Ultrafast dynamics of a nucleobase analogue illuminated by an ultrashort intense X-ray pulse of SACLA

The advent of X-ray Free Electron Lasers (XFELs) has opened new avenues in research fields such as the dynamic imaging of matter. X-ray time-resolved study on the time scale of femtoseconds allows us to monitor, for the first time, atoms and electrons in action. X-ray single-shot imaging of non-crystallized nanometer-size objects, such as bio-macromolecules, has been transformed from a remote goal into a tangible reality. A fundamental issue connecting these two realms of XFEL-based research is radiation damage. The amount of energy deposited in a target by a single XFEL pulse is sufficiently high to cause its total destruction. A question to be answered from the viewpoint of structural imaging is whether the time scale of these changes is sufficiently slow for the collected data to capture structural information about the original object. Our present study addresses this question.

The experimental approach we are taking is the three-dimensional momentum correlation measurement of the atomic ions emitted via the Coulomb explosion of a molecule, called Coulomb Explosion Momentum Imaging (CEMI). We expect that highly charged ions will be created by an intense XFEL pulse in the femtosecond time scale [1] and that detailed information of the Coulomb explosion can be extracted from the CEMI data [2]. We have illuminated an iodine-containing nucleobase analogue (5-iodouracil) by an ultrashort (10 fs) high-intensity X-ray pulse of SACLA. The CEMI data were simulated on the basis of theoretical models to analyze the ultrafast radiation damage to I-containing molecules [3,4].

We conducted the experiments at experimental hutch 3 (EH3) at SACLA **BL3** [5]. The XFEL beam with a photon energy of 5.5 keV was focused by a Kirkpatrick-Baez (KB) mirror system onto a molecular beam of 5-iodouracil in an ultrahigh-vacuum reaction chamber. The focus size was ~1 μm (FWHM) and the resulting peak fluence was 26 μJ/μm^2. We detected ionic fragments using a recoil-ion momentum spectrometer and determined the three-dimensional momentum of each fragment ion. We evaluated the kinetic energy distributions, two-body momentum correlations and three-body momentum correlations of fragment ions. We found that the dynamics of charge build-up, charge redistribution and early-stage fragmentation leaves an imprint on the final momentum vectors of the fragment ions [3].

Representative results of two-body momentum correlations are shown in Fig. 1. We denote the distributions of cos(θ) between the momenta of various ejected ion pairs as SP$_2$(A; B), where the cosine of the angle θ between the momenta of the two ionic fragments A and B is given by cos(θ) = $\overrightarrow{P_A}\cdot\overrightarrow{P_B}/|\overrightarrow{P_A}||\overrightarrow{P_B}|$. The observed maxima in the SP$_2$(I^{q+}; H$^+$), SP$_2$(I^{q+}; O$^+$) and SP$_2$(I^{q+}; N$^+$) distributions correspond to the geometric structure of 5-iodouracil, whereas the maxima in the SP$_2$(I^{q+}; C$^+$) distribution do not correspond to the molecular structure. These differences result from the dissociation dynamics in 5-iodouracil after the illumination with the XFEL pulse.

We carried out numerical calculations at two different levels in order to understand how the XFEL-illuminated molecule breaks. In the first approach, we adopted a Coulomb explosion model with charge evolution (CCE-CE model), where only the Coulomb repulsions between the ions were taken into account [3,4]. We introduced two effects of charge dynamics into the classical Coulomb explosion model: the build-up of molecular charge with time owing to the multiple XFEL ionization and the charge redistribution that occurs among atoms. We evaluated the momentum correlations of fragment ions emitted from 5-iodouracil, as depicted by red lines in Fig. 1. We found good agreement with the experimental results when we chose specific time scales of charge build-up in the molecule (~10 fs) and of charge redistribution over the molecule (~2 fs).

