

Chapter 1

Introduction

Learning Objectives

- To understand the origin of electromagnetic radiation.
- To determine the frequency, wavelength, wavenumber and energy change associated with an infrared transition.
- To appreciate the factors governing the intensity of bands in an infrared spectrum.
- To predict the number of fundamental modes of vibration of a molecule.
- To understand the influences of force constants and reduced masses on the frequency of band vibrations.
- To appreciate the different possible modes of vibration.
- To recognize the factors that complicate the interpretation of infrared spectra.

Infrared spectroscopy is certainly one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. As a consequence of the improved instrumentation, a variety of new sensitive techniques have now been developed in order to examine formerly intractable samples.

Infrared spectrometers have been commercially available since the 1940s. At that time, the instruments relied on prisms to act as dispersive elements,

but by the mid 1950s, diffraction gratings had been introduced into dispersive machines. The most significant advances in infrared spectroscopy, however, have come about as a result of the introduction of Fourier-transform spectrometers. This type of instrument employs an interferometer and exploits the well-established mathematical process of Fourier-transformation. Fourier-transform infrared (FTIR) spectroscopy has dramatically improved the quality of infrared spectra and minimized the time required to obtain data. In addition, with constant improvements to computers, infrared spectroscopy has made further great strides.

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. In this introductory chapter, the basic ideas and definitions associated with infrared spectroscopy will be described. The vibrations of molecules will be looked at here, as these are crucial to the interpretation of infrared spectra.

Once this chapter has been completed, some idea about the information to be gained from infrared spectroscopy should have been gained. The following chapter will aid in an understanding of how an infrared spectrometer produces a spectrum. After working through that chapter, it should be possible to record a spectrum and in order to do this a decision on an appropriate sampling technique needs to be made. The sampling procedure depends very much on the type of sample to be examined, for instance, whether it is a solid, liquid or gas. Chapter 2 also outlines the various sampling techniques that are commonly available. Once the spectrum has been recorded, the information it can provide needs to be extracted. Chapter 3, on spectrum interpretation, will assist in the understanding of the information to be gained from an infrared spectrum. As infrared spectroscopy is now used in such a wide variety of scientific fields, some of the many applications of the technique are examined in Chapters 4 to 8. These chapters should provide guidance as to how to approach a particular analytical problem in a specific field. The applications have been divided into separate chapters on organic and inorganic molecules, polymers, biological applications and industrial applications. This book is, of course, not meant to provide a comprehensive review of the use of infrared spectroscopy in each of these fields. However, an overview of the approaches taken in these areas is provided, along with appropriate references to the literature available in each of these disciplines.

1.1 Electromagnetic Radiation

The visible part of the electromagnetic spectrum is, by definition, radiation visible to the human eye. Other detection systems reveal radiation beyond the visible regions of the spectrum and these are classified as radiowave, microwave,

infrared, ultraviolet, X-ray and γ -ray. These regions are illustrated in Figure 1.1, together with the processes involved in the interaction of the radiation of these regions with matter. The electromagnetic spectrum and the varied interactions between these radiations and many forms of matter can be considered in terms of either classical or quantum theories.

The nature of the various radiations shown in Figure 1.1 have been interpreted by Maxwell's classical theory of electro- and magneto-dynamics – hence, the term *electromagnetic radiation*. According to this theory, radiation is considered as two mutually perpendicular electric and magnetic fields, oscillating in single planes at right angles to each other. These fields are in phase and are being propagated as a sine wave, as shown in Figure 1.2. The magnitudes of the electric and magnetic vectors are represented by E and B , respectively.

