

Studies of the Jahn-Teller Effect IV. The Vibrational Spectra of Spin-Degenerate Molecules

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STUDIES OF THE JAHN–TELLER EFFECT
 IV. THE VIBRATIONAL SPECTRA OF
 SPIN-DEGENERATE MOLECULES

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The physical theory necessary for interpreting the vibrational spectra of spin-degenerate molecules is developed in this paper. Particular attention is paid to those molecules whose behaviour is expected to be markedly different from that of both orbitally non-degenerate molecules and those with purely spatial degeneracy. These include certain Kramers degenerate molecules, whose Raman spectra are expected to contain reverse-polarized contributions, and also tetrahedral and octahedral molecules in fourfold degenerate states. The case of a fourfold degenerate octahedral molecule is investigated in the limits of strong vibronic coupling by one of the Jahn–Teller active vibrations (e_g and t_{2g}). It turns out that the forbidden t_{2u} vibration may be infra-red active, that the Raman spectrum may contain reverse-polarized contributions and that both infra-red and Raman spectra may contain strong progressions of bands involving multiple excitations of the vibronically active vibration.

1. INTRODUCTION

This paper, which concerns molecules in spin-degenerate states, is intended to supplement some previous work (Child & Longuet-Higgins 1961; this paper will be referred to as III) on the vibrational spectra of orbitally degenerate molecules. Such spectra are expected to exhibit certain novel features, which can be attributed to two causes. First, there are considerable differences between the distributions of the outer electrons in electronically degenerate and non-degenerate molecules. This leads in turn to essential differences between their dipole moments and optical polarizabilities and hence to different group-theoretical selection rules for interpreting their vibrational spectra. And secondly, the motions of the electrons in degenerate molecules may be extremely sensitive to distortions in certain normal co-ordinates of the nuclear framework, whereas the electrons and the nuclei in non-degenerate molecules move much more independently. These effects will also be found to be important for certain spin-degenerate molecules.

In § 2, selection rules are derived for determining which vibrations give bands in infra-red and Raman spectra. Tables containing these vibrations are given for the important point groups. Section 3 deals with the estimation of the intensities of those vibrational bands

which are allowed for spin degenerate molecules but forbidden for non-degenerate ones. For this purpose molecules are classified according to the symmetries of the orbital states from which their full electronic states are derived. It turns out that the most complicated cases are those octahedral molecules whose electronic states stem from orbitally triply degenerate states. Sections 4 and 5 are devoted to a more detailed discussion of molecules of this type; IrCl_6^{2-} and ReF_6 provide examples. The ground state of IrCl_6^{2-} is a Kramers doublet and there can be no Jahn–Teller effect (Jahn 1938), but turns out that its Raman spectrum may contain certain reverse polarized ($\rho_n = 2$) contributions. The case of an octahedral molecule in a fourfold spin-degenerate state, such as ReF_6 , is more involved; two vibrations (with symmetries e_g and t_{2g}) may cause vibronic coupling (Moffitt & Thorson 1957) and the general problem of finding vibronic functions and energy levels is best tackled by numerical methods. This has not been attempted. Instead § 5 is limited to a discussion of the vibrational spectra of those molecules in which there is strong coupling with only one of the vibronically active vibrations. In these cases approximate wave functions and energy levels may be derived algebraically. Section 6 contains a summary of our main results. Character tables for the important extended point groups are included in the appendix.

2. GROUP-THEORY CONSIDERATIONS

In discussing the vibrational spectra of electronically degenerate molecules we shall frequently require to expand matrix elements of the form

$$A_{ij} = \langle e_i | A | e_j \rangle \quad (2.1)$$

in powers of the molecular symmetry co-ordinates Q , since the components $|e_j\rangle$ of the electronic state and those operators A in which we shall be interested depend on Q . The most important co-ordinates for our purposes are those whose first power appears in the expansions of the matrices $[A_{ij}]$. These co-ordinates, which must have the same symmetry properties as the relevant A_{ij} , may be identified by means of group-theory arguments. A may stand for the electronic Hamiltonian or one of the components of the dipole moment or optical polarizability operators, according to whether one is discussing vibronic coupling in the molecule or the intensity of its infra-red or Raman spectrum.

First, as Renner (1934) has pointed out, one must in general describe the vibronic state of an electronically degenerate molecule by a ket such as

$$|en\rangle = \sum_j |e_j\rangle |n_j\rangle, \quad (2.2)$$

the vibrational factors $|n_j\rangle$ being solutions of the equation

$$\sum_j [H_{ij} + (T - E) \delta_{ij}] |n_j\rangle = 0. \quad (2.3)$$

In equation (2.3), T is the nuclear kinetic energy, E the total vibronic energy and H_{ij} the matrix elements of the electronic Hamiltonian within the degenerate state $|e\rangle$. The molecule may experience a linear Jahn–Teller effect in those co-ordinates which belong to the same representation as the elements H_{ij} .

Secondly, the oscillator strength for optical absorption corresponding to the vibrational transition $|en'\rangle \leftarrow |en''\rangle$ at frequency ν is given by

$$f = \frac{4\pi m \nu}{3\hbar e^2} |\langle en' | \mathbf{M} | en'' \rangle|^2, \quad (2.4)$$

where the components of the dipole moment operator \mathbf{M} may be taken in the real forms M_λ , λ standing for x , y or z , or in the complex combinations M_ρ , defined by

$$M_0 = M_z, \quad M_{\pm 1} = \sqrt{\frac{1}{2}} (M_x \pm iM_y). \quad (2.5)$$

Now, using equation (2.2) and integrating over the electronic co-ordinates, we find that

$$\langle en' | \mathbf{M} | en'' \rangle = \sum_{ij} \langle n'_i | (\mathbf{M})_{ij} | n''_j \rangle. \quad (2.6)$$

In other words, in discussing the infra-red spectrum of an electronically degenerate molecule, we shall be concerned as much with transitions during which the electronic state changes as with those in which it remains the same. The intensities of the former depend on the off-diagonal elements $(\mathbf{M})_{ij}$ and those of the latter on the diagonal elements $(\mathbf{M})_{ii}$. The symmetries of these matrix elements will, therefore, indicate which vibrational co-ordinates may be active in infra-red absorption.

Similarly, the corresponding Raman scattering cross-sections are given by

$$\sigma = \frac{64\pi^4\nu_s^4}{c^4} (G^0 + G^s + G^a), \quad (2.7)$$

ν_s being the frequency of the scattered light and G^0 , G^s and G^a being defined by

$$\left. \begin{aligned} G^0 &= \frac{1}{3} |\langle en' | \alpha_{-11} + \alpha_{00} + \alpha_{1-1} | en'' \rangle|^2, \\ G^s &= \sum_{\rho\sigma} |\langle en' | \alpha_{\rho\sigma} | en'' \rangle - \frac{1}{3} \delta_{-\rho, \sigma} \langle en' | \alpha_{-11} + \alpha_{00} + \alpha_{1-1} | en'' \rangle|^2, \\ G^a &= \sum_{\rho\sigma} |\langle en' | \beta_{\rho\sigma} | en'' \rangle|^2. \end{aligned} \right\} \quad (2.8)$$

$\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$ are defined by equations (5.14) and (5.20) of III; they are respectively the symmetric and antisymmetric parts of the polarizability tensor. α is responsible for scalar and symmetric tensor scattering, with depolarization ratios ρ_n equal to zero and $\frac{6}{7}$, respectively, while β causes pseudo-vector scattering ($\rho_n = 2$). These matrix elements may also be written in the forms

$$\left. \begin{aligned} \langle en' | \alpha_{\rho\sigma} | en'' \rangle &= \sum_{ij} \langle n'_i | (\alpha_{\rho\sigma})_{ij} | n''_j \rangle, \\ \langle en' | \beta_{\rho\sigma} | en'' \rangle &= \sum_{ij} \langle n'_i | (\beta_{\rho\sigma})_{ij} | n''_j \rangle. \end{aligned} \right\} \quad (2.9)$$

A knowledge of the transformation properties of the elements $(\alpha_{\rho\sigma})_{ij}$ and $(\beta_{\rho\sigma})_{ij}$ will therefore enable us to give group-theory selection rules for the Raman active vibrations of the molecule.

It is important to realize that the matrices $[(M_\rho)_{ij}]$, $[(\alpha_{\rho\sigma})_{ij}]$ and $[(\beta_{\rho\sigma})_{ij}]$ may not be Hermitian since M_ρ , $\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$ are not necessarily real linear operators, although they may be expressed in terms of the Hermitian operators M_λ , $\alpha_{\lambda\mu}$ and $i\beta_{\lambda\mu}$.

We now investigate the behaviour of the elements A_{ij} under the time-reversal operator * (Wigner 1932). The states $|e_i^*\rangle$ satisfy the same equations as the $|e_i\rangle$ except that the time t is everywhere replaced by $-t$ and all other quantities by their complex conjugates. The relations we shall obtain are conveniently expressed in terms of the real operators H , M_λ , $\alpha_{\lambda\mu}$ and $i\beta_{\lambda\mu}$, rather than H , M_ρ , $\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$. In the notation of (5.14) and (5.20) of (III),

$$\alpha_{\lambda\mu} = \frac{1}{2} [M_\lambda f^s(H) M_\mu + M_\mu f^s(H) M_\lambda] \quad (2.10)$$

and
$$i\beta_{\lambda\mu} = \frac{1}{2} i [M_\lambda f^a(H) M_\mu - M_\mu f^a(H) M_\lambda], \quad (2.11)$$

and it follows that

$$\left. \begin{aligned} H &= \bar{H} = H^*, \\ M_\lambda &= \bar{M}_\lambda = M_\lambda^* \\ \alpha_{\lambda\mu} &= \bar{\alpha}_{\lambda\mu} = \alpha_{\lambda\mu}^* \end{aligned} \right\} \quad (2.12)$$

and

but
$$i\beta_{\lambda\mu} = \overline{(i\beta_{\lambda\mu})} = -(i\beta_{\lambda\mu})^*. \quad (2.13)$$

The behaviour of the states $|e_i\rangle$ under time reversal depend on whether they represent even or odd electron systems. For even-electron systems Jahn (1938) has shown that

$$|e_i^{**}\rangle = |e_i\rangle, \quad (2.14)$$

in which case the A_{ij} transform according to the same rules as were derived in our previous paper on molecules with purely orbital degeneracy (III).

In the case of odd-electron systems, however,

$$|e_i^{**}\rangle = -|e_i\rangle. \quad (2.15)$$

Consequently, if $A = \bar{A} = A^*$ ($A = H, M_\lambda$ or $\alpha_{\lambda\mu}$, for instance)

$$\begin{aligned} \langle e_i^* | A | e_j \rangle &= \overline{\langle e_j | A | e_i^* \rangle} = [\langle e_j | A | e_i^* \rangle]^* \\ &= -\langle e_j^* | A | e_i \rangle = \frac{1}{2}[\langle e_i^* | A | e_j \rangle - \langle e_j^* | A | e_i \rangle]. \end{aligned} \quad (2.16)$$

Now Jahn has also shown that the bras $\langle e_i^*|$, which are linear combinations of the $\langle e_i|$, may be chosen to span the same representation as the kets $|e_i\rangle$, in identically the same form. It follows that if the electronic states $|e_i\rangle$ belong to the representation Γ , with symmetrized and antisymmetrized squares $[\Gamma^2]$ and $\{\Gamma^2\}$, respectively, and if A belongs to the representation Γ_A , then the A_{ij} belong to the representation $\{\Gamma^2\} \times \Gamma_A$. Hence, if Γ_0 is the totally symmetric representation, Γ_{\parallel} and Γ_{\perp} the representations of M_z and (M_x, M_y) and Γ_s the representation to which the symmetric part of the polarizability tensor belongs:

(i) co-ordinates belonging to $\{\Gamma^2\} \times \Gamma_0$ but not to Γ_0 are active in vibronic coupling (Jahn 1938);

(ii) co-ordinates belonging to $\{\Gamma^2\} \times \Gamma_{\parallel}$ give parallel infra-red bands;

(iii) co-ordinates belonging to $\{\Gamma^2\} \times \Gamma_{\perp}$ give perpendicular infra-red bands;

(iv) co-ordinates belonging to $\{\Gamma^2\} \times \Gamma_0$ give polarized contributions to the Raman spectrum;

(v) co-ordinates belonging to $\{\Gamma^2\} \times \Gamma_s$ give depolarized contributions to the Raman spectrum;

(iv) the molecule may have a permanent dipole moment if $\{\Gamma^2\} \times \Gamma_{\parallel}$ or $\{\Gamma^2\} \times \Gamma_{\perp}$ contains Γ_0 ;

(vii) directly (Rayleigh) scattered light may contain a polarized contribution if $\{\Gamma^2\} \times \Gamma_0$ contains Γ_0 and, a depolarized contribution if $\{\Gamma^2\} \times \Gamma_s$ contains Γ_0 .

