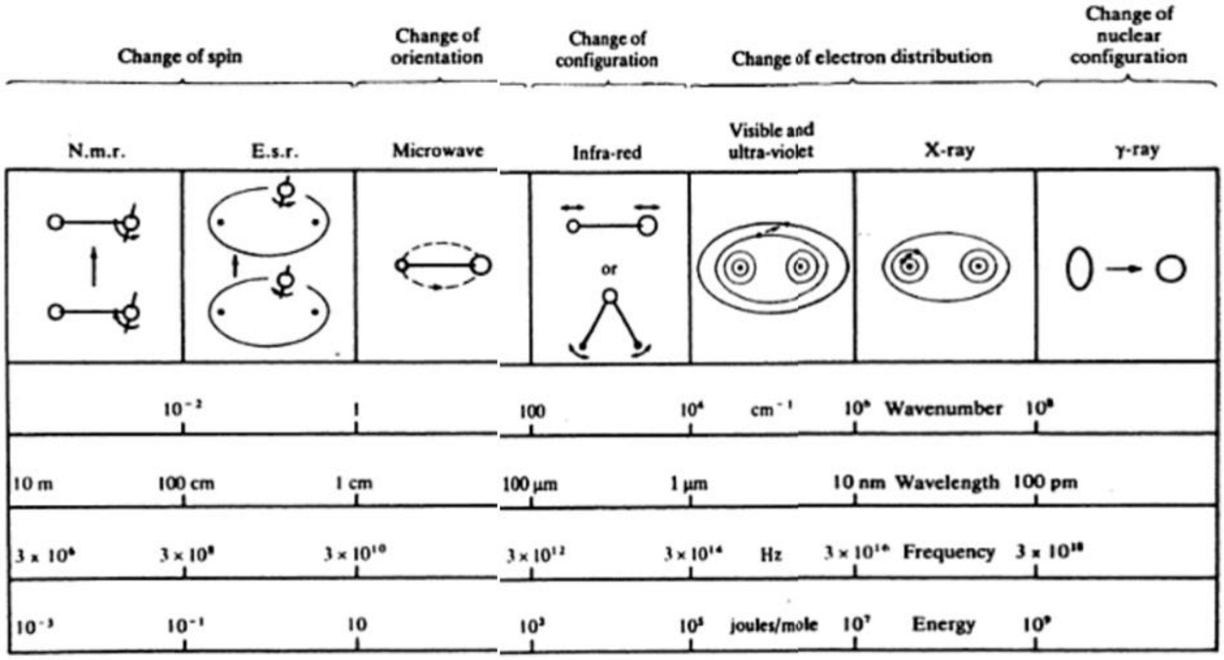
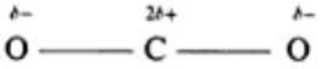
# Infra-red Spectroscopy

## Introduction

Infra-red region: $3 \times 10^{12}$–$3 \times 10^{14}$ Hz; 100 µm–1 µm wavelength. Vibrational spectroscopy. One of the most valuable spectroscopic regions for the chemist. Separations between levels are some $10^4$ joules/mole (Chapter 3).

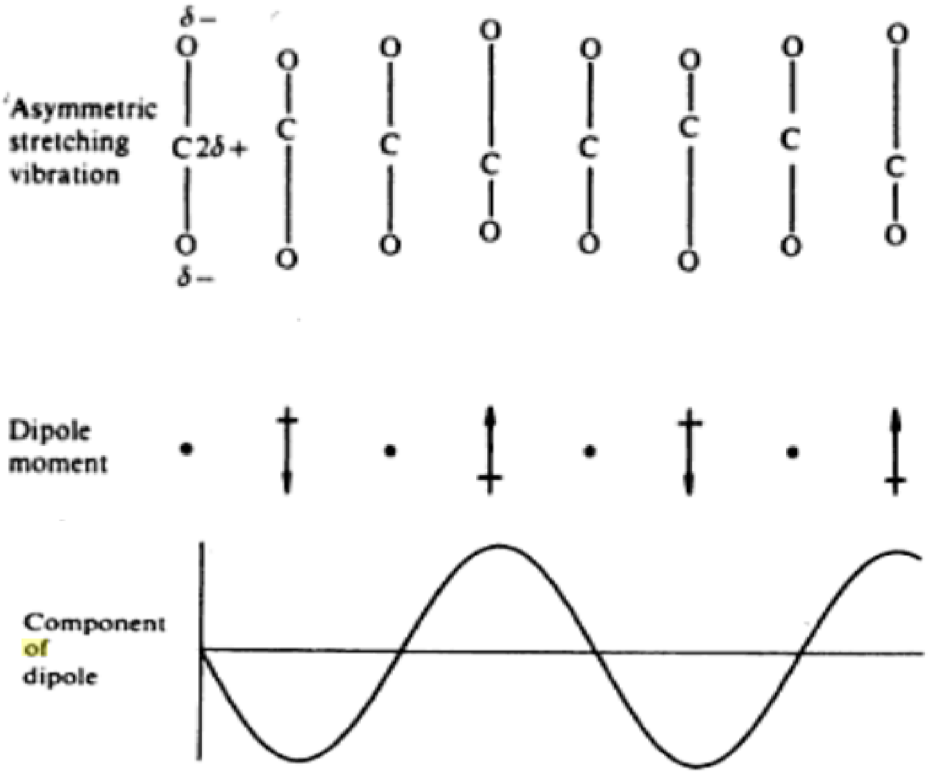


The infra-red region. Here it is a vibration, rather than a rotation, which must give rise to a dipole change. Consider the carbon dioxide molecule as an example, in which the three atoms are arranged linearly with a small net positive charge on the carbon and small negative charges on the oxygens:



$$\overset{\delta-}{\mathrm{O}} — \overset{2\delta+}{\mathrm{C}} — \overset{\delta-}{\mathrm{O}}$$

During the mode of vibration known as the 'symmetric stretch', the molecule is alternately stretched and compressed, both C—O bonds changing simultaneously, as in Fig. 1.6. Plainly the dipole moment remains zero throughout the whole of this motion, and this particular vibration is thus 'infra-red inactive'.



