# Charge Migration and Molecular Dissociation Following Multiphoton Multiple Ionization of Iodine-Substitute Molecules by X-Ray Free-Electron Laser Pulses from SACLA

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**Abstract:** We have studied charge migration and dissociation in iodine-contained molecules using XFEL from SACLA and applying the ion momentum coincidence technique to fragmentation of highly charged molecular ions produced via XFEL at the iodine site.
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## 1. Introduction

X-ray free-electron lasers (XFELs) provide extremely intense femtosecond x-ray pulses that promise access to high-resolution structure determination, while outrunning any radiation damage. Achievement of this goal, however, requires the ability to describe the dynamics of samples containing heavy atoms in high-intensity x-ray pulses. Samples containing substituted heavy atoms are highly sensitive to x-ray absorption due to high cross sections of inner shell ionization of these atoms. Such an x-ray absorption event deposits a large and concentrated amount of energy into a single molecule consisting of predominantly light atoms. Deep core ionization of the heavy atom is followed by the Auger decay cascade creating a multiply charged ionic state. Part of the initially absorbed energy is also spent to violent molecular dissociation as the electronic decay sequence progresses. Understanding these dynamic processes provides useful input for dynamic imaging using XFELs.

In early 2012, a new XFEL facility, the SPring-8 Angstrom Compact free electron LAser (SACLA) started user operation in Japan [1]. We have studied charge migration and dissociation in iodine-substituted molecules, iodomethane ($CH_3I$) and 5-iodouracil ($C_4H_3IN_2O_2$) molecules, using very intense and short XFEL pulses from SACLA. The extreme intensity of the XFEL radiation creates conditions under which the heavy atoms in the molecule absorbs a number of x-ray photons before and during the electronic relaxation and dissociation process [2,3]. This multiphoton absorption thus results in highly charges molecular states, unique for studying the charge distribution and migration during the electronic relaxation and initial stages of the dissociation. Also, the dynamics of often violent multifragment Coulomb explosions can be observed.

## 2. Experiment

The experiment has been carried out at the experimental hutch 3 (EH3) of the beamline 3 (BL3) of SACLA [4]. The XFEL beam is focused by the Kirkpatrick-Baez (KB) mirror system to a focal size of ~1 μm (FWHM) in diameter. The sample vapor seeded by He was introduced as a pulsed supersonic jet to the focal point of the XFEL beam. After crossing the gas jet at right angle, the XFEL beam exits the vacuum chamber via beryllium window. The relative XFEL pulse energy was measured shot-by-shot by a PIN photodiode. The photon energy was set at 5.5 keV. The peak fluence was 26 $\mu J/\mu m^2$ in average. The absolute value of the peak fluence was determined via the calibration using Ar [2,5].

Ions produced at the focal point were extracted towards ion momentum spectrometer equipped with microchannel plates (MCPs) and a delay-line anode. We used a velocity map imaging (VMI) [6] electric field condition. Signals from delay-line anode and MCPs were recorded by the digitizer and analyzed by a software discriminator. The arrival time and arrival position of each ion were determined.

## 3. Results and discussion

In the multiple ionization of iodomethane, we have extracted momentum-correlated $I^{m+}$-$C^{n+}$ ion-pairs up to $m$ = 15 and $n$ = 4 emitted from a single molecule. Taking three proton emissions from a single molecule into account, we found that highly charged parent molecules with charge state of up to +22 were produced. Such highly charged states are produced via sequential phtoabsorption and Auger cascade cycles [2]. We have obtained kinetic energy distributions of $I^{m+}$ and $C^{n+}$ for each pair of charge states ($m,n$). Measured kinetic energies were significantly lower than energies estimated by the Coulomb repulsion force at the equilibrium bond lengths of the neutral $CH_3I$ molecule in the ground state. This indicates that the bond lengths are elongated during multiple ionization and charge migration processes. Charge-state dependence of the average kinetic energy is reproduced by a simple model assuming charge buildup and migration within molecule proceed with time. During the charge buildup and migration processes, we also assumed that three hydrogen atoms receive charge first from iodine, and then carbon atom receives charge. We found that these charge buildup and migration proceeds within XFEL pulse duration of 10 fs from the model, also with help of *ab initio* calculations based on density functional theory (DFT).

Kinetic energy distribution of ions emitted from 5-iodouracil were also compared with calculated energy distribution assuming the Coulomb explosion at the equilibrium bond lengths of the neutral molecule. Compared with the case of $CH_3I$ molecule, the measured kinetic energy distributions are similar with calculated energy distribution. However, significant discrepancies appear for protons and carbon ions. Measured kinetic energies of proton were significantly lower than estimated energies. It indicates that protons were emitted before the charge buildup is completed in the molecule. On the other hands, measured kinetic energies of carbon ions were close to calculated energies on average. However, measured energy distribution has two peaks whereas calculated distribution has only one peak. We also found that protons and oxygen ions were emitted within molecular plane whereas carbon ion emissions have no angular correlation. These observations illustrate that emission processes for protons and oxygen ions are direct dissociation from the geometry of the ground state molecule, whereas these for carbon ions are via sequential dissociation after loss of memory for the initial geometry. These behaviors of ion emissions can be correlated to the molecular structure, i.e. the carbon atoms compose an aromatic ring of the molecule whereas hydrogen and oxygen atoms located at outside of the ring. All these observations and interpretations of the data are well supported by the DFT-based *ab initio* calculations.

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