Femtosecond charge and molecular dynamics of I-containing organic molecules induced by intense X-ray free-electron laser pulses†


Received 19th April 2016, Accepted 27th May 2016
DOI: 10.1039/c6fd00085a

We studied the electronic and nuclear dynamics of I-containing organic molecules induced by intense hard X-ray pulses at the XFEL facility SACLA in Japan. The interaction with the intense XFEL pulse causes absorption of multiple X-ray photons by the iodine atom, which results in the creation of many electronic vacancies (positive

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6fd00085a
charges) via the sequential electronic relaxation in the iodine, followed by intramolecular charge redistribution. In a previous study we investigated the subsequent fragmentation by Coulomb explosion of the simplest I-substituted hydrocarbon, iodomethane (CH₃I). We carried out three-dimensional momentum correlation measurements of the atomic ions created via Coulomb explosion of the molecule and found that a classical Coulomb explosion model including charge evolution (CCE-CE model), which accounts for the concerted dynamics of nuclear motion and charge creation/charge redistribution, reproduces well the observed momentum correlation maps of fragment ions emitted after XFEL irradiation. Then we extended the study to 5-iodouracil (C₄H₃IN₂O₂, 5-IU), which is a more complex molecule of biological relevance, and confirmed that, in both CH₃I and 5-IU, the charge build-up takes about 10 fs, while the charge is redistributed among atoms within only a few fs. We also adopted a self-consistent charge density-functional based tight-binding (SCC-DFTB) method to treat the fragmentations of highly charged 5-IU ions created by XFEL pulses. Our SCC-DFTB modeling reproduces well the experimental and CCE-CE results. We have also investigated the influence of the nuclear dynamics on the charge redistribution (charge transfer) using nonadiabatic quantum-mechanical molecular dynamics (NAQMD) simulation. The time scale of the charge transfer from the iodine atomic site to the uracil ring induced by nuclear motion turned out to be only ~5 fs, indicating that, besides the molecular Auger decay in which molecular orbitals delocalized over the iodine site and the uracil ring are involved, the nuclear dynamics also play a role for ultrafast charge redistribution. The present study illustrates that the CCE-CE model as well as the SCC-DFTB method can be used for reconstructing the positions of atoms in motion, in combination with the momentum correlation measurement of the atomic ions created via XFEL-induced Coulomb explosion of molecules.

1. Introduction

X-ray free-electron lasers (XFELs)¹⁻³ provide extremely intense femtosecond X-ray pulses that promise direct observations of atoms in action during various types of reactions.⁴⁻⁸ Creating such “molecular movies” of atomic motions is indeed a grand challenge of femtochemistry.⁹⁻¹¹ X-ray scattering experiments on gas-phase reactions with XFELs are, however, still very challenging, though not impossible.¹²⁻¹³ An alternative approach, photoelectron diffraction combined with the XFEL pulses, was suggested for visualizing the atomic motion in gas-phase intramolecular reactions¹⁴,¹⁵ and proof-of-principle experiments were carried out.¹⁶⁻¹⁸

Another promising approach for probing atoms in action is the three-dimensional momentum correlation measurement for the atomic ions created via Coulomb explosion of the molecule,¹⁹⁻²¹ called Coulomb Explosion Momentum Imaging (CEMI) throughout the present paper. In CEMI, the ultrafast creation of highly charged ions is the key for monitoring the dynamics of intermediate states. Intense XFEL pulses create extremely highly charged ions on the femtosecond time scale by multiple inner-shell ionization²²⁻²⁴ and are thus also expected to realize femtosecond time-resolved CEMI. For small molecules containing a heavy atom, CEMI by inner-shell X-ray absorption provides insight into the interplay of electron and ion/atom dynamics relevant to radiation damage at the atomic scale.²⁵⁻²⁹ As an example, Erk et al. studied the ionization...
and fragmentation of methylselenol (CH$_3$SeH) molecules by intense (>10$^{17}$ W cm$^{-2}$), 5 fs X-ray pulses (~2 keV) with CEMI. They found signatures of ultrafast charge redistribution from the inner-shell ionized Se atom to other atoms and noted significant displacements of atoms in the course of multiple ionization. Later, they extended the CEMI technique to probe laser-induced photodissociation of CH$_3$I and I$_2$.

Recent calculations of the double hole state of glycine (NH$_2$CH$_2$COOH), created after K-shell ionization and subsequent Auger decay, revealed that the double hole is transferred within 3 to 4 fs between the two functional end groups of the glycine molecule, driven solely by specific nuclear displacements and non-Born–Oppenheimer effects. The calculations also showed that the concurrent valence electron redistribution caused by nuclear dynamics is much faster than previously anticipated. It was noted that the non-Born–Oppenheimer effects affect the apparent electron densities and are thus relevant for X-ray imaging experiments, in which the ionization of inner atomic shells is unavoidable.

We have ourselves studied, by CEMI, the charge and molecular dynamics in I-containing organic molecules induced by intense XFEL pulses delivered from the hard X-ray FEL facility SACLA in Japan. In a first study we investigated the charge redistribution and fragmentation in the simplest I-substituted hydrocarbon, iodomethane (CH$_3$I), using very short (~10 fs) and intense XFEL pulses. We also simulated the momentum correlations of fragment ions emitted after XFEL irradiation by adopting a Coulomb explosion model, where only the Coulomb repulsions between charged atoms (ions) are the forces in a classical molecular dynamics (MD) simulation and there are no forces to form chemical bonds. The charge of a molecule builds up in time owing to the multiple XFEL ionization and charge redistribution occurs among atoms. These two effects are introduced into the classical Coulomb explosion model by their characteristic time constants. The present model, which accounts for the concerted dynamics between nuclear motion and charge build-up/charge redistribution, may be called the classical Coulomb explosion model with charge evolution (CCE-CE model). Fitting the simulation results to the experimental data, we were able to estimate the specific time scales of charge build-up in the molecule (~9 fs) and of charge redistribution over the molecule (~3 fs).

To deepen the understanding of the charge build-up, charge redistribution and fragmentation processes induced by XFEL pulses in more complex systems, we have extended our CEMI study to 5-iodouracil C$_4$H$_3$IN$_2$O$_2$ (5-IU). The kinetic energy distributions as well as the momentum correlations of fragments are derived from the observed momentum vectors of each fragment ion. Comparing the simulation results obtained by the CCE-CE model with the experimental data, we discussed the electronic and nuclear dynamics of 5-IU under XFEL irradiation and confirmed that the charge build-up takes ~10 fs, while the charge redistributes from the I atom to the other atoms and localizes in a couple of fs. We found that within the 10 fs XFEL pulse duration, the C–H bonds are significantly elongated, say, by a factor of two or more, but the other bonds are elongated only up to 5 to 10%.

