

CORIOLIS INTERACTIONS, INTENSITY PERTURBATIONS AND POTENTIAL FUNCTIONS IN POLYATOMIC MOLECULES

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1. INTRODUCTION

The effect of Coriolis interaction on vibration-rotation spectra is familiar in the case where a pair of otherwise degenerate vibrational levels interact with each other, as in symmetric top molecules. This situation was first discussed by Teller¹ and later by Johnston and Dennison², and Jahn³; more recently Boyd and Longuet-Higgins⁴ have reviewed the theory in some detail. Meal and Polo⁵ have discussed the derivation and properties of Coriolis zeta interaction constants, and Boyd and Longuet-Higgins⁴, Meal and Polo⁵ and Lord and Merrifield⁶ have discussed the sum rules that occur amongst the zetas that relate degenerate pairs of vibrations. Coriolis zeta constants also play an important role in formulating the general theory of the vibration-rotation Hamiltonian⁷⁻⁹ and some of their properties have been studied in this connection.

Despite these developments in the theory of zeta constants, there have been few discussions of the effect on rovibrational spectra of Coriolis interactions between non-degenerate vibrational levels; most of the treatments of the theory in this more general situation are due to Nielsen⁷ and his co-workers. Recently several examples of such perturbations in rovibrational spectra have been observed¹⁰⁻¹²; useful information may come from such observations in several ways. Firstly, such perturbations yield observed values of zeta constants relating pairs of non-degenerate normal vibrations, and since these are sensitive functions of the form of the normal coordinates they provide data for force constant calculations of precisely the kind required to supplement the vibration frequencies, in order to obtain a unique solution to the force field. Secondly, such perturbations may give information about otherwise inactive or unobserved vibrations, and thus enable a more complete assignment to be made; examples of this occur in ethylene¹⁰ and diborane¹¹. Thirdly, Coriolis interactions give rise to certain characteristic intensity perturbations, which give direct information on the relative signs of transition moments, which may otherwise be very hard to obtain. In particular it is possible to relate the signs of transition moments due to two vibrations in different symmetry species. There is, at present, no other method of obtaining such relations experimentally.

The object of this paper is to review the theory of these interactions and to consider some examples in detail. The theory is developed by using a matrix perturbation method, which gives more physical insight into the nature of the interaction than is obtained from the contact transformation

method used by previous workers. The general features of the method are outlined, and formulae are given for the matrix elements which are required to apply this theory in particular cases. The general selection rules governing Coriolis interactions, which result from symmetry considerations, are given. Some specific examples are considered, with regard to the effect of the interactions on both the positions and the intensities of lines in rovibrational bands. A simple classical model is described for a pair of Coriolis-interacting vibrations, which shows a close analogy to the quantum mechanical results and gives further physical insight into the cause of both the frequency and the intensity perturbations.

2. GENERAL THEORY

The following approximate quantum mechanical Hamiltonian for a vibrating-rotating molecule provides a model for the discussion of the theory of Coriolis interactions:

$$H = \frac{(J_x - p_x)^2}{2I_x} + \frac{(J_y - p_y)^2}{2I_y} + \frac{(J_z - p_z)^2}{2I_z} + \frac{1}{2} \sum_r (P_r^2 + \lambda_r Q_r^2) \quad (1)$$

Here J_α is the component of total angular momentum about the molecule fixed α axis, and I_α is the corresponding principal moment of inertia; Q_r and P_r are a typical normal coordinate and its conjugate momentum, and λ_r is the force constant in that coordinate; finally p_α is the component of vibrational angular momentum about the α axis, defined by:

$$p_z = \sum_a -i\hbar[x_a(\partial/\partial y_a) - y_a(\partial/\partial x_a)] \quad (2)$$

etc., with cyclic permutations of x , y and z , where (x_a, y_a, z_a) are mass adjusted Cartesian displacement coordinates of the atom a in the molecule.

Coriolis interactions arise through the presence of the terms in the vibrational angular momentum. If we neglect the explicit effects of anharmonicity and the dependence of the effective moments of inertia on the vibrational coordinates, the Hamiltonian (1) consists of the Hamiltonian of a rigid rotor H_r , plus an assembly of simple harmonic vibrators H_v , plus terms involving the vibrational angular momenta H' :

$$\begin{aligned} H &= H_r + H_v + H' \\ H_r &= J_x^2/2I_x + J_y^2/2I_y + J_z^2/2I_z \\ H_v &= \frac{1}{2} \sum_r (P_r^2 + \lambda_r Q_r^2) \\ H' &= -p_x J_x/I_x - p_y J_y/I_y - p_z J_z/I_z \\ &\quad + p_x^2/2I_x + p_y^2/2I_y + p_z^2/2I_z \end{aligned} \quad (3)$$

The wave-functions and energy levels obtained from H_r ¹³ and H_v ¹⁴ are familiar. Thus the terms H' may be treated as a perturbation, and the solutions to the complete Hamiltonian may be expanded in terms of the basis functions obtained as solutions to $H_r + H_v$. The matrix of the complete

Hamiltonian will contain off diagonal elements due to the terms in H' , and the diagonalization of this matrix (which may be carried out exactly, or by first or second order perturbation theory, as may be appropriate) will give both the perturbations to the energy levels and the wave-functions. Then, by forming terms between pairs of energy levels, and using the wave-functions in appropriate expressions for the transition moments, both the positions and the intensities of the rotational lines in the spectrum may be predicted.

Determination of matrix elements

Rotational perturbations arise mainly from the first three terms in H' , given in (3), since the last three terms do not involve any rotational operators (and the vibrational angular momentum is generally small compared to the rotational angular momentum). Only perturbations from these first three terms will be considered in this discussion. If the basis functions are written as vibration-rotation product functions, being solutions to H_v and H_r respectively, of the form:

$$\psi_{\text{vib.}}\psi_{\text{rot.}} \equiv |v;r\rangle \equiv |v\rangle|r\rangle, \text{ or } \psi_{\text{vib.}}^*\psi_{\text{rot.}}^* \equiv \langle v|\langle r| \quad (4)$$

then it is observed that the matrix elements of the first three terms in H' always factorize into a vibration-rotation product:

$$\langle v;r| -p_z J_z / I_z |v';r'\rangle = (-1/I_z) \langle v|p_z|v'\rangle \langle r|J_z|r'\rangle \quad (5)$$

The non-zero matrix elements of the components of total angular momentum are given by standard formulae for the rotational wave-functions of a symmetric top:

$$\langle J,k|J_z|J,k\rangle = k\hbar \quad (6)$$

$$\langle J,k|J_x \pm iJ_y|J,k \pm 1\rangle = \hbar[J(J+1) - k(k \pm 1)]^{1/2} \quad (7)$$

where k is the signed quantum number of angular momentum about the top axis, which is taken to be z . Although we shall not always be concerned with symmetric top molecules, the asymmetric top effects may often be neglected, and when this is not true they are best handled by retaining the symmetric rotor basis functions and including further perturbation terms to represent the asymmetry in the inertial axes. The matrix elements of the vibrational angular momenta are obtained by expressing the vibrational angular momenta in terms of the normal coordinates. It is found:

$$p_z = \sum_r \sum_s \zeta_{r,s}^z [Q_r P_s - Q_s P_r] \quad (8)$$

where the Coriolis zeta constants are defined by:

$$\zeta_{r,s}^z = \sum_a [(\partial x_a / \partial Q_r) (\partial y_a / \partial Q_s) - (\partial x_a / \partial Q_s) (\partial y_a / \partial Q_r)] \quad (9)$$

Each of the zeta constants relates a pair of normal coordinates through

† Here the phases of the rotational wave-functions have been chosen as in Hougen¹⁵.

