Br$_2$ molecular elimination in 248 nm photolysis of CHBr$_2$Cl by using cavity ring-down absorption spectroscopy

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Elimination of molecular bromine is probed in the B $^3\Pi_{ou}^+ - X ^1\Sigma_{g}^+$ transition following photodissociation of CHBr$_2$Cl at 248 nm by using cavity ring-down absorption spectroscopy. The quantum yield for the Br$_2$ elimination reaction is determined to be 0.05±0.03. The nascent vibrational population ratio of Br$_2$(v=1)/Br$_2$(v=0) is obtained to be 0.5±0.2. A supersonic beam of CHBr$_2$Cl is similarly photofragmented and the resulting Br atoms are monitored with a velocity map ion-imaging detection, yielding spatial anisotropy parameters of 1.5 and 1.1 with photolyzing wavelengths of 234 and 267 nm, respectively. The results justify that the excited state promoted by 248 nm should have an $A''$ symmetry. Nevertheless, when CHBr$_2$Cl is prepared in a supersonic molecular beam under a cold temperature, photofragmentation gives no Br$_2$ detectable in a time-of-flight mass spectrometer. A plausible pathway via internal conversion is proposed with the aid of ab initio potential energy calculations. Temperature dependence measurements lend support to the proposed pathway. The production rates of Br$_2$ between CHBr$_2$Cl and CH$_2$Br$_2$ are also compared to examine the chlorine-substituted effect. © 2007 American Institute of Physics. [DOI: 10.1063/1.2426334]

I. INTRODUCTION

Trihalomethanes such as CHBr$_2$Cl, CHBrCl$_2$, and CHBr$_3$ are observed in the troposphere and detected in drinking water and rivers.$^{1-3}$ As reported, the atmospheric lifetimes of these trihalomethanes are about 120 days by the reaction with OH, while the lifetimes with respect to photolysis near the earth surface (0–5 km) are found to be 20–60 days.$^4$ It turns out that UV photolysis is the major removal process for these species. Understanding the related UV photochemistry is therefore extremely important for the assessment of their environment impact.

For halogen-substituted methanes, irradiation with UV light may lead to a transition of a nonbonding electron of the halogen atom to the antibonding orbital of the C–X bond (X denotes halogen). Such a $(n,s)$ band excitation rapidly causes bond elongation and then bond rupture. Therefore, the release of a single halogen atom is considered as the dominant process of the photolysis in the UV region. Molecular halogen decomposition is seldom reported in the UV photodissociation of trihalomethanes, and there even exists a controversy on the mechanism of the molecular halogen production. For instance, McGivern et al. demonstrated that the C–Br bond cleavage was the only primary dissociation channel in single-photon dissociation of CHBr$_3$ at 193 nm by using photofragment translational spectroscopy.$^5$ The CHBr$_3$ fragment with sufficient internal energy may undergo secondary dissociation to give rise to comparable yields of HBr and CBr. When the light was changed to 248 nm, prompt C–Br bond fission was still the dominant channel.$^6$ Nevertheless, the molecular bromine photofragments were observed following an additional photon absorption of the CHBr$_2$ fragment. The secondary photodissociation of CHBr$_2$ results in three competing fragmentation channels, including CHBr + Br, CBr + HBr, and CH + Br$_2$. On the other hand, Xu et al. using a velocity map ion-imaging detection first observed a channel for the elimination of molecular bromine in the 234 and 267 nm photolysis of bromoform, and reported quantum yields of 0.26 and 0.16, respectively.$^7$ They measured the CHBr and CHBr$_2$ signal intensities to determine the branching ratios of Br$_2$ elimination and C–Br bond fission. But the laser power dependence of the fragment yields was not examined. In a recent work, we have also observed the channel of Br$_3$ molecular elimination following photodissociation of bromoform at 248 nm by using cavity ring-down spectroscopy (CRDS) technique.$^8$ A plot of rotational intensity of Br$_2$ as a function of the laser energy in a logarithmic scale yields a straight line with a slope equal to 1. However, whether the line may be extrapolated through the origin was not checked such that the probability for optical saturation or partial saturation may not be ruled out. This is one aim for the present work in order to clarify whether it is possible for a trihalomethane to release molecular halogen as a primary product in the UV photolysis.

