

Raman Spectroscopy

1.0 General Considerations

Raman spectroscopy is a light scattering experiment. The Raman effect depends on a change in polarizability of the molecule as radiation interacts with the molecule. The result is an inelastic light scattering process. This means that there is an exchange of energy between the light and the vibrations of the molecule. The frequency of the incident light is shifted and the molecule is left in an altered vibrational state. This is shown in the Figure below. The incident photon in this experiment is the $v = 0$ state and the scattering process leaves the molecule in the $v = 1$ state. The process shown in the Figure is a resonant Raman process since the incident light is in resonance with an absorptive transition. In this case the absorptive transition is Franck-Condon active. However, this FC activity is not required for a Raman process to be observed.

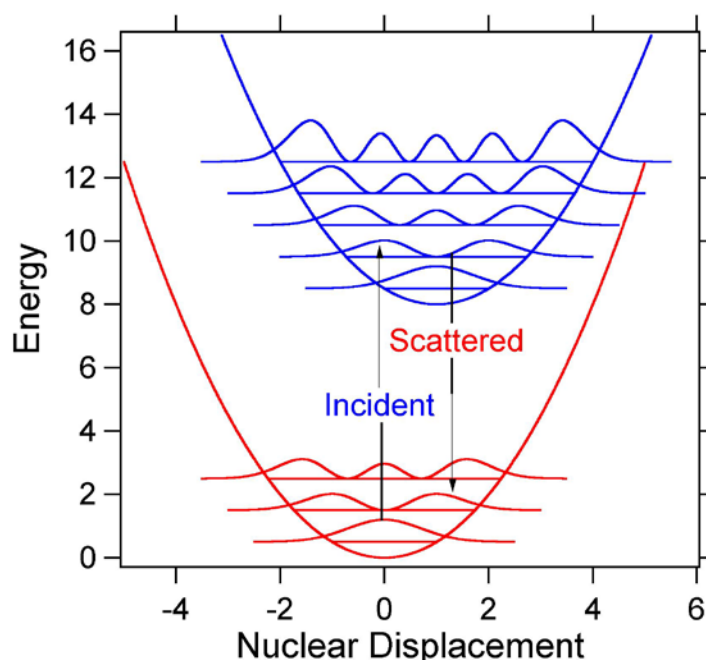
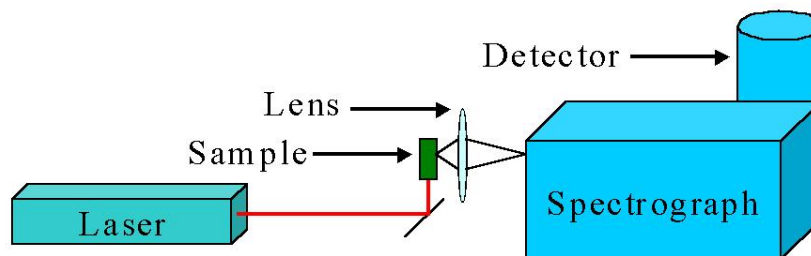


Figure 1. Illustration of the Raman effect.

In a typical Raman experiment polarized light impinges on the sample. The scattered light is detected using a spectrograph and an array detector to obtain a spectral region that will have peaks due to scattered intensity. The wavenumber shift of the peaks relative to the incident laser corresponds to the wavenumber of Raman active vibrational modes of the molecule. Figure 1 shows this effect for a specific resonant excited state excitation. If the laser wavenumber is not in resonance with an absorptive transition we can refer to the process as non-resonant Raman scattering. The further from resonance one tunes the laser, the lower is the Raman scattered intensity. Some books refer to “pre-resonant” Raman scattering when the laser frequency is near resonance. As will be shown below, one can always refer to non-resonant scattering as off-resonant (i.e. detuned from resonance).

2.0 Experimental configuration

Experimental Apparatus



Inelastic light scattering produces a frequency shift. There is exchange of energy between the vibrations of the molecule and the incident photon.

Figure 2. Raman scattering apparatus.

The scattered light can have two polarization components, parallel or perpendicular to the incident polarization. These polarizations are detected using an analyzing polarizer in front of the entrance slit of the spectrograph. The depolarization ratio is an important experimental observable and can give information that leads to vibrational mode assignment. In resonance Raman the intensity of the Raman scattered signal depends on the displacement of the potential energy surface of the excited state and on the excited state dynamics. This dependence is more complicated than the Franck-Condon factors in absorption spectroscopy.

2.1 The definition of polarization

For Z-polarized incident radiation we can detect scattered light using a 90 degree geometry shown below. The incident light propagates along the X-direction and the scattered light along the Y-direction. The uppercase letters here refer to the laboratory coordinate system.

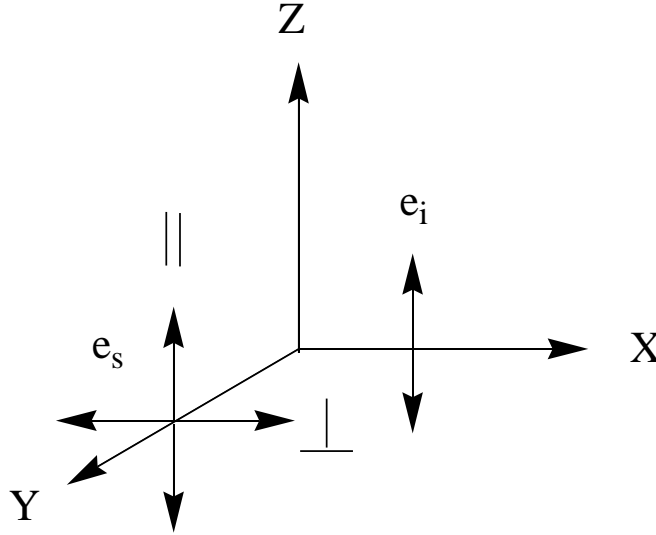


Figure 3. Definition of Raman polarization.

