

Capturing roaming fragments in formaldehyde by time-resolved Coulomb explosion imaging

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Abstract: Roaming fragments in dissociation reactions of the formaldehyde molecule are directly observed in real time by a combination of time-resolved Coulomb explosion imaging and quasi-classical trajectory simulation.

In conventional molecular or radical dissociation reactions, molecules follow the minimum energy paths from reactants to products. Alternative dissociation pathway called “roaming” was discovered in the dissociation reaction of formaldehyde (H_2CO) [1]. In this roaming pathway, the roaming fragment (H atom) walks around the remaining HCO. Since the first observation of roaming in 2004, footprints of roaming reaction have been reported in a wide variety of molecular systems [2-5]. However, roaming fragments themselves have not been observed directly because each molecule follows its own pathway. Recently, we have successfully captured roaming fragments in the dissociation of formaldehyde by using a combination of Coulomb explosion imaging and quasi-classical trajectory simulation [6].

Coulomb explosion imaging experiments were performed at Advanced Laser Light Source (INRS-EMT, Canada) on the multi-kHz beam line. Ultraviolet pump pulses (304 nm) were obtained by frequency quadrupling of the output of an optical parametric amplifier. Time-delayed ultrashort intense probe pulses (8 fs) were obtained by pulse compression with a pressure-gradient hollow-core fiber and chirped mirrors. These pulses were focused on an effusive molecular beam of deuterated formaldehyde (D_2CO). The ions generated by the probe pulse were collected with a uniform-electric-field ion momentum imaging spectrometer.

Figure 1 shows the two-dimensional plots of the total kinetic energy release (KER) with the angle between two deuteron momentum vectors for three-body breaking (D^+ , D^+ , CO^+) channel at different pump-probe time-delays Δt . The onset of molecular dynamics occurred already before 100 fs. This indicates that the S_1/S_0 relaxation occurs five-orders of magnitude faster than that previously assumed [7]. The existence of the fast relaxation process was verified by photoelectron experiments at Nagoya University and *ab initio* calculation. From the simulation including all critical steps (S_1/S_0 relaxation, dynamics on the S_0 state, and Coulomb explosion), we could identify the areas corresponding to roaming, molecular and radical dissociation channels in the two-dimensional plots as shown in the upper left subplot in

Fig. 1. The broad angular distribution in the KER range < 5 eV reflects that one deuteron moves freely around the parent molecule in the radical dissociation channel. The limited angular distribution in the 5-12 eV corresponds to weak interaction between D and DCO in the roaming channel. The narrow angular distribution around 150 degrees reflects the strong repulsive force between the deuterons in the molecular dissociation channel.

The present results provide a new method for detecting weak statistic dynamics hidden in overwhelming background and could be extended to a vast variety of molecular systems.

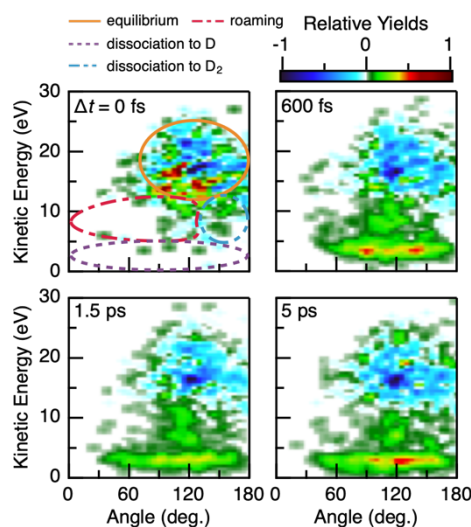


Fig. 1 Two-dimensional plots of kinetic energy versus deuteron momentum angle at the pump-probe time-delay Δt . The distribution at $\Delta t = -300$ fs was subtracted as background. Indicated in the upper left subplot are the areas corresponding to each reaction pathway identified by using *ab initio* calculations.

References

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