

Spectroscopic Study of the $\tilde{A}^1A'' - \tilde{X}^1A'$ System of CHBr

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We report fluorescence excitation and emission spectra of the CHBr molecule generated *via* pyrolysis of CH₃Br in a molecular beam experiment. The 193 nm attenuation cross sections were estimated from the reduction of the CHBr signal as a function of the excimer laser fluence. The derived 193 nm absorption cross section for CHBr [$(3.24 \pm 0.59) \times 10^{-17} \text{ cm}^2$] is slightly higher than the absorption cross section previously determined for CHCl [$(2.6 \pm 0.8) \times 10^{-17} \text{ cm}^2$], but the difference is within the estimated uncertainties in the measured cross section.

Key Words : Pyrolysis, Carbene, Absorption, Cross section, Spectroscopy

Introduction

Simple carbenes are important intermediates in a number of gas-phase reaction environments, including the interstellar media, such as plasma processing. Consequently, there has been much interest in their spectroscopy, in part for the development of sensitive diagnostics for their detection. A considerable number of spectroscopic investigations have provided detailed experimental information on the ground and first excited singlet states (\tilde{X}^1A' and \tilde{A}^1A'' for the unsymmetrical molecules) of the monohalocarbenes and dihalocarbene.¹⁻⁴ The methylene radical has a triplet ground electronic state (\tilde{X}^3B_1),⁵ while all of the mono- and dihalogenated derivatives have singlet ground states (\tilde{X}^1A_1 for the symmetrical dihalocarbenes). Considerable information is now available on the electronic transition to the first excited electronic state (\tilde{A}^1B_1) of a number of halocarbenes, and vibrational energies and rotational constants in both ground and excited electronic states have been determined.²⁻¹⁹ This has allowed determination of molecular geometries and information on the relevant potential energy surfaces. The \tilde{X}^1A_1 and \tilde{A}^1B_1 states coalesce to a degenerate electronic state at linear geometry, thus leading to the Renner-Teller effect which couples the two states.

Previously, UV photodissociation dynamics of several halocarbenes has been reported.¹⁷⁻¹⁹ The internal state distributions of the CCl and CF fragments from the 193 and 248 nm photolysis of CCl₂ and CFCl, respectively, have been determined. In addition, it was also possible to determine attenuation cross sections of the parent molecules by monitoring their densities versus the fluence of the excimer laser. These cross sections could be equated with absorption cross sections if the probability of the excited-state dissociation is unity.

The fluorescence decay lifetimes of the vibronic levels of the \tilde{A} state of a number of halocarbons have been measured.¹²⁻¹⁴ The lifetimes of HCF (\tilde{A}^1A'') vibronic levels with $K_a' \geq 1$ show a distinct increase with increasing excitation energy, as expected from the Renner-Teller interaction with

the \tilde{X}^1A' state.¹⁴ The lifetimes of HCCl (\tilde{X}^1A'') levels increase slightly with increasing energy; this dependence was ascribed to a homogeneous perturbation.¹² A different dependence of the lifetime upon excitation was observed for both CFCl and CFBr. The fluorescence lifetimes of CFCl (\tilde{A}^1A'') levels were found to be roughly constant for excitation energies $< 3000 \text{ cm}^{-1}$ above the \tilde{A}^1A'' zero-point energy level. In contrast to the extensive study of the \tilde{X}^1A_1 and \tilde{A}^1B_1 electronic states of the halocarbenes, there is relatively little information available on the higher excited states. Rydberg states of HCF and DCF have been observed by resonance-enhanced multiphoton ionization (REMPI).¹⁵ Quantum chemical calculations have mainly addressed the ground and lowest excited singlet and triplet states (\tilde{X}^1A_1 , \tilde{A}^1B_1 , and \tilde{a}^3B_1), although several studies have investigated higher excited states, for example in the CF₂ and CCl₂ molecules.¹⁶⁻²² Cai *et al.*²² have calculated CCl₂ excitation energies, equilibrium geometries, and vibrational frequencies of the seven lowest electronic states. They have also estimated oscillator strengths for dipole-allowed transitions from the ground electronic state.