A polarization analyzer between the sample and the detector can be used to distinguish the polarization of scattered light. If the polarization in the scattered light is the same as the incident we refer to this as $I_{||}$, I_{ZZ} or I_{pol} . If the polarization in the scattered light is perpendicular to the incident we refer to this as I_{\perp} , I_{XZ} or I_{dep} . The depolarization ratio ρ is $\rho = I_{dep}/I_{pol}$.

2.2 Collection of the light

Although we discuss the light scattered along Y it must be understood that light is in fact scattered into all directions. The solid angle of a sphere is 4π steradians and the solid angle collected is $d\Omega$ where $d\Omega < 4\pi$. The f-number of a lens is the ratio of the diameter, D of the lens divided by its focal length, F . The two parameters needed to calculate the f-number are shown in Figure 4.

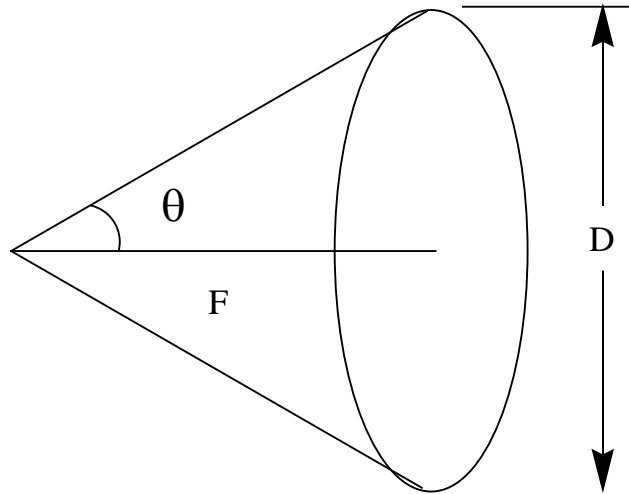


Figure 4. Illustration of collection optics for Raman scattered light.

The solid angle for collection can be calculated by integration to angle θ , which is determined by the ratio of the inverse tangent of the radius of the lens to the focal length.

$$\theta = \arctan\left(\frac{\text{Radius}}{\text{Focal length}}\right) \quad (2.1)$$

Once this angle shown in Figure 4 has been calculated, the fraction of the light collected (relative to 4π steradians) is given by,

$$\frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\theta \sin\theta' d\theta' \quad (2.2)$$

For example, if the f-number of a collection lens is 1, as shown in Figure 4, $D = F$ and we have $\theta = \arctan(1/2) = 26.56^\circ = 0.147\pi$ radians. The solid angle here can be calculated by integrating the differential volume element $d\Omega = d\phi \sin\theta d\theta$ over the limits 0 to 2π and 0 to 0.147π .

$$\frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{0.147\pi} \sin\theta d\theta = (2\pi)[-cos\theta]_0^{0.147\pi} \approx 0.1 \quad (2.3)$$

When we evaluate the integral over the limits shown we find that the second term is approximately 0.1. So the solid angle defined by f/1 collection optics is 0.4π steradians. This arrangement leads to collection of about 10% of the total light scattered from the sample.

3.0 Definition of the differential cross section

The part of the cross-section $d\sigma$ that contributes to the detected scattered intensity is the ratio of the power at the detector dP to the incident intensity I_0 . From $dP = I_0 d\sigma$ we obtain

$$d\sigma = \frac{dP}{I_0} \quad (3.1)$$

The differential power dP is proportional to the solid angle $d\Omega$ subtended by the detector. The scattered irradiance is the power per steradian at the detector such that $dP = I_s d\Omega$. Note the difference between irradiance and intensity. Incident light $dP = I_0 d\sigma$ where I_0 is in units of W/cm^2 . Scattered light $dP = I_s d\Omega$ where I_s is in units of W/sr . Thus, the differential cross section is

$$\frac{d\sigma}{d\Omega} = \frac{I_s}{I_0} \quad (3.2)$$

which has units of cm^2/sr . The Raman cross section is related to square of the projection of the polarizability tensor onto the incident e_i and scattered e_s directions in the laboratory frame.

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{16\pi^4 \nu_s^3 \nu_i}{c^4} (\hat{e}_s \cdot \alpha_{si} \cdot \hat{e}_i)^2 \quad (3.3)$$

Or in terms of the angular frequency

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{\omega_s^3 \omega_i}{c^4} (\hat{e}_s \cdot \alpha_{si} \cdot \hat{e}_i)^2 \quad (3.4)$$

Based on this definition we can determine the total Raman scattering cross section σ_R by

$$\sigma_R = \int \left(\frac{d\sigma}{d\Omega}\right) d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \left(\frac{d\sigma}{d\Omega}\right) \sin\theta d\theta \quad (3.5)$$

4.0 Symmetry and Raman activity

The transition polarizability is a tensor. The transition polarizability tensor can be written as,

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{yx} & \alpha_{zx} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{zy} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix} \quad (4.1)$$

In form this has the appearance of the ground state polarizability tensor. As is evident in 3.34, the only difference between transition polarizability and ground state polarizability is the final state $|f\rangle$, which is the same as the initial state in the ground state polarizability and is different by one or more vibrational quanta in the transition polarizability. Thus, the elements of the transition polarizability tensor can be symmetry, α_{xx} , α_{yy} , or α_{zz} or non-totally symmetric, α_{xy} , α_{xz} , or α_{yz} .

