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THE CAUSES OF ℓ-TYPE DOUBLING IN THE 3P(E'')
RYDBERG STATE OF AMMONIA

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ABSTRACT

Expressions are developed for the rotational levels of an electronically degenerate planar XY_3 molecule. It is shown that there can be strong ℓ-type doubling only in levels with no vibrational angular momentum and that this doubling has two main causes, namely, a rotational-electronic interaction and a rotational-Jahn-Teller interaction. The ℓ-type doubling of other levels is largely quenched by vibronic coupling.

Estimates of the observed ℓ-type doubling in the 3P(E") state of ammonia indicate that the two above contributions act in opposite senses. A mechanism which accounts for the variation of the observed ℓ-type doubling with vibronic is suggested.

INTRODUCTION

As is well-known a molecule in an electronically degenerate state may experience a dynamical Jahn-Teller effect[1], and its detailed rotational structure may provide a measure of the strength of this effect[2]. It is therefore interesting to examine the observations of Douglas and Hollas[3] on the rotational structure of the 3P(E") Rydberg state of ammonia, for evidence of vibronic coupling. Of particular interest are the possible causes of the reported strong ℓ-type doubling, since it is known that one possible cause is the Jahn-Teller effect.

The molecule is known to be planar in the 3P(E") state, and the first part of this paper involves a derivation of the formulae for the rotational levels of an electronically degenerate planar XY_3 molecule, first in the harmonic approximation, i.e. without either vibronic coupling or purely vibrational anharmonicity, and then in the presence of weak vibronic coupling. Using a slightly different perturbation procedure from the familiar Van Vleck transformation[4] we first derive an expression for an effective rotational Hamiltonian akin to the spin-Hamiltonian extensively employed in the theory of magnetic resonance[5]. It is then shown that in the harmonic approximation, first order ℓ-type doubling can occur only in levels in which there is no vibrational angular momentum, because the levels with a non-zero vibrational angular momentum which would be doubled are already split apart by Coriolis interactions. Strong second

order perturbations on these levels might however be regarded as pseudo ℓ-type doubling. In the harmonic approximation there are two main perturbing forces, both arising from second-order Coriolis interactions, one (q^E) being purely electronic in origin and the other (q^{VIB}) purely vibrational. Only q^E contributes to the true ℓ-type doubling. The main effects of vibronic coupling are to add a term q^{JT} to the term q^E, which increases or decreases the true ℓ-type doubling depending on the sign of the Jahn-Teller effect, and to quench the pseudo ℓ-type doubling mentioned above.

In the second part of the paper we review the experimental results and make order of magnitude estimates of the term q^E and the vibronically induced term q^{JT}. In view of our uncertain knowledge of the electronic structure of the molecule, these estimates may later prove unreliable, but they do indicate that q^E and q^{JT} probably have opposite signs. We suggest a possible mechanism for the large variation in the ℓ-type doubling from one vibronic state to another. Finally, we consider the information that couldbe gained by an analysis of the ND_3 spectrum.

THE ROTATIONAL LEVELS OF AN ELECTRONICALLY DEGENERATE PLANAR XY_3 MOLECULE

Formulas for the rotational levels of an electronically degenerate symmetrical X_3 molecule have been derived elsewhere[2], and the theory for the XY_3 system follows the same lines. One must however allow for certain second-order Coriolis interactions which were not considered in the

previous case.

Barring accidental degeneracy, the degenerate electronic state of the molecule must have symmetry E' or E", and in general one must allow for Jahn-Teller interactions between electronic and vibrational degrees of freedom. In the first instance however, these effects and indeed all other vibrational anharmonicities will be neglected; the vibronic state of the molecule will be taken to be a simple product of harmonic oscillator states and one of the two component electronic states, $|e_+\rangle$ or $|e_-\rangle$ say. We shall then go on to investigate the effects of vibronic coupling.

The Harmonic Approximation

Let H_r denote the rotational Hamiltonian. Then for an electronically degenerate planar symmetrical top molecule

$$H_{\underline{r}} = \tfrac{1}{2}\left\{\tfrac{1}{2}\mu_\perp[(J_+-\ell_+-p_+)(J_--\ell_--p_-) + (J_--\ell_--p_-)(J_+-\ell_+-p_+)] + \mu_{\parallel}\,(J_z-\ell_z-p_z)^2 + \mu_{++}(J_+-\ell_+-p_+)^2 + \mu_{--}(J_--\ell_--p_-)^2\right\}. \quad (1)$$

where

$$(J_{\pm}-\ell_{\pm}-p_{\pm}) = (J_x-\ell_x-p_x) \pm i(J_y-\ell_y-p_y). \quad (2)$$

$\underset{\sim}{J}$, $\underset{\sim}{\ell}$ and $\underset{\sim}{p}$ being the operators for total, electronic and vibrational angular momentum respectively. The tensor μ is the reciprocal of the effective instantaneous inertia tensor[6], and

$$\mu_\perp = \tfrac{1}{2}(\mu_{xx}+\mu_{yy}) \quad , \quad \mu_\parallel = \mu_{zz}$$
$$\mu_{\pm\pm} = \tfrac{1}{4}(\mu_{xx}-\mu_{yy} \mp 2i\mu_{xy}); \quad (3)$$

the other components of μ are zero.

To a good approximation $\underset{\sim}{\mu}$ is a function only of nuclear position, while $\underset{\sim}{p}$ depends on the positions and momenta of the nuclei and $\underset{\sim}{\ell}$ on those of the electrons. H_r therefore couples different vibrational-electronic states together. Suppose degenerate vibronic state has energy E_e and components $|en_\alpha\rangle$ characterized by three quantum numbers. In second-order perturbation theory, the matrix elements of H_r within this level can be written

$$\langle en_\alpha|H_r|en_\beta\rangle + \sum \frac{\langle en_\alpha|H_r|f\rangle\langle f|H_r|en_\beta\rangle}{E_e - E_f}. \qquad (4)$$

In other words, in this approximation H_r is equivalent to the operator

$$H_r^{(2)} = H_r + \sum_f{}' \frac{H_r|f\rangle\langle f|H_r}{E_e - E_f}, \qquad (5)$$

as far as interactions <u>within</u> the degenerate level are concerned. In the present case this operator can be reduced to the form

$$H_r^{(2)} = \frac{2\pi}{\hbar}\left[BJ^2 + (C-B)J_z^{\,2} - 2C\,\zeta\,J_z + \tfrac{1}{2}q_+J_+^{\,2} + \tfrac{1}{2}q_-J_-^{\,2}\right] + \text{const} \qquad (6)$$

keeping only terms no higher than quadratic in the rotational operators, and we shall give expressions for the operators $\underset{\sim}{\mu}$, B, C, $C\zeta$, and q_+ in terms of the coordinates and momenta of the nuclei and the electrons.

If m and M denote the masses of an X and a Y atom respectively and if $\mathcal{M} = 3mM/3m+M$, in the system shown in Fig. 1 a suitable set of mass-adjusted symmetry coordinates may be

taken to be

$$A_1' \quad : \qquad S_1 = \frac{1}{\sqrt{12}}(2x_1 - x_2 - \sqrt{3}y_2 - x_3 + \sqrt{3}y_3),$$

$$A_2'' \quad : \qquad S_2 = \frac{1}{3}(\sqrt{\mathcal{M}/m}\,(z_1+z_2+z_3) - 3\sqrt{\mathcal{M}/m}\,z_o),$$

$$E' \quad : \quad \begin{cases} S_{3a} = \frac{1}{\sqrt{12}}(2x_1 - x_2 + \sqrt{3}y_2 - x_3 - \sqrt{3}y_3), \\ S_{3b} = \frac{1}{\sqrt{12}}(2y_1 - \sqrt{3}x_2 - y_2 + \sqrt{3}x_3 - y_3), \end{cases}$$

$$E' \quad : \quad \begin{cases} S_{4a} = \frac{1}{3}\sqrt{\mathcal{M}/m}\,(x_1+x_2+x_3) - 3\sqrt{\mathcal{M}/M}\,x_o), \\ S_{4b} = \frac{1}{3}(\sqrt{\mathcal{M}/m}\,(y_1+y_2+y_3) - 3\sqrt{\mathcal{M}/M}\,y_o). \end{cases} \qquad (7)$$

With this choice of phase, S_3 and S_4 span the representation E' in identically the same way. The normal coodinates of the system may therefore be expressed in terms of the S's in the following way

$$Q_1 = S_1 \quad , \qquad Q_2 = S_2,$$

$$Q_3 = \cos\theta\, S_3 + \sin\theta\, S_4 \,,$$

$$Q_4 = -\sin\theta\, S_3 + \cos\theta\, S_4. \qquad (8)$$

The expansions of the components of as far as the quadratic terms in the normal coordinates take the form

$$\mu_{\perp} = (2/I_o)\left[1 - 2(Q_1/Q_o) + 3(Q_1/Q_o)^2 + 3\cos^2\theta\,(Q_3/Q_o)^2 + 3\sin^2\theta(Q_4/Q_o)^2\right] \qquad (9)$$

$$\mu_{\parallel} = (2/I_o)\left[1 - 2(Q_1/Q_o) + 3(Q_1/Q_o)^2\right]$$

$$\mu_{++} = \mu^*_{--} = (2/I_o)\left[\cos\theta(Q_{3\pm}/Q_o) + \sin\theta\,(Q_{4\pm}/Q_o)\right]$$

