Br₂ elimination in 248-nm photolysis of CF₂Br₂ probed by using cavity ring-down absorption spectroscopy

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By using cavity ring-down absorption spectroscopy technique, we have observed the channel of Br₂ molecular elimination following photodissociation of CF₂Br₂ at 248 nm. A tunable laser beam, which is crossed perpendicular to the photolyzing laser beam in a ring-down cell, is used to probe the Br₂ fragment in the B 3Πg→X 1Σg⁺ transition. The vibrational population is obtained in a nascent state, despite ring-down time as long as 500–1000 ns. The population ratio of Br₂(v=1)/Br₂(v=0) is determined to be 0.4±0.2, slightly larger than the value of 0.22 evaluated by Boltzmann distribution at room temperature. The quantum yield of the Br₂ elimination reaction is also measured to be 0.04±0.01. This work provides direct evidence to support molecular elimination occurring in the CF₂Br₂ photodissociation and proposes a plausible pathway with the aid of ab initio potential-energy calculations. CF₂Br₂ is excited probably to the 1B₁ and 3B₂ states at 248 nm. As the C–Br bond is elongated upon excitation, the coupling of the 1A¹(1B₁) state to the high vibrational levels of the ground state X 1A°(1A₁) may be enhanced to facilitate the process of internal conversion. After transition, the highly vibrationally excited CF₂Br₂ feasibly surpasses a transition barrier prior to decomposition. According to the ab initio calculations, the transition state structure tends to correlate with the intermediate state CF₂Br+Br(CF₂Br⋅⋅⋅Br) and the products CF₂+Br₂. A sequential photodissociation pathway is thus favored. That is, a single C–Br bond breaks, and then the free-Br atom moves to form a Br–Br bond, followed by the Br₂ elimination. The formed Br–Br bond distance in the transition state tends to approach equilibrium such that the Br₂ fragment may be populated in cold vibrational distribution. Observation of a small vibrational population ratio of Br₂(v=1)/Br₂(v=0) agrees with the proposed mechanism. © 2005 American Institute of Physics. [DOI: 10.1063/1.2047570]

I. INTRODUCTION

Investigation of halomethanes has received wide attention, not only due to their important applications in industry and agriculture as refrigerants, flame retardants, aerosols, and pesticides, but also due to their impact on atmospheric chemistry. Their photolysis in stratosphere, particularly for chlorine- and bromine-containing fluorocarbons, may seriously cause ozone-depletion cycle. Despite low concentration of bromine atom resided in the atmosphere, its catalytic reaction rates on depleting stratosphere ozone is proposed up to be 100 times more rapid than chlorine atom.2 Halons and methyl bromides are well-known sources of atmospheric bromine.3,4

CF₂Br₂ (or Halon 1202) has been investigated for several decades, but the mechanisms of its photochemistry are not well understood. In ultraviolet photolysis of CF₂Br₂, three major dissociation channels are energetically attainable:5

\[
\text{CF}_2\text{Br}_2 \rightarrow \text{CF}_2\text{Br} + \text{Br}, \quad \Delta H = 274 \text{ kJ/mol},
\]

\[
\text{CF}_2\text{Br}_2 \rightarrow \text{CF}_2 + \text{Br}_2, \quad \Delta H = 231 \text{ kJ/mol},
\]

