
Chapter 1

Introduction, Basic Theory and Principles

1.1 INTRODUCTION

The main spectroscopies employed to detect vibrations in molecules are based on the processes of infrared absorption and Raman scattering. They are widely used to provide information on chemical structures and physical forms, to identify substances from the characteristic spectral patterns ('fingerprinting'), and to determine quantitatively or semi-quantitatively the amount of a substance in a sample. Samples can be examined in a whole range of physical states; for example, as solids, liquids or vapours, in hot or cold states, in bulk, as microscopic particles, or as surface layers. The techniques are very wide ranging and provide solutions to a host of interesting and challenging analytical problems. Raman scattering is less widely used than infrared absorption, largely due to problems with sample degradation and fluorescence. However, recent advances in instrument technology have simplified the equipment and reduced the problems substantially. These advances, together with the ability of Raman spectroscopy to examine aqueous solutions, samples inside glass containers and samples without any preparation, have led to a rapid growth in the application of the technique.

In practice, modern Raman spectroscopy is simple. Variable instrument parameters are few, spectral manipulation is minimal and a simple interpretation of the data may be sufficient. This chapter and Chapter 2 aim to set out the basic principles and experimental methods to give the reader a firm understanding of the basic theory and practical considerations so that the technique

can be applied at the level often required for current applications. However, Raman scattering is an underdeveloped technique, with much important information often not used or recognized. Later chapters will develop the minimum theory required to give a more in-depth understanding of the data obtained and to enable comprehension of some of the many more advanced techniques which have specific advantages for some applications.

1.1.1 History

The phenomenon of inelastic scattering of light was first postulated by Smekal in 1923 [1] and first observed experimentally in 1928 by Raman and Krishnan [2]. Since then, the phenomenon has been referred to as Raman spectroscopy. In the original experiment sunlight was focussed by a telescope onto a sample which was either a purified liquid or a dust-free vapour. A second lens was placed by the sample to collect the scattered radiation. A system of optical filters was used to show the existence of scattered radiation with an altered frequency from the incident light – the basic characteristic of Raman spectroscopy.

1.2 BASIC THEORY

When light interacts with matter, the photons which make up the light may be absorbed or scattered, or may not interact with the material and may pass straight through it. If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state. It is this change which is measured in absorption spectroscopy by the detection of the loss of that energy of radiation from the light. However, it is also possible for the photon to interact with the molecule and scatter from it. In this case there is no need for the photon to have an energy which matches the difference between two energy levels of the molecule. The scattered photons can be observed by collecting light at an angle to the incident light beam, and provided there is no absorption from any electronic transitions which have similar energies to that of the incident light, the efficiency increases as the fourth power of the frequency of the incident light.

Scattering is a commonly used technique. For example, it is widely used for measuring particle size and size distribution down to sizes less than 1 μm . One everyday illustration of this is that the sky is blue because the higher energy blue light is scattered from molecules and particles in the atmosphere more efficiently than the lower energy red light. However, the main scattering technique used for molecular identification is Raman scattering.

The process of absorption is used in a wide range of spectroscopic techniques. For example it is used in acoustic spectroscopy where there is a very small energy difference between the ground and excited states and in X-ray absorption spectroscopy where there is a very large difference. In between these extremes are many of the common techniques such as NMR, EPR, infrared absorption, electronic absorption and fluorescence emission, and vacuum ultraviolet (UV) spectroscopy. Figure 1.1 indicates the wavelength ranges of some commonly used types of radiation.

Radiation is often characterized by its wavelength (λ). However, in spectroscopy, because we are interested in the interaction of radiation with states of the molecule being examined and this being usually discussed in terms of energy, it is often useful to use frequency (ν) or wavenumber ($\bar{\omega}$) scales, which are linearly related with energy. The relationships between these scales are given below:

$$\lambda = c/\nu \quad (1.1)$$

$$\nu = \Delta E/h \quad (1.2)$$

$$\bar{\omega} = \nu/c = 1/\lambda \quad (1.3)$$

It is clear from Equations (1.1)–(1.3) that the energy is proportional to the reciprocal of wavelength and therefore the highest energy region is on the left in Figure 1.1 and the longest wavelength on the right.

The way in which radiation is employed in infrared and Raman spectroscopies is different. In infrared spectroscopy, infrared energy covering a range of frequencies is directed onto the sample. Absorption occurs where the frequency of the incident radiation matches that of a vibration so that the molecule is promoted to a vibrational excited state. The loss of this frequency of radiation from the beam after it passes through the sample is then detected. In contrast, Raman spectroscopy uses a single frequency of radiation to irradiate the sample and it is the radiation scattered from the molecule, one vibrational unit of energy different from the incident beam, which is detected. Thus, unlike infrared absorption, Raman scattering does not require matching of the incident radiation to the energy difference between the ground and excited states. In Raman scattering, the light interacts with the molecule and distorts (polarizes) the cloud of electrons round the nuclei to form a short-lived state

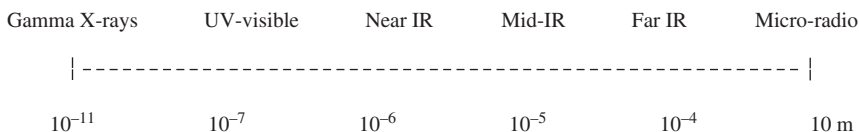


Figure 1.1. The electromagnetic spectrum on the wavelength scale in metres.

called a ‘virtual state’, which is discussed in Chapter 3. This state is not stable and the photon is quickly re-radiated.

The energy changes we detect in vibrational spectroscopy are those required to cause nuclear motion. If only electron cloud distortion is involved in scattering, the photons will be scattered with very small frequency changes, as the electrons are comparatively light. This scattering process is regarded as elastic scattering and is the dominant process. For molecules it is called Rayleigh scattering. However, if nuclear motion is induced during the scattering process, energy will be transferred either from the incident photon to the molecule or from the molecule to the scattered photon. In these cases the process is inelastic and the energy of the scattered photon is different from that of the incident photon by one vibrational unit. This is Raman scattering. It is inherently a weak process in that only one in every 10^6 – 10^8 photons which scatter is Raman scattered. In itself this does not make the process insensitive since with modern lasers and microscopes, very high power densities can be delivered to very small samples but it does follow that other processes such as sample degradation and fluorescence can readily occur.