In the present paper we review the above experimental and CCE-CE model studies, but also present new numerical simulations for 5-IU obtained by a higher-level approach and discuss what is behind the validity of the CCE-CE model. The employed approach is a semi-empirical one in which the forces on
atoms are calculated by the self-consistent charge density-functional based tight-binding (SCC-DFTB) method. Chemical bonds are explicitly taken into account in the SCC-DFTB approach, unlike in the case of the CCE-CE model. The SCC-DFTB approach has been applied to simulate the fragmentation of C$_{60}$ (ref. 32) and of its highly charged cations such as C$_{60}^{60+}$. This approach has been also used to simulate the dissociation processes of doubly-ionized thiophene (C$_4$H$_4$S) molecules triggered by X-ray photoionization from the 2p core level of the S atom. In this paper, we present the results of SCC-DFTB simulations for 5-IU. Good agreement with the experimental results was obtained by incorporating the effects of vibrational and electronic excitation upon XFEL-induced multiple ionization into the SCC-DFTB approach. Another approach we employed to evaluate the contribution of molecular dynamics to the charge dynamics is a molecular dynamics (MD) simulation based on a first-principles electronically nonadiabatic quantum-mechanical (NAQ) method, abbreviated as the NAQMD approach. We carried out NAQMD simulations for a high charge state of 5-IU to investigate the charge transfer dynamics in this molecule exposed to an XFEL pulse. The CCE-CE model deals with the charge redistribution in a molecule phenomenologically, assuming that it occurs, for example, as a result of molecular Auger decay in the later stage of the Auger cascades. The NAQMD approach, on the other hand, can simulate the electronic dynamics induced by the nuclear motion that occurs after the Auger decay, in real-time and real-space. The time scale of intramolecular charge transfer for 5-IU, estimated from the NAQMD simulation, was $\sim$5 fs, elucidating that nuclear dynamics play also a significant role in the ultrafast charge redistribution. These two approaches at the higher levels show that the CCE-CE model captures well the essential features of Coulomb explosion in a pragmatic way. The consistency between the experiment and all these computational approaches validates our understanding of the electronic and nuclear dynamics in Coulomb explosion under XFEL irradiation of sample molecules. The present study thus demonstrates that the CCE-CE model as well as the SCC-DFTB approach, combined with the experimental CEMI technique, can be used for the characterization of ultrafast dynamics of the molecular samples and provide a solid basis for time-resolved CEMI with XFEL.

In the following section, the experimental methods, as well as the CCE-CE, SCC-DFTB and NAQMD simulations are described. The results for all these methods are presented in Section 3 and the motions of individual atoms extracted from CCE-CE model simulations as well as the advantages and disadvantages of each theoretical approach are discussed in Section 4. Section 5 is the Conclusion.

2. Methods

2.1. Experimental

The experiments for CH$_3$I and 5-IU have been carried out at experimental hutch 3 of beam line 3 of SACLA, where the XFEL beam is focused by a Kirkpatrick–Baez (KB) mirror system to a focal spot of $\sim$1 $\mu$m FWHM in diameter. The photon energy was set at 5.5 keV, corresponding to the energy above the L-absorption edge of the iodine atom. The repetition rate of the XFEL pulses was 10 Hz. The temporal FWHM of the pulse was estimated to be $\sim$10 fs. The pulse energies were measured by the beam-position monitor located upstream of the beam line. The relative X-ray pulse energy passing through the interaction point was
also measured shot-to-shot by a p–intrinsic–n photodiode. The shot-to-shot pulse energy fluctuation was \( \sim 7\% \) (14\% FWHM), and the peak fluence was 26 \( \mu \)J \( \mu \)m\(^{-2}\) on average. The absolute value of the peak fluence was determined just after the experiment via the calibration using Ar.\(^{24}\)

The CH\(_3\)I (>99.5\%) reagent was purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. The CH\(_3\)I sample was provided as a liquid and it was introduced to the focal point of the XFEL beam as a pulsed supersonic gas jet seeded in helium gas. 5-IU (>99.0\%) was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. The 5-IU sample was heated up to 190 \( ^\circ \)C in the reservoir with a modified electromagnetic solenoid valve,\(^{39}\) and the resulting sample vapor was seeded in helium gas.

The molecular beam was crossed with the focused XFEL beam at the reaction point, and the emitted ions were projected onto a microchannel plate (MCP) in front of a delay-line anode. The three dimensional momentum vectors of the emitted ions were determined by using both the arrival time and the position of each ion. A three-layer type delay-line anode (Roentdek HEX80) was employed to minimize the detection dead time.\(^{40}\) The design of the ion spectrometer used was basically the same as the one described in ref. 41 but the electrodes were modified to extract high energy ions from the reaction point.\(^{29}\) The maximum acceptable kinetic energy was \( \sim 80\, q \) eV for a multiply charged ion with charge \( q \).

In the 5-IU experiments, the CEMI data have been recorded for \( 6.3 \times 10^6 \) XFEL shots, keeping the particle hit rate at less than 0.1 events per XFEL shot so that the false coincidences become negligible in the coincidence data analysis.

### 2.2. CCE-CE model simulations

We carried out CCE-CE simulations to translate the experimental results to spatiotemporal motion. The charge build-up induced by an XFEL pulse as well as the charge redistribution from the iodine atom to its counterparts (CH\(_3\) for iodomethane and C\(_4\)H\(_3\)N\(_2\)O\(_2\) for 5-IU, respectively) have been taken into account in the CCE-CE model.\(^{28}\) Briefly, several photons were absorbed within the XFEL pulse duration (\( \sim 10 \) fs) by the deep atomic inner shells of iodine in the present experiments. In parallel and partly also subsequently to the XFEL pulse, Auger cascades should be a dominant mechanism of charge multiplication which will generate charges at an exponentially decreasing rate. The multiplication process is modelled statistically by assuming that the total charge of a molecule (\( Q^\text{tot} \)) increases with time \( t \) as

\[
Q^\text{tot} = Q^\text{max} \left( 1 - \exp\left( -\frac{t}{\tau} \right) \right),
\]

where \( \tau \) is a charge build-up time constant and \( Q^\text{max} \) is the final charge. The charge redistribution from iodine to the rest of the molecule is represented by the rate constant \( R \) as

\[
\frac{dQ^{\text{Body}}[t]}{dt} = RdQ^{\text{I}}[t].
\]

here \( Q^{\text{I}}[t] \) and \( Q^{\text{Body}}[t] \) represent the charge of the iodine atom and of the rest of the molecule, respectively. Although the model itself is empirical and does not concern the physical mechanisms behind the charge redistribution, we note that it typically happens during the later stages of the Auger cascades that involve
molecular orbitals, not localized on the iodine atom. Nuclear dynamics after the Auger decay may further proceed the charge redistribution (charge transfer) as well, as will be discussed later. In the CCE-CE model, all these contributions are taken into account by a single parameter $R$.

