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Infrared Spectroscopy

In contrast to the relatively few absorption peaks observed in the ultraviolet region for most organic compounds, the infrared spectrum provides a rich array of absorption bands. Many of the absorption bands cannot be assigned accurately; those that can, however, provide a wealth of structural information about a molecule.

Either the wavelength (μ) or wave number (cm^{-1}) (see p. 1) is used to measure the position of a given infrared absorption. The ordinary infrared region extends from 2.5 to 15 μ (4000 to 667 cm^{-1}); the region from 0.8 to 2.5 μ ($12,500$ to 4000 cm^{-1}) is called the *near infrared* and the region from 15 to 200 μ (667 to 50 cm^{-1}) is called the *far infrared*. As is the case in ultraviolet spectroscopy, absorptions that occur at shorter wavelengths (higher frequency) are of higher energy. The wave number is directly proportional to the absorbed energy ($K = E/hc$), whereas the wavelength is inversely proportional to the absorbed energy ($\lambda = hc/E$; $\lambda = 1/K$).

3.1 MOLECULAR VIBRATION

A molecule is not a rigid assemblage of atoms. A molecule can be said to resemble a system of balls of varying masses, corresponding to the atoms of a molecule, and springs of varying strengths, corresponding to the chemical bonds of a molecule. There are two kinds of fundamental vibrations for molecules: *stretching*, in which the distance between two atoms increases or decreases, but the atoms remain in the same bond axis, and *bending* (or deformation), in which the position of the atom changes relative to the original bond axis. The various stretching and bending vibrations of a bond occur at certain quantized frequencies. *When infrared light of that same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased.* When the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat.

A nonlinear molecule that contains n atoms has $3n - 6$ possible *fundamental* vibrational modes that can be responsible for the absorption of

infrared light. Thus, such simple molecules as methane and benzene have, theoretically, nine and thirty possible fundamental absorption bands, respectively. In order for a particular vibration to result in the absorption of infrared energy, that vibration must cause a change in the dipole moment of the molecule. Thus, molecules that contain certain symmetry elements will display somewhat simplified spectra. The C=C stretching vibration of ethylene and the symmetrical C—H stretching of the four C—H bonds of methane do not result in an absorption band in the infrared region. The predicted number of peaks will not be observed also if the absorption occurs outside the region ordinarily examined, if the vibrations result in absorptions that are so close that they cannot be resolved, or if the absorption is of very weak intensity.

Additional (nonfundamental) absorption bands may occur because of the presence of overtones (or harmonics) that occur with greatly reduced intensity, at $\frac{1}{2}$, $\frac{1}{3}$, . . . of the wavelength (twice, three times, . . . the wave number), combination bands (the sum of two or more different wave numbers), and difference bands (the difference of two or more different wave numbers).

Some of the various stretching and bending vibrations that can exist within a molecule are shown schematically in Fig. 3-1. Bending vibrations generally require less energy and occur at longer wavelength (lower wave number) than stretching vibrations. Stretching vibrations are found to occur in the order of bond strengths. The triple bond (absorption at $4.4\text{--}5.0\ \mu$, $2300\text{--}2000\ \text{cm}^{-1}$) is stronger than the double bond (absorption at $5.3\text{--}6.7\ \mu$, $1900\text{--}1500\ \text{cm}^{-1}$), which in turn is stronger than the single bond (C—C, C—N, and C—O absorption at $7.7\text{--}12.5\ \mu$, $1300\text{--}800\ \text{cm}^{-1}$). When the single bond involves the very small proton (C—H, O—H, or N—H), stretching vibrations occur at much higher frequency ($2.7\text{--}3.8\ \mu$, $3700\text{--}2630\ \text{cm}^{-1}$). The O—H bond absorbs near $2.8\ \mu$ ($3570\ \text{cm}^{-1}$) and

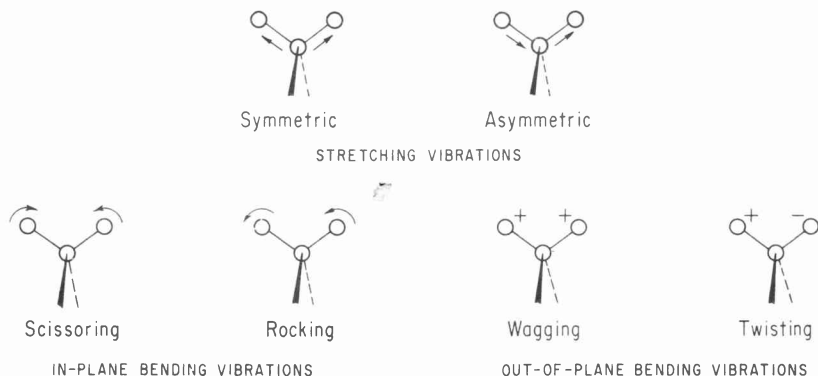


Fig. 3-1 Vibrations of a group of atoms (+ and — signify vibrations perpendicular to the plane of the paper).

the O—D bond absorbs near 3.8μ (2630 cm^{-1}); in this case the strengths of the bonds are nearly the same but the mass of one atom is doubled.