Normal modes of vibration can be analyzed in terms of symmetry in order to assign Raman spectra. Franck-Condon active modes are totally symmetric. These modes can be Raman active since vibration along the normal mode coordinates gives rise to a transition polarizability as required by the Kramers-Heisenberg-Dirac model described in Chapter 12. In molecules of high symmetry, the totally symmetric modes can be identified in the character table as those modes that contain x^2 , y^2 and z^2 . Depending on the symmetry of the molecule, the total symmetric mode may contain, $x^2 + y^2 + z^2$ (O_h and T_d), $x^2 + y^2$ and z^2 (D_{4h}) or x^2 , y^2 and z^2 (lower symmetry point groups). The relationship between x^2 , y^2 and z^2 ultimately determines the depolarization discussed in Section 2.1 (see also 4). Examination of the character tables shows that infrared and Raman active modes are mutually exclusive in molecules with a center of symmetry (i.e. molecules that contain an inversion center, i). In molecules of lower symmetry, that do not contain the symmetry operation, i , vibrational modes can be both infrared and Raman active.

Non-totally symmetric vibrational modes can be Raman active provided that they contribute to changes in the polarizability tensor. In the character tables, these are the modes that transform as xz , xy and yz .

5.0 The depolarization ratio

The depolarization ratio is defined experimentally as the ratio of the perpendicular to parallel scattered radiation. Thus,

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \quad (5.1)$$

in terms of intensity or

$$\rho = \frac{\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\perp}}{\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\parallel}} \quad (5.2)$$

in terms of the differential scattering cross sections. The depolarization ratio can be used to correct the Raman scattering cross section for orientation. It can be shown that

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta,\phi} = \left\{1 - \left(\frac{1-\rho}{1+\rho}\right)\cos^2\theta\right\} \left(\frac{d\sigma}{d\Omega}\right)_{90^\circ} \quad (5.3)$$

and the Raman scattering cross section is

$$\sigma_R = \frac{8\pi}{3} \left(\frac{1+2\rho}{1+\rho}\right) \left(\frac{d\sigma}{d\Omega}\right)_{90^\circ} \quad (5.4)$$

5.1 Orientation averaging of the depolarization ratio

Thus far we have considered the elements of the transition polarizability tensor in the molecular frame x, y, and z. In a Raman experiment we measure the scattering in the lab frame X, Y, and Z. The scattering signal is the average of all molecular orientations in the lab frame. Traditional methods of carrying out the orientation averaging involve the use of direction cosines.

For a rank 2 tensor (e.g. transition polarizability) we can write down three rotational invariants, Σ^J , that are linear combinations of the α_M^J that are independent of reference frame. These are

$$\Sigma^J = \sum_{M=-J}^J (\alpha_M^J)^2 \quad (5.3)$$

where $J = 0, 1, 2, \dots$ and $M = 0, \pm 1, \dots, \pm J$. Each Σ^J is called an invariant because it is independent of orientation. The length of a vector is independent of its orientation. That is the same thing as saying that for the vector μ , the combination $\mu_x^2 + \mu_y^2 + \mu_z^2$ is a rotational invariant. A second rank tensor has three invariants,

$$\Sigma^0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2$$

$$\begin{aligned}
\Sigma^1 &= \frac{1}{2} \left((\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{xz} - \alpha_{zx})^2 + (\alpha_{zy} - \alpha_{yz})^2 \right) \\
\Sigma^2 &= \frac{1}{2} \left((\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{xz} + \alpha_{zx})^2 + (\alpha_{zy} + \alpha_{yz})^2 \right) \\
&\quad + \frac{1}{3} \left((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \right)
\end{aligned} \tag{5.4}$$

The invariants are

Σ^0 isotropic part

Σ^1 anti-symmetric anisotropy

Σ^2 symmetric anisotropy

The isotropic part of the polarizability is proportional to the square of the trace of the polarizability tensor $\Sigma^0 = (\text{Tr}\alpha)^2/3$. The trace of tensor α (written as $\text{Tr}\alpha$) is the sum of diagonal elements of the tensor. Therefore, Σ^2 represents the deviation of the polarizability from spherical symmetry. The lab frame components $|\alpha_{zz}|^2$ and $|\alpha_{xz}|^2$ can be written as linear combinations of the invariants.

$$\begin{aligned}
(\alpha_{zz})^2 &= \frac{1}{3} \Sigma^0 + \frac{2}{15} \Sigma^2 \\
(\alpha_{xz})^2 &= \frac{1}{6} \Sigma^1 + \frac{1}{10} \Sigma^2
\end{aligned} \tag{5.5}$$

The depolarization ratio is

$$\rho = \frac{(\alpha_{xz})^2}{(\alpha_{zz})^2} \tag{5.6}$$

assuming the scattering geometry shown above. Using the invariants the depolarization ratio is

$$\rho = \frac{5\Sigma^1 + 3\Sigma^2}{10\Sigma^0 + 4\Sigma^2} \tag{5.7}$$

6.0 The depolarization ratio in non-resonant Raman scattering

The form of α in the molecular frame depends on the symmetry of the vibration. For non-resonant Raman the polarizability tensor is symmetric and therefore the anti-symmetric anisotropy Σ^1 is zero. Inspection of the anti-symmetric anisotropy shows that it is zero when $\alpha_{\rho\sigma} = \alpha_{\sigma\rho}$. Σ^2 depends on non-zero off diagonal terms and on differences in the diagonal terms. It is not necessarily zero in non-resonant Raman scattering.

