

Probing C₆₀ Fullerenes from within Using Free Electron Lasers

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Abstract: Fullerenes, such as C₆₀, are ideal systems to investigate energy redistribution following substantial excitation. Ultra-short and ultra-intense free electron lasers (FELs) have allowed molecular research in a new photon energy regime. FELs have allowed the study of the response of fullerenes to X-rays, which includes femtosecond multi-photon processes, as well as time-resolved ionization and fragmentation dynamics. This perspective: (1) provides a general introduction relevant to C₆₀ research using photon sources, (2) reports on two specific X-ray FEL-based photoionization investigations of C₆₀, at two different FEL fluences, one static and one time-resolved, and (3) offers a brief analysis and recommendations for future research.

Keywords: fullerenes; C₆₀; photoionization; fragmentation; free electron laser; femtosecond; dynamics; pump probe

1. Introduction

The behavior of C₆₀ in relation to ionizing radiation is important because it sheds light on the fundamental many-body problem due to the numerous nuclei–electron responses exhibited in a large molecule. Investigating C₆₀ using different light sources may reveal responses, which may impact other research fields. We thus studied C₆₀ using short wavelength lasers, and in particular, with free electron lasers (FELs), which are still relatively new light sources compared to table-top lasers or synchrotron facilities. FELs have opened up new research opportunities because they deliver photons in a new energy regime for many scientific fields, from physics to chemistry, as well as to matter under extreme conditions and biology [1]. These VUV/X-ray lasers are accelerator-based tools, which are a hybrid between synchrotron radiation facilities and typical table-top lasers. FELs produce high brightness radiation with typical femtosecond (fs) pulse duration [2] and have been available since 2005, with the first VUV FLASH FEL at DESY in Germany [3]. There are currently several X-ray FELs around the world in addition to XUV FELs. The first X-ray FEL, the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory [1,2], was commissioned and made available to scientists in 2009. It was used to carry out the static and time-resolved work reported here. The LCLS so far has a repetition rate up to 120 Hz, including a fs time scale where the pulse duration can be as short as 2–3 fs and as long as 500 fs [1,2]. Since 2017, the LCLS FEL also provides pulses as short as ~280 attoseconds (as) in the soft X-ray regime, which is an unprecedented technical progress that already impacts current X-ray as research [4].

X-ray FELs have opened up the possibility to investigate the ultra-fast response of matter to intense femtosecond X-ray pulses as well as to their pulse duration. The initial research on atoms and small molecules uncovered new aspects of this response, such as rapid sequences of inner-shell photoionization and the Auger–Meitner decay [5,6]. More recently, fullerenes were investigated with FELs because they bridge the gap between molecules and nanoparticles and are model systems for studying the dynamical behavior of large systems when exposed to intense, X-ray short pulses. Fullerenes have displayed molecular [7] and bulk [8] behavior and have proven to be an excellent testing ground for experiments and theories [9]. The behavior of C₆₀ in relation to ionizing radiation is intriguing due to the numerous nuclei–electron responses exhibited, since it consists



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of a cage of 60 atoms with 240 valence electrons [10]. The interaction of such a large system is key to investigating many-body problems induced on the system's electrons by the photon electric field. The photon interaction with the electronic fullerene's degrees of freedom results in electronic dynamics, which leads to nuclei dynamics, since they are inter-connected. Thus, the investigation of the interaction of C₆₀ with photons has been carried out extensively, theoretically and experimentally [11], to advance, in some cases, the quantitative understanding of the electronic and nuclear structure of these large molecules.

The photon used by the scientific community to study C₆₀ varied from IR to X-rays, and some studies were static, while others were time dependent, in order to understand the ultra-fast dynamics that arises in these systems subsequent to photoabsorption. The time-resolved experiments and calculation of the interaction of C₆₀ with photons have the ultimate goal to control ultra-fast molecular dynamics and understand the chemical transformation at the fs timescale. These studies include probing the multi-electron interactions in fullerenes as well as between the electrons and the carbon nuclei [12].

