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Tracking Ultrafast Bond Dissociation Dynamics with 0.1-Å Resolution by Femtosecond Extreme Ultraviolet Absorption Spectroscopy

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Abstract

Visualizing the real-time dissociation of chemical bonds represents a challenge in the study of ultrafast molecular dynamics due to the simultaneous need for sub-ångström spatial- and femtosecond temporal resolution. Here, we follow the C—I dissociation dynamics of strong-field-ionized 2-iodopropane ($2\text{-C}_3\text{H}_7\text{I}$) with femtosecond XUV absorption spectroscopy. By probing the iodine $4d$ core-level absorption, we resolve a continuous XUV spectral shift on the sub-100-fs timescale that accompanies the dissociation of the $2\text{-C}_3\text{H}_7\text{I}^+$ spin-orbit-excited $^2E_{1/2}$ state to yield atomic I in the $^2P_{3/2}$ state. In combination with ab initio calculations of the C—I distance-dependent XUV transition energy, we reconstruct the temporal evolution of the C—I distance from the Franck-Condon region to the asymptotic region with 10-fs, 0.1-Å resolution. The C—I bond elongation appears to couple to coherent vibrational motion along the $\text{HC}(\text{CH}_3)_2$ umbrella mode of the $2\text{-C}_3\text{H}_7^+$ fragment, whose effect on the I $4d$ XUV transition even at C—I distances of 3.5 Å points to the long-range nature of XUV absorption probing. Our results suggest that femtosecond XUV absorption spectroscopy, in combination with ab initio simulations of XUV transition energies, can be used to resolve the ultrafast structural dynamics of large polyatomic molecules.

TOC graphic

One of the holy grails of femtochemistry is to observe how molecular structures evolve in real-time during the course of chemical reactions.¹ In a pioneering study, Zewail applied optical pump-probe spectroscopy to investigate the photodissociation dynamics of the $\tilde{A}$ state of ICN.²⁻³ The results showed a dependence of the onset of the transient signal on the wavelength of the probe pulse: a shorter probe wavelength is associated with a larger delay in the signal onset, suggesting that a shorter probe wavelength captures the appearance of the wave packet further away from the Franck-Condon region. Combining this data with knowledge of the relevant potential energy curves thus allows tracking of the location of a wave packet as it propagates along the repulsive potential energy curve. Beyond this pioneering work, observations of structural dynamics have also been made with complementary spectroscopic approaches, such as time-resolved Coulomb explosion imaging⁴⁻⁵ and photoelectron spectroscopy,⁶ both of which have revealed changes in molecular structure that accompany vibrational wave packet motion. More recently, advances in the generation of ultrashort X-ray and electron pulses^{7,8} have enabled the direct observation of ultrafast structural dynamics in both the gas phase⁹⁻¹¹ and the condensed phase.¹²⁻¹⁴

Time-resolved extreme ultraviolet (XUV) absorption spectroscopy has emerged as a powerful tool for investigating ultrafast molecular dynamics. By probing the electronic transition between core levels and valence levels, XUV absorption spectroscopy offers element specificity and exquisite sensitivity to changes in the valence electronic structure.¹⁵ The ultrafast dissociation dynamics of small molecules that are induced by strong-field ionization¹⁶⁻¹⁹ or single-photon excitation²⁰⁻²⁴ have both been investigated by using this technique. Most of these studies have relied on measuring the timescales for the

disappearance of the parent molecule and/or the appearance of the fragment species. In addition to these population dynamics, encoded in changes in the amplitudes of the XUV absorption signal, the resonant XUV transition energy should also shift with time as the XUV absorption spectrum evolves from that of the initially photoexcited/photoionized molecule to that of the fragment. When applied to the prototypical case of CH_3I photodissociation in the $\tilde{A}$ state, femtosecond XUV absorption spectroscopy provided a glimpse of the wave packet en route to dissociation.²¹ The limited time resolution in that study, however, prevented the observation of a continuous shift in the XUV transition energy that one might expect to observe during the ~ 90 -fs bond dissociation process.²⁵

