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Core-to-valence spectroscopic detection of the CH_2Br radical and element-specific femtosecond photodissociation dynamics of CH_2IBr

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Element-specific single photon photodissociation dynamics of CH_2IBr and core-to-valence absorption spectroscopy of CH_2Br radicals are investigated using femtosecond high-harmonic extreme ultraviolet (XUV) transient absorption spectroscopy. Photodissociation of CH_2IBr along both the C–I or C–Br reaction coordinates is observed in real-time following excitation at 266 nm. At this wavelength, C–I dissociation is the dominant reaction channel and C–Br dissociation is observed as a minor pathway. Both photodissociation pathways are probed simultaneously through individual 4d(I) $N_{4/5}$ and 3d(Br) $M_{4/5}$ core-to-valence transitions. The 3d(Br) $M_{4/5}$ pre-edge absorption spectrum of the CH_2Br radical photoproduct corresponding to the C–I dissociation channel is characterized for the first time. Although the radical's singly occupied molecular orbital (SOMO) is mostly localized on the central carbon atom, the 3d(Br) $\rightarrow \pi^*$ (SOMO) resonances at 68.5 eV and 69.5 eV are detected 2 eV below the parent molecule 3d(Br) $\rightarrow \sigma^*$ (LUMO) transitions. Core-to-valence XUV absorption spectroscopy provides a unique probe of the local electronic structure of the radical species in reference to the Br reporter atom. The measured times for C–I dissociation leading to I and I* atomic products are 48 ± 12 fs and 44 ± 4 fs, respectively, while the measured C–Br dissociation time leading to atomic Br is 114 ± 17 fs. The investigation performed here demonstrates the capability of femtosecond time-resolved core-level spectroscopy utilizing multiple reporter atoms simultaneously.

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I. INTRODUCTION

The UV photodissociation of halogenated methanes is an important source of both reactive halogen atoms and halomethyl radicals that have an impact on atmospheric chemistry.^{1–5} Reactive halogens have an adverse impact via ozone depletion,^{4,5} and the possible role of halomethyl radical intermediates in the chemistry of the troposphere has been identified.^{1–3} In a landmark paper by Welz *et al.*,¹ the reaction of the CH_2I halomethyl radical with molecular oxygen is shown to produce the simplest and first experimentally observable Criegee intermediate. Halomethyl radicals display important bonding characteristics, attributed to the π -bonding interaction between the lone pair electrons on the halogen atom with the unpaired radical electron, resulting in anomalously short C–X (X = F, Cl, Br, I) bonds compared to closed-shell analogs.^{6–8} The partial C–X π -bond causes an extra stability of these radicals. The electronic structure has the $\pi^*(\text{C–X})$ orbital as the singly occupied molecular orbital (SOMO) with electron delocalization onto the halogen. The magnitude of the carbon-halogen interaction in halomethyl radicals depends on the π -donor ability of the halogen atom, which is known to increase going down the periodic table from fluorine to iodine.⁶

The reactivity of various halomethyl radicals in the atmosphere can vary dramatically,^{2,3} and these differences can have significant implications in the atmospheric photochemistry of multiply substituted halomethanes (e.g., CH_2IBr , CH_2ICl , etc.). In particular, the wavelength of UV radiation

absorbed by these species governs the branching ratio of C–X dissociation and therefore determines which reactive halogen and halomethyl radical is released.^{9–11} In CH_2IBr considered here, UV excitation at 248 nm leads to a dominant C–I dissociation pathway, while 210 nm excitation produces almost exclusively cleavage of the stronger C–Br bond.¹⁰ Depending on the wavelength of light absorbed, either CH_2Br radicals or CH_2I radicals can be released from the photodissociation of the parent molecule.

In the present study, we investigate the multichannel photodissociation dynamics of the bichromophoric system, CH_2IBr , with 266 nm excitation, by probing the local electronic structure of the major halomethyl radical photoproduct, CH_2Br , and the formation times of the Br and I atoms. This is accomplished through femtosecond time-resolved core-level transient absorption spectroscopy.

Core-level spectroscopies involving X-ray, or extreme ultraviolet (XUV), radiation are powerful techniques to probe the oxidation states, spin-states, chemical environment, and electronic structure of molecules.^{12–20} Due to the highly localized nature of core orbitals on specific atoms in a molecule, core-to-valence transitions probed by X-ray and XUV absorption are element-specific. By tuning the energy of the X-ray or XUV radiation near the binding energy of a core orbital localized on an individual element, one can selectively interrogate specific atomic sites. The local chemical environment, oxidation state, and local electronic structure involving these atomic sites are encoded in the near-edge and pre-edge

structures of the core-to-valence transitions.^{17,19} Furthermore, since the unoccupied valence electronic structure is directly probed, core-to-valence absorption spectroscopy is exceptionally well-suited to detect open-shell radical species. In particular, the core transitions into the SOMO can act as a unique fingerprint of the radical.²¹ Although there are still very limited published examples of core-to-valence absorption spectra of elusive radical reaction intermediates, the method has been exploited in a few static absorption experiments, in combination with the element-specificity of the technique, to identify and characterize the radical intermediates and even to uncover the spatial localization of the SOMO on certain atomic sites.^{21–24}

The powerful advantages of X-ray and XUV absorption spectroscopy, when extended into the time-domain, make it an ideal candidate to study multichannel reaction dynamics. In the present study, the element-specificity of the technique is exploited to monitor photodissociation along both the C–I and C–Br reaction coordinates of CH₂IBr through the 4d(I) N_{4/5} and 3d(Br) M_{4/5} core-to-valence transitions in the 45–58 eV and 64–73 eV ranges, respectively. The large spectral separation of the core-orbital binding energies allows for the atomic-site specific dynamics to be probed individually, yet simultaneously, as well as a function of time. Furthermore, the unique sensitivity to chemical environment and electronic structure of the core-to-valence transitions is leveraged to identify the major radical photoproduct and to probe the local electronic structure involving the halogen atom.

