# Femtosecond-resolved observation of the fragmentation of buckminsterfullerene following X-ray multiphoton ionization

N. Berrah<sup>®</sup><sup>1\*</sup>, A. Sanchez-Gonzalez<sup>®</sup><sup>2</sup>, Z. Jurek<sup>3</sup>, R. Obaid<sup>®</sup><sup>1</sup>, H. Xiong<sup>1</sup>, R. J. Squibb<sup>4</sup>, T. Osipov<sup>5</sup>, A. Lutman<sup>5</sup>, L. Fang<sup>6</sup>, T. Barillot<sup>2</sup>, J. D. Bozek<sup>7</sup>, J. Cryan<sup>8</sup>, T. J. A. Wolf<sup>®</sup><sup>8</sup>, D. Rolles<sup>9</sup>, R. Coffee<sup>5</sup>, K. Schnorr<sup>10</sup>, S. Augustin<sup>9</sup>, H. Fukuzawa<sup>®</sup><sup>11</sup>, K. Motomura<sup>11</sup>, N. Niebuhr<sup>®</sup><sup>12</sup>, L. J. Frasinski<sup>2</sup>, R. Feifel<sup>4</sup>, C. P. Schulz<sup>13</sup>, K. Toyota<sup>3</sup>, S.-K. Son<sup>®</sup><sup>3</sup>, K. Ueda<sup>11</sup>, T. Pfeifer<sup>10</sup>, J. P. Marangos<sup>®</sup><sup>2</sup> and R. Santra<sup>®</sup><sup>3,14</sup>

X-ray free-electron lasers have, over the past decade, opened up the possibility of understanding the ultrafast response of matter to intense X-ray pulses. In earlier research on atoms and small molecules, new aspects of this response were uncovered, such as rapid sequences of inner-shell photoionization and Auger ionization. Here, we studied a larger molecule, buckminsterfullerene ( $C_{60}$ ), exposed to 640 eV X-rays, and examined the role of chemical effects, such as chemical bonds and charge transfer, on the fragmentation following multiple ionization of the molecule. To provide time resolution, we performed femtosecond-resolved X-ray pump/X-ray probe measurements, which were accompanied by advanced simulations. The simulations and experiment reveal that despite substantial ionization induced by the ultrashort (20 fs) X-ray pump pulse, the fragmentation of  $C_{60}$  is considerably delayed. This work uncovers the persistence of the molecular structure of  $C_{607}$  which hinders fragmentation over a timescale of hundreds of femtoseconds. Furthermore, we demonstrate that a substantial fraction of the ejected fragments are neutral carbon atoms. These findings provide insights into X-ray free-electron laser-induced radiation damage in large molecules, including biomolecules.

decade ago, femtosecond X-ray free-electron lasers (XFELs) launched a new scientific era with prospects for an impact comparable to that of the ultrafast optical lasers revolution<sup>1</sup>. Photoionization and photon scattering studies using single, intense X-ray pulses have yielded exciting results in this new regime of ultrafast, intense X-ray-matter interactions. These investigations with intense X-rays ranged from the response of atoms<sup>2</sup> and molecules<sup>3-7</sup> to the response of clusters<sup>8,9</sup>. Intense, ultrafast X-rays were further used to create and probe the physics of solid-density plasmas<sup>10</sup>. The knowledge of how matter behaves under such conditions is crucial for advancing fundamental understanding and is also key for applications of XFEL-based coherent scattering studies that have retrieved molecular structure from nanosized crystals<sup>11</sup> and that aspire to reveal the structure of individual biological molecules<sup>12</sup> at (or close to) atomic resolution.

Recently, the generation of pairs of synchronized femtosecond X-ray pulses<sup>13</sup> has made it possible to carry out time-resolved studies that enable previously unexplored time-resolved tracking and probing and that ultimately enable the understanding of the time evolution of X-ray-induced photoprocesses. These investigations are still in their infancy<sup>14,15</sup> and are non-existent in the case of large polyatomic molecules, which was a strong motivation for this work on buckminsterfullerene. We chose this system because it is an

excellent target to initially test our understanding of fundamental processes. The system's simple atomic composition, symmetric structure and bonding are directly amenable to our theoretical calculations and to experimental measurements.

Pump-probe XFEL investigations of molecules allow the exploration of charge and nuclear dynamics after inner-shell photoabsorption. The ionization mechanism is such that photons interact directly with the electrons in the molecules, which couple to the nuclei, initiating ultrafast and concerted motion of both the electrons and the atoms forming the molecule. The photon-energy conversion is determined by this motion, which takes femtoseconds to picoseconds. In the X-ray multiphoton regime, there is so much ionization that the electrostatic repulsion energy stored within the molecule becomes comparable to the total molecular binding energy. Unravelling the subsequent dynamics presents theorists with challenges because of the response of a large number of degrees of freedom and the formation of highly excited states. Our experimental work, which reveals new physical and chemical processes, has validated state-of-the-art simulation methodology, providing a solid basis for the reliable interpretation of processes in systems even larger than C<sub>60</sub>. Future XFEL-based experimental research into a wide range of systems will benefit from these theoretical advances.

