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Transition state region in the A-Band photodissociation of allyl iodide—A femtosecond extreme ultraviolet transient absorption study

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Femtosecond extreme ultraviolet (XUV) transient absorption spectroscopy based on a high-harmonic generation source is used to study the 266 nm induced A-band photodissociation dynamics of allyl iodide ($\text{CH}_2=\text{CHCH}_2\text{I}$). The photolysis of the C—I bond at this wavelength produces iodine atoms both in the ground ($^2\text{P}_{3/2}$, I) and spin-orbit excited ($^2\text{P}_{1/2}$, I*) states, with the latter as the predominant channel. Using XUV absorption at the iodine $\text{N}_{4/5}$ edge (45–60 eV), the experiments constitute a direct probe of not only the long-lived atomic iodine reaction products but also the fleeting transition state region of the repulsive $n_1\sigma^*\text{C—I}$ excited states. Specifically, three distinct features are identified in the XUV transient absorption spectrum at 45.3 eV, 47.4 eV, and 48.4 eV (denoted transients A, B, and C, respectively), which arise from the repulsive valence-excited $n\sigma^*$ states and project onto the high-lying core-excited states of the dissociating molecule via excitation of 4d(I) core electrons. Transients A and B originate from $4d(\text{I}) \rightarrow n(\text{I})$ core-to-valence transitions, whereas transient C is best assigned to a $4d(\text{I}) \rightarrow \sigma^*(\text{C—I})$ transition. The measured differential absorbance of these new features along with the I/I* branching ratios known from the literature is used to suggest a more definitive assignment, albeit provisional, of the transients to specific dissociative states within the A-band manifold. The transients are found to peak around 55 fs–65 fs and decay completely by 145 fs–185 fs, demonstrating the ability of XUV spectroscopy to map the evolution of reactants into products in real time. The similarity in the energies of transients A and B with analogous features observed in methyl iodide [Attar *et al.* J. Phys. Chem. Lett. **6**, 5072, (2015)] together with the new observation of transient C in the present work provides a more complete picture of the valence electronic structure in the transition state region. The results provide a benchmark for theoretical calculations on the nature of core-excited states in halogenated hydrocarbons, especially in the transition state region along the C—I reaction coordinate. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4944930>]

I. INTRODUCTION

The advent of ultrashort laser pulses brought the emergence of femtosecond transition state (TS) spectroscopy, leading to temporal mapping of chemical reactions on their intrinsic time scales.^{1,2} While the kinetics of reactants and products corresponding to bound wells in the potential energy surface have been routinely tracked with such short pulses, spectroscopic detection of the fleeting TS is much more challenging and only reported for a few elementary reactions.^{3–7} However, this elusive part of the potential energy surface that separates reactants from products is critical to understand chemical reactions at a molecular level.⁸ Diverse chemical reactions have been explored with ultrafast pump-probe techniques based on laser-induced fluorescence,³ mass spectrometry,^{9,10} photoelectron spectroscopy,^{11–13} diffraction,¹⁴ and Coulomb explosion.¹⁵ Due to the short dwell time of reactants in the TS region, molecules are often directly launched into the TS

configuration as a stable negative ion precursor or as a van der Waals/hydrogen-bonded intermolecular complex to follow the ensuing dynamics.¹⁶

Femtosecond X-ray sources, equipped with the requisite spectral and temporal resolution, have emerged as an efficient tool to unravel reactive intermediates as well as transition states.^{17–20} Ultrafast X-ray absorption and scattering have been instrumental in the recent past to enable the real-time observation of structural transitions in molecules in the course of a chemical reaction.^{21,22} The ability of extreme ultraviolet (XUV) and soft X-rays to directly interrogate the inner valence states of atoms constitutes a powerful spectroscopic probe for electronic structure.^{23,24} Synchrotrons efficiently deliver energy-tunable X-ray pulses with high spectral resolution but lack the temporal resolution to map out dissociation processes that last only a few vibrational time-periods. With the incorporation of chopping/slicing methods of a synchrotron stored electron bunch, pulse durations on the order of one hundred femtoseconds have been achieved at the cost of low photon flux.^{25,26} This limitation is easily overcome using free electron lasers, which provide femtosecond time resolution coupled with a bright flux of photons of several hundred eV to several keV. Table-top X-ray sources employing high-

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harmonic generation can provide pulses ranging from vacuum ultraviolet to extreme ultraviolet and into the soft X-ray regime with pulse durations ranging from several tens of femtoseconds to attoseconds. As such, they have the potential to create successive snapshots of rapid electronic and nuclear motions leading to molecular dissociation on the order of a few vibrational time-periods.²⁷

Recently, we investigated the TS region in the C—I bond dissociation of methyl iodide at 266 nm using femtosecond XUV transient absorption spectroscopy.²⁸ The photodissociation of halogenated hydrocarbons constitutes a class of benchmark reactions in chemistry and has been the subject of an unprecedented number of studies.^{29–36} Electronic excitation of alkyl iodides is known to consist of multiple bands, the lowest energy of which is a continuum in the 220–300 nm range, referred to as the A-band.^{37–39} Accessed via a $n(5p, I) \rightarrow \sigma^*(C—I)$ excitation, the A-band absorption spans five electronic states, which arise from spin-orbit interactions and has been studied extensively.³² In the electric dipole approximation, transitions to only three of these states are allowed: a strong parallel transition to the 3Q_0 and two weak perpendicular transitions to the 3Q_1 and 1Q_1 states. In the asymptotic limit, the former correlates with the spin-orbit excited $^2P_{1/2}$ state of atomic I, while the latter two correlate with the $^2P_{3/2}$ state, hereafter denoted as I^* and I , respectively. Crossing of the 3Q_0 and 1Q_1 curves (Figure 1) causes the ground state I atom to be produced both adiabatically (via direct excitation) and non-adiabatically (via curve-crossing) and has been examined by experiments^{29–34} as well as theories.^{35,36}

