

CH radical production from 248 nm photolysis or discharge-jet dissociation of CHBr₃ probed by cavity ring-down absorption spectroscopy

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The A-X bands of the CH radical, produced in a 248 nm two-photon photolysis or in a supersonic jet discharge of CHBr₃, have been observed via cavity ring-down absorption spectroscopy. Bromoform is a well-known photolytic source of CH radicals, though no quantitative measurement of the CH production efficiency has yet been reported. The aim of the present work is to quantify the CH production from both photolysis and discharge of CHBr₃. In the case of photolysis, the range of pressure and laser fluences was carefully chosen to avoid postphotolysis reactions with the highly reactive CH radical. The CH production efficiency at 248 nm has been measured to be \( \Phi = N(\text{CH})/N(\text{CHBr}_3) = (5.0 \pm 2.5) \times 10^{-3} \) for a photolysis laser fluence of 44 mJ cm\(^{-2}\) per pulse corresponding to a two-photon process only. In addition, the internal energy distribution of CH(X \(^2\)I) has been obtained, and thermalized population distributions have been simulated, leading to an average vibrational temperature \( T_{\text{vib}} = 1800 \pm 50 \text{ K} \) and a rotational temperature \( T_{\text{rot}} = 300 \pm 20 \text{ K} \). An alternative technique for producing the CH radical has been tested using discharge-induced dissociation of CHBr₃ in a supersonic expansion. The CH product was analyzed using the same cavity ring-down spectroscopy setup. The production of CH by discharge appears to be as efficient as the photolysis technique and leads to rotationally relaxed radicals. © 2006 American Institute of Physics.

I. INTRODUCTION

The vacuum ultraviolet (vuv) solar photodissociation of bromoform (CHBr₃), mostly at the Lyman-\( \alpha \) wavelength (121.6 nm), has been the subject of numerous discussions in the past (see for instance Ref. 1, and references therein). This mechanism is indeed a dominant source of stratospheric atomic bromine, one of the most destructive species of stratospheric ozone.

In the laboratory, the photolysis of bromoform has been extensively studied by using laser beams at various fixed wavelengths, mainly 266 nm, \(^{2,6} \) 248 nm, \(^{7} \) and 193 nm. \(^{8} \) The Br, Br₂, CHBr, CBr, CH(X \(^2\)I), and CH(\(^2\)Δ) products have been probed by using various techniques, e.g., photofragment translational spectroscopy, \(^{9,10} \) ion velocity imaging, \(^{11} \) laser induced fluorescence (LIF), \(^{3,6-8,12} \) and cavity ring-down spectroscopy (CRDS).\(^{13,14} \) All the above photolysis experiments were performed with significantly high laser fluences, resulting in multiphoton processes whose interpretation is not trivial. As an example, the excitation mechanism for the production of Br₂ is still controversial. Although the dissociation into Br₂ is energetically allowed by one-photon absorption, either at 248 or at 193 nm photon energy, a debate exists as to whether this dissociation proceeds through one- or two-photon absorption.\(^{15,14} \) This issue has been summarized recently by Zou et al.\(^{10} \)

In this context, very few investigations have been carried out by using the CRDS technique coupled with a photolytic production of radicals. In the case of CHBr₃, only two CRDS studies are reported in the literature. They concern the spectroscopic detection of Br₂ and CBr₂ fragments.\(^{13,14} \)

In addition to the production of brominated fragments, bromoform is an efficient precursor of CH radicals (methylidyne) and will be studied in the present paper as a CH radical source. Indeed, CH plays a primary role in the carbon chemistry of interstellar and circumstellar media, as well as in planetary atmospheres, and thus it has been the subject of many laboratory studies. This radical has been studied as an important reactant with other molecules.\(^{3,5,8,15-17} \) It has been characterized by several techniques, mostly by LIF, yielding

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information on the internal energy distribution in its ground state\textsuperscript{2} or in its excited states\textsuperscript{4,12,13,18,19} following 266, 248, and 193 nm photolysis. Depending on its nascent state population, production of this radical by 248 nm photolysis of CHBr\textsubscript{3} requires either a two-photon or a three-photon photolysis scheme for CH\textsuperscript{+}/H\textsubscript{2}O\textsubscript{849} \textsuperscript{X}/H\textsubscript{9016}/H\textsubscript{2}O\textsubscript{850} or CH/CH\textsubscript{2}/H\textsubscript{9004}/H\textsubscript{2}O\textsubscript{850}/H\textsubscript{9018}/H\textsubscript{2}O\textsubscript{850}, respectively.\textsuperscript{12} Note that the multiphoton mechanism for CH production, involving either a direct or a sequential dissociation, is not well understood yet. However, progress has been made very recently by Chikan et al.,\textsuperscript{19} who have been able to explain the CHBr\textsubscript{3} dissociation mechanisms, following single and multiple photon excitations in the 10–20 eV energy range. The reactivity of excited CH in the A\textsuperscript{2}Σ\textsuperscript{+}/H\textsubscript{9004} or B\textsuperscript{2}Σ\textsuperscript{−}/H\textsubscript{9018}/H\textsubscript{2}O\textsubscript{850} states has also been studied via quenching measurements.\textsuperscript{5} Nevertheless, in none of the previous experiments has the absolute number density of the CH photolytic fragments been reported.

