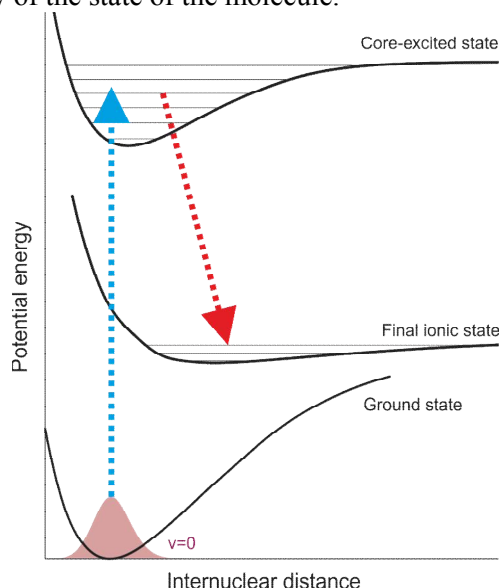


Figure 1: Schematic representation of the excitation of a molecular core level electron from the ground state of a diatomic molecule to a core excited state, bound in this case but with a different equilibrium internuclear distance, as indicated by the blue arrow. The nuclear geometry of the core-excited molecule responds to the new potential energy surface of the core-excited state and is probed by deexcitation to the final ionic state at a delayed time dictated by the core-hole lifetime.

The first observation of this phenomenon was reported in 1986 for HBr following the excitation of a Br 3d electron to the σ^* molecular resonance at 70.6eV [1]. The subsequent resonant Auger spectrum was found to have bands that appeared at constant kinetic energy, regardless of the exciting energy, while others dispersed with the photon energy, appearing to break the conservation of energy requirement. These non-dispersing bands were ascribed to Auger decay from excited atomic Br. Population of the σ^* molecular resonance in HBr initiates a dissociation of the molecule with the light hydrogen atom separating sufficiently from the bromine atom that it is no longer a molecule with the electronic deexcitation resulting from the core-hole occurs. The excess energy is carried by the kinetic energy of the hydrogen atom and energy conservation is preserved. The phenomenon is a general one in light atoms and several review articles of this type of work have appeared recently [2-4].

An interesting case has been O_2 where excitation of an O 1s electron to an antibonding σ^* molecular resonance initiates a molecular dissociation that similarly results in emission of Auger electrons with atomic character [5, 6]. In this case, however, because the empty molecular orbital is the $3\sigma_u$, transitions from the 1s core levels selectively excite molecules with their bond axis in the plane of the polarization of the synchrotron radiation. The molecular dissociation, which takes place on the same time scale as the Auger decay, is much faster than the rotational frequency of the molecule and this orientation is then preserved in the dissociating molecules with oxygen atoms moving apart in the plane of the polarization. Specific Auger lines were found to exhibit Doppler splitting resulting from excited oxygen atoms undergoing an Auger deexcitation and emitting an electron while moving towards and away from the electron detector when it was positioned in the polarization plane of the synchrotron. In contrast, electron spectra measured in the plane perpendicular to the polarization exhibited no such Doppler splitting. Subsequent studies have identified Doppler splitting in other diatomic molecules such as NO [7] and more complex molecules such as CF_4 [8], CH_3F [9], SF_6 [10-12] and CF_3SF_6 [13].

Utilizing the momenta of the oxygen atoms and the Doppler shifted electron energies, Liu and co-workers were recently able to apply this phenomena to a fundamental problem in physics, the nature of the interference between coherent paths [14]. The familiar Young's double slit interference pattern arises from the coherent interference of light "waves" passing through two slits simultaneously and if either of the slits is blocked and light can travel through only one, the interference pattern collapses. At the beginning of quantum mechanics, two familiar names, Bohr and Einstein disagreed as to the nature of this observation and devised a strategy to tag which slit the light passed through using a so called moving double slit. In their thought experiment, the momentum transferred by the light to the slit as it diffracted off would be transferred to a weakly held slit, causing it to move and thus identifying which slit the light had travelled through and therefore collapse the interference pattern. The idea was not technically feasible for many years but using oxygen atoms and their emitted Auger electrons, an analogous case can be constructed.

