

PHYSICAL CHEMISTRY

Fundamentals of Molecular Spectroscopy

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Introduction

Spectroscopy may be defined as the subject which deals with experimental measurement of energy gaps between different energy levels of a molecule (or ion or atom). All branches of spectroscopy is based on the fundamental relation,

$$\Delta E = h\nu \quad (1)$$

where ΔE , denotes the energy gap, h , the Planck constant (6.626×10^{-34} J s) and ν , is the frequency of the photon absorbed or emitted. According to equation (1) the energy must be equal to the energy ($h\nu$) of the photon. In a molecule, there are different types of energy levels-rotation, vibration and electronic. These gives rise to rotational, vibrational and electronic spectroscopy. Apart from these there is nuclear magnetic resonance (NMR) spectroscopy which involves nuclear spin states and electron spin resonance (ESR) spectroscopy for electronic spin states (for systems having unpaired electrons).

Different branches of spectroscopy involve photons of different energy i.e. frequencies and hence, different regions of the electromagnetic spectrum. In table 1 we list the wavelength range used in different branches of spectroscopy.

Table 1. Wavelength range used in different spectroscopy

Wavelength*	Name of radiation	Nature of energy level
150-400 nm	Ultraviolet (UV)	Electronic
450-750 nm	Visible	Electronic
1 μm -100 μm	Infrared (IR)	Vibrational
100 μm – 1 cm	Microwave	Rotational
1 cm-10 m	Radiowave	Nuclear spin levels

*1 nm= 10^{-9} m, 1 μm = 10^{-6} m

For vibrational and rotational spectroscopy it is a common practice to use the wavenumber ($\frac{1}{\lambda}$, in cm^{-1}).

Electromagnetic Radiation

According to Maxwell's theory, light is a transverse electromagnetic wave. If a light wave propagates along X-axis there is an oscillating electric field E along Y-axis and an oscillating magnetic field H along Z-axis. The oscillations (displacements) of E and H are simple harmonic

in nature and hence, can be described as sine or cosine function. If ν and λ denote the frequency and wavelength of light, and c ($3 \times 10^{10} \text{ m s}^{-1}$) is the velocity of light,

$$\nu\lambda = \frac{c}{n} \quad (2)$$

n , is refractive index of the medium and is unity in vacuum. For a simple harmonic motion we can write the electric field E as

$$E = E_0 \cos 2\pi\nu t \quad (3)$$

If the wave propagates a distance x along X-axis in time t ,

$$x = ct \quad (4)$$

Combining equations (3) and (4)

$$E = E_0 \cos \frac{2\pi\nu x}{c} \quad (5)$$

It is evident if $x = n\lambda$, i.e. an integral multiple of the wavelength, the values of oscillating electric field is identical to that at $x=0$, (since, $\nu\lambda=c$). In other words, for a transverse wave same values of E (H or displacement) repeats after one wavelength. In the presence of light (with electric field E), an electron of charge e , experience a force eE according to the Coulomb's law. For an electron moving with a velocity v there is an additional force Hev due to the magnetic field H of the light wave according to the Biot-Savart Law. Through these two interactions light affects electrons in an atom or a molecule and causes transitions between different states.

Lambert-Beer Law

Absorption spectroscopy is based on the Lambert-Beer law. This law may be understood as follows. As shown in fig. 1, let I_0 is the intensity of light before a sample and I , the intensity after the sample. If the sample absorbs a part of light $I_0 > I$. Then the law states that fraction of light ($\frac{dI}{I}$) absorbed by the sample is proportional to the concentration (c) of the absorbing species and the length of the sample dl so that,

$$\frac{dI}{I} = \epsilon c dl \quad (6)$$

the proportionality constant, ϵ is known as the extinction coefficient. On integration of this equation one obtains the Lambert-Beer law in the familiar form

$$\log \left(\frac{I_0}{I} \right) = \epsilon c l \quad (7)$$

The quantity $\log \left(\frac{I_0}{I} \right)$ is called the optical density or absorbance of the sample.

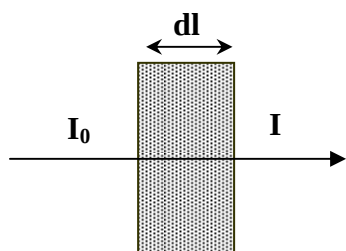


Fig.1. Schematic representation of absorption of light by a sample.

Basic Features of a Spectrometer

A spectrometer determines which photons are absorbed by a molecule and what is the extent of absorption (i.e. magnitude of ϵ). An absorption spectrometer in general consists of three different items- (a) a lamp or source of radiation; (b) a monochromator which disperse or separates photons of different frequency and (c) a detector which measures intensity of the light.

(a) Lamp : The nature of lamp varies from one branch of spectroscopy to another.

