Dr. Sangeeta Kumar

Department of Chemistry

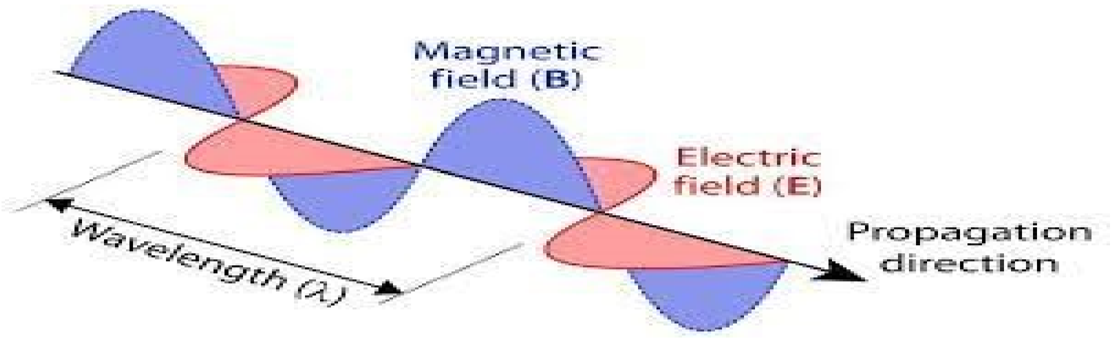
Sri Tika Ram Kanya Mahavidyalaya, Aligarh

SPECTROSCOPY

Spectroscopy is a study of interaction of electromagnetic radiation with matter. As a result of such an interaction, energy is either absorb or emitted by matter, thus, absorption or emission takes place in discrete amount called quanta.

This electromagnetic radiation has dual nature, both wave like and particle like. Electromagnetic radiation is made-up of protons, whose energy is given by the Planck's equation E = hν where 'h' is the Planck's constant.

The term electromagnetic radiation is used for radiant energy, starting from the lowest energy radiation called Radio waves, to the highest energy radiation, called gamma rays and cosmic rays. These rays travel with the velocity of light. There is an oscillating electric field and an oscillating magnetic field, in mutually perpendicular direction and perpendicular to the direction of propagation of light.



Following is the increasing order of energy of the electromagnetic radiation.

Energy increasing (Joules) →

Radio frequency region	Microwave region	Far IR near region	visible region	Ultraviolet region Near Far	X-rays	Gamma region
Radios, TVs, and transistors work in this region	Microwave oven works in this region	Sensation of heat	Colour seen due to this region of light	Forms ozone, responsible for skin cancer, tanning	Used for X-Rays of Bones and chest	
Change of nuclear spin takes place	Change of orientation takes place	Change of configuration	Change of electron distribution	Change of electron distribution	Change of nuclear configuration	
NMR Spectroscopy	Pure rotational or MW spectroscopy	Vib - Rot or IR spectroscopy	Visible Spectroscopy	UV –VIS spectroscopy	X-Ray crystallography	

Units of Energy used in Spectroscopy:

Unit of energy is joules. However, by convention other units of energy are also used such as wave number (cm^{-1}) or frequency (Hz).

Since $E = h\nu$ joules (1)

And since $\nu = \frac{c}{\lambda}$ (2)

$$E = \frac{hc}{\lambda} \qquad (3)$$

$$= hc\cdot\frac{1}{\lambda} \qquad (4)$$

$$= hc.\,\bar{\nu} \qquad (5)$$

$$\text{Or,} \quad \bar{\nu} = \frac{E}{hc} \qquad (6)$$

Where ‘c’ velocity of light is expressed in cm/s.

Thus, unit of wave number, $\bar{\nu}$ is cm^{-1}

The third unit of energy is Hz (frequency). where frequency $\nu = \frac{E}{h} Hz$

Thus, joules, wave number (cm^{-1}) and Hz are the commonly used units of energy.

Born Oppenheimer Approximation

A molecule has several energies, translational, rotational, vibrational, and electronic. The total energy can be represented as:

$$E_{total}=E_{trans} + E_{rot} + E_{vib} + E_{elec} \qquad (7)$$

It is interesting that $E_{rot} \approx 10^3\, E_{trans}$

$E_{vib} \approx 10^3\, E_{rot}$

$E_{elec} \approx 10^3\, E_{vib}$

Even more interesting is the fact that Translational energy is not quantized, while rotational, vibrational, and electronic energies are quantized.