Since bromoform is known as an efficient source of CH radicals, it is highly interesting to evaluate the rate of production by controlling the photolysis experimental conditions. The aim of this work is to quantify this production in terms of radical formation efficiency. A very efficient technique for measuring ground state concentrations is CRDS. We have applied this technique to a gas mixture of Ar/CHBr\textsubscript{3} within well defined experimental conditions of partial pressure and laser fluence in order to control, in particular, the multiphoton process for the ground state CH production. This is, to our knowledge, the first measurement of photolytic CH by CRDS.

Alternatively, another well-known source of CH radicals arises from discharge in bromoform. We have carried out a complementary approach yielding CH from a discharge in a He/CHBr\textsubscript{3} molecular beam. In order to compare the efficiency of photolysis and discharge-induced productions, the experiment has been carried out using the same CRDS probe technique within the same optical cavity arrangement. In both experiments, the CH(X\textsuperscript{2}Π) radical was detected on the A-X absorption bands around 430 nm. Internal vibrational and rotational energy distributions deduced from these two experiments are also presented in this paper.

II. EXPERIMENT

Photolysis and discharge experiments for measurements of the CH radical production from CHBr\textsubscript{3} were performed in a low pressure chamber apparatus equipped with CRDS mirrors as shown in Fig. 1. The experimental parameters for the CRDS detection are defined in Sec. II A below. The conditions for the CH production and detection are detailed in Sec. II B.

A. Principle of cavity ring-down absorption

CRDS is based on the principle of measuring the intensity decay rate of a laser pulse coupled to a stable optical cavity. Briefly, the laser intensity collected at the exit mirror of the ring-down cavity decays exponentially with time as

\[ I(t, \lambda) = I_0(0, \lambda) \exp \left( \frac{-t}{\tau(\lambda)} \right), \]

where \( I_0(0, \lambda) \) is the laser intensity at the entrance of the cavity and \( \tau(\lambda) \) is the ring-down time constant. When there is no absorber in the cavity, the corresponding ring-down time constant is then noted \( \tau_0(\lambda) \), and the decay rate is only

![FIG. 1. Scheme of the experimental CRDS setup with a typical ring-down decay signal in the insert. M\textsubscript{1} and M\textsubscript{2} are the CRDS mirrors and \( D \) is the cavity length. (a) Detail of the interaction zone in the 248 nm photolysis experiment of CHBr\textsubscript{3}; \( \ell_p \): effective absorption length of the CH radicals produced by photolysis (\( \ell_p=20 \) mm), \( \omega_0 \): focal waist radius of the CRDS laser in the center of the cavity (\( \omega_0=252 \) \( \mu \)m). (b) Detail of the interaction zone in the supersonic jet-discharge experiment; \( \ell_d \): effective absorption length of the CH radical produced in the discharge (\( \ell_d=70 \) mm, \( \omega_0 \); see (a)).](Image)
related to the empty cavity losses, meaning that, if scattering losses are negligible, it can be expressed as a function of the mirror reflectivity \( R(\lambda) \), the cavity length \( D \), and the light speed \( c \) such as

\[
\frac{1}{\tau_0(\lambda)} = -\frac{c \ln R(\lambda)}{D}.
\]

When an absorbing species is present in the cavity (here the CH radical produced either by photolysis or by discharge in CHBr\( _3 \)), the decay rate increases due to the additional loss by absorption. Assuming a thin absorbing medium, the decay rate is given by

\[
\frac{1}{\tau(\lambda)} = \frac{1}{\tau_0(\lambda)} + \frac{c\ell\sigma(\lambda)N}{D},
\]

where \( \ell \) is the effective absorption length along the cavity axis (so-called \( \ell'_p \) in the photolysis experiment or \( \ell_d \) in the discharge experiment; see Fig. 1 and Sec. II B below), \( \sigma(\lambda) \) is the absorption cross section at a given wavelength, and \( N \) is the absorber number density in the interaction region.

By measuring the ring-down time constant for a species for which the absorption cross section is known, with and without this absorber in the cavity, one has access to the absorber absolute number density with high sensitivity, due to the special property of the CRDS technique which avoids the shot-to-shot laser intensity fluctuations.

B. Experimental details for CH production and detection

In the 248 nm photolysis experiment, argon buffer gas (Air Liquide) was bubbled in a small reservoir of liquid CHBr\( _3 \) (Lancaster Chemicals, 97\% CHBr\( _3 \) in ethanol used without further purification) at room temperature. The gas mixture flowed slowly in the vacuum cell at a steady total pressure between 0.27 and 2.7 mbars.