6.1 Totally symmetric modes

The polarizability tensor for a totally symmetric vibrational mode preserves this symmetry. These are the modes that we think of as Franck-Condon active modes in absorption spectroscopy. The Cartesian Raman tensor for any totally symmetric mode is of the form:

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \quad (6.1)$$

For molecules with spherical symmetry $a = b = c$.

Symmetric top molecules have two equal components, so $a = b \neq c$.

Asymmetric top molecules have $a \neq b \neq c$.

We can show this in the following simplified model, which we will assume that the small tensor elements are equal to zero. We can represent the three possible Raman tensors in this approximation as follows.

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{pmatrix}$$

Spherically symmetric

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Symmetric top

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Asymmetric top

For example, the Raman polarizability tensor for any totally symmetric mode of a totally symmetric molecule (CCl_4 or SF_6) has three equivalent diagonal components and so

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \quad (6.2)$$

Thus, $\Sigma^1 = \Sigma^2 = 0$ and $\rho = 0$. It is often convenient to write out the totally and non-totally symmetric part of the polarizability,

$$\alpha = \bar{\alpha} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \beta \quad (6.3)$$

where we define the average polarizability:

$$\bar{\alpha} = \frac{\text{Tr} \alpha}{3} = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3} \quad (6.4)$$

and the tensor β is the anisotropy of the polarizability:

$$\beta = \begin{pmatrix} (\alpha_{xx} - \bar{\alpha}) & \alpha_{yx} & \alpha_{zx} \\ \alpha_{xy} & (\alpha_{yy} - \bar{\alpha}) & \alpha_{zy} \\ \alpha_{xz} & \alpha_{yz} & (\alpha_{zz} - \bar{\alpha}) \end{pmatrix} \quad (6.5)$$

This equation assumes that the Raman tensor is symmetric (and is only valid for non-resonant Raman scattering). Non-symmetric molecules β can be non-zero even for totally symmetric modes.

On the other hand if $a = b \neq c$, which corresponds to planar molecules such as benzene and metalloporphyrins, which usually means $\alpha_{xx} + \alpha_{yy} = \alpha$ and $\alpha_{zz} = 0$. We have

$$\begin{aligned}\Sigma^0 &= \frac{1}{3}(\alpha_{xx} + \alpha_{yy})^2 = \frac{4\alpha^2}{3} \\ \Sigma^1 &= 0 \\ \Sigma^2 &= \frac{1}{3}((\alpha_{yy})^2 + (\alpha_{xx})^2) = \frac{2\alpha^2}{3}\end{aligned}$$

The result is

$$\rho = \frac{3\Sigma^2}{10\Sigma^0 + 4\Sigma^2} = \frac{3\left(\frac{2\alpha^2}{3}\right)}{10\left(\frac{4\alpha^2}{3}\right) + 4\left(\frac{2\alpha^2}{3}\right)} = \frac{1}{8} \quad (6.6)$$

Finally, for asymmetric top molecules we have $a \neq b \neq c$, which be approximated in the simplest case as means $\alpha_{xx} = \alpha$ and $\alpha_{zz} = \alpha_{yy} = 0$. We have

$$\begin{aligned}\Sigma^0 &= \frac{1}{3}(\alpha_{xx})^2 = \frac{\alpha^2}{3} \\ \Sigma^1 &= 0 \\ \Sigma^2 &= \frac{1}{3}((\alpha_{xx})^2 + (\alpha_{xx})^2) = \frac{2\alpha^2}{3}\end{aligned}$$

The result is

$$\rho = \frac{3\Sigma^2}{10\Sigma^0 + 4\Sigma^2} = \frac{3\left(\frac{2\alpha^2}{3}\right)}{10\left(\frac{\alpha^2}{3}\right) + 4\left(\frac{2\alpha^2}{3}\right)} = \frac{1}{3} \quad (6.7)$$

Thus, we see that the depolarization ratio for totally symmetric modes varies from 0 to 1/3 depending on the relative magnitude of the diagonal tensor elements, α_{xx} , α_{yy} , and α_{zz} .

6.2 Non-totally symmetric modes

Non-totally symmetric modes are the modes that responsible for vibronic coupling or Herzberg-Teller coupling in absorption spectroscopy. For these modes $\text{Tr}\alpha$ vanishes and only β contributes to the non-resonant Raman scattering cross section. Since $\text{Tr}\alpha$ vanishes for non-totally symmetric modes we also have $\Sigma^0 = 0$. For non-resonant Raman, we assume that $\alpha_{\sigma\rho} = \alpha_{\rho\sigma}$, so that we can write,

$$\Sigma^0 = 0$$

$$\Sigma^1 = 0$$

$$\Sigma^2 = 2 \left((\alpha_{xy})^2 + (\alpha_{xz})^2 + (\alpha_{yz})^2 \right)$$

From which we see that only Σ^2 is non-zero. The depolarization ratio then becomes,

$$\rho = \frac{5\Sigma^1 + 3\Sigma^2}{10\Sigma^0 + 4\Sigma^2} = \frac{3\Sigma^2}{4\Sigma^2} = \frac{3}{4} \quad (6.8)$$

Thus, we see that the depolarization ratio is equal to $\frac{3}{4}$ regardless of the precise symmetry of the non-totally symmetric modes. In non-resonant Raman scattering ρ is never larger than $\frac{3}{4}$.