<sup>1</sup>Physics Department, University of Connecticut, Storrs, CT, USA. <sup>2</sup>Department of Physics, Imperial College London, London, UK. <sup>3</sup>Center for Free-Electron Laser Science, DESY, Hamburg, Germany. <sup>4</sup>Department of Physics, University of Gothenburg, Gothenburg, Sweden. <sup>5</sup>LCLS, SLAC National Accelerator Laboratory, Menlo Park, CA, USA. <sup>6</sup>Center for High Energy Density Science, University of Texas, Austin, TX, USA. <sup>7</sup>Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, Gif-sur-Yvette, France. <sup>8</sup>Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA. <sup>9</sup>J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS, USA. <sup>10</sup>Max-Planck-Institut für Kernphysik, Heidelberg, Germany. <sup>11</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan. <sup>12</sup>Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany. <sup>13</sup>Max Born Institute, Berlin, Germany. <sup>14</sup>Department of Physics, Universität Hamburg, Germany. \*e-mail: nora.berrah@uconn.edu



**Fig. 1** Comparison between the experimental and theoretical data for the atomic carbon ion yields as a function of the time delay between the X-ray pump and the X-ray probe. a-h, Experimental data (a-d) and modelling results (e-h) for  $C^{1+}$  (a,e),  $C^{2+}$  (b,f),  $C^{3+}$  (c,g) and  $C^{4+}$  (d,h). The experimental error bars correspond to one s.d. and originate from the error in ion counts estimated as the square root of the count within each data run. Error bars smaller than the marker size are omitted. The simulation provides absolute yields, which are rescaled by applying the same constant factor to all curves to match the experimental  $C^{1+}$  yield.

Here, we focus on the role of chemical effects by experimentally and theoretically investigating the complex ionization and fragmentation dynamics of gas-phase  $C_{60}$ . We perform a pump–probe study in which the X-ray pump pulse induces a substantial degree of ionization. We then use 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 experimentally observed fragment ions is interpreted by numerical simulations. This investigation gives new insight into the dynamics of molecular fragmentation of a partially ionized system and reveals 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 applications of high-intensity X-ray beams.

#### Results

In this investigation, C<sub>60</sub> fullerene was irradiated with 640 eV photons, which was sufficient to K-shell ionize the carbon atoms, at the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory. The time-resolved measurements were conducted using two X-ray pulses13 interacting with gas-phase C<sub>60</sub>. The pump and probe pulses intersected the C60 beam in the interaction region of an ion time-of-flight (TOF) magnetic bottle spectrometer<sup>16,17</sup> capable of detecting the generated ions (see Methods). In this experiment, the pump pulse induced ionization and structural dynamics, whereas the delayed probe pulse interrogated the transformation of  $C_{60}$  and enabled the identification of the parent fragments created by the pump. We varied the time delay between the pump and probe pulses from 25 to 925 fs and recorded the evolution of the transformation of C<sub>60</sub> into fragment ions. The pulse durations of the first and second pulses were 20 fs and 10 fs, respectively. The measured total energy was  $0.77 \pm 0.01$  mJ, while the estimated energy was 45% for the pump pulse (peak intensity of  $4 \times 10^{15} \text{W} \text{ cm}^{-2}$ ) and 55% for the probe pulse. For the theoretical modelling, we employed XMDYN Rev. 279818, a molecular dynamics-based simulation tool with recent additions that include the treatment of chemical bonds via classical force fields<sup>17</sup> and valence-electron charge transfer<sup>9,19</sup> (see Methods). With these experimental conditions, multiphoton ionization and Auger decay lead to multiple charged C60 molecules, which break into atomic and molecular fragments<sup>17,20</sup>. In this work, we focus our investigation on the atomic C ion fragments, as their yields show the strongest time-delay dependence for characterizing the molecular time evolution.

In Fig. 1 we compare the experimental and theoretical atomic ion yields for  $C^{1+}$  to  $C^{4+}$  as a function of pulse delay. The experimental yields were determined by integrating the individual ion peaks in the TOF spectra (see Methods) shown in Supplementary Fig. 1. All measured signals are affected by the spatially non-uniform X-ray intensity distribution. In the theoretical data, this is taken into consideration through volume integration (see Methods). For both the measurements and the calculations, the  $C^{1+}$  ion yield changes little as a function of time delay between 25 and 925 fs. However, the ion yields for  $C^{2+}-C^{4+}$  increase steadily over a time-delay range of approximately 600 fs, then flatten out at longer delays. The experimental and modelling data are in good agreement.

We determined the charge state of the C<sub>60</sub> molecule after ionization with the intense XFEL pump pulse, characteristic to our experiment. We used the capability of our modelling to find that the volume-integrated signals correspond, with good accuracy, to the response of  $C_{60}$  at a fixed X-ray fluence of ~6 × 10<sup>9</sup> photons  $\mu$ m<sup>-2</sup> (60 J cm<sup>-2</sup>) (Supplementary Fig. 2). At this pump-only fluence, the average of the total  $C_{\rm 60}$  charge is  ${\sim}13$  with a standard deviation of  $\pm 5$  due to the stochastic nature of the ionization processes (Supplementary Fig. 3). A simple estimate for the total accumulated electrostatic energy (representing the C<sub>60</sub><sup>13+</sup> ion by a sphere possessing 13 positive charges spread uniformly over its surface) yields approximately +350 eV. By contrast, as a consequence of chemical bonding, the bound molecule originally had a potential energy on the order of -400 eV (the average C-C bond dissociation energy in  $C_{60}$  is 4.6 eV; ref. <sup>21</sup>). Thus, a remarkable amount of energy-more than 80% of the full binding energy-is available for driving the fragmentation. In other words, strong fragmentation can be expected in this regime. There is enough energy in the system for the formation of a significant fraction of atomic fragments. The details of the fragmentation dynamics can only be revealed by a detailed, time-resolved experimental and simulation study, which we undertook and report here.

