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A Note Concerning *l*-Type Doubling in Axially Symmetric Molecules, in Particular with Reference to Molecules Belonging to the Symmetry Groups C_{4v} and V_d

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The theory of the *l*-type doubling for axially symmetric polyatomic molecules is applied to molecules belonging to the symmetry groups C_{4v} and V_d. It is shown that here *l*-type doubling may be expected in *both* degenerate Coriolis levels (referring to a positive and a negative product of the quantum numbers K and l, respectively). A detailed analysis of a pyramidal XY_4 model reveals that the doubling in these two levels is of the same order. On the basis of our discussion a microwave absorption pattern is predicted for the transitions $J=1\rightarrow J=2$, $\Delta K=0$, where a molecule of C_{4v} or V_d symmetry is in an excited degenerate vibration state. An interesting example may be provided by IF_5 if this molecule has the C_{4v} structure recently proposed.

I. INTRODUCTION

CERTAIN anomalies in the microwave spectrum of methyl cyanide and methyl iso-cyanide have led to an investigation[1,2] of the *l*-type doubling in axially symmetric polyatomic molecules, belonging to the group C_{3v}. It had been known that when a degenerate vibration is excited each state where $K\neq 0$ suffers a degenerate Coriolis-type splitting,[3] resulting in two levels, one where the product Kl is positive and one where it is negative, separated by a frequency interval $4Kl\zeta C_v$, where $C_v=h/8\pi^2 I_{zz}^{(e)}c$, and ζ is the Coriolis coupling constant. The sign of ζ determines which of the two Coriolis components, each of which is still twofold degenerate, has the higher energy. It has been shown[2] that the hamiltonian contains terms which in principle may further remove, in second order of approximation, this degeneracy. A detailed analysis reveals, however, that in this order of approximation only the Coriolis level $K=l=1$ (taken to be the upper level) splits (Fig. 1(a)). Moreover, a more general argument on the basis of group theory (see Sec. II below) proved that even in higher approximations the degeneracy of the level $K=l=1$ cannot possibly be removed. The microwave absorption pattern thus predicted (Fig. 1(b)) is in agreement with experiment (provided the difference in centrifugal stretching of the two Coriolis components is taken into account).

In the case of linear molecules the Coriolis splitting mentioned above is absent, since always $K=l$. Here too, for $K\neq 0$, *l*-type doubling will occur.[4–6]

It is now tempting to inquire into the question of whether it is generally true for all axially symmetric molecules (the linear ones considered as a limiting case) that only the level $K=l=1$ is subject to *l*-type doubling, while for other K values, in particular $K=-l=1$ (if such a state exists) the degeneracy concerned is not removed. In the present paper we shall show that no general rule can be established and shall investigate for which type of molecule a splitting of both Coriolis components may be expected.

II. GROUP THEORETICAL DISCUSSION

For C_{3v} molecules the following argument was suggested by Dennison and reported by Nielsen.[2] All vibrational states $l=\pm 1$ are characterized by vibrational wave functions belonging to the irreducible representation E of the C_{3v} group. The rotational wave functions will belong to the C_3 subgroup, and those for $K=\pm 1$ will be of the species E. Hence, there will be four complete rotation-vibration wave functions of symmetry $E\times E=2A+E$, out of which we can form four independent linear combinations, two of which are symmetrical with respect to permutations corresponding to rotations, whereas the other two form a degenerate pair.[7] Apparently the levels $K=l=1$, for which the internal angular momentum of the framework spinning

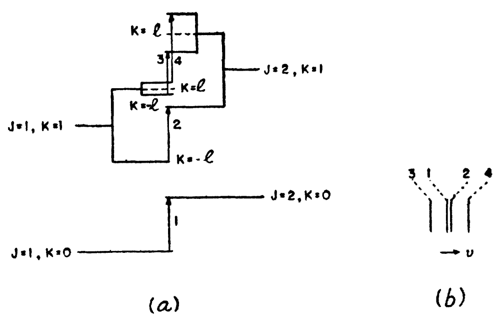

FIG. 1. (a) Rotation levels of an axially symmetric molecule, belonging to the group C_{3v}, for $J=1$ and $J=2$, showing *l*-type doubling, when the molecule is in a vibration state where $l=1$, for $K=l$. (See reference 2.) (b) Microwave absorption pattern predicted on the basis of *l*-type doubling (Fig. 1 (a)) and assuming the centrifugal stretching of both Coriolis components to be alike. (See reference 2.)

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[1] H. H. Nielsen, Phys. Rev. **75**, 1961 (1949).

[2] H. H. Nielsen, Phys. Rev. **77**, 130 (1950).

