

Capturing roaming fragments in the dissociation of formaldehyde in real-time

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In conventional chemical reactions, molecules follow the minimum energy paths from reactants to products. However, the molecules sometimes take a little extra “walk”.

Two possible pathways for the dissociation of formaldehyde molecules (H_2CO) are considered: the dissociation to $\text{H}_2 + \text{CO}$ (molecular dissociation channel), and the dissociation to $\text{H} + \text{HCO}$ (radical dissociation channel). In alternative “roaming” dissociation pathways, the roaming fragment (H atom) walks around the remaining parent molecule (HCO, see Fig. 1). Since the first observation of “roaming” in the dissociation reaction of H_2CO in 2004 [1], footprints of roaming reactions have been reported in a wide variety of molecular systems. The outcomes of roaming processes have been observed using high-resolution spectroscopy to determine the product state distributions in almost all experimental roaming studies. In the case of H_2CO , the roaming outcomes show a characteristic combination of hot H_2 vibrational- and cold CO rotational-level populations, which is distinct from the populations in conventional molecular and radical dissociation channels.

Previous time-resolved experiments have focused on the time-resolved measurement of roaming outcomes rather than a roaming fragment itself [2-5]. One reason is that both the onset and duration of roaming are strongly stochastic. For H_2CO , roaming occurs on the vibrationally hot electronic ground S_0 state. Even though the roaming process itself occurs at the femtosecond time scale, the overall time scales (excitation, relaxation, vibration and roaming on the hot S_0 state, and dissociation) span hundreds of femtoseconds to tens of nanoseconds.

Recently, a roaming fragment itself has been captured in real-time by a combination of Coulomb explosion imaging and quasi-classical trajectory analysis [6]. Here a comprehensive

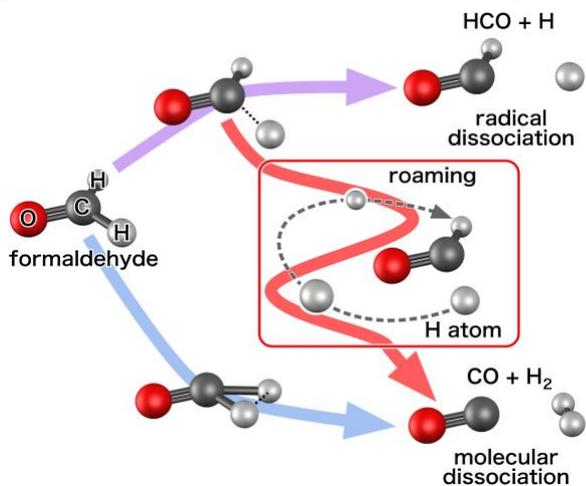


Fig. 1. Scheme representing the three dissociation pathways of a formaldehyde molecule (H_2CO): conventional molecular (blue arrow at the bottom) and radical (purple arrow at the top) dissociation, and roaming (red arrow in the middle).

picture is presented; the ultrafast dynamics triggered in neutral formaldehyde molecules upon femtosecond ultraviolet (UV) photoexcitation.

The Coulomb explosion imaging experiment was performed at the Advanced Laser Light Source (INRS-ÉMT, Canada) on the multi-kHz beamline. UV pump pulses were obtained by frequency quadrupling of the output of an optical parametric amplifier. Time-delayed probe pulses were obtained by pulse compression with a pressure-gradient hollow-core fiber and chirped mirrors. Both the pump and probe laser pulses were focused on an effusive molecular beam of deuterated formaldehyde (D_2CO). The ions generated by the probe pulses were collected with a uniform-electric-field ion imaging spectrometer. The three-dimensional momentum of each fragment ion was retrieved using a time- and position-sensitive delay-line detector. The total kinetic energy release (KER) E_{kin} and the angle θ between two deuteron momentum vectors can be expressed as