A significant discovery made about electromagnetic radiation was that the velocity of propagation in a vacuum was constant for all regions of the spectrum. This is known as the velocity of light, c , and has the value $2.997\,925 \times 10^8 \text{ m s}^{-1}$. If one complete wave travelling a fixed distance each cycle is visualized, it may be observed that the velocity of this wave is the product of the *wavelength*, λ (the distance between adjacent peaks), and the *frequency*, ν (the number of cycles

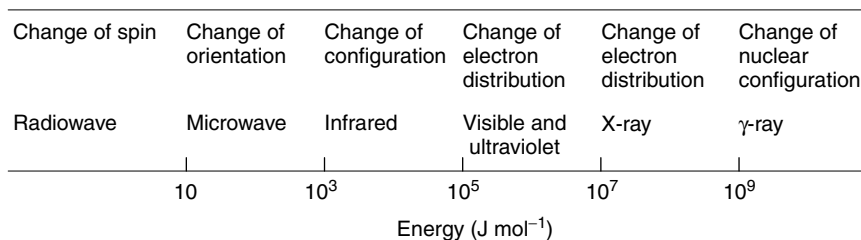


Figure 1.1 Regions of the electromagnetic spectrum. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

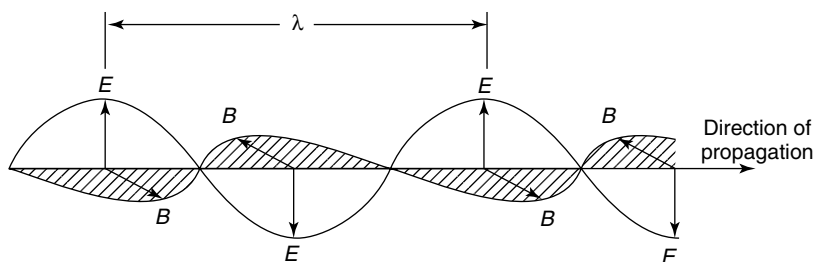


Figure 1.2 Representation of an electromagnetic wave. Reproduced from Brittain, E. F. H., George, W. O. and Wells, C. H. J., *Introduction to Molecular Spectroscopy*, Academic Press, London, Copyright (1975), with permission from Elsevier.

per second). Therefore:

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

The presentation of spectral regions may be in terms of wavelength as metres or sub-multiples of a metre. The following units are commonly encountered in spectroscopy:

$$1 \text{ \AA} = 10^{-10} \text{ m} \quad 1 \text{ nm} = 10^{-9} \text{ m} \quad 1 \text{ }\mu\text{m} = 10^{-6} \text{ m}$$

Another unit which is widely used in infrared spectroscopy is the *wavenumber*, $\bar{\nu}$, in cm^{-1} . This is the number of waves in a length of one centimetre and is given by the following relationship:

$$\bar{\nu} = 1/\lambda = \nu/c \quad (1.2)$$

This unit has the advantage of being linear with energy.

During the 19th Century, a number of experimental observations were made which were not consistent with the classical view that matter could interact with energy in a continuous form. Work by Einstein, Planck and Bohr indicated that in many ways electromagnetic radiation could be regarded as a stream of particles (or quanta) for which the energy, E , is given by the Bohr equation, as follows:

$$E = h\nu \quad (1.3)$$

where h is the Planck constant ($h = 6.626 \times 10^{-34} \text{ J s}$) and ν is equivalent to the classical frequency.

Processes of change, including those of vibration and rotation associated with infrared spectroscopy, can be represented in terms of quantized discrete energy levels E_0 , E_1 , E_2 , etc., as shown in Figure 1.3. Each atom or molecule in a system must exist in one or other of these levels. In a large assembly of molecules, there will be a distribution of all atoms or molecules among these various energy levels. The latter are a function of an integer (the *quantum number*) and a parameter associated with the particular atomic or molecular process associated with that state. Whenever a molecule interacts with radiation, a quantum of energy (or

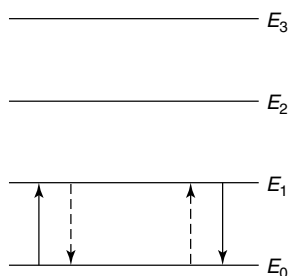


Figure 1.3 Illustration of quantized discrete energy levels.

