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# STUDIES OF THE JAHN–TELLER EFFECT

## III. THE ROTATIONAL AND VIBRATIONAL SPECTRA OF SYMMETRIC-TOP MOLECULES IN ELECTRONICALLY DEGENERATE STATES

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CONTENTS

We have developed the physical theory required for interpreting the infra-red, Raman and microwave spectra of molecules in orbitally degenerate electronic states in which spin-orbit coupling is unimportant. Formulae are obtained which relate the oscillator strengths and scattering cross-sections to the electrical and mechanical properties of the molecule, and group-theoretical selection rules are derived and applied to the common point groups.

Among other results we find:

(*a*) that in an electronically degenerate state a molecule may exhibit a dipole moment which would be symmetry-forbidden if the electronic state were non-degenerate,

(*b*) that certain lines in the Raman spectrum may have depolarization ratio greater than $\frac{6}{7}$, because of the possibility of pseudo-vector scattering, and

(*c*) that in both the infra-red and Raman spectra a Jahn–Teller active vibration may give rise to overtones of extremely high intensity but irregular spacing.

## 1. Introduction

The selection rules which govern the appearance of optical transitions at microwave and infra-red frequencies are well known for molecules in electronically non-degenerate states, and the same is true of the Raman spectra of such molecules. Furthermore, the intensities of these transitions are related in a known manner to the dipole moment and polarizability tensor regarded as functions of the vibrational normal co-ordinates. For molecules in electronically degenerate states, however, the theory is far from complete, though Thorson (1958) has discussed the infra-red spectra of tetrahedral and octahedral molecules in degenerate electronic states. There is thus a gap which must be filled before one can use observed rotational and vibrational spectra to obtain detailed information about the electrical and mechanical properties of molecules exhibiting the Jahn–Teller effect, and it is the purpose of the present paper to fill this gap.

Section 2 summarizes what is known about the lower vibronic levels of a doubly degenerate electronic state; a convenient example is the hypothetical molecule $X_3$, of symmetry $D_{3h}$, in an $E'$ state. Appropriate quantum numbers are introduced for the weak and strong coupling cases and also certain primitive matrix elements which are needed for the discussion of spectral intensities. Sections 3 to 5 are concerned respectively with the microwave, infra-red and Raman spectra of Jahn–Teller degenerate molecules; in the course of these sections attention is also given to the Zeeman and Stark effects, and to the intensity of Rayleigh scattering.

Section 6 summarizes the results, and discusses their application to molecules in which spin-orbit coupling is unimportant. In the appendix are tabulated values of the primitive matrix elements needed for the calculation of spectral intensities in the first-order coupling case.

## 2. Vibronic levels of a doubly degenerate electronic state

Let us consider a hypothetical $X_3$ molecule of symmetry $D_{3h}$ in an electronic state of species $E'$. Then as shown by Jahn & Teller (1937) there will be at least one mode of vibration which resolves the electronic degeneracy, the resolved electronic wave functions

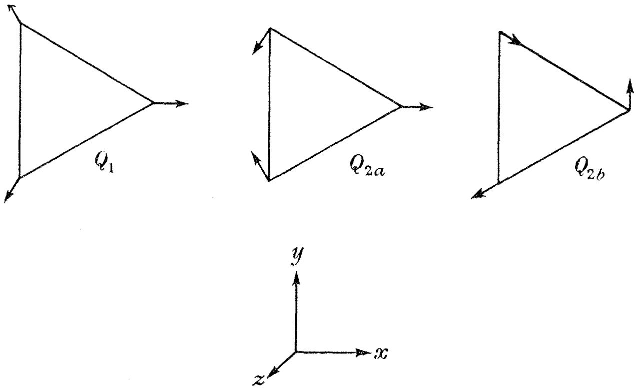

Figure 1. The vibrational symmetry co-ordinates of the $D_{3h}$ molecule $X_3$.

being, say, $\langle Q; q|e_a\rangle$ and $\langle Q; q|e_b\rangle$, where $Q$ denotes the vibrational symmetry co-ordinates and $q$ the electronic co-ordinates. For $X_3$ there are in fact three vibrational symmetry co-ordinates, depicted in figure 1. $Q_1$ is totally symmetric (of species $A_1'$); the degenerate co-ordinates $Q_{2a}$ and $Q_{2b}$ (of species $E'$) are those which resolve the electronic degeneracy.

It has been shown by several authors (Renner 1934; Sponer & Teller 1941; Moffitt & Liehr 1957; Moffitt & Thorson 1958; Longuet-Higgins, Öpik, Pryce & Sack 1958—we shall refer to this last paper as II) that in a situation of this sort a good approximation to the vibronic wave function is

$$\langle Q, q|n, e\rangle = \langle Q|n_a\rangle\langle Q;\, q|e_a\rangle + \langle Q|n_b\rangle\langle Q;\, q|e_b\rangle, \tag{2·1}$$

where the functions $\langle Q|n_a\rangle$ and $\langle Q|n_b\rangle$ are to be thought of as the first and second member of a two-component vibrational wave function.

Figure 2 shows schematically the forms assumed by the electronic states $|e_a\rangle$ and $|e_b\rangle$ when $Q_{2a}$ is positive and $Q_{2b}$ vanishes.

It will be noted that $|e_a\rangle$ is symmetric, and $|e_b\rangle$ antisymmetric, about the $xz$ plane; when it is necessary to make an assumption about their relative energies we shall assume that $|e_a\rangle$ has the lower electronic energy, but this is purely arbitrary and the alternative assumption could be made without affecting our analysis in any essential way.

An alternative and much more convenient form for the vibronic wave function is (Hobey & McLachlan 1960)

$$\langle Q,q|n,e\rangle = \langle Q|n_+\rangle\langle Q;\, q|e_+\rangle + \langle Q|n_-\rangle\langle Q;\, q|e_-\rangle, \tag{2·2}$$

where $|e_+\rangle$ and $|e_-\rangle$ are not themselves solutions of the electronic wave equation, but are, for any nuclear configuration, orthogonal combinations of $|e_a\rangle$ and $|e_b\rangle$ such that

$$\langle e_+|\,\partial/\partial Q\,|e_-\rangle = 0.$$

For $X_3$ we choose $|e_+\rangle$ and $|e_-\rangle$ to be such that for $Q_{2a}$ positive, and $Q_{2b} = 0$,

$$|e_+\rangle = \surd\tfrac{1}{2}(|e_a\rangle + \mathrm{i}|e_b\rangle), \quad |e_-\rangle = \surd\tfrac{1}{2}(|e_a\rangle - \mathrm{i}|e_b\rangle). \tag{2·3}$$

The form (2·2) has the advantage over (2·1) that the vibrational wave equation is then relatively simple; if $H$ is the electronic Hamiltonian and $T$ the nuclear kinetic energy, then $|n_+\rangle$ and $|n_-\rangle$ are determined by the coupled differential equations

$$\begin{bmatrix} \langle e_+|H|e_+\rangle + T - E & \langle e_+|H|e_-\rangle \\ \langle e_-|H|e_+\rangle & \langle e_-|H|e_-\rangle + T - E \end{bmatrix} \begin{bmatrix} |n_+\rangle \\ |n_-\rangle \end{bmatrix} = 0, \tag{2·4}$$

$E$ being the total vibronic energy. The electronic matrix elements will depend, of course, on the vibrational configuration $Q$, since $H$, $|e_+\rangle$ and $|e_-\rangle$ depend upon $Q$ parametrically.

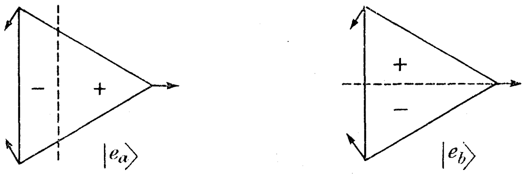

FIGURE 2. The real components of the electronic state for positive $Q_{2a}$ and vanishing $Q_{2b}$.

To obtain solutions of (2·4) one expands the $\langle e_\pm|H|e_\pm\rangle$ in powers of the $Q$, up to terms of the second order. A clockwise rotation $C_3$ of the vibronic state through $\frac{2}{3}\pi$ about the $z$ axis induces the following transformations in $|e_+\rangle$ and $|e_-\rangle$

$$C_3|e_+\rangle = \omega|e_+\rangle, \quad C_3|e_-\rangle = \omega^{-1}|e_-\rangle, \quad \omega = \mathrm{e}^{\frac{2}{3}\pi \mathrm{i}}. \tag{2·5}$$

If we replace $Q_{2a}$ and $Q_{2b}$ by the complex combinations

$$Q_\pm = Q_{2a} \pm \mathrm{i}Q_{2b}, \tag{2·6}$$

then these will be found to transform according to

$$C_3\, Q_+ = \omega^2 Q_+, \quad C_3\, Q_- = \omega^{-2} Q_-. \tag{2·7}$$

Using the fact that the co-ordinate $Q_1$ and the Hamiltonian $H$ are totally symmetric, and that $\omega^3 = 1$, we conclude that the second-order expansion of (2·4) must be

$$\begin{bmatrix} W_0 + \frac{1}{2}\omega_1^2 Q_1^2 + \frac{1}{2}\omega_2^2 Q_+ Q_- + T - E & fQ_- + f_1 Q_1 Q_- + gQ_+^2 \\ fQ_+ + f_1 Q_1 Q_+ + gQ_-^2 & W_0 + \frac{1}{2}\omega_1^2 Q_1^2 + \frac{1}{2}\omega_2^2 Q_+ Q_- + T - E \end{bmatrix} \begin{bmatrix} |n_+\rangle \\ |n_-\rangle \end{bmatrix} = 0, \tag{2·8}$$

where the origin of $Q_1$ has been chosen to eliminate terms linear in $Q_1$ from $\langle e_+|H|e_+\rangle$ and $\langle e_-|H|e_-\rangle$ (these matrix elements must be equal by the definition of $|e_+\rangle$ and $|e_-\rangle$).

If the off-diagonal terms in $Q_1$ are neglected, equation (2·8) may be factorized by the substitutions

$$\langle Q|n_+\rangle = \langle Q_1|v_1\rangle\langle Q_2|n_{2+}\rangle, \quad \langle Q|n_-\rangle = \langle Q_1|v_1\rangle\langle Q_2|n_{2-}\rangle \tag{2·9}$$

into the pair of equations

$$(\tfrac{1}{2}\omega_1^2 Q_1^2 + T_1 - E_1)\,|v_1\rangle = 0, \quad T_1 = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_1^2}, \tag{2·10}$$

$$\begin{bmatrix} \tfrac{1}{2}\omega_2^2 Q_+ Q_- + T_2 - E_2 & fQ_- + gQ_+^2 \\ fQ_+ + gQ_-^2 & \tfrac{1}{2}\omega_2^2 Q_+ Q_- + T_2 - E_2 \end{bmatrix} \begin{bmatrix} |n_{2+}\rangle \\ |n_{2-}\rangle \end{bmatrix} = 0, \quad T_2 = -\frac{\hbar^2}{2}\left(\frac{\partial^2}{\partial Q_{2a}^2} + \frac{\partial^2}{\partial Q_{2b}^2}\right), \tag{2·11}$$

where

$$E = W_0 + E_1 + E_2. \tag{2·12}$$

(Note that we are employing mass-adjusted vibrational symmetry co-ordinates, so that the nuclear masses do not appear explicitly in the kinetic energy.) Equation (2·10) is the simple harmonic oscillator equation, so that

$$E_1 = (v_1 + \tfrac{1}{2})\,\hbar\omega_1, \tag{2·13}$$

but (2·11) is less easy to solve, because of the first- and second-order coupling terms $fQ_\mp$ and $gQ_\pm^2$. The case $g = 0$ (first-order coupling only) has, however, been studied in some detail (see II), and it will be helpful if we outline the results which have already been obtained, and translate them into a notation which is especially convenient for the purpose in hand.

If not only $g$ but also $f$ were zero, the vibronic levels arising from (2·11) would form the pattern depicted in figure 3 where $|n_{2-}\rangle$ vanishes for the levels labelled + and $|n_{2+}\rangle$ vanishes for the − levels; the non-vanishing component would be one of the states $|v_2, l\rangle$‡ of the isotropic 2-dimensional harmonic oscillator, with

$$l = v_2, v_2 - 2, \ldots, -v_2, \quad E = (v_2 + 1)\,\hbar\omega_2. \tag{2·14}$$

Now the only non-zero matrix elements of the type $\langle v', l'|\,Q_-\,|v'', l''\rangle$ are those for which $v' = v'' \pm 1$, $l' = l'' - 1$, and the only non-vanishing elements of the type $\langle v', l'|\,Q_+\,|v'', l''\rangle$ are those for which $v' = v'' \pm 1$, $l' = l'' + 1$. It follows that the coupling terms $fQ_\pm$ in (2·11) have the effect of mixing together the levels connected by dashed lines in figure 3. If we define a quantum number $j$§ as being equal to $l - \tfrac{1}{2}$ for the (+) levels and $l + \tfrac{1}{2}$ for the (−) levels, then first-order coupling only mixes levels with the same value of $j$, so that $j$ remains a good quantum number so long as second-order coupling is unimportant. The values of $j$ for the

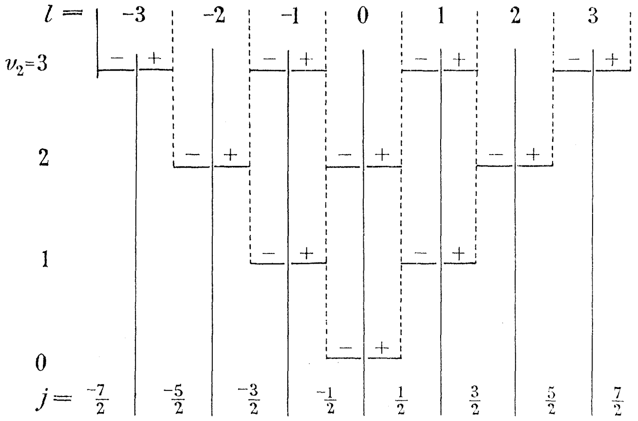

FIGURE 3. The vibronic levels of $X_3$ when there is no electronic-vibrational coupling.

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‡ In II $v_2 + 1$ was called $n$, and $l$ was referred to as $m$.

§ The quantum number $j$ was unfortunately called $l$ in II, and $\tfrac{1}{2}\bar{\Lambda}$ in the papers of Moffitt *et al.*

levels in figure 3 are shown at the foot of the diagram; it is clear that $j$ can only have the half-odd values $j = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots$, with the restriction $|j| < v_2+1$. The identity of any level is established by specifying the values of $v_2$ and $j$ only; we may therefore, in weak coupling, replace the symbols $|n_{2\pm}\rangle$ by the more explicit designations $|v_2, j_\pm\rangle$.

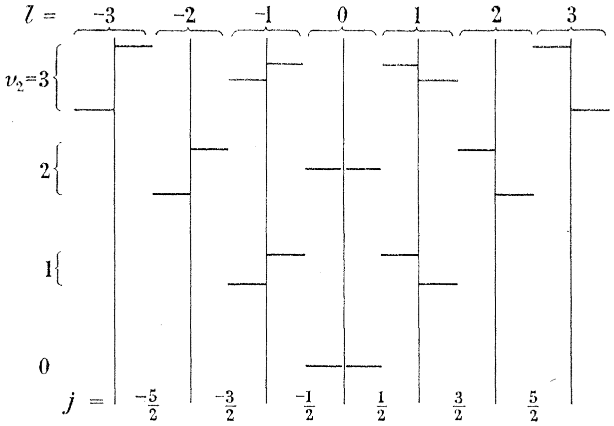

FIGURE 4. The vibronic levels of $X_3$ in weak first-order coupling ($D = 0{\cdot}125$).

The effect of the coupling terms $fQ_\pm$ on the energies of the levels is indicated in figure 4. A convenient measure of the strength of the first-order coupling is Moffitt & Thorson's parameter‡

$$D = f^2/2\hbar\omega_2^3, \tag{2·15}$$

which is the depth of the displaced potential minimum in units of $\hbar\omega_2$. In figure 4 the energies plotted are those which were calculated for $D = 0{\cdot}125$, a relatively small value. It is clear that the energy is mainly determined by the principal quantum number $v_2$ of the degenerate vibration, though the spacing of the levels is decidedly irregular (see II). Also, one may still usefully define an $l$ value for the state $|v_2, j\rangle$; this value is $j+\frac{1}{2}$ or $j-\frac{1}{2}$ according to which of these two numbers has the same parity as $v_2$.

Of particular importance is the manner in which the vibrational wave functions depend on the phase angle $\phi$ of the degenerate vibration, defined by

$$r\,\mathrm{e}^{\pm \mathrm{i}\phi} = Q_\pm = Q_{2a} \pm \mathrm{i}Q_{2b}. \tag{2·16}$$

Since $|v_2, j_+\rangle$ is a combination of vibrational states with $l = j-\frac{1}{2}$, and $|v_2, j_-\rangle$ is a combination of vibrational states with $l = j+\frac{1}{2}$,

$$\langle r, \phi | v_2, j_+\rangle = \rho_+(r)\,\mathrm{e}^{\mathrm{i}(j-\frac{1}{2})\phi}, \quad \langle r, \phi | v_2, j_-\rangle = \rho_-(r)\,\mathrm{e}^{\mathrm{i}(j+\frac{1}{2})\phi}, \tag{2·17}$$

in the notation of II. $|v_2, j_+\rangle$ and $|v_2, j_-\rangle$ thus transform like $Q_+^{j-\frac{1}{2}}$ and $Q_+^{j+\frac{1}{2}}$, respectively, so that

$$C_3\,|v_2, j_+\rangle = \omega^{2j-1}\,|v_2, j_+\rangle \quad C_3\,|v_2, j_-\rangle = \omega^{2j+1}\,|v_2, j_-\rangle. \tag{2·18}$$

The complete vibronic wave function

$$|v_1, v_2, j\rangle = |v_1\rangle\,(|v_2, j_+\rangle\,|e_+\rangle + |v_2, j_-\rangle\,|e_-\rangle) \tag{2·19}$$

therefore transforms according to the rule

$$C_3\,|v_1, v_2, j\rangle = \omega^{2j}\,|v_1, v_2, j\rangle. \tag{2·20}$$

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‡ The parameter $D$ is one half of the quantity called $k^2$ in II.

Thus for $2j$ a multiple of 3 we obtain $A'$ levels, and for other values of $2j$ the vibronic species is $E'$, The further classification of the $A'$ levels we shall leave till we have considered second-order coupling.

