

Deuterium Isotope Effect on Internal Conversion of Ethylene Studied by Time-Resolved Photoelectron Spectroscopy

*Alexie Boyer, Alexander Humeniuk, Shutaro Karashima and Toshinori Suzuki**

Department of Chemistry, Graduate School of Science, Kyoto University,

Kitashirakawa-Oiwakecho, Sakyo-Ku, Kyoto 606-8502, JAPAN

* Email: suzuki@kuchem.kyoto-u.ac.jp

ABSTRACT

The effect of deuterium isotopes on the internal conversion of ethylene is studied using extreme ultraviolet time-resolved photoelectron spectroscopy. For deuterium-labeled ethylene, the timescale for ultrafast internal conversion is increased by a factor of approximately $\sqrt{2}$, in agreement with the results of *ab initio* multiple spawning calculations, indicating the essential role played by hydrogen motion in the conversion process. Following internal conversion, a metastable species with an electron binding energy of ~ 9 eV is produced, and it decays with a similar time constant for both isotopologues.

1. INTRODUCTION

Ethylene (C_2H_4) undergoes ultrafast internal conversion (IC) from the $^1\pi\pi^*$ excited state to the ground state (S_0), which is the paradigm for the *cis-trans* photoisomerization of olefins.¹⁻¹⁵ The electronic transition to $^1\pi\pi^*$ gives rise to a broad photoabsorption spectrum centred around 160 nm, which overlaps with the vibrationally resolved transitions to the $\pi 3s$ Rydberg state starting at 175 nm.^{16, 17} Previous experimental studies performed at 159 nm revealed that $\pi 3s$ Rydberg state plays a negligible role in the photoexcited dynamics.^{4, 18, 19} Photoexcitation of ethylene immediately induces a C=C bond twisting motion, and additional pyramidalization at the carbon atom or largescale C-H bending motion towards an ethylidene ($\text{CH}_3\text{-CH}$)-like structure allows access to the conical intersection (COIN) between $^1\pi\pi^*$ and S_0 .^{3, 20} A previous study has shown that the nuclear wave packet reaches the C=C twisted geometry in less than 10 fs, and then population transfer from $^1\pi\pi^*$ to S_0 occurs within the next 20–30 fs.¹⁹ A vibrationally excited S_0 state is formed in less than 45 fs, eventually producing H, H_2 , C_2H_2 , or C_2H_3 .

The branching ratio and the energy distributions for these products have been extensively measured using photofragment translation spectroscopy.⁷⁻⁹ For partially deuterium-labeled ethylene, the results indicated migration of H and D atoms prior to dissociation. However, Rice-Ramsperger-Kassel-Marcus (RRKM) calculations failed to reproduce the yields for the 1,1- H_2 and 1,2- H_2 molecular elimination processes and their wavelength dependence,^{10, 11} indicating the non-statistical nature of the dynamics. In principle, the nuclear dynamics can be more accurately simulated using trajectory or wave packet calculations; however, such attempts have been made only up to a few hundred femtoseconds, to our knowledge, and the ground-state dynamics remain elusive.^{12, 13}

Regarding the large-amplitude motions of hydrogen atoms involved in the IC of ethylene, one might expect to observe a significant isotope effect on ultrafast timescales. However, theoretical calculations predict it to be minor^{4, 12, 21} and previous experiments using

time-resolved mass spectroscopy have failed to detect any significant isotope effects.^{15, 22} In the present study, we decided to gain further insights into the ultrafast dynamics of ethylene by investigating the effects of deuteration using extreme ultraviolet (EUV) time-resolved photoelectron spectroscopy (TRPES)^{18, 19} on ethylene-d₄ with a time resolution of 39 fs. We also revisit our previous measurements for ethylene-h₄ to extend the observation time window up to 25 ps and extract longer timescales associated with the formation of photoproducts.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental apparatus used in this study has been described previously.²³⁻²⁵ Briefly, a 1 kHz Ti:sapphire regenerative amplifier (35 fs, 800 nm, 6 mJ) was used as the driving laser to produce vacuum UV (VUV) and EUV radiation. Filamentation four-wave mixing in Ar was used to generate VUV pump pulses (160 nm), while high-order harmonic generation in Ar and a time-preserving monochromator²⁶ were used to generate the EUV probe pulses (21.7 eV). The pump and probe pulses were focused into a gas jet of 5% C₂H₄ or C₂D₄ in a helium carrier gas. The molecules were photoexcited by the VUV pulses and ionized by the time-delayed EUV pulses. Photoelectrons were detected using a magnetic bottle time-of-flight electron energy analyzer.²⁷ The cross-correlation between the pump and probe pulses was estimated to be ~39 fs. Gaseous C₂D₄ (purity > 98%) was purchased from Cambridge Isotope Laboratories. Due to the limited amount of C₂D₄ available for the measurements, the S/N ratio was lower than that for C₂H₄.

