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# *PR* separations of band envelopes produced by prolate and oblate top molecules

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**Abstract**—A study of *PR* separations produced by a relatively large number of prolate and oblate asymmetrical top molecules reported in the literature revealed that under certain conditions the branch separations of type $A(\|)$, type $B(\perp)$ and type $C(\perp)$ bands (prolate molecules) are in the proportion of

$$1:1/S(\tilde{\beta}):3/2$$

whereas the separations produced by type $A(\perp)$, type $B(\perp)$ and type $C(\|)$ bands (oblate molecules) are in the proportion of

$$\tfrac{2}{3}:1/S(\tilde{\beta}):1 \quad \text{and}$$
$$\tfrac{2}{3}:\tfrac{2}{3}:1 \quad \text{for planar oblate compounds.}$$

The branch separation of the parallel bands is found to obey the relation:

$$\Delta\nu(PR) = 10S(\tilde{\beta})(\tilde{B}T/9)^{1/2}\ \text{cm}^{-1}$$

For $\rho^* < \frac{3}{4}$ and $-1 < \varkappa < +1$ the proposed $\tilde{\varkappa}$ values fairly match those as calculated by Gerhard and Dennsion and Badger and Zumwalt as well. The method of predicting branch separations is therefore simplified while the agreement with the values observed by experiment is quite satisfactory.

## INTRODUCTION

FOR several decades spectroscopists have used the formulas of GERHARD and DENNISON [1] to predict *PR* separations of band envelopes produced by symmetrical top molecules. Even slightly unsymmetrical top molecules could be succesfully subjected to these calculations. About six years later, BADGER and ZUMWALT [2] carried out calculations concerning the band envelopes of unsymmetrical rotator molecules. While Gerhard and Dennison used $\beta$ and the separation function $S(\beta)$ as parameters, Badger and Zumwalt preferred $\varkappa$ (rather than Wang's $b$) and $\rho^*$ as molecular parameters.

Recently, HOLLAS [3] computed band envelopes of large symmetrical top molecules and found that compounds having large moments of inertia resemble top molecules to a greater extend than molecules with small moments of inertia having the same degree of asymmetry.

It was the purpose of this work to find a correlation between molecular parameters and *PR* separations observed by experiment.

[1] S. L. GERHARD and D. M. DENNISON, *Phys. Rev.* **43**, 197 (1933).
[2] R. M. BADGER and L. R. ZUMWALT, *J. Chem. Phys.* **6**, 711 (1938).
[3] J. M. HOLLAS, *Spectrochim. Acta* **22**, 81 (1966).

## NOTATION

The notation used in this paper is the one recommended by the Joint Commission for Spectroscopy [4], so that

$$A \geqslant B \geqslant C$$

for both prolate and oblate top molecules; $A$, $B$ and $C$ are the rotational constants expressed in reciprocal centimeters. Thus $A > B = C$ holds for prolate symmetrical top molecules while $A = B > C$ applies to oblate symmetrical top molecules. As a consequence, a band described as "type $A$" is parallel in prolate tops and perpendicular in oblate tops. Likewise, a "type $C$" band, being perpendicular in prolate tops, is parallel in oblate tops. A "type $B$" band is of the perpendicular type in prolate tops and oblate tops as well.

Furthermore, in prolate tops the type $A(\|)$ band results from transitions parallel to the minor axis of inertia whereas type $B(\perp)$ and type $C(\perp)$ bands arise from dipole vibrations perpendicular to this axis. Consequently in oblate tops, the type $C(\|)$ band results from dipole changes parallel to the major axis of inertia while type $A(\perp)$ and type $B(\perp)$ bands proceed from transitions perpendicular to this axis.

## $PR$ SEPARATION OF SYMMETRICAL TOP MOLECULES

(a) *Parallel bands*

According to Gerhard and Dennison, the $PR$ separation of parallel bands is found to obey the following relation:

$$\begin{aligned}
\Delta\nu(PR) &= S(\beta)(kT/\pi^2 I_b)^{1/2} && \text{which can be transformed into} \\
\Delta\nu(PR) &= 5S(\beta)(2BT/9)^{1/2}\ \mathrm{cm}^{-1} && \text{where} \qquad (1)\\
\log S(\beta) &= 0{\cdot}721/(\beta + 4)^{1{\cdot}13} && \text{and} \\
\beta + 1 &= A/B && \text{for prolate } (\beta > 0) \text{ and} \\
\beta + 1 &= C/B && \text{for oblate } (\beta < 0) \text{ symmetrical tops.}
\end{aligned}$$