In this paper, we extend previous XUV studies²⁸ of the TS region in the A-Band photodissociation of the C—I bond to allyl iodide ($CH_2=CHCH_2I$). It is a well-known precursor

used to generate the resonance-stabilized allyl radical either by pyrolysis or photolysis.^{40–42} Having been identified as a key component in combustion as well as in the interstellar medium, the ground and excited electronic states of allyl radical have been extensively characterized by optical spectroscopy^{43,44} as well as electronic paramagnetic resonance techniques.^{45,46} However, the photochemistry of the precursor itself is not as well studied as that of allyl radical or even other alkyl halide prototypes.^{47–54} The UV absorption spectrum of allyl iodide comprises two broad bands, a stronger band at ~ 200 nm and a weaker one at ~ 270 nm.^{38,50,55} While the absorption at shorter wavelengths is ascribed to transitions involving promotion of an electron to the π^* orbital, encompassing both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, the latter involves an $n \rightarrow \sigma^*$ transition, similar to methyl iodide. This is the band that we excite in our experiments to initiate the photodissociation. Recently, Kohguchi *et al.* have shown that the photodissociation of allyl iodide at 266 nm produces internally cold allyl radicals compared to that at shorter wavelengths (213 nm).⁵⁶ This is due to different photodissociation mechanisms operating at long and short wavelengths. At 266 nm, direct dissociation occurs on the repulsive $n_I\sigma_{C-I}^*$ excited-state surfaces and the excess energy gets channeled into translational energy of the product fragments. In contrast, 213 nm excitation causes an initial local $\pi\pi^*$ excitation followed by predissociation to the no^* states, which produces vibrationally hot allyl radicals.

An important feature of photodissociation reactions involving multiple excited-state surfaces is the branching ratio of the product fragments.^{57,58} As already mentioned, the A-band photodissociation of halogenated hydrocarbons is known to produce a halogen atom in both spin-orbit excited ($^2P_{1/2}, I^*$) and ground ($^2P_{3/2}, I$) states, respectively.^{53,59–61} The branching ratio of the dual I/I^* channels in the photodissociation of allyl iodide was measured by Fan and Pratt by making use of the different wavelength- and electric field-dependent photoionization cross sections of the atoms.⁵⁸ They obtained $I^*/(I + I^*)$ ratios of 0.61 ± 0.10 at 193 nm and 0.90 ± 0.10 at 266 nm, which is higher than that reported for CH_3I (0.76 at 266 nm).³² This led them to infer that at 266 nm, excitation to the 3Q_0 state in allyl iodide is the dominant channel with only a minor excitation to the 1Q_1 surface. From the observed spectral intensity in the resonance-enhanced multiphoton ionization (REMPI) spectrum of the iodine fragments and referencing those to the known branching ratios of CH_3I , Kohguchi *et al.* have recently measured the $I^*/(I + I^*)$ ratio to be 0.83 ± 0.08 at 266 nm.⁵⁶ Additionally, state-resolved scattering images of product iodine atoms showed a unimodal velocity distribution in the $^2P_{1/2}$ state but a bimodal velocity distribution in the $^2P_{3/2}$ state.⁵⁶ The number of peaks in the translational energy distribution was explained as being correlated with the number of excited-state surfaces leading to the respective products. The authors concluded that the different curvatures of the 1Q_1 and 3Q_1 potential energy surfaces, both culminating in the ground state I atom at the asymptotic limit, produced allyl radicals with different internal energies leading to two peaks in the translational energy of the I atom. On the other hand, I^* produced from a single 3Q_0 repulsive surface yielded a single peak in its velocity distribution.

FIG. 1. Potential energy curves representing the A-Band photodissociation of alkyl iodides along the C—I coordinate. A strong parallel transition from the ground state (GS) to the 3Q_0 surface (blue) correlates with the $R + I^*$ ($^2P_{1/2}$) products in the asymptote. Perpendicular transitions to the 1Q_1 and 3Q_1 surfaces (red) are much weaker and correlate with the $R + I$ ($^2P_{3/2}$) products in the asymptote. The width of the lines used to depict the excited-state surfaces are in the ratio of their calculated oscillator strengths ($^3Q_0: ^1Q_1: ^3Q_1 = 0.81: 0.17: 0.02$) from the ground state equilibrium bond length (See Ref. 70). A conical intersection between the 3Q_0 and 1Q_1 surfaces leads to non-adiabatic population transfer from the 3Q_0 to the 1Q_1 surface.

The photodissociation of CH_3I at 266 nm monitored via transient XUV absorbance of the iodine $\text{N}_{4/5}$ edge revealed distinct transient features at 45.6 eV and 47.3 eV (labelled transients A and B, respectively), arising as the molecules traverse along the repulsive $n\sigma^*$ excited potential energy surfaces.²⁸ These features were assigned to $4d(\text{I}) \rightarrow n(\text{I})$ transitions (in the vicinity of the $4d \rightarrow 5p$ resonances of atomic iodine), which were shown to be equivalent in electronic configuration to the $(4d_{5/2})^{-1}\sigma^*$ and $(4d_{3/2})^{-1}\sigma^*$ final states accessed from XUV absorption of the molecular ground state. A third weak feature was also observed at 48.4 eV, albeit not reproducibly, due to the low signal amplitude that made it inconspicuous from the underlying noise level. In this work, we revisit the TS region in the C—I bond dissociation process using allyl iodide as the reactant, for two reasons. First, with the increase in the mass of the departing hydrocarbon fragment (from methyl to allyl), the bond dissociation is expected to be slower, increasing the TS lifetime. Second, by incorporating a resonance-stabilized radical in the photoproduct, additional stabilization may be provided to the TS. Both factors are envisaged to facilitate the observation, characterization, and assignment of the transients. High-level *ab initio* calculations of a number of linear and branched alkyl iodides in the ground as well as first excited states have shown that the shape of the potential energy curves and the location of the conical intersection between the $^3\text{Q}_0/1\text{Q}_1$ surfaces are not very sensitive to chemical substitution.⁶² The present study is motivated by our previous work on probing the TS region of the 266 nm photodissociation of CH_3I by femtosecond XUV core-level spectroscopy. We detect the reactive transients on the repulsive valence-excited $n\sigma^*$ states accompanying C—I bond dissociation in allyl iodide through the evolution of the core-to-valence I N-edge resonances, clearly observe a third transient feature C, and assign them to specific valence and core-excited states.

