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Chapter 8

Light Scattering and the Raman Effect

8.1 Background

The Raman effect is a light-scattering phenomenon. When light of frequency ν_1 or ν_0 (usually from a laser or, in the pre-laser era, from a mercury arc lamp) irradiates a sample (Figure 8.1), it can be scattered. The frequency of the scattered light can either be at the original frequency (referred to as *Rayleigh scattering*) or at some shifted frequency $\nu_S = \nu_1 \pm \nu_{\text{molecular}}$ (referred to as *Raman scattering*). The frequency $\nu_{\text{molecular}}$ is an internal frequency corresponding to rotational, vibrational, or electronic transitions within a molecule. The vibrational Raman effect is by far the most important, although rotational and electronic Raman effects are also known. For example, the rotational Raman effect provides some of the most accurate bond lengths for homonuclear diatomic molecules.

In discussing the Raman effect some commonly used terms need to be defined (Figure 8.2). Radiation scattering to the lower frequency side (to the "red") of the exciting line is called *Stokes scattering*, while the light scattered at higher frequencies than that of the exciting line (to the "blue") is referred to as the *anti-Stokes scattering*. Finally, the magnitude of the shift between the Stokes or the anti-Stokes line and the exciting line is called the *Raman shift*, $\Delta\nu = |\nu_1 - \nu_S|$.

Classical Model

When an electric field is applied to a molecule, the electrons and nuclei respond by moving in opposite directions in accordance with Coulomb's law. The applied electric field therefore induces a dipole moment in the molecule. As long as the applied electric field is not too strong, the induced dipole moment is linearly proportional to the applied electric field, and is given by

$$\mu_{\text{ind}} = \alpha \mathbf{E}, \quad (8.1)$$

in which the proportionality constant α is called the *polarizability* and is a characteristic of the molecule.

The intensity of the scattered light is proportional to the square of the magnitude of the induced oscillating dipole moment. If some internal motion of the molecule (vi-

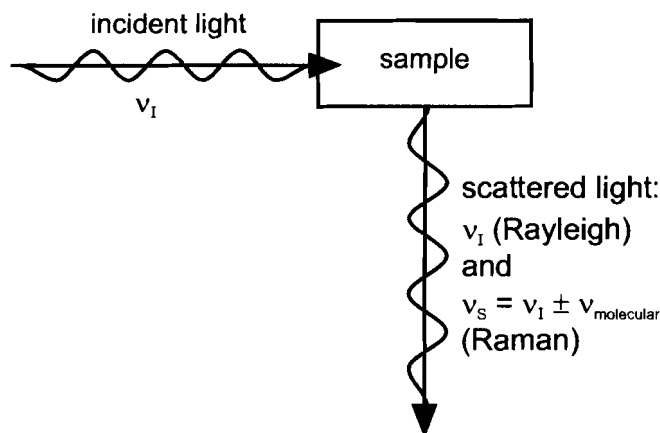


Figure 8.1: Scattering of light by a sample.

brational, rotational, or electronic) modulates this induced oscillating dipole moment, then additional frequencies can appear. Classically, this means that the polarizability has a static term α_0 and a sinusoidal oscillating term with amplitude α_1

$$\alpha = \alpha_0 + \alpha_1 \cos(\omega t) \quad (8.2)$$

with $\omega (= \omega_{\text{molecular}})$ being some internal angular frequency. As usual, it is convenient to use angular frequency $\omega (= 2\pi\nu)$ for theoretical work and frequency ν (or wavenumber, $\tilde{\nu}$) for experimental work. For example, a vibrational mode Q_i has

$$\alpha_1 = \left. \frac{\partial \alpha}{\partial Q_i} \right|_{Q_i=0} Q_i, \quad (8.3)$$

so that if the polarizability does not change with vibration, that is, if $(\partial\alpha/\partial Q_i)|_0 = 0$, then there is no vibrational Raman effect. Classically, the oscillating polarizability causes the induced dipole moment to oscillate at frequencies other than the incident ω_I . To see this, let us represent the applied electric field \mathbf{E} as $\mathbf{E}_0 \cos \omega_I t$. Upon substituting (8.2) into the magnitude of (8.1), we get

$$\mu_{\text{ind}} = \alpha E = \alpha E_0 \cos \omega_I t \quad (8.4)$$

$$\begin{aligned} \mu_{\text{ind}} &= (\alpha_0 + \alpha_1 \cos \omega t) E_0 \cos \omega_I t \\ &= \alpha_0 E_0 \cos \omega_I t + \alpha_1 E_0 \cos \omega_I t \cos \omega t \\ &= \alpha_0 E_0 \cos \omega_I t + \frac{\alpha_1 E_0 \cos(\omega_I - \omega)t + \alpha_1 E_0 \cos(\omega_I + \omega)t}{2}. \end{aligned} \quad (8.5)$$

The trigonometric identity

$$\cos \theta \cos \phi = \frac{\cos(\theta - \phi) + \cos(\theta + \phi)}{2} \quad (8.6)$$

has been used in the final step of equation (8.5). The first term is unshifted in frequency and corresponds to Rayleigh scattering (Figure 8.2). The lower frequency term with $\omega_I - \omega$ corresponds to Stokes scattering, while the higher frequency term with $\omega_I + \omega$

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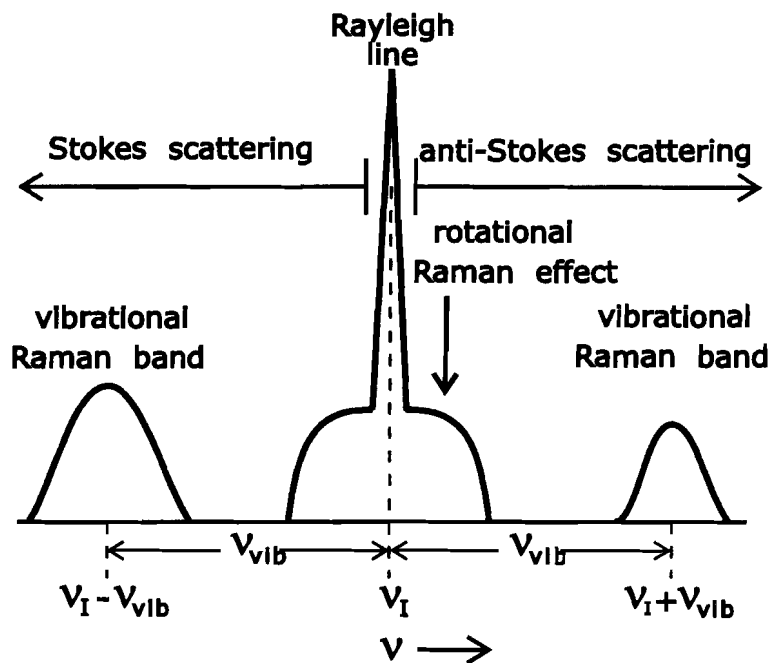


Figure 8.2: Schematic diagram of a Raman spectrum showing vibrational and rotational Raman effects.

corresponds to anti-Stokes scattering (Figure 8.3). This simple classical derivation (8.5) is very deceptive, since it predicts that Stokes and anti-Stokes scattering have the same intensity: this is not usually the case.

The energy-level diagram for Stokes and anti-Stokes scattering shows that anti-Stokes scattering will be weaker because the population in the excited vibrational level is less than that in the ground state (Figure 8.3). For a classical oscillator the scattering (Rayleigh and Raman) is proportional to the fourth power of the frequency (see section 8.4 and problem 7). (The sky is blue because air molecules Rayleigh scatter more blue than red sunlight.) Thus if we introduce the Boltzmann distribution of vibrational populations, the ratio of the intensities of the bands is given by

$$(8.4) \quad \frac{\text{Anti-Stokes intensity}}{\text{Stokes intensity}} = \frac{(\nu_I + \nu_{\text{vib}})^4 e^{-h\nu_{\text{vib}}/kT}}{(\nu_I - \nu_{\text{vib}})^4} \quad (8.7)$$

for a nondegenerate vibration.

There is one additional complication. For highly symmetric molecules such as CH₄, the induced dipole is in the same direction as the applied electric field. For less symmetric molecules, however, μ_{ind} and \mathbf{E} can point in different directions because the molecular response to the applied electric field can be different along the X-, Y- and Z-axes in the laboratory frame. In matrix notation, equation (8.1) becomes

$$(8.6) \quad \mu_{\text{ind}} = \alpha \mathbf{E} \quad (8.8)$$

or

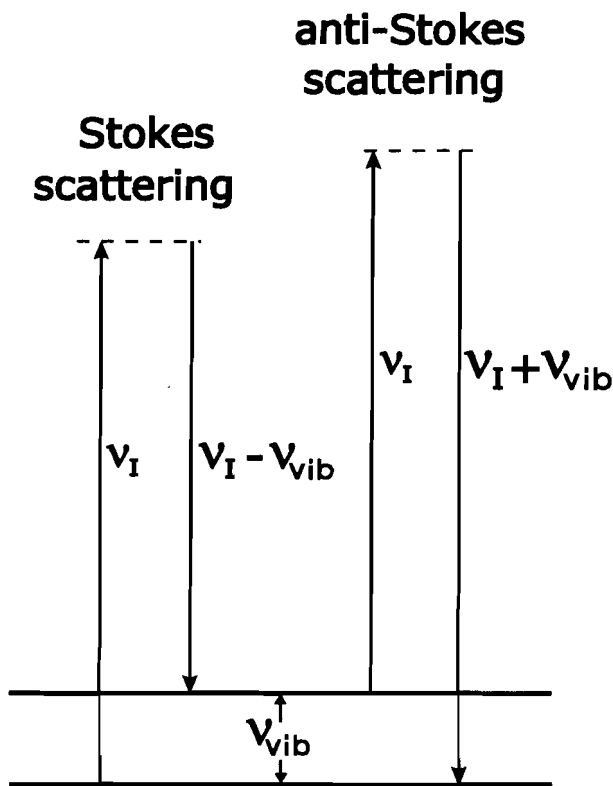


Figure 8.3: Energy-level diagram showing Stokes and anti-Stokes scattering.

$$\begin{pmatrix} \mu_X \\ \mu_Y \\ \mu_Z \end{pmatrix} = \begin{pmatrix} \alpha_{XX} & \alpha_{XY} & \alpha_{XZ} \\ \alpha_{XY} & \alpha_{YY} & \alpha_{YZ} \\ \alpha_{XZ} & \alpha_{YZ} & \alpha_{ZZ} \end{pmatrix} \begin{pmatrix} E_X \\ E_Y \\ E_Z \end{pmatrix}, \tag{8.9}$$

in which α is a 3×3 symmetric matrix. This symmetric matrix is called the *polarizability tensor*.

