Quantum yields and energy partitioning in the ultraviolet photodissociation of 1,2 dibromo-tetrafluoroethane (Halon-2402)

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The photodissociation of 1,2 dibromo-tetrafluoroethane (Halon-2402) has been investigated at 193 nm using photofragment translational spectroscopy with vacuum ultraviolet ionization and at 193, 233, and 266 nm using state-selected translational spectroscopy with resonance-enhanced multiphoton ionization. The product branching ratios, angular distributions, and translational energy distributions were measured at these wavelengths, providing insight into the ultraviolet photodissociation dynamics of CF₂BrCF₂Br. The total bromine atom quantum yields were found to be 1.9±0.1 at both 193 and 233 nm and 1.4±0.1 at 266 nm. The first C–Br bond dissociation energy was determined to be 69.3 kcal/mol from ab initio calculations. The second C–Br bond dissociation energy was determined to be 16±2 kcal/mol by modeling of the bromine quantum yield. In addition, variational Rice–Ramsperger–Kassel–Marcus theory was used to calculate the secondary dissociation rates for a range of dissociation energies above threshold. These results suggest that CF₂BrCF₂Br photofragments with sufficient internal energies will undergo secondary dissociation prior to collisional stabilization under atmospheric conditions. Based on the measured translational energy distributions and product branching ratios, a model is proposed to describe the wavelength-dependent bromine quantum yield and the implications of these results to atmospheric chemistry are discussed. © 2000 American Institute of Physics.

I. INTRODUCTION

The role of anthropogenic chlorine and bromine containing molecules in stratospheric ozone depletion has been well established.¹ The importance of bromine and its chemistry in the atmosphere is receiving renewed interest based on predictions that bromine is almost 100 times more destructive to stratospheric ozone than chlorine on an atom-for-atom basis.²,³ One of the major sources of anthropogenic bromine in the stratosphere are the halons. Recent measurements of the halogenated species in the tropical tropopause found that 1,2 dibromo-tetrafluoroethane, henceforth referred to as CF₂BrCF₂Br, constitutes 0.134 of the total organic bromine (21±1 pptv) detected in the tropical tropopause (between 30 °S and 30 °N latitudes).⁴ Since transport from the troposphere into the stratosphere occurs mainly in this region, the concentration of CF₂BrCF₂Br in tropical tropopause provides a good measure of the relative mixing ratio in the stratosphere. The title compound has found widespread use as a fire suppressant and, although the production of CF₂BrCF₂Br in development countries has been halted by the Copenhagen Amendment to the Montreal Protocol, its release continues from current inventories. Since the lifetime of this compound in the atmosphere is 25–40 years, it will make a significant contribution to stratosphere ozone depletion for an extended period of time.⁵

Although there are two C–Br bonds in this system, it has been assumed that the total bromine atom quantum yield, Φ[Br,Br*], for this molecule follows the trend of other bromomethanes and is unity.⁶ However, unlike the polybrominated methane derivatives, the second C–Br bond in CF₂BrCF₂Br is significantly weaker than a typical C–Br bond, due to the energy associated with forming the carbon–carbon double bond⁷ that largely offsets the energy necessary to break the second C–Br bond. As a result there is sufficient energy following UV absorption to ensure that both C–Br bonds break, resulting in a Φ[Br,Br*], of 2.0. The primary C–Br bond cleavage results in either ground state bromine (²P₃/2), denoted as Br, or excited state bromine (²P₁/₂), denoted as Br*, and an energized C₂F₄Br radical which may contain sufficient energy to undergo secondary dissociation

$$\text{BrCF}_2\text{CF}_2\text{Br} \rightarrow \text{C}_2\text{F}_4\text{Br} + \text{Br,Br*}, \quad (1)$$

$$\text{C}_2\text{F}_4\text{Br} \rightarrow \text{C}_2\text{F}_4 + \text{Br.} \quad (2)$$

An important issue from a dynamical perspective is whether the distribution of available energy following the initial
C–Br bond cleavage (see Table I) ensures that sufficient energy remains in the C₂F₄Br fragment for it to undergo secondary reaction and whether the breakage of bonds can be characterized as stepwise or concerted. A more atmospherically relevant question is whether the loss of one or both Br atoms changes the atmospheric impact of this molecule.