The UV absorption spectrum of CH₂IBr is characterized by two broad resonances peaking at 270 nm and 215 nm, referred to as the A band and B band, respectively.¹⁰ The A band is assigned to n(I) → σ^* (C–I) transitions, which represent the promotion of a nonbonding electron localized on the iodine atom to an antibonding orbital of the C–I bond. The higher energy B band is assigned as n(Br) → σ^* (C–Br). As noted, previous studies provide the intuitive picture of the bichromophoric photoexcitation where the n(I) → σ^* (C–I) transition leads primarily to C–I bond fission and excitation of the n(Br) → σ^* (C–Br) leads primarily to C–Br bond fission. Preferential dissociation of the stronger C–Br bond when exciting the B band occurs by a direct ultrafast dissociation mechanism, circumventing intramolecular vibrational redistribution (IVR), which might have played a role in the bond break-

ing. Due to the overlap of these bands between 215 nm and 270 nm, photoexcitation in this region can induce both n(I) → σ^* (C–I) and n(Br) → σ^* (C–Br) transitions, leading to dissociation along both the C–I and C–Br coordinates.¹⁰ At 248 nm, there is appreciable C–Br dissociation, with a lower limit of 1.2:1 for C–I:C–Br bond fission at this wavelength.¹⁰

In the experiments described here, the multichannel 266 nm photodissociation dynamics of CH₂IBr are investigated in real-time by the novel method of femtosecond time-resolved UV-pump, XUV-probe transient absorption spectroscopy. The extremely broad bandwidth of the XUV probe produced by high harmonic generation allows, for the first time, simultaneous observation of C–I and C–Br dissociation channels in real-time. With this capability, C–I dissociation following 266 nm excitation is observed to be the dominant pathway and also leads to a faster dissociation than the C–Br bond at this wavelength. The difference in dissociation times is rationalized in terms of the acceleration of the fragments in the Frank-Condon regions of the different excited state potentials and also the larger percentage of energy deposited as internal excitation during C–Br dissociation compared to C–I dissociation. The major radical product formed in the 266 nm photodissociation of CH₂IBr is CH₂Br, which is detected through XUV core-to-valence absorption spectroscopy for the first time, obtaining the 3d(Br) → SOMO transitions.

The remainder of this paper is organized as follows: The experimental methods applied in the studies presented here are described in Sec. II. The static XUV absorption spectrum of CH₂IBr, the differential XUV absorption spectra following 266 nm photodissociation, and transient absorption time scans are presented in Secs. III A–III C, respectively. The experimental results are discussed in more detail in Sec. IV and the paper concludes with a summary of significant results and outlook in Sec. V.

II. EXPERIMENTAL METHODS

The experimental apparatus is presented in Fig. 1 and has been described in detail.^{25,26} Previously, experiments on this apparatus were initiated by strong field ionization and dissociative ionization with 800 nm light. Here, the apparatus has

FIG. 1. Experimental setup of the UV-pump, XUV-probe transient absorption apparatus. The XUV probe is produced by high harmonic generation utilizing a semi-infinite gas cell. The high harmonics are refocused by a toroidal mirror into the sample chamber. The XUV spectrometer consists of another toroidal focusing mirror and a uniform line spaced reflection grating (600 lines/mm), which disperses the harmonics onto an x-ray CCD camera (PIXIS:XO 100B).

been modified to permit single-photon dissociation in the ultraviolet for the first time. The pump arm of the pump-probe set up has been altered to include a third-harmonic generator, producing 266 nm pulses, 80 fs, 20 μ J at 1 kHz. The 266 nm pump is focused to a beam diameter of 100 μ m in a heated sample gas cell filled with 5–10 Torr (0.67–1.3 kPa) of CH_2IBr gas. The CH_2IBr reservoir, the sample line, and the sample gas cell are all heated to $\sim 80^\circ\text{C}$ in order to reach an appropriate and constant gas pressure and to avoid formation of condensation in the sample cell. Constant pressure in the cell is confirmed by monitoring the overall flux of the XUV in regions of non-resonant absorption by the gaseous sample. Under experimental conditions, the sample flow is continuous and any gaseous dissociation products are removed from the interaction region in between each laser pulse. Solid buildup of dissociation products in the sample cell can occur; however, the lack of accumulation of dissociation products within the XUV focal volume is also confirmed by monitoring the constant XUV flux in regions of non-resonant absorption by the gaseous sample.

In the probe arm, broadband XUV probe pulses are produced via high harmonic generation (HHG) in a semi-infinite gas cell filled with 110 Torr of neon gas. The HHG process is driven by 800 nm (1.6 mJ) + 400 nm (25 μ J), 40 fs, linearly polarized light, which produces both even and odd harmonics of the fundamental 800 nm driving laser. The residual 800 nm and 400 nm beams are blocked by two 0.6 μ m Al filters. XUV energies up to ~ 72 eV are transmitted through the filters, but there is a sharp cut off in the Al transmission of XUV radiation at ~ 72 eV. The resulting XUV beam is focused to a beam diameter of 40 μ m in the gas cell, where it overlaps the 266 nm pump beam at a 1° crossing angle. The transmitted XUV photons are spectrally dispersed onto a CCD camera where the transmitted intensity is recorded as a function of photon energy. The spectrum is then referenced to another spectrum taken in the absence of the sample gas in order to obtain the optical density (OD) of the sample as function of photon energy. The XUV transient absorption signal is obtained by measuring the OD in the presence of the pump pulse relative to the static absorption in the absence of the pump pulse to yield the change in optical density (ΔOD). Each transient absorption timescan is recorded in 10- or 20-fs steps, averaging 32 scans with an integration time of 0.2 s at each time delay. For every time step, the spectrum is referenced to a “pump off” spectrum by utilizing an electronic shutter to block the pump beam in between each “pump on” spectrum, which helps to correct for any long-term fluctuations in the XUV flux. Measuring the cross-correlation of the 266 nm pump and the XUV probe to extract the instrument response function (IRF) was achieved using the ponderomotive shift in the XUV absorption transition energies of Xe Rydberg states in the presence of the moderately intense, non-resonant field of the 266 nm pump. Since the bound electron energy levels shift in accordance with the instantaneous field strength,²⁷ the shifting of the XUV absorption energies maps the cross-correlation of the pump and probe directly. The FWHM of the resulting cross-correlation trace is used as a fixed IRF in the fitting routine of the pump-probe time traces.

