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Emerging Photon Technologies for Probing Ultrafast Molecular Dynamics

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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The understanding of physical and chemical changes at an atomic spatial scale and on the time scale of atomic motion is essential for a broad range of scientific fields. A new class of femtosecond, intense, short wavelength lasers, the free electron lasers, has opened up new opportunities to investigate dynamics in many areas of science. For chemical dynamics to advance however, a rigorous, quantitative understanding of dynamical effects due to intense x-ray exposure is also required. We illustrate this point by reporting here an experimental and theoretical investigation of the interaction of C₆₀ molecules with intense x-ray pulses, in the multiphoton regime. We also describe the potential of new available instrumentation and explore their potential impact in physical, chemical and biological sciences when they are coupled with emerging photon technologies.

1 Introduction

The understanding of how nuclear and electron dynamics inside molecules can influence chemical reactions presents important implications in Physics, Chemistry and Biology with unforeseeable impacts. Nuclear motion occurs on femtosecond time scales and Angstrom spatial scales while electron motion is often much faster, particularly for tightly bound inner-valence and core electrons. New tools developed in the past two decades have made it possible to develop probes that can match many of these spatio-temporal requirements. Ultrafast infrared and optical wavelength lasers led to the detection of molecular vibrational, rotational and dissociative motion of molecules [1-6], as well as some degree of quantum control of valence electrons. The more recent advancements in attosecond lasers promise direct control of the electronic motion as well [7]. All of these investigations contribute to the fundamental understanding of dynamic phenomena which could ultimately lead to the *control* of chemical reactions with an unprecedented temporal resolution.

Technological advances in building short pulse lasers in all wavelength regimes coupled with advanced instrumentation can also contribute, when paired with theoretical calculations and modeling, to answer the key questions about energy flow and transient processes in molecular dynamics. Emerging photon technologies have enabled a new class of femtosecond lasers to join the ultrafast laser family, namely the vacuum ultraviolet (vuv) [8] and x-ray free electron lasers (FELs) [9]. They are new powerful femtosecond photonic tools, spanning a wide photon energy range from the infrared (IR) to the hard x-rays. The FELs are tunable, covering a wide

photon energy range and they are intense enabling a wide class of experiments, from non-linear science to time-resolved dynamics in physics, chemistry and biology, including chemical dynamics, the topic of the Faraday Discussion 171.

Ultrafast x-rays from FELs have photon energies sufficient to access core and inner-shell electrons, and like synchrotrons but unlike visible optical lasers, they enable inside-out ionization. The element-specificity of x-ray absorption, i.e. the ability to target specific atoms within molecules and select specific shells in those atoms (by tuning with high resolution the photon energy to specific spectral regions) [10,14] can be used to chart photochemical reactions and bioprocesses with atomic spatial resolution and femtosecond temporal resolution. Furthermore, the core-shell ionization and Auger decay processes, which are dominant in FEL-based work, lead to multiply charged fragments that are compared to strong-field optical and infrared laser cases. Thus FEL-based findings are relevant to the general optical laser community. Femtosecond optical laser pulses have led to the development of transition state spectroscopy and femtosecond chemistry [15], and have been applied in pump-probe experiments to map out time-dependent nuclear motion in molecules [16]. Similar schemes are being used with accelerator-based FELs [17,18] which are complementary to table-top optical lasers offering the opportunity to interrogate molecular dynamics.

The understanding of dynamics depends upon investigating the intertwined electronic and nuclear motion which may require theoretical models beyond the Born–Oppenheimer approximation and including electron correlation. We need to understand the

electronic structure because it determines the potential energy surfaces along which the nuclear motion evolves. This is very difficult, however, due to the different interactions and the large number of degrees of freedom that must be considered in order to completely describe even the smallest molecule. Here, we argue that judicious Molecular Dynamics (MD) modeling can result in advancing our understanding of molecular femtosecond dynamics as we show in this joint experimental and theoretical work.

