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"Pseudo-parallel" Infrared Bands of Oblate Symmetric Tops: Cyclopropane ν_{11}

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New high resolution data on the cyclopropane ν_{11} infrared band have been investigated in detail using an l-type resonance calculation computer program. An analysis has been made based on the computer simulation technique both to simulate the shape of the observed P, Q and R branches in detail and to obtain a precise match to the frequency of all the fine structure "lines" in the P and R branches. Our results represent an improvement on previous values of the band constants. In addition, we have shown conclusively that the observed P and R branch "lines" arise from clusters of closely spaced ${}^PP_K(J)$ and ${}^RR_K(J)$ lines of a given J and that in this band the peaks of these "lines" correspond to the most intense $K = J$ component or very close to it.

INTRODUCTION

Of the four perpendicular infrared active fundamentals of normal cyclopropane, only two, namely ν_9 at 1438 cm^{-1} and ν_{10} at 1028 cm^{-1}, have previously been resolved and their line positions measured *(1)*. The positions of the other two fundamentals, ν_8 at 3024 cm^{-1} and ν_{11} at 868 cm^{-1}, were also measured by Duncan *(1)* but their fine structure was not well resolved and line positions were not published. Cartwright and Mills *(2)*, however, have now presented an analysis of Duncan's experimental data on three of the fundamentals, ν_9, ν_{10} and ν_{11}, using a computer simulation technique in which the l-type resonance perturbation present in all three bands is calculated exactly.

The ν_{11} band has now been remeasured *(3)* under high enough resolution to resolve the J structure in the P and R branches. For this band, $X_t = (C_v - B_v - C_e\zeta) \simeq 0$[1], and it is thus of the "pseudo-parallel" type which was first resolved in the infrared spectrum of nitrogen trifluoride, another oblate symmetric top molecule, by Popplewell, Masri and Thompson *(4)*. We have made a detailed investigation of the ν_{11} band of cyclopropane and have obtained an analysis which is rather different from those given previously *(1, 2)*. The results of our investigation are the subject of the present paper.

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[1] $(C_v - B_v - C_e\zeta)$ should strictly be written in the form $(C_v - (C\zeta)_v - B_v)$ where $(C\zeta)_v = C_e\zeta^z +$ (higher order terms). For ν_{11} of cyclopropane, an order of magnitude analysis of the neglected terms in $(C\zeta)_v$ when approximated by $C_e\zeta^z$ leads to an expected maximum error in $\zeta^z \sim 0.006\ \text{cm}^{-1}/C_e$.