[3] See, for example, E. Teller and L. Tisza, Z. Physik **73**, 791 (1932); M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

[4] G. K. Herzberg, Revs. Modern Phys. **14**, 219 (1942).

[5] H. H. Nielsen and W. H. Shaffer, J. Chem. Phys. **11**, 140 (1943).

[6] H. H. Nielsen, Phys. Rev. **78**, 296 (1950).

[7] E. Bright Wilson, Jr., J. Chem. Phys. **3**, 818 (1935).

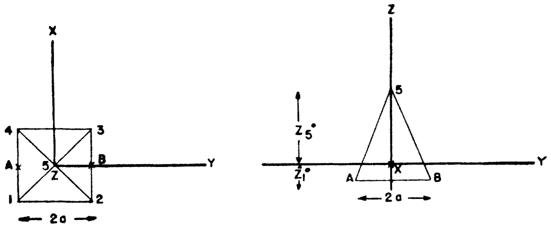

FIG. 2. The XY_4 model (see text).

around its axis, $L=|K-l|$, is zero, have the A symmetry, while the other two ($K=-l=1$, hence $L=\pm 2$) form a degenerate pair. Since this degeneracy cannot be removed by a perturbation which has the same symmetry as the molecule, the level of species E will remain degenerate in any order of approximation and cannot suffer l-type splitting.

For axially symmetric molecules belonging to other symmetry groups, the argument follows essentially along the same lines. A difference will only arise if the direct product of an E irreducible representation of the symmetry group concerned with itself (or with another irreducible representation of species E of the same group) will no longer be equal to $2A+E$ (or $2B+E$). In particular we wish to inquire whether in a given case this direct product might no longer contain an E component; this might, in principle, result in l-type doubling for both levels $K=l=1$ and $K=-l=1$. A quick survey of the character table of the symmetry groups concerned shows that the only important case where such a situation arises presents itself in the C_{4v} group (or V_d group). Here $E\times E=2A+2B$, and hence splitting of both Coriolis levels is possible. It remains of interest to inquire whether the splitting in both levels is of the same order. This question cannot be answered by group theory but necessitates a detailed analysis of a particular molecule. In the next paragraphs we shall report such an analysis for the simplest system with C_{4v} symmetry, the pyramidal XY_4 molecule.

III. NORMAL COORDINATES FOR PYRAMIDAL XY_4

The model assumed has, in its equilibrium configuration, the form of a pyramid as drawn in Fig. 2. The X particle of mass M is situated at the apex (5) and a Y particle of mass m at each base corner (1, 2, 3, and 4). The base is a square with length $2a$. A right-handed body-fixed coordinate system x, y, z is attached to the molecule so as to satisfy the Eckart conditions:[8, 9]

(a) The center of gravity is at the origin:

$$\sum_{i=1}^{4}(mx_i^o)+Mx_5^o=0, \text{ etc.}$$

(b) The angular momentum of vibration vanishes in zeroth approximation:

$$\sum_{i=1}^{4} m(x_i^o\dot{y}_i-y_i^o\dot{x}_i)+M(x_5^o\dot{y}_5-y_5^o\dot{x}_5)=0, \text{ etc.}$$

It follows from simple geometrical considerations that the moments of inertia in the equilibrium configuration, $I_{\alpha\alpha}^{(e)}$, are given by

$$I_{xx}^{(e)}=I_{yy}^{(e)}=4m\{a^2+(z_1^o)^2\}+[16m^2(z_1^o)^2/M], \tag{1a}$$

$$I_{zz}^{(e)}=8ma^2. \tag{1b}$$

Herzberg[10] has drawn schematically the nine normal vibrations which have the symmetry A_1 (twice), B_1 (twice), B_2 (one), and E (four), respectively. In order to relate the normal coordinates to the displacement coordinates (for small displacements), δx_i, δy_i, δz_i, etc., we introduce the following symmetry coordinates:

Symmetry A_1

$$q_1=(x_3+x_4)-(x_1+x_2)+(y_2+y_3)-(y_1+y_4)$$
$$q_2=z_5-\tfrac{1}{4}(z_1+z_2+z_3+z_4),$$

Symmetry B_1

$$q_3=(x_1+x_4)-(x_2+x_3)+(y_1+y_2)-(y_3+y_4)$$
$$q_4=(z_1+z_3)-(z_2+z_4),$$

Symmetry B_2

$$q_5=(x_1+x_2)-(x_3+x_4)+(y_2+y_3)-(y_1+y_4), \tag{2}$$

Symmetry E

$$q_6=x_5-\tfrac{1}{4}(x_1+x_2+x_3+x_4)$$
$$q_7=(y_1-y_2)+(y_3-y_4)$$
$$q_8=y_5-\tfrac{1}{4}(y_1+y_2+y_3+y_4)$$
$$q_9=(x_1-x_2)+(x_3-x_4).$$