Figure 1.2 shows the basic processes which occur for one vibration. At room temperature, most molecules, but not all, are present in the lowest energy vibrational level. Since the virtual states are not real states of the molecule but are created when the laser interacts with the electrons and causes polarization, the energy of these states is determined by the frequency of the light source used. The Rayleigh process will be the most intense process since most photons scatter this way. It does not involve any energy change and consequently the light returns to the same energy state. The Raman scattering process from the ground vibrational state m leads to absorption of energy by the molecule and its promotion to a higher energy excited vibrational state (n). This is called Stokes

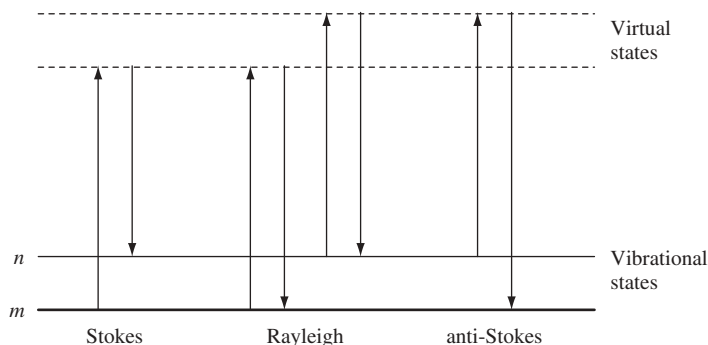


Figure 1.2. Diagram of the Rayleigh and Raman scattering processes. The lowest energy vibrational state m is shown at the foot with states of increasing energy above it. Both the low energy (upward arrows) and the scattered energy (downward arrows) have much larger energies than the energy of a vibration.

scattering. However, due to thermal energy, some molecules may be present in an excited state such as n in Figure 1.2. Scattering from these states to the ground state m is called anti-Stokes scattering and involves transfer of energy to the scattered photon. The relative intensities of the two processes depend on the population of the various states of the molecule. The populations can be worked out from the Boltzmann equation (Chapter 3) but at room temperature, the number of molecules expected to be in an excited vibrational state other than any really low-energy ones will be small.

Thus, compared to Stokes scattering, anti-Stokes scattering will be weak and will become weaker as the frequency of the vibration increases, due to decreased population of the excited vibrational states. Further, anti-Stokes scattering will increase relative to Stokes scattering as the temperature rises. Figure 1.3 shows a typical spectrum of Stokes and anti-Stokes scattering from cyclohexane separated by the intense Rayleigh scattering which should be off-scale close to the point where there is no energy shift. However there is practically no signal close to the frequency of the exciting line along the x -axis. This is because filters in front of the spectrometer remove almost all light within about 200 cm^{-1} of the exciting line. Some breakthrough of the laser light can be seen where there is no energy shift at all.

Usually, Raman scattering is recorded only on the low-energy side to give Stokes scattering but occasionally anti-Stokes scattering is preferred. For example, where there is fluorescence interference, this will occur at a lower energy than the excitation frequency and consequently anti-Stokes scattering can be used to avoid interference. The difference in intensities of Raman bands in Stokes and anti-Stokes scattering can also be used to measure temperature.

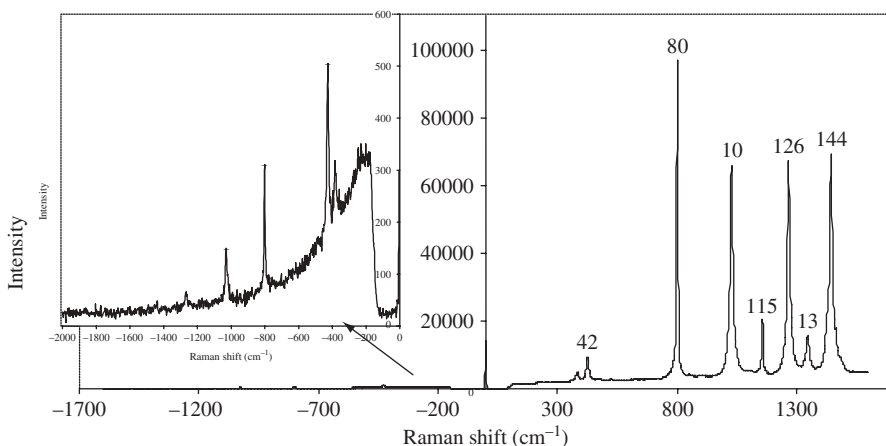


Figure 1.3. Stokes and anti-Stokes scattering for cyclohexane. To show the weak anti-Stokes spectrum, the y -axis has been extended in the inset.

Figure 1.2 illustrates one key difference between infrared absorption and Raman scattering. As described above, infrared absorption would involve direct excitation of the molecule from state m to state n by a photon of exactly the energy difference between them. In contrast, Raman scattering uses much higher energy radiation and measures the difference in energy between n and m by subtracting the energy of the scattered photon from that of the incident beam (the two vertical arrows in each case).

The cyclohexane spectrum in Figure 1.3 shows that there is more than one vibration which gives effective Raman scattering (i.e. is Raman active); the nature of these vibrations will be discussed in Section 1.3. However, there is a basic selection rule which is required to understand this pattern. Intense Raman scattering occurs from vibrations which cause a change in the polarizability of the electron cloud round the molecule. Usually, symmetric vibrations cause the largest changes and give the greatest scattering. This contrasts with infrared absorption where the most intense absorption is caused by a change in dipole and hence asymmetric vibrations which cause this are the most intense. As will be seen later, not all vibrations of a molecule need, or in some cases can, be both infrared and Raman active and the two techniques usually give quite different intensity patterns. As a result the two are often complementary and, used together, give a better view of the vibrational structure of a molecule.

One specific class of molecule provides an additional selection rule. In a centrosymmetric molecule, no band can be active in both Raman scattering and infrared absorption. This is sometimes called the mutual exclusion rule. In a centrosymmetric molecule, reflection of any point through the centre will reach an identical point on the other side (C_2H_4 is centrosymmetric, CH_4 is not). This distinction is useful particularly for small molecules where a comparison of the spectra obtained from infrared absorption and Raman scattering can be used to differentiate *cis* and *trans* forms of a molecule in molecules such as a simple azo dye or a transition metal complex.

Figure 1.4 shows a comparison of the infrared and Raman spectra for benzoic acid. The x -axis is given in wavenumbers for which the unit is cm^{-1} . Wavenumbers are not recommended SI units but the practice of spectroscopy is universally carried out using these and this is unlikely to change. For infrared absorption each peak represents an energy of radiation absorbed by the molecule. The y -axis gives the amount of the light absorbed and is usually shown with the maximum absorbance as the lowest point on the trace. Raman scattering is presented only as the Stokes spectrum and is given as a shift in energy from the energy of the laser beam. This is obtained by subtracting the scattered energy from the laser energy. In this way the difference in energy corresponding to the ground and excited vibrational states (n and m in Figure 1.2) is obtained. This energy difference is what is measured directly by infrared. The scattering is measured as light detected by the spectrometer and the maximum amount of light detected is the highest point on the trace.