It is clear that for $\beta = 0$ the molecule is a spherical top with $\Delta\nu(\|PR) = \Delta\nu(\perp PR)$ and $S(\beta) = \sqrt{2}$. There is no distinction between a parallel and a perpendicular band so that the $PR$ separation of spherical top molecules is

$$\Delta\nu(PR) = 10(BT/9)^{1/2}\ \mathrm{cm}^{-1} \qquad (2)$$

For $\beta = \infty$ the molecule is linear while again $\Delta\nu(\|PR) = \Delta\nu(\perp PR)$ but now $S(\beta) = 1$, hence

$$\Delta\nu(PR) = 5(2BT/9)^{1/2}\ \mathrm{cm}^{-1} \qquad (3)$$

(b) *Perpendicular bands*

In the curves, as drawn by Gerhard and Dennison, the absorption coefficient of a perpendicular band is given as a function of the frequency. Instead of the frequency however, a quantity $x$ is introduced which is proportional to the frequency according to the relation

$$\begin{aligned}
x &= (\nu/\alpha)\sigma^{1/2} && \text{where } \sigma = h^2/8\pi^2 I_b kT \text{ and } \alpha = h/4\pi^2 I_b \text{ so that} \\
\nu - \nu_0 &= 2x(kc/h)^{1/2}(BT)^{1/2} && \text{where } \nu_0 \text{ is the band origin, hence} \\
\Delta\nu(PR) &= 10\hat{x}(BT/9)^{1/2}\ \mathrm{cm}^{-1} && (4)
\end{aligned}$$

[4] Joint Commission for Spectroscopy, *J. Chem. Phys.* **23**, 1997 (1955).

Table 1

| Shape of the molecule | ß | $S(ß)$ | $\hat{x}(\parallel)$ | $\hat{x}(\perp)$ |
|---|---|---|---|---|
| Oblate ($A = B > C$) | $-\frac{1}{2}$ | 1·496 | 0·748 | 1·058 |
| | $-\frac{1}{3}$ | 1·466 | 0·846 | 1·037 |
| Spherical ($A = B = C$) | 0 | 1·414 | 1·000 | 1·000 |
| Prolate ($A > B = C$) | $+\frac{1}{2}$ | 1·355 | 1·173 | 0·958 |
| | $+\frac{3}{4}$ | 1·330 | 1·245 | 0·941 |
| Linear ($A = \infty$, $B = C$) | $\infty$ | 1·000 | 0·707 | 0·707 |

where $\hat{x}$ represents the value of $x$ corresponding to the maxima of the $P$ and $R$ branches. Obviously, for $\hat{x} = 1$ the molecule is a spherical top (ß = 0) whereas for $\hat{x} = \sqrt{2}/2$ the molecule is linear (ß = $\infty$). Naturally it is of interest to know the function $\hat{x} = f(ß)$. Unlike Gerhard and Dennison however, only one range is considered for the moment, namely $-\frac{1}{2} < ß < \frac{3}{4}$.

For the sake of simplicity we assumed $\hat{x}$ to be a function of ß and $S(ß)$ so that in the approximation to which we worked, $\hat{x}$ was found to be proportional to ß and $S(ß)$ according to the following expression (Table 1):

$$\hat{x} = \tfrac{1}{2}S(ß)(2ß + 2)^{1/2} \quad \text{(perpendicular bands)} \tag{5}$$

$$\hat{x} = \tfrac{1}{2}S(ß)\sqrt{2} \quad \text{(parallel bands)} \tag{5a}$$

For $-\frac{1}{2} < ß < \frac{3}{4}$ we therefore have the following $PR$ separations:

$$\text{type } A(\perp): \Delta\nu(PR) = 5S(ß)(2CT/9)^{1/2}\ \text{cm}^{-1} \text{ (oblate symmetrical tops)} \tag{6}$$

$$\text{type } C(\perp): \Delta\nu(PR) = 5S(ß)(2AT/9)^{1/2}\ \text{cm}^{-1} \text{ (prolate symmetrical tops)} \tag{7}$$

Combining relations 1, 6 and 7 it is obvious that

$$\Delta\nu(\perp PR) = (ß + 1)^{1/2}\Delta\nu(\parallel PR) \tag{8}$$

## *PR* Separation of Asymmetrical Top Molecules

### (a) *Parallel bands*

When formula (1) is applied to predict $PR$ separations of type $A(\parallel)$ and type $C(\parallel)$ bands of asymmetrical top molecules, it shall be observed that the calculated values are generally higher than those found by experiment. In order to diminish the differences between calculated and observed frequencies, $2\tilde{B}$ has to be substituted for $B$, hence

$$\tilde{ß} + 1 = A/2\tilde{B} \text{ or}$$
$$\tilde{ß} + 1 = C/2\tilde{B}$$

where $\tilde{B}$ equals $BC/B + C$ and $AB/A + B$ for prolate and oblate top molecules respectively so that $\tilde{ß} = ß$ and $S(\tilde{ß}) = S(ß)$ for symmetrical top molecules whereas $\tilde{ß} > ß$ and therefore $S(\tilde{ß}) < S(ß)$ with asymmetrical top molecules. Furthermore, $2\tilde{B} = B$ for symmetrical tops while $2\tilde{B} < B$ with asymmetrical top molecules. As a result, (1) is transformed into

$$\Delta\nu(PR) = 10S(\tilde{ß})(\tilde{B}T/9)^{1/2}\ \text{cm}^{-1} \tag{9}$$

For planar oblate molecules however, $S(ß) \approx \frac{3}{2}$ and $\tilde{B} = C$ so that

$$\text{type } C(\parallel): \Delta\nu(PR) = 5(CT)^{1/2}\ \text{cm}^{-1} \tag{9a}$$