Atomic, molecular and cluster physics experiments have been carried out with both vuv and x-ray FELs for investigating non-linear physics but also for revealing nuclear dynamics when using multiphoton ionization as a clock to determine the average time interval between the photoabsorption events [19], for molecular transformation during isomerisation [17], and for uncovering the time-scale of nucleobase ultraviolet photo-protection [20] relevant to chemical dynamics. Fundamental atomic experiments have provided insight into the nature of the interaction of light atoms such as Ne [21,22] and heavy atoms such as Xe [23] with x-ray FELs when tuning the intensity and/or pulse duration attributes of the x-ray FELs. Even with the first experiments that started in the fall of 2009 when the LCLS was still being commissioned, the ability to tune the pulse duration from sub-10fs to 250fs enabled molecular investigations to observe transparency effects [21, 24] and multiple core hole formation as a rebirth to electron spectroscopy for chemical analysis (ESCA) [12,25-30].

We report in this paper, which is a follow-up to an earlier work [31], on the nature of the interaction and response of a large molecule, C_{60} , with intense femtosecond photon pulses. Here we focus our investigation on the wavelength, pulse duration and pulse energy photoionization dependence of a special molecule, C_{60} . We argue with this paper that femtosecond dynamic experimental investigation in C_{60} under intense x-ray exposure of different wavelengths and pulse duration paired with classical mechanics-based Molecular Dynamics (MD) modeling can provide useful quantitative insights to the scientific community. We also explore here a future dynamical investigation with recently emerging instrument technologies paired with ultrafast x-ray photons.

Buckminsterfullerene (C_{60}) is a system that keeps being studied because it connects to many fields of research. It is a highly symmetric compound consisting entirely of C-C bonds forming many novel materials like graphene or carbon nanotubes. We were motivated to investigate and understand the interaction of a molecule like C_{60} with short and intense radiation because the interaction of x-ray FEL with matter is still terra-incognita since these lasers are less than five years old and there is no published experimental data yet on large system like C_{60} . Furthermore, theoretical models of large molecular femtosecond dynamics under ultrafast and intense x-ray laser exposure are available and need to be systematically tested since the wavelength, pulse duration and fluence can be varied. Although our primary interest is of fundamental nature, our results impact matter under extreme conditions because this community interprets their data using fundamental atomic and molecular physics results. Our findings also bear on radiation damage which happens *within* 10-100

femtosecond x-ray pulse duration. This issue is very important because it impacts x-ray imaging in all of the sciences and our contribution is at the fundamental molecular level. Neutze et al.[32] predicted the potential radiation damage for biomolecular imaging with femtosecond x-ray pulses. More recently, Chapman et al. [33], Nugent et al. [34] and Barty et al.[35] provided data on this topic with the current FELs. Our experimental and theoretical study of the C_{60} fragmentation dynamics under high x-ray fluence provides key insight into molecular dynamics in carbon-bonded molecules. The reported work enables a thorough understanding of the influence of intra-pulse radiation damage on high resolution x-ray diffraction imaging just like our previous work [21,24] uncovered electronic damage under intense radiation.

2 Experimental and Theoretical Methodology

The experiment was conducted at the atomic, molecular and optical physics (AMO) hutch of the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory using the High Field Physics instrument [24,36]. X-ray optics focused the incoming x-ray pulses to a peak focal intensity of 10^{16} – 10^{18} W/cm². A collimated molecular beam of C_{60} molecules from a resistively heated oven crossed the x-ray path at the focus. A magnetic bottle spectrometer allowed kinetic energy (KE) resolved ion time-of-flight spectroscopy with high collection efficiency, even at several hundred eV ion KE. A 2 meter long ion drift path provided high ion mass-to-charge and KE resolution while avoiding overlap of different fragment ion species [22, 31].

The last decade has seen several theoretical models developed to study the evolution of samples irradiated by x-ray FEL pulses [31, 37-45]. In this work we utilized the XMDYN [42] tool to model finite samples irradiated by high intensity x-ray pulses. The approach uses an atomistic description of C_{60} combined with a molecular dynamics treatment of the real space dynamics. The electronic configurations of the individual atoms/ions were tracked and utilized. Cross sections and rates for photoionization, fluorescent and Auger relaxation processes were calculated by the XATOM toolkit [43,44] and the Monte Carlo algorithm was implemented to describe these stochastic events. At an ionization event a new classical (free) electron was 'created' within the model and launched with the proper velocity. XMDYN treats these electrons together with the atoms and atomic ions within a sample as classical particles. The fullerene-specific classical Brenner force field [45] accounted for the chemical bonds between atoms, and the Coulomb forces for the interaction between the charged particles. The Newton equations were solved numerically to evolve the system in real space.