The non-adiabatic dynamics following excitation to the ¹ $\pi\pi^*$ state were simulated using the ab initio multiple spawning (AIMS) method^{28, 29} as implemented in Molpro.³⁰ The electronic structure was described using multi-reference second-order perturbation theory (MS-CASPT2) and the 6-31G* basis set. The active space consisted of 4 electrons in 3 orbitals (HOMO-1 (σ), HOMO (π) and LUMO (π^*)), and the lowest 3 singlet states were included in

the AIMS dynamics. Initial conditions for 10 trajectories were sampled from the Wigner distribution of the harmonic vibrational wavefunction in S_0 , which was calculated with second-order Møller-Plesset perturbation theory (MP2) and the cc-pVDZ basis set. Default parameters were used for most of the AIMS settings. The width of the frozen Gaussian functions for deuterium was taken to be the same as that for hydrogen (4.7 Bohr^{-2}).³¹ Trajectories were propagated for 300 fs with adaptive time-stepping with an initial step size of 1 fs.

3. RESULTS AND DISCUSSION

The results for C_2D_4 are shown in Figure 1(a). The low S/N ratio hampered the measurements for C_2D_4 in the electron binding energy (eBE) region $> 10 \text{ eV}$. We observe a rapid shift of the photoelectron (PE) signal from the Franck-Condon region (eBE $\sim 3.5 \text{ eV}$) toward higher eBE. The initial step of the dynamics is driven by C=C twisting that leads the wave packet to the COIN ($\sim 6.0\text{--}7.5 \text{ eV}$) before relaxation to the vibrationally excited S_0 ($\sim 8.5\text{--}9.8 \text{ eV}$), and photoproducts such as acetylene, H_2 and H are finally generated by dissociation. To extract the time constants associated with these elementary steps, we performed least-squares fitting of the PE signal intensity ($I(E, t)$) using a single exponential decay function:

$$I(E, t) = g(t) \otimes \left[H(t - t_d(E)) \times e^{-\frac{t - t_d(E)}{\tau(E)}} \right], \quad (1)$$

where $g(t)$ is the Gaussian cross-correlation function between the pump and probe pulses, $H(x)$ is the Heaviside function, t_d is the latency time and τ is the decay time constant. We focus here on the values of $t_d(E)$ and $\tau(E)$ shown in Figures 1(b) and 1(c), respectively, and a comparison with the corresponding values for C_2H_4 (dashed black lines). The $t_d(E)$ values are quite similar for the two isotopologues, while $\tau(E)$ for C_2D_4 is slightly larger.

