Electron-induced dissociation dynamics studied using covariance-map imaging

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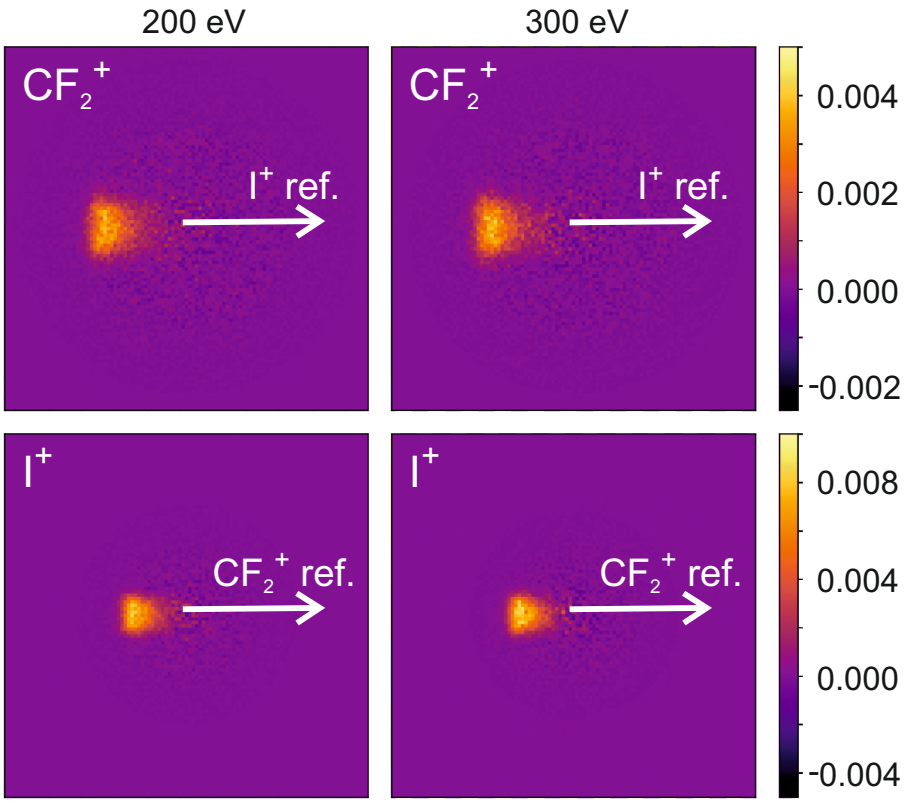

Figure S1 Recoil-frame covariance images obtained for the (CF_2^+,I^+) channel following electron ionisation of CF_3I at electron energies of 200 and 300 eV. Very little difference is seen between the covariance maps obtained at the two energies, implying that there has been little change to the (CF_2^+,I^+) dissociation channel in this electron energy range.