7.0 Raman scattering results from a transition polarizability

In the molecular frame of reference the transition polarizability can be expressed using the Kramers-Heisenberg-Dirac (KHD) expression

$$(\alpha_{\rho\sigma})_{if} = \frac{1}{\hbar} \left\{ \sum_n \left(\frac{\langle i|\mu_\rho|n\rangle\langle n|\mu_\sigma|f\rangle}{\omega + \omega_{nf} + i\Gamma_n} - \frac{\langle i|\mu_\sigma|n\rangle\langle n|\mu_\rho|f\rangle}{\omega - \omega_{ni} - i\Gamma_n} \right) \right\} \equiv \langle i|\alpha_{\rho\sigma}|f\rangle \quad (7.1)$$

The transition polarizability $\alpha_{\rho\sigma}$ is expressed as a function of the incident radiation frequency ω_0 . The transition polarizability is a Cartesian tensor where ρ and σ are direction x,y,z in the molecular frame. The first term is an anti-resonant term and the second term is a resonant term. Both terms are important for off-resonance or non-resonant Raman scattering. Only the second term is important for resonant Raman scattering. In the resonant term the energy denominator would approach infinity were it not for the damping term $i\Gamma_n$. Γ_n arises due to the finite lifetime of the intermediate state. The shorter the lifetime in the intermediate state, the smaller the Raman cross section. This is particularly important for resonant Raman scattering. The states involved can be defined in terms of all $3N - 6$ vibrational modes by writing:

$$\begin{aligned} |i\rangle &= |\phi_g(q; Q) \rangle |\chi_{gv}(Q_1)\chi_{gv}(Q_2) \dots \chi_{gv}(Q_{3N-6}) \rangle \\ |n\rangle &= |\phi_e(q; Q) \rangle |\chi_{ev_1'}(Q_1)\chi_{ev_2'}(Q_2) \dots \chi_{ev_{3N-6}'}(Q_{3N-6}) \rangle \\ |f\rangle &= |\phi_g(q; Q) \rangle |\chi_{gv''}(Q_1)\chi_{gv''}(Q_2) \dots \chi_{gv''}(Q_{3N-6}) \rangle \end{aligned} \quad (7.2)$$

Notice that only one of the modes actually changes its quantum number in the Raman process (the first one labeled by Q_1). The remaining modes end up in the same state that they started in. The potential energy surface is a $3N - 6$ dimensional surface and the Raman process is occurring along only one dimension. This can be represented as follows:

$v \rightarrow v''$

$$\{v_1, v_2, \dots, v_{3N-6}\} \rightarrow \{v''_1, v_2, \dots, v_{3N-6}\}$$

The quantum numbers v and v'' represent the two states shown.

As shown in Eqn. 7.1, polarizability arises due to state mixing. The KHD expression shows mixing of the ground state with one or more higher electronic states. In other words the states $|i\rangle$ and $|f\rangle$ refer to two different vibrational states in the ground electronic state. The states $|n\rangle$ refer to a set of vibrational states in one or more electronic state. When we consider resonant Raman scattering we will consider resonance with a single electronic state. For non-resonant Raman scattering the intermediate must be a superposition. In practice, we cannot calculate the magnitude of the non-resonant Raman cross section due to the complex nature of a superposition state. We can, however, determine the polarization, symmetry properties, and selection rules for non-resonant Raman scattering.

8.0 Introduction of the vibronic coupling operator: approach to resonance

If the frequency of exciting radiation is far removed from the resonant frequency, i.e. $\omega_0 \ll \omega_{ge}$ then vibrational energy terms in the energy denominator can be ignored compared to $\omega_0 - \omega_{ge}$ and $\omega_0 + \omega_{ge}$. The transition polarizability becomes

$$(\alpha_{\rho\sigma})_{0v''} = \frac{1}{\hbar} \left\{ \sum_{ev} (\mu_{ge}^0)_\rho (\mu_{ge}^0)_\sigma \left(\frac{\langle 0|v'\rangle \langle v'|v''\rangle}{\omega_0 + \omega_{eg}} - \frac{\langle 0|v'\rangle \langle v'|v''\rangle}{\omega_0 - \omega_{eg}} \right) \right\} \quad (8.1)$$

The quantities $\langle 0|v\rangle$ and $\langle v|v''\rangle$ are vibrational overlaps. The square of a vibrational overlap is a Franck-Condon factor so the Raman excitation profile bears a defined relationship to the absorption spectrum. Here the v quantum numbers refer to the intermediate state vibrational energy levels. Since excitation is off-resonance there are in principle many vibrational and electronic states that can contribute. The above approach is a sum-over-states approach. We can use the closure relation $\sum_v |v\rangle \langle v| = 1$ to simplify the expressions.

$$\begin{aligned} (\alpha_{\rho\sigma})_{0v''} &= \frac{2}{\hbar} \left\{ \sum_{ev} (\mu_{ge}^0)_\rho (\mu_{ge}^0)_\sigma \left(\frac{\delta_{0v''}}{\omega_{eg} - \omega_0} \right) \right\} \\ (\alpha_{\rho\sigma})_{00} &= \frac{2}{\hbar} \left\{ \sum_{ev} (\mu_{ge}^0)_\rho (\mu_{ge}^0)_\sigma \left(\frac{1}{\omega_{eg} - \omega_0} \right) \right\} \end{aligned} \quad (8.2)$$

The bottom equation describes Rayleigh scattering. The initial and final vibrational states are the same in Rayleigh scattering. There are no selection rules. All molecules are active Rayleigh scatterers. The Kroenecker delta in the top equation is $\delta_{0v''} = \langle 0|v''\rangle$ where $\delta_{0v''} = 0$ if $0 \neq v''$. Thus the first term and the second term are the same here. This means that non-resonant Raman scattering will not occur within the Condon approximation. This observation, first made by Albrecht, represents a paradox for Raman scattering. In reality the restriction that Raman scattering can only be observed for a breakdown of the Condon approximation is a result of the simplicity of the model. We can call this breakdown, Albrecht's paradox. Obviously, totally symmetric modes are observed in non-resonant Raman spectra of molecules.