In these equations I_o is the principal parallel moment of inertia, $3mR_o^2$, of the molecule in its symmetrical configuration,

and

$$Q_o^{\,2} = I_o, \quad Q_i^{\,2} = Q_{ia}^{\,2} + Q_{ib}^{\,2}, \qquad Q_{i\pm} = Q_{ia} \pm Q_{ib} \quad (i = 3,4).$$

In the harmonic approximation the states of Q_1 and Q_2 may be written $|v_i\rangle$, and those of Q_3 and Q_4 $|v_i, \ell_i\rangle$. $v_i = 0,1,2\ldots$ then specifies the energy of the state and, for the degenerate vibrations, $\ell_i = v_i, v_i-2, -v_i$ gives the vibrational angular momentum. It is now a matter of simple geometry to derive the forms of the various quantities in equation (1) and we shall merely give expressions for the various contributions to $H_r^{(2)}$.

If P_i is the momentum conjugate to Q_i

$$p_x = \zeta_{23}\,(Q_2P_{3b} - Q_{3b}P_2) + \zeta_{24}\,(Q_2P_{4b} - Q_{4b}P_2),$$

$$p_y = \zeta_{23}\,(Q_2P_{3a} - Q_{3a}P_2) + \zeta_{24}\,(Q_2P_{4a} - Q_{4a}P_2),$$

and
$$p_z = \zeta_3\,(Q_{3a}P_{3b} - Q_{3b}P_{3a}) + \zeta_4\,(Q_{4a}P_{4b} - Q_{4b}P_{4a}) + \zeta_{34}\,(Q_{3a}P_{4b} - Q_{4b}P_{3a} + Q_{4a}P_{3b} - Q_{3b}P_{4a}) \,. \tag{10}$$

where the Coriolis coupling constants ζ depend on the transformation angle θ:

$$\zeta_3 = -\zeta_4 = \cos 2\theta \,, \quad \zeta_{34} = \sin 2\theta,$$
$$\zeta_{23} = -\sin\theta \,, \quad \zeta_{24} = \cos\theta. \tag{11}$$

Vibrational Coriolis interactions arise from the terms involving products of the type $J_\alpha P_\beta$ in equation (1). In allowing for the terms which first contribute in second-order (i.e. those involving ζ_{23}, ζ_{24} and ζ_{34} in equation (9)), we make use of a device due to Moffitt and Thorson[7]. The relevant terms involve products of the type $Q_iP_j - Q_jP_i$, which connect the harmonic oscillator state $|v_i, v_j\rangle$ only with the states $|v_i \pm 1, v_j \pm 1\rangle$. Such a term which may be compactly written M_{ij},

provides the following vibrational contribution to the matrix element $\langle en_\alpha | H_r^{(2)} | en_\beta \rangle$ in equation (5)

$$\langle v_i, v_j | H_{ij}^{(2)} | v_i, v_j \rangle = \sum \frac{\langle v_i, v_j | M_{ij} | v_i', v_j' \rangle \langle v_i', v_j' | M_{ij} | v_i, v_j \rangle}{E_i + E_j - E_i' - E_j'}$$

$$= \sum \frac{\langle v_i, v_j | M_{ij} | v_i' v_j' \rangle (E_i - E_i' - E_j + E_j') \langle v_i', v_j' | M_{ij} | v_i, v_j \rangle}{(E_i - E_i')^2 - (E_j - E_j')^2} \tag{12}$$

$$= \sum \frac{\langle v_i, v_j | [(H_i - H_j), M_{ij}] | v_i', v_j' \rangle \langle v_i', v_j' | M_{ij} | v_i, v_j \rangle}{(E_i - E_i')^2 - (E_j - E_j')^2}$$

Now, since vibrational energy levels are equally spaced and $|v_i', v_j'\rangle = |v_i \pm 1, v_j \pm 1\rangle$, all terms in the sum have the same energy denominator, $c^2\hbar^2(\omega_i^2 - \omega_j^2)$. We can therefore perform the sum over the complete set $|v_i', v_j'\rangle$ to obtain the following result

$$H_{ij}^{(2)} = \frac{[(H_i - H_j), M_{ij}] M_{ij}}{c^2\hbar^2(\omega_i^2 - \omega_j^2)} = \frac{M_{ij}[M_{ij}, (H_i - H_j)]}{c^2\hbar^2(\omega_i^2 - \omega_j^2)}$$

$$= \frac{\left[[(H_i - H_j), M_{ij}], M_{ij}\right]}{2c^2\hbar^2(\omega_i^2 - \omega_j^2)} \quad . \tag{13}$$

The double commutator in equation (13) is evaluated with the help of the well-known relations

$$[Q_i, P_i] = i\hbar \quad , \quad [H_i, Q_i] = -i\hbar P_i \quad \text{and} \quad [H_i, P_i] = i\hbar(2\pi c\omega_i)^2 Q_i \tag{14}$$

In these equations ω_i has the conventional spectroscopic significance; it has dimensions of a reciprocal length. For $M_{ij} = M(Q_i P_j - Q_j P_i)$, using the fact that as far as interactions within a given vibrational level are concerned the expectation

value of the same as P_i^2 is the same as the expectation value of $(2\pi c\omega_i)^2 Q_i^2$, it turns out that

$$H_{ij}^{(2)} = -\pi c M^2 \left[\left(\frac{3\omega_i^2+\omega_j^2}{\omega_i^2-\omega_j^2} \right) Q_i^2 + \left(\frac{3\omega_j^2+\omega_i^2}{\omega_j^2-\omega_i^2} \right) Q_j^2 \right] , \qquad (15)$$

So much for second-order vibrational effects.

The electronic contributions to the rotational constants depend on how the components of $\underset{\sim}{\ell}$ affect the electronic states $|e_\pm\rangle$ which have e' symmetry. On symmetry grounds ℓ_z can only couple them to other states with the same symmetry, $|e'_\pm\rangle$ say, whereas $\ell_\pm$ can connect $|e_\pm\rangle$ either with other degenerate states of e" symmetry $|e''_\pm\rangle$ or with non-degenerate states of a''_1 or a''_2 symmetry, $|a\rangle$. If the components of degenerate states are taken to be complex conjugates of one another, it proves convenient to define the following types of electronic matrix element

$$\begin{aligned}
\langle e_+|\ell_z|e_+\rangle &= -\langle e_-|\ell_z|e_-\rangle = \hbar\zeta_e , \\
\langle e'_+|\ell_z|e_+\rangle &= -\langle e'_-|\ell_z|e_-\rangle = \hbar\zeta_{ae'} , \\
\langle e''_+|\ell_+|e_+\rangle &= -\langle e''_-|\ell_-|e_-\rangle = \hbar\zeta_{ee''} , \\
\langle a|\ell_-|e_+\rangle &= -\langle a|\ell_+|e_-\rangle = \hbar\zeta_{ea} . \qquad (16)
\end{aligned}$$

The signs in these relations follow from the identity $\underset{\sim}{\ell}^* = -\underset{\sim}{\ell}$.

Expressions for the rotational operators B, C, $C\zeta$, and $q_\pm$ in equation (6) can now be derived quite straightforwardly and we shall merely quote the results, correct to terms quadratic in the normal coordinates. Note however

(i) that terms in equation (1) which do not involve $\underset{\sim}{J}$ contribute only to the constant in equation (6);

(ii) that the terms $\mu_{\pm\pm} J_{\pm} P_{\pm}$ do not contribute until order Q^4;

