3

Classical Theory of Rayleigh and Raman Scattering

Se non è vero, è molto ben trovato.

Giordano Bruno

3.1 INTRODUCTION

We now consider an approach to the theory of Rayleigh and Raman scattering in which both the electromagnetic radiation and the material system are treated classically. Although the classical theory cannot deal with all aspects of Rayleigh and Raman scattering it does provide useful insights into some facets of such scattering, particularly the frequency dependence, and also some aspects of the selection rules.

3.2 FIRST-ORDER INDUCED ELECTRIC DIPOLE

In this section we develop in more detail the procedures outlined in Chapter 2, Section 2.3, confining ourselves to Rayleigh scattering and vibrational Raman scattering. Our objective is to calculate for a molecule the frequency-dependent linear induced electric dipole vectors $p^{(1)}$, making use of the relationship

$$p^{(1)} = \alpha \cdot E \tag{3.2.1}$$

where E is the electric field vector of the incident, plane wave, monochromatic radiation of frequency ω_1, and $\boldsymbol{\alpha}$ is the polarizability tensor[‡] of the molecule. The polarizability tensor will, in general, be a function of the nuclear coordinates and hence of the molecular vibrational frequencies. We may therefore obtain the frequency-dependent induced electric dipole vectors $p^{(1)}$, by introducing into eq. (3.2.1) the frequency dependence of E and $\boldsymbol{\alpha}$. The amplitude of a linear induced electric dipole of a particular frequency enables the scattered intensity to be calculated using eq. (2.2.1).

We shall consider the scattering system to be one molecule which is free to vibrate, but does not rotate; that is, the molecule is space-fixed in its equilibrium configuration, but the nuclei may vibrate about their equilibrium positions. The variation of the polarizability with vibrations of the molecule can be expressed by expanding each component $\alpha_{\rho\sigma}$ of the polarizability tensor $\boldsymbol{\alpha}$ in a Taylor series with respect to the normal coordinates of vibration, as follows:

$$\alpha_{\rho\sigma} = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l \ldots \tag{3.2.2}$$

where $(\alpha_{\rho\sigma})_0$ is the value of $\alpha_{\rho\sigma}$ at the equilibrium configuration, $Q_k, Q_l \ldots$ are normal coordinates of vibration associated with the molecular vibrational frequencies $\omega_k, \omega_l \ldots$, and the summations are over all normal coordinates. The subscript '0' on the derivatives indicates that these are to be taken at the equilibrium configuration. We shall, for the time being, neglect the terms which involve powers of Q higher than the first. This approximation is often referred to as the electrical harmonic approximation.[§] We shall also fix our attention initially on one normal mode of vibration Q_k. We may then write eq. (3.2.2) in the special form

$$(\alpha_{\rho\sigma})_k = (\alpha_{\rho\sigma})_0 + (\alpha'_{\rho\sigma})_k Q_k \tag{3.2.3}$$

where

$$(\alpha'_{\rho\sigma})_k = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \tag{3.2.4}$$

The $(\alpha'_{\rho\sigma})_k$ are components of a new tensor $\boldsymbol{\alpha}'_k$ which we shall call a derived polarizability tensor, as all its components are polarizability derivatives with respect to the normal coordinate Q_k. The properties of the components of the derived polarizability tensor differ in some respects from $(\alpha_{\rho\sigma})_0$, the components of the equilibrium polarizability tensor $(\boldsymbol{\alpha})_0$, as we shall see subsequently. As eq. (3.2.3) is valid for all tensor components we may write

$$\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \boldsymbol{\alpha}'_k Q_k \tag{3.2.5}$$

where $\boldsymbol{\alpha}_k$ is a tensor with components $(\alpha_{\rho\sigma})_k$ and Q_k, a scalar quantity, multiplies all components of $\boldsymbol{\alpha}'_k$. Assuming simple harmonic motion, that is, mechanical harmonicity[§],

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[‡] Chapter A14 treats the polarizability tensor.
[§] Mechanical harmonicity in a molecular vibration means that the restoring force is proportional to the first power of the displacement Q_k. Similarly, electrical harmonicity means that the variation of the polarizability in a vibration is proportional to the first power of Q_k.

the time dependence of Q_k is given by

$$Q_k = Q_{k_0} \cos(\omega_k t + \delta_k) \tag{3.2.6}$$

where Q_{k_0} is the normal coordinate amplitude and δ_k a phase factor. Combining eq. (3.2.6) with eq. (3.2.5) we obtain the time dependence of the polarizability tensor resulting from the kth molecular vibration:

$$\boldsymbol{\alpha}_k = \boldsymbol{\alpha}_0 + \boldsymbol{\alpha}'_k Q_{k_0} \cos(\omega_k t + \delta_k) \tag{3.2.7}$$

We now introduce into eq. (3.2.1) the frequency dependence[‡] of $\boldsymbol{E}$ given by

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos \omega_1 t \tag{3.2.8}$$

and of $\boldsymbol{\alpha}_k$ given by eq. (3.2.7). We then obtain

$$\boldsymbol{p}^{(1)} = \boldsymbol{\alpha}_0 \boldsymbol{E}_0 \cos \omega_1 t + \boldsymbol{\alpha}'_k \boldsymbol{E}_0 Q_{k_0} \cos(\omega_k t + \delta) \cos \omega_1 t \tag{3.2.9}$$

Using the trigonometric identity

$$\cos A \cos B = \tfrac{1}{2}\{\cos(A + B) + \cos(A - B)\} \tag{3.2.10}$$

the second term in eq. (3.2.9) may be reformulated and we may then write the expression for $\boldsymbol{p}^{(1)}$ in the form

$$\boldsymbol{p}^{(1)} = \boldsymbol{p}^{(1)}(\omega_1) + \boldsymbol{p}^{(1)}(\omega_1 - \omega_k) + \boldsymbol{p}^{(1)}(\omega_1 + \omega_k) \tag{3.2.11}$$