For weak first-order coupling, then, the vibronic levels may be adequately characterized by three quantum numbers $v_1, v_2, j$. The first determines the energy in the totally symmetric mode, the second largely determines the energy in the degenerate mode, and the third, which is half-odd, determines the transformation properties of the vibronic wave function.

When there is strong coupling, $v_1$ remains a good quantum number but $v_2$ loses its determining influence on the energy. Provided, however, that second-order coupling can still be neglected $j$ remains a good quantum number; this is its particular usefulness. It turns out that when $D \gg 1$ (equation 2·15) the vibronic levels at the bottom of the potential energy 'moat' have energies given approximately by the formula (see II)

$$E_2(u_2,j) = -D\hbar\omega_2 + (u_2+\tfrac{1}{2})\,\hbar\omega_2 + j^2/2r_0^2, \tag{2·21}$$

where $-D\hbar\omega_2$ is the depth of the moat, $r_0 = \surd(2\hbar D/\omega_2)$ is its radius, and $u_2$ is a new quantum number having the values 0, 1, 2, ... independently of $j$. (The level $|u_2,j\rangle$ actually arises from the level $|v_2,j\rangle$ where $v_2 = u_2+|j|-\frac{1}{2}$.) It turns out that if the vibronic level $|v_1,u_2,j\rangle$ is expressed in the form

$$|v_1,u_2,j\rangle = |v_1\rangle\,(|u_2,j_a\rangle\,|e_a\rangle + |u_2,j_b\rangle\,|e_b\rangle),$$

then if $|e_a\rangle$ is the electronic state of lower energy for given $Q$, the component $|u_2,j_b\rangle$ is small. The wave function of the other component is, to a fair approximation,

$$\langle r,\phi|u_2,j_a\rangle = u(r)\,\mathrm{e}^{\mathrm{i}j\phi}, \tag{2·22}$$

where $u(r)$ is $r^{-\frac{1}{2}}$ times a one-dimensional harmonic oscillator function of $(r-r_0)$, with energy $(u_2+\frac{1}{2})\,\hbar\omega_2$. One may indeed think of the molecule undergoing radial oscillations about $r = r_0$, and at the same time executing a cyclic motion in the phase co-ordinate $\phi$. Setting

$$|u_2,j_a\rangle\,|e_a\rangle \equiv |u_2,j_+\rangle\,|e_+\rangle + |u_2,j_-\rangle\,|e_-\rangle, \tag{2·23}$$

we find that the complex components of the vibrational wave function are now related by the approximations

$$|u_2,j_+\rangle \simeq \surd\tfrac{1}{2}\,\mathrm{e}^{-\frac{1}{2}\mathrm{i}\phi}|u_2,j_a\rangle, \quad |u_2,j_-\rangle \simeq \surd\tfrac{1}{2}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\phi}|u_2,j_a\rangle. \tag{2·24}$$

Figure 5 illustrates the disposition of the low-lying levels in strong first-order coupling; the energies are taken from the tables given in II for $D = 10$ ($k^2 = 20$). It will be observed how

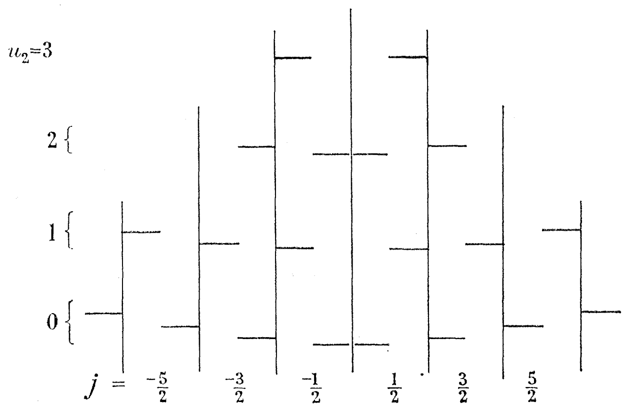

FIGURE 5. The vibronic levels of $X_3$ in very strong first-order coupling ($D = 10$)

much more nearly the energy is determined by the value of $u_2$ than of $v_2$ ($= u_2 + |j| - \frac{1}{2}$). In reality, of course, such strong first-order coupling would inevitably be accompanied by strong second-order coupling; thus the potential energy moat for $X_3$ would not really be equally deep all round, but would have a depth depending on the phase angle $\phi$: there would be three absolute minima in the potential energy surface, separated by saddle points over which the molecule would have to pass to get from one to the next. In second order the $\phi$-dependence of the electronic potential energy is determined by the coupling constant $g$, whose sign we will suppose to be such as to yield an absolute minimum for some positive rather than negative value of the co-ordinate $Q_{2a}$. The effect of the perturbation $gQ^2_{\pm}$ on the first-order vibronic energy levels of $X_3$ is actually to mix levels differing in their $j$ values by multiples of 3. Thus the levels with $j = \frac{3}{2}$ get mixed with the levels for which $j = -\frac{3}{2}$ and $j$ ceases to be a good quantum number. The absolute value of $j$ remains, however, a fairly good quantum number provided $g$ is not too large, and in figure 6 we see how the levels may be expected to split under the influence of weak second-order coupling. The energies in figure 6 have actually been guessed rather than calculated, as there is little point in inserting special values for the parameters; but there can be no doubt that the splitting of the $|j| = \frac{3}{2}$ levels will be more important than that of the others, at least to begin with. Of particular significance for the present discussion is the splitting of the levels with $v_2 = 1$ into three sublevels, of species $A'_1$, $A'_2$ and $E'$; as we shall see, this splitting may be directly observable in the vibrational spectra.

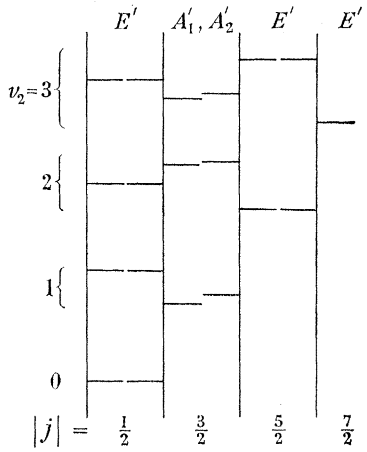

FIGURE 6. The vibronic levels of $X_3$ in weak first- and second-order coupling.

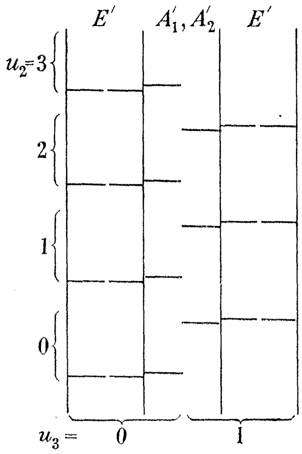

FIGURE 7. The vibronic levels of $X_3$ in strong first- and second-order coupling.

When the first- and second-order coupling constants are both large, three deep wells appear in the potential energy surface, and the molecular symmetry is effectively reduced from $D_{3h}$ to $C_{2v}$. There will, however, be a finite probability of tunnelling from one well to another, and if this is taken into account one may still classify the vibronic levels according to their species in $D_{3h}$. The vibronic energy level diagram then assumes the form shown in figure 7. Here the new quantum number $u_3$ has replaced $|j|$; it represents the number of vibrational quanta in the normal mode which is antisymmetric with respect to the $xz$ plane in the distorted molecule, and whose excitation enables the molecule to tunnel from one minimum to the next.

The levels have been arranged in figure 7 so as to exhibit their correlation with the levels of figure 6. The energy is once again given by a relatively simple approximate formula, namely

$$E_2 = \text{const.} + (u_2 + \tfrac{1}{2})\,\hbar\omega_2 + (u_3 + \tfrac{1}{2})\,\hbar\omega_3, \tag{2·25}$$

but there are slight departures from this formula owing to the finite tunnelling probability.

Having described the arrangement of the lowest energy levels in the various coupling cases (we shall not here be concerned with the upper levels, which are much more difficult to deal with) we now turn to the calculation of various matrix elements which will later appear in expressions for the intensities of rotational and vibrational transitions. These are all of the general form

$$[\langle n'_+|, \langle n'_-|]\begin{bmatrix}\langle e_+|A|e_+\rangle & \langle e_+|A|e_-\rangle \\ \langle e_-|A|e_+\rangle & \langle e_-|A|e_-\rangle\end{bmatrix}\begin{bmatrix}|n''_+\rangle \\ |n''_-\rangle\end{bmatrix}, \tag{2·26}$$

where $A$ is an operator involving the electronic co-ordinates, but depending on the vibrational co-ordinates $Q$ parametrically (the electronic Hamiltonian is itself such an operator). Expansion of the matrix $\langle e_\pm|A|e_\pm\rangle$ to the first order in the normal co-ordinates reduces the problem to that of evaluating the following types of expression

$$a = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}Q_- & 0 \\ 0 & Q_-\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix}, \quad a^* = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}Q_+ & 0 \\ 0 & Q_+\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix},$$

$$b = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}0 & Q_- \\ Q_+ & 0\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix},$$

$$c = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}0 & 0 \\ Q_- & 0\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix}, \quad c^* = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}0 & Q_+ \\ 0 & 0\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix},$$

$$d = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}1 & 0 \\ 0 & -1\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix},$$

$$e = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}0 & 0 \\ 1 & 0\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix}, \quad e^* = [\langle n'_{2+}|, \langle n'_{2-}|]\begin{bmatrix}0 & 1 \\ 0 & 0\end{bmatrix}\begin{bmatrix}|n''_{2+}\rangle \\ |n''_{2-}\rangle\end{bmatrix}.$$

In first-order coupling each of these 'primitive' elements may be evaluated for given $D$ (the first-order distortion parameter) by simply expanding the vibrational components $[|n_{2+}\rangle, |n_{2-}\rangle]$ of the initial and final states in terms of the 2-dimensional harmonic oscillator states $|v_2, l\rangle$ and making use of the standard formulae

$$\left.\begin{aligned}\langle v_2, l|\,Q_-\,|v_2+1, l+1\rangle &= \langle v_2+1, l+1|\,Q_+\,|v_2, l\rangle = \surd\{(v_2+l+2)\,\hbar/2\omega_2\},\\ \langle v_2, l|\,Q_-\,|v_2-1, l+1\rangle &= \langle v_2-1, l+1|\,Q_+\,|v_2, l\rangle = \surd\{(v_2-l)\,\hbar/2\omega_2\},\end{aligned}\right\} \tag{2·27}$$

all other elements $\langle v'_2, l'|\,Q_\pm\,|v''_2, l''\rangle$ being zero. The secular equations determining the expansion coefficients (and the vibronic energy) were derived in II and solved for a series of values of the first-order distortion parameter $D$; the reader is referred to that paper for the details of the method. At this juncture we merely draw attention to the conditions which the quantum numbers of the initial and final states must satisfy for each type of matrix element not to vanish, and consider separately the cases of weak and strong first-order coupling. When discussing the case of strong first-order coupling we shall limit ourselves to the lowest levels, for which the radial wave function is of the form (2·22); our 'selection rules' break down if $|e_b\rangle$ makes a large contribution to the upper state.

(*a*) The primitive element

$$a = \langle n'_{2+} |\, Q_- \,| n''_{2+} \rangle + \langle n'_{2-} |\, Q_- \,| n''_{2-} \rangle \tag{2·28}$$

vanishes exactly unless $j' = j'' - 1$. In weak coupling, furthermore,

*either* $\qquad |n''_{2+}\rangle \simeq |v''_2, l''\rangle, \quad |n''_{2-}\rangle \simeq 0, \quad l'' = j'' - \tfrac{1}{2},$

*or* $\qquad |n''_{2-}\rangle \simeq |v''_2, l''\rangle, \quad |n''_{2+}\rangle \simeq 0, \quad l'' = j'' + \tfrac{1}{2}.$

In the former case, if $a$ is not to vanish, we must have

$$0 \neq \langle n'_{2+}| \simeq \langle v'_2, l'|, \quad l' = j' - \tfrac{1}{2},$$

and in the latter case $0 \neq \langle n'_{2-}| \simeq \langle v'_2, l'|$, $l' = j' + \tfrac{1}{2}$. In either case we must have $v'_2 = v''_2 \pm 1$, so that $l' = l'' - 1$ (as can be seen most easily by inspection of figure 3). For weak coupling, therefore, and $v'_2 = v''_2 + 1$ we obtain

$$a = \langle v''_2 + 1, l'' - 1 |\, Q_- \,| v''_2, l'' \rangle = \surd\{(v''_2 - l'' + 2)\, \hbar/2\omega_2\}. \tag{2·29}$$

In strong coupling we have, by (2·24)

$$\begin{aligned} a &= \langle u'_2, j'_+ |\, Q_- \,| u''_2, j''_+ \rangle + \langle u'_2, j'_- |\, Q_- \,| u''_2, j''_- \rangle \\ &= \tfrac{1}{2}\langle u'_2, j'_a|\, \mathrm{e}^{\frac{1}{2}\mathrm{i}\phi}\, r\, \mathrm{e}^{-\mathrm{i}\phi}\, \mathrm{e}^{-\frac{1}{2}\mathrm{i}\phi} \,| u''_2, j''_a \rangle + \tfrac{1}{2}\langle u'_2, j'_a|\, \mathrm{e}^{-\frac{1}{2}\mathrm{i}\phi}\, r\, \mathrm{e}^{-\mathrm{i}\phi}\, \mathrm{e}^{\frac{1}{2}\mathrm{i}\phi} \,| u''_2, j''_a \rangle \\ &= \langle u'_2 |\, r \,| u''_2 \rangle, \end{aligned}$$

since $j' = j'' - 1$. Bearing in mind that

$$\langle r | u'_2 \rangle = r^{-\frac{1}{2}} w'(r - r_0),$$

where $w'$ is a harmonic oscillator function of $r - r_0$ with $r_0 = \surd(2\hbar D/\omega_2)$, we obtain

$$\begin{aligned} \langle u'_2 |\, r \,| u''_2 \rangle &= \int r^{-\frac{1}{2}} w'(r - r_0)\, r r^{-\frac{1}{2}} w''(r - r_0)\, r\, \mathrm{d}r \\ &= \int w'(s)\, (s + r_0)\, w''(s)\, \mathrm{d}s \\ &= r_0\, \delta(u'_2, u''_2) + \int w'(s)\, s w''(s)\, \mathrm{d}s. \end{aligned}$$

Thus for $u'_2 = u''_2$

$$a = r_0 = \surd(2\hbar D/\omega_2), \tag{2·30}$$

and for $u'_2 = u''_2 + 1$,

$$a = \surd\{(u''_2 + 1)\, \hbar/2\omega_2\}. \tag{2·31}$$

(*b*) The primitive element

$$b = \langle n'_{2+} |\, Q_- \,| n''_{2-} \rangle + \langle n'_{2-} |\, Q_+ \,| n''_{2+} \rangle$$

vanishes unless $j' = j''$, because $\langle r, \phi | n_{2+} \rangle$ and $\langle r, \phi | n_{2-} \rangle$ vary as $\mathrm{e}^{\mathrm{i}(j-\frac{1}{2})\phi}$ and $\mathrm{e}^{\mathrm{i}(j+\frac{1}{2})\phi}$, respectively. In the weak coupling case we again have $v'_2 = v''_2 \pm 1$, so that $l' = l'' + 1$ or $l' = l'' - 1$ (see figure 3). For excitation, $v'_2 = v''_2 + 1$; thus when $l' = l'' + 1$

$$b = \langle v''_2 + 1, l'' + 1 |\, Q_+ \,| v''_2, l'' \rangle = \surd\{(v''_2 + l'' + 2)\, \hbar/2\omega_2\}, \tag{2·32}$$

and when $l' = l'' - 1$

$$b = \langle v''_2 + 1, l'' - 1 |\, Q_- \,| v''_2, l'' \rangle = \surd\{(v''_2 - l'' + 2)\, \hbar/2\omega_2\}. \tag{2·33}$$

In strong coupling $b = \langle u_2', j_+' | \, Q_- \, | u_2'', j_-'' \rangle + \langle u_2', j_-' | \, Q_+ \, | u_2'', j_+'' \rangle$

$= \langle u_2' | \, r \, | u_2'' \rangle$ provided that $j' = j''$.

Hence for $u_2' = u_2''$, just as above, $$b = \surd(2\hbar D/\omega_2) \tag{2·34}$$

and for $u_2' = u_2''+1$, $$b = \surd\{(u_2''+1)\,\hbar/2\omega_2\}. \tag{2·35}$$

(*c*) Denoting $\langle n_{2-}' | \, Q_- \, | n_{2+}'' \rangle$ by $c$, and using the $\phi$-dependence of $\langle r, \phi | n_{2+} \rangle$ and $\langle r, \phi | n_{2-} \rangle$, we deduce that $c$ vanishes in first-order coupling unless

$$j' = j'' - 2.$$

In weak coupling $c$ is zero unless $v_2' = v_2'' \pm 1$; taking $v_2' = v_2''+1$ we obtain

$$c = \langle v_2''+1, \, l''-1 | \, Q_- \, | v_2'', \, l'' \rangle = \surd\{(v_2''+l''+2)\,\hbar/2\omega_2\}. \tag{2·36}$$

In strong coupling we have, for $j' = j''+2$,

$$c = \langle u_2', j_-' | Q_- \, | u_2'', j_+'' \rangle = \tfrac{1}{2} \langle u_2' | \, r \, | u_2'' \rangle.$$

Therefore $c$ vanishes unless $u_2' = u_2''$ or $u_2' = u_2'' \pm 1$; for $u_2' = u_2''$

$$c = \surd(\hbar D/2\omega_2), \tag{2·37}$$

and for $u_2' = u_2''+1$ $$c = \surd\{(u_2''+1)\,\hbar/8\omega_2\}. \tag{2·38}$$

(*d*) The primitive element $\langle n_{2+}' | n_{2+}'' \rangle - \langle n_{2-}' | n_{2-}'' \rangle$, which we denote by $d$, vanishes unless $j' = j''$.

In weak coupling we have the additional restriction $v_2' = v_2''$. If $j'' - \tfrac{1}{2}$ has the same parity as $v_2''$, the second term vanishes, and if $j'' + \tfrac{1}{2}$ has the same parity as $v_2''$ the first term vanishes. In the former case

$$d = \langle v_2'', \, l'' | v_2'', \, l'' \rangle = 1, \tag{2·39}$$

and in the latter case $$d = -\langle v_2'', \, l'' | v_2'', \, l'' \rangle = -1. \tag{2·40}$$

In strong first-order coupling we obtain

$$\begin{aligned} d &= \tfrac{1}{2} \langle u_2', j_a' | \mathrm{e}^{\frac{1}{2}\mathrm{i}\phi} \, \mathrm{e}^{-\frac{1}{2}\mathrm{i}\phi} | u_2'', j_a'' \rangle - \tfrac{1}{2} \langle u_2', j_a' | \mathrm{e}^{-\frac{1}{2}\mathrm{i}\phi} \, \mathrm{e}^{\frac{1}{2}\mathrm{i}\phi} | u_2'', j_a'' \rangle \\ &= 0, \end{aligned} \tag{2·41}$$

whatever the relative values of $u_2'$ and $u_2''$.