Early in 1960, Mann and Thrush studied photodissociation of CF₂Br₂ using flash photolysis to obtain CF₂ product, which was ascribed to the molecular elimination channel (2).6 Later, Sam and Yardley irradiated CF₂Br₂ in gas cell with a 248-nm excimer laser, acquiring the fluorescence of CF₂. They then suggested that the results might come from the molecular elimination and the subsequent resonant absorption of CF₂ ground state.7 Wampler et al. carried out similar a experiment in gas cell, supporting the proposed mechanism by Sam and Yardley.8 Despite the proposal favoring molecular elimination mechanism, note that the other moiety Br₂ has not been detected thus far. Krajnovich et al. studied the photolysis of CF₂Br₂ at 248 nm using the crossed laser-molecular-beam technique.9 By measuring laboratory angular and time-of-flight distributions of the CF₂Br and Br primary products, they concluded that the only primary reaction channel observed was a single C–Br bond fission channel (1). The molecular elimination channel did not occur to a detectable extent. The obtained CF₂ radicals came from a secondary photodissociation of some of the CF₂Br primary products. Cameron et al. extended the photolysis wavelengths from 223 to 260 nm.5 They analyzed the rotational, vibrational, and translational energy distributions partitioning...
in the CF$_2$ radical, and concluded that CF$_2$ should be accompanied by the production of two Br fragments. Two-step processes were suggested. CF$_2$Br+Br was formed in the first step, followed by spontaneous production of CF$_2$+Br as a result of some of the CF$_2$Br with sufficient energy deposited. Park et al. further used a two-dimensional photofragment ion image technique. At photolysis wavelength of 234 nm, they observed concurrently three channels of reactions including single C–Br bond fission, three-body dissociation, and molecular elimination with quantum yields of 0.84, 0.15, and trace, respectively. Nevertheless, when the wavelength was changed to 265 nm, the major primary dissociation channel was the single bond fission.

Another distinct approach to photodissociation dynamics of CF$_2$Br$_2$ is by infrared (IR) multiphoton excitation. For instance, by using laser-induced fluorescence (LIF) technique, Stephenson and co-worker determined the vibrational, rotational, and translational energies partitioning in the CF$_2$ radical fragmented from IR multiphoton dissociation. They also observed LIF spectra of Br$_2$ from $v=2$ to confirm that the CF$_2$ was obtained primarily from the molecular elimination channel. Abel et al. determined branching ratios and energy thresholds for both of Br$_2$ elimination and C–Br bond fission resulting from the highly vibrationally excited CF$_2$Br$_2$. The competition between these two reaction channels was governed by the individual rate constants, which depended on energy and angular momentum initially deposited in CF$_2$Br$_2$.

Thus far, the Br$_2$ elimination channel in ultraviolet photolysis of CF$_2$Br$_2$ is supported mostly by indirect evidences to observe the other CF$_2$ moiety, except for the 234-nm photolysis experiment in which trace Br$_2^*$ was ever found in the time-of-flight mass spectra. Therefore, this is the aim of this work to investigate detailed optical spectra of the Br$_2$ fragment by using a cavity ring-down absorption spectroscopy (CRDS), different from those applied previously in this subject. As an emerging absorption technique, CRDS has been widely applied in the studies of spectroscopy, kinetics, dynamics, and photochemistry in the gas or condensed phases. This technique is based upon the measurement of the decay rate of light trapped in an optical cavity with high reflectance. When a pulsed laser radiation is guided into an optical cavity, the small amount of light trapped inside the cavity reflects between two highly reflective mirrors ($R > 99.9\%$) with a small fraction transmitting through each mirror for each pass. The decay rate of the light leaking out of the cavity is related to the absorption coefficient of the sample in the cavity. Therefore, the CRDS method may ignore fluctuation of incident radiation intensity, with better sensitivity than conventional absorption methods due to a longer optical path. It has been developed as a promising alternative, when modern fluorescence or ionization techniques may not be effectively applied.

In this work, we employ the CRDS technique to measure the nascent vibrational spectra of the molecular bromine fragment in the CF$_2$Br$_2$ photodissociation with an excimer laser at 248 nm. The vibrational branching ratio of Br$_2(v=1)$ to Br$_2(v=0)$ is determined to be 0.4±0.2. With the aid of ab initio potential-energy calculations by Cameron and Bacskay, we may gain insight on the molecular dissociation pathway. The quantum yield of the molecular elimination channel may also be determined to be 0.04±0.01, as the photon number density absorbed and the Br$_2$ concentration produced in the beam-crossed region are given. The result turns out to be larger than the trace amount found in the 234-nm photolysis. Such direct observation of Br$_2$ may help clarify the puzzle regarding existence of molecular elimination in the subject reaction.