The following are the primary dissociation channels for CHBr$_2$Cl and their corresponding endothermicities:$^{9-11}$

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The molecular bromine along with \( \text{Br}_2 \) first acquired. Then, the quantum yields for the production of brational spectra of the fragmented molecular bromine were investigated by using CRDS technique. The rovibronically disfavored. In this sense, while detecting the \( \text{Br}_2 \) should be much less, since the C–Cl bond cleavage is energetically disfavored. In this sense, while detecting the \( \text{Br}_2 \) molecular elimination, the interference from the secondary photodissociation of \( \text{CHBr}_2 \) may be minimized. This is the main reason to choose this trihalomethane for investigation.

The UV absorption spectrum of \( \text{CHBr}_2 \text{Cl} \) was measured, showing two absorption bands with one maximum near 210 nm and the other near 240 nm.\(^4\) When the light wavelength becomes shorter in the 106–200 nm region, a diffused emission band of \( \text{CHCl}(\tilde{A} 1^{\tilde{A}}^\text{A}) \) was observed in the 500–800 nm region in the excitation of \( \text{CHBr}_2 \text{Cl} \).\(^1\) Despite the researches in photodissociation of \( \text{CHBr}_2 \text{Cl} \) are very limited, information regarding its reactions with atoms or radicals is abundant. For instance, the reaction of \( \text{CHBr}_2 \text{Cl} \) with Cl was found to yield a rate constant of 2.2 \( \times 10^{-13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 296 K, being more active by a factor of 2 than with \( \text{CH}_4 \).\(^4\) While considering calculated potential barriers, the major pathway for the above reaction was expected to be via \( \text{H} \) abstraction, and then \( \text{Br} \) abstraction, whereas Cl abstraction was impeded by a large barrier of 19.9 kcal/mol over the moderate temperature region.\(^3\) For the ion-molecule reactions, \( \text{H}_2\text{O}^+ + \text{CHBr}_2\text{Cl} \) was found with a rate constant close to the collisional value of 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 300 K.\(^4\) Reaction rate constants and branching ratios of \( \text{CHBr}_2\text{Cl} \) with anions \( \text{O}^- \), \( \text{O}^-_2 \), and \( \text{OH}^- \) in helium buffer gas at 300 K were investigated using an ion flow tube.\(^5\) In condensed phase, Phillips and co-workers reported the transient resonance Raman spectra of \( \text{CHBr}_2 \) following UV photolysis of \( \text{CHBr}_2\text{Cl} \) in methanol solution, and the spectra of iso\( \text{CHBrCl}_2\text{Br} \) and iso\( \text{CHClBr}_2\text{Br} \) species in cyclohexane solution.\(^6\) \( \text{CHBr}_2\text{Cl} \) also serves as a precursor following its photolysis at 193 or 248 nm for studies of midinfrared spectroscopy of \( \text{CHCl} \) and kinetics of the \( \text{CH} + \text{D}_2 \) reaction.\(^7\)

In this work, single-photon dissociation of \( \text{CHBr}_2\text{Cl} \) at 248 nm is investigated by using CRDS technique. The rovibrational spectra of the fragmented molecular bromine were first acquired. Then, the quantum yields for the production of the molecular bromine along with \( \text{Br}_2(v=1)/\text{Br}_2(v=0) \) branching were determined. With the aid of \( \text{ab initio} \) potential energy calculations, insight into the molecular dissociation pathway may be gained. Temperature-dependence measurement of the \( \text{Br}_2 \) product was further performed to support the proposed pathway. Finally, the Cl-substituted effect on the production rate of \( \text{Br}_2 \) with respect to \( \text{CH}_2\text{Br}_2 \) was examined.

