# Ultrafast Coulomb Explosion of Formaldehyde in 7 and 35 fs Intense Laser Fields Studied by Triple Ion-Coincidence Momentum Imaging

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**Abstract:** Ultrafast three-body Coulomb explosion of formaldehyde ($H_2CO$) in intense laser fields has been studied. The pulse duration dependence of the Newton plot of the fragment ions revealed the ultrafast molecular dynamics in the dication states.

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## 1. Introduction

Molecules irradiated with such intense laser pulses promptly eject several electrons to form highly charged states, which then undergo rapid bond breaking process by strong Coulombic repulsion between the constituent atoms. Since the momenta of the resultant fragment ions reflect sensitively the geometrical structure of the target molecule at the time of the laser irradiation, the "Coulomb explosion" process provides a unique means to visualize the instantaneous structure in reaction processes [1-3]. The pump-probe CEI using intense few cycle laser pulses has been applied for the photodissociation [1] and isomerization reactions [2,3]. In particular, CEI is advantageous in the direct probing of the geometrical structure to the large amplitude motion of energized molecules as demonstrated for hydrogen migration in $C_2D_2^{2+}$, $DCCD^{2+} \leftrightarrow CCD_2^{2+}$. In the present study, we performed an ion coincidence momentum imaging of three-body Coulomb explosion of formaldehyde ($H_2CO$) in 7 fs and 35 fs intense laser fields, (i) to understand the dynamics of formaldehyde in intense laser fields and (ii) to clarify the feasibility of applying the Coulomb explosion imaging to directly visualize the "roaming" hydrogen process [4].

## 2. Experimental

The output of a Ti:sapphire laser amplifier system (35 fs, 800 nm, 1 kHz) was compressed by a pulse compressor consisting of a 800-mm-long hollow fiber placed in an Ar cell and broadband dispersive mirrors (Tokai Optical) to generate sub-10 fs intense laser pulses. The obtained few-cycle laser pulses were introduced into an ultrahigh vacuum chamber ($<10^{-8}$ Pa) and focused by a concave mirror ($f$ = 75 mm). The gaseous $H_2CO$ sublimated from solid formaldehyde at ~ 50°C was introduced as a skimmed effusive beam into the interaction region in the vacuum chamber. The fragment ions produced by Coulomb explosion were guided to a fast position sensitive detector (Roentdek HEX80), by parallel-plate electrodes in a velocity mapping configuration. The momenta of the respective ions in the laboratory frame, $\mathbf{p}_i = (p_x^i, p_y^i, p_z^i)$ ($i$ = 1, 2, ...), are determined from the ($x$, $y$) position and the time-off-flight $t$ at the arrival at the detector for every single event of the Coulomb explosion process.

## 3. Results and Discussion

Three types of three-body Coulomb explosion pathways, $H_2CO^{3+} \rightarrow$ (i) $H^+ + H^+ + CO^+$, (ii) $H^+ + CH^+ + O^+$ and (iii) $H^+ + C^+ + OH^+$, are identified in 7-fs intense laser fields ($1.3 \times 10^{15}$ W/cm$^2$) with branching ratios of 0.93: 0.05: 0.02. The Newton diagram obtained for the major pathway (i) shows that the momenta of the two protons has an angular peak at $\theta_{HH}$ = 114° (see Fig.1(a)). This agrees well with that obtained ($\theta_{HH}$ = 120.5°) by a classical simulation of the Coulomb explosion from the geometric structure of $H_2CO$ in the ground $X^1A_1$ state, $R$(C-H) = 1.102 Å and ∠H-C-H = 121.1°. When a longer pulse (35 fs) is employed, on the other hand, the Newton plot shows a significant change in the distribution (Fig.1(b)). In addition to the shift of the $\theta_{12}$ distribution peak to ~105°, an asymmetric energy partitioning between two $H^+$ ions was observed. This suggests that the hydrogen motion is fast enough to deform the geometrical structure within 35 fs. In other words, an ultrashort laser pulse in the sub-10fs range is prerequisite for the probing of the roaming dynamics.