We explain here the delay-dependent yields of  $C^{2+}$ ,  $C^{3+}$  and  $C^{4+}$ from the pump-probe data shown in Fig. 1 by identifying the parent fragments generated with only the pump pulse. Figure 2a shows the simulated real-time evolution of the parent fragments after the pump pulse (the probe pulse is not used), demonstrating that a substantial fraction of the ejected fragments subsequent to the ionization of  $C_{60}$  are neutral carbon atoms. In fact, beyond about 300 fs, we calculate an even larger number of C-neutral than  $C^{1+}$ ions. Figure 2b, simulated at 925 fs, shows the fraction of pump and probe ions with respect to the fragments after pump only, allowing



**Fig. 2** | **Identification of the parent fragments responsible for the observed C ion charge states. a**, Simulated real-time evolution of the volume-integrated yield using only the pump pulse (probe pulse is not used) to identify the parent fragments (fragments that are responsible for the observed atomic ions when the probe pulse is also applied), which are found to be neutral C and C<sup>1+</sup> ion. The pump pulse is centred at t = 0 fs. **b**-**e**, On the basis of simulations, the relative weight of the parent of the final C charge states, C<sup>1+</sup> (**b**), C<sup>2+</sup> (**c**), C<sup>3+</sup> (**d**) and C<sup>4+</sup> (**e**) at a pump-probe time delay of 925 fs.



**Fig. 3** | **KE** evolution of the ion charge states as a function of the pump-probe delay. **a**-**h**, Experimental data (**a**-**d**) and modelling results (**e**-**h**) for for  $C^{1+}$  (**a**,**e**),  $C^{2+}$  (**b**,**f**),  $C^{3+}$  (**c**,**g**) and  $C^{4+}$  (**d**,**h**). The black dashed line indicates the peak position of the KE distribution at each delay. For the simulation we had low statistics for  $C^{4+}$ .

us to deduce that the probe pulse generates C<sup>2+</sup> predominantly through the ionization of neutral C by a photoionization and Auger decay (P-A) sequence, while C<sup>3+</sup> is created similarly after ionization of C1+ by a P-A sequence. C4+ is formed from neutral C via two P-A sequences or from C1+ by a P-A sequence and a valence ionization or secondary ionization. Figure 2a also shows the timescales for the formation of C and C1+ parent ions, which correlate well with the rise times seen in Fig. 1 for the appearance of C<sup>2+</sup>, C<sup>3+</sup> and C<sup>4+</sup> pump and probe ions, thus supporting this interpretation. On the basis of the measurement and modelling, we conclude that the production of C<sup>2+</sup>, C<sup>3+</sup> and C<sup>4+</sup> is primarily due to the ionization of C and C<sup>1+</sup> fragments by the probe pulse. Furthermore, we conclude that the measurement confirms the finding in the modelling (Fig. 2) that C and C1+ fragment yields continue to rise steadily for several hundred femtoseconds after the X-ray pulse has ended. Optical laser experiments on C<sub>60</sub> have reported the ejection of neutral C fragments under experimental conditions that differ from those used in the current work—conditions that either consider a lower degree of molecular ionization<sup>22</sup> or use nanosecond laser pulses<sup>23</sup>. Our work provides evidence of neutral atomic-fragment ejection under intense, femtosecond XFEL pulses.

The Fig. 1 data and modelling support the argument that the fragmentation dynamics of  $C_{60}$  is due to multiple X-ray photons

absorbed from the pump pulse. The simulation (Supplementary Fig. 4) shows a clear correlation between the number of photons absorbed per  $C_{60}$  and the atomic ion fragment yields; the appearance of atomic fragments is negligible when only one photon is absorbed by the fullerene molecule (see the inset of Supplementary Fig. 4), while the number of atomic fragments increases when multiple photons are absorbed.

To investigate the importance of specific physical phenomena, we used the ability to switch them on and off in the simulations. In particular, we investigated the effect of chemical bonds and valence charge transfer<sup>9</sup>. A straightforward consequence of charge transfer is the energy redistribution among atomic sites, which is due not only to molecular vibrations mediated by chemical bonds but also to Coulomb interaction, even if only a fraction of the atoms are ionized on average. Our modelling demonstrates that chemical bonds and valence charge transfer are important in the photoionization case of C60, since we find no time-delay dependence in the yield of the C<sup>2+</sup>, C<sup>3+</sup> and C<sup>4+</sup> ions without inclusion of such chemical effects (Supplementary Fig. 5). This finding helps us to better understand how the probe pulse works: a multiply charged atomic fragment can reach the ion detector unchanged only if it is formed at a sufficiently large distance from other fragments to suppress valence charge transfer. In our simulations, the critical distance<sup>20,24,25</sup> is between 5Å



