

Analysis of the P Branch of the ν_6 Fundamental of Carbon Suboxide

In this note, we present an analysis of the $\nu_6(\pi_u)$ band of C_3O_2 . The carbon suboxide sample was prepared by the decomposition of malonic acid as described previously (1, 2). In Fig. 1 we show the Fourier transform spectrum of the ν_6 region at a resolution of 0.04 cm^{-1} . The peak absorption occurs near 550 cm^{-1} , which was the value reported for ν_6 in previous studies of this region (2-4). The high resolution spectrum in Fig. 1 shows a series of Q branches beginning at 540 cm^{-1} and extending to higher frequency. Miller and Fateley (2) also noted fine structure in the ν_6 band, but no previous assignments have been made to date.

The appearance of the ν_6 band is qualitatively similar to the ν_2 and $2\nu_6$ Raman bands (5, 6) as well as the $\nu_2 + \nu_7$ infrared band (7, 8). In each of these cases the ground state transition is the lowest lying Q branch and the "hot" bands are shifted to a higher frequency. We thus expect the peak near 540 cm^{-1} to be the ground state transition and the structure at higher frequency to be due to "hot" bands. Duckett *et al.* have, in fact, reached the same conclusion (7).

Figure 2 shows an expanded plot of the region below the first Q branch. The series of nearly uniformly spaced lines is undoubtedly the P branch from the ground state transition. The J values can be unambiguously assigned by constraining the ground state constants (9) and requiring the band origin to be consistent with the position and shape of the unresolved Q branch. Table I gives the results of a least-squares analysis, fitting the observed P lines to the formula:

$$P(J) + F(J) = \nu_0 + B'J(J - 1) - D'J^2(J - 1)^2 + H'J^3(J - 1)^3, \tag{1}$$

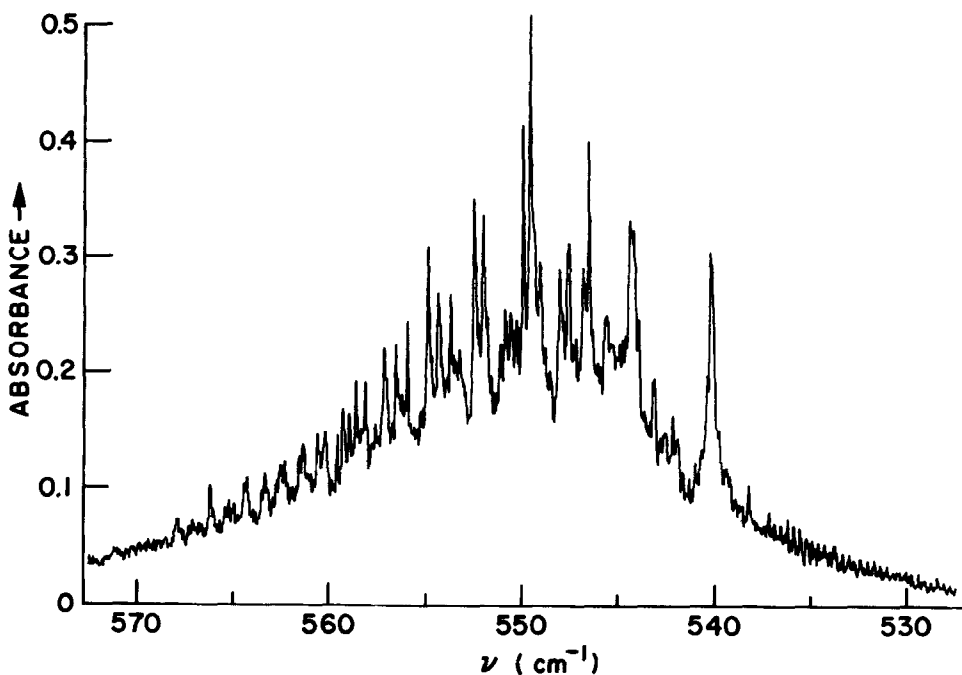


FIG. 1. Fourier transform spectrum of the ν_6 band of C_3O_2 at $\approx 0.04\text{ cm}^{-1}$ resolution, 10^{-2} Torr, and 40-m path length.