In the present work, we report the fluorescence excitation and emission spectra of the CHBr molecule from the pyrolysis from CH₃Br in a molecular beam experiment. We have estimated the 193 nm absorption cross section by monitoring the decrease in the CHBr density as a function of the excimer laser fluence.

Experiment

The apparatus employed in this study is a slight modification of the molecular beam apparatus employed in the earlier studies.¹⁷⁻¹⁹ The CHBr molecule was prepared in a supersonic beam by flash pyrolysis of a dilute mixture (5-10% mole fraction) of CH₃Br in argon (total pressures of 1 atm) by passage through a resistively heated SiC tube (0.5 mm ID, 2 mm OD) attached to a pulsed solenoid valve (General Valve). The experimental chamber housing the molecular beam was evacuated with a 10 in. diffusion pump

equipped with a water-cooled baffle. Fluorescence excitation spectra (for detection of CHBr) were recorded 1.5 cm downstream of the beam source using the fundamental of a Nd:YAG laser-pumped dye laser (Continuum ND6000). The spectral bandwidth in the visible was 0.1 cm^{-1} , and pulse energies of up to 1 mJ in a 0.5 cm dia. beam were employed. The bandwidth and pulse energies in the visible were somewhat smaller and larger, respectively (0.1 cm^{-1} and 5 mJ). The analyzed CHBr spectra were recorded with laser pulse energies of 200 μJ .

An excimer laser (Lambda Physik COMPex 102) was employed as the 193 nm. The output of the excimer laser was overlapped with the tunable probe laser beam with a dichroic mirror, and both beams co-propagated into the molecular beam apparatus. Excimer laser pulse energies of up to ~ 10 mJ in a 0.5 cm dia. at the entrance of the apparatus were employed. The excimer and probe laser beams were perpendicular to the molecular beam. The excimer laser was unpolarized, and the polarization of the visible probe laser was perpendicular to the molecular beam direction. The delay times between the pulsed molecular beam source, the excimer laser, and the tunable probe laser were controlled with a digital delay generator (Stanford Research Systems). The delay between the excimer and probe lasers was typically 100 ns.

Fluorescence emitted perpendicular to both the molecular and laser beams was imaged onto the entrance slit of a $\frac{1}{4}$ m monochromator and detected with a photomultiplier (Thorn EMI 9816, for visible detection), whose output was directed to a gated integrator and then to a computer. To reduce the intensity of scattered laser light, the monochromator was set to transmit fluorescence to the red of the laser excitation wavelength. The integrator gate width was set to 500 ns for collection of CHBr spectra. In this case, only a small part of the fluorescence decay profile was observed because the molecular flight time through the observation zone was short compared to the long radiative lifetime of the CHBr \tilde{A}^1A'' state, as noted by Guss *et al.*¹¹

Results and Discussions

The CHBr molecule could be detected only when the heater in the pyrolysis jet source was on. In order to measure the degree of internal excitation of the CHBr precursor, laser fluorescence excitation spectra were recorded in its $\tilde{A}^1A'' - \tilde{X}^1A'2_0^23_0^2$ band system. Figure 1 shows laser fluorescence excitation spectra of the overlapped ($2_0^23_0^2$) bands, recorded with source backing pressures of 1 atm. Figure 2 presents the dependence of CHBr laser fluorescence excitation signals on the pyrolysis beam source heater current (source backing pressure 1 atm). This signal could be detected only when pyrolysis beam source heater was on. On the basis of the measurements reported in Figure 2, a pyrolysis heater current of 2.1 A was employed for the generation of CHBr.

From the reduction of the CHBr laser-induced fluorescence signal as a function of the fluence of the excimer laser, it was possible to estimate the 193 nm attenuation cross section.