On the other hand if $A = \bar{A} = -A^*$ (as for the components of $i\beta$)

$$\langle e_i^* | A | e_j \rangle = \overline{\langle e_j | A | e_i^* \rangle} = [\langle e_j | A | e_i^* \rangle]^* = \langle e_j^* | A | e_i \rangle = \frac{1}{2}[\langle e_i^* | A | e_j \rangle + \langle e_j^* | A | e_i \rangle]. \quad (2.17)$$

We conclude that vibrations belonging to $[\Gamma^2] \times \Gamma_a$ will give a reverse-polarized contribution to the Raman spectrum, Γ_a being the representation to which the antisymmetric part of the polarizability tensor belongs. The molecule may exhibit reverse-polarized Rayleigh scattering if $[\Gamma^2] \times \Gamma_a$ contains Γ_0 .

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Tables 1 and 2 indicate the symmetries of those co-ordinates for which the group-theoretical selection rules differ from those derived for non-degenerate molecules. The existence of Kramers degeneracy causes no changes in the familiar selection rules for co-ordinates active in infra-red absorption and in isotropic and symmetric-tensor Raman scattering, since in this case $\{\Gamma^2\} = \Gamma_0$. However, certain types of vibration may cause

TABLE 1. VIBRATIONS RESPONSIBLE FOR PSEUDO-VECTOR RAMAN SCATTERING IN KRAMERS DEGENERATE MOLECULES

| point group | Γ_a | Γ | $[\Gamma^2]$ | γ_a | point group | Γ_a | Γ | $[\Gamma^2]$ | γ_a |
|-------------|----------------|--------------------------------------|--------------------|-----------------------|-------------|-------------------|---|----------------------------|--|
| D_3^* | $A_2 + E$ | $E_{\frac{3}{2}}$ | $A_2 + E$ | a_1, a_2, e | D_{3h}^* | $A_2' + E''$ | $E_{\frac{3}{2}}, E_{\frac{5}{2}}$ | $A_2' + E'$ | a_1', e', e'' |
| | | $E_{\frac{3}{2}}$ | $A_1 + 2A_2$ | a_1, a_2, e | | | $E_{\frac{3}{2}}$ | $A_1' + 2A_2'$ | a_1', a_2', e'' |
| C_{3v}^* | $A_2 + E$ | $E_{\frac{3}{2}}$ | $A_2 + E$ | a_1, a_2, e | D_{4h}^* | $A_{2g} + E_g$ | $\left\{ E_{\frac{1}{2}g}, E_{\frac{1}{2}u} \right\}$ | $A_{2g} + E_g$ | a_{1g}, a_{2g}, e_g |
| | | $E_{\frac{3}{2}}$ | $A_1 + 2A_2$ | a_1, a_2, e | | | $\left\{ E_{\frac{3}{2}g}, E_{\frac{3}{2}u} \right\}$ | | |
| C_{4v}^* | $A_2 + E$ | $E_{\frac{3}{2}}, E_{\frac{5}{2}}$ | $A_2 + E$ | a_1, a_2, b_1, b_2 | D_{5h}^* | $A_2' + E_1'$ | $E_{\frac{1}{2}}, E_{\frac{3}{2}}$ | $A_2' + E_1'$ | a_1', e_1', e_1'' |
| D_{2d}^* | $A_2 + E$ | $E_{\frac{3}{2}}, E_{\frac{5}{2}}$ | $A_2 + E$ | a_1, a_2, b_1, b_2 | | | $E_{\frac{3}{2}}, E_{\frac{7}{2}}$ | $A_2' + E_2'$ | a_1', e_1', e_2' |
| D_{3d}^* | $A_{2g} + E_g$ | $E_{\frac{3}{2}g}, E_{\frac{1}{2}u}$ | $A_{2g} + E_g$ | a_{1g}, a_{2g}, e_g | | | $E_{\frac{5}{2}}$ | $A_1' + 2A_2'$ | a_1', a_2', e_1' |
| | | $E_{\frac{3}{2}g}, E_{\frac{3}{2}u}$ | $A_{1g} + 2A_{2g}$ | a_{1g}, a_{2g}, e_g | D_{6h}^* | $A_{2g} + E_{1g}$ | $\left\{ E_{\frac{1}{2}g}, E_{\frac{1}{2}u} \right\}$ | $A_{2g} + E_{1g}$ | a_{1g}, a_{2g}, e_{2g} |
| D_{4d}^* | $A_2 + E_1$ | $E_{\frac{3}{2}}, E_{\frac{7}{2}}$ | $A_2 + E_1$ | a_1, a_2, e_2 | | | $\left\{ E_{\frac{3}{2}g}, E_{\frac{3}{2}u} \right\}$ | $A_{2g} + B_{1g} + B_{2g}$ | $a_{1g}, b_{1g}, b_{2g}, e_{1g}, e_{2g}$ |
| | | $E_{\frac{3}{2}}, E_{\frac{5}{2}}$ | $A_2 + E_3$ | a_1, e_1, e_3 | T_d^* | T_1 | $E_{\frac{3}{2}}, E_{\frac{5}{2}}$ | T_1 | a_1, e, t_1, t_2 |
| | | | | | O_h^* | T_{1g} | $\left\{ E_{\frac{1}{2}g}, E_{\frac{1}{2}u} \right\}$ | T_{1g} | $a_{1g}, e_g, t_{1g}, t_{2g}$ |
| | | | | | | | $\left\{ E_{\frac{3}{2}g}, E_{\frac{3}{2}u} \right\}$ | | |

Γ_a is the representation of the antisymmetric part of the polarizability tensor, Γ the symmetry of the electronic state and $[\Gamma^2]$ its symmetrized square. γ_a indicates the species of those vibrations which may have $G^a > 0$. $E_{\frac{1}{2}}$ and $E_{\frac{3}{2}}$ of T_d^* and O_h^* would be written Γ_6 and Γ_7 respectively in Bethe's notation.

TABLE 2. INFRA-RED AND RAMAN ACTIVE VIBRATIONS OF OCTAHEDRAL AND TETRAHEDRAL MOLECULES IN $U_{\frac{3}{2}} (\Gamma_8)$ STATES

| point group | T_d^* | O_h^* |
|----------------|-------------------------|---------------------------------------|
| Γ_M | T_2 | T_{1u} |
| Γ_o | A_1 | A_{1g} |
| Γ_s | $E + T_2$ | $E_g + T_{2g}$ |
| Γ_a | T_1 | T_{1g} |
| Γ | $U_{\frac{3}{2}}$ | $U_{\frac{3}{2}g}, U_{\frac{3}{2}u}$ |
| $\{\Gamma^2\}$ | $A_1 + E + T_2$ | $A_{1g} + E_g + T_{2g}$ |
| $[\Gamma^2]$ | $A_2 + 2T_1 + T_2$ | $A_{2g} + 2T_{1g} + T_{2g}$ |
| γ_M | a_1, e, t_1, t_2 | $a_{2u}, e_u, t_{1u}, t_{2u}$ |
| γ_o | a_1, e, t_2 | a_{1g}, e_g, t_{2g} |
| γ_s | a_1, a_2, e, t_1, t_2 | $a_{1g}, a_{2g}, e_g, t_{1g}, t_{2g}$ |
| γ_a | a_1, a_2, e, t_1, t_2 | $a_{1g}, a_{2g}, e_g, t_{1g}, t_{2g}$ |

Co-ordinates with species in which they are active: γ_M , infra-red absorption; γ_o , polarized Raman scattering; γ_s , depolarized Raman scattering; γ_a , reverse-polarized Raman scattering.

reverse-polarized Raman scattering and these are listed in table 1. Table 2 concerns molecules belonging to the point groups T_d and O_h , in fourfold degenerate states (Γ_8 in Bethe's notation); these are the only common species with more than twofold spin degeneracy.

There seems to be no accepted nomenclature for the representations of the extended groups of low symmetry. In accordance with Mulliken's notation doubly degenerate representations in table 1 are given the letter E and a subscript J to show that they form

part of the basis for the representation with angular momentum J , the chosen value of J being the lowest for which this is true. Similarly in table 2 the fourfold degenerate representations are given the symbol $U_{\frac{3}{2}}$.

3. INTENSITIES

In discussing the optical properties of a molecule one requires to know not only which vibrational co-ordinates may on symmetry grounds give rise to a Jahn–Teller effect or to bands in its infra-red and Raman spectra, but also whether or not such phenomena are effectively forbidden on other grounds. It is the purpose of this section to develop a method for estimating the magnitudes of the matrix elements A_{ij} of (2.1) upon which the intensities of these effects depend. We shall express the electronic states $|e_i\rangle, |e_j\rangle, \dots$ which include electron spin, in terms of the orbital states $|e_a\rangle, |e_b\rangle, \dots$ from which they are derived. Then, since the operators $M_\rho, \alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$ do not affect the electron spin, the quantities A_{ij} may be expressed in terms of corresponding elements A_{ab} which are capable of fairly ready physical interpretation (III).

There are several distinct cases to be considered:

- (i) molecules in states arising from orbitally non-degenerate states;
- (ii) dihedral molecules in states arising from orbitally degenerate states;
- (iii) molecules belonging to the cubic point-groups (T_d and O_h) in states arising from orbitally doubly degenerate states (E);
- (iv) tetrahedral and octahedral molecules in states derived from triply degenerate states (T).

Before discussing these situations in detail, we note that there can be no matrix elements A_{ij} between states which differ in their orientations of electron spin. Therefore, in the absence of spin-orbit coupling, which may be represented by

$$H_s = \sum_e \zeta_e \mathbf{l}_e \cdot \mathbf{s}_e = \sum_e \zeta_e [l_{ez} s_{ez} + \frac{1}{2}(l_{e+} s_{e-} + l_{e-} s_{e+})], \quad (3.1)$$

the optical and mechanical properties of the molecule would be exactly the same as those of a similar molecule with no electron spin. (The one-electron operators \mathbf{l}_e and \mathbf{s}_e in equation (3.1) transform in the same way as angular momentum operators; they affect the orbital part and the spin part of the wave function, respectively.)

Case (i)

The familiar selection rules for interpreting infra-red and Raman spectra (Herzberg 1945) were derived for molecules in orbitally non-degenerate states $|a\rangle$. Any novel effects in the spectra of such molecules with non-zero spin S may be attributed to spin-orbit coupling. Excited states $|f\rangle |m'_s\rangle$ may be mixed with the $(2S+1)$ components of the ground state, and to the first order in H_s

$$|a, m_s\rangle = |a\rangle |m_s\rangle + \sum_{e,f} \zeta_e |f\rangle |m'_s\rangle \langle f | \mathbf{l}_e | a\rangle \cdot \langle m'_s | \mathbf{s}_e | m_s\rangle / (E_a - E_f). \quad (3.2)$$

The matrix elements in which we are interested may therefore be written

$$\begin{aligned} \langle a, m'_s | A | a, m_s\rangle &= \langle a | A | a\rangle \delta_{m'_s, m_s} \\ &+ \left[\sum_{e,f} \zeta_e \frac{\langle a | A | f\rangle \langle f | \mathbf{l}_e | a\rangle \cdot \langle m'_s | \mathbf{s}_e | m_s\rangle + \langle a | \mathbf{l}_e | f\rangle \cdot \langle m'_s | \mathbf{s}_e | m_s\rangle \langle f | A | a\rangle}{(E_a - E_f)} \right]. \end{aligned} \quad (3.3)$$

The diagonal term $\langle a|A|a\rangle\delta_{m_s',m_s}$ in this expression provides just those contributions which are expected from an electronically non-degenerate molecule. The other terms depend upon the spin-orbit coupling constants ζ_e and their effect will probably not be appreciable unless spin-orbit coupling is strong. It is worth noting that the vibrational spectra of $\text{IrF}_6(^4A_2)$ do not appear to differ from those of a non-degenerate octahedral molecule (Claassen & Weinstock 1960), although $\zeta_e \sim 3400 \text{ cm}^{-1}$.

Case (ii)

Certain dihedral molecules in orbitally doubly degenerate states are expected to show a Jahn–Teller effect and their vibrational spectra may exhibit some ‘anomalies’; the case of a molecule with D_{3h} symmetry has been discussed in some detail (III). We shall find that, if such molecules have total spin $S \neq 0$ these effects may be quenched by sufficiently strong spin-orbit coupling.