$$E_{\text{kin}} = \sum_i^n \frac{|\mathbf{p}_i|^2}{2m_i},$$

and

$$\theta = \cos^{-1} \left(\frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{|\mathbf{p}_1| |\mathbf{p}_2|} \right),$$

where \mathbf{p}_i and m_i are the momentum and the mass of the i -th fragment, and $i = 1, 2$, corresponding to the two deuterons, respectively. The relationship between the molecular geometry before the Coulomb explosion and the distributions of the resulting E_{kin} and θ is as follows: a large E_{kin} and a θ of approximately 120 degrees is the equilibrium geometry (orange circle in Fig. 2), a small E_{kin} and broad θ distribution due to weak interactions between deuterons is the radical dissociation channel (purple), an intermediate E_{kin} and a θ of approximately 180 degrees due to strong Coulomb repulsion between deuterons is the molecular dissociation channel (light-blue), and an intermediate E_{kin} and limited θ distribution is the roaming pathway (red).

The obtained two-dimensional plots of E_{kin} with θ for the three-body breaking (D^+ , D^+ , CO^+) channel of D_2CO^{3+} at the pump-probe time delays Δt between 0 fs and 5 ps are shown in Fig. 2. In the KER region < 12 eV, the onset of molecular dynamics occurred already before 100 fs. Although the relaxation from the electronically excited S_1 state to the hot S_0 state was previously predicted to occur in tens of nanoseconds, the present result indicates that the dissociation occurs at the femtosecond timescale due to strong coupling between vibrational states during irradiation of femtosecond UV pump pulses. The existence of the fast relaxation process was verified by photoelectron experiments at Nagoya University and *ab initio* calculation. The angular distribution in the KER range < 5 eV is broader than in the 5-12 eV range. The broader angular distribution below 5 eV reflects that one deuteron moves freely around the parent molecule, showing the contribution of the radical dissociation channel in this range. Both the intermediate

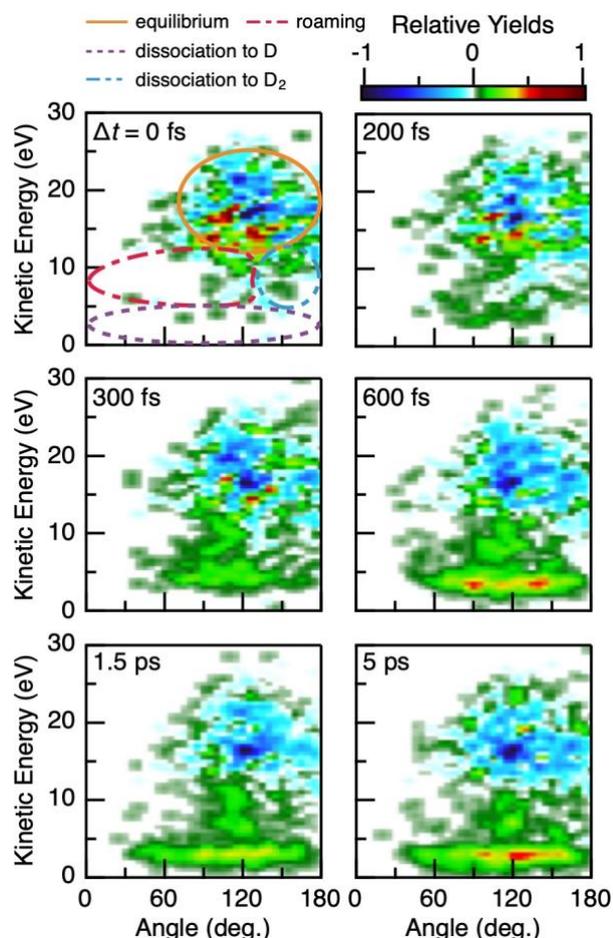


Fig. 2. Two-dimensional plots of kinetic energy versus deuteron momentum angle at the pump-probe time-delay Δt . The distribution at $\Delta t = -300$ fs was subtracted as background. Indicated in the upper left subplot are the areas corresponding to each reaction pathway identified by using *ab initio* calculations (Fig. 3).

energy distribution and limited angular distribution in the 5-12 eV range show the characteristics of the roaming pathway.