photon) is either emitted or absorbed. In each case, the energy of the quantum of radiation must exactly fit the energy gap $E_1 - E_0$ or $E_2 - E_1$, etc. The energy of the quantum is related to the frequency by the following:

$$\Delta E = h\nu \quad (1.4)$$

Hence, the frequency of emission or absorption of radiation for a transition between the energy states E_0 and E_1 is given by:

$$\nu = (E_1 - E_0)/h \quad (1.5)$$

Associated with the uptake of energy of quantized absorption is some deactivation mechanism whereby the atom or molecule returns to its original state. Associated with the loss of energy by emission of a quantum of energy or photon is some prior excitation mechanism. Both of these associated mechanisms are represented by the dotted lines in Figure 1.3.

SAQ 1.1

Caffeine molecules absorb infrared radiation at 1656 cm^{-1} . Calculate the following:

- (i) wavelength of this radiation;
- (ii) frequency of this radiation;
- (iii) energy change associated with this absorption.

1.2 Infrared Absorptions

For a molecule to show infrared absorptions it must possess a specific feature, i.e. an electric dipole moment of the molecule must change during the vibration. This is the *selection rule* for infrared spectroscopy. Figure 1.4 illustrates an example of an ‘infrared-active’ molecule, a *heteronuclear* diatomic molecule. The dipole moment of such a molecule changes as the bond expands and contracts. By comparison, an example of an ‘infrared-inactive’ molecule is a *homonuclear* diatomic molecule because its dipole moment remains zero no matter how long the bond.

An understanding of molecular symmetry and group theory is important when initially assigning infrared bands. A detailed description of such theory is beyond the scope of this book, but symmetry and group theory are discussed in detail in other texts [1, 2]. Fortunately, it is not necessary to work from first principles each time a new infrared spectrum is obtained.

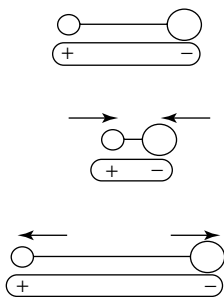


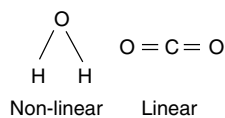
Figure 1.4 Change in the dipole moment of a heteronuclear diatomic molecule.

Infrared absorptions are not infinitely narrow and there are several factors that contribute to the broadening. For gases, the Doppler effect, in which radiation is shifted in frequency when the radiation source is moving towards or away from the observer, is a factor. There is also the broadening of bands due to the collisions between molecules. Another source of line broadening is the finite lifetime of the states involved in the transition. From quantum mechanics, when the Schrödinger equation is solved for a system which is changing with time, the energy states of the system do not have precisely defined energies and this leads to lifetime broadening. There is a relationship between the lifetime of an excited state and the bandwidth of the absorption band associated with the transition to the excited state, and this is a consequence of the *Heisenberg Uncertainty Principle*. This relationship demonstrates that the shorter the lifetime of a state, then the less well defined is its energy.

1.3 Normal Modes of Vibration

The interactions of infrared radiation with matter may be understood in terms of changes in molecular dipoles associated with vibrations and rotations. In order to begin with a basic model, a molecule can be looked upon as a system of masses joined by bonds with spring-like properties. Taking first the simple case of diatomic molecules, such molecules have three degrees of translational freedom and two degrees of rotational freedom. The atoms in the molecules can also move relative to one other, that is, bond lengths can vary or one atom can move out of its present plane. This is a description of stretching and bending movements that are collectively referred to as *vibrations*. For a diatomic molecule, only one vibration that corresponds to the stretching and compression of the bond is possible. This accounts for one degree of vibrational freedom.

