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Single vibronic level emission spectroscopy of the $\widetilde{A}^1A'' \rightarrow \widetilde{X}^1A'$ system of bromochlorocarbene

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Abstract

In a search for transitions to the low-lying $\tilde{a}^3A''$ state, we have recorded single vibronic level (SVL) emission spectra of bromochlorocarbene, CBrCl, which probe the vibrational structure of the $\widetilde{X}^1A'$ state up to ~5500 cm^{-1} above the vibrationless level. These spectra reveal many previously unassigned levels, and a complete set of vibrational parameters was determined for the $\widetilde{X}^1A'$ state. The derived parameters are compared with recent ab initio predictions.

Keywords: Emission spectroscopy; Carbenes; Single-triplet gap

1. Introduction

Carbenes are an important class of reactive intermediates which contain a divalent carbon, giving rise to singlet and triplet configurations of similar energy but very different reactivity [1–6]. The singlet–triplet splitting (ΔE_{ST}) is used to predict the reactivity of carbenes in environments where both states can be populated, and the mono- and dihalocarbenes have served as important benchmarks for comparison of experiment and theory [7–22]. For example, in CHCl the experimental value for $T_{00}(\tilde{a} - \widetilde{X})$ of 2172(2) cm^{-1}, derived from single vibronic level (SVL) emission spectroscopy [17,21], is within 2 cm^{-1} of a "best" theoretical estimate at the CCSD(T)/aug-cc-pVQZ level [19].

Of the halocarbenes, the magnitude of the singlet–triplet splitting has been the most controversial for the symmetric dihalocarbenes CCl_2 and CBr_2. Calculations predict a singlet ground state for both, with $\Delta E_{ST} \sim 20$ kcal mol^{-1} (~7000 cm^{-1}) for CCl_2 [19,23–45] and ~17 kcal mol^{-1} (~5900 cm^{-1}) for CBr_2 [30–32,34,35,38–40,42,44,46,47]. In contrast, the photoelectron studies of Lineberger and co-workers [7,9] place the singlet–triplet splitting at 3(±3) kcal mol^{-1} for CCl_2 and 2(±3) kcal mol^{-1} for CBr_2 [9]. Recent theoretical treatments have indicated that the photoelectron spectra may contain contributions from a quartet state of the anion, which might explain this discrepancy [44,45].

Recently, the technique of SVL emission spectroscopy has been applied to examine the singlet–triplet gap in the dihalocarbenes. Miller and co-workers obtained emission spectra of CCl_2 [16], and reported unassigned structure beginning ~5000 cm^{-1} (~14 kcal mol^{-1}) above the $\widetilde{X}^1A_1$ origin which was attributed to levels of the $\tilde{a}^3B_1$ state. In a recent study [48], we tested for the presence of $\tilde{a}^3B_1$ levels in the high energy region of the CCl_2 emission spectrum using K'_a-sorted emission spectra. The K'_a-sorted spectra discriminate between singlet and triplet levels via the $(A'' - \overline{B}'')$ rotational constant, which is significantly larger for pure triplet levels, due to the larger equilibrium bond angle of the triplet state. In the region between ~3500 and 9000 cm^{-1} above the vibrationless level of the $\widetilde{X}^1A_1$ state, we found only a very modest increase in $(A'' - \overline{B}'')$, and ~86% of the lines observed between 5000 and 9000 cm^{-1} could be assigned to $\widetilde{X}^1A_1$ levels within 3 standard deviations of our Dunham expansion fit, which included more than 140 levels in total.

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Following the development of an improved discharge recipe for the clean production of CBr_2, we subsequently reported SVL emission spectra of $C^{79}Br^{81}Br$ and $C^{81}Br_2$ which probed the vibrational structure of the $\widetilde{X}^1A_1$ state up to ~7000 cm^{-1} above the vibrationless level [49]. These spectra revealed many previously unassigned levels, and a nearly complete set of vibrational parameters was determined, which were in good agreement with ab initio predictions [49]. In this work no evidence was found for perturbations due to the low-lying triplet state, although analysis of the spectra was complicated by a polyad structure arising from the near 3:1 resonance of bending and symmetric stretching frequencies.

In comparison with CCl_2 or CBr_2, relatively few studies of the spectroscopy of CBrCl have been reported. Infrared and laser induced fluorescence (LIF) spectra were first obtained in cold matrices [50–53], with a few gas-phase studies following [53–56]. The most comprehensive of these is the recent report of Richmond et al. [56] who measured fluorescence excitation and emission spectra which revealed 20 ground state and 50 excited state levels. Nearly complete sets of vibrational parameters were obtained for the $\widetilde{X}^1A'$ and $\widetilde{A}^1A''$ states; in the latter case, for all four isotopomers. However, the SVL emission spectra were only measured up to a vibrational energy of ~2000 cm^{-1}, well below the ab initio estimate for ΔE_{ST} of ~6000–6600 cm^{-1} [19,39,57]. In this report, we have extended the SVL emission studies to higher energy in an effort to probe the region of the triplet origin. A complete set of vibrational parameters was determined for the ground state, and these are compared with theoretical predictions.