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rotation about one of the axes. The sign of a particular $\zeta_{r,s}^\alpha$ evidently depends on the choice of positive sense of Q_r , and of Q_s , and on the order of the subscripts r and s . The symmetry properties and sum rules relating to zeta constants follow from their definition in (9)^{5,8,9,16}; the most important of these results, originally due to Jahn³, states that a $\zeta_{r,s}^\alpha$ can only differ from zero if the product of the symmetry species of Q_r and Q_s contains the rotation R_α .

Since the vibrational basis functions are assumed to be simple products of harmonic oscillator functions in the normal coordinates, the non-zero matrix elements of the vibrational angular momenta follow directly from (8). It is found:

$$\langle v_r + 1, v_s | p_\alpha | v_r, v_s + 1 \rangle = -i\hbar \zeta_{r,s}^\alpha [\sigma_r + 1] \sigma_s + 1]^{\frac{1}{2}} \Omega_{rs} \quad (10)$$

$$\langle v_r + 1, v_s + 1 | p_\alpha | v_r, v_s \rangle = -i\hbar \zeta_{r,s}^\alpha [(v_r + 1)(v_s + 1)]^{\frac{1}{2}} \Phi_{rs} \quad (11)$$

where $\Omega_{rs} = \frac{1}{2}[(v_r/v_s)^{\frac{1}{2}} + (v_s/v_r)^{\frac{1}{2}}]$ and $\Phi_{rs} = \frac{1}{2}[(v_r/v_s)^{\frac{1}{2}} - (v_s/v_r)^{\frac{1}{2}}]$. Terms of the type (10) are of greater importance than terms of the type (11), since the former may connect levels of similar energy (*e.g.*, two singly excited fundamental states) whereas the latter will generally connect levels of very different energy. In the particular case of the interaction of two singly excited fundamentals equation (10) specializes to give:

$$\langle 1, 0 | p_\alpha | 0, 1 \rangle = -i\hbar \zeta_{r,s}^\alpha \Omega_{r,s} \quad (12)$$

In the case of symmetric top molecules the wave-functions of the doubly degenerate normal vibrations will be functions of a pair of coordinates (Q_{r1}, Q_{r2}) which transform into each other under certain operations of the molecular point group. The wave-functions of the doubly degenerate vibrations are usually characterized by the quantum numbers v_r and l_r (rather than v_{r1} and v_{r2}), where $v_r = v_{r1} + v_{r2}$ and l_r is the eigenvalue of the operator [$Q_{r1}P_{r2} - Q_{r2}P_{r1}$] in units of \hbar :

$$\langle v_r^l | Q_{r1}P_{r2} - Q_{r2}P_{r1} | v_r^l \rangle = l_r \hbar \quad (13)$$

The diagonal matrix elements of p_z for a symmetric top follow from (13). Off diagonal matrix elements of p_z , and of p_x and p_y , are more complicated; they involve the formulae for the matrix elements of the coordinates and moments for a two dimensional harmonic oscillator, which are as follows¹⁷:

$$\begin{aligned} & \langle v_r + 1, l_r \pm 1 | P_r \pm | v_r, l_r \rangle \\ &= -\langle v_r, l_r | P_r \mp | v_r + 1, l_r \mp 1 \rangle \\ &= i\hbar \left[\frac{\gamma_r}{2} \right]^{\frac{1}{2}} (v_r \pm l_r + 2)^{\frac{1}{2}} \end{aligned} \quad (14)$$

$$\begin{aligned} & \langle v_r + 1, l_r \pm 1 | Q_r \pm | v_r, l_r \rangle \\ &= \langle v_r, l_r | Q_r \mp | v_r + 1, l_r \mp 1 \rangle \\ &= \hbar \left[\frac{1}{2\gamma_r} \right]^{\frac{1}{2}} (v_r \pm l_r + 2)^{\frac{1}{2}} \end{aligned} \quad (15)$$

where $P_r \pm = P_{r1} \pm iP_{r2}$, $Q_r \pm = Q_{r1} \pm iQ_{r2}$, and $\gamma_r = 2\pi v_r/\hbar$.

From these expressions all the matrix elements of the vibrational angular

momenta involving doubly degenerate states of a symmetric top may be deduced; however since the results depend on the molecular point group, and the symmetry species of the states, they cannot be usefully stated in a general way.

Equations (6) to (15) give all the formulae which are required to evaluate the matrix of the Coriolis perturbation terms in the Hamiltonian.

Rovibration line intensities

The intensity of a particular rovibration line in the spectrum depends on the square of the transition moment between the states involved in the transition, and the effect of the Coriolis perturbation on the line intensities may be evaluated by using the expressions for the true (perturbed) wave-functions in terms of the basis functions to evaluate the transition moments. In the rigid-symmetric-rotor simple-harmonic-oscillator basis functions, the transition moments relative to an axis fixed in space may be resolved along the molecule fixed x , y and z axes, and factorized into vibration-rotation products, in the following way:

$$\begin{aligned} \langle v'', r'' | \mu_z | v', r' \rangle &= \langle v'' | \mu_z | v' \rangle \langle r'' | (zf) | r' \rangle \\ &+ \frac{1}{2} \langle v'' | \mu_x - i\mu_y | v' \rangle \langle r'' | (xf) + i(yf) | r' \rangle \\ &+ \frac{1}{2} \langle v'' | \mu_x + i\mu_y | v' \rangle \langle r'' | (xf) - i(yf) | r' \rangle \end{aligned} \quad (16)$$

where (xf) , (yf) and (zf) denote direction cosines of the molecule fixed x , y and z axes relative to the space fixed axis f . The rotational matrix elements of the three terms in (16) satisfy the selection rule $\Delta k = 0, +1$ and -1 respectively, so that for a given transition in the basis functions only one of the three terms can be non-zero; the actual values of the rotational matrix elements (the Hönl-London formulae) are given in Townes and Schawlow¹⁸ in the phase convention adopted here.

