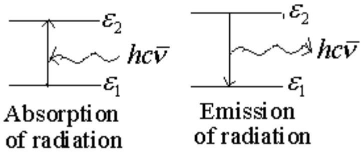
MOECULAR SPECTROSCOPY

Introduction

This chapter deals with interaction of radiation with molecules. Quantum mechanics states that the energy of the molecules is quantized and certain selected energy values are permitted. These energy values are represented in discrete energy levels. When energy is absorbed in the form of radiation, molecule is promoted from lower energy level to higher energy level.



$$\varepsilon_2 - \varepsilon_1 = \Delta\varepsilon = hc\bar{\nu} ,$$

where $\bar{\nu}$ is the frequency of radiation in cm^{-1} (wave number) absorbed by the molecule.
This frequency can be experimentally determined by spectrometer. Radiation of several frequencies is absorbed for transition of different energy levels of the molecules and produces absorption spectra.
But when the molecule transits from higher level to lower level, the energy is emitted in the form of radiation. These frequency lines give emission spectra. The energy of the photon emitted is equal to the energy spacing.

$$\varepsilon_2 - \varepsilon_1 = hc\bar{\nu}$$

The frequency of radiation absorbed or emitted is related with the molecular properties and hence the latter is calculated.

Molecular Energy and Range of Radiation for Interaction

Electromagnetic radiation can be grouped into several regions depending on the wavelength (λ) or frequency (ν). These are listed below:

Region:	$\gamma - X$ rays	UV – Vis	Infra-red (IR)	Microwave	Radio wave
Wave length (λ):	3 pm – 3 nm	3 nm – 800 nm	800 nm – 3 mm	3 mm – 30 cm	30 cm – 3 km

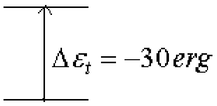
The molecular energy is classified depending on their motion. There are three kinds of molecular motion: the translational motion of the molecule as a whole; the rotational motion; and the vibrations of the nuclei within the molecule. These motions are approximately assumed to be independent and we shall discuss separately.

(1) Translational energy (ε_t)

This energy of the molecule is due to its translational motion when it moves from one point to another point in space. This energy is quantized. It is expressed as

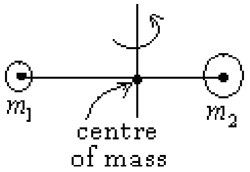
$$\varepsilon_t = n^2\left(\frac{h^2}{8mL^2}\right),$$ taking the particle's motion in one-dimensional box.

n is the translational quantum number and its value is 0, 1, 2, 3, etc.
The energy gap of the two successive translational energy levels is very small of about $\Delta\varepsilon_t \approx 10^{-30}$ erg. Hence, the radiation absorbed for transition from one level to its higher level has frequency very close and forms a continuous spectrum. It means that the frequency lines in the spectrum are not separated and this spectrum is of no use for the study of molecular properties. This is why we talk rotational spectra, vibrational spectra, electronic spectra but we do not talk translational spectra.



(2) Rotational energy (ε_r)

This energy is due to rotational motion of the molecule. The molecule is rotating along the axis passing through the centre of mass and perpendicular to the bond axis. The rotational energy is given as

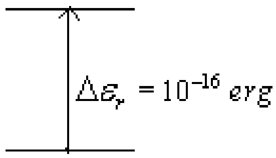


$$\varepsilon_r = J(J+1)\frac{h^2}{8\pi^2 I} ,$$

where J is the rotational quantum number having values 0, 1, 2, 3, etc.

I = moment of inertia = μr^2, μ = reduced mass of the molecule and r = bond length of the diatomic molecule.

Rotational energy-gap between two consecutive levels is of 10^{-16} erg.



The wave length of radiation absorbed for such rotational transition is calculated as $\Delta\varepsilon = hc\bar{\nu} = hc/\lambda$ or, $\lambda = hc/\Delta\varepsilon$.

Putting the values, we have $\lambda = \dfrac{6.627\times10^{-27}\, erg\ \sec\times 3\times10^{10}\, cm\ \sec^{-1}}{10^{-16}\, erg}$ = 0.2 cm.

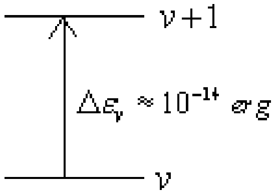
The wave length corresponds to the microwave region of radiation. It means that if the molecules in the gaseous state at low pressure (to avoid interaction among the molecules) are kept in the exposure of microwave radiation, the molecules suffer rotational transition. This is why the rotational spectra are often called microwave spectra.

(3) Vibrational energy (ε_v)

This energy corresponds to the vibrations of the nuclei within the molecule. The nuclei is stretched and compressed periodically along the equilibrium position. The energy due to vibration of the molecule is given by

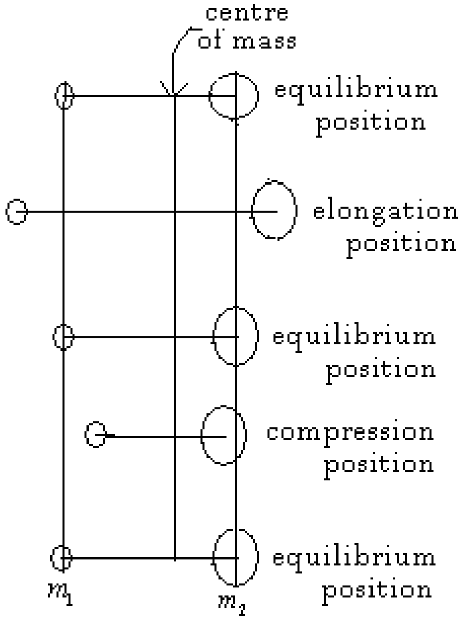
$\varepsilon_v = \left(v + \frac{1}{2}\right) hc\bar{\nu}_0$, where $\bar{\nu}_0 = \dfrac{1}{2\pi c}\sqrt{\dfrac{k}{\mu}}$ is the frequency of the molecular vibration in cm^{-1} and v is vibrational quantum number having values 0, 1, 2, 3, etc.

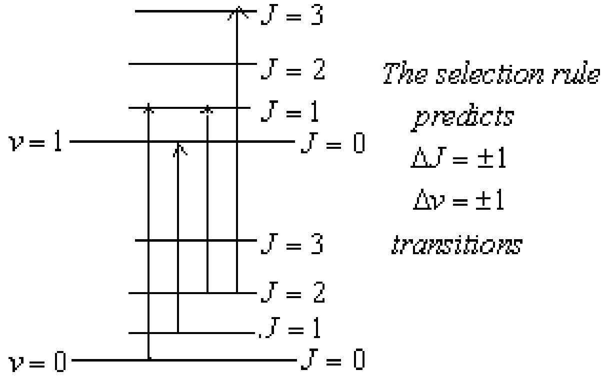
The energy spacing of the vibrational energy levels is approximately given as



The wave length of radiation required for vibrational transition of the molecule, $\lambda = hc/\Delta\varepsilon$ = 0.02 cm = 0.2 mm.

This wave length corresponds to infra-red region of radiation.





Since vibrational energy spacing is much greater than rotational energy spacing, vibrational transition is always accompanied with rotational transition. Thus the vibrational spectra are always associated with rotational spectra and IR spectra are due to vibration-rotation spectra.

More over, since rotational energy gap is of the order of thermal energy of the molecule, hence temperature of the gas under study is to be kept carefully controlled. A small fluctuation of temperature can cause rotational transition without absorbing microwave radiation.

For one degree change of temperature, the change of thermal of the molecule is

$$\Delta\varepsilon_{thermal} \approx k(T+1) - kT = k = 1.36\times10^{-16}\, erg .$$

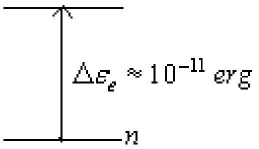
This thermal energy is sufficient to cause rotational transition and for that reason the temperature of the gas under study need carefully controlled. But such control of temperature is not required for the study of vibrational spectra since energy gap of vibrational energy level ($\Delta\varepsilon_v$) is sufficient high for transition from small temperature fluctuation.

(3) Electronic Energy

This energy correspond to the transition of electron from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). The electronic energy,

$$\varepsilon_e = -\frac{2\pi^2 m Z^2 e^4}{h^2}\left(\frac{1}{n^2}\right),$$ where n is the electronic quantum number having values 1, 2, 3, etc.

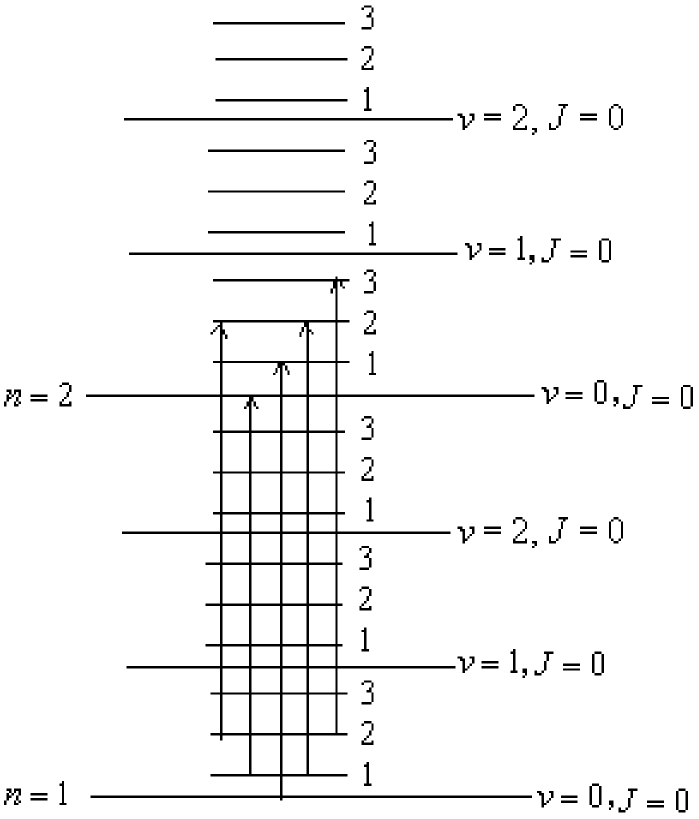
The electronic energy spacing is high and the radiation absorbed for electronic transition have wave length visible to ultraviolet region of radiation.



The wave length of radiation absorbed $\lambda = \frac{hc}{\Delta\varepsilon_e} = 200\ nm$.

For that reason the electronic spectra is called Visible-UV spectra.

Since the electronic energy spacing is very high in comparison to the vibrational and rotational energy spacings, electronic transition is always accompanied with vibrational and rotational transitions. Thus, electronic spectra are associated with vibrational and rotational spectra. It makes electronic spectra most complex while the rotational spectra are simplest one.



Selection rule

$\Delta\nu = any\ value$

$\Delta J = \pm 1$

Spectroscope and Spectroscopy

A spectroscope is an instrument that separates polychromatic light into monochromatic parts i.e. light into spectrum. In simple spectroscope, a prism is used to separate visible ranges into constituent colours. When a scale for reading the monochromatic wave number is attached, the instrument is termed the spectrometer.

A spectrograph makes a photographic record of the spectrum and in a spectrophotometer; a photographic cell is added with spectrometer for measuring quantitatively the light intensity at each wave length. Spectroscopy involves the measurement and interpretation of the interaction of the substance with electromagnetic radiation. So spectroscopy is the recording, study and analysis of this spectrum. Thus, spectrophotometer is invariably used to study the molecular spectra.

Intensity of the spectral lines

Mainly three factors control the intensity of the spectral lines.

(1) Transition probability: It is the likelihood of a system in one state changing to another state.
This is given by the selection rule and is discussed mathematically below.
(2) Population: The number of atoms or molecules initially present in the state from which the transition occurs.
(3) Concentration or path length of the sample: The amount of the material present that give rise to spectrum.

Transition probability from m state to n state

This probability is given by $P_{mn} = \int \psi_m \, \mathrm{p} \, \psi_n \, d\tau$,

where **p** = electric dipole moment operator $= \Sigma q_i r_i$. P_{mn} is also called transition (dipole) moment.

When $P_{mn} \neq 0$, the transition is allowed and when $P_{mn} = 0$, transition is not allowed.

Let us see the selection rule for a particle of charge q in one-dimensional box of length from the state m to state n. For allowed transition, the transition probability would be non-zero.

There is one particle, so $p = \Sigma q_i r_i = q \times x$, where x is the displacement of the particle from the origin.

The transition probability, $P_{mn} = \int_0^L \psi_m (q \times x) \psi_n dx = \frac{2q}{L} \int_0^L x \sin \frac{n\pi x}{L} \times \sin \frac{n\pi x}{L} dx$

or, $P_{mn} = \frac{q}{L} \int_0^L x \left[\cos(m-n)\frac{\pi x}{L} - \cos(m+n)\frac{\pi x}{L} \right] = \frac{q}{L} \int_0^L x \cos(m-n)\frac{\pi x}{L} dx - \int_0^L x \cos(m+n)\frac{\pi x}{L} dx$

or, $$P_{mn} = \frac{qL}{\pi^2}\left[\frac{\cos(m-n)\pi - 1}{(m-n)^2} - \frac{\cos(m+n)\pi - 1}{(m+n)^2} \right].$$

If m and n are both even number or both odd number, then $m - n$ and $m + n$ are even number and $P_{mn} = 0$ i.e. transitions are not allowed.

If m is even and n is odd or vice versa, then $m - n$ and $m + n$ are odd and $P_{mn} \neq 0$. Transitions are allowed.

So, the selection rule for transitions in one dimensional box is $\Delta n = \pm 1, \ \pm 3, \pm 5$, etc are allowed.

Selection rule and Boltzmann population in different energy levels

Spectroscopy ordinarily deals with a collection of identical molecules distributed among states according to Boltzmann distribution law,

$$\frac{n_2}{n_1} = e^{-\Delta\varepsilon/kT}$$, where $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$, difference of energy between two energy levels.

The selection rule for transition of different energy levels for absorption, say $\Delta n = 1$.

Some of the molecules in the $n = 0$ level will absorb radiation and make a transition to $n = 1$ level when exposed to radiation of appropriate frequency.

Some of the molecules in the $n = 1$ level will absorb radiation of appropriate frequency and go to $n = 2$, etc.

Thus, several frequency radiations are absorbed by a sample when exposed to radiation of suitable region of radiation.

Source of radiation, Dispersion element and Detectors used in Spectroscopy

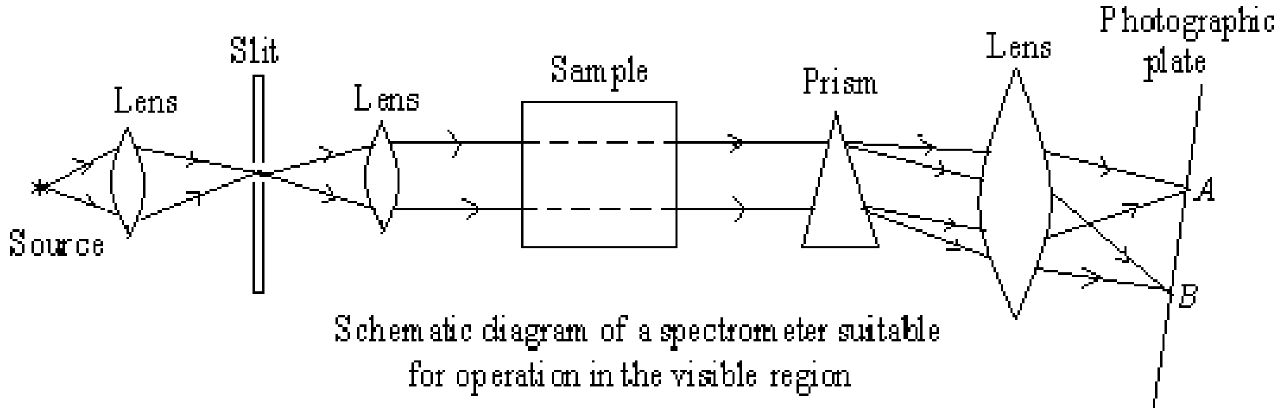
Spectral region	Source	Dispersing elements	Detectors
UV (250 nm – 400 nm)	H_2 discharge tube	Quartz prism	Photo multiplier tube
Visible (400 nm – 800 nm)	Tungsten lamp	Glass prism	Photo multiplier tube
IR (800 nm – 10^{-2} cm)	Heated ceramic element	Rock salt crystal	Thermocouple
Microwave (10^{-2} cm – 3 cm)	Klystron tube	–	Quartz crystal detector

Range of scales with symbol

z	a	f	p	n	μ	m	c	d	Da	k	M	G	T
zepto	alto	femto	pico	nano	micro	milli	centi	deci	deka	kilo	Mega	giga	tera
10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{1}	10^{3}	10^{6}	10^{9}	10^{12}

Experimental technique of Spectroscopy experiment

Experimental technique for absorption spectroscopy in the UV-visible and IR regions are same. Here one passes a beam of light containing a continuous range of frequencies through the sample, disperses the radiation using prism or diffraction grating and at each frequency compares the intensity of a reference beam that did not pass the sample.



Schematic diagram of a spectrometer suitable for operation in the visible region

The above figure is a highly simplified schematic diagram of a spectrometer suitable for use in the visible and UV regions spectrum. A ‘white’ light source is focused by lens 1 onto a narrow slit and is then made into parallel beam by lens 2. After passing through the sample it is separated into its constituent frequencies by a prism and is then focused on to a photographic plate by lens 3. Rays have been drawn to show the points at which two frequencies ν_1 and ν_2 are focused.

If the sample container is empty, the photographic plate, after development, should ideally show an even blackening over the whole range of frequencies covered (i.e. from A to B).

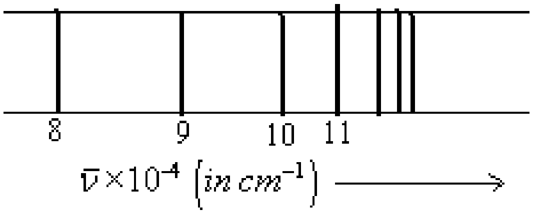
If now we imagine the sample space to be filled with a substance having only two possible energy levels, ε_1 and ε_2, the photographic plate, after development, will show blackening at all points except at the frequency

$$\nu = {(\varepsilon_2 - \varepsilon_1)}/{h} \quad .$$

since energy at the frequency will have been absorbed by the sample in raising each molecule from state 1 to state 2. Further if, as is almost always the case, there are many possible energy levels, ε_1, $\varepsilon_2, \varepsilon_3, \varepsilon_k$ available to the sample, a series of absorption lines will appear on the photographic plate at frequencies given by

$$\nu = {(\varepsilon_j - \varepsilon_k)}/{h} \; .$$

Now-a-days, photographic plate is rarely used and oscilloscope is used to detect the frequency lines of the absorbed light.



Absorption spectra of H-atom (Balmer series)

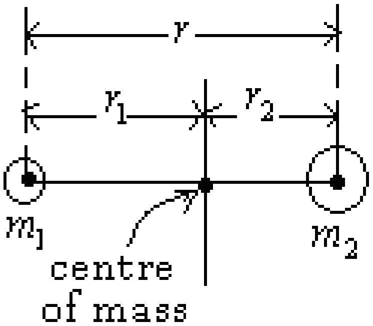
ROTATIONAL SPECTRA OF DIATOMIC MOLECULES

Introduction

Rotational spectra is generally studied by absorption of radiation in the microwave region of radiation (10^7 Å to 10^9 Å or, 0.1 cm to 10 cm except for light diatomic molecules).

Let us consider a diatomic molecule consisting of atoms of masses m_1 and m_2 connected by a chemical bond of length r . The molecule is executing rotational motion along an axis passing through the centre of mass. The model is compared with rigid spheres connected by a rod of very thin breath. The bond length does not change due to rotation and so the potential energy (V) of the molecule is taken zero.

Moment of Inertia (I)



The moment of inertia, $I = m_1r_1^2 + m_2r_2^2$.

But the centre of mass satisfies the condition, $m_1r_1 = m_2r_2$.

Adding m_2r_1 in both sides, we get $m_1r_1 + m_2r_1 = m_2r_2 + m_2r_1$

or, $(m_1 + m_2)r_1 = m_2(r_2 + r_1)$

But, $r_2 + r_1 = r$, bond length of the molecule so, $r_1 = \dfrac{m_2}{m_1 + m_2} r$.

Similarly, $r_2 = \dfrac{m_1}{m_1 + m_2} r$. **[Burdwan Univ. 2015]**

Putting the values in the expression of moment of inertia of the molecule, we get

$I = m_1\left(\dfrac{m_2}{m_1 + m_2} r\right)^2 + m_2\left(\dfrac{m_1}{m_1 + m_2} r\right)^2 = \dfrac{m_1m_2}{m_1 + m_2} r^2$, where $\dfrac{m_1m_2}{m_1 + m_2} = \mu$, called reduced mass of the molecule. Hence the moment of inertia of the molecule,

$I = \mu r^2$. Two-particle rotation is mathematically transformed into one particle.

Problem:

Calculate the reduced mass of $^{127}I\,^{35}Cl$. The bond length of the molecule is 2.32Å. Calculate the moment of inertia. **[Burdwan Univ. 1993]**

Solution: The reduced mass of the molecule, $\mu = \dfrac{m_1m_2}{m_1 + m_2}$, here $m_1 = \dfrac{127}{N_A}$ gm and $m_2 = \dfrac{35}{N_A}$ gm,

where N_A is Avogadro number and it is 6.023×10^{23} . Putting the values, we get reduced mass of the molecule, $\mu = \dfrac{127\times35}{(127+35)\times6023\times10^{23}} gm = 4.55\times10^{-23}$ gm.

The moment of inertia, I = $4.55\times10^{-23} gm \times \left(2.32\times10^{-8} cm\right)^2 = 2.45\times10^{-38}$ gm cm^2.

Implication of reduced mass

If one atom is very lighter than the other atom, say, $m_1 << m_2$, then the reduced mass of the molecule, $\mu = \frac{m_1 m_2}{m_1 + m_2} \approx \frac{m_1 m_2}{m_2} \approx m_1$.The reduced mass of the molecule is closed to the mass of the lighter atom. It implies that only the lighter atom is rotating and keeping the heavier atom almost fixed at the centre of mass. The reduced mass is thus a measure of contribution of the atoms to the rotational process.

When $m_1 = m_2 = m$ (say), then the reduced mass, $\mu = \frac{1}{2} m$ indicating that both the atoms are contributing the rotational process to the same extent.

Expression of Rotational Energy (using semi classical method)

The total energy of the rotating molecule is ε_r = KE + PE. But the molecule is assumed to be rigid rotator and hence PE = 0. Thus the rotational energy of the of the molecule, ε_r = KE = $\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$.

v_1 = linear velocity of one atom = ωr_1 and v_2 = linear velocity of the other molecule = ωr_2, where ω is the angular velocity of both the atoms.

Thus, $\varepsilon_r = \frac{1}{2} m_1 (\omega r_1)^2 + \frac{1}{2} m_2 (\omega r_2)^2 = \frac{1}{2} \omega^2 \left(m_1 r_1^2 + m_2 r_2^2 \right) = \frac{1}{2} \omega^2 I$, since I = $m_1 r_1^2 + m_2 r_2^2$.

So, $\varepsilon_r = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$. But L = angular momentum of the molecule = $\sqrt{J(J+1)}\, \frac{h}{2\pi}$ (quantum condition).

Thus, the rotational energy of the molecule, $\varepsilon_r = J(J+1) \frac{h^2}{8\pi^2 I} = J(J+1)Bhc$, where, $B = \frac{h}{8\pi^2 Ic}$ and J is the rotational quantum number and it has the values 0, 1, 2, 3, etc i.e. any (+ve) integer including zero.
The energy of the rotating molecule is thus quantized.
However this energy expression can be obtained by solving the Schrödinger equation of the rigid rotator,

$$\nabla^2 \psi + \frac{8\pi^2 \mu}{h^2} (\varepsilon_r - 0) \psi = 0, \text{ where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2}$$

and r is bond length and μ is reduced mass of the molecule.
The rotational energy can be shown in the as having energy levels by putting J = 0, 1, 2, 3, 4, etc.

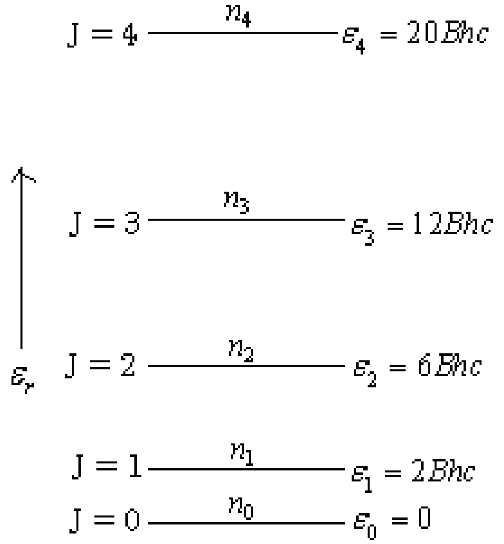


Figure: Rotational energy levels with population of molecules in the various energy levels.

n's are the population of molecules in the various energy levels.
This shows that rotational levels are not equispaced.
The energy spacing is increasing as the J is increasing.

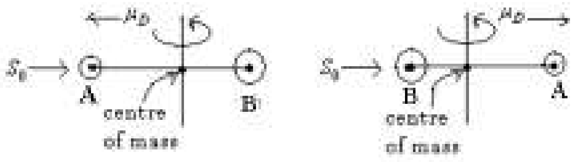
Conditions of Rotational Transition

(1) Molecules require to possess permanent dipole moment for being microwave active. It means that only those molecules can absorb or emit microwave radiation which have permanent dipole moment.

Thus homonuclear diatomic molecules (A—A type) are microwave inactive though they have rotational motion.

Heteronuclear diatomics (A—B type) are microwave active and they give rotational spectra. Thus HCl, CO, HBr, CH_3Cl, etc are microwave active in gaseous phase.

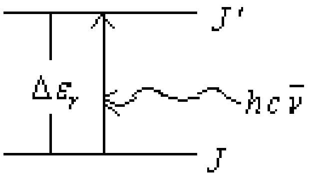
To a stationary observer S_0, a rotating polar molecule looks like an oscillating dipole that can stir the electromagnetic field of radiation.



(2) Selection rule states that rotational transition occurs in the adjacent levels only. $\Delta J = \pm 1$.
For absorption spectra, $\Delta J = +1$ and for emission spectra, $\Delta J = -1$.

Rotational Spectra

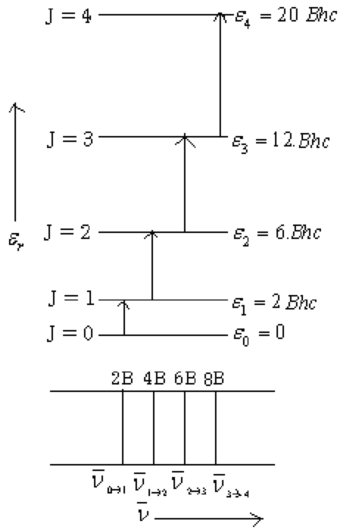
In absorption spectra, the molecule transits from lower rotational energy level (say, J) to higher rotational energy level (say, J$'$).
The energy difference between the rotational levels,
$\Delta\varepsilon_r = \varepsilon_{J''} - \varepsilon_J = J'(J'+1)Bhc - J(J+1)Bhc$.



But for absorption spectra, $J' = J+1$ so, $\Delta\varepsilon_r = (J+1)(J+2)Bhc - J(J+1)Bhc = 2Bhc(J+1)$.

The molecule acquires the energy of transition by absorption of microwave radiation of photon energy $hc\bar{\nu}$. One absorbed photon can transit one molecule for one transition.
Thus, $hc\bar{\nu} = 2Bhc(J+1)$ or, $\bar{\nu} = 2B(J+1)$,
where $\bar{\nu}$ is the frequency (in cm^{-1}) of radiation absorbed by the molecule for rotational transition,
B = $\dfrac{h}{8\pi^2\mu r^2 c}$ and J = lower rotational quantum number having values 0, 1, 2, 3, etc. These frequencies of radiation absorbed by the molecule can be accurately determined by the instrument, spectrometer.
Rotational spectral lines are obtained by putting J = 0, 1, 2, 3, etc. Rotational spectral lines along with specific transitions are shown as.

Thus it is seen that frequency lines of rotational spectra of diatomic molecule are equispaced though the rotational energy levels are not equispaced.



Applications

(A) The separation of frequency lines ($\Delta\bar{\nu}$) of rotational spectra is equal to 2B. It is possible to calculate the bond distance (r) of the diatomic polar molecule from this frequency separation.

$$\Delta\bar{\nu} = 2B = 2\times\frac{h}{8\pi^2\mu r^2 c} \quad \text{or,} \quad r = \sqrt{\frac{2h}{8\pi^2\mu c(\Delta\bar{\nu})}}.$$

Problem:

The rotational spectrum of $^1H\,^{35}Cl$ shows the separation of frequency lines is 20.3 cm^{-1}. Calculate the bond length of the molecule.

Solution:

The reduced mass of the molecule, $^1H\,^{35}Cl$,

$\mu = \dfrac{m_1m_2}{m_1+m_2} = \dfrac{1\times35}{(1+35)\times6.023\times10^{23}}\,gm = 1.63\times10^{-24}\,gm.$ So, the bond length (r) of the molecule is

$$r = \sqrt{\frac{2\times6.627\times10^{-27}\,erg\,\sec}{8\times(3.14)^2\times1.63\times10^{-24}\,gm\times3\times10^{10}\,cm\,\sec^{-1}\times20.3\,cm^{-1}}} = 1.29\times10^{-8}\,cm = 1.29\text{Å}.$$

Problem:

If there is +2 % error in the determination of rotational constant, B of a diatomic molecule, calculate the % of error in its bond length measurement. **[Calcutta Univ. 2005]**

Solution: $B = \dfrac{h}{8\pi^2 \mu r^2 c} = \dfrac{A}{r^2}$ or, $\ln B = \ln A - 2\ln r$ or, $\dfrac{dB}{B} = -2\dfrac{dr}{r}$, but $\dfrac{dB}{B} = 2\%$ so, $\dfrac{dr}{r} = -1\%$.

So the % of error in the bond length measurement is -1%.

Problem:

An estimated bond length of the species CN is 0.117 nm. Predict the positions of the first three lines in the microwave spectrum of CN. (Atomic weight of C and N are 12.011 and 14.0067 respectively).

(Answer: $\bar{\nu}_1 = 3.132\ cm^{-1}, \bar{\nu}_2 = 6.264\ cm^{-1}, \bar{\nu}_3 = 9.396\ cm^{-1}$ **)** **[Calcutta Univ. 2013]**

Problem:

If the J = 2 to 3 rotational transition for a diatomic molecule occurs at λ = 2.00 cm, find λ for the J = 6 to 7 transition of this molecule. **(Answer:** **[Calcutta Univ. 2013]**

Problem:

How many times does a molecule of $^1H\,^{35}Cl$ rotates per sec. in the J = 1 rotational level? Given, B ($^1H\,^{35}Cl$) = 10.6 cm^{-1}. **[Burdwan Univ. 1989]**

Answer: $\varepsilon_r = \dfrac{1}{2}I\omega^2 = \dfrac{1}{2}I\left(2\pi\nu_0\right)^2 = 2\pi^2 I(\nu_0)^2 = J(J+1)\dfrac{h^2}{8\pi^2 I}$ or, $\nu_0{}^2 = J(J+1)\dfrac{h^2}{16\pi^4 I^2}$

or, $\nu_0 = \sqrt{J(J+1)}\dfrac{h}{4\pi^2 I}$ or, $\nu_0 = \sqrt{J(J+1)}\dfrac{2hc}{8\pi^2 Ic}$ or, $\nu_0 = \sqrt{J(J+1)}2Bc$ **.**

Now putting the values, we have $\nu_0 = \sqrt{1(1+1)} \times 2 \times 10.6\, cm^{-1} \times 3 \times 10^{10}\ cm\,\sec^{-1} = 8.99 \times 10^{11}\sec^{-1}$.

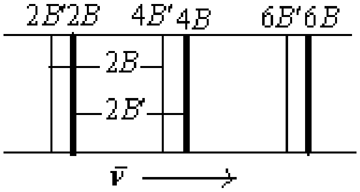
Thus, the $^1H\,^{35}Cl$ rotates about 9×10^{11} times per sec.

(B) Isotopic mass of an element can be determined from rotational spectral lines of the molecules having two isotopes of the same element. For example, in a mixture of $^1H\,^{35}Cl$ and $^1H\,^{37}Cl$ in which the abundance ratio is 3:1, the spectral lines of $^1H\,^{37}Cl$ is slightly to the left lower frequency side of the spectrum than $^1H\,^{35}Cl$.

The intensity ratio will be also 3:1 depending on their abundance ratio.

[**Intensity** of spectral lines depends mainly on three factors: (i) transition probability (ii) population and (iii) conc. or path length of the sample.]

The ratio of frequency-spacing of the two molecules $^1H\,^{35}Cl$ and $^1H\,^{37}Cl$ are $2B$ and $2B'$. Thus, $\dfrac{\Delta\bar{\nu}'}{\Delta\bar{\nu}} = \dfrac{2B}{2B'} = \dfrac{I'}{I} = \dfrac{\mu'}{\mu}$.



(Since r is not affected by isotopic substitution, only reduced mass is affected.)

Or, $\dfrac{\Delta\bar{\nu}'}{\Delta\bar{\nu}} = \left(\dfrac{m_1 m_2'}{m_1 + m_2'}\right) \Big/ \left(\dfrac{m_1 m_2}{m_1 + m_2}\right) = \dfrac{m_2'\left(m_1 + m_2\right)}{m_2\left(m_1 + m_2'\right)}$. Thus knowing $\Delta\bar{\nu}'$, $\Delta\bar{\nu}$ and m_1, m_2, it is possible to determine the mass (m_2') of ^{37}Cl isotope of the element. **Isotopic shift** is $\Delta\bar{\nu} = \dfrac{\bar{\nu} - \bar{\nu}'}{\bar{\nu}} = \left(1 - \dfrac{\bar{\nu}'}{\bar{\nu}}\right) = \left(1 - \dfrac{\mu}{\mu'}\right)$.

Problem: The line spacings in the microwave spectrum of ^{13}CO and ^{12}CO are 3.68 cm^{-1} and 3.84 cm^{-1}, respectively. Find out the isotopic mass of ^{13}C . [$m_O = 15.9994$ in ^{12}C scale] **[Calcutta Univ. 2014]**

Answer:

Problem: In the microwave spectrum of HCl (contaminated with DCl), the DCl spectral line will appear (recorded in increasing cm^{-1}),

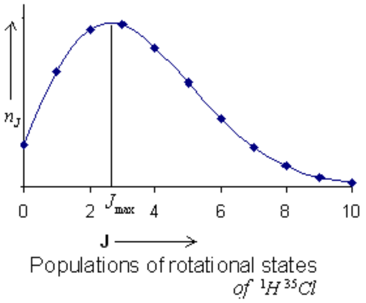
(a) close to the right of HCl line	(b) close to the left of HCl line
(c) far to the right of HCl line	(d) far to the left of HCl line **[Answer (d)]**

Relative population in different rotational energy levels

It is expected that relative intensities of the spectral lines will depend on the relative population of the energy levels. Greater is the number of molecules that can transit to the next higher level, greater will be the intensity of the absorbed radiation the

. The population of one level relative to the other level is given by Boltzmann distribution law, $\frac{n_2}{n_1} = \frac{g_2}{g_1} \times e^{-\Delta\varepsilon/kT}$, where g is the degeneracy factor of the rotational level and it is given by $g_J = (2J+1)$ and $\Delta\varepsilon$ = energy spacing between 2 and 1 levels i.e. $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$.