2. Experimental section

The apparatus, pulsed discharge nozzle, and data acquisition procedures have been described in detail in recent studies [20–22]. The carbene CBrCl was produced using a pulsed electrical discharge through a mixture of CBr_2Cl_2 seeded in high purity Ar. The discharge was initiated by a 1 kV pulse of ~100 μs duration, through a current limiting 10 kΩ ballast resistor. The timing of laser, nozzle, and discharge firing was controlled by a digital delay generator (Stanford Research Systems DG535), which generated a variable width gate pulse for the high voltage pulser (Directed Energy GRX-1.5K-E). The laser system consisted of an etalon narrowed dye laser (Lambda-Physik Scanmate 2E) pumped by the second or third harmonic (532 or 355 nm) of a Nd:YAG laser (Continuum NY-61). The laser beam was not focused, and typical pulse energies were ~1–2 mJ in a ~3 mm diameter beam.

A mutually orthogonal geometry of laser, molecular beam, and detector was used, where the laser beam crossed the molecular beam at a distance of ~1 cm downstream. Fluorescence was collected and collimated by a 2 in diameter, *f*/2.4 plano-convex lens, and focused into the spectrograph (Acton SR303i with ISTAR intensified CCD) using a *f*-matching *f*/3.0 plano-convex lens, also 2 in. in diameter. A removable mirror assembly was used to direct the output of an Fe:Ne hollow cathode lamp into the spectrograph for wavelength calibration; these spectra were typically obtained immediately after the emission spectra, and were acquired using a slit width of 10 μm and 500 shot accumulation.

The emission spectra were acquired in photon counting mode (10 000 shot typical accumulation) with a slit width of 50–100 μm, using a 600 lines/mm grating blazed at 500 nm. The integration gate (typically 8 μs) was set to fully encompass the fluorescence decay of the emitting level under our experimental conditions, and the spectrograph was operated in a "step and glue" mode, where the grating was sequentially stepped and spectra recorded at each grating position in order to cover the entire spectral region of interest. Spectra were calibrated in each range by first fitting the Ne I emission lines to a Gaussian lineshape function, using Origin 7.5 software. The observed positions were then compared against the known values [58], and the deviations fit to a second-order polynomial to obtain a calibration curve which was applied to the corresponding emission spectrum. Bands in the emission spectra were also fit to a Gaussian lineshape function, and background spectra were obtained with the laser blocked to check for emission lines from species in the discharge.

3. Results and discussion

As noted in the introduction, the most complete analysis of the $\widetilde{A}^1A'' \leftarrow \widetilde{X}^1A'$ system of CBrCl was performed by

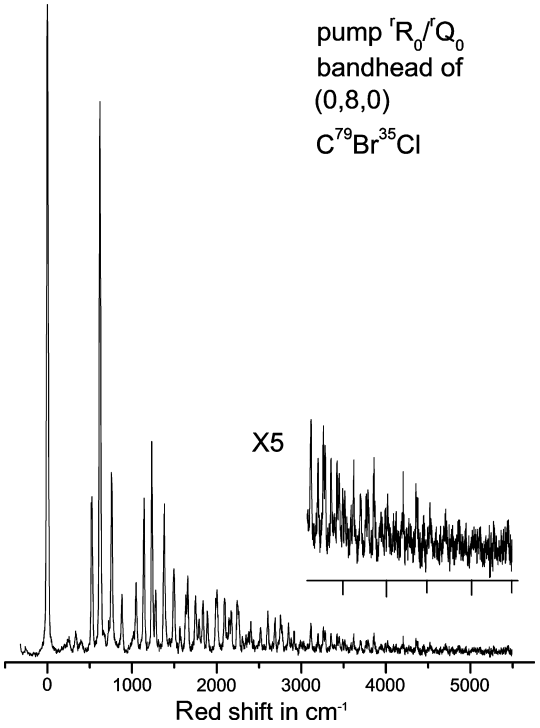

Fig. 1. Single vibronic level emission spectrum of $C^{79}Br^{35}Cl$ obtained by pumping the $^rR_0/^rQ_0$ bandhead of (0,8,0). The *x*-axis labels the shift in frequency from the excitation line, and thus the vibrational energy in the $\widetilde{X}^1A'$ state. Inset in the panel is an expanded (×5) view of the high energy region.