UNIT 8 MOLECULAR SPECTROSCOPY- II

8.1 INTRODUCTION

In the previous unit, we have explained the different types of energy levels in a molecule. We also discussed how the transition between energy levels is responsible for the different types of absorption spectra. Later we discussed the rotational spectra in detail and used the same to calculate the moment of inertia and bond length for a diatomic molecule.

In this unit, firstly we study infrared spectra of diatomic molecules. Then we talk about the infrared spectra of polyatomic molecules. We discuss the applications of infrared spectra in the characterisation of group frequencies. We also take up ultraviolet and visible spectra in detail. We then explain how electronic spectra are useful in the identification of chromophores in a molecule. Finally we discuss applications of ultraviolet and visible spectra for quantitative analysis.

Objectives

After studying this unit, you should be able to:

- describe the condition for absorption of infrared radiation,
- explain the infrared spectra of diatomic molecules,
- calculate the force constant of simple diatomic molecules from their infrared spectra,
- state the number of vibrational modes for the polyatomic molecules,
- identify some specific functional groups present in organic compounds on the basis of infrared spectra,
- explain the significance of $\lambda_{\text{max}}$ and $\epsilon$ values of a compound,
- state different types of electronic transitions in a molecule, and
- describe simple applications of ultraviolet and visible spectra in qualitative and quantitative analysis.

8.2 REQUISITE FOR INFRARED ABSORPTION

In the previous unit, we dealt with the rigid rotator model for the diatomic molecule, assuming that the bond is inflexible. The atoms in a molecule actually do not remain in fixed positions but vibrate about some mean positions. We have already noted that the absorption of infrared radiation by a molecule increases its vibrational energy. From the study of infrared absorption spectrum, we can, therefore, derive information about the spacings of the allowed vibrational energies. As in rotation spectra, all types of molecules cannot interact with infrared radiation. Only those molecules which show change in dipole
moment during a vibration can exhibit infrared spectra. Homonuclear diatomic molecules such as $O_2$, $N_2$ or $Cl_2$ do not show change in dipole moment during vibration; therefore, they do not exhibit infrared spectra.

You are aware that the infrared radiation absorbed by a gaseous molecule changes both the vibrational and the rotational energies of the molecule. This further adds to the complexity of infrared spectrum. We first consider the diatomic molecule undergoing vibrational and rotational energy changes simultaneously, and then we focus our attention on the group frequencies of polyatomic molecules.

### 8.3 INFRARED SPECTRA OF DIATOMIC MOLECULES

Let us consider in detail, the absorption spectrum of gaseous hydrogen chloride, as a typical example of a diatomic molecule. Figure 8.1 shows the absorption spectrum of gaseous hydrogen chloride in the wave number region $2600-3100$ cm$^{-1}$. The most important features to note are the regular spacings of about $20$ cm$^{-1}$ between adjacent lines and the fact that the spectrum is centred at about $2890$ cm$^{-1}$.

![Fig. 8.1: Infrared spectrum (2600-3100 cm$^{-1}$) of gaseous hydrogen chloride.](image)

The spectra of hydrogen chloride molecule can be understood in terms of vibrational and rotational transitions. You are aware that energy needed for rotational transition is less than that for vibrational transition. The numerous vibrational transitions accompanied by the rotational transitions are responsible for the multiple lines in its infrared spectrum as shown in Fig. 8.1. This is explained in more detail in the next section.

### 8.4 THEORY OF INFRARED ABSORPTION SPECTRA

The quantum theory predicts that only certain vibrational energies ($E_{vib}$) are allowed. These values are governed by the expression:

$$E_{vib} = (v + \frac{1}{2}) \ h\nu_0$$

where $v$ is the vibrational quantum number, with possible values of 0, 1, 2, etc. and $\nu_0$ is the fundamental frequency.

The lowest two energy levels, $v = 0$ and $v = 1$, will have $E_{vib}$ values of $1/2\ h\nu_0$ and $3/2h\nu_0$, respectively, so that the difference between them (i.e., the energy of the $v = 0 \rightarrow v = 1$ transition) is $h\nu_0$. The appropriate frequency of the electromagnetic radiation associated with this energy change is the fundamental frequency ($\nu_0$). It should also be noted that even in the ground vibrational state, the molecule has the vibrational energy, $1/2\ h\nu_0$. This is called the **zero point energy**.

When a molecule has rotational and vibrational changes simultaneously, the total energy associated with these changes is the sum of the rotational and vibrational energies, i.e.,

$$E_{vib} + E_{rot} = (v + \frac{1}{2}) \ h\nu_0 + \frac{\hbar^2}{8\pi^2 I} \ J \ (J + 1)$$
Allowed energy levels are illustrated in Fig. 8.2. Note that the vibrational energy levels are much more widely spaced than the rotational energy levels.

When a molecule absorbs energy in the infrared region of electromagnetic spectrum, it can change its vibrational and rotational levels and these energy changes account for the features of a typical spectrum (Fig. 8.1). The infrared absorption spectrum in the gas phase is much complicated due to the rotational fine structure (Fig. 8.3 a). We can avoid this complication by taking the spectrum for liquid (Fig. 8.3 b) or solid samples. For such cases, the rotational fine structure becomes buried and a broad peak is observed for a vibrational energy change. The interpretation of the infrared spectra is thus made simple even for polyatomic molecules.

![Diagram of energy levels and transitions](image)

**Fig. 8.2**: Vibrational energy levels with rotational sublevels for a diatomic molecule.

When a molecule absorbs energy in the infrared region of electromagnetic spectrum, it can change its vibrational and rotational levels and these energy changes account for the features of a typical spectrum (Fig. 8.1). The infrared absorption spectrum in the gas phase is much complicated due to the rotational fine structure (Fig. 8.3 a). We can avoid this complication by taking the spectrum for liquid (Fig. 8.3 b) or solid samples. For such cases, the rotational fine structure becomes buried and a broad peak is observed for a vibrational energy change. The interpretation of the infrared spectra is thus made simple even for polyatomic molecules.