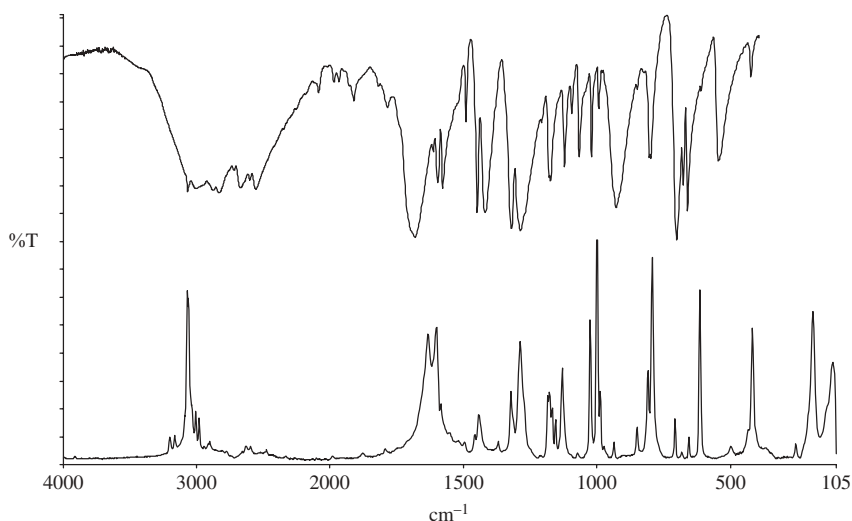


Figure 1.4. Infrared and Raman spectra of benzoic acid. The top trace is infrared absorption given in % transmission (%T) so that the lower the transmission value the greater the absorption. The lower trace is Raman scattering and the higher the peak the greater the scattering.

Strictly speaking, Raman scattering should be expressed as a shift in energy from that of the exciting radiation and should be referred to as Δcm^{-1} but it is often expressed simply as cm^{-1} . This practice is followed in this book for simplicity. Although different energy ranges are possible, the information of interest to most users is in the $3600\text{--}400\text{cm}^{-1}$ (2.8–12 micron) range in infrared spectroscopy and down to 200cm^{-1} in Raman spectroscopy since this includes most modes which are characteristic of a molecule. In some applications, much larger or smaller energy changes are studied and modern Raman equipment can cope with much wider ranges. One specific advantage of Raman scattering is that shifts from the laser line of 50cm^{-1} or lower can easily be recorded with the correct equipment. Many modern machines for reasons of cost and simplicity are not configured in a suitable way to measure shifts below $100\text{--}200\text{cm}^{-1}$. The intensities of the bands in the Raman spectrum are dependent on the nature of the vibration being studied and on instrumentation and sampling factors. Modern instruments should be calibrated to remove the instrument factors but this is not always the case; these factors are dealt with in the next chapter. Sampling has a large effect on the absolute intensities, bandwidths observed and band positions. Again these will be dealt with later. This chapter will concentrate on the effect on Raman scattering of the set of vibrations present in a molecule and set out a step-by-step approach to interpretation based on simple selection rules.

1.3 MOLECULAR VIBRATIONS

Provided that there is no change in electronic energy, for example, by the absorption of a photon and the promotion of an electron to an excited electronic state, the energy of a molecule can be divided into a number of different parts or ‘degrees of freedom’. Three of these degrees of freedom are taken up to describe the translation of the molecule in space and three to describe rotational movement except for linear molecules where only two types of rotation are possible. Thus, if N is the number of atoms in a molecule, the number of vibrational degrees of freedom and therefore the number of vibrations possible is $3N - 6$ for all molecules except linear ones where it is $3N - 5$. For a diatomic molecule, this means there will be only one vibration. In a molecule such as oxygen, this is a simple stretch of the O–O bond. This will change the polarizability of the molecule but will not induce any dipole change since there is no dipole in the molecule and the vibration is symmetric about the centre. Thus the selection rules already discussed would predict, and it is true, that oxygen gas will give a band in the Raman spectrum and no band in the infrared spectrum. However in a molecule such as nitric oxide, NO, there will be only one band but, since there is both a dipole change and a polarizability change, it will appear in both the infrared and Raman spectrum.

A triatomic molecule will have three modes of vibration. They are a symmetrical stretch, a bending or deformation mode and an asymmetrical stretch as shown in Figure 1.5. The very different water (H_2O) and carbon dioxide (CO_2) molecules clearly demonstrate these vibrations. These diagrams use ‘spring and ball’ models. The spring represents the bond or bonds between the atoms. The stronger the bond the higher the frequency. The balls represent the atoms and the heavier they are the lower the frequency. The expression which relates the mass of the atoms and the bond strength to the vibrational frequency is Hooke’s

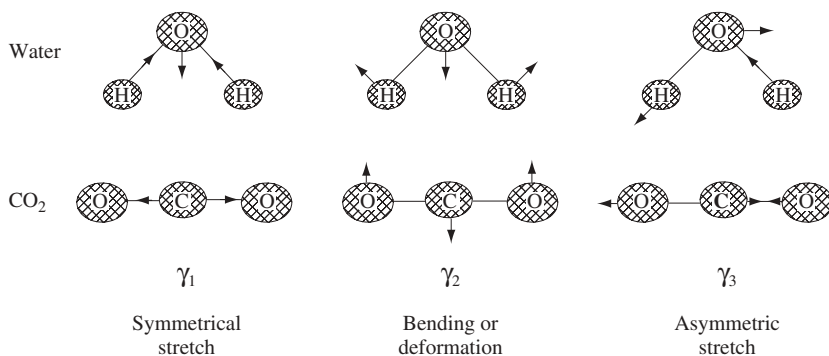


Figure 1.5. Spring and ball model – three modes of vibration for H_2O and CO_2 .

law which is dealt with in Chapter 3, but for the present, it is clear that strong bonds and light atoms will give higher frequencies of vibration and heavy atoms and weak bonds will give lower ones.