II. EXPERIMENT

The experiment employs a sub-70 fs UV pump pulse (266 nm, 4.7 eV) to trigger the photodissociation reaction and a broadband sub-40 fs XUV probe pulse (35–73 eV) to subsequently monitor it as a function of time. The output of a Spectra Physics Spitfire regenerative amplifier seeded with a Mai Tai oscillator (798 nm central wavelength, 60 nm bandwidth, 600 mW, 84 MHz repetition rate) and amplified in a dual stage arrangement by two Empower pump lasers (527 nm Nd:YLF, 28 W) is used to generate the pump and probe pulses. This commercial laser system is capable of delivering 12 mJ sub-35 fs pulses at 1 kHz repetition rate; however, only ~3 mJ of the output is utilized for the generation of the pump and probe pulses required for this experiment. Approximately, 0.7 mJ of the fundamental 800 nm pulses is used to generate the third harmonic at 266 nm (~25 μJ , 5–10 μJ used in the experiment), which serves as the pump beam. In another arm, the fundamental (800 nm, 1.65 mJ) and the second harmonic (400 nm, 25 μJ) beams are focused and overlapped, spatially and temporally, in a semi-infinite gas cell containing ~50 torr of Argon (or ~100 torr of Ne) to generate odd and

even harmonics of the fundamental, respectively, which serve as the broadband probe pulse (spectrum shown in Figure S1, supplementary material).⁶³ The residual fundamental is blocked using two 600 nm thick Al foils, which imposes an energetic cutoff on the harmonics at 73 eV, corresponding to absorption at the Al L-edge. The diverging XUV is focused into the sample cell using a 60 cm focal length toroidal mirror (with object-plane distance of 72 cm) set at a 5° grazing incidence angle. The time delay between the UV pump and the XUV probe pulses is controlled using a motorized delay stage capable of tuning the relative delays with a precision of 1 fs. The diameters of the UV and XUV beams at the focus are ~120 μm and ~40 μm , respectively. Pump energies used in the experiments are typically varied between 5 and 10 μJ and adjusted by rotating the $\omega + 2\omega$ mixing BBO (β -barium borate) crystal in the third harmonic generation setup from its optimum position, without altering the beam size or beam path. Alternatively, a variable aperture is also used in front of the focusing lens and the lens is used in a slightly defocused geometry in order to eliminate effects on spot size at the focus due to changing beam size.

The experimental apparatus (Figure S2)⁶³ used to carry out the measurements has been described previously.^{64,65} Briefly, the pump and probe pulses are focused at a ~1° crossing angle into a T-shaped sample cell containing a 200 micron clear hole through which the vapor of allyl iodide is made to exit. The transmitted pump beam emerges at an angle and is blocked, while the transmitted XUV probe is subsequently refocused by a toroidal mirror and spectrally dispersed by a grating (600 lines/mm) onto a CCD camera (PIXIS 400B, Princeton Instruments). The energy resolution of the spectrometer in the energy range of 45 eV–60 eV is estimated to be ~0.22 eV. The transmission spectrum of the XUV probe is recorded both in vacuum (I_0) and in the presence of the sample (I) to measure the optical density [$-\log(I/I_0)$], which yields the static XUV absorption spectrum of the molecule. The spectra are averaged over 256 X-ray camera images in order to improve the signal-to-noise ratio, with the CCD integration time set to 0.1 s (i.e., 100 laser pulses per image).

Transient absorption spectra are recorded by monitoring the XUV absorbance in the presence and absence of the pump pulse. An electronic shutter is used to intermittently block the pump beam every 0.1 s (i.e., 100 laser pulses) in order to compare the pump-on spectrum with the pump-off spectrum and measure the change in absorbance of the sample due to the pump pulse. In order to account for drifts in the high harmonic spectrum over time, pump-on spectra are acquired alternately with pump-off spectra. Both pump and probe pulses are horizontally polarized. The transient absorption spectra are acquired at several adjustable pump-probe time delays and the time-resolved spectra so obtained are used to trace the kinetics of the C—I bond dissociation. In order to map out the kinetics of the product channels in the reaction, several pump-probe spectra are measured at discrete time-points, acquiring 100 laser pulses per time-point, and averaged over a total of 32 or 64 measurements at each time delay for improved signal-to-noise ratio. The time-points are chosen at intervals of 10 fs immediately after

time-zero along the rising edge of the products and at greater intervals of 20 fs or 50 fs thereafter in the plateau region. The instrument response function (IRF) is measured as a separate *in situ* pump-probe cross-correlation measurement in neon; the resonant energies of the core-excited Rydberg states undergo a ponderomotive shift in the presence of the 266 nm field, providing a metric for the temporal resolution of the setup. The cross-correlation yields an IRF of 71 ± 14 fs (error denotes standard deviation evaluated over 15 measurements) for our setup, also providing a way to establish the zero time-delay between the pump and probe pulses. Throughout this paper, positive delay time is used to denote that the UV pump pulse precedes the XUV probe pulse. Error bars along the y-axis (OD or Δ OD) denote one standard deviation of the mean over all measurements (256 measurements for static spectra and 32 or 64 measurements over a specified set of time-points in a pump-probe experiment) made at that particular energy and/or time-delay.