![Spectra of CO in gas phase and CCl₄ solution](image)

**Fig. 8.3**: The spectra of CO (a) in the gas phase (b) in CCl₄ solution.

Now, we consider the theoretical basis of vibration spectra. It is simpler to understand the vibration of a diatomic molecule by classical mechanics than by quantum mechanics. If molecule undergoes only vibrational motion, we can explain the origin and changes in vibrational spectra using the ideas of the harmonic oscillator model, illustrated in Fig. 8.4. According to this model, each chemical bond acts like a spring; it connects two atoms of masses, \(m_1\) and \(m_2\), undergoing simple harmonic motion.

Such a system obeys Hooke's law; that is, when the masses are stretched or compressed away from the resting position, the restoring force is proportional to the extent of displacement \(\Delta x\) from that position. Algebraically stated,

\[
\text{Restoring force} = -k \Delta x
\]  \((8.3)\)
In figure 8.4, the diagram at the top illustrates the two masses at the resting position, while the one below when the two masses are compressed.

The distance of separation between the two particles at the resting position is \( x_0 \). But when the two particles are compressed, the distance of separation accordingly decreases to the extent \( \Delta x \).

Again the full circles represent the position of the masses at the resting position while the dotted circle in the bottom figure represent the position of one of the masses on compression. The distance through which the latter mass has been displaced is given by \( \Delta x \).

Fig. 8.4 : Ball and spring representation of a diatomic molecule.

where \( k \) is the proportionality constant known as force constant; it is the restoring force per unit displacement from the resting position. The negative sign in Eq. 8.3 indicates that the restoring force tends to pull the spring back to its original position. When the spring is compressed, it exerts a force to expand; when it is stretched, it exerts a force to pull back.

A set of masses that are connected by the spring, naturally tends to settle into a specific motion, when disturbed. The masses vibrate with a frequency that depends on the masses and the strength of the spring. Such vibrations, which occur at characteristic frequencies, are what we measure in infrared spectra. For the simple harmonic motion of the spring, it can be shown that the frequency of oscillation, \( \nu \), is given by,

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{k (m_1 + m_2)}{m_1 m_2}} \quad \ldots (8.4)
\]

where \( \mu \) is the reduced mass (being equal to \( \frac{m_1 m_2}{m_1 + m_2} \)) and \( k \) is the force constant of the spring. Similarly, the behaviour of chemical bonds can be interpreted in terms of a fundamental frequency, \( \nu_0 \), given by Eq. 8.5.

\[
\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \ldots (8.5)
\]

where \( \mu \) is the reduced mass of the two connected atoms, and by analogy, \( k \) is the force constant of the bond. The energy of a classical oscillator is equal to \( \frac{1}{2} k \xi^2 \) or \( 2\pi^2 \nu_0^2 \xi^2 \) (From Eq. 8.5, \( k = 4\pi^2 \mu \nu_0^2 \)) and hence can be varied continuously. But it can be shown that the energy of quantum mechanical oscillator is \( (\nu + 1/2) h \nu_0 \), with \( \nu_0 \) having the same value as obtained for a classical oscillator. Now, on substituting the value of fundamental frequency from Eq. 8.5 in Eq. 8.1, we can get,

\[
E_{\text{vib}} = (\nu + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \ldots (8.6)
\]

The allowed vibrational energies for a diatomic molecule, as given by Eq. 8.6 are shown schematically in Fig. 8.5, where energy is plotted against internuclear distance. This representation contains information both about the energy levels and the energy changes that occur during the vibration. The energy levels are seen to be equally spaced with a spacing of \( h/2\pi \sqrt{k/\mu} \) or more simply, \( h \nu_0 \). The selection rule for a harmonic vibrational transition, as per the solution of Schrödinger equation, is \( \Delta \nu = \pm 1 \). This means that the increase or decrease in the vibrational quantum number is by one unit only. That is, a molecule can absorb energy and get excited to the next higher vibrational level or emit a part of its energy to be transferred to the next lower vibrational level. Also the selection rule \( \Delta \nu = \pm 1 \) indicates that the energy difference between two vibrational levels involved in a transition would always be equal to the spacing \( (h \nu_0) \), and we would accordingly expect all lines in the spectrum to fall in the same place (see the diagram at the foot of Fig. 8.5).

Thus, for an ideal harmonic oscillator, the spectral absorption must occur exactly at the vibration frequency calculated from Eq. 8.6.
Fig. 8.5: The allowed vibrational energy levels and the transitions between them.

To express the position of a spectral band in wave number (m⁻¹) unit, Eq. 8.7 is to be used.

\[ \tilde{\nu} = \frac{E_{\text{vib}}}{hc} = (v + \frac{1}{2}) \frac{1}{2mc} \sqrt{\frac{k}{\mu}} \]  

...(8.7)

The literature values of the position of the spectral bands are in cm⁻¹ units. Since

1 m⁻¹ = 10⁻² cm⁻¹, \( \tilde{\nu} \) can be obtained in cm⁻¹ unit as per the equation,

\[ \tilde{\nu} = (v + \frac{1}{2}) \frac{10^{-2}}{2mc} \sqrt{\frac{k}{\mu}} \]  

...(8.8)

Using Eq. 8.7 or Eq. 8.8, you can construct an energy level diagram from vibrational spectrum; alternatively, you can draw conclusions about the spectrum from an energy level diagram.

In reality, the molecules do not exhibit the simple harmonic motion exactly. That is, the resulting vibrational motion is anharmonic in nature and the mathematical calculation of the vibrational energy levels is necessarily more complex. The corresponding curve is modified in the manner shown in Fig. 8.6. We observe in this diagram that the spacing of the vibrational energy levels become closer with increasing energy (or increasing vibrational quantum number) due to the anharmonic nature of the vibration.