Here, we employ femtosecond XUV absorption spectroscopy to investigate the strong-field dissociative ionization dynamics of 2-iodopropane ($2\text{-C}_3\text{H}_7\text{I}$) and observe the continuous evolution of the XUV differential absorption (ΔA) spectrum from that of the dissociative $^2E_{1/2}$ state of the $2\text{-C}_3\text{H}_7\text{I}^+$ parent ion to the atomic I $^2P_{3/2}$ fragment. This spectral shift occurs on the 100-fs timescale, in good agreement with the time constant for the disappearance of the $2\text{-C}_3\text{H}_7\text{I}^+ \ ^2E_{1/2}$ ion and the appearance of the I ($^2P_{3/2}$) atom. By combining the experimental time-dependent XUV absorption spectrum with ab initio simulations of the XUV transition energy, we successfully reconstruct the temporal evolution of the C—I bond distance ($R_{\text{C-I}}$) during the dissociation process with 0.1-Å resolution. Interestingly, the time-dependent $R_{\text{C-I}}$ exhibits a modulation with a frequency of 1100 cm^{-1} , suggesting that C—I dissociation is coupled to the umbrella mode of the $2\text{-C}_3\text{H}_7^+$ fragment.

Figure 1. (a) Differential XUV absorption spectra as a function of pump-probe time delay. (b) Plot of the differential absorption spectra collected at 2-ps time delay to multiple Gaussian functions. The experimental data is shown with red symbol, and the solid black line is the fit. Resonances due to $2\text{-C}_3\text{H}_7\text{I}^+$, neutral $\text{C}_3\text{H}_7\text{I}$, neutral I , and singly charged I^+ are displayed in different colors.

Femtosecond XUV pulses are produced by focusing 0.8-mJ, 5.6-fs pulses with a center wavelength of 786 nm into an argon-filled gas cell to drive high-order harmonic generation. The sample target comprises a quasi-static gas cell with a path length of 3 mm filled with 8 mbar of $2\text{-C}_3\text{H}_7\text{I}$ and heated to 353 K. A weaker replica of the few-cycle pulse is loosely focused to a peak intensity of $1.9 \times 10^{14} \text{ W/cm}^2$ to strong-field-ionize $2\text{-C}_3\text{H}_7\text{I}$. The XUV pulse transmitted through the sample target is spectrally dispersed on a thermoelectrically cooled X-ray CCD camera. The spectral resolution is 47 meV FWHM in the XUV photon energy range employed in the present study. Further details of the home-built femtosecond XUV absorption spectroscopy setup can be found in ref. 26.

The XUV differential absorption spectrum collected as a function of pump-probe time delay is shown in Figure 1a. The negative differential absorption features at 50.5 and

52.3 eV are due to bleaching of the iodine (I) $4d_{5/2} \rightarrow \sigma_{C-I}^*$ and $4d_{3/2} \rightarrow \sigma_{C-I}^*$ transitions of the neutral 2-C₃H₇I molecule, respectively, in good agreement with the peaks observed in the static XUV photoabsorption spectrum (see the Supporting Information). The pronounced positive differential absorption signal in the range of 45.5 – 48.7 eV arise from the I $4d$ core level transitions of the 2-C₃H₇I⁺ parent ion and its dissociative ionization products. A fit of the differential absorption spectrum collected at 2-ps time delay (Figure 1b) to multiple Gaussian peaks reveals transitions from the I $4d$ core levels of the $^2E_{3/2}$ state of the 2-C₃H₇I⁺ parent ion and its spin-orbit-excited $^2E_{1/2}$ state, as well as those of the atomic I ($^2P_{3/2}$) and I⁺ (3P_2) species. The assignment of the observed spectral features is summarized in the Supporting Information. Note that the ionization energies to give the 2-C₃H₇I⁺ ion $^2E_{3/2}$ and $^2E_{1/2}$ states are 9.1755 and 9.6903 eV, respectively.²⁷ Given the 1.58-eV central photon energy of the few-cycle laser pulses used for strong-field ionization, at least 6 photons are required to access these ion states. The appearance of the I⁺ (3P_2) ion, however, suggests that the ion $\tilde{A}$ state, located 11.1 eV above the neutral ground state,²⁸ is also produced by strong-field ionization. In this case, we can infer that strong-field ionization of 2-C₃H₇I under our experimental conditions involves a 7-photon process. The population of even higher-lying excited states of 2-C₃H₇I⁺ can be excluded based on the absence of their dissociation products, i.e., spin-orbit-excited I ($^2P_{1/2}$) and I⁺ (3P_1 and 3P_0) atomic species.