The components of the orbitally degenerate state may be chosen in the real forms $|e_a\rangle$ and $|e_b\rangle$ or in the complex combinations

$$|e_{\pm}\rangle = \sqrt{\frac{1}{2}}(|e_a\rangle \pm i|e_b\rangle), \quad (3.4)$$

and we can arrange that if C_p represents a rotation of the co-ordinate system of the molecule by an angle $2\pi/p$ around its figure axis

$$C_p|e_{\pm}\rangle = e^{\pm 2\pi ni/p}|e_{\pm}\rangle, \quad (3.5)$$

where n is some integer.

Consider now the effect of first-order spin-orbit coupling on the $2(2S+1)$ -fold degenerate electronic state of the molecule. If \mathbf{l} is quantized along the figure axis then l_z but neither l_x nor l_y can have non-zero matrix elements within the manifold $|e\rangle$, because \mathbf{l} is an operator of the second type discussed in § 2 (i.e. $\mathbf{l} = \bar{\mathbf{l}} = -\mathbf{l}^*$) and l_x and l_y together form the basis of some doubly degenerate representation, whereas l_z belongs to the same non-degenerate representation as $\{E^2\}$. Furthermore, from equation (3.5)

$$C_p\langle e_+|l_{ez}|e_+\rangle = \langle e_+|l_{ez}|e_+\rangle = \mu_e, \quad \text{say}$$

$$\text{and so} \quad \langle e_-|l_{ez}|e_-\rangle = [\langle e_-|l_{ez}|e_-\rangle]^* = -\langle e_+|l_{ez}|e_+\rangle = -\mu_e, \quad (3.6)$$

$$\text{but} \quad C_p\langle e_-|l_{ez}|e_+\rangle = e^{(4\pi ni/p)}\langle e_-|l_{ez}|e_+\rangle = 0$$

because n is not an integral multiple of $\frac{1}{2}p$ for any degenerate representation. It is also convenient to define a quantity σ_e such that

$$\langle m_s|s_{ez}|m_s\rangle = -\langle -m_s|s_{ez}| -m_s\rangle = \sigma_e m_s.$$

We then deduce that the first-order corrections to the energies of the states $|e_+\rangle|m_s\rangle$ and $|e_-\rangle|m_s\rangle$ are $(\sum\zeta_e\mu_e\sigma_e)m_s$ and $-(\sum\zeta_e\mu_e\sigma_e)m_s$ and hence that the initial electronic state is split into $2S+1$ degenerate pairs $|e_+\rangle|m_s\rangle$ and $|e_-\rangle| -m_s\rangle$ with the states $|e_+\rangle| -S\rangle$ and $|e_-\rangle|S\rangle$ lying lowest if $\sum\zeta_e\mu_e\sigma_e > 0$. This is Kramers degeneracy. Note also that if $S \neq 0$, in this order of perturbation there can be no matrix elements of the operators H , M_{ρ} , $\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$ between the components of the electronic ground state. Therefore provided that $\sum\zeta_e\mu_e\sigma_e$ is much

greater than the change in energy due to Jahn–Teller distortion in the absence of electron spin, the special effects due to orbital degeneracy are completely quenched by first-order spin-orbit coupling.

In ζ_e is a very large ($> 3500 \text{ cm}^{-1}$) the ground state may be appreciably contaminated with some excited states by second-order spin-orbit coupling. Arguments similar to those used in (i) then lead us to expect small anomalous terms in the matrices $[A_{ij}]$ if $S = \frac{1}{2}$ but not otherwise.

Case (iii)

An orbital angular momentum operator \mathbf{l} can have no non-zero matrix elements between the components of an E representation of a cubic point-group. The electronic wave functions and energy levels are therefore unaffected by first-order spin-orbit coupling. Hence unless ζ_e is very large, the optical properties of such a molecule will be independent of any spin-degeneracy. The effects of twofold orbital degeneracy are not quenched but on the other hand no additional effects are expected. A tetrahedral molecule in a 2E state (VCl_4 , for instance) provides a convenient example. This state would be classified as $U_{\frac{3}{2}}$ in the extended tetrahedral group and according to table 2 co-ordinates with symmetries e and t_2 may be involved in vibronic coupling. However, in this case we should expect no Jahn–Teller effect in the t_2 co-ordinates, since they would be vibronically inactive if the molecule had no spin degeneracy.

Second-order spin-orbit coupling may give rise to additional small terms in the matrices $[A_{ij}]$, but these will be important only if ζ_e is of the same order as the excitation energy to the state connected by H_s to the ground state. In the example quoted, these might include small vibronic coupling terms in the t_2 co-ordinates.

Case (iv)

Those octahedral and tetrahedral molecules whose electronic state has spin degeneracy as well as threefold orbital degeneracy will be treated in more detail, an octahedral molecule in a 2T_2 state being taken as an example. First-order spin-orbit coupling splits such a state into a Kramers doublet $[E_{\frac{3}{2}}]$ and a quartet ($U_{\frac{3}{2}}$). With the help of appropriate tables of coupling coefficients (Griffith 1961) we may write down the matrices of H , M_{ρ} , $\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$ within an orbital T_2 state, from which the analogous matrices within the $E_{\frac{3}{2}}$ and $U_{\frac{3}{2}}$ states may be derived.

The components of a T_2 electronic state may be chosen in the real forms $|yz\rangle$, $|zx\rangle$ and $|xy\rangle$ in which case the linear terms in the normal co-ordinates

$$Q_1(a_{1g}), \quad Q_{2a}, Q_{2b}(e_g), \quad Q_{3x}, Q_{3y}, Q_{3z}(t_{1u}), \quad Q_{4x}, Q_{4y}, Q_{4z}(t_{1u}), \\ Q_{5x}, Q_{5y}, Q_{5z}(t_{2g}) \quad \text{and} \quad Q_{6x}, Q_{6y}, Q_{6z}(t_{2u})$$

(Herzberg 1945) in the required matrices are as follows:

$$[\langle T | H | T \rangle] = \begin{bmatrix} k_2(Q_{2a} - \sqrt{3} Q_{2b}) & \sqrt{3} k_5 Q_{5z} & \sqrt{3} k_5 Q_{5y} \\ \sqrt{3} k_5 Q_{5z} & k_2(Q_{2a} + \sqrt{3} Q_{2b}) & \sqrt{3} k_5 Q_{5x} \\ \sqrt{3} k_5 Q_{5y} & \sqrt{3} k_5 Q_{5x} & -2k_2 Q_{2a} \end{bmatrix}. \quad (3.8)$$

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(For all representations of all point groups the matrix $[H_{ij}]$ may contain linear terms in the totally symmetric co-ordinate Q_1 but these may be removed by taking a suitable choice of origin for Q_1 .)

$$[\langle T | M_z | T \rangle] = \begin{bmatrix} (\mu_3 + \mu'_3) Q_{3z} + (\mu_4 + \mu'_4) Q_{4z} & 0 & \mu''_3 Q_{3x} + \mu''_4 Q_{4x} - \mu''_6 Q_{6x} \\ +\sqrt{3} \mu'_6 Q_{6z} & (\mu_3 + \mu'_3) Q_{3z} + (\mu_4 + \mu'_4) Q_{4z} & \mu''_3 Q_{3y} + \mu''_4 Q_{4y} + \mu''_6 Q_{6y} \\ 0 & -\sqrt{3} \mu'_6 Q_{6z} & \\ \mu''_3 Q_{3x} + \mu''_4 Q_{4x} - \mu''_6 Q_{6x} & \mu''_3 Q_{3y} + \mu''_4 Q_{4y} + \mu''_6 Q_{6y} & (\mu_3 - 2\mu'_3) Q_{3z} + (\mu_4 - 2\mu'_4) Q_{4z} \end{bmatrix}, \quad (3.9)$$

with similar expressions for $[\langle T | M_x | T \rangle]$ and $[\langle T | M_y | T \rangle]$. The constants μ_i , μ'_i and μ''_i have the dimensions of dipole moment derivatives with respect to Q_i ; μ'_i and μ''_i would not arise in the case of an electronically non-degenerate molecule. When discussing the Raman spectra of an octahedral molecule, it is convenient to replace α_{xx} , α_{yy} , α_{zz} by the equivalent set

$$\left. \begin{aligned} \alpha^0 &= \frac{1}{\sqrt{3}} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \\ \alpha_{z^2} &= \frac{1}{\sqrt{6}} (\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}), \\ \alpha_{x^2-y^2} &= \frac{1}{\sqrt{2}} (\alpha_{xx} - \alpha_{yy}), \end{aligned} \right\} \quad (3.10)$$

because α^0 has symmetry A_{1g} and α_{z^2} and $\alpha_{x^2-y^2}$ may be taken as bases for the irreducible representation E_g ; α_{yz} , α_{zx} , α_{xy} and β_{yz} , β_{zx} , β_{xy} already form bases for the T_{2g} and T_{1g} representations, respectively. The expansions, as far as terms linear in Q , of typical components of the polarizability tensor then take the following forms:

$$[\langle T | \alpha^0 | T \rangle] = \begin{bmatrix} \alpha_0 + \alpha_1 Q_1 + \alpha'_2 (Q_{2a} - \sqrt{3} Q_{2b}) & \alpha'_5 Q_{5z} & \alpha'_5 Q_{5y} \\ \alpha'_5 Q_{5z} & \alpha_0 + \alpha_1 Q_1 + \alpha'_2 (Q_{2a} + \sqrt{3} Q_{2b}) & \alpha'_5 Q_{5x} \\ \alpha'_5 Q_{5y} & \alpha'_5 Q_{5x} & \alpha_0 + \alpha_1 Q_1 - 2\alpha'_2 Q_{2a} \end{bmatrix},$$

$$[\langle T | \alpha_{z^2} | T \rangle] = \begin{bmatrix} \alpha_2 Q_{2a} + \alpha'_0 + \alpha'_1 Q_1 & \alpha''_5 Q_{5z} & -\frac{1}{2} \alpha''_5 Q_{5y} \\ -\alpha''_2 (Q_{2a} + \sqrt{3} Q_{2b}) & \alpha_2 Q_{2a} + \alpha'_0 + \alpha'_1 Q_1 & -\frac{1}{2} \alpha''_5 Q_{5x} \\ \alpha''_5 Q_{5z} & -\alpha''_2 (Q_{2a} - \sqrt{3} Q_{2b}) & \\ -\frac{1}{2} \alpha''_5 Q_{5y} & -\frac{1}{2} \alpha''_5 Q_{5x} & \alpha_2 Q_{2a} - 2\alpha'_0 - 2\alpha'_1 Q_1 + 2\alpha''_2 Q_{2a} \end{bmatrix},$$

$$[\langle T | \alpha_{xy} | T \rangle] = \begin{bmatrix} (\alpha_5 + \alpha''_5) Q_{5z} & \alpha''_0 + \alpha'_1 Q_1 - 2\alpha''_2 Q_{2a} & \alpha^{iv}_5 Q_{5x} \\ \alpha''_0 + \alpha'_1 Q_1 - 2\alpha''_2 Q_{2a} & (\alpha_5 + \alpha''_5) Q_{5z} & \alpha^{iv}_5 Q_{5y} \\ \alpha^{iv}_5 Q_{5x} & \alpha^{iv}_5 Q_{5y} & (\alpha_5 - 2\alpha''_5) Q_{5z} \end{bmatrix}, \quad (3.11)$$

$$[\langle T | i\beta_{xy} | T \rangle] = \begin{bmatrix} 0 & i\beta'_0 + i\beta'_1 Q_1 - 2i\beta'_2 Q_{2a} & i\beta'_5 Q_{5x} \\ -i\beta'_0 - i\beta'_1 Q_1 - 2i\beta'_2 Q_{2a} & 0 & i\beta'_5 Q_{5y} \\ -i\beta'_5 Q_{5x} & -i\beta'_5 Q_{5y} & 0 \end{bmatrix}. \quad (3.12)$$

In expressions (3.11) and (3.12) α_0 , α'_0 , α''_0 and β'_0 are constants and α_i , α'_i , α''_i , α^{iv}_i and β'_i have the dimensions of polarizability derivatives with respect to Q_i . The quantities with

single or multiple primes give rise to phenomena which do not occur in electronically non-degenerate systems.

In the absence of spin-orbit coupling these are the matrices required to determine the optical and mechanical properties of the molecule. Thorson (1958) has shown how the constants defined by equations (3.8) to (3.12) may be estimated from a detailed knowledge of the electronic states of the molecule. For instance, according to expression (3.9) the constants μ''_3 , μ''_4 and μ''_6 are defined by the equation

$$\langle yz | M_z | xy \rangle = \mu''_3 Q_{3x} + \mu''_4 Q_{4x} - \mu''_6 Q_{6x}, \quad (3.13)$$

and they may in principle be determined by expanding $|yz\rangle$, $|xy\rangle$ and M_z in terms of the normal co-ordinates Q . Unfortunately, sufficiently detailed information about the electronic states of any particular molecule is not readily available. Thorson argues, however, that since all the anomalous factors arise as a result of vibronic coupling, either between the components of the ground state or between the ground state and certain excited states, they will probably all be equally important. In other words, the presence of a strong Jahn-Teller effect in a particular molecule would lead us to expect the factors with primes in (3.9) to (3.12) to be large, and vice versa.