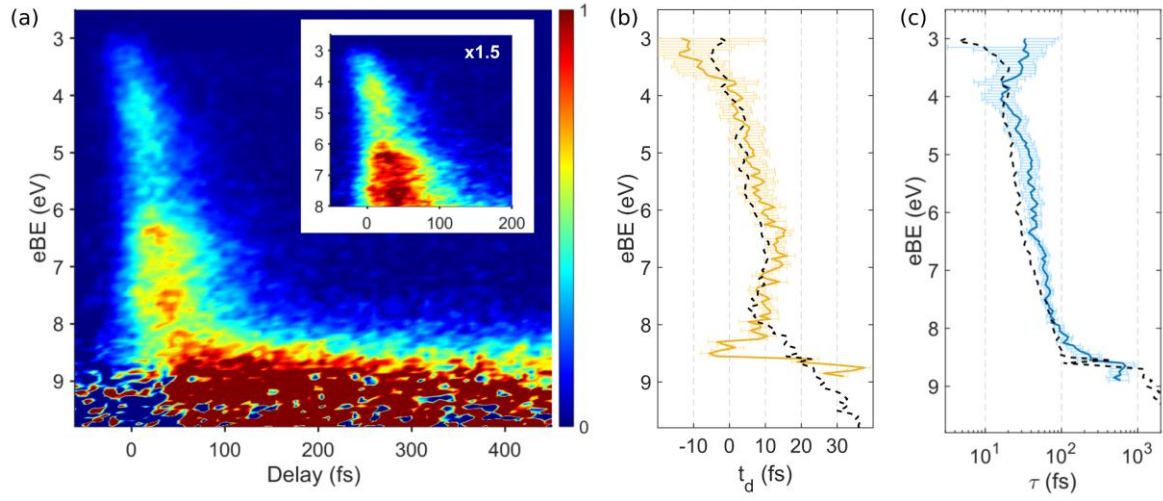


Figure 1. (a) TRPE spectra of C₂D₄. The inset shows the excited state and COIN regions with enhanced intensity ($\times 1.5$). The fitting parameters t_d and τ are plotted as functions of eBE in (b) and (c), respectively. The error bars correspond to the standard deviation of the fitting parameters. Black dashed lines are the corresponding values for C₂H₄.¹⁹

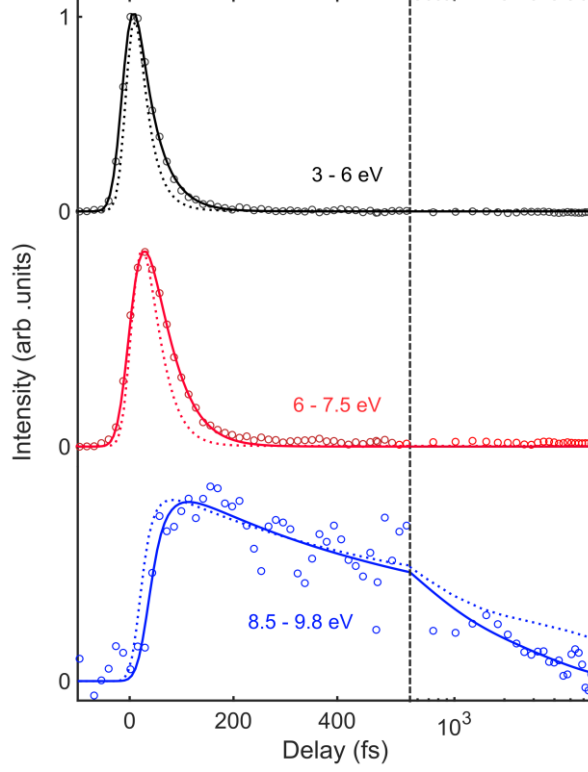


Figure 2. Time profiles of photoelectron signal integrated for 3.0–6.0, 6.0–7.5, 8.5–9.8 eV energy ranges together with fitting curves (solid lines). Dashed lines correspond to the data for C₂H₄.¹⁹

The photoelectron signal intensities integrated for three different eBE regions of 3.0–6.0, 6–7.5 and 8.5–9.8 eV are shown in Figure 2. These regions roughly correspond to the eBE values for $^1\pi\pi^*$, COIN and the S₀ product(s), respectively. The PE intensity in each region can be expressed using the following formulae:

$$I_{ES}(t) = g(t) \otimes \left[H(t - t_d) \times e^{-\frac{t-t_d}{\tau_{ES}}} \right], \quad (2)$$

$$I_{COIN}(t) = g(t) \otimes \left[H(t - t_d) \frac{\tau_{COIN}}{\tau_{ES} - \tau_{COIN}} \times \left[e^{-\frac{t-t_d}{\tau_{ES}}} - e^{-\frac{t-t_d}{\tau_{COIN}}} \right] \right], \quad (3)$$

$$I_{GS}(t) = g(t) \otimes \left[H(t - t_d') \frac{\tau_{GS}}{\tau_{COIN} - \tau_{GS}} \times \left[e^{-\frac{t-t_d'}{\tau_{COIN}}} - e^{-\frac{t-t_d'}{\tau_{GS}}} \right] \right], \quad (4)$$