The population of a J th rotational level is thus given by $n_J = C\, g_J\, e^{-\varepsilon_J/kT}$, where C is proportionality constant.



Populations of rotational states of $^1H^{35}Cl$

Putting the values of g_J and ε_J, we have $n_J = C(2J+1)\, e^{-J(J+1)Bhc/kT}$.

At J = 0 level, let the population is n_0, we have C = n_0 and so $n_J = n_0\,(2J+1)\, e^{-J(J+1)Bhc/kT}$

The expression of n_J consists of two terms – the non-exponential term which increases the value of n_J and exponential term decreases the value of n_J with increase of J at constant temperature (T). At lower value of J, non-exponential dominates while at larger value of J, exponential term dominates. This is Gaussian distribution, so when n_J is plotted against J, the value of n_J increases, reaches to a maximum and then decreases with increase of J. The value of J (J$_{max}$) at which n_J attains maximum, can be calculated by using the condition of maximum and minimum. We have

$$\frac{dn_J}{dJ} = n_0\,(2+0)\, e^{-J(J+1)Bhc/kT} + n_0\,(2J+1)\, e^{-J(J+1)Bhc/kT}\left[-(2J+1)\right]\times\frac{Bhc}{kT}$$

$$= n_0\; e^{-J(J+1)Bhc/kT}\left[2-(2J+1)^2\,\frac{Bhc}{kT}\right] = 0$$ .The term within bracket corresponds to the maximum value.

So, $(2J+1)^2\,\frac{Bhc}{kT} = 2$ or, $(2J+1)^2 = \frac{2kT}{Bhc}$ or, $(2J+1) = \sqrt{\frac{2kT}{Bhc}}$ or, $2J = \sqrt{\frac{2kT}{Bhc}} - 1$

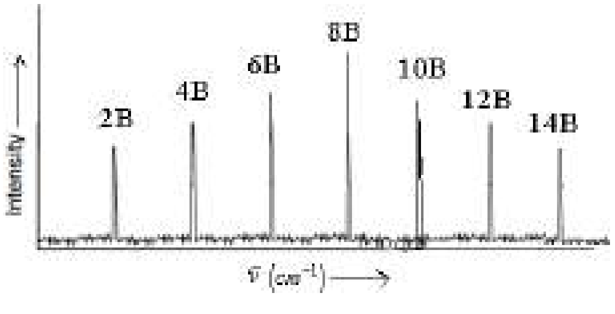
or, $J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$. For $^1H\,^{35}Cl$, B = 10.5 cm^{-1}, so at 25 °C , the rotational level which is maximum populated is $J_{max} = \sqrt{\frac{1.38\times10^{-16}\,erg\;K^{-1}\times 300K}{2\times10.5\,cm^{-1}\times 6.627\times10^{-27}\,erg\,\sec\times 3\times10^{10}\;cm\,\sec^{-1}}} - \frac{1}{2} = 3.2 - \frac{1}{2} = 2.7$.

But J is integer so J_{max} = 3.

Problem: Find the maximum populated rotational energy level of $^{12}C^{16}O$ molecule at 25 °C for which B = 1.93 cm^{-1} . **[Answer: J_{max} = 7].**

Intensity of the rotational frequency lines

Rotational transitions will be most intense from the J_{max} level. The intensity of the rotational frequency lines increases with increase of J and attains maximum and then decreases like the plot of the n_J vs. J curve.



Width of spectral frequency lines

Different lines in a spectrum have different width. This width of frequency of radiation can be explained on the basis of Heisenberg uncertainty principle.

The principle states $\Delta\varepsilon \times \Delta t = \frac{h}{4\pi}$, where Δt = life time of the molecule in the excited state and (τ)

$\Delta\varepsilon$ = uncertainty of energy of the molecule absorbed or emitted.

$\Delta\varepsilon = hc\Delta\bar{\nu}$, where $\Delta\bar{\nu}$ = width or uncertainty in frequency of radiation absorbed or emitted by the molecule.

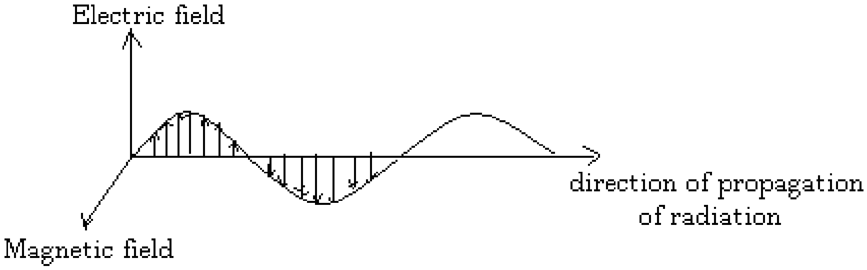
$$\text{Thus,}\quad hc\Delta\bar{\nu} \times \tau = \frac{h}{4\pi} \quad \text{or,} \quad \Delta\bar{\nu} = \frac{h}{4\pi hc} \times \frac{1}{\tau}.$$

This shows that greater is the life-time of the molecule in excited state, shorter is the width of frequency lines.

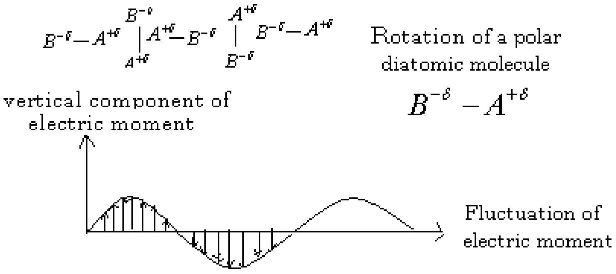
Interaction of a polar molecule with radiation

In electromagnetic radiation, electric field and magnetic field oscillate perpendicular to each other and also perpendicular to the direction of propagation of radiation.

One complete fluctuation of electric field occurs within the wave length (λ) of radiation. Hence frequency of fluctuation of electric field is equal to the frequency of radiation.



Now if we consider the rotation of a polar diatomic molecule ($A - B$ type), the dipole moment (μ_D) of say vertical component is also fluctuating and the frequency of fluctuation of vertical component of μ_D is equal to the frequency of molecular rotation.



When the frequency of fluctuation of electric field of radiation is equal to the frequency of fluctuation of electric moment generated due to rotation motion of polar molecule, the resonance develops between the polar molecule and radiation. It means that when the frequency of rotation of polar molecule is equal to the frequency of radiation, the molecule interacts with radiation. It can withdraw energy from radiation or give up energy to the radiation.

For non-polar molecules, there is no fluctuation of electric moment due to rotation and hence they can not interact with radiation and are microwave inactive.

Even polar diatomic molecules ($A - B$ type) when rotates along the bond axis, there is no fluctuation of electric moment and so this rotation is microwave inactive.

Problem: Is the rotation of AB type molecule about the bond axis effective in producing rotational transitions?

[BU 1988, Q 1(b), m = 2]

.

Rotational Spectra of Polyatomic Molecules

There are three modes of rotation in the polyatomic molecules along three mutually perpendicular axes x, y, z.

For linear molecules, the nuclei all exist on the bond axes (x- axis) and all the mass of the molecule lie on that axis. The moment of inertia about this axis is zero ($I_x = 0$). The moment of inertia about the other two axes y, z are same by symmetry ($I_y = I_z$). Thus linear molecule has only one value of moment of inertia like diatomic molecule. It is then calculated by $I = \sum_i m_i r_i^2$ and the spectra of these linear molecules are essentially similar with the diatomic molecule.

For non-linear polyatomic molecules, on the basis of relationship among different moment of inertia $\left(I_x, I_y, I_z\right)$, they are classified into three types:

(i) Spherical top molecules, such as CH_4, SF_6 in which $I_x = I_y = I_z$.

(ii) Symmetrical top molecules, such as CH_3Cl, NH_3 in which $I_x \neq I_y = I_z$.

(iii) Asymmetric top molecules, such as H_2O, CH_3OH in which $I_x \neq I_y \neq I_z$.

Spherical top molecules have no permanent dipole moment and so these molecules are microwave inactive. The spectra of symmetrical top and asymmetric top molecules are more complex than the linear molecules because of the occurrence of more than one principle axes of moment of inertia.

INFRA-RED SPECTRA
(VIBRATIONAL-ROTATIONAL SPECTRA)

Introduction

Vibrational transition of a molecule is effected by absorption of infra-red radiation of wave length 10^4 to 10^7 Å. Since vibrational transition requires much more energy than rotational transition, so absorption of infra-red radiation causes vibrational and rotational transitions simultaneously. This is why, vibrational and rotational spectra fall jointly in the infra-red spectra (IR spectra).

Analysis of frequency lines in the IR spectra provides information about the flexibility of the bond, bond dissociation energy, bond length of the molecule. Further this helps to identify the functional groups, unsaturation, isotopic mass, etc. In a word, it now becomes an important tool for structural study and so IR spectra are called finger print of a molecule.

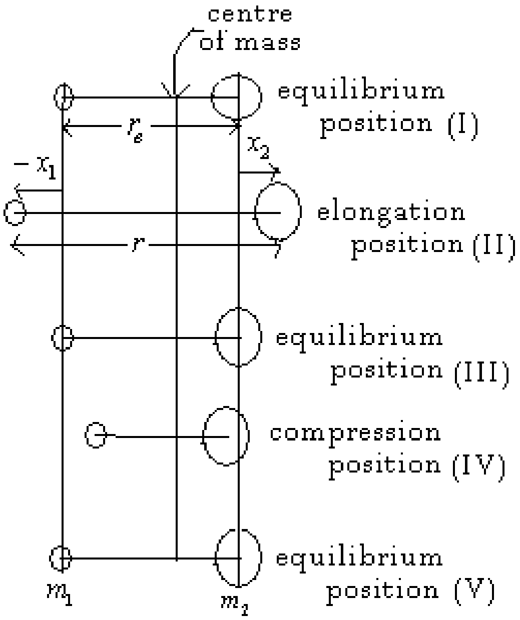
Different stages of vibration of a diatomic molecule

The diatomic molecule consists of two atoms of masses m_1 and m_2, and is connected by a bond. It has only one mode vibration and is symmetrical stretching vibration. The bond is like a spring connecting two balls of masses m_1 and m_2 (spring and ball model). The atoms are executing periodic displacement along the bond axis (say x-axis).

Right hand side displacement is taken (+ve) while left hand side displacement is (-ve) with centre of mass is at the origin. During the displacement of the atoms, the centre of mass remains fixed.

I to V positions complete one period of vibration. The time required for one complete vibration is τ_0 and the frequency of the molecular vibration, $\nu_0 = 1/\tau_0$.

Bonding electrons bring back the vibrating nuclei from elongation while inner shell electrons by repulsion push back from the compression.



Hooke's Law for SHO Model

This molecular vibration is assumed to be simple harmonic motion and it obeys Hooke's law i.e. restoring force (F) is proportion to the displacement (x). That is, $F \propto x$ or, $F = -kx$, where k is force stretching constant and it depends on the nature of the bond. It has the unit dyne cm^{-1} in CGS system and Nm^{-1} in SI system.

The above law can be written as $m\dfrac{d^2x}{dt^2} = -kx$ or, $\dfrac{d^2x}{dt^2} = -\dfrac{k}{m}x$

The vibration of one atom affects the other atom to keep centre of mass fixed at the origin and restoring force (mass × acceleration) experienced by both the atoms is proportional to the amount the bond stretched $(x_2 - x_1)$. Applying the Hooke's law for the vibration of two atoms, we get

$\dfrac{d^2x_2}{dt^2} = -\dfrac{k}{m_2}(x_2 - x_1)$ and $-\dfrac{d^2x_1}{dt^2} = -\dfrac{k}{m_1}(x_2 - x_1)$ [Atom of mass m_1 is stretched in the (–ve) direction]

Taking difference of the two

$\dfrac{d^2(x_2 - x_1)}{dt^2} = -k\left(\dfrac{1}{m_1} + \dfrac{1}{m_2}\right)(x_2 - x_1)$ or, $\dfrac{d^2x}{dt^2} = \left(-\dfrac{k}{\mu}\right)x$, where $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$ in which μ is reduced mass of the molecule and x is net displacement, $x = (x_2 - x_1)$.

However, if r_e and r are taken internuclear distance when the molecule is at equilibrium and at stretched condition then $x = r - r_e$ and the Hooke's law for the vibration becomes $\dfrac{d^2(r - r_e)}{dt^2} = -\dfrac{k}{\mu}(r - r_e)$ or, $\dfrac{d^2r}{dt^2} = -\dfrac{k}{\mu}(r - r_e)$.

Significance of reduced mass in the vibrating system

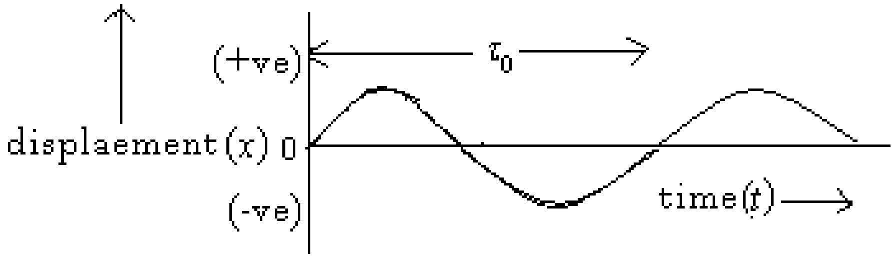
This signifies that when a heavy atom (say, m_2) is bonded with light atom (m_1), the reduced mass of the molecule is close to the lighter atom. Situation resembles that the lighter atom is only vibrating heavier atom remains almost fixed in its position. The centre of mass of the molecule lies very close to the centre of the heavy atom. Thus, magnitude of μ signifies the contribution of the atoms towards the vibration of the molecule. When the two atoms are of same masses, $m_1 = m_2 = m$, μ = (½) m indicating that both atoms are contributing the molecular vibration to the same extent.

Expression of force stretching constant

The Hooke's law for the molecular motion comes up with the formulation $\dfrac{d^2x}{dt^2} = \left(-\dfrac{k}{\mu}\right)x$. This is an eigen value equation in which x is the eigen function of the operator $\dfrac{d^2}{dt^2}$ with the eigen value $\left(-{}^{k}\!/\!{}_{\mu}\right)$, a fundamental property of the vibrating system.

The general solution of this differential equation is $x = A\sin\left(\sqrt{{}^{k}\!/\!{}_{\mu}}\;t\right) + B\cos\left(\sqrt{{}^{k}\!/\!{}_{\mu}}\;t\right)$. But in the molecular vibration, when $t = 0$, $x = 0$, so putting these values, we get B = 0. Thus appropriate solution is a sine function and the displacement (x) is oscillating periodically with time (t) with the time period (τ_0).

$x = A\sin\left(\sqrt{{}^{k}\!/\!{}_{\mu}}\;t\right)$, where A is the amplitude of the function, x.



Again, for one cycle of oscillation, time required is τ_0 and sine function also changes the angle 2π. Then $\sqrt{k/\mu}\,\tau_0 = 2\pi$ or, $\frac{1}{\tau_0} = \nu_0 = \frac{1}{2\pi}\sqrt{k/\mu}$, since $\frac{1}{\tau_0} = \nu_0$ so, $k = 4\pi^2\mu\nu_0{}^2$ or, $k = 4\pi^2\mu\left(c\,\bar{\nu}_0\right)^2$, where $\bar{\nu}_0$ is the frequency of molecular vibration in cm^{-1} unit. . This is expression of force stretching constant (k).

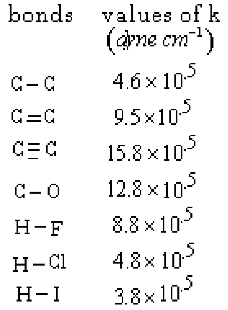
Problem: The wave number of vibration of $^1H\,^{35}Cl$ molecule is 2991 cm^{-1}. Calculate the force constant (k) of the $H-Cl$ bond. **[Burdwan Univ. 1995]**

Answer: $k = 4\pi^2\mu\left(c\,\bar{\nu}_0\right)^2$, putting the values, we get

$$k = 4(3.14)^2\left(\frac{1\times 35}{36\times 6.023\times 10^{23}}\,gm\right)\left(3\times10^{10}\,cm\sec^{-1}\times 2991\,cm^{-1}\right)^2 \text{ erg} = 5.11\times10^5 \text{ dyne cm}^{-1}.$$

Values of k of some typical groups

Force stretching constant (k) measures the flexibility of a bond. Greater the value of k less is its flexibility and more rigidity of the bond. By flexibility, we mean how easily the bond can be stretched; the bond angle can be distorted. The following values of k reflect the above concept.



bonds	values of k (dyne cm^{-1})
C−C	4.6×10^{-5}
C=C	9.5×10^{-5}
C≡C	15.8×10^{-5}
C−O	12.8×10^{-5}
H−F	8.8×10^{-5}
H−Cl	4.8×10^{-5}
H−I	3.8×10^{-5}

For one type of group, the group frequency ($\bar{\nu}_0$) increases with the increase of k and decreases with the increase of reduced mass (μ) of the group.

Since, $\bar{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$, $\bar{\nu}_0$ decreases from C≡C to C=C to C−C as $k_{C\equiv C} > k_{C\square C} > k_{C-C}$.

Again, k of the $H-X$ molecules, where X = F, Cl, Br, I decreases due to more flexibility of the bonds and $\bar{\nu}_0$ is also decreased and μ is increased from $H-F$ to H–Cl to H–Br to H–I.

Problem: The fundamental vibrational frequency of H–Cl is 2885 cm^{-1}. Assuming that H–Cl and D–Cl may be treated as simple harmonic oscillator, Calculate the fundamental frequency of D–Cl.
(Atomic mass of Cl = 35 Dalton). **[IIT-KGP, 2003]**

Answer : We have $k = 4\pi^2\mu\left(c\,\bar{\nu}_0\right)^2$, but k is same for H–Cl and D –Cl

so, $$\left(\bar{\nu}_0\right)_{D-Cl} = \left(\bar{\nu}_0\right)_{H-Cl}\times\sqrt{\frac{\mu_{H-Cl}}{\mu_{D-Cl}}} = 2885\,cm^{-1}\times\sqrt{\frac{(35/36)}{(70/37)}} = 2068\ cm^{-1}.$$

Expression of vibrational energy (ε_v)

Vibrational energy (ε_v) of a molecule can be obtained by solving the Schrödinger equation of one-dimensional simple harmonic oscillator (SHO). The equation is

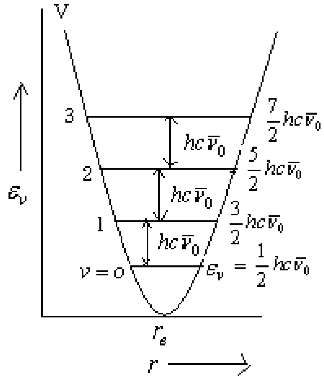
$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}\left(\varepsilon_v - V\right)\psi = 0$ when the oscillator is oscillating along x-axis. V = PE and it is $\frac{1}{2}k\,x^2$.

Putting the value of V and solving, we get the vibrational energy, $\varepsilon_v = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$ but, $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$,

so, the expression of vibrational energy of the molecule,

$$\varepsilon_v = \left(v + \frac{1}{2}\right)h\nu_0 \qquad \text{or,} \qquad \varepsilon_v = \left(v + \frac{1}{2}\right)hc\bar{\nu}_0 ,$$

where $\bar{\nu}_0$ is the frequency of the molecular vibration in cm^{-1} and v is the vibrational quantum number having the values 0, 1, 2, 3, etc i.e. any positive integer including zero.
The vibrational energy when plotted it gives the following diagram



Two aspects of molecular vibrational energy

(1) The vibrational energy levels are equispaced and the energy spacing is $\Delta\varepsilon_v = hc\bar{\nu}_0$ i.e. difference between two successive energy levels is $hc\bar{\nu}_0$ (like energy ladder).

(2) The lowest value of vibration energy (zero-point energy) is obtained by putting v = 0. So, ZPE, $\varepsilon_0 = \frac{1}{2}hc\bar{\nu}_0$.

This means that even at absolute zero temperature, the molecule possesses some energy and this is why the zero term is used in the energy value The molecule thus executes vibrational motion even at absolute zero temperature and it is never at rest.

The existence of zero-point energy is also supported by the Heisenberg uncertainty principle. If the molecule would be at rest then uncertainty in position (Δx) would be zero.

Hence uncertainty in momentum, $\Delta p_x = \frac{h}{4\pi}\Big/\Delta x = \frac{h}{4\pi}\Big/0 = \infty$ and $\Delta p_x = \infty$ is not possible.

Criteria of vibrational transition of molecules

(1) Only those molecules execute vibrational transition whose dipole moment (μ_D) changes due to vibration,

That is, $\frac{d\mu_D}{dx} \neq 0$. This means that the molecule must be an oscillating dipole for infrared active.

Thus all vibrating molecules can not absorb or emit infrared radiation and so do not give IR spectra.

(a) Homonuclear diatomic molecules (A – A type) are thus IR inactive, since $\frac{d\mu_D}{dx} = 0$.

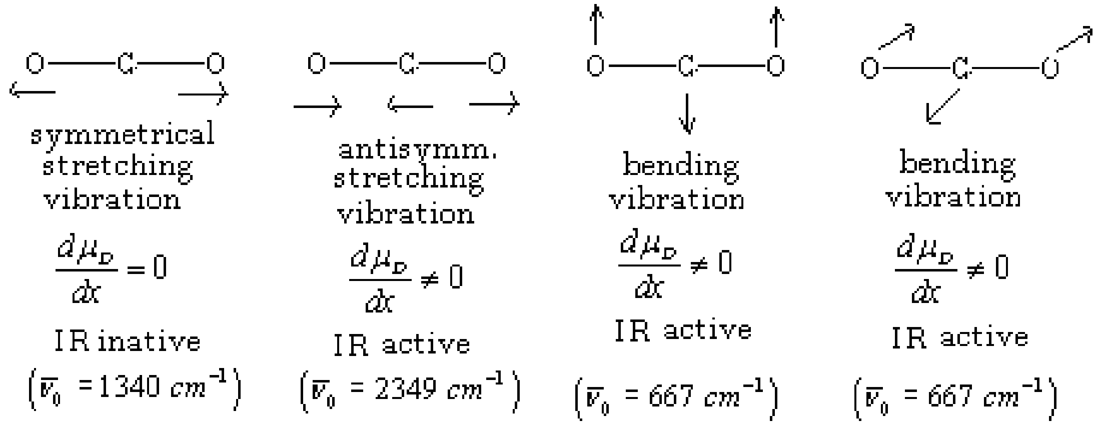
Thus, H_2 , N_2 , O_2 , etc are IR inactive.

(b) Heteronuclear diatomic molecules (A – B type) are always IR active since $\frac{d\mu_D}{dx} \neq 0$ and these molecules give IR spectra. HCl, HBr, CO, NO, etc are IR active and vibrational transition always occur.

(c) Non-polar molecules like CO_2 will show vibrational transitions in some modes of vibrations in which

$$\frac{d\mu_D}{dx} \neq 0 .$$

CO_2 is a linear molecule and so number of modes of vibration is (3N – 5), where N is the number of atoms in the molecule. Out of these (3N – 5) modes, (N – 1) are stretching modes and (2N – 4) are bending modes of vibration. Thus CO_2 molecule can vibrate in 4 modes out of which two are stretching and two are bending vibrations.

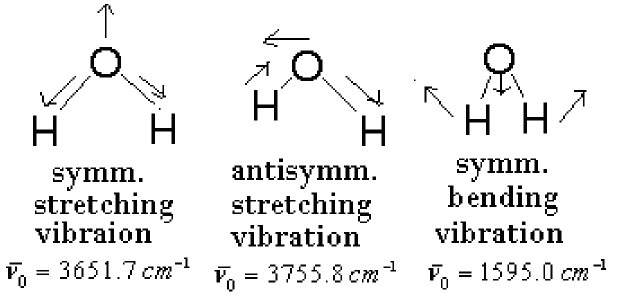


Antisymmetric and two bending modes of vibrations are IR active but the bending modes are doubly degenerate and so it leads to one IR spectra. In the antisymmetric stretching mode, the dipole moment oscillates parallel to the bond axis while in the bending vibrations, the dipole moment oscillates perpendicular to the bond axis.

The number of vibrational modes of H_2O is three out of which two are stretching vibrations and one is bending vibration.

These are shown here.
[Note that during vibration of the molecule, the centre of mass remains fixed in its original position]

(N – 1) are stretching modes and (2N – 5) are bending modes of vibration



(2) Vibrational transitions obey the selection rule,

$\Delta v = \pm 1$ i.e., transition occurs only in adjacent vibrational levels. For absorption spectra, $\Delta v = +1$.

When the dipole moment oscillates parallel to bond axis, the selection rule for absorption spectra is

$$\Delta v = +1 \quad \text{and} \quad \Delta J = \pm 1 \text{.(parallel band)}$$

When the dipole moment oscillates perpendicular to the bond axis, the selection rule for absorption spectra is

$$\Delta v = +1 \quad \text{and} \quad \Delta J = 0, \pm 1 \text{.(perpendicular band)}$$

Population in the vibrational energy levels

The population of the molecules in the different vibrational energy levels is guided by Boltzmann energy distribution law, $\frac{n_2}{n_1} = e^{-\Delta\varepsilon_v/RT}$, as this system is non-degenerate. For CO molecule at 27 °C,

$$\Delta\varepsilon_{0\to 1} \approx 42\times 10^{-14} \text{ erg/molecule and } kT = 1.38\times 10^{-16} \times 300 = 4.14\times 10^{-14} \text{ erg/molecule.}$$

Thus, $\frac{n_1}{n_0} = e^{-10.145} \approx 40\times 10^{-6} = \frac{40}{10^6}$. It means that if 10^6 (one million) CO molecules are in $v = 0$ level, then only 40 CO molecules occupy $v = 1$ level at 27 °C. So at ordinary temperature, ground vibrational level contains most of the molecules and other vibrational levels are thinly populated.

The vibrational transition occurs thus mainly from the ground vibrational level ($v = 0$) and the frequency line for the transition $v = 0$ to $v = 1$ will be most intense in the IR spectra.

Vibrational spectra

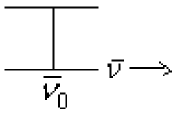
For the transition of the molecules from v to v' by absorption of IR radiation,

$$\Delta\varepsilon = \varepsilon_{v'} - \varepsilon_v = \left(v' + \frac{1}{2}\right)hc\bar{\nu}_o - \left(v + \frac{1}{2}\right)hc\bar{\nu}_o = \left(v' - v\right)hc\bar{\nu}_o \ .$$

But selection rule states that for absorption spectra, $v' - v = +1$ and the energy of the photon absorbed for transition is $hc\bar{\nu}$ so, $hc\bar{\nu} = hc\bar{\nu}_o$ or, $\bar{\nu} = \bar{\nu}_o$.

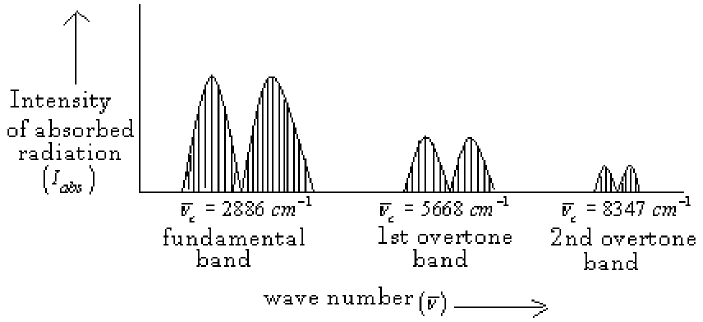
That is, frequency of radiation ($\bar{\nu}$) absorbed is equal to the frequency of the molecular vibration ($\bar{\nu}_o$).

Since the vibrational energy levels are equispaced so, there will be only one frequency line in the vibrational spectra for transition from any vibrational level to the next higher vibrational level. The IR spectral line given here is for any transition from v to $v+1$ level.

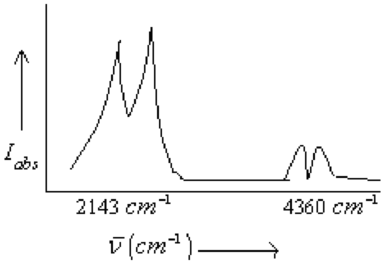


Experimental observation of IR spectra

Experimentally it is observed that IR spectra consists of several bands and each band is having a fine structure.



Rough sketch of IR absorption spectra of $^{1}H^{35}Cl$ (imaginary)



IR spectra of $^{12}C^{16}O$ (low resolution) of fundamental and first overtone band with centre frequency

$$\Delta\varepsilon = hc\bar{\nu}_0 = 6.627\times10^{-27}\,erg\,\sec\times3\times10^{10}\,cm\sec^{-1}\times2143\,cm^{-1} = 4.26\times10^{-13}\,erg.$$

This experimentally observed IR spectra could be explained by considering the following two aspects.

(1) Rotational transition requires smaller energy than the vibrational transition and hence rotational transitions are accompanied with the vibrational transitions under the exposure of IR radiation. Thus vibrational and rotational spectra are obtained simultaneously and the fine structure of each band is due to superimposition of rotational spectra.

(2) The molecule executes anharmonic motion and Hooke's law is not obeyed. The potential energy (V) differs. Selection rule is violated and it is $\Delta v = \pm1, \pm2, \pm3, etc$. For $\Delta v = \pm1$, we have fundamental band. $\Delta v = \pm2$, we get 1st overtone, $\Delta v = \pm3$, we have 2nd overtone, etc.

But fundamental band is most intense and 1st overtone, 2nd overtone bands less and less intense.

IR spectra of diatomic molecule assuming harmonic oscillator and rigid rotator model

Let us discuss the first aspect of the IR spectra of diatomic molecule. Born- Oppenheimer approximation assumes that a diatomic molecule can execute rotation and vibration motions quite independently. It means that vibrational motion of the molecule does not interfere its rotational motion. Thus the energy terms of these motions can be added up.

$$\varepsilon_{v,J} = \varepsilon_v + \varepsilon_J\,,$$

where ε_v = vibrational energy and ε_J = rotational energy of the molecule.
For the transition of vibrational level and rotational level, the energy required for the molecule,

$$\Delta\varepsilon_{v,J} = \Delta\varepsilon_v \pm \Delta\varepsilon_J$$

The molecule acquires this energy by absorption of radiation and so $\Delta\varepsilon_{v,J} = hc\bar{v}$, where $\bar{v}$ is the frequency of radiation in cm^{-1}, $\Delta\varepsilon_v = hc\bar{v}_0$, where $\bar{v}_0$ is the frequency of molecular vibration in cm^{-1} and $\Delta\varepsilon_J = 2Bhc\left(J+1\right)$, where J is the rotational quantum number having values 0, 1, 2, 3, etc and $B = h/\left(8\pi^2 Ic\right)$..

Putting the values, we have $$hc\bar{v} = hc\bar{v}_0 \pm 2Bhc\left(J+1\right)$$

or, $$\bar{v} = \bar{v}_0 \pm 2B\left(J+1\right)$$

With $\Delta J = -1$, i.e. J+1 to J, we have $\bar{v} = \bar{v}_0 - 2B\left(J+1\right)$ and putting J = 0, 1, 2, 3, etc, we get a series of fine lines and it is called P-series.
With $\Delta J = +1$, i.e. J to J+1, we have $\bar{v} = \bar{v}_0 + 2B\left(J+1\right)$ and putting J = 0, 1, 2, 3, etc, we get R-series of fine lines.
With $\Delta J = 0$, we have $\bar{v} = \bar{v}_0$, the centre line frequency of the band or in some cases, very closely spaced lines are obtained and then it is called Q-series.

P-series	R-series
$\bar{v} = \bar{v}_0 - 2B\left(J+1\right)$	$\bar{v} = \bar{v}_0 + 2B\left(J+1\right)$
(J = 0, 1, 2, 3, etc. are inserted).	(J = 0, 1, 2, 3, etc. are inserted)
$\bar{v}_1 = \bar{v}_0 - 2B$	$\bar{v}_1 = \bar{v}_0 + 2B$
$\bar{v}_2 = \bar{v}_0 - 4B$	$\bar{v}_2 = \bar{v}_0 + 4B$
$\bar{v}_3 = \bar{v}_0 - 6B$	$\bar{v}_3 = \bar{v}_0 + 6B$
$\bar{v}_4 = \bar{v}_0 - 8B$	$\bar{v}_4 = \bar{v}_0 + 8B$

The spectrum consists of equally spaced lines on each side of the band centre ($\bar{v}_0$), with spacing 2B between any two adjacent lines.
For linear stretching vibration, $\Delta J = 0$ is not permitted by the selection rule and so there is gap between 1st line of P-series and 1st line of R-series.

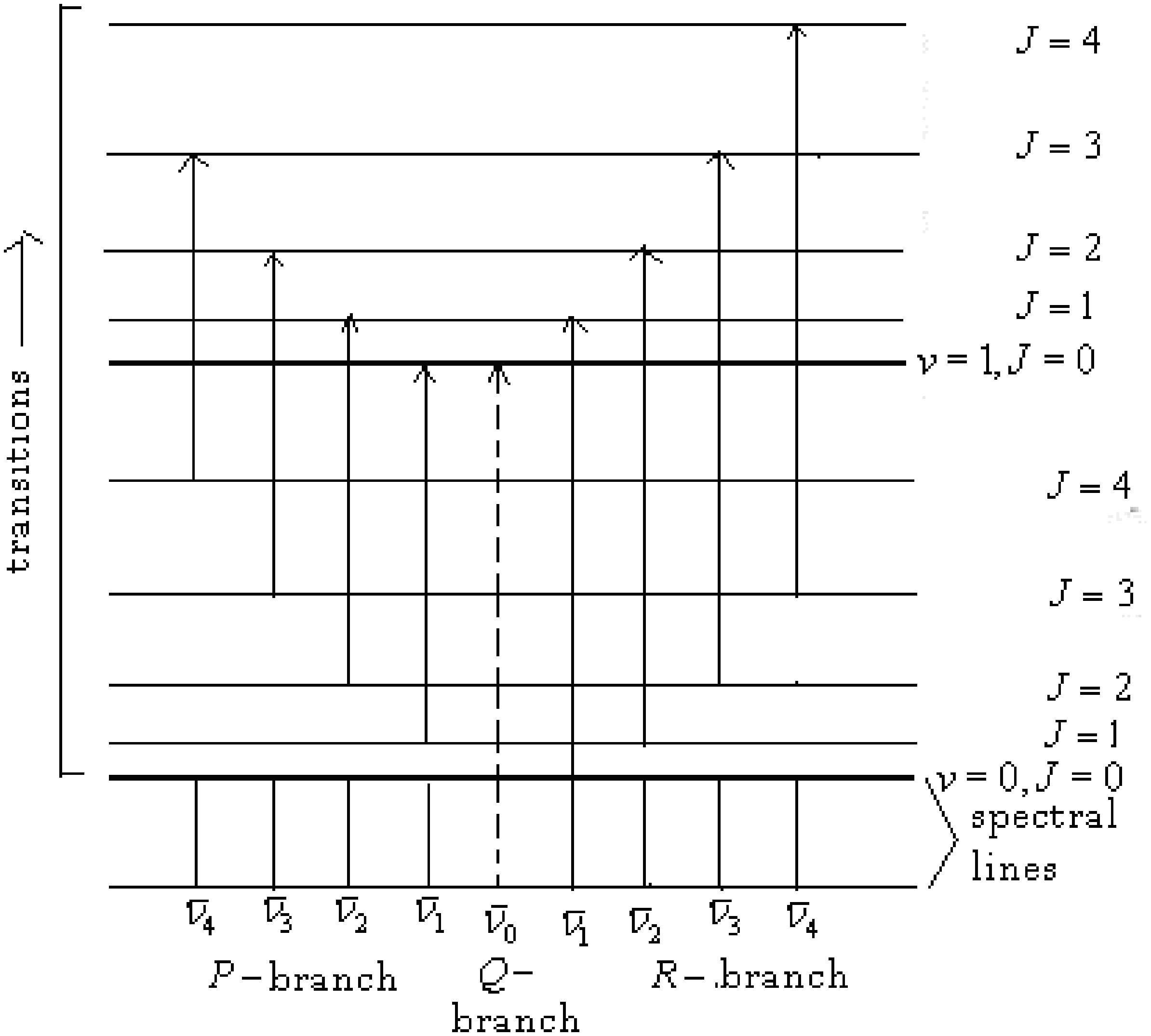
But for vertical vibration, such as for vibration of NH_3 (called inversion of umbrella) and bending vibration of linear molecules, like CO_2 $\Delta J = 0$ is permitted and Q-series appears whose rotational frequency lines are closely spaced.
The frequency of the centre of the band is $\bar{v}_0$ and it is frequency of the molecular vibration from which the force constant (k) of the molecule can be determined using the relation, $k = 4\pi^2\mu\left(c\bar{v}_0\right)^2$.