The polarizability tensor α can be simplified by working in the appropriate principal axis system of the molecule, analogous to the principal axis system for the moment of inertia tensor (Chapter 6). As the polarizability tensor is a real, symmetric matrix, it is always possible to construct an orthogonal transformation matrix \mathbf{X} from the normalized eigenvectors of α . The matrix \mathbf{X} represents a rotation of the coordinate system, $\mathbf{r}' = \mathbf{X}^{-1}\mathbf{r}$ or $\mathbf{r} = \mathbf{X}\mathbf{r}'$, with $\mathbf{r}' = (x, y, z)$. As discussed in Chapter 3, the diagonalized matrix α' is related to α by the similarity transformation

$$\alpha' = \mathbf{X}^{-1}\alpha\mathbf{X}. \tag{8.10}$$

The α' matrix consists of the eigenvalues of α and has the form,

$$\alpha' = \begin{pmatrix} \alpha_{x'x'} & 0 & 0 \\ 0 & \alpha_{y'y'} & 0 \\ 0 & 0 & \alpha_{z'z'} \end{pmatrix}, \tag{8.11}$$

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or $\alpha_x = \alpha_{x'x'}$, $\alpha_y = \alpha_{y'y'}$, and $\alpha_z = \alpha_{z'z'}$ if the molecular principal axis system is assumed. Note that unless required by symmetry, the principal axes of polarizability of a molecule do not coincide with the principal axes of the moment of inertia.

The polarizability ellipsoid of a molecule is defined by the equation

$$\mathbf{r}'\boldsymbol{\alpha}\mathbf{r} = 1 \quad (8.12)$$

or

$$\alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2 = 1 \quad (8.13)$$

in the principal axis system. The ellipsoid has maximum total dimensions equal to $2/\sqrt{\alpha_x}$, $2/\sqrt{\alpha_y}$, and $2/\sqrt{\alpha_z}$ along the x -, y -, and z -axes. For a spherical top, $\alpha_x = \alpha_y = \alpha_z$ so the ellipsoid is a sphere; for a symmetric top or linear molecule, $\alpha_x = \alpha_y$ and the ellipsoid has a circular cross section in the xy -plane. For the normal case of light scattering with wavelength λ substantially greater in size than that of the molecule, the molecule behaves as if it were represented in shape by the polarizability ellipsoid.

For a diatomic molecule such as H_2 or HCl , it is convenient to label the polarizability parallel to the molecular z -axis as α_{\parallel} ($= \alpha_z$), and the polarizability perpendicular to the z -axis as α_{\perp} ($= \alpha_x = \alpha_y$). The mean polarizability is given by

$$\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3 \quad (8.14)$$

and the polarizability anisotropy γ is defined as

$$\gamma = \alpha_{\parallel} - \alpha_{\perp}. \quad (8.15)$$

The mean polarizability $\bar{\alpha}$ can be deduced, for example, from a measurement of the optical refractive index (see problem 7) and the anisotropy γ from a measurement of the depolarization ratio ρ (see below) of Rayleigh scattering.

Polarizability is an important molecular property that plays a role in, for example, intermolecular interactions. The polarizability of a molecule can be calculated by the methods of *ab initio* quantum chemistry. The results of such a calculation¹ of $\bar{\alpha}$ and γ for H_2 are displayed in Figure 8.4 as a function of the internuclear distance, r . At large r , the value of $\bar{\alpha}$ approaches that of two H atoms, while at short r the value of $\bar{\alpha}$ tends to that of the He atom. At $r = r_e = 0.742 \text{ \AA}$, $\partial\bar{\alpha}/\partial r \neq 0$ so there will be a vibrational Raman effect for H_2 . As the bond stretches from equilibrium, the electrons are less tightly held by the nuclei so the polarizability increases. In general for both heteronuclear molecules such as HCl and homonuclear molecules such as H_2 , the polarizability ellipsoid will change as the molecule vibrates, leading to a vibrational Raman effect. The Raman effect is thus less restrictive than normal dipole-allowed infrared vibrational spectroscopy, which has no allowed transitions for a homonuclear molecule because $\partial\boldsymbol{\mu}/\partial r = 0$.

Simple arguments based on changes in the polarizability as a function of the normal coordinates Q_i can be made for a typical polyatomic molecule such as CO_2 . As shown in Figure 8.5, motion along the symmetric stretching coordinate Q_1 , will change the mean polarizability so that $\partial\bar{\alpha}/\partial Q_1 \neq 0$ and ν_1 is Raman active. The situation is different for ν_2 and ν_3 because of the high symmetry. The polarizability again changes with Q but the values at $+Q$ and $-Q$ are identical by symmetry, (i.e., $\bar{\alpha}(Q)$ is an even function) so at $Q = 0$, $\partial\bar{\alpha}/\partial Q = 0$ for ν_2 and ν_3 (Figure 8.5). For the dipole moments $\boldsymbol{\mu}$ the opposite situation prevails with $\partial\boldsymbol{\mu}/\partial Q_1 = 0$, $\partial\boldsymbol{\mu}/\partial Q_2 \neq 0$, and $\partial\boldsymbol{\mu}/\partial Q_3 \neq 0$, so ν_1 is Raman active but ν_2 and ν_3 are infrared active. This is an example of the *rule*

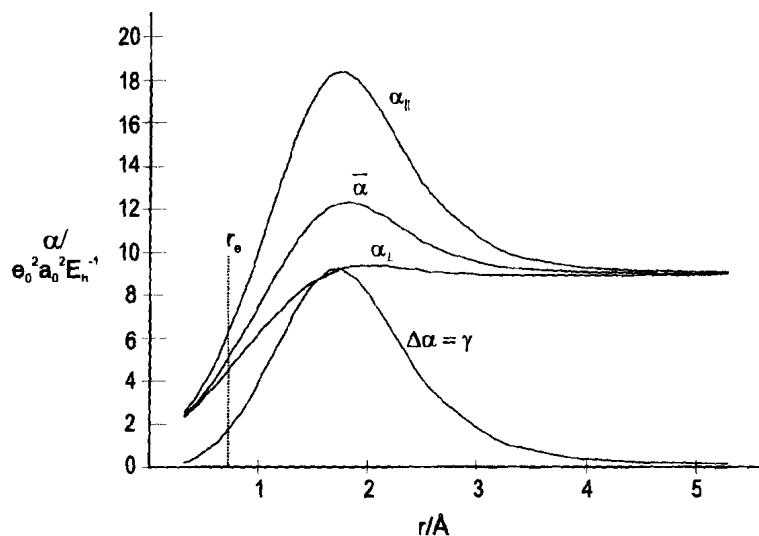


Figure 8.4: The polarizability of H_2 as a function of internuclear distance r calculated by *ab initio* methods.¹

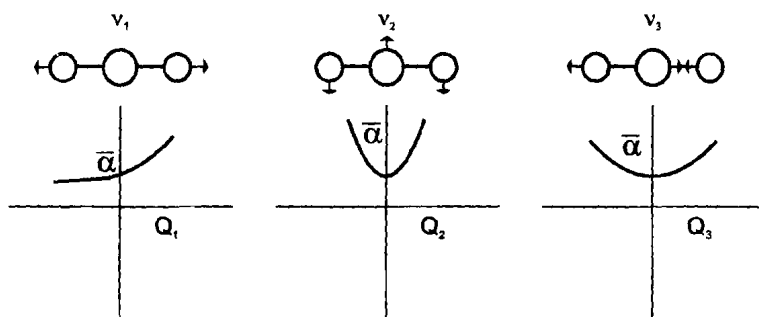


Figure 8.5: The polarizability of CO_2 as a function of the three normal coordinates Q_1 , Q_2 , and Q_3 (shown schematically).

of *mutual exclusion* that applies to molecules with a center of symmetry, and will be discussed later.

Quantum Model

The quantum mechanical theory of the Raman effect was developed in the early 1930s by Placzek.² The starting point is the same as in Chapter 1 with a two-level system with energy levels E_1 and E_0 as depicted in Figure 1.8. An oscillating electric field is applied to the system, $\mathbf{E} = \mathbf{E}_0 \cos \omega t$, with the wavelength λ assumed to be much bigger than the molecular dimensions. In the case of Rayleigh and Raman scattering, the electric field is not in resonance (i.e., $\omega \neq (E_1 - E_0)/\hbar = \omega_{10}$), but instead induces an oscillating dipole moment that re-radiates. In quantum mechanics this means that we are looking for (see equation (1.66)) the transition dipole moment,

$$\mathbf{M}_{10}(t) = \langle \Psi_1 | \boldsymbol{\mu} | \Psi_0 \rangle, \quad (8.16)$$

with $\Psi_1(t)$ and $\Psi_0(t)$ being the solutions of the time-dependent Schrödinger equation (1.29) for the two-level system. The intensity of the scattered radiation is proportional to $|\mathbf{M}_{10}|^2$. The interaction of electromagnetic radiation and the system is taken into account with the electric-dipole interaction term, equation (1.26), namely

$$\hat{H}' = -\boldsymbol{\mu} \cdot \mathbf{E}_0 \cos(\omega t). \quad (8.17)$$

In this case $\boldsymbol{\mu}$ is an induced moment, and $\boldsymbol{\mu}$ and \mathbf{E}_0 need not point in the same direction.

Rather than solving the Schrödinger equation as outlined in Chapter 1, perturbation theory (Chapter 4) will be used to obtain an expression for the transition dipole moment, $\mathbf{M}_{10}(t)$. In what follows the states in the molecule are labeled as $|n\rangle = |0\rangle, |k\rangle = |1\rangle$, and $|r\rangle$, with $|r\rangle$ being the additional states in the molecule not depicted in Figure 1.8. The application of the small perturbing electric field, equation (1.6), alters the wavefunction Ψ_n of the system so that

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \dots \quad (8.18)$$

The zeroth-order solution to the time-dependent Schrödinger equation,

$$\hat{H}^{(0)}\Psi_n^{(0)} = i\hbar \frac{\partial \Psi_n^{(0)}}{\partial t}, \quad (8.19)$$

is

$$\Psi_n^{(0)} = \psi_n^{(0)} e^{-iE_n t/\hbar} = \psi_n^{(0)} e^{-i\omega_n t}, \quad (8.20)$$

with $\psi_n^{(0)}$ being the solution of the corresponding time-independent equation,

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}. \quad (8.21)$$

The perturbed Schrödinger equation is

$$\left(\hat{H}^{(0)} - \boldsymbol{\mu} \cdot \mathbf{E}_0 \cos(\omega t) \right) \Psi_n = i\hbar \frac{\partial \Psi_n}{\partial t}, \quad (8.22)$$

and using equation (8.18) to first order leads to

$$\left(\hat{H}^{(0)} - \boldsymbol{\mu} \cdot \mathbf{E}_0 \cos(\omega t) \right) \left(\Psi_n^{(0)} + \Psi_n^{(1)} \right) = i\hbar \frac{\partial}{\partial t} \left(\Psi_n^{(0)} + \Psi_n^{(1)} \right), \quad (8.23)$$

or, equivalently, when the zeroth-order equation is subtracted, to

$$\hat{H}^{(0)}\Psi_n^{(1)} - i\hbar \frac{\partial \Psi_n^{(1)}}{\partial t} = \boldsymbol{\mu} \cdot \mathbf{E}_0 \cos(\omega t) \Psi_n^{(0)}. \quad (8.24)$$

The first-order correction can be obtained by assuming (with some foresight) a solution of the form

$$\Psi_n^{(1)} = \psi_n^+ e^{-i(\omega_n + \omega)t} + \psi_n^- e^{-i(\omega_n - \omega)t}. \quad (8.25)$$