Max Born and Oppenheimer suggested that the translational energy can be neglected and the total energy of a molecule can be given by

$$E_{total} \approx E_{rot} + E_{vib} + E_{elec} \qquad (8)$$

Equation (8) is called the Born Oppenheimer Approximation

When molecule absorbs energy in the microwave region, it gives rise to Pure rotational or Microwave spectroscopy. Absorption in Infra-red region is due to vibrational transition which is also accompanied by rotational transition, also called Vib-Rot or IR spectroscopy.

Microwave Spectroscopy

Spectroscopy in microwave region is associated with rotation of molecule. It is convenient to resolve the rotation of molecules through the central gravity about three mutually perpendicular directions. Thus, a body has three principal moments of inertia, one about each axis, designated as I_A, I_B, and I_C. Based on the moments of inertia of molecules, they may be classified as

1.**Linear molecule**: All atoms in such a molecule are arranged in a straight line. All homonuclear, heteronuclear diatomic molecules fall in this category as well as OCS, CO_2, HCN, HCl

The three directions of rotation would be

(a) Rotation about bond axis (b) and (c) end on end rotation in two mutually perpendicular direction,

Here, $I_A = 0$ and $I_B = I_C$

H-Cl, H-C≡N, O=C=S are the examples of this type of molecule.

2.**Symmetric top molecule**: in a tetrahedral molecule like CAB_3 like $CHCl_3$ OR CH_3F OR CH_3Cl, the rotation about the C-H, C-F or C-Cl bond will be like a spinning top and hence the name.

the rotation about these bonds will not be 0. Therefore $I_A \neq 0$ and rotation about the other two axis will be identical, $I_B = I_C$ but not equal to I_A.

Or $I_B = I_C \neq I_A$ and $I_A \neq 0$

3. **Spherical top molecule:**

When a molecule is spherically symmetrical or the three movements of inertia are identical, it is called a spherical molecule like CH_4, $CHCl_3$, CBr_4 etc.

Such molecule has no dipole and thus shows no rotational spectrum.

4. **Asymmetric top molecule:** Such molecule has the three moments of inertia different,

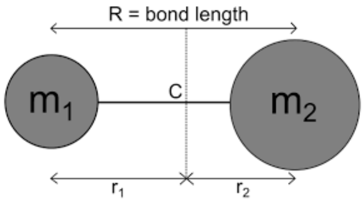
$I_A \neq I_B \neq I_C$

Example: H_2O. SO_2, etc.

Rotational spectrum: Rotational energy is quantized. This implies that only certain value of energy is allowed. The molecule cannot have any arbitrary value of rotational energy.

These values of energies can be calculated by solving the Schrodinger wave equation for the system represented by that molecule.

For simplicity, we shall consider the diatomic molecules. The treatment can be extended to symmetrical and unsymmetrical molecules.



Rigid Diatomic molecule:

Considering a simple diatomic molecule having two atoms of mass m_1 and m_2, separated by a distance r_0 . If the centre of gravity of the molecule is C, at a distance r_1 from the centre of the atom whose mass is m_1 and its distance from atom whose mass is m_2 is r_2 then,

$$r_1 + r_2 = R$$

We can show that $r_1 = \frac{m_2 R}{m_1+m_2}$

and $r_2 = \frac{m_1 R}{m_1+m_2}$

And the moment of inertia $I = \frac{m_1\, m_2\, R^2}{m_1+m_2} = \mu R^2$

Where $\mu = \frac{m_1 m_2}{m_1+m_2}$ μ is called the reduced mass of the system.

The Schrodinger wave equation has been solved for the rigid diatomic molecule and the allowed rotational energy levels are given by

$$E_J = h^2/8\pi^2 I.\ J(J+1) \qquad \text{where } J = 0,1,2,3,... \qquad (9)$$

In this equation, h is the Planck's constant, I is the moment of inertia and J is the rotational quantum number which can take value from 0,1, 2......