III. RESULTS AND DISCUSSION

A. Static XUV absorption spectrum

Figure 2 shows the static XUV absorption spectrum of allyl iodide in the region of the I $N_{4/5}$ edge. The spectrum is measured using neon harmonics and is corrected for the underlying non-resonant valence and core-level ionization (Figure S3).^{63,65,66} Four distinct peaks are observed in the spectrum, similar to those reported earlier in case of CH_3I ²⁸ and CH_2IBr .⁶⁵ They represent two distinct core-to-valence transitions involving the 4d core electron of I atom, one to the antibonding orbital (σ^*) of the C—I bond and the other to the high-lying 6p Rydberg state of I. Each transition is further composed of a doublet due to the $d_{5/2,3/2}$ spin-orbit splitting (1.7 eV) of the core holes. Gaussian functions with a variable width are used to fit each peak in order to identify the center

FIG. 2. Static XUV absorption spectrum of allyl iodide. Hollow black circles are the experimentally measured datapoints and error bars indicate the standard deviation evaluated over all data sets. Each peak is fitted to a Gaussian function shown as solid gray lines. The overall fit to all the peaks obtained by summing the individual Gaussian functions is shown by the solid red line.

frequency of the transitions. The observed peak positions are 50.7 eV, 52.4 eV, 54.6 eV, and 56.2 eV, similar to the core-to-valence transitions observed in CH_3I and CH_2IBr .^{28,65,66} The spin-orbit splitting is therefore found to be 1.7 eV and 1.6 eV for the two core-to-valence excited states, $(4d)^{-1}\sigma^*$ and $(4d)^{-1}6p$, respectively. It must be mentioned that the smaller sub-structures in the ~ 54 eV and ~ 56 eV peaks of CH_3I representing the $4d \rightarrow 6p(e)$ and $4d \rightarrow 6p(a_1)$ transitions could not be resolved in the case of allyl iodide.²⁸ Also, as a single Gaussian function does not capture the shape of the $4d \rightarrow 6p$ resonances exactly because of the unresolved sub-structure, slight differences (0.1 eV in the present case) may occur in the measured spin-orbit splitting from the known value of 1.7 eV.

B. Transient absorption at long time delays and dissociation kinetics

Figure 3 shows a transient XUV absorption spectrum of allyl iodide measured between 400 fs and 1200 fs (in steps of 50 fs) after irradiation with a 266 nm pulse and averaged over all the time-points. As evident from the time scales characterizing C—I bond dissociation,⁶⁵ the result is representative of spectra obtained in the final product region of the reaction coordinate, specifically, where the growth of the reaction products plateaus out. The power of the pump pulse was kept sufficiently low ($<5 \mu\text{J}$) in order to remain in the regime of single-photon excitation and avoid spurious ion peaks arising from multiphoton ionization of the molecule, based on our prior knowledge of the photochemistry of halogenated hydrocarbons and the spectroscopic positions of the ionic species therein (confirmed by power dependence studies of the corresponding peaks).⁶⁵ The negative Δ OD features in the region between 49 eV and 57 eV in Figure 3

FIG. 3. Transient XUV absorption spectrum of allyl iodide at low pump power ($<5 \mu\text{J}$) measured in the long delay limit (between 400 fs and 1200 fs). Positive peaks represent the product I atom absorption (see text for assignment), while negative peaks represent the ground state depletion of the parent molecule. Each peak is fitted to a Gaussian function shown in solid gray line. The overall fit to all the peaks is shown by the solid red line. Error bars correspond to one standard deviation over all data sets.

arise from depleted population in the ground state of the parent molecule induced by the UV pump and therefore resemble an inverted version of the static XUV absorption spectrum shown in Figure 2. This part of the spectrum does not contain any new features due to the UV excitation and is therefore not discussed any further. Two new sharp features with positive ΔOD are apparent at 46.1 eV and 46.8 eV that correspond to the known 4d electronic transitions of I atom products of the C—I bond dissociation induced by the pump pulse. Specifically, they represent the $^2P_{3/2} \rightarrow ^2D_{5/2}$ and $^2P_{1/2} \rightarrow ^2D_{3/2}$ transitions of atomic iodine, respectively. A third peak could be identified at 47.6 eV at slightly higher pump energies (~ 8 to $10 \mu J$), as shown in Figure S4.⁶³ This corresponds to the weaker $^2P_{3/2} \rightarrow ^2D_{3/2}$ transition of atomic I in the ground state and is in agreement with the transient XUV absorption spectra of CH_2IBr and CH_3I presented in our earlier papers.^{28,65} (It must be noted that the peak center appears on the low energy side of the known position for the transition at 47.8 eV due to contribution of ions generated by multiphoton absorption). While the first and third peaks correspond to I atoms produced in the ground state, the central peak corresponds to I^* . The lower peak amplitude of the $^2P_{3/2} \rightarrow ^2D_{3/2}$ transition (47.6 eV) of ground state I in allyl iodide compared to CH_3I ²⁸ at comparable pump excitation powers is already indicative of the higher $I^*/(I + I^*)$ branching ratio in allyl iodide (0.9 for allyl iodide versus 0.76 for CH_3I).^{32,58}

