Supporting Information for

Charge and Nuclear Dynamics Induced by Deep Inner-Shell Multiphoton Ionization of CH_3I Molecules by Intense X-ray Free-Electron Laser Pulses

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Momentum filter

In the experiment, we measured all three components of the ions' momenta (p_x, p_y, p_z) using a multicoincidence ion spectrometer based on a position sensitive detector. Here, we define the *x*, *y*, and *z* directions as the XFEL propagation direction, the molecular beam direction, and the spectrometer axis direction, respectively. In order to extract only true I^{m+}–C^{n+} coincident ion pairs, *i.e.* resulting from a single CH_3I molecule, we applied a momentum filter based on the momentum conservation law, as described below.

Figure S1a depicts a two-dimensional momentum-sum map for the I^{5+}–C^{2+} coincidences. The horizontal axis is the sum of p_x for the two ions, and the vertical axis is the sum of p_y. The clear observation of an island of high intensity on the map indicates that the two momenta are correlated, whereas the diffuse background arises from the inevitable false coincidences, *i.e.*, associating ions resulting from two different molecules. In order to perform the momentum filtering, we first redraw the momentum sum map with the I momenta always aligned with the direction of the *x* axis, as shown in Figure S1b.

One can see that the map is elongated in the *x* direction and the island exhibits an offset from the zero position, where it would be if the two ions would strictly satisfy the momentum conservation

law. The offset indicates that part of the momentum balancing that of the iodine is carried by the departing hydrogens – and represents the "missing" momentum in the sum. For efficient filtering based on the momentum correlation, the map (and each individual event) needs to be corrected for the missing momentum. The correction coefficient (k_{mn} in the main text) is obtained from the experiment, adjusting the iodine momentum so that the island in the map becomes centered at zero and the entire map becomes circular. In the case of Figure S1b, the suitable value of the coefficient k was 0.751, and by multiplying the I^{5+} momentum with that value, Figure S1c was obtained. By this procedure we obtained the values of k_{mn} for all ion pairs.

We extracted true coincidence events by limiting the accepted ion pairs to be within a small radius circle around the origin, in the corrected momentum sum maps. Furthermore, the contribution of false coincidences to the ion-pair counts and various other statistics could be estimated by interpolating the diffuse background under the correlated momentum island. The same procedure was also applied to y–z and z–x planes to further increase the accuracy of the result.

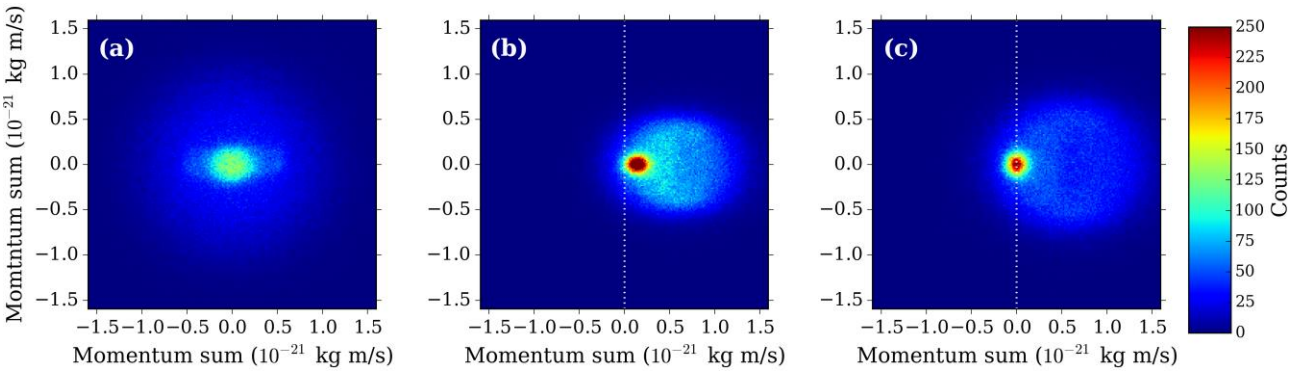

Figure S1. The two-dimensional momentum-sum maps for the I^{5+}–C^{2+} coincidences. Vertical dotted lines in (b) and (c) indicate zero position to guide the eye.

Figure S2 depicts the ion time-of-flight spectrum obtained after momentum filtering as described above.

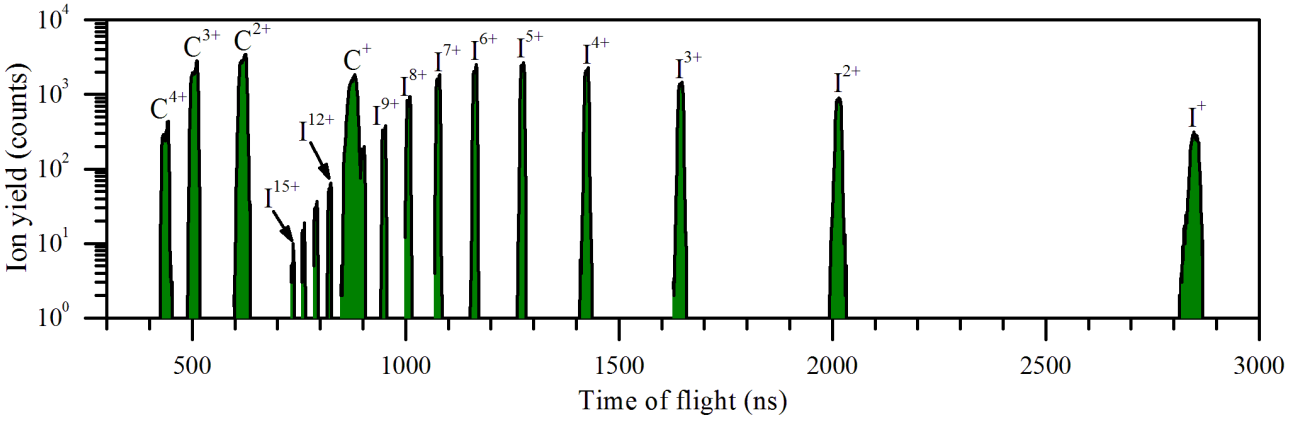

Figure S2. The ion time-of-flight spectrum after momentum filtering.