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Chapter 4 Molecular Spectroscopy

Introduction of molecular spectra and its types

Molecular spectroscopy is the study of the interaction of electromagnetic waves and matter which gives us more information related to the structure of matter. Any matter consists of atoms and molecules. The atoms are bounded together to form molecules. In this chapter, we discuss rotational energy levels, vibration energy level and electronic spectra of molecules.

Molecular spectra

EM radiations given out by atoms and molecules, The EM spectrum is classified various regions due to the frequency and wavelength range.



Types of Molecular spectra

We know that molecules can remains in the ground state as well as excited states. The transition between the allowed energy states of a molecule with the emission or absorption of radiation gives to molecular spectra. The frequency of emitted or absorbed spectra is given by

 $v = \frac{E_2 - E_1}{h}$ if $E_2 > E_1$ i.e. absorption $v = \frac{E_1 - E_2}{h}$ if $E_1 > E_2$ i.e. emission

The energy levels of molecule are more complex than atom.

We can classify molecular spectra into three distinct regions

- 1. Rotational spectra
- 2. Vibration spectra
- 3. Electronic spectra

1. Rotational energy levels of diatomic molecules- For example H-Cl molecules



Consider a diatomic molecules, like H-Cl,

here two atoms are separated by a rigid distance r and has mass m_1 and m_2 as shown in figure. The lowest energy level of a diatomic molecule arises from rotation about its centre of mass. In diatomic molecules, r = bond length i.e. distance between two atoms, m_1 and m_2 masses of two atoms. These atoms rotate about the axis that passes through C, centre of mass. The moment of inertia about an axis passing through C and perpendicular to line joining the atoms is,

$$I = m_1 r_1^2 + m_2 r_2^2$$

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i.e. m_1 r_1 = m_2 r_2 -----2
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Equating equation 1 and 2

$$\mathbf{r}_1 = \mathbf{r} - \mathbf{r}_2$$

Put in eqⁿ 2
$$m_1(r - r_2) = m_2 r_2$$

 $m_1 r - m_1 r_2 = m_2 r_2$
 $m_1 r = m_1 r_2 + m_2 r_2$
 $m_1 r = (m_1 + m_2) r_2$
 $\frac{m_1}{(m_1 + m_2)} r = r_2$ and $r_1 = \frac{m_2}{(m_1 + m_2)} r$

Now put the values of r_1 and r_2 in momentum of inertia I then,

$$I = m_1 \left(\frac{M_2}{m_1 + m_2}r\right)^2 + m_2 \left(\frac{M_1}{m_1 + m_2}r\right)^2$$
$$I = \frac{m_1 m_2}{(m_1 + m_2)}r^2$$

 $I = \mu r^2$ Where, μ is reduced mass

Energy of molecules rotating about a given axis with angular velocity ω is,

$$E = \frac{1}{2}I\omega^2$$

The angular momentum of the molecules has magnitude L= I ω Thus energy of the rotation is given as, $E = \frac{L^2}{2I}$

According to classical theory, radiation of any frequency may be absorbed by a molecule with a permanent dipole moment so there is no restriction on the rotational frequency of the molecules, but quantum theory requires that a molecule may only possess angular momentum is given as,

 $L = \sqrt{l(l+1)} \frac{h}{2\pi} \qquad l = \text{Orbital quantum number and } l = 0, 1, 2, \dots h = \text{Planks constant.}$ So, energy of rigid rotator or rotational spectra is,

$$E = l(l+1).\frac{h^2}{l.8\pi^2}$$

Energy different between two rotational levels is usually represent in cm⁻¹i.e. wave number to given energy ΔE is given by,

∆E=h**υ**

 $\mathbf{U} = \frac{\Delta \mathbf{E}}{h} \qquad \text{but } \mathbf{U} = \frac{c}{\lambda}$ $\frac{c}{\lambda} = \frac{\Delta \mathbf{E}}{h} \qquad \text{And } \overline{\mathbf{v}} = \frac{1}{\lambda}$ So, $\overline{\mathbf{v}} = \frac{\Delta \mathbf{E}}{hc} \text{ cm}^{-1} \quad \text{and rotational energy is,}$

$$E = l(l+1) \cdot \frac{h^2}{l \cdot 8\pi^2}$$

 $E_J = B l(l + 1)$ Where $B = \frac{h^2}{l.8\pi^2}$

Rotational energy level of diatomic molecules,



The selection rule for a rotational transition is,

 $\Delta l = \pm 1$

A molecule has to possess a dipole moment.