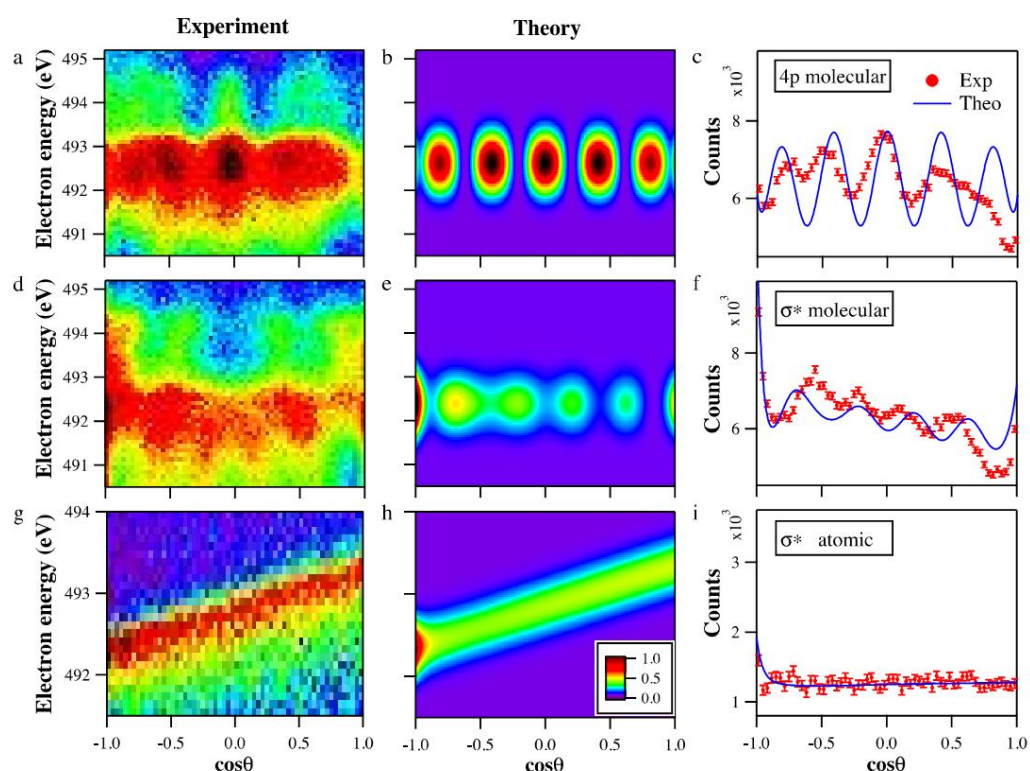


Figure 2: Intensity maps of the electron emission energy as a function of the angle θ between the momentum of the electron and the O^+ ion. The figure is organized into three columns corresponding to the experimental data, the theoretical results and a line out of the two data sets showing high contrast. The top three panels a, b, c illustrate excitation of a bound electronic state corresponding to Auger decay from intact molecules. The middle three panels d, e, f show the electron emission map for a dissociative state but at early times before molecular dissociation has occurred. The bottom three panels g, h, i show intensity maps for the late electron emission case where the kinetic energies of the atoms are modified by the Doppler effect. Reproduced from [14].

Oxygen molecules photoexcited from the $1s$ core level to the $3\sigma_u$ state will dissociate some of the collection of molecules into two atoms, one of which carries the core hole. The atom with the core hole can be on the left or the right hand side and when the core hole decays, the ejected Auger electron will come from the left or right hand side and if the origin of the electron is determined, no interference pattern is expected. Since the Auger Doppler effect will tag individual oxygen atomic ions with the recoil momentum of the ion from the ejection of the energetic Auger electron it is possible to determine which atom released the electron and the measured electron intensity map shows no

interferences. When the Auger decay occurs in the intact molecule, however, it is impossible to identify the atomic origin of the electron due to the molecular orbital nature of the O1s electron, and the two paths will interfere producing an interference pattern. To accomplish these measurements a coincidence spectrometer called EPICEA was used at PLEIADES beamline at Synchrotron SOLEIL. The spectrometer measures the electron kinetic energy along with coincident ion momentum. Electron spectra can then be sorted and binned based on various criteria such as the momentum of the corresponding ion.