We are now in a position to derive the matrices of H , M_ρ , $\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma}$ between the components of the $E_{\frac{3}{2}}$ and $U_{\frac{3}{2}}$ states into which a 2T_2 state splits under spin-orbit coupling. It is convenient to define the electronic states

$$\left. \begin{aligned} |1\rangle &= -(i/\sqrt{2}) (|yz\rangle + i|zx\rangle), \\ |0\rangle &= i|xy\rangle \\ \text{and} \quad | -1\rangle &= (i/\sqrt{2}) (|yz\rangle - i|zx\rangle), \end{aligned} \right\} \quad (3.18)$$

which may be combined with the spin states $|\pm\frac{1}{2}\rangle$ with the help of the $t_2^n - p^{6-n}$ isomorphism (Abragam & Pryce 1951), to give

$$\left. \begin{aligned} |+\rangle &= \sqrt{\frac{1}{3}} |0, \frac{1}{2}\rangle - \sqrt{\frac{2}{3}} |1, -\frac{1}{2}\rangle, \\ \text{and} \quad |-\rangle &= -\sqrt{\frac{2}{3}} |-1, \frac{1}{2}\rangle + \sqrt{\frac{1}{3}} |0, -\frac{1}{2}\rangle \end{aligned} \right\} \quad (3.19)$$

with $E_{\frac{3}{2}}$ symmetry, and

$$\left. \begin{aligned} |\kappa\rangle &= |1, \frac{1}{2}\rangle, \\ |\lambda\rangle &= \sqrt{\frac{2}{3}} |0, \frac{1}{2}\rangle + \sqrt{\frac{1}{3}} |1, -\frac{1}{2}\rangle, \\ |\mu\rangle &= \sqrt{\frac{1}{3}} |-1, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |0, -\frac{1}{2}\rangle \\ \text{and} \quad |\nu\rangle &= |-1, -\frac{1}{2}\rangle, \end{aligned} \right\} \quad (3.20)$$

which have symmetry $U_{\frac{3}{2}}$.

For the $E_{\frac{3}{2}}$ case (a Kramers doublet), according to §2, we expect neither a Jahn-Teller effect nor any novel features in the infra-red spectrum or in the polarized or depolarized contributions to the Raman spectrum. We shall therefore require only the matrices of the components of β ; it turns out that $[\langle E_{\frac{3}{2}} | i\beta_{xy} | E_{\frac{3}{2}} \rangle]$ for instance takes the form

$$[\langle E_{\frac{3}{2}} | i\beta_{xy} | E_{\frac{3}{2}} \rangle] = \begin{bmatrix} \beta'_0 + \beta'_1 Q_1 - 2\beta'_2 Q_{2a} & \beta'_5 (Q_{5y} - iQ_{5x}) \\ \beta'_5 (Q_{5y} + iQ_{5x}) & -\beta'_0 - \beta'_1 Q_1 + 2\beta'_2 Q_{2a} \end{bmatrix}. \quad (3.21)$$

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The analogous matrices for the $U_{\frac{3}{2}}$ case are more conveniently expressed in terms of the states

$$\begin{aligned} |\alpha\rangle &= \sqrt{\frac{1}{2}}(|\kappa\rangle + i|\mu\rangle), & |\gamma\rangle &= \sqrt{\frac{1}{2}}(|\nu\rangle + i|\lambda\rangle), \\ |\beta\rangle &= \sqrt{\frac{1}{2}}(|\kappa\rangle - i|\mu\rangle), & |\delta\rangle &= \sqrt{\frac{1}{2}}(|\nu\rangle - i|\lambda\rangle), \end{aligned} \quad (3\cdot22)$$

but even so the expressions are rather cumbersome. They will therefore be given terms of certain 4×4 matrices defined as follows:

$$\begin{aligned} \tau_0 &= \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \\ \tau_a &= \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, & \tau_b &= \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}, \\ \tau_x &= \frac{1}{\sqrt{3}} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}, & \tau_y &= \frac{1}{\sqrt{3}} \begin{bmatrix} 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \\ -i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix}, & \tau_z &= \frac{1}{\sqrt{3}} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \\ \pi_x &= \frac{1}{3} \begin{bmatrix} 0 & 0 & 1 & 2\bar{\omega} \\ 0 & 0 & 2\omega & 1 \\ 1 & 2\bar{\omega} & 0 & 0 \\ 2\omega & 1 & 0 & 0 \end{bmatrix}, & \pi_y &= \frac{1}{3} \begin{bmatrix} 0 & 0 & i & 2i\omega \\ 0 & 0 & 2i\bar{\omega} & i \\ -i & -2i\omega & 0 & 0 \\ -2i\bar{\omega} & -i & 0 & 0 \end{bmatrix}, & \pi_z &= \frac{1}{3} \begin{bmatrix} 1 & 2 & 0 & 0 \\ 2 & 1 & 0 & 0 \\ 0 & 0 & -1 & -2 \\ 0 & 0 & -2 & -1 \end{bmatrix}, \\ & & \omega &= e^{\frac{2}{3}\pi i}. \end{aligned} \quad (3\cdot23)$$

Typical matrices may then be written

$$[\langle U_{\frac{3}{2}} | H | U_{\frac{3}{2}} \rangle] = k_2 [Q_{2a}\tau_a + Q_{2b}\tau_b] + \sqrt{3}k_5 [Q_{5x}\tau_x + Q_{5y}\tau_y + Q_{5z}\tau_z]. \quad (3\cdot24)$$

$$\begin{aligned} [\langle U_{\frac{3}{2}} | M_z | U_{\frac{3}{2}} \rangle] &= [\mu_3 Q_{3z} + \mu_4 Q_{4z}] \tau_0 + [\mu'_3 Q_{3z} + \mu'_4 Q_{4z}] \tau_a + \mu'_6 Q_{6z} \tau_b \\ &+ [\mu''_3 Q_{3x} + \mu''_4 Q_{4x} - \mu''_6 Q_{6x}] \tau_y + [\mu''_3 Q_{5y} + \mu''_4 Q_{4y} + \mu''_6 Q_{6y}] \tau_x. \end{aligned} \quad (3\cdot25)$$

$$[\langle U_{\frac{3}{2}} | \alpha^0 | U_{\frac{3}{2}} \rangle] = [\alpha_0 + \alpha_1 Q_1] \tau_0 + \alpha'_2 [Q_{2a}\tau_a + Q_{2b}\tau_b] + \alpha'_5 [Q_{5x}\tau_x + Q_{5y}\tau_y + Q_{5z}\tau_z]; \quad (3\cdot26)$$

$$\begin{aligned} [\langle U_{\frac{3}{2}} | \alpha_{z^2} | U_{\frac{3}{2}} \rangle] &= \alpha_2 Q_{2a} \tau_0 + [\alpha'_0 + \alpha'_1 Q_1 - \alpha''_2 Q_{2a}] \tau_a + \alpha''_2 Q_{2b} \tau_b - \frac{1}{2} \alpha''_5 [Q_{5x}\tau_x + Q_{5y}\tau_y - 2Q_{5z}\tau_z]; \\ [\langle U_{\frac{3}{2}} | \alpha_{xy} | U_{\frac{3}{2}} \rangle] &= \alpha_5 Q_{5z} \tau_0 + \alpha''_5 Q_{5z} \tau_a + [\alpha''_0 + \alpha''_1 Q_1 - 2\alpha''_2 Q_{2a}] \tau_z + \alpha''_5 [Q_{5x}\tau_y + Q_{5y}\tau_x]. \end{aligned} \quad (3\cdot27)$$

$$[\langle U_{\frac{3}{2}} | i\beta_{xy} | U_{\frac{3}{2}} \rangle] = [\beta'_0 + \beta'_1 Q_1 - 2\beta'_2 Q_{2a}] \pi_z - \beta'_5 [Q_{5x}\pi_y - Q_{5y}\pi_x]. \quad (3\cdot28)$$

4. AN OCTAHEDRAL MOLECULE IN AN $E_{\frac{3}{2}}$ STATE (Γ_7) (A KRAMERS DOUBLET)

We shall now consider the case of an octahedral molecule in a Kramers doublet state which arises from an orbitally degenerate state with symmetry T as a result of spin-orbit coupling; IrCl_6^{2-} provides a convenient example. In §2, it was shown that such a system does not experience a Jahn-Teller effect, a conclusion which is supported by the e.s.r. spectrum of IrCl_6^{2-} (Griffiths, Owen & Ward 1953). Its vibrational-electronic state may

therefore be described in terms of a simple product $|+\rangle|n_+\rangle$ or $|-\rangle|n_-\rangle$ according to whether the molecule is in the electronic state $|+\rangle$ or $|-\rangle$ (see equation (3.19)). The vibrational factors are, to as good an approximation as in the electronically non-degenerate case, simple products of harmonic oscillator functions of appropriate degeneracy, i.e.

$$|n\rangle = |v_1\rangle |v_2, l_2\rangle |v_3, l_3, l_{3z}\rangle |v_4, l_4, l_{4z}\rangle |v_5, l_5, l_{5z}\rangle |v_6, l_6, l_{6z}\rangle, \quad (4.1)$$

where the principal quantum number $v_i = 0, 1, 2, \dots$ for all i . There is one angular quantum number l_2 for the e_g vibration ($l_2 = v_2, v_2 - 2, \dots, -v_2$) and two angular quantum numbers for the triply degenerate vibrations Q_3 to Q_6 which takes the values

$$l_i = v_i, v_i - 2, \dots, 0 \text{ or } 1, \\ l_{iz} = l_i, l_i - 1, \dots, -l_i.$$

Also, according to §2, the infra-red spectrum and the polarized and depolarized contributions to the Raman spectrum are not expected to differ from those of an electronically non-degenerate molecule. They need therefore concern us no longer. A novel feature, however, is the possibility of reverse-polarized Raman scattering, whose intensity in the case of a molecule like IrCl_6^{2-} may be calculated with the aid of equations (3.21), (3.22) and (4.1) and the following expressions

$$|\langle v_1 + 1 | Q_1 | v_1 \rangle|^2 = (v_1 + 1) \hbar/2\omega_1, \quad (4.2)$$

$$\sum_{l_2} \{ |\langle v_2 + 1, l_2' | Q_{2a} | v_2, l_2 \rangle|^2 + |\langle v_2 + 1, l_2' | Q_{2b} | v_2, l_2 \rangle|^2 \} = (v_2 + 2) \hbar/2\omega_2 \quad (4.3)$$

and

$$\sum_{l_i, l_{iz}} |\langle v_i + 1, l_i', l_{iz}' | Q_{ix} | v_i, l_i, l_{iz} \rangle|^2 + |\langle v_i + 1, l_i', l_{iz}' | Q_{iy} | v_i, l_i, l_{iz} \rangle|^2 \\ + |\langle v_i + 1, l_i', l_{iz}' | Q_{iz} | v_i, l_i, l_{iz} \rangle|^2 = (v_i + 3) \hbar/2\omega_i \quad \text{for } i = 3 - 6. \quad (4.4)$$

(see, for instance, Nielsen 1959). In these equations ω_i is the frequency of vibration in the mode Q_i . All matrix elements of the type $\langle v_i' | Q_i | v_i'' \rangle$ are subject to the selection rule $\Delta v_i = \pm 1$ and in discussing Stokes-Raman scattering we shall be interested only in those for which $v_i' = v_i'' + 1$. Moreover, all transitions are doubly degenerate and we need consider only those for which the system is initially in the state $|+\rangle|n_+\rangle$. We conclude therefore that the reverse-polarized contribution to the Stokes-Raman spectrum contains three bands, namely: a Q_1 band for which

$$G^a = \frac{8}{9} \beta_1'^2 \left(\sum_{n_+} |\langle n_+' | Q_1 | n_+'' \rangle|^2 + \sum_{n_-} 2 |\langle n_-' | Q_1 | n_+'' \rangle|^2 \right) = \frac{8}{9} \beta_1'^2 (v_1'' + 1) \hbar/2\omega_1,$$

a Q_2 band with

$$G^a = \frac{8}{9} \beta_2'^2 \left(\sum_{n_+} |\langle n_+' | 2Q_{2a} | n_+'' \rangle|^2 + \sum_{n_-} 2 |\langle n_-' | Q_{2a} | n_+'' \rangle|^2 + 6 |\langle n_-' | Q_{2b} | n_+'' \rangle|^2 \right) \\ = \frac{16}{9} \beta_2'^2 (v_2'' + 2) \hbar/2\omega_2$$

and a Q_5 band for which

$$G^a = \frac{8}{9} \beta_5'^2 \left\{ \sum_{n_+} (|\langle n_+' | Q_{5x} | n_+'' \rangle|^2 + |\langle n_+' | Q_{5y} | n_+'' \rangle|^2) + \sum_{n_-} (2 |\langle n_-' | Q_{5z} | n_+'' \rangle|^2 \right. \\ \left. + |\langle n_-' | Q_{5y} + iQ_{5x} | n_+'' \rangle|^2) \right\} \\ = \frac{16}{9} \beta_5'^2 (v_5'' + 3) \hbar/2\omega_5.$$

There is also a reverse-polarized contribution to the Rayleigh scattered light, with $G^a = \frac{8}{9} \beta_0'^2$.