In the present article, we have investigated the photodissociation of C₂F₄BrCF₂Br in a molecular beam at wavelengths ranging from 266 to 193 nm using two complementary experimental techniques. We have performed state-selected ion time-of-flight mass spectrometry (TOF-MS) measurements to measure the Br and Br⁺ relative branching ratios, angular distributions, and translational energy distributions. We have also performed photofragment translational spectroscopy (PTS) experiments at 193 nm using tunable photoionization detection to identify all of the dissociation products. This technique provides a broad overview of the dissociation and complements the state-specific measurements. We have unambiguously determined that ϕ_{Br,Br⁺} is near 2.0 at both 193 and 233 nm, and 1.4 at 266 nm. A model, based on the experimental distributions, provides a reasonable description of the wavelength-dependent Br quantum yields for this molecule. In addition, we present ab initio results on the C–Br bond dissociation energies in both C₂F₄Br and CF₂BrCF₂Br and compare them to the experimental bond energies. The atmospheric significance of the results will also be discussed.

TABLE I. Anisotropy parameters and average total translational energies for primary C–Br bond cleavage.

<table>
<thead>
<tr>
<th>Anisotropy parameter, β</th>
<th>Total translational energy (kcal/mol)</th>
</tr>
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<tbody>
<tr>
<td>193 nm</td>
<td>Br 0.67±0.10 26±1</td>
</tr>
<tr>
<td></td>
<td>Br⁺ 1.20±0.10 22±1</td>
</tr>
<tr>
<td>233 nm</td>
<td>Br 1.26±0.10 21±1</td>
</tr>
<tr>
<td></td>
<td>Br⁺ 1.39±0.10 18±1</td>
</tr>
<tr>
<td>266 nm</td>
<td>Br 1.10±0.10 19±1</td>
</tr>
<tr>
<td></td>
<td>Br⁺ 1.28±0.10 16±1</td>
</tr>
</tbody>
</table>

II. EXPERIMENT

A. Photofragment translational spectroscopy experiments

These experiments were carried out at the Chemical Dynamics Beamline at the Advanced Light Source at Lawrence Berkeley National Laboratory. A complete description of the apparatus can be found elsewhere. Briefly, a continuous molecular beam of <1% C₂F₄BrCF₂Br seeded in helium was collimated with conical skimmers and intersected at 90° with the output of an excimer laser operating on the ArF transition (193 nm). There was no change in the shape of any of the TOF spectra over a laser fluence range of 60–500 mJ/cm², providing strong evidence that all of the observed signals are the result of single photon absorption. Neutral photodissociation products traveled 15.2 cm where they were ionized by tunable vacuum ultraviolet (VUV) undulator radiation, mass selected, and counted as a function of time. The characteristics of the VUV undulator radiation used for product photoionization have also been previously described. The nozzle was heated to 100 °C to minimize clustering in the beam and no evidence for clusters was observed.

B. State-selected ion time-of-flight experiments

The state-selected ion time-of-flight experiments were conducted at Texas A & M University using a differentially pumped molecular beam apparatus that has been previously described. A pulsed molecular beam of ~3% CF₂BrCF₂Br in helium was collimated by a conical skimmer and intersected by either one or two laser pulses.

The bromine atoms were probed using 2+1 resonance-enhanced multiphoton ionization (REMPI) transitions in the wavelength region between 233 and 267 nm. The tunable laser pulses were generated by a dye laser that was pumped by 355 nm light from the third harmonic of a Nd:YAD laser operating at 10 Hz. Two laser experiments were performed by overlapping the output of an excimer laser operating on the ArF (193 nm) transition with the probe beam from the dye laser. The excimer light was polarized with a pile-of-plates polarizer and the reported anisotropy parameters were corrected for the incomplete (85%) polarization. The time delay between the pump and probe pulses was typically 0–50 ns.

Ions were detected using a two-stage Wiley–McLaren time-of-flight mass spectrometer in either “noncore sampled” or “core-sampled mode,” using a set of dual Chevron microchannel plates. In noncore sampled mode, the signal was sent to a 400 MHz digital oscilloscope, which was interfaced to a Pentium PC. Subtracting off-resonance traces from on-resonance signals effectively removed the minor pump-oil related background contribution to the TOF spectra. A fast photodiode was used to trigger the data acquisition. In core-sampled mode, a copper plate with a 3.0-mm-diam pinhole was placed approximately 29 cm from the interaction region, allowing only a “core” of the ion packet to strike the detector. The core-sampled signal was averaged using a multichannel scaler with a 5 ns bin size. In order to minimize cluster contributions, the pulsed valve nozzle was typically held at 70 °C, and an early part of the molecular beam pulse was probed. No significant change in the TOF profiles was observed as a function of the delay time between the laser and the molecular beam pulse, indicating that cluster formation was negligible.