**Fig. 4 | Real-space and real-time simulation dynamics of**  $C_{60}^{13+}$  **induced by a single XFEL pulse centred at** t = 0 **fs. a**, the maximum C displacement for two situations: (1) a model that does not include chemical effects such as bonds and charge transfer and (2) a full model that includes both chemical bonds and charge transfer. We show the standard deviation of the maximum displacement across simulations (wider shaded band) and the standard error of the average maximum displacement calculated using bootstrapping (very narrow shaded band). The inset represents a zoom of the first 30 fs real space and real time dynamics. **b**, snapshots of a trajectory calculated with the full model with the colour-coded charged states. Since the underlying quantum processes such as photoionization are stochastic in nature, the time evolution proceeds differently from pulse to pulse. The panels depict an exemplary realization of these stochastic dynamics between 0 and 200 fs. The average final ionization state in the present study is equal to the ionization degree reached in a biological sample during a 10 fs hard X-ray imaging pulse (see Methods).

and 8 Å, depending on the charge state of the atomic ion fragment. Hence, if the probe pulse arrives before fragmentation has evolved, the formation of  $C^{2+}$ ,  $C^{3+}$  and  $C^{4+}$  is suppressed.

To better understand the ionization and fragmentation mechanisms, we examine the kinetic energy (KE) of the C fragment ions, shown in Fig. 3, as a function of time delay (see Methods), providing further support for the interpretation of our results. The main trends observed in the experimental and theoretical data are in qualitative agreement. The KEs of the  $C^{2+}-C^{4+}$  charge states initially decrease, consistent with an overall expansion, then the spectra converge at long delays. The low KE values might indicate that the electrostatic Coulomb energy added to C60 via pump-induced ionization is not converted primarily into the production of fast fragments but into maximizing the number of fragments. The asymptotic KEs of the detected C<sup>2+</sup> and C<sup>3+</sup> ions reflect the asymptotic KEs with which C-neutral and C<sup>1+</sup>, respectively, are ejected after the pump pulse. Thus, Fig. 3 indicates for both experiment and simulation that neutral C atoms are born with noticeably lower KEs than the C<sup>1+</sup> ions. The KEs are higher in the simulation than in the experiment. This points to more efficient intramolecular energy redistribution in the experiment, which might be a signature of electron delocalization effects specific to the highly delocalized  $\pi$  electrons of the fullerene molecule not captured by the model.

# Discussion

With the experimental parameters used, the fragmentation dynamics are characterized by a multistep process in which the pump pulse does not induce a Coulomb explosion (supported by the observation of low-ion KEs) and bonds are still intact to a large degree, such that the fragmentation is not barrierless. Thus, the system has time to explore the high-dimensional configuration space to find a pathway that takes the system to the dissociative side of the barrier. This is similar to the reason why chemical reactions involving a barrier appear to be slow; in most encounters of the reaction partners, there is not enough energy to overcome the barrier. In rare cases in which the energy is sufficient, the reaction is ultrafast. As a consequence,  $C_{60}$  with ~13 positive charges does not undergo instantaneous fragmentation; the fragmentation is delayed relative to the pump pulse due to the still-existing chemical bonds. The probe pulse reveals that the gradual increase of the C<sup>2+</sup>-C<sup>4+</sup> yield, as a function of the pumpprobe delay, is not a consequence of gradually increasing interatomic distances. Indeed, Fig. 1 exposes the fact that 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. Furthermore, during this structural transformation, it takes more time for those fragments to eject neutral and singly charged atomic ion fragments (Supplementary Fig. 6). Once the atoms (atomic ions) are on the dissociative side of the potential energy surface, they separate from the other fragments quickly enough such that this part of the process is, for our purposes, practically instantaneous. Although there is not enough time to reach strict thermal equilibrium within a fragment, energy is transferred among the neutral C atoms, which is ultimately responsible for the ejection of atomic fragments. Partially thermalized larger units evaporate atomic neutral C and C<sup>1+</sup> 200 to 300 fs after irradiation. These characteristic times agree well with the rise times extracted from the delay-dependent experimental ion yields of C<sup>2+</sup> and C<sup>3+</sup>, respectively, shown in Fig. 1. The key insight that emerges from this time-resolved work is that the fragmentation is not prompt but delayed relative to the pump pulse due to chemical effects such as charge transfer and still-existing chemical bonds.

We illustrate the impact of the chemical effects by showing (Fig. 4a) the maximum atomic displacement, based on molecular dynamics simulations, for two situations: (1) the chemical phenomena (bonding and charge transfer) are removed and (2) the full model, including both chemical bonding and charge transfer. This is a real-time simulation using only one pulse. As can be seen, chemical effects significantly minimize the maximum displacement of C atoms. This clearly demonstrates that  $C_{60}$  is structurally resistant, on time scales of tens of femtoseconds, against the impact of X-ray multiphoton ionization. Specifically, for up to 30 fs after the peak of the X-ray pulse, the maximum atomic displacement does not exceed 2 Å. This outcome reveals that during the

entire 20 fs X-ray pulse, the C<sub>60</sub> structural changes remain below the critical resolution considered sufficient in biomolecular studies (for example, in the context of distinguishing peptides from a protein or the bases of a nucleic acid<sup>26</sup>). Therefore, this finding may have implications regarding the role of chemical effects in reducing radiation damage of biological systems imaged at XFELs. Proteins have chemical bonds of similar strength<sup>27</sup> to C<sub>60</sub>, and, under imaging conditions, experience a similar degree of ionization as C<sub>60</sub> does in our study (see Methods). Figure 4b shows simulation snapshots of the real-time evolution of C<sub>60</sub><sup>13+</sup> for the full model, illustrating the ionization and fragmentation dynamics of C<sub>60</sub> irradiated by femtosecond X-rays.