(iii) that since J_x and J_y do not commute, the terms involving $J_{\pm}(\ell_{\pm}+p_{\pm})$ provide contributions not only to B and $q_{\pm}$ but also to ζ as well. The final results are given in conventional form below

$$B = B_e - \alpha_B^{(e)} - \sum_{i=1}^{4} \alpha_B^{(i)} (Q_i/Q_i^{\circ})^2 ,$$

$$C = C_e - \alpha_C^{(e)} - \sum_{i=1}^{4} \alpha_C^{(i)} (Q_i/Q_i^{\circ})^2 , \qquad (17)$$

where $$\alpha_B^{(e)} = -\sum\left(\frac{E_e^{\,2}}{\Delta E_{ee''}}\right)\zeta^2_{ee''} - \sum\left(\frac{E_e^{\,2}}{\Delta E_{ea}}\right)\zeta^2_{ea},$$

$$\alpha_B^{(1)} = -3B_e^{\,2}/\omega_1 + 10\,\alpha_B^{(e)}\,B_e/\omega_1$$

$$\alpha_B^{(2)} = -2\left[\zeta^2_{23}\left(\frac{3\omega_2^{\,2}+\omega_3^{\,2}}{\omega_2^{\,2}-\omega_3^{\,2}}\right) + \zeta^2_{24}\left(\frac{3\omega_2^{\,2}+\omega_4^{\,2}}{\omega_2^{\,2}-\omega_4^{\,2}}\right)\right] B_e^{\,2}/\omega_2 ,$$

$$\alpha_B^{(3)} = -\left[3\cos^2\theta + \zeta^2_{23}\left(\frac{3\omega_3^{\,2}+\omega_2^{\,2}}{\omega_3^{\,2}-\omega_2^{\,2}}\right)\right] B_e^{\,2}/\omega_3 ,$$

$$\alpha_B^{(4)} = -\left[3\sin^2\theta + \zeta^2_{24}\left(\frac{3\omega_4^{\,2}+\omega_2^{\,2}}{\omega_2^{\,2}-\omega_4^{\,2}}\right)\right] B_e^{\,2}/\omega_4 ,$$

$$\alpha_C^{(e)} = -\sum\left(\frac{C_e^{\,2}}{\Delta E_{ee'}}\right)\zeta_{ee'}^2 \quad ,$$

$$a_C^{(1)} = -6C_e^{\,2}/\omega_1 \quad ,$$

$$a_C^{(2)} = 0 \quad ,$$

$$\alpha_C^{(3)} = -\zeta_{34}^2\left(\frac{3\omega_3^{\,2}+\omega_4^{\,2}}{\omega_3^{\,2}-\omega_4^{\,2}}\right) C_e^{\,2}/\omega_3 \quad ,$$

$$\alpha_C^{(4)} = -\zeta_{34}^2\left(\frac{3\omega_4^{\,2}+\omega_3^{\,2}}{\omega_4^{\,2}-\omega_3^{\,2}}\right) Ce^2/\omega_4 \quad , \qquad (18)$$

$$B_e = 2C_e = \hbar\mu_{\parallel}^{\,e}/4\pi c$$

$$\Delta E_{ef} = E_e - E_f \quad , \quad (f = a, e' \text{ or } e'').$$

$$C\zeta = C_e[\zeta_e'\hat{\ell}_z + \zeta_3' P_{3z} + \zeta_4' P_{4z}]$$

where $$\zeta_e' = \zeta_e + \sum\left(\frac{B_e}{\Delta E_{ee''}}\right)\zeta_{ee''}^2 - \sum\left(\frac{B_e}{\Delta E_{ea}}\right)\zeta_{ea}^2 \quad ,$$

$$\zeta_3' = \zeta_3 + 2\left(\frac{3\omega_2^{\,2}+\omega_3^{\,2}}{\omega_2^{\,2}-\omega_3^{\,2}}\right)\zeta_{23}^2 \ (B_e/\omega_2)\ (Q_2/Q_2^{\,o})^2 \quad , \qquad (19)$$

$$\zeta_4' = \zeta_4 + 2\left(\frac{3\omega_2^{\,2}+\omega_4^{\,2}}{\omega_2^{\,2}-\omega_4^{\,2}}\right)\zeta_{24}^2 \ (B_e/\omega_2)\ (Q_2/Q_2^{\,o})^2 \quad ,$$

$$\hat{\ell}_z \,|e_\pm\rangle = \pm|e_\pm\rangle$$

$$P_{iz}|v_i,\ell_i\rangle = \ell_i\,|v_i,\ell_i\rangle \qquad (i = 3,4).$$

And finally

$$q_+ = q_-^* = q_+^E + q_+^{JT} + q_+^{VIB} + q_+^{EV}, \qquad (20)$$

where

$$q_+^E = \sum\left(\frac{2B_e^2}{\Delta E_{ea}}\right)\zeta_{ea}^2\,\ell_-^2 ,$$

$$q_+^{JT} = 2\cos\theta\, B_e\sqrt{B_e/\omega_3}(Q_{3-}/Q_3^{\circ})+2\sin\theta\, B_e\sqrt{B_e/\omega_4}(Q_{4-}/Q_4^{\circ})^2 ,$$

$$q_+^{VIB} = -\zeta_{23}^2\left(\frac{3\omega_3^2+\omega_2^2}{\omega_3^2-\omega_2^2}\right)(B_e^2/\omega_3)(Q_{3+}/Q_3^{\circ})^2-\zeta_{24}^2\left(\frac{3\omega_4^2+\omega_2^2}{\omega_4^2-\omega_2^2}\right)(B_e^2/\omega_4)(Q_{4+}/Q_4^{\circ})$$

$$q_+^{EV} = \frac{1}{4B_e^2}\,q_-^E(q_+^{JT})^2$$

$$\ell_-^2\,|e_+\rangle = -|e_-\rangle \qquad (21)$$

The ratios (Q_i/Q_i°) in these expressions are dimensionless quantities;

$$\langle v_i|(Q_i/Q_i^{\circ})^2|v_i\rangle = v_i + \tfrac{1}{2}d_i \quad ;$$

$$\langle v_i+1,\ell_i+1|(Q_{i+}/Q_i^{\circ})|v_i,\ell_i\rangle = \sqrt{\tfrac{1}{2}(v_i+\ell_i+2)} \quad ; \qquad (22)$$

$$\langle v_i-1,\ell_i+1|(Q_{i+}/Q_i^{\circ})|v_i,\ell_i\rangle = \sqrt{\tfrac{1}{2}(v_i-\ell_i)}.$$

Most of the terms in these expressions have essentially been obtained before[8], with the help of the traditional contact transformation[4]; they are given here for the sake of completeness, and apart from the contributions to $q_\pm$, we would merely like

to draw attention to the electronic terms $\alpha_B^{(e)}$ and $\alpha_C^{(e)}$ in B and C respectively and to the fact that the effective Coriolis constants ζ_3, and ζ_4, may depend on v_2.

In the harmonic approximation there are two main types of contribution to $q_\pm$ - the purely electronic terms $q_\pm^E$ and the purely vibrational terms $q_\pm^{VIB}$. The terms $q_\pm^{JT}$, which are odd functions of Q, average to zero in this approximation, and the terms $q_\pm^{EV}$, which are of order $(B_e/\Delta E)x(B_e/\omega)xB_e$ must generally be much smaller than $q_\pm^E$ or $q_\pm^{VIB}$. We shall therefore consider only the first-order affects of $q_\pm^{EV}$.

In the absence of $q_\pm$, the rotational vibronic state can be taken in the form $|\lambda;v_1;v_2;v_3,\ell_3;v_4,\ell_4\rangle\,|J,K\rangle$ where λ takes the value ± 1 for the electronic states $|e_\pm\rangle$ and the rotational states $|J,K\rangle$ satisfy the equations

$$\begin{aligned} J^2|J,K\rangle &= J(J+1)\hbar^2|J,K\rangle, \\ J_z|J,K\rangle &= J_z\hbar|J,K\rangle, \\ J_+^2|J,K\rangle &= \sqrt{[J(J+1)-K(K\mp1)][J(J+1)-(K\mp1)(K\mp2)]}\,\hbar^2|J,K\mp2\rangle \end{aligned} \tag{23}$$

(The third of these equations follows from the commutation rule

$$[J_x,J_y] = -i\hbar J_z \tag{24}$$

for the components of $\underset{\sim}{J}$ referred to axes fixed in the molecule[9].) For q = 0 therefore, according to equations (6) and (19) the term values of these rotational levels are given by the following formula

$$F_v(\lambda;\ell_3,\ell_4;J,K) = B_vJ(J+1) + (C_v-B_v)K^2-2C_e(\lambda\zeta_e'+\ell_3\zeta_3'+\ell_4\zeta_4')K \tag{25}$$

In this approximation the states $|\lambda;\ell_3,\ell_4;J,K\rangle$ and $|-\lambda;-\ell_3,-\ell_4;J,-K\rangle$ have the same energy.

When $q \neq 0$ the state of the molecule is a linear combination of these basic states, but there is no simple general formula for the corresponding energy levels. We shall therefore consider only two special cases to illustrate the main effects involved.

Case (1) : $v_3 = v_4 = 0$

When Q_3 and Q_4 are not excited, the vibronic state is doubly degenerate, and only $q_{\pm}^{E}$ can couple the component states together. The rotational levels are given by the well-known formulas for ℓ-type doubling.

$$F_v(\pm 1;0,0;J,K) = B_v J(J+1)+(C_v-B_v)K^2 \mp 2C_e\zeta_e' K. \pm \frac{(q^E)^2[J(J+1)-K(K\mp 1)][J(J+1)-(K\mp 1)(K\mp 2)]}{16(C_v-B_v-C_e\zeta_e')(K\mp 1)} \tag{26}$$

except that for the A_1 and A_2 levels with $|K| = 1$

$$F_v(\pm 1;0,0;J,\pm 1) = B_v J(J+1)+(C_v-B_v) - 2C_e\zeta_e' \pm \tfrac{1}{2}q^E J(J+1) \tag{27}$$

In these equations

$$q^E = -\sum\left(\frac{2B_e^{\,2}}{\Delta E_{ea}}\right)\zeta_{ea}^2 \tag{28}$$

Either the upper or the lower signs in equation (26) are taken together.