Non-linear physics and strong-field table-top laser research with C₆₀ was extensively studied, and the photoionization mechanisms were found to be wavelength and pulse duration dependent [13]. The single-active-electron (SAE) method was used to calculate the ionization of C₆₀ in intense, 4×10^{13} W/cm² laser pulses with durations between 27 and 70 fs and for a wide range of wavelengths ranging from 395 to 1800 nm [14], which agreed with the measurements. For a long I.R. wavelength of 1800 nm and 70 fs pulse duration, the SAE picture predicts "over the barrier" ionization for a peak intensity of 10^{15} W/cm², leading to non-fragmented parent molecule but highly charged C₆₀^{q+} (q = 1–12) [12] ions. At a short wavelength of 355 nm, the excitation of C₆₀ with 10 ns pulses led to fragmentation by delayed ionization and C₂ emission as well as other fragments, even for small intensities of about 2×10^6 W/cm² [15].

We investigated and we report here on two studies regarding the X-ray ionization and fragmentation of C₆₀ under high- and mid-fluence X-ray femtosecond pulses from the LCLS. One study is static, and the other one is time resolved. The results of the static study demonstrated that intense X-ray FEL multiply ionizes the parent molecules before breaking into molecular ions as well as into highly charged atomic C states. This work contributed toward understanding the radiation damage, and in particular, electronic damage, due to X-ray radiation, which is essential to understand for the progress of bio-molecular imaging. The result of the time-resolved study gave new insights into the dynamics of the C₆₀ fragmentation subsequent to mid-fluence absorption of the X-ray photon. It demonstrated the importance of chemical effects and charge transfer in stabilizing the molecule against fragmentation over several hundred femtoseconds after the X-ray pump pulse. We conclude this article by identifying and providing recommendations for future research opportunities using *as* pump-probe techniques.

2. Materials and Methods

The measurement of the ions resulting from the ionization and fragmentation dynamics of C₆₀ under X-ray exposure was achieved by using a magnetic bottle spectrometer [16] at the LCLS AMO hutch. The method is described elsewhere [16]; thus, our description here is brief. The C₆₀ sample was produced via a collimated molecular beam using an evaporative oven introducing the gas phase C₆₀ into the vacuum chamber. The oven was resistively heated and had a small nozzle and skimmer through which the C₆₀ molecules entered the interaction region. The oven was heated to ~700–800 K, and a liquid-nitrogen-cooled dump opposite the skimmer captured the target after it passed through the interaction region. X-ray optics focused the incoming X-ray pulses to a peak focal intensity of $\sim 10^{15}$ W cm⁻². The magnetic bottle spectrometer consisted of a 2 m long ion drift path, providing high ion mass-to-charge and KE resolution. The pulse energies of the two beams, centroid photon energy and pulse duration were recorded and used as statistical filters in the analysis. The interaction region, defined by the intersection of the focused X-ray beam and the molecular

beam, covered a volume around the focus with an inhomogeneous X-ray spatial fluence distribution. Therefore, the measured data contain contributions from a wide range of fluence (volume integrated signal), with peak X-ray fluence only at the center of the focus. To model the interaction region, the X-ray spatial fluence distribution was calibrated using the ion yields from Ar. This spatial fluence distribution was then applied in the modeling of the X-ray interaction with C_{60} to account for low- and high-fluence regions, allowing quantitative comparison of theoretical predictions to the experimental data.

3. Results

3.1. Photoionization of C_{60} with High-Fluence X-ray FEL Pulses

One of the scientific motivations to study C_{60} with fs X-ray FELs is because these sources target atomic orbitals instead of molecular orbitals, and they allow simple measurements of the response of inner-shell electrons (localized with each atom forming the molecule) compared to the complex response of the molecular orbitals composed of all valence electrons. Probing inner-shell electrons with short wavelengths allows an efficient probing of physical and chemical phenomena from within, since it is an inside-out ionization. Inner-shell photoionization was carried out with synchrotron radiation [17], but the difference between these two light sources is that FELs have a fs time structure and are super intense [18] compared to synchrotrons. A synchrotron pulse on average has about 10^4 photons while FELs have about 10^{12} , allowing the investigation of non-linear processes as well as time-resolved photoionization and fragmentation of the molecules [19].

