

**HYPERPOLARIZABILITY AND FORBIDDEN  
RAMAN LINES**

**by**

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**A THESIS**

**submitted to**

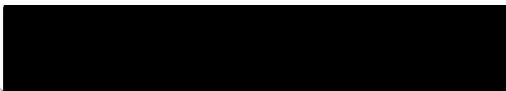
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# HYPERPOLARIZABILITY AND FORBIDDEN

## RAMAN LINES

### CHAPTER I

#### INTRODUCTION

In the Raman spectrum of certain molecules and ions weak transitions occur which are forbidden to take place when one considers the symmetry of the free molecule. An article by Gray and Waddington ( 6, p. 901-908 ) presents a summary of the articles which have been written on the azide ion which is usually assumed to have  $D_{\infty h}$  symmetry, i. e., a linear symmetric triatomic ion. Many investigators of this ion have observed its  $\nu_2$  and  $\nu_3$  bands in the Raman spectrum. In lead azide a partial covalent bond has been postulated to exist between the lead and the azide which destroys the symmetry for the azide ion. However, for the azide salts of the alkali metals this could not be postulated. It was stated that the normal selection rules are relaxed under the influence of the perturbing electric fields of neighboring ions.

It has also been noted by Welsh, et al., ( 11, p. 99-110 ) that carbon dioxide at high density shows the existence of both the  $\nu_2$  and  $\nu_3$  bands in the Raman spectrum. They suggested that the molecule was distorted under an influence of the field of neighboring molecules in such a way that the molecule took on  $C_{\infty v}$  type symmetry, i. e., the molecule remained linear but

one carbon oxygen bond became longer than the other. This conclusion was drawn from the fact the  $\nu_2$  band had a double maximum while the fainter  $\nu_3$  band was narrow, indicating a strong Q branch with rotational wings of low intensity. They made no depolarization measurements.

Evans and Bernstein ( 3, p. 1127-1133 ) found that in concentrated solution of carbon disulfide using cyclopentane as a solvent that the existing  $\nu_2$  and  $\nu_3$  bands were both polarized ( $\rho_n = 0.63$  for both bands ) and that the  $\nu_2$  bands of carbon disulfide showed no indication of a double peak. A triatomic molecule with  $C_{\infty v}$  symmetry requires that there be two polarized ( $\nu_1, \nu_3$ ) bands and one depolarized band ( $\nu_2$ ). Hence it was concluded that distortion in a carbon disulfide molecule under the influence of a perturbing neighboring field is not only along the SCS axis but also at a right angle to this axis. They gave the distorted carbon disulfide molecule a symmetry of  $C_s$ . They also found the ratio of the intensity of the  $\nu_3$  band to the  $\nu_1$  band of carbon disulfide to be proportional to the volume-fraction of carbon disulfide cyclopentane to the four-thirds power.

This paper will be an attempt to discuss the appearance of such forbidden bands, retaining the symmetry of the free molecule.

## CHAPTER II

## CLASSICAL THEORY OF THE RAMAN EFFECT

The introduction of an atom or molecule into an electric field  $\vec{E}$  induces an electric dipole moment  $\vec{P}$  in the system. If a component of the electric dipole is expanded by a Taylor's series expansion in terms of the components of the electric field,

$$(1) \quad \mu_F = (\mu_F)_0 + \sum_{F'} \left( \frac{\partial \mu_F}{\partial E_{F'}} \right)_0 E_{F'} + \frac{1}{2} \sum_{F'} \sum_{F''} \left( \frac{\partial^2 \mu_F}{\partial E_{F'} \partial E_{F''}} \right)_0 E_{F'} E_{F''} + \dots$$

Thus, the induced dipole, neglecting quadratic and higher terms of the components of the electric field, is

$$(2) \quad P_F = \sum_{F'} \left( \frac{\partial \mu_F}{\partial E_{F'}} \right)_0 E_{F'}$$

Let  $\alpha_{FF'} = \left( \frac{\partial \mu_F}{\partial E_{F'}} \right)_0$  be the components of the polarizability.

It can be shown ( 12, p. 44 ) that a set of axes in a molecule exists such that

$$(3) \quad P_x = \alpha_x E_x \quad ; \quad P_y = \alpha_y E_y \quad ; \quad P_z = \alpha_z E_z$$

If light of frequency  $\nu_0$  falls on an ion or molecule, the varying electric field produced by the light may be represented by

$$(4) \quad E_z = E_{z0} \cos(2\pi\nu_0 t)$$

This field produces a varying dipole moment which itself causes

emission of light of the same frequency as the incident light. For a classical oscillating dipole the intensity of the emitted radiation,  $I$ , is given by

$$(5) \quad I = \frac{16\pi^4 \nu^4}{3c^3} P_0^2$$

( see appendix 6). This accounts for the Rayleigh scattering which is responsible for the phenomena of dispersion and the Tyndall effect. The polarizability must change if internuclear distances change ( vibrations ) or if the molecule undergoes rotation, since the polarizability depends on the orientation of the molecule. By expanding the components of the polarizability,  $\alpha_g$  in terms of the normal coordinates of the molecule

$$(6) \quad \alpha_g = \alpha_{g0} + \sum_K \left( \frac{\partial \alpha_g}{\partial Q_K} \right)_0 Q_K + \dots$$

is a normal coordinate of the molecule and changes with a frequency characteristic of the molecule.

$$(7) \quad Q_K = Q_K^0 [\cos(2\pi \nu_K t)].$$

Now, combining equations 3, 4, 6, and 7

$$(8) \quad P_g = [\alpha_{g0} + \sum_K \left( \frac{\partial \alpha_g}{\partial Q_K} \right)_0 \cos(2\pi \nu_K t)] E_{g0} \cos(2\pi \nu_0 t)$$

$$(9) \quad P_g = \alpha_{g0} E_{g0} \cos(2\pi \nu_0 t) + \sum \left( \frac{\partial \alpha_g}{\partial Q_K} \right)_0 Q_K^0 E_{g0} \left[ \frac{1}{2} \cos 2\pi (\nu_0 + \nu_K) t + \frac{1}{2} \cos 2\pi (\nu_0 - \nu_K) t \right]$$

Thus, when one considers small changes in  $\alpha$  with vibration, the induced dipole moment changes not only with the frequency  $\nu_0$  of the incident light but also with frequencies  $\nu_0 \pm \nu_k$  ( or with frequencies  $\nu_0 \pm 2\nu_k$  for rotations ). The Raman lines displaced toward the longer wave lengths are called Stokes lines ( $\nu_0 - \nu_k$ ) and those displaced toward the shorter wave lengths ( $\nu_0 + \nu_k$ ) are called anti-Stokes lines. Thus, one should expect displacements on either side of the excitation line equal to  $\nu_k$  for vibrations and  $2\nu_k$  for rotations. Classically  $\nu_k$  is fixed while  $2\nu_k$  can take on any value. Hence, one should expect a continuous spectrum about the exciting Rayleigh line due to rotation and that the long wave length component of the displacement should have the same intensity as the short wave length displacement. These two expectations are not observed. Thus, although the classical treatment gives a qualitative picture of the Raman effect it does not give a quantitative picture. ( 12, p. 43-48 )

## CHAPTER III

## QUANTUM THEORY OF THE RAMAN EFFECT

If there are  $N_k$  molecules in the  $k^{\text{th}}$  state which are of a lower energy and  $N_n$  in the  $n^{\text{th}}$  state which is of a higher energy, the average intensity of the line arising from the transition  $k \rightarrow n$  is proportional to  $N_k (\nu_0 - \nu_{nk})^4$  while that arising from the transition  $n \rightarrow k$  is proportional to  $N_n (\nu_0 + \nu_{nk})^4$ . Thus,

$$(10) \quad \frac{I_A}{I_S} = \left( \frac{\nu_0 + \nu_{nk}}{\nu_0 - \nu_{nk}} \right)^4 \frac{N_n}{N_k} = \left( \frac{\nu_0 + \nu_{nk}}{\nu_0 - \nu_{nk}} \right)^4 e^{-\frac{h\nu_{nk}}{KT}}$$

since  $N_n/N_k$  is the Boltzman factor between the two states. This simple derivation explains why the intensity of the Stokes lines are generally more intense than those of the anti-Stokes lines.

The mean rate of total radiation of an induced dipole is given classically by equation (5). The hypothesis is made (Dirac radiation theory) that the classical formulas can be converted into quantum formulas by replacing  $P_0^2$  by  $4|[P^0]|^2$  in which

$$(11) \quad [P^0]^{nm} = \int \Psi_n^* P^0 \Psi_m d\tau$$

thus,

$$(12) \quad I = \frac{64\pi^4 \nu_{nm}^4}{3c^3} \left[ \left| \int \Psi_n^* P^0 \Psi_m d\tau \right| \right]^2$$

Now,

$$(13) \quad [P_x^0]^{nm} = E_x^0 \int \alpha_{xx} \psi_n \psi_m^* d\tau \\ + E_y^0 \int \alpha_{xy} \psi_n \psi_m^* d\tau + E_z^0 \int \alpha_{xz} \psi_n \psi_m^* d\tau$$

Similar equations hold for  $[P_y^0]^{nm}$  and  $[P_z^0]^{nm}$ .  $E_x^0$ ,  $E_y^0$ , and  $E_z^0$  are the components of the amplitudes of the incident light wave, and the integrals

$$(14) \quad [\alpha_{xx}]^{nm} = \int \alpha_{xx} \psi_n \psi_m^* d\tau, \dots$$

are the matrix elements of the six components of the polarizability tensor. In the Raman effect the electric vector of the incident illumination, acting on the charges of the molecule, perturbs its wave function. If the integrals  $[P]^{nm}$  are calculated using perturbed wave functions (including time factors), it is found that for  $n=m$  there are terms of the same frequency  $\nu_0$  as the incident light, but for  $n \neq m$  there are terms with the frequency  $\nu_0 \pm \nu_{nm}$ . The terms with unshifted frequency are responsible for Rayleigh scattering while those of frequency  $\nu_0 \pm \nu_{nm}$  give rise to the Raman effect. A Raman transition is allowed if at least one of the six quantities  $[\alpha_{rr'}]^{nm} \neq 0$ . For the approximation that the wave function can be written as a product of a rotational function,  $\psi_R$ , with quantum numbers  $R$  and a vibrational wave function,  $\psi_v$ , the integral

$$(15) \quad [\alpha_{gg'}]^{nm} = \int \psi_R^* \psi_{R'} d\tau_R \int \psi_v^* \alpha_{gg'} \psi_{v'} d\tau_v$$

since  $\alpha_{gg'}$  ( in molecular-fixed axes ) does not involve the coordinates of rotation ( 12, p. 52 ). The orthogonality of the rotational wave functions, therefore, leads to the result

$$(16) \quad [\alpha_{gg'}]^{nm} = \delta_{RR'} [\alpha_{gg'}]^{vv'}$$

Consequently  $[\alpha_{gg'}]^{nm}$  is zero unless the rotational states are the same. These integrals can be treated exactly the same way as the integrals of the electric moment; that is to say, they vanish unless the symmetry of the set of functions  $\psi_v^* \psi_{v'}$  for the two levels under consideration has some species in common with the species of  $\alpha_{xx}$ ,  $\alpha_{xy}$ , etc. For fundamentals this requires that the normal vibrations for a given frequency fall into one of the species associated with the  $\alpha$ 's, if this frequency is to occur in the Raman effect. ( 12, p. 48-53 )



# CHAPTER IV

## HYPERPOLARIZABILITY

As in the case of the polarizability, a component of the electric dipole moment may be expanded in terms of the components of the electric field acting upon the molecule in question.