## Condition:

### Dipole Changes during Vibrations and Rotations

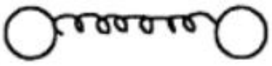
In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. Only under these conditions, the alternating electrical field of the radiation interact with the molecule and cause the changes in the amplitude of one of its motions. The charge distribution around a molecule such as HCl is not symmetric. Thus, HCl has a significant dipole moment and it is said to be polar ($H^{+\delta}$, $Cl^{-\delta}$). As the HCl molecule vibrates longitudinally, a regular fluctuation in its dipole moment occurs. Thus, a field is developed that can interact with the electrical field associated with the radiation. No net change in dipole moment occurs during the vibration or rotation of homonuclear species such as $H_2$, $O_2$, $N_2$ or $Cl_2$ and therefore such molecules cannot absorb in the infrared.

### Types of Molecular Vibrations

Vibrations may basically be characterised into the following two categories.

(i) Stretching and (ii) bending.

A stretching vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms, but the atoms remain in the same bond axis.



Stretching vibrations are of two types:

### *(i) Symmetrical stretching*

In this stretching both the atoms move in and out simultaneously. For example, symmetrical stretching of > $CH_2$ group is shown in Fig. 4.12.

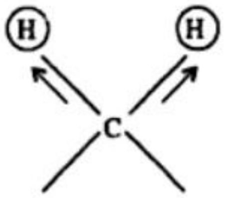


Fig. 4.12. Symmetrical stretching.

### *(ii) Asymmetrical stretching*

In this stretching, one atom moves 'in' while the other moves 'out'. It is represented for >$CH_2$ group in Fig. 4.13.

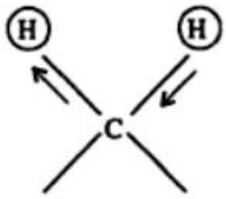
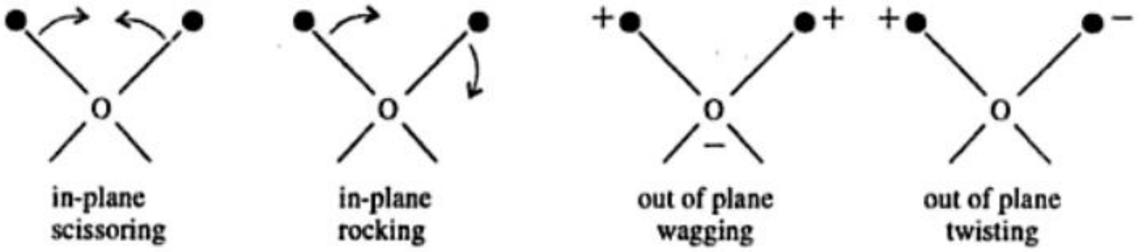


Fig. 4.13. Asymmetrical stretching.

Bending vibrations are characterised by a change in the angle between the two bonds and are of four types as shown in Fig. 4.14.

(i) scissoring (ii) rocking (iii) wagging and (iv) twisting



(+) indicates motion from plane toward reader

(–) indicates motion from plane away from reader

Fig. 4.14

## Model of Stretching Vibrations

**Simple harmonic motion:** When two masses are connected by a spring, a disturbance of one of these masses along the axis of the spring results in a vibration called a simple harmonic motion.

### 3.1.2 The Simple Harmonic Oscillator

In Fig. 3.1 we have plotted the energy in the form of Eq. (3.2), i.e. as a parabola. The zero of curve and equation is at $r = r_{eq.}$, and any energy in excess of this, for example at $\varepsilon_2$, arises because of extension or compression of the bond. The figure shows that if one atom (Cl) is considered to be stationary on the $r = 0$ axis, the other (H) will oscillate between H′ and H″. In the case of HCl, it is a good approximation to say that, during vibrations, the heavy chlorine atom stays virtually still and it is the much lighter hydrogen which moves. However, only the *distance* between the two atoms is important and for any diatomic molecule we can always imagine ourselves to be sitting on one atom and watching the other move—from our point of view the atom we are on is stationary and can be assumed fixed on the $r = 0$ axis. Thus diagrams like Fig. 3.1 apply to *any* diatomic molecule.

If the energy of the HCl molecule of Fig. 3.1 is increased to $\varepsilon_1$ the oscillation will become more vigorous—that is to say the degree of compression and extension will be greater—but the vibrational frequency will not change. An elastic bond, like a spring, has a certain intrinsic vibrational frequency, dependent on the mass of the system and the force constant, but is independent of the amount of distortion. Classically it is simple to show that the oscillation frequency is:

$$\omega_{osc.} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{Hz} \tag{3.3}$$

where $\mu$ is the reduced mass of the system (cf. Eq. (2.9)). To convert this frequency to wavenumbers, the unit most usually employed in vibrational spectroscopy, we must divide by the velocity of light, $c$, expressed in cm s$^{-1}$ (cf. Sec. 1.1), obtaining:

$$\bar{\omega}_{osc.} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1} \tag{3.4}$$

Vibrational energies, like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system may be calculated from the Schrödinger equation. For the simple harmonic oscillator these turn out to be:

$$E_v = (v + \tfrac{1}{2})h\omega_{osc.} \quad \text{joules} \quad (v = 0, 1, 2, \ldots) \tag{3.5}$$

where $v$ is called the *vibrational quantum number*. Converting to the spectroscopic units, cm$^{-1}$, we have:

$$\varepsilon_v = \frac{E_v}{hc} = (v + \tfrac{1}{2})\bar{\omega}_{osc.} \quad \text{cm}^{-1} \tag{3.6}$$

as the only energies allowed to a simple harmonic vibrator. Some of these are shown in Fig. 3.2.

In particular, we should notice that the *lowest* vibrational energy, obtained by putting $v = 0$ in Eq. (3.5) or (3.6), is

$$E_0 = \tfrac{1}{2}h\omega_{osc.} \quad \text{joules} \quad (\omega_{osc.} \text{ in Hz})$$

or

$$\varepsilon_0 = \tfrac{1}{2}\bar{\omega}_{osc.} \quad \text{cm}^{-1} \quad (\bar{\omega}_{osc.} \text{ in cm}^{-1}) \tag{3.7}$$

The implication is that the diatomic molecule (and, indeed, *any* molecule) can never have zero vibrational energy; the atoms can never be completely at rest relative to each other. The quantity $\frac{1}{2}h\omega_{osc.}$ joules or $\frac{1}{2}\bar{\omega}_{osc.}$ cm$^{-1}$ is known as the zero-point energy; it depends only on the classical vibration frequency and hence (Eq. (3.3) or (3.4)) on the strength of the chemical bond and the atomic masses.