Here

$$\boldsymbol{p}^{(1)}(\omega_1) = \boldsymbol{p}_0^{\text{Ray}} \cos \omega_1 t \tag{3.2.12}$$

with

$$\boldsymbol{p}_0^{\text{Ray}} = \boldsymbol{\alpha}^{\text{Ray}} \cdot \boldsymbol{E}_0 \tag{3.2.13}$$

and

$$\boldsymbol{\alpha}^{\text{Ray}} = \boldsymbol{\alpha}_0 \tag{3.2.14}$$

Also

$$\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_k) = \boldsymbol{p}_{k_0}^{\text{Ram}} \cos(\omega_1 \pm \omega_k \pm \delta_k)t \tag{3.2.15}$$

with

$$\boldsymbol{p}_{k_0}^{\text{Ram}} = \boldsymbol{\alpha}_k^{\text{Ram}} \cdot \boldsymbol{E}_0 \tag{3.2.16}$$

and

$$\boldsymbol{\alpha}_k^{\text{Ram}} = \tfrac{1}{2}\boldsymbol{\alpha}'_k Q_k \tag{3.2.17}$$

The cosine functions in eqs. (3.2.12) and (3.2.15) define the frequencies of the induced dipoles; and eqs. (3.2.14) and (3.2.17) define the classical Rayleigh and Raman scattering tensors introduced in eqs. (2.3.8) and (2.3.9) in Chapter 2.

[‡] Chapter A17 treats the frequency dependence of $\boldsymbol{E}$.

We have used the familiar trigonometric representation[‡] of sinusoidal phenomena in this treatment of the classical theory. However, as the exponential representation[‡] is used in all subsequent treatments, the appropriate equations are repeated below in the exponential representation:
for eq. 3.2.6

$$Q_k = \tfrac{1}{2}Q_{k_0}\{\exp-\mathrm{i}(\omega_k t + \delta_k) + \exp \mathrm{i}(\omega_k t + \delta_k)\} \tag{3.2.18}$$

for eq. 3.2.8

$$\boldsymbol{E} = \tfrac{1}{2}\boldsymbol{E}_0\{\exp-\mathrm{i}\omega_1 t + \exp \mathrm{i}\omega_1 t\} \tag{3.2.19}$$

for eq. 3.2.12

$$\boldsymbol{p}^{(1)}(\omega_1) = \tfrac{1}{2}\boldsymbol{p}_0^{\mathrm{Ray}}\{\exp-\mathrm{i}\omega_1 t + \exp \mathrm{i}\omega_1 t\} \tag{3.2.20}$$

for eq. 3.2.15

$$\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_k) = \tfrac{1}{2}\boldsymbol{p}_0^{\mathrm{Ram}}\{\exp-\mathrm{i}[(\omega_1 \pm \omega_k)t \pm \delta_k] + \exp \mathrm{i}[(\omega_1 \pm \omega_k)t \pm \delta_k]\} \tag{3.2.21}$$

3.3 FREQUENCY DEPENDENCE OF THE FIRST-ORDER INDUCED ELECTRIC DIPOLE

We see from eq. (3.2.11) that the linear induced electric dipole has three distinct frequency components: $\boldsymbol{p}^{(1)}(\omega_1)$, which gives rise to radiation at ω_1, and so accounts for Rayleigh scattering; $\boldsymbol{p}^{(1)}(\omega_1 - \omega_k)$, which gives rise to radiation at $\omega_1 - \omega_k$, and so accounts for Stokes Raman scattering; and $\boldsymbol{p}^{(1)}(\omega_1 + \omega_k)$, which gives rise to radiation at $\omega_1 + \omega_k$, and so accounts for anti-Stokes Raman scattering. It should be noted that, whereas the induced dipole $\boldsymbol{p}^{(1)}(\omega_1)$ has the same phase as that of the incident field, the induced dipoles $\boldsymbol{p}^{(1)}(\omega_1 \pm \omega_k)$ are shifted in phase relative to the incident field by δ_k. The quantity δ_k defines the phase of the normal vibration Q_k relative to the field and will be different for different molecules.

The time dependence of the electric field of the electromagnetic radiation of frequency ω_1 and the linear induced electric dipoles $\boldsymbol{p}^{(1)}$ which it can produce are compared in Fig. 3.1. In Fig. 3.1(a) the scattering molecule is not vibrating ($\omega_k = 0$) and the total induced electric dipole then has only one frequency component $\boldsymbol{p}^{(1)}(\omega_1)$ In Fig. 3.1(b), the scattering molecule is vibrating with frequency ω_k and the total induced electric dipole is resolvable into three frequency components:

$$\boldsymbol{p}^{(1)}(\omega_1), \ \boldsymbol{p}^{(1)}(\omega_1 - \omega_k) \quad \text{and} \quad \boldsymbol{p}^{(1)}(\omega_1 + \omega_k)$$

This relatively simple classical treatment provides us with a useful qualitative picture of the mechanisms of Rayleigh and Raman scattering. Rayleigh scattering arises from the electric dipole oscillating at ω_1 induced in the molecule by the electric field of the incident radiation, which itself oscillates at ω_1. Raman scattering arises from the electric dipoles oscillating at $\omega_1 \pm \omega_k$, which are produced when the electric dipole oscillating at ω_1 is

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[‡] Chapter A17 treats the trigonometric and exponential representations of sinusoidal phenomena such as electromagnetic waves.
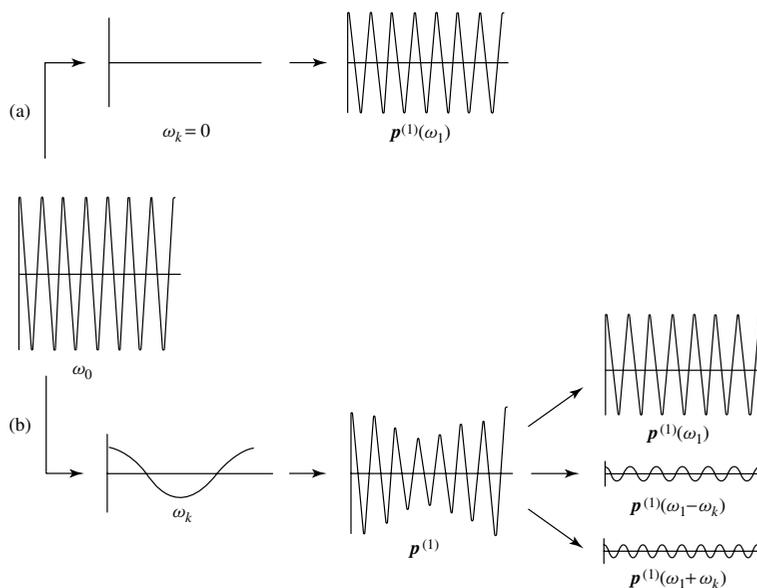
Figure 3.1 Time dependence of the linear induced dipoles $\boldsymbol{p}^{(1)}$ produced by electromagnetic radiation of frequency ω_1: (a) scattering molecule not vibrating $\omega_k = 0$: $\boldsymbol{p}^{(1)} = \boldsymbol{p}^{(1)}(\omega_1)$; (b) scattering molecule vibrating with frequency ω_k: $\boldsymbol{p}^{(1)} = \boldsymbol{p}^{(1)}(\omega_1) + \boldsymbol{p}^{(1)}(\omega_1 - \omega_k) + \boldsymbol{p}^{(1)}(\omega_1 + \omega_k)$.