FIG. 2. The static XUV absorption spectrum of CH_2IBr . The transitions marked A, B and C, D correspond to excitation of I(4d) core electrons to $\sigma^*(\text{C-I})$ and 6p,7p(I) unoccupied valence orbitals, respectively. The transitions marked E, F correspond to excitation of Br(3d) core electrons to the $\sigma^*(\text{C-Br})$ orbital. There is underlying non-resonant absorption throughout the spectrum due to valence and core-level ionization. The broad, underlying absorption edge at energies above 56 eV corresponds to a delayed onset of 4d(I) core-level ionization, referred to as a “giant resonance.”

III. RESULTS

A. Static XUV absorption spectrum of CH_2IBr

In Fig. 2, the static XUV absorption spectrum of CH_2IBr is plotted. The absorption spectrum is obtained from the spectrally dispersed XUV transmission through 5–10 Torr of CH_2IBr gas, referenced to the XUV transmission in the absence of the sample gas. The spectrum contains I $N_{4/5}$ and Br $M_{4/5}$ edge and pre-edge features (i.e., transitions originating from the 4d and 3d core orbitals of I and Br atoms, respectively). The resonant pre-edge transitions are labelled with letters A–F and overlap with an underlying, non-resonant contribution due to valence and core-level ionization. The assignments of the pre-edge transitions are given in Table I. The broad, underlying absorption edge at energies above 56 eV corresponds to a delayed onset of 4d(I) core-level ionization, referred to as a “giant resonance.”²⁸ Note that the slight discontinuities in absorption at 59.9 eV, 63.1 eV, 64.7 eV, 66.2 eV, etc. are caused by the sharp contrast in the flux at the peaks and valleys of the high harmonic photon flux. Discontinuation in absorption occurs near the regions of low flux in the harmonic valleys.

TABLE I. Static XUV absorption pre-edge transitions of CH_2IBr .

Peak	Photon energy (eV)	Assignment
A	50.6	$4d(\text{I}) \rightarrow \sigma^*(\text{C-I}), 4d_{5/2}^{-1}$
B	52.3	$4d(\text{I}) \rightarrow \sigma^*(\text{C-I}), 4d_{3/2}^{-1}$
C	54.8	$4d(\text{I}) \rightarrow 6p,7p, (4d_{5/2}^{-1})$
D	56.5	$4d(\text{I}) \rightarrow 6p,7p, (4d_{3/2}^{-1})$
E	70.5	$3d(\text{Br}) \rightarrow \sigma^*(\text{C-Br}), 3d_{5/2}^{-1}$
F	71.5	$3d(\text{Br}) \rightarrow \sigma^*(\text{C-Br}), 3d_{3/2}^{-1}$

FIG. 3. The static XUV absorption spectrum of CH_2IBr in the iodine window (a) and bromine window (b) after subtracting the contributions by non-resonant valence and core-level ionization. The solid black circles represent the experimental absorption data points. The dashed black lines are Gaussian functions fit to each peak in the experimental data and the solid red line is the sum of the Gaussian fitting functions for each plot. The peaks are marked with letters A–F and assigned in Table I.

The I $N_{4/5}$ pre-edge resonant transitions occur between 48 and 58 eV, while the Br $M_{4/5}$ pre-edge resonances occur between 68 and 72.5 eV. After subtracting the contributions by non-resonant valence ionization and the 4d(I) “giant resonance,” these specific energy regions are plotted in Figs. 3(a) and 3(b), respectively. Again, each distinct transition is labelled with letters A–F (same as Fig. 2) and the assignments are given in Table I. The solid black circles represent the experimental absorption data points. The dashed black lines are Gaussian functions fit to each peak in the experimental data and the solid red line is the sum of the Gaussian fitting functions for each plot. Free fit parameters include the peak position, width, and amplitudes of the Gaussian function. The peak energies of each transition are taken as the central peak positions of the Gaussian functions. In Fig. 3(a), there are slight discontinuities in the absorption at 51.8 eV and 53.2 eV caused by valleys in the harmonic flux near those energies as previously noted.

The large spectral separation (~ 20 eV) of transitions originating from the I or Br core orbitals in the same molecule highlights the element and atomic-site specificity inherent to

core-level spectroscopy. A spin-orbit doublet is observed for each core-to-valence transition in the figures and Table I. The doublets have distinct energy separations due to the spin-orbit splitting that characterizes the core-holes in the 4d(I) and 3d(Br) orbitals. The extracted I $4d_{5/2,3/2}$ and Br $3d_{5/2,3/2}$ spin-orbit splittings are 1.7 eV and 1.0 eV, respectively, which is in agreement with previous literature values.^{28–31}

It is valuable to compare the energetics of this static spectrum to the reported XUV absorption spectra of methyl iodide²⁸ and methyl bromide.²⁹ In fact, the $4d(\text{I}) \rightarrow \sigma^*(\text{C-I})$ and $3d(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$ resonances of CH_2IBr are observed at the same energies, respectively, within our spectral resolution, as the analogous transitions of CH_3I and CH_3Br . This observation is reasonable due to the atomic-site specificity of the core-valence transitions and the nearly identical C–I and C–Br bond lengths in the monosubstituted species compared to those of CH_2IBr .