(b) *Perpendicular bands*

Badger and Zumwalt carried out calculations concerning the band envelopes of asymmetrical rotator molecules. Using formula 4, $\hat{x}$ was claimed to depend on $\rho^* = (A - C)/B$ and $\varkappa = (2B - A - C)/(A - C)$ while the envelopes of the three types of band were calculated and drawn for nine different sets of molecular parameters $\rho^*$ ($= \frac{1}{3}, \frac{1}{2}, \frac{3}{4}$ and $\frac{5}{4}$) and $\varkappa$ ($= -\frac{1}{2}$, 0 and $+\frac{1}{2}$). The majority of molecules studied and reported in the literature however possesses molecular parameters different from the sets given above so that sometimes a laborious extrapolation has to be carried out to calculate the $\hat{x}$ values and corresponding branch separations of the three types of band. In the approximation to which we worked, the $\hat{x}$ values (Table 2) were found to resemble those as calculated by Badger and Zumwalt for

Table 2

| | $-1 \leqslant \varkappa \leqslant -\frac{1}{2}$ | $-1 \leqslant \varkappa \leqslant 0$ | $-1 \leqslant \varkappa \leqslant 0$ | |
|---|---|---|---|---|
| Prolate molecules | $\rho^* \leqslant \frac{3}{4}$ | $\frac{3}{4} < \rho^* \leqslant 3$ | $\rho^* > 3$ | |
| $\hat{x}$, type $A(\parallel)$ bands | $S(\tilde{\beta})/(\rho + 1)^{1/2}$ | $S(\tilde{\beta})/(\rho + 1)^{1/2}$ | $6/5(\rho + 1)^{1/2}$ | $\rho = B/C$ |
| $\hat{x}$, type $B(\perp)$ bands | $S(\tilde{\beta})(A/\tilde{B})^{1/2}/2\rho$ | $1/(\rho + 1)^{1/2}$ | $1/(\rho + 1)^{1/2}$ | $\tilde{\beta} + 1 = A/2\tilde{B}$ |
| $\hat{x}$, type $C(\perp)$ bands | $S(\tilde{\beta})(A/\tilde{B})^{1/2}/2$ | $3S(\tilde{\beta})/2(\rho + 1)^{1/2}$ | $9/5(\rho + 1)^{1/2}$ | $\tilde{B} = BC/B + C$ |
| Oblate molecules | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant 0$ | |
| | $\rho^* \leqslant \frac{1}{3}$ | $\frac{1}{3} < \rho^* \leqslant \frac{1}{2}$ | $\rho^* > \frac{1}{2}$ | |
| $\hat{x}$, type $A(\perp)$ bands | $S(\tilde{\beta})(C/\tilde{B})^{1/2}/2$ | $S(\tilde{\beta})(C/\tilde{B})^{1/2}/2$ | $\frac{2}{3}S(\tilde{\beta})/(\rho+1)^{1/2}$ | $\rho = B/A$ |
| $\hat{x}$, type $B(\perp)$ bands | $S(\tilde{\beta})(C/\tilde{B})^{1/2}/2\rho$ | $S(\tilde{\beta})(C/\tilde{B})^{1/2}/2$ | $1/(\rho + 1)^{1/2}$ | $\tilde{\beta} + 1 = C/2\tilde{B}$ |
| $\hat{x}$, type $C(\parallel)$ bands | $S(\tilde{\beta})/(\rho + 1)^{1/2}$ | $S(\tilde{\beta})/(\rho + 1)^{1/2}$ | $S(\tilde{\beta})/(\rho + 1)^{1/2}$ | $\tilde{B} = AB/A + B$ |
| Oblate molecules | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant 0$ | |
| (planar) | $\rho^* \leqslant \frac{1}{3}$ | $\frac{1}{3} < \rho^* \leqslant \frac{1}{2}$ | $\rho^* > \frac{1}{2}$ | |
| $\hat{x}$, type $A(\perp)$ bands | $\frac{3}{4}$ | $\frac{3}{4}$ | $(C/B)^{1/2}$ | |
| $\hat{x}$, type $B(\perp)$ bands | $3A/4B$ | $\frac{3}{4}$ | $(C/B)^{1/2}$ | |
| $\hat{x}$, type $C(\parallel)$ bands | $3(C/B)^{1/2}/2$ | $3(C/B)^{1/2}/2$ | $3(C/B)^{1/2}/2$ | |

$\rho^* < \frac{3}{4}$ and $-\frac{1}{2} \geqslant \varkappa \geqslant +\frac{1}{2}$. The $\hat{x}$ values proposed for $\rho^* > \frac{3}{4}$ were found to agree with the branch separations observed by experiment.