CF₂BrCF₂Br 99% was obtained from Aldrich Chemical Co. and used without further purification.

III. RESULTS AND ANALYSIS

A. Photofragment translational spectroscopy experiments at 193 nm

Center-of-mass translational energy distributions, P(E_T), were obtained from the TOF spectra using the forward convolution (FC) technique. For all of the PTS TOF spectra presented, the circles represent the data and the lines represent the forward convolution fit. TOF spectra were obtained for masses C₂F₄⁺ (m/z 100) and Br⁺ (m/z 79, 81). No signal was observed at any other masses including C₂F₄Br⁺ (m/z 179, 181) using a VUV ionization energy of 15 eV.
TOF spectra for m/z 79 (Br\(^{+}\)) at laboratory angles of 10° and 15° are shown in Fig. 1. Two contributions to the TOF spectra were observed and are shown using dashed lines in the figure. The narrow feature at early arrival times results from primary C–Br bond cleavage. The second contribution at longer times is due to secondary Br fragments that arise from the spontaneous dissociation of C\(_2\)F\(_4\)Br. The relative intensity of the fast to slow components in the TOF indicates that the primary to secondary Br yield is 1.0:0.97 suggesting an overall Br quantum yield of 1.98 ± 0.09. The primary Br TOF spectrum has been fit using the \(P(E_T)\) distribution shown in the top panel of Fig. 2. The distribution is nearly Gaussian in shape with a maximum at 26 ± 1 kcal/mol and a full width at half maximum (FWHM) of 10 kcal/mol.

Figure 3 shows C\(_2\)F\(_4\) (m/z 100) TOF spectra at a laboratory angle of 20° and a photoionization energy of 15 eV. Only one contribution to the m/z 100 spectra is present and is due to the formation of C\(_2\)F\(_4\) from the secondary fragmentation of C\(_2\)F\(_3\)Br. The secondary fragments in both the m/z 79 and m/z 100 TOF spectra were fit using the \(P(E_T)\) distribution shown in the lower panel of Fig. 2. The distribution is peaked near zero with an average energy of 5 kcal/mol. A secondary angular distribution with forward–backward symmetry, consistent with an intermediate lifetime longer than a rotational period, was used in the forward convolution fitting.

**B. State-selected ion time-of-flight experiments**

The FC technique was used to fit the experimental TOF profiles, and details can be found elsewhere.\(^{10,21}\) We find this approach preferable to a direct inversion of the TOF profiles, which ignores instrumental broadening factors and is valid only for high velocities. Briefly, the photofragment velocity distribution in terms of the projection of the fragment velocity on the detector axis, \(v_z\), the angle between the laser electric field, \(\mathbf{E}\), and the detector axis, \(\mathbf{z}\), is given by:

\[
\int_{v_z} f(v_z, \chi) \frac{g(v)}{2v} \left[ 1 + \beta P_2(\cos \chi) P_2\left(\frac{v_z}{v}\right) \right] dv,
\]

where \(\beta\) is the spatial anisotropy parameter, \(P_2(\chi)\) is the second Legendre polynomial, and \(g(v)\) is the center-of-mass speed distribution. In the noncore sampled fitting, the dependence of \(f(v_z, \chi)\) on \(\beta\) was eliminated by co-adding normalized profiles with \(\chi = 90°\) and \(\chi = 0°\) with a 2:1 weighting. A trial speed distribution, \(g(v)\), was adjusted to obtain a best fit to the co-added angular profile. A one-parameter fit to the individual horizontal and vertical profiles was then used to obtain \(\beta\). For core-sampled experiments, the presence of the coring aperture discriminates against fragments with large
velocity components perpendicular to the flight axis, thereby increasing the velocity resolution. The difference between core-sampled and noncore sampled fitting has been described previously. A speed-dependent $v_{\text{max}}$ array was calculated at each set of ion-optic voltage settings and used in the subsequent forward convolution fitting. By interactively adjusting a trial speed distribution $g(v)$ and anisotropy parameter, $\beta$, we can obtain best fits to both vertical ($\chi=0^\circ$) and horizontal ($\chi=90^\circ$) data simultaneously.