II. EXPERIMENTAL SETUP

The CRDS apparatus used for photodissociation study has been described in our previous work. In brief, a 20-ns-
pulsed excimer laser emitting at 248 nm was used for photolysis of CF₂Br₂, while a 5–8-ns-pulsed Nd: yttrium aluminum garnet (YAG) laser-pumped dye laser working on Coumarin 503 dye (515–524 nm) was used to probe the released Br₂ fragment in the $B^3Π_u^+ ← X^1Σ_g^+$ transition. Both lasers were operated at a repetition rate of 10 Hz. Prior to entering the ring-down cell, the energy of photolyzing laser was controlled in the range of 10–30 ± 1 mJ, whereas the probe laser was fixed at 4.0 ± 0.2 mJ. Then, the former laser was focused with a 25-cm focal length cylindrical lens onto the ring-down cell at right angle to the cavity, while the latter beam, in a 20-ns time delay, was injected along the axis of the cavity. The two laser beams were overlapped in the center of the flow cell. The volume of the overlapping region was evaluated by multiplication of beam width and height of the photolyzing laser and beam diameter of the probe laser. In order to remain mostly the TEM₀₀ mode, the probe beam was guided through a spatial filter made of a pair of lenses of 10- and 5-cm focal lengths and a pinhole with 70-μm diameter.

A four-armed stainless-steel reaction chamber was substituted for a glass-made ring-down cell designed previously.⁴ The short arms were mounted with two quartz windows, 40 cm set apart, while the long arms were sealed with two mirrors, 65 cm set apart, with high reflectances of 99.98% at 488 nm and 99.95% at 515 nm, a diameter of 25.4 mm, and a radius of curvature of 1 m. The probe beam was injected through the front mirror into the ring-down cell, but only a small fraction could be coupled into the cavity by transmission through one of cavity end mirrors. The mirrors were mounted in such a way that their positions may be slightly adjusted to trap a laser pulse inside the cavity by ensuring that it retroreflects back and forth between two mirrors. A photomultiplier tube was positioned behind the rear mirror to record the intensity of the light pulse leaking out of the mirror. The intensity envelope composed of each transmitted pulse exhibited an exponential decay, because of a constant loss of light at each mirror surface. The temporal profile of the ring-down signal was recorded on a transit digitizer and transferred to a personal computer. The ring-down time for each laser pulse may be determined by a best fit of the acquired exponential decay. When sample is introduced in the flow cell, the ring-down time relies on its absorption coefficient and thus changes with the laser wavelength. The corresponding absorption spectrum of the sample may be obtained as a result of the varied wavelengths. The related data analysis was handled by using a laboratory-developed program based on MATLAB environment.

CF₂Br₂ and CCl₃Br were used as photolysis reagents in this work. They were purified by repeated freeze-pump-thaw cycles at 77 K and each was introduced in the ring-down cell with the pressure at 1–3 Torr monitored by an MKS pressure gauge. The Br₂ absorption spectra were obtained by scanning the wavelength of the probe laser with a spectral resolution of 0.1 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Br₂ spectra and nascent population ratio

The CRDS spectra of Br₂ ν =0 and 1 levels in the $B^3Π_u^+ ← X^1Σ_g^+$ transition are obtained in Figs. 1 and 2, respectively, upon photodissociation of CF₂Br₂ at 248 nm. The spectral assignments of Br₂ isotope variants are referred to the report by Barrow et al.²² The Br₂ signals disappear when the photolyzing laser is off. To confirm the acquired spectra resulting from the Br₂ fragment, the CRDS spectra of a pure Br₂ compound, less than 0.1 Torr substituted in the cell, were measured for comparison [Figs. 1(b) and 2(b)]. Agreement between these two spectra reveals only the Br₂ fragment occurring in the 515–524-nm region in the photolysis of
CF$_2$Br$_2$. The bands from (35,0) to (39,0) corresponding to the $v=0$ level are observed in the 515.5–518-nm range, while the bands from (39,1) to (44,1) for the $v=1$ level occur in the 522.5–524-nm range.