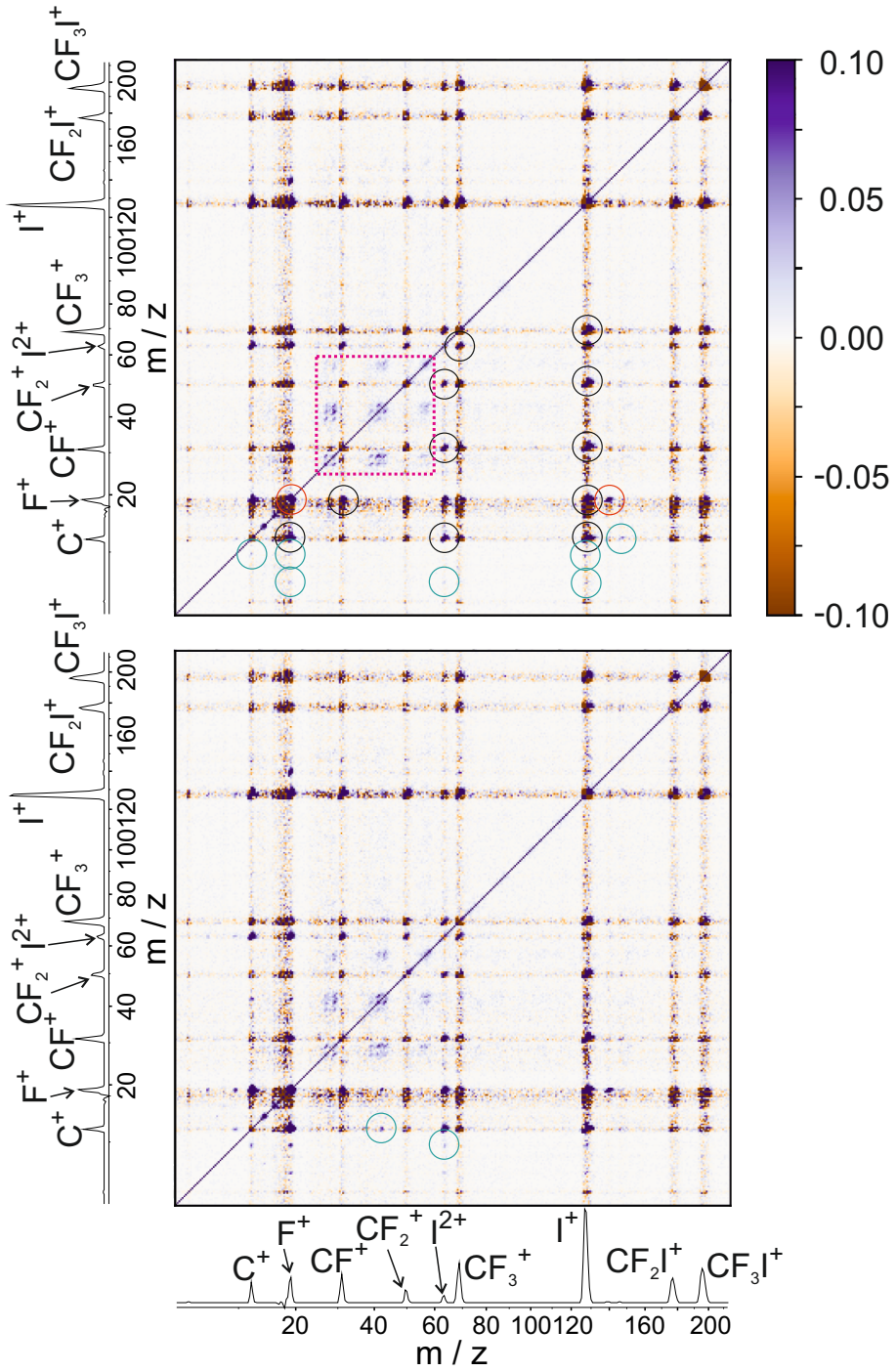

Figure S2 ToF-ToF covariance maps obtained following electron ionisation of CF_3I at electron energies of 200 and 300 eV, plotted on a more saturated colour scale than in figure 5 of the main text. Covariance signals observed at 100 eV are highlighted with black circles. New covariance signals are highlighted with either a red or turquoise circle, corresponding to strong and weak covariance signals, respectively. The covariance signals in the magenta box correspond to a hydrocarbon contaminant and can be ignored. All features observed in the 200 eV covariance map are also observed in the 300 eV covariance map.