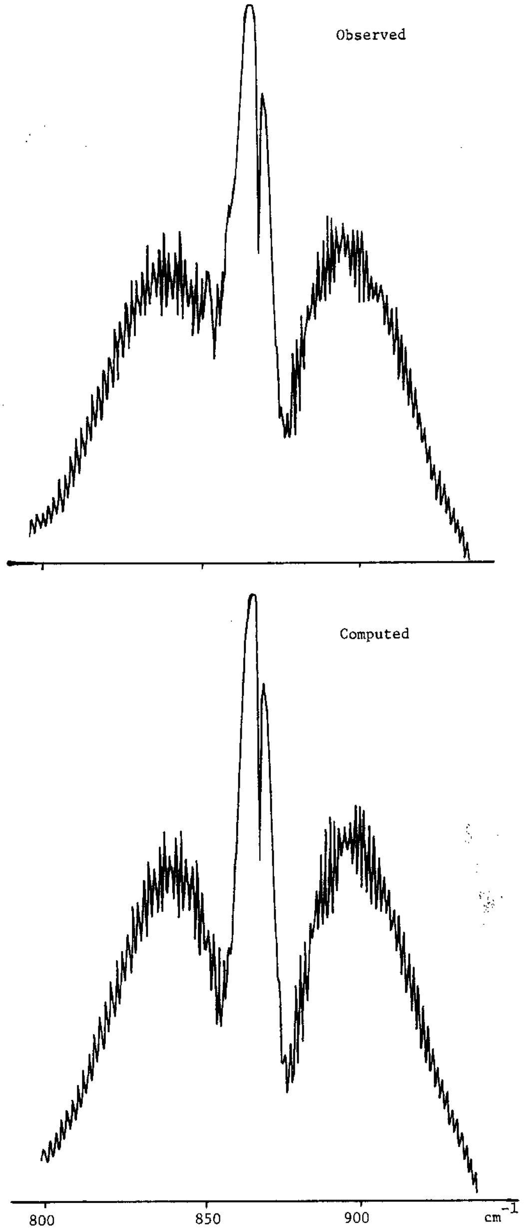

Fig. 1. Observed and Computed Spectra for cyclopropane ν_{11}

RESULTS

The ν_{11} band of cyclopropane is shown in Fig. 1. The band consists of a broad "split" Q branch, with the low frequency maximum more intense than the high one, and a series of well-resolved "lines" in the P and R branches with frequencies given in Table I.

TABLE I

CYCLOPROPANE ν_{11} : P AND R "LINES" (IN CM^{-1})

	$P(J)$				$R(J)$			
J	Obsd	Calcd-Obsd (this work)	$K_{\max}$	Calcd-Obsd (CM)[a]	Obsd	Calcd-Obsd (this work)	$K_{\max}$	Calcd-Obsd (CM)[a]
5					878.53			
6					79.95	−0.04	6	−0.01
7	857.43	0	7	+0.03	81.38	−0.03	6	0
8	55.91	−0.06	8	−0.02	82.77	+0.07	7	+0.03
9	—				—			
10	—				86.37	+0.02	10	+0.05
11	50.72	−0.02	11	−0.09	87.99	−0.06	10	−0.12
12	49.24	−0.10	12	−0.22	89.42	+0.07	11	−0.04
13	—				90.95	0	12	−0.13
14	45.63			−0.13	92.30	+0.10	12	−0.03
15	44.08	−0.05	15	−0.27	93.77			
16	—				95.95			
17	40.57				97.34	+0.12	16	−0.09
18	38.95	−0.02	18	−0.35	99.08	−0.01	18	−0.36
19	37.37	+0.02	18	−0.36	900.53	0	18	−0.41
20	—				1.92	+0.08	19	−0.36
21	33.75	+0.08	21	−0.48	3.45	+0.08	20	−0.40
22	32.20	+0.04	21	−0.51	4.96	+0.06	20	−0.51
23	30.33				—			
24	28.78	−0.07	24	−0.83	—			
25	27.11	−0.02	24	−0.79	9.85	−0.02	24	−0.60
26	25.31	−0.04	25	−0.73	11.38	−0.03	25	−0.63
27	23.57	−0.02	26	−0.97	13.01	0	26	−0.77
28	21.79	0	27	−0.85	14.48	0	27	−0.85
29	20.10	0	28		15.92	+0.06	28	−0.87
30	18.36	−0.01	29	−1.16	17.43	+0.09	29	−0.93
31	16.44	+0.09	31	−1.04	18.90	+0.13	30	−0.97
32	814.89	0	31		920.37	+0.09	31	−1.07
33	—				921.83	+0.19	32	
34	811.32	−0.05	34	−1.37	23.50	+0.02	33	−1.27
35	9.65			−1.52	25.08	−0.01	34	−1.48
36	7.78				—			
37	806.13	−0.11	36	−1.80	28.16	−0.09	36	−1.61
38					29.60	−0.08	36	−1.62
39					931.16	−0.08	38	−1.73
41					934.10	−0.02	40	−2.00

[a] Calculated from Cartwrights and Mills' band constants (Table II).