With the aid of the Eckart conditions given above, we easily obtain from Eq. (2) the expressions for the instantaneous coordinates of the particles x_i, y_i, z_i, etc., and those for the distance between pairs of particles δS_{ij}, in terms of the symmetry coordinates q_i. The details concerned are irrelevant for our purpose. For the kinetic energy we finally obtain the expression

$$2T=\tfrac{1}{8}m\{q_1^2+q_3^2+2q_4^2+q_5^2+2q_7^2+2q_9^2\}$$
$$+\mu q_2^2+\mu'(q_6^2+q_8^2), \tag{3}$$

where

$$\mu=4mM/(4m+M), \tag{4a}$$

$$\mu'=\mu+[4m(z_1^o)^2/a^2]. \tag{4b}$$

The quadratic portion of V appears to have cross terms only in those pairs of symmetry coordinates that

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[8] C. Eckart, Phys. Rev. **47**, 552 (1935).

[9] E. Bright Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 262 (1936).

[10] G. K. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1945), Vol. 2.

TABLE I. Values of $\overset{(\alpha)}{l}_{is''}$ and $\overset{(\alpha)}{l}_{is\sigma}$.

	1	2	3	4	5	$s1$	$s'1$	$s2$	$s'2$
x_1	$-\frac{1}{4}\sqrt{2}\alpha_{12}$	$-\frac{1}{4}\sqrt{2}\beta_{12}$	$\frac{1}{4}\sqrt{2}\alpha_{34}$	$\frac{1}{4}\sqrt{2}\beta_{34}$	$\frac{1}{4}\sqrt{2}$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$	$-\frac{1}{2}\beta$	$\frac{1}{2}\alpha$
x_2	$-\frac{1}{4}\sqrt{2}\alpha_{12}$	$-\frac{1}{4}\sqrt{2}\beta_{12}$	$-\frac{1}{4}\sqrt{2}\alpha_{34}$	$-\frac{1}{4}\sqrt{2}\beta_{34}$	$\frac{1}{4}\sqrt{2}$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$	$\frac{1}{2}\beta$	$-\frac{1}{2}\alpha$
x_3	$\frac{1}{4}\sqrt{2}\alpha_{12}$	$\frac{1}{4}\sqrt{2}\beta_{12}$	$-\frac{1}{4}\sqrt{2}\alpha_{34}$	$-\frac{1}{4}\sqrt{2}\beta_{34}$	$-\frac{1}{4}\sqrt{2}$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$	$-\frac{1}{2}\beta$	$\frac{1}{2}\alpha$
x_4	$\frac{1}{4}\sqrt{2}\alpha_{12}$	$\frac{1}{4}\sqrt{2}\beta_{12}$	$\frac{1}{4}\sqrt{2}\alpha_{34}$	$\frac{1}{4}\sqrt{2}\beta_{34}$	$-\frac{1}{4}\sqrt{2}$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$	$\frac{1}{2}\beta$	$-\frac{1}{2}\alpha$
x_5	0	0	0	0	0	$\mu(M\mu')^{-\frac{1}{2}}\alpha$	$\mu(M\mu')^{-\frac{1}{2}}\beta$	0	0
y_1	$-\frac{1}{4}\sqrt{2}\alpha_{12}$	$-\frac{1}{4}\sqrt{2}\beta_{12}$	$\frac{1}{4}\sqrt{2}\alpha_{34}$	$\frac{1}{4}\sqrt{2}\beta_{34}$	$-\frac{1}{4}\sqrt{2}$	$-\frac{1}{2}\beta$	$\frac{1}{2}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$
y_2	$\frac{1}{4}\sqrt{2}\alpha_{12}$	$\frac{1}{4}\sqrt{2}\beta_{12}$	$\frac{1}{4}\sqrt{2}\alpha_{34}$	$\frac{1}{4}\sqrt{2}\beta_{34}$	$\frac{1}{4}\sqrt{2}$	$\frac{1}{2}\beta$	$-\frac{1}{2}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$
y_3	$\frac{1}{4}\sqrt{2}\alpha_{12}$	$\frac{1}{4}\sqrt{2}\beta_{12}$	$-\frac{1}{4}\sqrt{2}\alpha_{34}$	$-\frac{1}{4}\sqrt{2}\beta_{34}$	$\frac{1}{4}\sqrt{2}$	$-\frac{1}{2}\beta$	$\frac{1}{2}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$
y_4	$-\frac{1}{4}\sqrt{2}\alpha_{12}$	$-\frac{1}{4}\sqrt{2}\beta_{12}$	$-\frac{1}{4}\sqrt{2}\alpha_{34}$	$-\frac{1}{4}\sqrt{2}\beta_{34}$	$-\frac{1}{4}\sqrt{2}$	$\frac{1}{2}\beta$	$-\frac{1}{2}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\alpha$	$-\frac{1}{4}\mu(m\mu')^{-\frac{1}{2}}\beta$
y_5	0	0	0	0	0	0	0	$\mu(M\mu')^{-\frac{1}{2}}\alpha$	$\mu(M\mu')^{-\frac{1}{2}}\beta$
z_1	$\frac{1}{4}(\mu/m)^{\frac{1}{2}}\beta_{12}$	$-\frac{1}{4}(\mu/m)^{\frac{1}{2}}\alpha_{12}$	$-\frac{1}{2}\beta_{34}$	$\frac{1}{2}\alpha_{34}$	0	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$
z_2	$\frac{1}{4}(\mu/m)^{\frac{1}{2}}\beta_{12}$	$-\frac{1}{4}(\mu/m)^{\frac{1}{2}}\alpha_{12}$	$\frac{1}{2}\beta_{34}$	$-\frac{1}{2}\alpha_{34}$	0	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$
z_3	$\frac{1}{4}(\mu/m)^{\frac{1}{2}}\beta_{12}$	$-\frac{1}{4}(\mu/m)^{\frac{1}{2}}\alpha_{12}$	$-\frac{1}{2}\beta_{34}$	$\frac{1}{2}\alpha_{34}$	0	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$
z_4	$\frac{1}{4}(\mu/m)^{\frac{1}{2}}\beta_{12}$	$-\frac{1}{4}(\mu/m)^{\frac{1}{2}}\alpha_{12}$	$\frac{1}{2}\beta_{34}$	$-\frac{1}{2}\alpha_{34}$	0	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$-(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\alpha$	$(z_1{}^o/a)(m/\mu')^{\frac{1}{2}}\beta$
z_5	$-(\mu/M)^{\frac{1}{2}}\beta_{12}$	$(\mu/M)^{\frac{1}{2}}\alpha_{12}$	0	0	0	0	0	0	0