Case (2) : $v_3 = 0,\ v_4 = 1$

The case when $v_4 = 1$ is more involved because ℓ_4 can take the values ± 1 and the vibronic state is 4-fold degenerate. Moreover $q_{\pm}^{E}$ and $q_{\pm}^{VIB}$ can both couple different component states together. With the exceptions given below the rotational term values are now given by the basic formula

$$F_v(\lambda;0,\ell_4;J,K) = B_vJ(J+1) + (C_v-B_v)K^2-2C_e(\lambda\zeta_e'+\ell_4\,{}_4^{\prime})K \tag{29}$$

with additional perturbations

$$\pm\,(q^{(E)})^2\,\frac{[J(J+1)-K(K\mp1)][J(J+1)-(K\mp1)(K\mp2)]}{16[(C_v-B_v-C_e\zeta_e')(K\mp1)-C_e\,{}_4\zeta_4']}$$ for levels with $\lambda = \pm 1$

and $$\pm\,(q_1^{(4)})^2\,\frac{[J(J+1)-K(K\mp1)][J(J+1)-(K\mp1)(K\mp2)}{16[(C_v-B_v+C_e\zeta_4')(K\mp1)-C_e\lambda\zeta_4']}$$ for levels with $\ell_4 = \mp 1$; (30)

$$q_1^{(4)} = -\zeta_{24}^2\left(\frac{3\omega_4^2+\omega_2^2}{\omega_4^2-\omega_2^2}\right)\frac{B_e^2}{\omega_4}\,.$$

There are the following exceptions to these rules

(i) $$F_v(\pm1;0,\pm1;J,0)=B_vJ(J+1)-\frac{(q^{(E)}+q_1^{(4)})^2J(J+1)[J(J+1)-2]}{16[C_v-B_v-C_e(\zeta_e'-\zeta_4')]}$$

$$F_v(\pm1;0,\mp1;J,\pm2)=B_vJ(J+1)+4(C_v-B_v)-4C_e(\zeta_e'-\zeta_4') + \frac{(q^{(E)}+q_1^{(4)})^2J(J+1)[J(J+1)-2]}{16[C_v-B_v-C_e(\zeta_e'-\zeta_4')]} \tag{31}$$

(ii) $a^{(EV)}$ couples together the otherwise degenerate states with $\lambda = \pm 1$, $\ell_4 = \mp 1$, $K = \mp 1$. These levels are therefore split into levels lying $\frac{1}{2}q_o^{(EV)}J(J+1)$ above and below the position given by equations (29) and (30);

$$q_o^{(EV)} = q^{(E)}\,\frac{B_e}{\omega_4}\,\sin^2\theta \tag{32}$$

(iii) The states $|K,\lambda,\ell_4\rangle = |\mp1,\mp1,\pm1\rangle$, $|\pm1,\pm1,\pm1\rangle$ and $|\pm1,\mp1,\mp1\rangle$ may be very close together and the corresponding energy levels depend on the magnitudes of the zeroth order energy level separations $4C_e\lambda\zeta_e'$ and $4C_e\ell_4\zeta_4'$ compared with the coupling terms

$\frac{1}{2}q_1^{(4)}J(J+1)$ and $\frac{1}{2}q_0^{(E)}J(J+1)$ respectively. Equations (29) and (30) apply to the case when $|4C_e\lambda\zeta_e'| >> |\frac{1}{2}q_1^{(4)}J(J+1)|$ and $|4C_e\ell_4\zeta_4'| >> |\frac{1}{2}q_0^{(E)}J(J+1)|$. Otherwise the perturbed term values are given by

$$F_v = B_vJ(J+1) + (C_v-B_v) + \mathcal{E} .$$

where $\mathcal{E}$ is one of the three eigenvalues of the following matrix

$$\begin{bmatrix} -2C_e(\zeta_e'-\zeta_4') & , \frac{1}{2}q^{(E)}J(J+1) & , \frac{1}{2}q_1^{(4)}J(J+1) \\ \frac{1}{2}q^{(E)}J(J+1) & , -2C_e(\zeta_e'+\zeta_4') & , \quad 0 \\ \frac{1}{2}q_1^{(4)}J(J+1), & 0 & , +2C_e(\zeta_e'+\zeta_4') \end{bmatrix} \tag{33}$$

The positions of the J=1 rotational levels of states with $v_3 = 0$, $v_4 = 0$ and with $v_3 = 0$, $v_4 = 1$ are illustrated in Fig. 2. These diagrams apply in the harmonic approximation to a hypothetical molecule with $B_e = B_v = 10\ cm^{-1}$, $C_e = C_v = 3\ cm^{-1}$, $q^{(E)} = 0.2\ cm^{-1}$, $q_1^{(4)} = -0.1\ cm^{-1}$, $\zeta_e' = 0.8$ and $\zeta_4' = -0.15$.

It is clear from equations (31), (32), and (33) and from diagram 2(b) that the only true ℓ-type doubling in the $v_4 = 1$ state arises in the level with $|K, \lambda, \ell_4\rangle = |\mp1,\mp1,\pm1\rangle$ and this is due to the small term $q_+^{(EV)}$. The effects of the much larger terms $q_\pm^{(E)}$ and $q_\pm^{(VIB)}$ are largely quenched by Coriolis interactions. There will therefore be no strong ℓ-type doubling in this level unless ζ_e' or ζ_4' vanishes. The relatively large perturbations of the levels $|\pm1,\mp1,\pm1\rangle$, $|\pm1,\pm1,\pm1\rangle$ and $|\mp1,\pm1,\pm1\rangle$ is, however, due to the second order effect of the ℓ-type doubling terms.

Influence of the Jahn-Teller Effect

As is well known, the Jahn-Teller effect upsets the harmonic behaviour of certain molecular vibrations[10,11]. In the present case both Q_3 and Q_4 may be affected. The vibronic wave function is no longer a simple product of harmonic oscillator functions, and a single electronic function and the vibronic level specified by v_3 and v_4 is no longer $2(v_3+1)(v_4+1)$-fold degenerate. It is split into $(v_3+1)(v_4+1)$ degenerate pairs with the states arising mainly from $|v_3,\ell_3;v_4,\ell_4;e_+\rangle$ and $|v_3,-\ell_3;v_4,-\ell_4;e_-\rangle$ remaining degenerate[7]. If round brackets $|)$ are used to denote the perturbed vibronic states and if k_3 and k_4 are the dimensionless vibronic coupling parameters introduced by Longuet-Higgins et.al.[11], it turns out that in first-order perturbation theory

$$
\begin{aligned}
|v_3,\ell_3;v_4\ell_4;e_+) = {} & [1+(v_3+1)k_3^2 + (v_4+1)k_4^2]^{-\frac{1}{2}}\Big\{|v_3,\ell_3;v_4,\ell_4;e_+\rangle \\
& - \sqrt{\tfrac{1}{2}(v_3+\ell_3+2)}\,k_3\,|v_3+1,\ell_3+1;v_4,\ell_4;e_-\rangle + \sqrt{\tfrac{1}{2}(v_3-\ell_3)}\,k_3\,|v_3-1,\ell_3+1;v_4,\ell_4;e_-\rangle \\
& - \sqrt{\tfrac{1}{2}(v_4+\ell_4+2)}\,k_4\,|v_3,\ell_3;v_4+1,\ell_4+1;e_-\rangle + \sqrt{\tfrac{1}{2}(v_4+\ell_4)}\,k_4\,|v_3,\ell_3;v_4-1,\ell_4+1;e_-\rangle\Big\}
\end{aligned}
\tag{34}
$$

and

$$
\begin{aligned}
|v_3,-\ell_3;v_4,-\ell_4;e_-\rangle = {} & [1+(v_3+1)k_3^2 + (v_4+1)k_4^2]^{-\frac{1}{2}}\Big\{|v_3,-\ell_3;v_4;e_-\rangle \\
& -\sqrt{\tfrac{1}{2}(v_3+\ell_3+2)}\,k_3\,|v_3+1,-\ell_3-1,v_4,-\ell_4;e_+\rangle + \sqrt{\tfrac{1}{2}(v_3-\ell_3)}\,k_3\,|v_3-1,-\ell_3-1;v_4,-\ell_4;e_+\rangle \\
& -\sqrt{\tfrac{1}{2}(v_4+\ell_4+2)}\,k_4\,|v_3,-\ell_3;v_4+1,-\ell_4-1;e_+\rangle + \sqrt{\tfrac{1}{2}(v_4-\ell_4)}\,k_4\,|v_3,-\ell_3;v_4-1,-\ell_4-1;e_+\rangle\Big\}\,.
\end{aligned}
$$

The Q_3 and Q_4 contributions to the term value of this level are given by the following formula

$$
G(v_3,\pm\ell_3;v_4\pm\ell_4;e_\pm) = [v_3+1 - (\ell_3+1)k_3^2]\omega_3 + [v_4+1 - (\ell_4+1)k_4^2]\omega_4\,. \tag{35}
$$

It is more convenient to work in terms of the k_i than with Moffitt and Thorson's $D_i(=\frac{1}{2}k_i^2)$[10], because the signs of the k_i are important in this work. Equations (34) and (35) are valid for $k^2<0.1$.