Free electrons can ionize the sample when colliding with atoms (electron impact ionization) and this effect is included [37] in our model. Impact ionization is responsible for the generation of many low energy free electrons, which is significant even for the sixty atom large fullerene. Further important molecular effects were also introduced in XMDYN: (a) molecular Auger effect, when one of the two involved electrons is from an atom next to the atom with the initial core hole; (b) bond breaking due to the changes of the

atomic electronic configurations driven by the ionizations. The experiment had significant impact on the development of the model by motivating the inclusion of many of the processes above, while modeling helped to interpret the measured data and reveal further details not accessible in present experiments.

3 Results and Discussion

3A Molecular Fragmentation

The ionization of C_{60} with focused x-rays of 485, 600 and 800 eV was investigated. One of the challenges with the SASE FELs [8,9] is that the interaction region covers a volume around the focus with an inhomogeneous x-ray spatial fluence distribution. Thus the recorded data include contributions from the wide range of fluence with the peak x-ray fluence localized at the center of the focus. In addition, the photon and pulse energy vary for each x-ray pulse. This is both a challenge for the non-linear optics community but it is also an opportunity for the chemical dynamics community to observe and compare trends at different fluences since each laser shot represents an experiment which is recorded along with all the experimental parameters. The data can then be binned accordingly. It should be noted that the FEL pulse energy can be focused for non-linear studies [21-31] but it can also be defocused for other time-resolved studies that do not require intense pulses [20].

The wavelength and intensity of the photon pulses lead to K-shell multi-photon ionization of the parent molecule which highly charges-up and then fragments into smaller observable molecular and atomic ionic fragments. We believe that the molecular fragments are generated dominantly in the wings of the fluence distribution while the atomic fragments are generated in the central high-fluence region of the focus. Figure 1 shows the ionization with 600 eV photons pulses at 60 and 20 fs with the same pulse energy of 0.61 mJ. The spectra display the molecular ionic C_{60} charge states from C_{60}^{2+} to C_{60}^{8+} as well as the observed molecular ionic fragments ranging from C_{11}^{+} to C_2^{+} and C^{+} the start of the C ionic fragments. The latter are discussed in the next section. The large fragments were formed in lower fluence regions of the x-ray beam where the molecule does not fully dissociate into atomic ions. This trend agrees with the molecular dynamics model as shown in Fig.1b. Note that the calculations were carried out with shorter pulse durations than the quoted experimental values to obtain the best agreement. The used values in the calculations are given in parenthesis. Since the photon pulse durations are not measured, the experimental values quoted here correspond to the electron pulse durations which is the only parameter given to the experimenters. It has been shown however that the photon pulse duration can be 40-50% shorter than the electron pulse duration [21,24] which is in agreement with this work.

The photoionization fragmentation dynamics shown in Fig.1 seems to indicate that with the longer pulse duration of 60 (30)fs the resulting ion yield is on average slightly higher than at the shorter 20 (13) fs pulse duration. This is not surprising since the longer pulse duration allows for more cyclic photoionization and Auger decay

during the same pulse, as observed in atoms [21] and smaller

Figure 1 (a) Experimental integral signals of molecular peaks at two pulse duration. The photon energy is 600 eV; the pulse energy is 0.61 mJ. The C^{+} peak is out of scale in the current plots. (b) Calculations using parameters that model best the measurements at 60 fs (30 fs) and 30 fs (13 fs).

molecules [24].

Figure 2 shows the comparison of the molecular fragmentation at two pulse durations, 60 and 20 fs, for three photon energies, 485, 600 and 800 eV and for the same pulse energy. Although the K-shell photoionization cross section decreases from 485 to 800 eV (the K-edge for C is ~280 eV), the parent and molecular fragments ion charge states decrease systematically from 800 eV to 485 eV. This trend is not understood and could be due to one of the challenges we need to overcome, namely better understanding of the x-ray focal width at different wavelengths.