For trajectory simulations of 5-IU by the CCE-CE model, we prepared ensembles of initial positions and velocities of the atoms in the parent molecule. The initial positions and velocities were sampled from MD trajectories at an effective temperature $T$ to provide an initial distribution that mimics the vibrational wavefunctions. The MD trajectories were obtained by performing quantum chemical calculations at the B3LYP/3-21G(d) level of theory using the GAMESS package. The classical Coulomb explosion model such as the CCE-CE model counts on the idea that the Coulomb explosion process may be modelled through simple classical trajectory calculations of point charges; i.e., the effect of chemical bonds in a molecule (e.g., 5-IU) may not practically play a significant role in the Coulomb explosion processes. We evaluated the Coulombic repulsive forces between ions for the trajectory calculations. We constructed kinetic energy distributions (KED) of ions, two-body angular correlations and three-body angular correlations among the momenta of fragment ions from the results of the CCE-CE model simulations averaged over the distribution of final charges $Q_{\text{max}}$ estimated from CH$_3$I experiments. The charge distribution peaked at $Q_{\text{max}} = 10$, ranging from +4 to +14. We scanned the parameter space of charge build-up time $\tau$, charge redistribution rate $R$ and temperature $T$ so that the results of the CCE-CE model simulations reproduce the experimental observations.

### 2.3. SCC-DFTB simulations

Another theoretical approach we developed is an adaptation of the self-consistent charge density-functional based tight-binding (SCC-DFTB) theory for electronic structure calculations. We applied it to on-the-fly classical trajectory calculations for the fragmentation dynamics of 5-IU ions. The density-functional based tight-binding (DFTB) method used to describe molecular structures or chemical bonds is computationally extremely fast and semiquantitatively reproduces the results of density functional theory (DFT). The DFTB method is based on the zeroth- or second-order expansion of the Kohn–Sham total energy with respect to electron density fluctuations. The second-order expansion is the SCC-DFTB method, where the charge distribution in a molecule is obtained in an iterative self-consistent manner by taking into account charge interactions between atoms. This method is applicable to systems where the charge balance between atoms is crucial, as for instance in biomolecules and other heteroatomic molecules. We carried out all DFTB calculations by using the DFTB+ program package (ver. 1.2.2). The adopted Slater–Koster files were parameter sets halorg-0-1 (ref. 46) and mio-1-1. The forces on atoms for the use in the MD simulations are calculated by SCC-DFTB; this MD simulation is abbreviated as SCC-DFTB/MD. The initial positions and velocities of atoms in a neutral molecule just before the interaction with an XFEL pulse are taken from an equilibrium ensemble sampled from SCC-DFTB/MD trajectories at temperature $T$.

Core ionization takes place in molecules exposed to X-ray radiation, followed by internal electronic relaxations such as Auger processes, which may occur in cascades in iodine-containing molecules. During core ionization and subsequent...
electronic relaxation processes, the molecule experiences different potential surfaces and is consequently heated. Part of the electronic energy is converted to vibrational energy. For instance, in the case of C60, a vibrational energy of 10–20 eV is deposited for each core ionization accompanied by an Auger process, which amounts to 5–10 eV on average per unit charge increase. In reference to these values, we infer the vibrational energy deposited in 5-IU that reproduces the experimental results. To incorporate the increasing process of vibrational energy into the SCC-DFTB approach, we employed a sequential ionization model\textsuperscript{32,48} where the molecule is vertically ionized from the \( q - 1 \) charge state to the \( q \) charge state when \( Q^{\text{tot}} \) in eqn (1) reaches a positive integer \( q \).

In the sequential ionization model, the momentum vector of atom \( i \) is instantaneously changed from \( \vec{p}_i \) to \( \vec{p}'_i \), when the charge of the molecule switches to the higher one:

\[
\vec{p}'_i = \vec{p}_i + \Delta \vec{p}_i
\]

where \( \Delta \vec{p}_i \) is a momentum added according to the acquired vibrational energy upon each ionization. We assume that the momentum \( \Delta \vec{p}_i \) is constructed from momenta parallel to the bond axes between atom \( i \) and its surrounding atoms, in line with the experimental observation that only bond stretching is induced by core ionization;\textsuperscript{49} the momentum \( \Delta \vec{p}_i \) that atom \( i \) receives is the composition of momentum vectors parallel to its bond axes. Various modifications can be made. We examined if the results of simulations depend on the types of energy injection significantly or not. For 5-IU, the vertical component of \( \Delta \vec{p}_i \) to the molecular plane, \( \Delta p_{i,\perp} \), vanishes on average over all trajectories. We also designed a scheme in which nonzero \( \Delta p_{i,\perp} \) are replaced by \( \Delta p_{i,\perp} = 0 \). We carried out simulations for the two cases of \( \Delta p_{i,\perp} = 0 \) and \( \Delta p_{i,\perp} \neq 0 \) and found that the choice of \( \Delta p_{i,\perp} = 0 \) leads to better results, as discussed later.

We prepare the momenta along bond axes following a one-dimensional Maxwell–Boltzmann distribution. The magnitudes of \( \Delta p_i \) are then scaled by a factor so that the total kinetic energy of atoms increases by an average vibrational energy that the molecule gains per unit charge increase. Denoting this quantity by \( \epsilon \), we can express the total kinetic energy added up to the final charge state of \( Q^{\text{max}} \) as

\[
\Delta E = Q^{\text{max}} \epsilon.
\]

In other words, we assume that the vibrational energy deposited in the molecule is more or less proportional to the final charge of the molecule. If the acquired vibrational energy \( \Delta E \) is larger than the atomization energy \( \Delta H_a \) of 5-IU (\(~80\) eV), the molecule is immediately decomposed into individual atoms. As \( \Delta E \) approaches \( \Delta H_a \), all atoms are separated so that vibrational energy is no longer accumulated upon further ionization. We therefore assume that the upper limit of \( \Delta E \) is around \( \Delta H_a \).