Fig. 8.6: The energy of a diatomic molecule undergoing anharmonic vibration. Compare this curve with the dotted curve of a harmonic oscillator.
The selection rules for all $\Delta \nu$ transitions in an anharmonic oscillator may be given as,
$\Delta \nu = \pm 1, \pm 2, \pm 3, \ldots$.  

The transition in which

i) $\nu = 0$ to $\nu = 1$, gives fundamental band;

ii) $\nu = 0$ to $\nu = 2$, gives first overtone;

iii) $\nu = 0$ to $\nu = 3$, gives second overtone.

A typical vibrational spectrum with two overtones is shown in Fig. 8.7. Note the decreased intensity (as shown by lower value for $% T$) of the overtones as compared to the fundamental band.

![Fig. 8.7: Infrared spectrum of a diatomic molecule in solution: (a) fundamental band; (b) first overtone; (c) second overtone.]

Using the above discussion, we can calculate the fundamental frequency ($v_0$) or the force constant ($k$), if one of them is known for a simple diatomic molecule. The value of force constant indicates the strength of the bond. For example, hydrogen chloride ($^1\text{H}^3\text{Cl}$), has a force constant value of 480 N m$^{-1}$. We can calculate its fundamental frequency, once its reduced mass is known.

Reduced mass of $^1\text{H}^3\text{Cl}$

\[ \mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{1 \times 35}{(1 + 35)} \times \frac{10^{-3}}{6.022 \times 10^{-23}} \text{ kg.} \]

\[ = 1.615 \times 10^{-27} \text{ kg.} \]

Now, substituting the value of reduced mass and force constant in Eq. 8.5,

\[ v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.142} \sqrt{\frac{480 \text{ (N m$^{-1}$)}}{1.615 \times 10^{-27} \text{ (kg)}}} \]

\[ = 8.676 \times 10^{13} \text{ Hz} \]

\[ v = \frac{v_0}{c} = \frac{8.676 \times 10^{13} \text{ (s$^{-1}$)}}{2.998 \times 10^8 \text{ (m s$^{-1}$)}} \]

\[ = 2.894 \times 10^3 \text{ m$^{-1}$} \]

\[ = 2.894 \times 10^3 \text{ cm$^{-1}$} \]

It is worth recollecting that the spectrum of hydrogen chloride given in Fig. 8.1 is centered around 2890 cm$^{-1}$. Now let us focus our attention on the significance of the force constant. Again consider the model given in fig. 8.4. Notice the way the frequency changes with $k$ and the masses, $m_1$ and $m_2$. If the spring is stiffer, which means $k$ becomes larger, then the frequency rises and the vibration is faster. Conversely, if the spring is weaker, $k$ is reduced, and the frequency falls.

What happens if either of the masses is decreased and the same spring is retained? In that case, the value of $\mu$ decreases. Therefore, $1/\mu$ becomes larger, and as can be seen from Eq. 8.5, the fundamental frequency will rise. So decrease in mass yields the same effect as
increase in the strength of the spring, and vice versa. Based on this analogy, we can
generalise that the vibrational fundamental frequency is higher for,
i) stronger chemical bonds
ii) bonding between lighter atoms
The clause (i) suggests that we might expect the frequency to increase with bond order
among C–C, C=C and C = C groups and among C–N, C≡N and C = N groups. The trend
expected from this simple model is indeed observed experimentally as seen in Table 8.1.

Table 8.1 : Variation of Vibrational Wave Number Values with Bond Order

<table>
<thead>
<tr>
<th>Group</th>
<th>Wave number/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C – C</td>
<td>900</td>
</tr>
<tr>
<td>C = C</td>
<td>1650</td>
</tr>
<tr>
<td>C = C</td>
<td>2050</td>
</tr>
</tbody>
</table>

As per clause (ii) and the earlier discussion, we expect the frequency to decrease with increase
in the vibrating masses. To understand this, consider the case of HCl (which we shall
represent as HCl in the following discussion) and DCl (DC1). In case of HCl, the
vibrational band, is centred at 2890 cm⁻¹ and in case of DCl, it is centred at 2090 cm⁻¹. The
force constant, is the same for HCl and DCl.

According to Eq. 8.5, \( \nu_0 \) (HCl)/\( \nu_0 \) (DCl) should be related inversely to the square root of the
ratio of their reduced masses.

\[
\frac{\nu_0 \text{(HCl)}}{\nu_0 \text{(DCl)}} = \sqrt{\frac{\mu \text{(DCl)}}{\mu \text{(HCl)}}}
\]

Assume that the atomic masses of hydrogen, deuterium and chlorine are 1, 2 and 35,
respectively.

\[
\text{Hence } \frac{\nu_0 \text{(HCl)}}{\nu_0 \text{(DCl)}} = \sqrt{\frac{2 \times 35}{(2 + 35)}} \times \frac{10^{-3}}{6.022 \times 10^{23}} \times \frac{(1 + 35)}{35 \times 1} \times \frac{6.022 \times 10^{23}}{10^{-3}}
\]

\[
= 1.395.
\]

We can calculate the ratio \( \nu_0 \) (HCl)/\( \nu_0 \) (DCl) also from the above mentioned experimental \( \nu_0 \)
values of the two molecules given above.

\[
\frac{\nu_0 \text{(HCl)}}{\nu_0 \text{(DCl)}} = \frac{2890 \text{ (cm⁻¹)}}{2090 \text{ (cm⁻¹)}}
\]

\[
= 1.383.
\]

It is interesting to note that the values of the ratio, \( \nu_0 \) (HCl)/\( \nu_0 \) (DCl), obtained by both the
methods are nearly the same. To test your understanding of the above discussion, try the
following SAQ.

SAQ 1
Calculate the force constant for carbon monoxide, if this compound absorbs at \( 2.143 \times 10^4 \)
m⁻¹ and its reduced mass is \( 1.139 \times 10^{-26} \) kg.

