

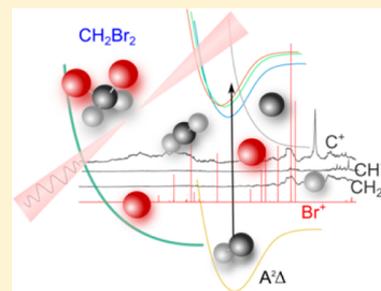
Resonance-Enhanced Multiphoton Ionization of CH₂Br₂: Rydberg States, Photofragmentation, and CH Spectra

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S Supporting Information

ABSTRACT: Mass-resolved (2 + *n*) resonance-enhanced multiphoton ionization (REMPI) spectra of CH₂Br₂ in the two-photon resonance excitation region from 71 200 to 82 300 cm⁻¹ were recorded and analyzed. Spectral structures allowed characterization of new molecular Rydberg states. C*(¹D₂) was found to be an important intermediate in the photodissociation processes. A broad spectral feature peaking at about 80 663 cm⁻¹ in the C⁺ spectrum and frequently seen in related studies is reinterpreted and associated with switching between three- and two-photon ionization of C*(¹D₂). Analysis of band structures due to transitions from the A²Δ state of CH* that were seen in the CH⁺ and C⁺ REMPI spectra allowed characterization of three electronic states of CH, assigned as E²Π, D²Π, and F²Σ⁺, which clarifies a long-term puzzle concerning the energetics of the CH radical. Predissociation of the E, D, and F states to form C*(¹D₂) occurs. Bromine atomic lines were observed and are believed to be associated with bromine atom formation via predissociation of CH₂Br₂ Rydberg states.

**■ INTRODUCTION**

Recently we have undertaken the task of making use of as well as developing the one-color mass-resolved resonance-enhanced multiphoton ionization (REMPI) technique to perform photofragmentation studies of molecules.^{1–9} This paper is a continuation of an ongoing series of spectroscopy and photofragmentation studies of halogenated methyl derivatives by REMPI for resonance excitations into medium- to high-energy Rydberg state regions of the molecules. In addition to being of interest for fundamental studies of photofragmentation processes in molecules, these compounds and their photofragmentation species are of great importance in both atmospheric chemistry and astrochemistry.^{10–14} Our recent REMPI studies of methyl bromide⁴ and CF₃Br⁶ confirmed and added information relevant to their Rydberg state structures and dissociation dynamics. The data revealed clear photodissociation processes to form bromine atoms in both cases. Interactions between Rydberg and ion-pair states are believed to play an important role in the photodynamics of both molecules.^{4,6,15} Unusual bond breaking and C/C* atom formation processes were observed for CH₃Br.⁴

Here we present corresponding REMPI studies of methylene bromide, CH₂Br₂. Very limited information is available on the Rydberg state energetics and relevant photofragmentation processes of CH₂Br₂. Early work on traditional single-photon absorption of the compound^{16,17} revealed a characteristic spectral structure of a weak, broad absorption band in the low-energy region (37 000 – 54 500 cm⁻¹) followed by a series of bands due to transitions to Rydberg states with Rydberg electrons of σ character.¹⁶ Three band series have been assigned to states associated with convergences to three separate ionization limits on the basis of photoelectron

studies.¹⁶ Photodissociation studies relevant to Rydberg state excitations of CH₂Br₂ have mostly been limited to uses of selected single-wavelength excitations. Fluorescence¹⁸ and ion detection studies¹⁹ have revealed several distinct competitive dissociative channels involving the formation of atoms and molecular fragments, such as Br, CH(A²Δ), and CH₂.

The electronic states of the methyldyne radical (CH) as well as its ion (CH⁺) are of great importance in astrochemistry¹⁴ and combustion chemistry. Since the pioneering work by Herzberg and Johns in 1969²⁰ on the spectroscopy of CH, there have been a number of conflicts and unsolved puzzles concerning the spectra due to transitions to high-energy electronic states. A number of detected resonance multiphoton ionization spectra remain to be assigned.²¹ Herzberg and Johns²⁰ reported a spectrum centered at 64 531 cm⁻¹ in single-photon absorption, which they assigned to the F²Σ⁺ state with the 2p σ^2 3p σ Rydberg state electron configuration. A corresponding spectrum could not be detected in multiphoton ionization studies, whereas a spectrum near 63 000 cm⁻¹ was assigned to the band origin of a 2²Σ⁺ upper state (named E'²Σ⁺).²¹ Three high-energy ²Π states were predicted to be found in the energy range from 59 900 to 65 000 cm⁻¹, one of which is a repulsive state.²² The $\nu' = 2$ and 0 levels of the lower-energy (D²Π) and higher-energy (E²Π) bound states, respectively, are predicted to be close in energy, which has caused misassignment and confusion in the literature.^{20,23} The observed band width and hence lifetime alteration and the sudden onset of predissociation processes^{21,23,24} observed in

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these systems are explained as the results of interactions between the $^2\Pi$ states.