This simple model is widely used to interpret vibrational spectra. However, the molecule actually exists as a three-dimensional structure with a pattern of varying electron density covering the whole molecule. A simple depiction of this for carbon dioxide is shown in Figure 1.6. If either molecule vibrates, the electron cloud will alter as the positive nuclei change position and depending on the nature of the change, this can cause a change of dipole moment or polarization. In these triatomic molecules, the symmetrical stretch causes large polarization changes and hence strong Raman scattering with weak or no dipole change and hence weak or no infrared absorption. The deformation mode causes a dipole change but little polarization change and hence strong infrared absorption and weak or non-existent Raman scattering.

As an example of this, Figure 1.7 illustrates the vibrations possible for carbon disulphide along with the corresponding infrared absorption and Raman scattering spectra.

Although this type of analysis is suitable for small molecules, it is more difficult to apply in a more complex molecule. Figure 1.8 shows one vibration from a dye in which a large number of atoms are involved. This is obtained from a theoretical calculation using density functional theory (DFT) which is discussed briefly later. It probably gives a depiction of the vibration which is close to the truth. However, even if it were possible to calculate the spectrum of every molecule quickly in the laboratory, which at present it is not, this type of diagram is only of limited utility to the spectroscopist. A comparison between molecules of similar type is difficult unless a full calculation is available for them all and each subtle change in the nuclear displacements is drawn out or accurately described for each one. This limits the ability to compare large numbers of molecules or to understand the nature of vibrations in molecules for which there is no calculation.

The usual approach to describing vibrations is to simplify the problem and break the displacements down into a number of characteristic features, which

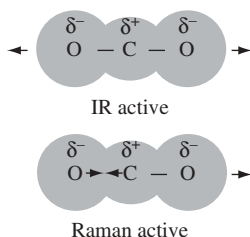


Figure 1.6. Electron cloud model of water and carbon dioxide showing an IR and a Raman active vibrations.

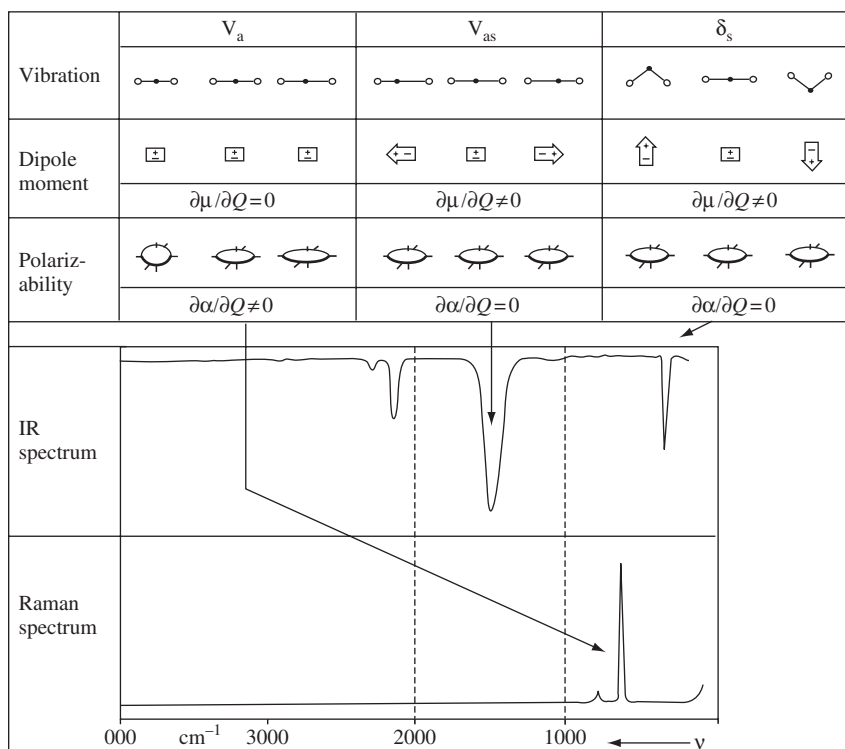


Figure 1.7. Dipole and polarization changes in carbon disulphide, with resultant infrared and Raman spectra. (Reprinted from A. Fadini and F.-M. Schnepel, *Vibrational Spectroscopy: Methods and Applications*, Ellis Horwood Ltd, Chichester, 1989.)

can relate to more than one molecule. In the vibration in Figure 1.8 which comes from a calculation to predict the energies of vibrations each azo dye, the biggest displacements of the heavier atoms is on one of the ring systems. The vibration would almost certainly be labelled vaguely as a ‘ring stretch’. In another vibration not shown the situation was much simpler. Large displacements were found on the two nitrogen atoms which form the azo bond between the rings, and the direction indicated bond lengthening and contracting during the vibrational cycle. Thus this vibration is called the azo stretch, and there is a change in polarizability just as there was for oxygen; so it should be a Raman-active vibration. We can search for these vibrations in the actual spectrum and hopefully match a peak to the vibration. This is called assigning the vibration. Thus, it is possible to describe a vibration in a few helpful words. In some cases this is fairly accurate as for the azo stretch, but in some cases, the description is not adequate to describe the actual movement. However, common bands can be assigned and reasonably described in many molecules.

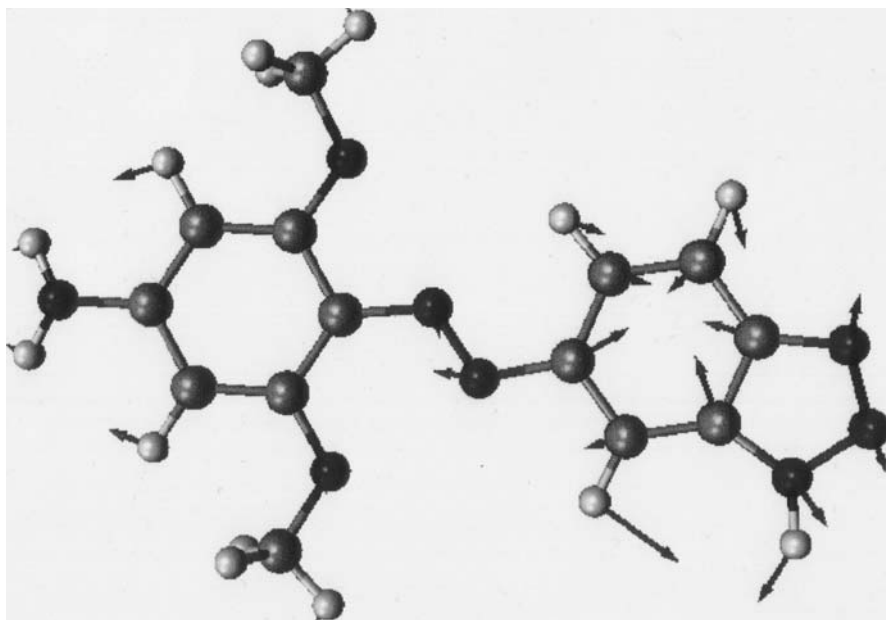


Figure 1.8. A displacement diagram for a vibration at about 1200cm^{-1} in a dye indicating the involvement of a number of atoms. The arrows show the direction of the displacement. Since the equilibrium position of the atoms is shown, during a complete vibration the arrows will reverse in direction.