Hence,

$$(17) \quad \mu_F = (\mu_F)_0 + \sum_{F'} \left( \frac{\partial \mu_F}{\partial E_{F'}} \right)_0 E_{F'} + \frac{1}{2} \sum_{F'} \sum_{F''} \left( \frac{\partial^2 \mu_F}{\partial E_{F'} \partial E_{F''}} \right)_0 E_{F'} E_{F''} + \dots$$

The components of the polarizability are

$$(18) \quad \left( \frac{\partial \mu_F}{\partial E_{F'}} \right)_0 = \alpha_{FF'}$$

Suppose that for a given vibration of a molecule all of the partial derivations of the components of the polarizability with respect to the normal coordinates of this particular vibration vanish, i. e., the line is forbidden by polarizability theory ( for a free molecule or ion the line would also be forbidden for the hyper-Raman effect because of the intensity dependence upon concentration ). ( See appendix 7 ). In this case the intensity of the emitted light will be dependent upon the partial derivatives of the components of the hyperpolarizability with respect to the normal coordinates of this particular vibration provided they do not vanish. The components of the hyperpolarizability are given by

$$(19) \quad \beta_{FF'F''} = \frac{1}{2} \left( \frac{\partial^2 \mu_F}{\partial E_{F'} \partial E_{F''}} \right)_0$$

In the hyper-Raman effect the induced dipole moment of a molecule may be represented as

$$(20) \quad p_F = \sum_{F'} \sum_{F''} \beta_{FF'F''} E_{F'} E_{F''}$$

The  $\beta_{FF'F''}$  in turn can be expanded in terms of the normal coordinates of the molecule.

$$(21) \quad \beta_{FF'F''} = (\beta_{FF'F''})_0 + \sum_R \left( \frac{\partial \beta_{FF'F''}}{\partial Q_R} \right)_0 Q_R + \dots$$

The  $(\beta_{FF'F''})_0$  can be shown to be all zero for molecules with a center of symmetry. The  $(\beta_{FF'F''})_0$  may be non-vanishing for molecules with no center of symmetry which will give rise to a pure rotational spectrum. If one separates  $E_F$  into the field, due to the light source,  $E_F$ , and the field due to the neighboring ions and molecules,  $\Delta E_F$ ,  $E_F$  becomes:

$$(22) \quad E_F = E_F + \Delta E_F$$

$E_F$  may be represented by

$$(23) \quad E_F = E_F^0 \cos(2\pi \nu_0 t)$$

where  $\nu_0$  is the frequency of the incident light.  $\Delta E_F$  may be represented as

$$(24) \quad \Delta E_F = \Delta E_{F0} + \Delta E_F^0 \cos(2\pi \nu_R t)$$

where  $\nu_R$  is a normal frequency of a neighbor and  $\Delta E_{F0}$  is the time independent part of the surrounding field. The normal

coordinate,  $Q_k$ , may also be written as

$$(25) \quad Q_k = Q_k^0 \cos(2\pi \nu_k t)$$

where  $\nu_k$  is the normal frequency of the molecule in question.

Combining these equations:

$$(26) \quad P_F = \sum_{F'} \sum_{F''} \sum_K \left( \frac{\partial P_{FF'F''}}{\partial Q_K} \right)_0 Q_K^0 \cos 2\pi \nu_K t [(\epsilon_F^0 \cos 2\pi \nu_0 t + \Delta \epsilon_F^0 \cos 2\pi \nu_K t)(\epsilon_{F'}^0 \cos 2\pi \nu_0 t + \Delta \epsilon_{F'}^0 \cos 2\pi \nu_K t) + \Delta \epsilon_{F''}^0 \cos 2\pi \nu_K t]$$

Expanding this becomes

$$(27) \quad P_F = \sum_{F'} \sum_{F''} \sum_K \left( \frac{\partial P_{FF'F''}}{\partial Q_K} \right)_0 Q_K^0 [\epsilon_F^0 \epsilon_{F'}^0 \cos 2\pi \nu_K t \cos^2 2\pi \nu_0 t + \epsilon_F^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_0 t) \Delta \epsilon_{F''}^0 + \epsilon_{F'}^0 \Delta \epsilon_{F''}^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_0 t)(\cos 2\pi \nu_K t) + \Delta \epsilon_{F'}^0 \epsilon_{F''}^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_0 t) + \Delta \epsilon_{F'}^0 \Delta \epsilon_{F''}^0 \cos 2\pi \nu_K t + \Delta \epsilon_{F_0}^0 \Delta \epsilon_{F''}^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_K t) + \Delta \epsilon_{F'}^0 \epsilon_{F''}^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_K t)(\cos 2\pi \nu_0 t) + \Delta \epsilon_{F'}^0 \Delta \epsilon_{F''}^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_K t) + \Delta \epsilon_{F'}^0 \Delta \epsilon_{F''}^0 (\cos 2\pi \nu_K t)(\cos 2\pi \nu_K t)^2]$$

Thus, the oscillating dipole due to the hyper-Raman effect will have frequencies of the following types:

$$2\nu_0 \pm \nu_k, \nu_0 \pm \nu_k, \nu_0 \pm \nu_k \pm \nu_{k'}, \nu_k, \nu_k \pm \nu_{k'}, 2\nu_{k'} \pm \nu_k.$$

A Raman apparatus is usually only designed to observe slight shifts from the exciting frequency. Hence, only the terms which involve  $\nu_0 \pm \nu_k$  and  $\nu_0 \pm \nu_k \pm \nu_{k'}$  are of importance. Terms of the type which involve frequencies  $\nu_0 \pm \nu_k$  are dependent upon  $\mathcal{E}_F^0 \Delta \mathcal{E}_{F'D}$ . Terms of frequencies  $\nu_0 \pm \nu_k \pm \nu_{k'}$  are dependent upon  $\mathcal{E}_F^0 \Delta \mathcal{E}_{F'}^0$ . It seems logical to consider the  $\Delta \mathcal{E}_F^0$  terms as being much smaller than  $\Delta \mathcal{E}_{F'D}$  terms. This being the case,

$$(28) \quad P_F = \sum_{F'} \sum_{F''} \sum_k \left( \frac{\partial R_{FF'F''}}{\partial Q_k} \right)_0 Q_k^0 \left[ \Delta \mathcal{E}_{F'D}^0 \mathcal{E}_{F''}^0 (\cos 2\pi \nu_k t) (\cos 2\pi \nu_0 t) \right. \\ \left. + \Delta \mathcal{E}_{F'D}^0 \mathcal{E}_F^0 (\cos 2\pi \nu_k t) (\cos 2\pi \nu_0 t) \right]$$

for observable lines in the hyper-Raman effect.

Depolarization Ratios: ( 12, p. 43-47 )

The two quantities most commonly measured are the relative intensities of the Raman shifts and their depolarization ratios. The depolarization ratios will now be discussed.

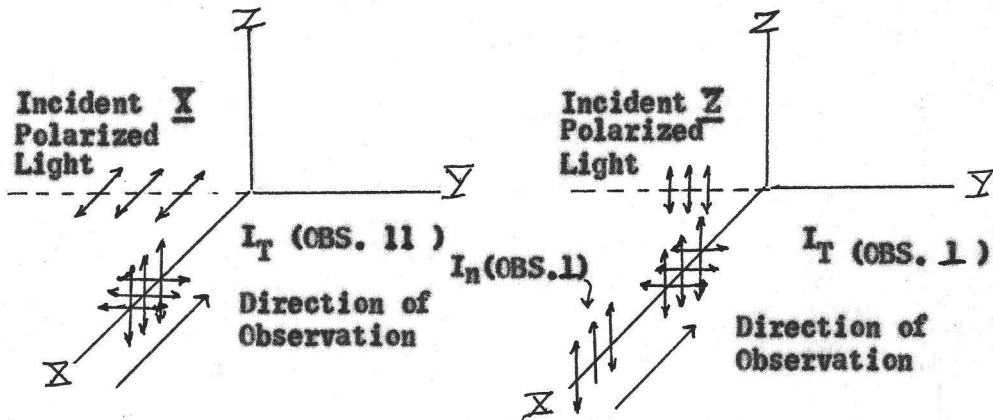
For the laboratory fixed axes, the total radiation emitted per unit solid angle in the  $\underline{X}$  direction is given by

$$(29) \quad I = \frac{2\pi^3 \nu^4}{c^3} (\mu_{0Y}^2 + \mu_{0Z}^2)$$

( see appendix 6 )

Consider that the direction of propagation of the incident

incident light coincides with the  $\underline{Y}$  axis.



If the incident light is plane polarized in the  $\underline{Y}$  direction and the total scattered intensity is observed along the  $\underline{X}$  axis, this total scattered intensity is represented by  $I_T(\text{OBS. 11})$ . If the incident light is Z-polarized and the total scattered intensity is observed along the  $\underline{X}$  axis, this total scattered intensity is represented by  $I_T(\text{OBS. 1})$ . If in this second case the scattered light is polarized parallel to the Z axis, the scattered intensity is represented by  $I_{11}(\text{OBS. 1})$ . If we now consider only lines which are forbidden in the first-order-Raman effect, but allowed in the hyper-Raman effect, the intensities according to equation (17) and (29) and the above definitions are

$$(30) \quad I_T(\text{OBS. 11}) = \frac{2\pi^3 \nu^4}{c^3} \left\{ \left[ \sum_{FF'} \beta_{YFF'} (\epsilon_X \delta_{FX} + \Delta \epsilon_F) (\epsilon_X \delta_{FX} + \Delta \epsilon_{F'}) \right]^2 + \left[ \sum_{FF'} \beta_{ZFF'} (\epsilon_X \delta_{FX} + \Delta \epsilon_F) (\epsilon_X \delta_{FX} + \Delta \epsilon_{F'}) \right]^2 \right\}$$

$$I_T (OBS. \perp) = \frac{2\pi^3 \nu^4}{c^3} \left\{ \left[ \sum_{FF'} \beta_{YFF'} (\epsilon_z \delta_{FZ} + \Delta \epsilon_F) (\epsilon_z \delta_{F'Z} + \Delta \epsilon_{F'}) \right]^2 \right. \\ \left. + \left[ \sum_{FF'} \beta_{ZFF'} (\epsilon_z \delta_{FZ} + \Delta \epsilon_F) (\epsilon_z \delta_{F'Z} + \Delta \epsilon_{F'}) \right]^2 \right\}$$

$$I_{||} (OBS. \perp) = \frac{2\pi^3 \nu^4}{c^3} \left[ \sum_{FF'} \beta_{ZFF'} (\epsilon_z \delta_{FZ} + \Delta \epsilon_F) (\epsilon_z \delta_{F'Z} + \Delta \epsilon_{F'}) \right]^2,$$

where  $\sum_{FF'} \beta_{YFF'} E_F E_{F'} = \sum_{FF'} \beta_{YFF'} (\epsilon_F + \Delta \epsilon_F) (\epsilon_{F'} + \Delta \epsilon_{F'})$ .