The prediction of zero-point energy is the basic difference between the wave mechanical and classical approaches to molecular vibrations. Classical mechanics could find no objection to a molecule possessing no vibrational energy but wave mechanics insists that it must always vibrate to some extent; the latter conclusion has been amply borne out by experiment.

Further use of the Schrödinger equation leads to the simple *selection rule* for the harmonic oscillator undergoing vibrational changes:

$$\Delta v = \pm 1 \tag{3.8}$$

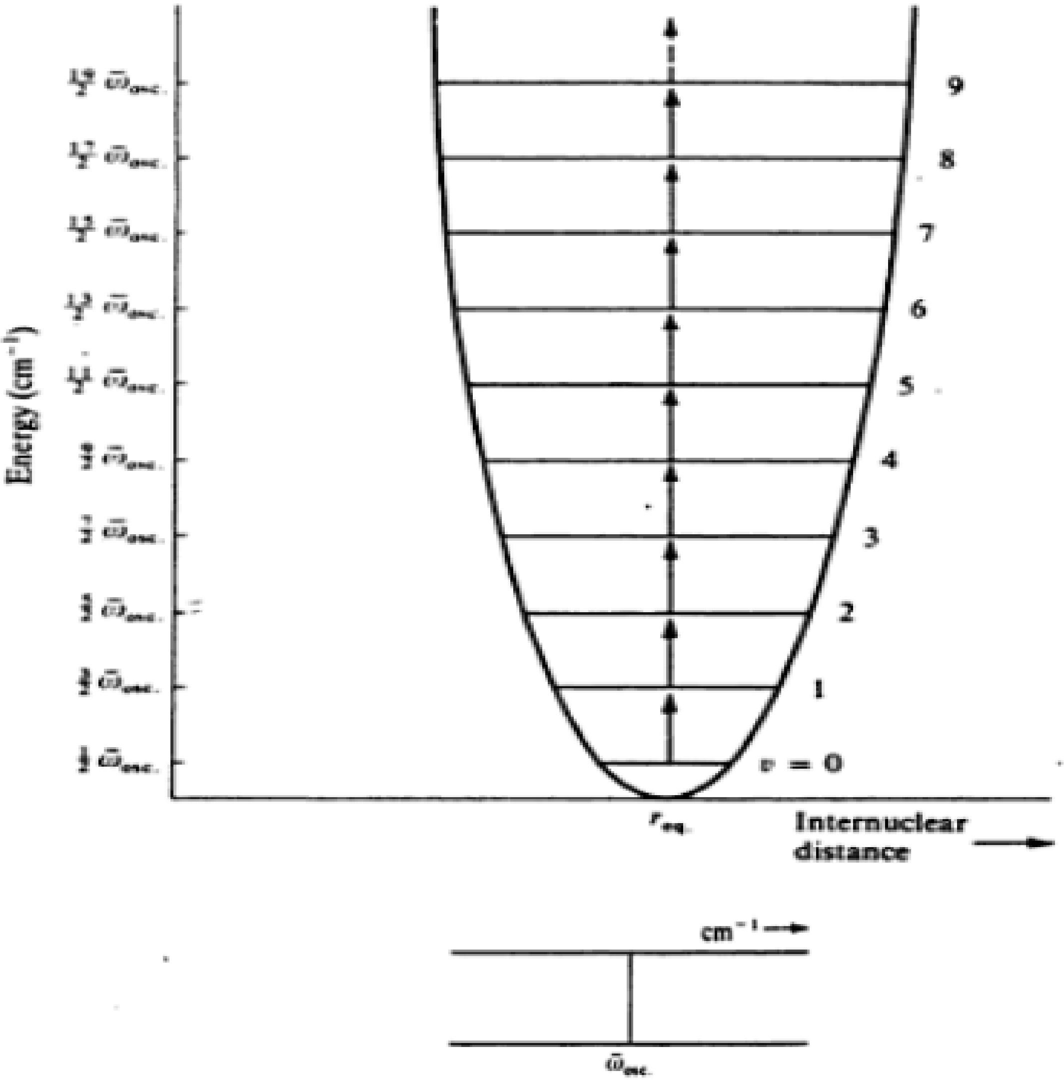


**Figure 3.2** The vibrational energy levels and allowed transitions between them for a diatomic molecule undergoing simple harmonic motion.

Applying the selection rule we have immediately:

$$\varepsilon_{v+1\to v} = (v+1+\tfrac{1}{2})\bar{\omega}_{\text{osc.}} - (v+\tfrac{1}{2})\bar{\omega}_{\text{osc.}} \\ = \bar{\omega}_{\text{osc.}} \quad \text{cm}^{-1} \tag{3.9a}$$

for emission and

$$\varepsilon_{v\to v+1} = \bar{\omega}_{\text{osc.}} \quad \text{cm}^{-1} \tag{3.9b}$$

for absorption, whatever the initial value of $v$.

Such a simple result is also obvious from Fig. 3.2—since the vibrational levels are equally spaced, transitions between any two neighbouring states will give rise to the same energy change. Further, since the difference between energy levels expressed in cm$^{-1}$ gives directly the wavenumber of the spectral line absorbed or emitted

$$\bar{\nu}_{\text{spectroscopic}} = \varepsilon = \bar{\omega}_{\text{osc.}} \quad \text{cm}^{-1} \tag{3.10}$$

This, again, is obvious if one considers the mechanism of absorption or emission in classical terms. In absorption, for instance, the vibrating molecule will absorb energy only from radiation with which it can coherently interact (cf. Fig. 1.8) and this must be radiation of its own oscillation frequency.

### 3.1.3 The Anharmonic Oscillator

Real molecules do not obey exactly the laws of simple harmonic motion; real bonds, although elastic, are not so homogeneous as to obey Hooke's law. If the bond between atoms is stretched, for instance, there comes a point at which it will break—the molecule dissociates into atoms. Thus although for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes—say greater than 10 per cent of the bond length—a much more complicated behaviour must be assumed. Figure 3.3 shows, diagrammatically, the shape of the energy curve for a typical diatomic molecule, together with (dashed) the ideal, simple harmonic parabola.