The time-resolved transient absorption spectra are analyzed to map out the dissociation kinetics by monitoring the change in the XUV absorption maxima of the reactant and product species as a function of time (Figure 4). The time behaviors are fitted to exponential functions convolved with a Gaussian component representing the instrument response function (~ 70 fs). The exponential rise-times of the I^* and I channels are obtained as 74 ± 4 fs and 104 ± 12 fs, respectively, whereas the decay of the parent molecule is characterized by a time constant of 99 ± 19 fs (errors

correspond to one standard deviation of measurements made over three time-scans). It is interesting to note that the rise time of the I atom product channel is slower compared to that of I^* despite the more steep slope of the repulsive 1Q_1 surface compared to the 3Q_0 . This is suggestive of a delayed onset of ground state I atoms, possibly if they are produced from a curve crossing of the 3Q_0 and 1Q_1 surfaces instead of a direct excitation on 1Q_1 . Moreover, our experiments do not detect any biexponential kinetics in the I atom channel, as would be expected from the reported bimodal translational energy distribution.⁵⁶ It is possible that the 3Q_1 state that was invoked to explain the bimodal behavior⁵⁶ is not accessed in the present work, as also seen in magnetic circular dichroism studies of the A-band²⁹ as well as photofragment angular distribution studies in methyl iodide.⁶⁷

C. Transient absorption at short time delays

Figure 5 shows a comparison of the transient absorption spectra acquired at high pump power ($\sim 8 \mu J$) at two separate pump-probe time delays, one at 70 fs (red squares) and another measured and averaged between 280 fs and 530 fs (black circles). These time scales represent spectroscopic windows into the TS region and the product region, respectively. Averaging is performed in the long time-delay limit where the product absorption reaches a plateau in order to improve the signal-to-noise ratio. On the other hand, a single time-point (70 fs) is chosen to represent the TS region where the new features attain maximum intensity, although the features are found to gradually rise and decay in the 0 fs to 180 fs time scale, as discussed later (Section III E). In the 70 fs time trace, enhanced absorptions can be clearly identified at ~ 45.3 eV, ~ 47.4 eV, and ~ 48.4 eV, labelled as transients A, B, and C in the figure, which are absent at long time delays. Transient A appears 0.8 eV to the red side of the $^2P_{3/2} \rightarrow ^2D_{5/2}$ (I) transition, while transients B and C appear 0.6 eV and

FIG. 4. Kinetics traces for rise of I^* (red circles), I (blue triangles), and ground state depletion of the parent molecule (black squares) obtained by plotting the change in the absorption maxima/minima of each peak as a function of pump-probe delay. Solid lines represent fits to the time traces involving an exponential rise convolved with a Gaussian instrument response function (~ 70 fs). The exponential rise-times of the I^* and I channels are obtained as 74 ± 4 fs and 104 ± 12 fs, respectively. The decay of the parent molecule is characterized by a time constant of 99 ± 19 fs (error bars correspond to one standard deviation).

FIG. 5. Comparison of transient absorption spectra of allyl iodide measured using $\sim 8 \mu\text{J}$ pump power at two separate pump-probe time delays of 70 fs (red squares) and between 280 and 530 fs (black circles). Transient peaks are identified at 45.3 eV (A), 47.4 eV (B), and 48.4 eV (C) in the 70 fs time trace, which disappear at long time delays. All three transients exhibit higher signal-to-noise ratio compared to spectra measured at lower pump power (see Figure S5).⁶³

0.9 eV to the blue side of ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{3/2}$ (I^*) and ${}^2\text{P}_{3/2} \rightarrow {}^2\text{D}_{3/2}$ (I) transitions, respectively. Interestingly, the spectroscopic positions of the transient features are similar to those identified in the photodissociation of CH_3I in our earlier work (although feature C was not always observed in CH_3I).²⁸ This suggests that these peaks arise from similar transitions on the evolving valence-excited-state surfaces of the molecule to the core-excited states and that the potential energy curves along the C—I reaction coordinate for the $n\sigma^*$ state are not affected by the type of alkyl substituent as the state is largely localized on the C—I bond. An important difference between the transient features observed in case of CH_3I and those seen in case of allyl iodide is that peak C is much more prominent in allyl iodide and exhibits experiment-to-experiment reproducibility. In order to confirm that the transients A, B, and C are not a result of any multiphoton absorption due to the $8 \mu\text{J}$ pump power used in the measurements, transient absorption spectra are also recorded at lower pump power ($5 \mu\text{J}$, Figure S5).⁶³ All three features are detected in the low pump power scan as well although the high pump power scan reveals them with better signal-to-noise ratio due to the higher fraction of excited molecules in the pump volume, at the cost of slight saturation of the ${}^2\text{P}_{1/2} \rightarrow {}^2\text{D}_{3/2}$ (I^*) peak in the XUV spectra at long time delays. (It must be mentioned that some multiphoton absorption sets in with the increase in pump power thereby populating the high-lying Rydberg states, which dissociate to produce ground state I atoms. This saturates the intensity ratio of the peaks (I^*/I) in the spectrum, as seen from comparison of Figures 5 and S5). As shown in Figure S6,⁶³ there is a fair degree of overlap between the absorption peaks of transient B (~ 47.4 eV) and the atomic I^* absorption at 46.8 eV, whereas the contributions of the atomic resonances to the transient features A and C are expected to be less as the transient peaks are energetically more separated from the atomic resonances.