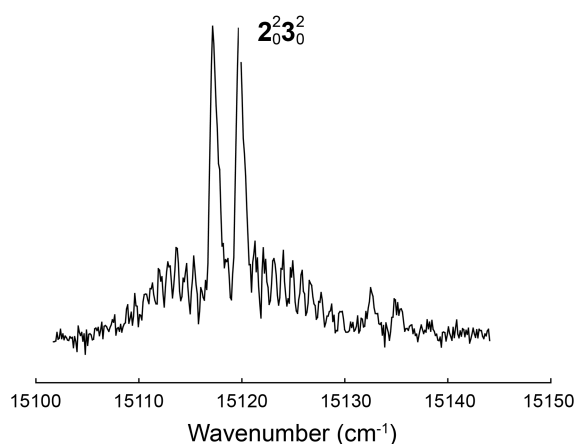


Figure 1. Laser-induced fluorescence excitation spectra of the bands of CHBr formed by pyrolysis of CH_3Br in a pulsed molecular beam source at 1 atm backing pressure.

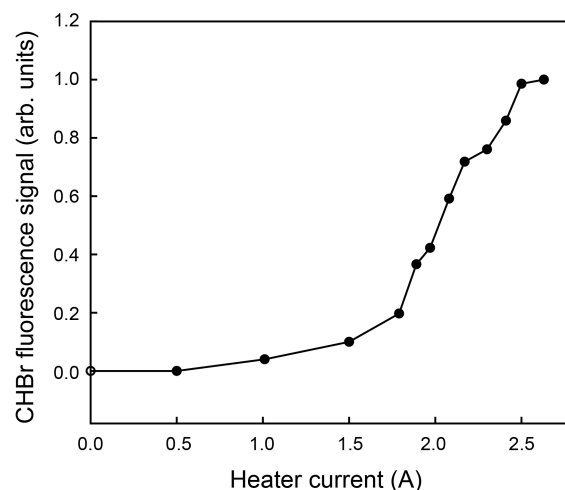


Figure 2. Dependence of CHBr laser-induced fluorescence excitation signals (detected in the $\tilde{A}^1A'' - \tilde{X}^1A'2_0^23_0^2$ band) on the pyrolysis beam source heater current (at backing pressure of 1 atm).

Figure 3 presents linear and semilogarithmic plots of the measured dependence of the CHBr fluorescence signal, with laser excitation in the $\tilde{A}^1A'' - \tilde{X}^1A'2_0^23_0^2$ band, on the 193 nm excimer laser fluence. The excimer laser pulse energy at the reaction spot was measured by inserting a power meter inside the vacuum chamber. As an iris is employed to define the area of the excimer laser beam, the fluence may be calculated directly from the pulse energy and beam cross sectional area A . The attenuation cross section s for CHBr was computed from the data in Figure 3 using the relationship presented by Rohrer and Stuhl:²³

$$N_e = N_a \exp(-\sigma n_p / A) \quad (1)$$

where N_a and N_e are the CHBr concentrations with the excimer laser off and on, respectively, and n_p is the number of photons in the light pulse.

A weighted least squares fit of the data presented in the lower panel of Figure 3 gives an attenuation cross section of $(3.24 \pm 0.59) \times 10^{-17} \text{ cm}^2$ for CHBr at 193 nm. The attenu-