3. X-ray free electron lasers:

The recent advent of x-ray free electron lasers, FEL's, with short intense pulses has opened new opportunities for pump-probe experiments. Drawing on experience from the first years at the LCLS FEL the various options for time-resolved experiments will be discussed.

3.1 Optical laser pump –FEL probe

Optical laser pump – FEL probe experiments were carried out in the first few months of user operation at the LCLS when an optical laser was used to align nitrogen molecules in the lab frame with subsequent ionization and Auger emission measured in the lab frame [15, 16]. These experiments found that the relative arrival time of the Ti:Sapphire laser and the LCLS x-ray pulses had a distribution with a standard deviation of approximately 120 fs (280 fs FWHM). Optical x-ray cross correlators based on spatial [17] and spectral [18] encoding of the relative arrival times of the beams have demonstrated resolutions of about 50 fs FWHM in the soft x-ray beamlines. Both techniques have been used in recent experiments at the AMO instrument at LCLS to improve the timing resolution from 260 fs to 65 fs in the charge transfer in iodomethane experiment for example [19].

3.2 Two pulse accelerator methods

Continued experience with the operating modes of the LCLS have led to the development of accelerator based methods for generating two x-ray FEL pulses. The first one utilizes a slotted spoiled foil spoiler in one of the bunch compressors of LCLS when the electron bunch is turned 90° so that the longitudinal direction of the beam is horizontally dispersed [20]. The slotted foil, with two slots, allows two spatially and hence temporally separated pulses to be generated with the emittance of the remainder of the electron bunch being spoiled by passing through the thin foil and hence not having the quality required to laser. Experimental verification of the method for generating ultrashort pulses has been carried out with laser field streaking to encode the pulse duration into the energy of photoelectrons emitted by photoionization with the generated x-ray pulse [21]. A second method which uses the slotted spoiler to create the two bunches then uses separate portions of the linear accelerator to control the pulse duration and relative delay, up to 40 fs, while even allowing for the generation of different wavelengths for the bunches [22]. Both of these methods, using different portions of the electron bunch, produce two pulses of light with no longitudinal phase coherence, unlike traditional split and delay methods used for optical laser pulses.

3.3 X-ray split and delay units

Several different x-ray split and delay devices have been developed at FELs to create and control two pulses of light for x-ray pump – x-ray probe experiments. The simplest was a split multilayer back-focussing mirror used at the FLASH FEL for pump-probe experiments and in particular to measure nonlinear autocorrelation traces of XUV pulses from FLASH where they determined the pulse duration to be 40 ± 10 fs [23]. In this design an on-axis back reflecting multilayer mirror was cut into two halves. One half was fixed and the other moved along the FEL beam on a high-precision stage. The multilayer coating of Mo/Si was optimized for reflectivity around 45.5 eV.

More complex and more versatile eight mirror grazing incidence devices have also been built and tested at the FLASH FEL [24, 25]. The incoming beam is split into two parts by a first mirror intercepting and reflecting only a portion of the beam while the rest of the beam passes over the mirror to a second mirror. The two spatially separated beams are then reflected through pathways that are

almost identical other than that the path length of one of the paths can be adjusted to vary the delay between the pulses. The two pulses are the recombined using mixing mirrors to provide overlap in the region of interest. While the alignment of the eight mirrors is a daunting task, the task needs only be completed once and assuming that the instrument is sufficiently stable, the beam paths will remain the same regardless of the wavelength.

3.4 The LCLS soft x-ray split and delay

The extended photon energy range of the LCLS versus FLASH presents challenges for the design of an x-ray split and delay unit. Due to the higher photon energies, much more grazing angles of incidence must be used, as low as 13 μ rad in order to adequately reflect light up to the Si K-edge at ~ 1800 eV. The lower angles of incidence then necessitate longer mirror substrates to accommodate the elongated beam footprint on the mirrors. A two mirror grazing incidence design was chosen for this device both because of spatial constraints, with over four meters of beam path required for an eight mirror device, and for cost reasons. The design has been described previously [26-28] and will be summarized here for completeness.