In this paper we present REMPI data for CH_2Br_2 and analysis relevant to further clarifying (i) the Rydberg state structure for the CH_2Br_2 molecule; (ii) its photodissociation into C/C^* , $\text{CH}(\text{A}^2\Delta)$, and Br/Br^* fragments; and (iii) the spectroscopy of the $\text{CH}(\text{A}^2\Delta)$ fragment.^{21,25}

EXPERIMENTAL SECTION

Mass-resolved ($2 + n$) REMPI data for jet-cooled CH_2Br_2 gas were sampled. Photoinduced ions were directed into a time-of-flight tube and detected by a microchannel plate (MCP) detector to record the ion yield as a function of mass and laser radiation wavenumber. Signals were fed into a LeCroy WaveSurfer 44MXs-A 400 MHz storage oscilloscope and averaged over 30 laser pulses. The apparatus used was similar to that described elsewhere.^{5,8,26} Tunable excitation radiation in the 480 to 560 nm wavelength region was generated by an excimer-laser-pumped dye laser system using a Lambda Physik COMPex 205 excimer laser and a Coherent ScanMatePro dye laser. The dyes C-540A, C-503, and C-480 were used. Frequency doubling was obtained with a β -barium borate (BBO) crystal (SHG-215, Sirah). The repetition rate was 10 Hz. The bandwidth of the dye laser beam was about 0.095 cm^{-1} . Typical laser intensities used were $0.1\text{--}0.3 \text{ mJ/pulse}$. The laser beam was focused on the molecular beam by a lens with a 20 cm focal length. The number of photons hitting the sample beam per pulse was estimated to be about 10^{14} . CH_2Br_2 vapor from a liquid sample cooled in a trap slightly below room temperature and mixed with argon was pumped through a $500 \mu\text{m}$ pulsed nozzle from a typical total backing pressure of about 1.0 bar into the ionization chamber. The pressure in the ionization chamber was lower than 10^{-6} mbar during the experiments. The nozzle was kept open for about $170 \mu\text{s}$, and the laser beam was fired about $500 \mu\text{s}$ after the nozzle was opened. Mass spectra were typically recorded in laser wavenumber steps of 0.05 or 0.1 cm^{-1} . REMPI spectra for certain ions as a function of excitation wavenumber were obtained by integrating the mass signal intensities for the ion. Laser calibration was based on ($2 + 1$) bromine atom REMPI signals recorded. The accuracy of the calibration was found to be about $\pm 2.0 \text{ cm}^{-1}$ on the two-photon wavenumber scale. Intensity drifts during the scan were taken into account, and the spectral intensities were corrected accordingly. Overall spectra were composed of several shorter scans, each of which was normalized. These scans were then normalized to each other using the intensities of bands common to neighboring sections.

RESULTS AND DISCUSSION

Mass-resolved REMPI data for CH_2Br_2 in the two-photon resonance excitation region from $71\,200$ to $82\,300 \text{ cm}^{-1}$ revealed signals for the ions H^+ , C^+ , CH^+ , CH_2^+ , and $^{79}\text{Br}^+$ ($i = 79, 81$). Figure 1 shows REMPI spectra for the ions C^+ , CH^+ , CH_2^+ , and $^{79}\text{Br}^+$, and those for the ions C^+ , CH^+ , and CH_2^+ are proportional in intensity. H^+ was detected only near $82\,260 \text{ cm}^{-1}$ as a strong signal corresponding to the ($2 + 1$) REMPI of H for the two-photon resonance excitation $\text{H}(n = 2) \leftarrow \leftarrow \text{H}(n = 1)$. All of the spectra for C^+ , CH^+ , CH_2^+ , and $^{79}\text{Br}^+$ showed a common broad underlying spectral structure, which suggests that it is determined by the initial step of the resonance excitations to Rydberg states, whereas the ionization step(s) could vary depending on the excitation wavenumber and ion.

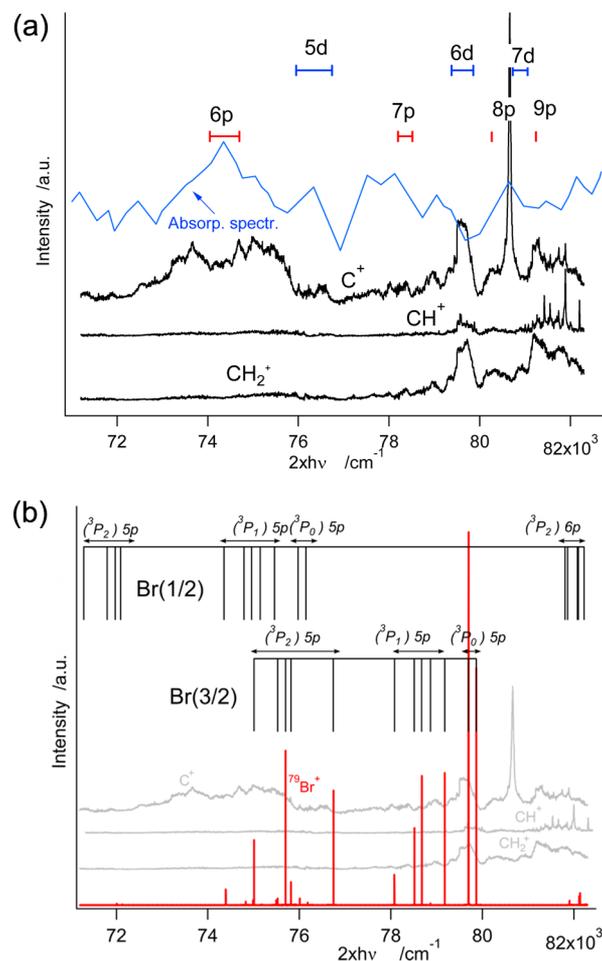


Figure 1. CH_2Br_2 : REMPI spectra of the ions (a) C^+ , CH^+ , and CH_2^+ and (b) $^{79}\text{Br}^+$ for the two-photon excitation region from $71\,200$ to $82\,300 \text{ cm}^{-1}$. The spectra of the ions C^+ , CH^+ , and CH_2^+ are proportional in intensity. In (a), ranges or positions of np and nd Rydberg states are marked (see Table 1), and the absorption spectrum derived by Causley and Russel^{16,36} (in blue) is included. In (b), bromine atomic line transitions are marked.