(*e*) Finally, we consider $\langle n_{2-}' | n_{2+}'' \rangle = e$, say. This is clearly zero unless $j' + \tfrac{1}{2} = j'' - \tfrac{1}{2}$, i.e. $j' = j'' - 1$.

In weak coupling we require, furthermore, $v_2' = v_2''$; if this condition is also satisfied, then

$$e = 1. \tag{2·42}$$

In strong coupling, on the other hand,

$$e = \langle u_2', j_-' | u_2'', j_+'' \rangle = \tfrac{1}{2} \langle u_2' | u_2'' \rangle.$$

Here again, therefore, $e$ vanishes unless $u_2' = u_2''$, when its value is

$$e = \tfrac{1}{2}. \tag{2·43}$$

The elements $a^*$, $c^*$ and $e^*$ show exactly the same limiting behaviour as $a$, $c$ and $e$, but they are subject to different selection rules on $j$. These rules are summarized below.

$$\begin{array}{ll} a\colon\ \Delta j = -1, & a^*\colon\ \Delta j = +1; \\ b\colon\ \Delta j = 0; & \\ c\colon\ \Delta j = -1, & c^*\colon\ \Delta j = +2; \\ d\colon\ \Delta j = 0; & \\ e\colon\ \Delta j = -1, & e^*\colon\ \Delta j = +1. \end{array}$$

Figure 8 indicates graphically which levels are connected to the state $|0, \frac{1}{2}\rangle$ by the various types of primitive elements, in the limits of (i) very weak or (ii) very strong first-order coupling. Matrix elements which are non-zero in both limits may be expected to be appreciable in the intermediate region also; the diagonal matrix element $d$, which is unity in weak coupling and zero in very strong coupling, will clearly have intermediate values in the intermediate coupling range. Inspection of the limiting formulae for the primitive elements $a$ and $b$ suggests that they may have identical values for related transitions, and this is indeed the case. The symmetry of figure 4 is connected with the fact that

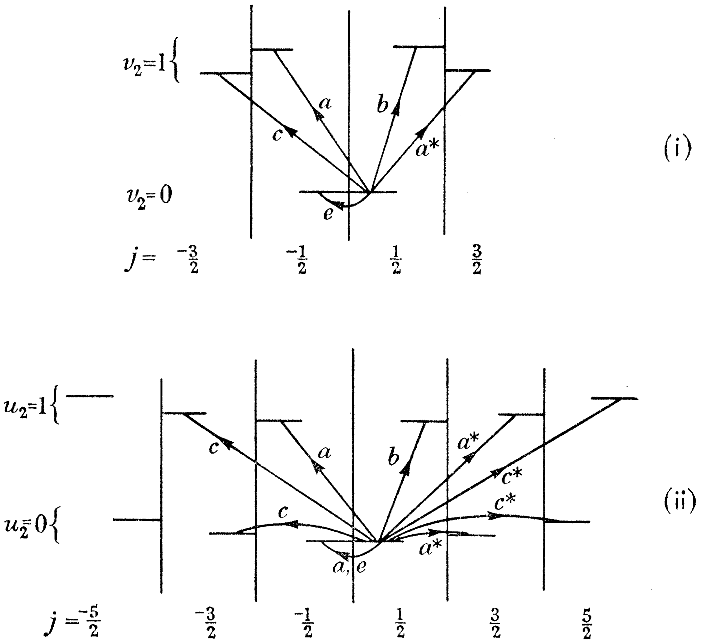

FIGURE 8. (i) The levels $|v_2, j\rangle$ which are connected with $|0, \frac{1}{2}\rangle$ in weak first-order coupling, and (ii) the levels $|u_2, j\rangle$ which are connected with $|0, \frac{1}{2}\rangle$ in strong first-order coupling, by primitive elements of the various types.

$$|v_1, v_2, j\rangle = |v_1, v_2, -j\rangle^*$$

so that
$$|v_2, j_+\rangle = |v_2, -j_-\rangle^*, \quad |v_2, j_-\rangle = |v_2, -j_+\rangle^*, \tag{2·44}$$

whatever the strength of the first-order coupling. As a result of this, the element $a$ connecting the state $|0, \frac{1}{2}\rangle$ with the state $|1, -\frac{1}{2}\rangle$ is equal to the element $b$ connecting $|0, \frac{1}{2}\rangle$ with $|1, \frac{1}{2}\rangle$ or $|0, -\frac{1}{2}\rangle$ with $|1, -\frac{1}{2}\rangle$. There is no such identity involving the primitive element $c$, however; this is clear from the fact that in strong coupling it falls to half the value expected by analogy with $a$.

The values of the primitive elements $a$, $b$ and $c$, in the dimensionless forms $a_0 = a\surd(\omega_2/\hbar)$, $b_0 = b\surd(\omega_2/\hbar)$, $c_0 = c\surd(w_2/\hbar)$, are tabulated in the appendix, for various pairs of states, along with the values of the dimensionless elements $d$ and $e$, for selected values of the distortion parameter $D$.

We may summarize this discussion of the primitive elements $a$ to $e$ by saying that for each there is a rigorous 'selection rule' involving the relative values of $j$ for the two states concerned; that in weak and strong first-order coupling there are subsidiary selection rules on $v_2$ and $u_2$, respectively. It is important to realize, however, that these subsidiary rules are relaxed in intermediate coupling, because of the mixing of vibronic levels with different values of $v_2$, or of $u_2$ as the case may be; this results in $a$ to $e$ having non-zero values for other pairs of states than those enumerated above, and is responsible for the appearance of overtones and combination bands in the vibrational spectra when the coupling is of intermediate strength.

## 3. Rotational spectra

We now consider the rotational levels of a symmetric-top molecule in a Jahn–Teller degenerate state, continuing with our example of the $D_{3h}$ molecule $X_3$ in an electronic $E'$ state.

As shown by Teller (1934) the rotational energy levels of a symmetric-top molecule differ from those of the rigid symmetric rotor by virtue of certain rotational-vibrational interaction terms, of which the most important is the first-order Coriolis coupling energy. The operator representing this energy is

$$-2AP_z p_z/\hbar^2, \tag{3·1}$$

where $A$ is $\frac{1}{2}\hbar^2$ divided by the principal moment of inertia, $P_z$ is the overall angular momentum about the figure axis, and $p_z$ is the angular momentum associated with the internal motion. This expression also applies to the vibronic levels of a degenerate electronic state, provided that $p_z$ is interpreted as the vibronic, rather than the vibrational, angular momentum. To determine the expectation value of (3·1) for a given vibronic level $|v_1, n_2\rangle$ and given $K$ (the quantum number for rotation about the figure axis) we separate $p_z$ into $p_z^e$, the electronic angular momentum, and $p_z^n$, the angular momentum associated with the degenerate mode $Q_2$. Then

$$\langle v_1, n_2|p_z|v_1, n_2\rangle = \langle n_{2+}|\langle e_+|p_z^e|e_+\rangle|n_{2+}\rangle + \langle n_{2-}|\langle e_-|p_z^e|e_-\rangle|n_{2-}\rangle + \langle n_{2+}|p_z^n|n_{2+}\rangle + \langle n_{2-}|p_z^n|n_{2-}\rangle. \tag{3·2}$$

In equation (3·2) the quantities $\langle e_\pm|p_z^e|e_\pm\rangle$ are implicit functions of $Q$; but if their variation with $Q$ is neglected, the off-diagonal terms $\langle e_+|p_z^e|e_-\rangle$ and $\langle e_-|p_z^e|e_+\rangle$ may be set equal to zero, which is their value for $Q = 0$. This accounts for the absence of cross-terms of the type

$$\langle n_{2+}|\langle e_+|p_z^e|e_-\rangle|n_{2-}\rangle, \quad \langle n_{2-}|\langle e_-|p_z^e|e_+\rangle|n_{2+}\rangle.$$

Now $p_z^n$ may be written in the form

$$p_z^n = \zeta_2(-\mathrm{i}\hbar\partial/\partial\phi), \tag{3·3}$$

where $\zeta_2$ is called the Coriolis coupling coefficient for the mode $Q_2$, and we may define an electronic Coriolis coefficient $\zeta_e$ by the equation

$$\langle e_+|p_z^e|e_+\rangle = \zeta_e\hbar = -\langle e_-|p_z^e|e_-\rangle. \tag{3·4}$$

Here $\zeta_e$ depends implicitly upon the co-ordinates $Q$, but we shall neglect its variation with $Q$. Using the fact that $|e_+\rangle$ and $|e_-\rangle$ are normalized electronic states, we may then write

$$\langle v_1, n_2|p_z|v_1, n_2\rangle = \zeta_e\hbar(\langle n_{2+}|n_{2+}\rangle-\langle n_{2-}|n_{2-}\rangle)+\zeta_2\hbar(\langle n_{2+}|-\mathrm{i}\partial/\partial\phi\,|n_{2+}\rangle$$
$$+\langle n_{2-}|-\mathrm{i}\partial/\partial\phi\,|n_{2-}\rangle). \qquad (3{\cdot}5)$$

Now $|n_{2+}\rangle$ varies as $\mathrm{e}^{\mathrm{i}(j-\frac{1}{2})\phi}$ and $|n_{2-}\rangle$ varies as $\mathrm{e}^{\mathrm{i}(j+\frac{1}{2})\phi}$, by the results obtained in § 2. We conclude that, since

$$\langle n_{2+}|n_{2+}\rangle+\langle n_{2-}|n_{2-}\rangle = 1, \qquad (3{\cdot}6)$$

$$\langle v_1, n_2|p_z|v_1, n_2\rangle = \hbar\{(\zeta_e-\tfrac{1}{2}\zeta_2)\,d+j\zeta_2\}, \qquad (3{\cdot}7)$$

where $d$ is the 'diagonal' primitive element

$$\langle n_{2+}|n_{2+}\rangle-\langle n_{2-}|n_{2-}\rangle$$

(see equations (2·39) and (2·40)). But the expectation value of $P_z$ is $K\hbar$, where the integral quantum number $K$ is to be thought of as having negative as well as positive values. It follows that for given $j$ and $K$ the first-order Coriolis energy is

$$-(2A/\hbar^2)\,\langle P_z p_z\rangle = -2AK\{(\zeta_e-\tfrac{1}{2}\zeta_2)\,d+j\zeta_2\} = -2AK\zeta,\ \text{say}. \qquad (3{\cdot}8)$$

In particular, for the $j=\frac{1}{2}$ component of the vibronic ground state we obtain (i) in weak coupling, when $d \simeq 1$,

$$\zeta \simeq \zeta_e \qquad (3{\cdot}9)$$

and (ii), in strong first-order coupling, when $d \simeq 0$,

$$\zeta \simeq \tfrac{1}{2}\zeta_2. \qquad (3{\cdot}10)$$

The first-order Coriolis coupling coefficient is thus a direct measure of the 'quenching parameter' $d$. This parameter will also determine the orbital contribution to the Zeeman splitting of each vibronic level; the splitting will be directly proportional to $d$ when the coupling is small.

A molecule of symmetry $D_{3h}$ in a non-degenerate electronic state cannot of course possess a permanent dipole moment, and consequently exhibits no microwave absorption spectrum. We shall now show that on the contrary if the electronic state is degenerate, there is a first-order Stark effect and also a microwave spectrum. In order to study these phenomena we need the matrix elements of the electric dipole moment between the various vibronic levels. These are obtained in the following manner.

With respect to the axes depicted in figures 1 and 2 the components of the instantaneous dipole moment operator will be denoted by $M_x$, $M_y$ and $M_z$. Since all the vibronic levels are symmetric with respect to the molecular plane, $M_z$ will have zero matrix elements between all the vibronic levels, and is therefore of no further interest here. It is convenient to replace the components $M_x$, $M_y$ by the complex combinations

$$M_1 = \surd\tfrac{1}{2}(M_x+\mathrm{i}M_y), \quad M_{-1} = \surd\tfrac{1}{2}(M_x-\mathrm{i}M_y); \qquad (3{\cdot}11)$$

the matrix elements of these operators between the vibronic levels then take the forms

$$\langle n'|M_{\pm1}|n''\rangle = [\langle n'_+|, \langle n'_-|]\begin{bmatrix}\langle e_+|M_{\pm1}|e_+\rangle & \langle e_+|M_{\pm1}|e_-\rangle \\ \langle e_-|M_{\pm1}|e_+\rangle & \langle e_-|M_{\pm1}|e_-\rangle\end{bmatrix}\begin{bmatrix}|n''_+\rangle \\ |n''_-\rangle\end{bmatrix}, \qquad (3{\cdot}12)$$

where the electronic matrix elements $\langle e_{\pm}|M_{\pm 1}|e_{\pm}\rangle$ depend implicitly upon the co-ordinates $Q$. To proceed we expand the matrices in (3·12) to first order in the vibrational co-ordinates; the transformation rules

$$C_3 M_1 = \omega M_1, \quad C_3 M_{-1} = \omega^{-1} M_{-1}, \tag{3·13}$$

taken in conjunction with those for $|e_+\rangle$ and $|e_-\rangle$, allow only the following constant and linear terms

$$\langle e_{\pm}|M_1|e_{\pm}\rangle = \begin{bmatrix} \surd\frac{1}{2}\lambda Q_- & \surd 2\kappa Q_+ \\ \surd 2(\mu_0+\mu_1 Q_1) & \surd\frac{1}{2}\lambda Q_- \end{bmatrix}, \quad \langle e_{\pm}|M_{-1}|e_{\pm}\rangle = \begin{bmatrix} \surd\frac{1}{2}\lambda Q_+ & \surd 2(\mu_0+\mu_1 Q_1) \\ \surd 2\kappa Q_- & \surd\frac{1}{2}\lambda Q_+ \end{bmatrix}. \tag{3·14}$$

(The factors $\surd\frac{1}{2}$ and $\surd 2$ have been inserted for future convenience.) The matrices (3·14) are simple linear combinations of the matrices appearing in § 2, (*a*) to (*e*). Thus the matrix elements of $M_{\pm 1}$ between two vibronic levels $|n_2'\rangle$ and $|n_2''\rangle$ may be written as

$$\langle n_2'|M_1|n_2''\rangle = \surd\tfrac{1}{2}\lambda a + \surd 2\kappa c + \surd 2(\mu_0+\mu_1 Q_1)\, e, \tag{3·15}$$

with a corresponding expression for the matrix element of $M_{-1}$.

In microwave absorption spectroscopy one is primarily concerned with the vibronic ground state; figure 8 shows that whether the first-order coupling is weak or strong the two components of this level are connected by an element of type $e$, though in intermediate and strong coupling they will also be connected by a primitive element of type $a$, because of the mixing between different levels of the same $j$. Writing $|v_1, v_2, j\rangle = |0, 0, \pm\frac{1}{2}\rangle$ for the two components of the vibronic ground state, we conclude that the matrices of $M_{\pm 1}$ between these two levels are

$$\langle 0, 0, \pm\tfrac{1}{2}|M_1|0, 0, \pm\tfrac{1}{2}\rangle = \begin{bmatrix} 0 & 0 \\ \surd 2\mu_{\perp} & 0 \end{bmatrix},$$

$$\langle 0, 0, \pm\tfrac{1}{2}|M_{-1}|0, 0, \pm\tfrac{1}{2}\rangle = \begin{bmatrix} 0 & \surd 2\mu_{\perp} \\ 0 & 0 \end{bmatrix}, \tag{3·16}$$

where

$$\mu_{\perp} = \mu_0 e + \tfrac{1}{2}\lambda a. \tag{3·17}$$

The matrices of $M_x$ and $M_y$ are therefore

$$\begin{bmatrix} 0 & \mu_{\perp} \\ \mu_{\perp} & 0 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & \mathrm{i}\mu_{\perp} \\ -\mathrm{i}\mu_{\perp} & 0 \end{bmatrix}; \tag{3·18}$$

consequently, when the molecule is placed in an electric field whose components with respect to the molecular axes are $\mathscr{E}_x$, $\mathscr{E}_y$, $\mathscr{E}_z$, the matrix of the perturbation

$$-(\mathscr{E}_x M_x + \mathscr{E}_y M_y + \mathscr{E}_z M_z) \tag{3·19}$$

takes the form

$$\begin{bmatrix} 0 & -\mu_{\perp}(\mathscr{E}_x + \mathrm{i}\mathscr{E}_y) \\ -\mu_{\perp}(\mathscr{E}_x - \mathrm{i}\mathscr{E}_y) & 0 \end{bmatrix}. \tag{3·20}$$

The eigenvalues of this matrix are

$$\pm\mu_{\perp}\surd(\mathscr{E}_x^2 + \mathscr{E}_y^2) = \pm\mu_{\perp}\mathscr{E}_{\perp}, \tag{3·21}$$

where $\mathscr{E}_{\perp}$ denotes the projection of the electric field on to the plane of the molecule. It is thus as though the electric field caused the molecule to develop a dipole moment of magnitude $\mu_{\perp}$ perpendicular to its axis and parallel or anti-parallel to $\mathscr{E}_{\perp}$. Hence the ground vibronic doublet will show a first-order Stark effect, and the dielectric constant will include a term which is inversely proportional to the temperature, the coefficient of $1/3kT$ being not $\mu_\perp^2$ but the expectation value of $(M_x^2+M_y^2)$, namely $2\mu_\perp^2$.

The fact that $M_1$ has a non-vanishing matrix element between the two vibronic levels $|0, 0, -\frac{1}{2}\rangle$ and $|0, 0, \frac{1}{2}\rangle$ means that the molecule will also possess a microwave spectrum. The selection rule for optical absorption is that if two internal states of a symmetric rotor are such that $\langle n'|M_1|n''\rangle$ $(=\langle n''|M_{-1}|n'\rangle^*)$ does not vanish, then the molecule can pass from $|n''\rangle$ to $|n'\rangle$ if at the same time the quantum number $K$ increases by unity (see, for example, Boyd & Longuet-Higgins 1952). Thus the $X_3$ molecule can undergo transitions from $|0, 0, \frac{1}{2}\rangle$ to $|0, 0, -\frac{1}{2}\rangle$ if at the same time $\Delta K = +1$. Since the vibronic energy does not change, this transition will be observed in the microwave region; the energy of the initial state will be

$$E'' = BJ''(J''+1)+(A-B)\,K''^2-2AK''\zeta, \quad \zeta = (\zeta_e-\tfrac{1}{2}\zeta_2)\,d+\tfrac{1}{2}\zeta_2, \tag{3·22}$$

where $d$ is positive, and that of the final state

$$E' = BJ'(J'+1)+(A-B)\,K'^2+2AK'\zeta, \quad K' = K''+1, \tag{3·23}$$

where we have used the fact that the vibronic angular momentum has equal and opposite values for the two states. The part of the spectrum for which $J' = J''$ therefore consists of a series of lines at frequencies determined by

$$\Delta E = \{A(1+2\zeta)-B\}\,(2K''+1). \tag{3·24}$$

The intensity of the transition is proportional to $\mu_\perp^2$.