In the SCC-DFTB approach, charge redistribution in real time is ignored and it is assumed that the electronic state instantaneously relaxes to the ground electronic state or an electronic state distribution characterized by the electronic temperature \( T_e \) which represents the width of the Fermi–Dirac distribution. The
charge distribution is that in the ground electronic state or the relaxed electronic state distribution. We set $T_e$ here to be in the range from a few eV to several eV to include the effects of electronic excitation on the charge distribution. The value of $T_e$ should be as high as the energies of excited states. The energy of the first absorption band of 5-IU was experimentally determined to be 4.4 eV (280 nm). According to our TD-DFT calculation at the B3LYP/CEP-121G level of theory implemented in the Gaussian 09 program package, the transition energy to the absorption band was 4.5 eV. The optimal value of $T_e$ was slightly higher than these values, i.e., $\sim 6$ eV. A more detailed discussion about the range of $T_e$ will be given in Section 3.5 and 4. In the present simulations, $T_e$ was set to be constant for different charge states, once $T_e$ was determined as a parameter. The final output of the simulation results is the average over the distribution of $Q_{\text{max}}$ estimated from CH$_3$I experiments, as in the case of the CCE-CE model.

### 2.4. NAQMD simulations

In order to examine the charge redistribution dynamics or charge transfer induced by the nuclear dynamics in a highly charged parent ion, which is generated through Auger cascades initiated by XFEL irradiation, we performed NAQMD simulations that include the effects of nonadiabatic electronic transitions with a surface-hopping approach. The nuclei are treated classically in the adiabatic representation, i.e., the atomic forces at the current nuclear positions are calculated from the potential surfaces of ground and excited electronic eigenstates. The switching probability from the current adiabatic state to another is computed from the density-matrix elements obtained by solving the time-dependent Kohn–Sham (TDKS) equations, and the occurrence of nonadiabatic transitions between adiabatic states is determined stochastically, according to the switching probability. In the present treatment, the electron configuration representing the current electronic state does not switch with another one unless the molecular structure changes toward a region where surface hopping can occur. By using the above NAQMD, we can investigate the charge dynamics solely driven by nuclear motion. We have previously applied it to investigate charge transfer in several photo-excited organic molecules. In the present study, we extend the method to the charge dynamics in 5-IU molecular ions with many holes.

### 3. Results

#### 3.1. Experimental results for CH$_3$I

Fig. 1a depicts the partial ion yields released from CH$_3$I recorded at a photon energy of 5.5 keV and peak fluence of 26 $\mu$J $\mu$m$^{-2}$. We observed only atomic ions H$^+$ (not shown), C$^n+$ with $n \leq 4$ and I$^m+$ with $m \leq 15$.

We extracted momentum-correlated iodine and carbon ion-pairs released from single molecules assuming three hydrogen atoms are released as three protons and the sum of momenta of three protons is parallel to C–I bond axis. Then we can apply the momentum conservation law as

$$\vec{p}(\text{I}^{m+}) \times k_{mn} + \vec{p}(\text{C}^{n+}) = 0,$$

where $\vec{p}(\text{I}^{m+})$ and $\vec{p}(\text{C}^{n+})$ are momenta of I$^{m+}$ and C$^{n+}$, respectively, and $k_{mn}$ is the momentum correlation coefficient that results from the missing momentum of...
the unobserved protons. The coefficients $k_{mn}$ for all observed combinations of $(m,n)$ are plotted in Fig. 2. Assuming three protons are released, we can estimate the total charges of ions released from a single molecule as $m + n + 3$. We then deduce that the maximum total charge reaches +22 as a result of multiphoton absorption and Auger cascade cycles.24

Fig. 3 depicts the kinetic energy distributions (KEDs) of $C^+$, $C^{2+}$, $C^{3+}$ and $C^{4+}$ in coincidence with $I^+$, $I^{6+}$, $I^{8+}$ and $I^{9+}$ from CH$_3$I. Fig. 4 depicts proton emission angular distributions with respect to the C–I axis in coincidence with $C^{2+}–I^{6+}$, $C^{3+}–I^{8+}$ and $C^{4+}–I^{9+}$.

![Fig. 1](image1.png)

Partial ion yields released from (a) CH$_3$I and (b) 5-iodouracil.

![Fig. 2](image2.png)

Momentum correlation coefficients $k_{mn}$. Filled symbols denote the experimentally determined values. Dashed lines denote the results of the instant charge distribution model ($\tau = 0$). Dotted lines, solid lines and chain lines denote the results of the CCE-CE model with a rate constant $R$ of 0.1, 0.37 and 1 fs$^{-1}$, respectively ($\tau = 9$ fs).
C$_3^+$–I$^8_+$ and C$_4^+$–I$^{9_+}$ ion pairs. The C–I axis is determined by the difference between the carbon and iodine momenta and the C–H axis by the difference of the carbon and hydrogen momenta. Thus the angle I–C–H formed by the three fragment ions is also affected by the motion of the carbon ions during the Coulomb explosion.

3.2. Experimental results for 5-IU

Fig. 1b depicts the partial ion yields released from 5-IU recorded at the same photon energy and the peak fluence as we employed for CH$_3$I. As we can see in the figure, atomic ions are the dominant fragments from 5-IU. We also observed singly charged polyatomic fragments, CC$_+^+$, CN$_+^+$, CO$_+^+$, CNH$_+^+$, and COH$_+^+$ but their fractions are much smaller than those of atomic fragments, indicating strong fragmentation of 5-IU by intense XFEL pulses. Multiply charged ions such as

![Graph](image-url)

Fig. 3  Kinetic energy distributions (KED) of C$_+^+$, C$_{2+}^+$, C$_{3+}^+$ and C$_{4+}^+$ in coincidence with I$_{4+}^+$, I$_{6+}^+$, I$_{8+}^+$ and I$_{9+}^+$. Filled symbols denote the experimental results. Dashed and solid lines denote the results for the instant charge distribution model ($\tau = 0$ fs) and the CCE-CE model ($\tau = 9$ fs and $R = 0.37$ fs$^{-1}$), respectively.

![Graph](image-url)

Fig. 4  Proton emission angular distributions with respect to C–I axis in coincidence with C$_{2+}^+$–I$_{6+}^+$, C$_{3+}^+$–I$_{8+}^+$ and C$_{4+}^+$–I$_{9+}^+$ ion pairs. Filled symbols denote the experimental results. Dashed and solid lines denote the results for the instant charge distribution model and the CCE-CE model, respectively.
doubly charged ions $\text{C}^{2+}$, $\text{O}^{2+}$, and $\text{N}^{2+}$, as well as the iodine ions $\text{I}^{q+}$ with $q \leq 4$, have also been observed. In contrast to $\text{CH}_3\text{I}$, the yields of the highly charged iodine ions are significantly suppressed for 5-IU. The predominance of the lower charge states of iodine ions suggests an efficient charge redistribution from iodine to the uracil ring before the break-up of 5-IU molecule.