A purely empirical expression which fits this curve to a good approximation was derived by P. M. Morse, and is called the Morse function:

$$E = D_{\text{eq.}}[1 - \exp\{a(r_{\text{eq.}} - r)\}]^2 \tag{3.11}$$

where $a$ is a constant for a particular molecule and $D_{\text{eq.}}$ is the dissociation energy.

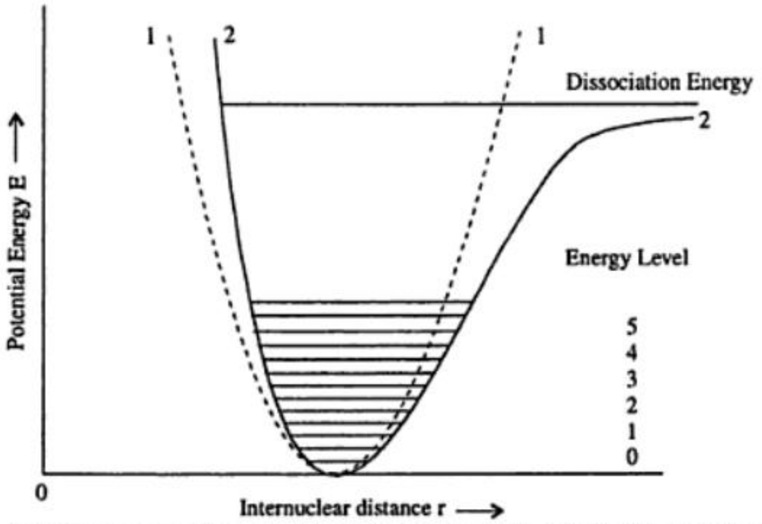


Fig. 4.16. Potential energy curves for (1) Harmonic oscillator and (2) Anharmonic oscillator.

When Eq. (3.11) is used instead of Eq. (3.2) in the Schrödinger equation, the pattern of the allowed vibrational energy levels is found to be:

$$\varepsilon_v = (v+\tfrac{1}{2})\bar{\omega}_e - (v+\tfrac{1}{2})^2\bar{\omega}_e x_e \quad \text{cm}^{-1} \quad (v = 0, 1, 2, \ldots) \tag{3.12}$$

where $\bar{\omega}_e$ is an oscillation frequency (expressed in wavenumbers) which we shall define more closely below, and $x_e$ is the corresponding anharmonicity constant which, for bond stretching vibrations, is always small and positive ($\approx +0.01$), so that the vibrational levels crowd more closely together with increasing $v$. Some of these levels are sketched in Fig. 3.4.

It should be mentioned that Eq. (3.12), like (3.11), is an approximation only; more precise expressions for the energy levels require cubic, quartic, etc., terms in $(v+\frac{1}{2})$ with anharmonicity constants $y_e$, $z_e$, etc., rapidly diminishing in magnitude. These terms are important only at large values of $v$, and we shall ignore them.

If we rewrite Eq. (3.12), for the anharmonic oscillator, as:

$$\varepsilon_v = \bar{\omega}_e\{1 - x_e(v+\tfrac{1}{2})\}(v+\tfrac{1}{2}) \tag{3.13}$$

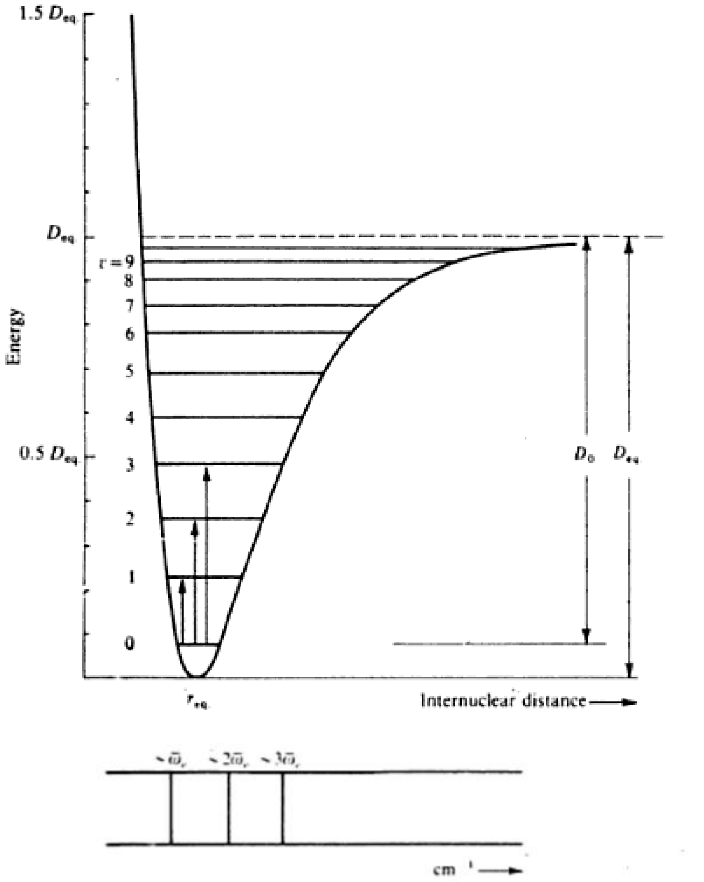


**Figure 3.4** Th rational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic o ions.

and compare with the energy levels of the *harmonic* oscillator (Eq. (3.6)), we see that we can write:

$$\bar{\omega}_{\text{osc.}} = \bar{\omega}_e\{1 - x_e(v + \tfrac{1}{2})\} \tag{3.14}$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing $v$. If we now consider the hypothetical energy state obtained by putting $v = -\frac{1}{2}$ (at which, according to Eq. (3.13), $\varepsilon = 0$) the molecule would be at the equilibrium point with zero vibrational energy. Its oscillation frequency (in $\text{cm}^{-1}$) would be:

$$\bar{\omega}_{\text{osc.}} = \bar{\omega}_e$$

Thus we see that $\bar{\omega}_e$ may be defined as the (hypothetical) *equilibrium oscillation frequency* of the anharmonic system—the frequency for infinitely small vibrations about the equilibrium point. For any real state specified by a positive integral $v$ the oscillation frequency will be given by Eq. (3.14). Thus in the ground state ($v = 0$) we would have:

$$\bar{\omega}_0 = \bar{\omega}_e(1 - \tfrac{1}{2}x_e) \quad \text{cm}^{-1}$$

and

$$\varepsilon_0 = \tfrac{1}{2}\bar{\omega}_e(1 - \tfrac{1}{2}x_e) \quad \text{cm}^{-1}$$

and we see that the zero-point energy differs slightly from that for the harmonic oscillator (Eq. (3.7)).