modulated by the molecule oscillating at frequency ω_k. The necessary coupling between the nuclear motions and the electric field is provided by the electrons whose rearrangement with nuclear motion impose a harmonic variation on the polarizability. Alternatively, we may use a musical analogy and say that the frequencies observed in Raman scattering are beat frequencies between the radiation frequency ω_1 and the molecular frequency ω_k.

3.4 CLASSICAL SCATTERING TENSORS $\boldsymbol{\alpha}^{\text{Ray}}$ AND $\boldsymbol{\alpha}_k^{\text{Ram}}$

It is evident that the necessary condition for Rayleigh scattering is that $\boldsymbol{\alpha}^{\text{Ray}}$ be non-zero. As all molecules are polarizable to a greater or lesser extent, the classical equilibrium polarizability tensor $\boldsymbol{\alpha}_0$ will always have some non-zero components and so $\boldsymbol{\alpha}^{\text{Ray}}$ is always non-zero. Thus all molecules exhibit Rayleigh scattering.

The corresponding necessary condition for Raman scattering associated with a molecular frequency ω_k is that $\boldsymbol{\alpha}_k^{\text{Ram}}$ be non-zero. This requires that at least one of the components $(\alpha'_{\rho\sigma})_k$ of the derived polarizability tensor $\boldsymbol{\alpha}'_k$ is non-zero. We recall from eq. (3.2.4) that $(\alpha'_{\rho\sigma})_k$ is the derivative of the $\rho\sigma$ component of the polarizability tensor with respect to the normal coordinate of vibration Q_k, taken at the equilibrium position. Thus, the condition for Raman activity is that, for at least one component of the polarizability tensor, a plot of that component against the normal coordinate must have a non-zero gradient at the equilibrium position.

3.5 SELECTION RULES FOR FUNDAMENTAL VIBRATIONS

3.5.1 General considerations

In principle we can now determine the Raman activity of vibrations in particular molecules. However, the selection rules in their classical form, although appearing deceptively simple in concept, become progressively more difficult to apply as the complexity of the molecule increases. The ensuing discussion of a few specific cases will illustrate this.

In dealing with these specific cases it will be instructive to consider the infrared activity as well as the Raman activity so that comparisons can be made. We note that according to classical theory the condition for vibrational infrared activity is that at least one of the dipole moment component derivatives with respect to the normal coordinate Q_k, taken at the equilibrium position, should be non-zero. This means that, for at least one of the components of the dipole moment vector, a plot of that component against the normal coordinate must have a non-zero gradient at the equilibrium position.

3.5.2 Diatomic molecules

We shall consider first a homonuclear diatomic molecule A_2 which has just one mode of vibration. Such a molecule has no permanent dipole moment in the equilibrium position because of the symmetry of the electron distribution. This symmetry does not change with small changes in the internuclear separation, and so the dipole remains zero during a vibration and hence the derivative is zero. The vibration is therefore infrared inactive. We turn now to the question of Raman activity. Clearly the molecule has a non-zero polarizability, and we may represent this by a polarizability ellipsoid[‡], so oriented at equilibrium that it has one principal axis along the bond direction and its other two principal axes at right angles to the bond direction. Such an ellipsoid is defined by a maximum of three polarizability components. However, as we are considering a σ bond, the polarizability will be the same in all directions at right angles to the bond, and the polarizability tensor is then defined by just two components which we may designate as $\alpha_\parallel$, the polarizability along the bond, and $\alpha_\perp$, the polarizability at right angles to the bond. For a given internuclear separation the mean polarizability a is then given by $\frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$ and the anisotropy γ by $(\alpha_\parallel - \alpha_\perp)$. We have now to ask how these polarizability components change during the vibration of the A_2 molecule. It is not as easy as many texts would imply to deduce conclusively the properties of $(\partial\alpha_\parallel/\partial Q_k)_0$ and $(\partial\alpha_\perp/\partial Q_k)_0$ from *a priori* considerations of how electron distributions are affected by a change of internuclear distance.

Let us consider the specific case of the hydrogen molecule H_2. We can see that as the internuclear separation tends to zero the polarizability tends towards that of a helium atom, and as the internuclear separation tends to infinity the polarizability tends to that of two hydrogen atoms. As we know that the polarizability of two hydrogen atoms is greater than that of a helium atom, we can infer that, in general terms, the polarizability does change with internuclear separation. However, these limiting cases do not define the form of the