3B Non Linear Physics

In our investigation, an average of 180 x-ray photons are absorbed per molecule in the x-ray focus, corresponding to 87 keV total energy transfer to the fullerene leading to the Coulomb explosion of the molecule generating highly charged atomic fragments ranging from C^{1+} to fully stripped C^{6+} at 150 fs as shown in Fig.3. The measurements were taken with 0.91 mJ pulse energy and 485 eV. We also show the carbon charge state distribution at 60 fs and

despite the same pulse energy the distribution is slightly different, but consistent with measurements carried out in Ne atoms [21] and N₂ molecule [24]. Namely, the long pulse duration allow for more highly charged states, in this case, C⁴⁺ and C⁵⁺. We do not observe fully stripped C at 60 fs since the pulse is not long enough to allow for the cyclic photoionization and Auger processes [21,24] to remove all six electrons from the C fragments. We also show in Fig. 4a,b the experimental and theoretical comparison of the C charge state distribution produced at 600 eV photon energy with 60 fs and 20 fs and with the same pulse energy of 0.61 mJ. The agreement between theory and experiment is good and the same trend is observed with the higher photon energy. That is if one keeps the pulse energy constant, one will generate less highly charged states at the shorter

Figure 2 Integral signals of molecular peaks at three different photon energies. (a) The pulse duration at 60 fs has pulse energy of 0.9 mJ. (b) The pulse duration at 20 fs has pulse energy of 0.5-0.55 mJ. The C⁺ peak is out of scale in the current plots.

Figure 3 Charge state distribution of atomic C ion fragments at pulse durations of 150 fs and 60 fs and the same pulse energy. The transmission of the spectrometer is included. The photon energy is 485 eV. Signals are normalized to the total C atomic ion yields.

pulse duration, close to or far from the C K-edge. This result is by far the *most nonlinear* sequential multiphoton process (during one x-ray laser pulse, C₆₀ absorbs many photons), in a molecule ever reported in the x-ray spectrum. The production of substantial yields of C⁵⁺ and C⁶⁺ as shown in Fig.3 for both 150 and 60 fs with similar pulse energy, has not been seen before in the published literature [46,47]. Note that multiphoton absorption---be it sequential or nonsequential---leads to a nonlinear dependence, in this case of C⁵⁺ and C⁶⁺ ion yield, on the pulse fluence.

We also investigated the C charge state distribution as a function of pulse energy. Fig. 5 displays our experimental and theoretical results for C₆₀ ionized at 485 eV, at 150 fs and for pulse energy varying between 1.2-0.6 mJ. We observe that C¹⁺ is the most intense at the lowest pulse energy. This trend however inverts starting at C³⁺ through C⁶⁺ where the highest ion yield is obtained at the highest pulse energy. The inset of Fig. 5 allows a close-up of how the highest C charge states ever observed from C₆₀ are created as the pulse energy increases and shows that 0.6mJ is high enough to produce fully stripped carbon. The calculation shown in Fig. 5b agrees well with measurements.

The comparison of our data to our MD calculations is very good as shown in the Fig. 4 and Fig. 5. The validation and refinement of molecular dynamics modeling at extreme fluence presented in this work is based on a direct comparison to dynamical quantities from experiment and is crucial in order to show that these approaches can make *quantitatively correct predictions*. Our experiment provides evidence that the charged particles produced by exposing an extended quantum system (C₆₀) to high-fluence x rays behave as if they were classical particles at different wavelength, pulse duration and pulse energies. Thus, we have *validated* a very fundamental assumption underlying all Molecular Dynamics approaches.

Figure 4 (a) Experimental charge state distribution of atomic C ion fragments at pulse durations of 60 fs and 20 fs with the same pulse energies. The transmission of the spectrometer is included. The photon energy is 600 eV. The pulse energy is 0.61 mJ. (b) Calculated charge state distribution. Signals are normalized to the total C atomic ion yields.

Figure 5 (a) Experimental charge state distribution of atomic C ion fragments at various pulse energies and the same pulse duration. The photon energy is 485 eV and the pulse duration is 150 fs. (b) Calculated charge state distribution.