Table 1: Design specifications for the LCLS soft x-ray split and delay

Energy range	250 – 1800 eV
Delay range	0 – 100 fs
Working Distance	1.2 m
Resulting KB focal length	2.2 m
Pump/probe intensity ratio	0 – 100%
Mirror pitch resolution	0.25 μ rad
Mirror position repeatability	10 nm
Mirror motion range	Rough ± 10 mm, Precise ± 30 μ m
Vacuum requirement	10^{-10} Torr

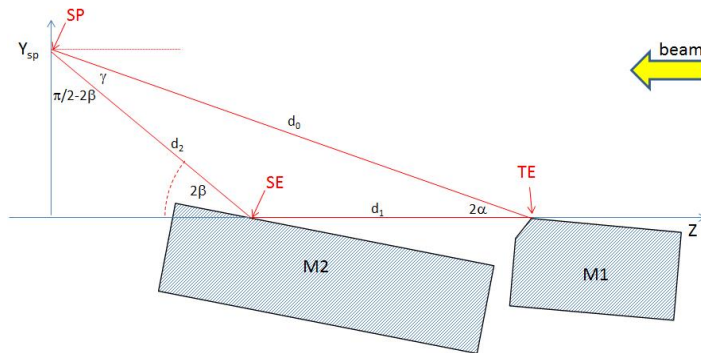


Figure 3: Optical layout of the x-ray split and delay device for soft x-rays at LCLS.

The completed design uses an edge polished plane mirror, M1 in Fig. 3, as the first mirror to intercept a variable portion of the incoming x-ray beam reflecting it towards the interaction region. Beam not reflecting off of the first mirror travels a further path to the second longer plane mirror, M2, reflecting off of it towards the interaction region. The delay between the two pulses is created by the path length difference the two portions of the pulse travel to the interaction region. Adjustment of the delay is accomplished by changing the vertical position and angle of the second mirror to change the path length difference while maintaining overlap of the two beams in the interaction region of the experiment 1.2 m downstream from the first mirror.

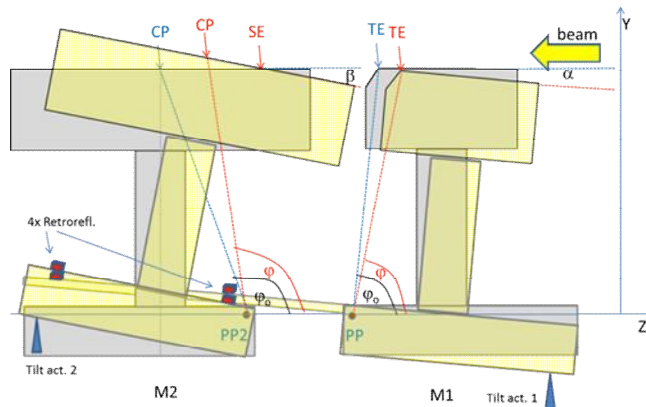


Figure 4: Tilt mechanism for the two mirrors with rotational axis at the PP and PP2 points on this figure respectively. As the rotational axes are not at the surface of the mirrors, angular changes introduce parasitic vertical motion that must be compensated to maintain overlap in the interaction region.

Detailed commissioning results will be presented elsewhere, but a few selected items are considered here. To verify the overlap of the two beams from the two mirrors when changing delay times, a series of different experiments were conducted, first using a microscope objective on a camera looking at a YAG screen inserted into the interaction region. Those results were compared with ion yield measurements of high charge states in Ar^{8+} to Ar^{11+} , sensitive to the total intensity on the target and therefore the overlap of the two beams. The results are shown below in Fig. 5 where the correspondence between the second mirror's pitch and position actuators is calibrated to optimize the overlap.

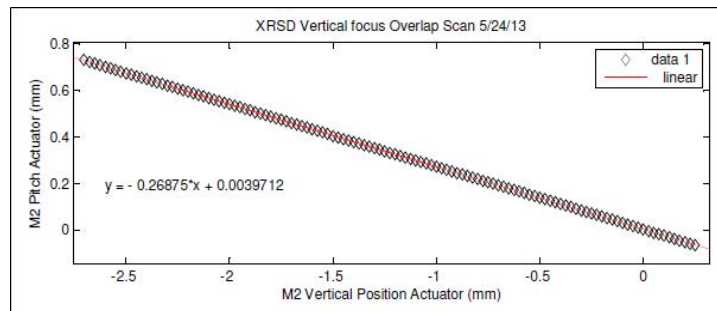


Figure 5: Motions of M2 pitch and displacement required to maintain overlap with the beam from the M1 mirror in the interaction region.