Equation (9) gives the energy in Joules, however, we are interested in energy in wave numbers, so we can convert joules to wave number as

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)\ cm^{-1} \qquad J=0,1,2,3..... \qquad (10)$$

Here, c, the velocity of light is expressed in cm/s so that we get the unit of E_J as cm^{-1}

Equation (10) is usually written as

$$\varepsilon_J = BJ(J+1)cm^{-1} \qquad . \qquad ....(11)$$

Where B is the rotational constant, given by

$$B = h/\ 8\pi^2 Ic \quad .... \qquad (12)$$

We can make a table for J and the corresponding value of E_J

J	0	1	2	3	4	5	6
E_J	0	2B	6B	12B	20B	30B	42B

For J=0, ε_J is 0 or the molecule is not rotating at all, for J=1, ε_1 is 2B. Thus, the rotating molecule has its lowest energy at $\varepsilon_1=2B$

For J=2, $\varepsilon_2= 6B$ and so on.

We can see that as quantum number increases, the value of ε_J also goes on increasing. In fact, the separation between two rotational energy level goes on increasing.

As the rotational energy level increases, there comes a point where the centrifugal force overcomes the strength of the bond and the molecular bond breaks. However, this rarely takes place at room temperature.

In order to consider the difference between rotational energy level, we can calculate the difference from the above table as:

(For rotational quantum numbers change by 1 unit),

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B\,cm^{-1}$$

$$\varepsilon_{J=2} - \varepsilon_{J=1} = 6B - 2B = 4B\,cm^{-1}$$

$$\varepsilon_{J=3} - \varepsilon_{J=2} = 12B - 6B = 6B\,cm^{-1}$$

$$\varepsilon_{J=4} - \varepsilon_{J=3} = 20B - 12B = 8B\,cm^{-1}$$

So, in general, in order to raise the molecules from J^{th} to $J+1^{\,th}$ level,

$$\begin{aligned}\varepsilon_{J+1} - \varepsilon_J &= B(J+1)(J+2) - BJ(J+1)\\ &= B(J^2+3B+2) - B(J^2+J)\\ &= B(2J+2)\\ &= 2\,B(J+1)cm^{-1} \qquad (13)\end{aligned}$$

We can see that on absorption of energy by change of 1 rotational quantum number, we get a spectrum having lines at 2B,4B ,6B, 8B….cm^{-1}

A lowering of quantum number by one unit would result in an emission spectrum, having lines at the same value.

We have considered rotational transition by one unit only, let us now state the selection rule for a rigid rotator.

Selection rules for Rotational spectroscopy:

1) Molecule must have a permanent dipole moment

2) $\Delta J = \pm 1$

The first selection rule implies that homonuclear diatomic molecule will not show rotational spectrum. Thus, molecule like O_2,Cl_2 , N_2 , H_2 etc. Will not show rotational spectrum, however, molecule like HCl, CO, HBr will show rotational spectrum.

Having discussed the selection rule and the spectrum, we need to know to what use this spectrum will be to us.

Recalling that $B = \frac{h}{8\pi^2 I_B C}$,

Here, h and c are universal constants, since every molecule has a unique value of 'B,' the value of I_B, that is, the moment of inertia of the molecule can be calculated, from which the bond length of the molecule can be calculated.

Let us calculate bond length of HCl molecule.

The value of B for HCl was found to have a value of 10.440254 cm^{-1}

If the sample whose value was taken as ^1H and ^{35}Cl, we can calculate I_{HCl} from the following formula: $B = \frac{h}{8\pi^2 I_B C}$

$$\therefore I_{HCl} = \frac{h}{8\pi^2 BC}$$

$$I = \frac{6.6\times10^{-27}\, erg\, sec}{8\times(3.14)^2\times10.440254\, cm^{-1}\times3\times10^{10}\ \frac{cm}{sec}}$$

$$I = \frac{6.6\times10^{-27}\, gm.cm^2/s\ \ 10^{-10}s}{8\times(3.14)^2\times10.440254\times3}$$

$$I = \frac{6.6\times10^{-37}\, gm\, cm^2}{8\times(3.14)^2\times10.440254\times3}$$