As reported previously, the rotational population becomes thermally equilibrated to lose its nascent nature during a ring-down time as long as 500–1000 ns. Nevertheless, the vibrational population may still preserve in a nascent state due to inefficient vibrational energy transfer. The vibrational population amounts to summation of each rotational line of the corresponding level. The bands (40,1) and (37,0) are used to estimate the population ratio of $v=1$ to $v=0$. The rotational lines composed of $P$ and $R$ branches in the bands (40,1) and (37,0) have been assigned up to $J=27$ and 35, respectively. Given the Franck-Condon factors of 0.005 57 and 0.004 25 for the bands (40,1) and (37,0), respectively, and Hönl-London factor for each rotational line, the branching ratio of Br$_2$($v=1$)/Br$_2$($v=0$) is estimated to be 0.4±0.2. The large uncertainty is found mainly due to the partially spectral overlap between isotope variants. Ignorance of the rotational lines $J>27$ may not contribute much uncertainty, since the rotational population is expected to reach thermal equilibrium. The lack of CRDS acquisition for the $v=2$ and higher levels is restricted to poor reflectivity of cavity mirrors in longer wavelength.

The Br-atom release from the C–Br bond fission has been considered as the major channel for the ultraviolet photolysis of most Br-containing hydrocarbons. To verify that the obtained Br$_2$ molecule should not stem from the secondary recombination of such two Br atoms, three experiments were further conducted. First, a precursor CCl$_3$Br to substitute for CF$_2$Br$_2$ was photolyzed at 248 nm in the ring-down cell under otherwise identical conditions. Figure 3 shows no detectable signals of Br$_2$ fragment in the photolysis, when the sample pressure was at 2.2 Torr and the photolysis-probe delay time was extended to 80 ns. The absorption cross section of CCl$_3$Br is $(4.8-4.9) \times 10^{-19}$ cm$^2$ at 248 nm, slightly smaller than the value of $7.12 \times 10^{-19}$ cm$^2$ for CF$_2$Br$_2$. With the experimental conditions similar to CF$_2$Br$_2$, extension of photolysis-probe delay time may increase the collision frequency of recombination. The lack of the Br$_2$ detection ensures that the secondary recombination should be negligible in this work. Second, the laser energy dependence was measured for a selective rotational line $P(37)$ of the Br$_2$ band (35,0) at 519.68 nm. As shown in Fig. 4, the plot of rotational intensity as a function of the incident laser energy, taking into account the origin coordinate, yields a straight line with a regression coefficient of 0.99, indicating that only a single photon is involved in the molecular elimination. Two photons are otherwise required for the recombination process, as dissociation channel (1) dominates. Note that consideration of the origin coordinate in the linear regression fit

![FIG. 3. Detection of CRDS spectra of Br$_2$ following photolysis of (a) CCl$_3$Br and (b) CF$_2$Br$_2$ at 248 nm.](image-url)

![FIG. 4. Plot of rotational intensity of Br$_2$ produced in 248-nm photolysis of CF$_2$Br$_2$ vs the incident laser energy. The origin coordinate is taken into account for the linear regression fit. The same plot with corresponding number density of Br$_2$ against the absorbed photon density yields a slope, indicative of the quantum yield 0.04±0.01 for the channel of molecular elimination.](image-url)
implies that the obtained one-photon absorption phenomena should not be interfered with by the effect of optical saturation or partial saturation. Third, the rotational line $P(37)$ at 519.68 nm was used again for the measurement of pressure dependence. As shown in Fig. 5, the plot of the Br$_2$ rotational intensity versus the CF$_2$Br$_2$ pressure ranging from 0.1 to 1.5 Torr yields a straight line. The linear dependence excludes the possibility of secondary recombination process, in which each Br atom is originated from an individual CF$_2$Br$_2$ molecule.

When a LIF technique was employed, as in our previous work on the CHBr$_3$ photodissociation, we failed to find any detectable $B^3Π_u \rightarrow X^1Σ^+_g$ signals of Br$_2$ fragmented from CF$_2$Br$_2$ at a pressure of 2.5 Torr. While a pure Br$_2$ compound was substituted, the LIF signals of the rotational lines in the (37,0) band appeared to be twice as wide as those detected by the CRDS method. The difficulty with LIF detection may rise from a low fluorescence quantum yield caused by predissociation with the repulsive $C^1Π_{tu}$ state.