The time-resolved XUV differential absorption spectrum exhibits XUV transition energies that oscillate as a function of time delay. These modulations originate from coherent vibrational wave packet dynamics that are launched by the intense laser field. The

Figure 2. Temporal traces of the ΔA signals for the (a) $2\text{-C}_3\text{H}_7\text{I}^+ \tilde{X}^+, {}^2E_{3/2}$, (b) $2\text{-C}_3\text{H}_7\text{I}^+ \tilde{X}^+, {}^2E_{1/2}$, (c) neutral I (${}^2P_{3/2}$) species. The dashed red lines are the experimental data, and the solid black lines are the exponential fits.

oscillation frequencies can be obtained either from the Fast Fourier Transform (FFT) of the time traces or from time-domain analysis of the first-moment time traces (see the Supporting Information). In the neutral depletion region, the retrieved vibrational frequency of $496 \pm 1 \text{ cm}^{-1}$ is assigned to the C—I stretching mode; the cosinusoidal oscillation phase of $-(0.45 \pm 0.04)\pi$ rad is consistent with vibrational motion launched by bond softening.²⁶ In addition, multiple oscillation frequencies observed about the dominant ${}^2E_{3/2} \rightarrow 4d_{5/2}^{-1}$ transition of the $2\text{-C}_3\text{H}_7\text{I}^+$ ion, along with their oscillation phases, suggests that strong-field ionization launches coherent vibrational motion via the displacive mechanism along the C—I stretching mode ($392 \pm 1 \text{ cm}^{-1}$) and both the C—C—I bending ($193 \pm 1 \text{ cm}^{-1}$) and $\text{HC}(\text{CH}_3)_2$ umbrella ($1126 \pm 2 \text{ cm}^{-1}$) modes of $2\text{-C}_3\text{H}_7\text{I}^+$. The experimentally observed vibrational frequencies are in good agreement with those values from literature^{27,29} (see the Supporting Information), suggesting that the combination of

strong-field ionization and femtosecond XUV absorption spectroscopy can be used to determine the vibrational frequencies of gas-phase molecular ions.^{26, 30-33}

Aside from bound-state coherent vibrational wave packet dynamics, it is evident from the appearance of atomic I ($^2P_{3/2}$) that strong-field-ionized 2-C₃H₇I also undergoes ultrafast dissociative ionization. It is known that cleavage of the C—I bond in the $^2E_{3/2}$ and $^2E_{1/2}$ states of 2-C₃H₇I⁺ yields the 2-C₃H₇⁺ fragment and the I atom in the $^2P_{3/2}$ state.²⁷ The time trace collected at 46.8 eV, corresponding to the peak of the 2-C₃H₇I⁺ $^2E_{3/2} \rightarrow 4d_{5/2}^{-1}$ transition at 2-ps time delay, reveals an ultrafast rise with a time constant of 54 ± 3 fs followed by a plateau (Figure 2a). The ultrafast rise is attributed to vibrational relaxation of the 2-C₃H₇I⁺ ion, hence dissipating the excess internal energy imparted by strong-field ionization. This ultrafast structural rearrangement gives rise to an enhanced Franck-Condon factor for the XUV probe transition. The subsequent ΔA signal remains constant up to 2 ps, indicating that the $^2E_{3/2}$ state of 2-C₃H₇I⁺ is stable with respect to C—I dissociation on the picosecond timescale. On the other hand, the ΔA signal of the 2-C₃H₇I⁺ $^2E_{1/2} \rightarrow 4d_{3/2}^{-1}$ transition at 46.4 eV (Figure 2b) exhibits a decay whose timescale is comparable to the rise of the ΔA signal for the atomic I $^2P_{3/2} \rightarrow ^2D_{5/2}$ at 46.0 eV (Figure 2c). Global analysis of both time traces suggests that the 2-C₃H₇I⁺ $^2E_{1/2}$ state undergoes C—I dissociation with a time constant of 121 ± 3 fs.

The observation of spin-orbit state-selective dissociation of 2-C₃H₇I⁺ is reminiscent of that recently reported for CH₃I⁺ and can be rationalized similarly in terms of ultrafast dissociation involving field-dressed states.¹⁹ Briefly, the wave packet that is initially launched on the dissociative $\tilde{A}$ state by strong-field ionization crosses the field-dressed