In order to explain non-resonant Raman scattering within the formalism of Eqn. 8.2, we must consider the coordinate dependence to the transition dipole moment, e.g. expand the transition dipole moment in a power series

$$\mu_{ge}(Q) = \mu_{ge}^0 + \sum_{i=1}^{3N-6} \left(\frac{\partial \mu_{ge}}{\partial Q} \right)_0 Q_i \quad (8.3)$$

and keep only the first term we find that the coordinate dependence of the transition moment can play a role. The reason for this is that even though $\langle 0|v''\rangle = 0$ for $0 \neq v''$, in general $\langle 0|Q|v''\rangle$ does not need to be zero. Thus, for Raman scattering to be allowed we use the linear term above and make the substitution

$$\mu_{ge}^0 \langle 0|v''\rangle \rightarrow \left(\frac{\partial \mu_{ge}}{\partial Q} \right)_0 \langle 0|Q|v''\rangle \quad (8.4)$$

The transition polarizability is

$$(\alpha_{\rho\sigma})_{0v''} = \frac{1}{\hbar} \left\{ \sum_e \left(\frac{(\mu_{ge}^0)_\rho \left(\frac{\partial \mu_{ge}}{\partial Q} \right)_\sigma \langle 0|Q|v''\rangle}{\omega_0 + \omega_{eg}} - \frac{(\mu_{ge}^0)_\sigma \left(\frac{\partial \mu_{ge}}{\partial Q} \right)_\rho \langle 0|Q|v''\rangle}{\omega_0 - \omega_{eg}} \right) \right\} \quad (8.5)$$

The selection rules arise from the requirement that $\langle 0|Q|v''\rangle$ does not vanish. We can define a polarizability derivative such that the transition polarizability is

$$(\alpha_{\rho\sigma})_{vv''} = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_i} \right) \langle v|Q_i|v''\rangle \quad (8.6)$$

where $\alpha'_{\rho\sigma}$ is the polarizability derivative also called the derived polarizability. The terms $\alpha'_{\rho\sigma}$ and $(\partial \alpha_{\rho\sigma} / \partial Q_i)$ are equivalent. For a harmonic oscillator $\langle v|Q|v''\rangle$ vanishes except when $v'' = v \pm 1$. Thus, the selection rule of $\Delta v = \pm 1$ applies to non-resonant Raman scattering as well as infrared spectroscopy (within the harmonic approximation).

9.0 Albrecht theory of resonant Raman Scattering

If the incident frequency ω_0 is in resonance with an electronic transition of the molecule the anti-resonant term (with $\omega_0 + \omega_{eg}$ in the denominator) can be neglected and only the resonant term contributes to Raman scattering. If we keep terms up to linear in Q , we may express the transition polarizability as a sum of two terms

$$(\alpha_{\rho\sigma})_{vv''} = A_{vv''} + B_{vv''} \quad (9.1)$$

These terms are called the Albrecht A and B terms. The first of these terms arises from the Condon approximation. The Condon approximation states that there is no nuclear coordinate

dependence to the wave function so that all terms in the expansion vanish except the μ_{ge}^0 term that does not depend on Q_i .

$$A_{v',v''} = \frac{1}{\hbar} \left\{ \sum_{ev} (\mu_{ge}^0)_\rho (\mu_{ge}^0)_\sigma \left(\frac{\langle 0|v'\rangle \langle v'|v''\rangle}{\omega_{ev',gv} - \omega_0 - i\Gamma_{ev}} \right) \right\} \quad (9.2)$$

In this expression the energy of an incident photon is equal to that of the energy difference between a ground state vibrational energy level gv' and an excited state level ev . The term $i\Gamma_{ev}$ is a phenomenological damping term. This term arises from dephasing and lifetime broadening in the excited state levels. One can envision the contribution of Γ as an energy width to each of the excited state energy levels.

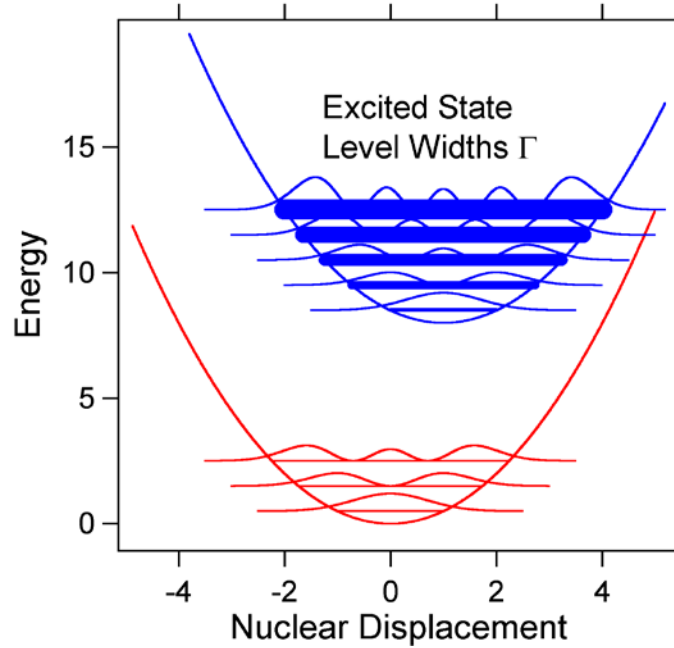


Figure 7 Depiction of the dependence of dephasing rate on the excited state quantum number.