An approximate value for the stretching frequency (ν , in cm^{-1}) of a bond is related to the masses of the two atoms (M_x and M_y , in grams), the velocity of light (c), and the force constant of the bond (k , in dynes/cm):

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{M_x M_y / (M_x + M_y)}}$$

Single, double, and triple bonds have force constants that are approximately 5, 10, and 15×10^5 dynes/cm, respectively.

The magnitude of the molar extinction coefficient in infrared spectroscopy varies from near zero to around 2,000. The value is proportional to the square of the change in the dipole moment of the molecule that the particular vibration causes. Absorption peaks caused by stretching vibrations are usually the most intense peaks in the spectrum.

3.2 MECHANICS OF MEASUREMENT

Infrared absorption spectra are usually obtained by placing the sample in one beam of a double-beam infrared spectrophotometer and measuring the relative intensity of transmitted (and therefore absorbed) light energy versus wavelength (or wave number). A common light source for infrared radiation is the Nernst glower, a molded rod containing a mixture of zirconium oxide, yttrium oxide, and erbium oxide that is heated to around $1,500^\circ$ by electrical means. Either optical prisms or gratings are used to obtain approximately monochromatic light; grating spectrophotometers give higher resolution. Glass and quartz absorb strongly throughout most of the infrared region, so they cannot be used as cell containers or as optical prisms. Metal halides (e.g., sodium chloride) are commonly used for these purposes. Recording spectrophotometers are available such that a complete spectrum ($2.5\text{--}25 \mu$, $4000\text{--}400 \text{ cm}^{-1}$) may be obtained in a matter of minutes.

When the spectrum is determined, a calibration line is usually recorded on the paper.† This is necessary because the recorder paper is fitted on a drum of the ordinary spectrophotometer, and it is not possible to place the paper in exactly the same position every time. One of several absorption peaks of polystyrene (Fig. 3-2) is commonly used for this purpose: 3.509μ (2850 cm^{-1}), 6.238μ (1603 cm^{-1}), or 11.035μ (906 cm^{-1}).

The spectrum may be determined if the sample is a gas, a solid, a liquid, or in solution. The sample should be dry, because water absorbs

† All infrared spectra here reproduced were recorded on a Perkin-Elmer Model 137 Infracord instrument; the 6.238μ (1603 cm^{-1}) polystyrene absorption was used to calibrate all spectra and appears on them.

(ii) **Bending Vibrations:** These types of vibrations are generally of four types; scissoring, rocking, wagging and twisting.

- Scissoring: In this type of bending vibrations, the two atoms approach each other
- Rocking: In this type of bending vibrations, the two atoms move in the same direction.
- Wagging: In this type of bending vibrations, the two atoms either move up or move below the plane with respect to the central atom.
- Twisting: In this type of bending vibrations, one atom move up and other below the plane with respect to the central atom.

In general, the molecular vibrations which lead to change in the dipole moment of the molecule shall give rise to the absorption bands in the infrared region and are said to be IR active radiations. Any molecular vibrations which do not lead to change in the dipole moment of the molecule shall not absorb in the infrared region and are said to be IR inactive radiations. Therefore, change in dipole moment in a molecule by absorption of radiation is basic requirement for a compound to be infrared active and exhibit IR spectrum.

10.11.3 Vibrational Spectroscopy

Polyatomic molecule composed of n -atoms has $3n$ degrees of freedom (translational, rotational and vibrational), six of which are translations and rotations of the molecule itself. This leaves $3n-6$ degrees of vibrational freedom ($3n-5$ if the molecule is linear). These degrees of freedom in a molecule are related to number of fundamental vibrational absorption bands. The various types of vibrational modes in different class of molecules are discussed below:

- Diatomic molecules:** The diatomic molecules are linear so vibrational degrees of freedom is $3n-5$ where $n = 2$ (number of atoms in the molecule). Hence, $3 \times 2 - 5 = 1$ (diatomic molecule have one mode of vibration). Further, homo-nuclear diatomic molecules do not undergo any vibrational energy change as the dipole moment is for the bond is zero and hence are IR inactive whereas hetero-nuclear diatomic molecules like HCl, CO, NO, etc. undergo variation in dipole moment leading to vibrational energy change and hence IR active.
- Tri-atomic molecules:** In case of *linear tri-atomic molecules* like CO_2 , CS_2 or BeCl_2 , the vibrational degrees of freedom = $3n-5$ (as linear molecule has only 2 modes of rotation). In tri-atomic molecule, $n=3$, hence vibrational degree of freedom in the above examples is = $3 \times 3 - 5 = 4$. For example, in CO_2 molecule, the theoretical number of vibrational modes should be equal to four and the IR spectra shows symmetrical stretching at 1340 cm^{-1} , asymmetrical stretching at 2350 cm^{-1} , two scissoring (bending) at 666 cm^{-1} . The two scissoring (bending) show absorptions at the same frequency but differ in their direction such vibrations are called as *degenerates*. So, in CO_2 basically there are three vibrational modes out of which one mode is doubly degenerate. In case of *non-linear (bent) tri-atomic molecules* like H_2O , NO_2 or SnCl_2 , the vibrational degrees of freedom = $3n-6$ (as non-linear molecule has 3 modes of rotation). In tri-atomic molecule, $n=3$, hence vibrational degree of freedom, in the non-linear (bent) tri-atomic molecules is = 3

$x\ 3-6 = 3$. e.g., In H_2O molecule, the theoretical number of vibrational modes should be equal to *three* and the IR spectra shows symmetrical stretching at 3652 cm^{-1} , asymmetrical stretching at 3756 cm^{-1} , scissoring (bending) at 1596 cm^{-1} .

- (iii) *Polyatomic molecules*: The common examples of polyatomic molecules are ethylene and benzene. The ethylene molecule is IR active due to asymmetrical C-H stretching whereas the benzene is IR inactive in symmetrical stretching mode as vibration of all C-H bonds result in zero dipole moment change.

In practice, infrared spectra do not normally display separate absorption signals for each of the $3n-6$ fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. *One selection rule that influences the intensity of infrared absorptions is that a change in dipole moment should occur for a vibration to absorb infrared energy.* Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode. The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. The expression for **frequency of oscillation** is derived from Hook's law and its relationship with atomic masses and force constant is given below:

$$\nu = \frac{1}{2\pi c} \left[\frac{k (M_a + M_b)}{(M_a M_b)} \right]^{1/2}$$

ν = Vibrational frequency (cm^{-1}); k = Force constant of bond (dyne/cm); c = velocity of light; M_a and M_b = Mass of atoms a and b (gm)

10.11.3.1 Simple harmonic model of vibrations in diatomic molecules: Consider a diatomic molecule HCl in the gaseous state. The two atoms combine to form a covalent bond. The formation of the bond between these atoms results from the balance of forces. These forces are (i) repulsive forces between the positively charged nuclei of the atoms and also between the negatively charged electrons of the atoms (ii) attractive forces between positively charged nucleus of one atom and negatively charged electrons of the other atom and vice-versa. The two atoms come closer up to a certain distance where the two types of forces are balanced. This distance is called as *inter-nuclear distance*, at which the energy of the system is minimum. This minimum distance is also called as *equilibrium distance* (r_{eq}) and referred as *bond length*.

In a vibrating diatomic molecule, the compression and extension of the bond may be compared to the motion of a spring (*simple harmonic motion*). So, like spring the diatomic molecule will obey Hook's law as given below:

$$f = -k(r - r_{\text{eq}})$$

where f is restoring force; k is force constant; r is inter-nuclear distance and r_{eq} is equilibrium distance. The energy curve in such a case is parabolic in nature and is given by the expression:

$$E = \frac{1}{2} k(r - r_{\text{eq}})^2$$

The above type of model of a diatomic vibrating molecule is known as *simple harmonic model*. The plot of energy vs. inter-nuclear distance is shown in *Figure 10.14*.

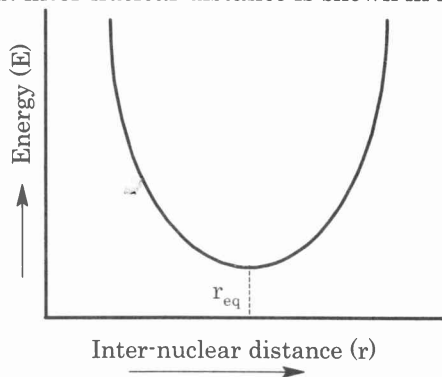


Figure 10.14: Energy curve in a simple harmonic oscillator

The frequency (ν) of oscillation for a molecule behaving like a simple harmonic oscillator is given by the following expression, where k is force constant and μ is reduced mass:

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \quad (\text{i})$$

Similarly, the vibrational wave number (w) is related to force constant (k) by the following expression where c is velocity of light:

$$w = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \quad (\text{ii})$$

The vibrational energy (E_ν) of a harmonic oscillator is given by the following expression where h is Plank's constant:

$$E_\nu = \left(\nu + \frac{1}{2} \right) h c w \quad (\nu = 0, 1, 2, \dots) \quad (\text{iii})$$

when $\nu = 0$, the vibrational energy (E_0) is called as the zero point energy of the vibrator.