The constants $\beta'_0, \beta'_1, \beta'_2$ and β'_5 are defined by equations (3·21) and (3·22). Although, as we have seen, it is difficult to estimate their magnitudes in IrCl_6^{2-} , for instance, these quantities will depend upon the extent to which the distortions Q_1, Q_2 and Q_5 mix the ground state of the Ir^{4+} ion with its excited states. It is important to realize that the rules derived by Placzek (1934) about the state of polarization of light scattered by electronically non-degenerate molecules do not necessarily apply even to Kramers degenerate systems; deductions about molecule configurations based on these rules may well be misleading.

5. AN OCTAHEDRAL MOLECULE IN A $U_{\frac{3}{2}}$ STATE (Γ_8)

The case of an octahedral XY_6 molecules in a fourfold spin-degenerate state ($U_{\frac{3}{2}}$) may be complicated by the effects of vibronic coupling. According to § 3 cases (i) and (iii), those molecules in $U_{\frac{3}{2}}$ states arising from states with spatial symmetries A or E are best treated initially as if they had no electron spin and they need not concern us here. For other $U_{\frac{3}{2}}$ molecules, namely, those whose electronic states arise from orbital T states, it is necessary to describe the vibronic states by kets such as

$$|en\rangle = |\alpha\rangle |n_\alpha\rangle + |\beta\rangle |n_\beta\rangle + |\gamma\rangle |n_\gamma\rangle + |\delta\rangle |n_\delta\rangle, \quad (5.1)$$

where $|\alpha\rangle, |\beta\rangle, |\gamma\rangle$ and $|\delta\rangle$ are the components of the electronic state and $|n_\alpha\rangle, |n_\beta\rangle, |n_\gamma\rangle$ and $|n_\delta\rangle$ are vibrational factors. As far as Q_1, Q_3, Q_4 and Q_6 are concerned the vibrational factors are simple products of the appropriate simple harmonic oscillator functions (see equation (4·1)), whereas the Q_2 and Q_5 vibrational states satisfy

$$[(H_2 - E_2 + H_5 - E_5)I + V_2 + V_5] |n_2, n_5\rangle = 0. \quad (5.2)$$

H_2 and H_5 in this equation are harmonic oscillator Hamiltonians for Q_2 and Q_5 , respectively

$$H_2 = \frac{1}{2}\omega_2^2(Q_{2a}^2 + Q_{2b}^2) - \frac{1}{2}\hbar^2 \left(\frac{\partial^2}{\partial Q_{2a}^2} + \frac{\partial^2}{\partial Q_{2b}^2} \right),$$

$$H_5 = \frac{1}{2}\omega_5^2(Q_{5x}^2 + Q_{5y}^2 + Q_{5z}^2) - \frac{1}{2}\hbar^2 \left(\frac{\partial^2}{\partial Q_{5x}^2} + \frac{\partial^2}{\partial Q_{5y}^2} + \frac{\partial^2}{\partial Q_{5z}^2} \right)$$

and V_2 and V_5 represent the vibronic coupling due to these vibrations. Equation (3·25) gives $V_2 + V_5$ in one form, but it is more convenient for our purposes to introduce polar co-ordinates as follows

$$\left. \begin{aligned} Q_{2a} &= \rho \cos \phi & \text{and} & & Q_{5x} &= r \sin \theta \cos \chi, \\ Q_{2b} &= \rho \sin \phi & & & Q_{5y} &= r \sin \theta \sin \chi, \\ & & & & Q_{5z} &= r \cos \theta \end{aligned} \right\} \quad (5.3)$$

and write

$$V_2 = k_2 \rho \begin{bmatrix} 0 & e^{-i\phi} & 0 & 0 \\ e^{i\phi} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{-i\phi} \\ 0 & 0 & e^{i\phi} & 0 \end{bmatrix} \quad \text{and} \quad V_5 = k_5 r \begin{bmatrix} \cos \theta & 0 & \sin \theta e^{-ix} & 0 \\ 0 & -\cos \theta & 0 & -\sin \theta e^{-ix} \\ \sin \theta e^{ix} & 0 & -\cos \theta & 0 \\ 0 & -\sin \theta e^{ix} & 0 & \cos \theta \end{bmatrix}; \quad (5.4)$$

k_2 and k_5 are defined by equation (3·8).

If both k_2 and k_5 are very small, the solutions of (5·2) may be obtained by perturbation theory (Moffitt & Thorson 1957). The Q_2 and Q_5 vibrational factors are products of the

harmonic oscillator states $|v_2, l_2\rangle$ and $|v_5, l_5, l_{5z}\rangle$ associated with $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$ or $|\delta\rangle$ and the associated energy levels are given by

$$\begin{aligned} E_2 &= (v_2 + 1) \hbar\omega_2 + \left(\frac{1}{2} \pm j_2\right) (k_2/\omega_2)^2 & \text{where } j_2 &= l_2 \pm \frac{1}{2}, \\ E_5 &= \left(v_5 + \frac{3}{2}\right) \hbar\omega_5 - \left\{\frac{3}{4} + j_5(j_5 + 1) - l_5(l_5 + 1)\right\} (k_5/\omega_5)^2, & \text{where } j_5 &= l_5 \pm \frac{1}{2}. \end{aligned} \quad (5.5)$$

We shall discuss the quantum numbers j_2 and j_5 in more detail later.

All transitions are fourfold degenerate and it will be sufficient to discuss only those taking place from the state $|\alpha\rangle |n'_\alpha\rangle$. Transitions to the states $|\alpha\rangle |n'_\alpha\rangle$, $|\beta\rangle |n'_\beta\rangle$, $|\gamma\rangle |n'_\gamma\rangle$ and $|\delta\rangle |n'_\delta\rangle$ will all be important in determining the vibrational spectra of the molecule.

We deduce from equations (3.26) and (4.4) that the infra-red spectrum contains the fundamentals of the Q_3 , Q_4 and Q_6 vibrations, with intensities proportional to

$$(\mu_i^2 + \mu_i'^2 + \frac{2}{3}\mu_i''^2) 3\hbar/2\omega_i \quad \text{if } i = 3 \text{ or } 4$$

$$\text{and} \quad (\mu_i'^2 + \frac{2}{3}\mu_i''^2) 3\hbar/2\omega_i \quad \text{for } i = 6, \quad (5.6)$$

(for transitions from the vibrational ground state $v'_i = 0$ for all i) whereas in non-degenerate molecules only Q_3 and Q_4 are infra-red active. However, it may well turn out that μ'_i and μ''_i are small for those degenerate molecules in which k_2 and k_5 are small.

Similarly, according to equations (3.27), (3.28) and (4.2) to (4.4) the Raman spectrum contains three bands:

the Q_1 fundamental for which

$$\begin{aligned} G^0 &= \alpha_1^2 \hbar/2\omega_1, \\ G^s &= (2\alpha_1'^2 + \alpha_1''^2) \hbar/2\omega_1, \\ G^a &= \frac{5}{3}\beta_1'^2 \hbar/2\omega_1, \end{aligned}$$

the Q_2 fundamental for which

$$\begin{aligned} G^0 &= \alpha_2'^2 \hbar/\omega_2, \\ G^s &= (\alpha_2^2 + 2\alpha_2''^2 + 2\alpha_2'''^2) \hbar/\omega_2, \\ G^a &= \frac{10}{3}\beta_2'^2 \hbar/\omega_2, \end{aligned}$$

and the Q_5 fundamental for which

$$\left. \begin{aligned} G^0 &= \frac{1}{3}\alpha_5'^2 3\hbar/2\omega_5, \\ G^s &= (\alpha_5^2 + \alpha_5'^2 + \frac{1}{3}\alpha_5''^2 + \alpha_5'''^2 + \frac{2}{3}\alpha_5^{iv}) 3\hbar/2\omega_5, \\ G^a &= \frac{10}{9}\beta_5'^2 3\hbar/2\omega_5. \end{aligned} \right\} \quad (5.7)$$

The vibrations Q_1 , Q_2 and Q_5 are Raman active in electronically non-degenerate octahedral molecules, but the Q_1 bands are subject to $G^0 \neq 0$, $G^s = G^a = 0$, while for the Q_2 and Q_5 bands $G^0 = G^a = 0$ and $G^s \neq 0$.

For many molecules, however, the vibronic coupling terms in equation (5.2) will be large enough to cause more drastic changes in both the vibronic energy levels and their associated wave functions. According to equation (5.4) the potential surfaces governing the Q_2 and Q_5 vibrations are the solutions of (Moffitt & Thorson 1957).

$$V = \frac{1}{2}\omega_2^2 \rho^2 + \frac{1}{2}\omega_5^2 r^2 \pm \sqrt{(k_2^2 \rho^2 + k_5^2 r^2)}; \quad (5.8)$$

they have two types of minimum

(a) tetragonal stationary points, at which $\rho = k_2/\omega_2^2$, $r = 0$ and $V = -\frac{1}{2}(k_2/\omega_2)^2$; these are stable if $|k_2/\omega_2| > |k_5/\omega_5|$, or

(b) trigonal points, which are stable if $|k_2/\omega_2| < |k_5/\omega_5|$; at these $\rho = 0$, $r = k_5/\omega_5^2$ and $V = -\frac{1}{2}(k_5/\omega_5)^2$.

We shall investigate the solutions of equation (5.2) for two extreme cases

$$\left| \frac{k_2}{\omega_2} \right| \gg \left| \frac{k_5}{\omega_5} \right| \quad \text{and} \quad \left| \frac{k_5}{\omega_5} \right| \gg \left| \frac{k_2}{\omega_2} \right|.$$

These situations will be treated as cases of strong vibronic coupling with Q_2 or Q_5 alone and V_5 or V_2 introduced as a perturbation as the case requires. The intensities of vibrational transitions depend on the initial and final wave functions, which will be only slightly affected by V_5 or V_2 as the case may be but these perturbations may cause appreciable changes in the vibronic energy levels.

If $k_5 = 0$ equation (5.2) is separable in the co-ordinates Q_2 and Q_5 . As far as Q_5 is concerned the solutions are the states $|v_5, l_5, l_{5z}\rangle$ of equation (4.1) with corresponding energies

$$E_5 = (v_5 + \frac{3}{2}) \hbar \omega_5. \quad (5.9)$$

Moreover, the equations involving Q_2 are two independent sets of coupled equations of the type which have already been solved in some detail (Moffitt & Thorson 1958; Longuet-Higgins, Öpik, Pryce & Sack 1958), namely

$$\begin{bmatrix} H_2 - E_2 & k_2 \rho e^{-i\phi} \\ k_2 \rho e^{i\phi} & H_2 - E_2 \end{bmatrix} \begin{bmatrix} |n_{2+}\rangle \\ |n_{2-}\rangle \end{bmatrix} = 0, \quad (5.10)$$

where the two-component state $|n_2\rangle$ is associated either with $|\alpha\rangle$ and $|\beta\rangle$ or with $|\gamma\rangle$ and $|\delta\rangle$. The operator

$$\hat{J}_2 = \begin{bmatrix} \hat{L}_2 + \frac{1}{2}\hbar & 0 \\ 0 & \hat{L}_2 - \frac{1}{2}\hbar \end{bmatrix}, \quad (5.11)$$

where $\hat{L}_2 = -i\hbar \partial/\partial\phi$, commutes with the Hamiltonian in (5.10) and hence the eigenvalues (j_2) of \hat{J}_2 are good quantum numbers. We are therefore led to choose the vibronic wave functions in the form

$$\langle \rho, \phi | n_2 \rangle = \langle \rho, \phi | w_2, j_2 \rangle = \begin{bmatrix} \langle \rho | w_{2+} \rangle e^{i(j_2 - \frac{1}{2})\phi} \\ \langle \rho | w_{2-} \rangle e^{i(j_2 + \frac{1}{2})\phi} \end{bmatrix}. \quad (5.12)$$