### II. EXPERIMENTAL SETUP

#### A. CRDS apparatus

The CRDS apparatus used for the photodissociation study has been described in our previous work.\(^8\) In brief, a 20 ns pulsed excimer laser at 248 nm was used for photolysis of \( \text{CHBr}_2\text{Cl} \), while a 5–8 ns pulsed neodymium doped yttrium aluminum garnet laser-pumped dye laser working on Coumarin 503 dye (515–524 nm) was triggered after a 20 ns delay to probe the released \( \text{Br}_2 \) fragment in the \( B^3\Pi_{\text{ou}} \rightarrow X^1\Sigma_{\text{g}}^+ \) transition. The energies of photolyzing and probe lasers were controlled in the 11–25 mJ range and at 4 mJ, respectively, prior to entering a four-armed stainless steel ring-down cell. The probe beam was injected through the front mirror into the ring-down cell, while a photomultiplier tube was positioned behind the rear mirror to detect the intensity of the light pulse leaking out of the mirror. The ring-down time for each laser pulse may be determined by a best fit of the acquired exponential decay. Its value varies with the absorption coefficient of the sample introduced. The reagents, \( \text{CHBr}_2\text{Cl} \), \( \text{CCl}_3\text{Br} \), and \( \text{CH}_2\text{Br}_2 \), were purified and each was introduced in the ring-down cell with the pressure of 0.4–3.5 Torr. The \( \text{Br}_2 \) absorption spectra, having a spectral resolution of 0.1 cm\(^{-1}\), were obtained with the aid of a laboratory-developed program based on a MATLAB environment. For the temperature dependence measurements, the whole chamber was wrapped with a heating tape and the temperature was monitored by a thermocouple positioned nearby the center region.

#### B. Time-of-flight mass spectrometer setup

Experiments were also performed with a time-of-flight mass spectrometer equipped with a velocity-map ion-imaging detector, so that the results could be compared with the current CRDS measurements and the upper state could also be definitively determined in terms of measurements of spatial anisotropy parameter.\(^21\) The saturation vapor of \( \text{CHBr}_2\text{Cl} \) was carried through a pulsed nozzle operating at 10 Hz, by \( \text{He} \) at 2 atm pressure, and expanded into the source chamber. After passing through a skimmer (diameter=200 \( \mu \text{m} \)) and a collimator, the supersonic molecular beam was intersected perpendicularly by a linearly polarized laser beam at either 234 or 267 nm in a two-stage ion lens region. These UV wavelengths happened to cause one-photon photodissociation of the precursor and the subsequent ionization of \( \text{Br} \) atoms via a \((2+1)\) resonance-enhanced multiphoton ionization (REMPI) process. The ions were then extracted and accelerated into a 36-cm-long field-free drift tube along the molecular beam direction, followed by velocity mapping onto a two-stage multichannel plate (MCP) and a phosphor screen. The MCP could be gated within a minimum duration of 200 ns for mass selection. The resultant ion imaging on the phosphor screen was recorded by a charge coupled device camera. The laser wavelength

\[
\begin{align*}
\text{CHBr}_2\text{Cl} &\rightarrow \text{CHBrCl} + \text{Br}, \quad \Delta H = 247 \text{ kJ/mol}, \\
\rightarrow \text{CHBr}_2 + \text{Cl}, \quad \Delta H = 302 \text{ kJ/mol}, \\
\rightarrow \text{CHCl} + \text{Br}_2, \quad \Delta H = 341 \text{ kJ/mol}, \\
\rightarrow \text{CCl} + \text{HBr}, \quad \Delta H = 242 \text{ kJ/mol}, \\
\rightarrow \text{CHBr} \rightarrow \text{BrCl}, \quad \Delta H = 379 \text{ kJ/mol}.
\end{align*}
\]
was scanned back and forth within the range of Doppler broadening to cover all the velocity components of the selected fragments. All the ion signals without gate restriction may be transferred to a transient digitizer for display of the mass spectrum.

