

Vibrational distribution of Br₂ molecule following photodissociation of CH₂Br₂ by using cavity ring-down absorption spectroscopy

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Abstract:

Cavity ring-down Spectroscopy (CRDS) is a relatively new direct absorption technique and its applications are developed very quickly in recent years. The method is based on measurement of the decay rate of a pulse light trapped in an optical cavity which is formed by a pair of highly reflective ($R > 99.9\%$) mirrors. A plot of decay rate as a function of laser frequency gives the absorption spectrum. As for photodissociation studies of CH₂Br₂, the major dissociation channels are found to be



We used a cavity ring-down spectroscopy (CRDS) to study of nascent Br₂ following photodissociation of CH₂Br₂. The quantum yield of Br₂ is found to be 0.21151 ± 0.05 following photodissociation of CH₂Br₂ at 248nm. According to the absorption spectrum, the nascent vibrational distribution was obtained. The excited parent molecules (CH₂Br₂) may transfer into highly vibrational levels of their electronic ground state via internal conversion. And the results agree with a given theoretical calculation.

1. Experimental Setup:

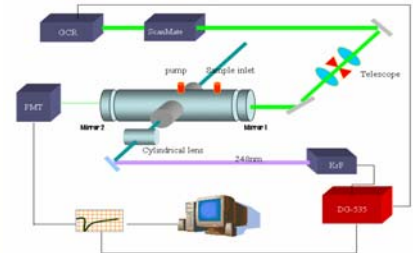


Fig. 1 Schematic diagram of pure Br₂ detection by using CRDS.

2. Results and Discussions:

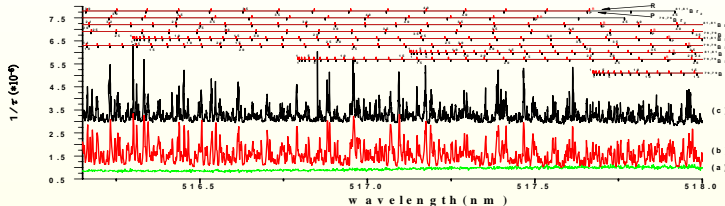


Fig. 2 The cavity ring-down absorption spectrum in ($v' \leq 0$) transition of (a) Br₂ without the photodissociation beam, 248nm, at a precursor pressure of 5.1 torr, (b) Br₂ with the photodissociation beam, 248nm, at a precursor pressure of 5.1 torr, and (c) pure Br₂ at pressure of 72 mtorr.

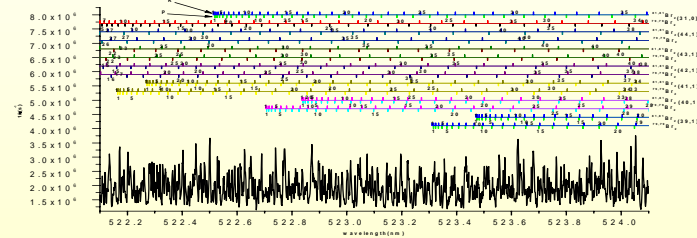


Fig. 3 The cavity ring-down absorption spectrum in ($v' \leq 1$) transition of Br₂ with the photodissociation beam, 248nm, at a precursor pressure of 5.1 torr.

$$P(J) \propto \frac{I(J)}{(FCF)(HLF)} \quad \frac{\sum P(J)(v''=1)}{\sum P(J)(v''=0)} = 0.7 \pm 0.2$$

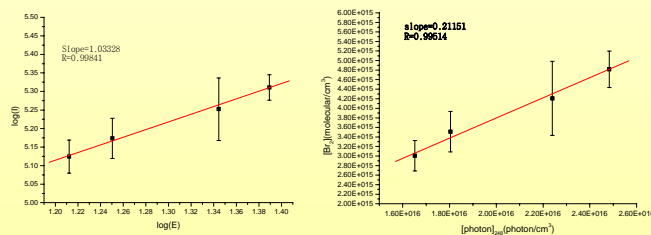


Fig. 4 The power dependence plot of photodissociation beam intensity vs. absorption signal for P(37) of the (35,0) band at 519.68nm. The slope is 1.03328, which means that Br₂ is resulted from one-photon absorption of CH₂Br₂.