We find in this work that secondary ionization by photo- and Auger electrons which occur weakly in isolated small molecules [24] or atoms [21], is significant in the dynamics of C_{60} under high photon dose rate conditions. Molecular influences on the Auger decay process, which are weak in van der Waals clusters, are also much stronger in C_{60} and must be incorporated in the calculations to account for the experimental data. The short C-C bond lengths also lead to far stronger Coulomb repulsion forces between the rapidly charging ions during the x-ray pulse, producing ion-ion forces more representative of biomolecules under high x-ray flux than seen in van der Waals clusters. Our findings allow the successfully tested model to be scaled to the higher photon energy typical of bio-molecular imaging. Thus, we argue that *quantitative radiation damage dynamics predictions* can be achieved in biomolecules at far higher intensity than currently available based on the reported work. This is important for high resolution diffraction imaging. Furthermore, our findings are of interest to the matter under extreme condition (MEC) [48,49] community using any source of photons (IR, UV, VUV, X-rays) because the formed plasmas are composed of highly charged ions and their modelling, often based on atomic calculation can now use experimental data.

4. Future Research Opportunities with Emerging Instrument Technologies

As FELs are improving their spectral and temporal resolution by using laser seeding [50] or self-seeding [51], the Berrah's group in collaboration with LCLS staff [52-55] and CAMP [56] scientists has built powerful instruments to advance scientific discoveries.

4A. The X-Ray Split and Delay for Time-Resolved Investigations.

We built an x-ray pump-x-ray probe instrument, called the x-ray split and delay (XRSD) [52,55] to carry out time-resolved experiments at the LCLS. The tool commissioned in June 2013 is now available for experiments. It consists of a compact two mirror device whose principle of operation is illustrated schematically in Fig.6. Briefly, two mirrors are located along the beam path such that the first mirror intercepts a portion of the beam and deflects it towards the interaction region. The second mirror intercepts the remaining portion of the beam downstream of the first mirror and deflects that portion through a slightly larger angle to intersect the beam from the first mirror in the interaction region of the experiment. In order to split the beam without significant losses, the first mirror was polished to its trailing edge where a short chamfer allows the beam not reflected by the mirror to pass over the edge to the second mirror. This design incorporates an extended second mirror requiring only vertical motion and pitch to properly intercept the delayed portion of the beam and reflect it towards the interaction

Fig. 6 Schematic of the two mirror soft x-ray split and delay.

region. This system was successfully commissioned in May 2013 [52,55] and has been already used in two experiments.

4B The LAMP Instrument

We built a modular system called LAMP that consists of: **i)** a chamber that houses two velocity map imaging (VMI) detectors to measure electrons and ion-ion coincidences resulting from the photo-absorption of fs x-ray photons [54], as well as **2i)** a chamber that houses two imaging detectors of the pn-CCD type that record scattering images or fluorescence resulting from the interaction of the photons with the samples [53]. This instrument was commissioned in November of 2013, was used successfully during an experiment that recorded the scattering of a biological system and is now available for experiments at the LCLS [53,54]. LAMP was designed similarly to the CAMP instrument [56] and it benefited from the first design and collaboration [54,56] to make significant improvements in its design and workmanship.

The LAMP-VMI system allows time-resolved nuclear dynamics experiments to be monitored via the detection of electron and ionic fragments resulting from photo-absorption of x-ray photons, as a function of pump probe delay and probe pulse intensity using the XRSD or using optical lasers synchronized to the FEL beam. With these new tools, we record the different fragmentation pathways by measuring multi-particles ion-ion coincidences/multi-particle correlations as a function of pump-probe delay to monitor the evolution of the kinetic energy release (KER) associated with different break-up patterns. We also simultaneously image the electrons momenta to capture the most detailed x-ray induced reaction in molecules and nano-systems. This instrument, available to any users, has the possibility to uncover new mechanisms in physics, chemistry and biology. The interpretation of the measurements can be done with molecular modeling and *ab initio* electronic structure calculations by comparing measured KER electron and ion spectra with classical and quantum-mechanical simulations. The identification of the various dynamic mechanisms can lead to improved understanding of the inner-working of molecular systems and to ultimately control chemical dynamics, the topic of this Faraday Discussion 171.