Strictly speaking the forms of the operators B, C, $C\zeta$ and $q_\pm$ in equation (6) will also be affected by vibronic coupling. For a weak Jahn-Teller effect however, any perturbations on the formulas given in equations (17) through (21) must be small and we shall neglect them.

The mean values of these operators when the vibronic state is described by equations (34) will not be the same as in the harmonic approximation though. In particular the mean values of $(Q_i/Q_i^o)^2$ and $C\zeta$ are no longer given by (22) and (23) respectively; we find instead that, to terms in k_i^2

$$\langle(Q_3/Q_3{}^o)^2\rangle = v_3+1 + [(\ell_3+1)(\ell_3+2) - (v_3+1)^2]k_3^2 \; ; \qquad (36)$$

with a similar formula for $\langle(Q_4/Q_4{}^o)^2\rangle$, and

$$\langle C\zeta\rangle = \pm C_e \left\{ \begin{array}{l} \zeta_e'[1-2(v_3+1)k_3^2 - 2(v_4+1)k_4^2] \\ \quad +\zeta_3'[\ell_3+(v_3+1)k_3^2] + \zeta_4'[\ell_4+(v_4+1)k_4^2] \end{array} \right\} . \qquad (37)$$

The upper and lower signs in equation (37) refer to the states given by the first and second equations (34) respectively.

In addition $q_\pm^{JT}$ can now mix together vibronic states which are degenerate or nearly so. It follows from equations (20), (22) and (34) that in this approximation there is only one new type of non-zero matrix element, Namely

$$(v_3,\ell_3;v_4,\ell_4;e_-|q_+^{JT}|v_3,\ell_3;v_4,\ell_4;e_+) = q^{(JT)}$$

$$= -4k_3\cos\ell B_e \quad B_e/\omega_3 - 4k_4 \sin\ell B_e \quad B_e/\omega_4 \qquad (38)$$

q_+^{JT} therefore connects together exactly the same states as q_+^E.

We have seen already that in the harmonic approximation there can be first order ℓ-type (or λ-type) doubling only in levels with $\ell_3 = \ell_4 = 0$. We now deduce that this doubling may be enhanced or reduced, depending on the signs of k_3 and k_4, as a direct result of the Jahn-Teller effect. Furthermore the pseudo ℓ-type doubling of levels with $\ell_3 = 0$, $\ell_4 = 0$ will be completely quenched by sufficiently strong vibronic coupling, since $|v_3,\ell_3;v_4,\ell_4;e_+)$ for instance remains degenerate only with $|v_3,-\ell_3;v_4,-\ell_4;e_-)$, but it is coupled by q_+^E and q_+^{JT} only with $|v_3,\ell_3;v_4,\ell_4;e_-)$ and by $q_\pm^{VIB}$ only with $|v_3,\ell_3\pm2;v_4\ell_4;e_-)$ or $|v_3,\ell_3;v_4,\ell_4\pm2;e_-)$ among levels with the same v_3 and v_4.

Finally we return to the special cases considered in the previous section.

<u>Case (1) : $v_3-v_4 = 0$</u>

Equations (26) and (27) must be replaced by

$$F_v(\pm1;0,0;J,K) = B_vJ(J+1) + (C_v-B_v)K^2 \pm 2C_e\zeta_vK$$

$$\pm q_v^2 \frac{[J(J+1)-K(K\mp1)][J(J+1)-(K\mp1)(K\mp2)]}{16(C_v-B_v-C_e\zeta_v)(K\mp1)} \qquad (26a)$$

and

$$F_v(\pm1;0,0;J,\pm1) = B_vJ(J+1)+(C_v-B_v)-2C_e\zeta_v\pm\tfrac{1}{2}q_vJ(J+1). \qquad (27a)$$

where according to (36), (37) and (38)

$$\zeta_v = \zeta_e'(1-2k_3^2-2k_4^2)+\zeta'_3k_3^2+\zeta_4'k_4^2$$

$$q_v = q^{(E)} + q^{(JT)} ,$$

and in B_v and C_v

$$\langle Q_i/Q_i^{\,o})^2\rangle = 1+k_i^2 \qquad \text{for } i = 3 \text{ or } 4.$$

<u>Case (2) : $v_3=0,\ v_4=1$</u>

According to (35) the vibronic state is split into two doublets, which may be distinguished by their values of $\lambda\ell_4$; the pair with $\lambda\ell_4 = +1$ lies lowest. Equations (29) and (30) for the rotational levels must be replaced by

$$F_v(\lambda;0,\ell_4;J,K) = -k_4^2\omega_4(1+\lambda\ell_4)+B_vJ(J+1)+(C_v-B_v)K^2$$
$$-2C_e(\lambda\zeta_e''+\ell_4\zeta_4'')K \tag{29a}$$
$$\pm\frac{[q^{(E)}+q^{(JT)}]^2[J(J+1)-K(K\mp1)][J(J+1)-(K\mp1)(K\mp2)]}{16[(C_v-B_v-C_e\zeta_4'')(K\mp1)-\ell_4(\frac{1}{2}k_4^2\omega_4+C_e\zeta_4'')]} \quad \text{when } \lambda = \pm1$$

$$\text{and } \pm\frac{(q_1^{(4)})^2[J(J+1)-K(K\mp L)][J(J+1)-(K\mp1)(K\mp2)}{16[(C_v-B_v+C_e\zeta_4'')(K\mp1)+\lambda(\frac{1}{2}k_4^2\omega_4-C_e\zeta_e'')]} \quad \text{when } \ell_4 = \mp1.$$

Similarly equations (31) become

$$F_v(\pm1;0,\pm1;J,0) = 2k_4^2\omega_4B_4J(J+1)-\frac{[q^{(E)}+q^{(JT)}+q^{(4)}]^2J(J+1)[J+1)[J(J+1)-2]}{16[C_v-B_vC_e(\zeta_e''-\zeta_4'')+\frac{1}{2}k_4^2\omega_4]}$$

$$F_v(\pm1;0\mp1;J,\pm2)-B_vJ(J+1)+4(C_v-B_v)-4C_e(\zeta_e''-\zeta_4'') \tag{31a}$$
$$+\frac{[q^{(E)}+q^{(JT)}+q^{(4)}]^2J(J+1)[J(J+1)-2]}{16[C_v-B_v-C_e(\zeta_e''-\zeta_4'')+\frac{1}{2}k_4^2\omega_4]}\ .$$

In these equations

$$\zeta_e'' = \zeta_e'[1-2k_3^2-4k_4^2]\ ,$$

and

$$\zeta_4'' = \zeta_4'[\ell_4+2k_4^2] \tag{39}$$

Finally the levels with $|K,\ \lambda,\ \ell_4\rangle = |\mp1,\ \mp1,\ \pm1,\rangle$, $|\pm1,\ \pm1,\ \pm1\rangle$ and $|\pm1,\ \mp1,\ \mp1\rangle$ give rise to three levels with term values

$$F_v = B_v J(J+1) + (C_v - B_v) + \mathcal{E} \tag{32a}$$

where $\mathcal{E}$ takes the ergonvalues of the matrix

$$\begin{vmatrix} -2C_e(\zeta_e''+\zeta_4''), & \frac{1}{2}(q^{(E)}+q^{(JT)})J(J+1) & , & \frac{1}{2}q_1^{(4)}J(J+1) \\ \frac{1}{2}(q^{(E)}+q^{(JT)})J(J+1) & , -2k_4^2\omega_4 - 2C_e(\zeta_e''+\zeta_4'') & , & 0 \\ \frac{1}{2}q_1^{(4)}\ J(J+1) & , & 0 & , -2k_4^2\omega_4+2C_e(\zeta_e''+\zeta_4'' \end{vmatrix}$$

$|\mp 1, \mp 1, \pm 1>$ will therefore be strongly perturbed by $|\pm 1, \pm 1, \pm 1>$ if the Jahn-Teller splitting $2k_4^2\omega_4 \simeq 4C_e\zeta_4''$. Similarly $|\mp 1, \mp 1, \pm 1>$ and $|\pm 1, \mp 1, \mp 1>$ will interact strongly if $2k_4^2\omega_4 \simeq 4C_e\zeta_e''$.