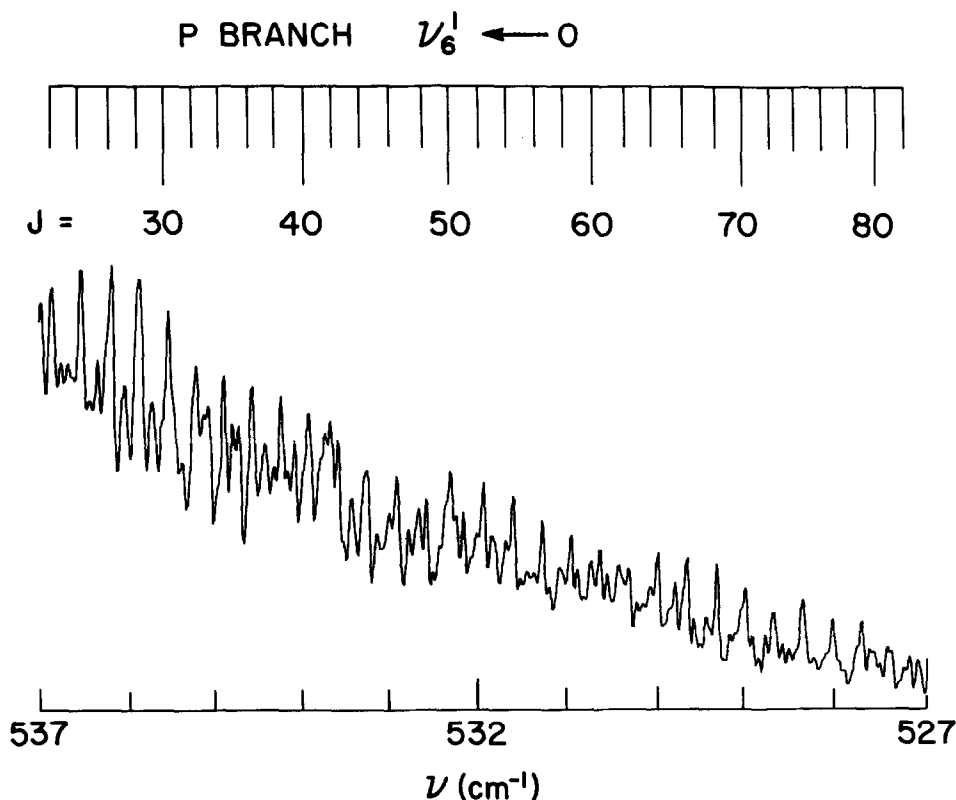


FIG. 2. Expanded plot of the P branch of the ν_6 ground state transition of C_3O_2 . Experimental conditions are the same as those for Fig. 1.

where $F(J)$ is the ground state rotational energy. The band origin is roughly 0.05 cm^{-1} above the Q -branch peak, consistent with the small negative $B' - B''$ expected for the $\nu_6 \leftarrow 0$ Q branch. Changing the J assignments by ± 2 still allows the lines to be fit well by Eq. (1), but the resulting band origins are $\approx 0.3 \text{ cm}^{-1}$ too low or too high.

The error analysis was done by assigning a statistical uncertainty of $\pm 0.0080 \text{ cm}^{-1}$ to each line position. Isolated lines can be measured to a relative precision about an order of magnitude greater, but most of the lines in Fig. 2 are blended. Lines which are badly overlapped were omitted from the fit. Since Eq. (1) is a cubic equation in $J(J - 1)$, a closed-form expression can be used to evaluate the least-squares parameters and their standard deviations (10). Systematic errors resulting from errors in the interferometer calibration or uncertainties in the ground state constants were ignored in the analysis, since these are in general small compared with the uncertainties reported in Table I.

Note that the $B' - B''$ value is negative, indicating an increased moment of inertia of the molecule in the ν_6 state. This sign is anomalous since a \perp vibration usually decreases the moment of inertia. A similar anomaly was found in the $\nu_4(\sigma_v)$ vibration where a negative $B' - B''$ was expected but a positive one was observed (1). In both cases the sign of $B' - B''$ is explained by the change in the ν_7 potential function. In ν_4 the potential barrier at the linear position increases, producing an average configuration that is more bent than it is in the ground state, while in ν_6 the barrier must decrease. The shift of the "hot" bands to higher frequency and the negative sign of $D' - D''$ are also consistent with a reduced potential barrier.