(i) Tungsten-halogen lamp: The most common lamp is the incandescent lamp (e.g. a tungsten halogen lamp). The tungsten filament lamp is used for absorption spectroscopy in the visible range. In this lamp, a tungsten lamp is heated by passing current. The heated filament emits light according to the principle of black body radiation. If $\lambda_{\max}$ is the wavelength corresponding to the maximum intensity, according to the Wien displacement law, $\lambda_{\max} T = \text{constant}$. This implies that $\lambda_{\max}$ is inversely proportional to the temperature of the filament. Thus with rise in temperature the $\lambda_{\max}$ gradually shifts to shorter wavelength. At a relatively lower

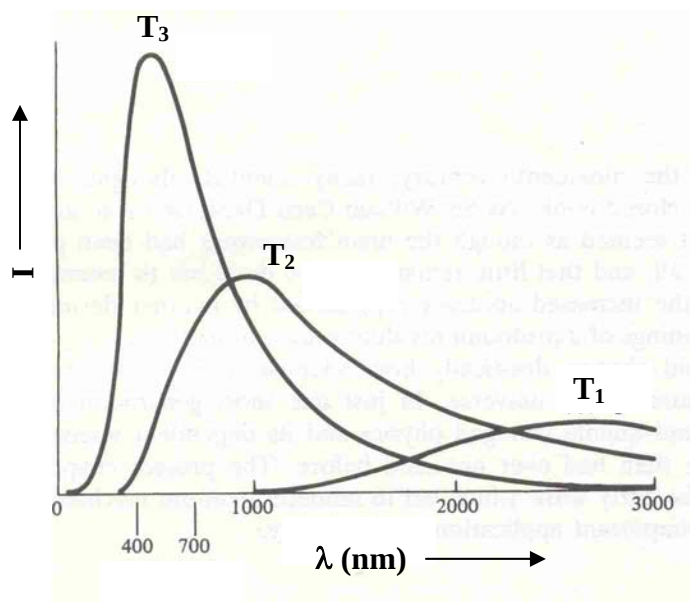


Fig.2. Intensity of the light emitted by a black body

temperature (T_1) the emitted light is in the infrared (>750 nm) region. At slightly higher temperature (T_2) the filament becomes “red-hot” i.e. with maximum around 600-700 nm. At a still higher temperature (T_3) the maximum shifts to shorter wavelength and light in the entire visible region is emitted. Such a filament is called “white hot.” The intensity of the light emitted by a black body at various temperatures are shown in fig. 2.

(ii) **Discharge lamp:** In a discharge lamp initially a high voltage is passed to ionize the gas to produce electrons (cathode rays). When an electron with very high kinetic energy collides with a molecule the electron lose a part of their kinetic energy and the lost energy is transferred to the molecule and the latter is excited to an upper electronic state. The most common discharge lamps are mercury, xenon, deuterium and nitrogen lamps.

(b) **Monochromator:** The monochromator separates lights of different wavelengths. In the old models of monochromator a prism is used as a dispersing element. Most modern monochromators use a grating as dispersive element, which reflects light in different angle according to the famous Bragg’s law.

(c) **Detector:** The function of the detector is to measure the intensity of light. The intensity of light is defined as the total energy (or number of photons times $h\nu$) passing through an unit area. To determine the number of photons one uses the celebrated photoelectric effect. For this purpose, the light is allowed to heat a photocathode. Each photon produces one electron and this gives rise to a current. In a spectrometer, instead of a photocell one uses a photomultiplier tube (PMT). In a PMT, the initial electron (primary electron) produced by the photocathode strikes an electrode (dynode) to produce ~ 4 secondary electrons. Subsequently the secondary electrons strike more dynodes. If there are N dynodes (or stages) the total number of electrons produced by one photon is $\sim 4^N$. Thus a photomultiplier produces large amount of current.

Separation of Rotational, Vibrational and Electronic Motion: Born-Oppenheimer Approximation

A molecule possesses translational, rotational, vibrational and electronic energy. Among these translational energies are continuous (i.e. un-quantized). Energy of the other energies is quantized with discrete energy levels and one may study the energy gap by spectroscopy. The rotational and vibrational levels arise from nuclear motion while the electronic energy levels originate from the electronic motion.

In order to get the different energies one needs to solve the Schrodinger equation which includes both the nuclear co-ordinate (R) as well as the electronic co-ordinate (r). The Schrodinger equation may be written as,

$$H(r, R) \Psi(r, R) = E\Psi \quad (8)$$

where the molecular Hamiltonian H is sum of nuclear kinetic energy (T_N) and electronic Hamiltonian H_e so that $H = T_N + H_e$.

Since the nuclei are several thousand times heavier than the electrons, the former is very sluggish. In order to separate the electronic and nuclear co-ordinates, Born and Oppenheimer proposed that the nuclei may be assumed to be stationary during the motion of the electrons. As a result of the Born-Oppenheimer approximation the total wave function $\Psi(r, R)$ may be written as a product of the electronic part (ψ_{el}) and the nuclear part (ψ_N) as, $\Psi(r, R) = \psi_{el}(r, R) \psi_N(R)$. It is further assumed that the electronic function varies very slowly over nuclear co-ordinate. Under these assumptions the Schrodinger equation may be separated as,

$$H_e \psi_{el}(r, R) = E_{el}(R) \psi_{el}(r, R) \text{ and } [T_N + E_{el}(R)] \psi_N(R) = E \psi_N(R) \quad (9)$$

In the last equation the electronic energy acts as the potential energy for the nuclear motion. Solution of the first equation of (9) gives the electronic energy while solution of the second gives nuclear kinetic arising from rotational and vibrational motion.