Comparison of this structure with the one-photon absorption spectrum,^{16,17} which has been interpreted as being due to transitions of halogen lone-pair $p\pi$ electrons to σ^* Rydberg orbitals, shows no clear correspondence between the two spectra. This suggests that the Rydberg states resonantly excited by two photons do not correspond to σ^* Rydberg orbitals but rather to $p\pi$ and $d\pi$ Rydberg orbitals, analogous to what is found for resonance excitation of the monohalomethanes.^{4,15}

The assignment of some spectral features to transitions to Rydberg states are listed in Table 1 and shown in Figure 1a. The assignments were based on the basic assumption that Rydberg states follow the standard expression

$$E([\Omega_c]nl\pi) = IE - \frac{R}{(n - \delta_l)^2} \quad (1)$$

where $E([\Omega_c]nl\pi)$ is the energy of the Rydberg state $[\Omega_c]nl\pi$, IE is the ionization energy of CH_2Br_2 corresponding to the formation of the ground-state parent ion ($83\,962 \text{ cm}^{-1}$),²⁷ R is the Rydberg constant, n is the principal quantum number, and δ_l is the relevant quantum defect parameter, which depends on the angular momentum quantum number, l . Expected quantum defect parameters or value ranges were based on the evaluation

Table 1. Spectral Peaks or Peak Ranges, Assignments (*nl*), and Quantum Defects (δ_l) or Quantum Defect Ranges ($\Delta\delta_l$) for Bands Due to Transitions from Ground-State CH_2Br_2 to Rydberg States

peak or peak range/ cm^{-1}	assignment (<i>nl</i>)	quantum defect (δ_l) or quantum defect range ($\Delta\delta_l$)
74050–74700	6p	2.56–2.67
75950–76745	5d	1.10–1.30
78195–78515	7p	2.51–2.64
79380–79860	6d	0.83–1.11
80265	8p	2.55
80730–81060	7d	0.85–1.17
81238	9p	2.65

of δ_l for Br, Br_2 , and CH_3Br .⁶ No clear evidence for spectral features due to transitions to Rydberg states converging to the first and second electronically excited ionic states,²⁷ analogous to those found in single-photon absorption studies,¹⁶ could be seen.

A characteristic broad “band” sticks out in the C^+ REMPI spectrum, peaking at about $80\,663\text{ cm}^{-1}$ (Figures 1a and 2).

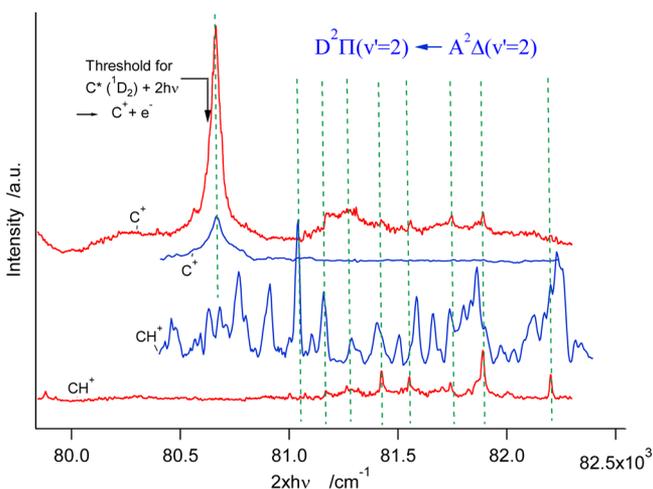


Figure 2. CH_2Br_2 and CHBr_3 : REMPI spectra of the ions C^+ and CH^+ for the two-photon excitation region from $79\,900$ to $82\,300\text{ cm}^{-1}$ for CH_2Br_2 (red; our data) and CHBr_3 (blue; data from refs 21 and 25). Broad peaks near the threshold for two-photon ionization of $\text{C}^*(^1\text{D}_2)$ ($80\,625.27\text{ cm}^{-1}$) due to an enhanced ionization probability are indicated. Sharp bands due to the single-photon resonance excitation from $\text{CH}^*(\text{A}^2\Delta(v'=0))$ fragments are seen in the CH^+ spectra as well as in our (CH_2Br_2) C^+ spectrum above $81\,000\text{ cm}^{-1}$. Dashed lines serve the purpose to guide the eye. The spectra in blue were scanned and reprinted from ref 25 with permission from Elsevier.