Another motivation to choose to carry out the photoionization of C_{60} with intense FELs was to understand the radiation damage of large systems because this finding could contribute to the understanding of biomolecular imaging using X-ray scattering techniques, which do not provide detailed spectroscopic information. C_{60} is considered a benchmark molecule because it consists of chemically bonded carbon atoms with representative bond lengths and damage processes to bio-molecules [20]. Although FELs provide the incident brightness needed to achieve diffraction-limited atomic resolution experiments, they, nevertheless, induce possible electronic and structural damage, altering the sample despite the use of short pulse durations [21].

We carried out an experimental and theoretical investigation of C_{60} dynamics with intense fs X-rays to provide a spectroscopic study that offers either a quantitative or qualitative understanding of molecular dynamics. To understand the effects of increased per-atom fluence dose in the photon–molecule interaction, we used the large photoabsorption cross-section of carbon 1 s electrons. We ionized C_{60} with 485 eV photon energy to reach conditions in which each atom in a C_{60} molecule in the X-ray focus absorbs multiple photons. The study was performed with three pulse durations (4 fs, 60 fs, 90 fs) to ascertain the effect of the pulse duration. The core ionization induces the Auger–Meitner process, resulting in many photo- and Auger–Meitner electrons due to the cyclic multiphoton ionization. This process leads to secondary ionization of C_{60} , and it fragments ions by the photo- and Auger–Meitner electrons, which are found to be weak in isolated small molecules and absent in atoms. These effects were found, however, to be very significant for the ionization and fragmentation of C_{60} under high photon dose rate conditions and had to be incorporated in the model calculation to account for the experimental data. The C_{60} molecule charges up to C_{60}^{8+} , based on our observation, and because of the short C–C bond lengths, it fragments via Coulomb repulsion into molecular and C ion charge states distribution from C^+ to C^{6+} at 90 fs pulse duration. At a shorter pulse duration, 4 fs, the higher charge state obtained is only C^{5+} , since the pulse is shorter, giving less multi-cyclic photoionization and Auger–Meitner decay. Our investigation focused on the production of charged atomic C states and not on the molecular fragments.

We show in Figure 1 some of the multi-ionized parent C_{60} as well as its fragmentation products, such as the molecular charged carbon chains, compared with the model [22]. Not all fragments are shown or taken into consideration in the calculation here; thus, the sum over all fractional fragmentation ion yields is not unity. Furthermore, we do not measure

the formation of neutral fragments in our experiment. As can be seen, there is not an agreement between the experimental molecular data and the model, which was tailored for the formation of charged atomic C states. The calculation is based on a model that follows both electronic and ionic dynamics in space and time, where the atoms/ions are treated as classical particles using Newtonian mechanics, but the rate equations and the cross sections are introduced quantum mechanically. The charges interact via Coulomb forces, and a non-relativistic equation of motion is used [22]. However, the molecular effects were not included, which is the reason for the discrepancy between the measurements and the calculation for the molecular fragment shown in Figure 1. Nonetheless, in the case of atomic carbon charge states, this model, which describes the charged particles behaving as if they were classical particles, agrees well with the experimental data, as shown in Figure 2.