Numerical solutions to equation (5.10) have been obtained for a range of values of a dimensionless parameter

$$D_2 = k_2^2/2\hbar\omega_2^3 \quad (5.13)$$

and the vibronic energy levels are generally found to be irregularly spaced. However, if k_2 is so large that the lowest vibronic states are determined almost entirely by the lower branch of the potential surface, an approximate algebraic solution is available. The radial contribution to these states may then be described as

$$\begin{bmatrix} |u_2\rangle \\ 0 \end{bmatrix} = \begin{bmatrix} \sqrt{\frac{1}{2}} (|w_{2+}\rangle - |w_{2-}\rangle) \\ \sqrt{\frac{1}{2}} (|w_{2+}\rangle + |w_{2-}\rangle) \end{bmatrix}, \quad (5.14)$$

and the wave function $\langle \rho | u_2 \rangle$ is $\rho^{-\frac{1}{2}}$ times a linear harmonic oscillator function centred on $\rho = k_2/\omega_2^2$; its associated energy levels are given by

$$E_2 = (u_2 + \frac{1}{2}) \hbar \omega_2 - \frac{1}{2} \left[\left(\frac{k_2}{\omega_2} \right)^2 - \left(j_2 \frac{\omega_2^2 \hbar}{k_2} \right)^2 \right]. \quad (5.15)$$

The perturbation V_5 causes a second-order correction

$$\Delta E = \sum_{w'_2, v'_5} \frac{|\langle w'_2, v'_5 | V_5 | u_2, v_5 \rangle|^2}{E_2 + E_5 - E'_2 - E'_5} \quad (5.16)$$

to the energy of low-lying states $|u_2, j_2, v_5\rangle$. Note that the summation is taken over the general states $|w'_2\rangle$ and not only the states $|u'_2\rangle$ which satisfy (5.14). Now according to the Franck–Condon principle, the numerators in (5.16) will be large only for vertical excitation. The denominators will therefore be replaced by the vertical excitation energy $2k_2^2/\omega_2^2$ so that (5.16) becomes

$$\begin{aligned} \Delta E &\doteq -\frac{\omega_2^2}{2k_2^2} \sum_{w'_2, v'_5} |\langle w'_2, v'_5 | V_5 | u_2, v_5 \rangle|^2 \\ &= -\frac{\omega_2^2}{2k_2^2} \langle v_5 | k_5^2 r^2 | v_5 \rangle \\ &= -\frac{1}{2} \left(\frac{k_5 \omega_2}{k_2 \omega_5} \right)^2 (v_5 + \frac{3}{2}) \hbar \omega_5. \end{aligned} \quad (5.17)$$

Therefore, if $|k_2/\omega_2| \gg |k_5/\omega_5|$ the lowest vibronic energy levels are given by

$$E_2 + E_5 = (u_2 + \frac{1}{2}) \hbar \omega_2 + (v_5 + \frac{3}{2}) \hbar \omega_5 (1 - \delta_5) - \frac{1}{2} \left[\left(\frac{k_2}{\omega_2} \right)^2 - \left(j_2 \frac{\omega_2^2 \hbar}{k_2} \right)^2 \right], \quad (5.18)$$

the apparent frequency of the Q_5 vibration being reduced by the factor $(1 - \delta_5)$, where

$$\delta_5 = \frac{1}{2} \left(\frac{k_5 \omega_2}{k_2 \omega_5} \right)^2. \quad (5.19)$$

The perturbation V_5 will make little difference to the vibronic wave functions and as far as Q_2 is concerned the system is equally likely to be in either of the states $|w_2, j_2(\alpha\beta)\rangle$ or $|w_2, j_2(\gamma\delta)\rangle$ where

$$\langle \rho, \phi | w_2, j_2(\alpha\beta) \rangle = \begin{bmatrix} \langle \rho | w_{2+} \rangle e^{i(j_2 - \frac{1}{2})\phi} \\ \langle \rho | w_{2-} \rangle e^{i(j_2 + \frac{1}{2})\phi} \\ 0 \\ 0 \end{bmatrix} \quad \text{and} \quad \langle \rho, \phi | w_2, j_2(\gamma\delta) \rangle = \begin{bmatrix} 0 \\ 0 \\ \langle \rho | w_{2+} \rangle e^{i(j_2 - \frac{1}{2})\phi} \\ \langle \rho | w_{2-} \rangle e^{i(j_2 + \frac{1}{2})\phi} \end{bmatrix}, \quad (5.20)$$

the other vibrations being in harmonic oscillator states $|v_1\rangle$ or $|v_i, l_i, l_{iz}\rangle$ as the case may be. Since all transitions are doubly degenerate it will be sufficient to discuss transitions from the state $|n''(\alpha\beta)\rangle$ to either $|n'(\alpha\beta)\rangle$ or $|n'(\gamma\delta)\rangle$; their intensities may be calculated by contracting the matrices (3.26) to (3.28) between the initial and final vibronic states.

According to table 2, Q_3 , Q_4 and Q_6 may all be active in infra-red absorption. We deduce from equations (3.26), (4.4) and (5.20) that in addition to the fundamentals of Q_3 and Q_4 , with intensities proportional to $\mu_3^2 \hbar / 2\omega_2$ and $\mu_4^2 \hbar / 2\omega_2$ respectively, the infra-red spectrum contains three sets of combination bands involving several quanta of excitation of Q_2 and

a single quantum of excitation of each of Q_3 , Q_4 and Q_6 . These sets of bands correspond to $\Delta j_2 = 0, \pm 1$ and their intensities are proportional to

$$\left. \begin{aligned} 2d_2^2 \mu_i'^2 \hbar / 2\omega_i & \text{ for } \Delta j_2 = 0, \\ 3e_2^{*2} \mu_i'^2 \hbar / 2\omega_i & \text{ for } \Delta j_2 = +1 \\ \text{and} & \\ 3e_2^2 \mu_i'^2 \hbar / 2\omega_i & \text{ for } \Delta j_2 = -1. \end{aligned} \right\} \quad (5.21)$$

In these expressions, the quantities

$$\left. \begin{aligned} e_2^* &= \langle w'_{2+} | w''_{2-} \rangle, \\ e_2 &= \langle w'_{2-} | w''_{2+} \rangle \\ \text{and} & \\ d_2 &= \langle w'_{2+} | w''_{2+} \rangle - \langle w'_{2-} | w''_{2-} \rangle \end{aligned} \right\} \quad (5.22)$$

are not subject to any general selection rules on w_2 (see the appendix to paper III). However, according to the Franck-Condon principle they will probably be largest for vertical excitation. We therefore expect to find a strong progression of combination bands at frequencies corresponding to $2(k_2/\omega_2)^2$. If $|k_2|$ is sufficiently large, for low-frequency transitions we may express $|w_{2+}\rangle$ and $|w_{2-}\rangle$ in terms of $|u_2\rangle$ of equation (5.14), in which case

$$\left. \begin{aligned} e_2^* &= e_2 = -\frac{1}{2} \delta_{u_2^-, u_2^+} \\ d_2 &= 0, \end{aligned} \right\} \quad (5.23)$$

and the low-frequency region of the spectrum contains only the Q_3 , Q_4 and Q_6 fundamentals.

As shown in table 2, Q_1 , Q_2 and Q_5 are expected to give rise to bands in the Raman spectrum, but the situation is complicated by the fact that Q_2 is also involved in vibronic coupling. The Q_1 and Q_5 fundamentals are expected to appear, with intensities given by equations (5.7) and also the fundamental of Q_2 . There may also be strong combination bands involving a single excitation of Q_1 or Q_5 and multiple excitations of Q_2 , in addition to strong overtones of Q_2 . The strongest lines in the high-frequency region of the spectrum will undoubtedly be the Q_2 overtones arising from the constant terms α_0 , α'_0 , α''_0 and β'_0 in equations (3.27) and (3.28) and previous calculations (III) indicate that they may well dominate the spectrum. They occur as three sets of lines, for which

$$\left. \begin{aligned} G^0 &= 0, \quad G^s = \alpha_0''^2 d_2^2, \quad G^a = 0 & \text{if } \Delta j_2 = 0, \\ G^0 &= 0, \quad G^s = 2\alpha_0'^2 e_2^{*2}, \quad G^a = \frac{4}{3}\beta_0'^2 e_2^{*2} & \text{if } \Delta j_2 = +1, \\ \text{and} & \\ G^0 &= 0, \quad G^s = 2\alpha_0'^2 e_2^2, \quad G^a = \frac{4}{3}\beta_0'^2 e_2^2 & \text{if } \Delta j_2 = -1, \end{aligned} \right\} \quad (5.24)$$

with maxima in the region of the frequency corresponding to vertical excitation.

The other situation which can be treated algebraically is the case of a deep trigonal minimum in the potential surface. As a first approximation we shall put $k_2 = 0$, when the Q_2 vibrations are described by the harmonic oscillator states $|v_2, l_2\rangle$ of equation (4.1) with energy

$$E_2 = (v_2 + 1) \hbar \omega_2, \quad (5.25)$$

and the Q_5 states are the solutions of one of the two independent equations

$$\begin{bmatrix} H_5 - E_5 + k_5 r \cos \theta & k_5 r \sin \theta e^{-i\chi} \\ k_5 r \sin \theta e^{i\chi} & H_5 - E_5 - k_5 r \cos \theta \end{bmatrix} \begin{bmatrix} |n_{5\alpha}\rangle \\ |n_{5\gamma}\rangle \end{bmatrix} = 0 \quad (5.26)$$

and

$$\begin{bmatrix} H_5 - E_5 - k_5 r \cos \theta & -k_5 r \sin \theta e^{-i\chi} \\ -k_5 r \sin \theta e^{i\chi} & H_5 - E_5 + k_5 r \cos \theta \end{bmatrix} \begin{bmatrix} |n_{5\beta}\rangle \\ |n_{5\delta}\rangle \end{bmatrix} = 0. \quad (5.26a)$$

The solutions of (5.26) and (5.26a) are so similar that we need consider only (5.26) for instance.

Moffitt & Thorson (1957) have shown that there are two good half-odd quantum numbers j_5 and m_5 , namely, the eigenvalues of \hat{J}_5^2 and \hat{J}_{5z} where,

$$\hat{\mathbf{J}}_5 = \hat{\mathbf{L}}_5 I + \frac{1}{2} \hbar \hat{\boldsymbol{\sigma}}; \quad (5.27)$$

$\hat{\mathbf{L}}_5$ is the angular momentum operator in Q_5 space and the components of $\hat{\boldsymbol{\sigma}}$ are the Pauli spin matrices. The solutions of equation (5.26), which are eigenfunctions of \hat{J}_5^2 and \hat{J}_{5z} may be obtained, by the methods for combining angular momenta in atomic spectroscopy (Condon & Shortley 1951) from the angular parts $|l_5, l_{5z}\rangle$ of the states $|v_5, l_5, l_{5z}\rangle$. For a given value of j_5 , either (i) $l_5 = j_5 - \frac{1}{2}$ and the resulting state is

$$|j_{5-}, m_5\rangle = \begin{bmatrix} \sqrt{\left(\frac{j_5 + m_5}{2j_5}\right)} |j_5 - \frac{1}{2}, m_5 - \frac{1}{2}\rangle \\ \sqrt{\left(\frac{j_5 - m_5}{2j_5}\right)} |j_5 - \frac{1}{2}, m_5 + \frac{1}{2}\rangle \end{bmatrix}, \quad (5.28)$$

or (ii) $l_5 = j_5 + \frac{1}{2}$ and we obtain

$$|j_{5+}, m_5\rangle = \begin{bmatrix} \sqrt{\left(\frac{j_5 - m_5 + 1}{2(j_5 + 1)}\right)} |j_5 + \frac{1}{2}, m_5 - \frac{1}{2}\rangle \\ -\sqrt{\left(\frac{j_5 + m_5 + 1}{2(j_5 + 1)}\right)} |j_5 + \frac{1}{2}, m_5 + \frac{1}{2}\rangle \end{bmatrix}. \quad (5.29)$$

The Q_5 vibronic state is some combination of these,

$$|n_5(xy)\rangle = |w_5, j_5, m_5\rangle = \sqrt{\frac{1}{2}} (|w_{5+}, j_{5+}, m_5\rangle + |w_{5-}, j_{5-}, m_5\rangle) \quad (5.30)$$

say, the radial factors $|w_{5+}\rangle$ and $|w_{5-}\rangle$ being the solutions of

$$\begin{bmatrix} H_{j_5} - k_5 r - E_5 & -(j_5 + \frac{1}{2}) \hbar^2 / 2r^2 \\ -(j_5 + \frac{1}{2}) \hbar^2 / 2r^2 & H_{j_5} + k_5 r - E_5 \end{bmatrix} \begin{bmatrix} \sqrt{\frac{1}{2}} (|w_{5+}\rangle - |w_{5-}\rangle) \\ \sqrt{\frac{1}{2}} (|w_{5+}\rangle + |w_{5-}\rangle) \end{bmatrix} = 0. \quad (5.31)$$

