

Assignment of the 278.2-nm Peak of the $\text{CCl } A^2\Delta - X^2\Pi$ System as the 0–0 P_1 Bandhead

Introduction. The $A^2\Delta - X^2\Pi$ spectrum of the CCl radical was first observed over a half-century ago (1). It has subsequently been the subject of extensive investigations, and the understanding of several of its features has changed (2–10). The near-equality of the equilibrium internuclear distances and vibrational frequencies of the A and X states results in crowded bands and badly overlapped sequences, of which the diagonal one is the strongest. One unresolved issue has been the identification of a peak at 278.2 nm ($35\,931\text{ cm}^{-1}$), which was clearly observed in some works (1, 2, 6, 9), but apparently not in others (3, 4, 7). It has tentatively been identified as the Q_1 bandhead of the 2–2 band (6, 7, 9), but this assignment poses several difficulties. For example, Larsson *et al.* (6) measured the lifetime of this peak, and found it to be longer than that of the known predissociative 1–1 bandheads—a surprising result. Recently, Sharpe and Johnson questioned the identification of the 278.2-nm peak, because their vibrational constants for the A and X states indicated that the 2–2 Q_1 bandhead should be at 278.0 nm (8).

In recent experiments on the reaction of $\text{C}(^1D)$ with HCl, we observed the $\text{CCl } A^2\Delta \leftarrow X^2\Pi$ spectrum, and in particular the peak at 278.2 nm and its relaxation (11). We therefore reinvestigated the $\Delta v = 0$ sequence of this transition, using two sources of CCl. Based on our simulated spectra and the relaxation behavior of the 278.2-nm peak, we identify the peak at 278.2 nm as the P_1 bandhead of the 0–0 band, formed at J'' between 60 and 70.

Experimental details. The experimental apparatus and procedures have been extensively described in Ref. (11). Briefly, $\text{CCl}(X^2\Pi)$ was generated by laser photolysis at 248 nm of mixtures of C_3O_2 with either HCl or ClCN. The product $\text{CCl}(X^2\Pi)$ was detected by laser-induced fluorescence (LIF) using a tunable dye laser between 277 and 292 nm. The bandwidth of the dye laser, 0.12 cm^{-1} FWHM, determined the linewidths. By varying the time between firing the photolysis and probe lasers (0.2–100 μsec), CCl with various amounts of internal excitation could be observed. At the shortest delays, CCl with substantial rotational and vibrational excitation is copiously produced in both mixtures. Increasing the pump-probe delay allowed the reaction product more time for collisions, so that the LIF spectrum showed more relaxation for longer delays. By 10 μsec , no further changes in relative intensities were observed.

Results. Figure 1 shows three CCl spectra produced by photolyzing $\text{C}_3\text{O}_2/\text{ClCN}$ mixtures, and obtained at progressively greater pump-probe delays. The well-known Q_1 and P_2 bandheads of the 0–0 band, and the Q_1 bandhead of the 1–1 band, are identified (3). By interpolation between the 0–0 bandheads, we measured the wavenumber of the 278.2-nm peak as $35\,930.5 \pm 0.5\text{ cm}^{-1}$, in good agreement with previous measurements (1, 2, 6, 9). The ratio of the 1–1 Q_1 bandhead intensity to the 0–0 Q_1 bandhead intensity decreased slightly as the pump-probe delay increased, as expected from normal slow vibrational relaxation (12). The 278.2-nm peak, however, disappeared much faster with increasing delay. This is consistent with the usual rapid rotational relaxation (12).

To estimate the rotational populations of the nascent CCl, we simulated the spectrum using spectroscopic constants reported by earlier workers. Rotational term values for both electronic states were calculated using the formulae and constants of Mélen *et al.* (7).¹ Using the constants of other groups (4, 5, 8, 10) shifted the relative positions of the bandheads by as much as 1 cm^{-1} , but did not affect their identification.

The simulated spectra at three temperatures are shown in Fig. 2. The temperatures were chosen to roughly match the experimental spectra displayed in Fig. 1. However, there is no reason to believe that the nascent vibrational, rotational, or spin–orbit populations produced in the reactions were thermal. In particular, the F_2 levels ($^2\Pi_{3/2}$) appear to have a larger population than the F_1 levels ($^2\Pi_{1/2}$), producing an unusually large ratio of the intensity of the 0–0 P_2 bandhead to that of the 0–0 Q_1 bandhead. The 0–0 P_1 bandhead occurs at $60 < J'' < 70$, corresponding to a term energy of 2500 to 3400 cm^{-1} .

¹ Equation (2) of Ref. (7) is missing a factor of $\frac{1}{2}$ before the radical.