Analogous signals were found for the C^+ ions in multiphoton ionization studies of bromoform (CHBr_3)²⁵ and for CH^+ in multiphoton ionization studies of ketene.²¹ These two signals were interpreted to originate from excitation of excited and ground-state CH fragments, respectively, and to involve transitions to repulsive states. By reference to a somewhat analogous observation of ours in REMPI studies of methyl bromide (CH_3Br),⁴ we offer a different interpretation. The broad signal peaking at $80\,663\text{ cm}^{-1}$ is due to an intensity enhancement in the C^+ signal because of an increased transition probability associated with switching from three-photon to two-photon ionization of $\text{C}^*(^1\text{D}_2)$ in the case of a scanning to higher wavenumbers. The threshold for that transformation,

that is, the minimum two-photon excitation of $\text{C}^*(^1\text{D}_2)$ to form C^+ , is $80\,625.27\text{ cm}^{-1}$ (see Figure 3).²⁷ Energetically, $\text{C}^*(^1\text{D}_2)$

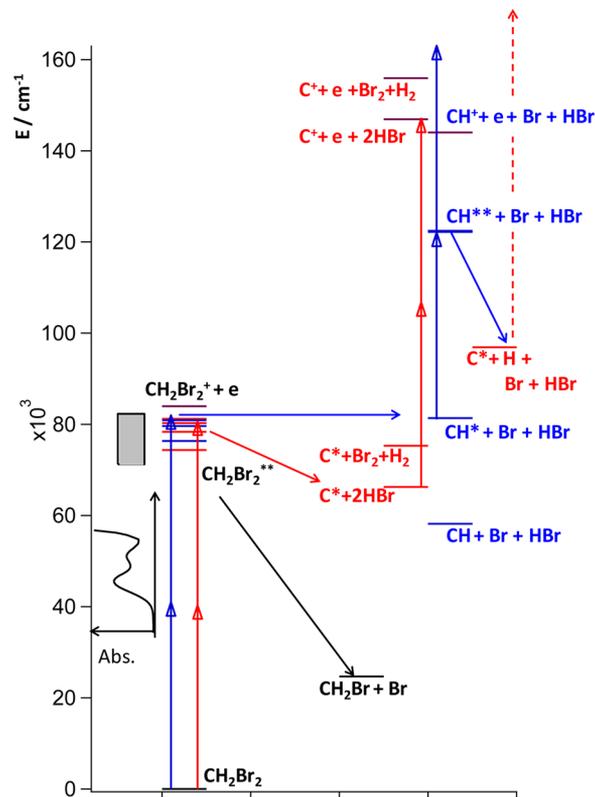
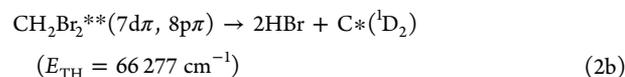
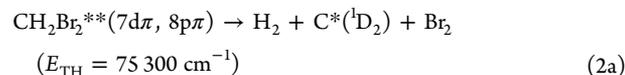


Figure 3. CH_2Br_2 REMPI: Energetics and excitation and photo-fragmentation processes in REMPI of CH_2Br_2 . The shaded area on the left is the scanning region dealt with in this paper. The relative single-photon absorption intensity³⁴ is tilted at the left. $\text{CH}_2\text{Br}_2^{**}$ represents molecular Rydberg states for *np* (red) and *nd* (blue) Rydberg electrons. C^* is the $^1\text{D}_2$ atomic state. CH^* is the excited $\text{A}^1\Delta$ state, and CH^{**} represents the “Rydberg-like” states $\text{E}^2\Pi(v'=0)$, $\text{D}^2\Pi(v'=2)$, and $\text{F}^2\Sigma^+(v'=0)$. The photoexcitation processes shown are for the two-photon wavenumber $80\,625.27\text{ cm}^{-1}$ (red), which corresponds to the threshold for two-photon ionization of $\text{C}^*(^1\text{D}_2)$, and the one-photon wavenumber $40\,991.5\text{ cm}^{-1}$ (blue), which corresponds to the resonance excitation $\text{D}(v'=2) \leftarrow \text{A}(v'=0)$ in CH. See the text for further clarification.

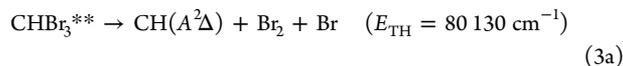
could be formed by dissociation of the $7d\pi$ and/or $8p\pi$ Rydberg state(s) of CH_2Br_2 (see Table 1) as follows:



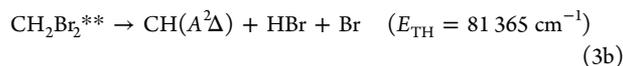
The energy thresholds (E_{TH}) for the dissociation products, derived from the bond energies^{28,19} and the level energy for C^* ,²⁷ are given in parentheses.

The CH^+ and C^+ REMPI spectra in the region from $81\,000$ to $82\,300\text{ cm}^{-1}$ (Figure 2) show bands of analogous structures. Some of these bands match those observed by Chen et al.²⁵ for CH^+ in one-color multiphoton ionization studies of CHBr_3 (see Figure 2). That spectrum was explained as being due to $(1+1)$ $\text{CH}(\text{A}^2\Delta)$ REMPI for the resonance transition $\text{D}^2\Pi(v'=2; J') \leftarrow \text{A}^2\Delta(v''=0, J'')$ after CHBr_3 photolysis. The spectra,

however, differ in complexity, with the spectrum for CHBr_3 showing a lot more bands or peaks. Comparison of the energetics for the two compounds CH_2Br_2 and CHBr_3 reveals a higher threshold energy for the possible formation of $\text{CH}(A^2\Delta)$ following two-photon resonance excitation for CH_2Br_2 compared with that for CHBr_3 :