where τ_{ES} , τ_{COIN} and τ_{GS} are the decay time constants, and t_d and t_d' are the latency times. The ground state decay signal can be fitted assuming dual exponential decay with fast (τ_{GS}^1) and slow (τ_{GS}^2) time constants. Because Figure 1(b) shows that the latency times in the 3.0–7.5 eV region are very similar, we used a single constant t_d here. The results of least-squares fitting are shown in Figure 2, and the time constants are summarized in Table 1. (The accuracy of the τ_{GS}^2 value for C_2D_4 is limited because the measurements were performed only up to 7 ps; the corresponding value for C_2H_4 is more accurate as it is obtained after revisiting an experiment with an observation window up to 25 ps – see Figure 3.) Similar to the 2D fitting results shown in Figure 1, the integrated photoelectron band intensities indicate that the latency time t_d for the excited-state dynamics is not much affected by the isotope substitution. On the other hand, the decay time constants τ_{ES} and τ_{COIN} are larger for C_2D_4 , which causes the appearance time ($t_d' = 49 \pm 7$ fs) for the S_0 transients to be later than that for C_2H_4 .

Interestingly, the time constants extracted from the decay of the PE signal in the 8.5–9.8 eV energy range (τ_{GS}^1 and τ_{GS}^2) are very similar for the two isotopologues. In this energy range, the PE spectra of vibrationally excited ground-state ethylene, ethylidene³² and vinyl radical³³ are expected to overlap. As we discussed in our previous paper,¹⁹ τ_{GS}^1 agrees reasonably well with the RRKM lifetime for ground-state ethylene, so that τ_{GS}^1 is ascribed to ethylene. As seen in Figure 3(a), the PE spectrum gradually shifts to ~9 eV, which is close to the PE band maximum (9.25 eV) for vinyl radicals.³³ Thus, τ_{GS}^2 is attributed to metastable vinyl radicals. As seen in Figure 3(b), the PE signal for ethylene-h4 on an extended timescale exhibits a long-lived component, which is also attributed to metastable vinyl radicals with a relatively low internal energy; because the vinyl radicals do not survive as the final product, they all should undergo dissociation on a longer timescale. It would be of interest to perform time-resolved mass spectrometry or ion imaging for this system to analyze these long-lived

states in the future. We have actually attempted to carry out an ion-imaging experiment using EUV probe pulses of 21.7 and 15.5 eV; however, dissociative ionization induced by the EUV probe pulses created a strong background, and measurement of the transient species was not possible. Therefore, a lower probe photon energy should be used for ion-imaging experiments.

Table 1. Extracted fitting parameters for C_2D_4 and C_2H_4 using equations (2)-(4).

	t_d [fs]	τ_{ES} [fs]	τ_{COIN} [fs]	t'_d [fs]	τ_{GS}^1 [fs]	τ_{GS}^2 [ps]
C_2D_4	8 ± 7^a	38 ± 4^a	27 ± 3^a	49 ± 7^a	445 ± 104^a	2.97 ± 0.84^a
C_2H_4	9 ± 1^b	25 ± 1^b	19 ± 1^b	27 ± 1^b	480 ± 40^b	2.77 ± 0.57^a
Ratio		1.52	1.42	1.81		

^aThis work. ^bParameters extracted from Karashima *et al.*¹⁹ at similar energy ranges to the C_2D_4 case.