**B. Quantum yield for molecular elimination**

The quantum yield for the channel of molecular elimination in the CF$_2$Br$_2$ photolysis can be determined from the ratio of Br$_2$ concentration produced in the beam-crossed region of photolysis/probe lasers to the photon number density absorbed in the same region. Following photolysis, the Br$_2$ concentration may be determined in terms of its absorption coefficient $α$, as evaluated by the equation

$$α = \frac{d}{c l} \left( \frac{1}{τ} - \frac{1}{τ_0} \right),$$

where $d=65$ cm, the distance between two high reflectance mirrors; $l=1.6±0.1$ cm, the optical length of the absorber; $c$, the light speed; and $τ$ and $τ_0$, the ring-down times of Br$_2$ as a result of the probe-laser wavelength in resonance or off resonance with 519.68 nm, respectively. If an empty cavity is used for the background measurement, an additional bound-free absorption may contribute to error in determining the term $(1/τ-1/τ_0)$. In this work the photolysis-probe delay time is fixed at 20 ns, which is short enough to ignore the diffusion loss of Br$_2$ fragment. The absorption cross section of Br$_2$ at 519.68 nm may be determined with the pure Br$_2$ compound substituted in the flow cell. According to Eq. (4) in which $l$ is replaced by $d$, the linear plot of the absorption coefficient against the number density of Br$_2$ yields an absorption cross section, $σ_{Br2}=(1.3±0.3)×10^{-19}$ cm$^2$. Given this absorption cross section, the Br$_2$ concentration produced in the interaction region may be evaluated from the ratio of $α/σ_{Br2}$.

Meanwhile, the absorbed photon number density $ϕ$ can be evaluated by using the following equation:

$$ϕ = \frac{E_{in} - E_{out}}{hνΔV},$$

where $h$ denotes Planck’s constant; $ν$, radiation frequency; $ΔV$, the volume of beam-crossed region; and $E_{in}$ and $E_{out}$ indicate the photon energy of incoming and outgoing radiations for photolysis. $E_{in}$ and $E_{out}$ may be estimated by using Lambert-Beer’s law, as expressed by

$$E_{in} = E_0 \exp(-αnl_1),$$  \hspace{1cm} (6)$$

$$E_{out} = E_0 \exp(-αnl_2),$$  \hspace{1cm} (7)$$

where $E_0$ is the photon energy of incident photolyzing laser pulse prior to the cell; $α$, the absorption cross section of CF$_2$Br$_2$ at 248 nm; $n$, the number density of CF$_2$Br$_2$ in the cell; and $l_1$ (or $l_2$) indicates the distance between the inner side of the entrance cell window and the front (or rear) edge of the beam-crossed region.

The cross section $σ$ of CF$_2$Br$_2$ at 248 nm is reported to be $7.12×10^{-19}$ cm$^2$. $l_1$ and $l_2$ are measured to be $3.77±0.02$ and $3.96±0.02$ cm, respectively. Given that the photolyzing beam energies are varied from $12.8±0.2$ to $30.2±0.3$ mJ/pulse, corresponding to the absorbed photon number density from $0.8×10^{17}$ to $2.1×10^{17}$ photons/cm$^3$, the Br$_2$ concentration can be produced from $3.8×10^{15}$ to $9.0×10^{15}$ molecules/cm$^3$ in linear proportion, as shown in Fig. 4. The slope gives rise to a quantum yield of $0.04±0.01$ for the molecular elimination channel. Our quantitative evaluation is larger than the trace amount of Br$_2(<0.01)$ obtained by Park et al. with radiation source at 234 nm. The dissociation channel of Br$_2$ elimination in the ultraviolet photolysis of CF$_2$Br$_2$ is usually ignored in the recent studies of
the supersonic beam experiments. Therefore, the related photodissociation mechanism, which actually exhibits distinct difference from the Br-release channel, is overlooked.