III. THEORETICAL METHODS

A. Ab initio electronic structure calculations

The Br₂ and Br dissociation channels on the adiabatic singlet ground-state potential energy surface of CHBr₂Cl are characterized. The geometries and the harmonic frequencies of reactant, transition states (TSs), and products are obtained at the level of the hybrid density functional theory, B3LYP/6-311G(d,p); the energies are further refined by the coupled cluster CCSD(T)/cc-pVTZ with B3LYP/6-311G(d,p) zero-point energy corrections. The vertical energies of the lowest excited states at the CCI optimized geometry with respect to the ground state $\tilde{X}^1A'$ CHBr₂Cl are determined by the Davidson-corrected multireference configuration interactions with single and double excitation (MRDCI) calculations, in which the cc-pVTZ basis functions are employed. The GAUSSIAN 98 (Ref. 24) and MOLPRO (Ref. 25) programs are utilized in the electronic structure calculations for the ground and excited states, respectively. For simplicity, the spin-orbit splitting of the Br atom is not taken into account for the ab initio calculations, but this would not have any effect on the mechanism proposed for the Br₂ elimination.

B. RRKM rate constant calculations

The Rice-Ramsperger-Kassel-Marcus (RRKM) and variational RRKM rate constants for Br₂ and Br dissociations at 248 nm, respectively, on the ground state CHBr₂Cl are predicted. The molecule is assumed to be a collection of harmonic oscillators, of which the harmonic frequencies and energies are obtained as described above. In particular, for the barrierless decomposition of the Br atom, intrinsic reaction coordinate (IRC) calculations of optimized geometries and corresponding harmonic frequencies as a function of C–Br bond length are performed at the level of B3LYP/6-311G(d,p) in order to locate the variational transition state.

IV. RESULTS AND DISCUSSION

A. Br₂ as primary product and its related spectra

The CRDS spectra of Br₂ $v=0$ and 1 levels in the $B^3\Pi_u←X^1\Sigma_g^+$ transition are obtained upon photodissociation of CHBr₂Cl at 248 nm. Figure 1 shows an example of the Br₂ ($v=0$) spectrum, which contains the bands from (36,0) to (39,0) in the 516.1–518 nm range, while the bands from (39,1) to (44,1) occur in the 522–524 nm range. The CRDS spectra for $v=2$ and higher levels are not observed due to poor reflectivity of cavity mirrors in the longer wavelength. The bands (41,1) and (37,0) are used to estimate the population ratio of $v=1$ to $v=0$, assigned up to $J=33$ and 35, respectively. Given the Franck-Condon factors for these two bands and the Hönl-London factor for each rotational line involved, the branching ratio of $Br_2(v=1)/Br_2(v=0)$ is estimated to be 0.5±0.2. Herein, only the $85^{\text{Br}}_2$ spectra are selective for the branching ratio determination. The assignments for the other two molecular isotopes are not shown in the figures to avoid spectral congestion. Despite a long ring-down time of 1000 ns, the nascent vibrational population may be preserved due to inefficient vibrational energy transfer. The large uncertainty in the analysis is mainly caused by the partial spectral overlap between different isotopic variants. Ignoring the rotational lines $>33$ may not contribute much uncertainty, since the rotational population is expected to reach thermal equilibrium.

In the following we conduct three further experiments to verify that the Br₂ fragment belongs to a primary product following the 248 nm photodissociation of CHBr₂Cl. First, a single-Br-containing molecule CCIBr, with absorption cross section of 4.8–4.9×10⁻¹⁹ cm² at 248 nm, as a substitute in the ring-down cell was photolyzed, yielding no detectable signals of Br₂ fragment, even when the sample pressure was increased to 3.5 Torr and the photolysis-probe delay time was prolonged to 80 ns. Then, the rotational line $P(37)$ of the
The Br$_2$ band (35.0) at 519.68 nm was selected for the measurements of laser energy and CHBr$_2$Cl-pressure dependence. As shown in Fig. 2, the plot of rotational intensity as a function of the incident laser energy yields a straight line, indicative of a single-photon involvement in the molecular elimination. Two photons are otherwise required for the secondary recombination and secondary photodissociation processes. Note that the plot has taken into account the origin point in the linear regression fit, implying that the effect of optical saturation or partial saturation should be negligible. Figure 3 shows the measurement of a linear CHBr$_2$Cl-pressure dependence of the Br$_2$ rotational intensity, as the pressure is varied from 0.8 to 2.0 Torr. All indications exclude the probability of atomic Br recombination and secondary photodissociation of CHBr$_2$ fragment.