B. XUV spectral observation of one-photon photodissociation of CH_2IBr at 266 nm

Figs. 4 and 5 show the transient absorption spectrum following 266 nm photodissociation of CH_2IBr . The transient absorption spectra at several delay times ranging from 500 fs to 1 ps, well after the dynamics have finished taking place, are averaged to obtain the final transient spectrum plotted in Figs. 4 and 5. Due to the extremely broadband nature of the XUV probe pulses, with energies spanning several tens of eV, core-to-valence transitions in the transient absorption spectrum are observed near both the 4d(I) $N_{4/5}$ and 3d(Br) $M_{4/5}$ edges simultaneously. In the range 44–58 eV, shown in Fig. 4, we observe resonances corresponding to promotion of 4d(I) core electrons into unoccupied valence orbitals. In the same spectrum, but zoomed into the energy range

FIG. 4. Transient absorption spectrum following 266 nm photodissociation of CH_2IBr , in the iodine window. The unfilled circles represent the experimental absorption data points. The dashed red lines are Gaussian functions fit to each peak in the experimental data and the solid black line is the sum of the Gaussian fitting functions for each plot. The peaks at 46.2 eV, 46.9 eV, and 47.9 eV correspond to atomic iodine transitions from the I(4d) core level, whereas the negative amplitude peaks at 50.6 eV, 52.3 eV, 54.8 eV, and 56.5 eV represent the depletion of the parent molecule following 266 nm photodissociation. There are several sharp positive features overlapping the 4d(I) $\rightarrow 6p, 7p$, ($4d_{3/2,5/2}^{-1}$) depletion of the parent molecule, which correspond to $4d(\text{I}) \rightarrow 6p, 7p$ transitions of atomic iodine, including the fitted peaks at 55.6 eV, 57.2 eV, 57.4 eV, and 57.8 eV.

FIG. 5. Transient absorption spectrum following 266 nm photodissociation of CH_2IBr , in the bromine window. Broad negative amplitude background from the depletion of the parent molecule $4d(\text{I})$ core-ionization at energies below 66 eV has been subtracted. The unfilled circles represent the experimental absorption data points. The dashed red lines are Gaussian functions fit to each peak in the experimental data and the solid black line is the sum of the Gaussian fitting functions for each plot. The peaks at 64.6, 65.1, and 65.6 eV correspond to atomic bromine transitions from the $\text{Br}(3d)$ core level. The weak resonance observed at 66.6 eV is attributed to CH_2IBr^+ ion formed by multiphoton ionization. The two broad product absorption features at 68.5 eV and 69.5 eV are attributed to $3d(\text{Br}) \rightarrow \text{SOMO}$ transitions of the CH_2Br radical intermediate and the negative amplitude peaks at 70.5 eV and 71.5 eV represent the depletion of the parent molecule following 266 nm photodissociation.

63–72.5 eV in Fig. 5, we observe resonances corresponding to promotion of $3d(\text{Br})$ core orbital electrons into unoccupied valence orbitals. We probe, separately, but simultaneously, time-resolved changes in the local chemical environments of both the iodine and bromine atomic centers. In the differential absorption spectra, the energy ranges will be referred to as: 44–58 eV, the “iodine window” and 63–72.5 eV, the “bromine window.” In both spectra, the open circles represent the experimental data. The individual peaks are fit to Gaussian functions, shown as dotted lines, and the sum of these Gaussian functions is represented by the solid black line. Focusing first on the transient spectrum in the iodine window shown in Fig. 4, the product absorption features at 46.2 eV, 46.9 eV, and 47.9 eV correspond to the well-known $4d \rightarrow 5p$ core-to-valence transitions of atomic iodine in both the spin-orbit ground state ($^2P_{3/2}$) and excited state ($^2P_{1/2}$).³² The three transitions, in ascending order of energy, are assigned to the $^2P_{3/2} \rightarrow ^2D_{5/2}$, $^2P_{1/2} \rightarrow ^2D_{3/2}$, and $^2P_{3/2} \rightarrow ^2D_{3/2}$ transitions of atomic iodine, respectively. The first and third of these resonances indicate C–I bond cleavage to form ground state I atoms while the middle peak represents the formation of spin-orbit excited I atoms, referred to as I^* atoms. Photodissociation specifically along the C–I coordinate forming both I and I^* photoproducts is observed through the appearance of these sharp atomic resonances in the iodine window. The four negative-amplitude peaks at 50.6 eV, 52.3 eV, 54.8 eV, and 56.5 eV represent the depletion of the parent molecule following 266 nm photodissociation. There are several sharp positive features overlapping the $4d(\text{I}) \rightarrow 6p, 7p, (4d_{3/2}^{-1})$ depletions of the parent molecule, which correspond to $4d(\text{I}) \rightarrow 6p, 7p, (4d_{5/2,3/2}^{-1})$ transitions of atomic iodine, including the fitted peaks at 55.6 eV, 57.2, 57.4, and

57.8 eV.³³ There is a slight discontinuation in the product absorption on the low energy side of the $^2P_{3/2} \rightarrow ^2D_{5/2}$ atomic iodine resonance at 45.7 eV, which is caused by the extremely low flux in the valley of the harmonics in this energy region. Finally, there is a weak resonance at 49.4 eV, which is likely due to the CH_2I radical formed in the minor C–Br dissociation channel, but could also be attributed to CH_2IBr^+ formed by a minor contribution from multiphoton ionization of the parent molecule. The $4d(\text{I})$ core-to-valence absorption spectrum of the CH_2I radical likely has a resonance in this energy region and this is being investigated in a forthcoming study involving the 266 nm photodissociation of CH_2I_2 .