The selection rules for the anharmonic oscillator are found to be:

$$\Delta v = \pm 1, \pm 2, \pm 3, \ldots$$

Thus they are the same as for the harmonic oscillator, with the additional possibility of larger jumps. These, however, are predicted by theory and observed in practice to be of rapidly diminishing probability and normally only the lines of $\Delta v = \pm 1, \pm 2$, and $\pm 3$, at the most, have observable intensity. Further, the spacing between the vibrational levels is, as we shall shortly see, of order $10^3\,\text{cm}^{-1}$ and, at room temperature, we may use the Boltzmann distribution (Eq. (1.12)) to show

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left\{-\frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300}\right\}$$

$$\approx \exp(-4.8) \approx 0.008$$

In other words, the population of the $v = 1$ state is nearly 0.01 or some one per cent of the ground state population. Thus, to a very good approximation, we may ignore all transitions originating at $v = 1$ or more and restrict ourselves to the three transitions:

1. $v = 0 \rightarrow v = 1$, $\Delta v = +1$, with considerable intensity.

$$\begin{aligned} \Delta\varepsilon &= \varepsilon_{v=1} - \varepsilon_{v=0} \\ &= (1 + \tfrac{1}{2})\bar{\omega}_e - x_e(1 + \tfrac{1}{2})^2\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\bar{\omega}_e\} \\ &= \bar{\omega}_e(1 - 2x_e) \quad \text{cm}^{-1} \end{aligned} \tag{3.15a}$$

2. $v = 0 \rightarrow v = 2$, $\Delta v = +2$, with small intensity.

$$\begin{aligned} \Delta\varepsilon &= (2 + \tfrac{1}{2})\bar{\omega}_e - x_e(2 + \tfrac{1}{2})^2\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\bar{\omega}_e\} \\ &= 2\bar{\omega}_e(1 - 3x_e) \quad \text{cm}^{-1} \end{aligned} \tag{3.15b}$$

3. $v = 0 \rightarrow v = 3$, $\Delta v = +3$, with normally negligible intensity.

$$\begin{aligned}\Delta\varepsilon &= (3 + \tfrac{1}{2})\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\bar{\omega}_e\} \\ &= 3\bar{\omega}_e(1 - 4x_e) \quad \text{cm}^{-1}\end{aligned} \tag{3.15c}$$

These three transitions are shown in Fig. 3.4. To a good approximation, since $x_e \approx 0.01$, the three spectral lines lie very close to $\bar{\omega}_e$, $2\bar{\omega}_e$, and $3\bar{\omega}_e$. The line near $\bar{\omega}_e$ is called the *fundamental absorption*, while those near $2\bar{\omega}_e$ *and* $3\bar{\omega}_e$ are called the *first* and *second overtones*, respectively. The spectrum of HCl, for instance, shows a very intense absorption at 2886 cm$^{-1}$, a weaker one at 5668 cm$^{-1}$, and a very weak one at 8347 cm$^{-1}$. If we wish to find the equilibrium frequency of the molecule from these data, we must solve any two of the three equations (cf. Eqs (3.15)):

$$\begin{aligned}\bar{\omega}_e(1 - 2x_e) &= 2886 \quad \text{cm}^{-1} \\ 2\bar{\omega}_e(1 - 3x_e) &= 5668 \quad \text{cm}^{-1} \\ 3\bar{\omega}_e(1 - 4x_e) &= 8347 \quad \text{cm}^{-1}\end{aligned}$$

and we find $\bar{\omega}_e = 2990\,\text{cm}^{-1}$, $x_e = 0.0174$. Thus we see that, whereas for the ideal harmonic oscillator the spectral absorption occurred *exactly* at the classical vibration frequency, for real, anharmonic molecules the observed fundamental absorption frequency and the equilibrium frequency may differ considerably.

The force constant of the bond in HCl may be calculated directly from Eq. (2.22) by inserting the value of $\bar{\omega}_e$:

$$\begin{aligned}k &= 4\pi^2\bar{\omega}_e^2 c^2 \mu \\ &= 516\,\text{N m}^{-1}\end{aligned}$$

4. $v = 1 \rightarrow v = 2$, $\Delta v = +1$, normally very weak

$$\begin{aligned}\Delta\varepsilon &= 2\tfrac{1}{2}\bar{\omega}_e - 6\tfrac{1}{4}x_e\bar{\omega}_e - (1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e) \\ &= \bar{\omega}_e(1 - 4x_e) \quad \text{cm}^{-1}\end{aligned} \tag{3.15d}$$

Thus, should this weak absorption arise, it will be found close to and at slightly *lower* wavenumbers than the fundamental (since $x_e$ is small and positive). Such weak absorptions are usually called *hot bands* since a high temperature is one condition for their occurrence. Their nature may be confirmed by raising the temperature of the sample when a true hot band will increase in intensity.

## Modes of vibration of linear and non linear molecules

will be equal to $3n$ where $n$ is the number of atoms in a molecule. A molecule having finite dimensions is made up of rotational, vibrational and translational degree of freedom *i.e.,*

$3n$ degree of freedom = translational + rotational + vibrational

Rotational degrees of freedom results from the rotation of a molecule about an axis through the centre of gravity. Since we are concerned only with the number of fundamental vibrational modes of a molecule, so we calculate only the number of vibrational degrees of freedom of a molecule.

The frequency associated with the fundamental vibration of the molecule is called fundamental frequency. Every molecule is associated with a number of fundamental vibrations given by the formula

$3N - 6$ for non-linear

and $3N - 5$ for linear

where N = Number of atoms present in a molecule.

Since only three co-ordinates are necessary to locate a molecule in space, so we can say that a molecule has always three translational degrees of freedom.

In case of linear molecule, there are only two degrees of rotation. It is due to fact that the rotation of such a molecule about its axis of linearity does not bring about any change in the position of the atoms while rotation about the other two axis changes the position of the atoms. Thus, for a linear molecule of $n$ atoms.