belong to the same species. This confirms that our choice of symmetry coordinates (2) was a suitable one and that we may introduce a set of normal coordinates $Q_1, \cdots, Q_9$ satisfying the relations

$$\begin{aligned} q_1&=2(2/m)^{\frac{1}{2}}(\alpha_{12}Q_1+\beta_{12}Q_2),\\ q_2&=\mu^{-\frac{1}{2}}(-\beta_{12}Q_1+\alpha_{12}Q_2),\\ q_3&=2(2/m)^{\frac{1}{2}}(\alpha_{34}Q_3+\beta_{34}Q_4),\\ q_4&=2m^{-\frac{1}{2}}(-\beta_{34}Q_3+\alpha_{34}Q_4),\\ q_5&=2(2/m)^{\frac{1}{2}}Q_5,\end{aligned}\tag{5a}$$

$$\begin{aligned} q_6&=(\mu')^{-\frac{1}{2}}(\alpha_{67}Q_6+\beta_{67}Q_7),\\ q_7&=2m^{-\frac{1}{2}}(-\beta_{67}Q_6+\alpha_{67}Q_7),\\ q_8&=(\mu')^{-\frac{1}{2}}(\alpha_{67}Q_8+\beta_{67}Q_9),\\ q_9&=2m^{-\frac{1}{2}}(-\beta_{67}Q_8+\alpha_{67}Q_9).\end{aligned}\tag{5b}$$

The α_{ij} and β_{ij} are related in a complicated way to the constants determining both the geometry and the force field of the molecule. For our purpose the explicit expressions need not be written down. For each ij, we have the normalizing condition

$$\alpha_{ij}{}^2+\beta_{ij}{}^2=1. \tag{6}$$

Within the scope of the present investigation, we are mainly interested in the degenerate modes of vibration. In order that our notation may conform to common usage, we rewrite Eqs. (5b) as follows (put $\alpha_{67}=\alpha$ and $\beta_{67}=\beta$):

$$\begin{aligned} q_6&=(\mu')^{-\frac{1}{2}}(\alpha Q_{s1}+\beta Q_{s'1}),\\ q_7&=2m^{-\frac{1}{2}}(-\beta Q_{s1}+\alpha Q_{s'1}),\\ q_8&=(\mu')^{-\frac{1}{2}}(\alpha Q_{s2}+\beta Q_{s'2}),\\ q_9&=2m^{-\frac{1}{2}}(-\beta Q_{s2}+\alpha Q_{s'2}).\end{aligned}\tag{7}$$

Here Q_{s1} and Q_{s2} denote the degenerate vibrations with frequency ω_s, and $Q_{s'1}$ and $Q_{s'2}$ those associated with $\omega_{s'}$.