Turning to the bromine window, in Fig. 5, the two negative-amplitude resonances marked at 70.5 eV and 71.5 eV represent the depletion of the $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$ transitions of the parent molecule following 266 nm photodissociation. The sharp product absorption features at 64.6, 65.1, and 65.6 eV are the well-known $^2P_{3/2} \rightarrow ^2D_{5/2}$, $^2P_{1/2} \rightarrow ^2D_{3/2}$, and $^2P_{3/2} \rightarrow ^2D_{3/2}$ transitions, respectively, of the Br atom in the ground state ($^2P_{3/2}$) and spin-orbit excited state ($^2P_{1/2}$).³¹ These atomic Br resonances indicate photodissociation along the C–Br coordinate following photoexcitation at 266 nm. The integrated absorption intensities of these atomic Br resonances are weaker than the analogous I atom resonances. As will be discussed further in Sec. IV C, dissociation along the C–I coordinate is indeed determined to be the major channel following 266 nm photoexcitation of CH_2IBr . The weak resonance observed at 66.6 eV is attributed to CH_2IBr^+ ion formed by multiphoton ionization. This peak matches the energy of the $\text{Br}(3d) \rightarrow \text{SOMO}$ resonance of the CH_2Br_2^+ ion.³¹ From pump laser-power-dependence analysis, shown in Fig. 6, the resonance attributed to the CH_2IBr^+ ion is the only feature in the transient spectra that displays a multiphoton power dependence. The power dependences of the Br and I absorption signals are close to one, as shown in the figure, while the power dependence of the peak at 66.6 eV is 3.8 ± 0.31 . This supports a three- or four-photon ionization of the parent molecule, which has an ionization potential of 9.7 eV.³⁴

The two broad product absorption features at 68.5 eV and 69.5 eV are attributed to $3d(\text{Br}) \rightarrow \text{SOMO}$ transitions of the CH_2Br radical intermediate, and the justification for the assignment is discussed further below. There is another product absorption feature that overlaps the $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$, $3d_{3/2}^{-1}$ depletion of the parent molecule at ~ 71.5 eV. This is evident by comparing the ratio of the intensities of the $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br}), 3d_{5/2}^{-1}$ and $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br}), 3d_{3/2}^{-1}$ resonances of the parent molecule static absorption at 70.5 eV and 71.5 eV, seen in Fig. 3(b), with the ratio of the depletion intensities of these resonances in Fig. 5. In the static absorption, the $3d_{5/2}^{-1} : 3d_{3/2}^{-1}$ ratio of integrated intensities is 1.32 ± 0.07 . The analogous ratio of the depletions, seen in Fig. 5, is 4.06 ± 1.31 . The overlapping product absorption at ~ 71.5 eV is attributed to a $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$ transition of the radical. The three resonances at 68.5 eV, 69.5 eV, and ~ 71.5 eV represent, to our knowledge, the first observation of core-to-valence absorption by a halomethyl radical. The detailed assignments of the radical peaks are discussed further in Sec. IV A.

FIG. 6. Integrated XUV absorbance of peaks centered at (a) 46.2 eV corresponding to atomic iodine, (b) 64.6 eV corresponding to atomic bromine, and (c) 66.6 eV corresponding to CH_2IBr^+ as a function of 266 nm pump power (intensity in the interaction region varies linearly with measured 266 nm power). The integrated XUV absorbances of atomic iodine and bromine resonances have a linear dependence on the 266 nm pump intensity, with slopes of 0.9 ± 0.17 and 1.0 ± 0.12 , respectively, indicating these atoms are each formed by single-photon excitation of the parent molecule. The integrated XUV absorbance of the resonance at 66.6 eV, on the other hand, has a nonlinear dependence on pump intensity with a slope of 3.8 ± 0.31 in the log-log plot. The peak at 66.6 eV therefore is assigned to CH_2IBr^+ , which is formed by 3–4 photon ionization of the parent molecule.

C. Timescales for the 266 nm photodissociation of CH_2IBr along the C–I and C–Br reaction coordinates

In the time domain, the multidimensional dissociation channels are tracked simultaneously with atomic-site specificity by monitoring the rises of each of the Br and I atomic

FIG. 7. Pump-probe time traces for the appearance of (a) the I atoms at 46.2 eV, (b) the I^* atoms at 46.9 eV, and (c) the Br atoms at 64.6 eV.

absorption signals. In the iodine window, time traces following the $^2\text{P}_{3/2} \rightarrow ^2\text{D}_{5/2}$ and $^2\text{P}_{1/2} \rightarrow ^2\text{D}_{3/2}$ resonances representing dissociation along the C–I coordinate to form both I and I^* photoproducts are plotted in Figs. 7(a) and 7(b), respectively. The time traces are fit to a single exponential growth function convoluted with the Gaussian IRF. The Gaussian IRF, with a FWHM of 91 ± 12 fs, is determined separately in a 266 nm + XUV cross correlation, as described in Sec. II. The 91 ± 12 fs FWHM of the Gaussian is fixed in the fitting of the time traces. The dissociation times are taken as the rise time of the exponential growth function. The measured I and I^* rise times are 48 ± 12 fs and 44 ± 4 fs, respectively. These dissociation times are essentially identical within the time

resolution of the experiment and 45 fs will be used later in the discussion. Dissociation along the C–Br coordinate to form ground-state Br atoms is traced by the $^2P_{3/2} \rightarrow ^2D_{5/2}$ resonance at 64.6 eV in the Br window in Fig. 7(c). The measured Br rise time is 114 ± 17 fs. In the kinetics scans, the signal-to-noise of the $^2P_{1/2} \rightarrow ^2D_{3/2}$ resonance of the Br* atomic species is too small to accurately fit the rise time of this spin-orbit excited atom. The atomic-site specificity of the XUV transient absorption technique allows for a simultaneous observation of multiple dissociation channels in real-time, elucidating distinct dissociation kinetics leading to each product. The distinctly different timescales of C–I and C–Br dissociation channels in this experiment suggest that the bond breaking pathways correlate with separate electronic excited states accessible by the 266 nm photon.

IV. DISCUSSION

A. XUV core-to-valence absorption by the CH₂Br radical intermediate

As noted, the differential absorption spectrum in the Br window after 266 nm photodissociation of CH₂IBr has taken place is shown in Fig. 5. There are two broad product absorption peaks at 68.5 eV and 69.5 eV, which are 2 eV below the $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$ depletions of the parent molecule, and another broad product absorption feature overlapping the parent molecule depletion at ~ 71.5 eV. The peaks at 68.5 eV and 69.5 eV are split by 1 eV, indicating that they represent the spin-orbit doublet of a $3d(\text{Br})$ core-excited electronic configuration. As for the absorption at 71.5 eV, the second peak in the $3d(\text{Br})$ spin-orbit doublet is expected to be at ~ 72.5 eV, but this is not observed due to the Al filter cut off in the XUV spectral profile above ~ 72 eV.