1. Photodissociation at 233 nm

Representative one-color core-sampled vertical ($\hat{e}\perp\hat{z}$) and horizontal ($\hat{e}\parallel\hat{z}$) TOF profiles of Br (upper panel) and Br$^+$ (lower panel) for dissociation wavelengths near 233 nm are shown in Fig. 4. The Br$^+$ TOF profile (lower panel) consists of a single component at large velocities and exhibits significant velocity anisotropy. The FC fit of the Br$^+$ TOF profiles gives a near Gaussian $P(E_T)$ distribution peaked at $18 \pm 1$ kcal/mol with a FWHM $\sim 10$ kcal/mol, which is consistent with a direct dissociation on a repulsive potential energy surface. Therefore, we attribute the Br$^+$ products to the primary C–Br bond fission. Based on the measured intensity change between vertical and horizontal geometries, an anisotropy parameter of $1.40 \pm 0.10$ was obtained, suggesting that the transition dipole moment is approximately parallel to the C–Br bond.

The Br TOF profiles, shown in the upper panel of Fig. 4, are substantially different and cannot be adequately fit with a single contribution. The fast feature has an anisotropy parameter of $1.20 \pm 0.10$ and an average translational energy of $21 \pm 1$ kcal/mol with a FWHM of $\sim 10$ kcal/mol. We attribute this feature to primary dissociation to give ground state Br. The observed spatial anisotropy suggests that the initial C–Br bond breaks rapidly ($\ll 1$ ps) and with unit efficiency following absorption of the photon. The slower feature exhibits little or no velocity anisotropy and is not observed in the Br$^+$ TOF profiles. Linear momentum conservation with the primary Br fragments provides an average velocity for the C$_2$F$_4$Br counter fragment of approximately 500 m/s. The secondary Br fragments will acquire an additional recoil from the spontaneous dissociation of the C$_2$F$_4$Br fragment. However, the average velocity for the secondary Br in the laboratory frame is symmetric about the C$_2$F$_4$Br velocity, implying that the C$_2$F$_4$Br fragments are relatively long lived. In addition, a forward–backward symmetric angular distribution of fragments was required to fit the secondary contribution to the 193 nm PTS data, and a faster C$_2$F$_4$Br dissociation at longer wavelengths with lower internal energy would not be expected. Rice–Ramsperger–Kassel–Marcus (RRKM) calculations on the C$_2$F$_4$Br dissociation (vide infra) also indicate that the C$_2$F$_4$Br fragment lives longer than the rotational period. Rotational averaging is expected to diminish the lab-frame anisotropy parameter, as observed in the TOF spectra. We therefore attribute the slow component of the TOF spectra to secondary Br atoms arising from the spontaneous dissociation of C$_2$F$_4$Br radicals.

The velocity distributions derived from fitting the TOF spectra are shown in Fig. 5. The relative intensities of primary and secondary contributions to the Br TOF spectra are

![FIG. 4. Core-sampled time-of-flight spectra for Br and Br$^+$ arising from CF$_2$BrCF$_2$Br photodissociation near 234 nm. The filled circles are the experimental data and the solid line is a forward convolution fit that includes both isotopes of bromine (for clarity the $^7$Br peaks are indicated with arrows). The dashed lines show the primary and secondary contributions to the TOF spectrum.](image1)

![FIG. 5. Translational energy distributions used to fit the Br fragment TOF profile at 233 nm. The primary and secondary components are indicated on the figure.](image2)
1.0 and 1.6, respectively. This ratio and the measured total Br/Br* branching ratio are necessary to provide a direct measure of the bromine atom quantum yield, \( \Phi_{[Br,Br^*]} \).

The branching ratio of Br and Br* was determined by scanning the probe laser over the Br/Br* Doppler profiles and correcting the ratio of integrated areas of the Br and Br* REMPI signals by the detection efficiency of Br and Br*. REMPI transitions. The photodissociation of CH₂Br was used to calibrate the Br/Br* detection efficiency, and the relative Br/Br* detection efficiencies were previously determined to be 0.46:1 for these states.\(^{17}\) The Br/Br* branching ratio measured in this manner includes Br from both the primary and secondary steps and, therefore, overestimates the primary Br/Br* branching ratio. Assuming that the first step in the dissociation is exclusively the loss of Br or Br*, the primary Br/Br* ratio may be derived by correcting for the relative contributions of primary to secondary Br. The total bromine atom quantum yield, \( \Phi_{[Br,Br^*]} \), at 233 nm is 1.93±0.09, implying that nearly all the \( \text{C}_2\text{F}_4\text{Br} \) radicals undergo secondary dissociation regardless of whether they arise from the \( \text{C}_2\text{F}_4\text{Br}^+ \) or \( \text{C}_2\text{F}_4\text{Br}^+ + \text{Br}^* \) channel. The Br/Br* total branching ratios and primary branching ratios for a number of photolysis wavelengths are shown in Table II.