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[‡] Chapter A14 treats the polarizability ellipsoid, and also the mean polarizability and the anisotropy.
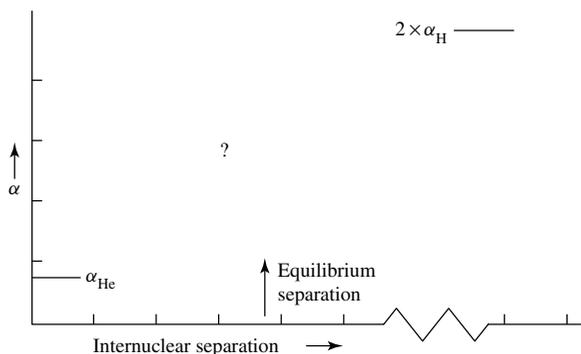
Figure 3.2 Polarizability and internuclear distance in the H_2 molecule with limiting values for zero and infinite internuclear distances.
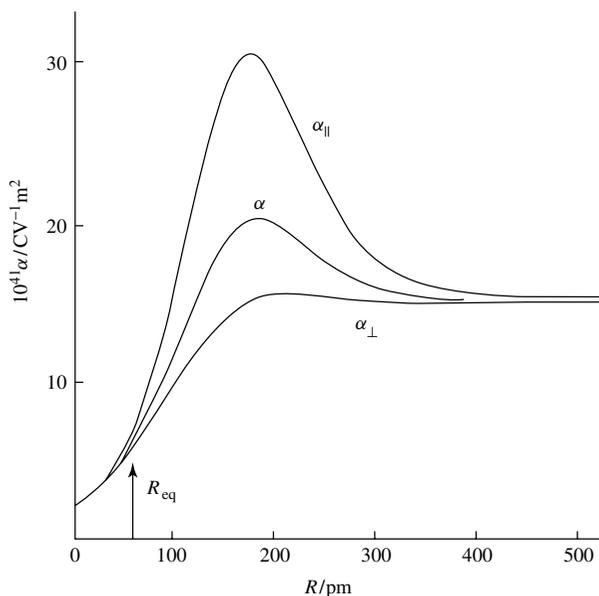
Figure 3.3 Plots of α, $\alpha_{\parallel}$, and $\alpha_{\perp}$ as functions of R, the internuclear distance, for the H_2 molecule. The mean polarizability α is shown only up to $R \approx 390$ pm so that the very close curves for $\alpha_{\parallel}$ and $\alpha_{\perp}$ above this distance remain distinct.

variation of the polarizability with internuclear separation, and in principle the derivative at the equilibrium internuclear separation could be positive, negative, or zero (Fig. 3.2). Also, as atoms have isotropic polarizabilities with $a \neq 0$ and $\gamma = 0$, whereas near the equilibrium position in H_2 we have $a \neq 0$ and $\gamma \neq 0$, the forms of the variation of a and γ with internuclear separation in H_2 must be different. For the fullest information, we must appeal to quantum mechanical calculations to ascertain the variation of the polarizability components with internuclear separation in the neighbourhood of the equilibrium position. The results of a typical calculation (Rychlewski, 1980) are presented in Fig. 3.3 and show
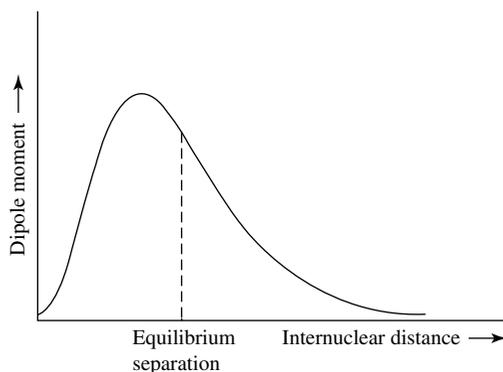
Figure 3.4   Variation of dipole moment with internuclear distance in a diatomic molecule AB (here the dipole moment derivative at the equilibrium separation is negative).

that both $(\partial\alpha_{\parallel}/\partial Q)_0$ and $(\partial\alpha_{\perp}/\partial Q)_0$ are non-zero and positive for values of the internuclear distance R up to about $R = 175$ pm. Further, the calculations show that $(\partial\alpha_{\parallel}/\partial Q)_0 > (\partial\alpha_{\perp}/\partial Q)_0$ and so $(\partial\gamma/\partial Q)_0$ is also non-zero and positive up to about $R = 175$ pm.

   These results for H_2 may be used to guide us towards some generalizations for other homonuclear diatomic molecules. In such molecules, we may also reasonably expect $(\partial\alpha_{\parallel}/\partial Q)_0$ and $(\partial\gamma/\partial Q)_0$ to be non-zero and of different magnitudes and hence $(\partial a/\partial Q)_0$ and $(\partial\gamma/\partial Q)_0$ to be non-zero. Thus, the vibrations of A_2 diatomic molecules will be Raman active. However the signs and relative magnitudes of these derivatives need not necessarily follow the pattern in H_2.

   We next consider the case of a heteronuclear diatomic molecule AB which also has just one mode of vibration. The arguments given above for polarizability changes in A_2 molecules can be expected to apply to AB molecules, and thus the vibration will be Raman active. The molecule AB will necessarily have a permanent dipole moment because there will be an asymmetry in its electron distribution. As the dipole moment must be zero for both infinitely large and zero internuclear separations, the normal form of the variation of the dipole moment component along the bond direction with internuclear distance will be as shown in Fig. 3.4. The components of the dipole at right angles to the bond direction are, of course, always zero. For infrared activity, the maximum dipole moment must occur at an internuclear distance different from the equilibrium distance, so that the derivative at the equilibrium position is non-zero. This is the case for all heteronuclear diatomic molecules and thus the vibration in AB molecules will be infrared active. The form of the plot of dipole moment against internuclear distance will, however, vary from one molecule to another, and thus the magnitude and sign of the derivative will also vary considerably. The A_2 and AB cases are compared in Fig. 3.5.

3.5.3 Polyatomic molecules

In polyatomic molecules, if we regard the total dipole moment as made up of contributions from individual bond dipoles (at least to a first approximation), then we may regard each

Figure 3.5 Comparison of polarizability and dipole moment variations in the neighbour-hood of the equilibrium position and vibrational Raman and infrared activities for an A_2 and an AB molecule.

heteronuclear bond as having a non-zero bond dipole derivative at the equilibrium position and combine such derivatives vectorially to determine infrared activities in particular modes of vibration, taking into account the relative phases of the motions in each bond.

Similarly, we may regard the total molecular polarizability as made up of contributions from individual bond polarizabilities (at least to a first approximation), and assume that these bond polarizabilities show the same qualitative behaviour as in H_2 (at least for σ bonds). However, in polyatomic molecules the forms of the vibrations are relatively complicated and involve, for example, the stretching and compression of more than one bond. The Raman activity of such a vibration depends on the components of the overall derived polarizability tensor which is formed by tensor addition of individual derived

bond polarizability tensors, taking into account the relative phases of the motions in each bond. It is profitable to consider only very simple polyatomic molecules as examples.