It may help the reader to understand the physical origin of these phenomena if we interpret $\mu_0$, etc., in terms of the real electronic functions $|e_a\rangle$ and $|e_b\rangle$ rather than the complex ones $|e_\pm\rangle$. When $Q_{2b}$ vanishes (see figure 2) the relation of the real electronic states to the complex ones is

$$|e_a\rangle = \surd\tfrac{1}{2}(|e_+\rangle+|e_-\rangle) \quad |e_b\rangle = -\mathrm{i}\,\surd\tfrac{1}{2}(|e_+\rangle-|e_-\rangle). \tag{3·25}$$

Therefore by (3·14), and with $Q_+ = Q_- = Q_{2a}$, the matrices of $M_x$ and $M_y$ between the real electronic states are, respectively

$$M_x{:}\begin{bmatrix} \mu_0+\mu_1 Q_1+(\lambda+\kappa)\,Q_{2a} & 0 \\ 0 & -\mu_0-\mu_1 Q_1+(\lambda-\kappa)\,Q_{2a} \end{bmatrix}, \tag{3·26}$$

$$M_y{:}\begin{bmatrix} 0 & -\mu_0-\mu_1 Q_1+\kappa Q_{2a} \\ -\mu_0-\mu_1 Q_1+\kappa Q_{2a} & 0 \end{bmatrix}, \tag{3·27}$$

where in each matrix the first row and column belong to $|e_a\rangle$, and the second to $|e_b\rangle$. Thus in a very direct sense $\mu_0$ is the dipole moment of the molecule in its symmetrical configuration (of minimum energy with respect to $Q_1$); this dipole moment is in the $x$ direction when $Q_{2b} = 0$ and is oppositely directed for the states $|e_a\rangle$ and $|e_b\rangle$ since its average value for the two components of an $E'$ state must necessarily vanish. $\mu_1$ is the dipole moment derivative with respect to $Q_1$; $\lambda$ and $\kappa$ are given by

$$\lambda, \kappa = \frac{1}{2}\frac{\partial}{\partial Q_{2a}}(\langle e_a|M_x|e_a\rangle \pm \langle e_b|M_x|e_b\rangle). \tag{3·28}$$

We conclude this section with a short account of the general conditions under which a Jahn–Teller symmetric-top molecule exhibits a degenerate dipole moment of this sort. The following group-theoretical results are more or less self-evident, so we shall merely state them without proof.

If $\Gamma$ is the species of the degenerate electronic state, then the lowest vibronic level is also of species $\Gamma$. The molecule will exhibit a dipole moment $\mu_{\parallel}$ parallel to its figure axis if $[\Gamma^2]$, the symmetrized square of $\Gamma$, includes $\Gamma_{\parallel}$, the irreducible representation to which $M_z$ belongs; it will exhibit a dipole moment perpendicular to the figure axis if $[\Gamma^2]$ includes $\Gamma_{\perp}$, the doubly degenerate representation according to which $M_x$ and $M_y$ transform.‡ These two situations are *not* mutually exclusive. In the former case microwave absorption can occur with the usual selection rules for a symmetric-top molecule; in the latter case the selection rule on $K$ is $\Delta K = \pm 1$ (according as $\Delta j = \mp 1$). The dielectric constant in either case is temperature-dependent, and the coefficient of $1/3kT$ is $(\mu_{\parallel}^2 + 2\mu_{\perp}^2)$.

It should be added that all these general results are subject to the proviso that spin-orbit coupling may be neglected.

## 4. Infra-red absorption spectra

In the infra-red we are mainly concerned with transitions in which the principal quantum numbers of the vibrations change by unity; but overtones and combination bands are also of interest.

The intensity of a band in the vibrational absorption spectrum of an $X_3$ molecule is proportional to the square of one of the matrix elements

$$\langle n'|M_1|n''\rangle = [\langle n'_+|, \langle n'_-|]\begin{bmatrix} \sqrt{\tfrac{1}{2}}\lambda Q_- & \sqrt{2}\kappa Q_+ \\ \sqrt{2}(\mu_0+\mu_1 Q_1) & \sqrt{\tfrac{1}{2}}\lambda Q_- \end{bmatrix}\begin{bmatrix} |n''_+\rangle \\ |n''_-\rangle \end{bmatrix} \tag{4·1}$$

and

$$\langle n'|M_{-1}|n''\rangle = [\langle n'_+|, \langle n'_-|]\begin{bmatrix} \sqrt{\tfrac{1}{2}}\lambda Q_+ & \sqrt{2}(\mu_0+\mu_1 Q_1) \\ \sqrt{2}\kappa Q_- & \sqrt{\tfrac{1}{2}}\lambda Q_+ \end{bmatrix}\begin{bmatrix} |n''_+\rangle \\ |n''_-\rangle \end{bmatrix}. \tag{4·2}$$

Since for every transition from $|0, 0, \tfrac{1}{2}\rangle$ there corresponds one of equal energy and intensity from $|0, 0, -\tfrac{1}{2}\rangle$, it will be sufficient to discuss transitions from only one of these components of the ground state, $|0, 0, \tfrac{1}{2}\rangle$, for instance.

We begin by considering the activity of the totally symmetrical vibration. For a non-degenerate state of a $D_{3h}$ molecule this could not appear in the infra-red spectrum, but for an electronic $E'$ (or $E''$) state this prohibition is relaxed. Since $Q_1$ has non-vanishing matrix elements only between states for which $v'_1 = v''_1 \pm 1$, we conclude that only one quantum of $Q_1$ at a time can be excited in infra-red absorption, the intensity of a band in which $Q_1$ participates being proportional to

$$|\langle 1|Q_1|0\rangle \sqrt{2}\mu_1 e|^2 = \mu_1^2 e^2 \hbar/\omega_1 \tag{4·3}$$

if the transition is brought about by $M_1$ and proportional to $\mu_1^2 e^{*2}\hbar/\omega_1$ if $M_{-1}$ is responsible, where $e$ and $e^*$ are the primitive elements defined in § 2.

Now the selection rule on the primitive element $e$ is $j' = j'' - 1$; hence the fundamental of $Q_1$, for which necessarily $v'_2 = v''_2$, is associated with a transition in which $v_1$ increases from 0 to 1, $v_2$ remains at zero and $j$ changes from $\tfrac{1}{2}$ to $-\tfrac{1}{2}$. In (4·3) therefore, $e$ stands for the

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‡ Mizushima & Venkateswarlu (1953) showed that a $D_{2d}$ molecule can in principle exhibit an anomalous dipole moment parallel to the figure axis if it is in a *vibrationally* degenerate state of species $E$. The group-theoretical principles involved are the same as those enunciated here.

element $\langle 0, \frac{1}{2}_- | 0, \frac{1}{2}_+ \rangle$. In intermediate coupling there are two sets of combination bands with one quantum of $Q_1$ and one or more quanta of $Q_2$. For one of these $j' = -\frac{1}{2}$ and the intensity is proportional to $\mu_1^2 e^2 \hbar/\omega_1$, and for the other $j' = \frac{3}{2}$ and the intensity is proportional to $\mu_1^2 e^{*2} \hbar/\omega_1$. In extreme coupling these combination bands will be much weaker because of the subsidiary selection rules on $e$, namely $v_2' = v_2''$ or $u_2' = u_2''$, as the case may be.

The transition moment associated with the fundamental of $Q_1$ will, of course, be perpendicular to the figure axis, and the symmetric fundamental will therefore appear as a perpendicular band. The appearance of totally symmetric vibrations as parallel or perpendicular bands in the infra-red spectrum is in fact determined by exactly the same group-theoretical selection rules as govern the appearance of a parallel or perpendicular dipole moment (see § 3, last two paragraphs).

Turning to the degenerate vibration itself, we deduce from (4·1) and (4·2) that the intensity of the transition $|v_1, n_2'\rangle \leftarrow |v_1, n_2''\rangle$ is proportional to either

$$|\langle n_2' | M_1 | n_2'' \rangle|^2 = \tfrac{1}{2} |\lambda a + 2\kappa c^* + 2\mu_0 e|^2 \tag{4·4}$$

or

$$|\langle n_2' | M_{-1} | n_2'' \rangle|^2 = \tfrac{1}{2} |\lambda a^* + 2\kappa c + 2\mu_0 e^*|^2. \tag{4·5}$$

Owing to the selection rules on $a$, $a^*$, $c$, $c^*$, $e$ and $e^*$, the intensities of transitions from $|0, 0, \frac{1}{2}\rangle$ will therefore depend on the following quantities

$$\left.\begin{aligned} |\langle 0, v_2', -\tfrac{1}{2} | M_1 | 0, 0, \tfrac{1}{2} \rangle|^2 &= \tfrac{1}{2} |\lambda a + 2\mu_0 e|^2, \\ |\langle 0, v_2', \tfrac{3}{2} | M_{-1} | 0, 0, \tfrac{1}{2} \rangle|^2 &= \tfrac{1}{2} |\lambda a^* + 2\mu_0 e^*|^2, \\ |\langle 0, v_2', \tfrac{5}{2} | M_1 | 0, 0, \tfrac{1}{2} \rangle|^2 &= 2\kappa^2 c^{*2}, \\ |\langle 0, v_2', -\tfrac{3}{2} | M_{-1} | 0, 0, \tfrac{1}{2} \rangle|^2 &= 2\kappa^2 c^2. \end{aligned}\right\} \tag{4·6}$$

Now the sign of $j$ is of no consequence in the determination of the energy of a vibrational level; we conclude that in first-order coupling the fundamental of $Q_2$ and its overtones will appear in the infra-red spectrum as three distinct sets of bands. For all these, of course, $|j''| = \frac{1}{2}$, but for those with $|j'| = \frac{1}{2}$ the intensity is proportional to

$$\tfrac{1}{2} |\lambda a + 2\mu_0 e|^2, \tag{4·7}$$

for those with $|j'| = \frac{3}{2}$ the intensity is determined by

$$\tfrac{1}{2} |\lambda a^* + 2\mu_0 e^*|^2 + 2\kappa^2 c^2, \tag{4·8}$$

and for those with $|j'| = \frac{5}{2}$ the intensity is proportional to

$$2\kappa^2 c^{*2}.$$

In very weak coupling $e$ and $e^*$ become very small for $v_2' \neq v_2''$ and the selection rule on $a$, $a^*$, $c$ and $c^*$ is $v_2' = v_2'' \pm 1$; therefore the fundamental is much stronger than the overtones in this case. Using the limiting expressions for $a$ and $c$ as given in (2·29) and (2·36) we conclude that for very weak coupling the intensities of the $|j'| = \frac{1}{2}$ and $|j'| = \frac{3}{2}$ components of the fundamental of $Q_2$ are approximately proportional to $\lambda^2 \hbar/2\omega_2$ and $(\lambda^2 + 4\kappa^2)\, \hbar/2\omega_2$, respectively.

In very weak coupling, then, the intensities of these two bands are both proportional to the squares of dipole moment derivatives (see equation (3·26)). But in the intermediate range, where most real cases are likely to be found, the two terms in (4·7) will both contribute

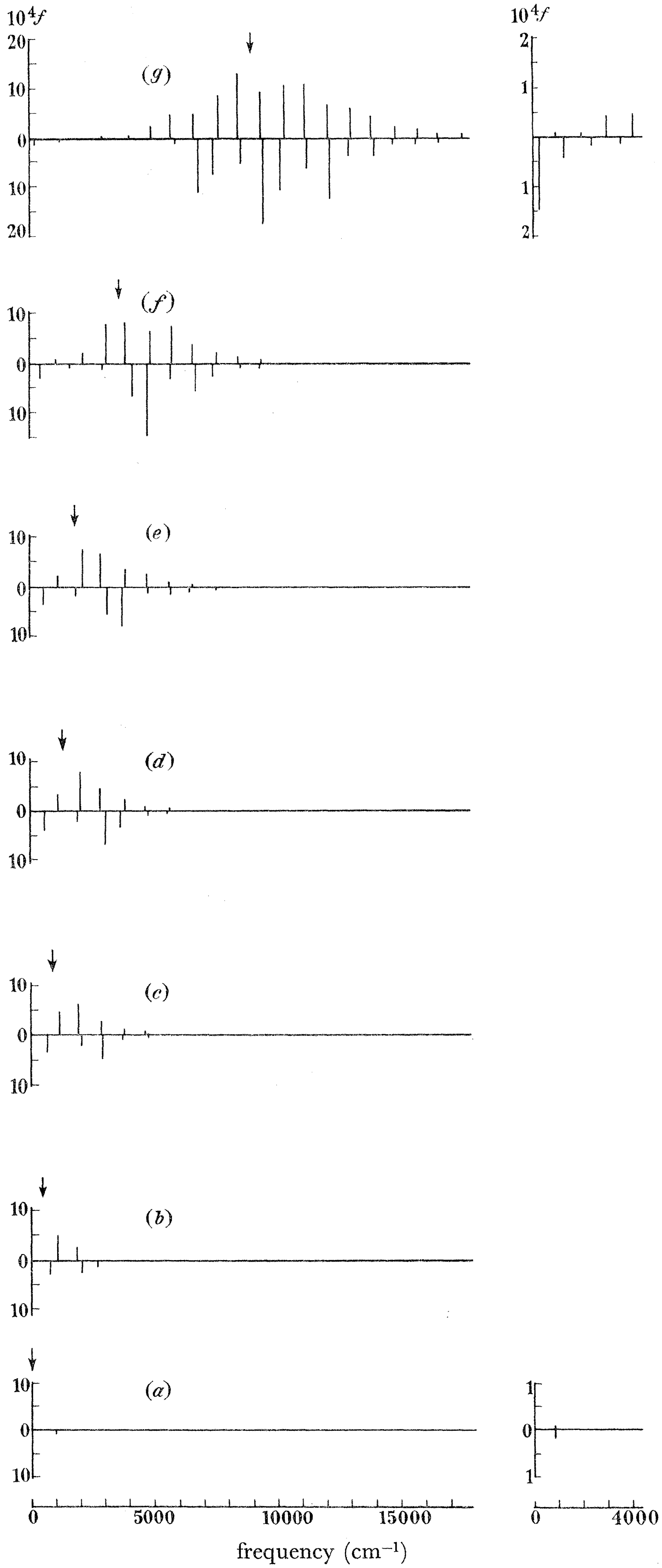

FIGURE 9. A series of synthetic infra-red absorption spectra for $X_3$, calculated for (*a*) $D = 0$; (*b*) $D = 0{\cdot}125$; (*c*) $D = 0{\cdot}25$; (*d*) $D = 0{\cdot}375$; (*e*) $D = 0{\cdot}50$; (*f*) $D = 1{\cdot}0$; (*g*) $D = 2{\cdot}5$. Lines above the axis refer to transitions in which $|j| = \frac{1}{2} \leftarrow \frac{1}{2}$; those below refer to transitions in which $|j| = \frac{3}{2} \leftarrow \frac{1}{2}$. Lines involving the symmetric vibration have not been plotted, nor lines for which $|j| = \frac{5}{2} \leftarrow \frac{1}{2}$.

significantly, and they may or may not reinforce one another, according to the relative signs of $\lambda$ and $\mu_0$. $\mu_0$, it is to be remembered, is not a dipole moment derivative, but the perpendicular dipole moment itself; it is as though when the molecule undergoes cyclic motion in the co-ordinate $\phi$, the perpendicular dipole moment is carried round and round, so that there is a contribution to the intensity of the same type as one finds in the pure rotational spectrum.

In intermediate coupling there will be a further splitting of the fundamental of $Q_2$ due to second-order effects. As shown in § 2, and illustrated in figure 6, the levels with $|j| = \frac{3}{2}$ will be resolved into levels of species $A_1'$ and $A_2'$ differing slightly in energy. The sign of the energy difference will depend upon the signs of the coupling constants $f$ and $g$, but in either case the lower-energy band due to the fundamental will be found to consist of two distinct sub-bands, each with half the intensity given by (4·8). The case of strong first-order coupling without second-order coupling is probably of academic interest only; but if there is strong first- *and* second-order coupling, the infra-red spectrum should be essentially that of a permanently distorted molecule of symmetry $C_{2v}$; there should be two distinct fundamental bands, one associated with $Q_{2a}$ and the other with $Q_{2b}$ (see equation (2·25)), though a further splitting might be observed (see figure 7) if the tunnelling frequency were sufficiently great between the three absolute potential energy minima.

Figure 9 (*a*) to (*g*) presents some 'synthetic' infra-red spectra for $X_3$, for various values of $D$. The appearance of such spectra will clearly depend a great deal on the choice of the relevant molecular constants; we have chosen values which might be appropriate for the *cyclo*-propenyl radical $C_3H_3$, namely

$$\omega_1/2\pi c = 1200\,\mathrm{cm}^{-1}, \quad \omega_2/2\pi c = 900\,\mathrm{cm}^{-1},$$
$$\mu_0 = 2{\cdot}0D, \quad \mu_1\sqrt{(\hbar/\omega_1)} = 0{\cdot}15D,$$
$$\lambda\sqrt{(\hbar/\omega_2)} = \kappa\sqrt{(\hbar/\omega_2)} = 0{\cdot}15D.$$

In each diagram the excitation energy is given in cm$^{-1}$; the vertical scale is the calculated oscillator strength, $f(\nu) = (4\pi m\nu/3\hbar e^2)\langle n'|\,M\,|n''\rangle^2$, where $\nu$ is the frequency in cycles/second. Adopting the above values of the molecular constants we find that the fundamental of $Q_1$ and the combination bands with $Q_2$ are very much weaker than the fundamental and the overtones of $Q_2$. We also find that the overtones of $Q_2$ with $|j'| = \frac{5}{2}$ are much weaker than those with $|j'| = \frac{1}{2}$ or $\frac{3}{2}$. We have therefore plotted in figure 9 only those lines which arise from transitions $\Delta v_1 = 0, \Delta v_2 \geqslant 1$ and $|j| = \frac{1}{2} \leftarrow \frac{1}{2}$ (above axis) or $|j| = \frac{3}{2} \leftarrow \frac{1}{2}$ (below axis). It should be stressed that in constructing figure 9 we have taken no account whatever of second-order coupling; the arrow in each diagram indicates the vertical excitation energy from the bottom of the moat to the upper branch of the (axially symmetrical) potential energy surface.