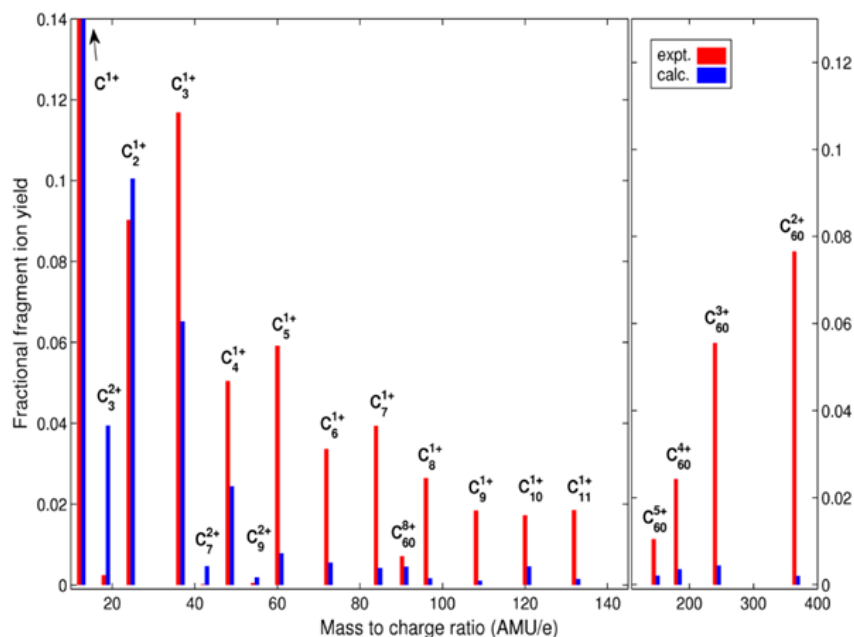


Figure 1. Sequential multi-photon ionization of C₆₀ displaying molecular ion fragments. The photon energy was 485 eV, the pulse duration was 90 fs, and the pulse energy was 0.61 mJ.

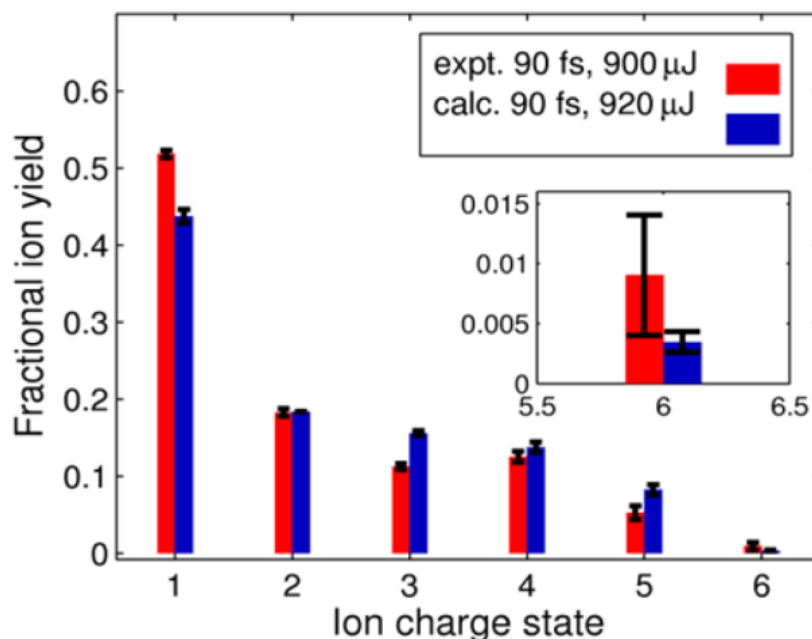


Figure 2. Charged atomic C state distribution measured with pulse duration of 90 fs and 900 μJ.

Figure 2 depicts the comparison between the experimental data and the model of the atomic C^{n+} ($n = 1-6$) ion charge states generated after the Coulomb explosion of C_{60}^{8+} . As can be seen, the pulse intensity allowed the formation of fully stripped C ions with 90 fs pulse duration. The model initially predicted more abundant charge states; however, the strong recombination of electrons with the C ions after the pulse ends led to the observed ion yield results [22].