From Eqs. (2), (5a), and (7), we finally obtain the constants $\overset{(\alpha)}{l}_{is\sigma}$, giving the displacement coordinates (x_i, y_i, z_i) in terms of the normal coordinates Q_i, according to

$$m_i{}^{\frac{1}{2}}\dot{\alpha}_i=\sum_{s''=1}^{5}\overset{(\alpha)}{l}_{is''}\dot{Q}_{s''}+\sum_{s\sigma s'\sigma'}\overset{(\alpha)}{l}_{is\sigma}\dot{Q}_{s\sigma}. \tag{8}$$

Values of the $\overset{(\alpha)}{l}_{is''}$ and $\overset{(\alpha)}{l}_{is\sigma}$ are given in Table I.

IV. l-TYPE DOUBLING IN PYRAMIDAL XY_4

The general form of that part of the hamiltonian for an axially symmetric polyatomic molecule which gives rise to l-type doubling in second-order approximation has been given by Nielsen:[11]

$$\begin{aligned} H^{(2)'}=&-\sum_{\alpha}\sum_{s\sigma}\sum_{s'\sigma'}(\hbar/2\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}(\overset{(e)}{I}_{\alpha\alpha})^2)\\ &\cdot\{[\overset{(\alpha\alpha)}{A}_{s\sigma s'\sigma'}-\sum_{\beta}(\overset{(\alpha\beta)}{a}_{s\sigma}\overset{(\alpha\beta)}{a}_{s'\sigma'}/\overset{(e)}{I}_{\beta\beta})\\ &-2\sum_{s''\sigma''}\overset{(\alpha)}{\zeta}_{s\sigma s''\sigma''}\overset{(\alpha)}{\zeta}_{s'\sigma's''\sigma''}\cdot\lambda_s/(\lambda_s-\lambda_{s''})]q_{s\sigma}q_{s'\sigma'}\\ &-2\sum_{s''\sigma''}[\overset{(\alpha)}{\zeta}_{s\sigma s''\sigma''}\overset{(\alpha)}{\zeta}_{s'\sigma's''\sigma''}\cdot\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}/(\lambda_s-\lambda_{s''})]\\ &\times(p_{s\sigma}p_{s'\sigma'}/\hbar^2)\}P_\alpha{}^2+\sum_{\alpha,\beta,\gamma}{}'\sum_{s\sigma}\sum_{s'\sigma'}(\hbar/2\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}\\ &\times\overset{(e)}{I}_{\alpha\alpha}\overset{(e)}{I}_{\beta\beta})\cdot\{[\overset{(\alpha\beta)}{A}_{s\sigma s'\sigma'}-(\overset{(\alpha\alpha)}{a}_{s\sigma}\overset{(\alpha\beta)}{a}_{s'\sigma'}/\overset{(e)}{I}_{\alpha\alpha}\\ &-(\overset{(\beta\beta)}{a}_{s\sigma}\overset{(\alpha\beta)}{a}_{s'\sigma'}/\overset{(e)}{I}_{\beta\beta})+(\overset{(\alpha\gamma)}{a}_{s\sigma}\overset{(\gamma\beta)}{a}_{s'\sigma'}/\overset{(e)}{I}_{\gamma\gamma})\\ &-2\sum_{s''\sigma''}\overset{(\alpha)}{\zeta}_{s\sigma s''\sigma''}\overset{(\beta)}{\zeta}_{s'\sigma's''\sigma''}\cdot\lambda_s/(\lambda_s-\lambda_{s''})]q_{s\sigma}q_{s'\sigma'}\\ &-2\sum_{s''\sigma''}[\overset{(\alpha)}{\zeta}_{s\sigma s''\sigma''}\overset{(\beta)}{\zeta}_{s'\sigma's''\sigma''}\cdot\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}/(\lambda_s-\lambda_{s''})]\\ &\times p_{s\sigma}p_{s'\sigma'}/\hbar^2\}P_\alpha P_\beta+\cdots,\end{aligned}\tag{9}$$

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[11] See reference 2. Some errors of sign and a few obvious misprints occur in Eqs. (2) and (3) of that paper. These have been corrected in Eq. (9) of the present publication.