Problem: The vibrational frequency and rotational constant of HCl are 3000 cm^{-1} and 10 cm^{-1} respectively. Calculate the frequencies of the 1st two lines of P and R branches of the vibrational-rotational spectrum of HCl. **[NET 2000]**

Solution: We have the expression as $\bar{\nu}_{1(P)} = \bar{\nu}_0 - 2B$ and $\bar{\nu}_{1(R)} = \bar{\nu}_0 + 2B$.

So, $\bar{\nu}_{1(P)} = 3000 - 20 = 2980$ cm^{-1} and $\bar{\nu}_{1(R)} = 3000 + 20 = 3020$ cm^{-1}.

Vibrational and rotational transition of a diatomic molecule



Selection rule of vibration-rotation transition for absorption spectra: $\Delta v = +1$ and $\Delta J = \pm 1$. From the spacing of two rotation lines, it is possible to calculate the bond length (r) of a diatomic molecule since, $\Delta \bar{\nu} = 2B$ and $B = \dfrac{h}{8\pi^2 \mu r^2 c}$. Thus the bond length of the molecule, $r = \sqrt{2h/(8\pi^2 \mu c)}$..

Anharmonic Oscillator

Now we can consider the anharmonic motion of the molecular vibration. The potential energy of this type of motion is expressed by Morse equation,

$$V(x) = D_e\left(1-e^{-ax}\right)^2,$$

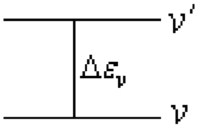
where D_e = depth of the PE minimum or depth of the PE well and $a = \sqrt{k/2D_e}$.

When this PE is included in the Schrödinger equation and solved, the following energy expression is obtained,

$$\varepsilon_v = \left(v+\frac{1}{2}\right)hc\bar{v}_0 - \left(v+\frac{1}{2}\right)^2 x_e\, hc\bar{v}_0 \quad , \qquad \text{(neglecting higher terms)}$$

where x_e is anharmonic constant for stretching vibration of the molecule and its value is small (about 0.01). Thus, the energy-difference of two vibrational levels is given by

$$\Delta\varepsilon_v = \left[\left(v'+\frac{1}{2}\right)hc\bar{v} - \left(v'+\frac{1}{2}\right)^2 x_e\, hc\bar{v}\right] - \left[\left(v+\frac{1}{2}\right)hc\bar{v}_0 - \left(v+\frac{1}{2}\right)^2 x_e\, hc\bar{v}_0\right]$$



$$= (v'-v)hc\bar{v}_0 - \left[\left(v'+\frac{1}{2}\right)^2 - \left(v+\frac{1}{2}\right)^2\right]x_e\, hc\bar{v}_0$$

$$= (v'-v)hc\bar{v}_0 - (v'-v)(v'+v+1)x_e\, hc\bar{v}_0$$

or, $$\Delta\varepsilon_v = (v'-v)\left[1-(v'+v+1)x_e\right]hc\bar{v}_0$$

For adjacent levels, $v' = v+1$, so $\Delta\varepsilon_v = \left[1-2(v+1)x_e\right]hc\bar{v}_0$, where v = 0, 1, 2, 3, etc.

$\Delta\varepsilon_{0\to1} = \left[1-2x_e\right]hc\bar{v}_0$, $\Delta\varepsilon_{1\to2} = \left[1-4x_e\right]hc\bar{v}_0$, $\Delta\varepsilon_{2\to3} = \left[1-6x_e\right]hc\bar{v}_0$, $\Delta\varepsilon_{3\to4} = \left[1-8x_e\right]hc\bar{v}_0$, etc.

This shows that energy levels of anharmonic oscillator are not equispaced and the energy spacing is decreasing as v is increasing. So, at certain limit of v and higher, vibrational levels converge, $\Delta\varepsilon_v = 0$ and continuum occurs.

Problem: Give three examples of three different model systems where (i) energy levels are equispaced, (ii) energy gap increases with increase in quantum number, (iii) energy gap decreases with increase in quantum number. **[Calcutta Univ. 2014]**

Answer: (i) Simple harmonic oscillator (ii) Rigid rotator (iii) Anharmonic oscillator.

Morse PE diagram

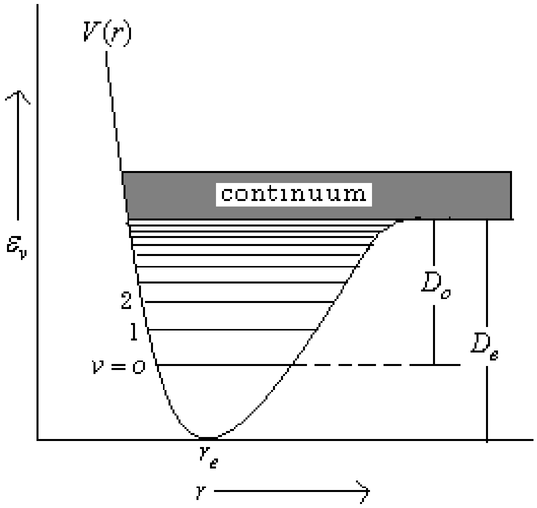
The Morse PE energy for anharmonic oscillator can also be written when $x = r - r_e$ as

$$V(r) = D_e\left[1-e^{-a(r-r_e)}\right]^2 .$$

When $V(r)$ is plotted against r,
the curve will be no longer be parabolic.
The PE rises more steeply in the compression and less steeply in the elongation.

D_o = spectroscopic dissociation energy and it is the energy difference between the dissociation level and ground level. It is the energy needed to break the bond.

D_e = energy difference between the dissociation level and the minimum of the PE curve i.e. it is the depth of the PE curve.



Thus, $D_o = D_e - \frac{1}{2}hc\bar{v}_0$, but $D_e = \frac{hc\bar{v}_0}{4x_e}$, so the dissociation energy of the bond, $D_o = \frac{hc\bar{v}_0}{4x_e} - \frac{1}{2}hc\bar{v}_0$.

Problem: The Morse potential is given by the expression $V(r) = D_e\left[1-\exp\left\{-b(r-r_e)\right\}\right]^2$.

(a) Sketch the potential schematically and comment on the value of V at $r = 0$ and $r = \infty$.

(b) Show for small displacement from the equilibrium position the above function is approximated by a simple harmonic potential. **[Burdwan Univ. 2012, Q 3(H)(ii), m = 5]**

Solution: (a) For the sketch of the potential, see the Text, page .

when r = r$_e$ in the expression of Morse potential, we have

$$V(r_e) = D_e\left[1-e^{-b(r_e-r_e)}\right]^2 = D_e\left[1-1\right] = 0.$$

Again, when $r = \infty$, we get $V(\infty) = D_e\left[1-e^{-b(\infty-r_e)}\right]^2 = D_e\left[1-e^{-b\times\infty}\right]^2 = D_e\left[1-0\right]^2 = D_e$.

(b) Now, expanding the exponential term in the Morse potential, we have

$$V(r) = D_e\left[1-\left\{1-b\left(r-r_e\right)-\frac{1}{2}b^2\left(r-r_e\right)^2 ---\right\}\right]^2 = D_e\left[1-\left\{1-b\left(r-r_e\right)\right\}\right]^2$$

Higher powers of $\left(r-r_e\right)$ is neglected as the displacement from the equilibrium is small so $\left(r-r_e\right)$ is small and the potential, $V(r) = D_e b^2\left(r-r_e\right)^2$.

This we can write, $V(r) = \frac{1}{2}k\left(r-r_e\right)^2$ which the potential of simple harmonic oscillator,

where $D_e b^2 = \frac{1}{2}k$ and $b = \sqrt{k/2D_e}$.

Vibrational Transition of Anharmonic Oscillator

Selection rule for anharmonic motion is $\Delta v = \pm 1, \ \pm 2, \ \pm 3$, etc. For absorption spectra, Δv = 1, 2, 3. When, Δv = 1, the frequency of vibration transition gives fundamental line and when rotational lines are superimposed, it is called fundamental band.

When Δv = 2, the band is called first overtone and when Δv = 3, the band is called second overtone, etc.

Since most molecules occupy the ground vibrational level, that is v = 0 so, transition for fundamental band occurs from v = 0 to v' = 1.Thus, putting v = 0 and v' = 1 in the expression of

$$\Delta\varepsilon_v = \left(v'-v\right)\left[1-\left(v'+v+1\right)x_e\right]hc\bar{v}_0,$$ we get

$\Delta\varepsilon_v = \left(1-2x_e\right)hc\bar{v}_0$. When this transition is effected by the absorption of IR radiation of photon energy $hc\bar{v}$, we have $hc\bar{v} = \left(1-2x_e\right)hc\bar{v}_0$ or, $\bar{v} = \left(1-2x_e\right)\bar{v}_0$.

This $\bar{v}$ is frequency of the central line of the fundamental band. The frequency lines of the fundamental band is obtained by adding the rotational lines associated with this transition, and it is

$$\bar{v} = \left(1-2x_e\right)\bar{v}_0 \pm 2B\left(J+1\right)$$

Similarly, the first overtone, v = 0 v' = 2, and centre band frequency is, $\bar{v} = 2\left(1-3x_e\right)\bar{v}_0$

and the band frequencies of the first overtone is $\bar{v} = 2\left(1-3x_e\right)\bar{v}_0 \pm 2B\left(J+1\right)$.

The second overtone, v = 0 v' = 3, centre band frequency is $\bar{v} = 3\left(1-4x_e\right)\bar{v}_0$

and the band frequencies of the second overtone is $\bar{v} = 3\left(1-4x_e\right)\bar{v}_0 \pm 2B\left(J+1\right)$.

It is seen that centre-band frequencies are $\left(\bar{v}\right)_{fundamental} : \left(\bar{v}\right)_{1st\ overtone} : \left(\bar{v}\right)_{2nd\ overtone} \approx 1:2:3$.

Thus, knowing these centre band frequencies, it is possible to calculate anharmonicity constant (x_e) and molecular frequency ($\bar{v}_0$). these values of the molecule will help to calculate dissociation energy (D_0) and force stretching constant (k) of the bond.

The **exact zero-point-energy** (when $v = 0$) is also calculated which is $\varepsilon_0 = \frac{1}{2}hc\bar{v}_0 - \frac{1}{4}x_e hc\bar{v}_0$.

For $^{1}H\,^{35}Cl$, $\left(\bar{\nu}\right)_{fundamental}$ = 2886 cm^{-1}, $\left(\bar{\nu}\right)_{1st\ overtone}$ = 2668 cm^{-1} and $\left(\bar{\nu}\right)_{2nd\ overtone}$ = 8347 cm^{-1}.

From these frequencies, we get $\bar{\nu}_0$ = 2990 cm^{-1} and x_e = 0.0174.

These values give $D_0 = 8.242\times10^{-12}$ erg = 118.194 kcal mol^{-1}, $k = 5.09\times10^{5}$ dyne cm^{-1}.

Problem: The fundamental and overtone transitions of $^{14}N\,^{16}O$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Calculate the exact zero point energy of the molecule.

[Calcutta Univ. 2014]

Solution: We have the relations, $\left(\bar{\nu}\right)_{fundamental} = \left(1-2x_e\right)\bar{\nu}_0$ and $\left(\bar{\nu}\right)_{1st\ overtone} = 2\left(1-3x_e\right)\bar{\nu}_0$.

But, $\left(\bar{\nu}\right)_{fundamental}$ = 1876.06 cm^{-1} and $\left(\bar{\nu}\right)_{1st\ overtone}$ = 3724.20 cm^{-1} ,

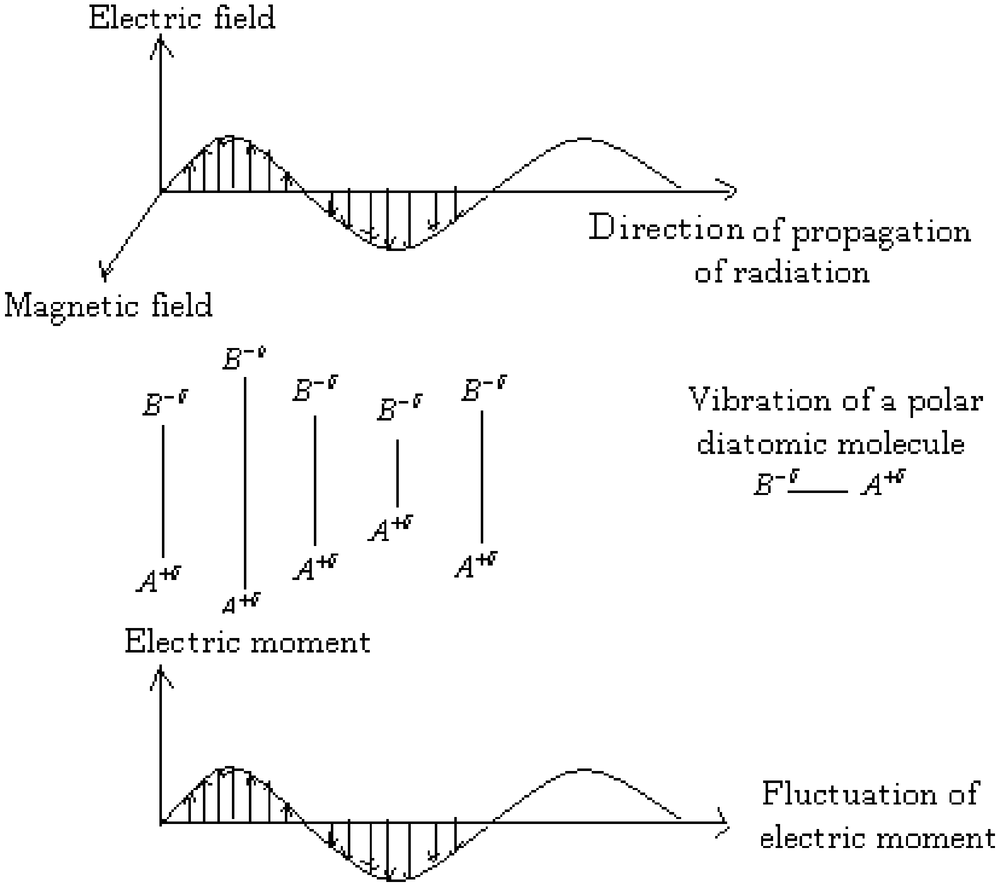
Putting these values and solving, we get $\bar{\nu}_0$ = 1902.29 cm^{-1} and x_e = 0.0069.

Exact zero point energy of the molecule, $\varepsilon_0 = \frac{1}{2}hc\bar{\nu}_0 - \frac{1}{4}x_e hc\bar{\nu}_0$. Putting the values of $\bar{\nu}_0$ and x_e , we get $\varepsilon_0 = 1.88\times10^{-13}$ erg.

Interaction of Radiation with Vibrating Molecule

In electromagnetic radiation, the electric field fluctuates and frequency of fluctuation of the electric field is equal to the frequency of radiation.

Due to vibration of a polar molecule, the dipole moment also fluctuates and the frequency of fluctuation is equal to the frequency of molecular vibration.



When the frequency of fluctuation (oscillation) of electric field due to radiation becomes equal to that generated from molecular vibration, resonance develops and interaction of the molecule with radiation occurs.
Under this condition, the molecule absorbs energy from radiation or emits radiation.

Problem:

The vibrational frequency of ${}^1H\,{}^{79}Br$ is $\bar{\nu}_0$ = 2649.7 cm^{-1} and $x_e\bar{\nu}_0$ = 45.2 cm^{-1}. Find the frequency (in cm^{-1}) of the fundamental and first overtone of the molecule. **[Calcutta Univ. 2011]**

Answer: We have $x_e = \left(45.2/2649.7\right) = 0.017$. Then the frequency of the centre of the fundamental band, $\bar{\nu}_{fund} = (1-2x_e)\bar{\nu}_0 = (1-2\times 0.017)\times 2649.7 = 2559.3\,\text{cm}^{-1}$. The centre frequency of the first overtone is $\bar{\nu}_{1st\ overtone} = 2(1-3x_e)\bar{\nu}_0 = 2(1-3\times 0.017)\times 2649.7 = 5029.13$ cm^{-1}.

Appearance of Q-branch in IR spectrum

For Q-branch, the transition occurs when $\Delta J = 0$ and this happens for perpendicular vibration of the molecules.

If the vibration is taken simple harmonic, the energy levels are identical and the frequency lines of P-branch and R-branch are all equispaced and are equal to 2B.

Transitions with $\Delta J = 0$, however corresponds to a Q-branch whose lines may be derived as $\bar{\nu}_c$. Thus the Q-branch consists of lines superimposed upon each other at the band centre $\bar{\nu}_c$., the one contribution arising for each of the populated J values. The resultant line is usually very intense.

If we take B values differ slightly in the upper and lower vibrational states, then we can write

$\bar{\nu} = \bar{\nu}_c + (B'-B)J(J+1)$, where J = 0, for 0 to 0 transition, J = 1 for 1 to 1 transition, J = 2 for 2 to 2 transition and so on.

$B' = h/8\pi^2 c\mu(r_e')^2$, rotational constant in the higher vibrational level and $B = h/8\pi^2 c\mu(r_e)^2$, rotational constant in the lower vibrational level. But $r_e' > r_e$, so $B' < B$. So, we see that the Q-branch line would become split into series of lines on the low frequency side of $\bar{\nu}_0$, since $B'-B$ = (- ve).

Normally $(B'-B)$ is so small that that the lines can not be resolved and that the Q-branch appears as a somewhat absorption centre around $\bar{\nu}_c$.

This Q-branch occurs for the molecules executing perpendicular (⊥) vibrations i.e. vibration of the atoms is up and down perpendicularly with the bond axis. Such as bending vibration of CO_2 molecule, HCN molecule, NH_3 molecule, etc

When the vibration is harmonic, $\bar{\nu}_c = \bar{\nu}_0$, the frequency of molecular vibration and when the vibration is anharmonic, $\bar{\nu}_c = (1-2x_e)\bar{\nu}_0$ for fundamental band and $\bar{\nu}_c = 2(1-3x_e)\bar{\nu}_0$ for 1st overtone, etc.

Again, since $B' < B$, the rotational lines are not accurately equispaced as

$$\bar{\nu} = \bar{\nu}_c + J'(J'+1)B' - J(J+1)B$$

For P-branch, $J \to J-1$ so putting $J' = J-1$, $\bar{\nu}_P = \bar{\nu}_c + (B'-B)J^2 - (B'+B)J$,

so 1st line frequency is $\bar{\nu}_P = \bar{\nu}_c + (B'-B) - (B'+B) = \bar{\nu}_c - 2B$,

2nd line frequency is $\bar{\nu}_P = \bar{\nu}_c + (B'-B)\times 2^2 - (B'+B)\times 2 = \bar{\nu}_c + 2B' - 6B$,

3rd line frequency is $\bar{\nu}_P = \bar{\nu}_c + (B'-B)\times 3^2 - (B'+B)\times 3 = \bar{\nu}_c + 6B' - 12B$.

For R-branch, $J-1 \to J$, so putting $J = J-1$, $\bar{\nu}_R = \bar{\nu}_c + (B'-B)J^2 + (B'+B)J$

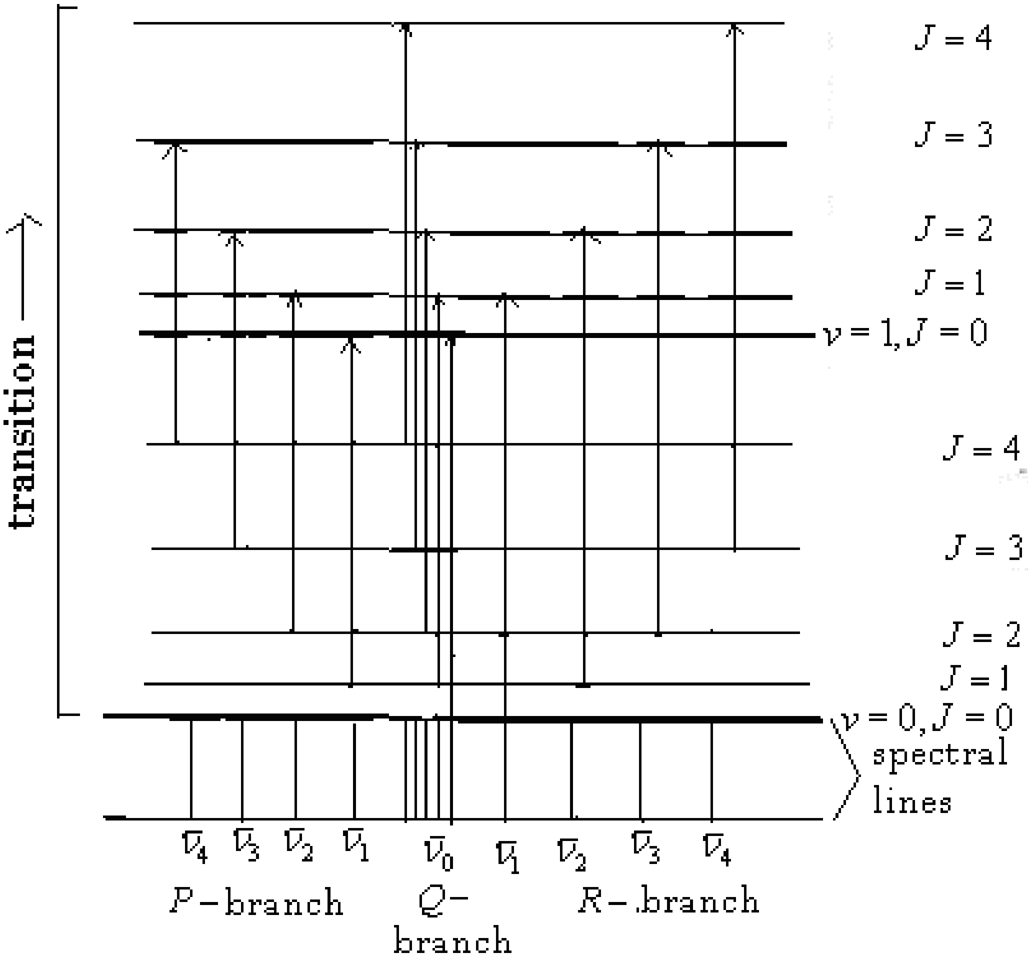
so 1st line frequency is $\bar{\nu}_R = \bar{\nu}_c + (B'-B) + (B'+B) = \bar{\nu}_c + 2B'$,

2nd line frequency is $\bar{\nu}_R = \bar{\nu}_c + (B'-B)2^2 + (B'+B)2 = \bar{\nu}_c + 6B' - 2B$

3rd line frequency is $\bar{\nu}_R = \bar{\nu}_c + (B'-B)3^2 + (B'+B)3 = \bar{\nu}_c + 12B' - 6B$

and so on.

Thus, the frequency gap of the P- branch is decreasing and that in the R-branch is increasing as J is increasing. The transitions along with IR spectra are shown in below:



Problem: If the bond length of a heteronuclear diatomic molecule is greater in the upper vibrational state, the gap between the successive absorption lines of P-branch

1. increases non-linearly 2. decreases non-linearly 3. increases linearly 4. decreases linearly

Answer: (2). **[NET, 2014, Dec.]**

Hot bands

At room temperature only, the lowest vibrational energy level $(v = 0)$ highly populated and so most of the vibrational transitions originate from this level. As the temperature is raised, molecules migrate from lowest level to $v = 1$. Thus a sufficient number of molecules occupy $v = 1$ level at higher temperature thereby permitting vibrational transitions to originate from $v = 1$ level. Such transitions from $v = 1$ to higher levels produce the spectral lines called **Hot bands.** As the temperature is increased, the intensity of hot bands also increases.

ELECTRONIC SPECTRA

Introduction

Electronic spectra are observed when there occurs redistribution of electrons in a molecule. When the electrons transit from filled molecular orbital (HOMO) to the vacant or partially filled molecular orbital (LUMO), photons are absorbed by the molecules for transition. The frequency of radiation for such transition falls in the visible and ultraviolet region since energy required for electronic transition is about 100 kcal/mole (about 7 $\times 10^{-12}$ erg/molecule). This is why electronic spectra is often called UV-Vis spectra.

Electronic spectra are studied in both absorption and emission spectroscopy. Electronic transition is always accompanied with vibrational and rotational transitions of the molecule. Therefore, electronic spectra is always associated with vibrational and rotational spectra and thereby it becomes most complicated.

Advantage

Instead of complex nature of the electronic spectra, it has certain advantages also.

(1) This spectra are studied in the visible and ultraviolet region of radiation and so experimental handling is easy. This means that recording is easy but interpretation is difficult.

(2) Homonuclear diatomic molecules give electronic spectra and molecular information about them can be obtained from the study of electronic spectra. These molecules do not show microwave and infrared spectra.

(3) Information about the excited state of the molecule and bond dissociation energy can be easily obtained from the study of electronic spectra.

Electronic spectra of diatomic molecules

When a diatomic molecule transits from lower electronic state to the higher electronic state, there occurs innumerable change of vibrational and rotational levels. Changes in vibrational levels are shown by coarse structure and each coarse structure is also associated with fine structure due to rotational transitions.

For vibrational transition in the coarse structure of electronic spectra, Born-Oppenheimer approximation is used.

$$\Delta\varepsilon = \Delta\varepsilon_{electronic} + \Delta\varepsilon_{vibrational} .$$

For a given electronic transition, there is no quantum mechanical restriction (i.e., selection rule) on the change of vibrational quantum numbers. Since most of the molecules occupy in the ground vibrational level ($v = o$), all types of transitions from this lowest vibrational level to any of vibrational level of higher electronic state is possible. Experimentally it is found that all such transitions are not equally intense. Only those transitions are intense which are in accordance to Frank-Condon principle. This principle states that

"The electronic transition occurs so quickly that the internuclear separation during the transition remains unchanged."

Thus, the electronic transitions are vertical transitions and these transitions give intense electronic spectral lines. Other transitions give less intense lines.

In the higher electronic state, following changes happen.

(1) Internuclear separation is slightly larger generally and so rotational constant B is thus less.

(2) The force constant (k) is slightly smaller and hence the molecular frequency of vibration $\left(\bar{v}_0\right)$ is smaller.

(3) The potential energy curve becomes flatter and so the molecule is less stable in the higher electronic state.

(4) The potential energy curve is displaced towards the larger internuclear distance $\left(r_e\right)$.

(5) Spacing of the successive vibrational levels in the higher electronic state is also smaller than those of the ground electronic state.

Each coarse structure is associated with band consisting of fine lines due to rotational transitions, thus making the electronic structure of very simple diatomic molecule quite complicated.

Quantitative approach

According to Born-Oppenheimer approximation, the total energy

$$\varepsilon_t = \varepsilon_e + \varepsilon_v + \varepsilon_r \qquad \text{[Neglecting the interaction among different molecular motions].}$$

The change of the energy levels is $\Delta\varepsilon_t = \Delta\varepsilon_e + \Delta\varepsilon_v + \Delta\varepsilon_r$,

where $\Delta\varepsilon_v = \left(v' + \frac{1}{2}\right)hc\bar{v}_0' - \left(v + \frac{1}{2}\right)hc\bar{v}_0$. [Neglecting anharmonicity of molecular vibration and taking molecular vibrational frequency is different in higher electronic state from the lower electronic state]

Again, $\Delta\varepsilon_r = J'\left(J'+1\right)B'hc - J\left(J+1\right)Bhc$, where the rotational constants are also different in different electronic states. Thus, $\Delta\varepsilon_t = \left[hc\bar{\nu}_e + \left\{\left(v'+\frac{1}{2}\right)hc\bar{\nu}_0' - \left(v+\frac{1}{2}\right)hc\bar{\nu}_0\right\}\right] + J'\left(J'+1\right)B'hc - J\left(J+1\right)Bhc$,

where $\bar{\nu}_e$ is the frequency (in cm^{-1}) of radiation if there would be electronic transition only and unaccompanied by vibrational and rotational transitions.

The photon of energy, $hc\bar{\nu} = \Delta\varepsilon_t$ is absorbed for the electronic transition, and hence

$$hc\bar{\nu} = \left[hc\bar{\nu}_e + \left\{\left(v'+\frac{1}{2}\right)hc\bar{\nu}_0' - \left(v+\frac{1}{2}\right)hc\bar{\nu}_0\right\}\right] + J'\left(J'+1\right)B'hc - J\left(J+1\right)Bhc$$

or,
$$\bar{\nu} = \left[\bar{\nu}_e + \left\{\left(v'+\frac{1}{2}\right)\bar{\nu}_0' - \left(v+\frac{1}{2}\right)\bar{\nu}_0\right\}\right] + J'\left(J'+1\right)B' - J\left(J+1\right)B.$$

This is the expression of frequency of radiation ($\bar{\nu}$) for electronic transition.

Taking the term within bracket [ ] as $\bar{\nu}_c$, the frequency of the central line of a band in coarse structure of the electronic spectra, we have $\bar{\nu} = \bar{\nu}_c + J'\left(J'+1\right)B' - J\left(J+1\right)B$.

For P branch of the band, transition of the rotational levels from $J \rightarrow J-1$, we get the frequency

$\bar{\nu}_P = \bar{\nu}_c + J\left(J-1\right)B' - J\left(J+1\right)B$ or, $\bar{\nu}_P = \bar{\nu}_c + \left(B'-B\right)J^2 - \left(B'+B\right)J$.

This will constitute the P branch of the fine structure. Each fine line is obtained by putting J = 1, 2, 3, etc. excluding zero.

Again for R branch, rotational transition occurs from $J-1 \rightarrow J$, where J = 1, 2, 3, etc excluding zero.

$\bar{\nu}_R = \bar{\nu}_c + J\left(J+1\right)B' - J\left(J-1\right)B$ or, $\bar{\nu}_P = \bar{\nu}_c + \left(B'-B\right)J^2 + \left(B'+B\right)J$.

This will constitute the R branch of fine structure.

From the frequency of different lines in the fine structure, it is possible to calculate the values of $\bar{\nu}_e$, B' and B of homonuclear diatomic molecules also. These values will provide the bond length (equilibrium internuclear distance) of the molecule in the ground electronic state and also in the higher electronic state.

Problem: The fundamental vibrational frequency for $^{23}Na\,^{35}Cl$ is 366 cm^{-1}. Calculate the fundamental vibrational frequency for $^{23}Na\,^{37}Cl$. Use integral masses.
The boiling point of NaCl is 1686 K. Determine the ratio of population in vibrational level v = 1 with respect to v = 0 for $^{23}Na\,^{35}Cl$ at the temperature. **[IISc 2003, Adm. Test to Int. Ph.D.]**

Solution: We have $\dfrac{\bar{\nu}_0\,(^{23}Na\,^{35}Cl)}{\bar{\nu}_0\,(^{23}Na\,^{37}Cl)} = \sqrt{\dfrac{\mu(^{23}Na\,^{37}Cl)}{\mu\left(^{23}Na\,^{35}Cl\right)}} = \sqrt{\left(\dfrac{23\times37}{23+37}\right)\Big/\left(\dfrac{23\times35}{23+35}\right)} = 1.0109$.

So, $\bar{\nu}_0\,(^{23}Na\,^{37}Cl) = \bar{\nu}_0(^{23}Na\,^{35}Cl)/1.0109 = 366/1.0109 = 362.05\,cm^{-1}$.

Again for $^{23}Na\,^{35}Cl$ molecule, the energy gap for two consecutive levels is

$\Delta\varepsilon_v = hc\bar{\nu}_0 = 6.627\times10^{-27}\,erg\,\sec\times3\times10^{10}\,cm\,\sec^{-1}\times366\,cm^{-1} = 7.274\times10^{-14}\,erg$.

The ratio of population, $\dfrac{n_1}{n_0} = e^{-\Delta\varepsilon_{0\rightarrow1}/kT} = e^{-7.274\times10^{-14}\,erg/1.36\times10^{-16}\,erg\,K^{-1}\times1686K} = 0.728$.

Electronic Spectra of Polyatomic Molecules

Electronic spectra of polyatomic molecules are very much complex and hence correlation of frequency of radiation absorbed with the specific transition of electrons is not made. Instead, types of electronic transition and the range of possible values of $\lambda_{\max}$ (wave length at which maximum absorption of radiation occurs) is suggested.

Different types of electrons in a molecule

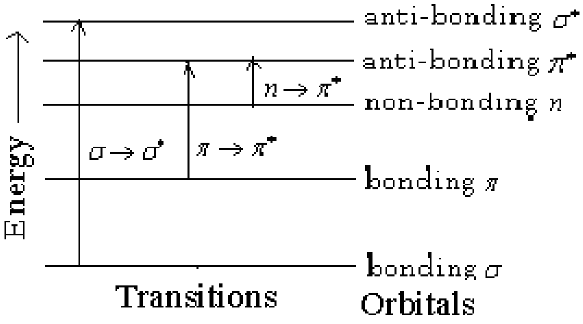
We encounter three types of electrons in molecules.

(a) σ - electrons: These electrons form σ - bonds in the molecule. Since σ - bond strongly binds the two bonded atoms, the σ - electrons are strongly bound between two the nuclei and great deal of energy is required for such transition type of transition ($\sigma - \sigma^*$).
For such transition, absorption of radiation of far ultra-violet region $(\lambda < 200\ nm)$ is required.

(b) π -electrons: These are π - bond forming electrons and are less firmly bound to the bond-forming nuclei. Therefore, less energy is required for excitation to antibonding molecular orbital(π^*).
Radiation responsible for $\pi \to \pi^*$ transition falls in the near ultra-violet region and λ being within 200 nm to 400 nm. These transitions occur in the molecules containing π - bonds. These transition gives strongly intense spectra.

(c) n -electrons: These are non-bonding electrons and present in the atoms to the right of carbon in the periodic table, notably in nitrogen, oxygen and halogens. It is attached to the single atom only and so least firmly bound in the molecule. Therefore, least energy is required for the transition of $n \to \pi^*$. n - electrons do not form bonds hence there is no antibonding orbitals associated with it. Radiation for such type of transition ($n \to \pi^*$) falls in the visible and ultra-violet region of radiation and λ lies between 400 nm to 750 nm.

We shall discuss here only $\pi \to \pi^*$ and $n \to \pi^*$ transitions only since these are common in the electronic spectra of polyatomic molecules. However, $\sigma \to \sigma^*$ transition falls below λ = 175 nm and this is outside of the available range of spectrometer (range < 185 nm).