Selection rules for rotational spectra. - A molecule must have a transitional dipole moment that is in resonance with an electromagnetic field for **rotational spectroscopy** to be used. Polar molecules have a dipole moment. A transitional dipole moment not equal to zero is possible.

Selection rules only permit transitions between consecutive rotational levels: $\Delta J=J\pm 1$, and require the molecule to contain a **permanent dipole** moment. Due to the dipole requirement, molecules such as **HF** and **HCl** have pure rotational spectra and molecules such as **H**₂ and **N**₂ are rotationally inactive.

2. Vibration energy Level-

The vibration spectra are form due to vibrational motion of diatomic molecules. Two atoms forming molecules have masses m_1 and m_2 are spattered by an equilibrium distance R_0 between them, at any instant during the vibration the separation between m_1 and m_2 become R. Therefore distance between two atoms is equal to $R-R_0$. The restoring force acting on the atoms is proportional to the change in equilibrium distance ($R-R_0$).

$$F \propto -(R-R_0)$$

Negative sign indicate that the force is directed towards the centre of mass,

Let, R-R₀ =x Then equation is, $F \propto X$

$$F = -KX$$

Where K is force constant.

But $F = ma = m \frac{d^2x}{dt^2}$ From above equation,

$$m\frac{d^2x}{dt^2} = -kx$$
$$\frac{d^2x}{dt^2} = -\frac{kx}{m}$$



In diatomic molecules we have two atoms having masses m_1 and m_2 joined by a bond which may be compared to an elastic spring as shown above figure. As there is no external force acting on the system, linear momentum remains constants, if m_1 and m_2 vibrate back and forth, relative to centre of mass in opposite directions and both reach extremes of their respective motion at the same time. Such two body oscillator is equivalent to motion of **SMO** of equal to reduced mass of the two body system.

$$m' = \frac{m_1 m_2}{m_1 + m_2}$$

Put m' in above equation,

$$\frac{d^2x}{dt^2} = -\frac{k}{m'}x$$

This is the equation of simple harmonic motion and according to classical physics; frequency of oscillation is given by,

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m'}}$$

In order to obtain energy levels of simple harmonic oscillator, Schrodinger one dimensional time independent equation is given by,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{h^2}(E-V)\psi = 0$$

Substituting m=m' and V= $\frac{1}{2}kx^2$ for the molecular oscillator, Schrödinger equation becomes,

V= potential energy of molecules

$$\frac{d^2\psi}{dx^2} + \frac{2\mathbf{m}'}{h^2} \left(E - \frac{1}{2}\mathbf{k}\mathbf{x}^2\right) \psi = 0$$
$$-\frac{d^2\psi}{dx^2} = \frac{2\mathbf{m}'}{h^2} \left(E - \frac{1}{2}\mathbf{k}\mathbf{x}^2\right) \psi$$
$$-\frac{h^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}\mathbf{k}\mathbf{x}^2 \psi = \mathbf{E}\psi$$

The energy levels of SHO are now given by the solution of above equation,

$$\mathrm{E}_{\mathrm{U}} = (\mathrm{U} + \frac{\mathrm{I}}{\mathrm{2}})hv_{\mathrm{0}}$$

Where, $U_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mathbf{m}'}}$

And $\upsilon = 0, 1, 2, 3$. is vibration quantum number.

For ground state U = 0 and hence ground state vibrational energy

 $E_0 = \frac{1}{2} h v_{\upsilon}$

Vibrational energy levels are equally spaced-

Vibration energy levels of diatomic molecules corresponding to vibrational quantum number $\upsilon = 0, 1, 2, 3,..$ etc. are shown in above diagram.



The energy levels are equally spaced. The energy of the ground state is not zero as in case of rotational energy levels but has values $\frac{1}{2} h \upsilon_0$

- $\upsilon = 0 E_0 = 1/2h\upsilon_0$
- $\upsilon = 1 E_1 = 3/2h\upsilon_0$
- $\upsilon=\!2~E_2\!\!=\!\!5/2h\upsilon_0$
- $\upsilon = 3 E_3 = 7/2h\upsilon_0$
- $\upsilon = 4 E_4 = 9/2h\upsilon_0$

Selection Rule-

According selection rules 'only those transitions are allowed between vibrations energy levels for which the vibrational quantum number \cup changes by one unit.

i.e. $\Delta \upsilon = \pm 1$

Electronic Spectra of Molecules-

In rotational or vibrational spectra, the energies are due to motion of atomic nucleus. The electrons in molecules can be excited to higher energy levels than ground state. The spacing between two levels is greater than spacing in rotational or vibrational energy levels.