TABLE II

BAND CONSTANTS DETERMINED FOR CYCLOPROPANE ν_{11}

	This work		Cartwright and Mills	
ν_0 (cm^{-1})	868.40	±0.10	868.5	±0.1
ζ^z	−0.955	±0.010	−0.96	
α^c (cm^{-1})	0.0018	±0.0003	0.0030	±0.0005
α^B (cm^{-1})	0.0013	±0.0005	0.0030	±0.0005
q (cm^{-1})	0.005	±0.001	0.0065	±0.0005

The two maxima in the Q branch are assigned to the ^PQ branch at lower frequency and the ^RQ branch at higher frequency and the splitting is attributed to l-type resonance in agreement with Cartwright and Mills. The feature at 853 cm^{-1} is assigned to the Q branch of the very weak parallel ν_7 fundamental. Since the Coriolis constant $\zeta^y_{7,11}$ coupling these two vibrations has a magnitude of only 0.02 (*1*), the Coriolis interaction between ν_7 and ν_{11} is unlikely to require a special treatment despite the proximity of the two bands.[2]

For our analysis of ν_{11} we have employed a computer simulation technique using a computer program similar to that described by Cartwright and Mills. The final band parameters obtained from the computer calculated spectrum which best reproduced the observed ν_{11} band are shown in Table II. The values assumed for C_0, B_0, and C_e were $C_0 = C_e = 0.42$ cm^{-1}, and $B_0 = 0.67024$ cm^{-1}. These are the same as those adopted by Cartwright and Mills. The values of the other five band constants were determined in this study by a process of iterative computation of the complete band contour so as to obtain the best match between calculated and observed features in the P, Q and R branches. Thus ν_0, ζ^z and α^C were determined by precisely matching the calculated and observed frequencies in the P and R branches. q was determined by obtaining the best match to both the relative intensities of the two Q branch maxima and their frequency separation. α^B was determined from the best match to the absolute positions of the two Q branch maxima relative to the band centre. It is believed that through this procedure we have obtained a unique solution for the band constants.

The agreement between our final calculated spectra and the observed one, compared in Fig. 1, is very encouraging. The detailed agreement between the P and R "line" positions in the observed and calculated spectra, shown in the second

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[2] This assumption has been confirmed by obtaining a computer simulation of the ν_7/ν_{11} Coriolis interaction using a computer program similar to that described by C. di Lauro and I. M. Mills [*J. Mol. Spectrosc.* **21**, 386 (1966)]. The results for both positive and negative signs for the interaction were almost identical with each other, and, apart from the ν_7 peak region between $P(9)$ and $P(10)$ of ν_{11}, were indistinguishable from ν_{11} spectra calculated without the Coriolis interaction.

For the ratio of the dipole moment derivatives, the coriolis perturbation calculation gave

$$(\partial\mu^z/\partial Q_7)/(\partial\mu^x/\partial Q_{11a}) \simeq 1/8.$$

column of Table I, is also very satisfactory. In view of the occurrence of "pseudo-parallel" bands in many oblate top spectra (*1*, *4*, *5*), it seems of interest to proceed further with an investigation of the detailed structure of the ν_{11} band of cyclopropane. Thus we have obtained computer printouts from our program of the perturbed frequencies and intensities of all the lines in the band. From these we have been able to determine unequivocally the origin of the observed features in the P and R branches of ν_{11}, and have, in this way, arrived at the J numbering of the P and R "lines" that we have given in Table I. These P and R features