To justify the assignment of these broad product absorption features, we first consider the possible photodissociation products containing a Br atom. As will be discussed in detail in Sec. IV C, the major photodissociation channel in this study leads to cleavage of the C–I bond to produce I/I* and a CH₂Br radical following one-photon absorption at 266 nm. To a relatively minor degree, there is overlapping absorption by the B band of CH₂IBr at 266 nm, leading to dissociation of the C–Br bond to form Br and Br* atoms. An alternative pathway including molecular dissociation to IBr is known to be negligible at wavelengths longer than 210 nm.¹⁰ Dissociation to form HI + CHBr and HBr + CHI have been ruled out by other studies at all UV wavelengths investigated.¹⁰ Therefore, the possible photodissociation products containing Br in this study are Br, Br*, and CH₂Br. Atomic Br and Br* do not have resonances at 68.5 eV, 69.5 eV, or 71.5 eV.³⁰ These features in the product absorption spectrum are thus at first assigned to the CH₂Br radical, and the rationalization of their assignments to specific $3d(\text{Br})$ core-to-valence transitions is further made by considering the energetics of the peaks in the context of the radical's frontier electronic structure.

Electronic structure calculations in conjunction with experimental data on the geometry of halomethyl radicals indicate there is π -donation by the halogen onto the radical carbon atom, forming a partial C–X π -bond.^{6,7,35,36} The fron-

FIG. 8. Molecular orbital picture for the ground state of the CH₂Br radical. The LUMO is the antibonding $\sigma^*(\text{C–Br})$ orbital. The SOMO takes on the character of a π^* orbital formed by the $2p_y$ of C and $4p_y$ of Br. The highest fully occupied molecular orbital (HFOMO) is a lone-pair orbital formed by the $4p_x$ of Br. The HFOMO – 1 is a π -bonding orbital formed by $2p_y$ of C and $4p_y$ of Br. The HFOMO – 2 is the σ -bonding orbital between C and Br.

tier electronic structure, specifically of the CH₂Br halomethyl radical, is depicted in a molecular orbital picture in Fig. 8. The lowest unoccupied molecular orbital (LUMO) is the antibonding $\sigma^*(\text{C–Br})$ orbital. The SOMO takes on the character of a π^* orbital formed by the $2p_y$ of C and $4p_y$ of Br, with a majority of the contribution by the C atom.³⁷ The highest fully occupied molecular orbital (HFOMO) is a lone-pair orbital formed by the $4p_x$ of Br. The HFOMO – 1 is a π -bonding orbital formed by $2p_y$ of C and $4p_y$ of Br, with most of the contribution from the Br atom. The HFOMO – 2 is the σ bonding orbital between C and Br. Due to the strong localization of the Br($3d$) core orbitals on the Br atom and the frontier orbitals on the Br and C atoms, the Br $M_{4,5}$ pre-edge absorption spectrum of the CH₂Br radical is expected to be dominated by transitions into the SOMO, $\pi^*(\text{C–Br})$ and LUMO, $\sigma^*(\text{C–Br})$. In the one-electron picture, the $3d(\text{Br}) \rightarrow \text{SOMO}, \pi^*(\text{C–Br})$ transitions of the radical should appear at energies below the $3d(\text{Br}) \rightarrow \text{LUMO}, \sigma^*(\text{C–Br})$ transitions of both the radical and the parent molecule.

In agreement with this picture, there are two peaks at 68.5 eV and 69.5 eV in the Br window of the differential absorption spectrum that are 2 eV below the $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$ depletions of the parent molecule and are split by the characteristic 1 eV spin-orbit splitting of $3d(\text{Br})$ core-excited electronic configurations. Due to the energetic position of this spin-orbit doublet relative to the $3d(\text{Br}) \rightarrow \sigma^*(\text{C–Br})$ depletions of the parent molecule, these peaks are assigned to the transitions $3d(\text{Br}) \rightarrow \pi^*(\text{C–Br}), 3d_{5/2}^{-1}$ and $3d(\text{Br}) \rightarrow \pi^*(\text{C–Br}), 3d_{3/2}^{-1}$, respectively.

In order to assign the overlapping absorption feature at 71.5 eV and rationalize its position in energy, the geometry of the radical is taken into consideration. Due to the partial C–Br π bond formed as indicated by the electronic structure depicted in Fig. 8, the C–Br bond in the CH₂Br radical is shorter compared to closed-shell analogs, such as CH₃Br and CH₂IBr.^{7,8,38} The shortened C–Br bond relative to the CH₂IBr parent molecule leads to a destabilization of the antibonding $\sigma^*(\text{C–Br})$ orbital of the radical (energetically

higher orbital) compared to the $\sigma^*(\text{C-Br})$ orbital of the parent molecule. NEXAFS studies on the R-dependence of σ^* resonances in a variety of different molecules have shown that, as a particular bond is contracted, the characteristic core-to- σ^* resonance shifts to higher energies.¹⁹ From this argument, one expects that transitions from the $3d(\text{Br})$ core orbital into the $\sigma^*(\text{C-Br})$ LUMO orbital of the CH_2Br radical would shift to higher energies relative to the analogous transitions in the parent molecule. This leads to the assignment of the product absorption peak at ~ 71.5 eV in Fig. 5 to the $3d(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$, $3d_{5/2}^{-1}$ transition of the radical, which is shifted to higher energy by ~ 1.0 eV compared to the analogous transition in the parent molecule. The second peak in the spin-orbit doublet, the $3d(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$, $3d_{3/2}^{-1}$ transition, is expected to be at 72.5 eV, but is cut off in this experiment due to the absorption by the Al filters at ~ 72 eV. Comparing the $3d(\text{Br}) \rightarrow \pi^*(\text{C-Br})$, $3d_{5/2}^{-1}$ resonance at 68.5 eV and $3d(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$, $3d_{5/2}^{-1}$ resonance at ~ 71.5 eV, there is approximately a 3 eV difference in energy between $3d(\text{Br}) \rightarrow \text{SOMO}$ states and $3d(\text{Br}) \rightarrow \text{LUMO}$ states.