Figure 3 shows what happens to the J=1 rotational levels of the $v_3 = 0$, $v_4 = 1$ states when there is a 15 cm^{-1} Jahn-Teller splitting of the $v_4 = 1$ vibronic level and when $q^{JT} = 0.3\ cm^{-1}$; all other rotational constants have the same values as in Fig. 2(a) and 2(b). Notice the strong accidental perturbation between the levels with $|K,\lambda,\ell_4) = |\pm 1,\mp 1,\mp 1)$ and $|\mp 1, \mp 1, \pm 1)$.

The following conclusions may be drawn from this work. First that there are three main possible contributions to the operators $q_\pm$ in equation (6) responsible for ℓ-type doubling, namely purely electronic terms $q_\pm^{(E)}$, purely vibrational terms $q_\pm^{(VIB)}$ and terms $q_\pm^{(JT)}$ directly induced by the Jahn-Teller effect. In weak vibronic coupling $q_\pm^{(E)}$ and $q_\pm^{(JT)}$ act in precisely the same way. Secondly, there can in general be no first order ℓ-type doubling in vibronic levels in which Q_3 or Q_4 is excited because the rotational sub-levels coupled together

by $q_{\pm}J_{\pm}^{2}$ are split by Coriolis interactions. Paradoxically therefore, ℓ-type doubling in electronically degenerate symmetric top molecules can arise only in vibronic states arising from those with $\ell_3 = \ell_4 = 0$, in which case it is caused by $q_{\pm}^{(E)}$ and $q_{\pm}^{(JT)}$; the terms λ-type or j-type doubling might therefore be more appropriate. Finally, the $2(v_3+1)(v_4+1)$-fold degenerate states in which Q_3 and Q_4 are excited are split by a linear Jahn-Teller effect into $(v_3+1)(v_4+1)$ degenerate pairs. This splitting tends to quench any pseudo ℓ-type doubling although there could be strong accidental perturbations between levels with $|K| = 1$ and the same value of J, belonging to different vibronic states; this situation is illustrated in Fig. 3. In the limit of a large linear Jahn-Teller effect however, the spectrum would show a set of well separated doubly degenerate vibronic levels each with Coriolis splitting appropriate to its combined vibrational and electronic angular momentum.

ℓ-TYPE DOUBLING IN THE 1600Å BAND SYSTEM OF AMMONIA

Careful investigation of the 1600Å band system of ammonia by Douglas and Hollas[3] has shown that the excited state involved in this transition is planar (D_{3h} symmetry) and has a degenerate electronic state belonging to the E" species. If the ground state of ammonia is considered to belong to the D_{3h} group, it would have an electronic configuration that may be represented as $(1s_N)^2(a'_1)^2(e')^4(a''_2)^2$, $^1A'_1$ where $(1s_N)$ represents the molecular orbital which consists mostly of the nitrogen 1s orbital, (a'_1) and (e') represent bonding

orbitals consisting of the nitrogen 2s, $2p_x$, and $2p_y$ and $2p_z$ orbitals mixed with the hydrogen 1s orbitals, and (a''_2) represents the nonbonding orbital consisting of the nitrogen 2s and $2p_z$ orbitals mixed with the hydrogen 1s orbital. In a planar state of ammonia, this last orbital consists entirely of the nitrogen $2p_z$ orbital. The excited state involved in the 1600Å transition probably has the configuration $(1s_N)^2(a'_1)^2(e')^4(a''_2)(3pe')$, $^1E''$ where (3pe') represents a Rydberg orbital similar to a 3p nitrogen orbital and belonging to the E' species [2]. A number of other bands arising from Rydberg states lie close to the 1600Å band and have been investigated[12]. Two of particular interest to our discussion are electronic states belonging to the $^1A'_1$ and $^1A''_2$ species with probable configurations $(1s_N)^2(a'_1)^2(e')^4(a''_2)(3pa''_2)$ and $(1s_N)^2(a'_1)^2(e')^4(a_2'')(3sa_1')$, respectively.

The spectrum of associated with the E" state shows a progression in the v_2 vibration, as well as strong ℓ-type doubling. The appearance of the ℓ-type doubling indicates that the v_3 and v_4 vibrations are not excited, a conclusion supported by the fact that no progressions appear in these vibrations. The upper state rotational constants derived from equations (26a) and (27a) are given in Table 1; Douglas and Hollas used slightly different expressions and our C_v and ζ_v coincide with their C_v* and ζ_v*.

Calculation of the Spectroscopic Constants

It is interesting to try to estimate the relative importance of $q^{(E)}$ and $q^{(JT)}$ in q_v, since this might provide some evidence for the presence of the elusive Jahn-Teller effect. Unfortunately our information about the molecule is insufficient to warrant more than order of magnitude estimates of $q^{(E)}$ and $q^{(JT)}$ and the results are not conclusive.

Our first approximation is to consider only the effects of the outermost electron and to assume further that it can be described by a pure 3p wavefunction. In this case

$$|e_{\pm}> = \frac{1}{2}\left(|p_x> \pm i|p_y>\right). \tag{40}$$

and in the first of equatins (16), $\zeta_e = \sqrt{2}$. Furthermore $|e_{\pm}>$ is connected by the components of ℓ only with the 3P(A') Rydberg state, in which the outer electron is assumed to have a pure $3p_z$ wavefunction. In other words $\zeta_{ee'} = \zeta_{ee''} = 0$ and, from the rules for combining angular momentum[13], $\zeta_{ea} = 2$. Therefore according to equation (28), q^E depends only on B_e and the single energy separation ΔE_{ea} between the E" and the A'_1 state mentioned above, but unfortunately this energy separation is not known. The spectrum arising from A'_1 state consists of a v_2 progression, but the correct numbering of the bands is uncertain. By extrapolation from the observed bands however, Douglas gives three possible values for the position of 0-0 band, namely 62870 cm^{-1}, 61207 cm^{-1}, and 59825 cm^{-1}. The corresponding band in the spectrum involving

the E" state has a frequency of 59225 cm^{-1}. Taking B_e = 10.6 cm^{-1}, we deduce that q^E = 0.12 cm^{-1}, 0.23 cm^{-1}, or 0.75 cm^{-1}. The contribution q^E could account for almost all of the experimentally observed q value or for only a small part of it. If the major contribution to the q value is that of q^E, then the variation of q with v_2 must be explained on the basis of the variation of q^E with v_2. As the molecule bends, the instantaneous wavefunction will contain mixtures of the $3pa''_2$ and the $3sa'_1$ orbitals or of the A'_1 and A''_2 states of the planar molecule. The appropriate value of q^E to use in equations (26a) and (27a) must be an average of the instantaneous value of q^E over the v_2 motion[14]. The average configuration of the molecule will be more bent for larger v_2 and this should mean a larger average mixing of the two states. This in turn would lead to a lower value of ζ_{ea} and to a larger value of ΔE_{ea} since the A''_2 state lies below the A'_1 state. The A''_2 state lies almost 13,000 cm^{-1} below the E" state and so the direct interaction of the A''_2 state and the E" state can be ignored. The result of all this would be a decrease in the absolute value of q^E. a change which is in the right direction to account for the observed change in q.

Turning now to $q^{(JT)}$, we must first make some assumptions about the frequencies ω_3 and ω_4 and about the transformation angle θ, which determines both the exact forms of Q_3 and Q_4 and the Coriolis constants ζ_3, ζ_4, ζ_{23}, ζ_{24} and ζ_{34} (see equation (10)). The $^{15}NH_3$ spectrum shows only a small isotope shift and so all vibrations probably have much the same frequency in the upper

and lower states unless the frequencies change in a compensating manner. We therefore assume the ground state mechanical frequencies $\omega_1 = 3577\ cm^{-1}$ and $\omega_4 = 1691\ cm^{-1}$ as approximations to the excited state frequencies[15]. The value $\omega_2 = 880\ cm^{-1}$ can be taken from the observed spectrum. The ground state frequencies ω_3 and ω_4 of ND_3 were also assumed to hold for the excited state of ND_3 and lead to $\cos\zeta = 0.7021$ with a choice of signs for the force constants which correspond to those for the ground state. As a rough check on these assumptions the value of $\alpha_B^{(2)}$ calculated from equation (18) may be compared with the observed value of $0.52\ cm^{-1}$. The calculated value is $0.48\ cm^{-1}$ which is satisfactory considering the neglect of both mechanical anharmonicity and vibronic coupling.