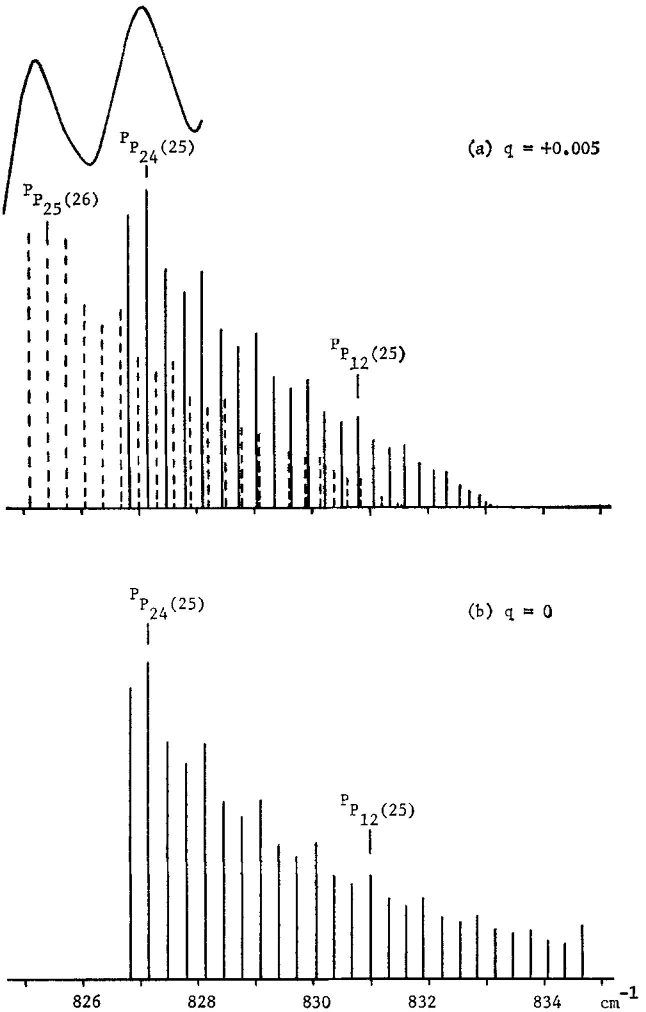

FIG. 2. Diagrams of the overall profile of the "line" ^PP (25) and of its K components for cyclopropane ν_{11} (a) with and (b) without l-type resonance.

arise from clusters of ${}^PP$ and ${}^RR$ lines with the same J value but with different K values; this clustering occurs because the coefficient of the K-dependent term $(C_v - B_v - C_e\zeta) \simeq 0$ in this type of band.[3] Hence our description of them as "pseudo-parallel" bands. The peaks of the observed features correspond very closely to the dominant high K components for which $K \simeq J$ since these are the most intense lines in the P and R branches. This effect is illustrated in Fig. 2 for the "line" ${}^PP$ (25). Figure 2(a) shows the individual ${}^PP_K$ (25) transitions beneath the overall computed profile of the ${}^PP$ (25) "line". For comparison, the adjacent ${}^PP_K$ (26) transitions are shown by broken lines (where they do not overlap the ${}^PP_K$ (25) transitions) beneath the overall computed profile of the ${}^PP$ (26) "line". The peak of the overall ${}^PP$ (25) "line" profile corresponds in position to the ${}^PP_{24}$ (25) component just as the peak of the ${}^PP$ (26) "line" profile corresponds to the ${}^PP_{25}$ (26) component. Figure 2(b) compares the same ${}^PP_K$ (25) transitions calculated from the unperturbed frequency and intensity expressions (*6*) in order to show the effects of l-type resonance. Clearly, the l-type resonance effects ar *not* very significant in the P "line" profiles in this band. To show that this situation is typical of all the P and R "lines" in the band, Table I includes the K component obtained from our computer printout which falls closest to each measured peak position in our final computer calculated spectrum. This component appears in the column headed "$K_{\max}$" in Table I. It is apparent from these figures that all the peaks in the P and R branches of the cyclopropane ν_{11} band correspond to the $K = J$ component or very close to it.

DISCUSSION

The band constants we have obtained for cyclopropane ν_{11} differ from those that have been obtained by previous workers (*1*, *2*). Accordingly, we have obtained a computer calculated spectrum using the band constants determined by by Cartwright and Mills (see Table II) in such a way as to reproduce the degree of resolution of the more highly resolved observed spectrum. The computed frequencies that were obtained in this way for the P and R branches may be compared with the observed values by examining the Calcd-Obsd (CM) column in Table I. As a result of the substantial discrepancies apparent in these figures at higher J values it would seem that our present analysis should be regarded as more reliable than that of Cartwright and Mills. This is probably due to the lower degree of resolution obtained in Duncan's spectra of the ν_{11} band.

In the rotational analysis given above, we have neglected the effects of centrifugal distortion. This is partly due to our lack of knowledge of all the constants $D_0{}^J$, D_0^{JK}, and $D_0{}^K$, but partly also on the basis of theoretical arguments and analogies with other oblate tops.