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

## **Online content**

Any methods, additional references, Nature Research reporting summaries, source data, statements of code and data availability and associated accession codes are available at https://doi.org/10.1038/ s41567-019-0665-7.

Received: 19 March 2019; Accepted: 12 August 2019; Published online: 23 September 2019

#### References

- Strickland, D. & Mourou, G. Compression of amplified chirped optical pulses. Opt. Commun. 55, 447–449 (1985).
- Rudek, B. et al. Ultra-efficient ionization of heavy atoms by intense X-ray free-electron laser pulses. *Nat. Photon.* 6, 858–865 (2012).
- 3. Rudenko, A. et al. Femtosecond response of polyatomic molecules to ultra-intense hard X-rays. *Nature* **546**, 129–132 (2017).
- Berrah, N. A perspective for investigating photo-induced molecular dynamics from within with femtosecond free electron lasers. *Phys. Chem. Chem. Phys.* 19, 19536–19544 (2017).
- Takanashi, T. et al. Ultrafast Coulomb explosion of a diiodomethane molecule induced by an X-ray free-electron laser pulse. *Phys. Chem. Chem. Phys.* 19, 19707–19721 (2017).
- Wolf, T. J. A. et al. Probing ultrafast ππ\*/nπ\* internal conversion in organic chromophores via K-edge resonant absorption. *Nat. Commun.* 8, 29 (2017).
- Glownia, J. M. et al. Self-referenced coherent diffraction X-ray movie of angstrom and femtosecond-scale atomic motion. *Phys. Rev. Lett.* 117, 153003 (2016).
- Gorkhover, T. et al. Femtosecond and nanometer visualization of structural dynamics in superheated nanoparticles. *Nat. Photon.* 10, 93–97 (2016).
- Kumagai, Y. et al. Radiation-induced chemical dynamics in Ar clusters exposed to strong X-ray pulses. *Phys. Rev. Lett.* **120**, 223201 (2018).
- 10. Vinko, S. M. et al. Creation and diagnosis of a solid-density plasma with an X-ray free-electron laser. *Nature* **482**, 59–62 (2012).
- Chapman, H. N. et al. Femtosecond X-ray protein nanocrystallography. Nature 470, 73–77 (2011).
- Neutze, R., Wouts, R., Van der Spoel, D., Weckert, E. & Hajdu, J. Potential for biomolecular imaging with femtosecond X-ray pulses. *Nature* 406, 752–757 (2000).
- Lutman, A. A. et al. Fresh-slice multicolour X-ray free-electron lasers. Nat. Photon. 10, 745–750 (2016).
- Liekhus-Schmaltz, C. E. et al. Ultrafast isomerization initiated by X-ray core ionization. *Nat. Commun.* 6, 8199 (2015).
- Picon, A. et al. Hetero-site-specific ultrafast intramolecular dynamics. *Nat. Commun.* 7, 11652 (2016).

- Mucke, M. et al. Covariance mapping of two-photon double core hole states in C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> produced by an X-ray free electron laser. *New J. Phys.* 17, 073002 (2015).
- 17. Murphy, B. F. et al. Femtosecond X-ray-induced explosion of  $C_{60}$  at extreme intensity. *Nat. Commun.* 5, 4281 (2014).
- Jurek, Z., Son, S.-K., Ziaja, B. & Santra, R. XMDYN and XATOM: versatile simulation tools for quantitative modeling of X-ray free-electron laser induced dynamics of matter. J. Appl. Cryst. 49, 1048 (2016).
- Schnorr, K. et al. Electron rearrangement dynamics in dissociating I<sub>2</sub><sup>n+</sup> molecules accessed by extreme ultraviolet pump-probe experiments. *Phys. Rev. Lett.* 113, 073001 (2014).
- Berrah, N. et al. Emerging photon technologies for probing ultrafast molecular dynamics. *Faraday Discuss.* 171, 471–485 (2014).
- Zdenek, S. & Eiji, O. Average bond dissociation energies of fullerene. Fuller. Sci. Technol. 5, 167–175 (1997).
- Boyle, M., Laarmann, T., Shchatsinin, I., Schulz, C. P. & Hertel, I. V. Fragmentation dynamics of fullerenes in intense femtosecond-laser fields: loss of small neutral fragments on a picosecond time scale. *J. Chem. Phys.* **122**, 181103 (2005).
- Lebeault, M.-A. et al. Decay of C<sub>60</sub> by delayed ionization and C2 emission: experiment and statistical modeling of kinetic energy release. *J. Chem. Phys.* 137, 054312 (2012).
- Erk, B. et al. Imaging charge transfer in iodomethane upon X-ray photoabsorption. Science 345, 288–291 (2014).
- Erk, B. et al. Inner-shell multiple ionization of polyatomic molecules with an intense X-ray free-electron laser studied by coincident ion momentum imaging. J. Phys. B 46, 164031 (2013).
- Podjarny, A. et al. X-ray crystallography at subatomic resolution. *Europhys.* News 33, 113–117 (2002).
- 27. Luo, Y. R. Comprehensive Handbook of Chemical Bond Energies (CRC Press, 2007).