Now the Jahn-Teller constants k_3 and k_4 in equation (38) are related to the coefficients K_3 and K_4 in the normal coordinate expansion of the vibronic matrix element

$$\langle e_+|H|e_-\rangle = K_3Q_{3-} + K_4Q_{4-} + - - -, \tag{41}$$

by the equations

$$k_i = Ki\sqrt{-1/(2\pi)^3\hbar c^3\omega_i^3}\ ; \quad i = 3,4. \tag{42}$$

In equation (41), H is the vibronic Hamiltonian. For an order of magnitude calculation we have taken the radial part of the 3p Rydberg orbitals in the form of a Slater orbital

$$R_{3p}(r) = \sqrt{\frac{(2c)^7}{6!}}\ r^2e^{-cr}, \tag{43}$$

and allowed only for the electrostatic interaction with the field due to the NH_3^+ framework. The constant c in equation (43) is determined by the effective nuclear charge on the

central atom. Self-consistent field molecular orbital calculations for NH_3^+ indicate an effective charge of +0.5e on each H atom and -0.5e on the N atom[16]. The spherical part of the potential of this system includes a contribution from the N atom, which was calculated from Slater's rules, and also a contribution from the 3 H atoms. For an N-H distance of 1.08 Å, the resultant is equivalent to an effective nuclear charge of 1.825 e on the central atom[17]. Accordingly, $c = \frac{1.825}{3a_0} = 1.15\ \text{Å}^{-1}$.

A straightforward calculation, which is most conveniently carried out in terms of the symmetry coordinates S_3 and S_4 of equation (7) then leads to the results

$$k_3 = -0.099 \sin^2\alpha,\ k_4 = 0.225 \sin^2\alpha, \qquad (44)$$

where α is the angle between the NH bonds and the figure axis of the molecule for values of α near $\pi/2$. In the planar configuration $\sin\alpha = 1$ and substitution in equation (38) leads to the value

$$q^{(JT)} = -0.38\ \text{cm}^{-1}. \qquad (45)$$

For $v_2 = 8$, the average value of α leads to $\sin^2\alpha = 0.86$[18]. This does not change the value of q^{JT} significantly and suggests that either most of the variation of q comes from q^E or that the Rydberg states do not have as simple an electronic structure as assumed here. These calculations are not capable of predicting the exact value of the various contributions to q_v, but the prediction of opposite sign for q^E and q^{JT} should be reliable.

Equation (27a) shows that ζ_v depends on ζ_e', ζ_3', ζ_4', k_3, and k_4. If we examine equations (19), we see that the same factors that would decrease the absolute value of q^E, namely a smaller value of ζ_{ea} and a larger value of ΔE_{ea} would also decrease the absolute value of ζ_e'. The second order Coriolis contributions to ζ_3' and ζ_4' also decrease as v_2 increases. If the variation in q is assumed to be due entirely to q^E and the measured variation in q as well as the vibrational frequencies given above are used to calculate the change in ζ_v, reasonable agreement is obtained (calculated change in ζ_v -0.048, observed change -0.043).

SUMMARY AND CONCLUSIONS

Formulae have been derived for the rotational energy levels of an electronically degenerate planar XY_3 molecule and applied to the 3P (E") Rydberg state of ammonia. The formulae indicate that there can be a large ℓ-type doubling only in molecules with no vibrational angular momentum, a fact that confirms the assignment of the observed spectrum to an upper state with v_3 and v_4 equal to zero. Theoretical estimates of the contributions to the ℓ-type doubling indicate two contributions, a rotational-electronic interaction and the Jahn-Teller rotational interaction, of comparable magnitude, but of opposite sign. A consistant explanation of the variation of the ℓ-type doubling constant and the effective Coriolis coupling

constant with a change in the out-of-plane bending quantum number is based on the variation of the rotational electronic interaction due to the shifting of electronic levels.

The size of the two contributions to the l-type doubling as well as a closer check on the theoretical calculations could be obtained from an analysis of the ND_3 spectrum particularly if k_4 is considerably greater than k_3. According to equations (28) and (38) $q^E = -(2\ B_e^2/\Delta E_{ea})\ \zeta_{ea}^2$ and $q^{JT} = -4k_3 \cos\theta\ B_e \sqrt{B_e/\omega_3}\ -4k_4 \sin\theta\ B_e \sqrt{B_e/\omega_4}$ where k_2 and k_4 are related to the electronic integrals K_3 and K_4 given by equation (42). In these formulas the unknown quantities $(\zeta_{ea}^2/\Delta E_{ea})$, K_3, and K_4 should not change on going from NH_3 to ND_3 while the other quantities change in a known manner. Determination of q for ND_3 would thus allow determination of the relative magnitude of these unknown electronic parameters, especially if k_4 is significantly greater than k_3 as indicated in equation (44).

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TABLE I. Experimental parameters from Douglas and Hollas[3] [a]

V_2	$B_v(cm^{-1})$ [b]	$C_v(cm^{-1})$ [c]	ζ_v	$q_v(cm^{-1})$
0	10.6[d]	5.16[d]		
1	10.11	5.21	0.841	0.758
2	9.48	5.33	0.837	0.530
3	8.99	5.37	0.821	0.529
4	8.48	5.35	0.822	0.429
5	8.00	5.46	0.822	0.258
8	6.92	5.55	0.798	0.170

[a] The B_v^* and ζ_v^* of ref. 3 is our B_v and ζ_v; we have also changed the extrapolations slightly. The parameters B_v, C_v, ζ_v, and q_v are defined in Eqs. (26a) and (27a).

[b] $B_v = 10.6 - 0.52\ v_2 + \ldots\ldots$

[c] $C_v = 5.16 + 0.05\ v_2 + \ldots\ldots$

[d] Obtained by extrapolation.

Figure Captions

Figure 1. The molecule fixed coordinate system for planar XY_3. The X atom is at 0 and the Y atoms at 1, 2, and 3 on the diagram.

Figure 2. The J = 1 rotational levels of a hypothetical electronically degenerate planar XY_3 molecule in the absence of vibronic coupling. (a) applies to vibrational levels with $v_3 = v_4 = 0$ and (b) to those with $v_3 = 0$, $v_4 = 1$. The spectroscopic constants chosen for the diagram are similar to those found for the 3P(E") state of ammonia and are described in detail in the text.

Figure 3. The J = 1 rotational levels of the first Q_4 vibronic state ($v_3 = 0$, $v_4 = 1$) of an electronically degenerate planar XY_3 molecule in the presence of a 15 cm^{-1} Jahn-Teller splitting. The other spectroscopic constants are similar to those found for the 3p(E") state of ammonia and are the same as those used in Fig. 2.

FOOTNOTES

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[18] For values of α close to $\pi/2$, sin θ goes as $1-\theta$ therefore, the sin θ of the average α gives the correct order of magnitude for the average of sin θ.