Substitution of the assumed solution (8.25) into equation (8.24), using $\cos(\omega t) = (e^{i\omega t} + e^{-i\omega t})/2$, and then equating terms with equal time dependence leads to two separate equations,

$$\hat{H}^{(0)}\psi_n^+ - (E_n + h\nu)\psi_n^+ = \boldsymbol{\mu} \cdot \mathbf{E}_0\psi_n^{(0)}/2, \quad (8.26)$$

and

$$\hat{H}^{(0)}\psi_n^- - (E_n - h\nu)\psi_n^- = \boldsymbol{\mu} \cdot \mathbf{E}_0\psi_n^{(0)}/2. \quad (8.27)$$

The right-hand side of equations (8.26) and (8.27) can be manipulated by the trick of inserting unity (Chapter 4), in the form $1 = \sum |\psi_r^{(0)}\rangle\langle\psi_r^{(0)}|$ so that we obtain

$$\boldsymbol{\mu}|\psi_n^{(0)}\rangle \cdot \mathbf{E}_0 = \sum_r |\psi_r^{(0)}\rangle\langle\psi_r^{(0)}|\boldsymbol{\mu}|\psi_n^{(0)}\rangle \cdot \mathbf{E}_0. \quad (8.28)$$

By defining the matrix element $\boldsymbol{\mu}_{rn}$ of $\boldsymbol{\mu}$ by

$$\boldsymbol{\mu}_{rn} = \langle\psi_r^{(0)}|\boldsymbol{\mu}|\psi_n^{(0)}\rangle, \quad (8.29)$$

we may write (8.26) and (8.27) as

$$\hat{H}^{(0)}\psi_n^+ - (E_n + h\nu)\psi_n^+ = \sum_r \boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0\psi_r^{(0)}/2 \quad (8.30)$$

and

$$\hat{H}^{(0)}\psi_n^- - (E_n - h\nu)\psi_n^- = \sum_r \boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0\psi_r^{(0)}/2. \quad (8.31)$$

The ψ_n^+ and ψ_n^- wavefunctions can also be expanded in terms of the complete, orthonormal set of $\psi_r^{(0)}$ functions, i.e., as

$$\psi_n^+ = \sum_r c_r^+ \psi_r^{(0)} \quad (8.32)$$

and

$$\psi_n^- = \sum_r c_r^- \psi_r^{(0)}, \quad (8.33)$$

which results in the expansion coefficients c_r^+ and c_r^- being given by

$$c_r^+ = \frac{\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0/2}{E_r - E_n - h\nu}, \quad (8.34)$$

and

$$c_r^- = \frac{\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0/2}{E_r - E_n + h\nu} \quad (8.35)$$

from equations (8.30) and (8.31). The time-dependent first-order correction (equation (8.25)) to the wavefunction is thus

$$\Psi_n^{(1)} = \frac{1}{2\hbar} \sum_r \psi_r^{(0)} \left(\frac{\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0}{\omega_{rn} - \omega} e^{-i(\omega_n + \omega)t} + \frac{\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0}{\omega_{rn} + \omega} e^{-i(\omega_n - \omega)t} \right), \quad (8.36)$$

with $\omega_{rn} \equiv (E_r - E_n)/\hbar$.

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(8.26)

Rayleigh scattering involves no frequency shift of the scattered light (i.e., $k = n$ for $\mathbf{M}_{kn}(t)$) and is based on the oscillating part of the quantum mechanical dipole moment, i.e.,

(8.27)

$$\begin{aligned} \mathbf{M}_{nn}(t) &= \langle \Psi_n | \boldsymbol{\mu} | \Psi_n \rangle \approx \langle \Psi_n^{(0)} + \Psi_n^{(1)} | \boldsymbol{\mu} | \Psi_n^{(0)} + \Psi_n^{(1)} \rangle \\ &\approx \langle \Psi_n^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle + \langle \Psi_n^{(0)} | \boldsymbol{\mu} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(1)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle \\ &= \mathbf{M}_{nn}^{(0)} + \mathbf{M}_{nn}^{(1)}(t) \end{aligned} \quad (8.37)$$

by the trick of
obtain

(8.28)

to first order. The term $\mathbf{M}_{nn}^{(0)}$, given by

(8.29)

$$\langle \Psi_n^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle = \langle \psi_n | \boldsymbol{\mu} | \psi_n \rangle = \boldsymbol{\mu}_{nn} \quad (8.38)$$

has no time dependence and is just the dipole moment of the molecule in state $|\psi_n\rangle$. This term does not result in any light scattering and hence can be discarded leaving, to first order, $\mathbf{M}_{nn}(t) \approx \mathbf{M}_{nn}^{(1)}(t)$, with $\mathbf{M}_{nn}^{(1)}(t)$ given as

(8.30)

$$\begin{aligned} \mathbf{M}_{nn}^{(1)}(t) &= \frac{e^{-i\omega t}}{2\hbar} \sum_r \left(\frac{\boldsymbol{\mu}_{nr}(\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0)}{\omega_{rn} - \omega} + \frac{\boldsymbol{\mu}_{rn}(\boldsymbol{\mu}_{nr} \cdot \mathbf{E}_0)}{\omega_{rn} + \omega} \right) \\ &+ \frac{e^{i\omega t}}{2\hbar} \sum_r \left(\frac{\boldsymbol{\mu}_{nr}(\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0)}{\omega_{rn} + \omega} + \frac{\boldsymbol{\mu}_{rn}(\boldsymbol{\mu}_{nr} \cdot \mathbf{E}_0)}{\omega_{rn} - \omega} \right). \end{aligned} \quad (8.39)$$

the complete,

(8.32)

Rayleigh scattering is thus proportional to $|\mathbf{M}_{nn}^{(1)}|^2$ obtained using equation (8.39).

In exactly the same way, the transition dipole moment $\mathbf{M}_{kn}^{(1)}(t)$ leads to transitions from state $|n\rangle$ to state $|k\rangle$ with

(8.33)

$$\begin{aligned} \mathbf{M}_{kn}^{(1)}(t) &= \frac{e^{i(\omega_{kn} - \omega)t}}{2\hbar} \sum_r \left(\frac{\boldsymbol{\mu}_{kr}(\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0)}{\omega_{rn} - \omega} + \frac{\boldsymbol{\mu}_{rn}(\boldsymbol{\mu}_{kr} \cdot \mathbf{E}_0)}{\omega_{rk} + \omega} \right) \\ &+ \frac{e^{i(\omega_{kn} + \omega)t}}{2\hbar} \sum_r \left(\frac{\boldsymbol{\mu}_{kr}(\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0)}{\omega_{rn} + \omega} + \frac{\boldsymbol{\mu}_{rn}(\boldsymbol{\mu}_{kr} \cdot \mathbf{E}_0)}{\omega_{rk} - \omega} \right). \end{aligned} \quad (8.40)$$

(8.34)

Once again, the zeroth order term,

(8.35)

$$\langle \Psi_k^{(0)} | \boldsymbol{\mu} | \Psi_n^{(0)} \rangle = \boldsymbol{\mu}_{kn} e^{i\omega_{kn}t} \quad (8.41)$$

has been discarded because it corresponds to a regular transition dipole moment of the type that has been discussed in Chapter 1, so that it does not contribute to Raman scattering.

tion (equation

(8.36)

For the Raman effect it is assumed that $\omega_{kn} = (E_k - E_n)/\hbar$ can be positive ($E_k > E_n$) for Stokes scattering or negative ($E_k < E_n$) for anti-Stokes scattering, and that enough energy is available from the incident photon to induce the transition from $|n\rangle$ to $|k\rangle$, i.e., $\omega > \omega_{kn}$ or $\omega - \omega_{kn} > 0$ (sometimes referred to as "Klein²⁻⁴ conditions"). In addition, the second term on the right-hand side of equation (8.40) has an oscillating dipole moment at a high angular frequency of $\omega_{kn} + \omega$, which is interpreted³ (somewhat surprisingly!) as a two-photon transition, and will not be considered further. The first

term on the right-hand side of equation (8.40) has the correct angular frequency $\omega_{kn} - \omega$ associated with the Raman effect.

The expression for the oscillating transition dipole moment for a Raman transition from state $|n\rangle$ to $|k\rangle$ is thus given in first-order perturbation theory as

$$\mathbf{M}_{kn}^{(1)}(t) = \frac{e^{i(\omega_{kn} - \omega)t}}{2\hbar} \sum_r \left(\frac{\boldsymbol{\mu}_{kr}(\boldsymbol{\mu}_{rn} \cdot \mathbf{E}_0)}{\omega_{rn} - \omega} + \frac{\boldsymbol{\mu}_{rn}(\boldsymbol{\mu}_{kr} \cdot \mathbf{E}_0)}{\omega_{rk} + \omega} \right). \quad (8.42)$$

Consider the applied electric field to be given in terms of its laboratory Cartesian components as

$$\mathbf{E}_0 = E_{0X}\hat{\mathbf{i}} + E_{0Y}\hat{\mathbf{j}} + E_{0Z}\hat{\mathbf{k}} \quad (8.43)$$

while the oscillating transition dipole moment also has Cartesian components,

$$\mathbf{M}_{kn}^{(1)} = M_{X,kn}\hat{\mathbf{i}} + M_{Y,kn}\hat{\mathbf{j}} + M_{Z,kn}\hat{\mathbf{k}}, \quad (8.44)$$

as do the matrix elements of the dipole moment:

$$\boldsymbol{\mu}_{rn} = \mu_{X,rn}\hat{\mathbf{i}} + \mu_{Y,rn}\hat{\mathbf{j}} + \mu_{Z,rn}\hat{\mathbf{k}}. \quad (8.45)$$

To make the meaning of equation (8.42) clearer, consider for example the X component of $\mathbf{M}_{kn}^{(1)}(t)$ on the left-hand side in response to the Z component of \mathbf{E}_0 on the right-hand side, in which case we may write

$$M_{X,kn}(t) = \frac{e^{i(\omega_{kn} - \omega)t}}{2\hbar} \sum_r \left(\frac{\mu_{X,kr}\mu_{Z,rn}}{\omega_{rn} - \omega} + \frac{\mu_{X,rn}\mu_{Z,kr}}{\omega_{rk} + \omega} \right) E_{0Z}, \quad (8.46)$$

for comparison with the corresponding term from equation (8.9), namely,

$$\mu_X = \alpha_{XZ}E_Z. \quad (8.47)$$

Before the comparison can be made, the substitution of $E_{0Z} \cos \omega t$ for E_Z in equation (8.47) needs to be made and then the kn -matrix element formed using the $\Psi_k^{(0)}(t)$ and $\Psi_n^{(0)}(t)$ wavefunctions to give

$$M_{X,kn} = \langle \Psi_k(t) | \hat{\alpha}_{XZ} | \Psi_n(t) \rangle E_{0Z} \cos \omega t. \quad (8.48)$$

Converting the cosine to its exponential form and using $\Psi_k^{(0)} = \psi_k^{(0)} e^{-i\omega_k t}$ and $\Psi_n^{(0)} = \psi_n^{(0)} e^{-i\omega_n t}$ leads to

$$M_{X,kn} = \frac{1}{2} \langle \psi_k^{(0)} | \hat{\alpha}_{XZ} | \psi_n^{(0)} \rangle E_{0Z} \left(e^{i(\omega_{kn} - \omega)t} + e^{i(\omega_{kn} + \omega)t} \right), \quad (8.49)$$

and once again the high frequency term with $\omega_{kn} + \omega$ can be ignored. Comparison of equations (8.46) and (8.49) leads to the conclusion that

$$\alpha_{XZ} = \frac{1}{\hbar} \sum_r \left(\frac{\mu_{X,kr}\mu_{Z,rn}}{\omega_{rn} - \omega} + \frac{\mu_{X,rn}\mu_{Z,kr}}{\omega_{rk} + \omega} \right) \quad (8.50)$$

or in general

$$\alpha_{ij} = \frac{1}{\hbar} \sum_r \left(\frac{\mu_{i,kr}\mu_{j,rn}}{\omega_{rn} - \omega} + \frac{\mu_{i,rn}\mu_{j,kr}}{\omega_{rk} + \omega} \right) \quad (8.51)$$

Figure 8.6: The dipole moment α_{ij} .

with $i, j = X, Y, Z$. The dipole moment α_{ij} is shown in Figure 8.6 for the case $i = X, j = Z$.