When an interaction is introduced which mixes together the basis functions, such as a Coriolis perturbation (or the effect of unequal moments of inertia in an asymmetric top), the effect on the line intensities may be evaluated in the following way. The true rovibration wave-functions consist of linear combinations of the basis functions with coefficients given by the appropriate eigenvectors of the Hamiltonian matrix. On substituting such an expression into the transition moment integral $\langle v'', r'' | \mu_z | v', r' \rangle$ a sum of terms each consisting of some coefficient times one of the transition moment integrals in the basis functions is obtained. On squaring this expression (and summing over necessarily degenerate transitions arising from different values of m , and from nuclear spin degeneracy) the true rovibrational line strength is found.

When two allowed vibration bands Coriolis interact, the general effect is to produce an asymmetry in the intensity distribution of the rotational structure in each band, as is shown in the examples below. Thus if the high frequency wing of a particular band is enhanced by the perturbation, then the low frequency wing is depleted, and vice-versa. This effect arises from cross-terms in the line strength factors in the following way: consider a

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transition $v', r' \leftarrow v'', r''$ where the excited state wave-function is a mixture of basis functions given by

$$|v'r'\rangle = a|v_1r_1\rangle + b|v_2r_2\rangle$$

Then for the line strength:

$$\begin{aligned} [\langle v''r'' | \mu_f | v'r' \rangle]^2 &= [a\langle v''r'' | \mu_f | v_1r_1 \rangle + b\langle v''r'' | \mu_f | v_2r_2 \rangle]^2 \\ &= a^2M_1^2 + b^2M_2^2 + 2abM_1M_2 \end{aligned} \tag{17}$$

where M_1 and M_2 are the unperturbed transition moments to the basis functions. The point to observe is that although the first two terms on the right of (17) are necessarily positive, the third term may be positive or negative, depending on the signs of a and b and the relative signs of M_1 and M_2 . Thus, mixing two strongly allowed transitions may give rise to a transition which is less strong than either of the original lines, or a transition which is stronger than either of the original lines; examples are shown below where these effects are quite dramatic. Moreover the sense of this intensity effect depends on the relative signs of M_1 and M_2 : it is in this way that the signs of transition moments in two different symmetry species may be related.

3. CORIOLIS SELECTION RULES

Just as selection rules can be derived for electric dipole radiation by considering which wave-functions are connected by non-zero matrix elements of the electric dipole moment operator, selection rules governing possible pairs of Coriolis interacting states can be similarly derived, by considering non-zero matrix elements of the Coriolis perturbation operator (8). Such selection rules will determine which pairs of basis functions can be mixed by the perturbation; so long as it is useful to think in terms of interactions between basis functions the concept of selection rules will be helpful.

These selection rules may be classified as overall selection rules, or vibrational selection rules (which are required to give a non-zero vibrational matrix element), or rotational selection rules (to give a non-zero rotational matrix element); they may be derived from consideration of the various formulae for the matrix elements given in Section 2. Moreover the vibration and rotation selection rules are correlated (as they are for dipole radiation): for example, the matrix elements of the perturbation operator may be written, in the case of a symmetric top:

$$\begin{aligned} \langle v,r | -p_z J_z / I_A - (p_x J_x + p_y J_y) / I_B | v',r' \rangle \\ = - (1/I_A) \langle v | p_z | v' \rangle \langle r | J_z | r' \rangle \\ - (1/I_B) [\langle v | p_- | v' \rangle \langle r | J_+ | r' \rangle + \langle v | p_+ | v' \rangle \langle r | J_- | r' \rangle] \end{aligned} \tag{18}$$

where $p_{\pm} = p_x \pm ip_y$ and $J_{\pm} = J_x \pm iJ_y$. In general the selection

rules require that not more than one of the three terms in (18) can differ from zero for a given pair of rovibrational levels, and evidently the selection rule will only be satisfied if the non-zero vibrational and rotational matrix elements occur in the same term.

All of these selection rules are summarized in *Tables 1 and 2*.

It is worth noting three special cases of the vibrational selection rules with regard to the activity of transitions to two Coriolis interacting vibrational levels from a third level. Let v and v' denote two interacting vibrational levels, due to rotation about the α axis, and let v'' denote a third level, from which we consider the possibility of observing transitions $v \leftarrow v''$ and $v' \leftarrow v''$. Suppose further that either the molecule is a symmetric top, or if it is an asymmetric top then its symmetry is sufficient to distinguish transition moments in the three principal axes x, y and z (this is true of the asymmetric top point groups D_{2h}, D_2 and C_{2v}). Then, if $\Gamma(v) \times \Gamma(v') \supset \Gamma(R_\alpha)$, one of the following situations must hold, where (α, β, γ) are any cyclic permutation of (x, y, z) :

$$(a) \left. \begin{aligned} \mu(v \leftarrow v'') &\sim T_\beta \\ \mu(v' \leftarrow v'') &\sim T_\gamma \end{aligned} \right\} \text{since } T_\beta \times T_\gamma \sim R_\alpha \quad (19)$$

$$(b) \left. \begin{aligned} \mu(v \leftarrow v'') &\sim T_\alpha \\ \mu(v' \leftarrow v'') &\sim T_\alpha R_\alpha \end{aligned} \right\} \text{since } T_\alpha \times T_\alpha R_\alpha \sim R_\alpha \quad (20)$$

In this case the transition ($v' \leftarrow v''$) is inactive, except in so far as it is made active by the perturbation.

(c) Neither of the transitions ($v \leftarrow v''$) nor ($v' \leftarrow v''$) is dipole active. The situation (a) might be described as an interaction between two allowed transitions; (b) as an interaction between an allowed and a forbidden transition; and (c) as an interaction between two forbidden transitions. These restrictions on activity will of course be relaxed if the molecular symmetry is not sufficient to distinguish transition moments in the three axes, when hybrid bands will appear.

Table 1. Selection rules for Coriolis interacting states

$p_\alpha J_\alpha$	Operator	Overall selection rule
		$\Delta J = 0$; only levels of the same rovibrational symmetry species interact
p_α	Vibrational operator	Vibrational selection rule
		In general: $\Gamma(v) \times \Gamma(v') \supset (R_\alpha)$ In harmonic approximation: $\Delta v_r = \pm 1, \Delta v_s = \pm 1, \Delta v_t = 0$ for $t \neq r$ or s , where $\Gamma(Q_r) \times \Gamma(Q_s) \supset \Gamma(R_\alpha)$

4. SPECIFIC EXAMPLES

I shall consider here only examples of interaction between non-degenerate vibrational levels. Also, I shall only discuss interactions between two allowed transitions, of the type described in (19), since I wish to emphasise the consequences of such interactions in perturbing the intensity distribution of the rotational structure.