Rotational Spectroscopy

Rotational spectroscopy refers to the study of transition between rotational energy levels. In order to calculate the rotational energy it is assumed that during rotation while all the nuclei in a molecule move the distance between the nuclei (i.e. bond distances) remain fixed. Such a rotating molecule with a fixed inter-nuclear distance is called a rigid rotator. We will now briefly discuss the Schrodinger equation of a rigid rotator.

The Rigid Rotator

The kinetic energy (T) of an atom of mass, m , is given by,

$$\begin{aligned} T = \frac{1}{2} m v^2 &= \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \\ &= \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \phi^2 \sin^2 \theta) \end{aligned} \quad (10)$$

where, r, θ, ϕ are the polar co-ordinates. For a rigid rotator, $\dot{r} = \frac{dr}{dt} = 0$, so that

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m r^2 (\dot{\theta}^2 + \phi^2 \sin^2 \theta) \quad (11)$$

Consider, a diatomic molecule in which two atoms of mass m_1 and m_2 are at a distance r_1 and r_2 from the centre of mass (origin) of the system. For the diatomic molecule the kinetic energy is sum of kinetic energy of the nuclei. For a rigid rotator, the potential energy is zero. So the total energy E_R is just equal to the kinetic energy. For the diatomic molecule the co-ordinates θ and ϕ are same for the two atoms. Thus one may write

$$E_R = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) (\dot{\theta}^2 + \phi^2 \sin^2 \theta) = \frac{1}{2} I (\dot{\theta}^2 + \phi^2 \sin^2 \theta) \quad (12)$$

where I is the moment of inertia of the diatomic molecule. I may be written as,

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \quad (13)$$

Where, μ is the reduced mass of the molecule and $r_0 = r_1 + r_2$, is the bond distance. Comparing equation (11) with equation (12) it is evident that a rigid rotator behaves like a particle of mass I placed at a distance unity (i.e. $r=1$) from the origin (centre of mass) of the system. Thus for a rigid rotator, using mass= I and energy= E_R , and noting potential energy $V=0$, the Schrödinger equation is

$$\nabla^2 \psi_R + \frac{8\pi^2 I E_R}{h^2} \psi_R = 0 \quad (14)$$

Solution of equation (14) gives rotational energy (E_R) and rotational wave-function (ψ_R). It may be shown that the rotational energy corresponding to the J -th level, E_J is given by,

$$E_J = J(J+1) \frac{h^2}{8\pi^2 I} \quad (15)$$

The rotational quantum number J may be zero or any positive integer e.g. $J=0, 1, 2, 3, \dots$. Each rotational is degenerate with $2J+1$ levels.

Rotational Transitions

Consider, transition from a rotational level of quantum number J to an upper level of quantum number J' . In this case, the energy of the photon absorbed is equal to $E_{J'} - E_J$ so that,

$$h\nu = E_{J'} - E_J = \frac{h^2}{8\pi^2 I} [J'(J'+1) - J(J+1)] \quad (16)$$

The frequency $\bar{\nu}$ of the photon absorbed, expressed in wavenumber, (cm^{-1}) is given by

$$\bar{\nu}_r = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{h}{8\pi^2 c I} [J'(J'+1) - J(J+1)] = B [J'(J'+1) - J(J+1)] \quad (17)$$

$B (= \frac{h}{8\pi^2 cI})$, is known as the rotational constant of the molecule and is expressed in cm^{-1} . The main aim of rotational spectroscopy is to determine B which gives I and finally the bond distance, r_0 .

Selection Rule: Position of Rotational Lines

According to the quantum mechanical theory, transitions between all rotational states are not allowed. Only transitions between states whose rotational quantum number differ by unity are allowed. Thus the selection rule for rotational transition is

$$\Delta J = \pm 1 \quad (18)$$

For absorption $\Delta J = 1$ and hence, in equation (16) $J' = J + 1$. Thus equation (16) may be written as

$$\bar{\nu}_r = B(J+1) \quad (19)$$

For transition from the lowest state ($J=0$), the rotational is observed at $2B$. The successive rotational lines are observed at frequencies $4B, 6B, 8B \dots$ for $J=1, 2, 3 \dots$, respectively. Evidently, the energy (frequency) spacing between two successive rotational lines is $2B$.

For example, for HCl, the first rotational line is observed at a frequency 20.8 cm^{-1} i.e. at a wavelength 0.48 mm . Hence, for HCl, the rotational constant, $B = 10.4 \text{ cm}^{-1}$. From the rotational constant of HCl, one may easily calculate that the moment of inertia of HCl is $2.66 \times 10^{-40} \text{ gm cm}^2$ and the H-Cl bond distance is $0.128 \text{ nm} = 1.28 \text{ angstrom}$ (i.e. $1.28 \times 10^{-8} \text{ cm}$).