and



The E_{TH} values are derived from the bond energies^{28,19} and the electronic energy for $\text{CH}(A^2\Delta)$.²⁹ These values correspond to a larger exothermicity for $\text{CH}(A^2\Delta)$ formation for resonance excitation in this spectral region for CHBr_3 compared with CH_2Br_2 , which suggests that the difference in the spectral structures is due to different rotational excitation in the $\text{CH}(A^2\Delta)$ fragments for comparable photon excitation of CHBr_3 and CH_2Br_2 . Alternatively, a rotationally hot $\text{CH}(A^2\Delta)$ formed from CHBr_3 could be the result of dissociation to $\text{CH}(A) + 3\text{Br}$ after three-photon excitation.³⁰ Our simulation of the $\text{CH}(A^2\Delta)$ spectrum for CHBr_3 revealed that the majority of the structure is indeed due to the $D^2\Pi(v'' = 2; J') \leftarrow A^2\Delta(v'' = 0, J'')$ transitions³¹ for rotationally excited (hot) $\text{CH}(A^2\Delta)$ species with a nonthermal (nonequilibrium) rotational distribution. The simulations were performed using the program PGOPHER.³² Some weak structures (bands), on both the high- and low-wavenumber sides of the $D \leftarrow A$ spectrum band origin, however, could not be reproduced by the simulation, suggesting that spectra due to transitions to more electronic states may also be involved. Resonance multiphoton ionization (MPI) spectra of CH radicals in the ground state ($X^2\Pi$) formed by photodissociation of ketene^{21,23} and *tert*-butyl nitrite²³ show features due to the two-photon resonance transition $D^2\Pi(v' = 2; J') \leftarrow X^2\Pi(v'' = 0, J'')$ for highly rotationally excited $\text{CH}(X^2\Pi)$ species. Our attempt to simulate the spectrum derived from ketene³¹ revealed that the spectrum is dominantly due to the $D \leftarrow X$ transition, whereas the MPI spectrum derived from *tert*-butyl nitrite was found to show additional unassigned peaks on the low-wavenumber side of the $D \leftarrow X$ band.²³

Our band-structured spectrum in the region from 81 000 to 82 300 cm^{-1} for CH^+ (Figure 2) could be simulated by assuming that it consisted of three one-photon electronic transitions from the $A^2\Delta(v' = 0)$ state for rotationally cold conditions (Figure 4). The spectroscopic parameters used in the simulation are listed in Table 2. The line widths (FWHM) were found to be rather large (about 10 cm^{-1}). The spectra with one-photon band origins of 40 762, 40 991.5, and 41 155 cm^{-1} were assigned to the upper electronic states $E^2\Pi(v' = 0)$, $D^2\Pi(v' = 2)$, and $F^2\Sigma^+(v' = 0)$ with principal electron configurations at the average internuclear distances (r_e) of $2p\sigma^23p\pi$, $2p\pi^3$, and $2p\sigma^23p\sigma$, respectively. The assignments are based on the following:

- The simulation of the 40 991.5 cm^{-1} band is based on known spectroscopic parameters for the $D^2\Pi(v' = 2)$ state.²⁵
- Herzberg and Johns²⁰ reported a spectrum centered at 64 531 cm^{-1} (41 313 cm^{-1} above the $A^2\Delta$ state) in single-photon absorption, which they assigned to the $F^2\Sigma^+$ upper state with the $2p\sigma^23p\sigma$ Rydberg state

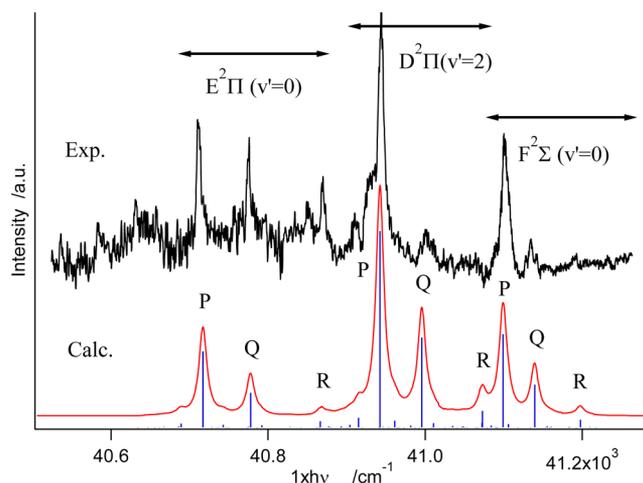


Figure 4. Simulation of a (1 + 1) $\text{CH}(A^2\Delta)$ REMPI spectrum derived from REMPI of CH_2Br_2 showing signals due to single-photon resonance transitions to the CH electronic states $E^2\Pi(v' = 0)$, $D^2\Pi(v' = 2)$, and $F^2\Sigma^+(v' = 0)$. Spectroscopic parameters are listed in Table 2. Line widths (FWHM) are about 10 cm^{-1} . The experimental spectrum is shown in black at the top. Calculated spectra are shown in red and blue at the bottom. It should be noted that the experimental $\text{CH}^*(A^2\Delta)$ spectra and CH^+ signals due to nonresonance transitions following two-photon resonance transitions of the parent molecule CH_2Br_2 were found to overlap.

configuration. Chen et al.²¹ could not identify the corresponding spectrum in the two-photon excitation of $\text{CH}(X)$ and assigned a relatively high intensity band at lower energy, near 63 000 cm^{-1} , to the $E'^2\Sigma^+$ upper state with the $2p\sigma^23p\sigma$ Rydberg state configuration, thus conflicting with the earlier assignment by Herzberg and Johns. Van Dishoeck predicted a $^2\Sigma^+$ state ($2p\sigma^23p\sigma$) close in energy to two $^2\Pi$ states and slightly higher in energy than a diabatic bound $^2\Pi$ potential.^{22,31} Although a transition from $A^2\Delta(v'' = 0, J'')$ with the principal electron configuration $2p\sigma^22p\pi^2$ to a $^2\Sigma^+$ state ($2p\sigma^23p\sigma$) would involve two-electron transfer, it may gain oscillator strength through mixing with nearby $^2\Pi$ states^{21,22} to give a weak absorption signal. All in all, we therefore assign the band at 41 155 cm^{-1} ($T_{00} = 64\,328 \text{ cm}^{-1}$) to the transition $F^2\Sigma^+(v' = 0; J') \leftarrow A^2\Delta(v'' = 0, J'')$.