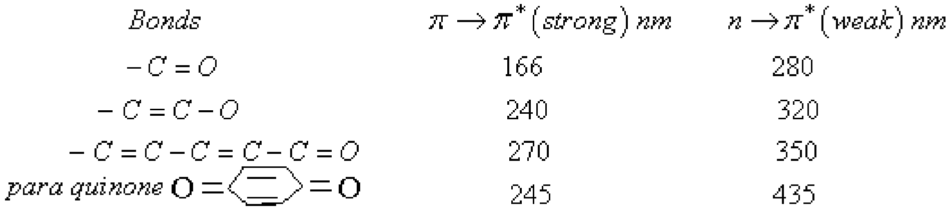
$\pi \to \pi^*$ transitions occurs in unsaturated compounds. Chromophores like $> c = c <$, $-c \equiv c-$ show this type of spectra. The group like $> c = o$ shows a strong absorption band around 170 nm due to $\pi \to \pi^*$ transition and a weaker absorption band around 280 nm for $n \to \pi^*$. (Unsaturated groups which cause absorption band at $\lambda > 175\ nm$ are called Chromophores).

$n \to \pi^*$ transition produces weak band of absorption since this transitions are often symmetrically forbidden and also excitation involves in different regions of the molecule.

When the double bond is a part of conjugated chain, the energies of the MO lie closer together due to increase of chain length molecule (particle in 1-d box) and the $\pi \to \pi^*$ transitions shift into visible region of radiation.

Bonds	$\lambda_{\max}(nm)$	$\varepsilon\ (cm^{-1} L\ mol^{-1})$
$-C = C-$	170	16,000
$-C = C - C = C-$	220	21,000
$-C = C - C = C - C = C-$	260	35,000

While oxygen containing molecules, we have both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and in conjugated polyenes, both $\lambda_{\max}$ and intensity (ε) of the above transitions increase considerably.



Bonds	$\pi \rightarrow \pi^*$ (strong) nm	$n \rightarrow \pi^*$ (weak) nm
$-C=O$	166	280
$-C=C-O$	240	320
$-C=C-C=C-C=O$	270	350
para quinone O= ⟨ ⟩ =O	245	435

Criteria of Rotational, Vibrational and Electronic Transitions of Molecules

Pure rotational spectra are shown by molecules possessing a permanent electric dipole moment or when the molecule rotates, the component dipole moment must change.

Vibrational spectra require a change of dipole moment during the vibration of the molecule (oscillating dipole).

Electronic spectra are shown by all molecules since changes in electronic distribution in a molecule are always accompanied by a change of dipole moment (μ_D). However, if the electronic redistribution occurs symmetrically, there is no net change in the dipole and the transition is forbidden. For example, in a molecule, $s \rightarrow p_z$ transition is allowed because it corresponds to the movement of charge along the z-axis. In contrast, a $1s \rightarrow 2s$ is spherically symmetrical. It, therefore, involves no change in dipole moment and so it is forbidden.

Thus, for the electronic transition, if there occurs some kind of transient dipole moment (it is called transition dipole moment), it absorbs visible and UV radiation. However, there may some electronic transition be forbidden but all molecules will show electronic spectra.

Chromophores:

Absorption of radiation of C = C double bond excites a π-electron to an antibonding π^* orbital. The Chromophore activity is thus due to a $\pi^* \leftarrow \pi$ transition (which read as π to π^* transition. Higher energy level is written first). Its energy is about 7 eV for a unconjugated double bond which corresponds to absorption at 180 nm (in the UV region) but when this double bond is a part of conjugation, the energy of MO lies closer together (one-dimensional box model) and λ shifts to the higher side. Further if the conjugation chain length is large, λ changes to the visible region.

Transition responsible for absorption of carbonyl compound is due to transition of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$.

The transition of lone pair of electrons in O-atom to π^* bond has typical energy value of 4 eV (equivalent to 290 nm). But the intensity of the transition is weak since in carbonyl, $\pi^* \leftarrow n$ is symmetrically forbidden.

Groups C = C, C = O, $-N=O$ which cause absorption at λ > 180 nm are called Chromophores (colour bringer). Position and intensity of the absorption are characteristic of each group.

C = C shows absorption peak at 180 – 190 nm with molar absorption coefficient, $\varepsilon = 10^4$ L mol^{-1} cm^{-1}.

C = O shows absorption peak at 270 – 290 nm with molar absorption coefficient, $\varepsilon = 10 - 30$ L mol^{-1} cm^{-1}.

Change in the Properties of a Molecule for Electronic Transition

When a molecule transits to the excited state by absorption of visible and ultraviolet region of radiation, there occur a lot of change in the physical and chemical properties of the substance. Excited state possesses higher energy and so the bonds become weaker.

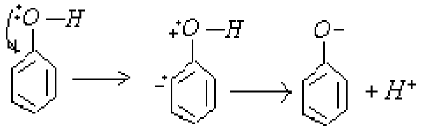
Transition from the ground bonding MO to antibonding MO can cause triple bond to become double bond, double bond to single bond and single bond to disrupt. The bond length is increased by about 15% or more. Bond angles may also change significantly. The change of the following properties is given here.

(1) Dipole moment:

By electronic transition of the molecule, there occurs an change in electronic distribution, so dipole moment of the molecule is changed. Non-polar molecule becomes polar in the excited state. Dipole moment of the polar molecules is increased.

(2) Acid properties: Acidity of the molecule is also changed in the excited state. Some examples are given as

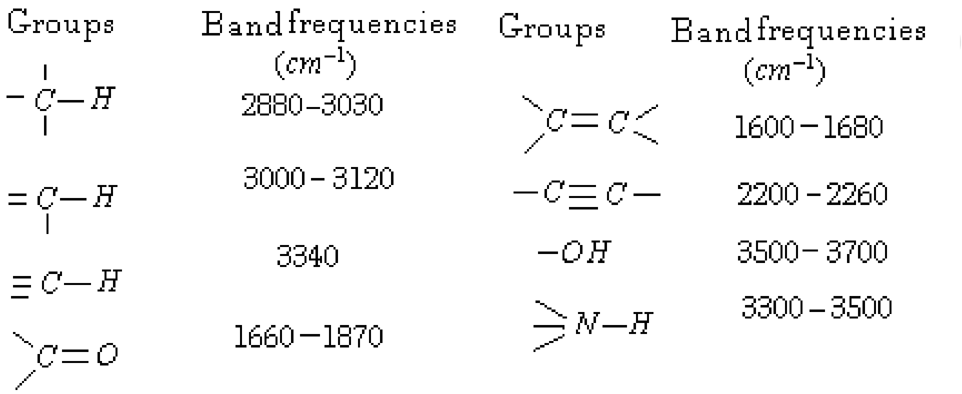
(a) Acidity of phenol→ In aqueous solution, phenol is a weak acid. But when it absorbs radiation of appropriate frequency, it gets excited due to $n \rightarrow \pi *$ transition. Lone pair of electrons on the oxygen atom is shifted to the antibonding MO ($\pi *$) which is on the ring only. This promotion increases the (+ve) character of oxygen atom and the phenol becomes stronger acid in the excited state. .



(b) Acidity of carboxylic acid 1→ In benzoic acid, the $\pi \rightarrow \pi^*$ transition transfers charge from the ring to the carboxylic group since antibonding MO is located on the group. The acid strength becomes less. The variation if often becomes as much as million times between the ground state and excited state.

Identification of organic compounds

The groups in the organic compound absorb light of frequencies within certain range depending on its nature. The some groups with range of absorbed frequencies (in cm^{-1}) are given bellow.



Groups	Band frequencies (cm^{-1})	Groups	Band frequencies (cm^{-1})
$-\overset{\vert}{\underset{\vert}{C}}-H$	2880–3030	$>C=C<$	1600–1680
$=\underset{\vert}{C}-H$	3000 - 3120	$-C\equiv C-$	2200 - 2260
$\equiv C-H$	3340	$-OH$	3500– 3700
$>C=O$	1660–1870	$\geqslant N-H$	3300 – 3500

Presence or absence of these groups may be established by the appearance or non-appearance of the absorption bands associated with these groups.

Burdwan University, 2010

Q 4(f) Write down the selection rule for allowed rotational and vibrational transition. (2)

Ans. According to rigid rotor model concept, the selection rule for rotational transition is $\Delta J = \pm 1$, It means that molecule transits in the successive levels only.

According to simple harmonic oscillator model concept, the selection rule for vibrational level is $\Delta v = \pm 1$, the molecule transits in the successive levels only.

But when the non-rigid model of molecule rotation is considered, the selection rule for rotational transition is violated and $\Delta J = \pm 1, \pm 2, \pm 3, etc.$ are allowed

Similarly when anharmonic motion of the molecule is considered, the selection rule for vibrational transition is also violated and $\Delta v = \pm 1, \pm 2, \pm 3, etc.$ are permitted.

Q 5(c)(i) The microwave spectrum of HI consists of a series of equally spaced lines with $\Delta \bar{\nu}$ = 128 cm^{-1}. Calculate the moment of inertia and the internuclear distance. (3)

Ans. We have $\Delta \bar{\nu} = \dfrac{2h}{8\pi^2 I\, c}$ or, $I = \dfrac{2h}{8\pi^2 (\Delta \bar{\nu}) c} = \dfrac{2 \times 6.627 \times 10^{-27}\, erg\ \sec}{8 \times (3.14)^2 \times 128\, cm^{-1} \times 3 \times 10^{10}\, cm\ \sec^{-1}}$ gm cm^{-1}

$= 4.37 \times 10^{-41}$ gm cm^{-1}, this is the moment of inertia of the molecule.

Again, $I = \mu r^2$, where μ = reduced mass of HI molecule = $\dfrac{1 \times 127}{(1+127) \times 6.023 \times 10^{23}} = 1.65 \times 10^{-24}\, gm$.

Hence, the internuclear distance, $r = \sqrt{I/\mu} = \sqrt{\dfrac{4.37 \times 10^{-41}\, gm\, cm^2}{1.65 \times 10^{-24}\, gm}} = 5.15 \times 10^{-9}\, cm$ = 5.15 nm.

(ii) Show that under harmonic oscillator approximation, the frequency of vibration of a diatomic molecule is equal to the frequency of photon absorbed by the molecule. (2)

Ans. See the Text for showing $\bar{\nu} = \bar{\nu}_0$.

(iii) What would be the zero-point energy of an oscillator if it is classical or quantum? (1)

Ans. The zero-point energy (ZPE) of classical oscillator is zero as, $\varepsilon_{vib} = nhc\bar{\nu}_0$, where n = 0, 1, 2, 3, etc.

But ZPE of quantum oscillator is $\dfrac{1}{2} hc\bar{\nu}_0$ as, $\varepsilon_{vib} = \left(v + \dfrac{1}{2}\right) hc\bar{\nu}_0$, where v = 0, 1, 2, 3, etc.

Q 8C(a) Using the formula for the energy levels for the Morse potential, $\varepsilon_n = h\nu\left(n + \dfrac{1}{2}\right) - \dfrac{(h\nu)^2}{4D_e}\left(n + \dfrac{1}{2}\right)^2$,

deduce the expression of energy spacing between adjacent levels.

For $^1H\, ^{35}Cl$, D_e = 7.41×10^{-19} J and ν =8.97×10^{13} sec^{-1}, calculate the smallest value of n for which $\varepsilon_{n+1} - \varepsilon_n$ < 0.5 ($\varepsilon_1 - \varepsilon_0$). (5)

Ans. $\varepsilon_{n+1} - \varepsilon_n = h\nu\left(n + \dfrac{3}{2}\right) - \dfrac{(h\nu)^2}{4D_e}\left(n + \dfrac{3}{2}\right)^2 - h\nu\left(n + \dfrac{1}{2}\right) - \dfrac{(h\nu)^2}{4D_e}\left(n + \dfrac{1}{2}\right)^2 = h\nu\left[1 - \dfrac{h\nu}{2D_e}(n+1)\right]$.

Thus, energy spacing, $\Delta\varepsilon = h\nu\left[1 - \dfrac{h\nu}{2D_e}(n+1)\right]$. Again, putting n = 0, we get $\varepsilon_1 - \varepsilon_0 = h\nu\left[1 - \dfrac{h\nu}{2D_e}\right]$.

Now for $^1H\, ^{35}Cl$ molecule, $h\nu\left[1 - \dfrac{h\nu}{2D_e}\right] < 0.5\, h\nu\left[1 - \dfrac{h\nu}{2D_e}\right]$ or, $n > \dfrac{D_e}{h\nu} - \dfrac{1}{2}$.

Now putting the values given for the molecule, we get $n > \dfrac{7.41 \times 10^{-19}\, J}{6.627 \times 10^{-34}\, J\, \mathrm{s} \times 8.97 \times 10^{13}\, s^{-1}} - \dfrac{1}{2}$

or, $n > 11.97$. Thus, the smallest value of $n = 12$.

Burdwan University, 2011

Q 4(d) Classify the following molecules in terms of spherical top, symmetric top and asymmetric top:
CH_3Cl, CH_4, NH_3, H_2O. (2)

Ans. CH_3Cl → Symmetric top, since $Iy = Iz \neq Ix$, $Ix \neq 0$.

CH_4 → Spherical top, since $Ix = Iy = Iz$

NH_3 → Symmetrical top, since $Ix = 2Iy = 2Iz$

H_2O → Asymmetric top, since $Ix \neq Iy \neq Iz$.

Ix, Iy and Iz are the moment of inertia, one about each axis. [See Fundamentals of molecular spectroscopy – C N Banwell]

Q 5(d)(i) Calculate the force constant for $H\,^{35}Cl$ molecule from the fact that the fundamental vibrational frequency is 8.667×10^{13} sec^{-1} and the reduced mass is 1.627×10^{13} kg. (3)

Ans. The force constant of the molecule is given by

$$k = 4\pi^2 \mu(\nu)^2 = 4 \times (3.14)^2 \times 1.6275 \times 10^{-27}\, kg \times \left(8.667 \times 10^{13}\, \sec^{-1}\right)^2 = 482.15\, N\, m^{-1}.$$

(ii) Find the value of $B\left(J_{\max} + \frac{1}{2}\right)^2$ at temperature, where B is the rotational constant and $J_{\max}$ is the rotational level with maximum population for a diatomic molecule. (3)

Ans. We have $J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$ and so the value of $B\left(J_{\max} + \frac{1}{2}\right)^2 = B\left(\sqrt{\frac{kT}{2Bhc}}\right)^2 = B\left(\frac{kT}{2Bhc}\right)$.

So the value of $B\left(J_{\max} + \frac{1}{2}\right)^2 = \frac{kT}{2hc}$.

Q 6C(ii) Show that the lines in the rotational spectrum of a diatomic molecule are equispaced under rigid rotor approximation. (3)

Ans. We have the energy expression of rotational level under rigid rotor model is

$$\varepsilon_J = J(J+1)Bch,$$

where $B = \frac{h}{8\pi^2 Ic}$, called rotational constant of the molecule. The spacing between two adjacent rotational energy level is $\Delta\varepsilon_J = \varepsilon_{J+1} - \varepsilon_J = 2Bhc(J+1)$, where $J = 1, 2, 3, etc$.

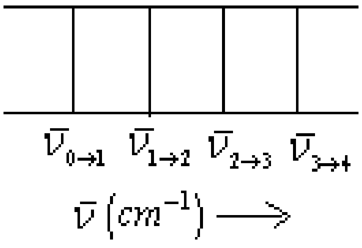
But $\Delta\varepsilon = h\bar{\nu}c$, the energy of the photon required to transit the molecule from J to $J+1$.

Thus, $\bar{\nu} = (J+1)2B$.

Putting the value of J = 0, 1, 2, 3, etc. we get $\bar{\nu}$ of the rotational lines of the spectrum.

The spectrum shows the rotational lines are equispaced and the frequency gap of the lines is $\Delta\bar{\nu} = 2B$.

The rotational spectrum of a diatomic molecule is shown in the adjoining figure.



(iv) Justify that the ground state vibrational level of a diatomic molecule is more densely populated. (3)

Ans. Population in different energy levels are controlled by Boltzmann distribution law. Let us consider the population in $v = 1$ level relative to $v = 0$ level,

$\frac{n_1}{n_0} = e^{\Delta\varepsilon_{0\to1}/kT}$. But $\Delta\varepsilon_{0\to1} >> kT$ so, $\frac{n_1}{n_0}$ is very small and thus $n_0 >> n_1$ it means that $v = 0$ level is densely populated than $v = 1$ level Higher levels are still of lower populated.

Burdwan University, 2012

Q 4(g) Sketch the IR active and IR inactive modes of vibration for carbon dioxide molecule. (2)

Ans. See Burdwan Univ. 2014 Q 6C(ii), page .

Q 5(d)(i) The Morse potential function, $V(r)$ for a diatomic molecule may be expressed as

$$V(r) = D_e\left[1 - e^{-\alpha(r-r_e)}\right]^2,$$

Calculate $V(r_e)$, $V(\infty)$ and α in the above expression. (1+1+2)

Ans. When $r = r_e$, the Morse function, $V(r_e) = De\left[1 - e^{-a(r_e-r_e)}\right]^2 = De\left[1 - e^0\right]^2 = De[1-1]^2 = 0$.

When $r = \infty$, the Morse function, $V(\infty) = De\left[1 - e^{-a(\infty-r_e)}\right]^2 = De\left[1 - e^{-\infty}\right]^2 = De[1-0]^2 = De$.

Expanding the expression of $V(r)$, we have

$$V(r) = D_e\left[1 - \left\{1 - \alpha(r-r_e) - \frac{1}{2}\alpha^2(r-r_e)^2 - - -\right\}\right]^2 = D_e\left[\alpha(r-r_e) + \frac{1}{2}\alpha^2(r-r_e)^2\right]^2.$$

When the displacement is small, higher powers of $(r - r_e)$ are neglected, the Morse potential becomes

$$V(r) = D_e\,\alpha^2(r-r_e)^2.$$

This Morse function is identical with potential energy of SHO which is $V(r) = \frac{1}{2}k(r-r_e)^2$.

Equating this PE with Morse potential, we get $\alpha = \sqrt{\frac{k}{2D_e}}$.

(ii) Justify that the ground state vibration level of a diatomic molecule is more densely populated. (2)

Ans. See the answer given in BU 2011, Q 6C(iv), page
and it means that $v = 0$ level is densely populated than $v = 1$ level.

Q 6(C)(i) Which of the following molecules may give rotational spectrum:

H_2, HCl, N_2, CO, DCL, CCl_4. (2)

Ans. The criteria of a molecule to give rotational spectrum is that the molecule must have permanent dipole moment (μ_D). Thus, HCl, CO, DCl give rotational spectrum.

(ii) Find the expression for the spacing between adjacent rotational levels under rigid rotor approximation. (2)

Ans. We have the energy expression of rotational level under rigid rotor model is

$$\varepsilon_J = J(J+1)Bch,$$

where $B = \frac{h}{8\pi^2 Ic}$, called rotational constant of the molecule. The spacing between two adjacent rotational energy level is $\Delta\varepsilon_J = \varepsilon_{J+1} - \varepsilon_J = 2Bhc(J+1)$, where $J = 1, 2, 3, etc$.

Thus, the spacing of the adjacent levels are: $\Delta\varepsilon_{0\to1} = 2Bhc$, $\Delta\varepsilon_{1\to2} = 4Bhc$, $\Delta\varepsilon_{2\to3} = 6Bhc$, etc.

(iii) The fundamental vibrational frequency of $H\,^{35}Cl$ is 8.67×10^{13} sec^{-1}. Calculate the fundamental vibrational frequency of $D\,^{35}Cl$ on the assumption that the force constant of the bond are equal.

Ans. The fundamental vibrational frequency is given by $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$.

Thus, $\frac{(\nu_0)_{D^{34}Cl}}{(\nu_0)_{H^{34}Cl}} = \sqrt{\frac{\mu_{H^{35}Cl}}{\mu_{H^{35}Cl}}} = \sqrt{\frac{(1\times 35)/36}{(2\times 35)/37}} = \sqrt{\frac{35}{36}\times\frac{37}{70}} = 0.717$,

hence, $(\nu_0)_{D^{34}Cl} = 0.717\times 8.67\times 10^{13}$ sec^{-1}.

Burdwan University, 2013

Q 4(d) Classify the following molecules in terms of symmetric top, spherical top and asymmetric top category: vinyl chloride, BCl_3, CCl_4 and H_2O. (2)

Ans. Symmetric top $(Iy = Iz \neq Ix) \rightarrow BCl_3$. Spherical top $(Ix = Iy = Iz) \rightarrow CCl_4$.

Asymmetric top $(Ix \neq Iy \neq Iz) \rightarrow$ vinyl chloride and H_2O.

Q 4(e) Write down primary condition(s) for a molecule to exhibit rotational and vibrational spectroscopy. (2)

Ans. For a molecule to give rotational spectra, the dipole moment of the molecule about any component must change while it is rotating and thus the molecule must be polar.

For a molecule to give infrared spectra, there mist be change of dipole moment (μ_D) while it is undergoing vibration and thus the molecule must be an oscillating dipole, $\frac{d\mu_D}{dx} \neq 0$.

Q 5c(i) Sketch the potential energy curve representing the simple harmonic motion having vibrational state $v = 0$ to $v = 0$. Point out D_0 and D_e in such curve. (3)

Ans. For harmonic motion,

$$PE(V) = \frac{1}{2}k(r - r_e)^2$$

The potential energy (V) vs. internuclear distance (r) is parabola.

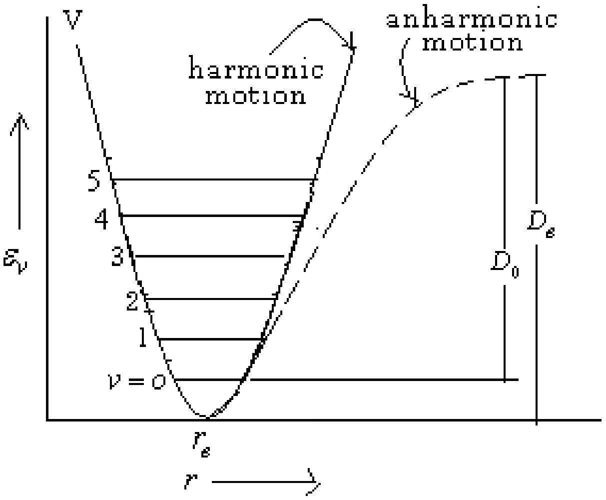
So there is no D_0 and D_e.

But for anharmonic motion, D_0 and D_e are shown in the adjoining curve.

D_0 = dissociation energy and

D_e = depth of the potential energy curve

Thus, $D_0 = D_e - \frac{1}{2}hc\bar{\nu}_0$.



Q 6C(i) Sketch the normal modes of vibration of water. (3)

Ans. See the Text, page .

(ii) The rotational spectrum of HCl molecule shows that the rotational lines are equally separated by 20.7 cm^{-1}. Calculate the internuclear bond length if reduced mass of HCl is given as 1.627×10^{-27} kg.

Ans. It is given $\Delta\bar{\nu} = 2B = 20.7\ cm^{-1}$ or, $B = 10.35\ cm^{-1}$. We have $B = \frac{h}{8\pi^2\mu r^2 c}$ or,. $r = \sqrt{\frac{h}{8\pi^2\mu c}}$.

Putting the values, we get

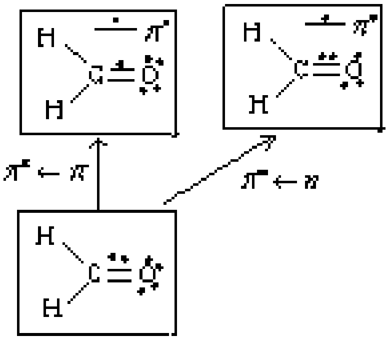
$$r=\sqrt{\frac{6.627\times10^{-27}\ J.\sec}{8\times\left(3.14\right)^2\times1.627\times10^{-24}\,gm\times3\times10^{10}\,cm\sec^{-1}\times10.35\,cm^{-1}}}=1.289\times10^{-8}\,cm.$$

(iii) Write down the electronic transition involved in formaldehyde. (2)

Ans. The molecule, formaldehyde contains $n-$bonding electrons and $\pi-$bonding electrons.

So there occur two types of electronic transitions,

viz. $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$.



Burdwan University, 2014

Q 4(d) Write down the selection rules for rotational and vibrational spectroscopy according to rigid rotor and harmonic oscillator model concept, respectively. (2)

Ans. According to rigid rotor model concept, the selection rule for rotational transition is $\Delta J=\pm1$,
It means that molecule transits in the successive levels only.
According to simple harmonic oscillator model concept, the selection rule for vibrational level is $\Delta v=\pm1$, the molecule transits in the successive levels only.

Q 5(d)(i) Calculate the force constant for $H\,{}^{35}Cl$ from the fact that the fundamental vibrational frequency is 8.667×10^{13} sec^{-1} and the reduced mass is 1.6275×10^{-27} kg. (2)

Ans. See the answer given, BU 2011, Q 5(d)(i).

(ii) The Morse function for diatomic molecule is written as $V(r)=De\left[1-e^{-a(r-r_e)}\right]^2$. Show that the Morse function gives $V(r_e)=0$ and $V(\infty)=De$. (2)

Ans. See the answer of BU 2012, Q 5(d)(i) (first two parts)

Q 5(e)(i) State and explain Franck-Condon principle. (2)

Ans. See the Text, page .

Q 6C(i) Deduce the expression for the rotational level having maximum population $\left(J_{\max}\right)$ using the concept of Boltzmann distribution, for rigid diatomic molecule. (4)

Ans. See the Text, page .

(ii) Show the IR active and IR inactive vibrational modes of CO_2 molecule. (2)

Ans. Antisymmetrical stretching and two bending modes of vibration are IR active while symmetrical stretching mode of vibrational mode is IR inactive.
in the above three modes dipole moment changes due to vibration and in the letter mode, dipole moment does not change due to vibration. See the Text, page

.

Calcutta University, 2010

Q 5(a) Explain how the bond length of a homonuclear diatomic may be determined spectroscopically. (2)

Ans. Homonuclear diatomic molecule responds only to the visible and UV light of radiation and there occurs electronic transition producing electronic spectra. From the fine structure of the electronic spectra, it is possible to determine rotational constant of the ground electronic state as well as higher electronic state of the molecule and from which the bond length of the molecule in both the states are calculated.

(b) The first rotational absorption of ${}^{12}C\,{}^{16}O$ occurs at 3.8424 cm^{-1} and that for ${}^{13}C\,{}^{16}O$ at3.6734 cm^{-1}. Calculate the atomic weight of C-13. Mention the assumption used, if any.
[Given, ${}^{16}O$ = 15.9994 and ${}^{12}C$ = 12.0000] (3+1)

Ans. 1st line of rotational absorption spectra is given by $\bar{\nu}_1 = 2B$ and $B = \dfrac{h}{8\pi^2 c\mu r^2}$. So $\dfrac{\bar{\nu}}{\bar{\nu}'} = \dfrac{\mu'}{\mu}$

Putting the values for ${}^{12}C\,{}^{16}O$ and ${}^{13}C\,{}^{16}O$, we get $\dfrac{3.8424\ cm^{-1}}{3.6734\ cm^{-1}} = \dfrac{m'(12.0000+15.9994)}{12.0000(m'+15.9994)}$,

where m' is the atomic weight of ${}^{13}C$. Solving the equation, we get the atomic weight of ${}^{13}C$ = 13.0005.
The assumption is that the internuclear distance (r) is not affected by the isotopic substitution.

(c) What are meant by fundamental, overtone and hot bands in vibrational spectroscopy? (3)

Ans. For anharmonic motion of the molecule, the vibrational transition from $v=0$ to $v=1$ in association with rotational transitions gives a series of fine lines, called fundamental bands.
For vibrational transition from $v=0$ to $v=2$ in association with rotational transition gives first overtone and for transition from $v=0$ to $v=3$ gives second overtone, etc.
For Hot bands, see the Text, page .

Q 6(a) State Franc-Condon principle and illustrate with suitable diagram. (3)

Ans. See the Text, page .

(c) What is the effect of anharmonicity in the vibrational spectra of a diatomic molecule AB? (2)

Ans. (i) Potential energy is changed and it is given by Morse function, $V(r) = D_e\left[1-e^{-\alpha(r-r_e)}\right]^2$

(ii) The spacing of the adjacent vibrational energy levels are decreased and it is

$$\Delta\varepsilon_V = \left[1-2(v+1)x_e\right]hc\bar{\nu}_0, \text{ where } v = 0, 1, 2, 3, \text{ etc.}$$

(iii) The selection rule is violated and it becomes $\Delta v = \pm1, \pm2, \pm3$, etc.

Calcutta University, 2011

Q 5(a) Show that the combined vibration-rotation spectrum of a diatomic molecule is generally found to consists of equally spaced lines on each side of the band origin. Assume the molecule as rigid rotator and harmonic vibrator. (4)

Ans. See the band of fine lines on both side of the band centre in the Text, page .

(c) The vibrational frequency of ${}^{1}H\,{}^{79}Br$ is ν_e = 2649.7 cm^{1} and $x_e\nu_e$ = 45.2 cm^{-1}. Find the frequencies (in cm^{-1}) of the fundamental and first overtone of ${}^{1}H\,{}^{79}Br$. (4)

Ans. The anharmonicity constant of the molecule, $x_e = \dfrac{x_e\nu_e}{\nu_e} = \dfrac{45.2\ cm^{-1}}{2649.7\ cm^{-1}} = 0.017$. The centre frequency of the fundamental band, $\nu_{fund} = (1-2x_e)\nu_e = (1-2\times0.017)\,2649.7\ cm^{-1} = 2559.6cm^{-1}$.

The centre band frequency of the first overtone, $\nu_{1st\ overt} = 2(1-3x_e)\nu_e$

$$= 2(1-3\times0.017)\,2649.7\ cm^{-1} = 5029.13\ cm^{-1}.$$

Q 6(a) Assuming the expression for rotational energy of a rigid diatomic molecule show that the spectral lines are equispaced. (3)

Ans. See the Text, page .

(c) Show different modes of CO$_2$ molecule and state which is Raman active. (4+1)

Ans. See the Text for different modes of CO$_2$ molecule in page .
Symmetrical stretching vibration is Raman active.

Calcutta University, 2012

Q 5(a) Write down the expression for energy $\left(E_J\right)$ in a rigid diatomic rotor. State the condition for such a rotor to be microwave active and state the corresponding spectroscopic selection rule. Also find the expression for transition energy. (6)

Ans. We have the energy expression of a rigid rotor, $E_J = J\left(J+1\right)Bch$, where B is called rotational constant and is equal to $B = \dfrac{h}{8\pi^2 Ic}$. I is moment of inertia and is equal to $I = \mu r^2$, where μ is reduced mass of the molecule.

Condition for microwave active is that the rotor must have permanent dipole moment. In other words, any component of dipole moment of the rotor must change during the rotation of the rotor.

The selection rule for rotational transition in spectroscopy is $\Delta J = \pm 1$, it means that the molecule transits between the adjacent rotational levels only.

The transition energy of the rigid rotor is $\Delta E_{J\rightarrow J+1} = \left(J+1\right)2B$, where, J is rotational quantum number and it has values 0, 1, 2, 3, etc.

(b) State and explain with diagram the Franck-Condon principle. (4)

Ans. See the Text, page .

Q 6(b) The rotational spectrum of ${}^{79}Br\,{}^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the bond length of the molecule. (4)

Ans. The reduced mass of the molecule, $\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{79\times 19}{\left(79+19\right)\times 6.023\times 10^{23}}$ = 2.543 × 10^{-23} gm.

The bond length, $r = \sqrt{\dfrac{h}{8\pi^2 \mu c}} = \sqrt{\dfrac{6.627\times 10^{-27}\, erg \sec}{8\times\left(3.14\right)^2 \times 2.543\times 10^{-23}\, gm \times 3\times 10^{10}\, cm \sec^{-1}}} = 1.05\times 10^{-8}\, cm$.

(c) A linear molecule has the formula AB_2. Discuss how would you ascertain whether the molecule has the structure BAB or ABB using its Raman and IR spectra together.

Ans. See the Text.

Calcutta University, 2013

Q 22(a) The symmetric stretching of CO_2 is IR inactive but Raman active. Explain. (2)

Ans. Symmetrical stretching vibration is IR inactive but this mode is Raman active. See Text for explanation.

(b) Infra-red Raman spectrum of Cl_2 molecule shows a series of Stokes lines separated by 0.98 cm^{-1} and a similar series of anti-stokes lines. Calculate the Cl–Cl bond length. (Atomic Wt. of chlorine = 35.45) (3)

Ans. See the Text for the answer.

Q 23(a) How does the IR absorption spectrum of a hypothetical diatomic molecule AB look like, when it behaves as (i) harmonic oscillator (ii) anharmonic oscillator. (2)

Ans. (i) The absorption spectrum will be of one band consisting of fine lines symmetrically spread over on both sides of centre frequency line and this line is absent for the molecule AB type.

(ii) This spectrum will consist of several bands and each band is having a fine structure. First band is of high intense and called fundamental band, second band is of less intense and is called first overtone, third band is of least intense and is called second overtone, etc.

The centre frequency line in these bands remain absent for this type of molecule and ratio of the centre lines are $\bar{\nu}_{fundamental} : \bar{\nu}_{1st\ overtone} : \bar{\nu}_{2nd\ overtone} \approx 1:2:3$.

(b) An estimated bond length of the species CN is 0.117 mm. Predict the positions of the first three lines in the microwave spectrum of CN. (Atomic weight of C and N are 12.011 and 14.0067 respectively). (3)

Ans. The reduced mass (μ) of the species, CN = $\dfrac{12.011\times 14.0067}{\left(12.011+14.0067\right)\times 6.023\times 10^{23}}\, gm = 1.0736\times 10^{-23}\, gm$.

The rotational constant, $B = \dfrac{h}{8\pi^2 \mu r^2} = \dfrac{6.627\times10^{-27}\,erg}{8\times(3.14)^2\times1.0736\times10^{-23}\,gm\times(0.0117\ cm)^2} = 0.0572\ \sec^{-1}$.

The position of the first three lines is 2B, 4B, 6B = $0.1143\sec^{-1}$, $0.2287\sec^{-1}$, $0.3429\ \sec^{-1}$.

Q 24(a) Show that for the rotational spectrum of a diatomic molecule, the rotational quantum number (to the nearest integral value) for the maximum populated level is given by

$J_{\max} = \left(\dfrac{kT}{2hcB}\right)^{1/2} - \dfrac{1}{2}$. The terms have their usual significance. (3)

Ans. See the Text, page .

(b) If the $J = 2$ to 3 rotational transition for a diatomic molecule occurs at λ = 2.00 cm, find λ for the $J = 6$ to 7 transition of this molecule. (2)

Ans. We have $\bar{\nu} = 2B(J+1)$ so, $\dfrac{\bar{\nu}_{2\to3}}{\bar{\nu}_{6\to7}} = \dfrac{\lambda_{6\to7}}{\lambda_{2\to3}} = \dfrac{(2+1)}{(6+1)} = \dfrac{3}{7}$ or,. $\lambda_{6\to7} = \lambda_{2\to3}\times\dfrac{3}{7} = 2.00\times\dfrac{3}{7} = 0.8571\,cm$.

Calcutta University, 2014

Q 22(a) Give three examples of three different model systems where (i) energy levels are equispaced, (ii) energy gap increases with increase in quantum number, (iii) energy gap decreases with increase in quantum number. (3)

Ans. (i) When the molecular model is taken as simple harmonic oscillator, the energy levels are equispaced.
(ii) When rigid rotor model is considered for molecular rotation, energy gap increases with increase in quantum number.
(iii) When the molecular vibration is anharmonic, the energy gap decreases with increase in quantum number.

(b) The line spacing in the microwave spectrum of ^{13}CO and ^{12}CO are 3.68 cm^{-1} and 3.84 cm^{-1}, respectively. Find out the isotopic mass of ^{13}C. [m_O = 15.9994 in ^{12}C scale]. (2)

Ans. We have $\dfrac{\Delta\bar{\nu}_1}{\Delta\bar{\nu}_2} = \dfrac{2B_1}{2B_2} = \dfrac{\mu_2}{\mu_1}$, where 1subscript is given for ^{13}CO and 2 subscript given for ^{12}CO.