### TABLE II. Br/Br* total and primary branching ratio.

<table>
<thead>
<tr>
<th>Total Br/Br*</th>
<th>Primary Br/Br*</th>
</tr>
</thead>
<tbody>
<tr>
<td>193 nm</td>
<td>8.3±0.2</td>
</tr>
<tr>
<td>233 nm</td>
<td>3.3±0.2</td>
</tr>
<tr>
<td>266 nm</td>
<td>2.1±0.2</td>
</tr>
</tbody>
</table>

### 2. Photodissociation at 266 nm

One-color noncore sampled TOF spectra are shown in Fig. 6 for the photodissociation of \( \text{C}_2\text{BrCF}_2\text{Br} \) at 266 nm. The Br TOF profiles (left panels) show a bimodal velocity distribution similar to that observed at 233 nm. The primary Br and Br* channels give anisotropy parameters of \( \beta = 1.10 \pm 0.10 \) and \( \beta = 1.28 \pm 0.10 \), indicating that both arise from a transition dipole moment of predominantly parallel character. The average translational energies are 19±1 and 16.1±1 for the primary Br and Br* channels, respectively. Performing a similar analysis to that described above for 233 nm, we attribute the fast and slow Br contributions to primary and secondary dissociation, respectively. Based on the FC fits, we find that the primary to secondary Br ratio is 1.0:0.9 and the primary Br/Br* branching ratio is 1.1±0.1, resulting in \( \Phi_{[Br,Br^*]} = 1.4 \). This value is lower than at 233 nm, implying that, because there is less available energy at 266 nm, not all \( \text{C}_2\text{F}_4\text{Br} \) fragments secondarily dissociate. The fraction of \( \text{C}_2\text{F}_4\text{Br} \) fragments that undergo secondary C–Br bond dissociation will depend on both the distribution of the internal energy following the primary dissociation step and the secondary C–Br bond strength. Using the primary \( P(E_T) \) distributions we can estimate the secondary C–Br bond dissociation energy by comparing the predicted Br quantum yield to the experimental measurement. The secondary C–Br bond energy provides a dividing line between stable and unstable \( \text{C}_2\text{F}_4\text{Br} \) radicals arising from the first step in the dissociation.

### 3. Photodissociation at 193 nm

The FC fitting of the two-color REMPI data using 193 nm photolysis gives average translational energies of 26±1 and 22±1 kcal/mol for the primary Br and Br* dissociation channels, respectively. These values result in a state-averaged translational energy of 25±1 kcal/mol, which is in excellent agreement with the PTS results. The anisotropy parameters of the primary Br and Br* are 0.5±0.1 and 0.9±0.1, respectively, indicating a stronger perpendicular contribution than observed at longer wavelengths. The Br/Br* branching ratio was found to be 3.8±0.2, and the ratio of primary to secondary Br is 1.2±0.1. From these ratios, the total bromine atom quantum yield, \( \Phi_{[Br,Br^*]} \), was found to be 1.9±0.1. The translational energy distribution associated with the secondary dissociation has an average value of 5±1 kcal/mol with FWHM of ~10 kcal/mol, which is consistent with the results derived from the PTS data. The secondary angular distribution was found to be nearly isotropic, consistent with a \( \text{C}_2\text{F}_4\text{Br} \) lifetime in excess of its rotational period.

### C. Ab initio and rate calculations

In order to provide additional insight into the mechanism for the photodissociation of \( \text{CF}_2\text{BrCF}_2\text{Br} \), we have performed \textit{ab initio} calculations to determine the primary and secondary C–Br bond strengths of \( \text{CF}_2\text{BrCF}_2\text{Br} \). All \textit{ab initio} calculations were performed using Gaussian 98\(^{24}\) on an
Origin 2000 Supercomputer and an SGI Power Challenge workstation. Geometries and frequencies for the ground state species were calculated at the MP2/6-311+G* level, and vibrational frequencies were left unscalled for the zero-point corrections and RRKM calculations. The ab initio methodology used to calculate the bond energies has been successful in calculating C–Br bond energies in haloalkanes with modest computational expense.25 This methodology corrects MP2/cc-pVTZ energies for correlation to the coupled cluster level including single and double excitations and perturbative treatment of triple excitations (CCSD(T)) and basis-set effects to the cc-pV5z level using correction factors derived from monohalogenated compounds. The primary C–Br bond energy is 69.3 kcal/mol, and the second C–Br bond dissociation energy is 19.3 kcal/mol from these calculations. Since the ab initio methodology yields good agreement with experiment for closed-shell compounds, we believe the value for the primary bond energy of CF2BrCF2Br to be accurate, though the value for the second bond energy appears to be overestimated. A schematic diagram of the sequential loss of bromine atoms is shown in Fig. 7.