We examine first a linear symmetric molecule ABA. Such a molecule has four modes of vibration: a symmetric stretching mode Q_1, an antisymmetric stretching mode Q_2, and two bending modes Q_{3a} and Q_{3b} which form a degenerate pair and have the same frequency of vibration. These vibrations are illustrated in Fig. 3.6, and in the following discussion we shall take the z axis as the bond axis. This ABA molecule has no permanent dipole because of the symmetry of the electron distribution. For the symmetric stretching mode

Molecule			
Mode of vibration			
Variation of polarizability with normal coordinate (schematic)			
Polarizability derivative at equilibrium position	$\neq 0$	$= 0$	$= 0$
Raman activity	Yes	No	No
Variation of dipole moment with normal coordinate (schematic)			
Dipole moment derivative at equilibrium position	$= 0$	$\neq 0$	$\neq 0$
Infrared activity	No	Yes	Yes

Figure 3.6 Polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for a linear ABA molecule.

Q_1, in which both A$-$B bonds are stretched simultaneously in one phase and compressed simultaneously in the other phase, the non-zero bond dipole derivatives in the two A$-$B bonds always act in opposition and cancel each other exactly; the vibration is therefore infrared inactive. However, for this vibration the non-zero bond polarizability derivatives in the two A$-$B bonds are additive and the vibration is Raman active. Specifically, as the axes of the molecular polarizability ellipsoid do not change in this vibration, the molecular polarizability derivatives $(\partial \alpha_{xx}/\partial Q_1)_0 = (\partial \alpha_{yy}/\partial Q_1)_0$ and $(\partial \alpha_{zz}/\partial Q_1)_0$ are non-zero; also, $(\partial \alpha_{xy}/\partial Q_1)_0 = (\partial \alpha_{yz}/\partial Q_1)_0 = (\partial \alpha_{zx}/\partial Q_1)_0 = 0$. Thus, $(\partial a/\partial Q_1)_0$ and $(\partial \gamma/\partial Q_1)_0$ are both non-zero.

The situation is quite different for the antisymmetric stretching mode Q_2, in which one A$-$B bond is stretched (or compressed) as the other A$-$B bond is compressed (or stretched). The non-zero bond dipole derivatives are additive and thus this vibration is infrared active. However, the bond polarizability derivatives cancel each other and we have for the molecular polarizability derivatives $(\partial \alpha_{xx}/\partial Q_2)_0 = (\partial \alpha_{yy}/\partial Q_2)_0 = (\partial \alpha_{zz}/\partial Q_2)_0 = (\partial \alpha_{xy}/\partial Q_2) = (\partial \alpha_{yz}/\partial Q_2)_0 = (\partial \alpha_{zx}/\partial Q_2)_0 = 0$ and so $(\partial a/\partial Q_2)_0$ and $(\partial \gamma/\partial Q_2)_0$ are both zero. Thus, the Q_2 mode is Raman inactive.

For the degenerate bending modes Q_{3a} and Q_{3b}, as far as infrared activity is concerned, it is readily seen that the dipole moment derivatives at right angles to the molecular axis are non-zero and thus these vibrations are infrared active. However, all six molecular polarizability derivatives are zero for both modes. Thus, $(\partial a/\partial Q_{3a})_0 = (\partial a/\partial Q_{3b})_0 = (\partial \gamma/\partial Q_{3a})_0 = (\partial \gamma/\partial Q_{3b})_0 = 0$ and both modes are Raman inactive. The general forms of the dipole moment and polarizability changes with the various normal coordinates are included in Fig. 3.6.

Finally, we consider the case of a non-linear ABA molecule. Such a molecule has three modes of vibration: Q_1, a symmetric stretching mode; Q_2, a symmetric bending mode; and Q_3, an antisymmetric stretching mode. The forms of these modes and the axis system are given in Fig. 3.7. We may perhaps leave it to the reader to endeavour to convince himself that: (a) Q_1 is infrared active and also Raman active with $(\partial \alpha_{xx}/\partial Q_1)_0$, $(\partial \alpha_{yy}/\partial Q_1)_0$ and $(\partial \alpha_{zz}/\partial Q_1)_0$ non-zero, and $(\partial \alpha_{xy}/\partial Q_1)_0 = (\partial \alpha_{yz}/\partial Q_1)_0 = (\partial \alpha_{zx}/\partial Q_1)_0 = 0$ so that both $(\partial a/\partial Q_1)_0$ and $(\partial \gamma/\partial Q_1)_0$ are non-zero; (b) Q_2 is also both infrared active and Raman active with the same dipole and polarizability components non-zero. The case of Q_3 calls for a little more explanation. It is quite easy to see that Q_3 is infrared active; Q_3 is also Raman active. This activity arises because the space-fixed z and y axes no longer remain axes of the polarizability ellipsoid during the whole of the vibration. Thus, although α_{yz} is zero, in the equilibrium configuration $(\partial \alpha_{yz}/\partial Q_3)_0$ is non-zero. This is the only non-zero component of the derived polarizability for this mode, and hence $(\partial a/\partial Q_3)_0 = 0$, although $(\partial \gamma/\partial Q_3)_0$ is non-zero. Figure 3.7 shows the forms of the dipole moment and polarizability changes with the various normal coordinates.

Comparison of the vibrational activities in the molecules considered above shows that, for those molecules with a centre of symmetry, those vibrations which are Raman active are infrared inactive, and *vice versa*. This can be shown to be a general rule which is often termed the rule of mutual exclusion. It can form the basis for distinguishing between two alternative configurations of a molecule, for instance between a linear and a non-linear configuration for an ABA molecule. In many other cases, it is also possible to distinguish

Molecule			z x out of plane y
Mode of vibration			
Variation of polarizability with normal coordinate (schematic)			
Polarizability derivative at equilibrium position	$\neq 0$	$\neq 0$	$\neq 0$
Raman activity	Yes	Yes	Yes
Variation of dipole moment with normal coordinate (schematic)			
Dipole moment derivative at equilibrium position	$\neq 0$	$\neq 0$	$\neq 0$
Infrared activity	Yes	Yes	Yes

Figure 3.7 Polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for a non-linear A−B−A molecule.

between alternative configurations of a molecule by comparing the predicted numbers of vibrational modes which are Raman and/or infrared active. This has proved to be a valuable method of structural elucidation. Its main limitation is that, whereas observation of a band is proof of its activity, the converse is not necessarily true. Some bands, although permitted in principle, may fail to be observed, either because they are inherently weak or because of limitations in the experimental technique. A careful study of the literature will teach the spectroscopist the importance of tempered judgement and guarded optimism!