The compound is regarded to be strongly asymmetrical when $-\frac{1}{2} < \varkappa < +\frac{1}{2}$. In this region and for $\rho^* \leqslant \frac{3}{4}$ the best results are obtained by extrapolation at constant $\rho^*$ using:

$$\hat{x} = \tilde{x}(1 \pm 2\varkappa) \mp 2\varkappa\hat{x}(\mp\tfrac{1}{2})$$

where $\tilde{x}$ represents the $\hat{x}$ value at $\varkappa = 0$ and $\hat{x}(\mp\frac{1}{2})$ the $\hat{x}$ value at $\varkappa = -\frac{1}{2}$ or $\varkappa = +\frac{1}{2}$ so that the following relations are to be used when $-\hat{x} < \varkappa < +\frac{1}{2}$:

$$\text{Prolate molecules, type } A(\parallel) \text{ bands: } 75\hat{x} = 75 - 2\rho^*(10 + 9\varkappa)$$
$$\text{type } C(\perp) \text{ bands: } 25\hat{x} = 25 + \rho^*(6 - 4{\cdot}3\varkappa).$$
$$\text{Oblate molecules, type } A(\perp) \text{ bands: } 15\hat{x} = 15 - 4\rho^*(1 + \varkappa)$$
$$\text{type } C(\parallel) \text{ bands: } 25\hat{x} = 25 + 2\rho^*(3 - 2{\cdot}2\varkappa).$$

Once the branch separations of the parallel bands are calculated, it is easy to find the $\Delta\nu(PR)$ of the perpendicular bands using the factors given in Table 3. For the sake of convenience some $\hat{x}$ values were calculated and tabulated (Table 4).

Table 3

| | | | |
|---|---|---|---|
| Prolate molecules | $-1 \leqslant \varkappa \leqslant -\frac{1}{2}$ | $-1 \leqslant \varkappa \leqslant 0$ | $-1 \leqslant \varkappa \leqslant 0$ |
| | $\rho^* \leqslant \frac{3}{4}$ | $\frac{3}{4} < \rho^* \leqslant 3$ | $\rho^* > 3$ |
| $\Delta\nu(PR)$ type $A(\parallel)$ | 1 | 1 | 1 |
| $\Delta\nu(PR)$ type $B(\perp)$ | $\frac{1}{2}[(\rho+1)/\rho](A/B)^{1/2}$ | $1/S(\tilde{\beta})$ | $\frac{5}{6}$ |
| $\Delta\nu(PR)$ type $C(\perp)$ | $\frac{1}{2}(\rho+1)(A/B)^{1/2}$ | $\frac{3}{2}$ | $\frac{3}{2}$ |
| Oblate molecules | $+1 \geqslant \varkappa \geqslant \frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant 0$ |
| | $\rho^* \leqslant \frac{1}{3}$ | $\frac{1}{3} < \rho^* \leqslant \frac{1}{2}$ | $\rho^* > \frac{1}{2}$ |
| $\Delta\nu(PR)$ type $A(\perp)$ | $\frac{1}{2}(\rho+1)(C/B)^{1/2}$ | $\frac{1}{2}(\rho+1)(C/B)^{1/2}$ | $\frac{2}{3}$ |
| $\Delta\nu(PR)$ type $B(\perp)$ | $\frac{1}{2}[(\rho+1)/\rho](C/B)^{1/2}$ | $\frac{1}{2}(\rho+1)(C/B)^{1/2}$ | $1/S(\tilde{\beta})$ |
| $\Delta\nu(PR)$ type $C(\parallel)$ | 1 | 1 | 1 |
| Oblate molecules | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant +\frac{1}{2}$ | $+1 \geqslant \varkappa \geqslant 0$ |
| (planar) | $\rho^* \leqslant \frac{1}{3}$ | $\frac{1}{3} < \rho^* \leqslant \frac{1}{2}$ | $\rho^* > \frac{1}{2}$ |
| $\Delta\nu(PR)$ type $A(\perp)$ | $\frac{1}{2}(\rho+1)^{1/2}$ | $\frac{1}{2}(\rho+1)^{1/2}$ | $\frac{2}{3}$ |
| $\Delta\nu(PR)$ type $B(\perp)$ | $\frac{1}{2}(\rho+1)^{1/2}/\rho$ | $\frac{1}{2}(\rho+1)^{1/2}$ | $\frac{2}{3}$ |
| $\Delta\nu(PR)$ type $C(\parallel)$ | 1 | 1 | 1 |