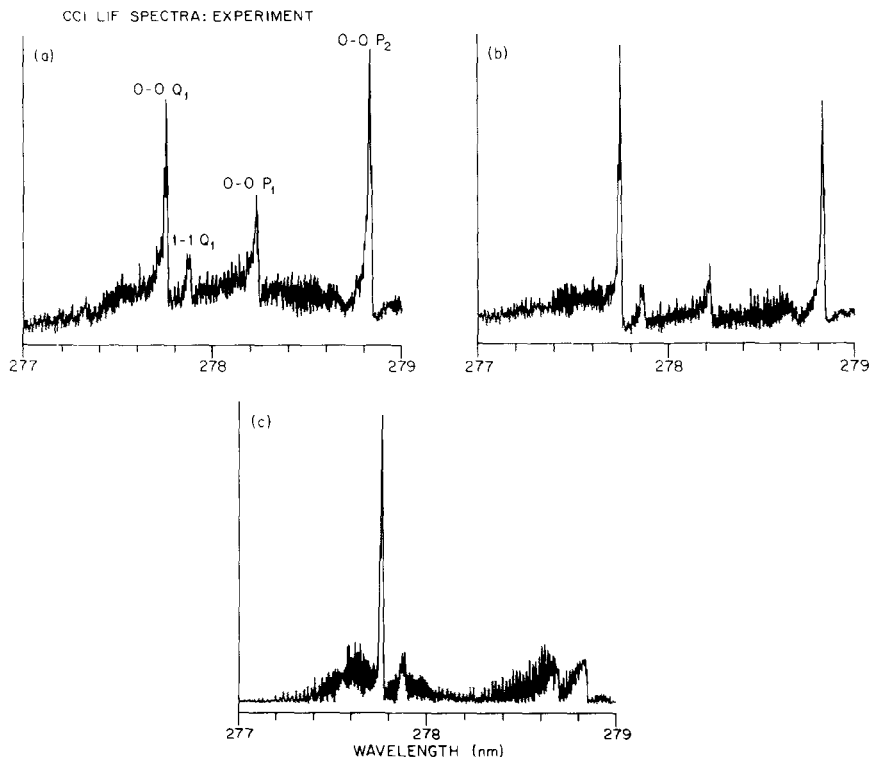


FIG. 1. Laser-induced fluorescence spectra of $\text{CCl } A^2\Delta-X^2\Pi$ produced in the photolysis of 50 to 70 mTorr of 1/9 $\text{C}_3\text{O}_2/\text{CICN}$ mixtures at three pump-probe delays. The peak at 278.2 nm disappears much more rapidly than the 1-1 Q_1 bandhead. Delay: (a) 0.5 μsec ; (b) 1.0 μsec ; (c) 100 μsec .

Discussion. Previous observations of the 278.2-nm peak have been done with CCl produced either in a discharge (1, 2, 9) or by 20-kV electron impact (6). Both these techniques are capable of generating species with considerable rotational, vibrational, and electronic excitation. However, the extent of excitation observed in discharges is very sensitive to the conditions of the discharge, including the nature and history of exposed surfaces, the presence of minor contaminants, the power into the discharge, the nature and density of any buffer gases, and flow speed (13). This may account for the intermittent observation of this head, which is formed at a high J .

The experimental results of Larsson *et al.* (6) are consistent with the identification of the 278.2-nm peak as the 0-0 P_1 bandhead. They measured a lifetime for this peak of 86 nsec, in contrast with 108 nsec for the 0-0 Q_1 bandhead and 35 nsec for the 1-1 Q_1 bandhead. Because the P_1 bandhead comprises only lines originating from high rotational levels, while the Q_1 bandhead contains essentially all the Q_1 lines, the small difference between lifetimes measured at the P_1 and Q_1 bandheads can be easily explained by rotational relaxation, or J -dependent fluorescence or predissociation rates. It is more difficult to account for an $A(v' = 2)$ lifetime greater than that of $A(v' = 1)$.

Venkataswarlu commented over 40 years ago that four bandheads (Q_1 , P_1 , Q_2 , and P_2) should be observed for this band system, and identified the 278.2-nm peak as a 0-0 P bandhead (2). However, other parts of his analysis, particularly the band numbering, have since been revised. It is indeed hard to see how the band system could have a P_2 bandhead without also having a P_1 bandhead, even if only at high J .

In conclusion, the assignment of the 278.2-nm peak to the 0-0 P_1 bandhead is in agreement with all past and present observations, and the peak location and height can be simulated using the known spectroscopic constants. The fast collisional relaxation of this peak explains its disappearance in high pressure environments.

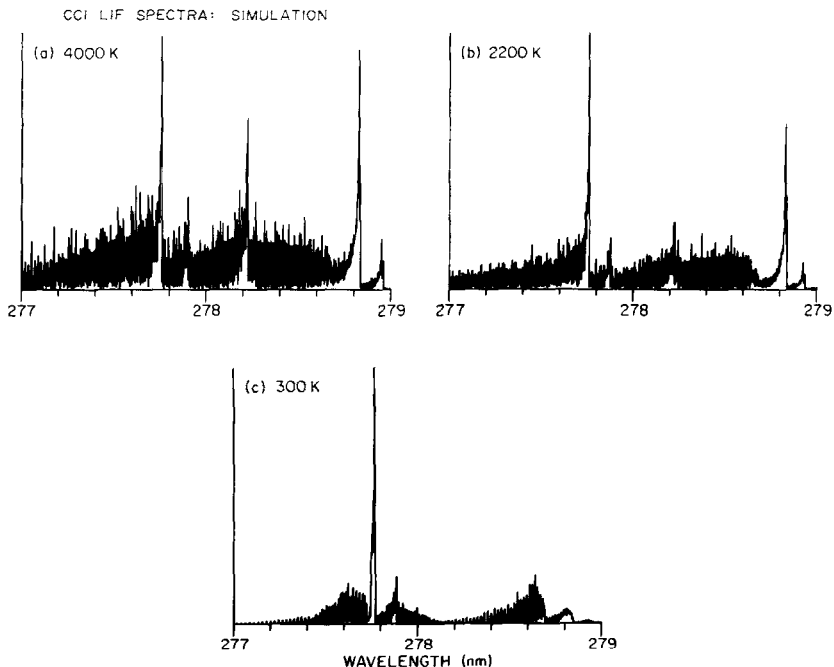


FIG. 2. Simulations of the CCl $A-X$ spectrum at three temperatures. Since the 0-0 P_1 bandhead is formed at a high J'' , it only appears at high temperatures. The 0-0 band temperature is stated. The 1-1 band temperature is 3000 K in (a) and (b), and 300 K in (c). The relative 0-0 and 1-1 band intensities have been adjusted to match the experimental spectra.

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