

Spectroscopy

VOLUME TWO

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4 Infrared and raman spectroscopy

4.1 INTRODUCTION TO INFRARED AND RAMAN SPECTROSCOPY

The infrared and Raman methods in general yield similar types of information. They both provide a means of studying pure rotational, pure vibrational, and rotation–vibration energy changes in the ground state of simple and even complex molecules; however, for complex molecules the type of information which may be derived is more limited.

The two methods are based on quite different physical principles. Infrared spectroscopy is mainly concerned with the absorption of energy by a molecule, ion, or radical from a continuum (where the absorption occurs somewhere in the region $10\,000\text{--}200\text{ cm}^{-1}$) or with the study of the emission of infrared radiation by species in excited states. In contrast, Raman scattering functions by an entirely different mechanism and depends on the collision of a quantum of incident light with a molecule. The molecule can be induced by the collision to undergo a pure rotational, or a vibrational, or a rotation–vibration change. The scattered light quantum now has a different frequency from that of the incident light, and the difference corresponds to the energy change which has taken place within the molecule. The incident light employed is monochromatic and normally lies in the visible region of the spectrum (see p. 225).

Not only do the mechanisms differ for the two techniques, but the criterion as to whether a particular transition will be observed in the infrared or Raman spectrum depends on widely different principles. For example, the occurrence of a vibrational transition in the infrared region is dependent on an overall change of the electric dipole moment during the particular vibration. The Raman criterion, however, depends on a change in the polarizability during the

vibration. In addition, the intensity of the infrared spectrum is dependent on the magnitude of the dipole moment change, whereas the Raman intensity is related to how readily polarizable the vibrating atoms and their bonds are.

The infrared and Raman techniques can be used to study gases, liquids, and solids. Both methods have been applied to a wide variety of problems, and both have yielded desirable knowledge such as internuclear distances and vibrational frequencies. They have also been useful in the determination, by the statistical method, of thermodynamic quantities such as entropy and heat capacity; these have been calculated from the spectral moments of inertia and vibrational frequency data. The infrared approach has been much more prolific so far in determining moments of inertia and internuclear distances of simple molecules, but the Raman method is rapidly developing in this direction, now that laser sources are commercially available.

The vibrational frequencies obtained by these methods have been extensively used to fingerprint certain groups in different molecules, but more fundamental than this has been the use of vibrational frequencies in force constant work and in structural determinations. In fact, the latter has been a major line of investigation for both techniques.

For an unsymmetrical molecule every fundamental vibration is concerned with a change of electric dipole moment and therefore satisfies the criterion for absorption in the infrared region; in such a molecule there is also a change in polarizability during the vibrations, and therefore a Raman spectrum is produced. Thus, either method could be employed to obtain vibrational frequencies, although the intensities of bands are likely to be different in the two spectra. In contrast, for molecules with a centre of symmetry, e.g. CO_2 , C_2H_2 , and SF_6 , the rule of Mutual Exclusion[†] applies and the fundamental frequencies which appear in the Raman spectrum do not appear in the infrared spectrum and vice versa; the two methods are then complementary (see p. 253).

This chapter is concerned mainly with outlining the different types of problems studied by each method. The procedure adopted has been to divide the chapter into three sections: (A) Infrared spectra; (B) Raman spectra; (C) Correlation of infrared and Raman spectra. This division is one of convenience, and it must not necessarily be supposed that the points common to the Raman and infrared methods are to be found only under Section C. In fact, some of the problems studied by the infrared method in Section A could well be studied by the Raman or even by both together. In a way, Section C is an attempt to stress that the methods often work hand in hand. This is especially true for the structural studies of polyatomic molecules.

[†] For molecules with a centre of symmetry, fundamental transitions which are active in the infrared are forbidden in the Raman and vice versa.

concludes that either $\text{Ni}(\text{CO})_3$ is planar and $\text{Ni}(\text{CO})_2$ is linear or the intensities of the a_1 modes for the non-planar and angular geometries are too weak to be observed. For more detailed accounts of the matrix techniques, readers are referred to the reviews given in ref. 4.26b.