Based on the available heat of formation data,26–29 the energy required for the loss of two Br atoms from CF2BrCF2Br is 82.9 kcal/mol. Combining the ab initio result for primary C–Br bond (69.3 kcal/mol) with relevant heat of formation information, the secondary C–Br bond energy is 13.6 kcal/mol. Krajnovich, Butler, and Lee reported an upper limit for the C2F4Br second C–Br bond energy of 19±3 kcal/mol from their PTS data analysis from the photodissociation of C2F4 and an initial C–Br bond energy of 69.3 kcal/mol.

The unimolecular rates for the secondary Br elimination channel were calculated using variational RRKM theory35 by minimizing the sum of states along the reaction coordinate:

\[
\frac{dN_i(E,J,R)}{dR} = 0. 
\]

For consistency all frequencies and energies used in the RRKM calculations, including reactant and product species, were obtained from ab initio theory. A direct count algorithm was used to determine the sum of states using the harmonic oscillator approximation for both sets of calculations. The frequencies of the conserved modes were assumed to change smoothly with the C–Br distance, \( R \), according to

\[
v^{(i)}(R) = v_r^{(i)}(R_\circ)\exp(-aR) + v_p^{(i)}(R_\circ)[1 - \exp(-aR)].
\]

where \( v^{(i)}(R_\circ) \) is the \( i \)th frequency of the reactant molecule at the equilibrium C–Br bond length, \( R_\circ \), \( v_r^{(i)}(R_\circ) \) is the corresponding product frequency, and \( a \) is a constant taken to be 1.2.34,35 The transitional modes were assumed to decay exponentially to the C2F4 rotational constant with the same value of \( a \). The sum of a Morse function and a centrifugal barrier was used to model the potential along the C–Br stretching coordinate. The centrifugal barrier was derived using the average rotational energy of the C2F4Br corresponding to \( J=75 \) derived from the soft fragment impulsive model36 following primary loss of bromine. Moments of inertia at each fixed geometry were obtained by changing only the C–Br bond length. One rocking mode and one wagging mode were treated as transitional modes. Variational RRKM calculations were performed at a series of energies above the threshold energy for Br loss from C2F4Br, and the rates are shown in Table III as a function of the energy above threshold. For the RRKM calculations, we have adopted an asymptotic energy of 16 kcal/mol for the secondary C–Br bond.
bond energy. Rate constants for Br loss increase from 2.5 \times 10^8 to 3.5 \times 10^{10} \text{s}^{-1} for energies above threshold between 1 and 10 kcal/mol. In all cases, the lifetime of the C_2F_4Br fragment under collisionless conditions was less than the temporal width of the laser pulses, ensuring that all secondary products were observed in the TOF-MS experiments.

IV. DISCUSSION

A. Product angular distributions and translational energy distributions

The positive anisotropy for the primary bromine fragment observed at all wavelengths under investigation indicates that the dissociation occurs on a repulsive potential prior to parent rotation and arises from a transition dipole moment predominately parallel to the C–Br bond. There are three electronic excited states that contribute to the first UV absorption band of haloalkane systems and are labeled \( ^3Q_1 \), \( ^3Q_0 \), and \( ^1Q_1 \). Among these states, the \( ^3Q_0 \) state diabatically correlates to excited state halogen atoms, while the \( ^3Q_1 \) and \( ^1Q_1 \) states correlate to ground state products. The transition is predominantly parallel at 266 nm, becomes increasingly parallel at 233 nm, and becomes more perpendicular at 193 nm. This behavior is very similar to other bromoalkanes and is the result of overlapping contributions from different parallel and perpendicular electronic states.\(^{10,17,38}\) Based on magnetic circular dichroism experiments, Gedanken and Rowe\(^{39}\) found that due to the smaller spin-orbit coupling of bromine relative to iodine, there was a decrease in the relative contribution of the parallel \( ^3Q_0 \) state relative to the perpendicular \( ^1Q_1 \) state in methyl bromide at short wavelengths when compared to methyl iodide. The present results are consistent with the significant contribution of the \( ^1Q_1 \) state near 193 nm but the overall dominance of the \( ^3Q_0 \) state.