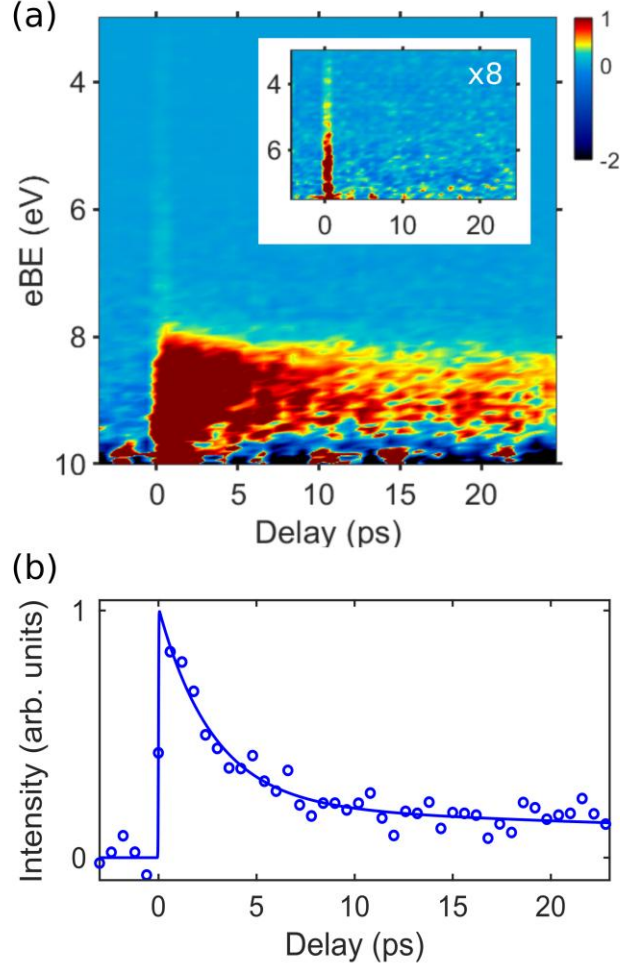


Figure 3. (a) TRPE spectra of C₂H₄ on 25 ps timescale. The inset shows the PE signal in the 3.0–9.8 eV energy range with enhanced intensity. (b) Integrated PE signals in 8.5–9.8 eV energy range fitted using double-exponential decay function to extract the slow component τ_{GS}^2 .

To compare with the experimental results, we performed MS-CASPT(4,3)/6-31G* AIMS calculations for ethylene-h₄ and ethylene-d₄ to identify the isotope effect on the internal conversion dynamics. The results for population transfer from the excited state $^1\pi\pi^*$ to the ground state S_0 are shown in Figure 4. The excited-state dynamics for ethylene-d₄ are slowed down by a factor of $\sqrt{2}$ compared to those for ethylene-h₄, which is expected based on the isotope mass ratio ($\sqrt{m_D/m_H}$). A similar scaling factor is observed in the experimental results

for τ_{ES} and τ_{COIN} . Unfortunately, the method did not enable us to calculate the dynamics on the longer timescale required to examine product formation, because the method based on the electronic structure becomes inaccurate for geometries that deviate significantly from the equilibrium structure.

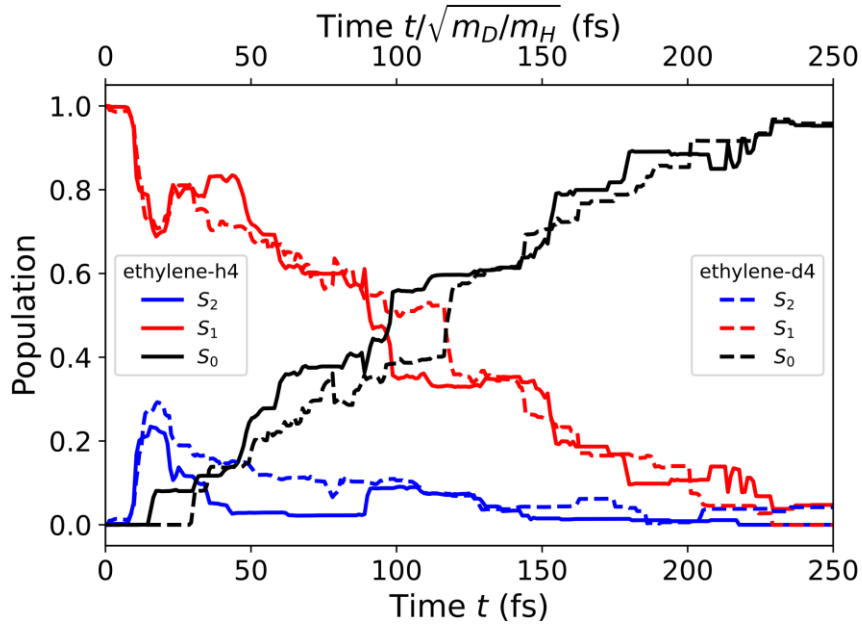


Figure 4. Adiabatic state populations for ethylene-h4 (solid) and ethylene-d4 (dashed) from AIMS simulations. For ethylene-d4, the time axis is scaled by a factor of $1/\sqrt{2}$.