Intensity of Rotational Lines: Maxwell Boltzmann Distribution

The intensity of a rotational line depends on the number of molecules present in the initial state J . At room temperature (300 K), the thermal energy, $k_B T = 208 \text{ cm}^{-1}$. Since the rotational energy gaps are of the order of a few cm^{-1} , many rotational levels are populated at room temperature. According to Maxwell Boltzmann Distribution law, the number of molecules (N_J) at a rotational level J is given by,

$$N_J = (2J+1) N_0 \exp [-(E_J - E_0)/k_B T] = (2J+1) N_0 \exp [-BJ(J+1)hc/k_B T] \quad (20)$$

Note that the factor $2J+1$ arises from the degeneracy of the rotational levels. For the most populated level,

$$\frac{dN_J}{dJ} = 0 \quad (21)$$

Using this condition it may be easily shown that the quantum number (J_{max}) for the most populated level (i.e. N_J highest) is

$$J_{\max} = \frac{1}{2} \left[\sqrt{\frac{2k_B T}{Bhc}} - 1 \right] \quad (22)$$

Non-Rigid Rotator

Though rotational lines are expected to be equispaced, in many cases the energy gap between successive rotational lines decreases slightly with increase in J. This discrepancy is attributed to the non-rigidity of a molecule. It is suggested that with increase in J as rotational energy increases the moment of inertia and hence, bond length increases. When this is taken into account the rotational energy is given by

$$E_J = BJ(J+1)hc - DJ^2(J+1)hc \quad (23)$$

The constant D is approximately given by

$$D = \frac{4B^3}{\omega^2} \quad (24)$$

where ω is the frequency of vibration of the molecule. Since B is of the order of 10 cm^{-1} and ω is $\sim 1000 \text{ cm}^{-1}$, D is $\sim 10^{-3} \text{ cm}^{-1}$ i.e. very small. Using equation (23) the expression of frequency of rotational line is given by

$$\bar{\nu}_r = 2BJ - 4DJ^3 \quad (25)$$

Isotope Effect

On isotopic exchange the reduced mass of a molecule changes. This causes a change in the moment of inertia and hence, the rotational energy. Suppose, for two isotopically substituted molecules (e.g. HCl and DCl) of moment of inertia I_1 and I_2 , the frequencies of the rotational lines are $\bar{\nu}_{1r}$ and $\bar{\nu}_{2r}$. From equation (19) it is easy to see that

$$\bar{\nu}_{1r} - \bar{\nu}_{2r} = \frac{h}{4\pi^2 c} J \left(\frac{1}{I_1} - \frac{1}{I_2} \right) \quad (26)$$

Vibrational Spectroscopy

The vibrational spectroscopy involves transition between different vibrational energy levels. The vibrational energy is calculated from the Schrodinger equation for a simple harmonic oscillator. We will now briefly discuss this equation in the next section.

Simple Harmonic Oscillator

The potential energy of a simple harmonic oscillator exhibits a quadratic dependence on the co-ordinate, e.g.

$$V = \frac{1}{2} k q^2 \quad (27)$$

where q , denotes the vibrational co-ordinate, i.e. inter-nuclear distance. Thus the Schrodinger equation for a simple harmonic oscillator is

$$\nabla^2 \psi_R + \frac{8\pi^2 m}{h^2} (E - \frac{1}{2} k q^2) \psi_R = 0 \quad (28)$$

From the solution of this equation, the vibrational energy of a linear harmonic oscillator is obtained as,

$$E_n = (n + \frac{1}{2}) h \nu_0 \quad (29)$$

where n is the vibrational quantum number and ν_0 is the classical frequency of vibration,

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (30)$$

In the last equation, k , denotes force constant and μ denotes reduced mass of the harmonic oscillator. The energy of the lowest state ($n=0$) is $\frac{1}{2} h \nu_0$ and is called zero point energy. The vibrational energy gap for the transition from the level n to n' is given by

$$\Delta E = (n' - n) h \nu_0 \quad (31)$$

The selection rule for vibrational transition is $\Delta n = \pm 1$. Thus the energy gap between two successive vibrational levels is $h \nu_0$. Thus a pure vibrational transition should be observed at this energy. The vibrational energy $h \nu_0$ is much greater than the thermal energy ($k_B T$) at room temperature and hence, at room temperature only the zeroth vibrational ($n=0$) level is populated with very small or negligible population of the upper vibrational levels ($n > 1$).

Anharmonic Vibration

In many cases, the potential energy of an oscillator deviates from that given in equation (27) and consists of terms beyond the quadratic term. Such an oscillator is called an anharmonic oscillator. In general, the potential energy of an anharmonic oscillator may be written as,

$$V = \frac{1}{2} k_1 q^2 + \frac{1}{6} k_2 q^3 + \frac{1}{24} k_3 q^4 \quad (32)$$

If one uses this potential in the Schrodinger equation (23) one may show that the energy of an anharmonic oscillator is given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu_0 - x\left(n + \frac{1}{2}\right)^2 h\nu_0 + y\left(n + \frac{1}{2}\right)^3 h\nu_0 + \dots \quad (33)$$

In the last equation x , y , .. are known as the anharmonicity constants. Considering only the first two terms in equation (33) the energy change for transition from a state of vibrational quantum number n to the next one $(n+1)$ is,

$$E_{n+1} - E_n = h\nu_0 - 2(n+1)xh\nu_0 \quad (34)$$

For a simple harmonic oscillator the vibrational energy gap between any two adjacent levels is the same ($h\nu_0$). From equation (34) it is evident that with increase in n the vibrational gap between two adjacent levels decreases because of anharmonicity.