In the present experiments, core-to-valence transitions observed in XUV absorption can directly probe the local electronic structure of the reporter atom due to the proximity of the available valence orbitals and the core electrons. The observation of $3d(\text{Br}) \rightarrow \text{SOMO}$ transitions (i.e., a significant transition dipole moment) in this region of Br core-level absorption at 68.5 eV and 69.5 eV suggests there is appreciable contribution to the radical SOMO by the Br atom. Due to the atomic-site specificity of core-orbitals, core-to-valence transitions involving unoccupied orbitals that do not have density on the reporter atom being probed are not observed.^{24,39} In the CH_2Br radical, the SOMO is a π^* orbital with character on both Br and C atoms due to π -donation by Br onto the carbon. The destabilization of the π^* orbital is related to the strength of the π -donation by the Br atom. Any shifting in the π^* orbital energy would be accompanied by a predictable shift in the $3d(\text{Br}) \rightarrow \pi^*$ resonances. Future studies can replace the hydrogen atoms with electron donating or withdrawing substituents to study the effect of these groups on the energetics of the $3d(\text{Br}) \rightarrow \pi^*$ resonances. This method has potential to illuminate the correlation between the SOMO energy and the reactivity of these halomethyl radicals in combustion-relevant reactions.

B. Element-specific photodissociation dynamics

The extremely broad bandwidth and atomic-site specificity of the XUV probe allows for simultaneous observation of C-I and C-Br dissociation channels in real-time. The time-traces of the I and I* atoms and Br atom signals reveal that, at 266 nm photoexcitation, dissociation along the C-I coordinate proceeds in approximately 45 fs while dissociation along the C-Br coordinate occurs in approximately 114 fs. First, the distinctly different timescales of C-I and C-Br dissociation channels in this experiment indicate that the bond breaking pathways correlate with separate electronic excited states accessible by the 266 nm photon. C-I dissociation occurs via excitation of $n(\text{I}) \rightarrow \sigma^*(\text{C-I})$ transitions in the A band of

CH_2IBr while C-Br dissociation occurs via overlapping excitation of $n(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$ transitions in the red wing of the B band. In a previous study on the recoil anisotropies involved in the photodissociation of CH_2IBr at 248 nm, both channels leading to either I or I* products are determined to have the same polarization dependence and are the result of excitation to an electronic state with the transition moment roughly parallel to the C-I bond.¹⁰ The C-Br dissociation, on the other hand, has a unique polarization dependence and is a result of excitation to an electronic state with the transition moment roughly parallel to the C-Br bond. The recoil anisotropy results are corroborated by the difference in the C-I and C-Br dissociation times reported here. In order to rationalize the difference in dissociation times along the different reaction coordinates, two effects are discussed.

The first is the acceleration of the recoiling fragments on different excited states with different repulsive slopes in the corresponding Frank-Condon regions. A 266 nm photon, for example, excites very near the peak of the A band ($n(\text{I}) \rightarrow \sigma^*(\text{C-I})$ transitions), but accesses only the red wing of the B band ($n(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$ transitions), closer to the asymptotic region of the repulsive potentials. In a groundwork study by Zewail *et al.* on the photodissociation of ICN,⁴⁰ the authors have shown that excitation onto the repulsive state using higher photon energies to access steeper parts of the potential results in a reduced dissociation time. In the case of CH_2IBr with 266 nm excitation, it is possible that the potential surface leading to C-I dissociation is steeper in the Frank-Condon region than the potential surface leading to C-Br dissociation in the red wing of the B band. However, without accurate potential energy curves for each excited state leading to the different I and Br atomic species, it is uncertain whether or not the potential at the maximum of the A band absorption is actually steeper than the potential in the red wing of the B band absorption. The direct observation here of slower C-Br dissociation compared to C-I dissociation following 266 nm excitation of CH_2IBr suggests that this is the case. With an appropriate decomposition of the near UV absorption spectral widths, at the temperatures used, and with the correct inclusion of conservation of linear momenta, some additional information about the slopes of these states could be inferred using the reflection principle.⁴¹ However, no such analysis is performed in the present study.

Another effect that can potentially lead to an observed difference in C-I and C-Br dissociation times is the vibrational/rotational energy deposited into the molecular fragments in each channel. For example, photofragment translational energy studies reveal that during dissociation of the C-I bond to form either I or I* at 248 nm excitation, approximately 65% and 64% of the available energy is deposited as internal energy into the CH_2Br radical, respectively.¹⁰ On the other hand, dissociation of the C-Br bond at this wavelength results in approximately 74% of the available energy being deposited as internal energy of the CH_2I radical. Under the “semi-rigid radical” interpretation of both CH_2Br and CH_2I ,⁴² the difference in the percentage of available energy that is deposited as internal energy is caused by the different mass combinations in each radical. In this sense, the CH_2I is the “softer” of the two radicals, which allows for a larger percentage of the

available energy to be converted into internal energy of the fragment. The distribution of energy between translational energy and internal energy of the fragments can affect photodissociation times, with the slower being the pathways leading to greater internal excitation of the fragments.⁴³

The difference in the dissociation times measured here for C–I and C–Br bond-breaking at 266 nm photoexcitation can likely be attributed to a combination of the two effects in the previous paragraphs. Accurate potential energy curves of each excited state involved in the photodissociation of C–I and C–Br bonds would help to determine the possible contribution of different instantaneous slopes of the potentials leading to each dissociation channel.