The 248 nm photolysis laser beam was delivered by a KrF excimer laser (ATL, Atlex 150, Lasertechnik GmbH; repetition rate of 10 Hz and laser pulse duration of 20 ns) with an output energy of 10–120 mJ/pulse. It passed unfocused through the center of the cell (\( \ell'_p = 20 \text{ mm} \) and height of 8 mm) and was crossed at a right angle by a probe dye laser beam propagating along the cavity axis. This probe laser beam was provided by an excimer (Lumonics, PM 886, XeCl) pumped dye laser (Lambda Physik, FL 2002) operating near 430 nm (Stilben 420 dye) in the region of the CH(\( A^2\Delta \leftarrow X^2\Pi \)) absorption bands. The dye laser spectral bandwidth was 0.20±0.02 cm\(^{-1}\) and its energy was measured to be less than 10 \( \mu\text{J} \) pulse at the cavity entrance after 20 m propagation from the laser output. In this configuration, no spatial filtering of the CRDS beam was needed since all transverse modes were eliminated due to their divergence, except for the TEM\(_{00}\) mode. The cavity spherical mirrors (Layertec GmbH, \( R \approx 99.93\% \) at 430 nm, 1 m curvature radius) were installed at \( D = 63.5 \text{ cm} \) apart from each other. Hence, the ring-down time constant \( \tau_0 \) for the empty cavity was about 3 \( \mu\text{s} \). The effective interaction volume was estimated to be \( \pi \times 0.25 \times 0.25 \times 20 \text{ mm}^3 \) in the overlapping region of the two laser beams [see Fig. 1(a) for a detailed description of the interaction region]. Both photolysis and CRDS lasers were synchronized in order to fire simultaneously.

In order to minimize particle deposition, both the CaF\(_2\) window of the photolysis beam entry and the CRDS mirrors were gently flushed with Ar. The transmitted beam light was collected at the exit of the rear mirror by a photomultiplier tube (Hamamatsu R955). The signal was amplified (LeCroy preamplifier VV100BTB) and processed by a personal computer equipped with a high speed acquisition card (Gage-scope CS 14100, v 1.1, 14 bits). A homemade LABVIEW program was used to make a shot-to-shot fitting of the signal to a single-exponential decay between 90\% and 7\% of the transmitted light (i.e., between 0.1\( \tau_0 \) and 2.3\( \tau_0 \) after the photolysis laser). The ring-down time measurement was performed with CHBr\(_3\) in the cavity by recording one scan with the photolysis laser off (\( \tau_0 \)) and one scan with the photolysis laser on (\( \tau \)). The 1/\( \tau_0 \) loss contribution was then subtracted from the 1/\( \tau \) measurement.

Discharge production of CH was also performed in the same vacuum chamber by adapting a nozzle and a pulsed discharge system to the gas entry [see Fig. 1(b)]. This second experimental configuration allowed working in supersonic expansion conditions. Since one of our objectives was to compare two different CH radical production methods (photolysis and discharge), the same CRDS probe method was used. The molecular beam consisted of Ar or a He/CHBr\(_3\) gas mixture with an upstream rare gas pressure of 6 bars (the rare gas flowed gently above a liquid surface of CHBr\(_3\)). The pulsed nozzle (General valve, 1 mm diameter aperture) was triggered to open 100 \( \mu\text{s} \) before the probe laser with an optimized opening duration of 200 \( \mu\text{s} \). The discharge was produced just at the exit of the nozzle with a bias voltage of ~900 V applied between two electrodes, the closest one to the nozzle being grounded [see Fig. 1(b)]. The molecular beam carrying the cooled CHBr\(_3\) molecules as well as the discharge products crossed the axis of the CRDS laser beam at a right angle 2.5 cm from the nozzle, resulting into an approximate effective interaction volume of \( \pi \times 0.25 \times 0.25 \times 70 \text{ mm}^3 \) (\( \ell_d = 70 \text{ mm} \)). The CH absorption signal was processed as described above.

All wavelengths reported in this article are given in air, and wavelength calibration was checked through comparison with the simulated spectra performed with the LIFBASE program.\(^{20}\)

III. RESULTS AND DISCUSSION

A. General considerations on CHBr\(_3\) photolysis

Figure 2 displays a panoramic overview of the excitation and relaxation channels for the bromoform molecule in the 0–13 eV energy region. The right panel shows the measured one-photon absorption cross section of CHBr\(_3\) retrieved from Refs. 21–23 and the left panel presents the different dissociation channels\(^{10}\) involving atomic and molecular bromine elimination, together with the excited state energies of the mother molecule.\(^{24}\)

It is worth noting that absorption begins to be significant above 4 eV. As shown in this figure, the lowest triplet states
FIG. 2. Left panel: Diagram of the thermodynamic dissociation thresholds for the CHBr3 molecule relevant for CH production adapted from Ref. 10, together with the CHBr3 energy levels extracted from Ref. 24. Each arrow on the diagram symbolizes the 248 nm one-photon energy. Right panel: One-photon absorption cross section (Ref. 36) of CHBr3 (straight line: Ref. 21, dashed line: Ref. 22, and Ly-α measurement: Ref. 23). Of CHBr3 are indeed accessible at the photon energy of 248 nm, i.e., 5 eV, with an absorption cross section of about $2 \times 10^{-18}$ cm$^2$. At this energy, two dissociation channels relevant for further CH production are thermodynamically opened, namely, CHBr2 + Br at 2.77 eV and CHBr + Br2 at 3.61 eV.