The polarizability α_{ij} is a tensor quantity and can be written as a sum of atomic or molecular polarizabilities. The effect also depends on the values of the wavefunctions $\psi_k^{(0)}$ and $\psi_n^{(0)}$ (8.51).¹

The same result can be obtained by using the perturbation theory

which is given in equation (8.51).

so that taking

leads to the polarizability α_{ij} . In terms of the dipole moment μ_{ij} the consequence is

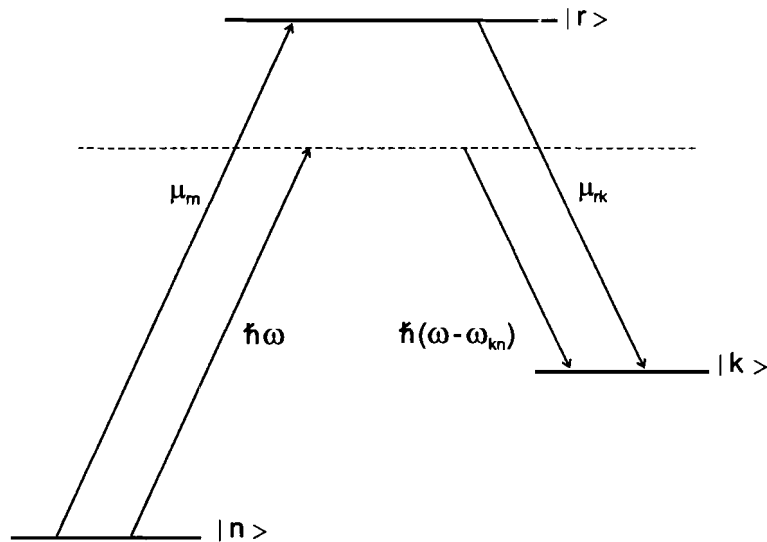


Figure 8.6: Energy-level diagram for the Stokes Raman scattering of $\hbar\omega$ into $\hbar(\omega - \omega_{kn})$ and the dipole matrix elements μ_{rn} and μ_{rk} that contribute to the polarizability tensor elements α_{ij} .

with $i, j = X, Y, Z$. The elements of the polarizability tensor are thus given by a sum of dipole matrix element products divided by energy denominators as depicted in Figure 8.6 for the case of Stokes Raman scattering of an incident photon at $\hbar\omega$ to $\hbar(\omega - \omega_{kn})$.

The polarizability, equation (8.51), contains resonance denominators that cause α_{ij} to become large if the frequency of the applied electric field approaches that of an atomic or a molecular transition—i.e., if ω approaches ω_{rn} . In this case, a single term in the sum dominates and results in the *resonance Raman effect*. The resonance Raman effect also leads to an enhancement in the Raman scattering, and with large (but finite!) values of α_{ij} , when an extra damping term is included in the denominator of equation (8.51).⁴

The selection rules for Raman transitions from state $|n\rangle$ to state $|k\rangle$ are, as usual, obtained by inspection of the transition dipole moment integral (8.42)

$$\mathbf{M}_{kn} = \langle \Psi_k | \boldsymbol{\mu} | \Psi_n \rangle, \tag{8.52}$$

which is given in equation (8.46) in terms of the polarizability tensor elements α_{ij} , equation (8.51). It is convenient to define formally a polarizability operator $\hat{\alpha}_{ij}$ as

$$\hat{\alpha}_{ij} \equiv \frac{1}{\hbar} \sum_r \left(\frac{\hat{\mu}_i |r\rangle \langle r| \hat{\mu}_j}{\omega_{rn} - \omega} + \frac{\hat{\mu}_j |r\rangle \langle r| \hat{\mu}_i}{\omega_{rk} + \omega} \right) \tag{8.53}$$

so that taking matrix elements

$$\alpha_{ij} = \langle k | \hat{\alpha}_{ij} | n \rangle = \int \psi_k^* \hat{\alpha}_{ij} \psi_n d\tau \tag{8.54}$$

leads to the polarizability tensor values, α_{ij} , of equation (8.51).

In terms of Raman selection rules, the time dependence of equation (8.52) is of no consequence, and they are determined by the symmetry of ψ_k , ψ_n , and $\hat{\alpha}_{ij}$ in equation

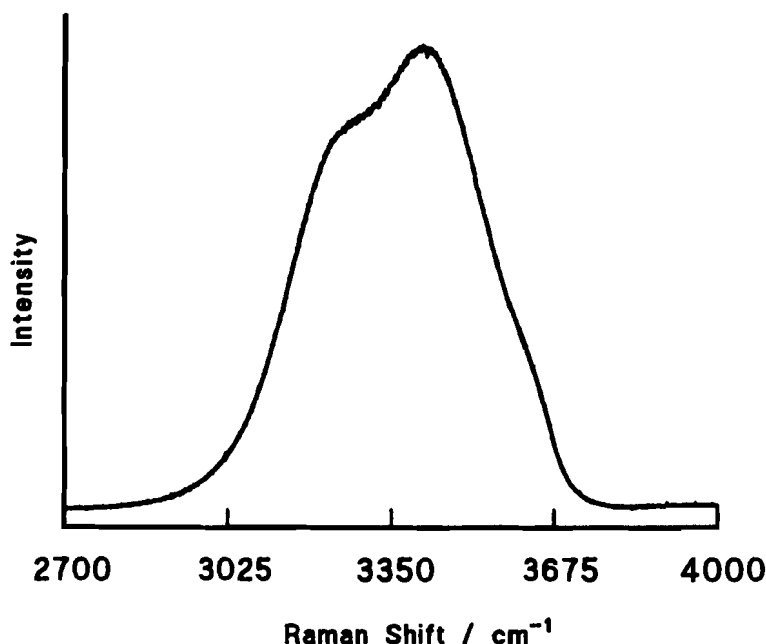


Figure 8.7: Raman spectrum of liquid H_2O in the O—H stretching region. The peak to the right is the ν_1 symmetric stretching mode, while the peak to the left is due to the $2\nu_2$ overtone and the O—H stretching mode of two (or more) hydrogen-bonded H_2O molecules.

(8.54). The $\hat{\alpha}_{ij}$ operator is made up of dipole moment operators $\hat{\mu}_i$ and $\hat{\mu}_j$, $i, j = x, y, z$. This means that in the molecular frame the six elements of the polarizability tensor (α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{xz} , and α_{yz}) all transform like the binary products of coordinates x^2 , y^2 , z^2 , xy , xz , and yz when the symmetry operations of the point group are applied. The symmetry of these binary products (or properly symmetrized combinations) are listed on the right side of character tables. Thus the direct product

$$\Gamma(\psi_1^*) \otimes \Gamma(\alpha_{ij}) \otimes \Gamma(\psi_0) \quad (8.55)$$

must contain the A_1 irreducible representation in order for the corresponding integral to be nonzero and give an allowed Raman transition from $|0\rangle$ to $|1\rangle$.

For example, x^2 , y^2 , and z^2 for the H_2O molecule have A_1 symmetry, while xy , xz , and yz have A_2 , B_1 , and B_2 symmetry, respectively. Thus the three normal modes of H_2O , $\nu_1(a_1)$, $\nu_2(a_1)$, and $\nu_3(b_2)$, are all Raman active (Figure 8.7).

Notice that if a molecule has a center of symmetry, then both ψ_0 (for fundamentals) and α_{ij} have g symmetry and consequently ψ_1 must also be of g symmetry. Thus all Raman active fundamental transitions have g symmetry, if the molecule has a center of symmetry. Correspondingly, all infrared active fundamentals must have u symmetry since μ has u symmetry. This leads to the *rule of mutual exclusion*, which states that no fundamental mode of a molecule with a center of symmetry can be both infrared and Raman active. Comparison of infrared and Raman band positions can thus be a simple but powerful tool in deducing molecular geometry.

For the tetrahedral molecule CCl_4 all four vibrational modes ($\nu_1(a_1)$ 459 cm^{-1} , $\nu_2(e)$ 218 cm^{-1} , $\nu_3(t_2)$ 762 cm^{-1} , $\nu_4(t_2)$ 314 cm^{-1}) (see Figure 8.8) are Raman active.

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Polarization

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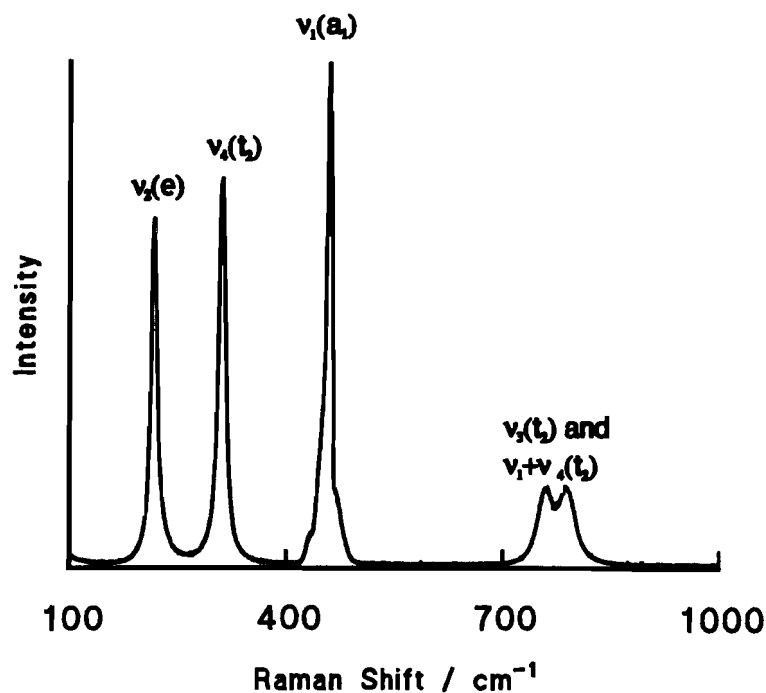


Figure 8.8: Vibrational Raman spectrum of liquid CCl_4 .