Table 4

| | $\hat{x}$, type $A(\parallel)$ | | | | $\hat{x}$, type $A(\perp)$ | | |
|---|---|---|---|---|---|---|---|
| $\varkappa$ | $-1$ | $-\frac{3}{4}$ | $-\frac{1}{2}$ | 0 | $+\frac{1}{2}$ | $+\frac{3}{4}$ | $+1$ |
| $\rho^*$ 0 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 |
| $\frac{1}{3}$ | 0·971 | 0·961 | 0·951 | 0·910 | 0·864 | 0·861 | 0·846 |
| $\frac{1}{2}$ | 0·958 | 0·944 | 0·927 | 0·865 | 0·803 | 0·775 | 0·748 |
| $\frac{3}{4}$ | 0·941 | 0·918 | 0·890 | 0·800 | | | |
| 1 | 0·926 | 0·894 | 0·854 | 0·733 | | | |
| $\frac{5}{4}$ | 0·912 | 0·872 | 0·819 | 0·651 | | | |
| $\frac{3}{2}$ | 0·901 | 0·849 | 0·780 | 0·532 | | | |
| 2 | 0·880 | 0·808 | 0·700 | | | | |
| $\frac{5}{2}$ | 0·864 | 0·772 | 0·608 | | | | |
| | $\hat{x}$, type $B(\perp)$ | | | | $\hat{x}$, type $B(\perp)$ | | |
| $\varkappa$ | $-1$ | $-\frac{3}{4}$ | $-\frac{1}{2}$ | 0 | $+\frac{1}{2}$ | $+\frac{3}{4}$ | $+1$ |
| $\rho^*$ 0 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 |
| $\frac{1}{3}$ | 1·120 | 1·069 | 1·016 | 0·976 | 0·936 | 0·896 | 0·846 |
| $\frac{1}{2}$ | 1·173 | 1·096 | 1·018 | 0·911 | 0·803 | 0·775 | 0·748 |
| $\frac{3}{4}$ | 1·245 | 1·125 | 1·012 | 0·762 | | | |
| 1 | 1·389 | 0·683 | 0·655 | 0·627 | | | |
| $\frac{5}{4}$ | 1·368 | 0·677 | 0·638 | 0·522 | | | |
| $\frac{3}{2}$ | 1·352 | 0·670 | 0·620 | 0·447 | | | |
| 2 | 1·320 | 0·655 | 0·578 | | | | |
| $\frac{5}{2}$ | 1·296 | 0·638 | 0·522 | | | | |
| | $\hat{x}$, type $C(\perp)$ | | | | $\hat{x}$, type $C(\parallel)$ | | |
| $\varkappa$ | $-1$ | $-\frac{3}{4}$ | $-\frac{1}{2}$ | 0 | $+\frac{1}{2}$ | $+\frac{3}{4}$ | $+1$ |
| $\rho^*$ 0 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 |
| $\frac{1}{3}$ | 1·120 | 1·116 | 1·108 | 1·079 | 1·050 | 1·044 | 1·037 |
| $\frac{1}{2}$ | 1·173 | 1·169 | 1·163 | 1·120 | 1·076 | 1·069 | 1·058 |
| $\frac{3}{4}$ | 1·245 | 1·242 | 1·246 | 1·180 | | | |
| 1 | 1·389 | 1·341 | 1·281 | 1·100 | | | |
| $\frac{5}{4}$ | 1·368 | 1·308 | 1·228 | 0·976 | | | |
| $\frac{3}{2}$ | 1·352 | 1·274 | 1·170 | 0·798 | | | |
| 2 | 1·320 | 1·213 | 1·050 | | | | |
| $\frac{5}{2}$ | 1·296 | 1·158 | 0·913 | | | | |

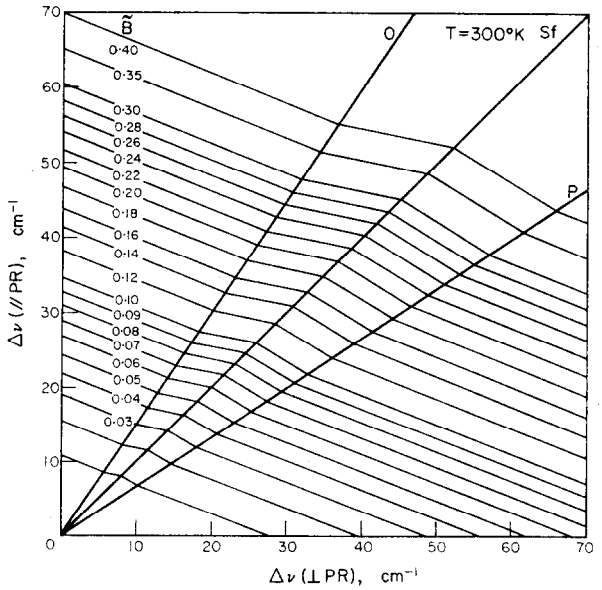


Fig. 1

## DISCUSSION

The most pronounced differences between calculated and observed $PR$ separations occur at the perpendicular bands. For one, the envelope of the $P$ and $R$ branches is such that an accurate measurement of their separation is not always possible. Secondly, many workers report $PR$ separations of type $B(\perp)$ bands while these values actually apply to the $QQ$ or $PQ$–$QR$ separations. These $Q$ branches should be prominent with molecules having a $\rho^* < \frac{3}{4}$ while for larger values the overlapping of the $P$ and $R$ branches coupled with a decrease of $Q$ intensity obstruct a clear distinction between a $QQ$ and a $PR$ separation [2]. Furthermore, many compounds show different $PR$ separations for the same type of band. This effect is believed to come from the various changes of rotational constants going from the ground to the excited states. If, in addition, the band types are mixed, one has the right to expect the observed frequencies to differ from the predicted values.