**B. Quantum yield for molecular elimination**

The quantum yield of Br$_2$ in the CHBr$_2$Cl photolysis at 248 nm can be determined by

\[
\phi = \frac{[\text{Br}_2]}{N_p},
\]

where [Br$_2$] indicates the Br$_2$ concentration produced in the beam-crossed region of photolysis/probe lasers and $N_p$ the photon number density absorbed in the same region. Following our previous work, Eq. (6) may be simplified as

\[
\phi = \frac{[\text{Br}_2]}{(E_0/h\nu\Delta V)(\ell_2 - \ell_1)n\sigma},
\]

where $E_0$ is the photolyzing laser energy prior to the cell, $h$ Planck’s constant, $\nu$ the radiation frequency, $\Delta V$ the volume of beam-crossed region, $n$ the number density of sample in the cell, $\sigma$ the absorption cross section at 248 nm, and $\ell_1$ (or $\ell_2$) indicates the distance between the inner side of the entrance cell window and the front (or rear) edge of the beam-crossed region. Note that the above equation requires the assumption that $\exp(-n\ell\sigma)$ may be expanded into $(1 - n\ell\sigma)$. Given the identical experimental conditions of $E_0$ and $n$ along with acquisition of a relative line intensity of Br$_2$ at 519.68 nm, the quantum yield of Br$_2$ in the CHBr$_2$Cl photolysis may thus be obtained of 0.05±0.03 by using CH$_2$Br$_2$ as a reference with a known quantum yield of 0.2±0.1, as evaluated in the following:

\[
\frac{\phi_{\text{CHBr}_2\text{Cl}}}{\phi_{\text{CHBr}_2}} = \frac{[\text{Br}_2]_{\text{CHBr}_2\text{Cl}}}{\sigma_{\text{CHBr}_2\text{Cl}}}/\frac{[\text{Br}_2]_{\text{CH}_2\text{Br}_2}}{\sigma_{\text{CH}_2\text{Br}_2}}.
\]

Here, \(\sigma_{\text{CHBr}_2\text{Cl}}\) and \(\sigma_{\text{CH}_2\text{Br}_2}\) are obtained to be 8.4×10$^{-19}$ (Ref. 4) and 3.7×10$^{-19}$ cm$^2$, respectively, in the absorption at 248 nm.

The RRKM theoretical calculations give rise to the rate constants of 4.6×10$^7$ and 3.5×10$^{12}$ s$^{-1}$ for the Br$_2$- and Br-elimination channels, respectively, both initiated from the ground state CHBr$_2$Cl. The RRKM calculations assume statistical equilibrium between the initial and the transition states. Before reaching that stage, the C–Br bond fission has already occurred following the repulsive limb of the excited state. This fact explains the discrepancy between our experimental findings and the theoretical results.
**Photolysis of CHBr₂Cl**