From the translational energy distributions of the state-selected fragments, the internal energy distribution of the C_2F_4Br radicals for the Br and Br* channels may be calculated precisely using the conservation equation

\[
E_{\text{int}}^{\text{C}_2\text{F}_4\text{Br}} = h\nu - D_0^0(\text{C–Br}) - E_{\text{trans}}^{\text{Br}} - E_{\text{elec}}^{\text{Br}},
\]

where \( D_0^0(\text{C–Br}) \) is the primary C–Br bond strength, \( E_{\text{trans}}^{\text{Br}} \) is the total translational energy for the primary dissociation step, and \( E_{\text{elec}}^{\text{Br}} \) is the electronic energy of the Br fragment relative to the ground spin-orbit state. Since only C_2F_4Br radicals with internal energies larger than the secondary C–Br bond energy will spontaneously dissociate to C_2F_4 and Br, the observed total quantum yield, \( \Phi_{\text{[Br,Br*]}} \), provides a measure of the secondary C–Br bond strength. A stronger secondary C–Br bond will result in fewer secondary Br products since fewer C_2F_4Br radicals contain sufficient internal energy to break the second C–Br bond. This is confirmed by our observation of a wavelength-dependent quantum yield. At 193 and 233 nm, the total bromine atom quantum yields are close to 2.0, indicating that almost all C_2F_4Br fragments from both the C_2F_4Br + Br and C_2F_4Br + Br* channels will experience secondary dissociation. At 266 nm, however, the bromine atom quantum yield is reduced to 1.4, suggesting that C_2F_4Br fragments derived from the C_2F_4Br + Br* channel do not have sufficient internal energy for secondary dissociation.

The secondary C–Br bond dissociation is correlated exclusively to ground state Br products, which appear as a slow component in the Br TOF profiles and are absent in the Br* TOF spectra. Analysis of the C_2F_4 product PTS data gives an average total translational energy of 5 kcal/mol, strongly indicating that the C_2F_4 molecules and slow Br fragment are derived from the same secondary dissociation channel. The present results may be compared to a prior distribution for the loss of an atom from a polyatomic molecule, in which \( P(f_T) = f_T^{0.5}(1-f_T)^{0.5} \), where \( f_T \) is the fraction of available energy partitioned into translation and \( s \) is the number of oscillators in the polyatomic product.\(^{40}\) For 193 nm dissociation, the available energy is 40 kcal/mol, assuming that the average translational energy of the C_2F_4Br fragment is 26 kcal/mol and the bond energies are 69.3 and 16 kcal/mol for the first and second steps, respectively. The average translational energy from the prior distribution is therefore 4 kcal/mol, in agreement with the PTS results. The agreement between the average values of the prior distribution and the observed \( P(E_T) \) distribution implies that little or no barrier exists for the secondary dissociation step. Secondary translational energy distributions at longer wavelengths are qualitatively consistent with the prior distribution, but the uncertainty of the primary translational energy distribution precludes a more detailed analysis.

The present results can be compared to the time-resolved UV study of C_2F_4I_2 reported by Zewail and co-workers.\(^{31,42}\) The authors observed a single prompt rise (\( \leq 1 \) ps) when probing the I* fragments but a biexponential appearance curve for ground state I atoms. The fast signal was consistent with direct bond dissociation, identical to the origin of the I* fragments. The slower component (30–150 ps) was due to spontaneous secondary bond cleavage. Based on the energetics of the CF_2BrCF_2Br system compared to C_2F_4I_2 we would expect to observe similar stepwise behavior.

B. Model for the wavelength dependent bromine quantum yield

As shown in Table II, the total quantum yield of bromine atoms, \( \Phi_{\text{[Br,Br*]}} \), depends strongly on the dissociation wavelength. Due to the small secondary C–Br bond energy, photodissociation at 193 and 233 nm results in internal energies of C_2F_4Br from both the Br and Br* channels that are sufficient to ensure complete secondary dissociation. At 266 nm, however, only C_2F_4Br radicals formed in coincidence with ground state Br with low translational energies will undergo secondary dissociation. In order to quantitatively evaluate the bromine atom quantum yield over the 193–266 nm wavelength region, functional forms of both the wavelength dependence of the Br/Br* branching ratios and the dependence of the translational energies on the photolysis energy must be determined.