This is in contrast to the infrared spectrum in which only ν_3 and ν_4 are observed. The partially resolved doublet near 775 cm^{-1} in the Raman spectrum is actually two Fermi resonance transitions (762 cm^{-1} , 790 cm^{-1}) made up of nearly equal mixtures of $\nu_3(t_2)$ and $\nu_1 + \nu_4(t_2)$.

Polarization

The typical Raman scattering geometry is shown in Figure 8.9. The intensity of light scattered parallel (I_{\parallel}) and perpendicular (I_{\perp}) to the incident electric field vector can easily be measured with polarizers. The ratio $\rho = I_{\perp}/I_{\parallel}$, called the *depolarization ratio*, is an important clue in the assignment of a vibrational Raman spectrum, because it depends on the symmetry of the vibrational mode.

From the theory of the Raman effect, it is known that a symmetric vibration has $0 \leq \rho \leq \frac{3}{4}$ for linearly polarized incident light.^{5,6} For a non-totally symmetric vibration, $\rho = \frac{3}{4}$ for linearly polarized incident light, and the band is said to be depolarized. If unpolarized light is used—as was done, for example, using a mercury arc lamp in the pre-laser era—then $\rho = \frac{6}{7}$ for a non-totally symmetric vibration.^{5,6} Thus a measurement of the depolarization ratio will often distinguish between totally symmetric and nonsymmetric vibrations. Totally symmetric vibrations, such as the C—Cl stretching mode ($\nu_1(a_1)$ 459 cm^{-1}) in CCl_4 , tend to be strong scatterers with depolarization ratios close to zero (Figure 8.10), whereas this mode is forbidden in the infrared spectrum.

The physical origin of polarized scattering for a symmetric vibration is easy to understand in classical terms. For example, in the case of a symmetric vibration for a spherical top, the induced dipole is always parallel to the incident radiation and the

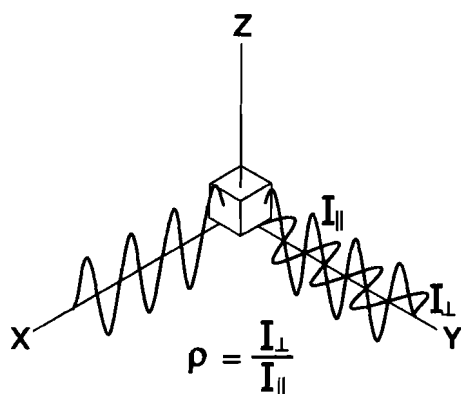


Figure 8.9: Parallel and perpendicular Raman scattering.

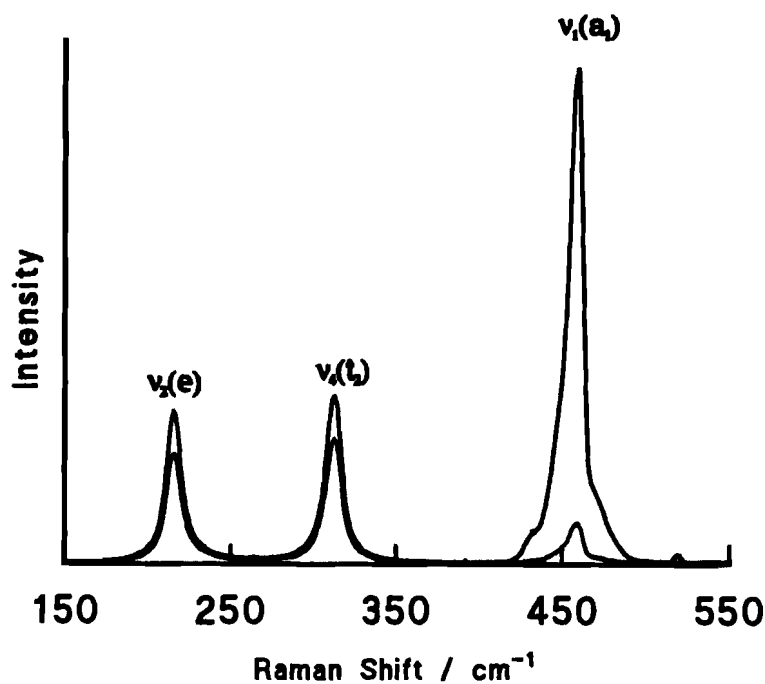


Figure 8.10: Vibrational Raman spectrum of liquid CCl_4 showing the depolarization of the bands. The upper trace corresponds to $I_{||}$ and the lower trace to I_{\perp} .

molecule behaves like a tiny sphere (Figure 8.11); i.e., the polarizability ellipsoid is a sphere. The scattered light is also polarized parallel to the incident light polarization and $\rho \sim 0$ (Figure 8.11). Molecules with O_h , T_d , or I_h symmetry behave in this way for totally symmetric (a_1) vibrations.

8.2 Rotational

The dipole moment is given in the

or, written explicitly

Since the polarizability ellipsoid is real symmetric, the diagonal elements α_{xx} , α_{yy} , α_{zz} are the molecular polarizabilities.

As far as the polarizability ellipsoid is concerned, therefore, the molecule behaves like a tiny sphere for all molecules.

The rotational Raman spectroscopy of CO_2 having $D_{\infty h}$ symmetry and C_{60} with I_h symmetry shows a depolarization ratio of 6 for a torque on a molecule.

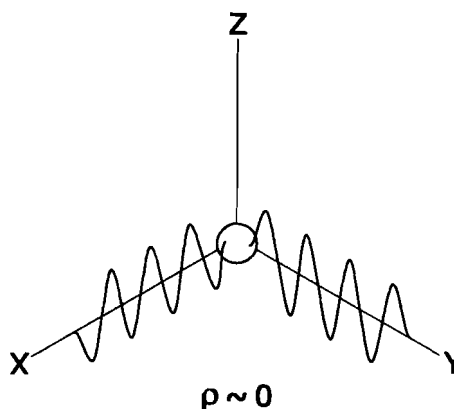


Figure 8.11: Polarized light scattering by a sphere.

8.2 Rotational Raman Effect

The dipole moment induced in a nonrotating molecule when an electric field is applied is given in the laboratory frame by

$$\boldsymbol{\mu} = \boldsymbol{\alpha}\mathbf{E}, \quad (8.56)$$

or, written explicitly in matrix format, by

$$\begin{pmatrix} \mu_X \\ \mu_Y \\ \mu_Z \end{pmatrix} = \begin{pmatrix} \alpha_{XX} & \alpha_{XY} & \alpha_{XZ} \\ \alpha_{XY} & \alpha_{YY} & \alpha_{YZ} \\ \alpha_{XZ} & \alpha_{YZ} & \alpha_{ZZ} \end{pmatrix} \begin{pmatrix} E_X \\ E_Y \\ E_Z \end{pmatrix}. \quad (8.57)$$

Since the polarizability tensor, like the moment of inertia tensor, is represented by a real symmetric matrix, it is always possible to find an orthogonal transformation which diagonalizes $\boldsymbol{\alpha}$. This new molecular coordinate system is obtained by a rotation of the molecular x -, y -, and z -axes such that the off-diagonal components of $\boldsymbol{\alpha}$ are eliminated,

$$\boldsymbol{\alpha}' = \begin{pmatrix} \alpha_x & 0 & 0 \\ 0 & \alpha_y & 0 \\ 0 & 0 & \alpha_z \end{pmatrix}. \quad (8.58)$$

As far as light scattering is concerned, the molecule is represented by the polarizability ellipsoid. A spherical top molecule has a spherical polarizability ellipsoid and therefore behaves like a tiny sphere when an electric field is applied. The oscillating electromagnetic field is applied and the scattered light is detected in the laboratory frame of reference. The rotation of the molecule therefore modulates the scattered light for all molecules except spherical top molecules (Figure 8.12).

The rotational Raman effect is less restrictive than is microwave rotational spectroscopy because symmetric linear molecules without dipole moments such as Cl_2 and CO_2 have pure rotational Raman spectra. However, spherical tops such as CH_4 , SF_6 , and C_{60} will not have observable rotational Raman spectra because an anisotropic polarizability tensor is required. In simple terms, an applied electric field can only exert a torque on a molecule if the molecule is more polarizable along one direction than another.

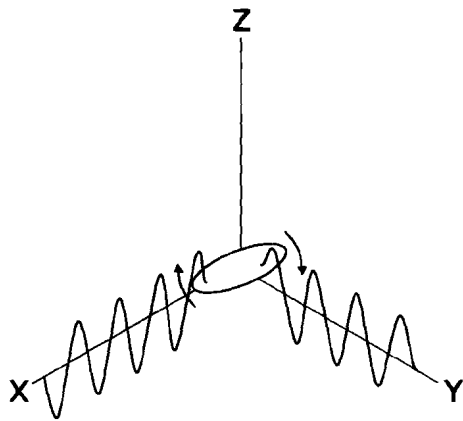


Figure 8.12: Light scattering by a rotating molecule is modulated by the rotational motion.

The rotational selection rules are obtained by evaluating the integrals

$$\begin{aligned} \int \psi_1^* \hat{\alpha}_{IJ} \psi_0 d\tau &= \int \psi_1^* \left(\sum_{i,j} \Phi_{Ii} \hat{\alpha}_{ij} \Phi_{jJ} \right) \psi_0 d\tau \\ &= \sum_{i,j} \alpha_{ij} \int \psi_1^* \Phi_{Ii} \Phi_{jJ} \psi_0 d\tau \quad i, j = x, y, z; \quad I, J = X, Y, Z, \end{aligned} \tag{8.59}$$

in which the Φ_{Ii} are the direction cosines, the ψ_i are rotational wavefunctions (ψ and Φ are both functions of the Euler angles θ, ϕ, χ , Figure 6.27) and α_{ij} is the polarizability component in the molecular frame. The direction cosines are required (Chapter 6) in order to transform between the laboratory and molecular coordinate systems. Selection rules for rotational Raman spectroscopy are derived from matrix elements of the *products* of the direction cosine matrix elements. As a result, $\Delta J = \pm 2$ transitions are possible. In simple terms, since there are two photons involved in a Raman transition, transitions with $\Delta J = \pm 2$ are possible.

Compare the previous results with pure rotational microwave transitions in which

$$\begin{aligned} \int \psi_1^* \hat{\mu}_I \psi_0 d\tau &= \int \psi_1^* \left(\sum_i \Phi_{Ii} \hat{\mu}_i \right) \psi_0 d\tau \\ &= \sum_i \mu_i \int \psi_1^* \Phi_{Ii} \psi_0 d\tau \quad I = X, Y, Z; \quad i = x, y, z. \end{aligned} \tag{8.60}$$

Again the integration is over the Euler angles, and μ_i are the dipole moment components averaged over vibrational and electronic variables. In this case the matrix elements of the direction cosines result in the selection rule, $\Delta J = \pm 1$.

v =

Figure 8.13

Diatomic

The selection rules for rotational Raman spectroscopy are $\Delta J = 0, \pm 2$. Only S and O lines correspond to $J' - J'' = 0$ and $J' - J'' = \pm 1$ respectively (Figure 8.13). The upper and lower lines are labeled $J = 0, \pm 1, \pm 2, \dots$ only R lines are observed. The transition is

where ν_0 is the vibrational frequency, ν_0 is spaced by $2B$ and ν_0 is the vibrational frequency of N_2 .