$^2E_{1/2}$ state at the trailing edge of the same intense pump pulse, which then dissociates to give $2\text{-C}_3\text{H}_7^+$ and atomic I ($^2P_{3/2}$). Stimulated emission to, and therefore dissociation from the $^2E_{3/2}$ state does not occur because the $\tilde{A} - ^2E_{3/2}$ crossing cannot be accessed within the 6-fs duration of the intense laser pulse. The disparate dissociation time constants – 0.76 ps in the case of CH_3I^+ vs. 121 fs for $2\text{-C}_3\text{H}_7\text{I}^+$ – can be attributed to the different dissociation energies of the two molecules. While both the $^2E_{3/2}$ and $^2E_{1/2}$ states of CH_3I^+ are bound by >2 eV along the C—I potential energy curve,^{34,35} the C—I dissociation energies of $2\text{-C}_3\text{H}_7\text{I}^+$ in the $^2E_{3/2}$ and $^2E_{1/2}$ states are expected to be only 0.643 eV and 0.128 eV, respectively.²⁷ The shallow minimum along the C—I dissociation coordinate for the $^2E_{1/2}$ spin-orbit excited state of $2\text{-C}_3\text{H}_7\text{I}^+$ leads to incomplete C—I bond dissociation and hence the baseline offset present in Figure 2b. It is noteworthy that the dissociation time constant of 121 fs is comparable to that reported for the neutral $\tilde{A}$ state (137 ± 12 fs).²⁵

Beyond measuring the dissociation time constant, the ~ 10 -fs time resolution afforded by our XUV absorption spectroscopy apparatus also allows us to reconstruct $R_{\text{C-I}}$ during the bond breaking process. As the $2\text{-C}_3\text{H}_7\text{I}^+ ^2E_{1/2}$ state dissociates, the initial $^2E_{1/2} \rightarrow 4d_{3/2}^{-1}$ transition at 46.4 eV is expected to transform into the atomic I $^2P_{3/2} \rightarrow ^2D_{5/2}$ transition at 46.0 eV as the wave packet propagates from the Franck-Condon region to the asymptotic region (Figure 3a). Indeed, such a continuous spectral shift is evident in the ΔA spectra collected at various time delays (Figure 3b). A plot of the peak positions vs. time delay reveals that the temporal evolution of the XUV transition is complete within 200 fs (Figure 3c, left panel). In order to reconstruct the time-dependent $R_{\text{C-I}}$, it is necessary to establish how the XUV transition energy (E_{XUV}) varies with $R_{\text{C-I}}$. To this end,

Figure 3. (a) The schematic potential energy curves of 2-C₃H₇I neutral ($\tilde{X}$), ion ($\tilde{X}^+$) and I $4d$ core-excited states. (b) The XUV differential absorption spectra for strong-field-ionized 2-C₃H₇I at various time delays. The peak position at each time delay is indicated with a red circle. (c) Plot of the 2-C₃H₇I⁺ $\tilde{X}^+ \ ^2E_{1/2}$ peak position as a function of time delay (left panel; dashed red line is the experimental data and solid black line is the fit) and the DFT-calculated I $4d$ to $5p$ XUV transition energy as a function of C—I distance R_{C-I} (right panel). Correlating the time delay and R_{C-I} for a given transition energy shift yields the reconstructed R_{C-I} as a function of time delay.

time-dependent density functional theory (TDDFT) calculations at the wB97XD/Def2SVP level of theory are used to compute E_{XUV} vs. R_{C-I} . The result shows a monotonic decrease of E_{XUV} with R_{C-I} (Figure 3c, right panel), in good agreement with the experimentally observed decrease in E_{XUV} as the C—I bond dissociates. Note that the plot starts from the Franck-Condon region, which, assuming a vertical strong-field ionization process, corresponds to the equilibrium geometry of neutral 2-C₃H₇I; for this species, ab initio calculation yields a C—I bond length of 2.18 Å.

Figure 4. Reconstructed C—I bond distance R_{C-I} as a function of time delay.

Compared to the experimentally observed XUV transition energies, the computed XUV transition energies are offset and have a different span from the Franck-Condon region ($t = 0$ and $R_{C-I} = 2.18$ Å in the left and right panels of Figure 3c, respectively) to the asymptotic region. As such, we vertically sectioned the curves in Figure 3c into the same number of equal-spaced segments, with the energy span of each segment representing the same fractional change in the XUV transition energy with either time delay or R_{C-I} . By determining the time delay t_i and C—I bond distance $R_{C-I,i}$ for each segment, we obtain a set of $\{R_{C-I,i}, t_i\}$, plotted in Figure 4. The uncertainty in the determination of the XUV transition energy beyond ~ 175 fs limits the useable range for reconstructing the time-dependent R_{C-I} to the time-delay range of 0 – 175 fs. The reconstructed temporal evolution of R_{C-I} shows that it takes 132 fs for the C—I bond length to double from its initial value of 2.18 Å. At short time delays, R_{C-I} increases gradually with time delay as the wave packet leaves the Franck-Condon region. While it moves along the repulsive potential, the wave packet continues to accelerate before reaching its terminal velocity in the asymptotic region. Given the 10-fs time resolution of the experimental setup and the initial wave packet velocity of 0.01 Å/fs, we obtain an estimated spatial resolution of 0.1 Å for our measurement.