$(\epsilon_x, \epsilon_y, \epsilon_z)$  is the electric vector of the external light source and  $(\Delta \epsilon_x, \Delta \epsilon_y, \Delta \epsilon_z)$  is the electric vector acting on the molecule in question due to the molecules which surround it. These equations apply only to a single radiator; for N radiators which are free to assume all orientations with respect to the observer's axes with equal probability, the equations are to be multiplied by N and the average of each expression is to be found as the radiator is allowed to assume all orientations. It can be shown ( see appendix 1 ) that the general formulas of transformation of  $\beta_{FF'}$  in laboratory fixed axes to in molecular fixed axes are given by

$$(31) \quad \beta_{FF'F''} = \sum_{gg'g''} \beta_{gg'g''} \Phi_{Fg} \Phi_{F'g'} \Phi_{F''g''}$$

Now consider,

$$(32) \quad \mathcal{U}_F = \sum_{F'F''} \beta_{FF'F''} E_{F'} E_{F''} = \sum_{F'F''} \beta_{FF'F''} (E_{F'} + \Delta E_{F'}) (E_{F''} + \Delta E_{F''})$$

If the incident light from the source is such that

$$E_X \neq 0, \quad E_Y = 0 = E_Z$$

then,

$$\mathcal{U}_F = \sum_{F'F''} \beta_{FF'F''} (E_{F'} \delta_{F'X} + \Delta E_{F'}) (E_{F''} \delta_{F''X} + \Delta E_{F''})$$

If we now consider only  $E_F \Delta E_{F'}$  type terms to be those which produce the hyper-Raman effect ( see equation 28 ), may be reduced for our purposes to

$$(33) \quad \mathcal{U}_F = \beta_{FF'F''} (E_{F'} \Delta E_{F''} \delta_{F'X} + E_{F''} \Delta E_{F'} \delta_{F''X})$$

Upon expansion this gives,

$$\begin{aligned} \mathcal{U}_F &= \beta_{FXX} (E_X \Delta E_X + E_X \Delta E_X) + \cancel{\beta_{FXY} E_X \Delta E_Y} \\ &\quad + \beta_{FXZ} E_X \Delta E_Z + \beta_{FYX} E_X \Delta E_Y + \beta_{YZX} E_X \Delta E_Z \end{aligned}$$

However,

$$\left( \frac{\partial^2 \mathcal{U}_F}{\partial E_{F'} \partial E_{F''}} \right) = \frac{\partial^2 \mathcal{U}_F}{\partial E_{F'} \partial E_{F'}}$$

$$(34) \quad \therefore, \quad \beta_{FF'F''} = \beta_{FF''F'}$$

Then

$$(35) \quad \overline{\mathcal{U}_F^2} = \frac{4}{3} \left( \sum_{F'} \beta_{FXX} \right)^2 E_X^2 \Delta E_R^2$$

Hence,

$$(36) \quad (\text{see next page})$$

$$(36) \quad \overline{\mu_F^2} = \frac{4}{3} \overline{\mathcal{E}_x^2 \Delta \mathcal{E}_n^2} \left[ \sum_{F'} \left( \sum_g \overline{\beta_{gg'g''}^2 \Phi_{Fg'}^2 \Phi_{xg'}^2 \Phi_{F'g''}^2} \right. \right. \\ \left. \left. + 2 \sum_{g < l} \overline{\beta_{gg'g''} \beta_{ll'l''} \Phi_{Fg} \Phi_{xg'} \Phi_{F'g''} \Phi_{Fl} \Phi_{xl} \Phi_{F'l''}} \right) \right. \\ \left. + 2 \sum_{F' < G} \sum_g \sum_l \overline{\beta_{gg'g''} \beta_{ll'l''} \Phi_{Fg} \Phi_{xg'} \Phi_{F'g''} \Phi_{Fl} \Phi_{xl} \Phi_{Gl''}} \right]$$

From equation (36) it is apparent that the intensity of the exciting light is proportional to  $\mathcal{E}_x^2$ . The term  $\Delta \mathcal{E}_n^2$  can be computed by introducing some assumptions regarding the inter-molecular forces ( see appendix 7 ). But  $\sum_{F'} \overline{\Phi_{F'g''}^2} = 1$  and  $\sum_{F'} \overline{\Phi_{F'g''} \Phi_{F'l''}} = \delta_{g''l''}$ . Also only the average value of  $\mu_F^2$  is needed. Since  $\sum_{F' < G} \overline{\Phi_{Fg} \Phi_{xg'} \Phi_{F'g''} \Phi_{Fl} \Phi_{xl} \Phi_{Gl''}} = 0$ ,  $\overline{\mu_F^2}$

reduces to

$$(37) \quad \overline{\mu_F^2} = \frac{4}{3} \overline{\mathcal{E}_x^2 \Delta \mathcal{E}_n^2} \left[ \sum_g \overline{\beta_{gg'g''}^2 \Phi_{Fg'}^2 \Phi_{xg'}^2} \right. \\ \left. + 2 \sum_{g < l} \overline{\delta_{l''g''} \beta_{gg'g''} \beta_{ll'l''} \Phi_{Fg} \Phi_{xg'} \Phi_{Fl} \Phi_{xl}} \right]$$

The depolarization ratio is "defined as the ratio of the scattered intensity which is polarized perpendicular to  $\vec{E}$ , that is, in the direction of propagation of the incident light, to the intensity parallel to  $\vec{E}$ ." ( 12, p. 47 ). " If the incident light is natural ( unpolarized ), the depolarization ratio may be computed by considering the scattered light to represent the sum of the intensities of the observations made parallel and perpendicular to the incident electric vector of a polarized beam. That part of the light from the parallel observation, being unpolarized, contributes one-half its



intensity to the scattered light polarized, respectively, parallel and perpendicular to  $\vec{E}$ :

$$(38) \quad \rho_n = \frac{I_T(\text{OBS. } \perp) - I_{||}(\text{OBS. } \perp) + \frac{1}{2} I_T(\text{OBS. } ||)}{I_{||}(\text{OBS. } \perp) + \frac{1}{2} I_T(\text{OBS. } ||)}$$

( 12, p. 47 )

Now let  $\epsilon_x = \epsilon_z$ ,  $\epsilon_y = 0$

Then

$$(39) \quad \rho_n = \frac{2 \sum_g \beta_{gg'g''}^2 \overline{\Phi_{Yg}^2} \overline{\Phi_{Xg'}^2} + 4 \sum_{g < i} \delta_{g''i''} \beta_{gg'g''} \beta_{ii'i''} \overline{\Phi_{Yg} \Phi_{Zg'}} \overline{\Phi_{Yi} \Phi_{Zi'}}}{\sum_g \beta_{gg'g''}^2 \overline{\Phi_{Yg}^2} \overline{\Phi_{Xg'}^2} + \sum_{g < i} \delta_{g''i''} \beta_{gg'g''} \beta_{ii'i''} \overline{\Phi_{Yg} \Phi_{Zg'}} \overline{\Phi_{Yi} \Phi_{Zi'}} + \sum_g \beta_{gg'g''}^2 \overline{\Phi_{Zg}^2} \overline{\Phi_{Zg'}^2} + 2 \sum_{g < i} \delta_{g''i''} \beta_{gg'g''} \beta_{ii'i''} \overline{\Phi_{Zg} \Phi_{Zg'}} \overline{\Phi_{Zi} \Phi_{Zi'}}$$

This may be written more concisely as

$$(40) \quad \rho_n = \frac{2 \sum_F \overline{\beta_{YXF}^2}}{\sum_F \overline{\beta_{YXF}^2} + \sum_F \overline{\beta_{ZZF}^2}}$$

## CHAPTER V

THE  $D_{2h}$  SYMMETRY POINT GROUP

First it will be necessary to determine which of the ten distinct  $\beta$ 's exist as linear combinations which transform as certain of the symmetry species of the group. One may observe the following transformations under the operations of the group:

$$\begin{aligned}
 (41) \quad & X'Y'Z' \xrightarrow{E} XYZ; \quad X'Y'Z' \xrightarrow{i} (-x)(-y)(-z) = -XYZ \\
 & X'Y'Z' \xrightarrow{C_2(z)} (-x)(-y)(z) = XYZ; \quad X'Y'Z' \xrightarrow{\sigma(xy)} (x)(y)(-z) = -XYZ \\
 & X'Y'Z' \xrightarrow{C_2(y)} (-x)(y)(-z) = XYZ; \quad X'Y'Z' \xrightarrow{\sigma(xz)} (x)(-y)(z) = -XYZ \\
 & X'Y'Z' \xrightarrow{C_2(x)} (x)(-y)(-z) = XYZ; \quad X'Y'Z' \xrightarrow{\sigma(yz)} (-x)(y)(z) = -XYZ
 \end{aligned}$$

( See appendix 2 for the character table of  $D_{2h}$  )

Hence, this shows that  $\beta_{xyz}$  transforms as  $A_u$  ( 12, p. 359-360). In a like manner it may be easily shown that  $\beta_{zzz}$ ,

$\beta_{xxz}$  and  $\beta_{yyz}$  transform as  $B_{1u}$ ,  $\beta_{yyx}$ ,  $\beta_{xxy}$ , and  $\beta_{zzy}$  transform as  $B_{2u}$ .

The character per unshifted atom ( see appendix 3) for E equals the number of coordinates. This is also the total number of linear combinations of the coordinates which will transform as the various species ( 12, p. 106). Hence, in the infrared there are three combinations; in the Raman there are six combinations. This shows that the ten hyperpolarizability components listed are all of the ones for this point group.

In order to illustrate that there are molecules which

allow vibrations which are inactive in the ordinary Raman effect to become active in the hyper-Raman effect, consider the ethylene molecule.

By standard methods ( 12, p. 106-113 ), it is found that the vibrational normal coordinates are of species:

The following table summarizes the number of frequencies active respectively in infrared absorption, the ordinary Raman, and the hyper-Raman effects.

	<u><math>n(\gamma)</math> IR</u>	<u><math>n(\gamma)</math> R</u>	<u><math>n(\gamma)</math> hyper-R</u>
<u>A<sub>g</sub></u>		3	
<u>B<sub>1g</sub></u>		0	
<u>B<sub>2g</sub></u>		1	
<u>B<sub>3g</sub></u>		2	
<u>A<sub>u</sub></u>			1
<u>B<sub>1u</sub></u>	2		2
<u>B<sub>2u</sub></u>	2		2
<u>B<sub>3u</sub></u>	1		1

$n(\gamma)$   
IR is the number of infrared modes.

$n(\gamma)$   
R is the number of Raman modes.

$n(\gamma)$   
hyper-R is the number of hyper-Raman modes.

Hence, by observing the  $D_{2h}$  character table the infrared frequencies are seen to be allowed in the hyper-Raman effect and an additional fundamental frequency is allowed in the hyper-Raman effect which is not allowed in either the infrared or Raman effect. ( 12, p. 106-109 )

Next the observable quantities  $\rho_n$  for the various species of the  $D_{2h}$  point group will be tabulated. First consider the  $B_{1u}$  species. Let  $Q$  represent a normal coordinate for this species. Then from the character table for  $D_{2h}$  in appendix 2, it follows that:

$$(42) \quad \frac{\partial \beta_{333}}{\partial Q} \neq 0 ; \quad \frac{\partial \beta_{xxz}}{\partial Q} \neq 0 ; \quad \frac{\partial \beta_{yzz}}{\partial Q} \neq 0 ;$$

$$\text{but all other } \frac{\partial \beta}{\partial Q} = 0$$

For simplicity of notation let

$$(43) \quad \frac{\partial \beta_{333}}{\partial Q} = \beta_{333} ; \quad \frac{\partial \beta_{xxz}}{\partial Q} = \beta_{113} ; \quad \frac{\partial \beta_{yzz}}{\partial Q} = \beta_{223}$$

Hence, since the order of cartesian subscripts is irrelevant, the non-vanishing terms for these species are

$\{\beta_{333}, \beta_{113}, \beta_{131}, \beta_{311}, \beta_{223}, \beta_{232}, \beta_{322}\}$   
From equation ( 40),  $\sum_F \beta_{YXF}^2$  and  $\sum_F \beta_{ZZF}^2$  need to be evaluated.

$$(44) \quad \sum_F \beta_{YXF}^2 = \sum_g \beta_{gg'g''}^2 \overline{\Phi_{Yg}^2} \overline{\Phi_{Xg'}^2} + 2 \sum_{g < i} \beta_{gg''i''} \beta_{gg'g''} \beta_{i'i''} \overline{\Phi_{Yg} \Phi_{Xg'} \Phi_{Yi} \Phi_{Xi'}}$$

$$(45) \quad \sum_g \beta_{gg'g''}^2 \overline{\Phi_{Yg}^2} \overline{\Phi_{Xg'}^2} = \beta_{333}^2 \overline{\Phi_{Y3}^2} \overline{\Phi_{X3}^2} + \beta_{113}^2 \overline{\Phi_{Y1}^2} \overline{\Phi_{X1}^2}$$

$$\begin{aligned}
 (45) \text{ continued } & + \beta_{131}^2 \overline{\Phi_{Y1}^2 \Phi_{X3}^2} + \beta_{311}^2 \overline{\Phi_{Y3}^2 \Phi_{X1}^2} \\
 & + \beta_{223}^2 \overline{\Phi_{Y2}^2 \Phi_{X2}^2} + \beta_{232}^2 \overline{\Phi_{Y2}^2 \Phi_{X3}^2} + \beta_{322}^2 \overline{\Phi_{Y3}^2 \Phi_{X2}^2} \\
 & = \frac{1}{15} \beta_{333}^2 + \frac{1}{3} \beta_{113}^2 + \frac{1}{3} \beta_{223}^2
 \end{aligned}$$