Total degrees of freedom $= 3n$

Translational degrees of freedom $= 3$

Rotational degrees of freedom $= 2$

∴ Vibrational degrees of freedom $= 3n - (3 + 2)$

$= 3n - 5$

Each vibrational degree of freedom corresponds to the fundamental mode of vibration and each fundamental mode corresponds to a band. Hence, theoretically there will be $3n - 5$ possible fundamental bands for the linear molecules. For example, $CO_2$ is a linear triatomic molecule.

Here number of atoms ($n$) $= 3$

∴ Total degrees of freedom $= 3n$

$= 3 \times 3 = 9$

and Vibrational degrees of freedom $= 3n - 5$

$= 9 - 5$

$= 4$

Therefore, there are four vibrational degrees of freedom should occur in case of $CO_2$ molecule.

In the case non-linear molecule, there are three degrees of rotation, as the rotation about all the three axes will result in a change in the position of the atoms. Thus, for a non-linear molecule having $n$ atoms

Total degrees of freedom $= 3n$

Translational degrees of freedom $= 3$

Rotational degrees of freedom $= 3$

∴ Vibrational degrees of freedom $= 3n - (3 + 3)$

$= 3n - 6$

For example, $C_6H_6$ is a non-linear molecule

Here number of atoms $= 12$

Total degrees of freedom $= 3n$

$= 3 \times 12 = 36$

Translational degrees of freedom $= 3$

Rotational degrees of freedom $= 3$

∴ Vibrational degrees of freedom $= 3n - 6$

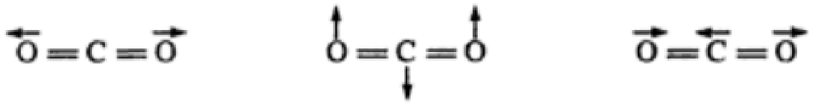
$= 36 - 6$

$= 30$

Hence, theoretically there should be 30 fundamental bands in the IR spectrum of benzene.

## 7.7.1 Normal Vibrations of $CO_2$ and $H_2O$ Molecules

The $CO_2$ molecule is linear and will have 4 normal vibrations. They are depicted in Fig. 7.5. The first and second vibrations are completely symmetric. Hence, they are called the symmetric stretching and symmetric bending modes respectively. There is an alternate way of looking at the system. These two vibrations are unchanged in character when the molecule is rotated by 180° about an axis perpendicular to the bond axis and passing through the carbon atoms.



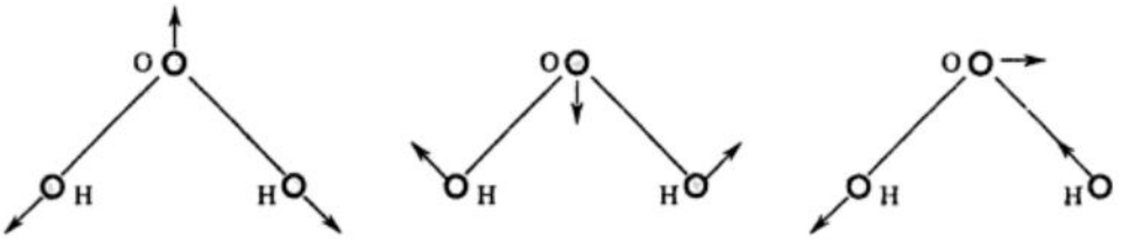
$\nu_1$—Symmetric stretching (1330 $cm^{-1}$)

$\nu_2$—Symmetric bending (667 $cm^{-1}$)

$\nu_3$—Asymmetric stretching (2349 $cm^{-1}$)

The vibrations are labelled as $\nu_1$, $\nu_2$ and $\nu_3$ (Fig. 7.5). By convention it is the practice to label vibrations in decreasing frequency within their symmetry type. Thus, the symmetric vibrations are labelled $\nu_1$ (highest frequency) and $\nu_2$ (next highest) and the asymmetric one as $\nu_3$. The $\nu_2$ vibration actually consists of 2 vibrations – one in the plane of the paper and the other in a plane perpendicular to it. Hence it is doubly degenerate. The observed vibrational frequencies are given in brackets.

The three normal modes of the nonlinear triatomic water molecule are as shown in Fig. 7.6.



$\nu_1$—Symmetric stretching (3652 $cm^{-1}$) Raman & IR active

$\nu_2$—Symmetric bending (1595 $cm^{-1}$) Raman & IR active

$\nu_3$—Asymmetric stretching (3756 $cm^{-1}$) Raman & IR active

**Fig. 7.6** The normal modes of water molecule.

## Force Constant

The difference in energy $\Delta E$ between two adjacent levels, $E_v$ and $E_{v+1}$ is given by

$$\Delta E = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

or

$$h\nu = \frac{\hbar}{2\pi}\sqrt{\frac{k}{\mu}}$$

or

$$\frac{c}{\lambda} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

or

$$\frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

or

$$\overline{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \text{... (4.24)}$$

where $K$ = stretching force constant and $\mu$ is the reduced mass given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ for the diatomic molecule } AB.$$

In the HCl molecule, the absorption of infrared radiation with $\overline{\nu} = 2890 \text{ cm}^{-1}$ corresponds to a transition from the ground state ($v = 0$) to the first excited state ($v = 1$). Since all the quantities are known, the value of force constant $k$ can be obtained to be $4.84 \times 10^5$ dynes/cm.

Calculation of reduced mass for HCl

$$\mu_{HCl} = \frac{m_H \cdot m_{Cl}}{m_H + m_{Cl}}$$

$$= \frac{\frac{1}{N} \cdot \frac{35.5}{N}}{\frac{1}{N} + \frac{35.5}{N}} = \frac{35.5}{36.5\, N}$$

$$= \frac{35.5}{365 \times 6.02 \times 10^{23}} = 1.62 \times 10^{-24} \text{ g}$$

# Applications of IR Spectra

## 7.10 HYDROGEN BONDING

Formation of the hydrogen bond (H–bond) also affects the vibrational frequencies of solids considerably. The H-bond is defined as the bond between an atom B and the hydrogen atom of a covalent bond A–H, forming the group A–H... B. Atoms A and B have electro-negativities greater than H. Generally, it can be considered as a proton shared by two lone pair electrons. It is an important form of molecular association and can be of both inter and intramolecular type. Different types of studies are needed to get a complete picture of H-bond. Spectroscopic methods offer the information needed to understand the strength of H-bond.

