Probing the nuclear dynamics of formaldehyde in 7 and 35 fs intense laser fields by coincidence momentum imaging

Chien-Ming Tseng¹, Mizuho Fushitani¹ ², and Akiyoshi Hishikawa¹ ² (IMS¹, SOKENDAI²)

Momenta of fragment ions produced by molecular Coulomb explosion in ultrashort intense laser fields provide valuable information on the molecular structure just before the explosion. This “Coulomb explosion imaging” is a powerful tool to visualize ultrafast reaction dynamics, e.g., hydrogen migration, as demonstrated for the acetylene-vinylidene isomerization of C₂H₂⁺, HCC₂⁺ ↔ CCH₂⁺ [1]. Here, we report an ion coincidence momentum imaging study of Coulomb explosion of formaldehyde (H₂CO) in 7 fs and 35 fs intense laser fields (800 nm, 1.3 × 10¹⁵ W/cm²) to understand the nuclear dynamics in intense laser fields and to seek the feasibility of applying the Coulomb explosion imaging to visualize the “roaming” hydrogen process discovered recently in the UV photodissociation of H₂CO [2].

The three-body explosion pathways identified at the present field intensity (1.3 × 10¹⁵ W/cm²) are:

\[
\begin{align*}
\text{H}_2\text{CO}^+ &\rightarrow \text{H}^+ + \text{H}^+ + \text{CO}^+ \quad (i) \\
&\rightarrow \text{H}^+ + \text{CH}^+ + \text{O}^+ \quad (ii) \\
&\rightarrow \text{H}^+ + \text{C}^+ + \text{OH}^+ \quad (iii)
\end{align*}
\]

The Newton diagram of the major three-body dissociation pathway (i) in Fig.1(a) shows that the distribution of momentum angle between two protons is peaked at θ₁₂ = 116°, preserving the original ∠H-C-H bond angle (∼116°) of H₂CO in the neutral ground state, in the 7 fs intense laser fields. On the other hand, when the longer laser pulses (35 fs) were employed, a shift in the θ₁₂ distribution peak (∼106°) as well as a broadening of the distribution were identified as shown in Figs. 1(b) and (d). In addition, an asymmetric energy partitioning between two H⁺ ions was observed in 35 fs laser fields.

![Fig.1](image-url)
According to the theoretical calculation of the potential surface of H$_2$CO$^{2+}$ [3], the $\angle$H-C-H bond angle is $\sim 60^\circ$ at the equilibrium geometry of H$_2$CO$^{2+}$(X $^1A_1$). This suggests that the structural changes from $\theta_{12}$ (= 116°) of H$_2$CO to smaller $\angle$H-C-H bond angles can occur after the vertical excitation from neutral ground state in a short time scale. Moreover, the potential energy curve is repulsive along the stretching coordinate of one C–H bond (see Fig. 2). Therefore, in the 35 fs laser fields, the wavepacket launched on the dication potential will move toward the equilibrium geometry with reducing $\theta_{12}$ and elongating one of the C–H bonds prior to the formation of the tri-cation at the peak laser intensity, resulting in the smaller angle $\theta_{12}$ (=106°) and the asymmetric energy partitioning between two H$^+$ ions. On the other hand, the wavepacket formed in the dication state in 7 fs laser fields should be ionized without significant structural changes because the laser field intensity reaches its maximum within few optical cycles.

In conclusion, we found the geometrical structure of H$_2$CO significantly deforms in the 35 fs intense laser fields reflecting the dynamics in the diatomic states, while it is almost frozen during the interaction with 7 fs intense laser pulse, showing that the Coulomb explosion imaging using few-cycle intense laser pulses provides a mean to directly probe the changes of the geometrical structure of formaldehyde in chemical reaction as demonstrated for acetylene [4]. Experiments to visualize “roaming hydrogen” in the UV photodissociation of H$_2$CO are in process.

Fig. 2. Schematic potential energy surfaces of formaldehyde along one C–H bond distance $R$(H–CHO) and the $\angle$H-C-H bond angle.

References