Broadly speaking, with molecules of relatively low symmetry all, or nearly all, vibrations are both infrared and Raman active. In molecules containing many atoms this might be thought to lead to vibrational spectra so rich in bands as to be unintelligible. In fact, in such molecules many of the vibrational frequencies are very close in value so that bands overlie each other and a relatively simple spectrum results. Thus even molecules such as DNA yield vibrational spectra with identifiable and characteristic features.

In some molecules, especially those of high symmetry, some vibrations may be both infrared and Raman inactive; however, such modes may be active in light-scattering spectra of non-linear origin, as for example in hyper-Raman spectra.

These qualitative considerations serve to indicate the importance of the symmetry of a molecule and its vibrational modes in determining infrared and Raman activity. It is also evident that the qualitative arguments used here would be difficult to apply to more complicated molecules. It would be difficult to infer with certainty the symmetry properties of the modes of vibration, let alone the behaviour of the dipole moment and the polarizability. Fortunately, there exist mathematical procedures which enable the symmetry properties of vibrational modes, dipole moment, and polarizability derivatives for molecules to be predicted for an assumed equilibrium configuration of the nuclei. We shall consider how such procedures operate after we have discussed quantum mechanical approaches to light-scattering phenomena. It should be noted in advance that these new procedures are completely independent of *special* assumptions regarding mechanical and electrical anharmonicity. They are derived solely on the basis of the symmetry of the vibrations and the electrical properties of the molecules and, consequently, have wide validity. However, these symmetry arguments tell us nothing about the intensity with which a vibrational band will appear in infrared or Raman spectra. Once again we emphasize that a vibration, while formally active, may be so weak as to be undetectable in practice.

3.6 SELECTION RULES FOR OVERTONES AND COMBINATIONS

In the foregoing we have been concerned entirely with fundamental vibrations; indeed, in the approximation of mechanical and electrical harmonicity, it would appear that only fundamental vibrations can occur. When anharmonicities are taken into account, overtone and combination bands are also permitted. Fortunately, in Raman spectra, unlike infrared spectra, such bands are almost invariably much weaker than the fundamentals. Vibrational Raman spectra are therefore usually much simpler than infrared spectra. However, it is worthwhile examining briefly the factors controlling the activity of overtone and combination bands in the Raman effect.

If mechanical anharmonicity is taken into account, the time dependence of the normal coordinate Q_k will not depend solely on $\cos(\omega_k t + \delta_k)$ as in eq. (3.2.6), but will include terms involving $\cos(2\omega_k t + \delta_{2k})$, $\cos(3\omega_k t + \delta_{3k})$ etc., which relate to overtones, and also terms involving $\cos(\omega_k t + \delta_{kl}) \cos(\omega_l t + \delta'_{kl})$ which relate to combination tones. As a consequence of the presence of these terms, there will be additional induced electric dipoles with frequencies $\omega_1 \pm 2\omega_k$ etc., and $\omega_1 \pm (\omega_k \pm \omega_l)$ etc. Thus, mechanical anharmonicity can lead to the observation of overtones and combinations in the Raman

effect. As $\boldsymbol{\alpha}'_k$ is unaffected by the introduction of mechanical anharmonicity, the same selection rules apply to the overtones and combination tones as to the fundamentals. For example, in a linear symmetric molecule ABA overtones of ω_1 (i.e $2\omega_1$, $3\omega_1$ etc.) would be Raman active, but not overtones of ω_2 or ω_3. Similarly, some combinations of ω_1 with ω_2 or ω_3 would be Raman active, but no combinations of ω_2 with ω_3.

The situation is different if electrical anharmonicity is taken into account. This means that the third (and possibly higher) terms in the Taylor series expansion of the polarizability in terms of the normal coordinates eq. (3.2.2) must be considered. The consequence of this is that there will again be additional induced electric dipoles with frequencies $\omega_1 \pm 2\omega_k$ etc. and $\omega_1 \pm (\omega_k \pm \omega_l)$ etc., but in this case these dipoles involve a new derived tensor with components of the type $(\partial^2\alpha_{\rho\sigma}/\partial Q_k^2)_0$, $(\partial^2\alpha_{\rho\sigma}/\partial Q_k \partial Q_l)_0$ and so on.

Thus overtones and combinations arising from electrical anharmonicity can be Raman active even if the fundamental vibration is not. For example, in a linear symmetric molecule ABA, although ω_2 and ω_3 are not Raman active, $2\omega_2$ and $2\omega_3$ are Raman active because, as can be seen from Fig. 3.6, although the first derivative of the polarizability is zero, the second derivative is not for ω_2 or ω_3.

3.7 COHERENCE PROPERTIES OF RAYLEIGH AND RAMAN SCATTERING

The classical treatment given earlier in Section 3.2 is based on a single scattering molecule which, although free to vibrate, is space-fixed in its equilibrium configuration. However in any experimental study scattering will be observed from a relatively large number of molecules and their orientations will not necessarily be fixed. For such an assembly of molecules there is an important difference between Rayleigh and Raman scattering. This difference arises because, as emphasized in Section 3.3, Rayleigh scattering is in phase with the incident radiation, whereas Raman scattering[‡] bears an arbitrary phase relation to the incident radiation. This is because the phase of Raman scattering depends on the phase of the molecular vibration (see eqs. 3.2.15 and 3.2.21) and this to a very good approximation varies arbitrarily from molecule to molecule. Thus the molecules act as independent sources of radiation irrespective of the degree of correlation between their positions. The situation is different for Rayleigh scattering because interference between the scattering from different molecules is possible and so the structural arrangement of the scattering molecules will play a role. For example, in the idealized case of a perfect crystal at absolute zero, this interference could result in the Rayleigh scattering averaging to zero. The strong dependence of Rayleigh scattering on the state of matter is illustrated by the fact that Rayleigh scattering from water is only 200 times stronger than from air, even though water contains 1200 times more molecules in the same volume. However, for scattering by an ideal gas, Rayleigh scattering is incoherent in non-forward directions and the intensity scattered by N molecules is simply N times that scattered by a single

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[‡] This statement specifically excludes higher-order coherent Raman-type processes such as CARS and CSRS, (see Chapter 1, Section 1.6) and SRGS and SRLS (see Chapter 1, Section 1.7).

molecule. In the forward direction the situation is less straightforward and depends on the relative contributions of the isotropic and anisotropic parts of the Rayleigh scattering.

With the coherence properties of Rayleigh and Raman scattering established we could proceed from the simple case of one space-fixed molecule to an assembly of freely rotating molecules and calculate the intensity and polarization properties of the scattered radiation as a function of the illumination–observation geometry.