A large number of studies on H-bonded systems show the following effects with the formation of a H-bond.

(i) Shifting of $\nu_{A-H}$ stretching vibration to lower frequencies with broadening and increase in intensity as the strength of the H–bond becomes stronger. Typical line widths of $\nu_{A-H}$ for weak, medium and strong H–bonded systems are of the order of 10, $10^2$ and $10^3$ $cm^{-1}$ respectively.

(ii) Shifting of $\delta_{A-H}$ deformation band to higher frequencies without appreciable changes in line width and intensity.

(iii) Appearance of new bands corresponding to H... B stretching and deformation at low frequencies.

(iv) Shifting of the vibrational modes involving the hydrogen bond acceptor atom B. This shift is generally much smaller than those found for donor A–H vibrations.

In IR and Raman spectroscopic studies, the main emphasis is on $\nu_{A-H}$ and $\delta_{A-H}$ frequencies since the effects on these are generally larger than those observed for the other frequencies. Also, the regions in which these frequencies occur are relatively free from vibrations of other molecules. Therefore, IR studies offer a powerful technique for understanding the nature and strength of hydrogen bonds in molecules.

### The 'Fingerprint' Region (Between 1500–700 $cm^{-1}$)

The region below 1600 $cm^{-1}$ is referred to as fingerprint region for many organic compounds. In this region significant differences occur in the spectra of substances which are very much alike. The absorption band in this region for a given functional group occurs at different frequencies depending on the skeleton of the molecule. As a consequence, a close match between two spectra in fingerprint region constitute strong evidence for the identification of the compound yielding the spectra. Most single bonds give rise to absorption bands at these frequencies because their energies are about the same. Strong interaction occurs below neighbouring bonds.

Important group frequencies that are found in the fingerprint region include the C—O—C stretching vibration in ethers and esters at about 1200 $cm^{-1}$ and the C—Cl stretching vibration at 700–800 $cm^{-1}$.

## Applications

It has wide applications in characterizing the functional groups. Some of the important applications are as follows :

(*i*) *Identification of substance.* It is very helpful in finding out whether a given sample of the organic substance is identical with another or not. If the IR spectra of the two compounds are same in identical conditions then the compound is identified. But this technique fails to distinguish between the two enantiomers of a substance because the IR spectra for the enantiomers are exactly the same.

(*ii*) *In determining the purity of a compound.* It is useful to check the purity of the compound by comparing its spectrum with that of the pure compound. Pure compound always shows a sharp peak whereas impure compound shows many extra poorly resolved bands.

(*iii*) *Presence of functional group.* In order to determining the molecular structure it is quite helpful in establishing the structure of the unknown organic compound by knowing the functional groups and the nature of the bond. For example, if the spectrum contains a strong absorption band 1900–1600 $cm^{-1}$, the presence of ($>C=O$) in a compound is suspected.

(*iv*) *Studying the progress of the reaction.* It determines the progress of a reaction by examine the spectra of small portion of compound of a reaction mixture in small interval of time. The rate of disappearance of characteristic absorption bands of a reactant and the increase of appearance of characteristic absorption bands of a product gives the exact idea of the formation of progress of a reaction.

(*v*) *Presence of conjugation or hydrogen bonding.* The presence of conjugation or hydrogen bonding can be easily detected by IR spectra as it shifts the stretching to the lower wave number. It also distinguishes between inter-molecular hydrogen bonding and intramolecular hydrogen bonding; the absorption position in the latter being independent of the change in concentration.

(*vi*) *In studying the reaction mechanism.* The reaction mechanism can be explained with the help of IR spectra. The IR spectra determine the formation of intermediates during the formation of products.