Figure 5. (a) Residual of the experimentally measured E_{XUV} , showing oscillatory features that are spaced apart by 30 fs (grey dashed lines). (b) The short-time Fourier transform spectrogram of the residual, revealing oscillation frequencies of 580 and 1100 cm^{-1} (dashed white lines). The spectrogram is calculated by employing a 100-fs-wide rectangular window.

Interestingly, the plot of E_{XUV} vs. time delay exhibits low-amplitude, periodic modulations (Figure 3c, left panel), which become more apparent after subtraction of a Gaussian fit to the experimental data. The residual time trace exhibit modulations with an oscillation period of 30 fs and a phase of $\sim\pi$ rad in the first ~ 100 fs (Figure 5a). The short-time Fourier Transform (STFT) of the time trace, computed by using a 100-fs-wide rectangular window, reveals a dominant oscillation frequency at 1100 cm^{-1} and a weaker component at 580 cm^{-1} (Figure 5b). According to ab initio calculations, the former is comparable to the 1094- cm^{-1} frequency of the $\text{HC}(\text{CH}_3)_2$ umbrella mode whereas the latter is assigned to the second overtone of the C–C–I bending mode (see the Supporting

Information). Both vibrational modes were previously observed in high-resolution mass-analyzed threshold ionization spectroscopy of 2-C₃H₇I.²⁷ The observed modulation of E_{XUV} by the HC(CH₃)₂ umbrella mode suggests that C—I dissociation is accompanied by coherent excitation of the umbrella mode. Ab initio DFT calculations show that the initial I—C—H (I—C—C) angle of 102.4° (110.0°) becomes 60.7° (102.7°) upon elongation of the C—I bond to 6 Å. This loss in pyramidalization of the HC(CH₃)₂ fragment is consistent with the oscillation phase of $\sim\pi$ rad, which implies the launching of vibrational motion along the umbrella mode from an extremum geometrical configuration.

In the case of the $\tilde{A}$ band photodissociation of CH₃I, the coupling of the C—I dissociation to the CH₃ umbrella mode is well-established based on photofragment translational energy³⁶⁻³⁸ and photoelectron kinetic energy³⁹ measurements as well as ab initio wave packet trajectory calculations.⁴⁰⁻⁴² Moreover, on-the-fly ab initio trajectory calculations performed on *t*-C₄H₉I reveal that the initial stages of C—I dissociation is accompanied by significant motion along the umbrella mode of the *t*-C₄H₉ fragment.²⁵ UV resonance Raman measurements show that iodoalkanes with larger alkyl groups support larger-amplitude vibration along the umbrella mode during photodissociation from the $\tilde{A}$ state.²⁹ The observed modulation of $R_{\text{C-I}}$ in our work suggests that the umbrella mode is, in fact, *coherently* excited upon ultrafast C—I dissociation. Furthermore, it is noteworthy that the modulation is observed out to ~ 100 fs, when the reconstructed C—I distance has reached ~ 3.5 Å. It is remarkable that the XUV transition, which nominally corresponds to that of the I atom, continues to be sensitive to structural changes of the 2-C₃H₇⁺ fragment even at such large C—I distances. The long-range nature of the core-level absorption probe is counterintuitive and warrants further investigation.

In conclusion, femtosecond XUV absorption spectroscopy reveals a continuous spectral shift that accompanies the ultrafast C—I dissociation dynamics of 2-C₃H₇I⁺ in the spin-orbit-excited $^2E_{1/2}$ state. The XUV absorption feature of the 2-C₃H₇I⁺ $^2E_{1/2} \rightarrow 4d_{3/2}^{-1}$ transition at 46.4 eV evolves within 200 fs to yield the atomic I $^2P_{3/2} \rightarrow ^2D_{5/2}$ transition at 46.0 eV. Combined with ab initio calculations of the XUV transition energy as a function of C—I bond distance, the measured time-resolved spectral shift is used to reconstruct the elongation of the C—I bond from the Franck-Condon region to the asymptotic region with 0.1-Å spatial resolution. The results reveal that the C—I bond increases from its initial value of 2.18 Å to 5 Å in 150 fs and that the C—I bond elongation appears to be modulated by the umbrella mode of the HC(CH₃)₂ fragment. The latter indicates that ultrafast dissociation is accompanied by coherent vibrational motion along the umbrella mode. The discernible coherent umbrella motion even as the C—I distance reaches 3.5 Å alludes to the long-range nature of XUV core-level absorption probing.