At 248 nm two-photon energy (i.e., 10 eV), Fig. 2 shows that three new dissociation channels are energetically accessible, namely,

\begin{equation}
\text{CHBr}_3 + 2h\nu \rightarrow \text{CHBr} + 2\text{Br} \quad \text{at} \quad 5.59 \text{ eV},
\end{equation}

\begin{equation}
\text{CHBr}_3 + 2h\nu \rightarrow \text{CH}(X^2\Pi) + \text{Br} + \text{Br}_2 \quad \text{at} \quad 7.06 \text{ eV},
\end{equation}

\begin{equation}
\text{CHBr}_3 + 2h\nu \rightarrow \text{CH}(X^2\Pi) + 3\text{Br} \quad \text{at} \quad 9.04 \text{ eV}.
\end{equation}

The above thresholds are extracted from Ref. 10. It is noteworthy from Fig. 2 that the production of excited CH in the $A^2\Delta$ state is not accessible by two-photon excitation at 248 nm and requires at least a three-photon process.

B. Control of the CHBr3 photolysis experimental parameters for CH(X) production

As mentioned in Sec. III A above, the CRDS technique was previously used in order to detect and measure the quantum yield of the Br$_2$ molecule.$^{14}$ To our knowledge, no such experimental scheme has been applied to probe the CH fragment production from CHBr3 photolysis. Unlike the bromine molecule which is a stable product, the CH radical is known to be very reactive. In order to measure the production and internal energy distributions of this radical, it is essential to check that the photolysis has been performed within the two following conditions:

(i) The CH($X^2\Pi$) number density must arise only from the primary two-photon photolysis process of CHBr3. Therefore further secondary production of CH(X) through relaxation of CH(A) produced via three or more photon absorptions must be eliminated by careful control of the laser fluence.

(ii) To avoid a rapid loss of the CH($X$) radical by reaction with the more abundant CHBr3 species before the detection step is completed, a low concentration of CHBr3 in Ar is required in order to minimize the reactive channels. Further collisions with the Ar buffer gas occur, but have no effect on CH reactivity.

The control of the conditions cited above is demonstrated in Figs. 3 and 4. Figure 3 displays the laser pulse energy dependence of the CRDS signal performed on the $R_1(1.5)$ line of the CH($A^2\Delta$ − $X^2\Pi$) absorption band system at 4303.9 Å for a constant total pressure of 2 mbar in the experimental chamber. The energy range of the measurements corresponds to laser pulse fluences between 9 and 78 mJ cm$^{-2}$ and to a photon flux between 9.5 and 84.6 $\times 10^{13}$ photons s$^{-1}$ cm$^{-2}$. The average accuracy on the measurements is better than 10%.

FIG. 3. Dependence of the CRDS signal as a function of the photolysis laser pulse energy plotted on a log-log scale, yielding a slope of 1.82 ± 0.30. The measurement has been performed on the $(0,0)$ $R_1(1.5)$ line of the CH($A^2\Delta$ − $X^2\Pi$) absorption band system at 4303.9 Å for a constant total pressure of 2 mbar in the experimental chamber. The energy range of the measurements corresponds to laser pulse fluences between 9 and 78 mJ cm$^{-2}$ and to a photon flux between 9.5 and 84.6 $\times 10^{13}$ photons s$^{-1}$ cm$^{-2}$. The average accuracy on the measurements is better than 10%.

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Figure 4 displays the total pressure dependence of the CRDS signal performed on the same spectral line at a constant laser pulse fluence of 44 mJ cm$^{-2}$. The signal is thus in the regime where it varies quadratically with laser intensity, as can be checked in Fig. 3. The pressure study clearly exhibits a linear dependence in the range of 0–2 mbar. This demonstrates that the rapid disappearance of CH($X$) by reaction is negligible within our experimental conditions.

In conclusion, the present experiment reveals to be a well-controlled technique for measuring the CH($X$) production after a two-photon photolysis of CHBr3 at 248 nm.
C. Internal population distribution of the photolytic CH(X) product

Figure 5(a) presents an experimental cavity ring-down absorption spectrum of \( CH(A \rightarrow X) \) produced by CHBr3 photolysis at 248 nm. The experimental conditions are a constant laser pulse fluence of 44 mJ cm\(^{-2}\), 1.2 bar of Ar bubbled through the CHBr3 reservoir, and a constant total pressure in the vacuum chamber of 1.33 mbar for the CHBr3/Ar mixture. These conditions ensure that the experiment is performed in a nonreactive regime for the CH(X) fragment and within a two-photon excitation process, as discussed in Sec. III B above.