(B) RAMAN SPECTROSCOPY

4.11 INTRODUCTION

In contrast to infrared spectroscopy, where we have been concerned with the *absorption* of infrared light, Raman spectroscopy depends on the frequency of the light *scattered* by molecules as they undergo rotations and vibrations. When monochromatic light of frequency ν_0 is directed at a cell containing a dust-free transparent substance, most of the light passes through unaffected. Some of the light, however (~ 0.1 per cent) is *scattered* by the sample molecules in all directions, as shown in Fig. 4.45. The scattered radiation contains photons which have the same frequency ν_0 as the incident light (elastic scattering), but in addition the emergent radiation contains other frequencies (due to inelastic scattering) such as $(\nu_0 - \nu_1)$ and $(\nu_0 + \nu_1)$. This was observed by Raman in 1928 but it had been predicted by Smekal in 1923. The lines of lower frequency than the incident light ($\nu_0 - \nu_1$) are known as *Stokes lines*, while the high-frequency lines ($\nu_0 + \nu_1$) are termed *anti-Stokes lines*.

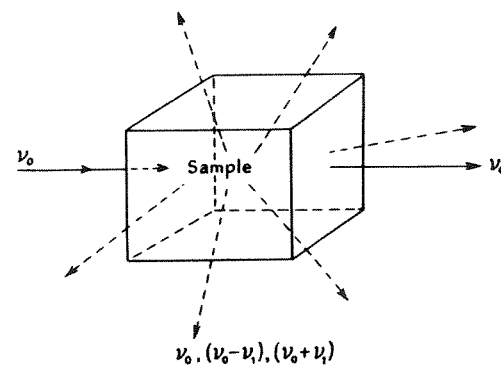


Fig. 4.45 Appearance of scattered light with frequencies ν_0 , $(\nu_0 + \nu_1)$, and $(\nu_0 - \nu_1)$.

Normally, an intense monochromatic source of light in the visible region is employed as the incident or exciting radiation. The 4358 Å line from a mercury Toronto arc was commonly used until the 1960s, but this has now been superseded by the highly monochromatic and intense lines available from various

gas lasers, e.g. 6328 Å red (helium–neon laser), 4880 Å blue and 5145 Å green (argon laser), 5681 Å yellow and 6471 Å red (krypton laser).

The Raman scattered light is due to rotations and vibrations of the compound under investigation. Since the wavenumber position of the exciting line is approximately $20\,000\text{ cm}^{-1}$ (i.e. 5000 Å), the Raman scattered light will have frequencies which are displaced from $20\,000\text{ cm}^{-1}$ by amounts which lie somewhere in the range $\pm 10\text{--}4000\text{ cm}^{-1}$. The exact wavenumber displacements, $\Delta\bar{\nu}$, will depend upon the rotational and vibrational energies of the particular compound causing the Raman scattering. The same displacement will occur on either side of the exciting line.

The total intensity of all the scattered light is only of the order of $10^{-3}\text{--}10^{-5}$ times the intensity of the incident light and a large part of this light has the same frequency ν_0 as the incident light and is known as Rayleigh scattering. Raman scattered light accounts for $< 10^{-7}$ of the intensity of the incident light, so the Raman effect is very weak indeed. It is therefore essential to use monochromators with very low stray-light characteristics otherwise the weak Raman effect will be 'swamped'. It is also necessary to use very sensitive detectors and efficient optical systems. The relative intensities of the Stokes and anti-Stokes lines are also worth mentioning at this stage. For vibrational transitions, the anti-Stokes (blue shifted) lines are usually considerably weaker than the Stokes (red shifted) lines (see p.234). Since the same frequencies are occurring in both sets of lines, there is no point in most cases in recording spectra on the anti-Stokes side of the exciting line and so most published spectra show the Stokes frequencies only. Figure 4.46 shows the Stokes and anti-Stokes lines of carbon tetrachloride examined as a liquid under low resolution. The detailed analysis of this compound will be dealt with later (see p.257) but the following general points require emphasis.