Fig. 5 shows the KEDs of atomic fragment ions, $\text{C}^+$, $\text{H}^+$, $\text{N}^+$, $\text{O}^+$ and $\text{I}^{q+}$ emitted from 5-IU. For the KED of fragment ions, we included all iodine ions $\text{I}^{q+}$ from $q = 1$ to 4 detected in coincidence with fragment ions. We show the KEDs for the individual charge states of the iodine ion in the ESI†.

The Coulomb explosion of 5-IU almost always create more than two ions, where the correlations among the momenta of emitted fragments are expected to provide us with rich information about fragmentation dynamics. Let us consider the angles formed between the momenta of atomic fragments in the Coulomb explosion of 5-IU. The cosine of angle $\theta$ between the momenta of two fragments A and B is defined by the scalar product of momentum vectors as follows:

$$\cos(\theta) = \frac{\vec{P}_A \cdot \vec{P}_B}{|\vec{P}_A| |\vec{P}_B|}.$$  

Fig. 5  Kinetic energy distributions (KED) of fragment ions emitted from XFEL-irradiated 5-iodouracil for (a) $\text{H}^+$, (b) $\text{O}^+$, (c) $\text{N}^+$, (d) $\text{C}^+$ and (e) $\text{I}^{q+}$. KED experimental data are summed over $\text{I}^{q+}$ of $q = 1$ to 4. The open circles, red dashed lines and blue lines are the experimental data, CCE-CE results and SCC-DFTB results, respectively. (f) Molecular structure of the neutral 5-IU molecule and the definition of the equilibrium angle between two atoms (the I atom and its nearest O atom).
The distributions of \( \cos(\theta) \) for the pair of A and B ions are denoted by \( \text{SP}_2(A,B) \) and are shown in Fig. 6a–d. Peaks observed in \( \text{SP}_2(I^q+\text{H}^+) \), \( \text{SP}_2(I^q+,O^+) \) and \( \text{SP}_2(I^q+,N^+) \) correspond to the angles in the equilibrium structure of the neutral 5-IU molecule. In order to see whether the momenta of three ions A, B and C lie on a plane or not, we calculated the following triple product from the observed momenta:

\[
\cos(\varphi) = \frac{(\vec{P}_A \times \vec{P}_B) \cdot \vec{P}_C}{|\vec{P}_A \times \vec{P}_B| |\vec{P}_C|}.
\]  

The experimental distribution of \( \cos(\varphi) \), \( \text{SP}_3(A,B,C) \), are displayed in Fig. 7a–d. Note that the distribution function \( \text{SP}_3 \) for three randomly oriented and uncorrelated vectors is flat against \( \cos(\varphi) \), so that the presented curves reflect directly the deviation from the random orientation of the three vectors. The Coulomb explosion that occurs preferentially in the plane then results in the distributions of \( \text{SP}_3(A,B,C) \) peaked around \( \cos(\varphi) = 0 \). In Fig. 7a–d, we chose four combinations of ions including an iodine ion and a hydrogen ion. Experimental results show evident peaks at \( \cos(\varphi) = 0 \) for \( \text{SP}_3(I^q+,\text{H}^+,\text{H}^+) \), \( \text{SP}_3(I^q+,\text{H}^+,O^+) \) and \( \text{SP}_3(I^q+,\text{H}^+,N^+) \), indicating that fragment ions tend to be emitted on the molecular plane of the parent molecule.

### 3.3. CCE-CE model simulations for CH\(_3\)I

We first tested our CCE-CE model by comparing with the results of the CH\(_3\)I experiments. The kinetic energies estimated by the model simulations are shown in Fig. 3. Dashed lines denote the results in the case where all charges are distributed instantaneously among atoms at the equilibrium structure of the neutral CH\(_3\)I in the ground state (the instant charge distribution model). The calculated energies appear to be overestimated. This disagreement indicates the
fact that the interatomic distances have considerably increased before the atoms reached their final charge states. It is thus essential to include the charge build-up time in order to obtain reasonable agreement of the model simulation with the measured kinetic energies of the ions. It also appeared that the charge redistribution rate $R$ introduced in our CCE-CE model is very sensitive to the momentum correlation coefficient $k_{mn}$ in Fig. 2. We scanned the combination of parameters of $\tau$ and $R$ and obtained a good agreement of the model simulation with both measured kinetic energies and momentum correlation coefficients $k_{mn}$ when we chose $\tau = 9$ fs and $R = 0.37$ fs$^{-1}$, as seen in Fig. 2 and 3. To illustrate the sensitivity of $R$ to the coefficient $k_{nn}$, $k_{in}$ values estimated with $R$ of 0.1 and 1 fs$^{-1}$ are also shown in Fig. 2. Comparisons between experiment and simulation for proton emission angular distributions are also shown in Fig. 4. The CCE-CE model also shows better agreement with the experimental results in the angular distributions. From the model simulation, we learned that charge build-up time and charge redistribution time must be considered in order to describe the molecular dynamics appropriately.

### 3.4. CCE-CE model simulations for 5-IU

We extended the CCE-CE model for 5-IU by incorporating the thermal vibration effects in addition to the charge build-up time and charge redistribution rate. We scanned the combination of parameters of $\tau$, $R$, and $T$, and found good agreement between experiment and classical MD when we adopted the parameter set of $T = 300$ K, $\tau = 10$ fs and $R = 0.5$ fs$^{-1}$. Calculated KED, $\text{SP}_2(A,B)$ and $\text{SP}_3(A,B,C)$ are displayed by red dashed lines in the Fig. 5–7, respectively. The values of $\tau$ and $R$ deduced from the 5-IU experiments are almost the same as those we obtained from CH$_3$I ($\tau = 9$ fs and $R = 0.37$ fs$^{-1}$). We emphasize that both the thermal vibrations (represented by $T$) and charge dynamics (represented by $\tau$ and $R$) in the molecules are important to reproduce momentum correlations for 5-IU. There are still discrepancies in the KEDs of iodine ions and carbon ions; they may be attributed to the neglect of chemical bonds in the classical MD.
3.5. SCC-DFTB results for 5-IU

The KED and \(SP_2(A,B)\) obtained by the SCC-DFTB approach are shown in Fig. 5 and 6, respectively, by blue lines. We adopted the same parameters of \(T = 300\) K and \(\tau = 10\) fs as in the case of the CCE-CE model simulations. We chose that \(T_e = 6\) eV, which provides the best fit with the experimental results. The injected energy per ionization, \(\epsilon\), was set to be 6 eV; the final accumulated energy \(\Delta E\) is 60 eV for \(Q^{\text{max}} = 10\). Shown in these figures are the results for the zero vertical momentum case (\(\Delta \vec{p}_{i \perp} = 0\)). We ran 1000 trajectories to obtain the KED and \(SP_2(A,B)\) for individual \(Q^{\text{max}}\) values, which were then averaged over the distribution of \(Q^{\text{max}}\) estimated from CH\(_3\)I experiments. The obtained KEDs are in good agreement with the experimental ones, except for that of \(H^+\). This approach also well reproduces the observed peaks in \(SP_2(I^+,H^+)\), \(SP_2(I^+,O^+)\), and \(SP_2(I^+,N^+)\); it holds the feature of the broad peak in \(SP_2(I^+,C^+)\).