The averages  $\overline{\Phi_{Yg}^2 \Phi_{Xg}^2}$ , and other similarly needed averages are calculated in appendix 4.

$$\begin{aligned}
 (46) \sum_{g < i} \delta_i'' g'' \beta_{gg'g''} \beta_{i'i'i''} \overline{\Phi_{Yg} \Phi_{Xg'} \Phi_{Yi} \Phi_{X i''}} &= \beta_{333} \beta_{113} \overline{\Phi_{Y3} \Phi_{X3} \Phi_{Y1} \Phi_{X1}} \\
 &+ \beta_{333} \beta_{223} \overline{\Phi_{Y3} \Phi_{X3} \Phi_{Y2} \Phi_{X2}} + \beta_{113} \beta_{223} \overline{\Phi_{Y1} \Phi_{X1} \Phi_{Y2} \Phi_{X2}} \\
 &+ \beta_{131} \beta_{311} \overline{\Phi_{Y1} \Phi_{X3} \Phi_{Y3} \Phi_{X1}} + \beta_{232} \beta_{322} \overline{\Phi_{Y2} \Phi_{X3} \Phi_{Y3} \Phi_{X2}} \\
 &= -\frac{1}{30} (\beta_{113} \beta_{333} + \beta_{223} \beta_{333} + \beta_{113} \beta_{223} + \beta_{113}^2 + \beta_{223}^2)
 \end{aligned}$$

Thus, from equations (44), (45), and (46),

$$\begin{aligned}
 (47) \sum_F \overline{\beta_{YXF}^2} &= \frac{4}{15} \beta_{113}^2 + \frac{4}{15} \beta_{223}^2 + \frac{1}{15} \beta_{333}^2 \\
 &\quad - \frac{1}{15} (\beta_{113} \beta_{333} + \beta_{223} \beta_{333} + \beta_{113} \beta_{223})
 \end{aligned}$$

Next, the value of  $\sum_F \overline{\beta_{22F}^2}$  is needed which is given by

$$(48) \sum_F \overline{\beta_{22F}^2} = \sum_g \beta_{gg'g''}^2 \overline{\Phi_{2g}^2 \Phi_{2g'}^2} + 2 \sum_{g < i} \delta_i'' g'' \beta_{gg'g''} \beta_{i'i'i''} \overline{\Phi_{2g} \Phi_{2g'} \Phi_{2i} \Phi_{2i''}}$$

The first term on the right-hand side of equation (48) may be expanded. Thus,

$$(49) \sum_g \beta_{gg'g''} \overline{\Phi_{Zg}^2 \Phi_{Zg'}^2} = \beta_{333}^2 \overline{\Phi_{Z3}^4} + \beta_{113} (\overline{\Phi_{Z1}^4} + 2 \overline{\Phi_{Z1}^2 \Phi_{Z3}^2}) \\ + \beta_{223}^2 (\overline{\Phi_{Z2}^4} + 2 \overline{\Phi_{Z2}^2 \Phi_{Z3}^2})$$

From the average values of the direction cosines,

$$(50) \sum_g \beta_{gg'g''} \overline{\Phi_{Zg}^2 \Phi_{Zg'}^2} = \frac{1}{5} \beta_{333}^2 + \frac{1}{3} \beta_{113}^2 + \frac{1}{3} \beta_{223}^2$$

The second term on the right-hand side of equation (48) may be expanded to give

$$(51) \sum_{g \neq i} \delta g'' i'' \beta_{gg'g''} \beta_{i i' i''} \overline{\Phi_{Zg} \Phi_{Zg'} \Phi_{Zi} \Phi_{Zi'}} = \frac{1}{15} \beta_{113} \beta_{333} \\ + \frac{1}{15} \beta_{223} \beta_{333} + \frac{1}{15} \beta_{113} \beta_{223} + \frac{1}{15} \beta_{113}^2 + \frac{1}{15} \beta_{223}^2$$

Thus, from equations (48), (50), and (51),

$$(52) \sum_F \overline{\beta_{ZZF}^2} = \frac{7}{15} \beta_{113}^2 + \frac{7}{15} \beta_{223}^2 + \frac{1}{5} \beta_{333}^2 \\ + \frac{2}{15} \beta_{113} \beta_{333} + \frac{2}{15} \beta_{223} \beta_{333} + \frac{2}{15} \beta_{113} \beta_{223}$$

Using equation (40),

$$(53) \rho_n = \frac{2[4\beta_{113}^2 + 4\beta_{223}^2 + \beta_{333}^2 - \beta_{113}\beta_{333} - \beta_{223}\beta_{333} - \beta_{113}\beta_{223}]}{[11\beta_{113}^2 + 11\beta_{223}^2 + 4\beta_{333}^2 + \beta_{113}\beta_{333} + \beta_{223}\beta_{333} + \beta_{113}\beta_{223}]}$$

The values of  $\rho_n$  are quite restricted as shown by determining the maximum and minimum values of  $\rho_n$ . For simplicity, let

$\beta_{113} = x$ ,  $\beta_{223} = y$ , and  $\beta_{333} = z$ . Hence,

$$(54) \rho_n = \frac{2[4x^2 + 4y^2 + z^2 - xy - yz - xz]}{[11x^2 + 11y^2 + 4z^2 + xy + yz + xz]}$$

$\rho_n$  will experience a relative extremum value when

$$(55) \frac{\partial \rho_n}{\partial x} = \frac{\partial \rho_n}{\partial y} = \frac{\partial \rho_n}{\partial z} = 0$$

Let

$$(56) \quad A = [11x^2 + 11y^2 + 4z^2 + xy + xz + yz]$$

Now, performing the indicated partial differentiation

$$(57) \quad \begin{aligned} \frac{\partial P_n}{\partial x} &= \frac{2[Bx - y - z]}{A} - \frac{[22x - y + z]}{A^2} = 0 \\ \frac{\partial P_n}{\partial y} &= \frac{2[By - x - z]}{A} - \frac{[22y + x + z]}{A^2} = 0 \\ \frac{\partial P_n}{\partial z} &= \frac{2[2z - y - x]}{A} - \frac{[8z + x + y]}{A^2} = 0 \end{aligned}$$

Three sets of solutions are obtained from these equations:

$$(58) \quad A\{x=y, z=3y\}, B\{x=-4y, z=3y\}, C\{y=-4x, z=3x\}$$

Solution A gives  $P_n = 4/13$ . Solutions B and C both give

$P_n = 6/7$ .  $4/13$  was found to be the absolute minimum and  $6/7$  was found to be the absolute maximum of  $P_n$ .

Similar solutions for  $P_n$  to the one for the  $B_{1u}$  species are obtained for the  $B_{2u}$  and  $B_{3u}$  species of  $\mathcal{D}_{2h}$ . The remaining species in  $\mathcal{D}_{2h}$  for which  $\beta$ 's appear is  $A_u$ . For this species  $\frac{\partial \beta_{xyz}}{\partial Q} \neq 0$ ; while the derivatives of the other nine of the ten  $\beta$ 's are zero. As before, let  $\frac{\partial \beta_{xyz}}{\partial Q} = \beta_{123}$ . The non-vanishing  $\beta$ 's become  $\{\beta_{123}, \beta_{132}, \beta_{213}, \beta_{231}, \beta_{312}\}$ . In this case the required terms for the determination of  $P_n$  are

$$(59) \quad \sum_g \beta_{gg'g''}^2 \overline{\Phi_{zg}^2} \overline{\Phi_{zg'}^2} = \frac{2}{5} \beta_{123}^2$$

$$\sum_{g < i} \delta_{i''g''} \beta_{gg'g''} \beta_{i'i'i''} \overline{\Phi_{zg}} \overline{\Phi_{zg'}} \overline{\Phi_{zi}} \overline{\Phi_{zi'}} = \frac{1}{5} \beta_{123}^2$$

$$\sum_g \beta_{gg'g''}^2 \overline{\Phi_{yg}^2 \Phi_{zg}^2} = \frac{4}{5} \beta_{123}^2$$

$$\sum_{g < i} \delta_{i''g''} \beta_{gg's''} \beta_{iil'i''} \overline{\Phi_{yg} \Phi_{zg} \Phi_{yi} \Phi_{zi'}} = -\frac{1}{10} \beta_{123}^2$$

Applying equation (40) to the equation given in (59)

$$(60) \quad \rho_n = 6/7$$

A summary of the  $\rho_n$ 's for the various species of this group and the  $D_{6h}$  and  $D_{\infty h}$  point groups will be found in appendix 5.

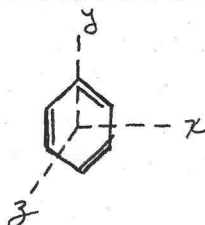


## CHAPTER VI

THE  $D_{6h}$  SYMMETRY POINT GROUP

As in the case of the  $D_{2h}$  group, let us determine which of the ten distinct linear combinations of the  $\beta$ 's are associated with the various species of the group. In a process similar to those of equations (41) it can be shown that  $\beta_{zzz}$  and  $\beta_{xxz} + \beta_{yyz}$  transform as  $A_{1u}$ ,  $\beta_{yyy} - 3\beta_{yxx}$  transforms as  $A_{2u}$ ,  $\beta_{xxx} - 3\beta_{xyy}$  transforms as  $B_{2u}$ ,  $(\beta_{yzz}, \beta_{xxz})$  and  $(\beta_{yyy} + \beta_{yxx}, \beta_{xxx} + \beta_{xyy})$  transform as  $E_{1u}$ , and  $(\beta_{xyz}, \beta_{xxz} - \beta_{yyz})$  transforms as  $E_{2u}$  (see appendix 3).

Benzene is a representative molecule of this group and a procedure similar to that which was carried out for ethylene of  $D_{2h}$  will be carried out for this molecule.



The  $z$ -axis is a six-fold symmetric axis.

The normal vibrations of  $C_6H_6$  are:

$$2A_{1g} + A_{2g} + 2B_{2g} + E_{1g} + 4E_{2g} + A_{2u} + 2B_{1u} + 2B_{2u} + 3E_{1u} + 2E_{2u}$$

Then, since the infrared active species are  $A_{2u}$  and  $E_{1u}$ , the ordinary Raman active species are  $A_{1g}$ ,  $E_{1g}$ , and  $E_{2g}$ , while the hyper-Raman active species are, as indicated above,  $A_{1u}$ ,  $A_{2u}$ ,  $B_{2u}$ ,  $E_{1u}$ , and  $E_{2u}$ , the numbers of active frequencies are

as given in the following table.

	$\frac{n(\gamma)}{\text{IR}}$	$\frac{n(\gamma)}{\text{R}}$	$\frac{n(\gamma)}{\text{hyper-R}}$
<u>A<sub>1g</sub></u>		2	
<u>A<sub>2g</sub></u>			
<u>B<sub>1g</sub></u>			
<u>B<sub>2g</sub></u>			
<u>E<sub>1g</sub></u>		1	
<u>E<sub>2g</sub></u>		4	
<u>A<sub>1u</sub></u>			
<u>A<sub>2u</sub></u>	1		1
<u>B<sub>1u</sub></u>			2
<u>B<sub>2u</sub></u>			2
<u>E<sub>1u</sub></u>	3		3
<u>E<sub>2u</sub></u>			2

Hence, the infrared frequencies are allowed in the hyper-Raman effect and six additional fundamental frequencies are allowed also which are not in either the infrared or Raman spectrum.