1.3.1 Group Vibrations

To assign vibrations to spectral peaks it is necessary to realize that two or more bonds which are close together in a molecule and are of similar energies can interact and it is the vibration of the group of atoms linked by these bonds which is observed in the spectrum. For example, the CH_2 group is said to have a symmetric and an anti-symmetric stretch rather than two separate CH stretches (Figure 1.9). It follows from this and from the geometry of the molecule that different types of vibrations are possible for different groups. Selected examples of a few of these for CH_3 and C_6H_6 are shown in Figure 1.9.

In contrast, where there is a large difference in energy between the vibrations in different bonds or if the atoms are well separated in the molecule, they can be treated separately. Thus, for CH_3Br , the C-H bonds in CH_3 must be treated as a group but the C-Br vibration is treated separately. In Figure 1.9, the selected vibrations of benzene are shown in two different ways. Firstly they are shown with the molecule in the equilibrium position with arrows showing the direction of the vibrational displacement. To illustrate what this means, they are also shown with the vibration at the extremes of the vibrational movement. To show

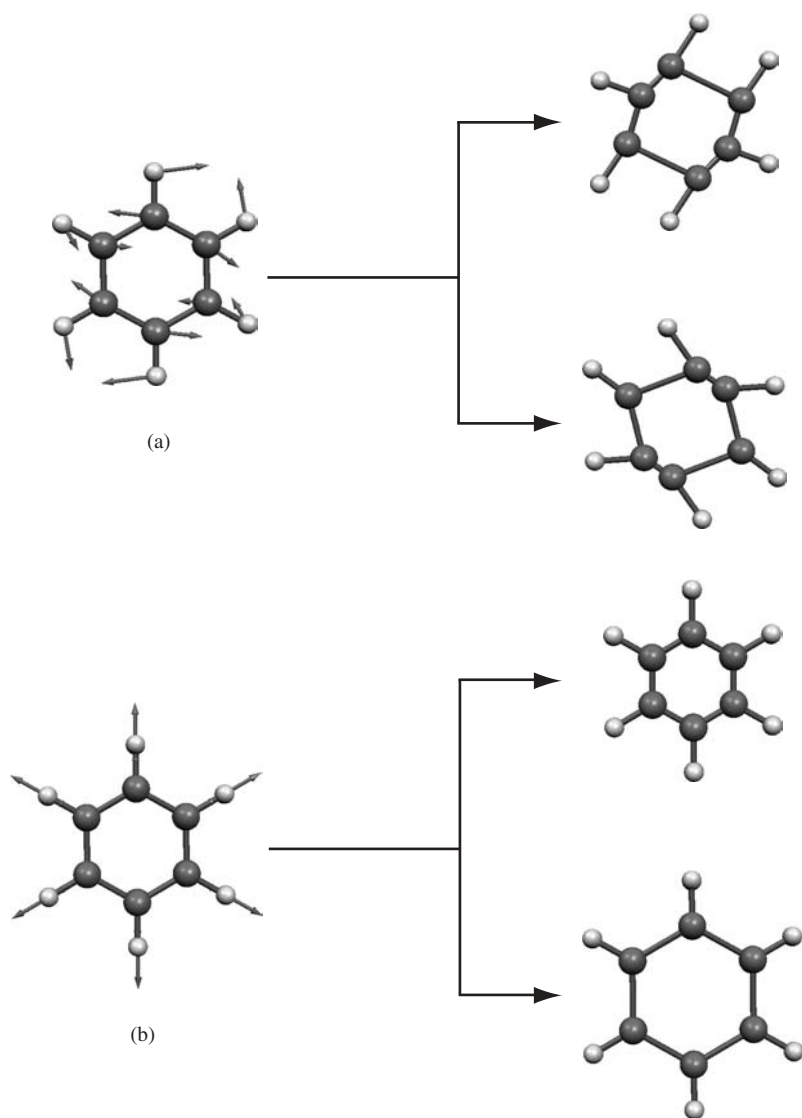


Figure 1.9. Selected displacement diagrams for benzene and for CH_3 in CH_3Br . (a) A quadrant stretch for benzene at about 1600 cm^{-1} . (b) The symmetric breathing mode at just above 1000 cm^{-1} . (c and d) Two C-H vibrations at about 3000 cm^{-1} . (e) The symmetric stretch of CH_3 in CH_3Br at above 3000 cm^{-1} . (f) An asymmetric stretch at above 3000 cm^{-1} . (g) A CH bend at about $1450\text{--}1500\text{ cm}^{-1}$. (h) A low frequency mode at below 600 cm^{-1} .