In summary, the static experimental and theoretical investigation of C_{60} with intense pulses resulted in demonstrating that an intense X-ray FEL multiply ionizes the parent molecules before breaking into molecular ions as well as into highly charged atomic C states. We learned that, in the case of charged atomic C, secondary ionization (collisional ionization by trapped electrons) and recombination of electrons with C ion fragments were extremely important to the interaction of C_{60} with intense photons because the interaction created a microplasma that allowed high kinetic energy electrons to also ionize the C_{60} atomic fragments. The calculation for the charged atomic C states will not have agreed with the measurement if it did not include these effects. These effects were not sufficient for the case of the molecular fragment ions, which was not the focus of our investigation. Our work with intense X-ray pulses also contributed a detailed understanding of electronic damage (photoelectron, Auger–Meitner electrons) due to X-ray radiation, which is essential for the progress of bio-molecular imaging [22].

3.2. Time-Resolved Photoionization of C_{60} with Mid-Fluence X-ray FEL Pulses

The instrumental advances that provided the generation of pairs of synchronized femtosecond X-ray FEL pulses [23] has made it possible to carry out time-resolved studies enabling tracking, probing and ultimately understanding the time evolution of X-ray-induced photo processes. We thus extended our static investigation of C_{60} by carrying out a time-resolved experimental and theoretical investigation of its dynamics with mid-fluence fs X-rays. Specifically, we examined the role of chemical effects, such as chemical bonds and charge transfer, on the fragmentation following multiple ionization of the molecules. The X-ray pump-probe investigations enabled probing charge and nuclear dynamics after inner-shell photoabsorption. In this mid-fluence X-ray multiphoton regime, like in the previous intense case, there is a high degree of ionization, challenging the time-resolved theoretical work because of the response of a large number of degrees of freedom and the formation of highly excited states.

We performed X-ray pump/X-ray probe measurements [23] in which the X-ray pump pulse with 640 eV photons from the LCLS enabled K-shell ionization of the carbon atoms and induced a substantial degree of ionization. We then used an X-ray probe pulse to observe the dynamics initiated by the pump pulse, by detecting molecular and atomic fragment ions. The time evolution of the observed fragment ions was interpreted by numerical simulations. The ion fragments were detected with an ion time-of-flight spectrometer [22], which recorded the evolution of C_{60} into fragment ions. The time delays between the pump and probe pulses were between 25 and 925 fs [23]. The pulse duration of the first and second pulses was 20 fs and 10 fs, respectively. The measured total energy was 0.77 ± 0.01 mJ, while the estimated energy of the two pulses was 45% for the pump (peak intensity of 4×10^{15} W/cm²) and 55% for the probe pulse. The theoretical modeling employed a molecular-dynamics-based simulation tool with recent additions to include the treatment of chemical bonds via classical force fields [22] and valence-electron charge transfer [24]. Under the current experimental conditions, multiphoton ionization and Auger–Meitner decay lead to multiply charged C_{60} molecules, stable up to C_{60}^{13+} , which break up into atomic and molecular fragments.

The examination of the charged atomic C fragments demonstrated a time-delay dependence to characterize the molecular time evolution. Figure 3 compares the experimental and theoretical atomic ion yields for C^{1+} to C^{4+} as a function of pulse delay, showing a qualitative good agreement between the experiment and modeling regarding only the dynamical behavior, not the absolute values of the yield of the charged atomic C states. As

can be seen, for both the measurements and the calculations, the behavior of the C^+ ion yield changes little as a function of time delay between 25 and 925 fs. However, the ion yield behavior for C^{2+} - C^{4+} increases steadily over a time-delay range of approximately 600 fs; then, a plateau is observed at a longer time delay.