8.5 INFRARED SPECTRA OF POLYATOMIC MOLECULES

So far, we have discussed the infrared spectra of simple diatomic molecules. Now, let us
consider the vibrational spectra of polyatomic molecules.
For polyatomic molecules, there are several possible ways in which the bonds can vibrate. These are called the vibrational modes and each vibration has an associated fundamental frequency \( v_0 \). For example, the fundamental modes for the linear molecule \( \text{CO}_2 \) are illustrated in Fig. 8.8. Of these, \( v_1 \) (the symmetric stretching mode) does not involve a dipole moment change and is "inactive" in the infrared region, there being no corresponding absorption of energy. However, absorption peaks are observed at \( v_2 \) (2349 cm\(^{-1}\)) and \( v_3 \) (667 cm\(^{-1}\)) because these modes of vibration involve dipole moment change. These are called asymmetric stretching (\( v_2 \)) and bending (\( v_3 \)) modes. We notice that less energy is involved in bending than in stretching; this is because, it is easier to bend a spring than to stretch. In symmetric stretching, both the bonds a and b are shortened or elongated to the same extent simultaneously. In asymmetric stretching, one of the bonds (a or b), is shortened, while the other is elongated.

During a stretching vibration, bond length varies; in a bending vibration, bond angle varies. Bending requires less energy than stretching.

In figure 8.8, the arrows attached to each atom show the direction of its motion during half of the vibration. The (+) sign near an atom shows that the atom is going above the plane while (-) sign indicates that the atom is going below the molecular plane. The two bending modes have same energy and are said to be degenerate and these two modes give rise to only one band.

The complexity of infrared spectra for molecules is increased as we progress from diatomic to triatomic and polyatomic molecules, because of the increase in the number of possible vibrations. For a nonlinear molecule with \( n \) atoms, the number of vibrational modes is \((3n-6)\), so that methane theoretically possesses 9, and ethane has 18. On the other hand, for a linear molecule, the number of vibrational modes is \( 3n-5 \). Actual number of observed vibration bands for a molecule is generally different from that calculated, because overtone and combination of overtones may increase the number of vibration bands or some other phenomenon may reduce the number of vibrations. In spite of these complications, it is often possible to obtain useful information about the structure of complex molecules from the infrared spectra, details of which we discuss in the following section. Before that try the following SAQ.

SAQ 2
How many normal modes of vibration do you expect for the following compounds?

(Hint: Using the materials in Units 3 and 4, find out whether a structure is linear or not.)

a) \( \text{CO}_2 \)  b) \( \text{SO}_2 \)  c) \( \text{CHCl}_3 \)

8.6 GROUP FREQUENCIES

We have stated earlier that for polyatomic molecules, infrared spectra is complex. So, it may not be easy to assign mode for every vibrational band. In such a case, the most important information we get is the recognition of group frequencies. To understand group frequencies, let us consider the organic compounds.
Organic compounds show spectra in which many bands are spread over the wide scan-range (4000–600 cm⁻¹). Each band is associated with a particular vibration (or a combination of these). The complexity of the spectra, as illustrated in Fig. 8.9, reflects the large number of vibrations, which depend on the structure of the molecule. Fortunately, we can, to a certain extent, associate some absorptions with stretching or bending vibrations characteristic of particular functional groups in a molecule; for example, the absorptions at 3050 and 1700 cm⁻¹ in the spectrum of acetophenone are typical of the stretching modes of C–H (aromatic) and C=O groups, respectively. These frequencies are called **group frequencies**. In this way, the infrared spectra allow recognition of the types of functional groups present in organic molecules. A list of some characteristic group frequencies is given in Table 8.2.

![Infrared spectrum of acetophenone, (C₆H₅COCH₃).](image)

**Table 8.2 : Characteristic Group Frequencies**

<table>
<thead>
<tr>
<th>Group</th>
<th>(Bond stretching vibration)/cm⁻¹</th>
<th>Group</th>
<th>(Bond stretching vibration)/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>=C–H</td>
<td>3300</td>
<td>=C–O</td>
<td>1700</td>
</tr>
<tr>
<td>=C–H</td>
<td>3020</td>
<td>=C–N</td>
<td>1150</td>
</tr>
<tr>
<td>=C–H</td>
<td>2960</td>
<td>=C≡N</td>
<td>2100</td>
</tr>
<tr>
<td>O–H</td>
<td>3680 (gas)</td>
<td>O–H</td>
<td>2050</td>
</tr>
<tr>
<td>N–H</td>
<td>3350</td>
<td>C≡C</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>3400 (liquid)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**SAQ 3**

Match each absorption band with the functional group.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Wave number/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) –C=O</td>
<td>2050</td>
</tr>
<tr>
<td>b) –N–H</td>
<td>3400</td>
</tr>
<tr>
<td>c) =C–H</td>
<td>1700</td>
</tr>
<tr>
<td>d) –C=C–</td>
<td>3350</td>
</tr>
<tr>
<td>e) –O–H</td>
<td>3020</td>
</tr>
</tbody>
</table>

**8.7 APPLICATIONS OF INFRARED SPECTRA**

The usefulness of infrared spectra lies not only in the calculations of the molecular parameters for small molecules, but also, for the characterisation of organic molecules. We
are considering some examples to illustrate further the importance of infrared spectra in identifying the structure of organic compounds:

**Example 1**: Pent-1-ene, $\text{CH}_3(\text{CH}_2)_2\text{CH} = \text{CH}_2$

The infrared spectrum of this compound is given in Fig. 8.10.

![Infrared spectrum of Pent-1-ene.](image)

The bands appearing at 3080 cm$^{-1}$, 2950 cm$^{-1}$ and 1640 cm$^{-1}$ are due to $\equiv \text{C-H}$, $\equiv \text{-C=H}$ and $\equiv \text{C}=$ stretching, respectively.