The general applicability of the SCC-DFTB approach depends on how the results are sensitive to \(\epsilon\) and \(T_e\). Almost the same results were obtained for the range of \(\epsilon = 3–9\) eV (\(\Delta E = 30–90\) eV for \(Q^{\text{max}} = 10\)), though the KED and \(SP_2(A,B)\) gradually became broader with increasing \(\epsilon\). Overall, the results are insensitive to the choice of \(\epsilon\) (or \(\Delta E\)). The dependence on \(T_e\) is not critical either around \(T_e = 6\) eV. While the peaks in the KED of \(N^+\) and \(O^+\) were shifted toward the higher energy side at extremely high \(T_e (>9\) eV), the KED for \(H^+\) and \(C^+\) were insensitive to \(T_e\). We would like to point out that 9 eV is equal to the ionization potential of 5-IU.\(^{60}\) All \(SP_2(A,B)\) remained unchanged for \(T_e > 3\) eV and the peaks in \(SP_2(A,B)\) disappear below \(T_e = 3\) eV. We also investigated the case of \(\Delta \vec{p}_{i \perp} \neq 0\). The results for \(\Delta \vec{p}_{i \perp} \neq 0\) were almost the same as those for \(\Delta \vec{p}_{i \perp} = 0\). The main differences that we noticed are as follows (see Fig. S5 and S6 of the ESI\(^\dagger\)): the KEDs of \(O^+\) and \(I^+\) for \(\Delta \vec{p}_{i \perp} \neq 0\) were broadened toward higher energy; the peak at \(\cos(\theta) = 0\) in \(SP_2(I^+,C^+)\) is shifted to \(\cos(\theta) = 1/4\) and a peak appears around \(\cos(\theta) = -1\).

3.6. NAQMD results for 5-IU

Finally, we carried out NAQMD simulations to estimate the time scale of the charge transfer induced by the nuclear motion in a molecular parent ion with a 6+ charge, as an example. As the initial state of 5-IU\(^6^+\), we assumed an electron charge transfer induced by the nuclear motion in a molecular parent ion with these MOs are mainly localized around the iodine atom. In contrast, HOMO \(\text{MOs})\) of a neutral 5-IU: HOMO, HOMO–1, and HOMO–4. As shown in Fig. S7,\(^\dagger\) these MOs are mainly localized around the iodine atom. In contrast, HOMO–2 and HOMO–3 do not have iodine atomic populations and thus their holes will not be created \(\text{via Auger cascades of the I atom. To investigate the charge dynamics in 5-IU}^{6^+}\), we first optimized the MOs so that the energy of the ground state electron configuration of 5-IU\(^6^+\) is minimized. We then transferred two electrons from HOMO–1 to LUMO of 5-IU\(^6^+\). These two MOs correspond to HOMO–4 and HOMO–2 of 5-IU; that is, the resultant electron configuration corresponds to the hole state in which six electrons are removed from HOMO, HOMO–1, and HOMO–4 of 5-IU. Fig. 8 shows the time evolution of the existence probability \(R_m(t)\) (\(\alpha = \text{iodine or the molecular counterpart}\)) of holes obtained from the ensemble average over 15 different trajectories. The initial positions and velocities of the nuclei are taken from a classical trajectory at \(T = 300\) K. The solid and dashed lines indicate \(R_m(t)\) for the iodine and the molecular counterpart, respectively. The holes transfer from the iodine to the molecular counterpart in...
The threshold time of the charge transfer in each trajectory is almost the same within ±1 fs. The value is in the same order of the charge redistribution time scale estimated from experiments (~3 fs for CH₃I and ~2 fs for 5-IU), indicating that ultrafast nuclear dynamics also play a significant role in charge redistribution.

4. Discussion

The experimental results of the CEMI presented in the above section were analyzed in detail using three theoretical approaches ranging from a classical model, namely, the CCE-CE model to a first-principles approach (the NAQMD approach). We confirmed that the CCE-CE model reproduces well the experimental observables such as the kinetic energy distributions of fragment ions both for CH₃I and 5-IU. The results obtained by the SCC-DFTB semi-empirical approach for fragmentation of 5-IU are in reasonable agreement with the results of our CCE-CE model simulations wherever comparisons are possible. The intramolecular charge redistribution in 5-IU induced by nuclear motion was investigated by using the first principles approach NAQMD. The results of the first principles approach NAQMD illustrates that besides Auger cascades, nuclear dynamics plays a significant role in the ultrafast intramolecular charge redistribution in 5-IU. (The charge transfer from the iodine to the molecular counterpart more or less follows the fast C–H stretching motion. The C–H and N–H bond

Fig. 8  Time evolution of the hole probability $R_a(t)$ of 5-U₆⁺ in NAQMD simulation. The red dashed line and black solid line denote $R_a(t)$ for iodine (I) and the molecular counterpart (molecule) region, respectively. The spatial distribution of the hole (one of the 15 trajectories) is also shown at time $t = (a)$ 0 fs, (b) 4.8 fs, and (c) 9.6 fs. The hole density is displayed at a contour level of 0.03e/$a_0^3$, where $a_0$ is the Bohr radius.
lengths increased by 25 pm in 5 fs on average.) Since the NAQMD approach is a higher level of theory, it is computationally demanding. It is thus practically impossible to generate a sufficient number of trajectories for the statistical analysis of molecular fragmentations. Let us now use our CCE-CE model to give insight into the motion of individual atoms in real space. We deduced the time evolution of interatomic distances from the results of the CCE-CE simulations for CH₃I and 5-IU. The temporal changes in interatomic distances are shown in Fig. 9 and 10 in which the interatomic distances are normalized by the values at $t = 0$.