So, $\dfrac{\Delta\bar{\nu}_1}{\Delta\bar{\nu}_2} = \dfrac{m_{^{12}C}\left(m_{^{13}C} + m_O\right)}{m_{^{13}C}\left(m_{^{12}C} + m_O\right)}$, putting the values, we get $\dfrac{3.68\ cm^{-1}}{3.84\ cm^{-1}} = \dfrac{12.0000\left(m_{^{13}C} + 15.9994\right)}{m_{^{13}C}\left(12.0000 + 15.9994\right)}$.

Solving the equation, we have the isotopic mass of $m_{^{13}C}$ = 12.9438.

Q 23(a) The fundamental and first overtone transitions of $^{12}N\,^{16}O$ are centre at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Calculate the exact zero point energy of the molecule. (3)

Ans. We have $\bar{\nu}_{fund} = \left(1-2x_e\right)\bar{\nu}_0$ and $\bar{\nu}_{1st\ over} = 2\left(1-3x_e\right)\bar{\nu}_0$, so $\dfrac{\bar{\nu}_{1st\ over}}{\bar{\nu}_{fund}} = \dfrac{\left(1-3x_e\right)}{\left(1-2x_e\right)}$. Putting the values, we get $\dfrac{3724.20\ cm^{-1}}{1876.066\ cm^{-1}} = \dfrac{\left(1-3x_e\right)}{\left(1-2x_e\right)}$. Now solving the equation, $x_e = 0.0069$.

Again, putting the value of x_e and $\bar{\nu}_{fund}$ in the relation $\bar{\nu}_{fund} = \left(1-2x_e\right)\bar{\nu}_0$,
we get $1876.066\ cm^{-1} = \left(1-2\times0.0069\right)\bar{\nu}_0$ or, $\bar{\nu}_0 = 1902.29\ cm^{-1}$.

The exact zero-point energy of the molecule, $\varepsilon_0 = \dfrac{1}{2}hc\bar{\nu}_0 - \dfrac{1}{4}x_e hc\bar{\nu}_0$. Putting the values, we get

$$\varepsilon_0 = \frac{1}{2} \times 6.627 \times 10^{-27}\, erg\ \sec \times 3 \times 10^{10}\, cm\ \sec^{-1} \times 1902.29\ cm^{-1} \left(1 - \frac{1}{2} \times 0.0069\right) = 1.88 \times 10^{-13}\, erg\ .$$

(b) The Raman shift of a given Raman spectrum line is independent of the value of the exciting frequency, ν_e . Explain. (2)

Ans. See the Text.

Q 24(a) What are meant by fundamental, overtone and hot band in vibrational spectroscopy? (3)

Ans. See CU 2010, Q 5(c), page .

(b) The wave number of the incident radiation in a Raman spectrometer is 20,487 cm^{-1} . What is the wave number of the scattered stokes radiation for the J = 0 to J = 2 transition of $^{14}N_2$ for which B = 1.99 cm^{-1} . (2)

Ans. See the Text.

PHOTOCHEMISTRY

Introduction:

Contents of the chapter

This chapter deals with the chemical reactions that result when the reacting substances are exposed to radiation. The activation of the reactant molecules is achieved by absorption of photon of appropriate energy. A photon of radiation, often called quantum, is the primary unit of radiation of energy $h\nu$, where ν is the frequency of radiation.

Absorption of visible and UV radiation supplies activation energy to the reactants.

These reactions are called photochemical reactions and are effected by absorption of radiation of visible and ultraviolet region of wavelength, approximately ranging from 1000 nm to 100 nm. The energy of the photon in this range varies from 35 kcal mol^{-1} to 286 kcal mol^{-1} which corresponds to the activation energy of the chemical reactions.

Radiation chemistry.

On the other hand, when photons of X-rays and γ-rays or high energy particles like α-particles, β-particles are used, they can ionize innumerable particles coming in their path. Their energies are so high that they can produce drastic or vast changes. These effects are studied in another chapter, called ‘radiation chemistry’.

Difference between photochemical reactions and thermal or dark reactions.

The differences between these two types of reactions are given below:

Photochemical activation and thermal activation.

(1) Photochemical reactions occur in presence of light and activation of reactant molecules is achieved by absorption of light energy (photochemical activation).

But thermal or dark reactions do not require the presence of light. Activation of reactant molecules is achieved from thermal energy of the molecules (thermal activation).

(2) Thermal reactions are always accompanied by the decrease of free energy ($\Delta G < 0$).

But photochemical reactions occur not only for the reactions with $\Delta G < 0$, but also for reactions with $\Delta G > 0$.

Absorption of light accelerates the rate of spontaneous reactions and can also make non-spontaneous reactions to occur spontaneously.

When spontaneous reactions ($\Delta G < 0$) occur photo chemically, light can act to speed up reaction i.e. it acts essentially as catalyst.

In the non-spontaneous reactions ($\Delta G > 0$), the radiant energy supplies the energy that can increase the free energy of the reactant molecules so that $G_{product} < G_{reactant}$ and

$$\Delta G = G_{product} - G_{reactant} = (-ve).$$

In photosynthesis of carbohydrate (non-spontaneous reaction, $\Delta G > 0$), under the action of sunlight and promoted by chlorophyll, CO_2 and H_2O are combined in plants to produce complex carbohydrate materials and O_2. On removal of light, the products oxidize slowly back to CO_2 and H_2O, releasing at the same time the energy accumulated from the sun’s radiations. Other non-spontaneous reactions that occurs photo chemically are

$3O_2 \rightarrow 2O_3$, dimerisation of anthracene : $2C_4H_{10} \rightarrow \left(C_{10}H_{10}\right)_2$,

decomposition of ammonia: $2NH_3 \rightarrow N_2 + 3H_2$, etc.

(3) Rate of the thermal reactions is highly influenced by the change of temperature.

The rate of thermal uncatalyzed reactions at any fixed conc. becomes doubles to trebles by the rise of 10^o temperature i.e. $\left({k_{T+10}}/{k_T}\right) \approx 2\ to\ 3$. (Arrhenius relation)

Thermal reactions are temperature-dependent while truly photochemical reactions are independent of temperature.

But the rate of truly photochemical reactions is not influenced by the change of temperature. Since activation energy is acquired not from thermal energy but from light, the rate of these reactions is dependent on intensity of the light used for irradiation.

The number of molecules activated is proportional to the intensity of light to which the reactant is exposed.

With sufficient intense light sources, it is possible to attain reaction rates at ordinary temperature which would not result thermally except at considerably elevated temperature.

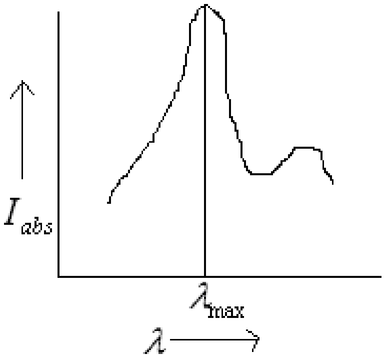
Any change of rate of photochemical reaction with temperature is due primarily to thermal reactions which follow the activated process.

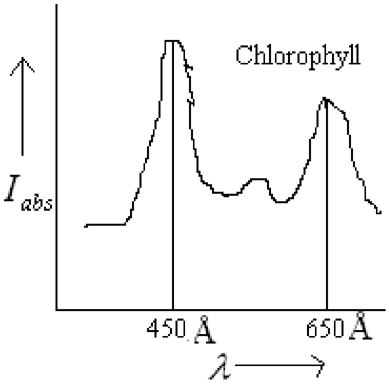
(4) More energy is often absorbed in photochemical reactions than it is required for activation, but this situation is rarely attained in thermal reactions.

Absorption of light:

Every substance has specific absorption peaks at certain wavelengths, called $\lambda_{\max}$

When light is passed through a solution or a given liquid, absorption does not occur at all wavelengths (λ). Light is considerably absorbed at a particular wavelength within a small range. At the shorter or longer wavelength side, absorption is very small. Thus if we plot intensity of light absorbed (I_{abs}) against wavelength (λ), we obtain maximum absorption at a particular wavelength, called $\lambda_{\max}$. Every substance has got its specific absorption curve and particular $\lambda_{\max}$ values. Absorption of light is governed by Lambert-Beers law for solution of the light absorbing substance.





Lambert-Beer's law:

Statement of the law

The law states that 'the rate of decrease of intensity of radiation with thickness (l) of absorbing solution is proportional to the intensity of radiation (I) and to the conc. (c) of the solute in solution. That is,

Mathematical statement of the law

$$-\frac{dI}{dl} = k\,c\,I$$

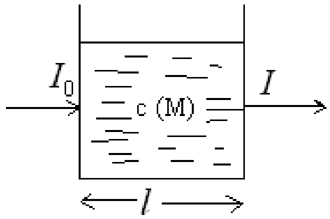
Where, c = molar conc. of the solution,
I = intensity of radiation and k is proportionality constant, called absorption coefficient of the solution.

Separating the variables and integrating, we get $-\int_{I_0}^{I}\frac{dI}{I} = kc\int_{0}^{l} dl$

Integrated form of the law

or, $\ln\frac{I_0}{I} = kcl$ or, $\log\frac{I_0}{I} = \left(\frac{k}{2.303}\right)cl$ or, $\log\frac{I_0}{I} = \varepsilon\, cl$,

where I_0 = intensity of incident radiation and
I = intensity of transmitted radiation.



Definition of the molar absorption coefficient (ε)

$k/2.303 = \varepsilon$, formerly called molar extinction coefficient but now called molar absorption coefficient or molar absorptivity of the substance. It depends on the nature of the substance that absorbs light and on the wavelength of the light used.
It may be defined as 'the reciprocal of thickness of one molar solution when the intensity of the incident radiation falls to one tenth of the initial value'.

Transmittance, opacity and absorbance

I_0/I is the opacity of the solution and I/I_0 is called transmittance.

$\log\frac{I_0}{I}$ = A, called absorbance or optical density of the solution.

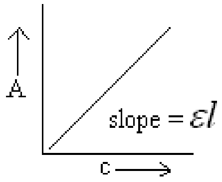
Absorbance (A) is extensive but molar absorptivity (ε) is intensive

A is an extensive property but molar absorption coefficient, ε is intensive one. Thus Lambert-Beer's law takes the simple form,

$$A = \varepsilon c l .$$

Determination of molar absorptivity of the substance (ε)

The absorbance (A) of the solution is measured by photocell, thermopile or chemical actinometer. The molar extinction coefficient (ε) is determined by plotting A vs. c and the value is obtained from the slope. For the purpose, solutions of different conc. of the light absorbing



substance are prepared and the absorbance is determined for these solutions using the light of wavelength, $\lambda_{\max}$ of the substance.

The intensity of light absorbed, $I_{abs} = I_0 - I = I_0 - I_0 10^{-\varepsilon c l} = I_0\left(1-10^{-\varepsilon c l}\right)$.

Beer's law for solution having several color absorbing solutes

For the solution containing several light absorbing substances, the Beer's law is

$$A = \varepsilon_1 c_1 l + \varepsilon_2 c_2 l + --- \quad or,\ A = \sum \varepsilon_i c_i l$$

where, ε_1, ε_2 are the molar absorption coefficient of the light absorbing solutes at a given λ of the light used and c_1, c_2 are their respective molar conc. of the solutes in the solution.

Magnitude of ε depends on the unit chosen for conc.

Magnitude of ε depends on the choice of conc. of the solution. If conc. is mol lit^{-1}, then unit of ε is the absorbance per unit length per unit conc. That is, unit of ε = cm^{-1} mol^{-1} lit.

Dimension of ε is $L^{-1} \times L^3 = L^2$.

When mol. wt of the solute is not known, % conc. is used.

When molecular weight of the solute is not known, conc. is expressed in % and $\varepsilon_{1cm}^{1\%}(325\,nm) = 30$ means that for the substance in solution at λ = 325 nm, a solution of 1% and length 1 cm has log (I_0/I) = 30.

The law forms the basis of spectrophotometric analysis.

From the value of ε and A, it is possible to determine the conc. of the light absorbing substance in solution and it is the basis of spectrophotometric analysis. The law is able to determine the conc. of the solution within error less than 1%.

Deviation:

Deviation originates when the structure of the solute is changed in solution.

This law holds good for wide range of conc. (a) unless the structure of the color substance is changed.

(b) Large amount of electrolyte may shift the absorption maximum and thus value of ε may be changed.

(c) Discrepancy may also be found when the color solute ionizes, dissociates or associates in solution and thus the nature of the species changes.

(d) Discrepancy also occurs when monochromatic light is not used.

Some related questions and answers:

Question (1) The optical density of a solution is never negative. – Why?

Answer: Optical density = log (I_0/I) is (+) ve always as $I_0 > I$, so I_0/I is greater than 1.

Question Find the dimension of molar extinction coefficient and write down its unit.

Answer: The dimension of molar extinction coefficient, $\varepsilon = A/cl = L^2$. Unit of ε is cm^{-1} mol^{-1} lit.

Question Complete the table

% T	Conc. (M)
50	0.001
60	—

Answer: 0.00074 (M)

Burdwan Univ. 1998

A dye solution of conc.0.01 g /cc absorbs 40% of blue light in a cell of thickness 1 cm. What would be the conc. to ensure 90% absorption in the same cell?

Answer: The absorbance, A = log (I_0/I) = log (100/60) = 0.2218. We have, $A = \varepsilon c l$.

Putting the values, 0.2218 = ε × 0.01 × 1 or, ε = 22.18 cm^{-1} g^{-1} cc.

Again for 90% absorption, log (100/10) = 22.18 × c × 1 or, c = 0.045 g/ cc.

Calcutta Univ. 1979

A 1×10^{-3} (M) solution of a dye (X) shows an absorbance of 0.20 at 450 mμ and an absorbance of 0.05 at 620 mμ. A 1×10^{-4} (M) solution of another dye (Y) shows 0.00 absorbance at 450 mμ and an absorbance 0.42 at 620 mμ. Calculate the conc. of each dye present together in a solution which exhibits an absorbance of 0.38 and 0.71 at 450 mμ and 620 mμ .respectively. The same cell is used in all measurements and its thickness is 1.00 cm.

Answer: For the dye (X), 0.20 = $\varepsilon_X\left(450\,m\mu\right)\times1\times10^{-3}\times1$ or, $\varepsilon_X\left(450\,m\mu\right)$ = 200 cm^{-1} mol^{-1} lit.

and 0.05 = $\varepsilon_X\left(620\,m\mu\right)\times1\times10^{-3}\times1$ or, $\varepsilon_X\left(620\,m\mu\right)$ = 50 cm^{-1} mol^{-1} lit.

For the dye (Y), 0 = $\varepsilon_Y\left(450\,m\mu\right)\times1\times10^{-4}\times1$ or, $\varepsilon_Y\left(450\,m\mu\right)$ = 0

and 0.42 = $\varepsilon_Y\left(620\,m\mu\right)\times1\times10^{-4}\times1$ or, $\varepsilon_Y\left(620\,m\mu\right)$ = 4200 cm^{-1} mol^{-1} lit.

For the mixture of the two dyes, $A=\varepsilon_X c_X l+\varepsilon_Y c_Y l$. Thus, 0.38 = 200 × c_X ×1 + 0 ×c_Y × 1

or, c_X = 1.9 × 10^{-3} (M).

Again, 0.71 = 50 × 1.9 ×10^{-3}× 1 + 4200 × c_Y ×1 or, c_Y = 1.46 ×10^{-4} (M).

Burdwan Univ. 1997

A mixture of dichromate and permanganate was analyzed spectrophotometrically at 440 nm and 545 nm as a means for simultaneous determination of these two species, and the observed absorbance values were 0.385 and 0.653 respectively at each wavelength for a 1.00 cm cell. Calculate conc. of dichromate and permanganate in the known mixture.

[Given, for Cr_2O_7'' : ε_{440} = 370 lit mol^{-1} cm^{-1} and ε_{545} = 10.8 lit mol^{-1} cm^{-1} and

for MnO_4' : ε_{440} = 92.8 lit mol^{-1} cm^{-1} and ε_{545} = 2350 lit mol^{-1} cm^{-1}]

Answer : $c_{Cr_2O_7''}$ = 4.71×10^{-4} (M) and $c_{MnO_4'}$ = 2.73 × 10^{-4} (M) .

Calcutta Univ. 2002

A 2 ×10^{-4} (M) solution of a dye when placed in a cell of 1.0 cm path length transmits 10.0% of 460 nm radiation incident on it. Calculate the value of the molar extinction coefficient of the dye. If the same solution be placed in a cell of 5.0 mm path length what would be its absorbance? Will the value of the molar extinction coefficient change if the measurement be made with 2 ×10^{-4} (M) solution in a 1.0 cm cell using radiation of λ = 500 nm? (5)

Answer: Ist part: A = ε c l, where, A = log (I_0/I). Putting the values, log (100/10) = ε × 2 ×10^{-4} × 1

or, ε = 5 × 10^3 cm^{-1} mol^{-1} lit.

2nd part: A = ε c l = 5 × 10^3 × 2 × 10^{-4} × 0.5 = 0.5.

3rd part: The molar absorption coefficient depends on the nature of the substance and the wavelength of the light used. Since the wavelength is changed in the experiment from 460 nm to 500 nm, the molar absorption coefficient (ε) of the substance will change.

Calcutta Univ. 2001

A light of wavelength λ having an intensity I_0 fall on a solution of conc. c and path length l. Write an expression for the intensity of light absorbed (I_a). Under what condition, will I_a be proportional to c? (3)

Answer:

1st part: The expression is given by Beer's law, A = ε c l, where, A = log (I_0/I).

Thus, log (I_0/I) = ε c l or, ln (I_0/I) = (2.303 ε) c l or, $I=I_0\,e^{-2.303\,\varepsilon cl}$.

But, $I_a=I_0-I$. Now putting the expression of I ,

we get, $I_a=I_0-I_0\,e^{-2.303\,\varepsilon cl}=I_0\left(1-e^{-2.303\,\varepsilon cl}\right)$.

2nd part: But when conc. c is low and ε is small in value,

$$I_a=I_0\left[1-\left(1-2.303\,\varepsilon cl---\right)\right]=\left(I_0\times2.303\varepsilon l\right)c=cons\tan t\times c$$

and I_a is proportional to conc. c.

Calcutta Univ. 2004

A 0.01 molar solution of a compound transmits 20% of the Na-D line when the absorbing path is 1.50 cm. What is the molar extinction coefficient of the substance? (2)

Answer: Beer's law is given as A = ε c l, where A = log (I_0/I) and ε is molar extinction coefficient of the compound

Thus putting the values, we have, log (100/20) = ε × 0.01 × 1.5 or, ε = 46.6 cm^{-1} mol^{-1} lit.

Calcutta Univ. 2014

Ethylene has a UV absorption peaks at 162 nm with molar absorption coefficient $\varepsilon = 1\times10^4$ cm^{-1} mol^{-1} lit. Calculate the absorbance of 162 nm radiation through a sample of ethylene gas at 25 °C and 10 torr for a cell of length 1 cm. (2)

Answer: We have Beer's law, $A = \varepsilon cl$.

But, $$c = \frac{P}{RT} = \frac{(10/760)\,atm}{0.082\,lit\,atm\,mol^{-1}K^{-1}\times 298K} = 5.38\times10^{-4}\,mol\,lit^{-1}.$$

Now the absorbance, $A = 1\times10^4\,cm^{-1}mol^{-1}lit\times5.38\times10^{-4}\,mol\,lit^{-1}\times1cm = 5.38$.

The laws of Photochemistry:

The photochemical reactions are governed by two basic laws. These are given below:

(1) The Grotthus – Draper law: This law states that

aThis law indicates qualitative relation between light energy absorbed and the subsequent chemical reaction occurred.

"Only those radiations which are absorbed can be effective in producing the chemical change."

However, it does not necessarily mean that the absorbed radiation will always bring about chemical change. The light absorbed may increase thermal energy and thereby temperature is increased. The absorbed radiation, in many cases, may be re-emitted in the form of resonance radiation, fluorescence and phosphorescence.

This law is purely qualitative and it does not indicate any relation between the absorbed light and the amount of chemical change.

(2) The Einstein's law of Photochemical Equivalence:

This law is quantitative one and is based on quantum aspect of light.

This law states that "Each of quantum of radiation absorbed activates one molecule in the primary step of a photochemical process."

The law states that each molecule takes one quantum of radiation for its activation and subsequent chemical reaction. Thus one molecule absorbs the entire quantum and the energy of the photon does not spread continuously over a number of molecules that are exposed to the light beam.

Efficiency of light energy to bring out chemical reaction is expressed by quantum yield.

This law is in a sense simply a quantum mechanical statement of the Grotthus - Draper law. It is, thus, another example of the break of classical mechanics.

This law is the quantitative formulation of the 1st law of photochemistry.

Einstein's law should not be interpreted to mean that one molecule would react per quantum of radiation but it means that only one molecule is activated by each quantum of radiation.

The efficiency of the absorbed light in bringing chemical change is expressed by a term, called quantum yield (φ). It is defined as

Definition of quantum yield of a photochemical reaction.

$$\text{Quantum yield } (\varphi) = \frac{Number\ of\ molecules\ reacting\ or\ formed}{Number\ of\ quantum\ of\ light\ absorbed}.$$

The energy corresponding to Avogadro number of photons (one mole photon) is called one einstein of energy. Thus the law can be stated as one mole of reactants will be activated by absorption of one einstein of radiation.

Definition of one einstein of light energy and its value in different units.

$$\text{One einstein of energy (E)} = N_A\, h\nu = {N_A hc}/{\lambda}. \text{ Where, c is the velocity of light.}$$

$$\text{or, one einstein} = \left(6.023\times10^{23}\,mol^{-1}\times6.625\times10^{-27}\,erg\ \sec\times3\times10^{10}\,cm\ \sec^{-1}/\lambda\right) erg\ mol^{-1} cm.$$

$$= \left(1.196\times10^{8}/\lambda\right)\ \text{erg mol}^{-1}\ \text{cm} = \left(2.86/\lambda\right)\ \text{cal mol}^{-1}\ \text{cm}.$$

One einstein energy is not an universal constant but it depends on the wavelength of light used.

$$\text{Thus, the quantum yield } (\varphi) = \frac{Number\ of\ moles\ reacting\ or\ formed}{Number\ of\ einstein\ of\ energy\ absorbed}.$$

Quantum yield is the rate of reaction per einstein absorbed in unit time in volume.

Therefore the quantum yield of a reaction is the number of moles of reacting or formed per einstein of energy absorbed. If unit time and unit volume of the reacting system are considered, then,

Quantum yield may also be viewed in different angle.

$$\varphi = \frac{moles\ reacting\ per\ unit\ time\ per\ unit\ volume\ (rate\ of\ the\ reaction)}{einstein\ of\ light\ absorbed\ per\ unit\ time\ per\ unit\ volume\ (I_{abs})} \quad \text{or,} \quad \varphi_X = \frac{d[X]/dt}{I_{abs}}.$$

In other words, it can be said that rate of a photochemical reaction is proportional to the intensity of light absorbed, I_{abs}, and the proportionality constant is quantum yield, φ. Thus for the reaction,

$$A + 2B \rightarrow C$$

$$\text{Rate of the reaction, } r = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[C]}{dt} = \varphi I_{abs}.$$

Though the intensity is the energy that falls on unit cross-sectional area per unit time, here I_{abs} is defined as the number of moles of photons absorbed per unit time and per unit volume.

φ is one in the primary step but overall photochemical reaction may have small or high value of φ

The quantum yield (φ) of a reaction may vary from small value to very high value. For the primary step (light absorbing step) of the photochemical reaction, generally the absorbed photon brings out the chemical change of one molecule and so quantum yield (φ) is unity. The departure of φ from unity in a photochemical reaction is due to the nature of the secondary steps which follows from the primary step.

Reasons for high quantum yield:

The following reasons may be considered for $\varphi > 1$.

Secondary chain reaction may lead to high value of quantum yield.

(1) The products formed in the primary step may initiate chain reaction.

The example is photochemical formation of hydrogen chloride. $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$.

The primary step : $Cl_2 + h\nu \rightarrow 2Cl$ (light absorbing step).

The products of the primary step initiate the propagation step of the chain reaction.

The secondary steps : $Cl + H_2 \rightarrow HCl + H$ and $H + Cl_2 \rightarrow HCl + Cl$. ------

These propagation steps continue till the reactants are consumed.

The quantum yield of formation of HCl is at least 10^5 i.e. one photon absorbed can produce about 10^5 HCl molecules.

Secondary thermal reaction may lead to high quantum yield.

(2) The products of primary step may undergo thermal reactions in the subsequent secondary steps. The example is photo-decomposition of hydrogen iodide, $2HI \xrightarrow{h\nu} H_2 + I_2$.

The primary step: $HI + h\nu \rightarrow H + I$, the secondary steps are, $H + HI \rightarrow H_2 + I$ and $I + I \rightarrow I_2$.

One photon dissociates two molecules of HI, so quantum yield of decomposition of HI is 2 i.e., $\varphi_{HI} = 2$.

Activated molecule may collide with normal molecule and both are decomposed.

(3) The activated molecule in the primary step may collide with the normal molecule and then both are decomposed. The example is photodecomposition of NOCl:

Primary step: $NOCl + h\nu \rightarrow NOCl^*$ (activated).

The secondary step: $NOCl^* + NOCl \rightarrow N_2 + Cl_2$, and the quantum yield, $\varphi_{NOCl} = 2$.

Primary product may act as catalyst

(4) The formation of product in the primary step may act as catalyst in the secondary steps and thus rate of the reaction is enhanced and quantum yield is greater than one.

Secondary steps may be exothermic.

(5) In exothermic reaction, heat evolved may activate other molecules and these molecules are decomposed by thermal reaction.

Reasons for low quantum yield:

Followings are the reasons for $\varphi < 1$.

Photo-physical process

(1) The activated molecule in the primary step may be deactivated through resonance or fluorescence or phosphorescence (photo physical processes) and thus $\varphi < 1$.

Deactivation of activated molecule

(2) The activated molecule may undergo collision with other molecules so they are deactivated, only producing thermal energy and thereby temperature is increased.

Secondary inhibition reaction

(3) The secondary process may involve a step which uses the product molecule as one of the reactants (inhibition step). The example is in the decomposition of HI from H_2 and I_2 one step is inhibition step.

$HI + h\nu \rightarrow H + I$, $H + HI \rightarrow H_2 + I$, $I + I \rightarrow I_2$ and $H + I_2 \rightarrow HI + I$ (inhibition step).

Due to the last step, the quantum yield of decomposition of HI is less than 2.

Reverse of primary process

(4) The primary photochemical step may be reversed (recombination of free radicals).

$Br_2 + h\nu \rightarrow 2Br$ (primary step) but, $2Br \rightarrow Br_2$ (reverse step).

Exception to the Einstein's law

Note: Exception to the Einstein's law have recently been reported in simultaneous two quantum absorptions in system illuminated with intensive and coherent radiation from laser.

$$A + 2h\nu \rightarrow A^{**}.$$

Excimer and exciplex.

When the A^* (excited molecule) collide with an unexcited A or B molecule to form Excimer $(AA)^*$ and exciplex $(AB)^*$

$$A + A \rightarrow (AA)^{*} \quad \text{and} \quad A + B \rightarrow (AB)^{*}$$

These species are stable only in common in solutions of aromatic hydrocarbons. The Excimer and exciplex then undergo fluorescence, $(AA)^{*} \rightarrow 2A + h\nu$ or, $(AB)^{*} \rightarrow A + B + h\nu$ or non-radiative decay to 2A or A + B.

Related problems:

Calcutta Univ. 2000

(1) When acetone vapor is irradiated with light of wave length 3130 Å, it decomposes to form ethane and CO, $(CH_3)_2CO + h\nu \rightarrow C_2H_6 + CO$.

Using reaction cell of 60.3 ml capacity and a temperature of 56°C, irradiation for 23000 sec at a rate of 85200 erg sec^{-1} produced a change in pressure from 760.0 mm to 790.4 mm. Calculate (i) the number of acetone molecules decomposed and (ii) the quantum yield. (4).

Answer: Let n moles of acetone is taken initially and x mole of acetone is decomposed in 23000 sec.

So after decomposition, total moles = n – x + x + x = n + x.

At time, t = 0, $n = \frac{PV}{RT} = \frac{\left(\frac{760.0}{760.0}\right) atm \times 60.3 \times 10^{-3} L}{0.083\, L\, atm\, mol^{-1} K^{-1} \times (273+56) K} = 2.208 \times 10^{-3}\ mol$.

After 23000 sec, $n + x = \frac{PV}{RT} = \frac{\left(\frac{790.4}{760}\right) atm \times 60.3 \times 10^{-3} L}{0.083\, L\, atm\, mol^{-1} K^{-1} \times (273+56) K} = 2.296 \times 10^{-3}\ mol$.

The number of moles decomposed in 23000 sec (x) = (2.296 – 2.208) × 10^{-3} mol

= 0.088 × 10^{-3} mol.

The number of acetone molecules decomposed = 0.088 × 10^{-3} mol × 6.023 × 10^{23} mol^{-1}

= 5.3 × 10^{19}

Number of photons absorbed = $\frac{85200\, erg\, sec^{-1} \times 23000\, sec}{\left(\frac{6.625 \times 10^{-27}\, erg\, sec \times 3 \times 10^{10}\, cm\, sec^{-1}}{3130 \times 10^{-8}\, cm}\right)} = 3.08 \times 10^{20}$

The quantum yield = $\varphi = \frac{number\ of\ acetone\ molecules\ decomposed}{number\ of\ photons\ absorbed} = \frac{5.3 \times 10^{19}}{3.08 \times 10^{20}} = 0.17.$

BurdwanUniv. 2000

(2) In the decomposition of ethylene iodide, $C_2H_4I_2$ + $h\nu$ → $2C_2H_4$ + I_2 with radiation of 424 nm, the iodine formed after 20 min required 41.14 ml of 0.005 (M) sodium thiosulphate solution. The intensity of light source was 9.15 erg sec^{-1}. Calculate the quantum yield.

Answer: The reaction between sodium thiosulphate and Iodine is $2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$

The number of moles of iodine formed after 20 min. = $\frac{0.005 \times 41.14}{10^3} \times \frac{1}{2} = 1.0285 \times 10^{-4} mol$.

Rate of formation of I_2 = $\frac{1.0285 \times 10^{-4}}{20 \times 60} = 8.57 \times 10^{-8} mol\ sec^{-1}$.

The number of einstein absorbed = $\frac{9.15}{\frac{1.196 \times 10^{8}}{424 \times 10^{-7}}} = 3.24 \times 10^{-12}$.

The quantum yield, $\varphi = \frac{Number\ of\ moles\ iodine\ reacted}{Number\ of\ einstein\ absorbed} = \frac{8.57 \times 10^{-8}}{3.24 \times 10^{-12}} = 2.645 \times 10^{4}$.

BHU Adm to M.Sc. 2011

(3) In a photochemical reaction, A → 2B + C, the quantum efficiency with 500 nm light is 2×10^2 mol $einstein^{-1}$. After exposure of 300 m moles of A to the light,, 2 m moles of B is formed. The number of photons absorbed by A is

(1) 1×10^{18} (2) 3×10^{18} (3) 6×10^{18} (4) 9×10^{18} .

Answer

1 m mol of A reacts to give 2 m mol of B, so $2\times10^{2}=\dfrac{1\times10^{-3}\,moles\ A\ reacted}{number\ of\ einstein\ absorbed}$ . .

Solving, we get the number of einstein absorbed = $0.5\times.10^{-5}$.
Number of photons absorbed = $0.5\times.10^{-5}\times6.023\times10^{23}=3\times10^{18}$. Option (2) is correct.

IIT- JAM, 2011

(4) A photochemical reaction was carried using a monochromatic radiation (490 nm) of intensity 100 W. When the sample was irradiated for 30 min, 0.3 mole of the reactant was decomposed. Estimate the quantum efficiency assuming 50% absorption.

Answer

The energy of one photon corresponding to the wave length (490 nm) of radiation

$$h\nu = hc/\lambda = 6.625\times10^{-34}\,Js\times3\times10^{8}\,m\,s^{-1}/490\times10^{-9}\,m = 4.056\times10^{-19}\,J$$

Number photons absorbed in 30 min = $100\,Js^{-1}\left(50/100\right)\times30\times60\,s/4.056\times10^{-19}\,J=2.22\times10^{23}$

Quantum efficiency = $\dfrac{Number\ of\ molecules\ reacting}{Number\ of\ photons\ absorbed}=\dfrac{0.3\times6.023\times10^{23}\,molecules}{2.22\times10^{23}\,photons}=0.82$ ·

GRE Sample Question

(5) The yield of HCl from the photochemical reaction, $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ is found to be 3.0×10^{-3} mol when 1.5×10^{15} photons are absorbed. Which of the following statements explain the observation?

(A) The process requires multiphoton absorption.
(B) The process violates Franck – Condon principle.
(C) The fluorescence quantum yield is 1.00.
(D) The reaction is a chain reaction.

Answer.

The quantum yield, $\varphi_{\mathrm{HCl}}=\dfrac{Number\ of\ molecules\ reacting}{Number\ of\ photons\ absorbed}=\dfrac{3.0\times10^{-3}\times6.023\times10^{23}\,molecules}{1.5\times10^{15}\,photons}$.

$=1.2\times10^{6}$.

The high quantum yield is the indicative of chain reaction. The correct answer is (D).

Calcutta Univ. 2009

(6) The photo-dissociation of gaseous hydrogen iodide to form normal hydrogen and iodine atoms requires radiation of 4040 Å or less.

(i) Determine the molar heat of dissociation of hydrogen iodide,
(ii) if the radiation of 2537 Å is used, how much energy will appear as kinetic energy of the atoms. (4)

Answer.

One einstein energy of radiation is the molar heat of dissociation, HI since the one mole of HI is dissociated by the absorption of wave length, 4040 Å
So, the one einstein of energy of radiation of 4040 Å

$$=\frac{N_A hc}{\lambda}=\frac{6.023\times10^{23}\,mol^{-1}\times6.627\times10^{-27}\,erg\ \sec\times3\times10^{10}\,cm\sec^{-1}}{4040\times10^{-8}\,cm\times4.2\times10^{10}\,erg\ kcal^{-1}}=70.58\,kcal\ mol^{-1}.$$

Energy corresponding to radiation of wave length, 2537 Å = $70.58\times\left(\dfrac{4040}{2537}\right)=112.4\,kcal\ mol^{-1}$ ·

The kinetic energy that will appear = (112.4 – 70.58) kcal = 41.82 kcal.

Question:

The C = O bond energy in acetone is 728 kJ mol^{-1}. Will a light of 250 nm be able to break the bond? (2 ½)

Answer:

No. The energy corresponding to radiation of 250 nm = 478.4 kJ mol^{-1}, so it is less than the energy required to break the bond.

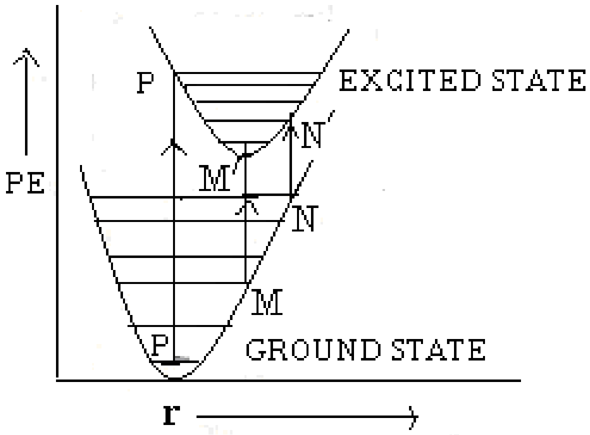
Primary processes in Photo-chemical reactions

Franck-Condon rule: when electron moves, internuclear distance remains unchanged in the molecule.