(1) It should be appreciated that the values of the observed Raman frequencies (in this case the vibrational modes of CCl_4) are completely independent of the laser line that is chosen to excite them. The Raman lines of CCl_4 will be displaced from the frequency of any particular exciting line by 218, 314 cm^{-1} , etc.

(2) The choice of a particular laser line is governed by the requirement that it should be sufficiently intense (i.e. $> 10\text{ mW}$ at the sample) and that the molecule itself should not show its normal electronic absorption or fluorescence spectrum in the region of the chosen line. Thus, the 4880 Å blue line is quite unsuitable for the routine investigation of deeply coloured red compounds such as KMnO_4 .

4.12 EXPERIMENTAL RAMAN SPECTROSCOPY

Raman spectra may be obtained from solids, liquids, gases, and solutions. All Raman spectrometers consist basically of four units – a source, sample optics, a monochromator, and a detector/electronics/recorder system. The sample optics (see Fig. 4.47) must be arranged so that as much scattered light as possible reaches the spectrometer, while the monochromator must have excellent stray-light

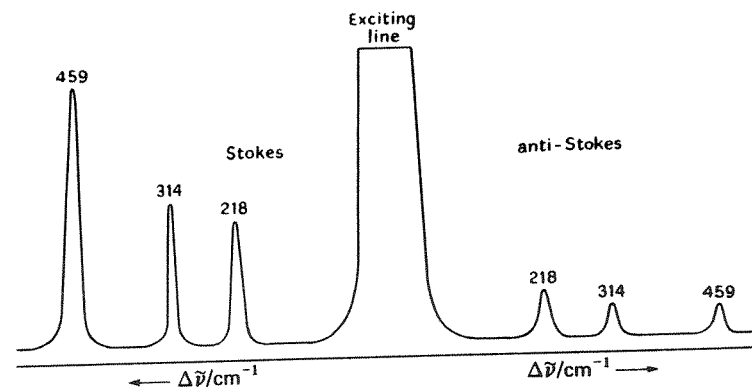


Fig. 4.46 Raman spectrum of CCl_4 liquid showing Stokes and anti-Stokes lines.

characteristics because of the very weak Raman effect. This leads to very sophisticated instrumentation involving double and even triple monochromators. Some general comments about sources and detectors will now be given.

4.12.1 Sources

Low-pressure mercury discharge lamps, which emit an intense blue line at 4358 Å, are frequently employed as radiation sources on older instruments. The discharge, however, produces several other mercury lines (e.g. 4047 Å) and these must be prevented from reaching the sample by surrounding the source with a filter solution (e.g. concentrated sodium nitrate solution). Otherwise the subsidiary lines will also act as exciting lines and a complicated spectrum of overlapping Raman lines would result. The mercury arc lamps have several other serious disadvantages as sources for Raman spectroscopy: (a) the blue line at 4358 Å effectively limits investigations to colourless compounds; even pale yellow liquids absorb this line; (b) comparatively large volumes ($\sim 5\text{ ml}$) of either a pure liquid or a very concentrated solution are required in order to obtain spectra of adequate intensity; (c) solids are difficult to illuminate using an arc source, and poor quality spectra are usually obtained.

The advent of stable lasers as exciting sources has completely revolutionised the usefulness of Raman spectroscopy. The majority of lasers in use are filled with noble gases, i.e. He–Ne mixture, Ar, or Kr. They produce highly monochromatic, coherent radiation and the diameter of the beam is usually about 2 mm. The beam is easily focused and the Brewster windows on the laser confer a specific polarization on the radiation. Power outputs ranging from 30 mW to one watt are readily obtainable from various commercial lasers, and all of these properties make lasers almost ideal sources for Raman spectroscopy. An obvious improvement would be a laser which was completely tunable over the whole of