Overlap was ultimately verified at a few positions by imprinting the beams into PMMA and imaging the resulting ablation craters with an optical microscope as shown below in Fig. 6.

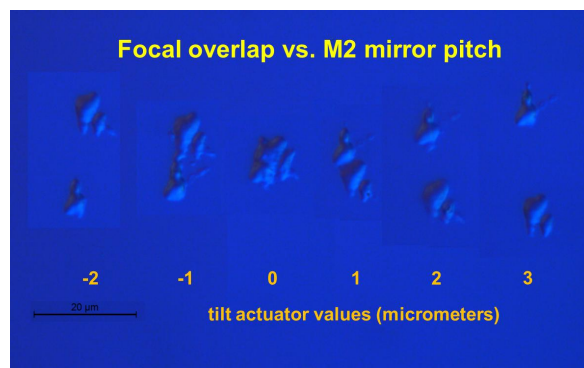


Figure 6: Imprints of the beams from the two mirrors while missteering the beam from the optimized overlap positions determined in the previous steps.

Following verification of proper performance of the mirrors and actuators, preliminary experiments were conducted on CH_3I to illustrate the total performance of the instrumentation. Recently published results on time-resolved ion yield spectra of laser dissociated CH_3I showed that highly charged iodine atoms with low kinetic energy resulted exclusively from laser induced dissociation of the iodine from the neutral methyl group followed by subsequent charging of the

separated iodine atom by FEL x-rays [19]. Using the XRSD instrument, we examined ion time-of-flight spectrum of highly charged iodine atoms from CH_3I as a function of the delay between the two x-ray pulses as shown in Fig. 7. It is apparent that the peak shapes for these highly charged iodine atoms are flat-topped when there is no delay between the two pulses and become more triangular as the delay between the two x-ray pulses is increased. We understand this to imply that low kinetic energy ions, which give rise to intensity in the center of the peak, are created only at long time delays when the iodine atom is well separated from the methyl fragment before the absorption of additional x-rays charges the atom to these high charge states. Further analysis and interpretation will be published shortly. A subsequent experiment on ultrafast isomerization in acetylene was performed utilizing the instrument and is recently published [29].

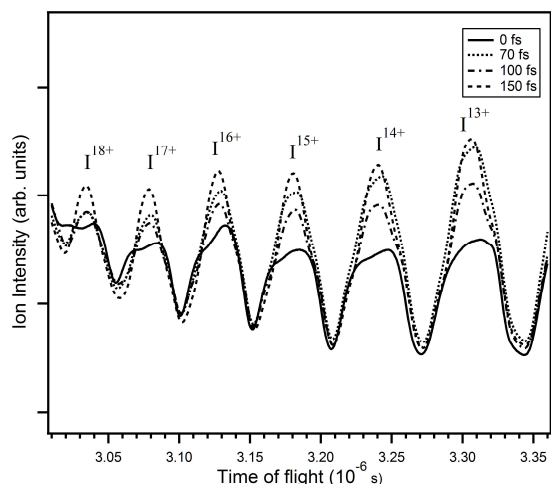


Figure 7: Ion time-of-flight spectra of CH_3I measured with 1600eV 50fs pulses from LCLS split and delayed with the XRSD to the delays indicated on the figure. The full peaks correspond to I^{18+} to I^{13+} from left to right across the figure as indicated.

Conclusion:

Ultrafast processes in molecules are studied using x-rays from both synchrotron radiation and x-ray free electron lasers. The long pulse durations of 10s of ps from synchrotron light sources are inherently mismatched with the fs time scales of ultrafast process in molecules. The natural lifetime of core holes provides a well-established method of time-resolved studies in systems where excitation of a core electron to an unoccupied molecular orbital initiates a dynamic molecular response which can be probed using the subsequently ejected Auger electrons. The advent of x-ray free-electron lasers with their fs short pulses of x-rays provides a more flexible means of probing ultrafast dynamics with x-rays. Different means of triggering and probing ultrafast dynamics were discussed and an example of a simple two mirror x-ray split and delay instrument was shown. Preliminary results on the ultrafast ionization of CH_3I were shown exhibiting temporal effects on the measured ion spectra.

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