Supplemental Material

Dissociative ionization and Coulomb explosion of CH_4 in two-color asymmetric intense laser fields

H. Hasegawa,[1] A. Matsuda,[1] T. Morishita,[2] L. B. Madsen,[3]
F. Jensen,[4] O. I. Tolstikhin,[5] and A. Hishikawa[1,6,*]

[1] *Graduate School of Science, Nagoya University, Furo-cho, Chikusa, Nagoya, Aichi, 464-8602, Japan*
[2] *Institute for Advanced Science, The University of Electro-Communications, 1-5-1 Chofu-ga-oka, Chofu-shi, Tokyo 182-8585, Japan*
[3] *Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark*
[4] *Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark*
[5] *Moscow Institute of Physics and Technology, Dolgoprudny 141700, Russia*
[6] *Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa, Nagoya, Aichi, 464-8602, Japan*

(Dated: August 9, 2023)

CONTENTS

* hishi@chem.nagoya-u.ac.jp

EFFECT OF ELECTRON MOMENTUM RECOIL ON SPATIAL ASYMMETRY OF FRAGMENT IONS

A separate ion momentum imaging study of dissociative ionization of CH_4 is carried out to clarify the effect of electron momentum recoil on the spatial asymmetry of fragment ejection. In order to measure precisely the ion momentum distributions, the polarization direction of the ω-2ω laser fields is directed along the time-of-flight axis of the coincidence momentum imaging system (see Fig.1). Since the direction is perpendicular to the molecular beam, the influence of the initial velocity spread is significantly suppressed. A longer flight tube and a higher ion-extraction field were employed to separate adjacent m/z ion signals with high kinetic energy along the laser polarization direction.

The obtained momentum distributions of CH_3^+ and H^+ are shown in Fig.S1. The momentum image of H^+ shows a similar distribution as observed with the polarization direction parallel to the molecular beam in Fig.2, because of the relatively large kinetic energy carried by H^+ formed by the dissociative ionization pathway (ii) $CH_4 \rightarrow CH_3 + H^+ + e^-$. On the other hand, the momentum image of CH_3^+ produced by the pathway (i) $CH_4 \rightarrow CH_3^+ + H + e^-$ show a narrower momentum distribution in the center than that in the parallel configuration in Fig.2. Accordingly, the total kinetic energy release (KER) spectrum in Fig.S2(a) is peaked at a slightly smaller value than in the corresponding spectrum recorded in the parallel configuration. The momentum image in Fig.S1(a) for CH_3^+ is isotropic, as expected from the long lifetime of the metastable CH_4^+ dissociating to $CH_3^+ + H$.

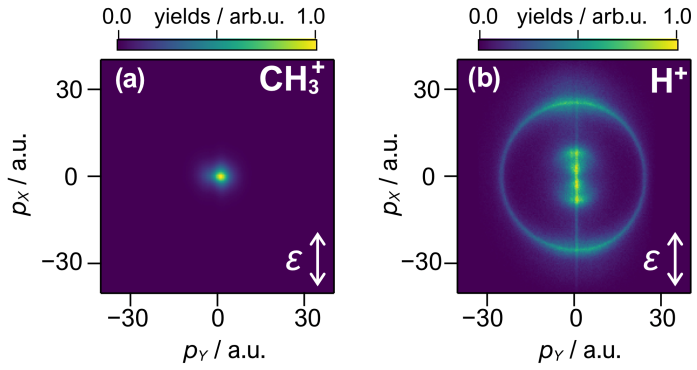

FIG. S1. Phase-averaged momentum image ($|p_Z| < 3$ a.u.) of (a) CH_3^+ and (b) H^+ fragment ions, respectively. The arrow with ε represents the direction of the laser polarization.

The asymmetry parameter $A_{CH_3^+}$ for the CH_3^+ fragment ion is shown in Fig.S2(b), exhibiting a clear oscillation as a function of the relative phase ϕ with an amplitude of $A_0 \sim 0.05$. Interestingly, it was also found that the parent ion CH_4^+ shows an asymmetric momentum distribution along the laser polarization direction. Figure S2(b) plots the phase dependence of the momentum $p_{CH_4^+,X}(\phi)$ at the distribution peak along the laser polarization direction (X-axis), where a clear oscillation with an amplitude of ~ 0.2 a.u. is observed.

The asymmetry and its phase dependence observed for the momentum distribution of the parent ion are attributed to momentum recoil from the tunneling electron. In order to understand how the momentum recoil affects the asymmetry of CH_3^+, the recoil momentum on CH_3^+ along the laser polarization direction is estimated as $p^{rc}_{CH_3^+}(\phi) = (m_{CH_3}/m_{CH_4})p_{CH_4^+,X}(\phi)$. The mean recoil momentum is subtracted from the momentum of CH_3^+ to estimate the net momentum distribution imposed by the fragmentation process, $\mathbf{p}'_{CH_3^+}(\phi) = \mathbf{p}_{CH_3^+}(\phi) - p^{rc}_{CH_3^+}(\phi)\mathbf{e}_X$, where $\mathbf{e}_X$ represents the unit vector along the X-axis. Figure S2(b) plots the asymmetry parameter obtained from the distribution of the net momentum $\mathbf{p}'_{CH_3^+}(\phi)$, where the uncertainties are estimated from the width of CH_4^+ momentum distribution. The dependence on KER is shown in Fig.S2(c). The obtained results show only a slight dependence on the phase with its amplitude close to the statistical uncertainty. This shows that the fragmentation process in the dissociative ionization pathway (i), $CH_4^+ \rightarrow CH_3^+ + H$, is not sensitive to the shape of the ω-2ω laser fields. This is consistent with the metastable decay from the CH_4^+ in the ground state discussed in main text, which smears out the effect of the asymmetric laser fields by molecular rotation prior to the dissociation.

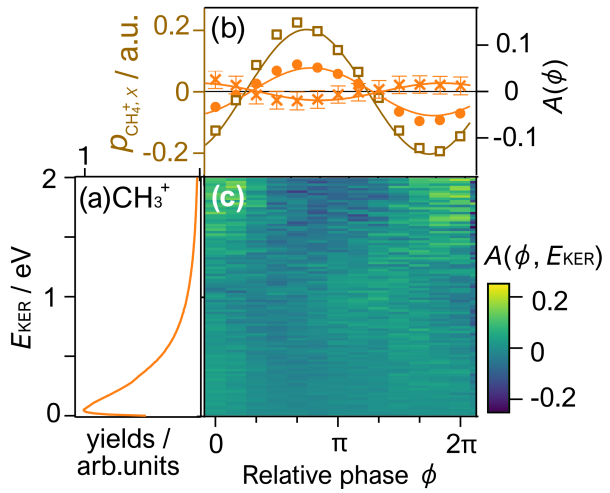

FIG. S2. (a) Total kinetic energy release (KER) spectra for $CH_4^+ \rightarrow CH_3^+ + H$. (b) Phase dependence of the momentum of the parent ion CH_4^+ (square), plotting the momentum value $p_{CH_4^+,X}$ at the distribution peak along the X-axis (laser polarization direction). The asymmetry parameters $A(\phi)$ for CH_3^+ (filled circle, right axis) is shown together with those obtained after the recoil momentum correction (cross, right axis). Solid lines are the results of the least-squares fitting to a cosine function. (c) Two-dimensional plot of the asymmetry parameter $A(\phi, E_{KER})$ of CH_3^+ obtained after the recoil momentum correction.