For comparison, Fig. 5(b) presents the corresponding simulated spectrum obtained with the LIFBASE program,\(^{26}\) where vibrational and rotational population distributions have been optimized to reproduce the experimental data and extract the CH(X) product internal population.

In our buffer gas pressure conditions, it is expected that collisional relaxation occurs with argon, affecting both nascent rotational and vibrational populations. Rotational thermalization is rapid, on the order of a few hundred nanoseconds,\(^7\) that is, a time scale shorter than the cavity ring-down time. It is thus expected that the rotational population of CH radicals produced in the bulk photolysis experiments performed at room temperature is completely thermalized at 300 K. This has been satisfactorily checked by the simulation, giving a rotational Boltzmann temperature \( T_{\text{rot}} = 300 \pm 20 \) K.

As for the vibrational distribution, thermalization is much slower\(^25\) and is not expected to be completed within the time scale of the ring-down cavity detection (i.e., \( \sim 7.5 \) \( \mu \)s). The simulation of Fig. 5(b) indicates an average vibrational temperature of \( T_{\text{vib}} = 1800 \pm 50 \) K, in satisfactory agreement with the observed spectrum of the CH(X) photolytic products [Fig. 5(a)]. This vibrational temperature implies a significant population of the \( v = 1 \) level. This is not surprising since there is probably an excess of internal energy deposited in the fragment after CHBr3 photolysis at 248 nm two-photon energy (maximum available excess energy of \( \sim 3 \) eV).

This vibrational temperature is lower than that obtained previously for a 248 nm photolysis of CHBr3, and measured either by degenerate four-wave mixing\(^7\) (\( T_{\text{vib}} = 3400 \) K) or by LIF (Ref. 26) (\( T_{\text{vib}} = 3000 \) K). This can be understood by the relatively long time typical of a cavity ring-down measurement, favoring partial vibrational relaxation of the CH(X) product.

D. Measurement of the CH(X) photolytic production efficiency

Two conditions are necessary to ensure an absolute concentration measurement by means of single wavelength absorption with the CRDS technique: (i) the signal must exhibit a pure monoexponential decay behavior and (ii) the line-width of the absorption feature must be much broader than the laser bandwidth as discussed by Zalicki and Zare\(^{27}\) and Yalin and Zare.\(^{28}\)

In our experiment, the sample absorption constituted only a small fraction of the cavity losses ensuring that the first requirement mentioned above was fulfilled. On the other hand, the laser bandwidth was about three times larger than...
the CH Doppler absorption linewidth, in contradiction with the second requirement. Nevertheless, according to Zalicki and Zare,27 a precise determination of the absolute absorber concentration can still be extracted from experimental data provided that integration over the whole experimental absorption line is performed. Indeed, such a data analysis reveals to be much less sensitive to finite laser bandwidth effects on the CRD signal as was checked by Luque et al.29

By assuming a small absorption to ensure the validity of the Beer-Lambert law, one can express the integrated absorption loss over a chosen rotational line (so-called RL) as a function of the CH number density $N_{\text{CH}}$ in the lower quantum state of the transition and as a function of the integrated single line absorption cross section $\sigma_{\text{CH}}$ such as

$$\int_{\text{RL}} \left[ \frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} \right] d\lambda = \sigma_{\text{CH}} N_{\text{CH}} f_{\text{L}}^\text{RL}. \quad (5)$$

For a Gaussian profile for both absorption and laser linewidths, this gives

$$\int_{\text{RL}} \left[ \frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} \right] d\lambda = \frac{2(2S'' + 1)(2J'' + 1)}{2(2S' + 1)(2J' + 1)} \frac{h B_{\text{CH}}}{\tau_0} \lambda_0 \times \frac{N_{\text{RL}}}{D}, \quad (6)$$

where $S'$, $S''$, $J'$, and $J''$ are the spin and rotational quantum numbers of the rotational transition with the Hund’s case (a) notation, $B_{\text{CH}}$ is the Einstein absorption coefficient for the relevant rotational line, and $\lambda_0$ is the center line wavelength.

The population of the lower quantum state (so-called $N_{\text{CH}}$) is given by

$$N_{\text{CH}}^\text{Q} = \frac{N_{\text{CH}}}{S_{J'P'}}, \quad (7)$$

where $S_{J'P'}$ is the Hönl-London factor of the rotational line RL as given in the LIFBASE program.20

In the general case, the total CH number density in the $X^2\Pi, v=0$ ground state can be expressed as

$$N_{\text{CH}}^\text{tot} = \frac{N_{\text{CH}}^\text{Q}}{f^\text{Q}}, \quad (8)$$

where $f^\text{Q}$ is a parameter depending on the initial quantum state of the chosen rotational line RL, on the rotational distribution in the $v=0$ level, and on the rotational partition function in the $v=0$ level.

Assuming a Boltzmann thermal rotational equilibrium in the $v=0$ level, and a Franck-Condon factor equal to 1 for the (0,0) band which precludes contributions from higher $(v',0)$ bands, the $f^\text{Q}$ factor depends very simply on the rotational temperature via the Boltzmann rotational distribution and the corresponding partition function as given for instance in Ref. 31.