Supporting Information

Description of ab initio calculation methods, optimized molecular geometries and vibrational frequencies obtained from ab initio calculations, static XUV photoabsorption spectrum, assignment of peaks observed in the differential XUV absorption spectrum collected at 2-ps time delay, FFT power spectrum and time-domain analysis of vibrational wave packet dynamics.

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References

- (1) Zewail, A. H. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. *J. Phys. Chem. A* **2000**, *104*, 5660-5694.
- (2) Dantus, M.; Rosker, M. J.; Zewail, A. H. Real-Time Femtosecond Probing of "Transition States" in Chemical Reactions. *J. Chem. Phys.* **1987**, *87*, 2395-2397.
- (3) Dantus, M.; Rosker, M. J.; Zewail, A. H. Femtosecond Real-Time Probing of Reactions. II. The Dissociation Reaction of ICN. *J. Chem. Phys.* **1988**, *89*, 6128-6140.
- (4) Stapelfeldt, H.; Constant, E.; Sakai, H.; Corkum, P. B. Time-Resolved Coulomb Explosion Imaging: A Method to Measure Structure and Dynamics of Molecular Nuclear Wave Packets. *Phys. Rev. A* **1998**, *58*, 426-433.
- (5) Ergler, T.; Rudenko, A.; Feuerstein, B.; Zrost, K.; Schröter, C. D.; Moshhammer, R.; Ullrich, J. Spatiotemporal Imaging of Ultrafast Molecular Motion: Collapse and Revival of the D_2^+ Nuclear Wave Packet. *Phys. Rev. Lett.* **2006**, *97*, 193001.
- (6) Zhang, Y.; Deb, S.; Jónsson, H.; Weber, P. M. Observation of Structural Wavepacket Motion: The Umbrella Mode in Rydberg-Excited N-Methyl Morpholine. *J. Phys. Chem. Lett.* **2017**, *8*, 3740-3744.
- (7) Miller, R. J. D. Femtosecond Crystallography with Ultrabright Electrons and X-rays: Capturing Chemistry in Action. *Science* **2014**, *343*, 1108-1116.
- (8) Bostedt, C.; Boutet, S.; Fritz, D. M.; Huang, Z.; Lee, H. J.; Lemke, H. T.; Robert, A.; Schlotter, W. F.; Turner, J. J.; Williams, G. J. Linac Coherent Light Source: The First Five Years. *Rev. Mod. Phys.* **2016**, *88*, 015007.
- (9) Ihée, H.; Lobastov, V. A.; Gomez, U. M.; Goodson, B. M.; Srinivasan, R.; Ruan, C.-Y.; Zewail, A. H. Direct Imaging of Transient Molecular Structures with Ultrafast Diffraction. *Science* **2001**, *291*, 458-462.