# Acknowledgements

This work was funded by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy, grant nos. DE-SC0012376 (N.B., R.O. and H.X.) and DE-FG02-86ER13491 (D.R.). Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under contract no. DE-AC02-76SF00515. We thank the Knut and Alice Wallenberg Foundation and the Swedish Research Council for support. This work was supported in part by the Hamburg Centre for Ultrafast Imaging centre of excellence of the Deutsche Forschungsgemeinschaft, EXC 1074, project ID 194651731 (Z.J., K.T., S.-K.S. and R.S.). A.S.-G. was funded by the Science and Technolgy Facilities Council (STFC). K.M., H.F. and K.U. acknowledge support by XFEL priority strategy program of MEXT. K.U. and H.F. acknowledge support by the Five-Star Alliance of the Network Joint Research Center of Materials and Devices, and by the TAGEN project. We thank A. LaForge for helpful discussions.

# Author contributions

A.S.-G. and Z.J. contributed equally to this work. N.B. conceived and coordinated the project. N.B., Z.J. and R.S. wrote the paper with contributions from all the authors. R.O. and H.X. developed and tested the C<sub>60</sub> source before the experiment, and R.O., H.X. and T.J.A.W. maintained the source during the experiment. R.J.S. and R.F. designed the spectrometer. A.L. prepared the two pulses for the X-ray pump-probe scheme. T.O., R.O., R.J.S., H.X. and R.F. prepared the experiment. T.O., J.C., A.S.-G., H.X., R.O., R.J.S., A.L., L.F., T.B., J.D.B., T.J.A.W., D.R., R.C., K.S., S.A., N.N., R.F., K.U., K.M., J.P.M., C.P.S., T.P., H.F. and N.B. carried out the experiment. Z.J., S.-K.S., K.T. and R.S. performed the theoretical work. A.S.-G., R.O., T.B., T.J.A.W. and L.J.F. contributed to the experimental data analysis.

#### **Competing interests**

The authors declare no competing interests.

# **Additional information**

Supplementary information is available for this paper at https://doi.org/10.1038/ s41567-019-0665-7.

Correspondence and requests for materials should be addressed to N.B.

**Peer review information** *Nature Physics* thanks Carl Caleman and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2019

# ARTICLES

#### Methods

Experiment. The measurement of the ions resulting from the ionization and fragmentation dynamics of C60 under X-ray exposure was performed using a magnetic bottle spectrometer<sup>16</sup> operated as a TOF attached to the LAMP instrument<sup>28</sup> at the LCLS Atomic, Molecular and Optical Physics (AMO) hutch. Since the method is described elsewhere<sup>17</sup>, our description here is brief. The C<sub>60</sub> sample was produced via a collimated molecular beam using an evaporative oven and the introduction of gas-phase C60 into the vacuum chamber. The oven was resistively heated and had a nozzle with diameter of 1 mm and a skimmer with diameter of 0.5 mm through which the  $C_{60}$  molecules entered the interaction region. The oven was heated to ~700-800 K and a dump cooled by liquid nitrogen opposite the skimmer captured the residual target after it passed through the interaction region<sup>17</sup>. X-ray optics focused the incoming 640 eV X-ray pulses with a combined pulse energy of 0.77 mJ, shared 45%/55% between the 20 fs pump and the 10 fs probe pulses, for a pump peak intensity of  $4 \times 10^{15}$  W cm<sup>-2</sup> (derived using Ar calibration measurements compared to modelling) and a focal area of  ${\sim}400\,\mu\text{m}^2.$  The magnetic bottle spectrometer, which was used as an ion TOF, consisted of a 2-m-long ion drift path providing high ion mass-to-charge and KE resolutions. The two X-ray pulses were created in the electron accelerator using the fresh-temporal slices technique<sup>13</sup>. In this procedure, two slices of one electron bunch that lase independently in separate undulators are used to introduce a delay between them through a magnetic chicane13.

The pulse energies of the two beams, the centroid photon energy and the 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 fluences (volume-integrated signal), with a peak X-ray fluence only at the centre of the focus. To model the interaction region, the X-ray spatial fluence distribution was calibrated using ion yields from Ar, which has well understood sequential multiphoton ionization behaviour<sup>20</sup>. This spatial fluence distribution was then applied in the modelling of the X-ray interaction with  $C_{60}$  to account for low- and high-fluence regions, allowing quantitative comparison of theoretical predictions with the experimental data.