**C. Photodissociation pathway**

Cameron and Bacsay have performed *ab initio* calculations for decomposition reaction of CF$_2$Br$_2$ using complete active space self-consistent field (CASSCF) computation with cc-pVDZ basis set in DALTON programs. As shown in Fig. 6, the transition state (TS), with only one imaginary vibrational frequency of 159 cm$^{-1}$, is located on the potential-energy surface (PES) at 259.7 kJ/mol above the electronic ground state of CF$_2$Br$_2$. The potential barrier is 30 kJ/mol larger than that determined previously by Abel et al. For the optimized TS structure, the C–Br–Br angle, F–C–F angle, C–Br bond length, C–F bond length, and Br–Br distance are 158.4$^\circ$, 108.4$^\circ$, 2.182 Å, 1.276 Å, and 2.578 Å, respectively. Intrinsic reaction coordinate (IRC) computation along the adiabatic reaction coordinate was also performed at CASSCF/cc-pVDZ level to relate the TS to the intermediate CF$_2$Br$^+$Br (or CF$_2$Br$^+$Br) on the one side and the products CF$_2$+Br$_2$ on the other side. But the TS failed to correlate directly to the reactant CF$_2$Br$_2$ and the final products.

According to the *ab initio* calculations of vertical excitation energies performed with a range of theoretical methods, the lowest singlet state $^1B_1$ and two nearby triplet states $^3A_2$ and $^3B_2$ are probably energetically accessible upon excitation at 248 nm. The $^3A_2$ or $^3B_2$ transition is dipole forbidden, whereas the $^3B_2$ or $^3A_1$ and $^1B_1$ or $^1A_1$ transitions should be both allowed, since the heavy atom effect may enhance the spin-changing transition probability. While further considering the measurement of anisotropy parameter by Krajnovich et al., the excited state should have the $^1B_1$ symmetry, because the transition dipole moment is polarized parallel to the Br–Br direction. If the photodissociation occurs directly from a repulsive limb of the excited state, the C–Br bond fission may lead to the products CF$_2$Br$^+$Br and the available energy is anticipated to substantially partition into the translational states of the fragments. As the C–Br bond is elongated upon excitation, the CF$_2$Br$_2$ structure changes to be $C_1$ symmetry and the subsequent $^1A'$ or $^3A_1$ coupling becomes strengthened. Thus a small fraction of population may have chance to transit to the high vibrational levels of the ground state X$^1A'$ prior to direct photodissociation. Following internal conversion, as shown in Fig. 6, the highly vibrationally excited CF$_2$Br$_2$ with internal energy about 483 kJ/mol, corresponding to 248-nm excitation, readily surpasses the transition barrier to undergo the Br$_2$ elimination.

Abel et al. have determined the branching ratio as 10% for the channel of Br$_2$ elimination as a result of IR multiphoton excitation of CF$_2$Br$_2$. The ratio increases up to 25% with increasing the incident laser energy. But if the energy is further increased, the competitive channel of C–Br bond fission is enhanced again to dominate substantially. The branching ratio of 10%–25% determined in the IR multiphoton dissociation may well be considered as the upper limit of

**FIG. 6. Ab initio** potential-energy calculations of CF$_2$Br$_2$ dissociation along an adiabatic reaction coordinate, reported by Cameron and Bacsay (Ref. 21). The structure-optimized transition state (TS), located at 259.7 kJ/mol above the ground potential-energy surface, correlates to both the intermediate CF$_2$Br$^+$Br (or CF$_2$Br$^+$Br) and the products CF$_2$+Br$_2$.

**FIG. 7. Schematic diagram for level-to-level coupling between the $^1A'$ ($^1B_1$) state and the high vibrational levels of the ground state X$^1A'$ ($^1A_1$). (a) a single-level excitation, which results in insignificant coupling efficiency; (b) a broad population distribution in the excited state, which enhances the coupling efficiency to facilitate internal conversion; and (c) high vibrational levels of ground state populated directly by IR multiphoton absorption.
the quantum yield for the molecular elimination in the 248-nm photolysis, depending on the coupling strength of internal conversion.