The most striking feature of figure 9 is the strong progression of $Q_2$ overtones with a maximum intensity near the position of the arrow. The appearance of so much intensity in the overtones is a result of the heavy mixing between unperturbed vibronic levels with the same value of $j$; the high intensity of the spectrum as a whole arises almost entirely from the terms $\mu_0 e$ and $\mu_0 e^*$ in (4·7) and (4·8). It is to be emphasized that such spectacular behaviour is limited to molecules in which optical transitions can take place between the components of a degenerate electronic state—that is, to those species with an anomalous dipole moment

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(see table 1). In such molecules a change in the phase of $Q_2$ induces a reorientation of $\mu_0$ within the molecule, but a variation of $Q_1$ has no such effect; this is why the intensity of the $Q_2$ progression is so much greater than that of the $Q_1$ fundamental. Another interesting feature of the spectra is the splitting of the $Q_2$ lines; this is a very direct manifestation of the dynamical Jahn–Teller effect.

When $D$ is very large the fundamental of $Q_2$ falls in intensity to a 'normal' value because in (4·7) and (4·8) the terms in $\mu_0$ become very small in comparison with those in $\lambda$ and $\kappa$. For instance, (4·7) becomes approximately

$$\begin{aligned}\tfrac{1}{2}\lvert\lambda a\rvert^2 = \tfrac{1}{2}\lambda^2\lvert\langle u_2''+1\,\lvert\, r\,\rvert\, u_2''\rangle\rvert^2 &= \tfrac{1}{2}\lambda^2\hbar(u_2''+1)/2\omega_2\\ &= \lambda^2\hbar/4\omega_2 \quad \text{when} \quad u_2''=0.\end{aligned}$$

Since $\lambda$ is an ordinary dipole moment derivative, the intensity of the band in question is of the same order as ordinary infra-red intensities, and at low frequencies the spectrum is not strikingly different from that of a non-degenerate molecule.

TABLE 1. THE INFRA-RED ACTIVE VIBRATIONS OF SYMMETRIC-TOP MOLECULES IN DEGENERATE ELECTRONIC STATES

| | $\Gamma_0$ | $\Gamma_\parallel$ | $\Gamma_\perp$ | $\Gamma$ | $[\Gamma^2]-\Gamma_0$ | $\gamma_\parallel$ | $\gamma_\perp$ |
|---|---|---|---|---|---|---|---|
| $D_3$ | $A_1$ | $A_2$ | $E$ | $E$ | $E$ | $A_2, E$ | $A_1, A_2, E$ |
| $C_{3v}$ | $A_1$ | $A_1$ | $E$ | $E$ | $E$ | $A_1, E$ | $A_1, A_2, E$ |
| $C_{4v}$ | $A_1$ | $A_1$ | $E$ | $E$ | $B_1+B_2$ | $A_1\;, B_1, B_2$ | $E$ |
| $D_{2d}$ | $A_1$ | $B_2$ | $E$ | $E$ | $B_1+B_2$ | $A_1, A_2, B_2$ | $E$ |
| $D_{3d}$ | $A_{1g}$ | $A_{2u}$ | $E_u$ | $E_g, E_u$ | $E_g$ | $A_{2u}, E_u$ | $A_{1u}, A_{2u}, E_u$ |
| $D_{4d}$ | $A_1$ | $B_2$ | $E_1$ | $E_1, E_3$ | $E_2$ | $B_2, E_2$ | $E_1, E_3$ |
| | | | | $E_2$ | $B_1+B_2$ | $A_1, A_2, B_2$ | $E_1, E_3$ |
| $D_{5d}$ | $A_{1g}$ | $A_{2u}$ | $E_{1u}$ | $E_{1g}, E_{1u}$ | $E_{2g}$ | $A_{2u}, E_{2u}$ | $E_{1u}, E_{2u}$ |
| | | | | $E_{2g}, E_{2u}$ | $E_{1g}$ | $A_{2u}, E_{1u}$ | $A_{1u}, A_{2u}, E_{1u}, E_{2u}$ |
| $D_{3h}$ | $A_1'$ | $A''$ | $E'$ | $E', E''$ | $E'$ | $A_2'', E''$ | $A_1', A_2', E'$ |
| $D_{4h}$ | $A_{1g}$ | $A_{2u}$ | $E_u$ | $E_g, E_u$ | $B_{1g}+B_{2g}$ | $A_{2u}, B_{1u}, B_{2u}$ | $E_u$ |
| $D_{5h}$ | $A_1'$ | $A_2''$ | $E_1'$ | $E_1', E_1''$ | $E_2'$ | $A_2'', E_2''$ | $E_1', E_2'$ |
| | | | | $E_2', E_2''$ | $E_1'$ | $A_2'', E_1''$ | $A_1', A_2', E_1', E_2'$ |
| $D_{6h}$ | $A_{1g}$ | $A_{2u}$ | $E_{1u}$ | $E_{1g}, E_{1u}, E_{2g}, E_{2u}$ | $E_{2g}$ | $A_{2u}, E_{2u}$ | $B_{1u}, B_{2u}, E_{1u}$ |
| $D_{7h}$ | $A_1'$ | $A_2''$ | $E_1'$ | $E_1', E_1''$ | $E_2'$ | $A_2'', E_2''$ | $E_1', E_3'$ |
| | | | | $E_2', E_2''$ | $E_3'$ | $A_2'', E_3''$ | $E_1', E_2', E_3'$ |
| | | | | $E_3', E_3''$ | $E_1'$ | $A_2'', E_1''$ | $A_1', A_2', E_1', E_2'$ |

$\Gamma_0$ is the totally symmetric representation, $\Gamma_\parallel$ is the species of $M_z$, $\Gamma_\perp$ is the species of $(M_x, M_y)$, and $\Gamma$ is the species of the degenerate electronic state. $[\Gamma^2]-\Gamma_0$ includes the species of all Jahn–Teller active vibrations. $\gamma_\parallel$ and $\gamma_\perp$ are the species of those vibrations whose fundamentals appear as parallel and perpendicular infra-red bands. If $\gamma_\parallel$ includes $\Gamma_0$, the molecule exhibits a parallel dipole moment; if $\gamma_\perp$ includes $\Gamma_0$, the molecule exhibits a perpendicular dipole moment.

The group-theoretical selection rules restricting the appearance of vibrational fundamentals in the infra-red spectrum are as follows. If, as before, $\Gamma$ denotes the species of the electronic state and $[\Gamma^2]$ is its symmetrized square, then a vibration of species $\gamma$ will give rise to a parallel fundamental band in the infra-red if $[\Gamma^2]\times\Gamma_\parallel$ includes $\gamma$, and to a perpendicular fundamental band if $[\Gamma^2]\times\Gamma_\perp$ includes $\gamma$, where $\Gamma_\parallel$ and $\Gamma_\perp$ are the species of $M_z$ and $(M_x, M_y)$, respectively. In table 1 the columns labelled $\gamma_\parallel$ and $\gamma_\perp$ indicate the species of those vibrations whose fundamentals give rise to parallel and perpendicular bands in the infra-red, for the point groups to which most symmetric-top molecules belong. The extent to which the normal selection rules are relaxed is indicated by the fact that in non-degenerate electronic states the only vibrations with active fundamentals are those of species $\Gamma_{\parallel}$ or $\Gamma_{\perp}$.

In general, a vibration whose fundamental is active will, in intermediate coupling, give rise to combination bands involving one quantum of the active fundamental and one or more quanta of the Jahn–Teller active vibration or vibrations (i.e. those whose species belong to $[\Gamma^2]-\Gamma_0$, where $\Gamma_0$ is the totally symmetric representation). This is because of the level mixing produced by the vibronic interaction.

## 5. Rayleigh and Raman spectra

In order to interpret the Raman spectra of Jahn–Teller molecules it is necessary to return to the fundamental formulae of Placzek (1934) for the intensities of Raman lines. Placzek distinguished three kinds of Raman scattering—scalar, symmetric-tensor and pseudo-vector scattering. For an assembly of randomly oriented molecules the intensities of these are additive. If the incident light is unpolarized, the light scattered by the scalar mechanism is found to be fully polarized, that scattered by the symmetric-tensor mechanism is slightly polarized (depolarization ratio $\rho_n = \frac{6}{7}$) and light scattered in a pseudo-vector fashion should be reverse polarized ($\rho_n = 2$). For molecules in non-degenerate electronic states the pseudo-vector scattering is symmetry-forbidden, but this is not necessarily so, as we shall demonstrate, for Jahn–Teller molecules.

Raman scattering is a two-quantum process involving the participation of intermediate vibronic states. If $|n'', e''\rangle$ and $|n', e'\rangle$ are the initial and final states, and $|n, e\rangle$ is any intermediate vibronic state, then the intensities of the three kinds of scattering depend upon matrix elements of the following types

$$\langle n', e'|\,c^0\,|n'', e''\rangle = \tfrac{1}{3}\sum_{ne}\left[\frac{1}{E-E''+h\nu}+\frac{1}{E-E'-h\nu}\right]\Big[\sum_{\rho}\langle n', e'|M_\rho|n, e\rangle\langle n, e|M_{-\rho}|n'', e''\rangle\Big]; \qquad (5\cdot1)$$

$$\begin{aligned}\langle n', e'|\,c^s_{\rho\sigma}\,|n'', e''\rangle = \tfrac{1}{2}\sum_{ne}\left[\frac{1}{E-E''+h\nu}+\frac{1}{E-E'-h\nu}\right]&[\langle n', e'|M_\rho|n, e\rangle\langle n, e|M_\sigma|n'', e''\rangle\\ &+\langle n', e'|M_\sigma|n, e\rangle\langle n, e|M_\rho|n'', e''\rangle]\\ &-\delta_{-\rho,\sigma}\langle n', e'|\,c^0\,|n'', e''\rangle; \qquad (5\cdot2)\end{aligned}$$

$$\begin{aligned}\langle n', e'|\,c^a_{\rho\sigma}\,|n'', e''\rangle = \tfrac{1}{2}\sum_{ne}\left[\frac{1}{E-E''+h\nu}-\frac{1}{E-E'-h\nu}\right]&[\langle n', e'|M_\rho|n, e\rangle\langle n, e|M_\sigma|n'', e''\rangle\\ &-\langle n', e'|M_\sigma|n, e\rangle\langle n, e|M_\rho|n'', e''\rangle]. \qquad (5\cdot3)\end{aligned}$$

In these equations $E''$, $E$ and $E'$ are the energies of the initial, intermediate and final vibronic states, and $\nu$ is the frequency of the incident light. The indices $\rho$, $\sigma$ in $M_\rho$, $M_\sigma$ and the $c_{\rho\sigma}$ stand for 0, 1 and $-1$; their meaning is precisely given by the definitions

$$M_0 = M_z, \quad M_1 = \sqrt{\tfrac{1}{2}}(M_x+\mathrm{i}M_y), \quad M_{-1} = \sqrt{\tfrac{1}{2}}(M_x-\mathrm{i}M_y). \qquad (5\cdot4)$$

Introducing the definitions

$$\left.\begin{aligned}G^0 &= 3\,|\langle n', e'|\,c^0\,|n'', e''\rangle|^2,\\ G^s &= \sum_{\rho\sigma}|\langle n', e'|\,c^s_{\rho\sigma}\,|n'', e''\rangle|^2,\\ G^a &= \sum_{\rho\sigma}|\langle n', e'|\,c^a_{\rho\sigma}\,|n'', e''\rangle|^2,\end{aligned}\right\} \qquad (5\cdot5)$$

Placzek showed that for randomly oriented molecules the molecular cross-sections for scalar, symmetric-tensor and pseudo-vector Raman scattering are proportional respectively to the three terms in (5·6)

$$\sigma = 64\pi^4\nu_s^4c^{-4}(G^0+G^s+G^a), \tag{5·6}$$

where $\nu_s$ is the frequency of the scattered light, the depolarization ratio for unpolarized incident light being

$$\rho_n = \frac{6G^s+10G^a}{30G^0+7G^s+5G^a}. \tag{5·7}$$

In order to simplify expressions (5·1) to (5·3) one notes that according to the Franck–Condon principle only vertical vibronic transitions have appreciable intensities. This makes it a reasonable approximation to replace the sum over the vibrational sublevels of the intermediate electronic state by an integral over the vibrational co-ordinates, at the same time replacing the excitation energy to a given vibronic level by the vertical excitation energy in a given vibrational configuration. For a transition between two electronically non-degenerate states we thus obtain, for example,

$$\begin{aligned}\tfrac{1}{2}\sum_{ne}\left[\frac{1}{E-E''+h\nu}+\frac{1}{E-E'-h\nu}\right][\langle n',e'|M_\rho|n,e\rangle\langle n,e|M_\sigma|n'',e''\rangle \\ +\langle n',e'|M_\sigma|n,e\rangle\langle n,e|M_\rho|n'',e''\rangle] \\ =\int \mathrm{d}Q\,\langle n'|\,Q\rangle\langle e'|\,\alpha_{\rho\sigma}(Q)\,|\,e''\rangle\langle Q\,|\,n''\rangle,\end{aligned} \tag{5·8}$$

where

$$\begin{aligned}\langle e'|\,\alpha_{\rho\sigma}(Q)\,|e''\rangle = \tfrac{1}{2}\sum_{e}\left[\frac{1}{W-W''+h\nu}+\frac{1}{W-W'-h\nu}\right] \\ \times[\langle e'|M_\rho|e\rangle\langle e|M_\sigma|e''\rangle+\langle e'|M_\sigma|e\rangle\langle e|M_\rho|e''\rangle],\end{aligned} \tag{5·9}$$

$|e'\rangle$, $|e\rangle$ and $|e''\rangle$ being the eigenstates of $H(Q)$, the electronic Hamiltonian for the nuclear configuration $Q$, and $W'$, $W$ and $W''$ the corresponding eigenvalues. If the vibronic levels $|n',e'\rangle$ and $|n'',e''\rangle$ have the forms

$$\left.\begin{aligned}|n',e'\rangle &= |n_a'\rangle\,|e_a\rangle+|n_b'\rangle\,|e_b\rangle,\\ |n'',e''\rangle &= |n_a''\rangle\,|e_a\rangle+|n_b''\rangle\,|e_b\rangle,\end{aligned}\right\} \tag{5·10}$$

then the obvious generalization of (5·8) is

$$\begin{aligned}\sum_{ne}\left[\frac{1}{E-E''+h\nu}+\frac{1}{E-E'-h\nu}\right][\langle n',e'|M_\rho|n,e\rangle\langle n,e|M_\sigma|n'',e''\rangle+\langle n',e'|M_\sigma|n,e\rangle\langle n,e|M_\rho|n'',e''\rangle] \\ =[\langle n_a'|,\langle n_b'|]\begin{bmatrix}\langle e_a|\,\alpha_{\rho\sigma}\,|e_a\rangle & \langle e_a|\,\alpha_{\rho\sigma}\,|e_b\rangle\\ \langle e_b|\,\alpha_{\rho\sigma}\,|e_a\rangle & \langle e_b|\,\alpha_{\rho\sigma}\,|e_b\rangle\end{bmatrix}\begin{bmatrix}|n_a''\rangle\\ |n_b''\rangle\end{bmatrix},\end{aligned} \tag{5·11}$$

where
$$\langle e_a|\,\alpha_{\rho\sigma}\,|e_b\rangle = \tfrac{1}{2}\langle e_a|\,\{M_\rho f_{ab}(H)\,M_\sigma+M_\sigma f_{ab}(H)\,M_\rho\}\,|e_b\rangle, \tag{5·12}$$

with
$$f_{ab}(H) = \left[\frac{1}{H-W_b+h\nu}+\frac{1}{H-W_a-h\nu}\right]. \tag{5·13}$$

Now the difference between $W_a$ and $W_b$ is relatively insignificant compared to the other energy differences concerned; we may therefore replace both of them by their average $\overline{W}$, and investigate instead the matrix elements of the electronic polarizability operator

$$\alpha_{\rho\sigma} = \tfrac{1}{2}\{M_\rho f^s(H)\,M_\sigma+M_\sigma f^s(H)\,M_\rho\}, \tag{5·14}$$

where $f^s(H)$ is defined as

$$\left[\frac{1}{H-\overline{W}+h\nu}+\frac{1}{H-\overline{W}-h\nu}\right]. \tag{5·15}$$

Having defined the operator $\alpha_{\rho\sigma}$ by equations (5·14) and (5·15) one may now with much greater convenience work in terms of the complex components $|e_+\rangle$ and $|e_-\rangle$. Introducing the definition

$$\langle n'|\,\alpha_{\rho\sigma}\,|n''\rangle = [\langle n'_+|, \langle n'_-|]\begin{bmatrix}\langle e_+|\,\alpha_{\rho\sigma}\,|e_+\rangle & \langle e_+|\,\alpha_{\rho\sigma}\,|e_-\rangle\\ \langle e_-|\,\alpha_{\rho\sigma}\,|e_+\rangle & \langle e_-|\,\alpha_{\rho\sigma}\,|e_-\rangle\end{bmatrix}\begin{bmatrix}|n''_+\rangle\\ |n''_-\rangle\end{bmatrix}, \tag{5·16}$$

we find that the scalar and symmetric-tensor scattering coefficients are now given by expressions of the same form as for the non-degenerate case, namely

$$G^0 = \tfrac{1}{3}|\langle n'|\,\alpha_{1-1}\,|n''\rangle+\langle n'|\,\alpha_{-11}\,|n''\rangle+\langle n'|\,\alpha_{00}\,|n''\rangle|^2 \tag{5·17}$$

and

$$G^s = \sum_{\rho\sigma}|\langle n'|\,\alpha_{\rho\sigma}\,|n''\rangle-\tfrac{1}{3}\delta_{-\rho,\sigma}\{\langle n'|\,\alpha_{1-1}\,|n''\rangle+\langle n'|\,\alpha_{-11}\,|n''\rangle+\langle n'|\,\alpha_{00}\,|n''\rangle\}|^2. \tag{5·18}$$

We also need an expression for the pseudo-vector scattering coefficient. This is

$$G^a = \sum_{\rho\sigma}|\langle n'|\,\beta_{\rho\sigma}\,|n''\rangle|^2, \tag{5·19}$$

where the operator $\beta_{\rho\sigma}$ is defined by the equation

$$\beta_{\rho\sigma} = \tfrac{1}{2}\{M_\rho f^a(H)\,M_\sigma - M_\sigma f^a(H)\,M_\rho\}, \tag{5·20}$$

with

$$f^a(H) = \left[\frac{1}{H-\overline{W}+h\nu}-\frac{1}{H-\overline{W}-h\nu}\right]. \tag{5·21}$$

Equations (5·14) to (5·21) provide the basis for the calculation of the intensities and depolarization ratios of Raman lines in the doubly degenerate Jahn–Teller case.