In equation (5.31), which is derived from (5.26) to (5.30) with the help of the standard expressions for the products $\cos \theta |l_5, l_{5z}\rangle$ and $\sin \theta e^{\pm i\chi} |l_5, l_{5z}\rangle$ (see, for instance, Condon & Shortley 1951, p. 53),

$$H_{j_5} = \frac{1}{2} \left\{ \omega_5^2 r^2 - \frac{\hbar^2}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - (j_5 + \frac{1}{2})^2 \right] \right\}. \quad (5.32)$$

There is no reason to suppose that the solutions of (5.25) can be expressed in a simple algebraic form and general solutions, which are $(2j_5 + 1)$ -fold degenerate since they are independent of m_5 , require numerical methods. However, approximate algebraic solutions are available for the lowest energy levels if k_5 is sufficiently large. The state of the system is then very nearly

$$\begin{bmatrix} |u_5\rangle \\ 0 \end{bmatrix} = \begin{bmatrix} \sqrt{\frac{1}{2}} (|w_{5+}\rangle - |w_{5-}\rangle) \\ \sqrt{\frac{1}{2}} (|w_{5+}\rangle + |w_{5-}\rangle) \end{bmatrix}, \quad (5.33)$$

whose radial wave function $v(r)$ satisfies

$$(H_{j_5} - k_5 r - E_5) v(r) = 0. \quad (5.34)$$

The substitution $v(r) = r^{-1}w(r)$ leads to

$$\left\{ \frac{d^2}{dr^2} + \frac{1}{\hbar^2} \left[2E_5 - \frac{(j_5 + \frac{1}{2})^2 \hbar^2}{r^2} + \left(\frac{k_5}{\omega_5} \right)^2 \right] - \frac{1}{2} \left(\frac{\omega_5}{\hbar} \right)^2 \left(r - \frac{k_5}{\omega_5^2} \right)^2 \right\} w(r) = 0. \quad (5.35)$$

If we now put $s = (\omega_5/\hbar)^{\frac{1}{2}} (r - k_5/\omega_5^2)$ and note that for small s $1/r^2 \doteq \omega_5^4/k_5^2$, we see that the function $u(s) = w(r)$ must satisfy

$$\left\{ \frac{d^2}{ds^2} + \frac{1}{\hbar\omega_5} \left[2E_5 - \left(\frac{j_5 + \frac{1}{2}}{k_5} \hbar\omega_5^2 \right)^2 + \left(\frac{k_5}{\omega_5} \right)^2 \right] - \frac{1}{2}s^2 \right\} u(s) = 0. \quad (5.36)$$

The solutions of equation (5.36), subject to the condition that $u(s) \rightarrow 0$ as $s \rightarrow \infty$ are linear harmonic oscillator functions for which

$$E_5 = (u_5 + \frac{1}{2}) \hbar\omega_5 - \frac{1}{2} \left[\left(\frac{k_5}{\omega_5} \right)^2 - \left(\frac{j_5 + \frac{1}{2}}{k_5} \hbar\omega_5^2 \right)^2 \right]. \quad (5.37)$$

It must be emphasized that these solutions apply only to those states which satisfy equation (5.31) and that the vibronic levels associated with the upper branch of the potential surface cannot be readily obtained by algebraic methods.

The solutions of (5.26a) are very similar. If the system is in the electronic states $|\beta\rangle$ and $|\delta\rangle$, its vibronic state is described in terms of

$$|n_5(\beta\delta)\rangle = \sqrt{\frac{1}{2}} (|w_{5-}, j_{5-}, m_5\rangle - |w_{5+}, j_{5+}, m_5\rangle), \quad (5.30a)$$

where $|w_{5+}\rangle$ and $|w_{5-}\rangle$ satisfy (5.31).

By following a procedure entirely analogous to that adopted for introducing V_5 in the tetragonal case (equations (5.16) to (5.19)) we deduce that if the system is in equilibrium near a trigonal stationary point, the apparent frequency of the Q_2 vibration is reduced by a factor $(1 - \delta_2)$, where

$$\delta_2 = \frac{1}{2} (k_2 \omega_5 / k_5 \omega_2)^2, \quad (5.38)$$

and for sufficiently large k_5 , the Q_2 and Q_5 vibrational energy levels are given by

$$E_2 + E_5 = (v_2 + 1) \hbar\omega_2 (1 - \delta_2) + (u_5 + \frac{1}{2}) \hbar\omega_5 - \frac{1}{2} \left[\left(\frac{k_5}{\omega_5} \right)^2 - \left(\frac{j_5 + \frac{1}{2}}{k_5} \hbar\omega_5^2 \right)^2 \right]. \quad (5.39)$$

We are now in a position to discuss the intensities of lines in the infra-red and Raman spectra of molecules for which $|k_5/\omega_5| \gg |k_2/\omega_2|$. According to equations (5.30) and (5.30a) the vibronic state of the molecule may be described in terms of a simple product of the states $|v_1\rangle$, $|v_2, l_2\rangle$, $|v_3, l_3, l_{3z}\rangle$, $|v_4, l_4, l_{4z}\rangle$ and $|v_6, l_6, l_{6z}\rangle$ and either of the states

$$|n_5(\alpha\gamma)\rangle = |w_5, j_5, m_5\rangle = \left[\begin{array}{c} \sqrt{\left(\frac{j_5 + m_5}{4j_5} \right)} |w_{5-}, j_5 - \frac{1}{2}, m_5 - \frac{1}{2}\rangle + \sqrt{\left(\frac{j_5 - m_5 + 1}{4(j_5 + 1)} \right)} |w_{5+}, j_5 + \frac{1}{2}, m_5 - \frac{1}{2}\rangle \\ 0 \\ \sqrt{\left(\frac{j_5 - m_5}{4j_5} \right)} |w_{5-}, j_5 - \frac{1}{2}, m_5 + \frac{1}{2}\rangle - \sqrt{\left(\frac{j_5 + m_5 + 1}{4(j_5 + 1)} \right)} |w_{5+}, j_5 + \frac{1}{2}, m_5 + \frac{1}{2}\rangle \\ 0 \\ 0 \end{array} \right] \quad (5.40)$$

and

$$|n_5(\beta\delta)\rangle = |w_5, j_5, m_5\rangle = \left[\begin{array}{c} 0 \\ \sqrt{\left(\frac{j_5 + m_5}{4j_5} \right)} |w_{5-}, j_5 - \frac{1}{2}, m_5 - \frac{1}{2}\rangle - \sqrt{\left(\frac{j_5 - m_5 + 1}{4(j_5 + 1)} \right)} |w_{5+}, j_5 + \frac{1}{2}, m_5 - \frac{1}{2}\rangle \\ 0 \\ \sqrt{\left(\frac{j_5 - m_5}{4j_5} \right)} |w_{5-}, j_5 - \frac{1}{2}, m_5 + \frac{1}{2}\rangle + \sqrt{\left(\frac{j_5 + m_5 + 1}{4(j_5 + 1)} \right)} |w_{5+}, j_5 + \frac{1}{2}, m_5 + \frac{1}{2}\rangle \end{array} \right]$$

For given w_5 and j_5 , $|n_5(\alpha\gamma)\rangle$ and $|n_5(\beta\delta)\rangle$ have the same energy and we need only consider transitions from $|n_5''(\alpha\gamma)\rangle$, say. These states are $(2j_5 + 1)$ -fold degenerate and the intensity of the given spectral line is obtained by averaging over all the possible initial values of m_5 with the help of the relations

$$\left. \begin{aligned} \overline{m_5^2} &= \frac{1}{3}j_5(j_5 + 1), \\ \frac{(j_5 + m_5 + 1)(j_5 - m_5)}{(j_5 + m_5)(j_5 - m_5)} &= \frac{2}{3}j_5(j_5 + 1), \\ \frac{(j_5 + m_5)(j_5 - m_5)}{(j_5 + m_5)(j_5 + m_5 - 1)} &= \frac{1}{3}j_5(2j_5 - 1), \\ \frac{(j_5 + m_5)(j_5 - m_5)}{(j_5 + m_5)(j_5 + m_5 - 1)} &= \frac{2}{3}j_5(2j_5 - 1). \end{aligned} \right\} \quad (5.41)$$

Using equations (5.40) and (5.41), together with the expressions (3.26), we deduce that at low temperatures the infra-red spectrum contains the Q_3 and Q_4 fundamentals with intensities proportional to $\mu_3^2\hbar/2\omega_3$ and $\mu_4^2\hbar/2\omega_4$, respectively, and combination bands involving a single excitation of Q_3 , Q_4 or Q_6 and multiple excitations of Q_5 . The intensities of these combination bands depend upon

$$\left. \begin{aligned} \left(\frac{1}{4}c_5^2\mu_i'^2 + \frac{1}{8}d_5^2\mu_i''^2\right) 3\hbar/2\omega_i & \text{ for } j_5 = \frac{1}{2} \leftarrow \frac{1}{2} \\ 2a_5^2\mu_i''^2 3\hbar/2\omega_i & \text{ for } j_5 = \frac{3}{2} \leftarrow \frac{1}{2}. \end{aligned} \right\} \quad (5.42)$$

and

(Since j_5 takes only positive values there can be no $\Delta j_5 = -1$ transitions from the vibronic ground state.) The quantities

$$\left. \begin{aligned} a_5 &= \langle w'_{5-} | w''_{5+} \rangle / 2(j_5'' + 1), \\ b_5 &= \langle w'_{5+} | w''_{5-} \rangle / 2j_5'', \\ c_5 &= \langle w'_{5+} | w''_{5+} \rangle - \langle w'_{5-} | w''_{5-} \rangle, \\ d_5 &= \langle w'_{5+} | w''_{5+} \rangle / 2(j_5'' + 1) - \langle w'_{5-} | w''_{5-} \rangle / 2j_5'', \\ e_5 &= \langle w'_{5+} | w''_{5+} \rangle / 2(j_5'' + 1) + \langle w'_{5-} | w''_{5-} \rangle / 2j_5'', \end{aligned} \right\} \quad (5.43)$$

and

are not subject to any general selection rules on w_5 but they are expected to be largest for vertical excitation. If k_5 is sufficiently large, only the Q_3 , Q_4 and Q_6 fundamentals occur in the low-frequency spectrum; the lowest energy levels are described in terms of the $|u_5\rangle$ of (5.33) and a_5 , b_5 , d_5 and e_5 are non-zero only if $\Delta u_5 = 0$, while c_5 is identically zero for all low frequency transitions.

Again the Raman spectrum contains the Q_1 , Q_2 and Q_5 fundamentals and also certain overtones and combination bands involving multiple excitations of Q_5 .

The intensities of the Q_1 and Q_2 bands depend on the squares of the polarizability derivatives α_1 to α_2''' and these bands will have normal intensities; but the fundamental of Q_5 and its overtones contain contributions whose intensities depend on the constants α_0' , α_0'' and β_0' and these may well dominate the spectrum. There are two sets of such progressions from the vibronic ground state, one corresponding to $j_5 = \frac{1}{2} \leftarrow \frac{1}{2}$ for which

$$G^0 = 0, \quad G^s = \frac{1}{2}\alpha_0'^2 c_5^2 + \frac{1}{4}\alpha_0''^2 d_5^2, \quad G^a = \frac{1}{12}\beta_0'^2 (d_5^2 + 4e_5^2), \quad (5.44)$$

and the other to $j_5 = \frac{3}{2} \leftarrow \frac{1}{2}$, in which case

$$G^0 = 0, \quad G^s = 3a_5^2\alpha_0''^2 \quad \text{and} \quad G^a = 5a_5^2\beta_0'^2. \quad (5.45)$$

Again these bands are expected to show maxima at the frequency corresponding to the vertical excitation energy $2(k_5/\omega_5)^2$. If k_5 is sufficiently large the low frequency region of

the spectrum will resemble that of a non-degenerate molecule, except that according to equations (5.7) and (5.44) all the bands may contain reverse polarized ($\rho_n = 2$) contributions.

According to its reported spectrum (Gaunt 1954) ReF_6 itself does not seem to belong to either of our limiting cases; the apparent frequencies of both the e_g (600 cm^{-1}) and t_{2g} (246 cm^{-1}) vibrations appear anomalously low, when compared with the corresponding frequencies for WF_6 (670 cm^{-1} and 322 cm^{-1}) (Burke, Smith & Neilsen 1951) and IrF_6 (643 cm^{-1} and 260 cm^{-1}) (Claassen & Weinstock 1960). It is probable therefore that Q_2 and Q_5 are equally important in vibronic coupling in ReF_6 . It would be interesting to investigate the infra-red and Raman spectra of this molecule at higher frequencies.