D. Assignment of the transients

In the XUV transient absorption study of the photodissociation of CH_3I , the spectroscopic positions of the observed transients (A and B) were validated using a one-electron transition picture.²⁸ The energies of the $4d \rightarrow n(\text{I})$ transitions from the valence-excited TS region were conjectured to lie between the core electron absorption energy on the repulsive $n\sigma^*$ states at the ground state equilibrium bond length (i.e., the Franck-Condon region) and the atomic $\text{I}/\text{I}^* 4d \rightarrow 5p$ resonance energies in the asymptote (at 46.2 eV and 46.9 eV). The former was calculated as the difference between the $4d(\text{I}) \rightarrow \sigma^*(\text{C—I})$ static XUV transition energies from the molecular ground state [$(4d_{3/2})^{-1}\sigma^*$ at 50.6 eV and $(4d_{5/2})^{-1}\sigma^*$ at 52.3 eV] and the $n(\text{I}) \rightarrow \sigma^*(\text{C—I})$ vertical excitation energy to the ${}^3\text{Q}_0$ and ${}^1\text{Q}_1$ surfaces (4.7 eV and 5.2 eV, respectively).³² This led to the prediction that the transients from the ${}^3\text{Q}_0$ surface would lie in the energy range 45.2 eV to 45.9 eV [${}^3\text{Q}_0 \rightarrow (4d_{5/2})^{-1}\sigma^*$] and 46.9 eV to 47.6 eV [${}^3\text{Q}_0 \rightarrow (4d_{3/2})^{-1}\sigma^*$], whereas those from the ${}^1\text{Q}_1$ surface would lie in the energy range 45.4 eV to 46.2 eV [${}^1\text{Q}_1 \rightarrow (4d_{5/2})^{-1}\sigma^*$] and 47.1 eV to 47.9 eV [${}^1\text{Q}_1 \rightarrow (4d_{3/2})^{-1}\sigma^*$]. Indeed, the experimentally observed values of 45.6 eV and 47.3 eV for transients A and B were found to be in close agreement with the predictions and they were accordingly assigned to the $(4d_{5/2})^{-1}\sigma^*$ and $(4d_{3/2})^{-1}\sigma^*$ core-excited states, respectively. Note the equivalence of the electronic configurations for the final states of the $4d \rightarrow n(\text{I})$ XUV transitions from the TS region and the $(4d)^{-1}\sigma^*$ states accessed via XUV absorption in the ground state.²⁸ However, any direct assignment to the ${}^3\text{Q}_0/{}^1\text{Q}_1$ surface was not possible in the absence of relevant reports on XUV absorption in the transition state region of related molecules. A third weak transient (C), identified at 48.4 eV, was not found to be reproducible from scan-to-scan because it was at the limit of the detection and was therefore not discussed further. However, it is quite clear from the above argument that such a transient essentially lies outside the energy range predicted for $4d \rightarrow n(\text{I})$ transitions (45.2 eV–47.9 eV) from the valence-excited states and may represent a transition to a higher-lying orbital, e.g., $4d \rightarrow \sigma^*$ in the TS region.

In close analogy with the above example, the transients A and B in the photodissociation of allyl iodide are easily explained based on the same one-electron picture. In addition, we find that to account for the origin of transient C, which is much more prominent in allyl iodide compared to methyl iodide, higher core-excited states (involving $4d \rightarrow \sigma^*$ transitions) must be invoked. Figure 6 shows a qualitative molecular orbital diagram of allyl iodide. The $n(\text{I})$ and $\sigma^*(\text{C—I})$ orbitals represent the HOMO and the LUMO, respectively, as in other alkyl halides.^{55,68} The π (HOMO–1) and π^* (LUMO+1) orbitals are built from C(2p) orbitals corresponding to the $\text{C}2=\text{C}3$ double bond and shown for the sake of completeness. The optical transition at 266 nm from the filled doubly degenerate non-bonding $n^4(5p)$ orbital to the vacant antibonding $\sigma^{*0}(\text{C—I})$ orbital of allyl iodide creates partially filled n^3 and σ^{*1} orbitals, the same as in CH_3I .²⁸ Therefore, these are the lowest two orbitals available for a transition of a 4d core electron from the $n\sigma^*$ excited-state

FIG. 6. Qualitative molecular orbital diagram of allyl iodide. The doubly degenerate non-bonding orbitals $n(I)$ and the antibonding orbital $\sigma^*(C-I)$ represent the HOMO and LUMO, respectively. The $\pi(C=C)$ and $\sigma(C-I)$ bonding orbitals represent the (HOMO-1) and (HOMO-2) orbitals, respectively. (It must be noted that the π and π^* orbitals correspond to the $C_2=C_3$ double bond and are shown here only for the sake of completeness). One-photon excitation at 266 nm (blue arrow) transfers an electron from the HOMO to the LUMO, leading to the electronic configuration $n^3\sigma^{*1}$. A time-delayed XUV pulse (green arrow) can then promote 4d core electrons of I atom (not shown) to the partially filled n or σ^* frontier molecular orbitals.

surfaces. Although the potential energy curves in the A-band of allyl iodide are not known, the assignments are based on the premise that they are similar to methyl iodide along the C—I reaction coordinate. This assumption is justified by similar I/I* branching ratios and translational energy distributions observed in the I/I* channels (unimodal and bimodal for I* and I, respectively) for both molecules.^{56,58,69} In addition, the shape of the potential energy curves and the location of the $^3Q_0/{}^1Q_1$ conical intersection are found to be invariant across a series of linear/branched alkyl iodide molecules.⁶² In this context, given the equiergic valence excitation, 4d static XUV absorption, and product I atom resonances in both molecules, transients A and B in allyl iodide are assigned to $(4d_{5/2})^{-1}\sigma^*$ and $(4d_{3/2})^{-1}\sigma^*$ core-excited states, respectively, accessed via $4d \rightarrow n(I)$ transitions from the $n\sigma^*$ states (i.e., similar to CH_3I).²⁸