Another consequence of anharmonicity is follows. Addition of the higher terms in the potential, makes the transition $\Delta n = \pm 2, \pm 3, \pm 4, \dots$ allowed. If $\Delta n = 1$, the transition is called fundamental transition and the corresponding frequency $(E_n - E_0)/h$ is denoted as ν_1 . For $\Delta n = 2$, the transition is called first overtone with a frequency ν_2 . Similarly, for second overtone, $\Delta n = \pm 3$ and the frequency is ν_3 . Evidently,

$$\begin{aligned} \nu_1 &= (1 - 2x)\nu_0 \\ \nu_2 &= (1 - 3x)2\nu_0 \\ \nu_3 &= (1 - 4x)3\nu_0 \end{aligned} \quad (35)$$

Since x is small obviously $\nu_1 : \nu_2 : \nu_3 \approx 1 : 2 : 3$.

Vibrational Spectrum and force Constants

It is evident from the position of the vibrational line one gets ν_0 and from this using equation (30) one obtains the force constant (k) of the vibration. In a molecule the force constants for various bonds and various functional groups are different. Thus the main application of vibrational spectroscopy is to detect different functional groups of a molecule. The most common vibrations are O-H stretching, C-H stretching and C=O stretching frequencies which appear at a frequency around 3500 cm^{-1} , 3000 cm^{-1} and 1800 cm^{-1} .

Isotope Effect in Vibrational Spectrum

For different isotopically substituted molecules, the force constant remains almost same because the latter depends on the electronic configuration. However the reduced mass of the system changes appreciably and this causes significant change in the vibrational frequency. If for two

isotopes the reduced masses are μ_1 and μ_2 , then the ratio of the vibrational frequencies ν_{01} and ν_{02} are

$$\frac{\nu_{01}}{\nu_{02}} = \sqrt{\frac{\mu_2}{\mu_1}} \quad (36)$$

For instance, in the case of HCl and DCl of the vibrational frequencies are 2885 cm^{-1} and 2061 cm^{-1} , respectively) and the ratio of reduced masses is $\sqrt{2}$. It is easy to verify that $\nu_{\text{HCl}}:\nu_{\text{DCl}} \approx \sqrt{2} = 1.414$.

Vibration Rotation Spectra

The vibrational transition is invariably accompanied by a change in the rotational quantum number. Thus one actually observes a transition from a state $(0, J)$ i.e. $n=0$, and rotational quantum number J to a state $(1, J')$. If one assumes that the rotational constant in the two vibrational states are same, one can write that the frequency of a vibration-rotation transition is given by,

$$\bar{\nu} = \nu_0 + B [J'(J'+1) - J(J+1)] \quad (37)$$

Obviously, if $\Delta J=0$ i.e. $J'=J$, there should be a pure vibration transition at a frequency ν_0 . However, a pure vibrational transition is never observed because the selection rule for rotational transition is $\Delta J=\pm 1$. Thus a vibration-rotation spectrum consists of two series of lines one at a frequency higher than ν_0 and another at a frequency lower than ν_0 . The series of lines which arise from rotational transitions are called rotational fine structure of a vibration spectrum. Such a spectrum involving simultaneous vibration and rotational transitions is called a vibration-rotation spectrum.

a) P Branch

The so called P branch of a vibration-rotation spectrum arises in the case $\Delta J=-1$ i.e. $J'=J-1$. From equation (17) in this case the frequency of transition is given by

$$\bar{\nu}_P = \nu_0 - 2BJ \quad (38)$$

Note that one can not have a line in P branch for $J=0$ because that would imply negative J' . Hence, in this case $J=1,2,3 \dots$

b) R Branch

The R branch corresponds to the case $\Delta J=+1$ i.e. $J'=J+1$. From equation (26)

$$\bar{\nu}_R = \nu_0 + 2B(J+1) \quad (39)$$

In this case $J=0, 1, 2, \dots$

In a vibration rotation spectra the pure vibration transition at ν_0 is not observed. The vibration energy is estimated from the position of the centre of the series of lines arises from R and P bands. In many molecules the rotational lines are very close. In this case, the spectrum looks like a band rather instead of separated lines. This vibration-rotation line is often referred to as a vibration band. The P and R –branches of a vibration-rotation spectrum are shown in fig. 3.

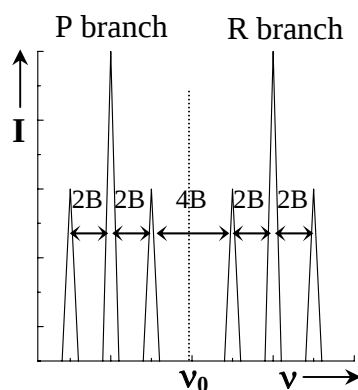


Fig.3. P and R branches of a vibration-rotation spectrum.

Raman Spectroscopy: Relative intensity of the Stokes and Anti-Stokes lines

The Raman effect refers to the shift in the frequency of light scattered by a system. If a light of frequency ν is incident on a system ordinarily the scattered light will also have the same frequency, ν . However, Raman first observed a weak scattered light at a frequency $\nu \pm \nu'$. The line at a frequency $\nu - \nu'$ is called the Stokes line and the one at $\nu + \nu'$ is called the anti-Stokes line. The frequency ν' is such that $h\nu'$ matches with the vibrational or rotational energy gap of the molecule. The origin of the Raman line may be understood in terms of the transitions depicted in Fig. 4 as follows.