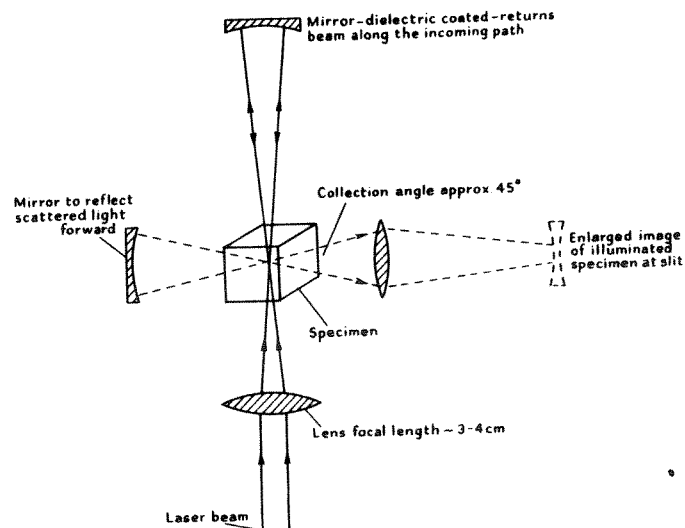


Fig. 4.47 A typical sample optics arrangement. (From ref. 4.27.)

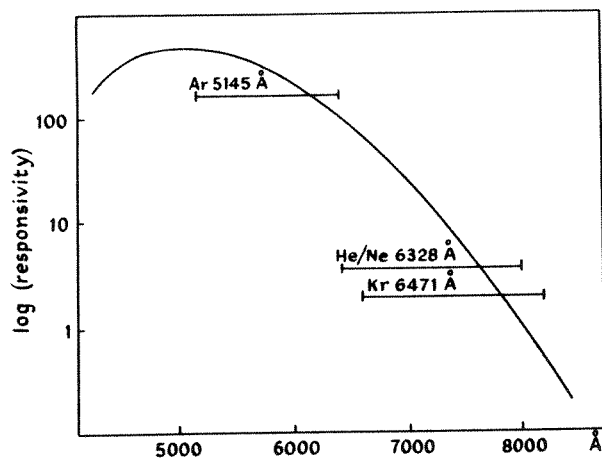


Fig. 4.48 The responsivity of the S20 photocathode surface. (From ref. 4.27.)

the visible region and extending into the infrared and ultraviolet regions; various dye lasers are a significant step in this direction.

4.12.2 Detectors

The early work in Raman spectroscopy used a camera and photographic plates to detect and record the spectrum. Exposure times varied from minutes to hours.

The normal detector for laser work is a multistage photomultiplier. It must be sensitive to a wide range of frequencies and it must have a very low noise character. A typical example is an I.T.T.F.W. 130 photomultiplier which has 16 stages and a cathode surface coated with Na, K, Cs, and Sb (the so-called S20 surface). The responsivity of the S20 photocathode surface is shown in Fig. 4.48 and the drop in sensitivity at the red end of the visible spectrum is apparent. This means that, all else being equal, a C-H stretching mode at $\sim 3000 \text{ cm}^{-1}$ will be much easier to detect using the $20\,490 \text{ cm}^{-1}$ (4880 Å) green line of an argon laser (it will appear at $20\,490 \pm 3000 \text{ cm}^{-1}$) than the red $15\,450 \text{ cm}^{-1}$ (6471 Å) line of a krypton laser (it will appear at $15\,450 \pm 3000 \text{ cm}^{-1}$).

4.12.3 Calibration

The usual method of checking the calibration of a spectrometer is to record the emission lines from the laser source being used. The standard wavenumber positions for the emission lines of neon, argon, and krypton can be found in ref.

4.2. For routine calibration checks, carbon tetrachloride and indene are frequently used. Table 4.9 gives the frequency shifts $\Delta\bar{\nu}$ for liquid indene.