Fig. 5 Plot of number density of Br₂ produced in 248 nm photolysis of CH₂Br₂ against the absorbed photon density, yielding a slope indicative of quantum yield 0.21151 ± 0.05 for the dissociation channel of molecular elimination.

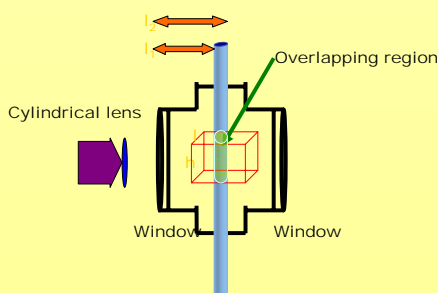


Fig. 6 The magnified diagram of overlapping region. h and l were determined by photolysis laser beam, while the overlapping width is equal to $l_2 - l_1$.

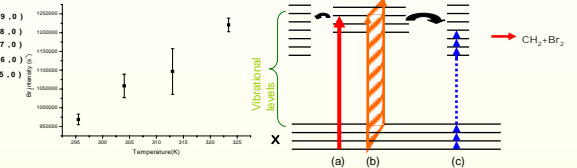


Fig. 7 The temperature dependence plot of photodissociation beam intensity vs. absorption signal for P(37) of the (35,0) band at 519.68nm.

Fig. 8 The schematic diagram of energy internal conversion between excited electronic state and ground electronic state of the (35,0) band at 519.68nm. (a) in molecular beam, (b) valid energy spread in bulk phase, (c) IR multiphoton excitation to high vibration level.

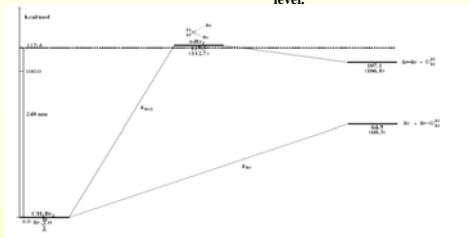


Fig. 9 The Br₂ and Br dissociation channels of CH₂Br₂, in which the energies in kcal/mol relative to CH₂Br₂ are computed with CCSD(T)/cc-pVTZ level of theory with B3LYP/6-311G(d,p) zero-point energy corrections at the B3LYP/6-311G(d,p) optimized geometries. The energies in parenthesis are obtained at level of B3LYP/6-311G(d,p).

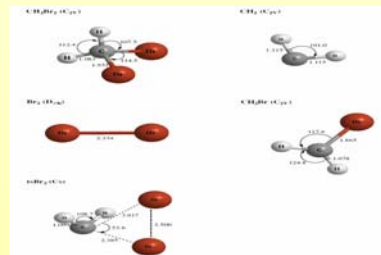


Fig. 10 The B3LYP/6-311G(d,p) optimized geometries of species along the Br₂ and Br dissociation channels of CH₂Br₂ on the adiabatic singlet ground state potential energy surface of CH₂Br₂. In which the point group is in parenthesis, the lengths in angstrom, and the angles in degree.

	248nm
(CH ₂ Br ₂ → CH ₂ + Br ₂)	$8.88 \times 10^7 \text{ s}^{-1}$
(CH ₂ Br ₂ → CH ₂ Br + Br)	$2.50 \times 10^{12} \text{ s}^{-1}$

Table 1 At 248 nm, the RRKM rate constant k_{Br_2} computed with zero-point energy corrected B3LYP/6-311G(d,p) energy and the variational RRKM rate constant k_{Br} computed with CCSD(T)/cc-pVTZ energy with B3LYP/6-311G(d,p) harmonic frequencies.

3. Conclusions:

- The Br₂ quantum yield following the photodissociation of CH₂Br₂ is 0.21151 ± 0.05 at 248 nm.
- The population ratio of Br₂ in $v''=1$ to $v''=0$ at Br₂ electronic ground state is 0.7 ± 0.2 .
- The present work under the room-temperature condition induces a much wider population distribution in the excited state, thus enhancing the coupling strength to facilitate the internal conversion.
- The theoretical calculations also can prove the Br₂ channel that we have seen in CRDS.