where

$$\lambda_s=(2\pi c\omega_s)^2, \tag{10}$$

$$q_{s\sigma}=(\hbar^2/\lambda_s)^{-\frac{1}{4}}Q_{s\sigma}, \tag{11}$$

$$\overset{(\alpha\alpha)}{A}_{s\sigma s''\sigma''}=\sum_i(\overset{(\beta)}{l}_{is\sigma}\overset{(\beta)}{l}_{is''\sigma''}+\overset{(\gamma)}{l}_{is\sigma}\overset{(\gamma)}{l}_{is''\sigma''}), \tag{12}$$

$$\overset{(\alpha\beta)}{A}_{s\sigma s''\sigma''}=-\sum_i \overset{(\alpha)}{l}_{is\sigma}\overset{(\beta)}{l}_{is''\sigma''}, \tag{13}$$

$$\overset{(\alpha\alpha)}{a}_{s\sigma}=2\sum_i m_i^{\frac{1}{2}}(\beta_i{}^0\overset{(\beta)}{l}_{is\sigma}+\gamma_i{}^0\overset{(\gamma)}{l}_{is\sigma}), \tag{14}$$

$$\overset{(\alpha\beta)}{a}_{s\sigma}=-\sum_i m_i^{\frac{1}{2}}(\alpha_i{}^0\overset{(\beta)}{l}_{is\sigma}+\beta_i{}^0\overset{(\alpha)}{l}_{is\sigma}), \tag{15}$$

$$\overset{(\alpha)}{\zeta}_{s\sigma s'\sigma'}=\sum_i(\overset{(\beta)}{l}_{is\sigma}\overset{(\gamma)}{l}_{is'\sigma'}-\overset{(\beta)}{l}_{is'\sigma'}\overset{(\gamma)}{l}_{is\sigma}). \tag{16}$$

In Eq. (9) P_α is the α-component of the total angular momentum, and $p_{s\sigma}$ is the momentum conjugate to $q_{s\sigma}$; the $q_{s\sigma}$ and $p_{s\sigma}$ can be replaced by their equivalents in cylindrical polar coordinates r, χ:

$$\begin{aligned} q_{s,1}&=r_s\cos\chi_s, \quad p_{s,1}=-i\hbar\left[\cos\chi_s\frac{\partial}{\partial r_s}-\frac{\sin\chi_s}{r_s}\frac{\partial}{\partial\chi_s}\right], \\ q_{s,2}&=r_s\sin\chi_s, \quad p_{s,2}=-i\hbar\left[\sin\chi_s\frac{\partial}{\partial r_s}+\frac{\cos\chi_s}{r_s}\frac{\partial}{\partial\chi_s}\right]. \end{aligned} \tag{17}$$

In our case, s can have two values, s and s'; σ takes on the values 1 and 2. In Eq. (9) $\sum'_{\alpha\beta\gamma}$ means that the summation is to be extended over α, β, and γ, where the three indexes may not all be identical. The s'', in our case, refer to the vibrations $Q_1, \cdots, Q_5$, all of which are nondegenerate, so that the subscript σ'' is superfluous.

Of all constants A, a, and ζ, only the following do not vanish (specific values calculated with the l's of Table I):

$$\begin{aligned} \overset{(xx)}{A}_{s1s1}&=\beta^2+4(z_1{}^0/a)^2(m/\mu')\alpha^2, \\ \overset{(xx)}{A}_{s2s2}&=\alpha^2, \\ \overset{(xy)}{A}_{s1s2}&=-\alpha^2(\mu/\mu'), \\ \overset{(xy)}{A}_{s2s1}&=-\beta^2, \\ \overset{(xz)}{a}_{s1}&=\overset{(zy)}{a}_{s2}=8m(\mu')^{-\frac{1}{2}}z_1{}^0\alpha. \end{aligned} \tag{18}$$

To obtain the corresponding constants for s', we merely have to interchange α and β