Table 4.9 Raman frequencies of liquid indene

$\Delta\bar{\nu}/\text{cm}^{-1}$	Intensity	$\Delta\bar{\nu}/\text{cm}^{-1}$	Intensity
205.0	w	1286.7	vw
533.7	ms	1361.6	wm
593.0	w	1393.6	wm
730.4	s	1457.6	wm
831.0	mw	1552.7	s
861.0	w	1589.8	w
947.8	w	1610.2	ms
1018.3	s	2892.2	ms
1067.8	mw	2901.2	m
1108.9	mw	3054.7	m
1154.3	vw	3068.2	w
1205.6	s	3112.7	w
1225.6	mw		

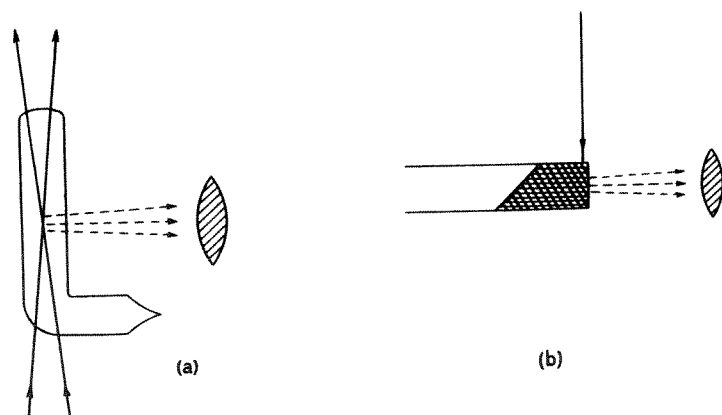


Fig. 4.49 Raman cells for gases, liquids, and solids. (a) Glass-sealed gas or liquid cell. (b) Powder in glass tube.

4.12.4 Examination of samples

The great ease with which samples in all three phases can be examined by laser Raman spectroscopy is one of the main reasons for the resurgence of interest in this technique. Figure 4.49 shows some typical presentations for gases, liquids, and solutions, and it is immediately obvious that samples can be measured (a) directly in reaction vessels, (b) in capillary tubes when only small amounts of liquid are available, (c) under a vacuum or controlled atmosphere, or (d) at various temperatures and pressures. Solids can be examined by holding the sample directly in the beam if the solid is rigid enough or a powder can be packed into a capillary tube.

Single crystals (approximately 1–2 mm long) can be mounted easily in the laser beam. If the crystal is glued on to a glass fibre and then held in a goniometer, as for X-ray work, the unique polarization properties of the laser light can be exploited. Raman spectra can be measured for the crystal in different orientations, and, as we shall see in Section C, this enables the chemist unambiguously to assign the vibrational frequencies of molecules or ions to particular symmetry classes.

4.13 CLASSICAL THEORY OF THE RAMAN EFFECT AND THE SELECTION RULE FOR RAMAN SCATTERING

When a molecule is introduced into an electric field of strength E an electric dipole moment P is induced in the molecule. If α is the polarizability of the molecule, the magnitude of the induced dipole moment is given by:

$$|P| = \alpha |E| \quad (4.97)$$

Classical theory of the Raman effect

When electromagnetic radiation of frequency ν_0 falls on the molecule this introduces a varying electric field, E , whose dependence on the time t is given by:

$$E = E^0 \cos 2\pi\nu_0 t \quad (4.98)$$

where E^0 is the amplitude of the electric field. Hence, from Equations (4.97) and (4.98):

$$P = \alpha E^0 \cos 2\pi\nu_0 t \quad (4.99)$$

Thus, the electromagnetic radiation induces a varying electric dipole moment which then permits emission of light identical in frequency with that of the incident radiation. This is *Rayleigh scattering*.