**Example 2**: 1-Butanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

![Infrared spectrum of 1-butanol.](image)

In Fig. 8.11, the infrared spectrum of 1-butanol is given. Broad band at 3400 cm$^{-1}$ indicates the presence of the O-H group in the molecule. This is due to the stretching of the O-H group. Broadening of the band suggests intermolecular hydrogen bonding. Here, intermolecular hydrogen bonding arises between hydrogen of the hydroxyl group of one molecule with the oxygen of the hydroxyl group of another molecule.

**Example 3**: Diethylamine ($\text{C}_2\text{H}_5\text{NH}$)

![Infrared spectrum of diethylamine.](image)
The infrared spectra of diethylamine is given in Fig. 8.12. As in the case of alcohols, amines have a broad band, although at lower wave number region (3350 cm$^{-1}$); it is due to N-H stretching. The broadening suggests that the hydrogen atom takes part in intermolecular hydrogen bonding of the type $\cdots$H -N $\cdots$N$\cdots$.

![Infrared spectrum of diethylamine](image)

**Fig. 8.13**: Infrared spectrum of ethyl acetate.

As an example of carbonyl compounds, the infrared spectrum of ethyl acetate is shown in Fig. 8.13. Note the intense band around 1700 cm$^{-1}$ which is characteristic of C=O stretching. Among the carbonyl compounds such as acids, esters, ketones and aldehydes, this is one of the prominent bands.

Finally, infrared spectra may also be employed for rapid quantitative analysis of a mixture of compounds. The infrared spectra are widely used in pollution detection and in milk analysis, etc. But the quantitative results obtained from infrared spectra are not as accurate as in the case of ultraviolet and visible spectra which we will discuss in Section 8.11.

Try the following SAQ before proceeding to the next section.

**SAQ 4**

From the infrared spectrum given in Fig. 8.14, identify the possible functional groups corresponding to the peaks indicated by the arrows.

![Infrared spectrum of the compound mentioned in SAQ 4](image)

**Fig. 8.14**: Infrared spectrum of the compound mentioned in SAQ 4.

### 8.8 MAIN FEATURES OF ULTRAVIOLET AND VISIBLE SPECTRA

We have already stated in Unit 7 that the absorption of radiation in the ultraviolet and visible regions of the electromagnetic spectrum results in transitions between electronic energy levels. Therefore, visible and ultraviolet spectra are also known as electronic spectra. The energy changes are relatively large, corresponding to 100-10$^4$ kJ mol$^{-1}$. This corresponds to wavelength range of 200-400 nm (ultraviolet region of electromagnetic spectrum) and 400-750 nm (visible region of electromagnetic spectrum). All molecules can undergo electronic
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transitions, but in some cases absorptions occur below 200 nm where atmospheric absorption necessitates the use of vacuum instrumentation.

The large energy changes involved in electronic transitions cause simultaneous change in rotational and vibrational energies also, as $E_{rot} > E_{vib} > E_{uv}$. For this reason, the spectra of simple molecules in the gaseous state contain narrow absorption peaks where each peak is representing a transition from a particular combination of vibrational and rotational levels in the electronic ground state to a different combination in the excited state. The allowed energy levels are shown in Fig. 8.15.

Such vibrational and rotational fine structure lines are not usually observed if the spectrum is run in solution because of physical interactions between solute and solvent molecules, causing collisional broadening of the lines. The resulting overlapping bands coalesce to give one or more broad band envelopes (see Fig. 8.16).

In some cases, however, vibrational fine structures are visible as in the case of spectrum of benzene (see Fig. 8.17) around $\lambda = 255$ nm.

Bands observed in ultraviolet and visible spectra are usually characterised by two parameters:

i) $\lambda_{max}$ Value: The value of the wavelength at which absorption maximum occurs is called $\lambda_{max}$ value. From Figs. 8.16 and 8.17, you can understand that $\lambda_{max}$ values are different for different molecules. For example, $\lambda_{max}$ for acetone is 279 nm, whereas for benzene, it is 255 nm.
ii) ε Value: The extent of absorption for a given concentration of a compound at any given wavelength is defined by molar absorptivity or molar extinction coefficient which is indicated as 'ε' value. It is related to the height of the absorption band. We shall define it precisely in Section 8.11. The parameters, \( \lambda_{\text{max}} \) (the position) and ε (the extent of absorption) are characteristic properties of a molecule. The parameters depend on the structure and concentration of the molecules in solution. Therefore, we extensively use ultraviolet and visible spectra in characterisation and also in quantitative estimation. Now, the origin of the absorption bands is discussed in the following section.

### 8.9 ELECTRONIC TRANSITIONS

According to molecular orbital theory, which we discussed in Unit 5, the interaction of atomic orbitals leads to the formation of bonding and antibonding molecular orbitals. Depending on the nature of the overlapping atomic orbitals, bonding molecular orbitals may be of \( \sigma \) type, the electron density being concentrated along the internuclear axis, or of the \( \pi \) type where the electron density is concentrated above and below the internuclear axis. Electron density probability contours for electrons occupying \( \sigma \) and \( \pi \) (bonding), \( \sigma^* \) and \( \pi^* \) (antibonding) orbitals are shown in Fig. 8.18a. The relative energies of these orbitals and that of nonbonding orbital \( n \), are given in Fig. 8.18b.