Transient C, found on the higher energy side of the ${}^2P_{3/2}$ to ${}^2D_{3/2}$ I atom resonance, appears 3.1 eV higher in energy compared to transient A. The sum of the core-hole splitting of the I atom (${}^2P_{3/2,5/2}$, 0.95 eV) and I* (${}^2D_{3/2,5/2}$, 1.7 eV) spin-orbit states at the asymptote of the potential energy curve represents the maximum possible separation between transients borne out of $4d \rightarrow n(I)$ transitions from the $n\sigma^*$ excited-state surfaces.²⁸ This value (~ 2.7 eV) does not encompass the empirical energy gap between transients A and C. The next available higher energy, partially filled orbital (σ^*) is therefore invoked to explain its origin. This particular core-to-valence excitation generates a state with three electrons in the $n(I)$ orbital and two electrons in the σ^* orbital, i.e., with the electronic configuration $(4d)^{-1}n^3\sigma^{*2}$. In view of this assignment, it might then be argued that transient C should

also be partnered with a spin-orbit counterpart ($4d_{3/2,5/2}$) that is 1.7 eV lower or higher in energy (i.e., at ~ 46.7 eV or ~ 50.1 eV). However, these regions of the transient absorption spectrum coincide with the rising edge of the I* product absorption and the falling edge of the ground state depletion, respectively (as seen in Figure 3), and therefore, no feature is observed in the experiment to corroborate the assignment to specific spin-orbit states. Transient C is therefore assigned to a $4d \rightarrow \sigma^*(C-I)$ transition, leading to a $(4d)^{-1}n^3\sigma^{*2}$ core-excited state; however, it remains unclear at present whether it corresponds to a $d_{3/2}$ or $d_{5/2}$ core-hole. It must be mentioned that the energies of these core-to-valence excited states are not known experimentally; however, the spectroscopic positions of the transients A, B, and C revealed in the femtosecond extreme ultraviolet transient absorption studies of methyl iodide and allyl iodide provide a benchmark for theoretical calculations on the nature of the core-excited states in alkyl iodides, especially in the TS region of the potential energy surface.

The differential absorbance of the new features observed in the transient absorption spectra of methyl iodide²⁸ and allyl iodide provides the basis for a preliminary assignment of the transients observed to specific electronic states in the A-band manifold. The experimentally measured absorption intensities of transients A and B in methyl iodide (after deconvolution of the atomic absorption due to overlapping resonances) were found to be 10 mOD and 28 mOD (i.e., ratio of $\sim 1:3$), respectively.²⁸ A complete nine-dimensional potential energy surface calculation of methyl iodide provided the oscillator strengths of the $n \rightarrow \sigma^*$ transition to the 3Q_0 , 1Q_1 , 3Q_1 states as 0.81:0.17:0.02 at the ground state equilibrium geometry.⁷⁰ However, the occurrence of nonadiabatic dynamics precludes the direct mapping of the measured peak intensities to computed oscillator strengths. Magnetic circular dichroism studies of CH_3I reveal that production of I atoms in the photodissociation is almost entirely due to the 3Q_0 to 1Q_1 curve crossing (94% of the absorption strength between 260 and 262 nm is carried by the 3Q_0 state).²⁹ As the 3Q_1 state contributes mostly in the red wing of the A-band absorption³² and has very low oscillator strength,⁷⁰ it is omitted from the present discussion. Assuming that the oscillator strengths for the $4d \rightarrow n(I)$ transitions are not much different for the two valence-excited states (3Q_0 and 1Q_1), the XUV transient absorbance is expected to correlate directly with the transient population in each valence-excited state. Since the empirical intensity ratio of the transients approximates the known I*/(I + I*) branching ratio, the results are suggestive that transients A and B in CH_3I may correlate with the 1Q_1 and 3Q_0 surfaces, respectively.

The appearance of the same transients (A and B) and an additional feature (C) in the photodissociation of allyl iodide offers additional insight into the origin of these transient features. The measured peak intensities of the transient features in allyl iodide were 6 mOD (transient A), 28 mOD (transient B, post subtraction of the asymptotic product I* atom absorption, as discussed later in Section III E), and 13 mOD (transient C), i.e., in the ratio $\sim 1:5:2$. It must be reiterated that while transients A and B were both assigned to $4d \rightarrow n(I)$ transitions, transient C was best assigned to a $4d \rightarrow \sigma^*(C-I)$

transition. The oscillator strengths in the A-band of allyl iodide are assumed to be similar to methyl iodide since the non-bonding and antibonding orbitals in both molecules are localized on the I atom and C—I bond, respectively. The experimentally measured I*/I branching ratio in allyl iodide is higher (9:1 measured by Fan *et al.* and 8.3:1.7 measured by Sumida *et al.*), suggesting that non-adiabatic dynamics is less facile.^{56,58} Nonetheless, due to the curve crossing, the branching ratio of the reaction products is not expected to directly follow the oscillator strengths of the different surfaces involved in the valence excitation. It must be noted that even without considering the new transient feature C, the relative peak intensities of transients A and B in allyl iodide are found to be similar to those in methyl iodide²⁸ (i.e., $B > A$), suggestive of their origin from the same valence-excited surfaces in both molecules. The feature C is observed for the first time in this work and although it most likely connects to the $(4d)^{-1}\sigma^*$ core-excited state, assigning it to a specific valence-excited state is not straightforward. Origin of transient C from the 1Q_1 state would be less likely, as this state has lower population in allyl iodide ($\sim 10\%$) compared to methyl iodide ($\sim 25\%$), yet feature C is more prominent in allyl iodide. Thus, it possibly originates from the 3Q_0 surface, in line with the high I*/I branching ratio (signifying high population and consequently higher probability of detection) in allyl iodide. This initial assignment could potentially be tested by characterizing the transient peak intensities in other alkyl iodides with systematically varying I*/(I + I*) branching fractions at the same excitation wavelength (0.67 in C_2H_5I ,⁷¹ 0.6 in C_3H_7I ,⁷² 0.32 in C_6H_5I ,⁷³ 0.27 in C_2H_3I ,⁷⁴ and 0.22 in $C_6H_{11}I$).⁷⁵ However, it must be mentioned that more thorough assignment of the transient species as a general feature of A-band photodissociation in halogenated hydrocarbons necessitates the availability of more quantitative information on the exact oscillator strengths of both the valence-excited and core-excited states, their slopes in the TS region, as well as the adiabaticity of the valence-excited states.