Determination of KE from the TOF spectra. The KE of the C ion charge state distributions is determined from the TOF profiles obtained for all of the X-ray pump-probe delay events. These data display the TOF shapes used to retrieve the KE distribution for all delay times. Simulations of the spectrometer were carried out using ion trajectory simulation software (SIMION v. 7.028) to determine the optimal positions of the lens elements and the corresponding voltages needed for effective ion collection. In SIMION, each fragment ion flies from an interaction volume defined by the molecular beam and the photon focal volume. All fragments flew with randomized direction into  $4\pi$  solid angles within KEs ranging between 0 and 200 eV. Their trajectories were traced until they hit the detector. To translate the ion TOF simulation to the real data, factors such as transmission loss, acceptance angle and focal volume need to be incorporated. These factors have strong dependence on the TOF signal shape given a certain ion KE. Previously<sup>17</sup>, the effect of transmission loss was considered by assuming an isotropic ion distribution in the Coulomb explosion. However, due to lower photon beam fluence in the current experiment compared with the experiment by Murphy et al.<sup>17</sup>, such an assumption is no longer valid. Thus, to take all of these factors into account, the spectrometer transfer function, H, is calculated from the SIMION v. 7.0<sup>28</sup> simulation to model the relationship

#### t = HK

where *t* is the TOF of a particular ion species and *K* is the KE. *K* is a column matrix of size  $n \times 1$  with *n* ranging from 0 to 200 eV at intervals of 1 eV. The simulation is performed for 1,000 ion species for each *K* to obtain the TOF information. Thus, a transfer matrix *H* of size 1,000 × 201 is constructed. To obtain the KE of the fragments in the experiment for a given TOF, the pseudoinverse (Moore–Penrose inverse) of *H* can be computed<sup>30</sup>. However, to avoid rank deficiency and overfitting of the data, we performed Tikhonov regularization<sup>31</sup> of the form

$$K = (H^{T}H + \lambda I)^{-1}H^{T}t$$

where  $\lambda$  is the regularization parameter, T is the transpose of H and I is the identity matrix. The regularization parameter ensures that the data are not overfitted during the minimization process. According to the simulations, light ions with low KE are collected with near 100% efficiency, while the transmission declines for more energetic ions within each ion species, as shown in Supplementary Fig. 7. Note that the transmission decreases faster for C<sup>1+</sup> than for the other ions.

**Spatial pulse intensity profile and volume integration.** An unavoidable feature of high-intensity measurements on molecules is that the detected signal accumulates contributions from a wide range of spatial regions across the intensity profile of the beam, meaning a range of fluences is sampled rather than a single fluence value.

This makes the interpretation of measured signals more difficult and can smear some features. For a comparison between experimental and theoretical data, one has to perform the same spatial accumulation (called 'volume integration') on the calculated results. To do that, the spatial intensity profile, averaged over many FEL pulses, has to be known. In our experiment we characterized the averaged spatial profile using Ar ion charge-state distributions measured under the same experimental conditions. We fitted the pulse profile parameters using the single-pulse data with the newly developed tool XCALIB Rev. 2646<sup>32</sup>. This methodology is similar to what was applied in previous work<sup>17</sup>, but with automated optimization. A single Gaussian spatial beam profile was used in the volume integration, and we assumed perfect overlap between the pump and probe pulses when evaluating the theoretical volume-integrated spectra. The temporal profile of the X-ray pulse (intensity) was also assumed to be Gaussian.

Fragmentation modelling. For the simulations, we employed an extended version9 of the tool XMDYN18, which is a code for modelling the dynamics of matter exposed to high-intensity X-ray radiation. In brief, it tracks the ionization dynamics using a Monte Carlo scheme, while the real-space dynamics of the particles are computed using the classical molecular dynamics technique. The atoms of the originally neutral sample are described as classical particles interacting via fullerene-specific (Brenner) classical force fields<sup>17</sup>. The bound electrons are assigned to atomic orbitals of the atomic sites (disregarding molecular states). The stochastic ionization induces changes of the occupation numbers of these orbitals, which are tracked in time. Probabilities of photoionization, Auger and fluorescent events for a discrete time step are calculated from atomic crosssection and rate data supplied by the ab initio tool XATOM Rev. 158218. Ionized electrons are also treated as classical particles. All charged particles interact via Coulomb forces. Bond breaking is treated as in Murphy et al.17. Other than the inner-shell photoionization processes, the model also contains collisional ionization and recombination. A new extension has been applied for describing valence-to-valence electron transfer between atomic sites, based on an over-thebarrier ionization picture9,29, which replaced the 'molecular description' of the Auger process that was used to redistribute accumulated charge among neighbours at an Auger decay event17.

We applied a multi-time-step position Verlet algorithm with 64 small steps in a 50-as-long step. Trajectories were computed up to 3 ps after the pulse. The volume-integrated signals were calculated based on spectra for 10 different fluence values, calculating 200 realizations for each fluence value to sample the stochastic ionization dynamics. A single Gaussian spatial beam profile was used in the volume integration. The temporal profile of the X-ray pulse (intensity) was also assumed to be Gaussian.

Accuracy of the applied force fields for highly excited  $C_{60}$ . We have compared the applied Brenner force fields in our work to a tight-binding model<sup>33</sup> in terms of fragmentation for vibronically highly excited  $C_{60}$ . In ref. <sup>33</sup>, the fragmentation of neutral  $C_{60}$  was investigated by assuming that it has an initially perfect buckyball geometry and that a different amount of total KE is distributed among the site according to thermal equilibrium. We found a good comparison between the fragment distributions extracted from the two models. We used 300 eV and 400 eV excitation energies because they surround the value of  $350 \,\text{eV}$ , the electrostatic potential energy for  $C_{60}^{-13+}$  that drives the fragmentation. Supplementary Fig. 8 shows the good comparison between our work and the work from ref. <sup>33</sup>. Thus, the applicability of the applied force fields under the conditions in this study is not only validated through our experiments but also with another computational method.