$$\begin{aligned} \overset{(x)}{\zeta}_{s21\cdot}&=-\overset{(y)}{\zeta}_{s11\cdot}=\alpha(\mu')^{-\frac{1}{2}}\{\beta_{12}\mu^{\frac{1}{2}}-\alpha_{12}(z_1{}^0/a)(2m)^{\frac{1}{2}}\}, \\ \overset{(x)}{\zeta}_{s22\cdot}&=-\overset{(y)}{\zeta}_{s12\cdot}=-\alpha(\mu')^{-\frac{1}{2}}\{\alpha_{12}\mu^{\frac{1}{2}}+\beta_{12}(z_1{}^0/a)(2m)^{\frac{1}{2}}\}, \\ \overset{(x)}{\zeta}_{s13\cdot}&=-\overset{(y)}{\zeta}_{s23\cdot}=-\beta\cdot\beta_{34}+\alpha\cdot\alpha_{34}(z_1{}^0/a)(2m/\mu')^{\frac{1}{2}}, \\ \overset{(x)}{\zeta}_{s14\cdot}&=-\overset{(y)}{\zeta}_{s24\cdot}=\beta\cdot\alpha_{34}+\alpha\cdot\beta_{34}(z_1{}^0/a)(2m/\mu')^{\frac{1}{2}}, \\ \overset{(x)}{\zeta}_{s25\cdot}&=-\overset{(y)}{\zeta}_{s15\cdot}=-\alpha(z_1{}^0/a)(2m/\mu')^{\frac{1}{2}}, \\ \overset{(z)}{\zeta}_{s1s2}&=\alpha^2(\mu/\mu')-\beta^2. \end{aligned} \tag{19}$$

Again, if s is replaced by s', we have to interchange α and β.

Substitution of Eqs. (12)–(19) in the expression for the hamiltonian, (9), yields

$$\begin{aligned} H^{(2)'}=\cdots-\bar{\sum_{+}}\sum_s(B_e/4\omega_s) \\ \times[\{1-\alpha^2[1+64(mz_1{}^0)^2/(\mu'\overset{(e)}{I}_{zz})]\}(e^{\pm i\chi_s}r_s)^2 \\ -\sum_{s''}(\overset{(x)}{\zeta}_{ss''})^2[\lambda_s/(\lambda_s-\lambda_{s''})](e^{\pm i\chi_s})^2 \\ \times\{r_s{}^2+[(p_{r_s}\pm ip\chi_s/r_s)/h]^2\}]\cdot\{P_x\mp iP_y\}^2/\overset{(e)}{I}_{xx} \\ -\bar{\sum_{+}}\sum_s(B_e/4\omega_s)\{-\alpha^2\mu/\mu'\}(e^{\pm i\chi_s}r_s)^2 \\ \cdot\{P_x\pm iP_y\}^2/\overset{(e)}{I}_{xx}. \end{aligned} \tag{20}$$

The matrix components of (20) can be evaluated with the aid of the relations given by Shaffer,[12] along the lines indicated by Nielsen.[2] Assume first that the vibration s is excited. Then for the first term in (20) the only nonvanishing components which are diagonal in V_s are $(V_s, l_s, K|H^{(2)'}|V_s, l_s\pm2, K\pm2)$, whereas for the second term only $(V_s, l_s, K|H^{(2)'}|V_s, l_s\pm2, K\mp2)$ will not be equal to zero. Hence, the following nondiagonal matrix elements will be responsible for the l-type

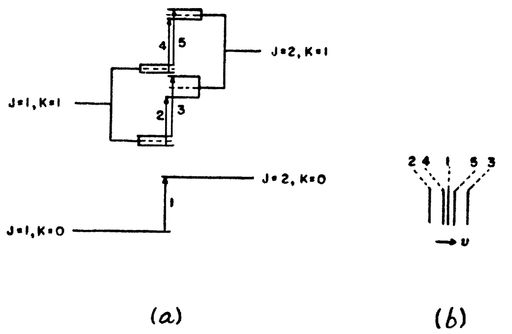

FIG. 3. (a) Rotation levels of an axially symmetric molecule, belonging to the group C_{4v}, for $J=1$ and $J=2$, showing l-type doubling, when the molecule is in a vibration state when $l=1$, both for $K=l$ and $K=-l$. (b) Microwave absorption pattern predicted on the basis of l-type doubling (Fig. 2 (a)) and assuming the centrifugal stretching of both Coriolis components to be alike.

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[12] W. H. Shaffer, Revs. Modern Phys. 16, 235 (1944).

doubling:

(a) For the level $K=l$:

$$(V_s, l_s, K|H^{(2)\prime}|V_s, l_s\pm 2, K\pm 2)$$

$$=hcB_e(B_e/2\omega_s)$$

$$\cdot\{1-\alpha^2[\mu a^2+12m(z_1^o)^2]/[\mu a^2+4m(z_1^o)^2]$$

$$+4\sum_{s''}[\{\overset{(x)}{\zeta}_{ss''}\}^2\lambda_s/(\lambda_s-\lambda_{s''})]\}$$

$$\cdot\{[J(J+1)-K(K\pm 1)]\cdot[(J(J+1)$$

$$-(K\pm 1)(K\pm 2)][(V_s\mp l_s)(V_s\pm l_s+2)]\}^{\frac{1}{2}}, \quad (21a)$$

where, making use of Eqs. (1b) and (4b), we have replaced $[1+64(mz_1^o)^2/(\mu' I_{zz}^{(e)})]$ by $[\mu a^2+12m(z_1^o)^2]/[\mu a^2+4m(z_1^o)^2]$.