We now apply these general results to the Raman spectrum of $X_3$, in an $E'$ electronic state. The first thing to do is to discover how the various electronic matrix elements $\langle e_\pm|\,\alpha_{\rho\sigma}\,|e_\pm\rangle$ transform under the operation $C_3$ applied to the vibronic state. Since $H$ is a totally symmetric operator, $f^s(H)$ is also totally symmetric, and so $\alpha_{\rho\sigma}$ transforms like $M_\rho M_\sigma + M_\sigma M_\rho$:

$$C_3\,\alpha_{\rho\sigma} = \omega^{\rho+\sigma}\alpha_{\rho\sigma}. \tag{5·22}$$

Next, it is clear that the operators $\alpha_{01}$, $\alpha_{10}$, $\alpha_{0-1}$, $\alpha_{-10}$ are all antisymmetric with respect to the molecular plane, so that their matrix elements between the various vibrational sublevels must all vanish. Using the transformation rules $C_3\,Q_\pm = \omega^{\pm 2}Q_\pm$ we conclude that to the first order in the vibrational co-ordinates the electronic matrix elements of the $\alpha_{\rho\sigma}$ must have the following forms, where the first row and column of each matrix belongs to $|e_+\rangle$, and the second to $|e_-\rangle$

$$\left.\begin{aligned}
\langle e_\pm|\,\alpha_{-11}\,|e_\pm\rangle &= \begin{bmatrix}\alpha_1+\delta_1 Q_1 & \gamma_1 Q_-\\ \gamma_1 Q_+ & \alpha_1+\delta_1 Q_1\end{bmatrix}, \quad \langle e_\pm|\,\alpha_{-1-1}\,|e_\pm\rangle = \begin{bmatrix}\gamma_2 Q_- & 2\gamma_4 Q_+\\ 2(\alpha_2+\delta_2 Q_1) & \gamma_2 Q_-\end{bmatrix},\\
\langle e_\pm|\,\alpha_{11}\,|e_\pm\rangle &= \begin{bmatrix}\gamma_2 Q_+ & 2(\alpha_2+\delta_2 Q_1)\\ 2\gamma_4 Q_- & \gamma_2 Q_+\end{bmatrix}, \quad \langle e_\pm|\,\alpha_{1-1}\,|e_\pm\rangle = \begin{bmatrix}\alpha_1+\delta_1 Q_1 & \gamma_1 Q_-\\ \gamma_1 Q_+ & \alpha_1+\delta_1 Q_1\end{bmatrix},\\
\langle e_\pm|\,\alpha_{00}\,|e_\pm\rangle &= \begin{bmatrix}\alpha_3+\delta_3 Q_1 & \gamma_3 Q_-\\ \gamma_3 Q_+ & \alpha_3+\delta_3 Q_1\end{bmatrix}.
\end{aligned}\right\} \tag{5·23}$$

It may be wondered why so many of the coefficients should be equal in these expressions. The reasons are to be found in the identities

$$\begin{aligned} \alpha_{-11} &= \tfrac{1}{2}(\alpha_{xx}+\alpha_{yy}), \quad \alpha_{-1-1} = \tfrac{1}{2}(\alpha_{xx}-\alpha_{yy}) - \tfrac{1}{2}\mathrm{i}(\alpha_{xy}+\alpha_{yx}), \\ \alpha_{11} &= \tfrac{1}{2}(\alpha_{xx}-\alpha_{yy}) + \tfrac{1}{2}\mathrm{i}(\alpha_{xy}+\alpha_{yx}), \quad \alpha_{1-1} = \tfrac{1}{2}(\alpha_{xx}+\alpha_{yy}), \end{aligned} \tag{5·24}$$

where the operators $\alpha_{xx}$, etc., are defined by equations of identical form to (5·14). Thus $\alpha_{-11}$ and $\alpha_{1-1}$ are real Hermitian operators, and $\alpha_{11}$, which is the complex conjugate of $\alpha_{-1-1}$, is the sum of a real and i times a real Hermitian operator. The equalities between certain of the coefficients then follow from the complex conjugacy of the states $|e_+\rangle$, $|e_-\rangle$.

As with the matrix elements of the dipole moment it may be helpful if we express the various coefficients $\alpha_1$ to $\delta_3$ in terms of quantities referring to the real electronic states $|e_a\rangle$ and $|e_b\rangle$ rather than the complex ones $|e_+\rangle$ and $|e_-\rangle$. Setting $Q_{2b} = 0$ so that $Q_+ = Q_- = Q_{2a}$, and using (5·24), we obtain straightforwardly

$$\left.\begin{aligned} \tfrac{1}{2}\{(\alpha_{xx})_a + (\alpha_{yy})_a\} &= \alpha_1 + \gamma_1 Q_{2a} + \delta_1 Q_1, \\ \tfrac{1}{2}\{(\alpha_{xx})_b + (\alpha_{yy})_b\} &= \alpha_1 - \gamma_1 Q_{2a} + \delta_1 Q_1, \\ \tfrac{1}{2}\{(\alpha_{xx})_a - (\alpha_{yy})_a\} &= \alpha_2 + (\gamma_2+\gamma_4)\, Q_{2a} + \delta_2 Q_1, \\ \tfrac{1}{2}\{(\alpha_{xx})_b - (\alpha_{yy})_b\} &= -\alpha_2 + (\gamma_2-\gamma_4)\, Q_{2a} - \delta_2 Q_1, \\ (\alpha_{zz})_a &= \alpha_3 + \gamma_3 Q_{2a} + \delta_3 Q_1, \\ (\alpha_{zz})_b &= \alpha_3 - \gamma_3 Q_{2a} + \delta_3 Q_1, \end{aligned}\right\} \tag{5·25}$$

where, for instance, $(\alpha_{xx})_a$ denotes $\langle e_a|\,\alpha_{xx}\,|e_a\rangle$. Equations (5·25) enable one to interpret all the quantities $\alpha_1$ to $\delta_3$ in terms of the real electronic polarizabilities of $|e_a\rangle$ and $|e_b\rangle$, and their derivatives with respect to $Q_1$ and $Q_{2a}$.

Returning to equation (5·16) and substituting into it the matrices given in (5·23) we see that for $v_1' = v_1''$, the matrix elements $\langle n'|\,\alpha_{\rho\sigma}\,|n''\rangle$ may be expressed in the forms

$$\left.\begin{aligned} \langle n'|\,\alpha_{-11}\,|n''\rangle &= \alpha_1\langle n_2'|n_2''\rangle + \gamma_1 b = \langle n'|\,\alpha_{1-1}\,|n''\rangle, \\ \langle n'|\,\alpha_{-1-1}\,|n''\rangle &= 2\alpha_2 e + \gamma_2 a + 2\gamma_4 c^* = \langle n''|\,\alpha_{11}\,|n'\rangle^*, \\ \langle n'|\,\alpha_{00}\,|n''\rangle &= \alpha_3\langle n_2'|n_2''\rangle + \gamma_3 b, \end{aligned}\right\} \tag{5·26}$$

where $a$, $b$, $c^*$ and $e$ are four of the primitive matrix elements defined in § 2. For $v_1' = v_1''+1$, on the other hand,

$$\left.\begin{aligned} \langle n'|\,\alpha_{-11}\,|n''\rangle &= \delta_1\langle v_1''+1|\,Q_1\,|v_1''\rangle = \langle n'|\,\alpha_{1-1}\,|n''\rangle, \\ \langle n'|\,\alpha_{-1-1}\,|n''\rangle &= 2\delta_2 e\langle v_1''+1|\,Q_1\,|v_1''\rangle = \langle n''|\,\alpha_{11}\,|n'\rangle,^* \\ \langle n'|\,\alpha_{00}\,|n''\rangle &= \delta_3\langle v_1''+1|\,Q_1\,|v_1''\rangle. \end{aligned}\right\} \tag{5·27}$$

So far we have said little about the operators $\beta_{\rho\sigma}$, defined by (5·20), which determine the intensity of pseudo-vector scattering. In the first place the tensor components $\beta_{01}$, $\beta_{10}$, $\beta_{0-1}$ and $\beta_{-10}$ have zero matrix elements between all the vibrational levels, since they are antisymmetric with respect to the molecular plane. Secondly, $\beta_{\rho\sigma}$ vanishes identically if $\rho$ and $\sigma$ are equal. There remain only $\beta_{-11}$ and $\beta_{1-1}$ to be considered, and these may be written in the forms

$$\beta_{-11} = \tfrac{1}{2}\mathrm{i}(\beta_{xy}-\beta_{yx}), \quad \beta_{1-1} = -\tfrac{1}{2}\mathrm{i}(\beta_{xy}-\beta_{yx}). \tag{5·28}$$

Both these operators are invariant under $C_3$, and each is Hermitian. It follows from this and from (5·28) that their off-diagonal elements between $|e_+\rangle$ and $|e_-\rangle$ vanish identically, leaving

$$\langle e_\pm|\beta_{-11}|e_\pm\rangle = \begin{bmatrix} \beta+\epsilon Q_1 & 0 \\ 0 & -\beta-\epsilon Q_1 \end{bmatrix}, \quad \langle e\pm|\beta_{1-1}|e_\pm\rangle = \begin{bmatrix} -\beta-\epsilon Q_1 & 0 \\ 0 & \beta+\epsilon Q_1 \end{bmatrix} \qquad (5·29)$$

as the most general first-order expansions in the vibrational co-ordinates. In terms of the real wave functions, therefore,

$$\beta+\epsilon Q_1 = \langle e_a|\beta_{xy}|e_b\rangle = \langle e_b|\beta_{yx}|e_a\rangle, \qquad (5·30)$$

where $\beta_{xy}$ is defined by an equation like (5·20). Thus the quantities $\beta$ and $\epsilon$, unlike the $\alpha$'s, the $\gamma$'s and the $\delta$'s, cannot be regarded as real polarizabilities or derivatives thereof; they are inescapably off-diagonal elements of polarizability operators in a basis of real electronic functions. They may, however, be of the same order of magnitude as the $\alpha$'s and $\delta$'s, and therefore cannot be neglected in any complete discussion of the Raman effect in Jahn–Teller molecules. From (5·29) it follows that for $v_1' = v_1''$

$$\langle n'|\beta_{-11}|n''\rangle = -\langle n'|\beta_{1-1}|n''\rangle = \beta d, \qquad (5·31)$$

and for $v_1' = v_1''+1$

$$\langle n'|\beta_{-11}|n''\rangle = -\langle n'|\beta_{1-1}|n''\rangle = \epsilon d\langle v_1''+1|Q_1|v_1''\rangle. \qquad (5·32)$$

Armed with equations (5·26), (5·27), (5·31) and (5·32) we are now in a position to calculate the intensities of the various Raman lines; we first consider Rayleigh scattering, which may be regarded as a special case of the Raman effect.

In Rayleigh scattering the vibronic energy does not change, but if the molecule is initially in the state $|v_1, v_2, j\rangle = |0, 0, \frac{1}{2}\rangle$, its final state may be either $|0, 0, \frac{1}{2}\rangle$ or $|0, 0, -\frac{1}{2}\rangle$. Referring to (5·17), (5·18) and (5·19), and using the selection rules on $a$, $b$, $c$, $d$ and $e$, we find that the Rayleigh scattering coefficients from $|0, 0, \frac{1}{2}\rangle$ into $|0, 0, \frac{1}{2}\rangle$ are

$$\left.\begin{aligned} G^0 &= \tfrac{1}{3}|2(\alpha_1+\gamma_1 b)+(\alpha_3+\gamma_3 b)|^2, \\ G^s &= 2|(\alpha_1+\gamma_1 b)-\tfrac{1}{3}(2\alpha_1+2\gamma_1 b+\alpha_3+\gamma_3 b)|^2+|(\alpha_3+\gamma_3 b)-\tfrac{1}{3}(2\alpha_1+2\gamma_1 b+\alpha_3+\gamma_3 b)|^2, \\ G^a &= 2\,|\beta d|^2, \end{aligned}\right\} \qquad (5·33)$$

and the coefficients for scattering from $|0, 0, \frac{1}{2}\rangle$ into $|0, 0, -\frac{1}{2}\rangle$ are

$$\left.\begin{aligned} G^0 = 0, \quad G^a &= 0, \\ G^s &= |2\alpha_2 e+\gamma_2 a|^2, \end{aligned}\right\} \qquad (5·34)$$

where the two terms in $G^s$ both arise from $\alpha_{-1-1}$. Since all the quantities on the right are real, the net result is

$$\left.\begin{aligned} G^0 &= \tfrac{1}{3}\{(2\alpha_1+\alpha_3)+(2\gamma_1+\gamma_3)\,b\}^2, \\ G^s &= \tfrac{2}{3}\{(\alpha_1-\alpha_3)+(\gamma_1-\gamma_3)\,b\}^2+\{2\alpha_2 e+\gamma_2 a\}^2, \\ G^a &= 2\{\beta d\}^2. \end{aligned}\right\} \qquad (5·35)$$

The average cross-section for Rayleigh scattering, per molecule, is therefore

$$\sigma = 64\pi^4 \nu_s^4 c^{-4}\{2(\alpha_1+\gamma_1 b)^2+(\alpha_3+\gamma_3 b)^2+(2\alpha_2 e+\gamma_2 a)^2+2(\beta d)^2\}. \qquad (5·36)$$

In this expression the quantities $a$ and $b$ are actually equal, for the reasons indicated in equation (2·44). But the terms in $\alpha_2$ and $\gamma_2$ have a different physical origin from the others, since they arise from a type of scattering in which the vibronic state changes. The other novel feature of (5·36) is the appearance of a term, $2\beta^2 d^2$, arising from pseudo-vector scattering; the light scattered by this mechanism has a polarization opposite to that of the incident light.

We now investigate the intensity of the fundamental band of the totally symmetric vibration $Q_1$. The calculation proceeds along parallel lines to that for Rayleigh scattering, since in (5·23) and (5·29) terms linear in $Q_1$ appear in the same places as the constants $\alpha_1$, $\alpha_2$, $\alpha_3$ and $\beta$, and nowhere else. Using the formula

$$\langle 1 | Q_1 | 0 \rangle = \surd(\hbar/2\omega_1), \tag{5·37}$$

we deduce that the net cross-section for the two Raman transitions $|1, 0, \pm\tfrac{1}{2}\rangle \leftarrow |0, 0, \tfrac{1}{2}\rangle$ is

$$\sigma = \frac{64\pi^4\nu_s^4}{c^4}\frac{\hbar}{2\omega_1}(2\delta_1^2 + \delta_3^2 + 4\delta_2^2 e^2 + 2\epsilon^2 d^2), \tag{5·38}$$

where $d$ and $e$ have the same definitions as in (5·36). Here the terms in $\delta_1$ and $\delta_3$ parallel those found in electronically non-degenerate molecules; $4\delta_2^2 e^2$ arises from a change in $j$ during the scattering process; $2\epsilon^2 d^2$ makes a reverse-polarized contribution to the scattered beam.

There are also two sets of combination bands in which one quantum of $Q_1$ is excited together with one or more quanta of $Q_2$. For one of these

$$|j'| = \tfrac{1}{2} \quad \text{and} \quad \sigma = \frac{64\pi^4\nu_s^4}{c^4}\frac{\hbar}{2\omega_1}(4\delta_2^2 e^2 + 2\epsilon^2 d^2), \tag{5·39}$$

and for the other

$$|j'| = \tfrac{3}{2} \quad \text{and} \quad \sigma = \frac{64\pi^4\nu_s^4}{c^4}\frac{\hbar}{2\omega_1} 4\delta_2^2 e^{*2}, \tag{5·40}$$

where now

$$d = \langle v_2', \tfrac{1}{2}{}_+ | 0, \tfrac{1}{2}{}_+ \rangle - \langle v_2', \tfrac{1}{2}{}_- | 0, \tfrac{1}{2}{}_- \rangle, \quad e = \langle v_2', -\tfrac{1}{2}{}_- | 0, \tfrac{1}{2}{}_+ \rangle, \quad e^* = \langle v_2', \tfrac{3}{2}{}_+ | 0, \tfrac{1}{2}{}_- \rangle.$$

Such combination bands will therefore be much weaker than the fundamental, but since, for the first set, the scattering coefficient contains a pseudo-vector term with no scalar term, they will be *reverse*-polarized, with depolarization ratio $\rho_n$ greater than $\tfrac{6}{7}$. This phenomenon is peculiar to molecules in electronically degenerate states.

There remain the Raman transitions in which one or more quanta of $Q_2$ are excited but $Q_1$ remains unexcited. For these, according to (5·26) and (5·31),

$$\left.\begin{aligned} G^0 &= \tfrac{1}{3}|(2\gamma_1 + \gamma_3)\, b|^2, \\ G^s &= 2|\gamma_1 b - \tfrac{1}{3}(2\gamma_1 + \gamma_3)\, b|^2 + |\gamma_3 b - \tfrac{1}{3}(2\gamma_1 + \gamma_3)\, b|^2 + |2\alpha_2 e + \gamma_2 a + 2\gamma_4 c^*|^2 \\ &\qquad + |2\alpha_2 e^* + \gamma_2 a^* + 2\gamma_4 c|^2, \\ G^a &= 2\,|\beta d|^2. \end{aligned}\right\} \tag{5·41}$$

We now assume the initial state to be the $j = \tfrac{1}{2}$ component of the ground vibronic doublet, and consider separately the following types of transition.