8.3 Vi

Diatomic

The selection rules for rotational Raman spectroscopy are $\Delta J = 0, \pm 2$. Only S and O lines are allowed. The transition is observed in Raman spectroscopy.

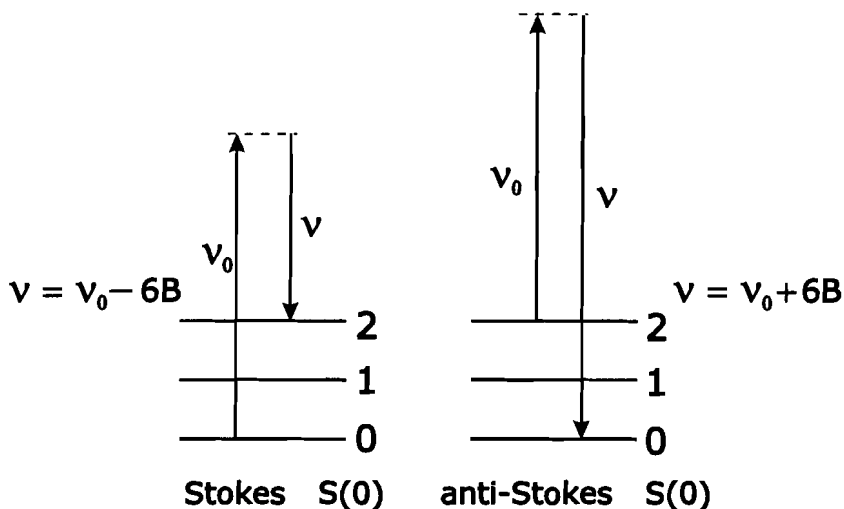


Figure 8.13: Stokes and anti-Stokes $S(0)$ transitions for the rotational Raman effect.

Diatomic Molecules

The selection rules for the rotational Raman effect in linear $^1\Sigma^+$ molecules are $\Delta J = 0, \pm 2$. Only S -branch transitions ($\Delta J = +2$) are observable since the $\Delta J = 0$ transitions correspond to the unshifted Rayleigh line. The definition of the S branch as $\Delta J = J' - J''$ means that both the Stokes and anti-Stokes transitions are S -branch lines (Figure 8.13), although this seems confusing at first sight. The definition of ΔJ is $J_{\text{upper}} - J_{\text{lower}}$, not $J_{\text{final}} - J_{\text{initial}}$, and as depicted in Figure 8.13, $J = 2$ is always above $J = 0$. As shown in Figure 8.13, $\Delta J = +2$ for both the Stokes and anti-Stokes $S(0)$ lines. The situation is analogous to microwave transitions of a linear molecule for which only R branch ($\Delta J = +1$) transitions occur in both emission $J + 1 \rightarrow J$ or absorption $J + 1 \leftarrow J$, although the initial and final states are different.

The transition frequencies are given by

$$\begin{aligned} \tilde{\nu} &= \tilde{\nu}_0 \pm (B(J + 2)(J + 3) - BJ(J + 1)) \\ &= \tilde{\nu}_0 \pm B(4J + 6) \end{aligned} \tag{8.61}$$

where \pm corresponds to anti-Stokes and Stokes transitions, respectively. The lines are spaced by about $4B$ from each other. Figure 8.14 shows the rotational Raman spectrum of N_2 .

8.3 Vibration-Rotation Raman Spectroscopy

Diatomic Molecules

The selection rules for vibration-rotation Raman spectroscopy for $^1\Sigma^+$ diatomic molecules are $\Delta v = \pm 1$ and $\Delta J = 0, \pm 2$. The vibrational transitions with $\Delta v = \pm 2, \pm 3, \dots$ are allowed weakly for the anharmonic oscillator, similar to infrared vibration-rotation spectroscopy.

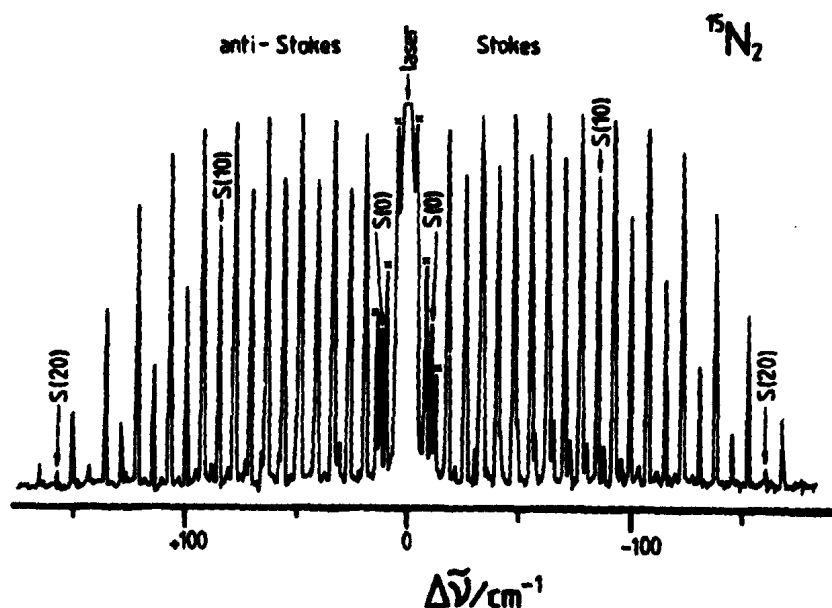


Figure 8.14: Rotational Raman spectrum of N_2 . Note the intensity alternation due to nuclear spin statistics and the x's that mark instrumental artifacts called grating ghosts.

The rotational selection rules $\Delta J = -2, 0, 2$ result in O , Q , and S branches, respectively, as shown in Figure 8.15. The vibration-rotation Raman spectrum of N_2 is shown in Figure 8.16.

The equations for the three branches are

$$\tilde{\nu}_S = \tilde{\nu}_0 - (6B' + (5B' - B'')J'' + (B' - B'')(J'')^2) \quad J'' = 0, 1, 2, \dots \quad (8.62)$$

$$\tilde{\nu}_Q = \tilde{\nu}_0 - ((B' - B'')J'' + (B' - B'')(J'')^2) \quad J'' = 0, 1, 2, \dots \quad (8.63)$$

and

$$\tilde{\nu}_O = \tilde{\nu}_0 - (2B' - (3B' + B'')J'' + (B' - B'')(J'')^2) \quad J'' = 2, 3, \dots \quad (8.64)$$

in which $\tilde{\nu}_0 = \tilde{\nu}_1 - \Delta G_{1/2}$ for the $1 \leftarrow 0$ Stokes spectrum. Notice that at high resolution (Figure 8.16), the Q -branch lines can be resolved at high J because of the $\Delta B J^2$ term in equation (8.63).

8.4 Rayleigh and Raman Intensities

Classical Theory

As discussed in Chapter 1, an oscillating classical dipole moment

$$\mu = \mu_0 \cos \omega t \quad (8.65)$$

Figure 8.16
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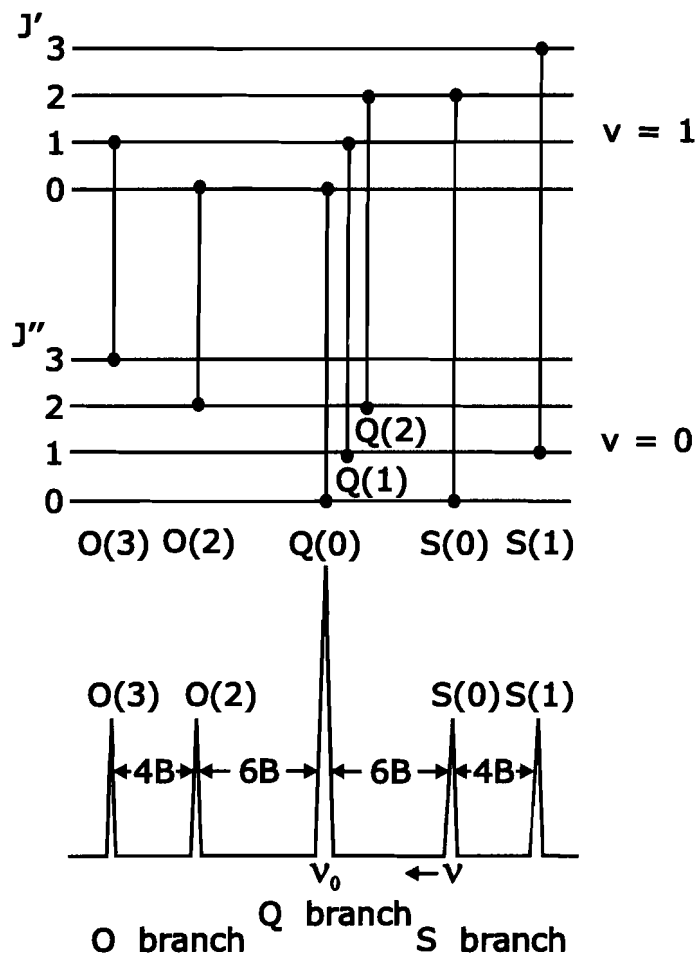


Figure 8.15: Energy-level diagram and spectrum for vibrational Raman scattering of a linear molecule.

radiates with total average power P (watts) given, from electromagnetic theory,⁷ by

$$\begin{aligned}
 P &= \frac{4\pi^3 \nu^4 |\mu_0|^2}{3\epsilon_0 c^3} \\
 &= \frac{4\pi^3 c}{3\epsilon_0 \lambda^4} |\mu_0|^2.
 \end{aligned}
 \tag{8.66}$$

In scattering, the incident electric field polarizes the molecule and induces a dipole moment, $\mu_{ind} = \alpha E$, equation (8.1). The electric field oscillation is given by

$$\mathbf{E} = \mathbf{E}_0 \cos \omega t
 \tag{8.67}$$

so μ_{ind} oscillates at the same angular frequency ω and radiates with a total average power

(8.65)

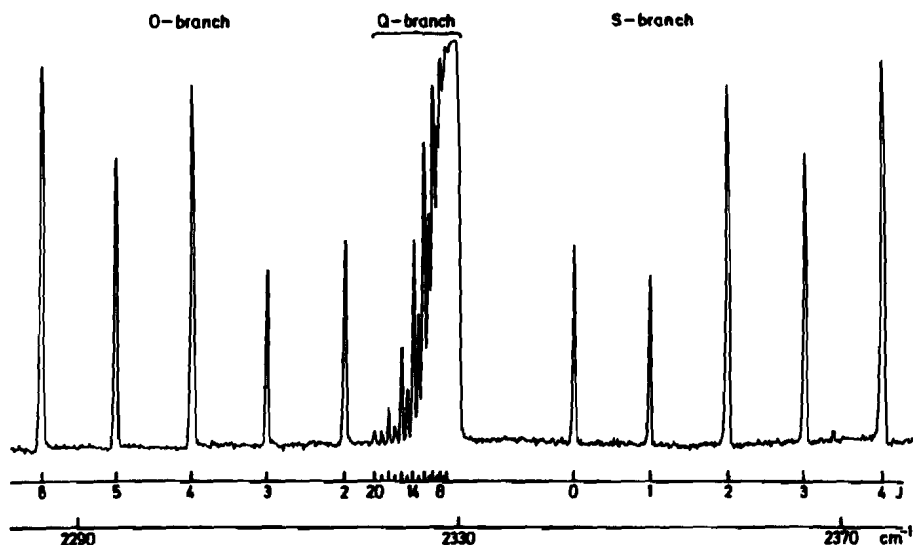


Figure 8.16: Vibration-rotation Raman spectrum of N_2 . Note the intensity alternation due to nuclear spin statistics.

$$P = \frac{4\pi^3 c (\alpha E_0)^2}{3\epsilon_0 \lambda^4} \quad (8.68)$$

In terms of the incident intensity $I = \epsilon_0 E_0^2 c / 2$ (equation (1.43)) the electromagnetic wave leads to

$$P = \frac{8\pi^3 \alpha^2 I}{3\epsilon_0^2 \lambda^4} \quad (8.69)$$

for the scattered power per molecule. A scattering cross section σ_{scat} can be defined as

$$\sigma_{\text{scat}} = \frac{P}{I} = \frac{8\pi^3 \alpha^2}{3\epsilon_0^2 \lambda^4} \quad (8.70)$$

and can be evaluated if a value for the mean polarizability $\alpha = \bar{\alpha}$ is available.