The $\hat{x}$ values of prolate molecules ($\rho^* > 3$) and planar oblate molecules ($\rho^* > \frac{1}{2}$) clearly show that $\Delta\nu(\|PR)/\Delta\nu(\perp PR)$ equals $\frac{2}{3}$ and $\frac{3}{2}$ respectively. Therefore, straight lines (Fig. 1) can be drawn for all values of $\tilde{B}$ so that intersections of these lines with those belonging to oblate (O) and prolate (P) molecules should give the expected $PR$ separations. For $\tilde{B} = 0{\cdot}20$ the $PR$ separations are expected to be about 39 and 26 cm$^{-1}$ for type $C(\|)$ and type $A(\perp)$ bands. Using the same $\tilde{B}$ value, 31 and 46·5 cm$^{-1}$ are predicted for type $A(\|)$ and type $C(\perp)$ bands. (Since the $PR$ separation of type $B(\perp)$ bands equals the $\Delta\nu(PR)$ of type $A(\perp)$ bands, $\Delta\nu(PR)$ type $B(\perp)$ is obviously found at the intersections of the parallel lines with O. For spherical top molecules

$$\Delta\nu(\|PR) = \Delta\nu(\perp PR) \text{ and } \tilde{B} = B/2$$

so that the straight line ($Sf$) with slope $m = 1$ is situated between O($m = \frac{3}{2}$) and P($m = \frac{2}{3}$).

The $PR$ separations of all compounds listed in Tables 5 and 6 were calculated using the $\hat{x}$ values as given in Tables 2 and 3. The agreement between predicted and observed values is quite satisfactory.

Table 5

| Compound | *PR* branch separation ($cm^{-1}$) | | | | | | Reference |
|---|---|---|---|---|---|---|---|
| | Type $A(\parallel)$ | | Type $B(\perp)$ | | Type $C(\perp)$ | | |
| | calc. | observed† | calc. | observed | calc. | observed | |
| (1) | 21·4 | $20^2$, 24 | 17·8 | 18 | | | [5] |
| (2) | 17·7 | 15, $16^4$, $17^2$, 18 | | | | | [6, 7] |
| (3) | 15·5 | 14, $16^3$, 17, 18 | | | | | [5] |
| (4) | 31·3 | $30^2$, 32, 33, $34^2$ | | | | | [8] |
| (5) | 16·4 | 13, 14, 15 | | | | | [8] |
| (6) | 18·8 | $18^2$, $19^5$, 20 | | | | | [9] |
| (7) | 14·1 | 12, 14, 15, $16^2$ | | | 21·2 | 17 | [9] |
| (8) | 13·7 | $13^3$, 15 | | | 20·6 | 17 | [9] |
| (9) | 18·3 | 16–19 | | | | | [10] |
| (10) | 13·3 | $12^2$, $13^2$ | | | | | [11]* |
| (11) | 21·7 | 21 | | | | | [10] |
| (12) | 18·9 | 18, $20^2$ | | | 28·3 | 30 | [12] |
| (13) | 15·5 | 14, 16, 17, 18 | | | | | [9] |
| (14) | 17·0 | 16 | | | | | [13] |
| (15) | 20·0 | 18, $19^2$, $20^4$, 21 | | | | | [14, 15] |
| (16) | 41·8 | 42 | | | | | [16] |
| (17) | 17·1 | 17 | 14·3 | $15^2$ | 25·7 | 26 | [17] |
| (18) | 20·5 | 20 | | | | | [18] |
| (19) | 15·8 | $15^4$ | 13·2 | 14 | | | [19]* |
| (20) | 26·3 | 22, $25^2$ | | | | | [20] |
| (21) | 10·1 | 9, $10^3$, 11, 12 | | | 15·3 | 14, 18 | [21] |
| (22) | 20·3 | | 16·9 | 17 | 30·5 | 22? | [22] |
| (23) | 13·7 | $13^2$, $15^2$ | 11·4 | $13^3$, $15^2$ | | | [23] |
| (24) | 22·5 | 23 | | | | | [24] |
| (25) | 46·6 | 40, 45, 50 | | | | | [25] |
| (26) | 25·5 | 26 | 21·0 | 20 | | | [24] |
| (27) | 13·1 | 13 | | | | | [26] |
| (28) | 26·9 | $27^2$ | 22·2 | 21 | | | [27] |
| (29) | 22·5 | 22 | | | | | [24] |
| (30) | 8·1 | 8, 9 | 6·8 | 9 | | | [28] |
| (31) | 30·8 | 31 | | | | | [29]* |
| (32) | 23·4 | 20, 24, 25, 26 | | | | | [30] |
| (33) | 27·1 | $26^2$ | 22·0 | 21 | | | [27] |
| (34) | 17·1 | $18^2$, $19^2$ | 14·4 | 15 | | | [31, 32] |
| (35) | 25·6 | $26^3$ | | | | | [24] |
| (36) | 12·0 | 11, 12, $13^2$ | 10·0 | 9, 10, 12, 14 | | | [33] |
| (37) | 9·3 | 10 | | | | | [34] |
| (38) | 23·6 | 22 | | | | | [24] |
| (39) | 10·4 | 10 | | | | | [35] |
| (40) | 10·9 | 11 | | | | | [36] |
| (41) | 11·2 | 12 | 9·4 | 10 | 16·8 | 16 | [37] |
| (42) | 11·7 | 13 | | | 17·6 | 20 | [38] |
| (43) | 10·3 | $8^2$, $10^2$ | 8·4 | $8^2$, $10^2$ | | | [39] |
| (44) | 16·5 | 13, 15, $16^2$ | 13·4 | 15 | 24·7 | 24 | [40] |
| (45) | 16·0 | 13, $15^2$, 16, 17, 19 | 13·0 | 12–16 | 24·0 | 24 | [41] |
| (46) | 12·4 | 13, 15 | | | 18·6 | 18 | [36] |
| (47) | 16·5 | 16, $17^2$ | 13·4 | 13 | 24·8 | 24 | [40] |
| (48) | 16·7 | 16, $17^5$, 18 | 13·3 | $11^4$, $12^3$, $13^3$ | | | [42] |
| (49) | 19·0 | $18^4$, 20, $22^2$ | 15·2 | 12, 16 | 28·5 | 29 | [43] |
| (50) | 15·5 | 15 | 17·6 | 14, 15 | 20·3 | 19 | [44] |
| (51) | 16·2 | 16 | 12·8 | 13 | 24·3 | 23 | [45]* |
| (52) | 15·6 | 16 | 12·2 | 10, 12, 15 | | | [18] |
| (53) | 15·0 | 15 | | | | | [46] |
| (54) | 19·8 | 16, 18, 19, $20^2$ | 15·5 | 14, $16^2$ | 29·7 | $25^2$ | [47] |
| (55) | 20·3 | $20^3$ | 15·6 | $16^2$ | 30·4 | 28 | [48] |
| (56) | 14·5 | 12 | | | | | [49] |
| (57) | 14·9 | 15–20 | | | | | [50] |
| (58) | 15·2 | $14^2$, 15 | 11·7 | 10, 12 | | | API 44 |
| (59) | 13·2 | 10, $12^3$, $13^3$ | 10·2 | 10, 11 | 19·8 | 14, 16 | [28] |
| (60) | 9·2 | 6, 8 | 7·3 | 7 | | | [28] |
| (61) | 19·9 | 19, 25 | 15·3 | 14, 17 | 29·9 | 32, 34 | [51] |
| (62) | 8·3 | 6, 7, 8 | | | 12·3 | 13 | [52] |