In the molecular beam experiments, the time-of-flight spectra of the fragmented ions following either 234 or 267 nm irradiation of CHBr₂Cl are obtained. As with the photodissociation of CH₂Br₂ or CF₂Br₂, no trace of Br₂ signals at (average) m/e=160 can be found in the molecular beam experiments upon UV light (>234 nm) irradiation. The mixed signal of Br⁺ (m/e=79 and 81) is ionized via (2+1)REMPI upon irradiation at either 234 or 267 nm, while the remaining peaks are obtained via nonresonant ionization. The Br ion images of fine-structure ground states following photodissociation process with CHCl group on the xy symmetry plane and the angle Br–C–Br bisected. The 1 A'' ← X 1 A' or the 2 1 A'' ← X 1 A' transitions are then defined, depending on whether the excitation transition is along the plane normal (z axis) or the CHCl plane (xy plane). According to our ab initio calculations, the ground state structure of CHBr₂Cl is optimized to have the Br–C–Br angle of 111.9°. When the transition dipole moment is along the z axis, the corresponding value of α is 34.1°, and in turn, β becomes 1.1, which is consistent with the observed values in the 234 or 267 nm photolysis. When the transition dipole moment is parallel to this axis, then α becomes 55.9° and β becomes 0.06. The x axis is normal to the yz plane which contains the BrBr group. If the transition dipole moment is parallel to this axis, then α corresponds to 90° and β becomes 1. β is evaluated to be between these two extreme values with the transition dipole moment lying on the xy plane, relying on the definition of the x and y axes. Apparently, the appropriate excited state should be with the A'' symmetry, although the radiations at 234 and 267 nm are substituted for 248 nm. The latter radiation may not cause the REMPI process for the bromine atoms in one-color-laser experiments.

**C. Photolysis in supersonic molecular beam**

In the molecular beam experiments, the time-of-flight spectra of the fragmented ions following either 234 or 267 nm irradiation of CHBr₂Cl are obtained. As with the photodissociation of CH₂Br₂ or CF₂Br₂, no trace of Br₂ signals at (average) m/e=160 can be found in the molecular beam experiments upon UV light (>234 nm) irradiation. The mixed signal of Br⁺ (m/e=79 and 81) is ionized via (2+1)REMPI upon irradiation at either 234 or 267 nm, while the remaining peaks are obtained via nonresonant ionization. The Br ion images of fine-structure ground states following photodissociation at 234 and 267 nm are acquired in Fig. 4. The corresponding speed and angular distributions of the product ions may be analyzed by inverse Abel transform. The details of image processing have been described elsewhere. The resulting anisotropy parameters β for Br are determined to be 1.5 and 1.1 at 234 and 267 nm, respectively.

β is related to the flight direction of Br in the C–Br fission with respect to the transition dipole moment, as expressed by

$$\beta = 2P_2(\cos \alpha),$$

where $P_2(\cos \alpha)$ is the second order Legendre polynomial and α is defined as the angle between the recoil velocity of Br atom and the transition dipole moment. According to the β values, the symmetry of excited state may be determined. We assume CHBr₂Cl remains in the C₆ symmetry during the photoexcitation process with CHCl group on the xy symmetry plane and the angle Br–C–Br bisected. The 1 A'' ← X 1 A' or the 2 1 A'' ← X 1 A' transitions are then defined, depending on whether the excitation transition is along the plane normal (z axis) or the CHCl plane (xy plane). According to our ab initio calculations, the ground state structure of CHBr₂Cl is optimized to have the Br–C–Br angle of 111.9°. When the transition dipole moment is along the z axis, the corresponding value of α is 34.1°, and in turn, β becomes 1.1, which is consistent with the observed values in the 234 or 267 nm photolysis. When the transition dipole moment is parallel to this axis, then α becomes 55.9° and β becomes 0.06. The x axis is normal to the yz plane which contains the BrBr group. If the transition dipole moment is parallel to this axis, then α corresponds to 90° and β becomes 1. β is evaluated to be between these two extreme values with the transition dipole moment lying on the xy plane, relying on the definition of the x and y axes. Apparently, the appropriate excited state should be with the A'' symmetry, although the radiations at 234 and 267 nm are substituted for 248 nm. The latter radiation may not cause the REMPI process for the bromine atoms in one-color-laser experiments.