- The diabatic bound $^2\Pi$ potential with the principal configuration $2p\sigma^23p\pi$ was predicted by van Dishoeck²² to be only slightly lower in energy than the $^2\Sigma^+$ ($2p\sigma^23p\sigma$) state (also see above). Excitation to this state would involve two-electron transfer from $A^2\Delta(v'' = 0, J'')$ at the average internuclear distance, whereas one-electron transfers could be involved for larger internuclear distances.²² Hence, the transition probability is likely to be small. We therefore assign the weak absorption band at 40 762 cm^{-1} ($T_{00} = 63\,935 \text{ cm}^{-1}$) to the transition $E^2\Pi(v' = 0; J') \leftarrow A^2\Delta(v'' = 0, J'')$.

The observation of an analogous structure but weaker signals in the C^+ REMPI spectrum (Figure 2), indicating the $\text{CH}^*(A^2\Delta)$ resonance excitation, most likely is due to couplings between the bound $^2\Pi/{}^2\Sigma^+$ excited states and the “close-in-energy” repulsive $^2\Pi$ state to form $\text{C}^*(^1\text{D}) + \text{H}$ by predissociation followed by two-photon ionization of $\text{C}^*(^1\text{D})$. Such predissociation processes can also explain the relatively large line widths (10 cm^{-1}) and hence the short lifetimes of the

Table 2. Energetic/Spectroscopic Parameters for Excited States of CH

parameter	$A^2\Delta(v' = 0)$	$E^2\Pi(v' = 0)$	$D^2\Pi(v' = 2)^b$	$F^2\Sigma(v' = 0)$
ν_0^c	–	–	40762	40991.5
$T_{v',0}^d$	–	23173.462 ^a	63935	64165
B_v	14.5821	14.5789 ^a	14.58	12.7
D_v	0.00156	0.0015646 ^a	0	0.00158

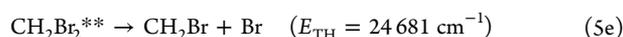
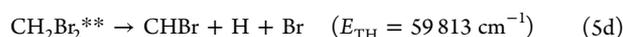
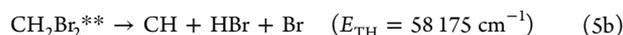
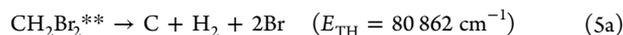
^aValues from ref 29 for comparison. ^bValues from ref 25. ^cBand origin for the transition from $A^2\Delta(v' = 0)$. ^dTerm value for the v' level with respect to $v'' = 0$ for the ground state $\text{CH}(X^2\Pi)$.

upper states (E , D , and F). On the basis of the equation relating lifetimes of upper states (τ) and line widths (FWHM) for long-lived lower states,^{1,8}

$$\tau \text{ (in ps)} > \frac{5.3}{\text{FWHM in cm}^{-1}} \quad (4)$$

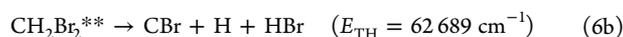
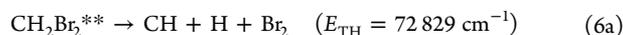
$\tau > 0.53$ ps. The lifetime of the lower state (A) has been found to be long (520 ns).³³

The observed bromine atomic lines (Figure 1b) could partly be due to (2 + 1) REMPI of bromine atoms formed by one-photon photodissociation via excitation to repulsive molecular valence states,³⁴ since a one-photon excitation corresponds to the low-energy tail of the weak absorption band in the near-UV spectral region³⁵ (see Figure 3). However, in view of the number of observations of photofragmentation via Rydberg states, these must also be partly or largely due to REMPI of bromine atoms formed by predissociation of Rydberg states following two-photon excitation. Thus, they will resemble analogous findings for other Br-containing compounds.^{4,6,7} Energetically,^{28,19} a number of Br atom formation channels following two-photon excitation to Rydberg states could be involved:



Among these, the simplest channel (eq 5e), involving only a single bond breaking, is likely to be dominant. Generally, lines due to transitions from the ground state, $\text{Br}(^2P_{3/2})$, are found to be more intense than those due to transitions from the spin-orbit excited state, $\text{Br}^*(^2P_{1/2})$ (Figure 1b), suggesting that dissociative channels forming ground-state Br are more favorable.