The results for CH₃I revealed that the H–C distance increases about two times from the initial length at $t = 10$ fs, whereas the I–C distance elongates less than several %. The results for 5-IU also revealed that the H–C and H–N distances elongate by 50–100% from the initial lengths at $t = 10$ fs as seen in Fig. 10a. The SCC-DFTB and NAQMD approaches have reproduced the ultrafast ejection of H⁺ as well. The changes of C–O, C–N and C–C are less than several % at $t = 10$ fs. The results of our simulations clearly indicate that the ultrashort escape time of hydrogen ions, which is comparable to the pulse width of XFEL, makes them sensitive to the intramolecular charge dynamics and its time scale. In contrast, the I–C length of 5-IU does not change in 30 fs, which is presumably due to the large iodine mass as well as the fact that the C₁ adjacent to the I atom is surrounded by three heavy atoms (iodine and two carbons), as shown in Fig. 10c. This effect was examined by evaluating the site dependence of SP₂(I⁺,C⁺) on C⁺ sites as well as the off-planar displacement of each carbon ion. Site-resolved $\text{SP}_2(I^+,C^+)$ is shown in the Fig. 10f. The angles between the momenta of I⁺ and that of its neighbor C₁ has a broad peak at $\cos(\theta) = 0$, indicating that C₁ tends to be emitted at right angles to the direction of I⁺ ejection. The off-planar motion of emitted ions is quantified by $\alpha(t)$ which is defined by the angle between $\vec{n}_0$ and $\vec{r}(t)$, where $\vec{n}_0$ is the normal vector of the molecular plane defined at $t = 0$ and $\vec{r}(t)$ is the position vector of an ion at $t$, respectively (see the definition in Fig. 10d). An increase of $\alpha(t)$ corresponds to the off-planar displacement of ions. The time evolution of $\alpha(t)$ shown in Fig. 10e indicates that the off-planar displacement of C₁ is apparently larger than those of other carbons. The results suggest a strong frustration of the Coulombic repulsive forces exerted on the C₁ site of 5-IU.

![Fig. 9](image.png) Simulated time evolution of H–C (solid lines) and I–C (broken lines) distances in C₂⁺–I₆⁺ (red), C₃⁺–I₈⁺ (blue) and C₄⁺–I⁹⁺ (green) ion-pair formations. The distances are normalized by those at time zero.
The success of the SCC-DFTB approach is attributed to the introduction of $T_e$. While the charge of the C atom adjacent to $I^+$ tends to be negative for 5-IU, it becomes positive for appropriate values of $T_e$; all the atoms are positively charged. As a result, the bond between $I^+$ and its adjacent C atom is weakened by Coulomb repulsion and $I^+$ are emitted almost parallel to the initial direction of the I–C bond axis of the molecule (or on the molecular plane), which is essential to reproduce, especially the two-body momentum correlations with $I^+$ observed in the experiments. In the range of $T_e > 3$ eV, all the atoms are positively charged if the total charge of the molecule is positive. This type of charge distribution is the key to reproduce the experimental results and reveals why the CCE-CE model is so successful. Another point to be noted is that the chemical bonds (covalent bonds in the case of 5-IU) in a molecule are almost broken, i.e., $\Delta E$ is as high as the atomization energy of the molecule when the Coulomb explosion is about to proceed. These two points are the reasons why the CCE-CE model and the SCC-DFTB approach provide nearly the same results, though differences exist.

As we have shown, the performance of the SCC-DFTB approach is overall satisfactory. There is however a serious discrepancy with the experiment. As shown in Fig. 5, the high energy components (>40 eV) in the KED of $H^+$ are not reproduced by the SCC-DFTB approach. We performed SCC-DFTB simulations at high temperatures of $T = 2000–3000$ K, which is as high as the zero point energy of the C–H or N–H stretching vibration, but the KED sharply dropped in the high energy region as in the lower temperature cases. This denies the possibility that the high energy components of $H^+$ originate from different molecular structures of short C–H or N–H distances. (The Coulomb explosion energies of $H^+$ in the

Fig. 10  (a) and (b) Time evolution of interatomic distances of the 5-iodouracil molecule averaged over the CCE-CE trajectories. Interatomic distances are normalized by the values at $t = 0$. (c) Definition of bonds. (d) Definition of $\alpha(t)$ to quantify the degree of off-planar ejection. (e) Time evolution of $|\cos(\alpha(t))|$. (f) Site-resolved $SP_2(I^+,C^+)$. 

Published on 31 October 2016. Downloaded by POSTECH Library on 02/11/2016 04:17:04.
explored region were smaller than 50 eV.) Those high-energy components presumably appear through different Coulomb explosion channels that have different charge distributions. The charge distribution that the SCC-DFTB approach affords is an averaged one over $T_e$ but almost unique for the structures at the moment of Coulomb explosion. Note that the CCE-CE model, where the charges of atoms are randomly selected under the constraint of the conservation of total charge, gives better agreement with the experimental KED of H$^+$. The reproduction of the high-energy components in the KED of H$^+$ is challenging. What is required to this end is nonadiabatic theory beyond the Ehrenfest dynamics on an average potential, such as Tully’s surface-hopping algorithm used in the NAQMD approach, but the conventional surface hopping methods or algorithms are time-consuming. A promising approach is a surface hopping algorithm recently proposed by C. Zhu et al., in which surface hopping is executed efficiently following the analytical switching probability determined only from excited state potential surfaces and their gradients. This algorithm, which efficiently simulates nonadiabatic molecular dynamics without calculating nonadiabatic coupling, is very fast and enables us to prepare a sufficient number of trajectories at a low computational cost.

The experimental results in Fig. 5 show that the fragment ions of peripheral H and O atoms have high kinetic energies, of which peaks are higher than or around 20 eV. This due to the fact that H$^+$ and O$^+$ immediately escape from the parent molecule (see Fig. 10a). One may thus expect that the fragment ions of ring atoms have lower kinetic energies. In fact, the kinetic energy distribution of N$^+$ is peaked around 20 eV, whereas the peak in the kinetic energy distribution of C$^+$ is much lower than 20 eV. The ring atoms C and N are almost considered the same type of atom without chemical bonds (the difference in mass is small): in the CCE-CE model, i.e., a free atom model, the kinetic energy distribution for N$^+$ is similar to that for C$^+$. While the experimental peak in the kinetic energy distribution of C$^+$ is lower than the peak in the CCE-CE simulation, the experimental peak of N$^+$ is higher than the CCE-CE peak. This suggests that N$^+$ tends to be released earlier than C$^+$ in the Coulomb explosion of 5-IU. The chemical environment of N is different from that of C. We attribute the difference between C$^+$ and N$^+$ to the existence of chemical bonds. This conclusion is reinforced by the fact that the SCC-DFTB approach reproduces the experimental KEDs for N$^+$ and C$^+$.