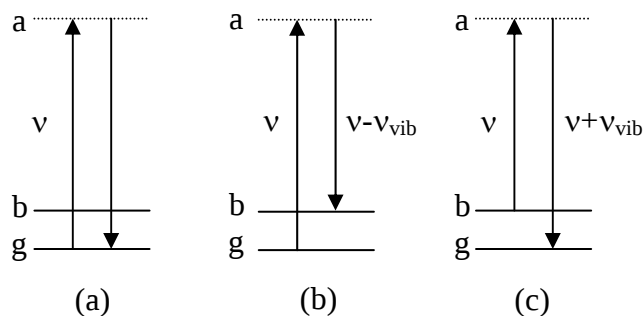


Fig. 4. Transitions involved in (a) Rayleigh; (b) Stokes and (c) Anti-stokes line

a) Rayleigh Line: In this case, the molecule in the ground state g on interaction of the external photon of frequency ν first goes to a virtual or non-stationary state, a (fig. 1a) . If from

this state the molecule comes back to the same state the scattered (or emitted) photon is of energy, $h\nu$ and the frequency is ν .

b) Stokes Line: In this case, instead of coming back to the same state the molecule returns to a higher vibrational (or rotational) state, b (fig. 1b). Thus the energy of the scattered light is less than that ($h\nu$) of the incident photon by the energy gap $E_b - E_g$. Since the energy gap $E_b - E_g$ is equal to the vibrational or rotational energy ($h\nu'$) the energy of the scattered light is $h\nu - h\nu'$ and the frequency is $\nu - \nu'$.

c) Anti-Stokes Line: In this case, the transition starts from a higher (“hot”) vibrational or rotational level, b (fig. 1c). From this level, the molecule goes to the virtual state a and then returns to the lowest state g . Thus the energy of the scattered light is more than that ($h\nu$) of the incident photon by the energy gap $E_b - E_g$. Thus, the frequency of the scattered light is $\nu + \nu'$.

Since population of the higher vibrational level (b) is much smaller than that in the lowest state (g) the anti-Stokes line in vibrational Raman spectrum is much weaker in intensity compared to the Stokes line. However, in the case of rotational levels often the anti-Stokes lines are more intense than the Stokes lines because of higher population in the higher rotational levels.

Raman Effect: Classical Theory and Polarizability

According to the classical theory, any scattered light (Rayleigh or Raman) arises from an oscillating dipole. The electric field of the incident light produces an induced dipole moment μ which is given by,

$$\mu = \alpha E \quad (40)$$

where α is the polarizability of the molecule. From equation (3) the electric field E of a radiation of frequency ν is given by, $E = E_0 \cos 2\pi \nu t$.

As result, from equation (40)

$$\mu = \alpha E_0 \cos 2\pi \nu t \quad (41)$$

According to equation (41) the induced dipole oscillates at a frequency ν and thus gives rise to the Rayleigh line. If the polarizability (α) of a molecule changes during vibrational and rotational motion the frequency in equation (41) is different from ν . This gives rise to the Raman effect.

a) Vibrational Raman Effect

The vibrational Raman effect arises from the change of α with the vibrational co-ordinate, q . The essential condition of Raman effect is

$$\frac{d\alpha}{dq} \neq 0 \quad (42)$$

One can expand α as a Taylor's series

$$\alpha = \alpha_0 + \frac{\beta}{A} q \quad (43)$$

where $\beta = \frac{d\alpha}{dq}$ and A is the amplitude of vibration. For simple harmonic vibration,

$$q = q_0 \cos 2\pi\nu_0 t \quad (44)$$

where ν_0 denotes the vibrational frequency. Thus

$$\alpha = \alpha_0 + \frac{\beta}{A} q_0 \cos 2\pi\nu_0 t \quad (45)$$

Substituting the value of α in equation (41)

$$\begin{aligned} \mu &= E_0 \cos 2\pi\nu t \left[\alpha_0 + \frac{\beta}{A} q_0 \cos 2\pi\nu_0 t \right] \\ &= \alpha_0 E_0 \cos 2\pi\nu t + \frac{1}{2} \frac{\beta}{A} q_0 E_0 [\cos 2\pi(\nu - \nu_0)t + \cos 2\pi(\nu + \nu_0)t] \end{aligned} \quad (46)$$

The last equation gives a classical explanation of the Raman effect. Evidently, in equation (46) the first, second and third terms respectively, gives rise to the Rayleigh, Stokes and anti-Stokes lines. It is also easy to see that according to this equation the selection rule for Raman effect is $\Delta n = \pm 1$.

b) **Rotational Raman Effect**

The classical theory of Raman effect is almost identical to that for the vibrational Raman effect. For rotational Raman effect, the essential condition is that the molecule must be anisotropic i.e. its polarizability changes with direction or orientation of the molecule. For rotational Raman, the polarizability changes because during molecular rotation the orientation of the molecule with respect to the electric field E of incident light changes. For a diatomic molecule if the rotational frequency is ν_R the time dependent polarizability is given by

$$\alpha = \alpha_0 \cos 2\pi(2\nu_R t) \quad (47)$$

In this case the factor $2\nu_R$ arises because during a complete rotation (by 2π) the molecule assumes same orientation twice (for rotation by π and 2π).