Next the observable quantities,  $P_n$ , for the various species of the  $D_{6h}$  point group will be calculated. First consider the  $B_{1u}$  species. Let  $Q$  represent a normal coordinate for this species. Hence:

$$(61) \quad \frac{\partial(P_{yyy} - 3P_{xyy})}{\partial Q} \neq 0, \quad \frac{\partial(P_{yyy} + P_{xyy})}{\partial Q} = 0$$

and all other of the linear combinations of the  $\frac{\partial P_i}{\partial Q}$  for this group are zero. From this it is found that

(62) see next page

$$(62) \quad \frac{\partial \beta_{zyy}}{\partial Q} = - \frac{\partial \beta_{xzy}}{\partial Q} \neq 0$$

and all other  $\frac{\partial \beta}{\partial Q}$ 's vanish. Let  $\frac{\partial \beta_{zyy}}{\partial Q} = \beta_{222}$  and  $\beta_{112}$ . Hence the non-vanishing terms for this species may be represented by  $\{\beta_{222}, \beta_{112}, \beta_{121}, \beta_{211}\}$ . In this case,

$$(63) \quad \begin{aligned} \sum_g \beta_{ggg}^2 \overline{\Phi_{zg}^2 \Phi_{zg}^2} &= \frac{8}{15} \beta_{222}^2 \\ \sum_{g < i} \delta_{i''g''} \beta_{ggg''} \beta_{iii''} \overline{\Phi_{zg} \Phi_{zg'} \Phi_{zi} \Phi_{zi'}} &= 0 \\ \sum_g \beta_{ggg}^2 \overline{\Phi_{yg}^2 \Phi_{zg}^2} &= \frac{2}{5} \beta_{222}^2 \\ \sum_{g < i} \beta_{ggg''} \beta_{iii''} \delta_{i''g''} \overline{\Phi_{yg} \Phi_{zg'} \Phi_{yi} \Phi_{zi'}} &= 0 \end{aligned}$$

Applying equation (40), to the equations of (63),

$$(64) \quad \rho_n = 6/7$$

The species  $B_{2u}$  has linear combination of the  $\beta$ 's similar to that of  $B_{1u}$ . This yields that  $\rho_n$  for  $B_{2u}$  is given by

$$(65) \quad \rho_n = 6/7$$

Also  $\beta_{xyz}$  of the degenerate pair  $(\beta_{xyz}, \beta_{xxz}, \beta_{yyz})$  of the species  $E_{2u}$  acts identically as the  $\beta_{xyz}$  of the species  $A_u$  of the point group  $D_{2h}$ . Hence,

$$(66) \quad \rho_n = 6/7$$

for the  $E_{2u}$  species.

Next, consider the  $\beta$ 's of the  $A_{2u}$  species. If  $Q$

represents a normal coordinate for this species, then

$$(67) \quad \frac{\partial \beta_{zzz}}{\partial Q} \neq 0, \quad \frac{\partial (\beta_{xxz} + \beta_{yyz})}{\partial Q} = 0, \quad \frac{\partial (\beta_{xz} - \beta_{yz})}{\partial Q} = 0$$

Thus, it is found that

$$(68) \quad \frac{\partial \beta_{zzz}}{\partial Q} \neq 0, \quad \frac{\partial \beta_{xxz}}{\partial Q} = \frac{\partial \beta_{yyz}}{\partial Q} \neq 0$$

and all of the other  $\frac{\partial \beta}{\partial Q}$  's are zero for this species. Let

$$(69) \quad \frac{\partial \beta_{zzz}}{\partial Q} = \beta_{333}, \quad \frac{\partial \beta_{xxz}}{\partial Q} = \beta_{113}, \quad \frac{\partial \beta_{yyz}}{\partial Q} = \beta_{223}$$

Hence, the non-vanishing terms for this species may be re-

presented by  $(\beta_{333} \beta_{113} \beta_{131} \beta_{311} \beta_{223} \beta_{232} \beta_{322})$ .

These  $\beta$ 's are exactly those obtained in the  $B_{1u}$  species of

the  $D_{2h}$  point group. This leads directly to

$$P_n = \frac{2[4\beta_{113}^2 + 4\beta_{223}^2 + \beta_{333}^2 - \beta_{113}\beta_{333} - \beta_{223}\beta_{333} - \beta_{113}\beta_{223}]}{[11\beta_{113}^2 + 11\beta_{223}^2 + 4\beta_{333}^2 + \beta_{113}\beta_{333} + \beta_{223}\beta_{333} + \beta_{113}\beta_{223}]}$$

for the  $A_{2u}$  species of  $D_{6h}$ . But, for this species

$\beta_{223} = \beta_{113}$ . This reduces  $P_n$  to

$$(70) \quad P_n = \frac{2[7\beta_{113}^2 + \beta_{333}^2 - 2\beta_{113}\beta_{333}]}{[23\beta_{113}^2 + 4\beta_{333}^2 + 2\beta_{113}\beta_{333}]}$$

Again the maximum and minimum values of  $P_n$  put a useful

restriction on the range of  $P_n$ . For simplicity, let

$\beta_{113} = x$  and  $\beta_{333} = y$ . Hence,

$$P_n = \frac{2(7x^2 + y^2 - 2xy)}{23x^2 + 4y^2 + 2xy}$$

As before the relative extremum values are found by setting

$$(71) \quad \frac{\partial P_n}{\partial x} = \frac{\partial P_n}{\partial y} = 0$$

This leads to the following set of equations:

$$(72) \quad \frac{\partial P_n}{\partial x} = \frac{28x - 4y}{23x^2 + 4y^2 + 2xy} - \frac{z(7x^2 + y^2 - 2xy)(46x + 2y)}{(23x^2 + 4y^2 + 2xy)^2}$$

$$\frac{\partial P_n}{\partial y} = \frac{4y - 4x}{23x^2 + 4y^2 + 2xy} - \frac{z(7x^2 + y^2 - 2xy)(8y + 2x)}{(23x^2 + 4y^2 + 2xy)^2}$$

Two sets of solutions are obtained from these equations:

$$(73) \quad A\{3x = y\} ; B\{2x = -y\}$$

Solution A gives  $\rho_n$  4/13. Solution B gives  $\rho_n$  6/7.

4/13 is found to be the absolute minimum and 6/7 is found to be the absolute maximum of  $\rho_n$  for species  $A_{2u}$  of the group  $D_{6h}$ .

The remaining species of  $D_{6h}$  which has linear combinations of  $\beta$ 's associated with it is  $E_{1u}$ . If  $Q$  be a normal coordinate for this species, then

$$(74) \quad \frac{\partial \beta_{xzz}}{\partial Q} \neq 0, \quad \frac{\partial (\beta_{xxx} + \beta_{xyy})}{\partial Q} \neq 0$$

while

$$(75) \quad 0 = \frac{\partial \beta_{yzz}}{\partial Q} = \frac{\partial (\beta_{yyx} + \beta_{xxy})}{\partial Q} = \frac{\partial (\beta_{xxz} + \beta_{yyz})}{\partial Q} = \frac{\partial (\beta_{xxx} - 3\beta_{xyy})}{\partial Q}$$

and so forth. Thus, it is found that

(76) see next page

$$(76) \quad \frac{\partial \beta_{xzz}}{\partial Q} \neq 0; \quad \frac{\partial \beta_{xxx}}{\partial Q} = \frac{3 \partial \beta_{xyy}}{\partial Q} \neq 0;$$

and all of the other  $\frac{\partial \beta}{\partial Q}$ 's are zero for this species and particular normal coordinate. Let

$$(77) \quad \frac{\partial \beta_{xzz}}{\partial Q} = \beta_{111}; \quad \frac{\partial \beta_{xxx}}{\partial Q} = \beta_{111}; \quad \frac{\partial \beta_{xyy}}{\partial Q} = \beta_{122}.$$

Hence, the non-vanishing terms for this species may be represented by  $\{\beta_{111}, \beta_{122}, \beta_{212}, \beta_{221}, \beta_{133}, \beta_{313}, \beta_{331}\}$ . This set is equivalent to the set of non-vanishing  $\beta$ 's of the  $B_{1u}$  species of the  $D_{2h}$  point group. This leads directly to

$$\rho_n = \frac{2[4\beta_{122}^2 + 4\beta_{133}^2 + \beta_{111}^2 - \beta_{122}\beta_{111} - \beta_{133}\beta_{111} - \beta_{122}\beta_{133}]}{[11\beta_{122}^2 + 11\beta_{133}^2 + 4\beta_{111}^2 + \beta_{122}\beta_{111} + \beta_{133}\beta_{111} - \beta_{122}\beta_{133}]}$$

for the  $E_{1u}$  species of  $D_{6h}$ . But, for this species  $\beta_{111} = 3\beta_{122}$ . This reduces  $\rho_n$  to

$$(78) \quad \rho_n = \frac{4[5\beta_{111}^2 + 18\beta_{133}^2 - 3\beta_{111}\beta_{133}]}{[50\beta_{111}^2 + 99\beta_{133}^2 + 12\beta_{111}\beta_{133}]}$$

Again the relative extremum values of  $\rho_n$  will be determined

by setting  $\frac{\partial \rho_n}{\partial x} = 0 = \frac{\partial \rho_n}{\partial y}$ , where  $x = \beta_{111}$  and  $y = \beta_{133}$ .

Hence

$$(79) \quad \rho_n = \frac{4[5x^2 + 18y^2 - 3xy]}{50x^2 + 99y^2 + 12xy}$$

$$(80) \quad \frac{\partial \rho_n}{\partial x} = \frac{4(10x - 3y)}{50x^2 + 99y^2 + 12xy} - \frac{4(6x^2 + 18y^2 - 3xy)(100x + 12y)}{(50x^2 + 99y^2 + 12xy)^2}$$

(80) continued

$$\frac{\partial P_n}{\partial Y} = \frac{12(12Y-X)}{50X^2+99Y^2+12XY} - \frac{12(5X^2+18Y^2-3XY)(66Y+4X)}{(50X^2+99Y^2+12XY)^2} = 0$$

Two sets of solutions are obtained from these equations:

~~$$\frac{\partial P_n}{\partial Y} = \frac{12(12Y-X)}{50X^2+99Y^2+12XY} - \frac{12(5X^2+18Y^2-3XY)(66Y+4X)}{(50X^2+99Y^2+12XY)^2}$$~~

Solution A gives  $P_n = 0.363$ . Solution B gives  $P_n = 0.732$ .0.363 was found to be the absolute minimum and 0.732 was found to be the absolute maximum of  $P_n$  for the species  $E_{lu}$ .A summary of the  $P_n$ 's for the various species of this group will be found in appendix 5.

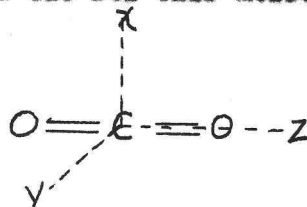
$$A \left\{ \frac{X}{Y} = \frac{270 + 3\sqrt{8940}}{140} \right\} \text{ and } B \left\{ \frac{X}{Y} = \frac{270 - 3\sqrt{8940}}{140} \right\}$$

## CHAPTER VII

THE  $D_{\infty h}$  SYMMETRY POINT GROUP

As in the case of the  $D_{2h}$  group, let us determine which of the ten distinct linear combinations of the  $\beta$ 's are associated with the various species of the group. In a process similar to that shown by equations (14), it can be shown that  $\beta_{zzz}$  and  $\beta_{xxz} + \beta_{xyz}$  transform as the species  $\Sigma_u^+$ ,  $(\beta_{yzz}, \beta_{xzz})$  and  $(\beta_{yyy} + \beta_{xyy}, \beta_{xxx} + \beta_{xyy})$  transform as the species  $\Pi_u$ ,  $(\beta_{xxz} - \beta_{yyz}, \beta_{xyz})$  transforms as the species  $\Delta_u$ , and  $(\beta_{xxx} - 3\beta_{xyy}, \beta_{yyy} - 3\beta_{xxy})$  transforms as the species  $\Gamma_u$  (see appendix 2).

Carbon dioxide is a representative molecule of this group and a procedure similar to that for ethylene of  $D_{2h}$  will be carried out for this molecule.



the z axis is the  
molecular symmetric axis

The normal vibrations of  $CO_2$  are of the types  $\Sigma_g^+ + \Sigma_u^- + \Pi_u$ .