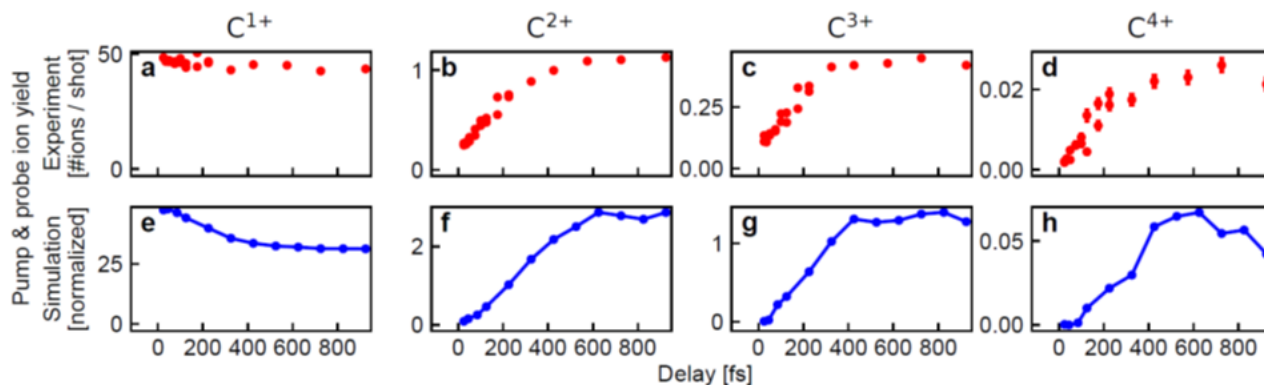


Figure 3. Comparison between experiment and modeling of the time-resolved ionization and fragmentation dynamics of C_{60} displaying charged atomic C fragments. The top panels show the measurements while the bottom panels show the calculations. Panels (a,e) show the C^{1+} ; (b,f) show the C^{2+} ; (c,g) show the C^{3+} ; and (d,h) show the C^{4+} fragment ions. See text for details.

Our analysis of the data guided by the calculation allowed us to understand the real-time evolution of the parent fragments after the pump pulse. Specifically, we found out that a substantial fraction of the ejected fragments, subsequent to the ionization of C_{60} , are neutral carbon atoms. We calculated that beyond about 300 fs, there is an even larger number of C neutral than C^+ ions. This modeling allowed us to deduce that the probe pulse generates C^{2+} predominantly through the ionization of neutral C by a photoionization and Auger–Meitner decay (P-A) sequence, while C^{3+} is created similarly after ionization of C^{1+} by a P-A sequence. C^{4+} is formed from neutral C via two P-A sequences or from C^{1+} by a P-A sequence and a valence ionization or secondary ionization. Based on the measurement and modeling, we concluded that the production of C^{2+} , C^{3+} and C^{4+} is primarily due to the ionization of C/ C^{1+} fragments by the probe pulse.

Our modeling demonstrated that chemical bonds and valence charge transfer are important in the photoionization of C_{60} , since we found no time-delay dependence in the yield of the C^{2+} , C^{3+} and C^{4+} ions without inclusion of such chemical effects. We found that the parent ion C_{60}^{13+} does not undergo instantaneous fragmentation because it is delayed, as shown in Figure 3. The fragmentation is delayed relative to the pump pulse due to the still existing chemical bonds because it takes time for the 60-atom system to break up into smaller fragments, most of which exist only transiently for several tens of femtoseconds. In addition, during this structural transformation, it takes additional time for those fragments to eject neutral and singly charged atomic ion fragments. We show the impact of the chemical effects in Figure 4 (top panel) by plotting the maximum atomic displacement for the parent ion C_{60}^{13+} based on MD simulations, for two situations: (1) chemical phenomena, such as bonding and charge transfer, are removed; (2) the full model that includes both chemical bonding and charge transfer.

It is clear that chemical effects minimize significantly the maximum displacement of C atoms, demonstrating evidently that C_{60} is structurally resistant, on time scales of tens of femtoseconds, against the impact of X-ray multiphoton ionization. Figure 4 (bottom panel) shows the simulation snapshots of the real-time evolution of C_{60}^{13+} for the full model, illustrating the ionization and fragmentation dynamics of C_{60} irradiated by femtosecond X-rays.