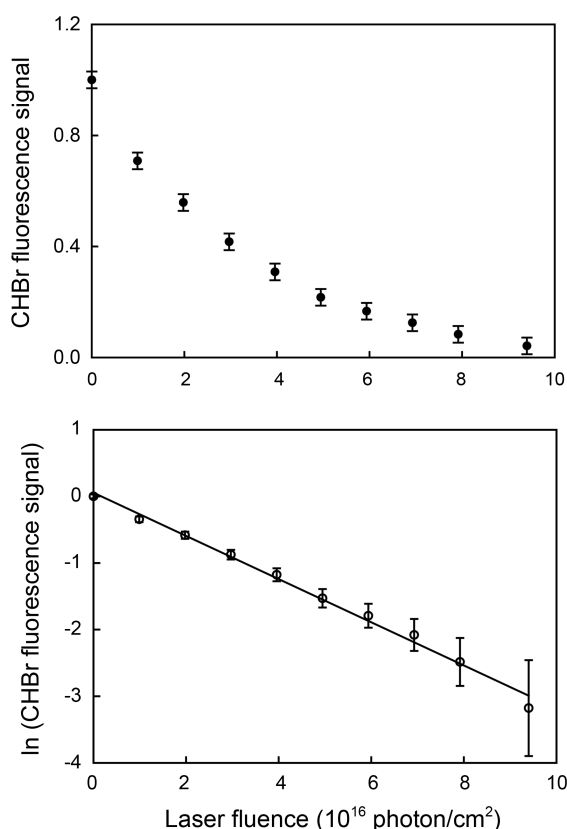


Figure 3. Linear (upper panel) and semilogarithmic (lower panel) plots of the CHBr laser-induced fluorescence signal as a function of the 193 nm laser fluence. The plotted line in the lower panel is a weighted linear least square fit to obtain the attenuation cross section.

ation of the CHBr laser fluorescence signal with excitation in the $\tilde{A} - \tilde{X} 2_0^2 3_0^2$ band was also investigated, while the cross sections were nearly the same regardless of the bands in the experimental uncertainty. In case the probability of the excited-state dissociation is unity, the derived attenuation cross sections can be equated with those of absorption.

Of the excited electronic states of CHBr, there is information available only for \tilde{a}^3A'' and \tilde{X}^1A' states from spectroscopic studies and quantum chemical calculations.²⁴ The absorption of a 193 nm photon accesses a higher electronic state. In previous work,¹⁷ we discussed the higher electronic state of the CCl_2 molecules. Lias *et al.*²⁵ have computed ionization potential for CCl_2 , CHF and CHCl from thermochemistry bracketing experiments in an ion cyclotron resonance spectrometer and obtained the values, $\text{IP}(\text{CCl}_2) = 10.36$, $\text{IP}(\text{CHF}) = 10.49$, and $\text{IP}(\text{CHCl}) = 9.84$ eV. The results of Lias *et al.* suggest that the ionization potential of CHBr is slightly lower than that of CHCl. This implies that the Rydberg states of CHCl and CHBr should have similar excitation energies. Kohn *et al.*²⁶ have calculated the bond angle of the CCl_2^+ ion at the MP2/6-31G level to be 135.3° . We thus expected that CCl_2 and CHCl Rydberg states have nonlinear equilibrium geometries. Also, we assume that CHBr Rydberg states have nonlinear equilibrium geometries.

Previously,¹⁹ we concluded that the absorption of a 193 nm photon CHCl accesses a Rydberg excited state, and a similar conclusion should apply for CHBr. The determined 193 nm absorption cross section for CHBr $[(3.24 \pm 0.59) \times 10^{-17} \text{ cm}^2]$ is slightly higher than the absorption cross section previously determined¹⁹ for CHCl $[(2.6 \pm 0.8) \times 10^{-17} \text{ cm}^2]$, but the difference is within the estimated uncertainties in the measured cross section.

Conclusion

In this paper, we report the fluorescence excitation and emission spectra of the CHBr molecule from the pyrolysis of CH_3Br in a molecular beam experiment. We have employed laser fluorescence excitation spectroscopy to observe the CHBr molecule and assume that CHBr Rydberg states have nonlinear equilibrium geometries. We have estimated the 193 nm absorption cross section by monitoring the decrease in the CHBr density as a function of the excimer laser fluence. The measured absorption cross section for CHBr is somewhat higher than that for CHCl.

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