We also analyzed how deuteration changes the reduced mass μ of normal modes that are initially excited. This allows to roughly estimate the factor by which the time constants are scaled if the wavepacket initially follows one of those normal modes. The reduced mass $\mu(m_H, m_C)$ is a function of the atomic masses $m_H = 1.0$ and $m_C = 12.0$. In ethylene-d4, the mass of deuterium $m_D = 2.0$ replaces m_H . For torsion around the CC bond, pyramidalization and the symmetric CC stretch vibration, the reduced mass becomes $m_H, \left(\frac{0.64}{m_H} + \frac{0.36}{m_C}\right)^{-1}$ and

$\left(\frac{0.26}{m_H} + \frac{0.74}{m_C}\right)^{-1}$, respectively. The fractions of the normal mode displacements on hydrogen and carbon atoms were taken from a B3LYP/6-31G* frequency calculation. Deuteration increases the period of oscillation by a factor of $\sqrt{\mu(m_D, m_C)/\mu(m_H, m_C)}$, which is $\sqrt{2} \approx 1.41$ for torsion, 1.38 for pyramidalization and 1.30 for the symmetric CC stretch.

4. CONCLUSION

We investigated the ultrafast dynamics of two isopologues, ethylene-h4 and ethylene-d4, using extreme ultraviolet time-resolved photoelectron spectroscopy. Deuteration increased the timescale for the elementary internal conversion steps by a factor of $\sqrt{2}$, in agreement with theoretical simulations, indicating the essential role of hydrogen atomic motion. The lifetime of long-lived reaction intermediates, which were most likely metastable vinyl radicals, was found to be similar for the two isotopologues.

AUTHOR INFORMATION

Corresponding Author *Toshinori Suzuki – Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan; Email: suzuki.toshinori.2n@kyoto-u.ac.jp.

Notes

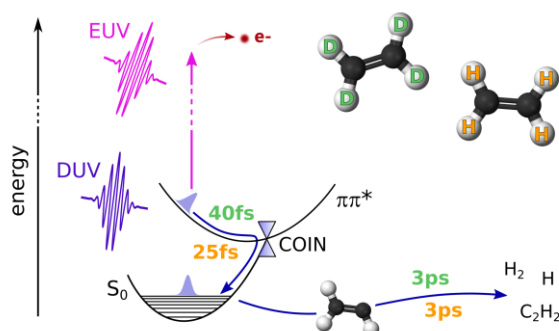
The authors declare no competing financial interests.

ACKNOWLEDGMENTS

This study was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant No. 21H04970. AB thanks the Japan Society for the Promotion of Science for the

postdoctoral fellowship. The computations were performed at the Research Center for Computational Science of the Institute for Molecular Science (Project: 23-IMS-C284).

TOC GRAPHIC



REFERENCES

- (1) Ohmine, I. Mechanisms of nonadiabatic transitions in photoisomerization processes of conjugated molecules: Role of hydrogen migrations. *The Journal of Chemical Physics* **1985**, *83*, 2348-2362. DOI: 10.1063/1.449276.
- (2) Ben-Nun, M.; Martínez, T. J. Photodynamics of ethylene: Ab initio studies of conical intersections. *Chemical Physics* **2000**, *259*, 237-248. DOI: 10.1016/S0301-0104(00)00194-4.
- (3) Barbatti, M.; Paier, J.; Lischka, H. Photochemistry of ethylene: A multireference configuration interaction investigation of the excited-state energy surfaces. *The Journal of Chemical Physics* **2004**, *121*, 11614-11624. DOI: 10.1063/1.1807378.
- (4) Sellner, B.; Barbatti, M.; Müller, T.; Domcke, W.; Lischka, H. Ultrafast non-adiabatic dynamics of ethylene including Rydberg states. *Molecular Physics* **2013**, *111*, 2439-2450. DOI: 10.1080/00268976.2013.813590.