6. CONCLUSIONS

The considerations of the preceding sections lead us to expect in the vibrational spectra of electronically degenerate molecules certain features which do not arise in the non-degenerate case. The mere fact of electronic degeneracy causes a breakdown in the familiar group-theoretical selection rules (Herzberg 1945) since bands in the infra-red and Raman spectrum may owe some or all of their intensity to what are effectively vibrational-electronic transitions, for which the initial and final electronic states happen to have the same energy.

In order to estimate the magnitudes of these effects in any particular spin-degenerate molecule, it is convenient to consider the orbital character of the state from which its full electronic state is derived. The vibrational spectra of those molecules in which the effect of spin-orbit coupling is small will have no strong features which can be attributed to their spin degeneracy. This applies not only to those molecules in which ζ is small, but also to all molecules in orbitally non-degenerate states and to tetrahedral and octahedral molecules in orbitally doubly degenerate states (E). Moreover, the special effects due to orbital degeneracy in electronically degenerate dihedal molecules (III) are quenched by strong spin-orbit coupling. The remaining case, namely, that of an octahedral or tetrahedral molecule whose electronic state arises from a spatially triply degenerate state, is therefore likely to prove the most interesting.

The ground electronic state of a molecule with octahedral symmetry, and an odd number of electrons may either be a Kramers doublet ($E_{\frac{3}{2}}, E_{\frac{3}{2}}$) or a quartet ($U_{\frac{3}{2}}$) state. In the former case the only novelty is the possibility of reverse-polarized Raman and Rayleigh scattering, so that any deductions based on Placzek's (1934) rules about depolarization ratios may be misleading. This might be exhibited by IrCl_6^{2-} . In the $U_{\frac{3}{2}}$ case, both the e_g and the t_{2g} vibrational co-ordinates may be involved in vibronic coupling, but we have limited our discussion to those cases in which vibronic coupling is very weak, or in which coupling by one of the vibronically active co-ordinates is very much more important than by the other. In those cases when vibronic coupling is weak, it turns out that the t_{2u} vibration (Q_6) may be infra-red active as well as the t_{1u} vibrations (Q_3 and Q_4); the depolarization ratios for bands in the Raman spectrum may have 'unexpected' values. If there is strong coupling with one of the vibronically active co-ordinates, its vibronic energy levels will in general be irregularly spaced, but for sufficiently strong coupling the lowest energy levels will have the same spacing as if there were no Jahn–Teller effect. The apparent frequency of vibration in the other vibronically active co-ordinate may be reduced. All

the u vibrations are expected to be infra-red active and the infra-red spectrum may contain in addition to their fundamentals strong progressions of combination bands between these vibrations and the vibronically active vibration. These progressions will have maxima in the region of the vertical excitation energy. Similarly the g vibrations (Q_1 , Q_2 and Q_5) are expected to be Raman active with 'anomalous' depolarization ratios and the Raman spectrum may contain a strong progression of overtones of the vibronically active vibration, as well as the Q_1 , Q_2 and Q_5 fundamentals.

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STUDIES OF THE JAHN-TELLER EFFECT. IV

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APPENDIX. CHARACTER TABLES FOR THE 'TWO-VALUED' REPRESENTATIONS OF THE IMPORTANT EXTENDED DIHEDRAL GROUPS

| | | | | | | | | | | | | | | | | | | | | | | |
|------------|-----|-----|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|------------------------------------|-------------|-------------|-------------|--|--|--|--|-----------------------------------|
| C_{3v}^* | E | R | $2C_3$ | $2C_3R$ | $6\sigma_v$ | | | | | | | | | | | | | | | | | |
| $E_{1/2}$ | 2 | -2 | 1 | -1 | 0 | | | | | | | | | | | | | | | | | |
| $E_{3/2}$ | 2 | -2 | -2 | 2 | 0 | | | | | | | | | | | | | | | | | |
| C_{4v}^* | E | R | $2C_4$ | $2C_4R$ | $2C_2$ | $4\sigma_v$ | $4\sigma_d$ | | | | | | | | | | | | | | | |
| D_{2d}^* | E | R | $2S_4$ | $2S_4R$ | $2C_2$ | $4C_2'$ | $4\sigma_d$ | | | | | | | | | | | | | | | |
| $E_{1/2}$ | 2 | -2 | $\sqrt{2}$ | $-\sqrt{2}$ | 0 | 0 | 0 | | | | | | | | | | | | | | | |
| $E_{3/2}$ | 2 | -2 | $-\sqrt{2}$ | $\sqrt{2}$ | 0 | 0 | 0 | | | | | | | | | | | | | | | |
| D_{3d}^* | E | R | $2C_3$ | $2C_3R$ | $6C_2$ | i | iR | $2S_6$ | $2S_6R$ | $6\sigma_d$ | | | | | | | | | | | | |
| $E_{1/2g}$ | 2 | -2 | 1 | -1 | 0 | 2 | -2 | 1 | -1 | 0 | | | | | | | | | | | | |
| $E_{3/2g}$ | 1 | -1 | -1 | 1 | i | 1 | -1 | -1 | 1 | 0 | | | | | | | | | | | | |
| $E_{1/2u}$ | 1 | -1 | -1 | 1 | $-i$ | 1 | -1 | -1 | 1 | 0 | | | | | | | | | | | | |
| $E_{3/2u}$ | 2 | -2 | 1 | -1 | 0 | -2 | 2 | -1 | 1 | 0 | | | | | | | | | | | | |
| $E_{1/2u}$ | 1 | -1 | -1 | 1 | i | -1 | 1 | 1 | -1 | 0 | | | | | | | | | | | | |
| $E_{3/2u}$ | 1 | -1 | -1 | 1 | $-i$ | -1 | 1 | 1 | -1 | 0 | | | | | | | | | | | | |
| D_{4d}^* | E | R | $2S_8$ | $2S_8R$ | $2C_4$ | $2C_4R$ | $2S_8^3$ | $2S_8^3R$ | $2C_2$ | $8C_2'$ | $8\sigma_d$ | | | | | | | | | | | |
| $E_{1/2}$ | 2 | -2 | β | $-\beta$ | $\sqrt{2}$ | $-\sqrt{2}$ | $-\alpha$ | α | 0 | 0 | 0 | | | | | | | | | | | |
| $E_{3/2}$ | 2 | -2 | $-\alpha$ | α | $-\sqrt{2}$ | $\sqrt{2}$ | $-\beta$ | β | 0 | 0 | 0 | | | | | | | | | | | $\alpha = 2 \cos \frac{1}{8}\pi,$ |
| $E_{5/2}$ | 2 | -2 | α | $-\alpha$ | $-\sqrt{2}$ | $\sqrt{2}$ | β | $-\beta$ | 0 | 0 | 0 | | | | | | | | | | | $\beta = 2 \cos \frac{3}{8}\pi$ |
| $E_{7/2}$ | 2 | -2 | $-\beta$ | β | $\sqrt{2}$ | $-\sqrt{2}$ | α | $-\alpha$ | 0 | 0 | 0 | | | | | | | | | | | |
| D_{3h}^* | E | R | $2C_3$ | $2C_3R$ | $4C_2$ | $2\sigma_h$ | $2S_3$ | $2S_3R$ | $6\sigma_v$ | | | | | | | | | | | | | |
| $E_{1/2}$ | 2 | -2 | 1 | -1 | 0 | 0 | $\sqrt{3}$ | $-\sqrt{3}$ | 0 | | | | | | | | | | | | | |
| $E_{3/2}$ | 2 | -2 | -2 | 2 | 0 | 0 | 0 | 0 | 0 | | | | | | | | | | | | | |
| $E_{5/2}$ | 2 | -2 | 1 | -1 | 0 | 0 | $-\sqrt{3}$ | $\sqrt{3}$ | 0 | | | | | | | | | | | | | |
| D_{4h}^* | E | R | $2C_4$ | $2C_4R$ | $2C_2$ | $4C_2'$ | $4C_2''$ | i | iR | $2S_4$ | $2S_4R$ | $2\sigma_h$ | $4\sigma_v$ | $4\sigma_d$ | | | | | | | | |
| $E_{1/2g}$ | 2 | -2 | $\sqrt{2}$ | $-\sqrt{2}$ | 0 | 0 | 0 | 2 | -2 | $\sqrt{2}$ | $-\sqrt{2}$ | 0 | 0 | 0 | | | | | | | | |
| $E_{3/2g}$ | 2 | -2 | $-\sqrt{2}$ | $\sqrt{2}$ | 0 | 0 | 0 | 2 | -2 | $-\sqrt{2}$ | $\sqrt{2}$ | 0 | 0 | 0 | | | | | | | | |
| $E_{1/2u}$ | 2 | -2 | $\sqrt{2}$ | $-\sqrt{2}$ | 0 | 0 | 0 | -2 | 2 | $-\sqrt{2}$ | $\sqrt{2}$ | 0 | 0 | 0 | | | | | | | | |
| $E_{3/2u}$ | 2 | -2 | $-\sqrt{2}$ | $\sqrt{2}$ | 0 | 0 | 0 | -2 | 2 | $\sqrt{2}$ | $-\sqrt{2}$ | 0 | 0 | 0 | | | | | | | | |
| D_{5h}^* | E | R | $2C_5$ | $2C_5R$ | $2C_5^2$ | $2C_5^2R$ | $10C_2$ | $2\sigma_h$ | $2S_5$ | $2S_5R$ | $2S_5^3$ | $2S_5^3R$ | $10\sigma_v$ | | | | | | | | | |
| $E_{1/2}$ | 2 | -2 | γ | $-\gamma$ | δ | $-\delta$ | 0 | 0 | β | $-\beta$ | $-\alpha$ | α | 0 | $\alpha = 2 \cos \frac{1}{10}\pi,$ | | | | | | | | |
| $E_{3/2}$ | 2 | -2 | $-\delta$ | δ | $-\gamma$ | γ | 0 | 0 | $-\alpha$ | α | $-\beta$ | β | 0 | $\beta = 2 \cos \frac{3}{10}\pi,$ | | | | | | | | |
| $E_{5/2}$ | 2 | -2 | 2 | -2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\gamma = 2 \cos \frac{1}{5}\pi,$ | | | | | | | | |
| $E_{3/2}$ | 2 | -2 | $-\delta$ | δ | $-\gamma$ | γ | 0 | 0 | α | $-\alpha$ | β | $-\beta$ | 0 | $\delta = 2 \cos \frac{3}{5}\pi$ | | | | | | | | |
| $E_{5/2}$ | 2 | -2 | γ | $-\gamma$ | δ | $-\delta$ | 0 | 0 | $-\beta$ | β | α | $-\alpha$ | 0 | | | | | | | | | |
| D_{6h}^* | E | R | $2C_6$ | $2C_6R$ | $2C_3$ | $2C_3R$ | $2C_2$ | $6C_2'$ | i | iR | $2S_3$ | $2S_3R$ | $2S_6$ | $2S_6R$ | $2\sigma_h$ | $6\sigma_d$ | $6\sigma_v$ | | | | | |
| $E_{1/2g}$ | 2 | -2 | $\sqrt{3}$ | $-\sqrt{3}$ | 1 | -1 | 0 | 0 | 2 | -2 | $\sqrt{3}$ | $-\sqrt{3}$ | 1 | -1 | 0 | 0 | 0 | | | | | |
| $E_{3/2g}$ | 2 | -2 | 0 | 0 | -2 | 2 | 0 | 0 | 2 | -2 | 0 | 0 | -2 | 2 | 0 | 0 | 0 | | | | | |
| $E_{5/2g}$ | 2 | -2 | $-\sqrt{3}$ | $\sqrt{3}$ | 1 | -1 | 0 | 0 | 2 | -2 | $-\sqrt{3}$ | $\sqrt{3}$ | 1 | -1 | 0 | 0 | 0 | | | | | |
| $E_{1/2u}$ | 2 | -2 | $\sqrt{3}$ | $-\sqrt{3}$ | 1 | -1 | 0 | 0 | -2 | 2 | $-\sqrt{3}$ | $\sqrt{3}$ | -1 | 1 | 0 | 0 | 0 | | | | | |
| $E_{3/2u}$ | 2 | -2 | 0 | 0 | -2 | 2 | 0 | 0 | -2 | 2 | 0 | 0 | 2 | -2 | 0 | 0 | 0 | | | | | |
| $E_{5/2u}$ | 2 | -2 | $-\sqrt{3}$ | $\sqrt{3}$ | 1 | -1 | 0 | 0 | -2 | 2 | $\sqrt{3}$ | $-\sqrt{3}$ | -1 | 1 | 0 | 0 | 0 | | | | | |

Character tables for the 'two-valued' representations of the groups D_3^* , D_4^* , D_5^* , D_6^* , T^* , T_d^* and O^* are given by Griffith (1961, table A8).