FIG. 7. Time traces of transients A (gray squares), B (blue circles), and C (red diamonds) obtained by plotting the change in absorption intensity at the respective resonance positions as a function of pump-probe delay.

E. Temporal dynamics in the transition state region

In order to elucidate the temporal characteristics of the transient features, spectral lineouts are taken at their respective absorption maxima at a number of pump-probe time delays. Such a kinetic trace is shown in Figure 7. The transient features are observed to appear in a characteristic time-window between 0 fs and 180 fs after the $n \rightarrow \sigma^*$ excitation initiated by the pump pulse, peaking at about ~ 60 fs. In contrast to the product I atom fragments, which rise in after time zero and

FIG. 8. Temporal lineouts of the absorption maxima of transients A (45.3 eV, gray squares), B (47.4 eV, blue circles), and C (48.4 eV, red diamonds) fitted to Gaussian functions (solid gray line, solid blue line, and solid red line, respectively) to represent their convolutions with the Gaussian instrument response function. The overlapping contribution of the product I* absorption is subtracted from transient B (as shown in Figure S7).⁶³ The transients are found to peak at 54 ± 8 fs (A), 64 ± 3 fs (B), and 59 ± 3 fs (C).

plateau out at longer delay times (Figure 4), these features are clearly ‘transient’ on the time scale of dissociation. Two points may be noted about these transient features. First, whereas transients A and C decay almost to zero at long time delays beyond 180 fs (Figure 7), transient B shows a finite non-zero absorbance. This is because the latter is overlapping with the high-energy wing of the I^* resonance and the product absorbance manifests as a finite non-zero absorbance in the long delay time limit after the transient has decayed. Second, within the energy and time resolution of the experimental setup, no discernible spectral shift is noted in the absorption maxima of the transients as a function of time, as might be expected with varying slopes of the potential energy curves along the reaction coordinate; on the contrary, the transient features only appear with increasing and decreasing amplitude as a function of time. Higher energy resolution of the XUV spectrometer and shorter pump pulses might be required to follow energy shifts in the transient energy maxima with change in pump-probe time delay. The temporal behavior of the transients is fitted to a Gaussian function in order to determine the peak positions and the peak widths, as shown in Figure 8. The I^* absorbance is deconvolved from transient B absorbance in order to extract its lifetime (see Figure S7);⁶³ such a procedure was not required for transients A and C as they are well separated from the product fragment absorption peaks (Figure S6).⁶³ The peak maxima for transients A, B, and C are obtained as 54 ± 8 fs, 64 ± 3 fs, and 59 ± 3 fs, respectively, whereas the peak widths (full width at half maximum) are obtained as 140 fs, 67 fs, and 93 fs, respectively. The transients are found to decay completely by 145 fs–185 fs, providing an estimate for the C—I bond dissociation time, which is also consistent with the rise times of the I/I^* peaks shown in Figure 4. These time constants also agree well with femtosecond clocking experiments, which monitored the product I atom rise in alkyl iodide molecules of comparable mass.⁶² The lifetimes of the transients and C—I bond dissociation times in allyl iodide are found to be greater compared to the case of methyl iodide (as expected) by a factor of 1.6–2.²⁸ This is reasonable to expect from a simple square root of reduced-mass (of the dissociating R and I product fragments) dependence of the reaction time.⁷⁶

IV. CONCLUSION

The importance of characterizing the TS region of chemical reactions in order to gain deeper insight into the nature of the excited potential energy surfaces as well as the reaction mechanism cannot be overemphasized. XUV/soft X-ray pulses produced by high harmonic generation can be used to selectively probe the reaction coordinate with temporal resolution ranging from picoseconds to attoseconds. Along with our earlier report on CH_3I photodissociation,²⁸ this work demonstrates the ability of core-level spectroscopy to monitor the progress of a reaction in real time as well as to characterize the fleeting TS region in chemical reactions.

Femtosecond core-to-valence transient absorption spectroscopy is applied to study the photodissociation of allyl iodide upon excitation of its A-band at 266 nm. This unimolecular reaction is seen to produce I atom fragments both in the

ground and spin-orbit excited states, revealing the multidimensional nature of the excited electronic state, as is well known for alkyl halides in general. Furthermore, in the course of the C—I bond breaking along the repulsive $n\sigma^*$ excited-state surfaces, three distinct peaks identified as transients A (45.3 eV), B (47.4 eV), and C (48.4 eV) constitute signatures of the evolving transient valence electronic structure. While the first two peaks are both borne out of $4d \rightarrow n(I)$ transitions (similar to CH_3I), the third peak is attributed to a $4d \rightarrow \sigma^*(\text{C—I})$ transition. The observation and assignment of transient C constitutes a new finding of this work and paints a more detailed picture of the transition state region of C—I bond dissociation. These transients are found to decay on a time scale of 145 fs–185 fs, thereby delineating time scales for the C—I bond dissociation in allyl iodide. The peak intensities of the transients are used to assign them to possible specific electronic states 3Q_0 and 1Q_1 within the framework of known I^*/I branching ratios. It is argued that transient A may arise from the 1Q_1 surface, whereas transients B and C may arise from the 3Q_0 surface. Furthermore, their spectroscopic positions and lifetimes provide a benchmark for theoretical calculations on the nature of the core-excited states involved.

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