Contrary to our CRDS results, the failure in the molecular-beam experiments to observe any significant contribution of the molecular elimination might rise from the following reason. In the molecular-beam experiments under a cold temperature condition, the precursor CF₂Br₂ may be populated in a single or only few rotational levels of the electronic ground state and also of the excited state upon photon absorption at 248 nm. The narrow population spread in the upper levels of excited state restricts the efficiency of level-to-level couplings of internal conversion, and thereby no appreciable amount of Br₂ product may be detected. In contrast, the present work under the room-temperature condition induces a much wider population distribution in the excited state, thus enhancing the coupling strength to facilitate the internal conversion. For comparison, schematic descriptions for supersonic beam experiment, IR multiphoton excitation, and our CRDS experiment are depicted in Fig. 7.

To support the photodissociation pathway proposed, temperature dependence of Br₂ elimination was further conducted with the selective rotational line \( P(37) \) at 519.68 nm. As shown in Fig. 8, the rotational intensity rises gradually up to 5% enhancement within temperature increment from 20 to 50 °C. Such positive temperature effect is under anticipation. As temperature increases, the higher levels of excited state are populated such that the increased density of states may strengthen the level-to-level couplings of internal conversion. In addition, a further wider population distribution has more chance to increase the coupling efficiency.

According to the \textit{ab initio} calculations of ground-state PES and TS structure, a sequential photodissociation mechanism seems to be favored. That is, a single C–Br bond breaks first, and then the free-Br atom moves to form a Br–Br bond, followed by the Br₂ elimination. When the departing atom attacks the Br atom of CF₂Br, the formed Br–Br distance tends to approach equilibrium such that the Br₂ fragment may be populated in cold vibrational distribution. It is reflected in the obtained vibrational population ratio of Br₂\((v=1)/\text{Br₂}(v=0)\), which is 0.4±0.2 close to the value of 0.22 evaluated by the Boltzmann distribution at room temperature. In contrast to the CF₂Br₂ case, the 248-nm photolysis of bromoform is found to follow a concerted mechanism analogously via internal conversion. The transition state, which lies along an adiabatic reaction coordinate of the ground-state PES, correlates to the CHBr + Br₂ products. Its structure has two elongated C–Br bonds with the Br–C-Br angle bent symmetrically. The elongation of both C–Br bonds may break concurrently along a symmetry plane. Such a photodissociation pathway leads to a vibrationally hot Br₂ fragment with the Br₂\((v=1)/\text{Br₂}(v=0)\) ratio equal to 0.8.

IV. CONCLUSION

This work demonstrates for the first time that Br₂ can be eliminated in the primary photodissociation of CF₂Br₂ at 248 nm by using CRDS technique. In spite of a small quantum yield, the molecular elimination channel should not be ignored in the ultraviolet photolysis. The branching ratio for this channel determined in the experiments of infrared multiphoton excitation may be considered as the upper limit for the ultraviolet photolysis. A photodissociation pathway is proposed with the aid of the \textit{ab initio} potential-energy calculations. As CF₂Br₂ is excited to the \( ^1B_1 \) or \( ^3B_2 \) states, elongation of the C–Br bond may strengthen the \( ^1A' \rightarrow X \rightarrow ^1A' \leftarrow ^1B_1 \rightarrow X \rightarrow ^1A_1 \) couplings to facilitate the process of internal conversion. The fraction of highly vibrationally excited CF₂Br₂ in the electronic ground state may then feasibly surpass the transition state to end with the molecular elimination. Unlike the molecular-beam experiments, the CRDS method performed at room temperature broadens the population distribution in the excited states, which enhances the efficiency of internal conversion. The sequential photodissociation mechanism is favored to cause Br₂ fragmented in lower vibrational levels. The nascent vibrational population ratio measured lends support to the proposed mechanism. In contrast to this work, the CHBr₃ photodissociation at 248 nm was previously reported to follow a concerted mechanism, leading to vibrationally hot Br₂ products.
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