A vibrational transition between two energy levels is possible for a harmonic vibrator only if that vibration causes a change in the dipole moment on interaction with electromagnetic radiation. Therefore, homo-nuclear diatomic molecules do not give vibrational spectrum in the IR region as single symmetric vibration in such molecules causes no change in the dipole moment. In case of CO_2 molecule (which is linear and centrosymmetric), although symmetric stretching vibration does not change the dipole moment hence IR inactive but the asymmetric stretching vibration and the bending vibration do change the dipole moment and hence IR active. For a transition from ν to $\nu+1$ level, the difference in energy is given by the following expression:

$$E_{\nu+1} - E_\nu = \left(\nu + \frac{3}{2} \right) h c w - \left(\nu + \frac{1}{2} \right) h c w = h c w \quad (\text{iv})$$

The force constant of the diatomic molecule can be calculated from the vibrational wave number as per following expression:

$$k = 4\pi^2 w^2 c^2 \mu \quad (\text{v})$$

10.11.3.2 Anharmonic vibrator: In real situations, molecules do not obey the laws of harmonic oscillator. During stretching of the bonds in a molecule, at some point the molecule dissociates into atoms and thus behaves as anharmonic vibrator. The energy curve for such a anharmonic oscillation in a diatomic molecule is given by *Figure 10.15*.

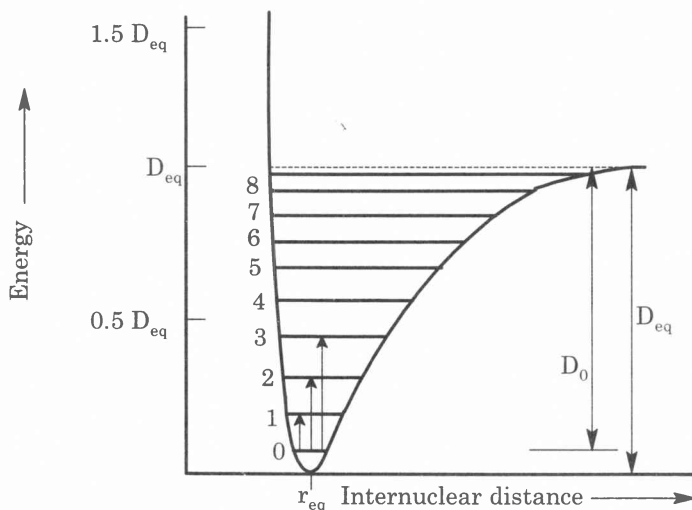


Figure 10.15: Vibrational transitions in a diatomic anharmonic vibrator

An empirical function known as Morse function fits the above curve (Figure 10.15) and is given by the following expression, where D_{eq} is the dissociation energy and a is a constant for a particular molecule:

$$E = D_{eq} [1 - \exp\{a(r_{eq} - r)\}]^{1/2} \quad (vi)$$

The above equation is inserted in *Schrödinger equation* to give the following expression for the vibrational energy levels:

$$E_v = \left(v + \frac{1}{2}\right)^2 h c w_e - \left(v + \frac{1}{2}\right)^2 - h c w_e x_e + \dots \quad (vii)$$

where w_e is *equilibrium vibrational wave number* and x_e is the *anharmonicity constant*.

The selection rules for anharmonic vibrator are $v = \pm 1, \pm 2, \pm 3, \dots$. But, practically only transitions corresponding to $v = \pm 1, \pm 2$ and ± 3 are observed, other lines go on decreasing in their intensity as the population of higher energy levels also go on decreasing. For example, the ratio of number of molecules in the $v = 1$ to $v = 0$ state is given by the following expression:

$$\frac{N_1}{N_0} = \exp\left(\frac{-h c w}{k T}\right) \quad (viii)$$

At $T = 300$ K, the value of $w = 1000$, so, the population ratio can be obtained as follows:

$$\frac{N_1}{N_0} = \exp\left[\frac{-6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300}\right] = 8.246 \times 10^{-3} \quad (ix)$$