Table 2. Correlation between vibration and rotation selection rules for Coriolis interacting levels

Molecule	Vibrational operator	Vibrational selection rule in terms of θ circle (Mills ¹⁹)		Rotational operator	Rotational selection rule
		G_n molecules	S_m molecules		
Symmetric Top	p_z, ip_y $p_x + ip_y$	$\Delta\theta = 0$	$\Delta\theta = 0$	J_x, iJ_y $J_x + iJ_y$ $J_x - iJ_y$	$\Delta k = 0$ $\Delta k = +1$ $\Delta k = -1$
		$\Delta\theta = +2\pi/n$	$\Delta\theta = \pi + 2\pi/m$		
Asymmetric Top	p_a p_b p_c	$\Delta\theta = -2\pi/n$	$\Delta\theta = \pi - 2\pi/m$	J_a J_b J_c	$\Delta K_{-1} = 0, \Delta K_{+1} = \pm 1$ $\Delta K_{-1} = \pm 1, \Delta K_{+1} = \mp 1$ $\Delta K_{-1} = \pm 1, \Delta K_{+1} = 0$
		$\Gamma(\nu) \times \Gamma(\nu') = \Gamma(R_a)$ $\Gamma(\nu) \times \Gamma(\nu') = \Gamma(R_b)$ $\Gamma(\nu) \times \Gamma(\nu') = \Gamma(R_c)$			

Prolate asymmetric tops

Interaction between B and C type bands

In a prolate asymmetric top, with a small value of I_A , the perturbation term $(-p_z J_z / I_A)$ may be large and thus produce important interactions; moreover if the asymmetry parameter $\kappa \sim -1$, the asymmetric top effects may often be neglected.

Consider the case of interaction between the two fundamental vibrational levels $(v_r = 1, v_s = 0)$ and $(v_r = 0, v_s = 1)$ where $Q_r \times Q_s \sim R_A$, and $Q_r \sim T_B$, $Q_s \sim T_C$, so that the two fundamental levels combine with the ground state to give B and C type perpendicular bands. If the molecule is close to a symmetric top about the A axis, and k is treated as a good quantum number (an approximation that will fail only for the lowest k values), the important perturbation term $(-p_z J_z / I_A)$ will be diagonal in J and k , and will connect together terms of the same J and k in the two levels. The Hamiltonian factorizes into (2×2) blocks:

$$\begin{array}{cc} |1,0; J,k\rangle & |0,1; J,k\rangle \\ \left[\begin{array}{c} \nu_r + F(J,k) \\ \text{(hermitian)} \end{array} \right. & \left. \begin{array}{c} + 2iA \zeta_{rs} \Omega_{rs} k \\ \nu_s + F(J,k) \end{array} \right] \end{array} \quad (21)$$

where ν_r and ν_s denote vibrational energies measured from the ground vibrational state, and $F(J,k)$ denotes the rigid symmetric rotor approximation to the rotational energy:

$$F(J,k) = \bar{B}J(J+1) + (A - \bar{B})k^2 \quad (22)$$

Diagonalizing (21) gives the energy levels:

$$E_{\pm}(J,k) = \frac{1}{2}(\nu_r + \nu_s) + F(J,k) \pm \frac{1}{2}\Delta_k \quad (23)$$

where

$$\Delta_k^2 = \delta^2 + 16A^2 k^2 \zeta_{rs}^2 \Omega_{rs}^2 \quad (23a)$$

and

$$\delta = \nu_r - \nu_s \quad (23b)$$

The perturbed wave-functions are given by:

$$\begin{array}{l} |\psi_+\rangle = a_k |\psi_r\rangle - i\sigma_{\zeta k} b_k |\psi_s\rangle \\ |\psi_-\rangle = -i\sigma_{\zeta k} b_k |\psi_r\rangle + a_k |\psi_s\rangle \end{array} \quad (24)$$

where

$$a_k = [(\Delta_k + \delta)/2\Delta_k]^{\frac{1}{2}} \quad (24a)$$

$$b_k = [(\Delta_k - \delta)/2\Delta_k]^{\frac{1}{2}}$$

and

$$\sigma_{\zeta k} = (\text{sign } \zeta_{rs}) (\text{sign } k) \quad (24b)$$

In (24), $|\psi_r\rangle$ and $|\psi_s\rangle$ denote the unperturbed vibrational wavefunctions $|1,0\rangle$ and $|0,1\rangle$. The sign index $\sigma_{\zeta k}$, equal to ± 1 , is simply the sign of the cross term in the original matrix; this decides the phases with which the

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basis functions are mixed by the perturbation. The square roots in (24a) are to be taken positive, and it is assumed that $\nu_r > \nu_s$; thus for small values of k [when the cross term is smaller than the difference between the diagonal terms in (21)] the upper energy levels E_+ correlate strongly with ν_r and the lower energy levels E_- with ν_s . For large values of k , however, the wavefunctions become strongly mixed, and a_k and b_k tend towards the limiting values $(1/\sqrt{2})$.

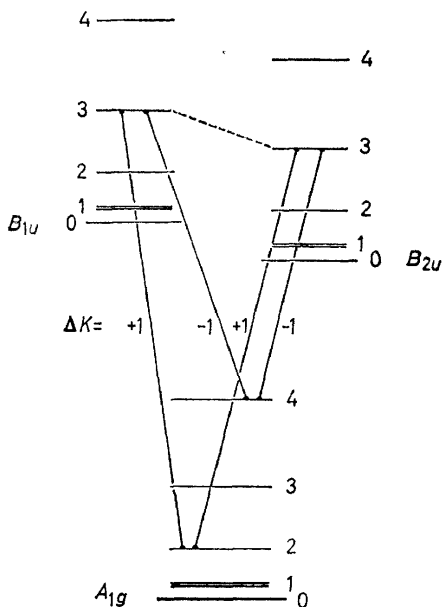


Figure 1. Energy level diagram for Coriolis interaction between B and C type bands in a prolate asymmetric top. Solid lines indicate allowed transitions; dotted lines indicate Coriolis interacting levels. Three vibrational levels are shown with symmetry species appropriate to the D_{2h} point group; rotational levels are shown for a single value of J and different values of K from 0 through 4

It should be noted that, in this case, since the perturbation is diagonal in all the rotational quantum numbers, it may be thought of as mixing vibrational wavefunctions only. The perturbation is indicated diagrammatically in Figure 1.