- (10) Blaga, C. I.; Xu, J.; DiChiara, A. D.; Sistrunk, E.; Zhang, K.; Agostini, P.; Miller, T. A.; DiMauro, L. F.; Lin, C. D. Imaging Ultrafast Molecular Dynamics with Laser-Induced Electron Diffraction. *Nature* **2012**, *483*, 194-197.
- (11) Minitti, M. P.; Budarz, J. M.; Kirrander, A.; Robinson, J. S.; Ratner, D.; Lane, T. J.; Zhu, D.; Glowacki, J. M.; Kozina, M.; Lemke, H. T.; *et al.* Imaging Molecular Motion: Femtosecond X-Ray Scattering of an Electrocyclic Chemical Reaction. *Phys. Rev. Lett.* **2015**, *114*, 255501.
- (12) Baum, P.; Yang, D.-S.; Zewail, A. H. 4D Visualization of Transitional Structures in Phase Transformations by Electron Diffraction. *Science* **2007**, *318*, 788-792.
- (13) Gao, M.; Lu, C.; Jean-Ruel, H.; Liu, L. C.; Marx, A.; Onda, K.; Koshihara, S.; Nakano, Y.; Shao, X.; Hiramatsu, T.; *et al.* Mapping Molecular Motions Leading to Charge Delocalization with Ultrabright Electrons. *Nature* **2013**, *496*, 343-346.
- (14) Pande, K.; Hutchison, C. D. M.; Groenhof, G.; Aquila, A.; Robinson, J. S.; Tenboer, J.; Basu, S.; Boutet, S.; DePonte, D. P.; Liang, M.; *et al.* Femtosecond Structural Dynamics Drives the Trans/Cis Isomerization in Photoactive Yellow Protein. *Science* **2016**, *352*, 725-729.
- (15) Loh, Z.-H.; Leone, S. R. Capturing Ultrafast Quantum Dynamics with Femtosecond and Attosecond X-ray Core-Level Absorption Spectroscopy. *J. Phys. Chem. Lett.* **2013**, *4*, 292-302.
- (16) Loh, Z.-H.; Leone, S. R. Ultrafast Strong-Field Dissociative Ionization Dynamics of CH₂Br₂ Probed by Femtosecond Soft X-Ray Transient Absorption Spectroscopy. *J. Chem. Phys.* **2008**, *128*, 204302.
- (17) Lin, M.-F.; Neumark, D. M.; Gessner, O.; Leone, S. R. Ionization and Dissociation Dynamics of Vinyl Bromide Probed by Femtosecond Extreme Ultraviolet Transient Absorption Spectroscopy. *J. Chem. Phys.* **2014**, *140*, 064311.
- (18) Chatterley, A. S.; Lackner, F.; Neumark, D. M.; Leone, S. R.; Gessner, O. Tracking Dissociation Dynamics of Strong-Field Ionized 1,2-Dibromoethane with Femtosecond XUV Transient Absorption Spectroscopy. *Phys. Chem. Chem. Phys.* **2016**, *18*, 14644-14653.

- (19) Wei, Z.; Li, J.; See, S. T.; Loh, Z.-H. Spin–Orbit State-Selective C–I Dissociation Dynamics of the $\text{CH}_3\text{I}^+ \tilde{X}$ Electronic State Induced by Intense Few-Cycle Laser Fields. *J. Phys. Chem. Lett.* **2017**, *8*, 6067-6072.
- (20) Attar, A. R.; Piticco, L.; Leone, S. R. Core-to-Valence Spectroscopic Detection of the CH_2Br Radical and Element-Specific Femtosecond Photodissociation Dynamics of CH_2IBr . *J. Chem. Phys.* **2014**, *141*, 164308.
- (21) Attar, A. R.; Bhattacharjee, A.; Leone, S. R. Direct Observation of the Transition-State Region in the Photodissociation of CH_3I by Femtosecond Extreme Ultraviolet Transient Absorption Spectroscopy. *J. Phys. Chem. Lett.* **2015**, *6*, 5072-5077.
- (22) Bhattacharjee, A.; Attar, A. R.; Leone, S. R. Transition State Region in the A-Band Photodissociation of Allyl Iodide—A Femtosecond Extreme Ultraviolet Transient Absorption Study. *J. Chem. Phys.* **2016**, *144*, 124311.
- (23) Attar, A. R.; Bhattacharjee, A.; Pemmaraju, C. D.; Schnorr, K.; Closser, K. D.; Prendergast, D.; Leone, S. R. Femtosecond X-Ray Spectroscopy of an Electrocyclic Ring-Opening Reaction. *Science* **2017**, *356*, 54-59.
- (24) Bhattacharjee, A.; Pemmaraju, C. D.; Schnorr, K.; Attar, A. R.; Leone, S. R. Ultrafast Intersystem Crossing in Acetylacetone via Femtosecond X-ray Transient Absorption at the Carbon K-Edge. *J. Am. Chem. Soc.* **2017**, *139*, 16576-16583.
- (25) Corrales, M. E.; Lorient, V.; Balerdi, G.; González-Vázquez, J.; de Nalda, R.; Bañares, L.; Zewail, A. H. Structural Dynamics Effects on the Ultrafast Chemical Bond Cleavage of a Photodissociation Reaction. *Phys. Chem. Chem. Phys.* **2014**, *16*, 8812-8818.
- (26) Wei, Z.; Li, J.; Wang, L.; See, S.-T.; Jhon, M. H.; Zhang, Y.; Shi, F.; Yang, M.; Loh, Z.-H. Elucidating the Origins of Multimode Vibrational Coherences of Polyatomic Molecules Induced by Intense Laser Fields. *Nat. Commun.* **2017**, *8*, 735.
- (27) Park, S. T.; Kim, S. K.; Kim, M. S. One-Photon Mass-Analyzed Threshold Ionization Spectroscopy of 1- and 2-Iodopropanes in Vacuum Ultraviolet. *J. Chem. Phys.* **2001**, *114*, 5568-5576.