In the equation $|P| = \alpha |E|$, both P and E are vectors, and in the case of an isotropic molecule both their directions are identical. This makes α a *scalar*. However, for non-isotropic molecules the application of an electric field in a fixed direction induces a moment in a different direction, and α becomes a *tensor*. In general, molecules are non-isotropic, and the three equations which take account of the unequal polarizability along the different principal axes of the molecule are:

$$P_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \quad (4.100)$$

$$P_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \quad (4.101)$$

$$P_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \quad (4.102)$$

where for example P_z is the induced electric dipole moment in the direction of the z -axis. The meaning of a coefficient such as α_{xy} is that it is the electric moment induced in the x -direction by a unit field E_y polarized along the y -axis. The tensor α is defined by these nine coefficients $\alpha_{xx}, \alpha_{xy}, \dots, \alpha_{zz}$. However, since $\alpha_{xy} = \alpha_{yx}, \alpha_{yz} = \alpha_{zy},$ and $\alpha_{zx} = \alpha_{xz}$, the tensor α is really defined by six coefficients.

These six coefficients together with the coordinates $x, y,$ and z may be expressed in the equation:

$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 + 2\alpha_{xy}xy + 2\alpha_{yz}yz + 2\alpha_{zx}zx = 1 \quad (4.103)$$

This is the equation of an ellipsoid. Thus, the polarizability of the molecule is divided into three components at right angles along the $x, y,$ and z axes, and the values of these components fix the dimensions of what is termed the polarizability ellipsoid. *If any of the six polarizability tensor components change during a rotation or a vibration, then the theoretical criterion for a Raman spectrum is satisfied.* For very small vibrational amplitudes the polarizability of the molecule is related to the normal vibrational coordinate, q_ν by the equation:

$$\alpha = \alpha^0 + \left(\frac{\partial \alpha}{\partial q_\nu} \right) q_\nu \quad (4.104)$$

where the attached zero refers to the coordinate values at the equilibrium configuration. An equation such as (4.104) holds for each of the six coefficients which define α .

The dependence of the normal vibrational frequency ν_v on the normal coordinate q_v is given by:

$$q_v = q_0 \cos(2\pi\nu_v t) \quad (4.105)$$

where q_0 is the normal coordinate of the initial position.

By substitution of equations of the type (4.98) into Equation (4.100):

$$P_x = (\alpha_{xx}E_x^0 + \alpha_{xy}E_y^0 + \alpha_{xz}E_z^0) \cos 2\pi\nu_0 t \quad (4.106)$$

On substitution of α from Equation (4.104) and q_v from Equation (4.105) the following expression is obtained:

$$P_x = (\alpha_{xx}^0 E_x^0 + \alpha_{xy}^0 E_y^0 + \alpha_{xz}^0 E_z^0) \cos 2\pi\nu_0 t + \left[\left(\frac{\partial \alpha_{xx}}{\partial q_v} \right) E_x^0 + \left(\frac{\partial \alpha_{xy}}{\partial q_v} \right) E_y^0 + \left(\frac{\partial \alpha_{xz}}{\partial q_v} \right) E_z^0 \right] q_0 \cos 2\pi\nu_v t \cos 2\pi\nu_0 t \quad (4.107)$$

Equation (4.107) can be readily transformed into:

$$P_x = (\alpha_{xx}^0 E_x^0 + \alpha_{xy}^0 E_y^0 + \alpha_{xz}^0 E_z^0) \cos 2\pi\nu_0 t + \frac{q_0}{2} \left[\left(\frac{\partial \alpha_{xx}}{\partial q_v} \right) E_x^0 + \left(\frac{\partial \alpha_{xy}}{\partial q_v} \right) E_y^0 + \left(\frac{\partial \alpha_{xz}}{\partial q_v} \right) E_z^0 \right] [\cos 2\pi(\nu_0 - \nu_v)t + \cos 2\pi(\nu_0 + \nu_v)t] \quad (4.108)$$