The strong (2 + 1) REMPI line of $\text{H}(n = 1)$ detected could be due to H atoms formed by predissociation of Rydberg states. Energetically,²⁸ a number of H atom formation channels following two-photon excitation to Rydberg states could be involved, such as



CONCLUSION

Mass-resolved (2 + n) CH_2Br_2 REMPI spectra for the two-photon resonance excitation region from 71 200 to 82 300

cm^{-1} were recorded and analyzed. H^+ , C^+ , CH^+ , CH_2^+ , and $^i\text{Br}^+$ ($i = 79, 81$) signals were detected (Figure 1). The spectra for all the ions except H^+ show structure due to two-photon resonance transitions to molecular Rydberg states. Quantum defect analysis revealed transitions to molecular states with np and nd bromine-atom-based Rydberg electrons (Table 1 and Figure 3). The spectrum for C^+ shows a broad spectral feature centered at $80\,663 \text{ cm}^{-1}$ associated with switching from three- to two-photon ionization of $\text{C}^*(^1D_2)$, indicating the importance of C^* formation in the photodissociation processes (Figures 2 and 3). The CH^+ and C^+ spectra show bands due to single-photon transitions from the $A^2\Delta(v' = 0)$ state of CH^* . Simulation analysis of the CH^+ spectrum revealed the structure to be due to transitions to three electronic states with band origins of $40\,762$, $40\,991.5$, and $41\,155 \text{ cm}^{-1}$ assigned as $E^2\Pi(v' = 0)$, $D^2\Pi(v' = 2)$, and $F^2\Sigma^+(v' = 0)$, respectively, for rotationally cold $\text{CH}^*(A^2\Delta(v' = 0))$ species. This finding clarifies, to some extent, a long-term puzzle concerning the CH spectroscopy and energetics for this region. Relevant energetic/spectroscopic parameters were determined or verified. The corresponding structure seen in the C^+ spectrum indicates predissociation processes of the upper states [$E(v' = 0)$, $D(v' = 2)$, and $F(v' = 0)$] via a repulsive $^2\Pi$ state to form $\text{C}^*(^1D_2)$ (Figure 3). The observed bromine atomic resonances are associated with bromine atom formation via predissociation of CH_2Br_2 Rydberg states as well as possible single-photon photodissociation (Figure 3).