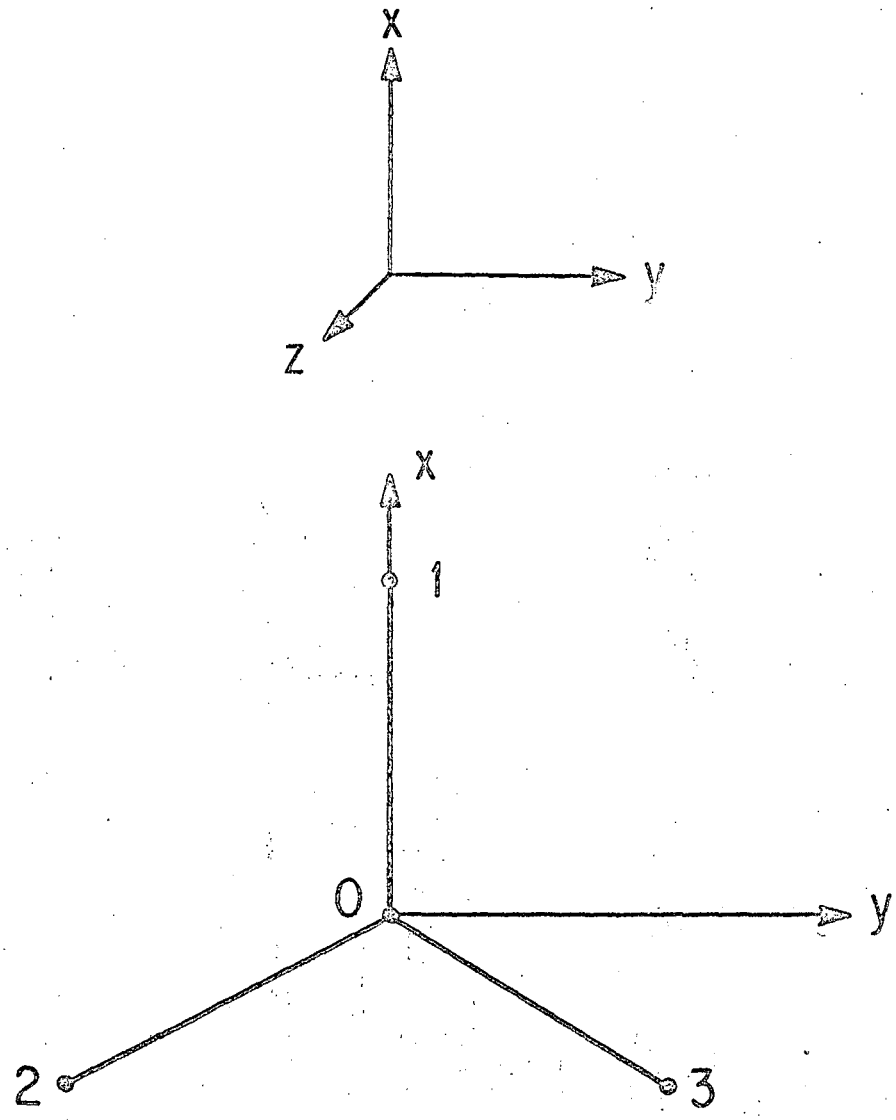
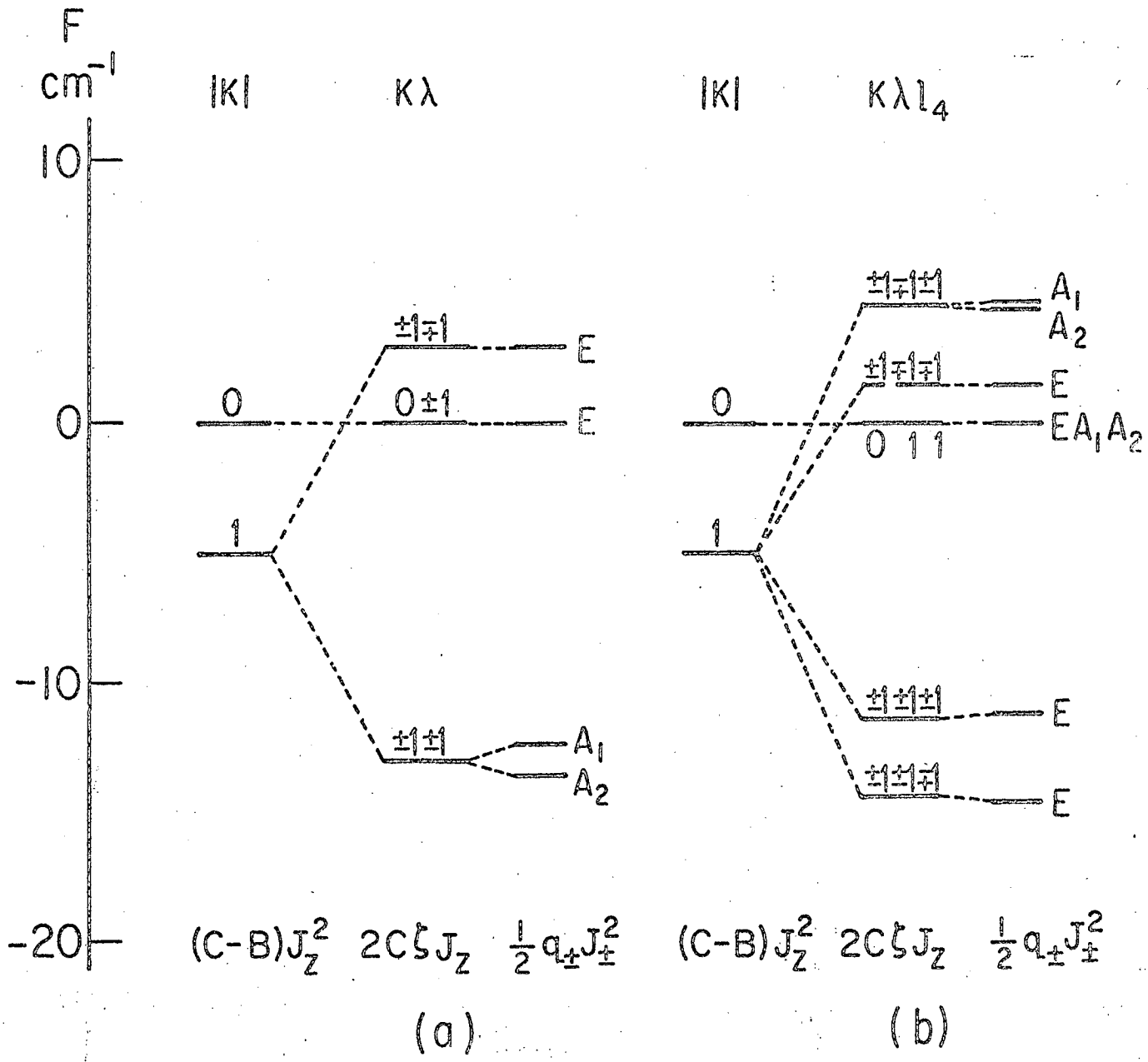


Fig. 1.



Figs. 2(a) and 2(b).

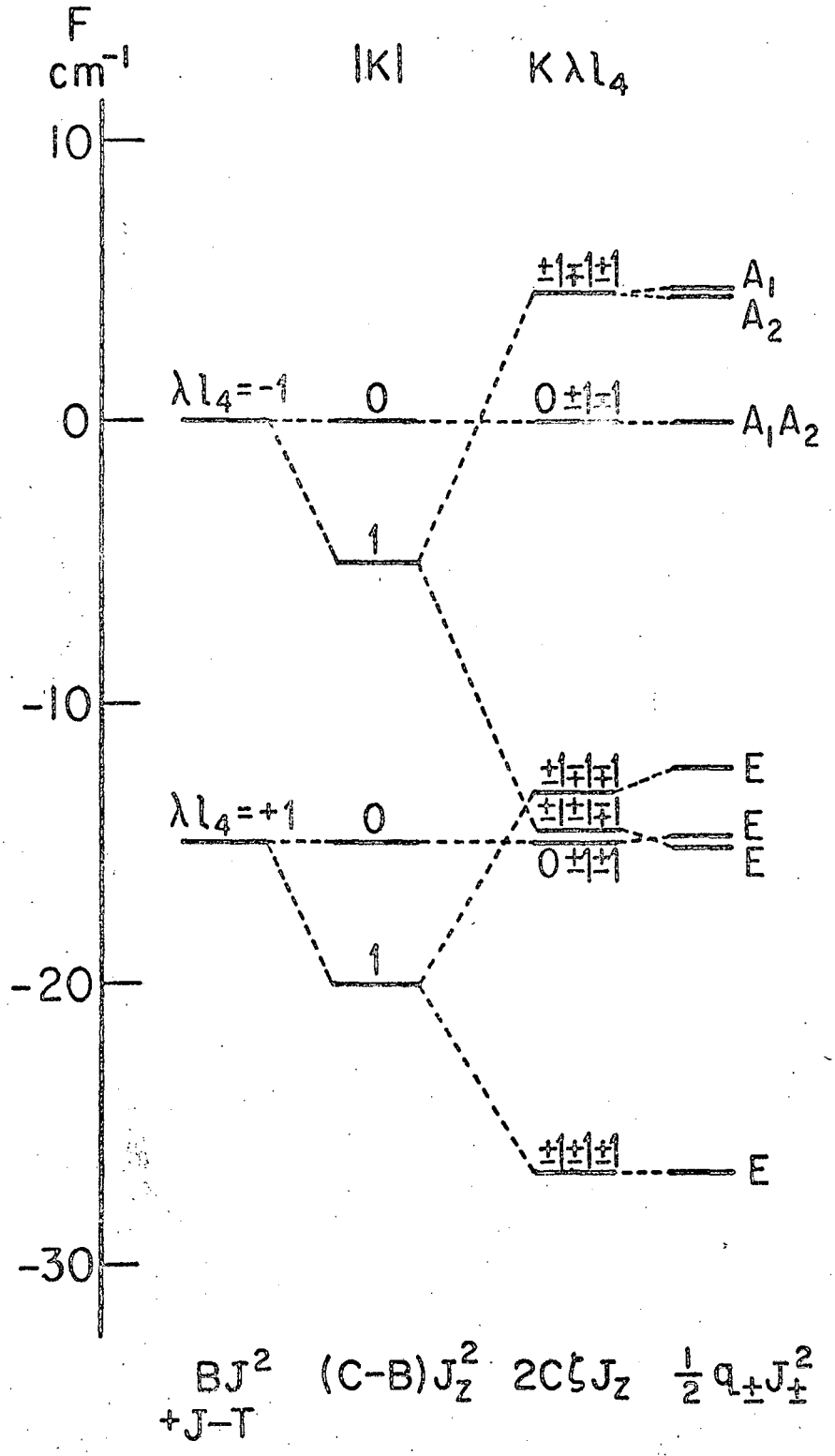

F
cm⁻¹
|K|
Kλl4
10
0
-10
-20
-30
λl4=-1
0
1
±1∓1±1
0±1-1
A1
A2
A1A2
λl4=+1
0
1
±1∓1∓1
±1±1∓1
0±1±1
E
E
E
±1±1±1
E
BJ²
+J-T
(C-B)Jz²
2CζJz
½q±J±²

Fig. 3.

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