![Shapes and relative energies of molecular orbitals](image)

When excitation takes place, an electron from one of the filled orbitals (\( \sigma \), \( \pi \) or \( n \)), gets excited to one of the vacant antibonding orbitals (\( \sigma^* \) or \( \pi^* \)). Since various excitations are possible, there are various absorptions, corresponding to these transitions:

\[
\sigma \rightarrow \pi^*, \sigma \rightarrow \sigma^*, \pi \rightarrow \pi^*, \pi \rightarrow \sigma^*, n \rightarrow \pi^* \quad \text{and} \quad n \rightarrow \sigma^*
\]

As expected, the \( \sigma \) electrons require a high energy for excitation to \( \sigma^* \) level. The order of decreasing energy for the absorptions is as follows:

\[
\sigma \rightarrow \sigma^* \rightarrow \pi \rightarrow \pi^* \rightarrow n \rightarrow \sigma^* \rightarrow n \rightarrow \pi^*
\]

Of all the possible transitions, the last three account for absorptions in the region 200 - 800 nm; while others demand much higher energy. This then explains why only molecules with \( n \) or \( \pi \) electrons give rise to characteristic spectra in the region 200 - 800 nm, whereas alkanes, for example, absorb in the region below 200 nm. It is observed in the case of organic molecules that the part of the molecule having \( n \) or \( \pi \) electrons, is essentially responsible for this absorption; these fragments are called chromophores. If two or more chromophores having \( \pi \) electrons are separated by a single bond in between, the system is said to be conjugated. For example, 1, 3-butadiene, benzene and crotonaldehyde are conjugated molecules. It has been found that for the conjugated molecules, \( \lambda_{\text{max}} \) values are somewhat larger. It is also reported that as conjugation length increases, \( \lambda_{\text{max}} \) also increases.
This is evident from Table 8.3, where $\lambda_{\text{max}}$ and $\varepsilon$ values for $\pi \rightarrow \pi^*$ transitions of a few chromophores are given. Note that $\lambda_{\text{max}}$ value of benzene is larger than that of butadiene, which in turn, is larger than that of ethylene. Again, $\lambda_{\text{max}}$ value of crotonaldehyde is larger than that of acetonitrile or ethylene.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Example</th>
<th>$\lambda_{\text{max}}$ /nm</th>
<th>$\varepsilon /$cm$^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}$</td>
<td>Ethylene</td>
<td>165</td>
<td>1500</td>
</tr>
<tr>
<td>$\text{CH}_2=\text{C} \equiv \text{CH}$</td>
<td>Acetone</td>
<td>188</td>
<td>90</td>
</tr>
<tr>
<td>$\text{CH}_2=\text{CH} \equiv \text{C} \equiv \text{O}$</td>
<td>Butadiene</td>
<td>217</td>
<td>2100</td>
</tr>
<tr>
<td>$\text{CH}_2=\text{C} \equiv \text{C} \equiv \text{O}$</td>
<td>Crotonaldehyde</td>
<td>217</td>
<td>1600</td>
</tr>
</tbody>
</table>

The positions ($\lambda_{\text{max}}$) and extinction coefficients ($\varepsilon$) of the absorption bands are sensitive to the substituents close to the chromophore, and also to the solvents used.

Try the following SAQs to check your understanding regarding ultraviolet and visible spectra.

**SAQ 5**
Identify the type of absorptions, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ among the following compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ /nm</th>
<th>Transition involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) CH$_3$OCH$_3$</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>b) CH$_2$SH</td>
<td>228</td>
<td></td>
</tr>
<tr>
<td>c) CH$_2$ = CH-CH=CH$_2$</td>
<td>217</td>
<td></td>
</tr>
<tr>
<td>d) CH$_2$ = CH$_2$</td>
<td>165</td>
<td></td>
</tr>
</tbody>
</table>

**SAQ 6**
Which of the following two will absorb at higher wavelength? Reason out your answers.

CH$_3$-CH=CH$_2$ or CH$_3$-CH=CH-CH=CH-CH$_3$.

8.10 **APPLICATIONS OF ULTRAVIOLET AND VISIBLE SPECTRA**

Electronic absorption spectra are useful in the characterisation of organic and inorganic compounds which show absorption in ultraviolet and visible regions of the electromagnetic spectrum. The transition metal complexes are often highly coloured and absorb in the visible region.

Also it is possible to estimate quantitatively the compounds absorbing in the ultraviolet and visible regions. This estimation is based on Beer-Lambert law. In the next section, we shall discuss this in detail.

8.11 **QUANTITATIVE ANALYSIS**

It is known to us that when light is passed through a sample as the absorbing medium, the intensity of the transmitted light is less than that of the incident light. This idea is expressed mathematically by Beer-Lambert law and it is useful in the quantitative estimation of compounds.
8.11.1 Beer-Lambert Law

Beer-Lambert law is actually a combined form of Lambert's law and Beer's law.

We shall now take Lambert's law. 

Lambert's Law
This law states that when a monochromatic beam of light is passed through a homogeneous medium absorbing this light, the absorption at each infinitesimally small section is proportional to the intensity of the incident light and the thickness of the layer. We can explain this using Fig. 8.19 given below:

![Fig. 8.19: Illustration of Lambert's Law](image)

Let us consider that the light enters the sample with the intensity \( I_0 \). When it goes out of the sample, the intensity of transmitted light is \( I \). Somewhere in the sample, let us consider a small section of thickness \( dx \). The light here enters with intensity \( I \) and goes out with intensity \( I - dl \). The change in intensity,

\[
I_0 - dl - I = -dl
\]

According to this law, this should be proportional to the thickness \( dx \) and the intensity \( I \) at that point, i.e.,

\[
-dl = kI dx
\]

or

\[
\frac{dI}{I} = k dx
\]

... (8.10)

where \( k \) is the proportionality constant. Now we can integrate it, knowing that the intensity varies from \( I_0 \) to \( I \), and the thickness of the sample varies from 0 to \( x \).