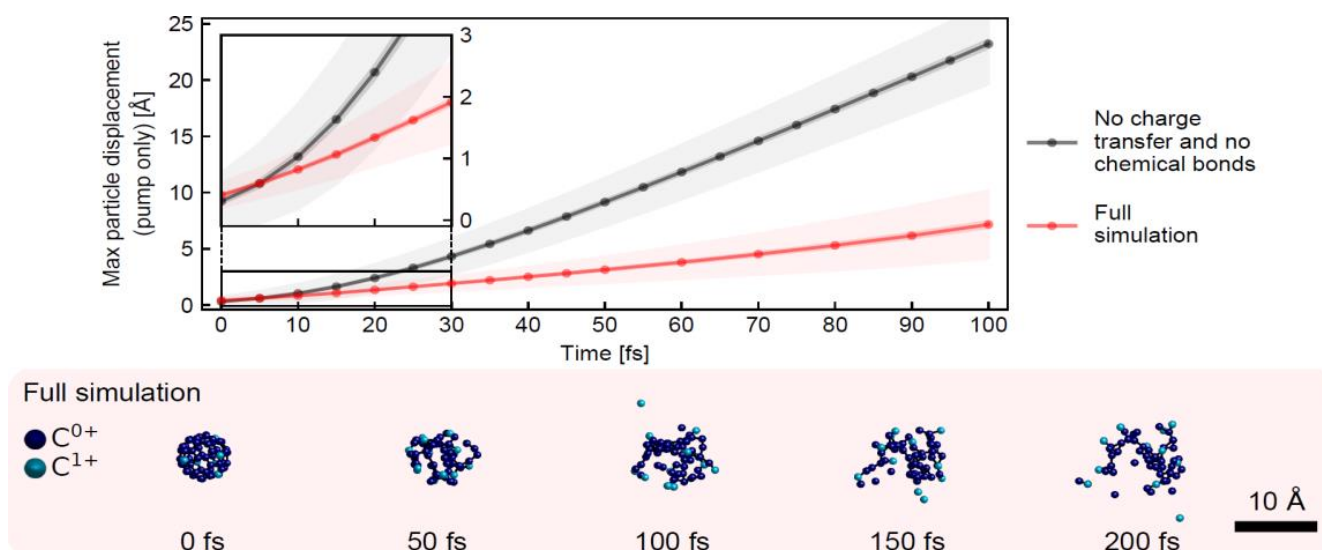


Figure 4. Movie snapshots of the real-space and real-time simulation dynamics of C_{60}^{13+} induced by XFEL pulse.

The implications of this work for the field of femtosecond molecular imaging is that charge transfer, nuclear arrangement, chemical bonds, and thus, the chemical structure are resistant to the intense electromagnetic environment created by XFEL irradiation. The impact of this work is that delayed fragmentation will play a critical role in most other intense X-ray multiphoton ionizations of molecules. With the advent of several new FELs all over the world, our results, which lay the foundation for a deeper understanding and quantitative modeling of XFEL-induced radiation damage, will impact biomolecular imaging.

In summary, this time-resolved investigation gave new insight into the dynamics of the C_{60} fragmentation subsequent to mid-fluence absorption of the X-ray photon. It revealed the importance of chemical effects, such as covalent bonding and charge transfer, in stabilizing the molecule against fragmentation over several hundred femtoseconds after the X-ray pump pulse. Such detailed understanding of X-ray-induced ionization dynamics and atomic motions in molecules is crucial for the applications of high-intensity X-ray beams [25].

4. Discussion

Our experimental work in the high- [22] and mid-fluence [25] X-ray regime, investigating the response of C_{60} to fs FEL pulses, revealed new physical and chemical processes that were validated either qualitatively or quantitatively by state-of-the-art simulation methodology. Specifically, the static X-ray high-fluence, 90 fs study showed that the Coulomb explosion subsequent to multiphoton ionization is so violent that it leads to fully stripped C atoms, and the model does not require the inclusion of detailed molecular effects. The most important effect that needed to be included in the calculation was the secondary electron collision with the ions fragments as well as the recapture of electrons by the ion fragments. On the other hand, the time-resolved mid-fluence study demonstrated that chemical bonds and the charge transfer effect were crucial to be included in the calculation to observe dynamics as a function of time delay. These effects had to be included to agree with the measurements that depicted dynamics as a function of time delay. In this situation, the simulations and the experiment revealed that despite significant ionization induced by the ultra-short (20 fs) X-ray pump pulse, the fragmentation of C_{60} was significantly delayed. This work uncovered the persistence of the molecular structure of C_{60} , which hinders fragmentation over a timescale of hundreds of femtoseconds. Furthermore, the calculation demonstrated that a substantial fraction of the ejected fragments is neutral carbon atoms. In fact, it is these neutral fragments' ejection from C_{60} , as the molecule cools