Then in analogy to equation (46) for rotational Raman one can write that

$$\mu = \frac{1}{2} \alpha_0 E_0 [\cos 2\pi(\nu - 2\nu_R)t + \cos 2\pi(\nu + 2\nu_R)t] \quad (48)$$

According to this equation the frequencies of Stokes and anti-Stokes lines are $\nu - 2\nu_R$ and $\nu + 2\nu_R$ respectively. In other words, the selection rule for Rotational Raman is $\Delta J = \pm 2$.

IR and Raman Spectra for centrosymmetric molecules: Mutual Exclusion

Usually a molecule has many vibrational degrees of freedom ($3N-6$ for a non-linear molecule). All the vibrational modes are not observed in simple Infra Red (IR) absorption and Raman spectra. According to quantum theory, for a centrosymmetric molecule if a particular vibrational mode is IR active (i.e. those for which IR transition is allowed), it can not display Raman effect. Conversely, a vibration which gives rise to Raman line (i.e. Raman active) is IR inactive. Thus it is said that for a centrosymmetric molecule, IR and Raman spectra are mutually exclusive.

Electronic Spectroscopy

The electronic spectroscopy involves transition between different electronic states. Let us consider the potential energy curve of a molecule. The potential energy (PE) curve refers to the plot of potential energy against the inter-nuclear co-ordinate. According to equation (27) the potential energy (V) for a simple harmonic oscillator is proportional to the square of the vibrational co-ordinate, q . Thus the plot of V against q should be a parabola (figure 5).

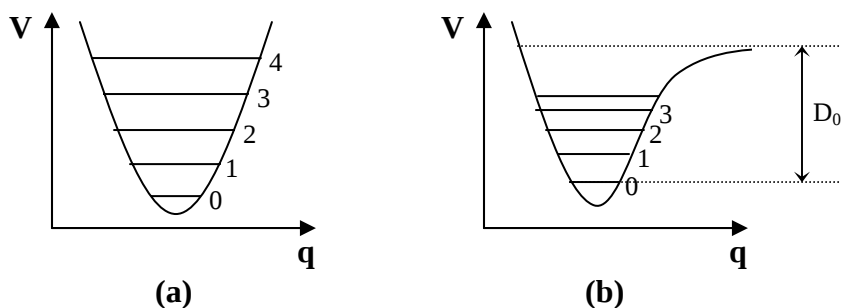


Fig. 5. (a) Potential energy diagram of a simple harmonic oscillator (b) Potential energy diagram of a real molecule.

In fig. 5a the horizontal lines correspond to different vibrational quantum numbers (n). In a particular electronic state the vibration energy of the molecule increases with increase in the vibrational quantum number. It is evident that for a simple harmonic motion, the inter-nuclear distance, q never becomes infinite. In other words, the molecule never dissociates. But in actual case, most molecules dissociate at an energy greater than the bond dissociation energy (D_0). The potential energy curve for a real molecule is shown in fig. 5b. In this case, it is evident that when the potential exceeds D_0 the inter-nuclear coordinate becomes infinite. The particular form of potential which gives rise to such a curve is called Morse potential, $U(r)$ and is given by

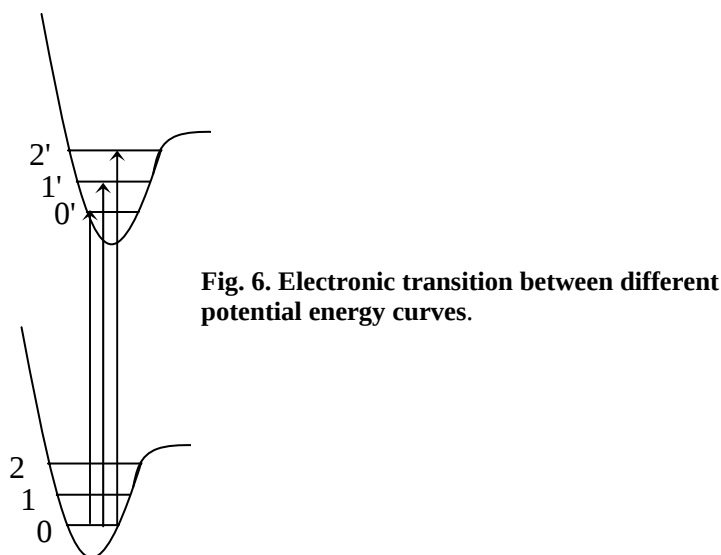
$$U(r) = D [1 - e^{-a(q-q_0)}]^2 \quad (49)$$

Obviously, at a distance $q=q_0$, the energy is zero and hence, q_0 is the equilibrium internuclear (bond) distance. D is equal to D_0 plus the zero point vibration energy ($\frac{1}{2} h\nu_0$). The particular form of the PE curve shown in fig. 5b in which the molecule remains bound at least for some energy corresponds to bound or bonded state. In some states the inter-nuclear distance is infinite at all energies. Such a curve corresponds to a dissociative state. If a molecule is excited to such a state the molecule dissociates immediately. Such dissociation by excitation is known as photo-dissociation.