Then we have,

\[
\int_{I_0}^{I} \frac{dI}{I} = k \int_0^x dx
\]

or

\[
\ln \frac{I}{I_0} = -kx
\]

or

\[
\frac{I}{I_0} = e^{-kx}
\]

\[
I = I_0 e^{-kx}
\]

... (8.11)

The intensity of light absorbed by the sample,

\[
l_{abs} = I_0 - I = I_0 - I_0 e^{-kx}
\]

\[
= I_0 (1 - e^{-kx})
\]

... (8.12)

Here '\( k \)' is the proportionality constant. It is obvious that larger the value of \( k \), greater is the absorption.
Beer's Law

Beer extended Lambert's law to solutions. According to this law, the value of \( k \) in Eq. 8.12 is proportional to the concentration of the solution.

\[
k = k'c
\]

...(8.13)

where \( k' \) is another proportionality constant and \( c \) is the concentration of the solution. In the combined form, these laws are known as Beer-Lambert law. It can be written by substitution of Eq. 8.13 in Eq. 8.11.

\[
I_0 = I_0 e^{-k'c}
\]

\[
= I_0 10^{-ke^{2.303}}
\]

\[
= I_0 10^{-ac}
\]

...(8.14)

where \( a = \frac{k}{2.303} \) is known as the absorption coefficient or extinction coefficient of the solute.

Also, \( \log \frac{I_0}{I} = acx \) ...(8.15)

where the term \( \log \frac{I_0}{I} \) is commonly called the absorbance and given the symbol \( A \).

Thus, Eq. 8.15 becomes,

\[
A = acx
\]

...(8.16)

Eq. 8.14 and Eq. 8.15 are termed as mathematical statements of Beer-Lambert law.

8.11.2 Molar Extinction Coefficient

The numerical value of the extinction coefficient, \( a \), depends on the units used for expressing the concentration of the absorbing solution. Concentration units such as molality, parts per million (ppm) (which is milligram per dm\(^3\)), grams per 100 cm\(^3\), etc. are often used.

However, a different symbol, \( \epsilon \) (epsilon), is used in place of \( a \) when the concentration is expressed as mol m\(^{-3}\). Eq. 8.16 may then be written as,

\[
A = \epsilon cx
\]

or \( \epsilon = \frac{A}{cx} \) ...(8.17)

If \( x \) and \( c \) are in units m and mol m\(^{-3}\), then \( \epsilon \) is in m\(^2\) mol\(^{-1}\) and is described as the molar decadic absorptivity or molar extinction coefficient. The \( \epsilon \) value is characteristic of a particular compound at a given wavelength. Usually for the wavelength of maximum absorbance (\( \lambda_{max} \)), molar decadic absorptivity, \( \epsilon \), is most commonly expressed as \( \epsilon_{max} \). Some typical values for \( \epsilon_{max} \) of organic compounds are already listed in Table 8.3.

Using Eq. 8.17 we can calculate \( \epsilon \) for a compound, if \( x \) and \( c \) are known, and if \( A \) is experimentally determined. It is important to realise that, once \( \epsilon \) has been determined, it is possible to estimate the concentration, \( c_i \), of a solution of unknown concentration by measuring its absorbance, \( A_i \), using the same cell. This feature is the basis of the quantitative application of Beer-Lambert law. Therefore,

\[
c_i = \frac{A_i}{\epsilon x}
\]

...(8.18)

We generally make measurements in cells of 1 cm thickness; for a compound, \( \epsilon \) is constant for a particular wavelength. In such a condition, Beer-Lambert law may be written

\[
A \approx c
\]

Hence, by measuring the values of \( A \) for different concentration values of the solution of a substance in the same cell and plotting the curve \( A \) vs. \( c \), a straight line will be obtained and this would pass through the origin as evident from Fig. 8.20. This calibration line may then be used to determine unknown concentration of a solution of the same material in the same solvent, after measurement of the absorbance. For example, for a solution of absorbance, \( A_i \), the concentration \( c_i \) is given by the interpolation of the curve in Fig. 8.20.
Quantitative measurements based on Beer-Lambert law are extensively used for ultraviolet and visible spectra and less in the case of infrared spectra. The reason is that $\varepsilon$ value for the molecules are larger in the ultraviolet and visible regions, whereas it is smaller in the infrared region.

8.11.3 Deviation From Beer-Lambert Law

As mentioned earlier, when Beer-Lambert law is obeyed, calibration plot will be obtained as a straight line passing through the origin. If there are deviations from Beer-Lambert law, the calibration plot will curve either upward (positive deviation) or downward (negative deviation) as indicated by OP and OR, represented in Fig. 8.21. The ideal curve is represented by OQ. The reasons for such deviations are both instrumental and chemical. To avoid deviation, we generally prefer dilute solutions.

Why don’t you try the following SAQ to test your “grip” of Beer-Lambert law?

SAQ 7

An organic compound has \( \lambda_{\text{max}} = 400 \) nm. The absorbance of its solution \( (c = 132 \text{ mg cm}^{-1}) \) was found to be 0.465. If a test solution of this compound gave an absorbance of 0.501, calculate its concentration. (Do not change the concentration units.)

8.12 SUMMARY

In this unit we have described the infrared, ultraviolet and visible spectra. We are summarising below what we have studied so far:
8.13 TERMINAL QUESTIONS

1. Calculate the frequency of O–H band, if the force constant and reduced mass of the atom pair are 770 N m\(^{-1}\) and 1.563 \times 10^{-27} kg, respectively.

2. How many normal vibrational modes are possible for ethane and benzene?

3. Characteristic group frequencies (in cm\(^{-1}\)) and functional groups are given below. Match the pairs.

i) 1650 
ii) 2100 
iii) 2960 
iv) 900

| i) 1650 | a) –C –C – |
| ii) 2100 | b) –C –H |
| iii) 2960 | c) –C = C– |
| iv) 900 | d) –C = N |

4. Of each pair of transitions, which would require radiation of lesser energy?

a) \(\pi \rightarrow \pi^*\) or \(\pi \rightarrow \pi^*\) in \(\text{CH}_3 - \text{C} = \text{N}\)

b) Stretching or rotational transition in \(\text{ICl}\)

c) \(\pi \rightarrow \pi^*\) or \(\pi \rightarrow \pi^*\) in \(\text{CH}_3 - \text{N} = \text{O}\)

d) \(-\text{C} = \text{C} - \text{stretching}\) or \(-\text{C} = \text{C} - \text{stretching}\).