Thus, since dipole moment is of species  $\Sigma_u^+ + \Pi_u$  and ordinary polarizability is of species  $2\Sigma_g^+ + \Pi_g + \Delta_g$ , the active modes are as given in the table. (see next page)



	$\frac{n(\gamma)}{IR}$	$\frac{n(\gamma)}{R}$	$\frac{n(\gamma)}{hyper-R}$
$\underline{\Sigma_g^+}$			
$\underline{\Sigma_g^-}$			
$\underline{\pi_g}$			
$\underline{\Delta_g}$			
---	---	---	---
$\underline{\Sigma_u^+}$	1		1
$\underline{\Sigma_u^-}$			
$\underline{\pi_u}$	1		1
$\underline{\Delta_u}$			
$\underline{\Gamma_u}$			
---	---	---	---

For a linear triatomic symmetric molecule, such as carbon dioxide, there are four fundamental frequencies of molecular vibration. The totally symmetric vibration associated with  $\Sigma_g^+$  is active only in the Raman effect, comparing only the Raman and infrared spectra, while on the same basis the anti-symmetric stretch of the molecule associated with the  $\Sigma_u^+$  species is active only in the infrared spectrum, and the degenerate bending motion, associated with the  $\pi_u$  species, is also active only in the infrared spectrum. Thus, it is readily seen that the existence of linear combinations of the  $\beta$ 's associated with both  $\Sigma_u^+$  and  $\pi_u$  insure that the infrared active fundamentals will also be active in the hyper-Raman effect.

Next, consider the species  $\Gamma_u$ . A consideration of

either  $B_{1u}$  or  $B_{2u}$  of the point group  $D_{6h}$  will show that

$\rho_n = 6/7$  for this species also.

If the  $\beta$ 's of the species  $\Sigma_u^+$  of  $D_{6h}$  are compared with the  $\beta$ 's of the species  $A_{2u}$  of  $D_{6h}$ , it is apparent that

$$(70) \quad \rho_n = \frac{2(7\beta_{113}^2 + \beta_{333}^2 - 2\beta_{113}\beta_{333})}{23\beta_{113}^2 + 4\beta_{333}^2 + 2\beta_{113}\beta_{333}}$$

for the  $\Sigma_u^+$  species and that the range of  $\rho_n$  is given by

$$(81) \quad \frac{4}{13} \leq \rho_n \leq \frac{6}{7}$$

The last species of  $D_{6h}$  in which linear combinations of the  $\beta$ 's are associated is  $\Pi_u$ . A comparison of the  $\beta$ 's of this species with those of the species  $E_{1u}$  of the point group  $D_{6h}$  shows that

$$(78) \quad \rho_n = \frac{4(5\beta_{111}^2 + 18\beta_{133}^2 - 3\beta_{111}\beta_{133})}{50\beta_{111}^2 + 99\beta_{133}^2 + 12\beta_{111}\beta_{133}}$$

for the species  $\Pi_u$ . The range of  $\rho_n$  again being given by

$$(82) \quad 0.363 \leq \rho_n \leq 0.732$$

A summary of the  $\rho_n$ 's for the various species of this group will be found in appendix 5.

## CHAPTER VIII

## CONCLUSION

Much work on this subject is yet to be done. The theoretical expectation for the concentration dependence of the hyper-Raman lines should be determined for cases of ion-ion, ion-dipole, dipole-dipole, etc., interactions in much more detail than in appendix 7. The quantum mechanical aspect of this work should be worked out to show the validity of the classical approach. However, the experimental side of the theory can not be overlooked. Although the values for the depolarization ratios for the  $\Sigma_u^+$  and  $\Pi_u$  species for carbon disulfide have been measured and fall within the theoretically predicted range, many more cases should be studied. A very interesting prediction is offered by the hyperpolarizability theory. For ethylene a fundamental mode of vibration is allowed in the hyper-Raman effect which is not allowed in either the infrared or the usual Raman effect. This mode corresponds to the  $A_u$  species. Theoretically this line should have a depolarization ratio of 6/7. In the case of benzene even more apparent should be the confirmation of the theory. Allowed fundamental modes of vibration in the hyper-Raman effect correspond to the species  $B_{1u}$ ,  $B_{2u}$ , and  $E_{2u}$ . All six of these allowed lines should have depolarization ratios of 6/7.

This theory should not be considered as a contradiction

or a rival theory of those previously presented in papers by Evans and Bernstein, and Welsh, et al. However, it should be considered as a complementary theory describing the same phenomena only considered from a slightly different point of view.

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## APPENDIXES

## APPENDIX I

GENERAL FORMULAS OF TRANSFORMATION FOR THE  $\beta_{FF'F''}$ 

In the hyper-Raman effect  $\mu_F$  is given by

$$(1) \quad \mu_F = \sum_{F'F''} \beta_{FF'F''} E_{F'} E_{F''}$$

also

$$(2) \quad E_F = \sum_g \Phi_{gF} E_g$$

where  $(E_1, E_2, E_3)$  is the electric vector of the incident light along the axes of the molecules and  $(E_x, E_y, E_z)$  is the electric vector of the incident light along the laboratory fixed axes.  $\{\Phi_{gF}\}$  are the direction cosines between the two systems. A product of two components of the electric field in the  $(X, Y, Z)$  system in terms of the  $(1, 2, 3)$  system is given by

$$(3) \quad E_F E_{F'} = \sum_g \sum_{g'} \Phi_{gF} \Phi_{g'F'} E_g E_{g'}$$

Now, combining equations (1) and (2)

$$(4) \quad \mu_F = \sum_{F'F''} \sum_{gg'} \beta_{FF'F''} E_g E_{g'} \Phi_{gF'} \Phi_{g'F''}$$

But,  $\mu$  in the  $(X, Y, Z)$  system is given by

$$(5) \quad \mu_F = \sum_l \mu_l \Phi_{lF}$$

in the  $(1, 2, 3)$  system. Let



$$(6) \quad \sum_l \mu_l \Phi_{lF} = \sum_{gg'} \left( \sum_{FF'} \beta_{FF'F''} \Phi_{gF'} \Phi_{g'F''} \right) E_g E_{g'} = A_F$$

Then, solving for  $\mu_l$

$$(7) \quad \mu_l = \begin{vmatrix} A_x & \Phi_{2x} & \Phi_{3x} \\ A_y & \Phi_{2y} & \Phi_{3y} \\ A_z & \Phi_{2z} & \Phi_{3z} \end{vmatrix}$$

since the  $\Phi_{gF}$  are the elements of an orthogonal matrix.

Expansion of the determinant gives

$$(8) \quad \mu_l = \left[ \sum_{gg'} \left( \sum_{FF'} \beta_{XFF'} \Phi_{gF} \Phi_{g'F'} \right) E_g E_{g'} \right] (\Phi_{2y} \Phi_{3z} - \Phi_{3y} \Phi_{2z}) \\ + \left[ \sum_{gg'} \left( \sum_{FF'} \beta_{YFF'} \Phi_{gF} \Phi_{g'F'} \right) E_g E_{g'} \right] (\Phi_{2z} \Phi_{3x} - \Phi_{3z} \Phi_{2x}) \\ + \left[ \sum_{gg'} \left( \sum_{FF'} \beta_{ZFF'} \Phi_{gF} \Phi_{g'F'} \right) E_g E_{g'} \right] (\Phi_{2x} \Phi_{3y} - \Phi_{3x} \Phi_{2y})$$

Hence,

$$(9) \quad \beta_{l g g'} = \sum_{FF'} \beta_{XFF'} \Phi_{gF} \Phi_{g'F'} (\Phi_{2y} \Phi_{3z} - \Phi_{3y} \Phi_{2z}) \\ + \sum_{FF'} \beta_{YFF'} \Phi_{gF} \Phi_{g'F'} (\Phi_{2z} \Phi_{3x} - \Phi_{3z} \Phi_{2x}) \\ + \sum_{FF'} \beta_{ZFF'} \Phi_{gF} \Phi_{g'F'} (\Phi_{2x} \Phi_{3y} - \Phi_{3x} \Phi_{2y}) \\ = \sum_{FF'F''} \beta_{FF'F''} \Phi_{lF} \Phi_{gF'} \Phi_{g'F''}$$

Thus, in general,

$$(10) \quad \beta_{g g' g''} = \sum_{FF'F''} \beta_{FF'F''} \Phi_{gF} \Phi_{g'F'} \Phi_{g''F''}$$

or

$$\beta_{FF'F''} = \sum_{g g' g''} \beta_{g g' g''} \Phi_{Fg} \Phi_{F'g'} \Phi_{F''g''}$$

## APPENDIX 2

TABLES OF CHARACTERS OF THE GROUPS  $D_{nh}$  ( $n=2, 6, \infty$ )

$D_{2h}=V_h$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$
$A_g$	1	1	1	1	1	1	1	1
$B_{1g}$	1	1	-1	-1	1	1	-1	-1
$B_{2g}$	1	-1	1	-1	1	-1	1	-1
$B_{3g}$	1	-1	-1	1	1	-1	-1	1
$A_u$	1	1	1	1	-1	-1	-1	-1
$B_{1u}$	1	1	-1	-1	-1	-1	1	1
$B_{2u}$	1	-1	1	-1	-1	1	-1	1
$B_{3u}$	1	-1	1	1	-1	1	1	-1

$A_g$   $d_{xx}, d_{yy}, d_{zz}$

$B_{1g}$   $R_z$   $d_{xy}$

$B_{2g}$   $R_y$   $d_{zx}$

$B_{3g}$   $R_x$   $d_{yz}$

$A_u$   $\beta_{xyz}$

$B_{1u}$   $T_z$   $\beta_{zzz}, \beta_{xxx}, \beta_{xyx}$

$B_{2u}$   $T_y$   $\beta_{yyy}, \beta_{xyy}, \beta_{yzz}$

$B_{3u}$   $T_x$   $\beta_{xxx}, \beta_{xyx}, \beta_{xzz}$

$D_{6h}$	E	$2C_6$	$2C_3$	$C_2$	$3C_2^1$	$3C_2''$	i	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0

$A_{1g}$		$d_{xx} + d_{yy}, d_{zz}$
$A_{2g}$	$R_z$	
$B_{1g}$		
$B_{2g}$		
$E_{1g}$	$(R_x, R_y)$	$(d_{yz}, d_{zx})$
$E_{2g}$		$(d_{xx} - d_{yy}, d_{xy})$
$A_{1u}$		
$A_{2u}$	$T_z$	$\beta_{zzz}, \beta_{xxz} + \beta_{yyz}$
$B_{1u}$		$\beta_{yyy} - 3\beta_{xyy}$
$B_{2u}$		$\beta_{xxx} - 3\beta_{xyx}$
$E_{1u}$	$(T_x, T_y)$	$(\beta_{yzz}, \beta_{xzz})$
		$(\beta_{yyy} + \beta_{xyy}, \beta_{xxx} + \beta_{xyx})$
$E_{2u}$		$(\beta_{xyx}, \beta_{xyy} - \beta_{yyz})$

$D_{\text{coh}}$	E	$2C_0^{\phi} \dots$	$\omega C_1$	$2S_0^{\phi} \dots$	$\omega C_2$	
$\Sigma_g^+$	1	1	...	1	1	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
$\Sigma_g^-$	1	1	...	-1	1	$R_z$
$\Pi_g$	2	$2\cos\phi$	...	0	2	$(R_x, R_y)$ ( $\alpha_{yz}, \alpha_{zx}$ )
$\Delta_g$	2	$2\cos 2\phi$	...	0	2	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
---	..	..	...	..	..	
$\Sigma_u^+$	1	1	...	1	-1	$T_z$
$\Sigma_u^-$	1	1	...	-1	-1	
$\Pi_u$	2	$2\cos\phi$	...	0	-2	$(T_x, T_y)$
$\Delta_u$	2	$2\cos 2\phi$	...	0	-2	
$\Gamma_u$	2	$2\cos 3\phi$	...	0	-2	
---	..	..	...	..	..	