The primary process in photochemical reaction is the light-absorbing step which follows the law of photochemical equivalence. The photon in the region of visible and ultraviolet radiation absorbed by a molecule causes the electronic transition. The electronic transition follows *Franck-Condon rule* according to which, the time required for electronic excitation is so small that the internuclear distance remains unchanged during the excitation.

This is due to the fact that electronic movement is much more rapid compared to nuclear movements. The period for electronic transition (may be calculated roughly from Bohr's model, the time required to circle a hydrogen nucleus) is about 10^{-16} sec while vibrational period is of the order of 10^{-13} sec. This suggests that nuclei will not change their positions when electronic configuration changes. The spectral transitions are drawn vertical as shown in the figure PP', MM', NN', etc.

PE vs. internuclear distance(r) diagram showing *Franck-Condon principle*



Franck-Condon principle further states that an electronic transition would occur when the molecules in the lower electronic state are in their extreme positions such as M, N, etc except in the lowest vibrational level when the excitation starts from equilibrium position, (P).

This is due to the fact that quantum mechanical results show that in the lowest energy state, contrary to classical ideas, the most probable inter-molecular distance is that corresponding to the equilibrium position. For the higher energy states, quantum mechanical result is more like the classical result and most probable configuration is at the ends of the vibration, where the atoms must stop and reverse their direction.

Photo-physical processes

After absorption of photon in the region of visible or UV radiation, the energy rich excited molecule may undergo *photo-physical processes* by way of fluorescence and phosphorescence or resonance radiation. By these processes, the excited molecule re-emits radiation and comes back to its ground state. In many instances, the excess energy gained by the molecule may be transformed into heat energy by collision with other molecules and thereby temperature is increased.

The absorption of photon on the other way may lead to chemical reactions. Such behavior can be explained by the potential energy curves. Four types of *primary processes* are possible. These are given below:

Photo-chemical processes

Type I:

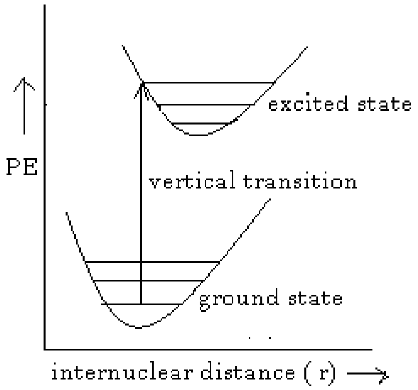
When the molecule in the higher electronic state also assumes a definite stable vibrational level as shown in the figure, there will be no direct dissociation of the molecule. The excess energy, in the usual course, may be dissipated by the *photo-physical processes* as outlined above. But the molecule may retain its energy until it can be used chemically. The spectrum will show fine structure.

(a) By combination with another molecule, such as

$$NOCl + h\gamma \rightarrow NOCl^*, \quad NOCl^* + NOCl \rightarrow 2NO + Cl_2$$

The photo chemically excited $NOCl^*$ collides with a normal NOCl molecule leading to chemical decomposition. The quantum yield (φ) = 2.

PE vs. r diagram for transition from ground state to stable vibration level of the excited state



Example of photosensitization

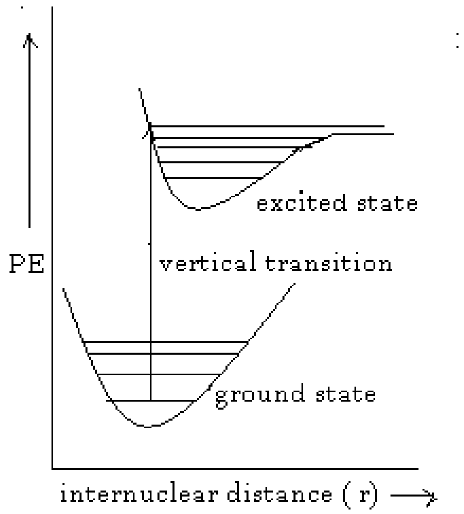
(b) By transferring the excitation energy to another molecule which in turn utilizes the energy for activation and produces the chemical change, such as, decomposition of oxalic acid by UO_2^{++} ion

$$UO_2^{++} + h\gamma \rightarrow (UO_2^{++})^* ; \quad (UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO + CO_2 + H_2O$$

The excited uranyl ion $(UO_2^{++})^*$ actually passes the energy to an oxalic acid molecule and the latter suffers decomposition.
This reaction is called photo sensitization reaction and (UO_2^{++}) is called photo sensitizer, acting the function of photochemical catalyst.

Type II:
If the molecule is raised to the higher electronic state and acquires a vibrational quantum level above the maximum stability level, the energy acquired is higher than the binding energy concerned, the molecule in the first oscillation will undergo dissociation. The spectrum will show continuum.

PE vs. r diagram for transition from ground state to excited state of above the vibration stability level.

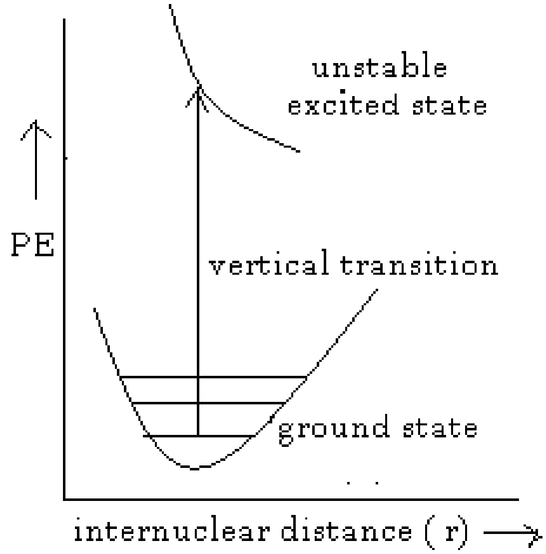


The product of dissociation may enter into a simple thermal chemical reaction or these may start chain reaction.

Example of photochemical chain reaction

(a) Thermal chemical reaction: Photo chemical decomposition of HI:
$HI + h\gamma \rightarrow H + I$: primary step (or light absorbing step)
$H + HI \rightarrow H_2 + I$, $I + I \rightarrow I_2$: secondary thermal steps.
Quantum yield = 2.
(b) Chain reaction: Photochemical combination of H_2 and Cl_2.
$Cl_2 + h\gamma \rightarrow 2Cl$: primary step (light absorbing step)
$Cl + H_2 \rightarrow HCl + H$; $H + Cl_2 \rightarrow HCl + Cl$; secondary chain propagation step.
The quantum yield (φ) is very high since the propagation steps continue till the reactants are exhausted.

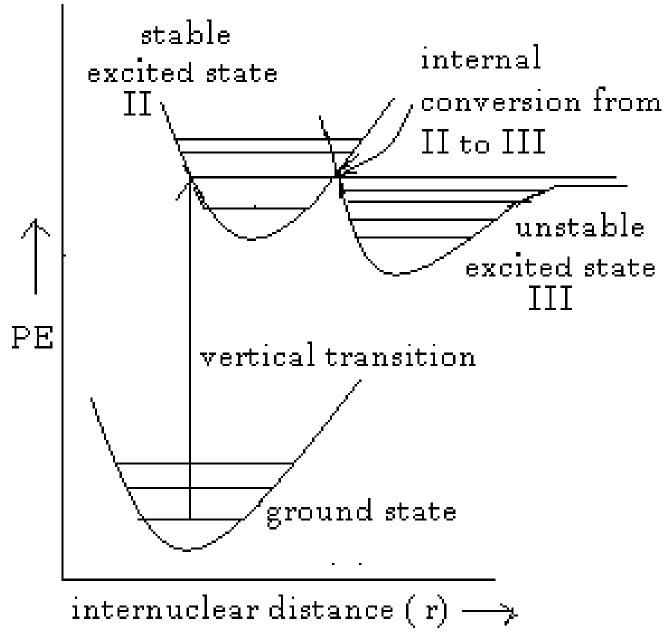
Type III:
The absorption of energy may raise the molecule to an electronic state which is quite unstable and the corresponding potential energy curve does not show any minimum. No sooner is the photon absorbed, the molecule breaks down into atoms and radicals. The fragments of dissociation are produced with different kinetic energy and a continuous spectrum is obtained without any fine structure.



PE vs. r diagram for transition from ground state to unstable excited state.

The products of dissociation may start secondary chemical changes as outlined in the type II.

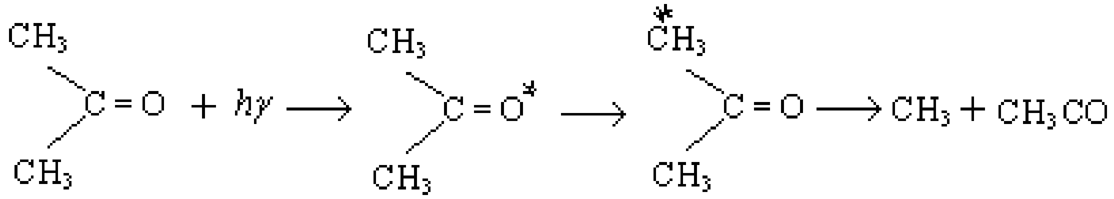
Type IV: Pre-dissociation:
Beside the above, the dissociation may occur in another way. In this case, stable and unstable upper levels overlap each other. Transition occurs from the lower level (I) to the stable upper level (II). During the course of vibration, the molecule may shift from the stable level (II) to the unstable level (III). When a shift of this type takes place, the molecule would dissociate producing atoms or radicals. The behavior is referred to as the pre-dissociation. The spectrum would show fine structure at lower levels of vibration followed by continuum: the latter may be followed by again fine structure.



PE vs. r diagram for transition from ground state to stable excited state and then to unstable state *(Pre-dissociation)*.

Photo-dissociation of acetone may be cited as example:

Example of photo-decomposition of acetone.



The photon absorption may primarily occur at C = O bond and subsequently on transfer, leads to the cleavage of C – C bond. The existence of free radicals has been experimentally detected. The secondary processes may follow as

$CH_3 + CH_3CO \rightarrow C_2H_6 + CO$; $CH_3CO \rightarrow CH_3 + CO$

That is, first excited electronic level of C = O is stable but that of C – C is relatively less stable and so latter is broken up by the absorption of radiation.

SOME TYPICAL EXAMPLE OF PHOTOCHEMICAL REACTIONS

(*A) Photochemical decomposition of hydrogen iodide ($2HI \xrightarrow{h\nu} H_2 + I_2$):*

Photochemical decomposition of HI is studied at wave length 282 nm and 253 nm.

The electronic spectrum of HI in the wave length region 200 nm to 330 nm shows continuum, indicating that HI molecule is dissociated in this λ - range by absorption of radiation.
The decomposition has been studied at 282 nm and 253 nm. The following mechanism has been suggested for the reaction (282 nm is equivalent to 101 kcal/mol).
Primary step: $HI + h\nu \rightarrow H + I$, rate = quantum yield (φ) × I_{abs} , but φ = 1 for the primary step and so rate = I_{abs} , it is the number of Einstein absorbed per unit time per unit volume of the reaction mixture.

Mechanism of the reaction

Secondary steps : $H + HI \xrightarrow{k_2} H_2 + I$; rate = $k_2 [H] [HI]$

$I + I \xrightarrow{k_3} I_2$; rate = $k_3 [I]^2$

However, this is followed by an inhibition step

Inhibition step: $H + I_2 \xrightarrow{k_4} HI + I$; rate = $k_4 [H] [\mathbf{I_2}]$

This step occurs when large amount of I_2 accumulates in the reaction vessel.
Following the above proposed mechanism, the rate of photo decomposition of HI is given as:

$$-\frac{d[HI]}{dt} = I_{abs} + k_2[H][HI] - k_4[H][I_2] \quad (1)$$

Using the steady state condition of H-atom, we get $\frac{d[H]}{dt} = I_{abs} - k_2[H][HI] - k_4[H][I_2] = 0$ (2)

Utilizing the relation (2), we get $-\frac{d[HI]}{dt} = 2k_2[H][HI]$. (3)

From the steady state equation of H-atom (2), $[H] = \frac{I_{abs}}{k_2[HI] + k_4[I_2]}$.

Rate equation of the reaction on the basis of the proposed mechanism.

Putting the expression of [H] in the equation (3), we have $-\frac{d[HI]}{dt} = \frac{2k_2[HI]I_{abs}}{k_2[HI] + k_4[I_2]}$

or, the rate equation for the photo decomposition of HI using the above proposed mechanism is:

$$-\frac{d[HI]}{dt} = \frac{2I_{abs}}{1 + \left(\frac{k_4}{k_2}\right)\frac{[I_2]}{[HI]}} . \quad (4)$$

Quantum yield (φ) of the reaction

The quantum yield of decomposition of HI is $\varphi_{HI} = \dfrac{\left(-d[HI]/dt\right)}{I_{abs}} = \dfrac{2}{1+\left(k_4/k_2\right)\dfrac{[I_2]}{[HI]}}$ (5)

Quantum yield = 2 at the initial stages of the reaction or when inhibition step is ignored.

This expression of φ_{HI} shows that at the initial stages of the reaction, $[I_2]/[HI]$ is small and

$$\varphi_{HI} = 2$$

but at the latter stages of the reaction, $[I_2]/[HI]$ is not negligible and so φ becomes less than 2.

If the inhibition step is ignored, then φ = 2 and independent of [HI]. However, I_{abs} is indirectly related with [HI] through Beer's law.

(B) Photochemical combination of H_2 and Br_2 ($H_2 + Br_2 \xrightarrow{h\nu} 2HBr$)

Br_2 is dissociated by absorption of radiation of $\lambda \le 510$ nm.

With the radiation of wave length (λ) less than 510 nm is reached, banded spectrum of Br_2 disappears and continuum is obtained. Bromine molecules are thus dissociated by the absorption of radiation of $\lambda \le 510$ nm (510 nm wave length is equivalent to 56 kcal/mol).
The mechanism of the reaction has been proposed as follows:

Mechanism of the photochemical reaction

Primary step: $Br_2 + h\gamma \rightarrow 2Br$; rate = I_{abs}, since φ = 1.

Secondary step: $Br + H_2 \xrightarrow{k_2} HBr + H$; rate = k_2 [Br] [H_2]

$H + Br_2 \xrightarrow{k_3} HBr + Br$; rate = k_3 [H][Br_2]

Inhibition step: $H + HBr \xrightarrow{k_4} H_2 + Br$; rate = k_4 [H] [HBr]

$Br + Br \xrightarrow{k_5} Br_2$; rate = k_5 $[Br]^2$

Following the above mechanism, the rate of formation of HBr is given as:

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (1)$$

Using steady state approximation of H and Br chain carriers, we get

$$\frac{d[Br]}{dt} = 2I_{abs} - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 = 0 \quad (2)$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0 \quad (3)$$

Formulation of the expression rate equation and quantum yield

Adding (2) and (3), we have $2I_{abs} = 2k_5[Br]^2$ or, $[Br] = \left(I_{abs}/k_5\right)^{1/2}$ (4)

Using equation (3) in equation (1), we have $\dfrac{d[HBr]}{dt} = 2k_3[H][Br_2]$ (5)

Now from equation (3) $[H] = \dfrac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} = \dfrac{k_2(I_{abs}/k_5)^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]}$ [from equation (4)]

Now putting [H] in equation (5), we get $\dfrac{d[HBr]}{dt} = \dfrac{2k_3k_2(I_{abs}/k_5)^{1/2}[H_2][Br_2]}{k_3[Br_2] + k_4[HBr]}$.

Or, the rate equation of the formation of HBr is $\dfrac{d[HBr]}{dt} = \dfrac{2k_2\sqrt{(I_{abs}/k_5)}\,[H_2]}{1+\left(k_4/k_3\right)\left([HBr]/[Br_2]\right)}$.

The quantum yield of the formation of HBr, $\varphi = \dfrac{rate\ of\ \ formation\ HBr}{I_{abs}} = \dfrac{\left(d[HBr]/dt\right)}{I_{abs}}$

or,

$$\varphi = \frac{2}{\sqrt{I_{abs}}} \times \frac{k_2\sqrt{\left(1/k_5\right)}\,[H_2]}{1+\left(k_4/k_3\right)\left([HBr]/[Br_2]\right)}.$$

From the above expression, it is clear that the rate of formation of HBr is proportional to the square root of light intensity (I_{abs}).

Critical discussion of the rate equation and the quantum yield

This mechanism is strictly applied at constant pressure. This is due to the fact that the reaction occurs from two moles of reactants to two moles of products i.e. volume remains constant and that becomes possible only if T and P are kept constant. If P changes, then volume changes and conc. can not be written as n/V.

Another point is to note that in spite of chain reaction, quantum yield of the photosynthesis of HBr is low (φ = 0.01) at ordinary temperature. This is due to the fact that the secondary step

$$Br + H_2 \xrightarrow{k_2} HBr + H; \quad rate = k_2 [Br] [H_2].$$

This step is slow due to high activation energy (≈ 18 kcal mol^{-1}) and so most of the bromine atoms produced in the primary step recombine to produce Br_2 molecules and thus giving low yield.

However, if temperature is increased, the rate of the step is also increased so the quantum yield of

$$\left(Arrhenius\ equation,\ k_2 = A_2\, e^{-E_2/RT} \right)$$

formation of HBr is increased. The recombination of Br-atoms (free radicals) is not affected by the increased of temperature.

It is interesting to note that as the intensity of radiation is increased, a greater proportion of the Br-atoms formed are converted into the Br_2. Thus most of the additional quanta are thus wasted and the process is less efficient (φ decreases).

(C) Photosynthesis of hydrogen chloride ($H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$)

Cl_2 is dissociated by absorption of radiation of $\lambda \leq 480$ nm.

It is one of the most interesting and perplexing photochemical reaction. When a mixture of chlorine and hydrogen is exposed to light, the continuous region of chlorine spectrum is obtained at the wavelength less than 480 nm. This indicates that chlorine is dissociated at $\lambda \leq 480$ nm and this is the primary step of this photochemical synthesis of HCl (510 nm wave length is equivalent to 56 kcal/mol).

The following steps may be suggested for the reaction.

Mechanism of the photochemical reaction

Primary step: $Cl_2 + h\nu \rightarrow 2Cl$; rate = I_{abs}, since the quantum yield = 1.

Secondary step: $Cl + H_2 \xrightarrow{k_2} HCl + H$; rate = k_2 [Cl] [H_2]

$H + Cl_2 \xrightarrow{k_3} HCl + Br$; rate = k_3 [H][Cl_2]

$Cl + wall \xrightarrow{k_4} destruction$; rate = k_4 [Cl]

The rate of formation of HCl is: $\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2]$ (1)

Applying steady state condition for conc. of H and Cl atoms, we have

$$\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] = 0 \qquad (2)$$

and $$\frac{d[Cl]}{dt} = 2I_{abs} - k_2[Cl][H_2] + k_3[H][Cl_2] - k_4[Cl] = 0 \qquad (3)$$

Adding equation (2) and (3), we get $2I_{abs} - k_4[Cl] = 0$ or, $[Cl] = 2I_{abs}/k_4$ (4)

By utilizing equation (2), the rate of formation of HCl becomes $\frac{d[HCl]}{dt} = 2k_2[Cl][H_2]$

Formulation of expression of rate equation and quantum yield.

Putting the expression of [Cl] from equation (4), the rate equation is:

$$\frac{d[HCl]}{dt} = 2k_2 \times \frac{2I_{abs}}{k_4} \times [H_2] \quad \text{or,} \quad \frac{d[HCl]}{dt} = \left(\frac{4k_2}{k_4}\right) I_{abs}[H_2]$$

The quantum yield of the formation of HCl, $\varphi = \dfrac{(d[HCl]/dt)}{I_{abs}}$ or, $\varphi = \left(\dfrac{4k_2}{k_4}\right)[H_2]$.

φ agrees well with experiment in absence of O_2 and when Cl_2 pressure is moderate.

The expression of φ is in agreement with the experimental results in absence of oxygen and when Cl_2 pressure is not too low. The rate is proportional to the intensity of the absorbed light and the H_2 pressure.

But when the chain termination step is the gas phase recombination of Cl-atoms with a third body, $Cl + Cl + M \xrightarrow{k_5} Cl_2 (M)$, the rate expression becomes $\dfrac{d[HCl]}{dt} = 2k_2[H_2]\left(\dfrac{2I_{abs}}{k_5[M]}\right)^{1/2}$

Expression of φ in presence of O_2

If a small amount of oxygen is present in the reaction mixture, the main chain termination step is $H + O_2 \rightarrow HO_2$ and this leads to the expression of rate $\dfrac{d[HCl]}{dt} = k\left(\dfrac{I_{abs}}{k_5[O_2]}\right)[Cl_2]$.

Calcutta Univ. 1997

The following mechanism has been proposed for the photochemical formation of HCl:

$Cl_2 + h\gamma \rightarrow 2Cl$ (rate = $\varphi_1 I_a$) ------- .(1), $Cl + H_2 \xrightarrow{k_2} HCl + H$ -----(2)

$H + Cl_2 \xrightarrow{k_3} HCl + Cl$ --------(3), $Cl \xrightarrow{k_4} \frac{1}{2} Cl_2$ ------------- (4)

Obtain the expression for the overall rate of formation of HCl. Comment on the quantum yield of the reaction.

Answer:

1st Part : See the note for the rate equation, $\dfrac{d[HCl]}{dt} = \left(\dfrac{2k_2\varphi_1}{k_4}\right) I_a[H_2]$.

2nd Part : Quantum yield of formation of HCl (φ) = $\dfrac{(d[HCl]/dt)}{I_a} = \left(\dfrac{2k_2\varphi_1}{k_4}\right)[H_2]$.

The comment is that quantum yield of formation of HCl (φ) is directly proportional to the conc. of H_2 .

(D) Photo dimerisation of anthracene ($2A \xrightarrow{h\nu} A_2$)

Observations of the experiment for dimerisation of anthracene

When a dilute solution of anthracene (A) in benzene or in other inert solvent, is exposed to UV light, the system exhibits fluorescence with small quantum yield (φ) of dimerisation of anthracene (A_2). As [A] is increased, the fluorescence falls off and quantum yield of A_2 increases towards to a limiting value and fluorescence is practically eliminated.

In other wards, fluorescence is quenched as the [A] is increased.

Experimental observations of the reaction are shown in figure

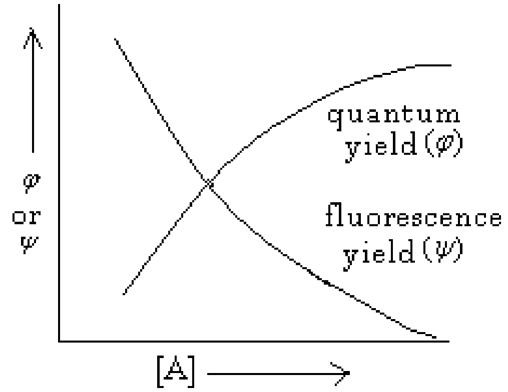


Figure shows the quenching of fluorescence exhibited by anthracene in solution

Qualitative argument to explain the observations

That is, when [A] is low, $\varphi \rightarrow 0$ but $\psi \rightarrow 1$ and when [A] is large, $\varphi \rightarrow 1$ and $\psi \rightarrow 0$.

This observation can be explained by the following qualitative argument:

When conc. of anthracene, [A] is low, there is little chance for the excited molecule to collide with normal anthracene molecule during the life-time of the excited state (10^{-8} sec).

The excitation energy is re-emitted in the form of fluorescence and the fluorescence yield (ψ) is high. But when the [A] is increased, the chances of collision of the excited molecules with normal molecules increases and thus quantum yield of formation of dimmer (φ) is increased and the fluorescence yield (ψ) is decreased.

Quantitative steps proposed to explain the observations

However this observation can be explained quantitatively by the proposed mechanism as outlined below:

Absorption step (primary step) : A + $h\gamma_e \rightarrow$ A* (excited anthracene)

Florescence step : A* $\xrightarrow{k_f}$ A + $h\gamma_f$ (energy of fluorescence photon)

Dimerisation or quenching step : A* + A $\xrightarrow{k_q}$ A_2 (dimmer anthracene)

Applying the steady state condition for the conc. of A*, we have

$$\frac{d[A^*]}{dt} = I_{abs} - k_f[A^*] - k_q[A^*][A] = 0 \text{ or, } \left(k_f + k_q[A]\right)[A^*] = I_{abs} \text{ or, } [A^*] = \frac{I_{abs}}{\left(k_f + k_q[A]\right)}.$$

Formulation of the expression of quantum yield (φ) and fluorescence yield (ψ)

The intensity of fluorescence, I_{fluor} is given by I_{fluo} = rate of the fluorescence step $= k_f[A^*]$.

The fraction of the excited molecules that fluoresce, is called the fluorescence yield (ψ) and is given as:

$$\psi = \frac{I_{fluor}}{I_{abs}} \quad \text{or,} \quad \psi = \frac{k_f[A^*]}{\left(k_f + k_q[A]\right)[A^*]} \quad \text{or,} \quad \psi = \frac{1}{1 + \left(k_q/k_f\right)[A]}.$$

This expression shows that as the conc. of anthracene, [A] is increased, the fluorescence yield (ψ) is decreased and when [A] is very high, $\psi \rightarrow 0$.

Again, the rate of dimerisation, $\frac{d[A_2]}{dt} = k_q[A^*][A]$, putting the expression of [A*], we get:

$$\frac{d[A_2]}{dt} = \frac{k_q[A]I_{abs}}{\left(k_f + k_q[A]\right)} \quad \text{or,} \quad \frac{d[A_2]}{dt} = \frac{I_{abs}}{1 + \left(k_f/k_q\right)/[A]}$$

The quantum yield of dimerisation, $\varphi = \frac{d[A_2]/dt}{I_{abs}}$ or, $\varphi = \frac{1}{1 + \left(k_f/k_q\right)/[A]}$.

Expressions of φ and ψ explains the observations quantitatively

This shows that as the conc. of anthracene, [A] is increased, the quantum yield of dimerisation of anthracene (φ) increases and when [A] is very high, φ tends to limiting value of one. However, the experimental value of φ is little less than unity due to the thermal dissociation of the dimmer, $A_2 \xrightarrow{thermal}$ 2A. This tends to decrease the quantum yield (φ) from unity. A typical value of φ for the reaction is 0.2.

Stern – Volmer relation :

Fluorescence intensity depends on the competition of fluorescence step and quenching step.

The intensity of fluorescence from an excited molecule A will depend on the efficiency of any competitive chemical quenching process. Let us consider the gas phase fluorescence from the excited anthracene molecule A* which is formed by, A + $h\gamma_e \rightarrow$ A*

This absorption step is followed by the second order quenching step, A* + Q $\rightarrow$ A + Q, with rate coefficient, k_q in competition with the fluorescence step with intensity of fluorescence, I_{fluor}

A* $\rightarrow$ A + $h\lambda_f$, with rate coefficient, k_f.

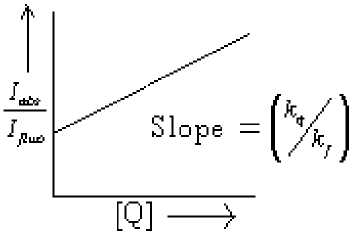
$$I_{fluor} = k_f[A^*], \text{ but } [A^*] = \frac{I_{abs}}{\left(k_f + k_q[Q]\right)}, \text{ thus } I_{fluo} = k_f \times \frac{I_{abs}}{\left(k_f + k_q[Q]\right)} \text{ or, } \frac{1}{I_{fluo}} = \frac{k_f + k_q[Q]}{k_f \times I_{abs}}.$$

This leads to Stern-Volmer relation between fluorescence intensity and absorption intensity as:

Ratio of absorption intensity and fluorescence intensity is shown by expression and also by graph.

$$\frac{I_{abs}}{I_{fluo}} = 1 + \left(k_q \middle/ k_f\right)[Q]$$

With increase of [Q], the fluorescence intensity is decreased and quenching step is dominated.



Calcutta Univ. 2007

The reaction A → B + C is supposed to proceed according to the following mechanism:

$$A + h\nu \rightarrow A^* ; A^* + M \xrightarrow{k_1} A + M : A^* \xrightarrow{k_2} B + C$$

Derive an expression for the quantum yield (φ) for the reaction. Plot $\frac{1}{\varphi}$ vs. [M]. (3+1)

Answer We have the expression of φ by using the steady state condition of $[A^*]$ as

$$\varphi = \frac{k_2}{k_2 + k_1[M]} \text{ and } \frac{1}{\varphi} = 1 + \left(\frac{k_1}{k_2}\right)(M) \cdot$$

Calcutta Univ. 2006

The reaction $2A \rightleftharpoons A_2$ occurs photochemically. The different steps in the reaction system are:
(i) $A \xrightarrow{h\nu} A^*$; (ii) $A^* + A \xrightarrow{k_2} A_2$; (iii) $A^* \xrightarrow{k_3} A + h\nu'$; (iv) $A_2 \xrightarrow{k_4} 2A$.
Applying the steady state concept to A^*, show that at photo stationary equilibrium, $[A_2] = \frac{I_{abs}}{k_4\left\{1 + \frac{k_3}{k_2[A]}\right\}}$. Also show that [A$_2$] is independent of [A] when A is in large excess. . (3+1)

Answer

Using steady state concept to A^*, we have $\frac{d[A^*]}{dt} = I_{abs} - k_2[A^*][A] - k_3[A^*] = 0$.

Or, $[A^*] = \frac{I_{abs}}{k_2[A] + k_3}$.

The rate of formation of the dimmer, $\frac{d[A_2]}{dt} = k_2[A][A^*] - k_4[A_2] = \frac{k_2[A] \times I_{abs}}{k_2[A] + k_3} - k_4[A_2]$

When the reaction attains photo-stationary equilibrium, $\frac{d[A_2]}{dt} = 0$, i.e. there is no change of A$_2$ with time. Thus, $\frac{k_2[A] \times I_{abs}}{k_2[A] + k_3} - k_4[A_2] = 0$ or, $k_4[A_2] = \frac{I_{abs}}{1 + \frac{k_3}{k_2[A]}}$ or, $[A_2] = \frac{I_{abs}}{k_4\left\{1 + \frac{k_3}{k_2[A]}\right\}}$.

When A is present in large excess, [A] is high and $\frac{k_3}{k_2[A]}$ is negligible small in comparison to 1.

So, $[A_2] = \frac{I_{abs}}{k_4}$ and $[A_2]$ is independent of [A].

Photochemical equilibrium or photostationary state

A reaction in which forward process is light sensitive but reverse process is thermal.

In reversible photochemical reactions, either or both processes may be sensitive to light. Let us first consider the reaction in which the forward reaction is light sensitive but backward reaction is light insensitive (dark reaction).

$$A + B \underset{thermal}{\overset{h\nu}{\rightleftharpoons}} C + D$$

The forward reaction occurs by absorption of radiation and as the reaction proceeds, the products are formed. The backward reaction starts and the rate of the backward reaction (R_b) is increased.

The rate of the forward reaction, (R_f) = $I_{abs.}$

But the rate of the backward reaction, (R_b) = k_2 [C][D].

R_f is constant if intensity of the radiation is kept constant. But R_b is increased as the products are being accumulated. Eventually a state is reached when

Formulation of photochemical equil^m.

R_f = R_b and equilibrium is attained.

Thus, at the equilibrium, I_{abs} = k_2 [C][D].

This equilibrium is called photochemical equilibrium. This differs from true thermal equilibrium. Now we see in details what the differences between photochemical equilibrium and thermal equilibrium are:

Comparison between thermal equil^m. and photochemical equil^m.

(1) Unlike the thermal equilibrium, the conc. of the products in photochemical equilibrium does not depend on the conc. of the reactants.

(2) If the source of the radiation is removed, forward light sensitive process stops and thermal process may occur but backward process continues and the equilibrium is changed and it shifts to true equilibrium or thermodynamic equilibrium. This is why the photochemical equilibrium is often called photostationary state.

(3) The photochemical equilibrium depends on the intensity of the radiation used but it does not depend on the temperature of the experiment. If temperature is increased, R_b is increased as the rate constant, k_2 is increased according to Arrhenius equation but R_f remains constant. With this higher rate of backward process, the products are depleted and the rate is decreased and becomes equal to the rate of the forward process. Thus, the equilibrium remains unaffected with change of temperature.

The examples of the this type of reaction are

(a) Dimerisation of anthracene (b) Decomposition of nitric oxide

$$2A \underset{thermal}{\overset{h\nu}{\rightleftharpoons}} A_2 \qquad 2NO_2 \underset{thermal}{\overset{h\nu}{\rightleftharpoons}} 2NO + O_2$$

The equilibrium constant, K_a remains constant for a fixed intensity of light and vary if the latter is changed. Further they do not correspond to the equilibrium constant obtained for reaction under purely thermal condition.

Absorption of light modifies the ΔG^0 of the reaction and hence the value of K_a

(4) In thermal equilibrium, the equilibrium constant (K_a) is related with standard free energy change of the reaction, $\Delta G^0 = -RT \ln K_a$ and $\Delta G^0 = G^0_{products} - G^0_{reactants}$ which again depends on the temperature at which the equilibrium exists.

But in photochemical equilibrium, these free energy relations are modified by the free energy supplied by light. Addition of the latter changes the ΔG^0 of the reaction and thereby also the equilibrium constant.

Reactions in which both forward and reverse processes are light sensitive.

Now let us consider the reactions where light affects both the forward and backward processes of the photochemical reactions.

$$A + B \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} C + D$$

The reaction occurs thermally at high T but photochemically it occurs at ordinary T.

The examples of this type of reactions are:

Dissociation of sulphur trioxide $2SO_3 \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} 2SO_2 + O_2$

(5) Both the direct and reverse reactions take place with appreciable velocity when exposed to UV light but in absence of light, it occurs with low velocity at ordinary temperature. Thermal equilibrium calculations show that to obtain 30% dissociation of SO_3 at 1 atm pressure, this substance must be heated to 630°C. On the other hand, it is found that photochemically SO_3 may be dissociated to the extent of 35% at 45°C.

Photochemical equilibrium is selective but thermal equil^m. is non-selective

(6) However photochemical equilibrium is selective towards absorption of radiation for activation energy but thermal reaction involves absorption of heat without selective for acquiring activation energy.

One application of photostationary state

The phenomenon of vision is explained by postulating a photostationary state. Light sensitive substance in the eye, called 'visual purple' is bleached forming 'visual yellow' on exposure to light, but it is regenerated in a thermal change with the result of photostationary state. In the dark, visual purple accumulates and results dazzle on exposure to light.

Photosensitization Reactions:

Light energy is absorbed in one species and reaction occurs in another species

In some class of reactions, the reactants are not sensitive to the light to which they are exposed and hence they do not take part in the primary step of absorption of radiation and subsequent dissociation. But if a suitable foreign substance is added to the reaction vessel in small amount, the reaction starts. In this case, the foreign substance absorbs light to which the reactants are exposed and gets excited. This excited foreign substance passes the energy to the reactant molecules which undergo dissociation. This class of reactions is called *photosensitization reactions* and the foreign substance is called *photo-sensitizer.*

Difference from catalyzed reactions:

Catalyst can accelerate only the spontaneous reaction but photo sensitizer can induce both spontaneous and non-spontaneous reactions

The photo-sensitizer, like catalyst, remains itself unchanged in mass and composition, and induces the change of the other substances. But the catalyst can not start a reaction, it can only accelerate the speed of the spontaneous reactions (in which $\Delta G < 0$), but photo-sensitizer can induce reactions not only spontaneous reactions but also in some non-spontaneous reactions (in which $\Delta G > 0$)

Most important example of photosensitization reaction involving an increase of free energy ($\Delta G > 0$) due to reaction is the photosynthesis of carbohydrate sensitized by chlorophyll.