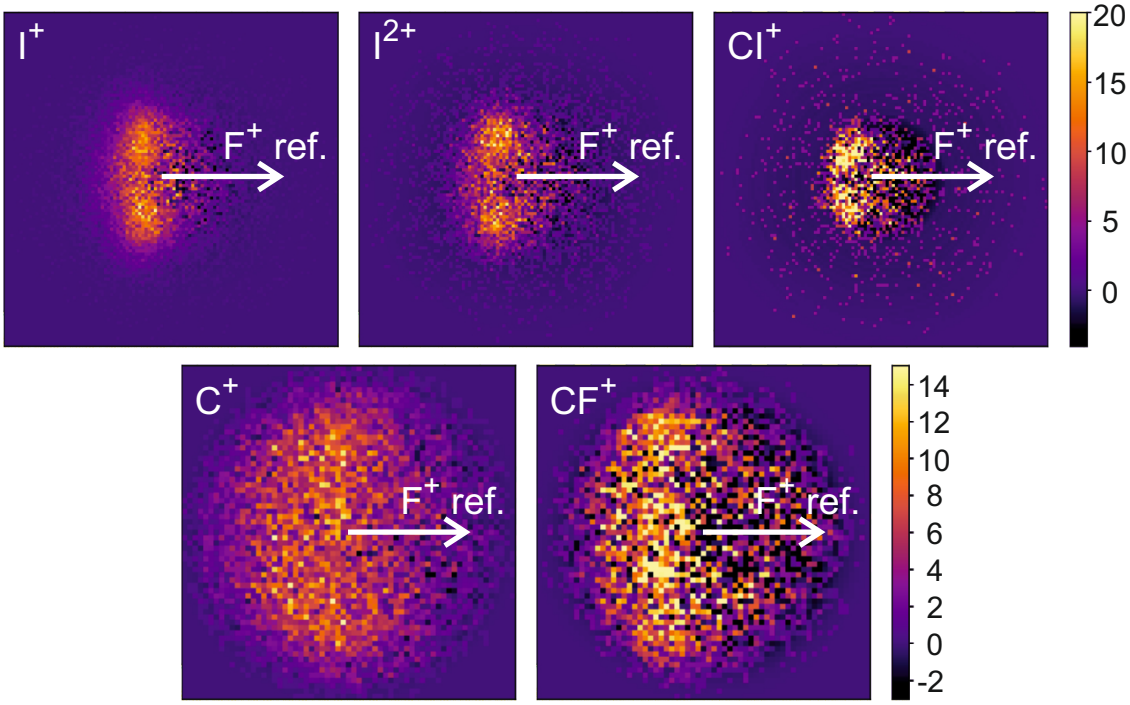

Figure S3 Recoil-frame covariance maps obtained following electron ionisation of CF_3I at 300 eV between F^+ and I^+, I^{2+}, C^+, CF^+, and CI^+, where F^+ is the reference ion. Note that where C^+ and CF^+ are signal ions, the corresponding covariance maps have been rebinned to a greater extent to improve the signal-to-noise ratio.

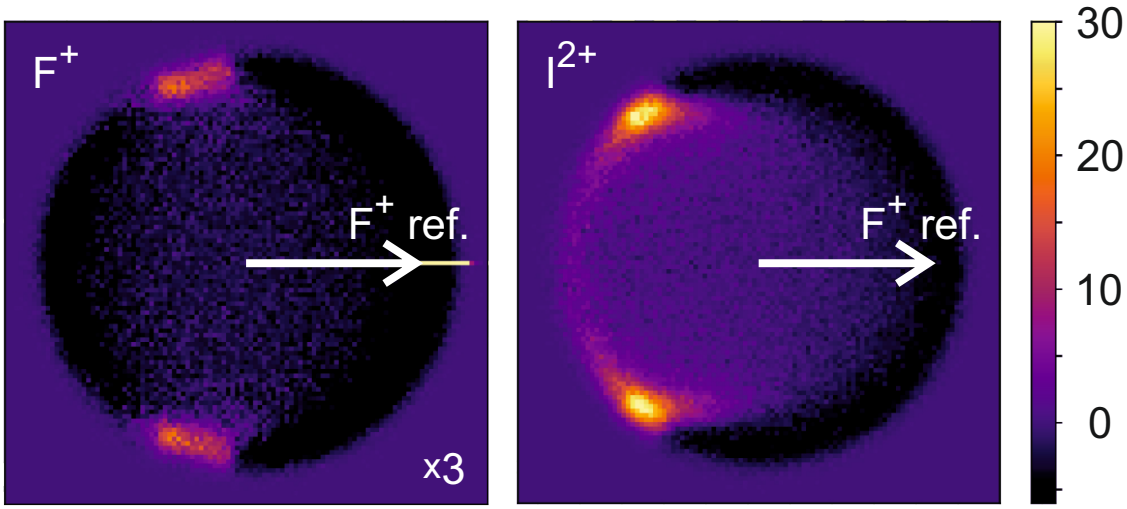

Figure S4 Simulated recoil-frame covariance map for the dissociation of CF_3I^{4+} to form I^{2+}, two F^+ and neutral fragments. The simulation parameters are detailed in section S1, and the results compared to experimental data in the main text.

S1 Simulation of the dissociation of CF_3I4+

To simulate the dissociation of CF_3I^{4+} to form I^{2+}, $2F^+$, and neutral fragments, we have employed a simple Coulomb model. For these simulations, the geometry of neutral CF_3I was first optimised at the at the MP2//LANL2DZ level of theory. Charges were placed on the individual ions in the optimised geometry, the force acting on each of the ions was calculated using Coulomb's law, and the Coulomb potential for each ion was determined. It was assumed that the neutral fragments had negligible velocity and could be neglected, that the ions travelled in the direction in which the force acted at the initial geometry, and that the potential energy was entirely converted to kinetic energy. The velocities of the F^+ and I^{2+} ions were calculated to be 10,800 ms^{-1} and 1,900 ms^{-1}, respectively, and the angle between the F^+ and I^{2+} velocity vectors was found to be 127°.

A Monte-Carlo simulation was then carried out, in which five molecules were dissociated per acquisition cycle, for a total of 50,000 acquisition cycles. Each molecule was defined such that the three ions were in the same randomly oriented plane, with F^+ and I^{2+} recoiling at an angle of $127° \pm 5$ with respect to one another. The velocity vectors of the ions were convoluted with a Gaussian with a standard deviation of 5% of the velocity for the corresponding ion. To imitate the experimental datasets, only two dimensions of the simulated 3D scattering distributions were retained. Recoil-frame covariance analysis was then performed on the generated dataset. The resulting covariance maps are shown in figure S4, and the recoil angle obtained is indicated in the (F^+,F^+) and (I^{2+},F^+) covariance maps shown in figures 6 and 7 of the main text, respectively.