To identify the contribution of the roaming process, a simulation using *ab initio* calculations including all the critical steps (relaxation, dynamics on the S_0 state, and Coulomb explosion) was performed. The molecular geometry for each trajectory and the corresponding two-dimensional plots of the simulated KER versus deuteron momentum angle are shown in Fig. 3. The left column contains the real-space representation of two deuterons with respect to the CO fragment (fixed at the origin) before the Coulomb explosion step. One deuteron is plotted on the x -axis and the other is on the xy -plane. The right panels show the simulated results with an *ab initio* potential energy surface of the triply charged state. Here, our generalized definition of roaming, where one of the deuterons exceeds the threshold distance ($R_{D-DCO} = 2.8$ Å) and then returns to the parent DCO molecule, was used to extract the corresponding geometry for the roaming pathway (Fig. 3B). In the molecular dissociation channel, both deuterons are far from CO (Fig. 3C). In the radical dissociation channel, one of the deuterons is close to CO and the other is far away (Fig. 3D). The remaining case, where both deuterons are close to CO, is the equilibrium geometry (Fig. 3E). The roaming trajectory is distinguishable from other molecular and radical dissociation pathways because of the characteristic distribution of the KER ranging from 10 to 16 eV and the angle between 90 and 140 degrees.

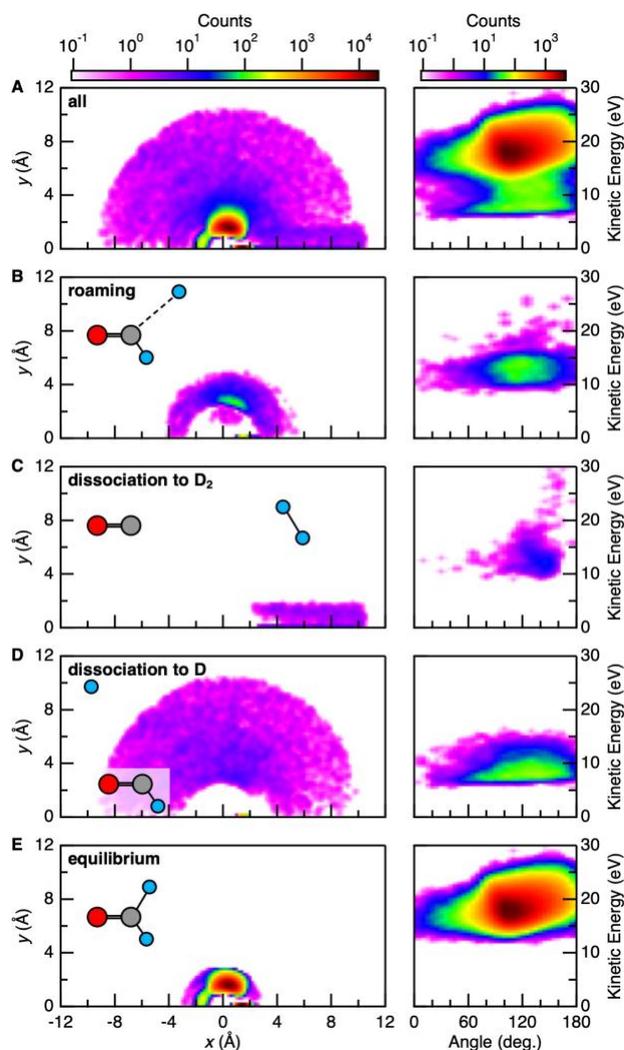


Fig. 3. (Left) The real-space representation of the molecular geometry for each reaction pathway before the Coulomb explosion. Typical geometries are represented on a relative scale. (Right) Two-dimensional plots of the simulated kinetic energy versus deuteron momentum angle.

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

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