By combining (23) with the expression for the rotational energy levels in the ground vibrational state, given by (22), expressions are obtained for the line positions in the two observed bands. Since the perturbation depends only on k , and is independent of J , only the relative positions of the sub-band origins are affected: these degrade away from each other in the two bands, being given by:

$$\begin{aligned}
 R,PQ_K(\nu^+) &= \frac{1}{2}(\nu_r + \nu_s) + (A - \bar{B}) \pm 2(A - \bar{B})K + \\
 &\quad + \frac{1}{2}[\delta^2 + 16A^2\zeta_{rs}^2\Omega_{rs}^2(K \pm 1)^2]^{\frac{1}{2}} \\
 R,PQ_K(\nu^-) &= \frac{1}{2}(\nu_r + \nu_s) + (A - \bar{B}) \pm 2(A - \bar{B})K - \\
 &\quad - \frac{1}{2}[\delta^2 + 16A^2\zeta^2\Omega^2(K \pm 1)^2]^{\frac{1}{2}}
 \end{aligned}
 \tag{25}$$

In these equations $K = |k|$, as is usual, and the upper and lower signs refer to R type ($\Delta K = +1$) and P type ($\Delta K = -1$) sub-bands respectively. The sub-band origins will usually be evident in the spectrum owing to the

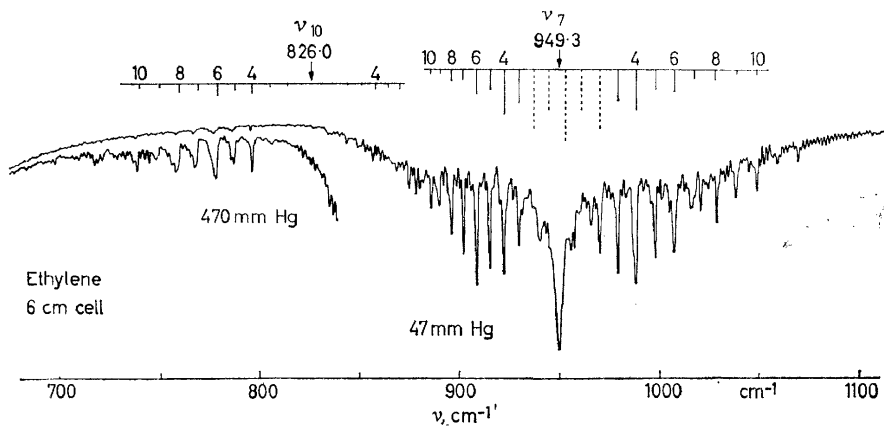


Figure 2. Spectrum of ethylene from 700 to 1100 cm^{-1} , with a resolving power $\sim 0.8 \text{ cm}^{-1}$, showing opposed degradation of the sub-band Q branches in the B and C type perpendicular fundamentals ν_7 and ν_{10} (after Smith and Mills¹⁰)

associated Q branch maxima; Figures 2 and 3 illustrate the effect in the CH_2 wagging and rocking vibrations of ethylene and allene— $1.1 - d_2$.

The perturbed line intensities are given by substituting (24) into the expressions for the transition moments. For the vibrational transition moments we find:

$$\begin{aligned} \langle \psi_0 | \mu_x \mp i\mu_y | \psi_+ \rangle &= a_k M_T \mp \sigma_{zk} b_k M_S \\ \langle \psi_0 | \mu_x \mp i\mu_y | \psi_- \rangle &= -i\sigma_{zk} b_k M_T \mp ia_k M_S \end{aligned}$$

where $M_T = \langle \psi_0 | \mu_x | \psi_T \rangle$ and $M_S = \langle \psi_0 | \mu_y | \psi_S \rangle$ are the unperturbed vibrational transition moments in the B and C axes, and the upper and

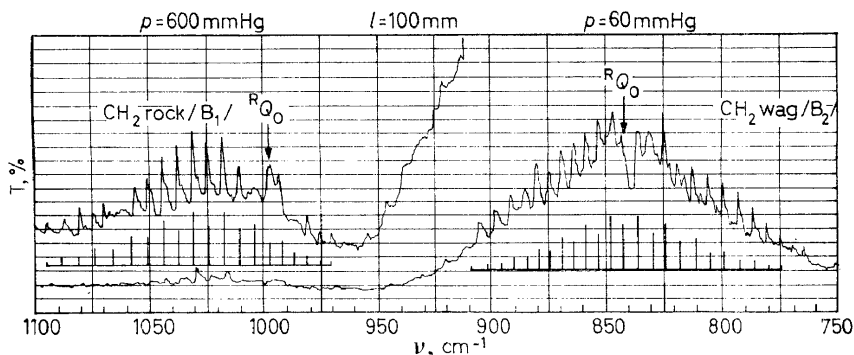


Figure 3. Spectrum of allene— $1.1 - d_2$ from 750 to 1100 cm^{-1} , with a resolving power $\sim 1 \text{ cm}^{-1}$, showing opposed degradation of the sub-band Q branches in B and C type perpendicular fundamentals, and intensity asymmetry in the weaker band

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lower signs correspond to $\Delta k = \pm 1$. Finally, writing $K = |k|$, and squaring to obtain the vibration line strengths S_+ and S_- , we obtain:

$$\begin{aligned} S_+ &= a_K^2 M_r^2 + b_K^2 M_s^2 \mp \sigma_c a_K b_K M_r M_s \\ S_- &= b_K^2 M_r^2 + a_K^2 M_s^2 \pm \sigma_c a_K b_K M_r M_s \end{aligned} \quad (26)$$

Here σ_c denotes the sign of ζ_{rs} only, and the upper and lower signs refer to $\Delta K = +1$ (*R* type) and $\Delta K = -1$ (*P* type) transitions.

The equations (26) show a two-fold effect of the perturbation on the sub-band intensities: the first two terms on the right hand side lead to a transfer of intensity from the stronger to the weaker band at high K , while the third term leads to an asymmetry of intensity about the band centre in both bands. Since a_K and b_K are defined as positive, the sense of the asymmetry is determined by the sign of (ζ_{rs}) (M_r) (M_s), or, for the two fundamental bands considered, the sign of

$$(\zeta_{r,s}^2) (\partial\mu^x/\partial Q_r) (\partial\mu^y/\partial Q_s) \quad (27)$$

If (27) is *positive*, we talk of a *positive perturbation*, in which [as shown by (26)] the *P*-type sub-bands of the high frequency band and the *R*-type sub-bands of the low frequency band are enhanced, and the *R*-type of the high frequency and *P*-type of the low frequency are depleted. If (27) is *negative*, we have a *negative perturbation*, and the converse intensity perturbation is observed. These effects correspond to the vibrational angular momentum, and the effective charge, rotating in the *same sense* or the *opposite sense* respectively, when the two vibrations are excited classically with a 90 degree phase shift; the classical model is discussed further in Section 5.