Bond dissociation energies of  $C_{60}$  and some organic molecules. We compare here the bond energies of  $C_{60}$  with those of some biologically relevant organic molecules, such as alanine dipeptide, based on the literature. A typical C–N amide bond (peptide bonds belong to this class of bonds) has dissociation energies in the range of 3 to 4 eV, while the C–C bonds in  $C_{60}$  have an average bond dissociation energy of 4.6 eV (ref.<sup>21</sup>, we introduced the C–C bond dissociation energy in the main text).

Furthermore, the C–N bond dissociation energies for various systems are<sup>27</sup> 4.28 eV for methyl isocyanide (CH<sub>3</sub>–NC), 4.28 eV for ethyl isocyanide (C<sub>2</sub>H<sub>5</sub>–NC) and 4.37 eV for *N*-methylacetamide (H<sub>3</sub>C(O)–NHCH<sub>3</sub>). We can thus conclude that the bond energy is about 4.3 eV. We also note that in alanine dipeptide, the equilibrium distance between the C and N atoms within a peptide bond is quite short<sup>34</sup>.

We conclude that the characteristic energies holding  $C_{60}$  together are similar to the dissociation energies associated with peptide bonds.

Hard X-ray imaging of a macromolecule. We compare our results to established serial femtosecond crystallography experiments with hard X-ray light, using a pump fluence that creates an equivalent degree of ionization to that encountered in those short-pulse experiments. We explain our reasoning by describing the relationship between the ionization state of a carbon bulk system (for example, a protein crystal) by the end of a ~10 fs hard X-ray imaging pulse and the state reached during the current C<sub>60</sub> experiment after the pump pulse.

A common set-up in serial femtosecond crystallography is to use 1 mJ XFEL imaging pulses of 10 keV photons, focused down to 1  $\mu$ m<sup>2</sup>, such that a peak fluence

# **NATURE PHYSICS**



of  $F = 5.5 \times 10^{11}$  photons  $\mu$ m<sup>-2</sup> is reached. The fraction of atoms photoionized during a pulse is  $1 - \exp(-\sigma F) \approx 0.002$ , where  $\sigma$  is the photoionization crosssection  $(41 \times 10^{-24} \text{ cm}^2)$  of carbon at the photon energy 10 keV. One photoelectron of 10 keV loses its energy due to collisional ionization within approximately 100 fs, therefore with the rate of 100 eV fs<sup>-1</sup> (ref. <sup>35</sup>). Shortly after most of the photoionization events, a ~250 eV Auger electron is also released and is assumed to promptly distribute its energy via collisional ionization. According to Ziaje at al.<sup>35</sup>, ~13.5 eV energy is needed on average to create a secondary electron. Therefore, in the case of T = 10 fs pulse duration, the average charge state per atom reached by the end of the pulse is:

 $[(1 - exp(-\sigma F)] \times (250 \text{ eV} + 100 \text{ eV} \text{ fs} \times 10 \text{ fs})/13.5 \text{ eV} \approx 0.21$ 

This value is approximately equal to the final average carbon charge observed in the present experiment,  $13/60 \approx 0.22$ , achieved because of the pump pulse. This state is only transiently present for an imaging experiment, but in our spectroscopy experiment this is the final ionization state existing over an extended time period, allowing more detailed information on the ionization dynamics to be extracted, as it was in this work.

In single-molecule imaging experiments, the targeted fluence regime requires  $\sim$ 100 nm focusing (which is not the case in this study), when photoionization alone ionizes  $\sim$ 20% of all atoms, leading to ionization of all atoms in the sample via the secondary ionization processes. Under such conditions, chemical phenomena disappear in the system and plasma dynamics becomes predominant.

#### Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

## Code availability

The released version of the software underlying the findings of this study is available from Z.J. and R.S (at xraypac@mail.desy.de). and more information is available at http://www.desy.de/~xraypac.

#### References

- Osipov, T. et al. The LAMP instrument at the Linac Coherent Light Source Free-Electron Laser. *Rev. Sci. Instrum.* 89, 035112 (2018).
- 29. Motomura, K. et al. Sequential multiphoton multiple ionization of atomic argon and xenon irradiated by X-ray free-electron laser pulses from SACLA. *J. Phys. B* **46**, 164024 (2013).
- 30. Greville, T. N. E. The pseudoinverse of a rectangular or singular matrix and its application to the solution of systems of linear equations. *SIAM Rev.* **1**, 38–43 (1959).
- 31. Tikhonov, A. & Arsenin, V. Solutions of Ill-Posed Problems (V. H. Winston and Sons, 1977).
- Toyota, K. et al. XCALIB: a focal spot calibrator for intense X-ray freeelectron laser pulses based on the charge state distributions of light atoms. *J. Synchrotron Radiat.* 26, 1017–1030 (2019).
- Horváth, L. & Beu, T. Tight-binding molecular dynamics simulations of radiation-induced fragmentation of C<sub>60</sub>. *Phys. Rev. B* 77, 075102 (2008).
- Sushko, G. B. et al. Studying chemical reactions in biological systems with MBN Explorer: implementation of molecular mechanics with dynamical topology. *Eur. Phys. J. D.* **70**, 12 (2016).
- 35. Ziaja, B. et al. Towards realistic simulations of macromolecules irradiated under the conditions of coherent diffraction imaging with an X-ray free-electron laser. *Photonics* **2**, 256–269 (2015).