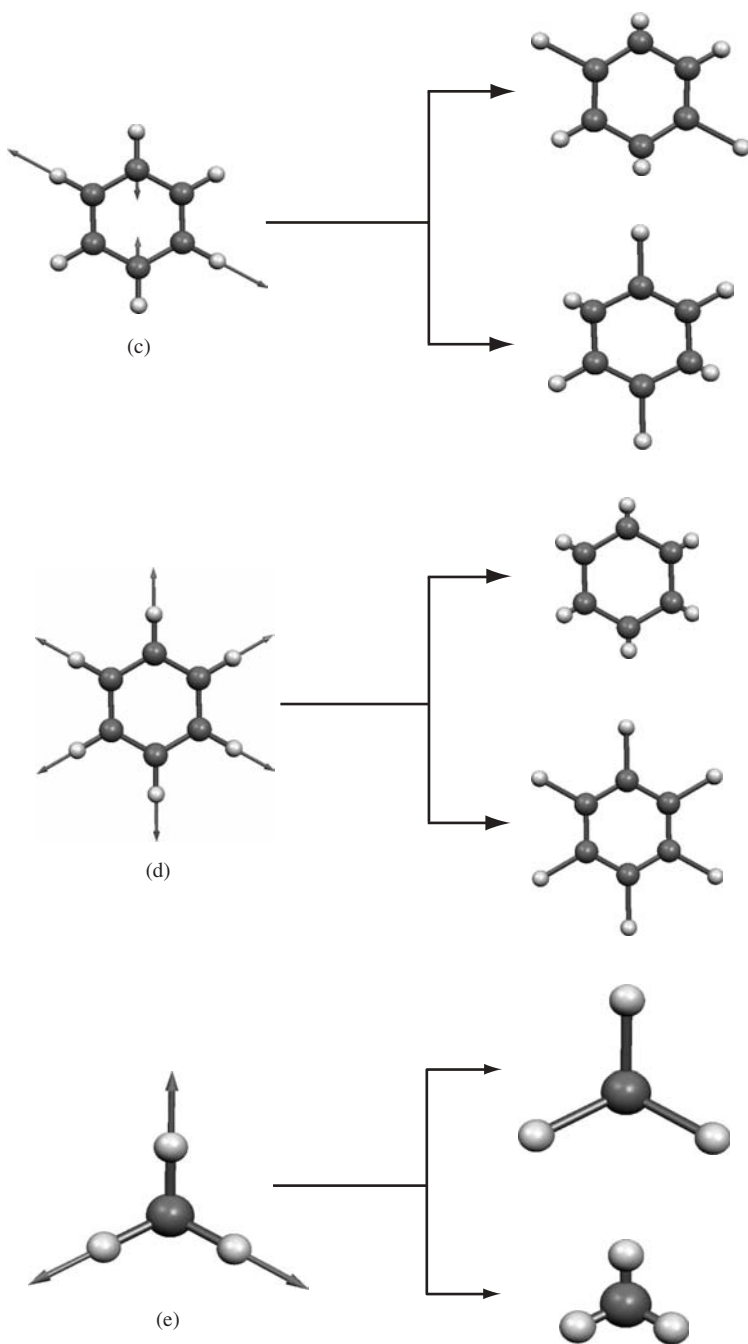


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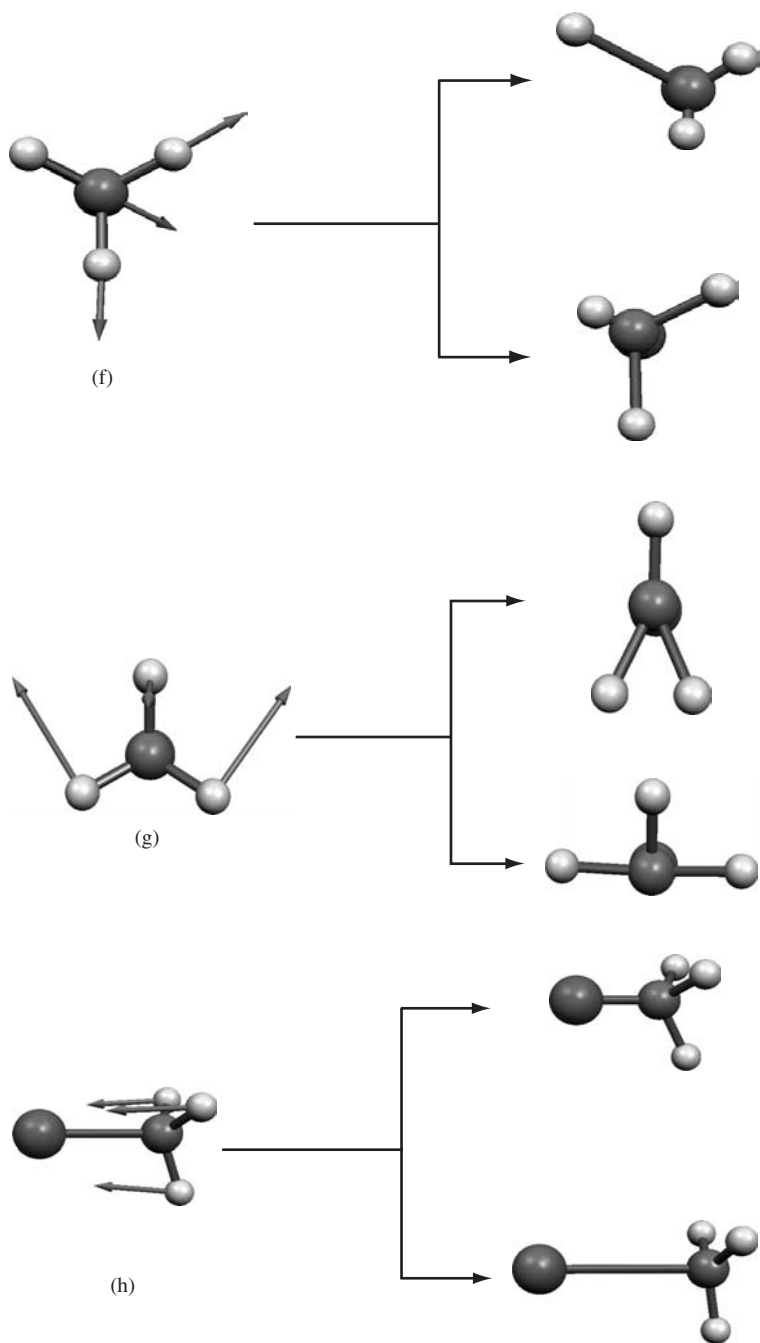


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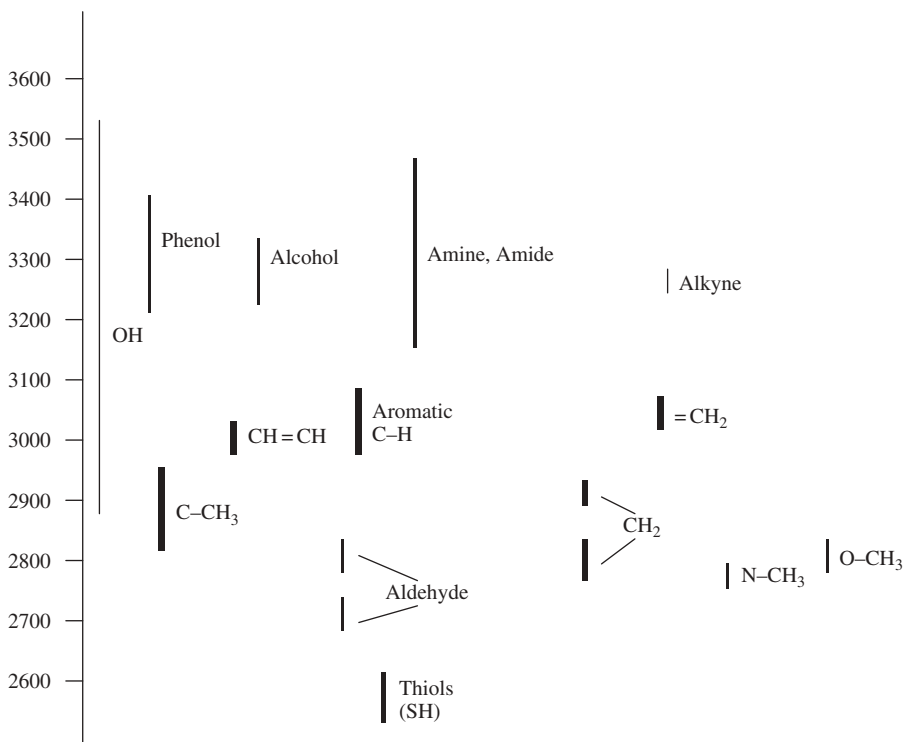
the selected CH_3 group vibrations, the molecule is completed using a bromine. As discussed, the C-Br bond vibrates at a much lower frequency and does not interact appreciably with the high CH_3 displacements shown.