* See footnote to Table 6. † See footnote to Table 6.

Table 6

| Compound | *PR* branch separation ($cm^{-1}$) | | | | | | Reference |
|---|---|---|---|---|---|---|---|
| | Type $C(\parallel)$ | | Type $B(\perp)$ | | Type $A(\perp)$ | | |
| | calc. | observed† | calc. | observed | calc. | observed | |
| (63) | 34·1 | 35, 36 | 22·8 | 23 | 22·8 | $23^2$, 24 | [54]* |
| (64) | 25·9 | 22 | 17·3 | 16 | 17·3 | $17^2$, 18, 19 | [55] |
| (65) | 33·0 | 33 | | | 25·3 | $22^2$, 23, 25 | [20] |
| (66) | 27·0 | 25, 29 | 18·0 | 16, 17, 18 | 18·0 | $17^2$, $18^2$ | [53] |
| (67) | 28·0 | 29 | 18·7 | $18^2$ | 18·7 | 17, $18^3$ | [54]* |
| (68) | 26·2 | 24 | 17·5 | 15, 18 | 17·5 | 15, $16^2$, 17 | [53] |
| (69) | 20·8 | 21 | 13·9 | 13 | 13·9 | 13 | [48] |
| (70) | 27·7 | | 18·5 | 20 | 18·5 | 17, 18 | [55] |
| (71) | 26·5 | 28 | 17·7 | | 17·7 | 16, 18, 20 | [56] |
| (72) | 53·2 | 52 | 40·8 | 39, $40^2$ | 40·8 | 42 | [57, 58]* |
| (73) | 34·3 | $35^2$, 36 | 22·8 | 22, 24 | 22·8 | 23, 24, 25 | [59] |
| (74) | 33·7 | 35, $37^2$, 41 | | | 22·5 | $20^2$, 22, $23^3$, 25 | [60] |
| (75) | 39·2 | 38, $40^2$, 41 | 26·3 | 20, $26^2$ | 26·3 | $26^2$, 28 | [61] |
| (76) | 15·1 | | | | 10·1 | 11 | [62] |
| (77) | 37·8 | | 25·2 | | 26·0 | $27^2$ | [63, 64]* |
| (78) | 31·5 | 30, 45 | | | 21·0 | 20, 24, 25, 27 | [65] |
| (79) | 33·8 | 34, 35, 38 | 22·7 | 25, 26, 27, 29 | 22·7 | 22, 25 | [61] |
| (80) | 28·0 | 27 | 18·7 | 12, 15, $16^2$ | 18·7 | 18, 19 | [53] |
| (81) | 55·4 | 55 | 37·4 | 35, 36, 37 | 37·4 | 36, 38 | [66]* |
| (82) | 33·8 | 33 | 22·7 | 22 | 22·7 | 23 | [67] |
| (82) | 33·9 | 33 | 22·7 | 22 | 22·7 | 23, 24 | [62, 68] |
| (83) | 29·9 | 29 | 19·9 | 20 | 19·9 | $19^2$, $20^2$ | [69]* |
| (84) | 31·6 | 32 | 21·2 | | 21·2 | 22 | [67] |
| (85) | 30·1 | 32 | 20·1 | | 20·1 | $21^2$, 22 | [70] |
| (86) | 29·8 | | 19·9 | | 20·0 | $20^2$ | [67] |
| (87) | 29·4 | 27, $32^2$ | 19·9 | | 19·9 | 19, $20^3$, 21, 24 | [71] |