off, that prohibits a strong Coulomb explosion. These findings, interpreted by the most advanced modeling and theory, provide insights into X-ray FEL-induced radiation damage in large molecules, including biomolecules [25]. In fact, this work seems to indicate that experiments conducted with up to 20 fs, with mid fluence, will not experience radiation damage due to the delayed ionization. Thus, bio-molecule X-ray diffraction at this fluence will not suffer the “diffract before destroy” scenario. Furthermore, our simulation [25] provides a solid basis for the reliable interpretation of processes in systems even larger than C_{60} . Future XFEL-based experimental research into a wide range of systems will benefit from our results and the theoretical advances needed to interpret the experimental work.

Recently, a time-resolved experiment was conducted with intense XUV photons at the FLASH-II FEL that probed the resonance structure at about 20 eV, and this work might reveal new insight regarding the ionization and fragmentation of C_{60} at lower photon energy [26]. In addition, an experiment was conducted with hard X-rays at LCLS to visualize the light-induced reshaping of C_{60} via X-ray diffraction. Specifically, time-resolved X-ray diffraction images of C_{60} molecules were recorded during and after their interaction with intense near-infrared fields, giving direct access to structural changes of the molecules and their neutral or ionic fragmentation, in real time [27].

The current experiments so far focused on measuring the charged fragments resulting from absorption of X-ray photons by neutral C_{60} to investigate the ionization processes or using X-ray diffraction to visualize the transformation of C_{60} . Future work could investigate the anion, C_{60}^- [28,29] or C_{60}^+ [30]. Additionally, what is missing are experiments that will use photoelectron spectroscopy to measure in detail the ionization and fragmentation dynamics. In particular, the electron-ion coincidence techniques could be used, especially with the now available high repetition rate at FELs sources, to measure the momenta of the ions as well as identify the possible coincidences among the fragments and to visualize the different coincidence channels. Furthermore, the use of ultra-fast electron diffraction (UED) techniques [31] will allow the imaging of the molecular changes as a function of time delay between the pump and probe pulse.

Finally, the exciting advent of *as* X-ray pulses from FELs opens up the opportunity to study the electronic dynamics that precedes the nuclear dynamics [32]. Specifically, inner-shell X-ray pump-probe studies with *as* pulses could allow the probing and understanding of the electronic dynamics on its natural timescale. Currently, *as* pulses from the LCLS-II X-ray FEL are provided to scientists with photon energies tunable across the soft X-ray regime and with spectral brightness six orders of magnitude greater than HHG sources [32]. This *as* capability will soon be reproduced at other FEL facilities around the world, enabling previously impossible *as* experiments in all research fields.

5. Conclusions

Intense and short X-ray FELs allowed new understanding of the interaction and response of C_{60} fullerenes in a new energy regime. Furthermore, FELs facilities offer the possibility to carry out time-resolved experiments that allow us to extract molecular movies of the system's transformation as it evolves as a function of time. Future work could focus on using shorter X-ray pulses, for example, *as* pulses, as well as using other experimental methodologies, such as electron spectroscopy, coincidence techniques or ultra-fast electron diffraction. The combination of X-ray *as* FEL facilities and differential experimental techniques will enable scientists to understand the first steps in the photoabsorption or scattering investigations, resulting in new breakthrough that will push the frontiers of science and may result in new discoveries.

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Conflicts of Interest: The authors declare no conflict of interest.

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