$\Sigma_g^+$	
$\Sigma_g^-$	
$\Pi_g$	
$\Delta_g$	
...	
$\Sigma_u^+$	$\beta_{zzz}, \beta_{xxz} + \beta_{yyz}$
$\Sigma_u^-$	
$\Pi_u$	$(\beta_{yzz}, \beta_{xzz})$ ( $\beta_{yyz} + \beta_{xxy}, \beta_{xxx} + \beta_{xyy}$ )
$\Delta_u$	$(\beta_{xxz} - \beta_{yyz}, \beta_{xyz})$
$\Gamma_u$	$(\beta_{xxx} - 3\beta_{xyy}, \beta_{yyy} - 3\beta_{xxy})$

## APPENDIX 3

CHARACTER FOR  $\beta$  FOR AN OPERATION R

To obtain the character of a transformation  $\chi^R$ , one needs only to note its definition, i. e.,

$$(1) \quad \chi^R = \sum_i R_{ii} \quad (12, \text{ p. } 92)$$

in which  $R_{ii}$  is a diagonal coefficient in the transformation

$$(2) \quad \eta'_i = \sum_{j=1}^{3N} R_{ij} \eta_j,$$

and then add up the  $R_{ii}$  terms of the transformation. Thus, in general for a rotation  $C_n^k$  and about the Z axis, the transformation is

$$(3) \quad \begin{aligned} X' &= \cos \frac{2\pi k}{n} X - \sin \frac{2\pi k}{n} Y \\ Y' &= \sin \frac{2\pi k}{n} X + \cos \frac{2\pi k}{n} Y \\ Z' &= Z \end{aligned}$$

Thus,

$$\chi^{C_n^k} = 1 + 2 \cos \frac{2\pi k}{n}$$

Next, for a general rotary reflection,  $S_n^k$

$$(4) \quad \begin{aligned} X' &= \cos \frac{2\pi k}{n} X - \sin \frac{2\pi k}{n} Y \\ Y' &= \sin \frac{2\pi k}{n} X + \cos \frac{2\pi k}{n} Y \\ Z' &= -Z \\ \chi^{S_n^k} &= -1 + 2 \cos \frac{2\pi k}{n} \end{aligned}$$

Hence,

$$(5) \quad \chi_{\mu}^R = \pm 1 + 2 \cos \frac{2\pi k}{n}$$

where the positive sign is used for proper rotations, simple rotations, and the negative sign is used for improper rotations, rotary reflections.

This concept can be extended for the transformation of the kind which involve the product of two coordinates. This would be the character of a transformation for polarizability components. Thus, in general for a rotation  $C_n^R$  the transformation is

$$\begin{aligned}
 (6) \quad (X')^2 &= (\cos \alpha X - \sin \alpha Y)^2 \\
 (Y')^2 &= (\sin \alpha X + \cos \alpha Y)^2 \\
 (Z')^2 &= Z^2 \\
 (X')(Y') &= (\cos \alpha X - \sin \alpha Y)(\sin \alpha X + \cos \alpha Y) \\
 (X')(Z') &= (\cos \alpha X - \sin \alpha Y)(Z) \\
 (Y')(Z') &= (\sin \alpha X + \cos \alpha Y)(Z)
 \end{aligned}$$

where  $\alpha = \frac{2\pi k}{n}$

Hence,

$$(7) \quad \chi_{\alpha}^{C_n^k} = 2 \cos \alpha (2 \cos \alpha + 1)$$

Now consider a general rotary reflection,  $S_n^k$ . The only changes from that of the rotation  $C_n^k$  are

$$\begin{aligned}
 (8) \quad (X')(Z') &= -(\cos \alpha X - \sin \alpha Y)(Z) \\
 (Y')(Z') &= -(\sin \alpha X + \cos \alpha Y)(Z)
 \end{aligned}$$

Hence, (see next page)

$$(9) \quad \chi_{\alpha}^{S_n^k} = 2 \cos \alpha (2 \cos \alpha - 1)$$

Thus,

$$(10) \quad \chi_{\alpha}^R = 2 \cos \alpha (2 \cos \alpha \pm 1)$$

The components of the hyperpolarizability transform as the product of three coordinates. Hence, the character of a transformation for the hyperpolarizability components may be found in the same way as in the previous two cases. Thus, in general for a rotation,  $C_n^k$ , the transformation is

$$(11) \quad \begin{aligned} (X')^3 &= (\cos \alpha) X - (\sin \alpha) Y)^3 \\ (Y')^3 &= (\sin \alpha) X + (\cos \alpha) Y)^3 \\ (Z')^3 &= Z^3 \\ (X')^2 (Y') &= (\cos \alpha) X - (\sin \alpha) Y)^2 (\sin \alpha) X + (\cos \alpha) Y \\ (X') (Y')^2 &= (\cos \alpha) X - (\sin \alpha) Y) (\sin \alpha) X + (\cos \alpha) Y)^2 \\ (X')^2 (Z') &= (\cos \alpha) X - (\sin \alpha) Y)^2 Z \\ (X') (Z')^2 &= (\cos \alpha) X - (\sin \alpha) Y) Z^2 \\ (Y')^2 (Z') &= (\sin \alpha) X + (\cos \alpha) Y)^2 Z \\ (Y') (Z')^2 &= (\sin \alpha) X + (\cos \alpha) Y) Z^2 \\ (X') (Y') (Z') &= (\cos \alpha) X - (\sin \alpha) Y) (\sin \alpha) X + (\cos \alpha) Y) Z \end{aligned}$$

Hence,

$$(12) \quad \chi_{\beta}^{C_n^k} = 2 \cos \alpha (4 \cos^2 \alpha + 2 \cos \alpha - 1)$$



Now consider a general rotary reflection,  $S_n^k$ . The only changes from that of the rotation  $C_n^k$  are

$$(13) \quad (z')^3 = -z^3$$

$$(x')^2 (z') = -(\cos \alpha) x - (\sin \alpha) y)^2 z$$

$$(y')^2 (z') = -(\sin \alpha) x + (\cos \alpha) y)^2 z$$

$$(x') (y') (z') = -(\cos \alpha) x - (\sin \alpha) y)(\sin \alpha) x + (\cos \alpha) y)z$$

Hence,

$$(14) \quad \chi_{\beta}^{S_n^k} = 2 \cos \alpha (4 \cos^2 \alpha - 2 \cos \alpha - 1)$$

Thus,

$$(15) \quad \chi_{\beta}^R = 2 \cos \alpha (4 \cos^2 \alpha \pm 2 \cos \alpha - 1)$$

## APPENDIX 4

## EULERIAN ANGLES AND THE AVERAGES OF NEEDED PRODUCTS OF DIRECTION COSINES

The Eulerian angles are defined as the three successive angles of rotation by means of which a given cartesian coordinate system may be transformed to another ( 5, p. 107-109 ).

Here the system as shown in Goldstein's Classical Mechanics will be used. Hence, the Eulerian angles are defined by the following three rotations:

$$(1) \quad \vec{\xi} = D \vec{X} ; \quad \vec{\xi}' = C \vec{\xi} ; \quad \vec{X}' = B \vec{\xi}'$$

where  $\vec{\xi}$ ,  $\vec{X}$ ,  $\vec{\xi}'$ , and  $\vec{X}'$  represent column matrices;  $\vec{X}$  represents the coordinates of the initial cartesian coordinate system and  $\vec{X}'$  represents the coordinates of the final system, D, C, and B are the matrices

$$(2) \quad D = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$C = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{pmatrix}$$

$$B = \begin{pmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The product matrix  $A = BCD$  will furnish the direction cosines which connect the initial and final cartesian coordinate systems.

$$(3) \begin{pmatrix} \cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & -\sin \psi \sin \phi - \cos \theta \sin \phi \cos \psi & \sin \theta \sin \phi \\ -\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & -\sin \psi \sin \phi \cos \theta \cos \phi & \cos \theta \cos \phi \\ \sin \theta \sin \phi & \sin \theta \cos \psi & \cos \theta \end{pmatrix}$$

There are only four distinct types of products of direction cosines which need to be evaluated. These are

$$\left\{ \overline{\Phi_{x1}^4}, \overline{\Phi_{x1}^2 \Phi_{y1}^2}, \overline{\Phi_{x1}^2 \Phi_{y2}^2}, \overline{\Phi_{x1} \Phi_{y1} \Phi_{x2} \Phi_{y2}} \right\}$$

For Eulerian angles the average of a function,  $f(\theta, \phi, \psi)$ , is given by

$$(4) \quad \overline{f(\theta, \phi, \psi)} = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi f(\theta, \phi, \psi) \sin \theta \, d\theta \, d\phi \, d\psi$$

Hence,

$$(5) \quad \overline{\Phi_{x1}^4} = 1/5$$

$$\overline{\Phi_{x1}^2 \Phi_{y1}^2} = 1/15$$

$$\overline{\Phi_{x1}^2 \Phi_{y2}^2} = 2/15$$

$$\overline{\Phi_{x1} \Phi_{y1} \Phi_{x2} \Phi_{y2}} = -1/30$$

## APPENDIX 5

SUMMARY OF THE FORM AND RANGE OF THE VARIOUS  $P_n$ 's OF THE SPECIES  
OF THE POINT GROUPS  $D_{2h}$ ,  $D_{6h}$ , AND  $D_{\infty h}$

$D_{2h}$	$P_n$
$A_u$	6/7
$B_{1u}$	$\frac{2[4\beta_{xyz}^2 + 4\beta_{yyz}^2 + \beta_{zzz}^2 - \beta_{xxz} \beta_{zzz} - \beta_{yyz} \beta_{zzz} - \beta_{xxz} \beta_{yyz}]}{11\beta_{xyz}^2 + 11\beta_{yyz}^2 + 4\beta_{zzz}^2 + \beta_{xxz} \beta_{zzz} + \beta_{yyz} \beta_{zzz} + \beta_{xxz} \beta_{yyz}}$
$B_{2u}$	$\frac{2[4\beta_{xxy}^2 + 4\beta_{yzz}^2 + \beta_{yyy}^2 - \beta_{xxy} \beta_{yyy} - \beta_{yzz} \beta_{yyy} - \beta_{xxy} \beta_{yzz}]}{11\beta_{xxy}^2 + 11\beta_{yzz}^2 + 4\beta_{yyy}^2 + \beta_{xxy} \beta_{yyy} + \beta_{yzz} \beta_{yyy} + \beta_{xxy} \beta_{yzz}}$
$B_{3u}$	$\frac{2[4\beta_{xxy}^2 + 4\beta_{xzz}^2 + \beta_{xxx}^2 - \beta_{xxy} \beta_{xxx} - \beta_{xzz} \beta_{xxx} - \beta_{xxy} \beta_{xzz}]}{11\beta_{xxy}^2 + 11\beta_{xzz}^2 + 4\beta_{xxx}^2 + \beta_{xxy} \beta_{xxx} + \beta_{xzz} \beta_{xxx} + \beta_{xxy} \beta_{xzz}}$

$D_{2h}$	$D$	Range of $P_n$
$A_u$	$\beta_{xyz}$	6/7
$B_{1u}$	$\beta_{zzz}, \beta_{xxz}, \beta_{yyz}$	$4/13 \leq P_n \leq 6/7$
$B_{2u}$	$\beta_{yyy}, \beta_{xxy}, \beta_{yzz}$	$4/13 \leq P_n \leq 6/7$
$B_{3u}$	$\beta_{xxx}, \beta_{xyy}, \beta_{xzz}$	$4/13 \leq P_n \leq 6/7$