Polyatomic molecules containing many (N) atoms will have $3N$ degrees of freedom. Looking first at the case of molecules containing three atoms, two groups of triatomic molecules may be distinguished, i.e. linear and non-linear. Two simple examples of linear and non-linear triatomics are represented by CO_2

**Figure 1.5** Carbon dioxide and water molecules.**Table 1.1** Degrees of freedom for polyatomic molecules. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Type of degrees of freedom	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N - 5$	$3N - 6$
Total	$3N$	$3N$

and H_2O , respectively (illustrated in Figure 1.5). Both CO_2 and H_2O have three degrees of translational freedom. Water has three degrees of rotational freedom, but the linear molecule carbon dioxide has only two since no detectable energy is involved in rotation around the $\text{O}=\text{C}=\text{O}$ axis. Subtracting these from $3N$, there are $3N - 5$ degrees of freedom for CO_2 (or any linear molecule) and $3N - 6$ for water (or any non-linear molecule). N in both examples is three, and so CO_2 has four vibrational modes and water has three. The degrees of freedom for polyatomic molecules are summarized in Table 1.1.

SAQ 1.2

How many vibrational degrees of freedom does a chloroform (CHCl_3) molecule possess?

Whereas a diatomic molecule has only one mode of vibration which corresponds to a stretching motion, a non-linear B–A–B type triatomic molecule has three modes, two of which correspond to stretching motions, with the remainder corresponding to a bending motion. A linear type triatomic has four modes, two of which have the same frequency, and are said to be *degenerate*.

Two other concepts are also used to explain the frequency of vibrational modes. These are the stiffness of the bond and the masses of the atoms at each end of the bond. The stiffness of the bond can be characterized by a proportionality constant termed the *force constant*, k (derived from Hooke's law). The *reduced mass*, μ , provides a useful way of simplifying our calculations by combining the individual atomic masses, and may be expressed as follows:

$$(1/\mu) = (1/m_1) + (1/m_2) \quad (1.6)$$

where m_1 and m_2 are the masses of the atoms at the ends of the bond. A practical alternative way of expressing the reduced mass is:

$$\mu = m_1 m_2 / (m_1 + m_2) \quad (1.7)$$

The equation relating the force constant, the reduced mass and the frequency of absorption is:

$$\nu = (1/2\pi) \sqrt{(k/\mu)} \quad (1.8)$$

This equation may be modified so that direct use of the wavenumber values for bond vibrational frequencies can be made, namely:

$$\bar{\nu} = (1/2\pi c) \sqrt{(k/\mu)} \quad (1.9)$$

where c is the speed of light.

A molecule can only absorb radiation when the incoming infrared radiation is of the same frequency as one of the fundamental modes of vibration of the molecule. This means that the vibrational motion of a small part of the molecule is increased while the rest of the molecule is left unaffected.

SAQ 1.3

Given that the C–H stretching vibration for chloroform occurs at 3000 cm^{-1} , calculate the C–D stretching frequency for deuteriochloroform. The relevant atomic masses are $^1\text{H} = 1.674 \times 10^{-27} \text{ kg}$, $^2\text{H} = 3.345 \times 10^{-27} \text{ kg}$ and $^{12}\text{C} = 1.993 \times 10^{-27} \text{ kg}$.

Vibrations can involve either a change in bond length (*stretching*) or bond angle (*bending*) (Figure 1.6). Some bonds can stretch in-phase (*symmetrical* stretching) or out-of-phase (*asymmetric* stretching), as shown in Figure 1.7. If a molecule has different terminal atoms such as HCN, ClCN or ONCl, then the two stretching modes are no longer symmetric and asymmetric vibrations of similar bonds, but will have varying proportions of the stretching motion of each group. In other words, the amount of *coupling* will vary.

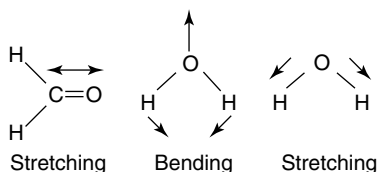


Figure 1.6 Stretching and bending vibrations.