Examples: (1) *Gas phase photo sensitization reactions*:

Photosensitization reaction between hydrogen and oxygen in presence of mercury vapor when exposed to radiation of $\lambda = 253.7$ nm leads to the formation of water and hydrogen peroxide.

Photo sensitization chain reaction between H_2 and O_2

Primary step: $Hg + h\gamma \rightarrow Hg^*$ (excited);

Secondary chain reaction: $Hg^* + H_2 \rightarrow Hg + 2H$;
Chain branching: $H + O_2 \rightarrow HO + O$ and $O + H_2 \rightarrow HO + H$;
Chain propagation: $OH + H_2 \rightarrow H_2O + H$;
Chain termination: $OH + OH \rightarrow H_2O_2$;

Energy corresponding to this $\lambda = 113$ kcal mol^{-1} and dissociation of H_2 requires 103 kcal mol^{-1}. Still the reaction does not occur in absence of mercury vapor as this radiation is not sensitive to H_2 gas. However, the mechanism is not yet clear.

(2) Liquid phase photo sensitization reactions.

Photosensitization reaction can be used in chemical actinometer to determine intensity of light

Decomposition of oxalic acid by uranyl ion is another example of photo sensitization reaction in solution. The reaction is used in chemical actinometer to determine the intensity of light experimentally. Uranyl ion acts as photo sensitizer. In absence of uranyl ion, quantum yield of decomposition of oxalic acid (φ) is very low and it is about 0.01 or less.

But when the oxalic acid with uranyl ion in solution exposed to radiation of λ ranging from 254 nm to 435 nm, φ becomes about 0.57 (average value)

$$UO_2^{++} + h\gamma \rightarrow (UO_2^{++})^* \text{ (excited)}; \quad (UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO + CO_2 + H_2O$$

(3) *Natural photo-sensitization reaction:*

Most important natural reaction for the survival of living organism

The typical example is the photo synthesis of carbohydrate in living plant in presence of chlorophyll by absorption of sun rays. Most plant and animal life on earth depends on this process in which green plants synthesize carbohydrate from CO_2 and H_2O. Chlorophyll contains a conjugated ring system that allows absorption of visible radiation and thus acts as photo sensitizer. The main absorption peaks of chlorophyll are at 450 nm (blue) and 650 nm (red). $6CO_2 + 6H_2O \xrightarrow[h\nu]{chlorophyll} (C_6H_{12}O_6) + 6O_2$

The reaction occurs in very complicated fashion and quantum yield, φ = 0.34. This reaction is non-spontaneous in absence of chlorophyll and $\Delta G^o = 688$ kcal mol^{-1}.

The reverse of this reaction provides energy for plants and animals.

Two main difficulties are encountered while dealing with this type of reactions.

These reactions face some difficulties

(i) It is difficult to propose the mechanism of the reactions and

(ii) It is difficult also to study the kinetics of the reactions.

Chemical actinometer:

Purpose of actinometry is to measure the intensity of radiation

Originally the term actinometry is used to designate the methods of measuring the solar radiations. At present the term means the method of measuring the number pf quanta or intensity of light used in the experiment.

The chemical actinometer uses several photochemical reactions of known quantum yield.

Oxalate actinometer:

This actinometer is popular for measuring the intensity of radiation within wave length of 254 nm to 435 nm. It uses the decomposition of oxalic acid photosensitized by uranyl ion. This ion absorbs the radiation of above wave length and gets excited. It transfers the absorbed energy to the oxalic acid which is then decomposed.

$$UO_2^{++} + h\gamma \rightarrow (UO_2^{++})^* \text{ (excited)}; \quad (UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO + CO_2 + H_2O$$

Reaction used in oxalate actinometer and its working principle

The amount of oxalic acid remaining after exposure can be determined by titration with standard $KMnO_4$ solution and the extent of decomposition is used to find the number of incident photons. The average quantum efficiency of the above reaction in the wave length region is 0.57. Thus knowing the amount of oxalic acid decomposed, the number of photons or einstein of energy absorbed can be determined.

Calculation:

$$\text{The quantum efficiency } (\varphi) = \frac{number\ of\ moles\ of\ oxalic\ acid\ decomposed}{number\ of\ einstein\ of\ light\ absorbed\,(E)}.$$

When 1 mole of oxalic acid is decomposed, it can be written: $0.57 = \frac{1}{E}$ or, $E = \frac{1}{0.57} = 1.75$.

It means that each mole of oxalic acid decomposed is equivalent to 1.75 einstein energy of the radiation. If time is noted for the exposure, intensity can be calculated.

Materials used in the actinometer:

Material used in the oxalate actinometer

The oxalic actinometer contains 0.04 (M) oxalic acid and 0.01 (M) uranyl sulphate solution mixture or in some cases, uranyl oxalate solution of appropriate conc. is taken as such.

Limitation of the method:

Limitation of the oxalate actinometer

Quantum yield (φ) for the process depends on the wave length (λ) of the light used. For example, φ of the reaction at 25 ^oC is decreased from 0.60 at 254 nm to 0.49 at 366 nm and then increased again to 0.58 at 435 nm. Thus the number of quanta absorbed per sec can be calculated from the value of wave length of the light used. This is done from the standard plot of φ vs. λ of the light.

Another limitation is that this method is used for a limited range of wave length of radiation from 254 nm to 435 nm only.

Related problems:

Problem 1: In a particular experiment, the actinometer contains 5.232 g anhydrous oxalic acid in 25 cc water together with uranyl sulphate. After exposure for 5 min, the remaining oxalic acid is titrated with 0.212 (M) $KMnO_4$ and 17.0 cc requires for complete titration of remaining oxalic acid. Calculate the amount of photon /sec and einstein /sec at this wavelength.
(Quantum efficiency of decomposition of oxalic acid at the wave length used is 0.53)

Solution: 17.0 cc 0.212 (M) $KMnO_4$ solution = $0.212 \times 17 \times 10^{-3} = 3.604 \times 10^{-3}$ mol of $KMnO_4$.
The reaction between $KMnO_4$ and oxalic acid is given by

$$2\,MnO_4^- + 5\,C_2O_4^{-2} + 16H^+ \rightarrow 2Mn^{+2} + 10\,CO_2 + 8\,H_2O$$

Thus, 3.604×10^{-3} mol of $KMnO_4$ is equivalent to $(5/2)\times3.604\times10^{-3} = 9.01 \times 10^{-3}$ mol oxalic acid.
The number of moles of oxalic acid decomposed = $(5.232 / 90) - 9.01\times 10^{-3} = 4.91 \times 10^{-2}$.
The number of einstein of radiation absorbed per sec = $(4.91\times10^{-2} / 0.53) / (5\times60)=3.09\times10^{-4}$.
The number of photons absorbed per sec = $3.09 \times 10^{-4} \times 6.023 \times10^{23} = 1.86 \times 10^{20}$.

Problem 2: In an experiment, the incident light of wave length 300 nm passes through an empty cell decomposes 6.201×10^{-3} mol oxalate ion in 2 hrs. When the cell contains acetone and it is irradiated for 10 hrs, it is found that 1.40×10^{-3} mol acetone is decomposed and the light that passes through the cell and not absorbed decomposes 2.631×10^{-2} mol of the oxalate. What is the quantum efficiency of the acetone decomposition?
(φ of uranyl oxalate is 0.570 at wave length 300 nm).

Solution:

$$I_{abs} = I_{incident} - I_{transmitted} \quad \text{But,} \quad I_{incident} = \frac{6.201\times10^{-3}}{0.57\times2} = 5.44\times10^{-3} \text{ einstein / hour.}$$

and

$$I_{transmitted} = \frac{2.631\times10^{-2}}{0.57\times10} = 4.61\times10^{-3} \text{ einstein / hour.}$$

Thus,

$$I_{absorbed} = 5.44\times10^{-3} - 4.62\times10^{-3} = 0.82\times10^{-3} \text{einstein / hour}$$

Thus the quantum efficiency of the acetone decomposition = $\dfrac{\left(1.40\times10^{-3}/10\right)}{0.82\times10^{-3}} = 0.17$.

Problem 3: Radiation of wave length 2540 Å was passed through a cell containing 10 ml of a solution of 0.0495 molar oxalic acid and 0.01 molar uranyl sulphate; after the absorption of 8.81×10^8 ergs of radiation, the oxalic acid was reduced to 0.0383 molar. Calculate the quantum yield for the photo chemical decomposition of oxalic acid at the given wave length. (4) **[CU, 2007, Q6(c)]**

Solution: Initial amount of oxalic acid = (0.0495 / 1000) × 10 = 0.000495 moles.
Final amount of oxalic acid after exposure = (0.0383 / 1000) × 10 = 0.000383 moles.
Amount of oxalic acid decomposed after irradiation = 0.000495 – 0.000383 = 0.000112 moles.

$$8.81\times10^8 \text{ erg of radiation } \equiv \frac{8.81\times10^8}{\left(1.196\times10^8 \big/ 2540\times10^{-8}\right)} = 0.000187 \text{ einstein.}$$

The quantum yield of decomposition of oxalic acid, $\varphi = 0.000112 / 0.000187 = 0.599$

PRIMARY PHOTO PHYSICAL PROCESSES:

Introduction:

What is meant by photo physical process?

When a molecule (A) is exposed to visible and ultra violet radiation, it is promoted to higher electronic state by absorption of radiation. If the molecule does not involve in photochemical reaction, it must return to its ground electronic state (S_o) through different photo physical processes. In these photo physical processes, the chemical identity of the molecule remains same but the excess absorbed energy is removed by different physical processes.

In gaseous system at moderate pressure, most energy is taken away by collision with environment molecules and radiation energy is converted into heat energy.

Different pathways for dissipation of excitation energy of the molecule

In condensed system or in gaseous state at reasonable high pressures, there are different pathways for the excited molecule to dissipate excitation energy. Some are intrinsic properties of the molecule and are unimolecular in which the excitation energy is re-emitted in the form of fluorescence and phosphorescence while others depend on external perturbations and may involve bimolecular collisions with environment.

Singlet (S) and Triplet (T) states:

These two terms represent the multiplicity of the spin vectors in spectroscopy and simply refers to the number of unpair electrons. If the systems have 0,1,2,3, etc. unpair electrons, it refers to singlet, doublet, triplet, quartet, etc.

Multiplicity of spin vectors

In molecules, generally the two terms, singlet and triplet are common with unpair electrons 0 and 2 respectively. These represent the multiplicity of spin vector (J) and is equal to $J = 2S + 1$, where S is the total spin quantum number of the molecule and is equal to $S = s_1 + s_2$.

Meaning of singlet term (S)

For an arrangement of opposite spins (↓↑), $s_1 = ½$ and $s_2 = -½$ and $S = 0$ hence the multiplicity, $J = 2S + 1 = 1$. Such an arrangement is represented by a single wave function and so gives rise to singlet state. The molecule is diamagnetic in the state due to absence of unpair electrons.

Meaning of triplet term (T)

For an arrangement of two parallel spins (↑↑), $s_1 = ½$ and $s_2 = ½$ and $S = s_1 + s_2 = ½ + ½ = 1$, and the multiplicity, $J = 2S + 1 = 3$. This corresponds to the three different orientations of the total spin vector along z-component ($M_s = 1, 0, –1$). These arrangements of parallel spin are represented by three degenerate wave functions in absence of magnetic field (one for each value of M_s) and give rise to triplet state (T). But the degeneracy is lifted when magnetic field is applied. The presence of unpair electron spins ascribes magnetic behavior in the molecule. The magnet moment observed in the molecule confirms the presence of two unpair electrons.

A triplet state (T) is always has a lower energy than the corresponding singlet state (S). This is roughly explained as two outer electrons have same spins, they can not come closer without violating Pauli Exclusion Principle. Since the electrons are further apart, there is a decrease in electronic repulsion and the energy of the molecule is lower.

Notations used:

Subscript and superscript of the terms, singlet and triplet

The singlet and triplet electronic levels are denoted by S and T respectively. Subscripts indicate the order of increasing energy, superscript indicates that the molecule is in higher vibrational level and so is having excess vibrational energy. Absence of superscript indicates that the molecule is in lowest vibrational level.

Jablonsky Potential Energy Diagram:

Description of the Jablonsky diagram

Let the system is initially in the ground state (S_o) with electrons in pair, called ground singlet state. Absorption of one quantum of radiation unpairs the electrons and promote to an excited electronic state, called first excited singlet (S_1^v).

The vertical axis measures the energy of the system while horizontal axis simply spreads the figure for clarity.

Radiative transitions are indicated by solid lines while non-radiative transitions by wavy lines. Because of Frank Condon principle, the molecule, after absorption of light, most likely is in an excited vibrational level. Collision with other molecules takes away this excess vibrational energy very rapidly and comes to zero vibrational level ($v = 0$) of the excited singlet state (S_1).

Allowed Electronic Transitions:

Quantum mechanical restriction for S → S and T→ S transitions

Quantum mechanically the allowed electronic transitions occur between the states of same spin multiplicity. A transition in which the spin is reversed is a forbidden transition. Thus, the singlet – singlet and triplet – triplet transitions are allowed whereas the singlet – triplet or triplet – singlet transitions are forbidden.
In some molecules, the singlet – triplet transition becomes weakly allowed as spin – orbit interaction in heavy atoms in the molecule can reverse the spins of the electrons.

Internal Conversion (IC) and Intersystem Crossing (ISC):

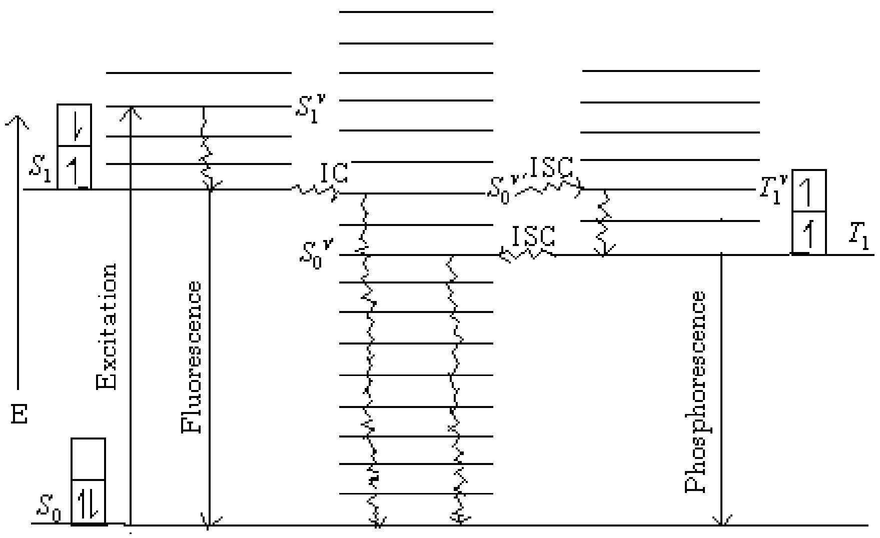
Radiationless transitions, IC and ISC

The crossing over of the molecule from singlet to singlet or triplet to triplet is known as internal conversion (IC) while that of singlet to triplet or vice versa is known as intersystem crossing (ISC). These IC and ISC are radiationless transition between two states and the rate of IC and ISC depends on the energy separation between the states involved. Larger the energy separation, lower is the rate.

Jablonsky Potential energy diagram:

This diagram is simplified sketch indicating different photo physical pathways, like photo excitation of the molecule, fluorescence, phosphorescence, internal conversion (IC) and intersystem crossing (ISC), etc.

Simplified sketch of Jablonsky PE diagram



Jablonsky PE diagram

Notations for various energy states of the molecule used in the diagram

Detailed notations in the diagram are given below:

S_0 = ground singlet (v = 0);

$S_0^{\,v}$ = ground singlet in higher vibrational level;

$S_0^{\,v'}$ = ground singlet in another higher vibrational level;

S_1 = excited singlet (v = 0);

$S_1^{\,v}$ = excited singlet in higher vibrational level;

T_1 = excited triplet (v = 0);

$T_1^{\,v}$ = excited triplet in higher vibrational level;

γ_f = frequency of the fluorescent light;

γ_p = frequency of the phosphorescent light.

The molecule after excitation can revert to the ground singlet state (S_0) by the three possible pathways as outlined below:

PATH I:

Let the molecule after excitation moves to excited electronic state of higher vibrational level, S_1^v (according to Franck-Condon principle). By collisions with other molecules, the excess vibrational energy is taken away by non-radiative process and the molecule comes to S_1.

Path I is fluorescence which is radiative transition

In non-radiative process, the environment acts as a heat sink for dissipation of extra energy as thermal energy. From this state, the molecule re-emits radiation and transits to the S_0 state. This radiative transition gives rise to fluorescence of energy ($h\gamma_f$). The frequency of the fluorescent radiation is less than that of excitation radiation since fluorescence occurs after some energy has been discarded into the solvent.

Since the transition $S_1 \rightarrow S_0$ is quantum mechanically permitted, it is very rapid it ceases almost immediately after the excitation radiation is switched off.

(Radiative life time, $\tau_o = \frac{1}{k_f}$ and $k_f = 10^6 - 10^9$ sec^{-1}, unimolecular reaction is 1st order and so life time is inversely proportion to the rate constant of the process.)

PATH II: The molecule from S_1 can cross to T_1^v through intersystem crossing (ISC) ($k_{ISC} = 10^4 - 10^6$ sec^{-1}) and then it follows rapid loss of excess vibrational energy through bimolecular collision with environment molecules and comes to T_1 . This is followed by radiative transition from $T_1 \rightarrow S_0$ ($k_p = 10^{-2} - 10^4$ sec^{-1}) with emission of phosphorescent radiation.

Path II is phosphorescence which is also radiative transition

The frequency of phosphorescent radiation is much smaller than that of incident radiation and slightly smaller than that of fluorescent light. That is

$$\gamma_p < \gamma_f < \gamma_e \text{ or, } \lambda_e < \lambda_f < \lambda_p$$

Since $T_1 \rightarrow S_0$ transition is forbidden by selection rule, the process of phosphorescence is slow and continued to even hours after the incident light is removed.

However, the intersystem crossing (ISC) is much slower and competes with the fluorescent emission in the molecule that exhibit phosphorescence.

This phosphorescent light is most intense for solid samples because environment then collides less effectively with the molecule. In that case, ISC step has time to occur as the singlet excited state slowly loses vibrational energy and falls past the intersection point.

The difference between these two radiative transitions is that fluorescence is an immediate conversion of absorbed light into re-emitted energy, but that in phosphorescence the energy is stored in some kind of reservoir from which it slowly leaks. Thus, phosphorescence is delayed fluorescence.

Path IIIA and path III B are non-radiative IC and ISC

PATH III A: Non-radiative internal conversion (IC) from $S_1 \rightarrow S_0^{v'}$ and rapid thermalisation of vibrational energy brings the molecule to S_0. There will be no emission of radiation in this pathway.

PATH III B: Reverse inter system conversion (ISC) may lead to $T_1 \rightarrow S_0^v$ level and then comes to S_0 by rapid thermal equilibriation with collision by other molecules. There is no emission of radiation in this pathway.

Various Rate Equations of the Photophysical Process:

Table shows the name of different processes, reactions and rate in photo physical pathways.

Process	Reactions		Rate
Excitation	$S_0 + h\gamma \rightarrow S_1$		I_{abs}
Fluorescence	$S_1 \rightarrow S_0 + h\gamma_f$	(path I)	$A_{10}[S_1]$
Internal conversion	$S_1 \rightarrow S_0$	(path III A)	$k_{IC}^S [S_1]$

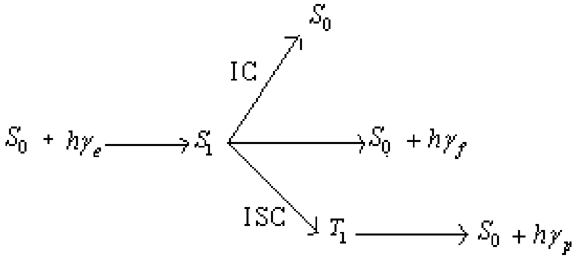
Fluorescence quenching	$S_1 + Q \rightarrow S_0 + Q$	(path III A)	$k_q^F[S_1][Q]$
Intersystem crossing	$S_1 \rightarrow T_1$	(path III B)	$k_{ISC}^S[S_1]$
Phosphorescence	$T_1 \rightarrow S_0 + h\gamma_p$	(path II)	$A_{TS}[T_1]$
Intersystem crossing (reverse)	$T_1 \rightarrow S_0$	(path III B)	$k_{ISC}^T[T_1]$
Phosphorescence quenching	$T_1 + Q \rightarrow S_0 + Q$	(path III B)	$k_q^P[T_1][Q]$

Where, k's are the rate constants for the various processes. A_{10} and $A_{T S}$ are the Einstein coefficients for spontaneous emissions. M = any atom or molecule that may be present.

Substances producing fluorescence and phosphorescence

Fluorescence producing substances are eosin, fluorescein, chlorophyll, etc.
Phosphorescence producing substances are ZnS and alkaline earth metal sulphides (generally called phosphor).
Sketch of the different pathways

Flow sheet of different pathways for dissipation of extra energy



Alternative Jablonsky PE diagram

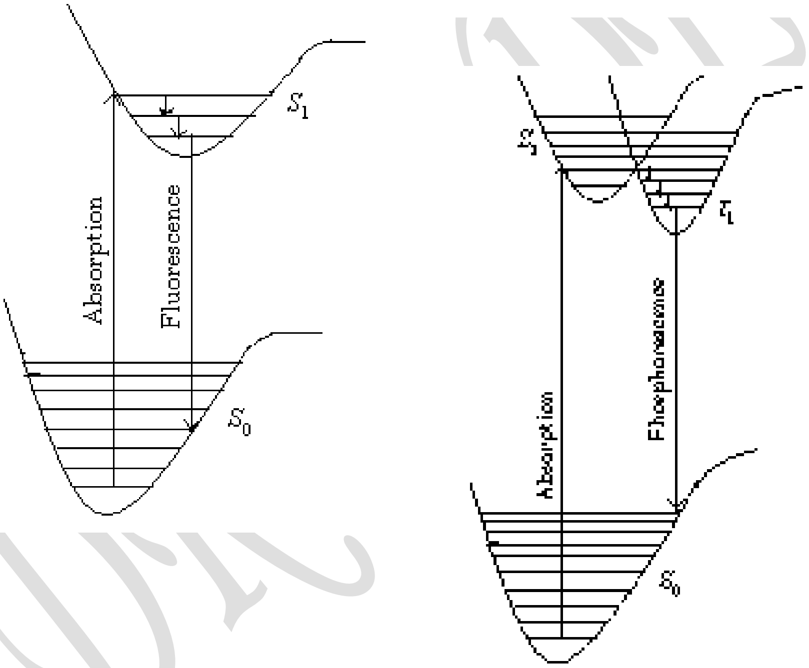


Fig.→ The alternative sketch of Jablonsky diagram showing fluorescence and phosphorescence.
Radiation occurs in a transition between states of the same multiplicity → Fluorescence and radiation emitted in a transition between states of different multiplicity → Phosphorescence.

Luminescence or Cold light:

The emission of visible light from a body due to some cause other than heat is called luminescence. It is the light without heat. It is of following type:

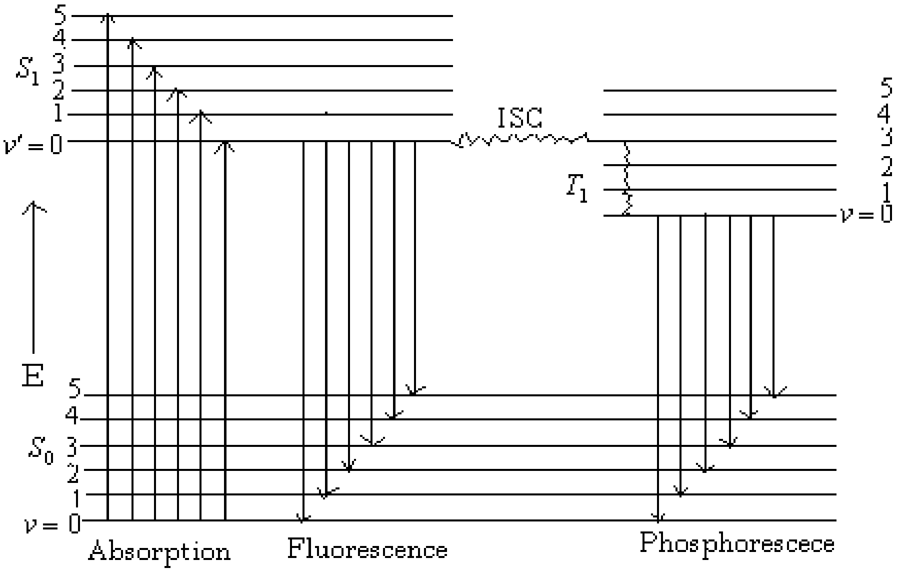
Different types of luminescence

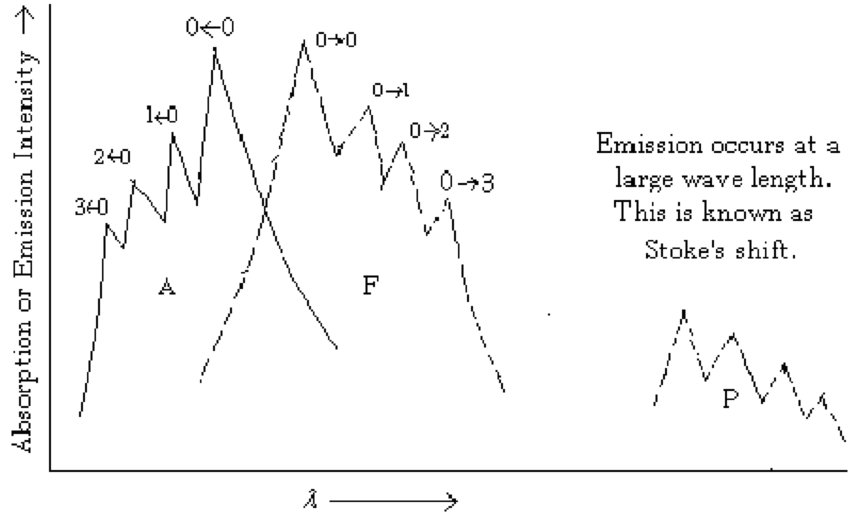
(1) Photoluminescence: This is caused by light and it is of two types (i) fluorescence (ii) phosphorescence.
(2) Chemiluminescence: This results from chemical reaction viz. oxidation of red phosphorus in aerial oxygen.
(3) Bioluminescence: It is observed in living organisms like fire fly or glow worm.

(4) Cathodoluminescence: It occurs when cathode is stimulated by bombardment of electrons.
(5) Electroluminescence: It results from the application of an electric field to matter.

Absorption and fluorescence spectra have approximately mirror-image relation:

As Radiative life time, $\tau_o = \frac{1}{k_f}$, hence the states that are populated rapidly are also depopulated readily. If only fluorescence is the process of emission (spontaneous) of an excited state, then the intensity distribution would be the same as that of absorption spectrum.
Absorption and fluorescence spectra have an approximately mirror-image relationship if the spacings of the ground state and excited state are similar.





Sketch of sequence of transition lines for absorption, fluorescence and phosphorescence

Burdwan Univ 2010

For a photochemical reaction 2A + B → 3C, express $\frac{d[A]}{dt}$ and $\frac{d[C]}{dt}$ in terms of I_a and quantum yield of φ. (2)

Answer:

Quantum yield $(\varphi) = \frac{\text{rate of the reaction}}{I_a} = \left(-\frac{1}{2}\frac{d[A]}{dt}\right)\Big/ I_a = \left(\frac{1}{3}\frac{d[C]}{dt}\right)\Big/ I_a$.

Thus $\left(-\frac{d[A]}{dt}\right) = 2\varphi I_a$ and $\frac{d[C]}{dt} = 3\varphi I_a$.

Burd. Univ. 2010 Mention the characteristic features of photochemical equilibrium. (2)

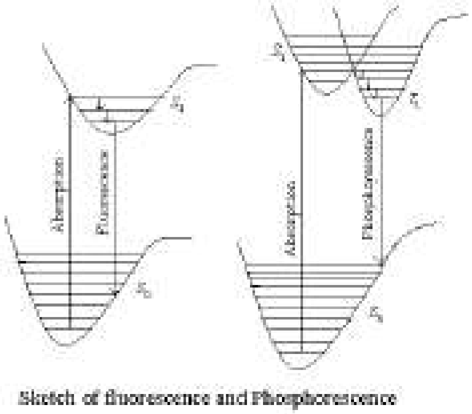
Answer: Let us start with photochemical dimerisation of anthracene (A) in which forward reaction is photochemical while backward reaction is thermal.

$$2A \underset{thermal(k_2)}{\overset{h\nu}{\rightleftharpoons}} A_2$$

As the product A_2 is formed by absorption of light, backward reaction also starts.
The rate of the forward reaction (R_f) = I_{abs} and the rate of the backward reaction (R_b) = $k_2[A_2]$
After sometime, $R_f = R_b$ and the reaction attains photochemical equilibrium.
Main characteristics of this equilibrium are given here:
(a) Equilibrium is not affected by temperature. It depends on the intensity of light absorbed.
(b) When radiation is withdrawn, equilibrium turns into thermal equilibrium. This is why it is called photostationary state.
(c) At equilibrium, $k_2[A_2] = I_{abs}$ and so the conc. of the product (A_2) does not depend on the conc. of the monomer (A).

Burd. Univ. 2010 What do you mean by 'Fluorescence' and 'Phosphorescence'? (2+2)

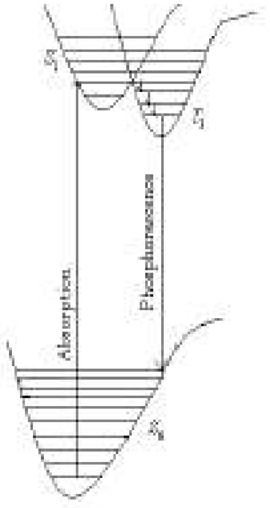
Answer: Fluorescence is the re-emission of radiation from an excited state to lower state of the molecule without spin reversal, i.e. from singlet to singlet or triplet to triplet.
Since these transitions are quantum mechanically allowed, fluorescence occurs immediately after the excitation and the process stops as soon as excitation source is switched off. The frequency of fluorescence radiation is smaller that of excitation.
Phosphorescence is also the re-emission of radiation from excited state to the lower state of the molecule with spin reversal, i.e. from triplet to singlet and from singlet to triplet. These transitions are not allowed quantum mechanically, so the process occurs very slowly and continues for long time even the excitation source is removed.
Phosphorescence is thus delayed fluorescence.



Sketch of fluorescence and Phosphorescence

Burd. Univ. 2013 Discuss 'intersystem crossing' and 'phosphorescence' in the context of a photophysical process. (2)

Answer: When a molecule is exposed to UV- VIS radiation, it absorbs radiation and promoted from ground singlet (S_0) to next higher singlet (S_1) following Franck-Condon principle. In its first vibration it shifts to the excited triplet (T_1) of higher vibration level through 'intersystem crossing'.
The excess vibrational energy is dissipated by collision with environment molecules and comes to ground vibration level of the triplet. Now the molecule re-emits energy in the form



of ‘phosphorescence’ and comes to ground singlet through triplet to singlet transition. This transition is not quantum mechanically allowed, so the process is slow and re-emission continues for later times after the excitation energy is stopped.

Burd. Univ. 2013

On passing monochromatic light through a 0.04 molar solution in a cell of 2 cm thickness, the intensity of the transmitted light was reduced to 50%.
Calculate the molar extinction co-efficient of the solution. (2)

Solution:

The Beer’s law is $\log\left(\frac{I_0}{I}\right)=\varepsilon c l$, the terms have usual meanings. Putting the data given,

we have, $$\log\left(\frac{100}{50}\right)=\varepsilon\times 0.04\, mol\, L^{-1}\times 2\, cm.$$

Solving, we get, molar extinction coefficient of the solution, $\varepsilon = 3.76\, L\, mol^{-1} cm^{-1}$.

Burd. Univ. 2013

Absorption and fluorescence spectra hold mirror image relationship – Comment. (2)

Answer:

See the text note, page. 26.

Burd. Univ. 2013

On irradiation of propionaldehyde at 30 °C with light having wavelength of 3020 Å, the quantum yield for CO is estimated to be 0.54. The intensity of incident light is 15,000 erg /sec. Find the rate of formation of CO. (3)

Solution:

The photo decomposition of propionaldehyde is $CH_3CHO \xrightarrow{h\gamma} CH_4 + CO$

The energy of one photon, $\varepsilon = \frac{hc}{\lambda} = \frac{6.625\times10^{-27}\, erg\, \sec\times 3\times10^{10}\, cm\, \sec^{-1}}{3020\times10^{-8}\, cm} = 6.58\times10^{-12}\, erg.$

The number of photons of incident light 15000 erg /sec = $\frac{15000\, erg/\sec}{6.58\times10^{-12}\, erg} = 2.28\times10^{15}\sec^{-1}$.

Now quantum yield, $\varphi = \frac{number\ of\ molecules\ CO\ formed\ per\sec}{number\ of\ photons\ absorbed\ per\sec}$.

Or, $number\ of\ molecules\ CO\ formed\ per\sec = 0.54\times 2.28\times10^{15} = 1.23\times10^{15}$

The rate of formation of CO = $= \frac{1.23\times10^{15}}{6.023\times10^{23}} = 2.04\times10^{-9}$ moles per sec.

TIFR, Adm. to Int. M Sc and Ph D, 2014

Phosphorescence is a slower process than fluorescence because
(A) phosphorescence occurs at longer wavelengths than fluorescence
(B) spin angular momentum is not conserved in phosphorescence process
(C) both A and B (D) none of the above **[Correct answer is B]**

Burd. Univ. 2014

Discuss “internal conversion” and “quantum yield” in the context of a photochemical process. (2)

Answer:

When the molecule shifts from singlet to singlet or triplet to triplet i.e. without spin reversal, the process is called internal conversion. The rate of the process depends on the energy separation between the two spin states. Greater is the energy separation, slower is the rate.
It is a non-radiative process.
Quantum yield (φ) of a photochemical process is defined as the ratio of number molecules reacting and number of photons absorbed. It provides the quantitative term defining the efficiency of the absorbed light for photochemical process. Higher the value of φ, greater is the efficiency of the absorbed light to yield more photochemical reaction.

Burd. Univ. 2014

Which of the following molecules would generate high phosphorescence quantum yield at low temperature? H_2O and $SeOCl_2$? (2)

Answer: SeOCl$_2$ molecule gives more phosphorescence quantum yield than H$_2$O. This is due to the fact that SeOCl$_2$ contains heavier atom Se and so in this case there will be easy spin reversal for greater spin-orbit interaction. Further at low temperature (below 11 ^{o}C), SeOCl$_2$ is in solid state and hence phosphorescence yield becomes more due to less collision with environment.

Burd. Univ. 2014

State and explain Franck-Condon principle. (2)

Answer: See the text.