The first term on the right-hand side of Equation (4.108) contains only one frequency factor ν_0 which is that of the incident radiation. This term is interpreted in terms of Rayleigh scattering. The second term on the right-hand side contains, in addition to the incident frequency ν_0 , the frequencies $(\nu_0 \pm \nu_v)$. Thus, the induced dipole moment can also oscillate with the two frequencies:

$$(\nu_0 + \nu_v) \quad \text{and} \quad (\nu_0 - \nu_v)$$

These two frequencies are interpreted as the vibrational Raman frequencies. The $(\nu_0 - \nu_v)$ and $(\nu_0 + \nu_v)$ frequencies are known, respectively, as the *Stokes* and *anti-Stokes lines*. The intensity of the Raman lines for a light source of fixed intensity is determined by the value of $(\partial\alpha/\partial q_v)_0$. In fact, the properties of Raman radiation (e.g. state of polarization, see later) are determined by the tensor $(\partial\alpha/\partial q_v)_0$. Equation (4.104) is important since the α_0 in the first term on the right-hand side determines the properties of Rayleigh radiation, while in the second term $(\partial\alpha/\partial q_v)_0$ determines the properties of Raman radiation.

For a pure rotational change of a diatomic molecule it can be shown that the three frequencies are ν_0 , $(\nu_0 - 2\nu_r)$, and $(\nu_0 + 2\nu_r)$, where $2\nu_r$ is the frequency corresponding to the increase of rotational energy. Thus, very simple classical considerations can explain the appearance of both vibrational and rotational changes and of Stokes and anti-Stokes lines. However, once the intensity of Stokes and anti-Stokes lines is considered, this classical theory is most

unsatisfactory, since it predicts that the Stokes and anti-Stokes lines should be of equal intensity, whereas, in practice for vibrational changes, the latter are very much less intense than the former. A quantum mechanical approach, however, predicts that the anti-Stokes lines will be much weaker than the Stokes lines for vibrational transitions (see p. 234).

As has been indicated already, the criterion for a vibrational Raman spectrum is that one or more of the dimensions of the polarizability ellipsoid must change during the vibration, in order that the vibration may interact with suitable electromagnetic radiation to produce a Raman effect. In the case of a diatomic molecule such as X_2 the polarizability components give an ellipsoid, and during the vibration $\leftarrow X-X \rightarrow$ the polarizability ellipsoid must change its dimensions. Thus, the condition for a Raman spectrum[†] is satisfied; it is also satisfied for $\leftarrow X-Y \rightarrow$. In order to decide which vibrational frequencies will appear as Raman frequencies each bond should be considered as associated with a polarizability ellipsoid, and the criterion for such a change is that the total polarization should change during the vibration. In the case of the parallel vibrations of carbon dioxide (see p. 170), for the $\bar{\nu}_1$ vibrational mode there is reinforcement and a strong Raman spectrum, but for the $\bar{\nu}_3$ vibrational mode the change in one polarizability ellipsoid tends to be cancelled out by the opposite change in the other, and there is no Raman spectrum.

For a molecule which possesses a centre of symmetry such as CO_2 there is a useful rule known as the *Mutual Exclusion Rule*. This states that, for molecules with a centre of symmetry, fundamental transitions which are active in the infrared are forbidden in the Raman and vice versa.^{††} For example, in the acetylene molecule (see p. 254) the frequencies $\bar{\nu}_3$ and $\bar{\nu}_5$ occur in the infrared but not in the Raman, while $\bar{\nu}_1$, $\bar{\nu}_2$, and $\bar{\nu}_4$ appear in the Raman but not in the infrared.

On many occasions both the infrared and Raman methods have to be employed to obtain a complete pattern of the different vibrational frequencies in a molecule; the two methods are often complementary, and when a certain group lacks strong features in the infrared spectrum, it often exhibits intense lines in the Raman spectrum and vice versa.

4.14 QUANTUM THEORY OF THE RAMAN EFFECT

The quantum theory treats monochromatic radiation of frequency ν_0 as a stream of photons having energy $h\nu_0$ where h is Planck's constant.

In Rayleigh scattering, the incident photons collide with a molecule and are

[†] This should be contrasted with the infrared method where the stretching of a homonuclear diatomic molecule is infrared-inactive under ordinary conditions.

^{††} It is not to be inferred that the transitions which are forbidden in the infrared appear in the Raman and vice versa. Some transitions may be forbidden to both methods.