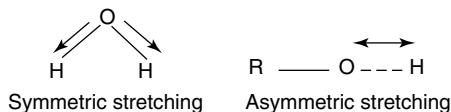


Figure 1.7 Symmetric and asymmetric stretching vibrations.

Bending vibrations also contribute to infrared spectra and these are summarized in Figure 1.8. It is best to consider the molecule being cut by a plane through the hydrogen atoms and the carbon atom. The hydrogens can move in the same direction or in opposite directions in this plane, here the plane of the page. For more complex molecules, the analysis becomes simpler since hydrogen atoms may be considered in isolation because they are usually attached to more massive, and therefore, more rigid parts of the molecule. This results in *in-plane* and *out-of-plane* bending vibrations, as illustrated in Figure 1.9.

As already mentioned, for a vibration to give rise to the absorption of infrared radiation, it must cause a change in the dipole moment of the molecule. The larger this change, then the more intense will be the absorption band. Because of the difference in electronegativity between carbon and oxygen, the carbonyl group is permanently polarized, as shown in Figure 1.10. Stretching this bond will increase the dipole moment and, hence, C=O stretching is an intense absorption. In CO₂, two different stretching vibrations are possible: (a) symmetric and (b) asymmetric (Figure 1.11). In practice, this ‘black and white’ situation does not prevail. The change in dipole may be very small and, hence, lead to a very weak absorption.

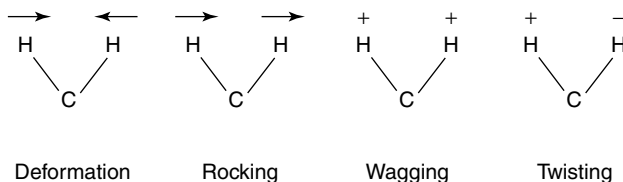


Figure 1.8 Different types of bending vibrations.

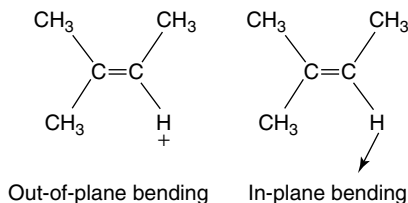


Figure 1.9 Out-of-plane and in-plane bending vibrations.



Figure 1.10 Dipole moment in a carbonyl group.

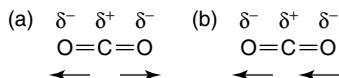


Figure 1.11 Stretching vibrations of carbon dioxide.

DQ 1.1

Which one of the vibrations shown in Figure 1.11 is ‘infrared-inactive’?

Answer

A dipole moment is a vector sum. CO_2 in the ground state, therefore, has no dipole moment. If the two $\text{C}=\text{O}$ bonds are stretched symmetrically, there is still no net dipole and so there is no infrared activity. However, in the asymmetric stretch, the two $\text{C}=\text{O}$ bonds are of different length and, hence, the molecule has a dipole. Therefore, the vibration shown in Figure 1.11(b) is ‘infrared-active’.

SAQ 1.4

Consider the symmetrical bending vibration of CO_2 , as shown in Figure 1.12. Will this vibration be ‘active’ in the infrared?



Figure 1.12 Symmetric bending vibration of carbon dioxide (cf. SAQ 1.4).

Symmetrical molecules will have fewer ‘infrared-active’ vibrations than asymmetrical molecules. This leads to the conclusion that symmetric vibrations will generally be weaker than asymmetric vibrations, since the former will not lead to a change in dipole moment. It follows that the bending or stretching of bonds involving atoms in widely separated groups of the periodic table will lead to intense bands. Vibrations of bonds such as $\text{C}-\text{C}$ or $\text{N}=\text{N}$ will give weak bands. This again is because of the small change in dipole moment associated with their vibrations.

There will be many different vibrations for even fairly simple molecules. The complexity of an infrared spectrum arises from the coupling of vibrations over a large part of or over the complete molecule. Such vibrations are called *skeletal* vibrations. Bands associated with skeletal vibrations are likely to conform to a

pattern or *fingerprint* of the molecule as a whole, rather than a specific group within the molecule.