This scattering causes the extinction of a beam of light of intensity I_0 falling on a sample through an equation similar to Beer's law, as depicted in Figure 1.12,

$$I = I_0 e^{-\sigma_{\text{scat}} N l} = I_0 e^{-\alpha_{\text{scat}} l} \quad (8.71)$$

with the cross section σ_{scat} due to scattering out of the beam rather than absorption. In general, when a beam of light of intensity I_0 is transmitted through a sample, the light can be absorbed (with $\sigma = \sigma_{\text{abs}}$) as discussed in Chapter 1 or scattered (with σ_{scat} including both Rayleigh and Raman effects) as discussed here, so that the total extinction of the beam ($\sigma_{\text{abs}} + \sigma_{\text{scat}}$) is given as

$$I = I_0 e^{-(\sigma_{\text{abs}} + \sigma_{\text{scat}}) N l} \quad (8.72)$$

The mean polarizability $\bar{\alpha}$ can be computed for use in equation (8.70) by *ab initio* methods (e.g., Figure 8.4 for H_2) or obtained from refractive index data (Problem 7). In this example, the Rayleigh scattering of light by air leads to the attenuation coefficient

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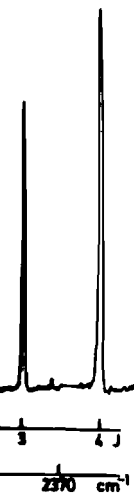
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8.4 Rayleigh and Raman Intensities

$$\alpha_{\text{scat}} = \frac{32\pi^3(n-1)^2\delta}{3\lambda^4 N}, \tag{8.73}$$

with N the air density in molecules/m³, n the refractive index of air (Chapter 1, Problem 2) and $\delta = 1.05$, a small correction for the anisotropy of the N₂ and O₂ molecules. Rayleigh scattering of sunlight leads to red sunsets and blue skies because of the λ^{-4} dependence of the attenuation coefficient α_{scat} of air.

Because Raman and Rayleigh scattering are so weak, a typical laboratory experiment does not involve measurement of the small intensity change in an incident laser beam as given by equation (8.71). Rather, a typical Raman experimental geometry is as shown in Figure 8.9, with the incident electric field \mathbf{E}_0 polarized parallel to the Z -axis and traveling in the X direction. The total scattered radiation, I' , is detected at 90° traveling in the Y direction, and polarized in the X and Z directions. A polarizer could be used to measure I'_{\parallel} and I'_{\perp} separately, but generally just the total intensity I' is detected. The observed intensity of the scattered light, I' , in this typical 90° scattering geometry is given from electromagnetic theory⁷ as

$$I' = \frac{\pi^2 \nu^4}{2\epsilon_0 c^3} |\mu_0|^2, \tag{8.74}$$

per molecule. The prime is used on the scattered intensity I' because the units are watts per steradian (not watts/m²). The incident radiation of intensity I_0 is an irradiance (Chapter 1) and has the usual units of watts/m². The oscillating electric field \mathbf{E}_0 is along the Z -axis so the induced moments needed for scattering are

$$\mu_Z = \alpha_{ZZ} E_{0Z} \tag{8.75}$$

$$\mu_X = \alpha_{XZ} E_{0Z}. \tag{8.76}$$

If there are N_0 molecules per m³ in the initial state $|0\rangle$ in the scattering volume V_S , and the incident intensity is $I_0 = \epsilon_0 c |E_0|^2 / 2$, then the scattered intensities become

$$I'_{\parallel} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \alpha_{ZZ}^2 N_0 V_S I_0, \tag{8.77}$$

$$I'_{\perp} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \alpha_{XZ}^2 N_0 V_S I_0, \tag{8.78}$$

and

$$I' = I'_{\parallel} + I'_{\perp} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} (\alpha_{XZ}^2 + \alpha_{ZZ}^2) N_0 V_S I_0. \tag{8.79}$$

The molecules in the sample, however, generally have random orientations except in the case of a single crystal, so that the polarizability elements must be averaged over the different molecular orientations.^{5,6} The transformation between the laboratory and molecular coordinate systems is given by direction cosines Φ_{li} (Chapter 6), and as shown in equation (8.59). The resulting average is given in terms of two quantities: the mean polarizability $\bar{\alpha}$ defined as

$$\bar{\alpha} \equiv (\alpha_x + \alpha_y + \alpha_z) / 3 \tag{8.80}$$

and the anisotropy γ , defined as

$$\gamma^2 \equiv ((\alpha_x - \alpha_y)^2 + (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2) / 2 \quad (8.81)$$

in the principal axis system. For the cases of linear and symmetric top molecules for which $\alpha_x = \alpha_y$, γ reduces to $\alpha_{\parallel} - \alpha_{\perp}$ (equation (8.15)). In particular, the required orientational averages are

$$\langle \alpha_{ZZ}^2 \rangle = \frac{45\bar{\alpha}^2 + 4\gamma^2}{45}, \quad (8.82)$$

$$\langle \alpha_{XZ}^2 \rangle = \frac{\gamma^2}{15}, \quad (8.83)$$

and

$$\langle \alpha_{ZZ}^2 \rangle + \langle \alpha_{XZ}^2 \rangle = \frac{45\bar{\alpha}^2 + 7\gamma^2}{45}. \quad (8.84)$$

The final intensity expressions for the scattered light are thus given in terms of $\bar{\alpha}$ and γ as

$$I'_{\parallel} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{45\bar{\alpha}^2 + 4\gamma^2}{45} \right) N_0 V_S I_0, \quad (8.85)$$

$$I'_{\perp} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{\gamma^2}{15} \right) N_0 V_S I_0, \quad (8.86)$$

and

$$I' = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{45\bar{\alpha}^2 + 7\gamma^2}{45} \right) N_0 V_S I_0. \quad (8.87)$$

The depolarization ratio $\rho = I_{\perp}/I_{\parallel}$ has the simple expression

$$\rho = \frac{3\gamma^2}{45\bar{\alpha}^2 + 4\gamma^2}. \quad (8.88)$$

As expected, for spherical tops $\gamma = 0$ so $\rho = 0$ and the scattered radiation is linearly polarized as if the molecule was spherical. Expressions (8.81) to (8.88) assume linearly polarized incident radiation as from a laser, but if unpolarized natural light is used, a slightly different set of expressions is obtained.⁶

As always some care with units is needed. The units of $\bar{\alpha}^2$ and γ^2 can be deduced from the basic equation (8.1) and are $\text{C}^2 \text{m}^4 \text{V}^{-2}$ or $\text{C}^4 \text{m}^4 \text{J}^{-2}$. The units to be used for the incident intensity I_0 are W m^{-2} and the scattered intensity I' is in W sr^{-1} , with N_0 in molecules per m^3 .

One of the main problems with scattering (Raman and Rayleigh) intensities, I' , is that equations such as (8.87) depend upon the particular experimental conditions, such as the 90° viewing geometry, the state of the incident polarization, the size of the scattering volume, and so forth. To remove at least some of the experimental parameters, a quantity called the differential scattering cross section ($d\sigma/d\Omega$) is defined by some authors as

$$\frac{d\sigma}{d\Omega} = \frac{I'}{N_0 V_S I_0} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{45\bar{\alpha}^2 + 7\gamma^2}{45} \right), \quad (8.89)$$

with units of m^2 per cross section. For such as (8.87)

Vibrations

The general specific case of the estimated in the band intensity summed for each (rather than

for a diatomic $\langle v' | \alpha_{ij} | r \rangle$

The first three are orthogonal harmonic $x = r - r_0$

for the $1 \leftarrow 0$ transition. The polarizability $1 \leftarrow 0$ at

Equation (8.87)

with

and

with units of m^2 per steradian. The concept of a differential scattering (or Raman) cross section is not particularly useful, and it is just as easy to use the full equations such as (8.87).

Vibrational Intensity Calculations

The general scattering intensity equations, (8.85) to (8.89), can be applied to the specific case of the vibrational Raman effect. Raman intensities of vibrational bands can be estimated in the "double harmonic" approximation analogous to infrared vibrational band intensities (Chapter 7). In the Raman case, the harmonic oscillator model is assumed for each vibrational mode as in the infrared, but it is the polarizability expansion (rather than the dipole expansion), that is truncated after the linear term: i.e.,

$$(8.84) \quad \alpha_{ij}(r) = \alpha_{e,ij} + \left. \frac{\partial \alpha_{ij}}{\partial r} \right|_{r_e} (r - r_e) \quad (8.90)$$

for a diatomic molecule. For the Raman transition from v to v' , the matrix element $\langle v' | \alpha_{ij}(r) | v \rangle$ is needed with

$$(8.85) \quad \langle v' | \alpha_{ij}(r) | v \rangle = \alpha_{e,ij} \langle v' | v \rangle + \left. \frac{\partial \alpha_{ij}}{\partial r} \right|_{r_e} \langle v' | r - r_e | v \rangle. \quad (8.91)$$

(8.86) The first term on the right-hand side of equation (8.91) is zero because ψ_v and $\psi_{v'}$ are orthogonal within a single electronic state, and the second term leads to the usual harmonic oscillator selection rules $\Delta v = \pm 1$ (Chapter 7). Using equation (7.56) with $x = r - r_e$ gives

$$(8.87) \quad \langle v + 1 | r - r_e | v \rangle = \left(\frac{\hbar}{2\mu_{AB}\omega} \right)^{1/2} \sqrt{v + 1} \quad (8.92)$$

for the $v + 1 \leftarrow v$ transition of the diatomic A—B with reduced mass μ_{AB} .