However, these developments are not pursued here for the classical theory because of its limited validity, as explained in the next section.

3.8 LIMITATIONS OF THE CLASSICAL THEORY

The classical theory gives the correct frequency dependence for Rayleigh scattering and vibrational Raman scattering. It also shows, correctly, the dependence of the Rayleigh scattering tensor on the equilibrium polarizability tensor $\boldsymbol{\alpha}_0$, and its prediction of the dependence of the vibrational Raman scattering tensor on the derived polarizability tensor $\boldsymbol{\alpha}'_k$ turns out to be correct in certain situations. For those who want to use Raman spectroscopy merely to obtain characteristic molecular vibrational frequencies and use them as molecular signatures for qualitative analysis, the classical theory might be deemed adequate.

However, as might be expected, the classical theory has many limitations. It cannot be applied to molecular rotations as classical theory does not ascribe specific discrete rotational frequencies to molecules. The result for the vibrational Raman scattering tensor given by eq. (3.2.17) is only partly correct. When quantum mechanics is used for the treatment of molecular vibrations, the classical amplitude Q_k is replaced by a quantum mechanical amplitude. Also, the classical theory cannot provide information as to how $\boldsymbol{\alpha}'_k$ is related to the properties of the scattering molecule, in particular its characteristic transition frequencies, and to the frequency of the incident radiation. The quantum mechanical theory which will be developed in subsequent chapters provides this information and forms the basis for a complete treatment of all aspects of Raman scattering. This treatment will reveal Raman scattering as a powerful and versatile tool which can be used to determine molecular parameters and to explore in some detail the spectroscopic properties not only of the ground electronic state but also of upper electronic states of molecules. Like our own signatures, Raman spectra, when properly analysed, can reveal much about the character as well as the identity of the molecular signatory.

3.9 EXAMPLE OF RAYLEIGH AND RAMAN SCATTERING

In this section and the following one, both of which deal with observed spectra, we use wavenumber $\tilde{\nu}$ instead of the angular frequency ω which was appropriate for the theoretical treatment earlier in this chapter.

The phenomena of Rayleigh and Raman scattering are illustrated in Fig. 3.8, which includes facsimiles of two of the first spectra published by Raman and Krishnan. Figure 3.8(a) shows the photographically recorded spectrum of the essentially monochromatic radiation from a mercury arc used to produce the scattering; the
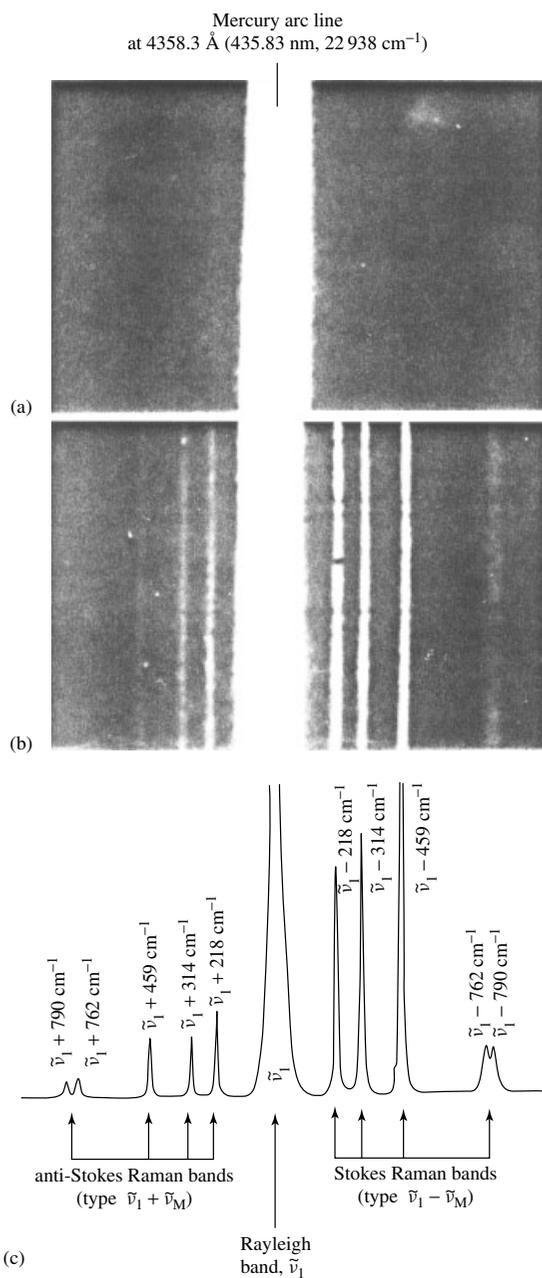
Figure 3.8 (a) Spectrum of a mercury arc in the region of 4358.3 Å (435.83 nm, $\tilde{\nu}_1 = 22\,938\,\text{cm}^{-1}$. (b) Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited by mercury arc radiation, $\tilde{\nu}_1 = 22\,938\,\text{cm}^{-1}$. (c) Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited by an argon ion laser, $\tilde{\nu}_1 = 20\,487\,\text{cm}^{-1}$ (4879.9 Å, 487.99 nm) and recorded directly. The spectra in (a) and (b) are facsimiles of spectra reported by Raman and Krishnan (1929) and were photographically recorded.

spectrum has one intense line[‡] at wavenumber $\tilde{\nu}_1 = 22\,938\,\text{cm}^{-1}$ (or wavelength 4358.3 Å, 435.83 nm). The mercury spectrum contains other lines in this region, but they are much weaker and need not be considered here. Figure 3.8(b) shows the photographically recorded spectrum of the radiation after scattering by carbon tetrachloride (liquid). This spectrum contains a strong band[‡] at $\tilde{\nu}_1 = 22938\,\text{cm}^{-1}$ due to Rayleigh scattering of the incident radiation, and a number of weaker bands whose absolute wavenumbers conform to the pattern $\tilde{\nu}_1 \pm \tilde{\nu}_M$ and are given by $\tilde{\nu}_1 \pm 218$, $\tilde{\nu}_1 \pm 314$, $\tilde{\nu}_1 \pm 459$, $\tilde{\nu}_1 - 762$ and $\tilde{\nu}_1 - 790\,\text{cm}^{-1}$. The first three pairs of bands arise from Stokes and anti-Stokes Raman scattering associated with $\tilde{\nu}_M$ values of 218, 314 and 459 cm^{-1}. The remaining two bands arise from Stokes Raman scattering associated with $\tilde{\nu}_M$ values of 762 and 790 cm^{-1}; the corresponding anti-Stokes bands are not observed. The $\tilde{\nu}_M$ values relate to fundamental vibrations of the carbon tetrachloride molecule.