$D_{6h}$	$\beta$	$P_n$
$A_{2u}$	$\beta_{zzz},$ $\beta_{xxz} + \beta_{yyz}$	$\frac{2(7\beta_{xxz}^2 + \beta_{zzz}^2 - 2\beta_{xxz}\beta_{zzz})}{23\beta_{xxz}^2 + 4\beta_{zzz}^2 + 2\beta_{xxz}\beta_{zzz}}$
$B_{1u}$	$\beta_{yyz} - 3\beta_{xxy}$	$6/7$
$B_{2u}$	$\beta_{xxx} - 3\beta_{xyy}$	$6/7$
$E_{1u}$	$(\beta_{yzz}, \beta_{xzz}),$ $(\beta_{yyz} + \beta_{xxy}, \beta_{xxx} + \beta_{xyy})$	$\frac{4(5\beta_{xxz}^2 + 18\beta_{xzz}\beta_{xxy} - 3\beta_{xxz}\beta_{xzz})}{50\beta_{xxz}^2 + 99\beta_{xzz}^2 + 12\beta_{xxz}\beta_{xzz}}$
$E_{2u}$	$(\beta_{xyz}, \beta_{xxz} - \beta_{yyz})$	$6/7$

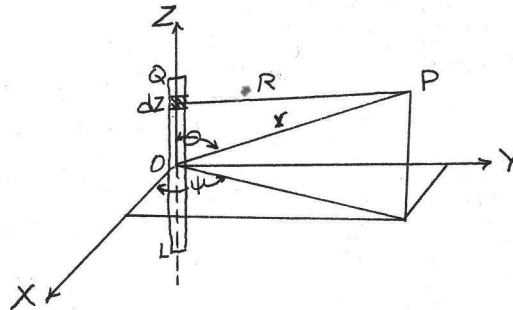
$D_{6h}$	Range of $P_n$
$A_{2u}$	$4/13 \leq P_n \leq 6/7$
$B_{1u}$	$6/7$
$B_{2u}$	$6/7$
$E_{1u}$	$0.363 \leq P_n \leq 0.732$
$E_{2u}$	$6/7$

Dosh	B	P <sub>n</sub>
$\Sigma_u^+ (B_{zzz}, B_{xxz} + B_{yyz})$	$\frac{2(7B_{xxz}^2 + B_{zzz}^2 - 2B_{xxz}B_{zzz})}{23B_{xxz}^2 + 4B_{zzz}^2 + 2B_{xxz}B_{zzz}}$	
$\Pi_u (B_{yyz}, B_{xzz})$ $(B_{yyy} + B_{xxy}, B_{xxx} + B_{xyy})$	$\frac{4(5B_{xxz}^2 + 18B_{xzz}^2 - 3B_{xxz}B_{xzz})}{50B_{xxz}^2 + 99B_{xzz}^2 + 12B_{xxz}B_{xzz}}$	
$\Delta_u (B_{xxx} - B_{yyz}, B_{xyz})$		6/7
$\Gamma_u (B_{xxx} - 3B_{xxy}, B_{yyy} - 3B_{xyy})$		6/7

Dosh	Range of P <sub>n</sub>
$\Sigma_u^+$	$4/13 \leq P_n \leq 6/7$
$\Pi_u$	$0.363 \leq P_n \leq 0.732$
$\Delta_u$	6/7
$\Gamma_u$	6/7

**THE AVERAGE INTENSITY FROM  
A CLASSICAL OSCILLATING DIPOLE**

"Consider a linear current element  $QOL$  of length  $L$  along the  $Z$  axis with its center at the origin." ( 8, p. 416 )



Let the current flowing through the element be given by

$$(1) \quad I = I_0 \sin \omega t$$

The magnetic induction  $\vec{B}$  and the electric field strength  $\vec{E}$  may be written in terms of a vector potential  $\vec{A}$  and a scalar potential  $\phi$ . Thus,

$$(2) \quad \vec{B} = \nabla \times \vec{A} \quad ; \quad \vec{E} + \frac{1}{c} \frac{\partial \vec{A}}{\partial t} = -\nabla \phi$$

A solution of  $\vec{A}$  and  $\phi$  may be given as a retarded potential:

$$(3) \quad \phi_p(t) = \frac{1}{K} \int \frac{1}{r} \rho(t - \frac{r}{v_c}) d\tau \quad ;$$

$$\vec{A}_p(t) = \frac{\mu}{c} \int \frac{1}{r} [\rho \vec{v}(t - \frac{r}{v_c})] d\tau$$

where

$$v_c = \frac{c}{\sqrt{\mu K}}$$

Hence, it is seen that the electric field intensity may be obtained by evaluating  $\phi_p(t)$  and  $A_p(t)$ . For our problem

$$(4) \quad \vec{A} = A_z \vec{z}_1$$

since  $\rho \vec{v}$  is directed along the Z axis where

$$(5) \quad A_z = \frac{I_0}{cS} \int_{-l/2}^{l/2} \frac{\sin w(t-R/c)}{R} S dz$$

and S is the cross sectional area of the conductor.

"R is the distance from P to the element of length dz."

(8, p. 416). The space is taken as free space so that

$\mu = K = 1$  and  $v_c = c$ . The solution of  $A_z$  after integration becomes

$$(6) \quad A_z = \frac{I_0 l}{cR} \sin w(t-z/c)$$

for the assumption that  $r \gg l/2$ . In spherical coordinates

$$(7) \quad \vec{A} = \vec{r}_1 A_z \cos \theta - \vec{\theta}_1 A_z \sin \theta$$

Thus, since  $\vec{H} = \nabla \times \vec{A}$

$$(8) \quad H_r = 0; \quad H_\theta = 0; \quad H_\phi = \frac{I_0 l}{cR} \sin \theta \left[ k \cos(wt - kr) - \frac{1}{R} \sin(wt - kr) \right].$$

The scalar potential is given by the Lorentz relation

$$(9) \quad \frac{\partial \phi}{\partial t} = -c \nabla \cdot \vec{A}$$

The solution of  $\phi$  from the previously obtained value of  $\vec{A}$



gives

$$(10) \quad \phi = \frac{-I_0 l \cos \theta}{wcr^2} \cos(wt - kr) + \frac{I_0 l k \cos \theta}{wcr} \sin(wt - kr)$$

Now the components of the electric field intensity may be solved for. Thus,

$$(11) \quad E_r = \frac{2I_0 l \cos \theta}{wr} \left[ \frac{k}{r} \sin(wt - kr) - \frac{1}{r^2} \cos(wt - kr) \right]$$

$$E_\theta = \frac{I_0 l \sin \theta}{wr} \left[ k^2 \cos(wt - kr) - \frac{k}{r} \sin(wt - kr) - \frac{1}{r^2} \cos(wt - kr) \right]$$

$$E = 0$$

The Poynting vector  $\frac{c}{4\pi} \vec{E} \times \vec{H}$  for the oscillating dipole becomes

$$(12) \quad \frac{c}{4\pi} \vec{E} \times \vec{H} = \frac{\vec{r}_1 I_0^2 \ell^2 k^2}{4\pi c r^2} (\sin^2 \theta) (\cos(wt - kr))^2$$

The time average of the Poynting vector becomes

$$(13) \quad \overline{\frac{c}{4\pi} \vec{E} \times \vec{H}} = \frac{\vec{r}_1 I_0^2 \ell^2 k^2 \sin^2 \theta}{8\pi c r^2}$$

- The total radiation may be obtained by integrating the Poynting vector over a surface of a sphere of radius  $r$ . The element of area is given by  $r^2 \sin \theta d\theta d\phi$ . After performing this integration, the result is

$$(14) \quad \int \left| \frac{c}{4\pi} \vec{E} \times \vec{H} \right| r^2 \sin \theta d\theta d\phi = \frac{16\pi^4 P_0^2 \nu^4}{3c^3}$$

where  $P_0^2 = \frac{I_0^2 \ell^2}{C^4 k^2}$  and  $\nu = \frac{\omega}{2\pi}$

## APPENDIX 7

THE DEPENDENCE OF THE INTENSITY OF A HYPER-RAMAN LINE  
UPON ION CONCENTRATION

In the Debye-Hückel theory the electrostatic potential,  $\phi$ , at a given point in the vicinity of a positive ( or negative ) ion is given by ( 4, p. 956-958 )

$$(1) \quad \phi = \frac{\pm Z_i \epsilon}{D} \frac{e^{-K\pi}}{\pi},$$

+ for a positive ion  
- for a negative ion

where  $\pi$  is the distance from the ion,  $D$  is the dielectric constant,  $\epsilon$  is the charge on one electron,  $Z_i$  is the number of charges on the ion, and  $K$  is given by

$$(2) \quad K^2 = \frac{4\pi\epsilon^2}{DKT} \sum n_i Z_i^2$$

where  $k$  is the Boltzman constant and  $n_i$  is the number of each kind of ion per cc.

The electric field at a distance  $r$  may be obtained by finding  $\frac{\partial \phi}{\partial \pi}$ . Hence,

$$(3) \quad \mathcal{E}_\pi = - \frac{\partial \phi}{\partial \pi} = \pm \frac{Z_i \epsilon e^{-K\pi}}{D \pi^2} (1 + K\pi)$$

However, the electric field at this point due to the ion itself is given by

$$(4) \quad \mathcal{E}'_\pi = \pm \frac{Z_i \epsilon}{D \pi^2}$$

Thus, the electric field on the ion itself due to the surrounding atmosphere is

$$(5) \quad \Delta \mathcal{E}_\lambda = \lim_{\lambda \rightarrow 0} [\mathcal{E}_\lambda - \mathcal{E}_\lambda'] = \lim_{\lambda \rightarrow 0} \left\{ \frac{\pm Z i \mathcal{E}}{D \lambda^2} [e^{-K\lambda} (1 + K\lambda) - 1] \right\}$$

If  $\lambda$  is small then  $e^{-K\lambda}$  and  $e^{K\lambda}$  may be expanded as

$$(6) \quad \begin{aligned} e^{-K\lambda} &= 1 - K\lambda + \frac{K^2 \lambda^2}{2} - \dots \\ e^{K\lambda} &= 1 + K\lambda + \frac{K^2 \lambda^2}{2} + \dots \end{aligned}$$

Using these expansions,

$$(7) \quad \frac{\pm Z i \mathcal{E} e^{-K\lambda}}{D \lambda^2} [1 + K\lambda - e^{K\lambda}] = \frac{\pm Z i \mathcal{E} e^{-K\lambda}}{D \lambda^2} \left( -\frac{K^2 \lambda^2}{2} \right)$$

Thus,  $\Delta \mathcal{E}_\lambda$  may be given by

$$(8) \quad \Delta \mathcal{E}_\lambda = \lim_{\lambda \rightarrow 0} [\mp Z i \mathcal{E} (1 - K\lambda + \dots)]$$

This reduces to

$$(9) \quad \Delta \mathcal{E}_\lambda = \mp \frac{Z i \mathcal{E} K^2}{2 D}$$

Equation (35) of the text gives

$$(10) \quad \overline{\mathcal{M}_F^2} = \frac{4}{3} \overline{\mathcal{E}_X^2} \overline{\Delta \mathcal{E}_\lambda^2} \left( \sum_{F'} \beta_{FXF'} \right)^2$$

and equation (29) of the text gives

$$(11) \quad I = \frac{2 \pi^3 \nu^4}{c^3} (\mathcal{M}_{OY}^2 + \mathcal{M}_{OZ}^2)$$

This means that the intensity in the hyper-Raman effect is proportional to  $(\Delta \mathcal{E}_\lambda)^2$  for a constant  $\mathcal{E}_F^\circ$ .

$$\begin{aligned}
 (12) \quad (\Delta \mathcal{E}_\lambda)^2 &= \frac{Z_i^2 \epsilon^2 K^4}{4 D^2} \\
 &= \frac{4 \pi^2 \epsilon^4 Z_i^2}{D^4 k^2 \tau^2} \left( \sum_i n_i^2 Z_i^4 + 2 \sum_{i \neq j} n_i n_j Z_i^2 Z_j^2 \right)
 \end{aligned}$$

The above argument ignores the complication that

$\Delta \mathcal{E}_x = -\frac{\partial \phi}{\partial x}$ , in contrast to  $\Delta \mathcal{E}_\lambda = -\frac{\partial \phi}{\partial \lambda}$ , is apparently indeterminate as  $\lambda \rightarrow 0$ . One resolution of this difficulty may involve the assumption of finite radius for the ions.