For $j' = j'' = \tfrac{1}{2}$, $a$, $a^*$, $c$, $c^*$, $e$ and $e^*$ vanish, so that

$$G = G^0 + G^s + G^a = (2\gamma_1^2 + \gamma_3^2)\, b^2 + 2\beta^2 d^2. \tag{5·42}$$

For $j' = j'' + 1 = \tfrac{3}{2}$, $a^*$ and $e^*$ are the only non-vanishing primitive elements, and therefore

$$G = G^s = (2\alpha_2 e^* + \gamma_2 a^*)^2. \tag{5·43}$$

For $j' = j''+2 = \frac{5}{2}$, $c^*$ is the only non-vanishing primitive element and

$$G = G^s = 4\gamma_4^2 c^{*2}. \tag{5·44}$$

For $j' = j''-1 = -\frac{1}{2}$ $$G = G^s = (2\alpha_2 e + \gamma_2 a)^2. \tag{5·45}$$

For $j' = j''-2 = -\frac{3}{2}$ $$G = G^s = 4\gamma_4^2 c^2. \tag{5·46}$$

Therefore when $|j''| = \frac{1}{2}$, we obtain the following intensity expressions for the three components of the fundamental of $Q_2$

$$|j'| = \tfrac{1}{2}: \quad G = (2\gamma_1^2+\gamma_3^2)\, b^2 + (2\alpha_2 e + \gamma_2 a)^2 + 2\beta^2 d^2, \tag{5·47}$$

$$|j'| = \tfrac{3}{2}: \quad G = (2\alpha_2 e^* + \gamma_2 a^*)^2 + 4\gamma_4^2 c^2, \tag{5·48}$$

$$|j'| = \tfrac{5}{2}: \quad G = 4(\gamma_4 c^*)^2. \tag{5·49}$$

In (5·47), because of (2·44), the elements $a$ and $b$ are actually equal. But $a^*$ in (5·48) bears no exact relation to $a$ in (5·47), because different transitions are involved in the two cases, nor is there any exact relation between $c$ in (5·48) and $c^*$ in (5·49).

An interesting feature of (5·47) and (5·48) is the presence of terms in $\alpha_2$ and $\beta$, when the coupling is of intermediate strength. According to (5·25) $\alpha_2$ is one-half the difference between the values of $\alpha_{xx}$ and $\alpha_{yy}$ for the real electronic state $|e_a\rangle$. It is as though, in intermediate coupling, the cyclic motion in the co-ordinate $\phi$ has the effect of rotating the electronic polarizability ellipsoid inside the molecule, so that the Raman intensity depends on a term of the same type as determines the intensity of a rotational Raman transition. The term in $\beta$ has no parallel in the non-degenerate case; it represents the contribution of the pseudo-vector scattering.

It can be asserted with confidence that in intermediate coupling the overtones of $Q_2$ will be very strong, and may indeed be much stronger than the fundamental. To show what happens we present in figure 10 a series of synthetic Raman spectra, based on (5·47) and (5·48), for various values of the first-order distortion parameter $D$. Again we have entirely neglected second-order coupling and, as in figure 9, the arrow marks the vertical excitation energy from the bottom of the moat, to the upper branch of the potential energy surface. In constructing figure 10 we adopted the following values for the molecular constants, again suggested by a rough calculation on $C_3H_3$

$$\alpha_1 = \beta = 5{\cdot}0\,\text{Å}^3, \quad \alpha_2 = 2{\cdot}5\,\text{Å}^3, \quad \alpha_3 = 2{\cdot}0\,\text{Å}^3,$$

$$\sqrt{\{(2\gamma_1^2+\gamma_3^2)\,\hbar/\omega_2\}} = 1{\cdot}0\,\text{Å}^3, \quad \gamma_2\sqrt{(\hbar/\omega_2)} = 0{\cdot}35\,\text{Å}^3, \quad \gamma_4 = 0,$$

$$\delta_1\sqrt{(\hbar/\omega_1)} = 0{\cdot}7\,\text{Å}^3, \quad \delta_2\sqrt{(\hbar/\omega_1)} = \epsilon\sqrt{(\hbar/\omega_1)} = 0{\cdot}35\,\text{Å}^3, \quad \delta_3\sqrt{(\hbar/\omega_1)} = 0{\cdot}15\,\text{Å}^3,$$

$$\omega_1/2\pi c = 1200\,\text{cm}^{-1}, \quad \omega_2/2\pi c = 900\,\text{cm}^{-1}, \quad \nu = 30\,000\,\text{cm}^{-1}.$$

The abscissa is the Stokes frequency shift in $\text{cm}^{-1}$; the ordinate is the molecular cross-section in units of $10^{-26}\,\text{cm}^2$. With the above values of the molecular constants it turns out that the fundamental of $Q_1$ and its combination bands with $Q_2$ are rather weak compared to the fundamental of $Q_2$ and its overtones. Figure 10 (*a*) to (*g*) therefore only shows those Raman lines which arise from excitation of $Q_2$ alone, although in general $Q_1$ will probably appear with fairly high intensity in the spectrum. The lines above the axis refer to transitions of the type $|j| = \frac{1}{2} \leftarrow \frac{1}{2}$, and those below to transitions for which $|j| = \frac{3}{2} \leftarrow \frac{1}{2}$.

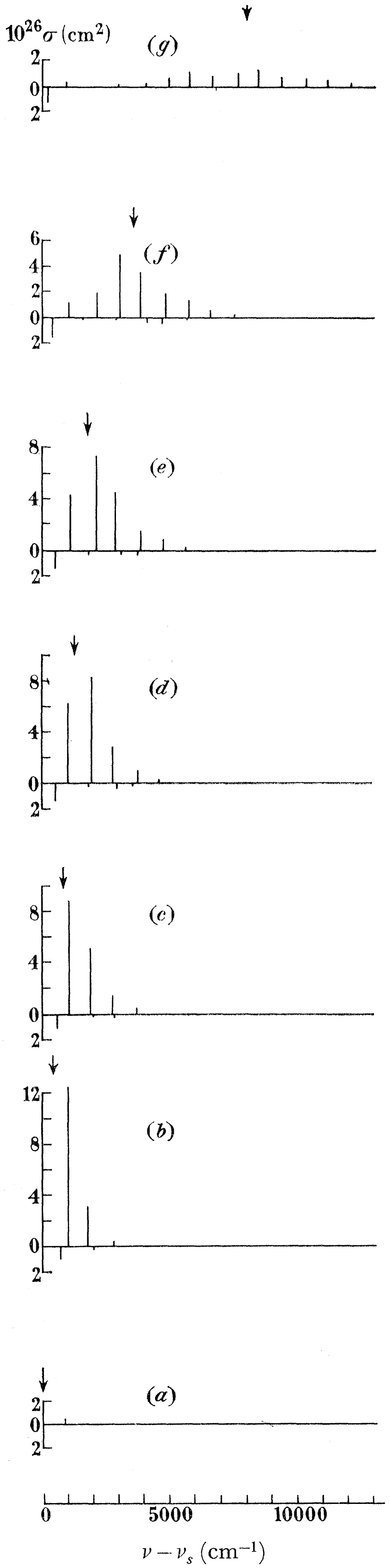

FIGURE 10. A series of synthetic Raman spectra for $X_3$, calculated for (*a*) $D = 0$; (*b*) $D = 0{\cdot}125$; (*c*) $D = 0{\cdot}25$; (*d*) $D = 0{\cdot}375$; (*e*) $D = 0{\cdot}50$; (*f*) $D = 1{\cdot}0$; (*g*) $D = 2{\cdot}5$. Lines above the axis refer to transitions for which $|j| = \frac{1}{2} \leftarrow \frac{1}{2}$; those below refer to transitions for which $|j| = \frac{3}{2} \leftarrow \frac{1}{2}$; lines involving the symmetric vibration have not been plotted, nor lines for which $|j| = \frac{5}{2} \leftarrow \frac{1}{2}$.

The outstanding feature of figure 10 is again the very high intensity of certain overtones of $Q_2$, especially those in the neighbourhood of the vertical excitation energy. These transitions owe their high intensity to the terms in $\alpha_2$ and $\beta$ in (5·47) and (5·48), terms which have no analogue for non-degenerate electronic states. Spectra of this kind are expected from species in which purely electronic Raman transitions are possible between the components of a degenerate electronic state, and from this point of view the spectra presented in figure 10 may be regarded as electronic Raman spectra exhibiting vibrational structure.

Another characteristic feature of these synthetic spectra is the doubling of each Raman line—a direct manifestation of the dynamical Jahn–Teller effect.

As with the infra-red spectrum, for large values of $D$ the fundamental of $Q_2$ has a 'normal' intensity. This is because in (5·47) and (5·48) the terms in $\alpha_2$ and $\beta$ become very small for the transitions $u_2 = 1 \leftarrow 0$, while the coefficients of $\gamma_1$, $\gamma_2$, $\gamma_3$ and $\gamma_4$, which are ordinary polarizability derivatives, are of the same order of magnitude as in non-degenerate situations. For example, when $u_2'' = 0$,

$$(\gamma_2 a)^2 \simeq \gamma_2^2 |\langle u_2''+1|r|u_2''\rangle|^2 \simeq \gamma_2^2 \hbar/2\omega_2.$$

In these circumstances only a search at higher values of $\nu$ would reveal the true nature of the Raman spectrum.

We will summarize in the next section the group-theoretical rules for Raman activity; but a remark should be made at this point about the reverse-polarized scattering. The cross-section for this is determined by the matrix elements of an operator

$$\beta_{-11} = \tfrac{1}{2}\mathrm{i}\{M_x f^a(H)\, M_y - M_y f^a(H)\, M_x\} = -\beta_{1-1} \tag{5·50}$$

having the property that

$$\langle e_a|\beta_{-11}|e_b\rangle = -\langle e_b|\beta_{-11}|e_a\rangle. \tag{5·51}$$

Terms linear in a normal co-ordinate $Q_i$ can therefore appear in the matrix $\langle e_\pm|\beta_{-11}|e_\pm\rangle$ only if the species of $Q_i$ is included in the *antisymmetrized* square, $\{\Gamma^2\}$, of the electronic species $\Gamma$. This is the essential reason why a term in $Q_1$ (and a constant term) appears in (5·28), but no terms in $Q_\pm$.

## 6. Generalizations

Our results may be generalized as follows:

(1) A symmetric top molecule will exhibit a dipole moment perpendicular to its axis if $[\Gamma^2]$, the symmetrized square of the electronic species, includes $\Gamma_\perp$, the representation generated by $(M_x, M_y)$. This is the case for molecules of symmetry $C_{3v}$ or $D_3$ in $E$ states, for $D_{3h}$ molecules in $E'$ or $E''$ states, for $D_{5h}$ molecules in $E_2'$ or $E_2''$ states, for $D_{7h}$ molecules in $E_3'$ or $E_3''$ states, etc. It cannot, however, happen with molecules of symmetry $D_{3d}$, $D_{4h}$, $D_{5d}$, $D_{6h}$, etc., since such molecules have centres of symmetry.

The presence of a perpendicular dipole moment is manifested in a first-order Stark effect and a pure rotation spectrum for which the selection rule on $K$ is $\Delta K = \pm 1$.

(2) A symmetric-top molecule with dihedral symmetry will exhibit an anomalous dipole moment parallel to its figure axis if $[\Gamma^2]$ includes $\Gamma_\parallel$, the species of $M_z$. This is the case for molecules of symmetry $C_{4v}$ or $D_{2d}$ in $E$ states, for $D_{4d}$ molecules in $E_2$ states, etc. (The symmetry group must comprise a four-fold axis of rotation or alternation, but must not include a centre of symmetry.) Again there is a first-order Stark effect and a pure rotation spectrum; but the selection rule for $K$ is now $\Delta K = 0$.

(3) In the infra-red spectrum a vibration of species $\gamma$ will appear as a fundamental if $\gamma$ is included in $[\Gamma^2]\times\Gamma_{\parallel}$ or in $[\Gamma^2]\times\Gamma_{\perp}$. In the former case the transition is seen as a parallel band, in the latter as a perpendicular band.

If a Jahn–Teller vibration (i.e. one belonging to $[\Gamma^2]-\Gamma_0$) is itself infra-red active, its fundamental will split into two or more bands of comparable intensity, because of the degeneracy of the first excited state being lifted by the vibronic interaction. The overtones will likewise be split, and in intermediate coupling may dominate the fundamental in intensity.

If the molecule has an anomalous dipole moment perpendicular to its axis, the totally symmetric vibrations are infra-red active and their fundamentals will appear as perpendicular bands. The intensity of a Jahn–Teller active vibration will in this case be found to depend not only on a dipole moment derivative but also on the magnitude of the anomalous dipole moment itself—as though the dipole moment were rotating inside the molecule. The case of an anomalous parallel moment we have not considered in detail, but similar effects are to be expected.

(4) In the Raman spectrum a vibration of species $\gamma$ will appear as a fundamental if $\gamma$ is included in $[\Gamma^2]$, $[\Gamma^2]\times\Gamma_s$ or $\{\Gamma^2\}\times\Gamma_a$. In table 2 the columns headed $\gamma_0$, $\gamma_s$ and $\gamma_a$ give the species of those vibrations which satisfy these three conditions. A new feature is the vibrations of species $\gamma_a$, for which the pseudo-vector scattering coefficient $G^a$ does not vanish; and if the species of a vibration appears under $\gamma_a$ but not under $\gamma_0$ it will give rise to a reverse-polarized line in the Raman spectrum ($\rho_n > \frac{6}{7}$).

The Jahn–Teller vibrations themselves are always Raman active; since their species necessarily appear under $\gamma_0$, but seldom under $\gamma_a$, they will usually give rise to partly polarized lines, a privilege normally reserved for totally symmetric vibrations. As in the infra-red spectrum, the fundamental of a Jahn–Teller vibration and its strong overtones will split into two or more series of lines, because of the vibrational degeneracy of the two-dimensional oscillator having been removed by the vibronic coupling.

Apart from these qualitative generalizations, is it possible to make any estimates of the relative intensities of the various lines in the vibrational spectra of a Jahn–Teller molecule? Thorson (1958) has discussed this question, with reference to the infra-red spectra of octahedral molecules, and his conclusions probably have general validity. Hence, as far as the infra-red is concerned the Jahn–Teller vibrations may give rise to strong bands, but the intensities of other vibrations should be much the same, in weak coupling, as if the molecule were non-degenerate. In strong coupling, of course, one expects the spectrum to become that of a molecule of lower symmetry.

The same can be anticipated in the Raman spectrum. Apart from the Jahn–Teller vibrations, which may give strong bands, the strongest fundamentals will, in all probability, be those which would be the strongest if there were no electronic degeneracy (i.e. if the valency shell were closed by the addition or removal of one or two electrons). In strong coupling, one should obtain the normal Raman spectrum of a less symmetrical molecule.

As to actual molecules exhibiting the Jahn–Teller effect in their infra-red and Raman spectra, an obvious field of study is the complexes of the transition elements, which have already been subjected to close scrutiny by many workers for signs of the dynamical Jahn–Teller effect. So far there is no compelling evidence for or against the quantitative dynamical

Table 2. The Raman active vibrations of symmetric-top molecules in degenerate electronic states

| | $\Gamma_0$ | $\Gamma_s$ | $\Gamma_a$ | $\Gamma$ | $[\Gamma^2]-\Gamma_0$ | $\{\Gamma^2\}$ | $\gamma_0$ | $\gamma_s$ | $\gamma_a$ |
|---|---|---|---|---|---|---|---|---|---|
| $D_3$ | $A_1$ | $A_1+2E$ | $A_2+E$ | $E$ | $E$ | $A_2$ | $A_1, E$ | $A_1, A_2, E$ | $A_1, E$ |
| $C_{3v}$ | $A_1$ | $A_1+2E$ | $A_2+E$ | $E$ | $E$ | $A_2$ | $A_1, E$ | $A_1, A_2, E$ | $A_1, E$ |
| $C_{4v}$ | $A_1$ | $A_1+B_1+B_2+E$ | $A_2+E$ | $E$ | $B_1+B_2$ | $A_2$ | $A_1, B_1, B_2$ | $A_1, A_2, B_1, B_2, E$ | $A_1, E$† |
| $D_{2d}$ | $A_1$ | $A_1+B_1+B_2+E$ | $A_2+E$ | $E$ | $B_1+B_2$ | $A_2$ | $A_1, B_1, B_2$ | $A_1, A_2, B_1, B_2, E$ | $A_1, E$† |
| $D_{3d}$ | $A_{1g}$ | $A_{1g}+2E_g$ | $A_{2g}+E_g$ | $E_g, E_u$ | $E_g$ | $A_{2g}$ | $A_{1g}, E_g$ | $A_{1g}, A_{2g}, E_g$ | $A_{1g}, E_g$ |
| $D_{4d}$ | $A_1$ | $A_1+E_2+E_3$ | $A_2+E_1$ | $E_1, E_3$ | $E_2$ | $A_2$ | $A_1, E_2$ | $A_1, A_2, B_1, B_2, E_1, E_2, E_3$ | $A_1, E_1$† |
| | | | | $E_2$ | $B_1+B_2$ | $A_2$ | $A_1, B_1, B_2$ | $A_1, B_1, B_2, E_1, E_2, E_3$ | $A_1, E_1$† |
| $D_{5d}$ | $A_{1g}$ | $A_{1g}+E_{1g}+E_{2g}$ | $A_{2g}+E_{1g}$ | $E_{1g}, E_{1u}$ | $E_{2g}$ | $A_{2g}$ | $A_{1g}, E_{2g}$ | $A_{1g}, A_{2g}, E_{1g}, E_{2g}$ | $A_{1g}, E_{1g}$† |
| | | | | $E_{2g}, E_{2u}$ | $E_{1g}$ | $A_{2g}$ | $A_{1g}, E_{1g}$ | $A_{1g}, A_{2g}, E_{1g}, E_{2g}$ | $A_{1g}, E_{1g}$ |
| $D_{3h}$ | $A_1'$ | $A_1'+E'+E''$ | $A_2'+E''$ | $E', E''$ | $E'$ | $A_2'$ | $A_1', E'$ | $A_1', A_1'', A_2', A_2'', E', E''$ | $A_1', E''$† |
| $D_{4h}$ | $A_{1g}$ | $A_{1g}+B_{1g}+B_{2g}+E_g$ | $A_{2g}+E_g$ | $E_g, E_u$ | $B_{1g}+B_{2g}$ | $A_{2g}$ | $A_{1g}, B_{1g}, B_{2g}$ | $A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_g$ | $A_{1g}, E_g$† |
| $D_{5h}$ | $A_1'$ | $A_1'+E_1''+E_2'$ | $A_2'+E_1''$ | $E_1', E_1''$ | $E_2'$ | $A_2'$ | $A_1', E_2'$ | $A_1', A_2', E_1', E_1'', E_2', E_2''$ | $A_1', E_1''$† |
| | | | | $E_2', E_2''$ | $E_1'$ | $A_2'$ | $A_1', E_1'$ | $A_1', A_1'', A_2'', E_1', E_1'', E_2', E_2''$ | $A_1', E_1''$† |
| $D_{6h}$ | $A_{1g}$ | $A_{1g}+E_{1g}+E_{2g}$ | $A_{2g}+E_{1g}$ | $E_{1g}, E_{1u}, E_{2g}, E_{2u}$ | $E_{2g}$ | $A_{2g}$ | $A_{1g}, E_{2g}$ | $A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1g}, E_{2g}$ | $A_{1g}, E_{1g}$† |
| $D_{7h}$ | $A_1'$ | $A_1'+E_1''+E_2'$ | $A_2'+E_1''$ | $E_1', E_1''$ | $E_2'$ | $A_2'$ | $A_1', E_2'$ | $A_1', A_2', E_1'', E_2', E_3', E_3''$ | $A_1', E_1''$† |
| | | | | $E_2', E_2''$ | $E_3'$ | $A_2'$ | $A_1', E_3'$ | $A_1', E_1', E_1'', E_2', E_2'', E_3', E_3''$ | $A_1', E_1''$† |
| | | | | $E_3', E_3''$ | $E_1'$ | $A_2'$ | $A_1', E_1'$ | $A_1', A_1'', A_2'', E_1', E_2', E_2'', E_3'$ | $A_1', E_1''$† |

$\Gamma_0$ is the totally symmetric representation, $\Gamma_s$ that of a traceless symmetric tensor, $\Gamma_a$ that of an antisymmetric tensor. $[\Gamma^2]$ and $\{\Gamma^2\}$ denote the symmetrized and antisymmetrized square of $\Gamma$, the electronic species. $\gamma_0, \gamma_s, \gamma_a$ indicate the species of those vibrations for which $G^0 > 0$, $G^s > 0$, $G^a > 0$. † indicates the species of those vibrations which give reverse-polarized Raman fundamentals ($\rho_n > \frac{6}{7}$).