For a chosen positive sense of each of the coordinates Q_r and Q_s , the sign of ζ_{rs}^2 is fixed, and it follows that the signs of $(\partial\mu^x/\partial Q_r)$ and $(\partial\mu^y/\partial Q_s)$ can be experimentally related from an observation of the sense of the intensity perturbation, even though Q_r and Q_s may lie in different symmetry species.

Examples of this type of perturbation are the interaction of the CH_2 wagging and rocking motions of formaldehyde, in which according to Hisatsune and Eggers²⁰, a negative perturbation is observed; the corresponding bands in allene $-1.1 - d_2$, shown in *Figure 3*²¹, where a negative perturbation is observed; and in butatriene, where, to judge from a spectrum recently published by Matsubara and Miller²², a negative perturbation is again observed. In all these cases the conclusion is that the dipole moment derivatives in the CH_2 wagging and rocking vibrations are related as in *Figure 4*, which is actually drawn for the allene molecule.

Finally it is interesting to consider what happens as the two perpendicular normal modes become more and more nearly degenerate: such a model, with near accidental degeneracy, would presumably be appropriate for studying the rovibration structure of the methyl-group perpendicular vibrations in CH_3NH_2 , or the isotopically-split degenerate vibrations in benzene with one ^{13}C atom substituted in the ring. In this case the correct vibrational wave-functions become 50/50 mixtures of $|\psi_r\rangle$ and $|\psi_s\rangle$ even for quite low values of k , because a_k and b_k reach their limiting values of $1/\sqrt{2}$ as soon as the interaction is large compared to $(\nu_r - \nu_s)$. If, in addition, $M_r = M_s$

(which would be approximately true for the examples above) then the intensity of one half of each band becomes completely suppressed, and the two remaining halves—in the limit— fit together to give the appearance of a single band.

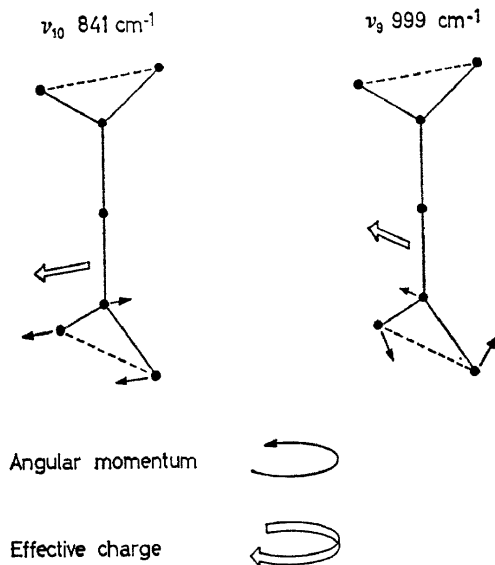


Figure 4. CH₂ wagging and rocking fundamentals in allene type molecules, showing the sign relation between angular momentum and effective charge, and hence between dipole moment derivatives in the normal coordinates

Symmetric top

Interaction due to rotation about the top axis

Once again we consider the case of interaction between two different vibrational levels, both of which are active in combination with the ground state. The only case which has been observed and analysed in detail is that of allene itself¹², which belongs to the point group D_{2d} ; in this case the CH₂ rocking and wagging fundamentals are both in the E species, and since $E \times E \supset A_2(R_z)$, they are connected by a Coriolis interaction. The effect is large since the fundamentals are not far apart, and both the ζ and the A rotational constant are large; the theory has been described in detail¹². The energy level interaction diagram is shown in Figure 5. The effect on the intensities is qualitatively very similar to the prolate asymmetric top case: allene shows a *negative* perturbation between the two bands in question, as shown in Figure 6, in accordance with the observation on allene $-1.1 - d_2$.

Interaction due to rotation about (x, y) axes

We shall consider briefly here the case of (x, y) axis interaction in a C_{3v} molecule, which we are currently studying for the CH₃F molecule. We consider interaction between the two upper states of an $A_1 \leftarrow A_1$ parallel fundamental, and an $E \leftarrow A_1$ perpendicular fundamental; since $A_1 \times E \supset E(R_x, y)$, these interact due to rotation about the x and y axes.

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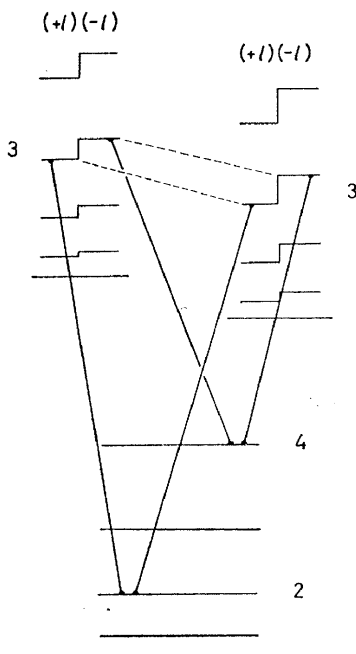


Figure 5. Energy level diagram for Coriolis interaction between two E species vibrational levels of a symmetric top molecule. Rotational levels are shown for a single value of J , and different values of K from 0 through 4

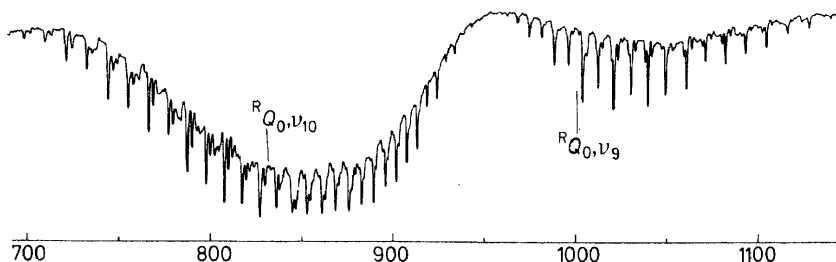


Figure 6. Spectrum of allene from 750 to 1100 cm^{-1} , with a resolving power $\sim 0.8 \text{ cm}^{-1}$, showing intensity asymmetry in the weaker band (after Mills, Smith and Duncan¹²)

By applying the general theory of Section 2 the Hamiltonian is found to factorize into (3×3) blocks, of which a typical one is:

$$\begin{array}{ccc}
 |0,1^{+1}; J,k+1\rangle & |1,0; J,k\rangle & |0,1^{-1}; J,k-1\rangle \\
 \left[\begin{array}{ccc}
 \nu_s + F(J,k+1) & +\sqrt{2B}\zeta_{r,s_1}^y \Omega_{rs}[J,k]^{\frac{1}{2}} & 0 \\
 -2A(k+1)\zeta_{s_1,s_2}^z & & \\
 & \nu_r + F(J,k) & -\sqrt{2B}\zeta_{r,s_1}^y \Omega_{rs}[J,k-1]^{\frac{1}{2}} \\
 & & \nu_s + F(J,k-1) \\
 & & +2A(k-1)\zeta_{s_1,s_2}^z
 \end{array} \right] \\
 \text{(hermitian)} & &
 \end{array} \quad (28)$$

Here $[J, k]$ denotes $[J(J + 1) - k(k + 1)]$. The corresponding interaction diagram is shown in *Figure 7*.