Electronic Excitation: Frank-Condon Principle

The electronic excitation corresponds to transition between different potential energy (PE) curves (fig. 6). Note, the equilibrium bond distances are not same in all electronic states. Usually, the bond distances in the excited electronic state is slightly larger and hence, in fig. 6 the PE curve in the excited state is displaced slightly to the right.

The time needed for an electronic transition is very fast. Therefore, during electronic transition the slower moving nuclei do not undergo any displacement and hence, the inter-nuclear distances remain fixed during an electronic transition. This is the famous Frank-Condon principle. Thus, the electronic transitions are represented by vertical lines (i.e. with no change in the inter-nuclear distance). Such an electronic transitions is referred to as a Frank-Condon transitions or vertical transitions.



It may be noted that at room temperature most of the molecules are in the lowest ($n=0$) vibrational level. Thus for absorption the transitions start from $n=0$ level. However, on excitation

the molecule may be excited to the lowest vibrational level ($n'=0$) of the upper electronic states as well as higher vibrational levels ($n'=1, 2, 3, \dots$) as shown. Evidently, the energy gap between successive absorption lines gives vibrational energy in the excited electronic state. It should be emphasized that the vibrational energy gap in the excited state is usually lower than that in the ground electronic state. Such a transition which involves change of both electronic and vibrational energy is called a vibronic transition. A vibronic transition is often very broad because of the large number of transitions involving vibrational and rotational states. Thus electronic transition in most cases appear as a band.

Nature of Molecular Orbitals

In a molecule there are different kinds of molecular orbitals (MO-s)- σ , π and n (non-bonding) ones. Out of these the non-bonding MO-s have energies roughly equal to the energy of the atomic orbitals (AO-s). The bonding MO-s are lower in energy compared to the atomic orbitals while energy of an anti-bonding orbital is higher than that of the corresponding atomic orbitals. The σ MO-s and π MO-s arise respectively, from axial and lateral overlap of the atomic orbitals. The σ bonding MO-s are the lowest in energy while the σ anti-bonding MO-s (σ^*) possess the highest energy. The π bonding MO-s possess higher in energy compared to the σ bonding MO-s while the π anti-bonding MO-s (π^*) possess lower energy than a σ anti-bonding MO. The relative energies of the σ , π and n bonding MO-s and also the corresponding anti-bonding MO-s are shown in fig. 7. From fig. 7 it is easy to see that the relative energies of different transitions are of the order, $n\pi^* < \pi\pi^* \sim n\sigma^* < \sigma\sigma^*$.

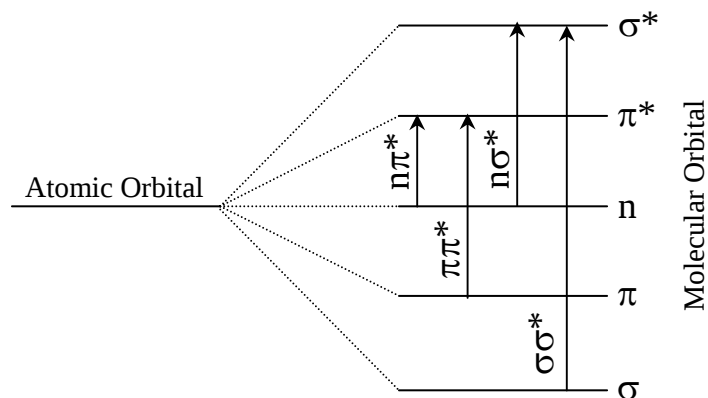


Fig. 7. Different kinds of molecular orbitals.

HOMO and LUMO

For spectroscopy the most important MO-s are the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). The lowest energy electronic transition refers to transition from HOMO to LUMO. As an example, in fig. 8 we have shown transition from a ground singlet state (S_0) in which there are two unpaired electron of opposite spin in the HOMO. When one electron is excited from the HOMO to the LUMO there may be two situations. Firstly, the excited electron in the LUMO may have opposite spin to that of the electron in the HOMO. In this case, the total spin is zero and the spin multiplicity $2S+1=1$. Such a state is called a singlet

state (S_1). Secondly, the two electrons may be of same spin. This gives rise to a triplet state T_1 since $2S+1=3$. The relative energies of the states are of the order $S_1 > T_1 > S_0$.

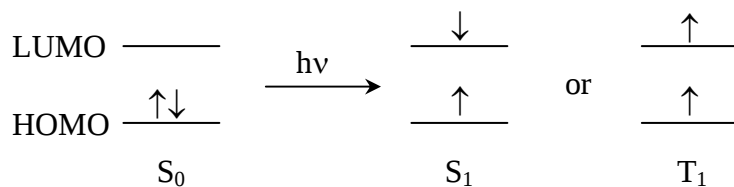


Fig. 8. HOMO-LUMO transitions: singlet, and triplet state

Suggested Reading

1) Fundamentals of

- Molecular Spectroscopy- C. N. Banwell and E. M. McCash
 2) Instrumental Methods of Analysis- H. H. Willard, L. L. Merrit, J. A. Dean, and F. A. Settle
 3) Elementary Quantum Mechanics- F. L. Pilar
 4) Theoretical Chemistry- S. Glasstone
 5) Applications of Absorption Spectroscopy of Organic Compounds- J. R. Dyer