In short, the CCE-CE model and the SCC-DFTB approach attained a level to reproduce the CEMI experiment semiquantitatively. Both can therefore serve as a Coulomb explosion simulator, though there is still room for improvement. Their advantages and disadvantages can be summarized as follows. The SCC-DFTB approach deals with chemical bonds appropriately, whereas the CCE-CE model ignores them. The SCC-DFTB approach hence predicts more accurately when fragments ions are ejected from the parent molecule and how much kinetic energies the fragment ions gain, except for H$^+$. The advantage of the CCE-CE model over the SCC-DFTB approach is the flexibility to allow various charge distributions for a molecule. In the CCE-CE model, intramolecular charge redistribution from the I atom to its molecular partner in 5-IU is well characterized by a rate equation with the charge redistribution rate $R$. In the SCC-DFTB approach, intramolecular charge redistribution is not handled in real time; instead, the charge redistributions that result from intramolecular charge redistribution are imitated by those obtained by the introduction of $T_e$. The best choice
at present is to do a cross-check on the results of simulations by making the most of the advantages of the CCE-CE model and the SCC-DFTB approach. The CCE-CE model is computationally cheaper than the SCC-DFTB approach, but the differences are no longer significant considering current computer resources.

5. Conclusion

We carried out CEMI measurements for halogenated molecules, CH$_3$I and 5-iodouracul (5-IU), by using intense XFEL pulses at SACLA. The CCE-CE model, which includes the charge dynamics and nuclear dynamics in the classical Coulomb explosion model, has been applied to the analysis of CEMI, i.e., 3D momentum correlations between fragment ions. We confirmed for CH$_3$I that the CCE-CE model reproduces the main features of the experimentally observed two-body momentum correlations and kinetic energies of fragment ions; we succeeded in determining the charge build-up time of $\tau = 9$ fs and the charge redistribution rate of $R = 0.37$ fs$^{-1}$. We then applied the model to 5-IU and reproduced the experimental observations by using the parameters of $T = 300$ K, $\tau = 10$ fs and $R = 0.5$ fs$^{-1}$. The effective temperature $T$ is introduced to prepare a proper initial distribution of the positions and velocities of the atoms. The initial distribution, sampled from trajectories of the thermal molecular vibration, is essential to reproduce the experimentally observed two-body momentum correlations. The range of optimal values of $\tau$ and $R$ was almost the same between CH$_3$I and 5-IU. The present results indicate that both the charge build-up and charge redistribution take place within the XFEL pulse duration of 10 fs, at the early stages of the Coulombic explosion. The charge transfer dynamics for 5-IU, induced by nuclear dynamics, was simulated by the first-principles NAQMD approach. The ultrafast charge transfer from the iodine atom to its molecular counterpart follows the ultrafast nuclear dynamics such as hydrogen motion. The estimated time scale of charge transfer is in the same order of the value of the charge redistribution rate $R$ used in the CCE-CE model.

We also developed a novel approach based on the SCC-DFTB method, where the effects of sequential ionization and concurrent electronic excitation are described in the framework of the sequential ionization model. The SCC-DFTB approach is more realistic than the CCE-CE model in the sense that the chemical bonds in molecules are accurately taken into account in the SCC-DFTB approach, though semiempirically. In the SCC-DFTB approach, bond dissociation processes are triggered by the excess vibrational energy injected to molecules during the Auger cascade, as well as Coulomb repulsion. For 5-IU, the SCC-DFTB approach employed the values of $T$ and $\tau$ used in the CCE-CE model, whose parameter set consistently reproduced the experimental observations of ion kinetic energy and two-body momentum correlation. The dynamics of charge redistribution, represented by $R$, cannot be explicitly treated in our SCC-DFTB approach. We had to introduce an electronic temperature $T_e$ in order to model the charge distribution that reflects electronic excitation and charge redistribution, i.e., the contribution from various excited electronic states.

The SCC-DFTB approach is robust. It reproduces the experimental results for reasonable choices of $\epsilon$ and $T_e$. The analysis of the SCC-DFTB results clarified why two apparently contradictory approaches, namely the CCE-CE model and the SCC-DFTB approach, function well. Our understanding of the mechanism of
XFEL-induced Coulomb explosion is founded on the consistency among the three theoretical approaches which are adapted or developed for this study. The present study demonstrates that both approaches can be used for extracting the physics of Coulomb explosion from the experimental data and therefore for reconstructing molecular structures. The successful extension from CH$_3$I to 5-IU suggests that the applicability is more general and that photo-induced ultrafast dynamics of many molecules can be adequately characterized by the laser–pump–XFEL–probe CEMI combined with CCE-CE and/or SCC-DFTB simulations. Such studies are in progress at both SACLA and LCLS.

**Author contributions**


**Conflict of interest**

The authors declare no conflict of interest.

**Acknowledgements**

The experiments were performed at SACLA with the approval of JASRI and the program review committee (No. 2012B8045). This study was supported by the X-ray Free Electron Laser Utilization Research Project and the X-ray Free Electron Laser Priority Strategy Program of the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), by the Japan Society for the Promotion of Science (JSPS), by the Proposal Program of SACLA Experimental Instruments of RIKEN and by the IMRAM project. H. K. acknowledges Grant-in-Aid for Scientific Research by MEXT (No. 24245001 and 16H04091). Part of the calculations was carried out by using supercomputing resources at the Cyberscience Center, Tohoku University and at the Research Center for Computational Science, Okazaki, Japan. K. Nak. is supported by Research Fellowships of Institute for Quantum Chemical Exploration for Young Scientists. S. O. acknowledges Grant-in-Aid for Scientific Research by MEXT (No. 15K17722) and also thanks the Supercomputer Center, Institute for Solid State Physics, the University of Tokyo for the use of facilities. Part of calculations was also carried out using the computer facilities at the Research Institute for Information Technology, Kyushu University. K. Nag. and S. O. acknowledge support by the Cooperative Research Program of “Network Joint Research Center for Materials and Devices” of Japan. E. Ku. acknowledges support by the Academy of Finland, and Y. H. J. by the National Basic Research Program of China (2013CB922200), the Natural Science Foundation of China (11420101003, 11274232 and 61308068). A. R. was supported
by the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy under contract No. DE-FG02-86ER13439. M. A. and D. E. Ki., acknowledge the Global Research Laboratory Program (No. 2009-00439) and the Max Planck POSTECH/KOREA Research Initiative Program (No. 2011-0031558) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science ICT & Future Planning. J. H. C. acknowledges support by the Shanghai Natural Science Foundation (No. 13ZR1464700) and the Knowledge Innovation Project of the Chinese Academy of Sciences (No. 255015061).

References