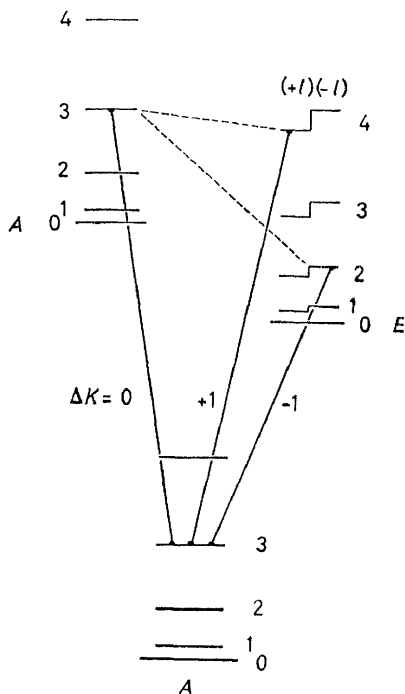


Figure 7. Energy level diagram for Coriolis interaction between an *A* and an *E* species vibration in a C_{3v} molecule, due to rotation about *x* and *y* axes. Rotation levels are shown for a single value of *J*, and different values of *K* from 0 through 4

The eigenvalues and eigenvectors of (28) cannot be expressed analytically, except in the approximation of second order perturbation theory. However Dr. di Lauro, working in my laboratory, has recently programmed for a computer the calculation of the line positions and intensities of the rotational structure of two bands interacting in this way, and has successfully reproduced the observed perturbations in the spectrum of two pairs of CH_3F fundamentals: $\nu_2(A_1)$ and $\nu_5(E)$, and $\nu_3(A_1)$ and $\nu_6(E)$. He has had similar success in explaining perturbations observed in $\nu_2(A_1)$ and $\nu_5(E)$ of CD_3Cl ²³.

Qualitatively the intensity perturbations follow the same pattern as that already described, except that in this case the perturbation increases with $[J(J + 1) - k(k + 1)]^{\frac{1}{2}}$, which is approximately equal to $(J - K)$, and is a measure of angular momentum perpendicular to the top axis. Thus in this case it is the *J* structure that is perturbed: if $\nu_r(A_1) > \nu_s(E)$, then in a *positive perturbation*, where the vibrational angular momentum and the effective charge rotate in the same sense,

$$\text{the sign of } (\xi_{r,s1}^y) (\partial\mu^z/\partial Q_r) (\partial\mu^x/\partial Q_{s1}) \quad (29)$$

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is *positive*, and the *P* branch of ν_r and the $^R R$ branches of ν_s are enhanced in intensity, and the *R* branch of ν_r and the $^P P$ branches of ν_s are depleted. For a *negative perturbation* the converse would be observed.

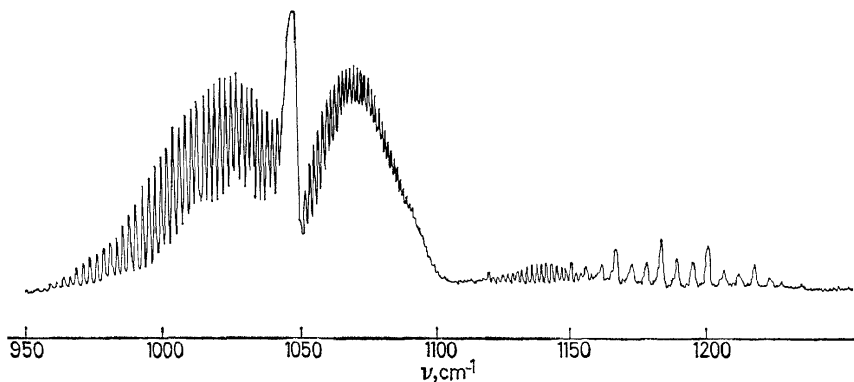


Figure 8. Spectrum of methyl fluoride from 950 to 1200 cm^{-1} , with a resolving power $\sim 0.8 \text{ cm}^{-1}$, showing the intensity asymmetry in the weak perpendicular band, evidenced by the enhancement of the $^P P$ structure

The ν_3 and ν_6 fundamentals of CH_3F are shown in Figure 8. In this case $\nu_6(E) > \nu_3(A_1)$. As usual the intensity perturbation shows best in the weaker band, ν_6 , in which it is evident that the $^P P$ branches are far more intense

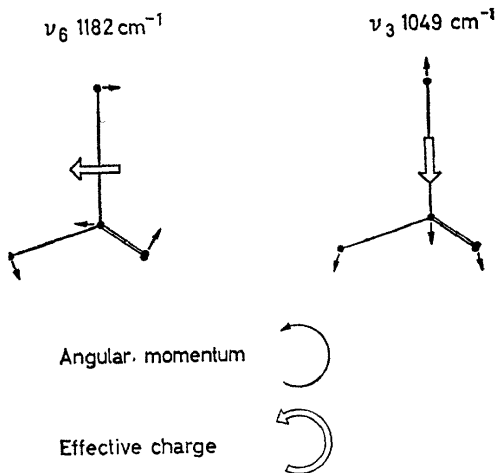


Figure 9. CH_3 rocking and CF stretching fundamentals in methyl fluoride, showing the sign relation between angular momentum and effective charge, and hence between dipole moment derivatives in the normal coordinates

than the corresponding $^R R$ branches, showing that there is a positive perturbation. The dipole moment derivatives are thus related as shown in Figure 9, which portrays approximate cartesian displacements for the two normal modes calculated from the force field of Aldous and Mills²⁴.

5. CLASSICAL MODEL

The following qualitative classical model provides a useful physical picture of the cause of the intensity asymmetry which results from Coriolis interaction between two allowed transitions, as described in the above examples.

Consider a simplified model of the CH_2 wagging and rocking perpendicular vibrations of an allene-type molecule, in which ν_1 and ν_2 represent the two vibrations, with which are associated an oscillation of effective mass and effective charge in the x and y molecular axes respectively (*Figure 10*). The heavy atoms in the molecule are disposed along the z axis.