Table 3. The infra-red and Raman activity of the vibrations of tetrahedral molecules in electronically degenerate states (neglecting spin-orbit coupling)

In $T_d$, $\Gamma_0 = A_1$, $\Gamma_M = T_2$, $\Gamma_s = E+T_2$, $\Gamma_a = T_1$

(i) $\Gamma = E$, $[\Gamma^2] = A_1+E$, $\{\Gamma^2\} = A_2$

| | infra-red activity | $G^0$ | $G^s$ | $G^a$ |
|---|---|---|---|---|
| $A_1$ | 0 | + | + | 0 |
| $A_2$ | 0 | 0 | + | 0 |
| $E$ | 0 | + | + | 0 |
| $T_1$ | + | 0 | + | 0 |
| $T_2$ | + | 0 | + | + |

There is no dipole moment or microwave spectrum.

(ii) $\Gamma = T_1$ or $T_2$, $[\Gamma^2] = A_1+E+T_2$, $\{\Gamma^2\} = T_1$

| | infra-red activity | $G^0$ | $G^s$ | $G^a$ |
|---|---|---|---|---|
| $A_1$ | + | + | + | + |
| $A_2$ | 0 | 0 | + | 0 |
| $E$ | + | + | + | + |
| $T_1$ | + | 0 | + | + |
| $T_2$ | + | + | + | + |

The molecule also exhibits a dipole moment and a microwave spectrum.

Table 4. The infra-red and Raman activity of the vibrations of octahedral molecules in electronically degenerate states (neglecting spin-orbit coupling)

In $O_h$, $\Gamma_0 = A_{1g}$, $\Gamma_M = T_{1u}$, $\Gamma_s = E_g+T_{2g}$, $\Gamma_a = T_{1g}$

(i) $\Gamma = E_g$ or $E_u$, $[\Gamma^2] = A_{1g}+E_g$, $\{\Gamma^2\} = A_{2g}$

| | infra-red activity | $G^0$ | $G^s$ | $G^a$ |
|---|---|---|---|---|
| $A_{1u}$ | 0 | 0 | 0 | 0 |
| $A_{2u}$ | 0 | 0 | 0 | 0 |
| $E_u$ | 0 | 0 | 0 | 0 |
| $T_{1u}$ | + | 0 | 0 | 0 |
| $T_{2u}$ | + | 0 | 0 | 0 |
| $A_{1g}$ | 0 | + | + | 0 |
| $A_{2g}$ | 0 | 0 | + | 0 |
| $E_g$ | 0 | + | + | 0 |
| $T_{1g}$ | 0 | 0 | + | 0 |
| $T_{2g}$ | 0 | 0 | + | + |

There is no dipole moment or microwave spectrum.

(ii) $\Gamma = T_{1g}$, $T_{2g}$, $T_{1u}$ or $T_{2u}$, $[\Gamma^2] = A_{1g}+E_g+T_{2g}$, $\{\Gamma^2\} = T_{1g}$

| | infra-red activity | $G^0$ | $G^s$ | $G^a$ |
|---|---|---|---|---|
| $A_{1u}$ | 0 | 0 | 0 | 0 |
| $A_{2u}$ | + | 0 | 0 | 0 |
| $E_u$ | + | 0 | 0 | 0 |
| $T_{1u}$ | + | 0 | 0 | 0 |
| $T_{2u}$ | + | 0 | 0 | 0 |
| $A_{1g}$ | 0 | + | + | + |
| $A_{2g}$ | 0 | 0 | + | 0 |
| $E_g$ | 0 | + | + | + |
| $T_{1g}$ | 0 | 0 | + | + |
| $T_{2g}$ | 0 | + | + | + |

There is no dipole moment or microwave spectrum.

theory, though Forman & Orgel (1959) have almost certainly found an example of a split fundamental in the infra-red spectrum of manganic acetyl-acetonate. For completeness, therefore, we give in tables 3 and 4 the relevant group-theoretical results for molecules of symmetry $T_d$ and $O_h$. It is to be firmly stressed that these tables have little or no relevance to the important case of strong spin-orbit coupling; but when the electronic degeneracy is due to an odd electron or hole in an $E$ orbital, spin-orbit coupling is of secondary importance, so that for $E$ states at least these tables have some interest. The points of most interest are perhaps the following:

(1) If a tetrahedral molecule is in an $E$ state all its vibrations are Raman active; those of species $T_2$ are reverse-polarized.

(2) If an octahedral molecule is in an $E_g$ or $E_u$ state all its $g$ vibrations are Raman active; those of species $T_{2g}$ are reverse-polarized.

(3) A tetrahedral molecule in a $T_1$ or $T_2$ state should have an apparent dipole moment, and exhibit a pure rotation spectrum.

It will be of great interest to see whether these somewhat novel expectations are borne out by experiment.

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## APPENDIX

Tables A 1 to A 6 give the numerical values of the following primitive matrix elements, for various values of the first-order distortion parameter $D$

$$
\begin{aligned}
a_0(v_2,-\tfrac{1}{2}) &= (\langle v_2,-\tfrac{1}{2}_{+}|\,Q_-\,|0,\tfrac{1}{2}_{+}\rangle+\langle v_2,-\tfrac{1}{2}_{-}|\,Q_-\,|0,\tfrac{1}{2}_{-}\rangle)\,\surd(\omega_2/\hbar),\\
a_0^*(v_2,\tfrac{3}{2}) &= (\langle v_2,\tfrac{3}{2}_{+}|\,Q_+\,|0,\tfrac{1}{2}_{+}\rangle+\langle v_2,\tfrac{3}{2}_{-}|\,Q_+\,|0,\tfrac{1}{2}_{-}\rangle)\,\surd(\omega_2/\hbar),\\
b_0(v_2,\tfrac{1}{2}) &= (\langle v_2,\tfrac{1}{2}_{-}|\,Q_+\,|0,\tfrac{1}{2}_{+}\rangle+\langle v_2,\tfrac{1}{2}_{+}|\,Q_-\,|0,\tfrac{1}{2}_{-}\rangle)\,\surd(\omega_2/\hbar)\\
&= a_0(v_2,-\tfrac{1}{2}),\\
c_0(v_2,-\tfrac{3}{2}) &= (\langle v_2,-\tfrac{3}{2}_{-}|\,Q_-\,|0,\tfrac{1}{2}_{+}\rangle)\,\surd(\omega_2/\hbar),\\
d(v_2,\tfrac{1}{2}) &= \langle v_2,\tfrac{1}{2}_{+}|0,\tfrac{1}{2}_{+}\rangle-\langle v_2,\tfrac{1}{2}_{-}|0,\tfrac{1}{2}_{-}\rangle,\\
e(v_2,-\tfrac{1}{2}) &= \langle v_2,-\tfrac{1}{2}_{-}|0,\tfrac{1}{2}_{+}\rangle,\\
e^*(v_2,\tfrac{3}{2}) &= \langle v_2,\tfrac{3}{2}_{+}|0,\tfrac{1}{2}_{-}\rangle.
\end{aligned}
$$

TABLE A 1. VALUES OF $a_0(v_2,-\tfrac{1}{2}) = b_0(v_2,\tfrac{1}{2})$

| | $D$ = 0·000 | 0·125 | 0·250 | 0·375 | 0·500 | 1·000 | 2·500 |
|---|---|---|---|---|---|---|---|
| $v_2$ = 0 | −0·000 | −0·831 | −1·051 | −1·190 | −1·297 | −1·608 | −2·288 |
| 1 | 1·000 | 0·838 | 0·759 | 0·714 | 0·690 | 0·665 | 0·690 |
| 2 | 0·000 | 0·059 | 0·111 | 0·132 | 0·133 | 0·089 | 0·029 |
| 3 | 0·000 | 0·008 | 0·021 | 0·037 | 0·052 | 0·068 | 0·010 |
| 4 | 0·000 | 0·002 | 0·008 | 0·012 | 0·017 | 0·038 | 0·018 |
| 5 | 0·000 | 0·000 | 0·002 | 0·005 | 0·009 | 0·018 | 0·016 |
| 6 | 0·000 | 0·000 | 0·000 | 0·002 | 0·003 | 0·013 | 0·015 |
| 7 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·006 | 0·015 |
| 8 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·004 | 0·012 |
| 9 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·007 |
| 10 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·005 |

TABLE A2. VALUES OF $a_0^*(v_2, \frac{3}{2})$

| | $D =$ 0·000 | 0·125 | 0·250 | 0·375 | 0·500 | 1·000 | 2·500 |
|---|---|---|---|---|---|---|---|
| $v_2 = 1$ | 1·000 | 1·181 | 1·299 | 1·392 | 1·472 | 1·736 | 2·365 |
| 2 | 0·000 | 0·040 | 0·061 | 0·078 | 0·095 | 0·160 | 0·342 |
| 3 | 0·000 | 0·014 | 0·033 | 0·040 | 0·039 | 0·031 | 0·032 |
| 4 | 0·000 | 0·001 | 0·006 | 0·017 | 0·029 | 0·028 | 0·005 |
| 5 | 0·000 | 0·000 | 0·002 | 0·004 | 0·007 | 0·030 | 0·009 |
| 6 | 0·000 | 0·000 | 0·001 | 0·002 | 0·004 | 0·009 | 0·010 |
| 7 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·007 | 0·014 |
| 8 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·004 | 0·010 |
| 9 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·009 |
| 10 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·011 |
| 11 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·018 |
| 12 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 |
| 13 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·005 |
| 14 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·005 |

TABLE A3. VALUES OF $c_0(v_2, -\frac{3}{2})$

| | $D =$ 0·000 | 0·125 | 0·250 | 0·375 | 0·500 | 1·000 | 2·500 |
|---|---|---|---|---|---|---|---|
| $v_2 = 1$ | 1·000 | 0·890 | 0·868 | 0·868 | 0·877 | 0·946 | 1·209 |
| 2 | 0·000 | 0·352 | 0·245 | 0·168 | 0·117 | 0·004 | 0·148 |
| 3 | 0·000 | 0·321 | 0·462 | 0·450 | 0·344 | 0·103 | 0·006 |
| 4 | 0·000 | 0·100 | 0·205 | 0·343 | 0·471 | 0·306 | 0·027 |
| 5 | 0·000 | 0·060 | 0·144 | 0·188 | 0·219 | 0·503 | 0·035 |
| 6 | 0·000 | 0·015 | 0·072 | 0·167 | 0·243 | 0·268 | 0·094 |
| 7 | 0·000 | 0·006 | 0·027 | 0·060 | 0·228 | 0·375 | 0·343 |
| 8 | 0·000 | 0·001 | 0·014 | 0·041 | 0·219 | 0·278 | 0·290 |
| 9 | 0·000 | 0·000 | 0·004 | 0·015 | 0·243 | 0·164 | 0·253 |
| 10 | 0·000 | 0·000 | 0·002 | 0·007 | 0·117 | 0·167 | 0·511 |
| 11 | 0·000 | 0·000 | 0·000 | 0·003 | 0·070 | 0·076 | 0·413 |
| 12 | 0·000 | 0·000 | 0·000 | 0·002 | 0·043 | 0·060 | 0·331 |
| 13 | 0·000 | 0·000 | 0·000 | 0·000 | 0·016 | 0·035 | 0·482 |
| 14 | 0·000 | 0·000 | 0·000 | 0·000 | 0·010 | 0·017 | 0·311 |
| 15 | 0·000 | 0·000 | 0·000 | 0·000 | 0·003 | 0·012 | 0·274 |
| 16 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·005 | 0·303 |
| 17 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·003 | 0·171 |
| 18 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·172 |
| 19 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·130 |
| 20 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·075 |

TABLE A4. VALUES OF $d(v_2, \frac{1}{2})$

| | $D =$ 0·000 | 0·125 | 0·250 | 0·375 | 0·500 | 1·000 | 2·500 |
|---|---|---|---|---|---|---|---|
| $v_2 = 0$ | 1·000 | 0·663 | 0·486 | 0·374 | 0·297 | 0·137 | 0·023 |
| 1 | 0·000 | 0·629 | 0·580 | 0·483 | 0·396 | 0·193 | 0·033 |
| 2 | 0·000 | 0·376 | 0·565 | 0·621 | 0·593 | 0·299 | 0·044 |
| 3 | 0·000 | 0·138 | 0·275 | 0·390 | 0·486 | 0·512 | 0·063 |
| 4 | 0·000 | 0·060 | 0·162 | 0·246 | 0·305 | 0·466 | 0·110 |
| 5 | 0·000 | 0·017 | 0·071 | 0·151 | 0·234 | 0·366 | 0·227 |
| 6 | 0·000 | 0·006 | 0·029 | 0·066 | 0·117 | 0·364 | 0·298 |
| 7 | 0·000 | 0·001 | 0·012 | 0·036 | 0·068 | 0·239 | 0·271 |
| 8 | 0·000 | 0·000 | 0·004 | 0·014 | 0·034 | 0·171 | 0·340 |
| 9 | 0·000 | 0·000 | 0·001 | 0·006 | 0·015 | 0·123 | 0·396 |
| 10 | 0·000 | 0·000 | 0·000 | 0·002 | 0·007 | 0·068 | 0·323 |
| 11 | 0·000 | 0·000 | 0·000 | 0·001 | 0·003 | 0·046 | 0·330 |
| 12 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·025 | 0·320 |
| 13 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·014 | 0·239 |
| 14 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·008 | 0·222 |
| 15 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·004 | 0·179 |
| 16 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·128 |
| 17 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·109 |
| 18 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·075 |
| 19 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·054 |

### TABLE A5. VALUES OF $e(v_2, -\frac{1}{2})$

| $D$ = | 0·000 | 0·125 | 0·250 | 0·375 | 0·500 | 1·000 | 2·500 |
|---|---|---|---|---|---|---|---|
| $v_2$ = 0 | 1·000 | 0·831 | 0·743 | 0·687 | 0·649 | 0·569 | 0·512 |
| 1 | 0·000 | 0·315 | 0·290 | 0·241 | 0·198 | 0·097 | 0·017 |
| 2 | 0·000 | 0·188 | 0·283 | 0·310 | 0·296 | 0·150 | 0·022 |
| 3 | 0·000 | 0·070 | 0·137 | 0·195 | 0·243 | 0·256 | 0·032 |
| 4 | 0·000 | 0·030 | 0·081 | 0·123 | 0·153 | 0·233 | 0·055 |
| 5 | 0·000 | 0·009 | 0·035 | 0·075 | 0·117 | 0·183 | 0·113 |
| 6 | 0·000 | 0·003 | 0·014 | 0·033 | 0·059 | 0·182 | 0·149 |
| 7 | 0·000 | 0·001 | 0·006 | 0·018 | 0·034 | 0·120 | 0·136 |
| 8 | 0·000 | 0·000 | 0·002 | 0·007 | 0·017 | 0·086 | 0·170 |
| 9 | 0·000 | 0·000 | 0·001 | 0·003 | 0·008 | 0·062 | 0·198 |
| 10 | 0·000 | 0·000 | 0·000 | 0·001 | 0·004 | 0·034 | 0·161 |
| 11 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·023 | 0·165 |
| 12 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·012 | 0·160 |
| 13 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·007 | 0·119 |
| 14 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·004 | 0·111 |
| 15 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·090 |
| 16 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·064 |
| 17 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·055 |
| 18 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·037 |
| 19 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·027 |

### TABLE A6. VALUES OF $e^*(v_2, \frac{3}{2})$

| $D$ = | 0·000 | 0·125 | 0·250 | 0·375 | 0·500 | 1·000 | 2·500 |
|---|---|---|---|---|---|---|---|
| $v_2$ = 1 | 0·000 | −0·359 | −0·418 | −0·446 | −0·461 | −0·487 | −0·500 |
| 2 | 0·000 | 0·165 | 0·174 | 0·166 | 0·158 | 0·131 | 0·074 |
| 3 | 0·000 | 0·110 | 0·212 | 0·241 | 0·211 | 0·103 | 0·039 |
| 4 | 0·000 | 0·024 | 0·072 | 0·149 | 0·234 | 0·199 | 0·031 |
| 5 | 0·000 | 0·012 | 0·039 | 0·062 | 0·084 | 0·279 | 0·036 |
| 6 | 0·000 | 0·003 | 0·017 | 0·047 | 0·078 | 0·122 | 0·068 |
| 7 | 0·000 | 0·001 | 0·005 | 0·014 | 0·033 | 0·143 | 0·206 |
| 8 | 0·000 | 0·000 | 0·003 | 0·009 | 0·017 | 0·096 | 0·160 |
| 9 | 0·000 | 0·000 | 0·001 | 0·003 | 0·009 | 0·049 | 0·122 |
| 10 | 0·000 | 0·000 | 0·000 | 0·001 | 0·003 | 0·046 | 0·219 |
| 11 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·019 | 0·163 |
| 12 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·014 | 0·118 |
| 13 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·007 | 0·161 |
| 14 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·003 | 0·098 |
| 15 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·002 | 0·079 |
| 16 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·001 | 0·083 |
| 17 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·044 |
| 18 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·041 |
| 19 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·030 |
| 20 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·000 | 0·017 |

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