- (5) Mori, T.; Glover, W. J.; Schuurman, M. S.; Martinez, T. J. Role of Rydberg states in the photochemical dynamics of ethylene. *The Journal of Physical Chemistry A* **2012**, *116*, 2808-2818. DOI: 10.1021/jp2097185.
- (6) Allison, T. K.; Tao, H.; Glover, W. J.; Wright, T. W.; Stooke, A. M.; Khurmi, C.; Van Tilborg, J.; Liu, Y.; Falcone, R. W.; Martínez, T. J.; et al. Ultrafast internal conversion in ethylene. II. Mechanisms and pathways for quenching and hydrogen elimination. *The Journal of Chemical Physics* **2012**, *136*, 124317. DOI: 10.1063/1.3697760.
- (7) Lin, J. J.; Hwang, D. W.; Lee, Y. T.; Yang, X. Site and isotope effects on the molecular hydrogen elimination from ethylene at 157 nm excitation. *The Journal of Chemical Physics* **1998**, *109*, 2979-2982. DOI: 10.1063/1.476888.
- (8) Lin, J. J.; Wang, C. C.; Lee, Y. T.; Yang, X. Site-specific dissociation dynamics of ethylene at 157 nm: Atomic and molecular hydrogen elimination. *The Journal of Chemical Physics* **2000**, *113*, 9668-9677. DOI: 10.1063/1.1321044.
- (9) Lee, S.-H.; Lee, Y. T.; Yang, X. Dynamics of photodissociation of ethylene and its isotopomers at 157 nm: Branching ratios and kinetic-energy distributions. *The Journal of Chemical Physics* **2004**, *120*, 10983-10991. DOI: 10.1063/1.1740711.
- (10) Chang, A. H. H.; Mebel, A. M.; Yang, X. M.; Lin, S. H.; Lee, Y. T. *Ab initio*/RRKM approach toward the understanding of ethylene photodissociation. *The Journal of Chemical Physics* **1998**, *109*, 2748-2761. DOI: 10.1063/1.476877.
- (11) Chang, A. H. H.; Hwang, D. W.; Yang, X. M.; Mebel, A. M.; Lin, S. H.; Lee, Y. T. Toward the understanding of ethylene photodissociation: Theoretical study of energy partition in products and rate constants. *The Journal of Chemical Physics* **1999**, *110*, 10810-10820. DOI: 10.1063/1.478999.

- (12) Tao, H.; Levine, B. G.; Martínez, T. J. Ab initio multiple spawning dynamics using multi-state second-order perturbation theory. *The Journal of Physical Chemistry A* **2009**, *113*, 13656-13662. DOI: 10.1021/jp9063565.
- (13) Hollas, D.; Šišťík, L.; Hohenstein, E. G.; Martínez, T. J.; Slaviček, P. Nonadiabatic ab initio molecular dynamics with the floating occupation molecular orbital-complete active space configuration interaction method. *Journal of Chemical Theory and Computation* **2018**, *14*, 339-350. DOI: 10.1021/acs.jctc.7b00958.
- (14) Farmanara, P.; Stert, V.; Radloff, W. Ultrafast internal conversion and fragmentation in electronically excited C₂H₄ and C₂H₃Cl molecules. *Chemical Physics Letters* **1998**, *288*, 518-522. DOI: 10.1016/S0009-2614(98)00312-1.
- (15) Kosma, K.; Trushin, S. A.; Fuss, W.; Schmid, W. E. Ultrafast dynamics and coherent oscillations in ethylene and ethylene-*d*₄ excited at 162 nm. *The Journal of Physical Chemistry A* **2008**, *112*, 7514-7529. DOI: 10.1021/jp803548c.
- (16) Merer, A. J.; Mulliken, R. S. Ultraviolet spectra and excited states of ethylene and its alkyl derivatives. *Chemical Reviews* **1969**, *69*, 639-656. DOI: 10.1021/cr60261a003.
- (17) Wu, C. Y. R.; Chen, F. Z.; Judge, D. L. Temperature-dependent photoabsorption cross sections in the VUV-UV region: Ethylene. *Journal of Geophysical Research: Planets* **2004**, *109*, E07S15. DOI: 10.1029/2003JE002180.
- (18) Kobayashi, T.; Horio, T.; Suzuki, T. Ultrafast deactivation of the $\pi^*(V)$ state of ethylene studied using sub-20 fs time-resolved photoelectron imaging. *The Journal of Physical Chemistry A* **2015**, *119*, 9518-9523. DOI: 10.1021/acs.jpca.5b06094.
- (19) Karashima, S.; Humeniuk, A.; Glover, W. J.; Suzuki, T. Ultrafast photoisomerization of ethylene studied using time-resolved extreme ultraviolet photoelectron spectroscopy. *The Journal of Physical Chemistry A* **2022**, *126*, 3873-3879. DOI: 10.1021/acs.jpca.2c02468.