**D. Photodissociation pathways**

As shown in Fig. 5, the ab initio calculations give rise to the fragmentation processes of CHBr₂Cl for both Br and Br₂ elimination channels. The optimized structures involved in the dissociation channels are also calculated (Fig. 6) and the corresponding energies are listed in Table I. For the TS structure, the Br–C–Br angle is suppressed to 59.8° and C–B bond lengths are elongated asymmetrically to 2.504 and 2.504 Å. The results are defined as the angle between the recoil velocity of Br atom and the transition dipole moment. According to the β values, the symmetry of excited state may be determined. We assume CHBr₂Cl remains in the C₆ symmetry during the photoexcitation process with CHCl group on the xy symmetry plane and the angle Br–C–Br bisected. The 1 A'' ← X 1 A' or the 2 1 A'' ← X 1 A' transitions are then defined, depending on whether the excitation transition is along the plane normal (z axis) or the CHCl plane (xy plane). According to our ab initio calculations, the ground state structure of CHBr₂Cl is optimized to have the Br–C–Br angle of 111.9°. When the transition dipole moment is along the z axis, the corresponding value of α is 34.1°, and in turn, β becomes 1.1, which is consistent with the observed values in the 234 or 267 nm photolysis. When the transition dipole moment is parallel to this axis, then α becomes 55.9° and β becomes 0.06. The x axis is normal to the yz plane which contains the BrBr group. If the transition dipole moment is parallel to this axis, then α corresponds to 90° and β becomes 1. β is evaluated to be between these two extreme values with the transition dipole moment lying on the xy plane, relying on the definition of the x and y axes. Apparently, the appropriate excited state should be with the A'' symmetry, although the radiations at 234 and 267 nm are substituted for 248 nm. The latter radiation may not cause the REMPI process for the bromine atoms in one-color-laser experiments.

**FIG. 4.** Ion images of the Br atoms photofragmented from CHBr₂Cl at (a) 234 and (b) 267 nm. The linearly polarized laser beam is along up and down directions.

**FIG. 5.** The Br₂ and Br dissociation channels of CHBr₂Cl, in which the energies in kJ/mol relative to CHBr₂Cl are computed with CCSD(T/cc-pVTZ level of theory with B3LYP/6-311G(d,p) zero-point energy corrections. The energies in parentheses are obtained at the level of B3LYP/6-311G(d,p). The vertical energies of CHBr₂Cl 1 1 A' and 1 1 A'' are computed with Davidson-corrected multireference CI/cc-pVTZ at optimized ground state (1 A') geometry.
2.706 Å, such that the associated Br–Br moiety may be released. The IRC computation along the adiabatic reaction coordinate was also performed to ensure that the Br$_2$ molecular elimination should be related with the ground state CHBr$_2$Cl.

According to the measurement of anisotropy parameter, 1 $^1A''$ is assigned to be the upper state. As the $(n, \sigma^*)$ band is excited, the elongation of C–Br bond may rapidly cause its rupture, and concomitantly enhance the 1 $^1A$$^\prime$$^\prime$$^\prime$$^\prime - X$$^\prime$$^\prime$ (or 1 $^1A'' - X$$^\prime$$^\prime$ as $C_1$ is used) coupling strength to facilitate the internal conversion, since the CHBr$_2$Cl structure becomes a $C_1$ symmetry. In addition, based on the \textit{ab initio} potential energy surface calculations, there exists a potential well of about 92 kJ/mol depth in the 1 $^1A''$ state to prolong the lifetime of excited CHBr$_2$Cl, and thus favors the occurrence of the internal conversion (Fig. 7). The energy deficit of 52 kJ/mol, upward from the excitation energy at 248 nm (Fig. 5), may be fulfilled while taking into account the minimum state of 1 $^1A''$ (adiabatic transition). Accordingly, a small fraction of population may have a chance to transit to the high vibrational levels of the ground state prior to direct photodissociation, followed by surpassing the transition barrier. By inspecting the calculations of fragmentation processes, a mechanism of asynchronous concerted photodissociation is favored. The two C–Br bonds are elongated asymmetrically in the TS structure, but both break simultaneously to form the Br$_2$ product. In this manner, the Br$_2$ population is slightly vibrationally hot, as observed in this work.