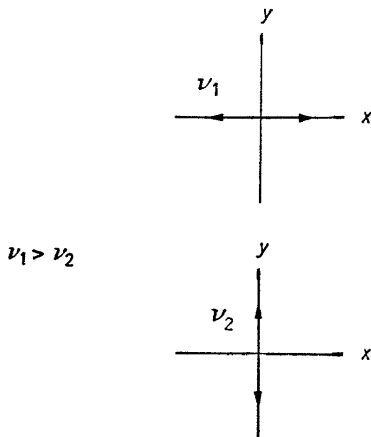


Figure 10. Diagrammatic representation of two normal vibrations, involving charge and mass oscillation in the x and y axes, in a prolate top molecule viewed along the z axis

Now consider the effect of superposing a rotation of the molecule about the z axis. The Coriolis forces set up in the two normal modes are shown by the dotted arrows in *Figure 11*. In the mode ν_1 , the Coriolis force tends to excite the mode ν_2 at the higher normal frequency of ν_1 ; similarly in ν_2 , there is a tendency to excite ν_1 at the lower frequency of ν_2 . As a result the effective mass follows an elliptical path in each normal mode; however in the higher frequency ν_1 the resulting vibrational angular momentum *opposes* the rotational angular momentum, whereas in the lower frequency ν_2 it is in the *same sense* as the rotation. This may be regarded as a consequence of the classical analysis of a forced harmonic oscillator: if the driving frequency exceeds the natural frequency, the displacement is always out of phase with the force, whereas if the driving frequency is less than the natural frequency it is in phase. The direction of motion of the effective mass around its elliptical path, referred to the molecule-fixed coordinates, is indicated on the left of *Figure 11* for each normal mode.

To predict the frequencies and the intensities of radiation absorbed one must consider the effective charge oscillation in each normal mode relative to axes fixed in space. Suppose first, that the effective charge displacements associated with the two normal coordinates satisfy the very simple model:

$$(\partial\mu^x/\partial Q_1) = (\partial\mu^y/\partial Q_2) \quad (30)$$

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Then it follows that the effective charge moves (in the molecule-fixed coordinate system) through the same elliptical path, and in the same sense, as the effective mass; in fact the ellipses of *Figure 11* may be thought of as representing exactly the effective charge movement in the two normal modes, referred to the molecular axes.

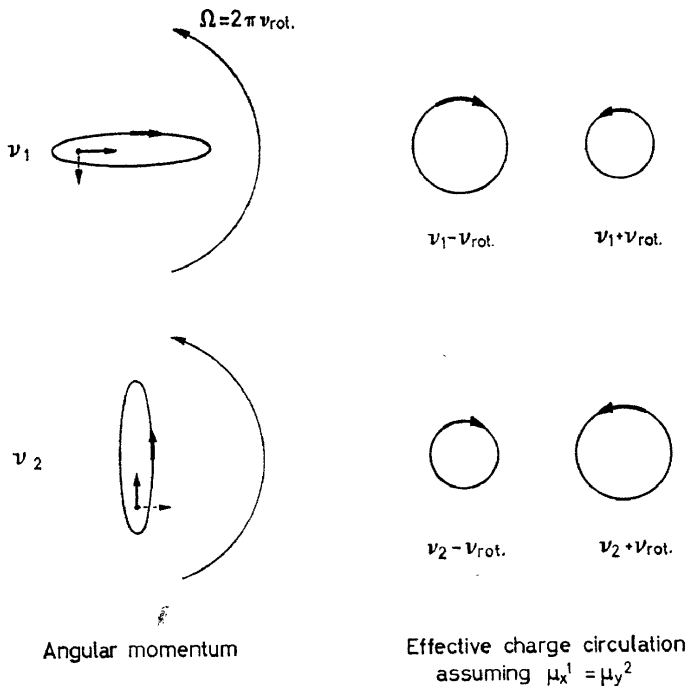


Figure 11. The effect of Coriolis forces, due to rotation about the z axis, on the model depicted in *Figure 10*

In order to refer this motion to space fixed axes this elliptically polarized motion of the effective charge is resolved into two circularly polarized motions, in opposite senses, the larger one having a radius equal to the sum of the major and minor axes of the original ellipse and the smaller one a radius equal to the difference. The effective charge rotates about the larger circle in the same sense as the original ellipse, and about the smaller circle in the opposite sense. This resolution is indicated on the right-hand side of *Figure 11*. Finally, the effect of rotating the molecular axes relative to space-fixed axes is simply to add or subtract the rotation frequency to the effective vibration frequency in the two circular motions, so that relative to space-fixed axes the effective charge rotates at $(\nu_{\text{vib.}} + \nu_{\text{rot.}})$ around one of the circles and at $(\nu_{\text{vib.}} - \nu_{\text{rot.}})$ around the other.

As the figure shows, the assumption of equation (30) leads to the prediction that the absorption at $(\nu_1 - \nu_{\text{rot.}})$ will be greater than that at $(\nu_1 + \nu_{\text{rot.}})$ in the higher frequency band, and vice-versa for ν_2 , the lower frequency band, owing to the different diameters of the two circles. This is exactly

the type of intensity asymmetry predicted quantum mechanically in the last section. Moreover it is evident that if we were to assume:

$$(\partial\mu^x/\partial Q_1) = -(\partial\mu^y/\partial Q_2) \quad (31)$$

then the effective charge would rotate around each ellipse in exactly the opposite sense to the effective mass (*i.e.*, the dipole moment would rotate in the *opposite* sense to the angular momentum), and in consequence the intensity perturbations would be reversed from those indicated in *Figure 11*. These two cases correspond exactly to the case of a *positive perturbation* [effective charge as in (30)] or a *negative perturbation* [as in (31)] as described in the quantum mechanical models of the last section.

Finally one may consider the effect of allowing the two vibrations ν_1 and ν_2 to become nearly degenerate. As the difference ($\nu_1 - \nu_2$) is decreased it is found that the corresponding elliptical motion in each of the normal coordinates of the rotating molecule tends towards a circular motion, opposing the overall rotation for the high frequency and in the same sense for the low frequency mode. When resolved into pure circular motions, referred to space fixed axes, it is found that the radius of the smaller circle (given by the difference of the major and minor axes of the ellipse) tends to zero, showing that ultimately one wing of each band loses all its intensity, leaving two half bands, as described above for the quantum mechanical model. This exact cancellation of the intensity in one wing of each band only holds when the two dipole moment derivatives are numerically equal to each other, as in the case of a symmetric top molecule where the symmetry has been reduced by a small isotopic substitution (*e.g.*, benzene with one ^{13}C atom) causing a small splitting of the doubly degenerate vibrations.

Although this classical picture adds nothing new to the exact quantum mechanical description, it gives a physical picture of the reason why these intensity perturbations occur and why the sense of the asymmetry is related to the relative signs of the dipole moment derivatives.

I should particularly like to express my thanks to all my recent coworkers at the University of Reading, whose work has been the foundation of the results presented in this paper.

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