In an attempt to determine the ν_7 potential in the ν_6 state, we have made tentative assignments of a few of the "hot" band Q branches and fitted these with an adjustable potential using the rigid bender model (11). The prominent peak near 544.5 cm^{-1} is certainly the transition from ν_7^1 , but the remaining

TABLE I

Observed Wavenumbers (vac. cm^{-1}) of P Lines of the $\nu_6 \leftarrow 0$ Transition of C_3O_2^a

J	P(J)	0-C $\times 10^3$
22	536.8533	18.3
24	536.5218	3.3
26	536.1904	-10.5
28	535.8740	-8.2
30	535.5432	-19.4
32	535.2412	-0.9
34	534.9248	4.0
36	534.6084	9.8
38	534.2776	2.0
46	532.9818	4.4
48	532.6499	-1.6
52	532.0028	4.4
54	531.6707	-0.6
56	531.3393	-4.7
58	531.0088	-7.5
60	530.6913	2.9
62	530.3748	14.4
64	530.0297	-2.5
66	529.7001	-3.7
68	529.3661	-9.2
70	529.0461	-0.5
72	528.7190	1.1
74	528.3970	8.0
76	528.0583	-1.6
78	527.7292	-1.5

^a The molecular constants in cm^{-1} determined by a least-squares fit to Eq. (1) are $\nu_0 = 540.2365 \pm 0.0086$, $B' - B'' = (-1.739 \pm 0.123) \times 10^{-4}$, $D' - D'' = (-0.987 \pm 0.448) \times 10^{-8}$, and $H' - H'' = (-4.2 \pm 4.6) \times 10^{-13}$. The uncertainties are one standard deviation. The rms error of the fit is 0.0078 cm^{-1} for 25 lines.

assignments are far less certain. Our analysis suggests that the barrier at the linear position is roughly 15 cm^{-1} , compared with a barrier height of 29 cm^{-1} in the ground state. This value is in good agreement with the estimate of Duckett *et al.* (7), which was made on the basis of lower resolution data. Higher resolution data are needed to complete the analysis of the "hot" band structure. This would be a particularly good problem to study with diode lasers, since the spectral region of interest is only 20 cm^{-1} wide, from 540 to 560 cm^{-1} .

REFERENCES

1. W. H. WEBER, P. D. MAKER, AND C. W. PETERS, *J. Chem. Phys.* **64**, 2149-2158 (1976).
2. F. A. MILLER AND W. G. FATELEY, *Spectrochim. Acta* **20**, 253-266 (1964).
3. D. A. LONG, F. S. MURFIN, AND R. L. WILLIAMS, *Proc. Roy. Soc. London A* **223**, 251-266 (1954).
4. H. D. RIX, *J. Chem. Phys.* **22**, 429-433 (1954).
5. J.-E. LOLCK AND S. BRODERSEN, *J. Mol. Spectrosc.* **72**, 445-462 (1978).
6. J.-E. LOLCK AND S. BRODERSEN, *J. Mol. Spectrosc.* **75**, 234-244 (1979).
7. J. A. DUCKETT, I. M. MILLS, AND A. G. ROBIETTE, *J. Mol. Spectrosc.* **63**, 249-264 (1976).
8. C. W. PETERS, W. H. WEBER, AND P. D. MAKER, *J. Mol. Spectrosc.* **66**, 133-149 (1977).
9. A. W. MANTZ, P. CONNES, G. GUELACHVILI, AND C. AMIOT, *J. Mol. Spectrosc.* **54**, 43-53 (1975).

10. See, for example, P. R. BEVINGTON, "Data Reduction and Error Analysis for the Physical Sciences," Chap. 8, McGraw-Hill, New York, 1969.
11. W. H. WEBER AND G. W. FORD, *J. Mol. Spectrosc.* **63**, 445-458 (1976).

W. H. WEBER
P. D. MAKER

*Physics Department
Research Staff
Ford Motor Company
Dearborn, Michigan 48121*

C. W. PETERS

*Physics Department
University of Michigan
Ann Arbor, Michigan 48109*

Received: August 7, 1978