If a vibrational population distribution is assumed among the lowest $v''$ levels, the total number of CH radicals formed in the $X^2\Pi, v=0$ electronic ground state is given by

$$N_{\text{CH}}^\text{tot} = \frac{N_{\text{CH}}^\text{Q}}{q_{\text{vib}}(v=0)} \times f^\text{Q}(T_{\text{CH}}) = \frac{N_{\text{CH}}^\text{Q}}{N_{\text{CH}}^\text{Q,CH}}, \quad (9)$$

where $q_{\text{vib}}(v=0)$ is the relative vibrational population of CH in the ground state.

As discussed in Sec. III C above, the best simulation reproducing the experimental spectrum obtained by photolysis of CHBr$_3$ corresponds to both a thermal rotational distribution, $T_{\text{rot}}=300$ K, and a thermal vibrational distribution, $T_{\text{vib}}=1800$ K. The rotational line $R_1(1.5)$ [using Hund’s case (a) notation] of the (0,0) band at 4303.9 Å is the strongest line in the experimental spectrum of Fig. 5, hence it has been used to determine the concentration $N_{\text{CH}}^\text{RL}$ of Eq. (5) above. $S_{J'P'}$, $q_{\text{vib}}(v=0)$, and the product $f^\text{Q}(T_{\text{CH}}) = f^\text{Q}(T_{\text{CH}}) \times q_{\text{vib}}(v=0)$ are extracted from the LIFBASE simulation.20

The following values used in Eqs. (5)–(9) are given below:

- $N_{\text{CH}}^\text{RL} = 3.15 \times 10^9$ molecules cm$^{-3}$ from our experimental spectrum, using Eqs. (5) and (6).
- $B_{\text{CH}} = 6.65 \times 10^{18}$ m$^3$ J$^{-1}$ s$^{-2}$, taken from Ref. 30.
- $S_{J'P'} = 3.015$ from Ref. 20.
- $f^\text{Q}(T_{\text{CH}}=300$ K)$=0.1076$ from Ref. 20.
- $q_{\text{vib}}(v=0)=0.8859$ from Ref. 20.

According to Eq. (9), the absolute number density for CH has been derived from our CRDS measurement of the $R_1(1.5)$ $v=0$ line to be $N_{\text{CH}}^\text{tot}=(3.6\pm1.0) \times 10^{10}$ molecules cm$^{-3}$. The uncertainty on this CH number density is an upper estimate, mainly due to the uncertainty on the quantum state relative population affecting the $R_1(1.5)$ line intensity. This population has been determined by simulating the rotational and vibrational distributions, with the assumption of given rotational and vibrational temperatures. The subsequent error accounts for 20% uncertainty on the $N_{\text{CH}}^\text{tot}$ measurement.

At this point, if one wants to compare this CH number density with the CHBr$_3$ mother molecule number density, it is necessary to evaluate the initial concentration of bromoform molecules in the interaction volume. Indeed, it is well known that bubbling conditions do not yield the vapor pressure value at the thermal equilibrium for the molecules evaporating from the liquid phase. For this purpose, a calibrated gas bulk mixture was used to measure the CHBr$_3$ absolute number density in our experiment. This calibrated mixture consisted of 4.5 mbars of CHBr$_3$ in 14 bars of argon, with a greater dilution than in the bubbling conditions described above. It was introduced in the vacuum chamber at a total pressure of 2.2 mbars corresponding therefore to $N_{\text{CHBr}_3}(1.8\pm0.4) \times 10^{12}$ molecules cm$^{-3}$ of CHBr$_3$ in the interaction volume with the photolysis laser. Then, by comparing the CRDS signal on the $R_1(1.5)$ line for this calibrated mixture with the corresponding signal for the bubbling mixture conditions of Fig. 5(a), a simple proportionality law yields an actual CHBr$_3$ number density of $(7.1\pm1.6) \times 10^{13}$ molecules cm$^{-3}$. This calibration was performed only on the $R_1(1.5)$ strongest line due to the weaker
CRDS signal obtained with the diluted calibrated gas mixture. The uncertainty on the CHBr₃ number density is mainly related to the concentration fluctuations observed during the different calibration measurements. These fluctuations have been estimated to be \( \sim \pm 20\% \).

Since the photolysis experiment was performed with 1.2 bar of argon gas bubbling through liquid CHBr₃ (pressure conditions given in Sec. III C), the CHBr₃ partial pressure in the mixture volume upstream from the chamber could be estimated at 1.9 mbar. This value is a reasonable estimate, expected to be lower than the maximum value, i.e., the vapor pressure of CHBr₃ at equilibrium, 7 mbars at 300 K.