Burd. Univ. 2014

Absorption of UV radiation decomposes acetone according to the reaction

$$(CH_3)_2CO \xrightarrow{h\nu} C_2H_6 + CO.$$

The quantum yield of the reaction at 280 nm is 0.2. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of $7.50\times10^{-3}\,J.\sec^{-1}$. Calculate the rate of formation of CO. (4)

Answer: Number of einstein energy absorbed per sec.

$$= \frac{Q\lambda}{N_A hc} = \frac{7.50\times10^{-3}\,J.\sec^{-1}\times280\times10^{-9}\,m}{6.023\times10^{23}\,mol^{-1}\times6.625\times10^{-34}\,J.\sec\times3\times10^{8}\,m\sec^{-1}} = 1.75\times10^{-8}\,mol\sec^{-1}.$$

Burd. Univ. 2015

Calculate the number of photons emitted in 1 s from a 100 W red lamp, assuming for simplicity that all the photons have an average wavelength of 694 nm. (2)

Answer: Number of photons emitted = $\frac{Q\lambda}{hc} = \frac{100\,J.\sec^{-1}\times694\times10^{-9}\,m}{6.625\times10^{-34}\,J.\sec\times3\times10^{8}\,m\sec^{-1}} = 3.49\times10^{20}\sec^{-1}$.

Burd. Univ. 2015

Write down the rate law for the photochemical reaction, $Cl_2 + h\nu \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Cl$. (2)

Answer: Rate of dissociation of Cl$_2$, $-\frac{d[Cl_2]}{dt}$ = Rate of forward reaction – Rate of backward reaction

$$= k_1 I_{abs} - k_2[Cl]^2.$$

So the rate law is given as $-\frac{d[Cl_2]}{dt} = k_1 I_{abs} - k_2[Cl]^2$.

Burd. Univ. 2015

In photobromination of cinnamic acid, radiation at 435 nm with intensity of $1.4\times10^{-3}\,J\,s^{-1}$ was 80.1% absorbed in a litre of solution during an exposure of 1105 s. The conc. of Br$_2$ is decreased by $7.5\times10^{-2}\,mol\;m^{-3}$ during this period. What is the quantum yield? (4)

Answer: Light energy, I$_{abs}$ = $\frac{1.4\times10^{-3}\,J.s^{-1}\times0.801\,litre^{-1}\times1105\,s\times435.8\times10^{-9}\,m}{6.023\times10^{23}\,mol^{-1}\times6.625\times10^{-34}\,J.s\times3\times10^{8}\,m\,s^{-1}} = 4.5\times10^{-6}\,mol\,lit^{-1}$.

Quantum yield, $\varphi = \frac{-\left(d[Br_2]/dt\right)}{I_{abs}} = \frac{7.5\times10^{-2}\,mol\times10^{-3}\,lit^{-1}}{4.5\times10^{-6}\,mol\,lit^{-1}} = 16.63$.

Burd. Univ. 2015

Photochemical equilibrium of dimerisation of anthracene ($2A \xrightarrow{h\nu} A_2$)may be represented by the following mechanism:

$$A + h\nu \rightarrow A^*;\ A^* + A \xrightarrow{k_2} A_2;\ A^* \xrightarrow{k_3} A + h\nu';\ A_2 \xrightarrow{k_4} 2A.$$

Apply steady state approximation on the conc. of A^*, calculate the rate of formation of A$_2$. Find the conc. of A$_2$ when the system is at photostationary state. (4)

Answer: Following the given mechanism, we have $\frac{d[A_2]}{dt} = k_2[A][A^*] - k_4[A_2]$. Now applying steady state approximation, we get $\frac{d[A^*]}{dt} = I_{abs} - k_2[A][A^*] - k_3[A^*] = 0$ or, $[A^*] = \frac{I_{abs}}{k_2[A] + k_3}$.

Putting in the rate equation, $\frac{d[A_2]}{dt} = k_2[A] \times \frac{I_{abs}}{k_2[A]+k_3} - k_4[A_2] = \frac{I_{abs}}{1+\left(k_3/k_2\right)/[A]} - k_4[A_2]$.

Thus the rate of formation of A_2 = $\frac{d[A_2]}{dt} = \frac{I_{abs}}{1+\left(k_3/k_2\right)/[A]} - k_4[A_2]$. But at the stationary state, $\frac{d[A_2]}{dt} = 0$, hence the conc. of A_2 at the stationary state, $[A_2] = \frac{I_{abs}}{k_4\left(1+\left(k_3/k_2\right)/[A]\right)}$.

Introduction: NMR spectra lie in the radio frequency region of electromagnetic radiation and it involves the reversal of spin angular momentum of the nucleus when kept in a magnetic field. This spectrum is very useful in elucidating the structure of molecules especially in the domain of organic chemistry.

Nature of nucleus: NMR spectroscopy deals with the interaction of nuclei with external magnet field. The protons and neutrons present in the atom spin on their own axis and each of them possesses angular momentum (1/2)$\hbar$ here 1/2 is the spin quantum number of each particle.

Each nucleus possesses a total spin angular momentum which results simply from the vector addition of the spin angular momentum of protons and neutrons. The net resultant spin angular momentum of the nucleus and its magnitude has certain discrete values i.e., it is quantized, that is

$$L = \sqrt{I(I+1)}\ \hbar,$$

where I is called spin quantum number of the nucleus or called nuclear spin.

Experimental facts show that

(1) A nucleus with an odd mass number has a half integral spin (i.e., 1/2, 3/2, 5/2, etc) .

(2) A nucleus with an odd number of protons and odd number of neutrons has an integral spin (1, 2, 3, etc).

(3) A nucleus with an even number of protons and even number of neutrons has zero spin (I = 0).

Thus: ^{1}H, ^{15}N, ^{19}F , ^{13}C have I = 1/2, ^{35}Cl has I = 3/2, ^{17}O has I = 5/2, and ^{2}H , ^{14}N have I =1 ^{10}B has I = 3. But ^{12}C, ^{16}O, ^{4}He have I = 0.

Angular momentum of the nucleus:

Angular momentum of the spinning nucleus is given by the relation, $L = \sqrt{I(I+1)}\ \hbar$. Again the angular momentum (L) is also space quantized i.e., it cannot have any arbitrary direction but can point only along certain directions. These directions are such that the component of L along certain reference axis (say, Z-axis) has only quantized values. The permitted values of Z-component of L (L_Z) are:

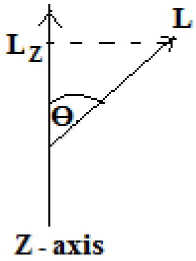
$$L_Z = m\,\hbar,$$

where m can take the following values:

(a) For integral values of I, m = - I, - (I-1), …0… + (I - 1), + I, and

(b) for half- integral values of I, m = - I, - (I - 1), …… - 1/2, +1/2, ……. +(I - 1), + I.

So there are total of (2I + 1) components for each value of I. These components are normally degenerate (i.e., all of them have same energy). But this degeneracy is lifted up when the nuclei is kept in an external magnet field and NMR spectroscopy originates due to this lifting up of degeneracy of energy.



$L_Z = L\cos\theta$ of which both L and L_Z are quantized and so θ can have only certain discrete values.

$L = \sqrt{I(I+1)}\ \hbar$ and $L_Z = m\hbar$, so $\sqrt{I(I+1)}\ \cos\theta = m$

For, ^{1}H, I = 1/2 and m = -1/2 and +1/2.

For ^{2}H , I = 1, and m = -1, 0, +1.

Magnetic moment of the nucleus:

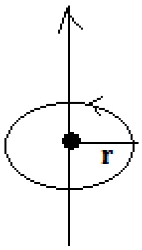
The spinning of a nucleus is equivalent to the circulation of positive charge around the axis of spinning. It produces a tiny magnet placed along the spin axis. The magnetic moment (μ_m) of the generated magnet is calculated by using **Ampere's law,** $\mu_m = i\,A$, where i = current strength,

A = area of cross section of the circular path.

i = (+ve) charge circulating per unit time.

= number of revolutions per sec × positive charge on the nucleus.

= $\dfrac{v}{2\pi r} \times pe$, where the nucleus of charge pe circulating with velocity v around the nucleus of radius r. p = number of protons present in the nucleus and e = electronic charge.



Thus, magnet moment, $\mu_m = i\,A = \dfrac{v}{2\pi r} \times \pi r^2 \times pe = \left(Mvr\right) \times \dfrac{pe}{2M} = L \times \dfrac{pe}{2M}$,

where M = nuclear mass and Mvr is angular momentum (L).

But $L = \sqrt{I\left(I+1\right)}\,\hbar$, hence, $\mu_m = \sqrt{I\left(I+1\right)} \times \left(\dfrac{p \times m_p}{M}\right)\left(\dfrac{e\hbar}{2m_p}\right)$, where m_p = mass of the proton.

Or, $\mu_m = \sqrt{I\left(I+1\right)}\left(\dfrac{p \times m_p}{M}\right) \times \mu_N$, where μ_N = nuclear magneton $= \dfrac{e\hbar}{2m_p}$.

μ_N is the magnetic moment of a single spinning proton (similar to Bohr magneton) and its value is:

$$\mu_N = \frac{e\hbar}{2m_p} = \frac{1.6\times10^{-19}C\times6.627\times10^{-34}J\,s}{2\times2\times3.14\times1.673\times10^{-27}kg} = 5.05\times10^{-27}\ J\big/\left(C^{-1}\times s^{-1}\times kg\right) = 5.05\times10^{-27}\ J/T\ .$$

$$(1\,Tesla = C^{-1}s^{-1}kg = A^{-1}s^{-2}kg = 10{,}000\ \text{Gauss})$$

Experimental evidence shows that a term, G (number) is required to include in the expression of μ_m. Though theoretical basis of G is not known, it is added to comply with the experimental results.

Hence $\mu_m = \sqrt{I\left(I+1\right)} \times \left(\dfrac{G\,p \times m_p}{M}\right)\mu_N$ or, $\mu_m = g\sqrt{I\left(I+1\right)}\ \mu_N$, where $g = \dfrac{G\,p \times m_p}{M}$,

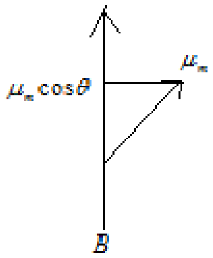
called g-factor that depends on the nature of the nucleus, while μ_N, nuclear magneton is a universal constant.

Potential energy of a nucleus in a magnetic field:

When a nucleus is placed in a homogeneous external magnetic field of strength B, it will behave as a tiny magnet and tend to orient itself with respect to the field. In that case, the potential energy is given by:

$$\in = -\left(\mu_m \cos\theta\right) \times B,$$

where $\mu_m \cos\theta$ is the component of the magnet moment along the axis of the field B and θ is the angle between the direction of magnetic moment (μ_m) and the external applied magnetic field (B).



$\mu_m \cos\theta$ = component of μ_m along B = $g\sqrt{I(I+1)}\cos\theta\,\mu_N$ = $g\,m\,\mu_N$,

as $\sqrt{I(I+1)}\cos\theta$ = m.

This component (m) has $(2I+1)$ orientations in space,

so m has $(2I+1)$ values. Thus the potential energy

$$\in = -gB\mu_N m$$

$\in$ is quantized and it can have certain discrete values.

Three cases may be distinguished on the sign of m.

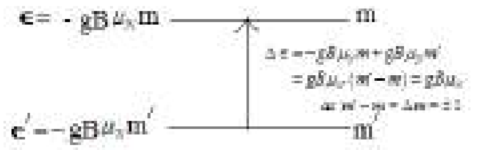
1. For negative value of m, the potential energy ($\in$) increases with the increase of magnet field (B). This is due to the fact that the orientation of the poles of the tiny magnet generated due to spinning motion of the nucleus is in the unfavorable position in the magnetic field (repulsive position).
2. For positive value of m, the potential energy ($\in$) decreases with the increase of magnet field (B). Here the orientation of the tiny magnet is in the favorable direction and this leads to more and more stabilized (attractive position) as the external field (B) is increased.
3. For zero value of m, the potential energy ($\in$) = 0. Here the orientation of the tiny magnet is perpendicular to the direction of the magnetic field (B).

Transition in magnetic energy levels:

Selection rule for the magnetic energy transition is: $\Delta m = \pm 1$.

Therefore, the energy gap between two adjacent magnetic energy levels is: $\Delta \in = gB\mu_N(\Delta m)$

or, $$\Delta \in = gB\mu_N .$$



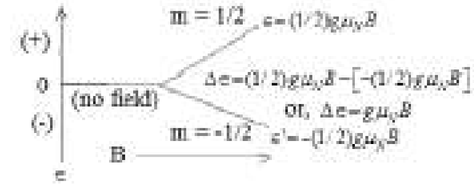
For such transition between two magnetic energy levels, the energy of the photon absorbed is $h\nu$ and thus

$h\nu = g\mu_N B$ and $\nu = (g\mu_N B)/h$, where ν is the frequency of the light absorbed for such transition and it depends on the magnetic field, B.

A typical magnetic field (B) of 1 T = 10,000 Gauss is easily attained in the laboratory and for ${}^1H$, $g = 5.585$, $\mu_N = 5.05\times10^{-27}\ J/T$, so the frequency of the light absorbed is calculated as, $\nu = \left(5.585\times5.05\times10^{-27}\ J/T\times1T\right)/6.627\times10^{-34}\,J\,s = 42.6\times10^{6}\,s^{-1}$, then $\nu = 42.6MHz$ that falls in the radio frequency region of electromagnetic radiation. [FM radio station broadcast from 88 to 108 MHz]

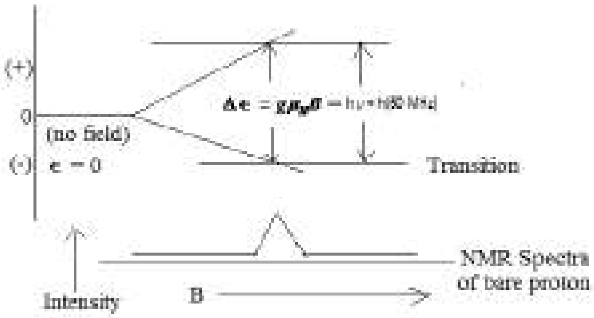
For bare proton (${}^1H$ nucleus), I = $1/2$ hence, so m = +1/2 and -1/2 (two orientations).

When the magnet field is applied, the energy is split up for these two orientations



The energy gap, $\Delta\in$ increases with the increase of B. When the energy of the photon is matched with the energy gap between two magnetic levels at the field strength (B), resonance builds up and the radiation is absorbed.

Either of the frequency of radiation (ν) or the external magnetic field (B) can be varied to match the energy of photon with the energy gap of the two levels but it is the usual practice to keep frequency of radiation fixed generally at 60 MHz and magnetic field strength (B) is increased. Resonance is built up when the equation $\nu = (gB\mu_N)/h$ is satisfied and energy transfer between the radiation and the nucleus occurs. Different kinds of nuclei (^1H, ^{13}C, ^{19}F, etc) have very different g - values, so their NMR absorption lines occur at very different frequencies. In a given experiment, one examines the NMR spectrum of only one kind of nucleus. We are considering only proton (^1H) NMR spectra.



Larmor precession:

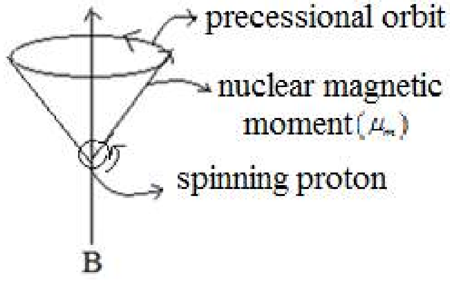
A spinning proton like the motion of a top in a gravitational field precesses around the field direction. This precessional motion results from the torque (defined as $\mu_m \times B$) on the angular momentum vector. This precessional motion of a proton can take place either parallel (shown in the figure) or antiparallel to the direction of the magnet field. This precession of a spinning charged body in a magnetic field is referred to as **Larmor precession.**

Frequency of Larmor precession,

$(\nu_0) = \dfrac{\mu_m \times B}{L}$ radians/sec. But $\mu_m = g\sqrt{I\left(I+1\right)}\,\mu_N$

and, $L = \sqrt{I(I+1)}\,\hbar$ so, $\nu_0 = \dfrac{g\sqrt{I\left(I+1\right)}\,\mu_N \times B}{\sqrt{I\left(I+1\right)}\,\hbar}$ radians/sec,

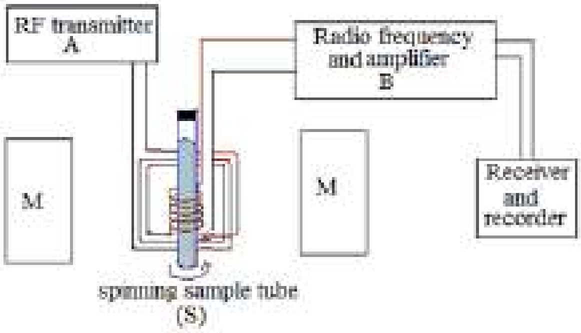
or, $\nu_0 = \dfrac{g\mu_N B}{\hbar} \times \dfrac{1}{2\pi}$ s^{-1} or, $\nu_0 = \dfrac{g\mu_N B}{h}$ Hz.



This is just equal to the frequency of radiation (ν) absorbed.

From the classical theory, it is supposed that when the frequency of radiation becomes equal to the frequency of Larmor precessional motion of the nucleus, it can interact and energy transfer occurs between radiation and spinning nucleus. The radio frequency beam is said to be in resonance with the magnetic nuclei and so the term is called **nuclear magnetic resonance**. However, the nuclei having I = 0 are NMR inactive. Further NMR spectra are obtained only in presence of external magnetic field while in vibrational and rotational spectra are obtained in absence of magnetic field.

Experimental set-up for NMR spectrometer: In 1946, Block and Purcell independently developed the experimental technique for study of NMR spectroscopy. The spectrometer consists of a tube (S) containing sample either liquid or solid placed between two poles of a huge magnet (M) of adjustable field strength. A coil (A) surrounding the sample emits a definite pre-adjusted radio frequency (40 – 60 MHz) from a transmitter, while another coil (B) picks up any radiation emitted. The latter is carried to a receiver and amplified and finally to a cathode ray oscillograph or recorder. The field strength (B) is gradually increased and radiation is only absorbed when the equation, $\nu_0 = g\mu_N B/h$ is satisfied for a given ν.



Schematic diagram of simple NMR spectrometer

When this condition is reached, there is resonance between two and absorption occurs. On further increase of field strength (B), there is no absorption until again a correspondence is reached. These absorptions are detected from oscilloscope or recorder.

PMR in organic compounds: In organic compounds, ^{12}C and ^{16}O are not magnetic active nuclei (I = 0), and these nuclei cannot interact with the external magnetic field, thus they do not show NMR spectroscopy. NMR spectra of organic compound are only due to the ^{1}H nuclei (proton) so it is called usually **proton magnetic resonance (PMR)** spectroscopy. The area under the PMR signals is directly proportional to the number of resonating ^{1}H nuclei in the organic compound. The position and area of PMR signal are the characteristics of the nature and number of ^{1}H nuclei present in the compound.

Chemical shift (δ): A proton (H^1) has only two magnetic energy levels and there is one energy level gap. so, we can expect one absorption peak in the resonance spectrum. But even at low resolution as many as two in CH_3OH and three in CH_3CH_2 OH absorption peaks are usually obtained. This is due to fact that different ^{1}H nuclei exist in different chemical environments in the molecule. The density of electron cloud around any particular nucleus is different in the different groups. The electronic field produces an induced magnetic field which acts in opposition to the external magnet field (B). Thus effective field (or actual field) observed by the nucleus is not equal to the external magnetic field (B) applied but a little less by a factor equal to the induced magnetic field produced by electron cloud surrounding the nucleus i.e.

$$B_{observed} = B_{applied} - B_{induced}.$$

But $B_{induced} \propto B_{applied}$ or, $B_{induced} = \sigma\, B_{applied}$, as induced field is directly proportional to the applied field. $B_0 = B - \sigma B = B(1-\sigma)$, where B_0 = actual field strength observed by the ^1H nuclei and B is applied field.

Hence $$\Delta \in = g\,B(1-\sigma)\mu_N$$

σ , is the screening constant that depends on the electron cloud density around the nucleus in a molecule. Larger the electron cloud density, greater is the value of σ and B_0 will be less for the nucleus.

Spacing of NMR signals is very close and could not be measured accurately. So NMR signal of ^1H nuclei is measured with respect to one reference substance and then multiplied by 10^6 to get a significant value. Variation of B_0 due to variation in the chemical (i.e., electronic) environment of the nucleus is called the chemical shift (δ) which is defined as,

$$\delta = \frac{B_{ref} - B_{sample}}{B_{ref}} \times 10^6\ ppm \quad ,$$

where B_{ref} and B_{sample} are the values of external magnetic field at which resonance occurs for H^1 nuclei present in the reference compound and the sample compound respectively.

Reference compound is dissolved in the same solution of the sample so that both are under the influence of the same external magnet field. The reference compound is universally selected for ^1H NMR in non-aqueous solvents is **tetra methyl silane (TMS)**, $(CH_3)_4Si$. The reasons for the selection are given below:

1. It gives a single intense peak, since the entire twelve nuclei ^1H are equivalent.
2. The ^1H nuclei in TMS are highly shielded as compared to those in organic compounds hence exhibit resonance at a very high field strength (1.4092 T for 60 MHz radiation) which can be easily recognized.
3. It has low boiling point (27^{o}C) and hence can be removed after the spectrum has been recorded. TMS also dissolves without reaction in most organic solvents.

Chemical shift (δ) is a dimensionless parameter and expressed in parts per million (ppm). It is independent of field strength (B). Chemical shift, (δ) for TMS is taken 0.0 ppm

Chemical shift is also denoted by τ which is defined by $\tau = 10 - \delta$. Thus for TMS, τ is 10.0 ppm.

Most organic molecules will have chemical shift between 0 and 10. For example, water has δ of about 4.7 ppm at ordinary temperature

NMR spectrum of CH_3OH:

Methyl alcohol (CH_3OH) has three identical C-H bonds and one O-H bond. The chemical environments of H-atoms in C-H bonds and O-H bond are different. Since O-atom is more electronegative than C, the electron density around H atom in O-H bond will be less than that on H atom in C-H bonds. That is, the shielding effect of H-nucleus in O-H is less than that of H-nuclei in C-H bonds

$$\sigma_{OH} < \sigma_{CH} \quad \text{hence,} \quad (B_0)_{OH} > (B_0)_{CH}$$

The observed (actual) field experienced by the hydroxyl proton will be greater than that by methyl protons. Now the spacing between two nuclear magnetic energy levels in presence of magnet field as

$$\Delta\epsilon = g\mu_N\, B_0$$

and it is greater for hydroxyl proton than that for methyl proton for the applied magnetic field (B). This effect will steadily increase with the increase of applied magnetic field. That is,

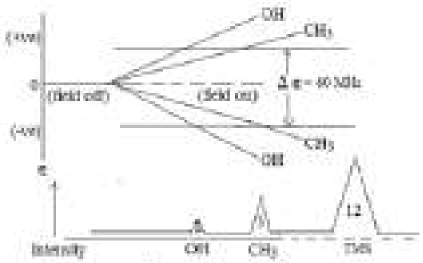
$$(\,\Delta\epsilon)_{OH} > (\,\Delta\epsilon)_{CH}.$$

Since NMR spectrometers are mostly operated by using a constant frequency oscillator (usually at 60 MHz) and varying the external magnet field, it is obvious that hydroxyl proton will be thrown into resonance at lower magnetic field than methyl protons as the external magnetic field is steadily increasing.

It means that hydroxyl proton will resonate at low end field and methyl protons at high end field.

The area under the signal of methyl protons will be three times larger than that under the hydroxyl proton. But area under TMS protons is twelve times than that of the hydroxyl proton. This is for the resonating protons in OH, CH_3 and TMS are 1, 3, and 12 respectively.

^{12}C and ^{16}O nuclei are NMR inactive as $I = 0$ for these nuclei.



NMR signals of CH_3OH with TMS
(under low resolution)

NMR spectrum of CH_3CH_2OH:

In ethyl alcohol (CH_3CH_2OH), we have three different types of protons
(1) hydroxyl proton (2) methylene protons and (3) methyl protons.

Out of these, the hydroxyl proton is expected to be least shielded as it is attached to the more electronegative O – atom. Consequently this proton will come into resonance at lowest end field. Out of the methylene and methyl protons, the H – atom in CH_2 group is expected to be less shielded than methyl protons as CH_2 group is directly attached to O – atom .Thus methylene protons will come into resonance earlier than those of methyl protons. Hence the NMR spectrum of CH_3CH_2OH will consist of three signals. The signal at the low end field is due to OH proton, at the high end field is due to methyl protons and in-between is due to methylene protons.

Area under the signals

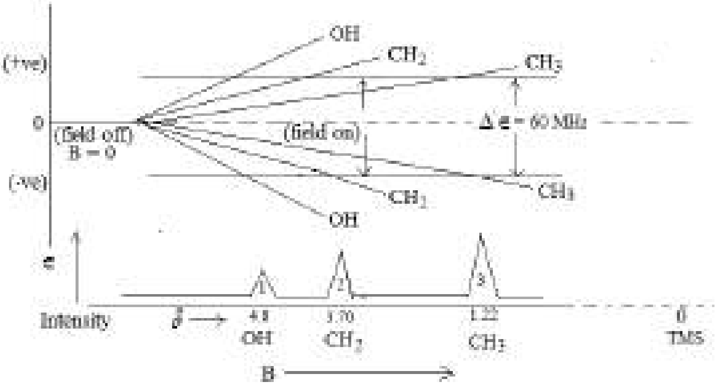
$OH : CH_2 : CH_3 = 1 : 2 : 3$.

Thus NMR studies reveal

(a) the presence of particular functional groups

(b) the relative number of nuclei present in the group and

(c) the relative positions of these groups from the multiplicities of the lines (under high resolution due to spin – spin splitting)



NMR signals of CH_3CH_2OH
(under low resolution)

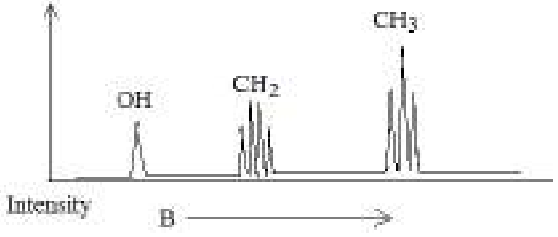
Spin – spin Splitting:

When NMR spectrum of CH_3CH_2OH is observed under high resolution, the lines in the spectrum are split into number of fine lines (multiplets).

The effect is caused by the interaction of the magnetic moments of one set of equivalent protons with those of another set.

This splitting is called spin – spin splitting.

However, equivalent nuclei of a particular set do not interact with one another because of selection rule.



In case of ethanol, the absorption peak due to CH_3 group is split into three components. This is due to the presence of neighboring CH_2 protons, each with spin 1/2.

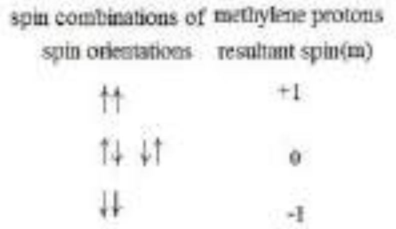
These protons in CH_2 group when coupled would produce three possible combinations.
1. Spins of both protons parallel to that of the methyl protons.
2. Spins of both the protons are antiparallel to that of the methyl protons.
3. Spin of first parallel and second antiparallel to that of methyl protons, and vice versa.

As a result of this pattern of coupling, the corresponding values of m will be +1, 0, -1 but zero value of m can be obtained in two ways. Possible spin combinations for the methylene protons are shown below:

The resonance absorption of methyl protons would therefore, be split into three peaks (a triplet) having relative intensities of 1 : 2 : 1.

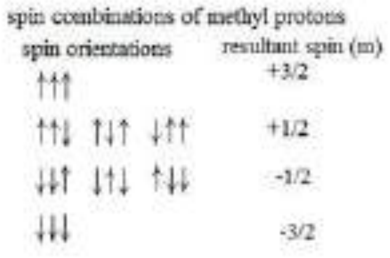
Similarly, the methylene (CH_2) protons are affected by three protons of neighboring CH_3 group. These three protons, each with 1/2 spin can couple in four different ways and corresponding m can have values, +3/2, +1/2, -1/2, -3/2. There will be four closely spaced spectral lines for the CH_2 group and the intensities of the spectral lines will be in the ratio 1 : 3: 3 : 1.

The hydroxyl proton is not affected by neighboring protons because it exchanges its position so rapidly with protons of other molecules that it does not produce splitting effect. Hence hydroxyl proton will have only one line.



spin combinations of methylene protons

spin orientations	resultant spin(m)
↑↑	+1
↑↓ ↓↑	0
↓↓	-1



spin combinations of methyl protons

spin orientations	resultant spin (m)
↑↑↑	+3/2
↑↑↓ ↑↓↑ ↓↑↑	+1/2
↓↓↑ ↓↑↓ ↑↓↓	-1/2
↓↓↓	-3/2

$$\text{Number of peaks in a group} = n + 1,$$

where n = number of equivalent protons in the adjacent group that interact with the proton being studied.

Intensities of the multiplets can be obtained from the co-efficient of the terms that result from the binomial expansion of $(1+x)^n$, where n = number of equivalent adjacent protons.

Thus for methylene group, number of peaks = 3 + 1 and intensities are obtained from the expansion of

$$(1+x)^3 = 1+3x+3x^2+x^3 \quad \text{so, the intensities are in the ratio } 1:3:3:1.$$

For methyl group, number of peaks = 2 + 1 = 3 and the intensities are obtained from the expansion

$$(1+x)^2 = 1+2x+x^2 \quad \text{i. e. in the ratio } 1:2:1$$

Some University Questions with Answers:

Q 1. What is nuclear magneton? Write an expression for the spin energy level of a nucleus having a nuclear spin I placed in a magnetic field, H. Compare the gap between the spin energy levels ^1H (I = 1/2) and ^2H (I = 1).

Ans. 1st part: Nuclear magneton (μ_N) is defined as, $\mu_N = \frac{e\hbar}{2m_p}$, terms having usual significance.

It the quantity used to define the magnetic moment of a spinning proton.

2nd part: The energy expression of spin energy level of a nucleus of spin I in a magnetic field H is given by $\in = -gH\mu_N\sqrt{I(I+1)}\cos\theta$, where θ is the angle between the magnetic moment and the filed direction. But $\sqrt{I(I+1)}\cos\theta = m$ that has values from $I, (I-1), ...-(I-1), -I$, so $\in = -gH\mu_N m$.

3rd part: For H^1 (I = ½), m = +1/2 and -1/2 , so the energy gap,

$\Delta\in = \left(\frac{1}{2}gH\mu_N\right) - \left(-\frac{1}{2}gH\mu_N\right) = gH\mu_N$, here $g = G\frac{pm_p}{M} = \frac{G\times 1\times m_p}{1} = Gm_p$

hence, $\Delta\in = \left(Gm_p\right)H\mu_N$.

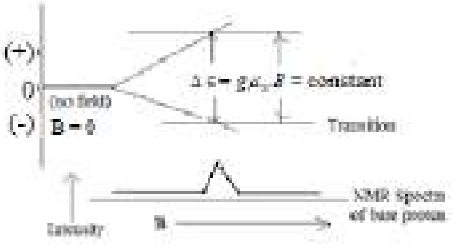
For H^2 (I = 1), m = 1, 0, -1. So the energy gap, $\Delta\in = \left(gH\mu_N\right) - \left(-gH\mu_N\right) = 2gH\mu_N$,

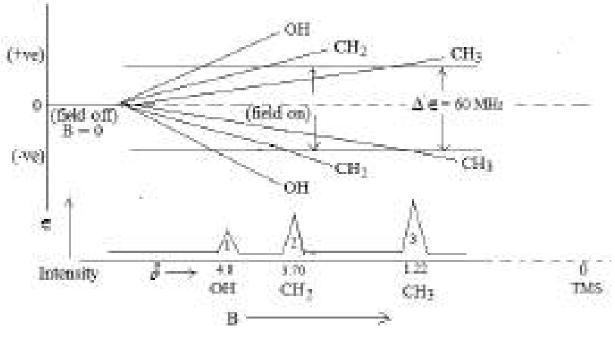
but $g = G\frac{pm_p}{M} = \frac{G\times 1\times m_p}{2} = \frac{1}{2}Gm_p$, hence $\Delta\in = \left(\frac{1}{2}Gm_p\right)\times 2H\mu_N = Gm_pH\mu_N$.

Thus the energy gap for ^1H and ^2H is same.

Q 2. How do the NMR spectra of a proton in chemical environment differ from that of a bare proton? Discuss with respect to the case of ethanol.

Ans. In case of bare proton, there is no electron cloud around the nucleus. The screening constant $(\sigma) = 0$. The applied field becomes same as the observed field. The NMR signal will occur at the lowest magnetic field of ^1H nuclei.





NMR signals of CH_3CH_2OH (under low resolution)

For ethanol, there are different types of ^1H nuclei from the viewpoint of electron cloud environment around the nucleus. $\sigma_{OH} < \sigma_{CH_2} < \sigma_{CH_3}$, hence $\left(B_0\right)_{OH} > \left(B_0\right)_{CH_2} > \left(B_0\right)_{CH_3}$. The energy gap of the different protons will be $\left(\Delta\in\right)_{OH} > \left(\Delta\in\right)_{CH_2} > \left(\Delta\in\right)_{CH_3}$ so hydroxyl proton will be thrown into resonance at lowest end of the magnetic field, methyl protons at the highest end and methylene protons at the middle end.

Q 3. What is nuclear magneton and nuclear g-factor?

Ans. The nuclear magneton, $\mu_N = \frac{e\hbar}{2m_p}$ and $g = G\frac{pm_p}{M}$. μ_N denotes the magnetic moment of bare proton and it is universal constant. g-factor is the property of the nucleus, where G is a number obtained from experimental data.

Q 4. The nucleus ^{13}C is NMR active but ^{12}C is not. Why?

Ans. Experiment shows that for nucleus with odd mass number, nuclear spin quantum number (I) = half integral and they are NMR active hence ^{13}C is NMR active while ^{12}C has even number of protons and even number of neutrons and I = 0. It is thus NMR inactive since magnetic moment μ_m of nucleus is zero.

Q 5. What is chemical shift in NMR spectroscopy? Sketch the NMR spectra that you expect to find for protons in ethanol (i) at low resolution and (ii) at high resolution. **Ans.** See the note, page 6 and 7.

Q 7. For an electron moving with a velocity v in a circular orbit of radius r, obtain expression for (i) angular momentum and (ii) magnetic moment.

Ans. (i) The angular momentum of the electron (L) is mvr, where m is the mass of the electron and (ii) magnetic moment according to Ampere's law $\mu_m = iA$, where i = current circulating per sec = number of revolution per sec × negative charge on the electron = $-\frac{v}{2\pi r}\times e$, A = area of cross section of the coil = πr^2. Thus, magnetic moment of electron,

$$\mu_m = \frac{v}{2\pi r}\times e \times \pi r^2 = \frac{evr}{2} ,$$

Q 8. Obtain an expression for Larmor frequency of precession of the proton around the applied magnetic field. **Ans.** The Larmor precession frequency is given by $\nu_0 = (g\mu_N B)/h$. See the text, page 4.

Q 9. NMR spectrum is said to quite different from the IR and electronic spectra. Discuss the most important point for this difference.

Ans. NMR spectra is obtained in presence of external magnetic field and it is used to split the energy levels. But for IR and electronic spectra, external magnet field is not required for absorption of radiation.

Q 10. Which of the following nuclei respond to NMR spectroscopy? $^1H,\ ^2H,\ ^{12}C,\ ^{13}C,\ ^{16}O.$ Give reasons in brief. **Ans.** $^1H,\ ^2H,\ ^{13}C$ respond to NMR spectroscopy as for the nuclei, $I \neq 0$. See text, page 1.

Q 11. In what position of the of the following energy scale does the NMR spectra belong? Far IR, IR, visible, UV, X-ray, none. Justify your answer. Ans. None, much larger wave length of radiation (radio wave) is required as the spacing of magnetic energy level is very small.

-- END --