When CHBr$_2$Cl is prepared in a supersonic beam under jet-cooled conditions, a single or only few rotational levels of the electronic ground state may be populated. Upon single photon absorption at 248 nm, the narrow population spread in the excited state restricts the efficiency of level-to-level coupling between the excited and ground states, and thereby no appreciable amount of Br$_2$ product may be detected. In contrast, the present work under the room temperature conditions induces a much broader population distribution in the excited state, thus enhancing the coupling strength to facilitate the internal conversion. In the following, temperature effects on Br$_2$ elimination may lend further support to the photodissociation pathway proposed. The rotational line

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.pdf}
\caption{The B3LYP/6-311G(d,p) optimized geometries of species along the Br$_2$ and Br dissociation channels of CHBr$_2$Cl on its adiabatic singlet ground state potential energy surface, in which the point group in parentheses, the length in angstrom, and the angle in degree.}
\end{figure}
P(37) of Br₂ at 519.68 nm was selected for the temperature-dependence measurements, as shown in Fig. 8, resulting in the intensity enhancement up to 14% within temperature increment from 27 to 52 °C. As the temperature increases, higher levels of excited state are populated such that the increased density of states may strengthen the level-to-level coupling, which results in more efficient internal conversion.

E. Chlorine effect on Br₂ elimination rate

It is worthwhile to inspect the Cl effect on the production rate of Br₂ between CHBr₂ and CHBr₂Cl. Given identical experimental conditions of laser energy and sample pressure, a relative line intensity of Br₂ at 519.68 nm, as normalized to its corresponding absorption cross section at 248 nm, shows that the Br₂ production rate for CHBr₂Cl is slower by four times than that for CH₂Br₂. According to the RRKM calculations, CHBr₂Cl and CH₂Br₂ in the 248 nm photolysis yield similar rate constants of 4.61 × 10⁷ and 4.44 × 10⁷ s⁻¹, respectively, for the Br₂ molecular elimination. This prediction is reasonable since the sum of states above the transition state and density of states in the reactant both are found to increase in the case of CHBr₂Cl. The Cl-substituted compound enlarges its density of states calculated at 5.0 × 10⁴ cm⁻¹, as compared with 1.9 × 10⁴ cm⁻¹ for CH₂Br₂. As in the temperature-dependence experiment, one may anticipate that the increase of the density of states should enhance the probability of level-to-level coupling. Why does the Br₂ production rate for CHBr₂Cl contrarily becomes slower? To answer this question, we have to consider the lifetimes of both excited states. We may anticipate the lifetime of CHBr₂Cl to be shorter from the following two aspects. First, the Cl-substituted halomethane causes the UV spectra redshifted. The C–Br bond fission may then become more rapid as a result of the increase of the available energy, and in turn, the less population in the excited state has the probability to go through the internal conversion. Second, the potential wells for the excited states of CHBr₂Cl and CH₂Br₂ are evaluated at 92 and 110 kJ/mol, respectively, for both Br atoms are symmetrically elongated. The fact suggests that the former excited state may allow a shorter time to undergo the internal conversion. The less lifetime is, the less efficient the level-to-level coupling becomes.

V. CONCLUSION

By using the CRDS technique, we have demonstrated molecular bromine elimination to be a primary photodissociation channel of CHBr₂Cl at 248 nm, excluding the probability of secondary atomic recombination and photofragmentation of energized CHBr₂ fragment. The quantum yield and the vibrational population ratio of Br₂ are determined. The upper state excited by 248 nm is also assigned by analyzing the anisotropy parameter. With the aid of the ab initio potential energy calculations, a photodissociation pathway
via the internal conversion is proposed. The asynchronous concerted mechanism is favored to cause Br2 fragmented vibrationally hot. A Cl-substituted effect is inspected to explain suppression of the production rate of Br3 in the photolysis of CHBr2Cl, with respect to the case of CH2Br2.

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FIG. 8. Temperature dependence of the line intensity of the Br2 rotation at 519.68 nm in photodissociation of CHBr2Cl at 248 nm.