1.3.2 An Approach to Interpretation

It is possible to give energy ranges in which the characteristic frequencies of the most common groups which are strong in either infrared or Raman scattering can occur. The relative intensities of specific peaks help to confirm that the correct vibration has been picked out.

For example, carbonyl groups $>\text{C}=\text{O}$ which are both asymmetric and ionic will have a dipole moment which will change when the group stretches in a manner analogous to oxygen. They have strong bands in the infrared spectrum

Table 1.1. Single vibration and group frequencies and possible intensities of peaks commonly identified in Raman scattering. The length of the vertical line represents the wavenumber range in cm^{-1} in which each type of vibration is normally found and the line thickness gives an indication of intensity with thick lines being the most intense.



but are weaker in the Raman spectrum. They are usually present at $\sim 1700\text{ cm}^{-1}$. Symmetrical groups such as unsaturated bonds ($-\text{C}=\text{C}-$) and disulphide bonds ($-\text{S}-\text{S}-$) are weak infrared absorbers, but strong Raman scatterers. The stretching modes for these vibrations are ~ 1640 and 500 cm^{-1} respectively. There are many more examples. It is the combination of the knowledge of approximate energy and likely relative intensity of particular vibrations which form the basis of the assignment mode used by most spectroscopists. For example, the $4000-2500\text{ cm}^{-1}$ is the region where single bonds ($\text{X}-\text{H}$) absorb. The $2500-2000\text{ cm}^{-1}$ is referred to as the multiple bond ($-\text{N}=\text{C}=\text{O}$) region. The $2000-1500\text{ cm}^{-1}$ region is where double bonds ($-\text{C}=\text{O}$, $-\text{C}=\text{N}$, $-\text{C}=\text{C}-$) occur. Below 1500 cm^{-1} , some groups, e.g. nitro ($\text{O}=\text{N}=\text{O}$) do have specific bands but many molecules have complex patterns of Carbon-Carbon and Carbon-Nitrogen vibrations. The region is generally referred to as the Fingerprint region. Significant bands below 650 cm^{-1} usually arise from inorganic groups, metal-organic groups or lattice vibrations. Tables 1.1–1.5 show the frequency ranges of

Table 1.2. Single vibration and group frequencies and an indication of possible intensities of peaks commonly identified in Raman scattering