The thickness of the blue excited state levels is dependent upon excited state lifetimes and dephasing processes. The various levels have different energy widths to illustrate the fact that the dephasing rate can depend on vibrational state. Without the dephasing rate Γ_{ev} the resonance term would approach infinity when $\omega_{ev,gv} = \omega_0$. The larger the dephasing terms $i\Gamma_{ev}$ the smaller the overall resonant Raman cross section. The terms $\langle v'|v\rangle$ and $\langle v|v''\rangle$ are Franck-Condon factors. In fact, these are the same Franck-Condon factors found in absorption spectroscopy. Just as in absorption spectroscopy there must be displacement along a normal mode coordinate upon electronic excitation in order for it to be Franck-Condon active.

The Albrecht B-term describes resonance Raman scattering of a vibronically active vibrational mode. In electronic absorption a vibronic mode is one which causes a transition to be

allowed by distortion of the molecule to lower the symmetry. In resonant Raman scattering a vibronic mode has a resonance enhancement pattern that is different from a Franck-Condon active mode for the same reason. The Franck-Condon active modes are the totally symmetric modes of the molecule and the vibronic modes are the non-totally symmetry modes of the molecule. The B term is more complicated than the A term. In the A term the transition moment for the ground to excited state electronic transition μ_{ge} is contributes and in B-term scattering it is the terms in $(\partial\mu_{ge}/\partial Q_i)_0 Q_i$ that contribute. In Albrecht theory the B-term is given by,

$$B_{v',v''} = \frac{1}{\hbar} \left\{ \sum_e \left(\frac{(\mu_{ge}^0)_\sigma \left(\frac{\partial \mu_{ge}}{\partial Q} \right)_\rho \langle 0|Q|v'' \rangle}{\omega_{ev',gv} - \omega_0 - i\Gamma_{ev}} \right) \right\} \quad (9.4)$$

10.0 Polarization in resonant Raman scattering

10.1 Totally symmetric modes

The polarizability depends on the symmetry of the electronic transition. For example, in a z-polarized transition a totally symmetric A-term mode has only one non-zero tensor component, α_{zz} . From this consideration we can readily calculate that $\rho = 1/3$, as shown above for asymmetric top molecules. A doubly degenerate resonant electronic state (i.e. a state that x,y polarized such as in porphyrins) results in two equal diagonal tensor components, e.g. $\alpha_{xx} = \alpha_{yy}$, which leads to $\rho = 1/8$. If the electronic transition is triply degenerate (i.e. if the molecule is spherically symmetric such as SF_6) then $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$. In this case $\rho = 1/\infty = 0$. These examples show that the limiting cases for the depolarization ratio of totally symmetric modes are $0 \leq \rho \leq 1/3$.

10.2 Vibronic coupling and anomalous polarization in non-totally symmetric modes

Vibronic coupling of two states can lead to Raman tensors in which $\alpha_{\sigma\rho} \neq 0$, but $\alpha_{\sigma\sigma} = 0$. Such vibrational modes are non-totally symmetric. The origin of coupling via non-totally symmetric modes can be found in the Herzberg-Teller coupling between two states. As a molecule vibrates along a non-totally symmetric mode coupling is induced with other electronic states. This coupling results in enhancement at molecule geometries that are distorted from the equilibrium geometry. This is precisely what is described in the B-term of Albrecht theory. B term enhancement can also lead to anomalous polarization in which $\rho > 3/4$. Vibronic coupling of two states can lead to Raman tensors in which $\alpha_{\sigma\rho} \neq \alpha_{\rho\sigma}$. A nonzero value of Σ^1 can lead to a depolarization ratio of greater than 3/4.

Anomalous polarization can be explained as follows using the Herzberg-Teller approach. Suppose that the electronic transition $g \rightarrow e$ is x polarized and the transition $g \rightarrow r$ is y polarized leading to a Raman activity of the fundamental transition of a non-totally symmetric vibration of symmetry $\Gamma_v = \Gamma_x \Gamma_y$. The transition is resonant with $|e0\rangle$ and $|e1\rangle$ intermediate states. Herzberg-Teller coupling requires that vibronic coupling to state mix $|e0\rangle$ with $|r1\rangle$ and $|e1\rangle$ with $|r0\rangle$. The vibronic intermediate states are:

$$|e0\rangle' = |e0\rangle + \frac{\langle r1 | \left(\frac{\partial H}{\partial Q} \right) Q | e0 \rangle}{\hbar\omega_{r1} - \hbar\omega_{e0}} |r1\rangle$$

$$|e1\rangle' = |e1\rangle + \frac{\langle r0 | \left(\frac{\partial H}{\partial Q} \right) Q | e1 \rangle}{\hbar\omega_{r0} - \hbar\omega_{e1}} |r0\rangle \quad (10.1)$$