(8.88) The polarizability tensor elements α_{ij} for the fundamental vibrational band ($v = 1 \leftarrow 0$) are

$$\alpha_{ij} = \left(\frac{\hbar}{2\mu_{AB}\omega} \right)^{1/2} \left. \frac{\partial \alpha_{ij}}{\partial r} \right|_{r_e} = \left(\frac{h}{8\pi^2 \mu_{AB} \nu_{10}} \right)^{1/2} \left. \frac{\partial \alpha_{ij}}{\partial r} \right|_{r_e}. \quad (8.93)$$

Equation (8.93) can be combined with equation (8.87) to yield the intensity expression

$$(8.89) \quad I' = \frac{h}{8\epsilon_0^2 \lambda^4 \mu_{AB} \nu_{10}} \left(\frac{45(\bar{\alpha}')^2 + 7(\gamma')^2}{45} \right) N_0 V_S I_0 \quad (8.94)$$

with

$$\bar{\alpha}' = \left(\frac{\partial \alpha_x}{\partial r} + \frac{\partial \alpha_y}{\partial r} + \frac{\partial \alpha_z}{\partial r} \right) / 3 \quad (8.95)$$

and

$$(8.89) \quad (\gamma')^2 = \left(\left(\frac{\partial \alpha_x}{\partial r} - \frac{\partial \alpha_y}{\partial r} \right)^2 + \left(\frac{\partial \alpha_y}{\partial r} - \frac{\partial \alpha_z}{\partial r} \right)^2 + \left(\frac{\partial \alpha_z}{\partial r} - \frac{\partial \alpha_x}{\partial r} \right)^2 \right) / 2. \quad (8.96)$$

In equation (8.94), the primes on $\bar{\alpha}$ and γ denote derivatives, while on I the prime indicates that the units are watts/sr rather than watts/m².

The lower state population density N_0 can be replaced by the total population density N using the usual relationship for a harmonic oscillator from statistical thermodynamics,

$$N_0 = \frac{N}{q} = \frac{N}{1 - e^{-h\nu_{10}/kT}}, \quad (8.97)$$

in which q is the partition function for a simple harmonic oscillator. The final intensity equation for Stokes vibrational Raman scattering for the fundamental band of a diatomic thus becomes

$$I' = \frac{h(\nu - \nu_{10})^4 N V_S I_0}{8\varepsilon_0^2 c^4 \mu_{AB} \nu_{10} (1 - e^{-h\nu_{10}/kT})} \left(\frac{45(\bar{\alpha}')^2 + 7(\gamma')^2}{45} \right). \quad (8.98)$$

For polyatomic molecules the polarizability is expanded in terms of the normal mode Q_k with

$$\alpha_{ij}(Q_k) = \alpha_{e,ij} + \left. \frac{\partial \alpha_{ij}}{\partial Q_k} \right|_0 Q_k. \quad (8.99)$$

The expression for the scattered intensity for mode Q_k is then

$$I'_k = \frac{h}{8\varepsilon_0^2 \lambda^4 \nu_k} \left(\frac{45(\bar{\alpha}'_k)^2 + 7(\gamma'_k)^2}{45} \right) N_0 V_S I_0, \quad (8.100)$$

with the definitions

$$\bar{\alpha}'_k \equiv \left(\frac{\partial \alpha_x}{\partial Q_k} + \frac{\partial \alpha_y}{\partial Q_k} + \frac{\partial \alpha_z}{\partial Q_k} \right) / 3 \quad (8.101)$$

and

$$(\gamma'_k)^2 \equiv \left(\left(\frac{\partial \alpha_x}{\partial Q_k} - \frac{\partial \alpha_y}{\partial Q_k} \right)^2 + \left(\frac{\partial \alpha_y}{\partial Q_k} - \frac{\partial \alpha_z}{\partial Q_k} \right)^2 + \left(\frac{\partial \alpha_z}{\partial Q_k} - \frac{\partial \alpha_x}{\partial Q_k} \right)^2 \right) / 2 \quad (8.102)$$

For a polyatomic molecule, the equation corresponding to (8.98) for Stokes Raman scattering by a fundamental mode Q_k is given similarly by

$$I'_k = \frac{h(\nu - \nu_k)^4 N V_S I_0}{8\varepsilon_0^2 c^4 \nu_k q_v} \left(\frac{45(\bar{\alpha}'_k)^2 + 7(\gamma'_k)^2}{45} \right), \quad (8.103)$$

with q_v the total vibrational partition function. The formula (8.88) for the depolarization ratio also applies, but with the polarizability derivatives, $\bar{\alpha}'$ and γ' , replacing the polarizabilities, $\bar{\alpha}$ and γ .

The units of polarizability, α , are not always easy to understand because the SI units of C m² V⁻¹ obtained from the basic equation (8.1) are often not encountered. If equation (8.1) is used with cgs units, then surprisingly the dimensions of α are cm³ so α values are traditionally reported in Å³ (1 Å³ = 10⁻²⁴ cm³). One can imagine that the polarizability ellipsoid has this "pseudo volume" in these non-SI units. The conversion from polarizabilities in Å³ to C m² V⁻¹ involves multiplication by the factor of $4\pi\varepsilon_0 \times 10^{-6}$, i.e.,

$$\alpha/(\text{C m}^2 \text{ V}^{-1}) = 1.112\,650\,1 \times 10^{-16} \alpha/(\text{cm}^3) \quad (8.104)$$

$$= 1.112\,650\,1 \times 10^{-40} \alpha/(\text{\AA}^3) \quad (8.105)$$

Ab initio computer programs use atomic units internally, and the atomic units for polarizability can be deduced from equation (8.51). The atomic units for α are $a_0^2 e^2 / E_h$, with a_0 the Bohr radius and E_h the hartree (1 hartree = $2 R_\infty = 219\,474.631\,2 \text{ cm}^{-1}$). The numerical conversion factor from atomic units is given as

$$\alpha/(\text{C m}^2 \text{ V}^{-1}) = 1.648\,777\,2 \times 10^{-41} \alpha/(a_0^2 e^2 E_h^{-1}). \quad (8.106)$$

8.5 Conclusions

There has been a renaissance in Raman spectroscopy with the availability of lasers, Fourier transform spectrometers, and sensitive array detectors. Although Rayleigh scattering is weak and Raman scattering even weaker (typically 10^{-6} of the incident radiation), Raman spectroscopy has a number of important attributes.

Raman spectroscopy has different selection rules than do direct electronic, vibrational, and rotational spectroscopies, so it provides complementary information, especially for centrosymmetric molecules. Raman spectroscopy uses visible light to obtain electronic, vibrational, and rotational information about molecules. Since the technology for generating, manipulating, and detecting visible light is often more advanced than the corresponding infrared and millimeter wave technology, this can provide an important experimental advantage. The water molecule is a relatively weak Raman scatterer but a strong infrared absorber. Because of this fact, Raman spectroscopy is often the technique of choice for the vibrational spectroscopy of molecules in aqueous environments. For example, the vibrational spectroscopy of biological samples (which are altered by dehydration) is usually best carried out by Raman scattering.

Problems

1. Which normal modes of ethylene are Raman active? (See Problem 1 of Chapter 7.)
2. For the molecules in Problem 2 of Chapter 7, which modes are infrared active and which are Raman active?
3. Discuss the Raman activity of the normal modes of the molecules in Problems 4, 5, 12, 14, 15, 16, and 17 of Chapter 7.
4. For the ICl molecule the following spectroscopic constants are listed in Huber and Herzberg's book:

$$\begin{aligned} \omega_e &= 384.293 \text{ cm}^{-1} \\ \omega_e x_e &= 1.501 \text{ cm}^{-1} \\ B_e &= 0.114\,158\,7 \text{ cm}^{-1} \\ \alpha_e &= 0.000\,535\,4 \text{ cm}^{-1}. \end{aligned}$$

- (a) Predict the pure rotational Raman spectrum. What will be the Raman shift of the two lines closest to the exciting laser line?
- (b) Predict the pattern of the Stokes vibration-rotation Raman spectrum for the fundamental band. What will be the Raman shifts of the $S(0)$ and $O(2)$ lines from the exciting laser line at 5145 \AA ?
5. Fill in the following table with a yes (Y) or a no (N) to indicate allowed spectroscopic transitions. Answer yes if one or more modes or transitions are allowed, and no if all modes or transitions are forbidden.

Molecule	Rotational	Vibrational	Rotational Raman	Vibrational Raman
H ₂ O				
SF ₆				
CS ₂				
N ₂ O				
Allene				
Benzene				
Cl ₂				

6. The vibrational Raman spectrum of the SO_3^{2-} anion of C_{3v} symmetry exhibits four bands in aqueous solution: 966 cm^{-1} (strong, p); 933 cm^{-1} (shoulder, dp); 620 cm^{-1} (weak, p); and 473 cm^{-1} (dp) (p = polarized; dp = depolarized). Assign the symmetries of the bands and describe the motion of the normal modes.
7. The attenuation of sunlight by Rayleigh scattering is described by equation (8.71).
- (a) Derive equation (8.73) using the Lorentz-Lorenz relationship between the mean polarizability $\bar{\alpha}$ and the refractive index n :

$$\bar{\alpha}N = 3\epsilon_0 \frac{n^2 - 1}{n^2 + 2}$$

N is the molecular density in molecules/ m^3 .

- (b) At 500 nm , what is the amount of direct sunlight ($1 - I/I_0$) removed by Rayleigh scattering as measured by a person on the earth's surface? Use the refractive index for air (at 1 atm) given in Question 2 of Chapter 1. Assume that the atmospheric pressure p (and the density N , the quantity $n - 1$, and consequently σ_{scat}) obey the barometric law, $p/p_0 = e^{-z/H}$, with z the height above the ground and the atmospheric scale height, H , taken as 8 km . Do the calculation for a solar zenith angle of 0° , i.e., the sun is directly overhead. Take the temperature as 15°C and ignore its variation with height.
8. The mean polarizability $\bar{\alpha}$ of N_2 gas has been found to be 1.778 \AA^3 by measurement of the refractive index (Problem 7) at 5145 \AA . The polarizability anisotropy γ has been determined to be 0.714 \AA^3 by measurement of the depolarization of scattered light from an argon ion laser operating at 5145 \AA .

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- (a) What was the measured depolarization ratio?
- (b) The argon ion laser beam has a power of 1 W and is focused to a 10 μm spot (i.e., approximately a cube with 10- μm sides) in N_2 at 1 atm pressure. A 2-cm diameter lens with a focal length of 10 cm collects the photons scattered at 90° . What is the scattered power detected, assuming no optical or detector losses? How many photons/s are detected?
9. Pecul and Coriani (*Chem. Phys. Lett.* **355**, 377 (2002)) have calculated the derivatives of the mean polarizability $\bar{\alpha}' = \partial\alpha/\partial r$ and $\gamma' = \partial\gamma/\partial r$ at r_e for N_2 . At 5145 \AA , they obtained $\bar{\alpha}' = 6.61$ and $\gamma' = 7.80$ in atomic units. (*Hint*: Atomic units for $\bar{\alpha}'$ and γ' are $a_0 e^2 E_h^{-1}$, while atomic units for $\bar{\alpha}$ and γ are $a_0^2 e^2 E_h^{-1}$.)
- (a) What is the depolarization ratio for the fundamental Stokes Raman vibrational band?
- (b) For the experimental conditions of Problem 8, compute the scattered power for the Stokes Raman fundamental band at 2330 cm^{-1} .

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