

NOTE

The Excitation Spectrum of Gas Phase Thiophosgene

It was erroneously reported recently that the $\text{CSCl}_2 \bar{a}^3A_2-\bar{X}^1A_1$ transition was observed by dye laser excitation spectroscopy (1). In that work a Rhodamine 6G dye laser was scanned through the 560-610-nm spectral region while emission was observed. We wish to report the extension of the spectrum to a short wavelength limit of 539 nm using a Rhodamine 110 dye laser and to correct the results reported for Rhodamine 6G.

Analysis of the Rhodamine 110 excitation spectrum (Fig. 1; uncorrected for dye laser intensity variation) shows that only emission from the \bar{A}^1A_2 state is definitely observed. The strong features marked on Fig. 1 match "hot" bands of the $\bar{A}-\bar{X}$ transition assigned by Brand *et al.* (2) from absorption data. Triplet bands (3) reported to have about the same intensity in absorption in this region are not observed here. The absence of the relatively strong $4_0^4 \bar{a}-\bar{X}$ transition at $18\,027.9 \text{ cm}^{-1}$ observed by Moule and Subramaniam (3) implies that, for our detection method, the triplet bands are reduced in intensity by at least a factor of 20 relative to singlet bands.

All bands reported by Brand *et al.* (2) between $17\,000$ and $18\,550 \text{ cm}^{-1}$ are observed with the exceptions of $2_1^0 3_0^1 4_2^3$, $3_0^1 4_2^3$, $2_0^1 3_0^1 4_2^1$, and $2_1^0 4_0^3$. This suggests that either these bands are too weak to be observed easily by excitation spectroscopy (due to small absorption strength or unusually rapid quenching) or they have been misassigned and belong to the $\bar{a}-\bar{X}$ transition.

Weak bands with multi-peaked contours are observed at $17\,660$, $17\,954$, and $18\,424 \text{ cm}^{-1}$. These are the most intense of the multi-peaked bands. Figure 2 contrasts the shape of the single peaked $3_0^1 4_2^1$ band with that of the multi-peaked, new band at $17\,954 \text{ cm}^{-1}$. Band contours in Fig. 2 are typical both of hot band $\bar{A}-\bar{X}$ transitions and the weak bands. The multi-peaked bands do not seem to belong to an impurity. Their contour could be caused by overlap of several weak vibronic bands of the $\bar{A}-\bar{X}$ transition or to parallel as opposed to perpendicular rotational selection rules.

An excitation spectrum gives information similar (but not identical) to that provided by a conventional absorption spectrum. In order for a transition to appear strongly in an excitation spectrum the molecule must have more than a large absorption cross section. The molecule must also fluoresce or phosphoresce before it is deactivated. For thiophosgene this means that the overlapping $\bar{a}^3A_2-\bar{X}^1A_1$ and $\bar{A}^1A_2-\bar{X}^1A_1$ transitions can be separated because of different photophysical behavior. Only the singlet-singlet transition appears in the excitation spectrum recorded with fluorescence detection. Spectrophone

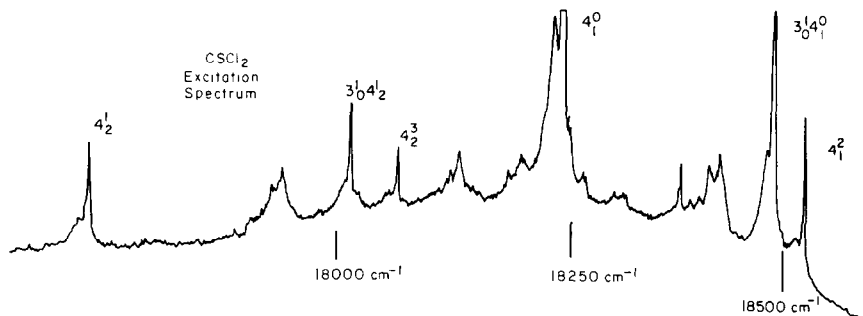


FIG. 1. CSCl_2 excitation spectrum recorded using a Rhodamine 110 dye laser. $\bar{A}^1A_2-\bar{X}^1A_1$ vibrational bands are labeled.

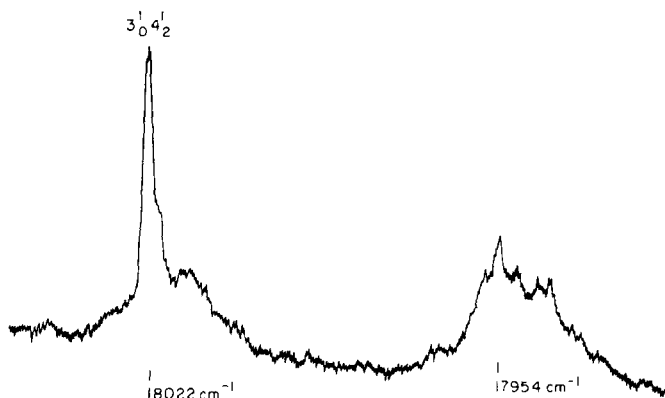


FIG. 2. Excitation spectrum of CSeCl_2 near the $3_0^1 4_2^1$ band of the $\bar{A}^1 A_2 - \bar{X}^1 A_1$ transition. This spectrum illustrates the difference between the contours of the $3_0^1 4_2^1$ band and the weak multi-peaked band near $17\,954\text{ cm}^{-1}$.

detection is quite sensitive to the triplet band (f). The $\sim 35\text{-}\mu\text{sec}$ lifetime of the singlet is much longer than the collisional quenching time (f) at the $\sim 400\text{-mTorr}$ pressure used in this experiment. The reported oscillator strength (f) of the triplet transition suggests that the triplet lifetime is six times longer than the singlet. The longer lifetime of the triplet is still not sufficient to account for the absence of $\bar{a}-\bar{X}$ bands from our excitation spectrum. The $\bar{a}^3 A_2$ state must also have a much larger quenching cross section than the $\bar{A}^1 A_2$ state. This is not unreasonable since the $\bar{a}^3 A_2$ state has A_1 , B_2 , and B_1 spin-electronic components and probably the A_1 component (by mixing with the $\bar{B}^1 A_1$ state) is most strongly connected radiatively with the ground state (I). Emission from the triplet state could thus be easily quenched by collisional population of weakly radiative B_1 and B_2 components.

A wavelength calibration error for the bands observed with Rhodamine 6G excitation by Lombardi *et al.* (I) led to the erroneous conclusion that triplet emission had occurred. This also suggests that the 528.7-nm Ar^+ laser line, for which thiophosgene emission spectra were reported (I), may be exciting the $^o P$ branch of the $\bar{A}-\bar{X}$ $1_0^1 3_0^1 4_2^1$ band or perhaps a weak unreported singlet band.

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REFERENCES

1. J. R. LOMBARDI, J. B. KOFFEND, R. A. GOTTSCHO, AND R. W. FIELD, *J. Mol. Spectrosc.* **65**, 446 (1977).
2. J. C. D. BRAND, J. H. CALLOMON, D. C. MOULE, AND T. H. GOODWIN, *Trans. Faraday Soc.* **61**, 2365 (1965).
3. D. C. MOULE AND C. R. SUBRAMANIAM, *J. Mol. Spectrosc.* **48**, 336 (1973).
4. R. N. DIXON, D. A. HAUER, AND C. R. WEBSTER, *Chem. Phys.* **22**, 199 (1977).
5. J. R. McDONALD AND L. E. BRUS, *Chem. Phys. Lett.* **16**, 587 (1972).

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