We define the production efficiency of CH(X) in the 248 nm two-photon photolysis process as the ratio between the total number density of CH(\( X^2S \)) detected in the experiment and the initial number of CHBr₃ present in the photolysis interaction volume: \( \Phi = \frac{N_{\text{tot}}^\text{CH}}{N_{\text{CHBr}_3}} \). Hence, from the relevant number densities extracted above, \( \Phi \) has been estimated to be \( (5.0 \pm 2.5) \times 10^{-4} \) for a 248 nm two-photon process and a photolysis laser fluence of 44 mJ cm\(^{-2}\)/pulse (corresponding to an unfocused laser output energy of 71 mJ/pulse). The large error on the \( \Phi \) value originates from two equivalent major sources of uncertainties affecting the CH and the CHBr₃ number density, as explained above. The subsequent production efficiency may be extrapolated to whatever laser pulse fluence, provided that it lies in the two-photon controlled excitation regime as was shown in Fig. 3, and to whatever mixture of CHBr₃ (vapor pressure) in Ar within the range \([0–1.6 \text{ mbar}]\) for the total pressure, as shown in Fig. 4.

Note that, to our knowledge, this is the first reported value for the CH radical production efficiency. This production efficiency should not be confused with the photodissociation quantum yield for a two-photon photolysis process at 248 nm, although it is related in some way. This process is very difficult to evaluate in our case due to the multiple photodissociation pathways and/or the lack of data for the two-photon absorption cross section of CHBr₃. Nevertheless, the value of \( \Phi \) is meaningful because CRDS is such a sensitive technique that it allows the detection of almost any CH radical produced in the interaction volume.

### E. CH(X) production in a CHBr₃ pulsed supersonic-jet discharge

As was mentioned in the Introduction, a discharge production of CH radicals has also been carried out using the same CRDS detection [see Fig. 1(b) for details]. For practical purposes, it has been chosen to couple the discharge with a supersonic free jet configuration (6 bars of argon passing over liquid CHBr₃) in order to optimize the bromoform density in the interaction volume. Two buffer gases, argon and helium, were tested in this supersonic expansion. By using argon, a worse signal-to-noise ratio was obtained than by using helium, with the occurrence of many additional extra lines arising from atomic and ionized discharge products. Hence argon buffer gas results have not been exploited here and only the results obtained with helium gas are shown. This issue also has been addressed by Deselnicu et al. in a very recent work \(^3\) on CHBr production using a pulsed electrical discharge through a mixture of CHBr₃ in Ar, He, or Ne with conditions very similar to ours. Among the three tested carrier gases, only He gave a satisfactory signal.

Even if the experimental conditions for CH production are rather different in discharge and photolysis experiments, it is interesting to compare both productions using the same detection scheme.

Figure 6 displays an experimental CRDS spectrum of CH(X) radical produced by discharge in a He/CHBr₃ supersonic expansion \([\text{Fig. 6(a)}]\) together with the simulated spectrum obtained with the LIFBASE program \(^20\) [Fig. 6(b)]. It is interesting to note that the optimized \((v^a, N^a, F^a)\) population distributions used to reproduce the experimental spectrum are not thermal, both rotationally and vibrationally.

As far as vibration is concerned, the distribution appears to be slightly nonthermal and significant population for \( v^a = 1 \) and \( v^a = 2 \) levels is found, as displayed in the insert of Fig. 6(b). For comparison, a thermal vibrational distribution with \( T_{\text{vib}} = 1700 \text{ K} \) is reported in this panel. This insert also displays the rotational distribution in the \( v^a = 0 \) level for both spin components \( F_1 \) and \( F_2 \) of each \( N^a \) level. A bimodal distribution was found to fit the observed spectrum with, in addition, a nonequal distribution between the two spin components \( F_1 \) and \( F_2 \). A similar nonthermal rotational distribution was assessed for the \( v^a = 1 \) and \( v^a = 2 \) levels, but is not shown in this figure. A nonthermal rotational distribution is not surprising in supersonic expansion conditions as well as in discharge conditions. Indeed, the discharge occurs upstream from the expansion, in a high pressure region where many collisions take place and where reactivity is very efficient. Hot CH radicals are produced in this discharge region and are further rotationally “cooled” when the expansion takes place. A simple comparison between Figs. 5(a) and 6(a) clearly shows that the CH radicals produced in the discharged are rotationally relaxed, significantly more than in the photolysis experiment discussed in Sec. III C. Nevertheless, the simulation of Fig. 6(b) shows that no thermalization is achieved in the rotational population. Moreover, the simulation reveals an unbalanced spin component population which is not understood so far. This might be a remnant effect of the electron impact process which might favor a particular spin component.