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[3] The influence of the normally weak ${}^PR$ and ${}^RP$ lines on the positions of the P and R branch features is considered negligible in this band. Thus the strongest ${}^RP$ lines have less than 10% of the intensity of the strongest ${}^PP$ lines, while the strongest ${}^PR$ lines are only 0.1% as intense as the strongest ${}^RR$ lines.

Now the preceding arguments have shown that the peaks in the P and R branches of the cyclopropane ν_{11} band correspond closely to the $K = J$ components of the ${}^PP(J)$ and ${}^RR(J)$ "lines". For the ${}^PP_J(J)$ components, the terms in the vibration rotation energy involving the centrifugal distortion constants may be written

$$4D_0^JJ^3 + D_0^{JK}(4J^3 - 3J^2 + J) + D_0^K(4J^3 - 6J^2 + 4J - 1).$$

If we carry through only the more important terms in J^3, we obtain

$$4(D_0^J + D_0^{JK} + D_0^K)J^3.$$

A similar expression holds for the ${}^RR_J(J)$ components. Thus any calculation including centrifugal distortion effects would require reliable estimates of all three of the distortion constants. The only accurate experimental values of a centrifugal distortion constant for cyclopropane are for D_0^J, the best estimate being 8.2×10^{-7} cm^{-1} (*7*). This is supported by the value $D_0^J \simeq 9.5 \times 10^{-7}$ cm^{-1} calculated from the harmonic force field (*8*), which also yielded an estimate of $D_0^{JK} \simeq -8.3 \times 10^{-7}$ cm^{-1}. On the other hand, no estimate of D_0^K is apparently available and for this reason we decided that an inclusion of centrifugal distortion terms in our analysis was not justified.

However, we do not believe that their omission is likely to be a significant source of error for the following reasons. If Duncan's calculated estimate (*8*) of D_0^{JK} is accepted, then the terms in D_0^J and D_0^{JK} will cancel leaving only the D_0^K term. Very roughly we might expect that $D_0^K/D_0^J \sim C/B$ which suggests that $D_0^K \sim 5 \times 10^{-7}$ cm^{-1} for cyclopropane. This would lead, for example, to a shift of only 0.05 cm^{-1} for the ${}^PP_{30}(30)$ line, which is well within the error limits of Table II. If, on the other hand, we make use of the formula $(D_0^{JK}/2D_0^J) \sim [(C/B)^4 - 1]$, applicable to planar molecules of D_{3h} symmetry (*9*), then D_0^{JK} is estimated to be about 14×10^{-7} cm^{-1}. Taking this value with the rough estimate of D_0^K above, the complete centrifugal distortion term above becomes vanishingly small. Finally, the values of the centrifugal distortion constants obtained for other oblate top molecules such as NF_3 (*10*) and CF_3H (*11*) lead to values of $(D_0^J + D_0^{JK} + D_0^K)$ which are vanishingly small. It, therefore, seems reasonable to have excluded the effects of centrifugal distortion in our analysis.

The error estimates for each of the band constants that we have determined in Table II have been arrived at in a similar fashion to that employed by Popplewell, Masri and Thompson (*4*). ν_0 can be chosen to within 0.10 cm^{-1}, including the uncertainty in obtaining exact superposition of calculated and observed spectra. For a $K = J = 30$ line, for example, a change of 0.01 in ζ_{11} leads to a shift of 0.25 cm^{-1} while a change of 0.0003 cm^{-1} in α_{11}^c leads to a shift of 0.27 cm^{-1}. Taking the interdependence of all the band constants into account, it is considered that ζ_{11} and α_{11}^c can be fixed to within ± 0.01 and ± 0.0003 cm^{-1}, respectively. It is difficult to make estimates of error in our values of q_{11} and

α_{11}^{B} since they were not determined from all the P and R "line" frequencies. However, it is believed that the uncertainties in these parameters are within the error limits given in Table II. Similar error limits have previously been suggested for l-type doubling constants estimated in this way (*2*).

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