Rayleigh and Raman scattering are now invariably excited by monochromatic radiation from a suitable laser and recorded directly, for example, photoelectrically. For comparison with Fig. 3.8(b), the Rayleigh and Raman spectra of carbon tetrachloride (liquid) excited with $20\,487\,\text{cm}^{-1}$ radiation (4879.9 Å, 487.99 nm) from an argon ion laser and directly recorded are shown in Fig. 3.8(c). In addition to all the bands observed previously, this spectrum contains the anti-Stokes bands at $\tilde{\nu}_1 + 762$ and $\tilde{\nu}_1 + 790\,\text{cm}^{-1}$, which were missing from the spectrum in Fig. 3.8(b). Their very low intensity explains why they were not observed in the early work.

The patterns of bands observed in the spectra in Figs. 3.8(b) and 3.8(c) are entirely consistent with the theory developed in Sections 3.2 and 3.3. These spectra also show that Rayleigh scattering is much more intense than Raman scattering, and that Stokes Raman scattering is more intense than anti-Stokes Raman scattering with the ratio of the intensity of anti-Stokes to Stokes Raman scattering decreasing rapidly as $\tilde{\nu}_M$ increases. However, in order to interpret and understand these observations and other characteristic properties of the scattered radiation which can be measured by appropriately designed experiments, a knowledge of the theoretical developments treated in subsequent chapters is required.

3.10 PRESENTATION OF RAMAN SPECTRA

For a given Raman band let us denote its absolute peak wavenumber by $\tilde{\nu}'$ and define its wavenumber shift from $\tilde{\nu}_1$, the wavenumber of the exciting radiation, as $\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}'$. With this definition $\Delta\tilde{\nu}$ is positive for Stokes Raman scattering ($\tilde{\nu}' = \tilde{\nu}_1 - \tilde{\nu}_M$) and negative for anti-Stokes Raman scattering ($\tilde{\nu}' = \tilde{\nu}_1 + \tilde{\nu}_M$). The characteristic molecular property, the wavenumber[§] $\tilde{\nu}_M$ is given by $|\Delta\tilde{\nu}|$; for Stokes Raman scattering $\Delta\tilde{\nu} = \tilde{\nu}_M$.

Raman spectra are normally presented in terms of $\Delta\tilde{\nu}$ and not $\tilde{\nu}'$ unless some dependence on $\tilde{\nu}'$ needs to be emphasized. For Stokes Raman scattering $\tilde{\nu}_M$ can be used as an equivalent alternative to $\Delta\tilde{\nu}$. It has been recommended by IUPAC that Raman spectra should be plotted with the abscissa linear in the wavenumber shift $\Delta\tilde{\nu}$ (unit: cm^{-1}) increasing to the left, and the ordinate linear and proportional to the intensity. As an

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[‡] See Chapter 1, Section 1.8.
[§] See also Chapter 1, pages 4 and 5.
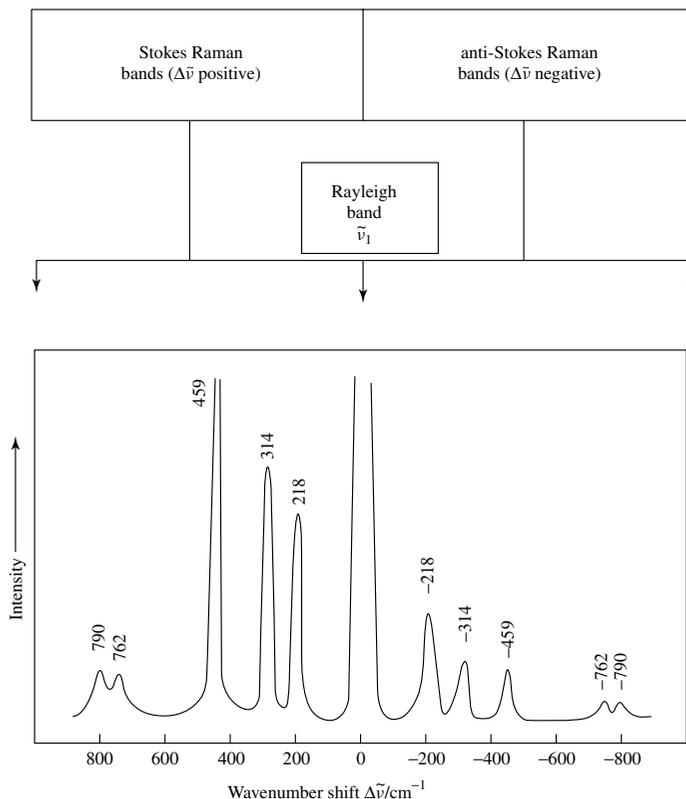
Figure 3.9 Rayleigh and Raman spectra of carbon tetrachloride (liquid) presented according to IUPAC recommendations. Note that normally only Stokes Raman bands are studied. It is then acceptable to label the abscissa as wavenumber/cm^{-1}.

example the directly recorded Raman spectrum of Fig. 3.8(c), which has the wavenumber shift increasing to the right in order to match the photographically recorded Raman spectrum of Fig. 3.8(b), has been redrawn in Fig. 3.9 to conform with the recommended conventions. The use of a quotient of a physical quantity and a unit, that is quantity calculus, in the labelling of the wavenumber axis should be noted. This practice means that the values of the quantities are presented as pure numbers. Quantity calculus should also be used for the intensity axis when the intensity has a specific unit; otherwise, the ordinate axis should be labelled 'intensity' with an arrow indicating that the intensity increases upwards as in Fig. 3.9.

For illustrative Raman spectra specially prepared for this book we shall follow the IUPAC conventions but Raman spectra taken from the literature will not be redrawn for conformity.

REFERENCES

Raman, C. V. and Krishnan, K. S. (1929). *Proc. Roy. Soc. Lond.* **122**, 23.
Rychlewski, J. (1980). *Molec. Phys.* **41**, 833.