The Newton plot observed for the 35-fs intense laser fields suggests a stepwise three-body dissociation where one of the C-H bonds stretches significantly prior to the explosion. For a more quantitative discussion, we performed a simulation for the sequential explosion based the free rotor model [5], where the three-body Coulomb

explosion proceeds via the formation of $HCO^{2+}$, $H_2CO^{3+} \rightarrow H^+ + HCO^{2+} \rightarrow H^+ + H^+ + CO^+$. The results of the simulation are plotted in Fig.1(b). While the results show an overall agreement with the observed distributions, a slight deviation from the observed distributions is seen, implying there remain some interactions between $H^+$ and $HCO^{2+}$ when the second step explosion occurs.

Here we briefly discuss the mechanism of the quasi-sequential explosion. Compared with $H_2CO$, the ground state dication $H_2CO^{2+}$ has a substantially small H-C-H bond angle ∠H-C-H = 61° and a large C-H bond length, $R$(C-H) = 1.303 Å at the equilibrium geometry, which is in a quasi-bound well separated by a shallow barrier from a Coulombic repulsive potential. The potential barrier can be overcome from the Frank-Condon region from the neutral state in the repulsive part of the dication potential, so that one of the C-H bonds can readily stretch on this potential energy surface. Therefore, when the ground state of $H_2CO^{2+}$ is populated by the intense laser pulses, ultrafast nuclear motion should be induced both along the ∠H-C-H bending coordinate and along the one C-H bond stretching coordinate, as observed the experimental results. If we assume that the multiple ionization proceeds sequentially, the double charged state should be formed in the rising edge of the laser pulse and the further ionization to the triply charged final state and the Coulomb explosion takes place near the peak of the laser pulse in competition with the nuclear motion in the double charged state. Thus, the longer duration of the laser pulse (35 fs), provides a sufficient time for the structure deformation on the dication states, while the deformation is not significant for the 7 fs laser pulses due to the steep intensity increase.

## 4. Summary

The three-body Coulomb explosion dynamics of formaldehyde ($H_2CO$) in intense laser fields was investigated by ion coincidence momentum imaging technique. It was shown from the momentum correlation of the fragment ions that, when few-cycle intense laser pulses (7 fs) are used, the geometrical structure of the molecule is essentially frozen along the H-C-H bending coordinate during the interaction with the laser pulse. This suggests that the structural changes associated with hydrogen migration or roaming triggered pump laser pulse can be clearly monitored by the Coulomb explosion imaging using few-cycle intense laser pulses as a probe. On the other hand, deformation of the geometrical structure both along the C-H stretching and H-C-H bending coordinates is suggested for the 35 fs laser pulses. The origin of the structural change was discussed in terms of the nuclear dynamics in the dication states populated in the rising edge of the laser pulse.

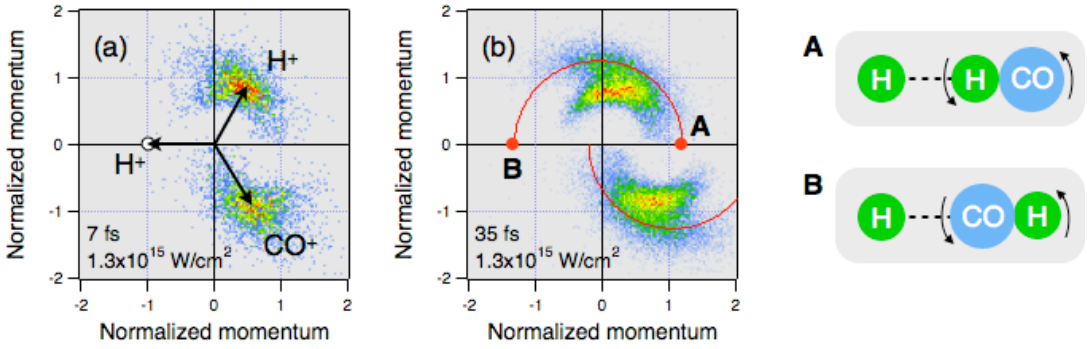


Fig. 1. Newton plot for the three-body Coulomb explosion of $H_2CO$ in intense laser fields ($1.3\times10^{15}$ W/cm$^2$) with a pulse duration of (a) 7 fs and (b) 35 fs. The momentum of one H+ is used for the normalization and is placed along the x-axis on the negative direction (open circle in (a)). The results of the free-rotor model simulation for sequential three-body explosion [5] are shown in (b). Two representative geometries (A and B) and the corresponding points in the Newton plot are indicated.

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