5. For each of the following molecules indicate the possible electronic excitations:

a) \(\text{CH}_3\text{CH}_2\text{CH}_3\) 

b) \(\text{CH}_3\text{CH} = \text{CH}_2\)

c) \(\text{CH}_3\text{CH} = \text{CH} = \text{CH} = \text{CH}_3\)

d) \(\text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3\)


7. Compound X exhibits molar extinction coefficient of 245 m\(^2\) mol\(^{-1}\) at 450 nm. What concentration of X in a solution will cause a 25% decrease in the intensity of 450 nm radiation, when the solution is placed in a 0.01 m absorption cell?

8.14 ANSWERS

Self-assessment Questions

1. The force constant can be calculated using the equation,

\[
\bar{v}_n = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

This can be rearranged as,

\[
k = \frac{4 \pi^2 c^2 \bar{v}_n^2 \mu}{4 \times 3.142^2 \times (2.998 \times 10^8 \text{ m s}^{-1})^2 \times 2.143 \times 10^3 \text{ (m}^{-1})^2 \times 1.139 \times 10^{-26} \text{ (kg)}}
\]

\[
k = 1857 \text{ (kg m}^2\text{s}^{-2}\text{)} \text{ (m}^{-2}\text{)}
\]

\[
k = 1857 \text{ (kg m}^{-2}\text{s}^{-2}\text{)} \text{ (m}^{-1}\text{)}
\]

\[
k = 1857 \text{ N m}^{-1}
\]

\[
\bar{v}_n = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]
2. The expected modes of vibration are:
   \( \text{CO}_2 \): linear; \( (3 \times 3 - 5) = 4 \)
   \( \text{SO}_2 \): Nonlinear; \( (3 \times 3 - 6) = 3 \)
   \( \text{CHCl}_3 \): Nonlinear; \( (3 \times 5 - 6) = 9 \)

3. Functional group | Wave number/cm\(^{-1}\)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\text{C}=\text{O} )</td>
<td>1700</td>
</tr>
<tr>
<td>( -\text{N}=\text{H} )</td>
<td>3350</td>
</tr>
<tr>
<td>( =\text{C}-\text{H} )</td>
<td>3020</td>
</tr>
<tr>
<td>( -\text{C}≡\text{C} )</td>
<td>2050</td>
</tr>
<tr>
<td>( -\text{O}-\text{H} )</td>
<td>3400</td>
</tr>
</tbody>
</table>

4. This infrared spectrum has peaks at 3300, 2100 and 1640 cm\(^{-1}\), indicating the presence of \( \equiv\text{C}-\text{H}, -\text{C}≡\text{C} \) and \( -\text{C}=\text{C} \) groups. (In fact, this is the infrared spectrum of 1-methoxy-but-1-en-3-yne).

5. a) \( n \rightarrow \sigma^* \)
   b) \( n \rightarrow \pi^* \)
   c) \( \pi \rightarrow \pi^* \)
   d) \( \pi \rightarrow \pi^* \)

6. \( \text{CH}_3-\text{CH}≡\text{CH}=\text{CH}-\text{CH} \) will have higher \( \lambda_{\text{max}} \) than \( \text{CH}_3-\text{CH}=\text{CH}_2 \) because of conjugation.

7. According to Beer-Lambert law, \( \lambda = \epsilon \). If \( A_1 \) and \( A_2 \) are the absorbance values of a substance in solutions of concentrations, \( c_1 \) and \( c_2 \), then \( A_1 = c_1 \) and \( A_2 = c_2 \).

\[
\frac{A_1}{c_1} = \frac{A_2}{c_2}
\]

\( A_1 = 0.465, c_1 = 132 \text{ mg cm}^{-3} \)
\( A_2 = 0.501, c_2 = ? \text{ mg cm}^{-3} \)

\[
c_2 = c_1 \frac{A_2}{A_1} = 132 \text{ (mg cm}^{-3} \text{)} \times \frac{0.501}{0.465}
\]

\[= 142 \text{ mg cm}^{-3}\]

Terminal Questions:

1. \( k = 770 \text{ N m}^{-1} \)
   \( \mu = 1.563 \times 10^{-27} \text{ kg} \)

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

\[
= \frac{1}{2 \times 3.142} \times \sqrt{\frac{770 \text{ (N m}^{-1})}{1.563 \times 10^{-27} \text{(kg)}}}
\]

\[= 1.117 \times 10^{14} \text{ Hz}\]

\[
\nu = \frac{v}{c} = 3.726 \times 10^{4} \text{ m}^{-1}
\]

\[= 3726 \text{ cm}^{-1}\]

2. Ethane has \( 3 \times 8 - 6 = 18 \) normal vibration modes; benzene has \( 3 \times 12 - 6 = 30 \) normal vibration modes.

3. (i) c    (ii) d    (iii) b    (iv) a
4. a) $n \rightarrow \pi^*$  
    b) rotational  
    c) N=O stretching  
    d) $C=\overset{\infty}{C}$ stretching.

5. a) $\sigma \rightarrow \sigma^*$  
    b) $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$  
    c) $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$.

6. As given in Sec. 8.11.

7. If the intensity of the incident light ($I_0$) is assumed to be 100%, then the intensity of the light transmitted ($I_t$) after passing through the solution of concentration $c$ is 75% (since there is 25% reduction in the intensity).

   i.e., $I_t = \frac{100}{75}$

   According to Beer-Lambert law,

   $\log \frac{I_0}{I_t} = \varepsilon c x$

   $\varepsilon = 245 \text{ m}^2 \text{ mol}^{-1}$

   $x = 10^{-2} \text{ m}$

   $c = ? \text{ mol m}^{-3}$

   $c = \frac{\log \frac{I_0}{I_t}}{\varepsilon x}$

   $= \frac{\log 100/75}{245 (\text{ m}^2 \text{ mol}^{-1}) \times 10^{-2} \text{ (m)}}$

   $= 0.0510 \text{ mol m}^{-3}$. 

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