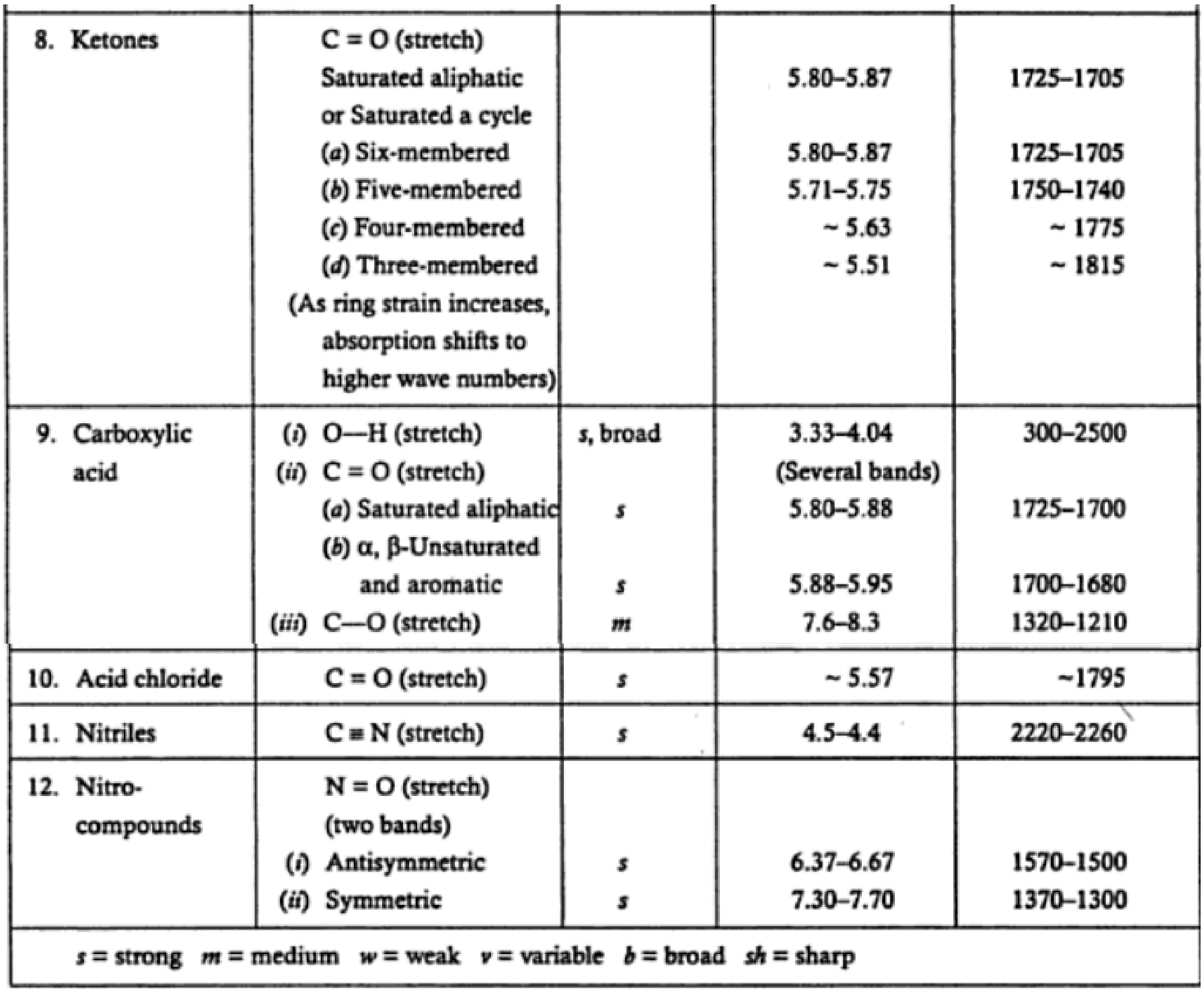
**Table 1**

| Class of compounds | Type of vibrations | Intensity | Approximate range | |
|---|---|---|---|---|
| | | | Wavelength (μ) | Frequency ($cm^{-1}$) |
| 1. Alkanes | (*i*) C—H (Stretch) | *m – s* | 3.38–3.51 | 2960–2850 |
| | (*ii*) $>CH_2$ (bend) | *m* | 6.85–6.89 | 1460–1450 |
| | (*iii*) $C—CH_3$ (bend) | *w* | ~ 7.27 | ~1375 |
| 2. Alkenes | (*i*) =C—H (stretch) | *m* | 3.29–3.32 | 3040–3010 |
| | (*ii*) C = C (stretch) | *w* | 6.02–6.35 | 1660–1600 |
| 3. Alkynes | (*i*) ≡C—H (stretch) | S | 3.05 | 3300 |
| | (*ii*) C≡C (stretch) | *m, w* or *v* | 4.42–4.76 | 2260–2100 |

| | | | | |
|---|---|---|---|---|
| 4. Aromatic hydrocarbon | (*i*) = C—H (stretch) | *w* | 3.28–33.3 | 3050–3000 |
| | (*ii*) C = C (stretch) | *v* | 6.25 | 1600 |
| | | *v* | 6.33 | 1580 |
| | | *m* | 6.67 | 1500 |
| | (*iii*) C—H (bending) | *m* | ~ 6.09 | ~ 1450 |
| | The number and position of these bonds depends upon the substitution pattern. For example | *m–s* | 14.28–11.11 | 900–700 |
| | **Mono substituted benzenes** | *s* | 14.5–14.1 | 710–690 |
| | (two bands) | *s* | 13.7–13.0 | 770–730 |
| | ***o*-Disubstituted** | | | |
| | (one band) | | | |
| | ***m*-Disubstituted** | *v, s* | 13.6–13.0 | 770–735 |
| | (two bands) | *m* | 14.5–14.1 | 710–690 |
| | ***p*-Disubstituted** | *m* | 13.3–12.5 | 800–750 |
| | (one band) | *s* | 12.5–11.9 | 840–800 |

| | | | | |
|---|---|---|---|---|
| 5. Alcohols and Phenols | Free O—H (stretch) | *sh* | 2.78–2.74 | 3650–3600 |
| | H-bonded O—H (stretch) | *sh* | 3.13–286 | 3500–3200 |
| | C—O (stretch) | *s* | 10–8 | 1250–1200 |
| 6. Ethers | C—O (stretch) | *s* | 10–7.7 | 1300–1000 |

| | | | | |
|---|---|---|---|---|
| 7. Amines | (*i*) N—H (stretch) | | | |
| | 1° Amines | | | |
| | (two bands) | *m* | 2.86–3.12 | 3500–3200 |
| | 2° Amines | | | |
| | (one band) | *m* | 2.88–3.12 | 3500–3200 |
| | (*ii*) N—H (bend) | | | |
| | 1° Amines | *m–s* | 6.06–6.29 | 1650–1550 |
| | 2° Amines | *w* | 6.06–6.24 | 1650–1550 |
| | (*iii*) C—N (stretch) | | | |
| | (*a*) Aliphatic | *w* | 8.2–9.8 | 1220–1020 |
| | (*b*) Aromatic | *s* | 7.35–9.25 | 1360–1080 |



| | | | | |
|---|---|---|---|---|
| 8. Ketones | C = O (stretch) | | | |
| | Saturated aliphatic | | 5.80–5.87 | 1725–1705 |
| | or Saturated a cycle | | | |
| | (*a*) Six-membered | | 5.80–5.87 | 1725–1705 |
| | (*b*) Five-membered | | 5.71–5.75 | 1750–1740 |
| | (*c*) Four-membered | | ~ 5.63 | ~ 1775 |
| | (*d*) Three-membered | | ~ 5.51 | ~ 1815 |
| | (As ring strain increases, absorption shifts to higher wave numbers) | | | |
| 9. Carboxylic acid | (*i*) O—H (stretch) | *s*, broad | 3.33–4.04 (Several bands) | 300–2500 |
| | (*ii*) C = O (stretch) | | | |
| | (*a*) Saturated aliphatic | *s* | 5.80–5.88 | 1725–1700 |
| | (*b*) α, β-Unsaturated and aromatic | *s* | 5.88–5.95 | 1700–1680 |
| | (*iii*) C—O (stretch) | *m* | 7.6–8.3 | 1320–1210 |
| 10. Acid chloride | C = O (stretch) | *s* | ~ 5.57 | ~1795 |
| 11. Nitriles | C ≡ N (stretch) | *s* | 4.5–4.4 | 2220–2260 |
| 12. Nitro-compounds | N = O (stretch) (two bands) | | | |
| | (*i*) Antisymmetric | *s* | 6.37–6.67 | 1570–1500 |
| | (*ii*) Symmetric | *s* | 7.30–7.70 | 1370–1300 |
| *s* = strong *m* = medium *w* = weak *v* = variable *b* = broad *sh* = sharp | | | | |