1.4 Complicating Factors

There are a number of factors that may complicate the interpretation of infrared spectra. These factors should be considered when studying spectra as they can result in important changes to the spectra and may result in the misinterpretation of bands.

1.4.1 Overtone and Combination Bands

The sound we hear is a mixture of harmonics, that is, a fundamental frequency mixed with multiples of that frequency. *Overtone bands* in an infrared spectrum are analogous and are multiples of the fundamental absorption frequency. The energy levels for overtones of infrared modes are illustrated in Figure 1.13. The energy required for the first overtone is twice the fundamental, assuming evenly spaced energy levels. Since the energy is proportional to the frequency absorbed and this is proportional to the wavenumber, the first overtone will appear in the spectrum at twice the wavenumber of the fundamental.

Combination bands arise when two fundamental bands absorbing at $\bar{\nu}_1$ and $\bar{\nu}_2$ absorb energy simultaneously. The resulting band will appear at $(\bar{\nu}_1 + \bar{\nu}_2)$ wavenumbers.

SAQ 1.5

A molecule has strong fundamental bands at the following wavenumbers:

C–H bending at 730 cm^{-1}

C–C stretching at 1400 cm^{-1}

C–H stretching at 2950 cm^{-1}

Determine the wavenumbers of the possible combination bands and the first overtones.

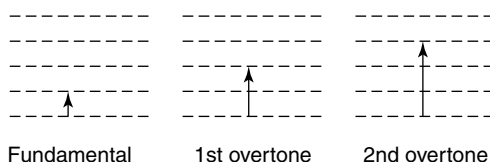


Figure 1.13 Energy levels for fundamental and overtone infrared bands.

1.4.2 Fermi Resonance

The Fermi resonance effect usually leads to two bands appearing close together when only one is expected. When an overtone or a combination band has the same frequency as, or a similar frequency to, a fundamental, two bands appear, split either side of the expected value and are of about equal intensity. The effect is greatest when the frequencies match, but it is also present when there is a mismatch of a few tens of wavenumbers. The two bands are referred to as a *Fermi doublet*.

1.4.3 Coupling

Vibrations in the skeletons of molecules become coupled, as mentioned in Section 1.4. Such vibrations are not restricted to one or two bonds, but may involve a large part of the carbon backbone and oxygen or nitrogen atoms if present. The energy levels mix, hence resulting in the same number of vibrational modes, but at different frequencies, and bands can no longer be assigned to one bond. This is very common and occurs when adjacent bonds have similar frequencies. Coupling commonly occurs between C–C stretching, C–O stretching, C–N stretching, C–H rocking and C–H wagging motions. A further requirement is that to be strongly coupled, the motions must be in the same part of the molecule.

1.4.4 Vibration–Rotation Bands

When the infrared spectra of gaseous heteronuclear molecules are analysed at high resolution, a series of closely spaced components are observed. This type of structure is due to the excitation of rotational motion during a vibrational transition and is referred to as a vibration–rotation spectrum [1]. The absorptions fall into groups called branches and are labelled P, Q and R according to the change in the rotational quantum number associated with the transition. The separation of the lines appearing in a vibration–rotation spectrum may be exploited to determine the bond length of the molecule being examined.

Summary

The ideas fundamental to an understanding of infrared spectroscopy were introduced in this chapter. The electromagnetic spectrum was considered in terms of various atomic and molecular processes and classical and quantum ideas were introduced. The vibrations of molecules and how they produce infrared spectra were then examined. The various factors that are responsible for the position and intensity of infrared modes were described. Factors such as combination and overtone bands, Fermi resonance, coupling and vibration–rotation bands can lead to changes in infrared spectra. An appreciation of these issues is important when

examining spectra and these factors were outlined in this chapter. For further reference, there is a range of books and book chapters available which provide an overview of the theory behind infrared spectroscopy [3–7].

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