As the second approach, we employed a semi-

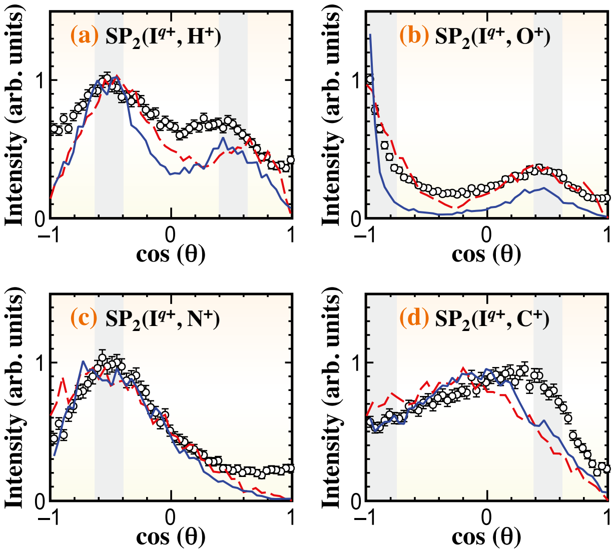

Fig. 1. Distribution of the normalized scalar product of momentum vectors, SP$_2$(A,B), as a function of cos(θ) = $\overrightarrow{P_A}\cdot\overrightarrow{P_B}/|\overrightarrow{P_A}||\overrightarrow{P_B}|$, displayed for fragment ion pairs **(a)** I^{q+} -H$^+$, **(b)** I^{q+} -O$^+$, **(c)** I^{q+} -N$^+$ and **(d)** I^{q+} -C$^+$. Gray shaded areas indicate the equilibrium angles between atoms in 5-iodouracil. The open circles, red dashed lines and blue lines are the experimental data, CCE-CE results and SCC-DFTB results, respectively. [4]

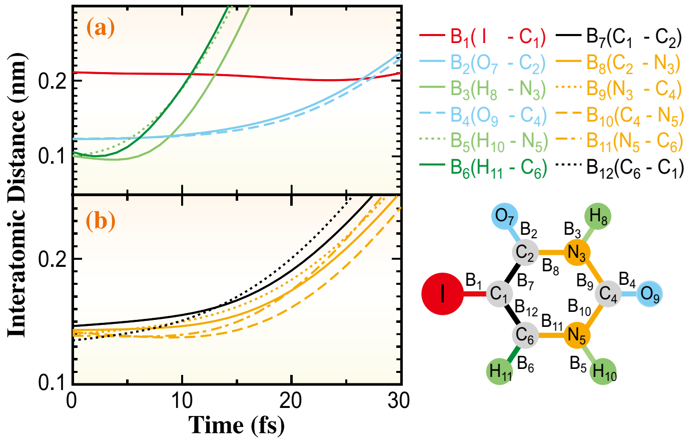

Fig. 2. Time evolution of interatomic distances in 5-iodouracil obtained by CCE-CE calculations. **(a)** Interatomic distance of I-C (red line), O-C (sky-blue lines), H-C (dark-green line), and H-N (light-green lines) pairs. **(b)** Interatomic distance of C-C (black lines) and C-N (orange lines) pairs. [4]

empirical method in which the forces on atoms were calculated by the self-consistent-charge density-functional-based tight-binding (SCC-DFTB) method [4]. Chemical bonds are explicitly taken into account in the SCC-DFTB method, unlike in the CCE-CE model. In the SCC-DFTB approach, bond dissociation processes are triggered by the excess vibrational energy injected into molecules during the Auger cascades as well as Coulomb repulsion. We introduced an electronic temperature T_e in order to reflect electronic excitation and charge redistribution, i.e., the contribution from various excited electronic states. The results of SCC-DFTB simulations are given by blue lines in Fig. 1. Good agreement with the experimental results was obtained by incorporating the effects of vibrational and electronic excitation on XFEL-induced multiple ionization into the SCC-DFTB approach. We clarified why two apparently contradictory approaches, namely, the CCE-CE model and the SCC-DFTB approach, function well by analyzing the SCC-DFTB results.

Based on the success of the numerical calculations, we deduced the temporal changes in interatomic distances as shown in Fig. 2. CCE-CE calculations revealed that the H-C and H-N distances increase by 50–100% from the initial lengths at $t = 10$ fs, whereas the changes in the C-O, C-N and C-C distances are less than several percent. The SCC-DFTB approach also reproduced the ultrafast ejection of H^+. The results of our simulations clearly indicate that the ultrashort escape time of hydrogen ions, which is comparable to the pulse width of the XFEL, makes their escape sensitive to the intramolecular charge dynamics and its time scale. In contrast, the I-C length of 5-iodouracil does not change in 30 fs, which is presumably due to the large iodine mass as well as the fact that the carbon atom adjacent to the I atom is surrounded by three heavy atoms (iodine and two carbons).

In summary, we investigated the radiation damage of the 5-iodouracil molecule illuminated by an X-ray pulse of SACLA and well reproduced the obtained experimental results of CEMI by using two different theoretical approaches. The consistency among the theoretical approaches and the experimental results deepened our understanding of the mechanism of XFEL-induced Coulomb explosion. The present results, obtained for a realistic biologically relevant molecule, give an important indication that, if sufficiently short XFEL pulses are used, the single-shot coherent diffraction imaging approach will enable the interrogation of target samples of single bio-macromolecules.

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