(b) For the level $K=-l$:

$$(V_s, l_s, K|H^{(2)\prime}|V_s, l_s\pm 2, K\mp 2)$$

$$=-hcB_e(B_e/2\omega_s)\alpha^2 I_{zz}^{(e)}/(I_{xx}^{(e)}+I_{yy}^{(e)})$$

$$\times\{[J(J+1)-K(K\pm 1)][J(J+1)$$

$$-(K\pm 1)(K\pm 2)]\cdot[(V_s\pm l_s)(V_s\mp l_s+2)]\}^{\frac{1}{2}}, \quad (21b)$$

where, using Eqs. (1a), (1b), (4a), and (4b), we have replaced (μ/μ') by $I_{zz}^{(e)}/(I_{xx}^{(e)}+I_{yy}^{(e)})$.

If the vibration s' is excited, then in Eqs. (21a), and (21b) we have to replace s by s' and interchange α and β.

V. DISCUSSION

The result, embodied in Eqs. (21a) and (21b), is that for the simple XY_4 model chosen, the l-type splitting of both Coriolis components, $K=l=1$ and $K=-l=1$, is of the same order. The actual magnitude of this splitting still depends on both the geometry and the force field (influencing our equations through the constants α and β) of the molecule under consideration. In particular, Eq. (21b) shows that the splitting of the level $K=-l=1$ would be a maximum in the case of planar XY_4 molecules (when $I_{zz}^{(e)}/(I_{xx}^{(e)}+I_{yy}^{(e)})=1$), and that this splitting goes to zero as $I_{zz}^{(e)}$ approaches zero (linear model!). There is no reason to expect the situation for other molecules belonging to the C_{4v} (and V_d) group to be essentially different. A possible sequence of rotational levels is drawn in Fig. 3(a) and a possible microwave absorption pattern in Fig. 3(b). Actually, the relative position of the lines 2 and 4 (or 5 and 3) is still uncertain, since it is undetermined which of the two Coriolis levels will suffer the largest splitting. The sign of $\zeta_{s_1s_2}^{(z)}$ will determine which of the two Coriolis components is the lower and which is the higher level; subsequently, the l-type doubling will be given by equations of the type (21a) and (21b).

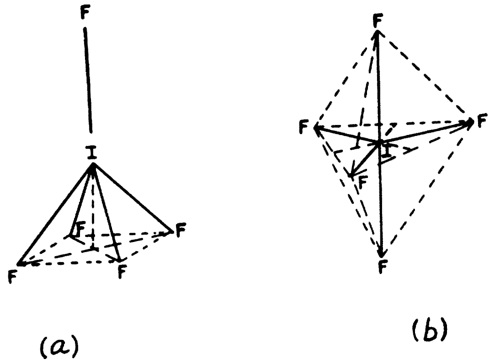

FIG. 4. (a) C_{4v} structure for IF_5. (b) Bipyramidal structure for IF_5.

Recently, Lord *et al.*[13] have proposed a structure for IF_5, which has C_{4v} symmetry (Fig. 4(a)). Their evidence is not quite conclusive, and at present it is not sure whether this molecule has, indeed, this structure or whether it should be represented by a bipyramidal model (Fig. 4(b)). If it has the C_{4v} symmetry as indicated, then IF_5 should show the "twofold l-type doubling," which we have discussed in this paper. Since the bipyramidal structure has no dipole moment around the z axis, it might show no microwave absorption at all. However, if two degenerate frequencies, s and s', lie close enough together, we might get a transition from a rotational level associated with frequency s to one associated with frequency s', a transition that might involve a transition moment around the z axis.[14] If such a microwave spectrum could be observed, only half of the levels (those for $K=l$) will undergo l-type doubling (D_{3h} symmetry!). If no microwave spectrum can be detected at all, the model proposed by Lord *et al.*[13] must be rejected.[15]

Allene, C_3H_4, belonging to the group V_d, should also show the "twofold l-type doubling" discussed in this paper. Again, this can only be detected in the microwave spectrum if a transition from an s rotational sublevel to an s' rotational sublevel is associated with a transition moment along the molecular axis.

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[13] Lord, Lynch, Schumb, and Slowinsky, J. Am. Chem. Soc. **72**, 522 (1950).

[14] A. H. Nielsen and R. M. Talley, J. Chem. Phys. (to be published).

[15] As far as we know, no direct dipole moment investigation on IF_5 has been reported.