- (20) Barbatti, M.; Ruckebauer, M.; Lischka, H. The photodynamics of ethylene: A surface-hopping study on structural aspects. *The Journal of Chemical Physics* **2005**, *122*, 174307. DOI: 10.1063/1.1888573.
- (21) Tao, H.; Allison, T. K.; Wright, T. W.; Stooke, A. M.; Khurmi, C.; Van Tilborg, J.; Liu, Y.; Falcone, R. W.; Belkacem, A.; Martinez, T. J. Ultrafast internal conversion in ethylene. I. The excited state lifetime. *The Journal of Chemical Physics* **2011**, *134*, 244306. DOI: 10.1063/1.3604007.
- (22) Stert, V.; Lippert, H.; Ritze, H. H.; Radloff, W. Femtosecond time-resolved dynamics of the electronically excited ethylene molecule. *Chemical Physics Letters* **2004**, *388*, 144-149. DOI: 10.1016/j.cplett.2004.02.077.
- (23) Karashima, S.; Humeniuk, A.; Uenishi, R.; Horio, T.; Kanno, M.; Ohta, T.; Nishitani, J.; Mitrić, R.; Suzuki, T. Ultrafast ring-opening reaction of 1,3-cyclohexadiene: Identification of nonadiabatic pathway via doubly excited state. *Journal of the American Chemical Society* **2021**, *143*, 8034-8045. DOI: 10.1021/jacs.1c01896.
- (24) Miura, Y.; Yamamoto, Y.-i.; Karashima, S.; Orimo, N.; Hara, A.; Fukuoka, K.; Ishiyama, T.; Suzuki, T. Formation of long-lived dark states during electronic relaxation of pyrimidine nucleobases studied using extreme ultraviolet time-resolved photoelectron spectroscopy. *Journal of the American Chemical Society* **2023**, *145*, 3369-3381. DOI: 10.1021/jacs.2c09803.
- (25) Karashima, S.; Miao, X.; Kanayama, A.; Yamamoto, Y.-i.; Nishitani, J.; Kavka, N.; Mitric, R.; Suzuki, T. Ultrafast ring closure reaction of gaseous *cis*-stilbene from $S_1(\pi\pi^*)$. *Journal of the American Chemical Society* **2023**, *145*, 3283-3288. DOI: 10.1021/jacs.2c12266.
- (26) Frassetto, F.; Cacho, C.; Froud, C. A.; Turcu, I. C. E.; Villoresi, P.; Bryan, W. A.; Springate, E.; Poletto, L. Single-grating monochromator for extreme-ultraviolet ultrashort pulses. *Optics Express* **2011**, *19*, 19169. DOI: 10.1364/OE.19.019169.

- (27) Kurahashi, N.; Thürmer, S.; Liu, S. Y.; Yamamoto, Y.-i.; Karashima, S.; Bhattacharya, A.; Ogi, Y.; Horio, T.; Suzuki, T. Design and characterization of a magnetic bottle electron spectrometer for time-resolved extreme UV and X-ray photoemission spectroscopy of liquid microjets. *Structural Dynamics* **2021**, *8*, 034303. DOI: 10.1063/4.0000107.
- (28) Ben-Nun, M.; Martínez, T. J. Ab initio molecular dynamics study of cis–trans photoisomerization in ethylene. *Chemical Physics Letters* **1998**, *298*, 57-65. DOI: 10.1016/S0009-2614(98)01115-4.
- (29) Levine, B. G.; Coe, J. D.; Virshup, A. M.; Martínez, T. J. Implementation of ab initio multiple spawning in the Molpro quantum chemistry package. *Chemical Physics* **2008**, *347*, 3-16. DOI: 10.1016/j.chemphys.2008.01.014.
- (30) MOLPRO, version 2023.2, a package of ab initio programs, H.-J. Werner, P. J. Knowles, and others, see <https://www.molpro.net>. (accessed April 2024).
- (31) Thompson, A. L.; Punwong, C.; Martínez, T. J. Optimization of width parameters for quantum dynamics with frozen Gaussian basis sets. *Chemical Physics* **2010**, *370*, 70-77. DOI: 10.1016/j.chemphys.2010.03.020.
- (32) Baek, S. J.; Choi, K.-W.; Choi, Y. S.; Kim, S. K. Spectroscopy and dynamics of methylamine. II. Rotational and vibrational structures of CH₃NH₂ and CH₃ND₂ in cationic D states. *The Journal of Chemical Physics* **2003**, *118*, 11040-11047. DOI: 10.1063/1.1575735.
- (33) Wu, X.; Zhou, X.; Hemberger, P.; Bodi, A. The ionization energy of the vinyl radical: a Mexican standoff with a happy ending. *Physical Chemistry Chemical Physics* **2019**, *21*, 22238-22247. DOI: 10.1039/C9CP04493K.