The forward convolution results show that the primary translational energy distributions are well described by a near symmetric functional form\(^{43}\) with a FWHM of ~13.
C2 F 4 Br radicals have sufficient internal energy to break the dissociation at wavelengths shorter than 230 nm, almost all the Br quantum yield, \( \Phi_{\text{Br}} \), secondary C–Br bond dissociation energy of 16 kcal/mol. The closed and open circles represent the ion TOF data and PTS data, respectively.

The ultraviolet photodissociation of CF₂BrCF₂Br will be released as active bromine upon absorption of a single UV photon, irrespective of the photolysis energy.

**V. CONCLUSIONS**

In the present study, we have examined the photodissociation of CF₂BrCF₂Br (Halon 2402) using both photofragment translational spectroscopy at 193 nm and state-selected translational spectroscopy at 193, 233, and 266 nm. At each wavelength, translational energy distributions, angular distributions, and branching ratios were determined. Forward convolution fitting of the observed Br spectra showed two components, corresponding to a fast primary loss of bromine followed by a slower spontaneous dissociation of the C₂F₂Br fragment. Based on the measured Br/Br* branching ratios and the primary to secondary branching ratios, we have determined the total bromine quantum yield at the three wavelengths. The results suggest that state-selected ion TOF is a viable method for studying three-body dissociation. Using these results, a model for the wavelength-dependent quantum yield has been developed that provides an estimate for the second C–Br bond resulting in a bromine atom quantum yield near 2. The atmospheric pressure in the lower stratosphere is 10–50 Torr, and temperature in this region is typically \( \sim 220 \) K. The collision frequency under these conditions ranges from 2 \( \times \) 10⁸ to 1 \( \times \) 10⁹ s⁻¹, suggesting that nascent C₂F₂Br radicals with internal energies near their dissociation threshold may be partially stabilized by collisions. The solar flux in the upper troposphere is concentrated in the wavelength region >290 nm, where the photolysis energy is insufficient to break both C–Br bonds and the bromine atom quantum yield will be unity. In the lower stratosphere where the solar flux has increasingly significant contributions from shorter wavelengths, the internal energies of C₂F₂Br radicals are much higher than the dissociation threshold. The unimolecular dissociation rates for these high-energy fragments are much faster than the collisional frequency, yielding a photolysis quantum yield of 2. The resulting C₂F₂ molecules will be removed primarily by reaction with OH radicals. Acerboni et al. determined the rate constant of this reaction at 298 K to be \( 1.13 \pm 0.33 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) implying that low stratospheric lifetime of C₂F₂ is approximately one day.

Despite the insufficient photolysis energy in the lower troposphere to break both C–Br bonds, surviving C₂F₂Br radicals will rapidly react with O₂, and the resulting peroxy radical C₂F₂BrO₂ will react primarily with NO to produce C₂F₂BrO and NO₂. The alkoxy radical, C₂F₂BrO, will likely undergo C–C bond fission, giving CF₂Br and CF₂O as products. It has been reported that 85% of C₂ClO radicals undergo thermal C–Cl bond fission and 15% undergo C–C bond fission. However, since the C–F bond is significantly stronger than the C–Cl bond, little C–F bond cleavage channel would be expected for C₂F₂BrO radical dissociation. Exclusive C–C bond breakage has been previously reported for C₂F₂O radicals. The CF₂Br will undergo subsequent oxidation to yield CF₂O and Br atom. The final CF₂O product will be effectively taken up by raindrops or aerosols. As a result, it may be expected that both Br atoms present in the CF₂BrCF₂Br will be released as active bromine upon absorption of a single UV photon, irrespective of the photolysis energy.
secondary C–Br bond dissociation energy. Though conditions in the upper troposphere will allow some of the C2F4Br fragments to be collisionally stabilized, subsequent oxidation will yield a second bromine and two CF2O fragments. As a result, the photodissociation of CF2BrCF2Br may be expected to yield two Br atoms and two CF2O fragments, regardless of the conditions in the upper atmosphere.

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43 Based on translational energy distributions of the form $P(E) = E_a f(E_1-a-E_1^2)$, we find that values of 10 for both parameters $a$ and $b$, respectively, reproduce the experimental distributions.