4C Tracking the Ionization Dynamics of C_{60} by Time-Resolved Measurements.

We explore briefly here a possible future study that can utilize the new tools described above to carry out a time-resolved experiment of the absorption and dissociation dynamics of C_{60} under various pulse durations and pulse energies. Our calculations led by the Santra's group predict, as shown in Fig. 7, that the ionization of C_{60} at high fluence occurs within the first few fs. The fast electrons will be ejected, followed within the first 20 fs-130 fs of the expansion dynamics of a nanoplasma formed of trapped electrons and C ions.

We plan to track the evolution of the ionization mechanisms by time-resolved measurement using x-ray pump-x-ray probe spectroscopy with the XRSD. We will take advantage of the *site specificity* of x-ray ionization by creating a hole (pump) on the K-shell site in C_{60} . We will then use a second, delayed x-ray pulse (probe) to interrogate the ionization/expansion of the system at various pump-probe delay times. We will record the photoelectron spectra and ion spectra simultaneously using the double VMI spectrometers in the LAMP end station. The varying delay will reveal the time-evolution of the ionized system.

Conclusions

The presented work reports on the fragmentation dynamics of C_{60} subsequent to absorption of x-ray FEL pulses of different photon energies (485 eV, 600 eV, 800 eV), pulse duration (20 fs, 60 fs, 150 fs) and pulse energy (0.6mJ-1.2mJ). Our findings seem to indicate that once a molecule, whether it is a small diatomic molecule like N_2 or a large molecule like C_{60} , absorbs photons from intense short x-ray pulses, it undergoes multi-photon ionization, followed by Coulomb explosion and dissociation. In addition, the data indicate that the fragment ions generated from a small or a large molecule behave the same way with respect to wavelength, pulse duration and pulse energy. However, from the radiation damage perspective, our modeling has shown that secondary ionization of C_{60} by photo- and Auger electrons, weak in isolated small molecules and absent in atoms, is significant in its dynamics under high dose rate conditions. Furthermore, our work revealed that molecular influences on the Auger decay process, which are weak in van der Waals clusters [57,58] are much stronger in C_{60} and must be incorporated in the calculations to account for the data. The short C-C bond lengths lead to far stronger repulsion forces between the rapidly charging ions during the x-ray pulse producing ion-ion forces more representative of chemically bonded systems than those seen in van der Waals clusters.

Our results on the fundamental interaction of C_{60} with intense femtosecond x-ray photons is interesting in its own right in chemical dynamics and atomic and molecular physics but it is also relevant to many fields of research, in particular to matter under extreme conditions as well as high resolution x-ray imaging and scattering experiments relevant to biology.

The world is on the threshold of a dramatic increase in the number of FEL photon sources which are planned to be even more intense — despite present severe world economic constraints — because of their importance to uncovering new science. In fact, advances in FEL technologies are pushing the pulse duration down to the attosecond realm [59]. It is therefore of utmost importance to understand, from a fundamental point of view, the interaction of atoms, molecules, nano-systems and bio-systems with short x-ray

Figure 7 Real space snapshots of the time evolution of a C_{60} molecule irradiated at the center of the focus of the x-ray free electron laser pulse, based on theoretical modelling. Carbon atoms (blue) and electrons (yellow) are shown as a function of time at fine spatial scale (a, b) and expanded spatial scale (c, d, e). The centre of the pulse is at $t = 0$ fs and the photon energy is 600 eV with 30 fs pulse duration and 0.6 mJ pulse energy.

radiation with the present and future generation of FEL photon sources.

Acknowledgements

This work was funded by the Department of Energy office of Science, Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under grant No. DE-FG02-92ER14299.A002. We would like to thank E. Kukk, M. Mucke, J. H. D. Eland, V. Zhaunerchyk, R. Feifel, L. Avaldi, P. Bolognesi, C. Bostedt, J. D. Bozek, J. Grilj, M. Guehr, L. J. Frasinski, D. T. Ha, K. Hoffmann, B. K. McFarland, C. Miron, K. Ueda, E. Sistrunk, R. J. Squibb and J. Glowonia for their contribution to the earlier work [31].

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