- (28) Boschi, R. A. A.; Salahub, D. R. The High Resolution Photoelectron Spectra of Some Iodoalkanes, Iodocycloalkanes, Iodoalkenes, and Fluoroiodohydrocarbons. *Can. J. Chem.* **1974**, *52*, 1217-1228.
- (29) Phillips, D. L.; Lawrence, B. A.; Valentini, J. J. Substituent Effects on Gas-Phase Photodissociation Dynamics: Resonance Raman Spectra of Ethyl Iodide, Isopropyl Iodide, and Tert-Butyl Iodide. *J. Phys. Chem.* **1991**, *95*, 9085-9091.
- (30) Fang, L.; Gibson, G. N. Investigating Excited Electronic States of I_2^+ and I_2^{2+} Produced by Strong-Field Ionization Using Vibrational Wave Packets. *Phys. Rev. A* **2007**, *75*, 063410.
- (31) Geißler, D.; Pearson, B. J.; Weinacht, T. Wave Packet Driven Dissociation and Concerted Elimination in CH_2I_2 . *J. Chem. Phys.* **2007**, *127*, 204305.
- (32) Hosler, E. R.; Leone, S. R. Characterization of Vibrational Wave Packets by Core-Level High-Harmonic Transient Absorption Spectroscopy. *Phys. Rev. A* **2013**, *88*, 023420.
- (33) Ando, T.; Iwasaki, A.; Yamanouchi, K. Strong-Field Fourier Transform Vibrational Spectroscopy of D_2^+ Using Few-Cycle Near-Infrared Laser Pulses. *Phys. Rev. Lett.* **2018**, *120*, 263002.
- (34) Walter, K.; Weinkauff, R.; Boesl, U.; Schlag, E. W. Molecular Ion Spectroscopy: Mass Selected, Resonant Two - Photon Dissociation Spectra of CH_3I^+ and CD_3I^+ . *J. Chem. Phys.* **1988**, *89*, 1914-1922.
- (35) Song, Y.; Qian, X.-M.; Lau, K.-C.; Ng, C. Y.; Liu, J.; Chen, W. High-Resolution Energy-Selected Study of the Reaction $CH_3X^+ \rightarrow CH_3^+ + X$: Accurate Thermochemistry for the CH_3X/CH_3X^+ ($X=Br, I$) System. *J. Chem. Phys.* **2001**, *115*, 4095-4104.
- (36) Sparks, R. K.; Shobatake, K.; Carlson, L. R.; Lee, Y. T. Photofragmentation of CH_3I : Vibrational Distribution of the CH_3 Fragment. *J. Chem. Phys.* **1981**, *75*, 3838-3846.
- (37) Van Veen, G. N. A.; Baller, T.; De Vries, A. E.; Van Veen, N. J. A. The Excitation of the Umbrella Mode of CH_3 and CD_3 Formed from Photodissociation of CH_3I and CD_3I at 248 nm. *Chem. Phys.* **1984**, *87*, 405-417.

- (38) Eppink, A. T. J. B.; Parker, D. H. Energy Partitioning Following Photodissociation of Methyl Iodide in the A Band: A Velocity Mapping Study. *J. Chem. Phys.* **1999**, *110*, 832-844.
- (39) Samartzis, P. C.; Bakker, B. L. G.; Parker, D. H.; Kitsopoulos, T. N. Photoelectron and Photofragment Velocity Imaging Following the Excitation of CH₃I to the A-Band Using fs, ps, and ns Laser Pulses. *J. Phys. Chem. A* **1999**, *103*, 6106-6113.
- (40) Guo, H. Three - Dimensional Photodissociation Dynamics of Methyl Iodide. *J. Chem. Phys.* **1992**, *96*, 6629-6642.
- (41) Amatatsu, Y.; Yabushita, S.; Morokuma, K. Full Nine - Dimensional Ab Initio Potential Energy Surfaces and Trajectory Studies of A - Band Photodissociation Dynamics: CH₃I* → CH₃+I, CH₃+I*, and CD₃I* → CD₃+I, CD₃+I*. *J. Chem. Phys.* **1996**, *104*, 9783-9794.
- (42) Alekseyev, A. B.; Liebermann, H.-P.; Buenker, R. J.; Yurchenko, S. N. An Ab Initio Study of the CH₃I Photodissociation. I. Potential Energy Surfaces. *J. Chem. Phys.* **2007**, *126*, 234102.