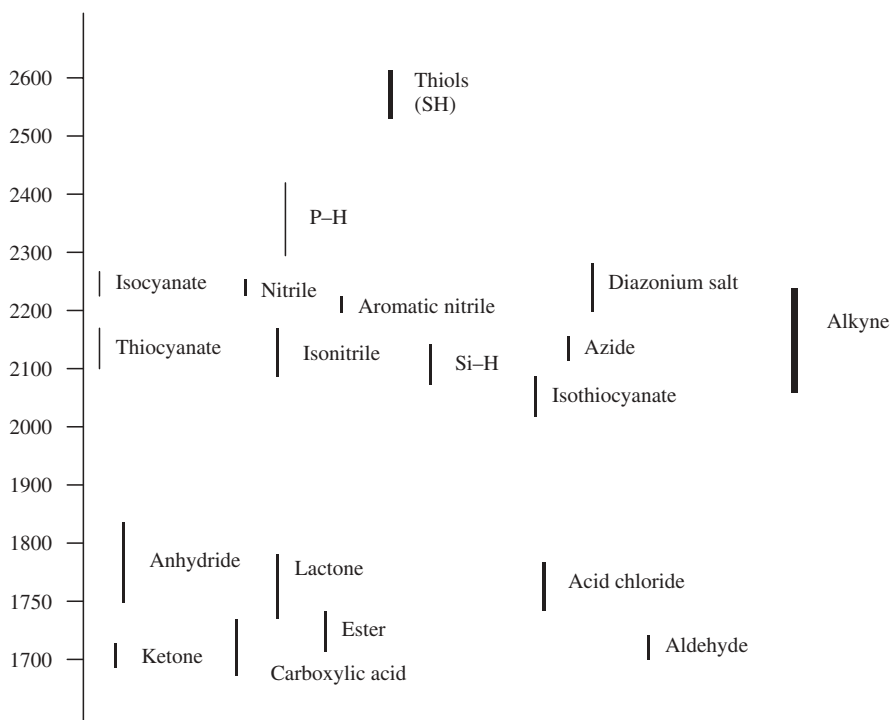
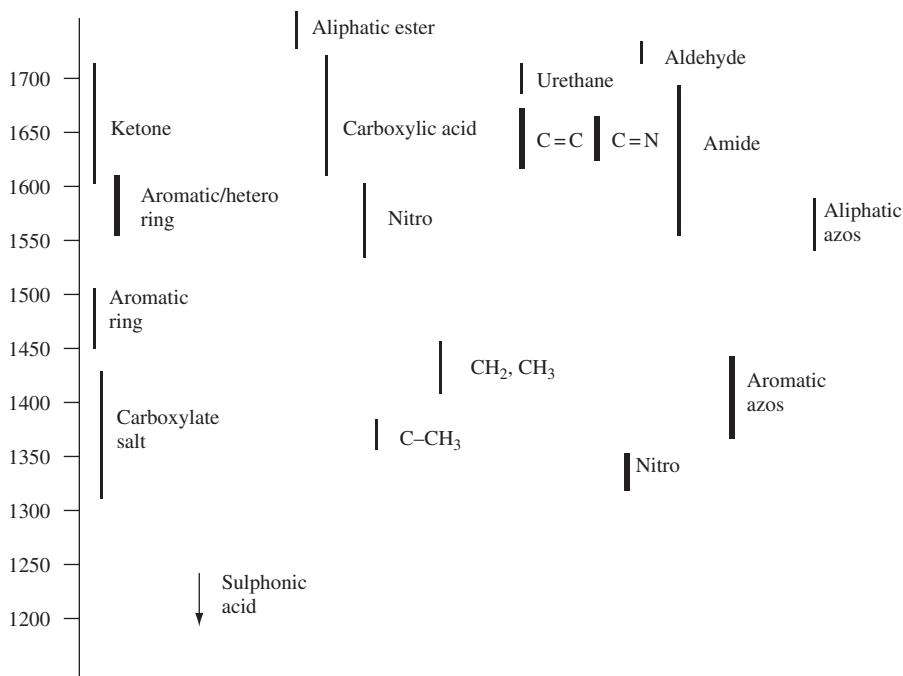
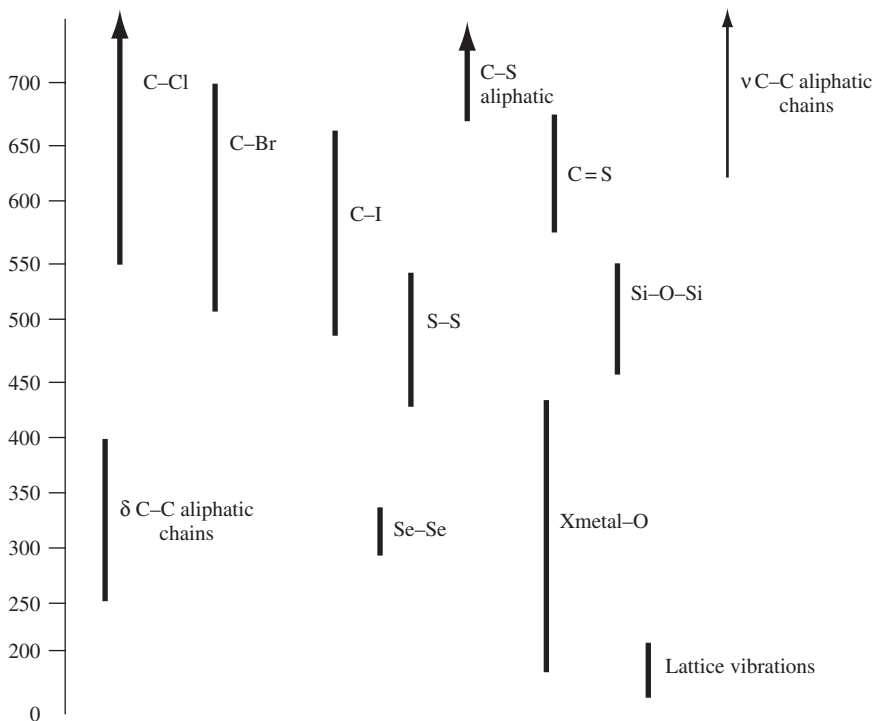


Table 1.3. Single vibration and group frequencies and an indication of possible intensities of peaks commonly identified in Raman scattering

many of the vibrations which give rise to strong bands in either Raman or infrared spectroscopy. The ranges are approximate for the groups in most structures but some groups in unusual structures may give bands outside these ranges. The thickness of the line indicates relative strength. These tables enable a beginning to be made on the assignment of specific bands. A more difficult problem is in estimating the relative intensities of the bands. Earlier in this chapter, we showed that there are reasons why in some circumstances bands which are strong in the infrared spectrum are not strong in the Raman spectrum. However, this cannot be taken as an absolute rule although it is the normal behaviour. Thus, the bands that we would expect to be strong in Raman scattering are the more symmetric bands in the spectrum.

This approach is often used in vibrational spectroscopy. However, to assign specific peaks in the spectrum to specific vibrations, modern laboratories use libraries in which complete spectra are stored electronically. Most spectrometers have software to obtain a computer-generated analysis of the similarities and differences with standards so that specific substances can be identified positively and easily. In other areas, the initial assignment is confirmed by

Table 1.5. Single vibration and group frequencies and an indication of possible intensities of peaks commonly identified in Raman scattering

Raman spectra are usually somewhat simpler. The most environmentally sensitive bands, e.g. OH and NH, are broad and weak and the backbone structural bands are strong and sharp. The extent of this difference can be illustrated from the fact that water can be used as a solvent to obtain the Raman spectra of organic molecules. This indicates the relative strength of bands in the organic molecule compared to the weakness of hydrogen bonded species such as the OH bands in water. It is this greater selectivity which leads to the simplicity of Raman spectra compared to infrared spectra. Thus, the Raman spectra of quite large molecules show clear bands. In Figure 1.4 the infrared spectrum is complex and has a strong band just above 1600 cm^{-1} from the carbonyl group due to the C=O vibration. The strong bands in the Raman spectrum are largely due to the aromatic group. The band at 2900 cm^{-1} due to the CH₂ group is hidden under the strong OH bands in the infrared spectrum but can be clearly seen in the Raman spectrum.

The above information makes it possible to start assigning and interpreting Raman spectra. If possible it is always good to run an infrared spectrum for

comparison. The phrase ‘interpretation of Raman spectra’ is used in many different ways. The spectrum of a molecule can be the subject of a full mathematical interpretation in which every band is carefully assigned or of a cursory look to produce the interpretation ‘Yes that is toluene’. However, to be able to carry out a complete, correct and relevant interpretation, the total Raman experiment must be considered. Raman spectroscopists have to make a number of choices in deciding how to examine a sample and the type of answer required may ultimately determine these choices. The simplicity and flexibility of Raman scattering are considerable advantages but if care is not taken in making the correct choices, poor or spurious results can be obtained. Chapter 2 describes the choices and provides the background information to enable the recording and interpretation of Raman scattering in a reliable and secure manner.

1.4 SUMMARY

In this chapter we have attempted to introduce the reader to the basic principles of Raman spectroscopy without going into the theory and details of practice too deeply, with a view to encouraging further interest. Chapter 2 outlines the practical choices to be made in carrying out the Raman experiment in full. Later chapters give the theoretical background required for full analysis of spectra, a guide to ways in which Raman spectroscopy has been successfully employed, and lead to the more sophisticated but less common techniques available to the Raman spectroscopist.

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