On the other hand, the discharge setup may induce substantial population of the product in the electronically excited states. It is expected that these electronic states have enough time to relax towards the ground state since the nozzle is located 2.5 cm above the interaction region (typical velocity in helium-free expansion: 1700 m s\(^{-1}\); typical radiative lifetime for the A state for instance: 500 ns). Finally, it is difficult to quantitatively interpret the populations deduced from the simulations of Fig. 6(b) since they arise from various processes, i.e., broadband energy electron impact formation, electronic relaxation of the CH radical, and partial thermalization of the \((v^a, N^a, F^a)\) levels in the expansion prior to the CRDS detection zone. The net result is that all the CH radicals reaching the detection zone are in their ground state.
Unlike in the photolysis experiment where CH fragments are directly detected in their production region, in the case of the discharge experiments, CH fragments are detected downstream from their production region. Hence, the measured total number of CH radicals is a lower limit due to the occurrence of loss processes in the collisional and reactive nozzle regions. Nevertheless, such a value is relevant in many situations where CH radicals are used as reactant species, downstream from a supersonic expansion. Note that the CH number density is not homogeneous, in principle, along the transverse dimension of the expansion which is probed by the CRDS laser beam. The number density should be considered therefore as an average value resulting from a spatially integrated CRDS signal. The CH number density in the detection region has been determined from the CRDS signal on the \( R_1(1.5) \) line of the spectrum obtained in discharge by using the same procedure as in the photolysis experiment. It was found to be \( N_{\text{CH}}^{\text{tot}} = (5.1 \pm 1.0) \times 10^9 \) molecules cm\(^{-3}\). Using the well-known formulas for describing the evolution of the density along the jet axis,\(^3\) one can extrapolate this number density near the CH production region, that is, at the exit of the nozzle. A number density near the discharge location, in the region where there are no more collisions, i.e., typically 2 mm from the discharge nozzle exit, can be derived: \( N_{\text{CH}}^{\text{min}} = (9.6 \pm 1.9) \times 10^{11} \) molecules cm\(^{-3}\).

Concerning the CHBr\(_3\) number density, the pulsed nozzle is open for 200 \( \mu \)s only every 100 ms. If we assume a relative steady situation upstream, the equilibrium vapor pressure of CHBr\(_3\) should be nearly reached (7 mbars). Hence, we can only evaluate an upper limit for the CHBr\(_3\) number density at the discharge nozzle exit: \( N_{\text{CHBr}_3}^{\text{max}} = (1.7 \pm 0.3) \times 10^{17} \) molecules cm\(^{-3}\) corresponding to \( (7.4 \pm 1.3) \times 10^{15} \) molecules cm\(^{-3}\), 2 mm from the discharge nozzle exit.

In conclusion, only a lower limit \( \Phi_{\text{min}} \) can be estimated for the radical production efficiency due to the lower limit CH number density and upper limit CHBr\(_3\) number density: \( \Phi_{\text{min}} = (1.3 \pm 0.4) \times 10^{-4} \). This lower limit differs by less than a factor of 4 with the photolysis value. Thus this study illustrates that CH production is as efficient by using either a two-photon photolysis or a discharge within the specific experimental conditions described in Sec. II.

**Fig. 6.** (a) Experimental CRDS spectrum of CH radical produced by discharge in a He/CHBr\(_3\) expansion. The two lines marked with an asterisk (at \( \lambda = 4300.13 \) Å and \( \lambda = 4311.21 \) Å) are assumed to be absorption lines of excited argon atoms (they also could be due to unknown impurities from the CHBr\(_3\) unpurified liquid). (b) Simulated spectrum of CH radical obtained by using the LIFBASE program (Ref. 20). Insert (upper part): Vibrational distribution deduced from the simulation in hatched bars. The thermal vibrational distribution at 1700 K is shown in hollow bars for comparison. Insert (lower part): Rotational distributions in the \( v'' = 0 \) level for \( F_1 \) and \( F_2 \) spin components as a function of the \( N'' \) rotational quantum number.
IV. CONCLUDING REMARKS

This paper describes the use of the sensitive CRDS technique to study the CH production from CHBr\textsubscript{3}. This quantitative detection method allowed us to evaluate, for the first time, the CH(X\textsuperscript{2}Π) production efficiency from the 248 nm two-photon photolysis process, i.e., $\Phi=(5.0\pm2.5)\times10^{-4}$ for a laser pulse fluence of 44 mJ cm\textsuperscript{-2}. This determination could not have been performed without a careful control of the photolysis experimental parameters as described in Sec. III B. Indeed, it has been demonstrated that the CH radicals probed in this experiment arise only from a two-photon photolysis process and undergo no further reactive collisions with the CHBr\textsubscript{3} mother molecule.

The determined production efficiency by two-photon photolysis of CHBr\textsubscript{3} may be quantitatively used for further experiments involving the CH radical as a reactive partner by extrapolating the experimental conditions described in Sec. III B.

In addition, we have demonstrated by using the same quantitative CRDS detection device that the two CH productions studied here, photolysis and discharge, are equivalent and therefore that a simple scheme using a discharge-induced production can be implemented to study the reactivity of the CH radical in combustion processes\textsuperscript{14} and various astrophysical media as discussed, for instance, by Canosa et al.\textsuperscript{15}

The experimental methodology described in this paper will be further applied to the UV photolysis of methane. A through investigation of the primary fragments arising from this photolysis is needed for the understanding of Titan atmosphere chemistry,\textsuperscript{35} with a special concern on the production of the CH radical, which is the starting point of the rich atmospheric carbonated chain reactions.

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