ASSOCIATED CONTENT

Supporting Information

(1) Calculated CH spectra due to the transitions $D^2\Pi(v' = 2; J') \leftarrow A^2\Delta(v'' = 0, J'')$ as a function of rotational temperature and comparison with experimental spectra from refs 21 and 25; (2) ab initio potential curves for CH derived by van Dishoeck (ref 22) and state energies derived from this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Matthíasson, K.; Wang, H.; Kvaran, Á. $(2 + n)$ REMPI of Acetylene: Gerade Rydberg States and Photorupture Channels. *Chem. Phys. Lett.* **2008**, *458*, 58–63.
- (2) Kvaran, Á.; Wang, H.; Matthíasson, K.; Bodi, A.; Jónsson, E. Two-Dimensional $(2 + n)$ Resonance Enhanced Multiphoton Ionization of HCl: Photorupture Channels via the $F^1\Delta_2$ Rydberg State and *ab Initio* Spectra. *J. Chem. Phys.* **2008**, *129*, No. 164313.
- (3) Kvaran, Á.; Matthíasson, K.; Wang, H. Two Dimensional $(2 + n)$ Resonance Enhanced Multiphoton Ionization of HCl: State Interactions and Photorupture Channels via Low-Energy Triplet Rydberg States. *J. Chem. Phys.* **2009**, *131*, No. 044324.
- (4) Kvaran, Á.; Wang, H.; Matthíasson, K.; Bodi, A. Two-Dimensional $(2 + n)$ REMPI of CH_3Br : Photodissociation Channels via Rydberg States. *J. Phys. Chem. A* **2010**, *114*, 9991–9998.
- (5) Matthíasson, K.; Long, J.; Wang, H.; Kvaran, Á. Two-Dimensional Resonance Enhanced Multiphoton Ionization of H^1Cl ; $i = 35, 37$: State Interactions, Photofragmentations and Energetics of High Energy Rydberg States. *J. Chem. Phys.* **2011**, *134*, No. 164302.
- (6) Kvaran, Á.; Sveinbjörnsson, K.; Long, J.; Wang, H. Two-Dimensional REMPI of CF_3Br : Rydberg States and Photofragmentation Channels. *Chem. Phys. Lett.* **2011**, *516*, 12–16.
- (7) Long, J.; Hróðmarsson, H. R.; Wang, H.; Kvaran, Á. Photofragmentations, State Interactions and Energetics of Rydberg and Ion-Pair States: Two Dimensional Resonance Enhanced Multiphoton Ionization of HBr via Singlet-, Triplet-, $\Omega = 0$ and 2 States. *J. Chem. Phys.* **2012**, *136*, No. 214315.
- (8) Long, J.; Wang, H.; Kvaran, Á. Photofragmentations, State Interactions, and Energetics of Rydberg and Ion-Pair States: Resonance Enhanced Multiphoton Ionization via E and $V(B)$ States of HCl and HBr. *J. Chem. Phys.* **2013**, *138*, No. 044308.
- (9) Long, J.; Kvaran, Á.; Wang, H. REMPI Spectra of HCl: Analysis of $F^1\Delta_2$ Spectral Perturbation. *Acta Phys. Sin.* **2013**, *16*, No. 163302.
- (10) Solomon, S. Stratospheric Ozone Depletion: A Review of Concepts and History. *Rev. Geophys.* **1999**, *37*, 275–316.
- (11) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed.; Wiley: New York, 2006.
- (12) Simpson, M. J.; Tuckett, R. P.; Dunn, K. F.; Hunniford, C. A.; Latimer, C. J. Vacuum-UV Negative Photoion Spectroscopy of CF_3Cl , CF_3Br , and CF_3I . *J. Chem. Phys.* **2009**, *130*, No. 194302.
- (13) Lunine, J. I. *Astrobiology: A Multidisciplinary Approach*; Pearson Addison Wesley: San Francisco, 2005.
- (14) Shaw, A. M. *Astrochemistry: From Astronomy to Astrobiology*; Wiley: Chichester, U.K., 2006.
- (15) Ridley, T.; Hennessy, J. T.; Donovan, R. J.; Lawley, K. P.; Wang, S.; Brint, P.; Lane, E. Evidence for Rydberg Doorway States in Photoion Pair Formation in Bromomethane. *J. Phys. Chem. A* **2008**, *112*, 7170–7176.
- (16) Causley, G. C.; Russel, B. R. Vacuum Ultraviolet Absorption Spectra of the Bromomethanes. *J. Chem. Phys.* **1975**, *62*, 848–857.
- (17) Molina, L. T.; Molina, M. J.; Rowland, F. S. Ultraviolet Absorption Cross Sections of Several Brominated Methanes and Ethanes of Atmospheric Interest. *J. Phys. Chem.* **1982**, *86*, 2672–2676.
- (18) Yang, S.-X.; Hou, G.-Y.; Dai, J.-H.; Chang, C.-H.; Chang, B.-C. Spectroscopic Investigation of the Multiphoton Photolysis Reactions of Bromomethanes (CHBr_3 , CHBr_2Cl , CHBrCl_2 , and CH_2Br_2) at Near-Ultraviolet Wavelengths. *J. Phys. Chem. A* **2010**, *114*, 4785–4790.
- (19) Sharma, P.; Vatsa, R. K.; Maity, D. K.; Kulshreshtha, S. K. Laser Induced Photodissociation of CH_2Cl_2 and CH_2Br_2 at 355 nm: An Experimental and Theoretical Study. *Chem. Phys. Lett.* **2003**, *382*, 637–643.
- (20) Herzberg, G.; Johns, J. W. C. New Spectra of the CH Molecule. *Astrophys. J.* **1969**, *158*, 399–418.
- (21) Chen, P.; Pallix, J. B.; Chupka, W. A.; Colson, S. D. Resonant Multiphoton Ionization Spectrum and Electronic Structure of CH Radical. New States and Assignments above $50\,000\text{ cm}^{-1}$. *J. Chem. Phys.* **1987**, *86*, 516–520.
- (22) van Dishoeck, E. F. Photodissociation Processes in the CH Molecule. *J. Chem. Phys.* **1987**, *86*, 196–214.
- (23) Chen, P.; Chupka, W. A.; Colson, S. D. Multiphoton Spectroscopy and Analysis of the $E^2\Pi \leftarrow X^2\Pi_r$ band of CH. *Chem. Phys. Lett.* **1985**, *121*, 405–407.
- (24) Wang, Y.; Li, L.; Chupka, W. A. $(2 + 1)$ Resonance-Enhanced Multiphoton Ionization Studies of the CH $D^2\Pi(v = 2)$ State. *Chem. Phys. Lett.* **1992**, *192*, 348–352.
- (25) Chen, Y.; Jin, J.; Pei, L.; Ma, X.; Chen, C. Resonance Multiphoton Ionization Spectroscopy of the $D^2\Pi(v = 2) \leftarrow A^2\Delta$ of CH Radicals. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *108*, 221–224.
- (26) Long, J.; Wang, H.; Kvaran, Á. Rydberg and Ion-Pair States of HBr: New REMPI Observations and Analysis. *J. Mol. Spectrosc.* **2012**, *282*, 20–26.
- (27) National Institute of Standards and Technology. NIST Chemistry WebBook. <http://webbook.nist.gov/chemistry/>.
- (28) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Prentice Hall, 2005; <https://archive.org/details/organicchemistry031426mbp>.
- (29) Bernath, P. F.; Brazier, C. R.; Olsen, T.; Hailey, R.; Fernando, W. T. M. L.; Woods, C.; Hardwick, J. L. Spectroscopy of the CH Free Radical. *J. Mol. Spectrosc.* **1991**, *147*, 16–26.
- (30) Chikan, V.; Fournier, F.; Leone, S. R.; Nizamov, B. State-Resolved Dynamics of the CH($A^2\Delta$) Channels from Single and Multiple Photon Dissociation of Bromoform in the 10–20 eV Energy Range. *J. Chem. Phys. A* **2006**, *110*, 2850–2857.
- (31) See the Supporting Information.
- (32) Western, C. M. *PGOPHER, A Program for Rotational, Vibrational and Electronic Spectra*; University of Bristol: Bristol, U.K.; <http://pgopher.chm.bris.ac.uk>.
- (33) Bauer, W.; Engelhardt, B.; Wiesen, P.; Becker, K. H. Lifetime Measurements of GeH and CH in the $A^2\Delta$, $v' = 0$ State by Laser-Induced Fluorescence. *Chem. Phys. Lett.* **1989**, *158*, 321–324.
- (34) Ji, L.; Tang, Y.; Zhu, R.; Wei, Z.; Zhang, B. Photodissociation Dynamics of CH_2Br_2 near 234 and 267 nm. *Spectrochim. Acta, Part A* **2007**, *67*, 273–280.
- (35) Gillotay, D.; Simon, P. C.; Dierckx, L. Temperature Dependence of Ultraviolet Absorption Cross-Sections of Brominated Methanes and Ethanes. *Aeron. Acta A* **1989**, *335*, 706.
- (36) Keller-Rudek, H.; Moortgat, G. K.; Sander, R.; Sörensen, R. The MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest. *Earth Syst. Sci. Data* **2013**, *5*, 365–373.