* The band separations were measured in this laboratory using a Perkin–Elmer Spectrophotometer model 225. The length of the gas cell was 10 cm while the temperature inside the cell was assumed to be about 320°K.

† The exponent, placed at some *PR* separations indicates the number of observed band structures having the same branch separation.

*Compounds**

(1) silyl phosphine, (2) butatriene, (3) α-chloromethylether (333°K), (4) methyl phosphine, (5) α-cyanomethylether (393°K), (6) α-fluoroacetonitrile, (7) α-bromoacetonitrile, (8) α-iodoacetonitrile (438°K), (9) vinylbromide, (10) 3-bromopropyne (320°K), (11) vinylchloride, (12) methylazide-$d_3$ (13) α-chloroacetonitrile, (14) trifluoroacetaldehyde, (15) vinylsilane, (16) dideuteromethyl fluoride, (17) monobromoethane, (18) monochloroethane, (19) 3-chloropropyne (320°K), (20) monofluoroethane, (21) 1,3,5-hexatriene, (22) disulphur dinitride, (23) acetyl hypochlorite, (24) propane-$d_3$ (25) ethylene, (26) propane, (27) 1,1-difluoro-2-chloroethylene, (28) dimethylamine, (29) propane-$d_6$, (30) 1,1-dichloro-2-bromoethylene, (31) formic acid (320°K), (32) propylene oxide, (33) dimethylamine-$d_1$, (34) methylthiocyanate, (35) propane-$d_2$, (36) 2,5-dimethyl*cyclo*tetrazenoborane, (37) hexafluoroacetone, (38) propane-$d_2$, (39) octafluoropropane, (40) *p*-benzoquinone, (41) 2-chlorothiophene, (42) trifluoroacetylchloride (43) *trans* dichlorodifluoroethylene, (44) trifluoroethylene, (45) maleic acid anhydride (423°K), (46) *p*-benzoquinone-$d_4$ (390°K), (47) trifluoroethylene-$d_1$, (48) dimethylketene, (49) methylnitrate, (50) dichlorodifluoromethane, (51) phosgene (320°K), (52) 1,1-dichloroethane, (53) trifluoroacetylfluoride, (54) 1-chloro-1-fluoroethylene, (55) thiocarbonylfluoride, (56) pentafluoroethane, (57) trifluoroacetic acid, (58) tetrafluoroethylene, (59) 1,1-dichloro-2-fluoroethylene, (60) bromotrichloroethylene (413°K), (61) 1,3,4-thiadiazole (353°K), (62) 1,1-difluoro-2,2-dibromoethylene, (63) furan (320°K), (64) pyrimidine-$d_4$, (65) 1,1-difluoroethane, (66) pyrazine-$d_2$,† (67) pyridine (320°K), (68) pyrazine-$d_4$†, (69) thiophosgene, (70) pyrimidine, (71) 1,4-dioxadiene, (72) ethyleneimine (320°K), (73) oxazole, (74) isoxazole† (423°K), (75) *cyclo*butene, (76) 1,4-naphtoquinone (423°K), (77) nitromethane, (78) isoxazole-$d_3$† (423°K), (79) *cyclo*butene-$d_6$, (80) pyrazine†, (81) ethylene oxide (320°K), (82) acetone†, (83) thiophene (320°K), (84) acetone-$d_3$†, (85) 1,2,5-thiadiazole, (86) acetone-$d_6$†, (87) isothiazole.†

* Unless stated otherwise, the spectra were run at room temperature.

† The dimensions of the moments of inertia were taken as a.m.u. $Å^2$ instead of g. $cm^2$. $10^{-40}$ as reported.

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