C. Multichannel dissociation branching ratio

The observation of both atomic Br and I resonances in the transient absorption spectra reveal the multichannel photodissociation process in CH₂IBr following 266 nm excitation. One photon at 266 nm (107 kcal/mol) or at 248 nm (115 kcal/mol), used in previous studies, has insufficient energy to break both the C–I and C–Br bonds; this would require approximately 118 kcal/mole.³⁴ Photoexcitation at 266 nm can therefore only lead to dissociation of either the C–I bond or the C–Br bond, but not both. Power dependence studies, shown in Fig. 6, taking the integrated absorbance intensities of I and Br resonances at several powers and fixed sample gas pressure, confirm that one-photon excitation leads to formation of both I and Br atomic species. The dissociation of either C–I or C–Br bonds results from overlapping excitation of either the A-band or the B-band and the branching ratio is wavelength dependent. At 248 nm used in previous studies, the authors found that the lower limit ratio of C–I:C–Br bond fission is 1.2:1.

In order to estimate the ratio of C–I:C–Br bond fission following 266 nm photoexcitation in the present experiments, the relative integrated absorbance intensities of the I atom and Br atom resonances in the ΔOD spectra are compared. The densities of each atomic species are proportional to the integrated absorbance of each corresponding resonance; however, a one-to-one comparison can only be made if the relative XUV absorption cross sections of these atomic species are known. To estimate this, we performed a recent separate experiment on the 266 nm photodissociation of IBr, which is the subject of a future work. In the case of IBr dissociation, the only possible products are I/I* and Br/Br* via the following pathways:

Previous state-selective ion time-of-flight experiments extracted the branching ratios of these four pathways and the

total I/I* and Br/Br* branching ratios have been determined.⁴⁴ In our experiments, 266 nm photodissociation of IBr is probed by XUV transient absorption and the individual I, I*, Br, and Br* XUV absorption peaks are integrated at a fixed time delay at which the dissociation process is complete. Assuming there are no overlapping or interfering peaks at the energies of the I, I*, Br, and Br* resonances, the relative integrated intensities can be compared with the published spin-orbit branching ratios. In this way, we can estimate the relative I:Br (²P_{3/2} → ²D_{5/2}) and I*:Br* (²P_{1/2} → ²D_{3/2}) integrated XUV absorption cross section ratios. The I:Br (²P_{3/2} → ²D_{5/2}) ratio is 0.6 ± 0.2 and the I*:Br* (²P_{1/2} → ²D_{3/2}) ratio is found to be 0.8 ± 0.3.

With this information, the integrated intensities of the individual atomic resonances following photodissociation of CH₂IBr are used to determine the ratio of C–I:C–Br bond fission at 266 nm photoexcitation, which is 4.8 ± 1.2. The ratio of 4.8 ± 1.2 for C–I:C–Br bond fission indicates that at this wavelength, 78%–86% of photoexcited CH₂IBr molecules undergo C–I dissociation.

V. CONCLUSIONS AND OUTLOOK

The multidimensional photodissociation of a bichromophoric molecule, CH₂IBr, following 266 nm excitation has been investigated with atomic-site specificity using femtosecond time-resolved XUV transient absorption spectroscopy. Dissociation of either the C–I or C–Br bonds has been characterized through the XUV spectral observation of atomic I and Br resonances. The major C–I dissociation channel is accompanied by formation of the CH₂Br radical. This has led to the first observation of core-to-valence absorption by a short-lived halomethyl radical. Product absorption features observed at 68.5 eV, 69.5 eV, and ~71.5 eV are assigned to 3d(Br) → π*, 3d_{5/2}⁻¹, 3d(Br) → π*, 3d_{3/2}⁻¹, and 3d(Br) → σ*, 3d_{5/2}⁻¹ transitions of CH₂Br, respectively. There is approximately a 3 eV difference in energy between 3d(Br) → SOMO states and 3d(Br) → LUMO states. The observation of the 3d(Br) → SOMO resonances of the CH₂Br radical indicates there is appreciable contribution to the radical SOMO by the Br atom. This provides direct support for the existence of a partial C–Br π-bond formed through π-donation by the halogen in this particular halomethyl radical. Future studies can replace the hydrogen atoms with electron donating or withdrawing substituents to study the effect of these groups on the energetics of the SOMO. This method has potential to illuminate the correlation between the SOMO energy and the reactivity of these halomethyl radicals in combustion-relevant reactions.

The broad bandwidth and atomic-site specificity of the XUV probe allows for simultaneous observation of C–I and C–Br dissociation channels in real-time. From the integrated intensities and relative cross sections of these atomic features, assuming there are no interfering peaks, we have estimated that 78%–86% of photoexcited parent molecules dissociate along the C–I coordinate. The minor C–Br dissociation channel is attributed to excitation of overlapping n(Br) → σ*(C–Br) transitions in the red wing of the B band. Kinetic

studies have been carried out in order to track, simultaneously, the rise of I and Br atomic species. The measured rise times of I, I*, and Br atomic species are 48 ± 12 fs, 44 ± 4 fs, and 114 ± 17 fs. The slower C–Br dissociation has been rationalized in terms of the difference between the repulsive slopes of the excited states accessed by the 266 nm photon and the relative internal energy deposited into the CH₂I radical during C–Br dissociation compared to the CH₂Br radical from C–I dissociation. The results are in agreement with previous studies that have shown the “steepness” of the repulsive excited state accessed in the Frank-Condon region and the distribution of energy between translational energy and internal energy of the fragments can largely affect the dissociation times.^{40,43} It is likely that both effects lead to the total difference in the measured dissociation times in this work.

The investigation performed here is the first demonstration of femtosecond time-resolved core-to-valence spectroscopy utilizing two or more reporter atoms simultaneously. The combination of element-specificity with ultrafast time-resolution and sensitivity to local electronic structure and chemical environment provides an exciting platform for future applications in molecular dynamics studies and spectroscopic investigations of elusive intermediates such as radicals.

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