Using the above states to write the Albrecht B-term leads to the following xy and yx Raman tensor components:

$$\begin{aligned} (\alpha_{xy})_{01} &= \frac{1}{\hbar^2} \left\{ \frac{\langle r0 | \left(\frac{\partial \mu_{ge}}{\partial Q} \right) | e1 \rangle (\mu_{ge}^0)_x (\mu_{gr}^0)_y \langle 0|Q|1 \rangle}{\omega_{r0} - \omega_{e1} \quad \omega_{e1,g0} - \omega_0 - i\Gamma_e} \right\} \\ (\alpha_{yx})_{01} &= \frac{1}{\hbar^2} \left\{ \frac{\langle r1 | \left(\frac{\partial \mu_{ge}}{\partial Q} \right) | e0 \rangle (\mu_{ge}^0)_x (\mu_{gr}^0)_y \langle 1|Q|0 \rangle}{\omega_{r1} - \omega_{e0} \quad \omega_{e0,g0} - \omega_0 - i\Gamma_e} \right\} \end{aligned} \quad (10.2)$$

The α_{xy} component dominates when the incident frequency is resonant with the $g0 \rightarrow e1$ transition, while the α_{yx} component is resonant with the $g0 \rightarrow e0$ transition. If the energy levels of the states e and r are well separated then the energy denominators are nearly equal:

$$\omega_{r0} - \omega_{e1} \approx \omega_{r1} - \omega_{e0} \quad (10.3)$$

If ω_0 is far from resonance then $\alpha_{xy} \approx \alpha_{yx}$. This is a non-resonant condition where the Raman tensor is symmetric, $\Sigma^1 = 0$, and $\rho = 3/4$. On the other hand, close to resonance with the 0-1 transition, we have $\alpha_{xy} \gg \alpha_{yx}$ and for ω_0 close to the frequency of the 0-0 transition, $\alpha_{yx} \gg \alpha_{xy}$. When the exciting radiation is midway between the 0-0 and 0-1 resonances, the relationship $\alpha_{xy} \approx -\alpha_{yx}$ results. This leads to $\Sigma^1 \neq 0$, while $\Sigma^0 = \Sigma^2 = 0$. At this frequency the depolarization ratio approaches infinity. Anomalous polarization was first observed in the vibronic bands of hemes.

Appendix. The integration of the rotational invariants in the molecular frame

Here we give an intuitive argument to explain the contributions of the various invariants to depolarization ratio. The crucial property of an invariant is that the excitation is independent of the orientation. Therefore, to determine the contribution to the polarization we only need to consider the interaction of the molecular polarizability with the X and Z polarized light waves in the laboratory frame. The totally symmetric invariant involves excitation and scattering from the same direction. for α_{zz} . Since the direction cosine from z in the molecular frame to Z in the lab frame is $\cos\theta$. The square of this value is

$$(\alpha_{zz})_{zz}^2 = |\mathbf{e}_z \cdot \alpha_{zz} \cdot \mathbf{e}_z|^2 = \frac{(\alpha_{zz})^2}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \cos^2\theta \sin\theta d\theta = \frac{(\alpha_{zz})^2}{3}$$

We can show that similar relationships will hold for α_{xx} and α_{yy} , gives the rotational invariant, which in this case is the average excitation of all three

$$(\alpha_{ZZ})_{\text{sym}}^2 = \frac{1}{3} \Sigma^0$$

Since each of the terms in this sum has the same properties with respect to the orientation average the total invariant is multiplied by the factor of 1/3 calculated above.

The off-diagonal terms are:

$$(\alpha_{ZZ})_{\text{ZX}}^2 = |\mathbf{e}_Z \cdot \alpha_{\text{ZX}} \cdot \mathbf{e}_Z|^2 = \frac{(\alpha_{\text{ZX}})^2}{4\pi} \int_0^{2\pi} \cos^2 \phi d\phi \int_0^\pi \cos^2 \theta \sin^2 \theta \sin \theta d\theta = \frac{(\alpha_{\text{ZX}})^2}{15}$$

Since the matrix is symmetric (by assumption)

$$(\alpha_{ZZ})_{\text{ZX}}^2 = |\mathbf{e}_Z \cdot \alpha_{\text{ZX}} \cdot \mathbf{e}_Z|^2 = \frac{(\alpha_{\text{ZX}})^2}{4\pi} \int_0^{2\pi} \cos^2 \phi d\phi \int_0^\pi \cos^2 \theta \sin^2 \theta \sin \theta d\theta = \frac{(\alpha_{\text{ZX}})^2}{15}$$

The second contribution to the symmetric anisotropy gives a similar value. Thus,

$$(\alpha_{ZZ})_{\text{sym-aniso}}^2 = \frac{2}{15} \Sigma^2$$

For the totally symmetric contribution to the perpendicular component we find.

$$(\alpha_{\text{XZ}})_{\text{XZ}}^2 = |\mathbf{e}_Z \cdot \alpha_{\text{XZ}} \cdot \mathbf{e}_X|^2 = \frac{(\alpha_{\text{XZ}})^2}{4\pi} \int_0^{2\pi} \cos^4 \phi d\phi \int_0^\pi \sin^4 \theta \sin \theta d\theta = \frac{(\alpha_{\text{XZ}})^2}{20}$$

As above since there are two identical tensor elements $\alpha_{\text{XZ}} = \alpha_{\text{ZX}}$ that have this relationship, so the factor is 1/10.

$$(\alpha_{\text{XZ}})_{\text{sym-aniso}}^2 = \frac{1}{10} \Sigma^2$$