Electronic transition involves radiation in visible and ultraviolet region. Each transition appears as a series of closely spaced lines called a band due to presence of different rotational and vibrational states in each electronic state. All molecule exhibits electronic spectra as a dipole moment changes due to change in electronic configuration of molecules. Hence homonuclear molecules such as H_2 , N_2 which has neither rotational nor vibrational spectra have **electronic spectra**.

Fluorescence-

A molecule in an excited state can lose energy and return to ground state in various way

- Molecule may emit photon of same frequency as frequency of photon which is absorbed and come to ground state in single state.
- Molecule give up some of its vibrational energy in collision with other molecule so transition takes place from lower vibrational level to to upper electronic state. Hence fluorescent radiation has lower frequency than that of absorbed radiation.



Molecules can also undergo

changes in electronic transitions during microwave and infrared absorptions. The energy level differences are usually high enough that it falls into the visible to UV range; in fact, most emissions in this range can be attributed to electronic transitions. Electronic transitions involve both the vibrational and rotational states. Electronic potential energy cures with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

Fluorescence has many applications

- 1. It is used to identify minerals and biochemical compound
- 2. Fabric brighteners are added to detergents it absorbs UV radiations and then fluoresce blue light
- 3. In a fluorescent lamp, a mixture of mercury vapors and inert gas such as argon inside a glass tube gives off UV radiation when an electric current is passed through it. Inside of tube is coated with fluorescent material (called phosphor). It gives visible light when excited through UV radiation.

Phosphorescence-



In figure, the molecule in its singlet (S=0) ground state absorbs photon and is raise to singlet excited state.

In collision the molecules can undergo radiation less transitions to lower vibrational level that may happen to have same energy as one of levels in triplet S=1to excited state. Transition from triplet to singlet state is not allowed by selection rule (Forbidden transition). Hence phosphorescence radiation may be emitted minute after the initial absorption.

Advantages of phosphorescence

It store light for several minutes or even hours and re-emits a significance amount of light over a long period of time. it can be recharged when expose d to light or other EM radiations.

Applications of UV-Vis spectroscopy

This technique is used to measures the amount of discrete wavelength of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.

The UV spectroscopy provides information on what is the sample and at what concentrations. This is done by measuring the intensity of light that passes through a sample and comparing it with respect to the intensity of light passing through a reference sample or blank. This technique is useful for multiple samples including liquids, solids, thin films and glass.

The basic component of a spectrometer includes, light source (UV and visible), monochromator, sample stage and detector as shown in figure, A tungsten filament, continuous over UV region is generally used as light source, detector is used as a photodiode go with monochromators to filter light of a particular wavelength fed to detector.



Diagram of UV –Vis spectroscopy

UV spectroscopy is used extensively in teaching, research and analytical laboratories for the quantitative analysis of all molecules that absorbs UV and visible electromagnetic radiations.

1. Quantitative analysis

a. Determination of concentration of the component: VU spectroscopy is used for the quantitative determination of compounds, it is based on Beer's law related to the absorbance A of a substance of a particular wavelength to the concentration, C as shown follows,

$$A = \log_{10} \frac{I_0}{I}$$

 I_0 is incident radiation and I is a intensity of transmitted radiations.

- b. UV Vis-spectroscopy can also used to study reaction rates--: it involves the measurement of absorption of either reactants or products at a fixed wavelength when reaction occurs. in reaction when product absorbs radiations at a particular wavelength as a function of time and rate of reaction is measured.
- 2. Qualitative analysis

UV spectroscopy is used in structure clarifications of organic compounds, detection of different organic compounds presence in a mixture and their separation by several analytical techniques such as thin layer chromatography.

a. Structure elucidation of organic compound

UV –Vis spectroscopy has been used for the structure elucidation of organic compounds. The particular wavelength indicates evidence of particular chromophore in the compound.

b. Determination of impurities

Thin layer chromatography (TLC) is a very simple technique which is used for qualitative analysis of reaction mixture. Many organic compounds absorbs UV light of various wavelengths, it is used for determination of impurities on organic compounds. The detector used for high performance liquid chromatography (HPLC).

3. Applications in nanotechnology

Nanoparticles have unique optical properties that are sensitive to size, shape, concentration, agglomeration state and refractive index near the surface of nanoparticle, which make UV-Vis a valuable tool for identifying, characterizing and studying nanoparticles. Optical study helps the researcher for the applications of properties of the materials for different use.

4. UV Vis spectroscopy also used for other purpose

Bacterial culturing, drug identification, nucleic acid purity, DNA and RNA analysis, Pharmaceutical industry, Beverage analysis, This technique also used in many other industries. e.g. color index is useful for monitoring transformer oil as a preventative measure to ensue electric power is being delivered safety.