$$I = 0.00267\, X\, 10^{-37}\ gmcm^2$$

$$I = 2.67\ \times\ 10^{-3}\ \times 10^{-37} gmcm^2$$

$$I = 2.67\ \times\ 10^{-40} gm\, cm^2$$

$$I\ =\ \frac{m_1\ +\ m_2}{m_1 + m_2} R^2$$

Method 1:

$$2.67\times10^{-40} gm\, cm^2\ = \frac{\frac{1}{6.023\times10^{23}}\times\ \frac{35}{6.023\times10^{23}}\ \ gm}{\frac{1}{6.023\times10^{23}}+\frac{35}{6.023\times10^{23}}}.R^2$$

$$R^2 \times \frac{35\, X\ 10^{-40}\qquad\qquad gm}{36\quad\times\ \ 6.023\times10^{23}} =\ 2.67\times10^{-40} gm\, cm^2$$

$$R^2\ = \frac{2.67\times10^{-40}\times36\times\ 6.023\times10^{23}}{35}\ cm^2$$

$$= 16.54\ \times10^{-17}\ \ cm^2$$

$$R^2 = 1.654\ \times10^{-16}\ \ cm^2$$

$$R\ \ = 1.286\times10^{-8}\ \ cm$$

R= 1.286A°

Method 2:

$$I = 2.67 \times 10^{-40}$$

$$\text{Since } I = \frac{m_1 m_2 r_o^2}{m_1+m_2}$$

$$m_1 = 1\,amu$$

$$=1/6.023 \times 10^{23}$$

$$= 1.66X10^{-24}gm$$

$$m_2 = \frac{35}{6.023\times10^{23}}gm$$

$$= 58.11 \times 10^{-24}gm$$

$$\text{But } \mu = \frac{m_1 m_2}{m_1+m_2}$$

$$= \frac{(1.66\times10^{-24})\times(58.11\times10^{-24})}{(1.66\times10^{-24})+(58.11\times10^{-24})}gm$$

$$= \frac{96.4626\times10^{-24}\times10^{-24}}{59.77\times10^{-24}}gm$$

$$= 1.613896 \times 10^{-24}gm$$

$$\text{Therefore, } r_o^2 = \frac{I}{\mu} = \frac{2.67\times10^{-40}}{1.613896\times10^{-24}}cm^2$$

$$r_0^2=1.654X\,10^{-16}cm^2$$

$$r_0=1.286X10^{-8}\,cm$$

$$r_0 = 1.286\,A^o$$

Ex.1. Calculate the moment of inertia and bond length of carbon monoxide molecule. The first line in rotational spectrum of carbon monoxide is 3.84235 cm^{-1}

Solution: $2B = 3.842335\ cm^{-1}$

Therefore $B=1.92118\ cm^{-1}$

$$Since\ B = \frac{h}{8\pi^2 IC}$$

$$\therefore\ I = \frac{h}{8\pi^2 BC}$$

$$= \frac{6.6\times10^{-27}\,erg\,sec}{8\times(3.14)^2\times1.92118cm^{-1}\times3\times10^{10}\,\frac{cm}{sec}}$$

$$= 14.5695 \times 10^{-40} gm\, cm^2 \ldots\ldots \left(erg = gm \frac{cm^2}{s^2} \right)$$

In order to calculate the moment of inertia

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$m_c = 12\, amu = \frac{12}{6.023 \times 10^{23}} gm$$

$$= 1.9923 \times 10^{-23} gm$$

$$m_o = 16\, amu = \frac{16}{6.023 \times 10^{23}} gm$$

$$= 2.656 \times 10^{-23} gm$$

$$\therefore \mu = \frac{(1.9923 \times 10^{-23}) \times (2.656 \times 10^{-23})}{(1.9923 \times 10^{-23}) + (2.656 \times 10^{-23})} gm$$

$$= \frac{5.2915 \times 10^{-46}}{4.6483 \times 10^{-23}} gm$$

$$= 1.138 \times 10^{-23} gm$$

$$\boldsymbol{Since\ I = \mu r_o^2}$$

$$\therefore R^2 = \frac{I}{\mu}$$

$$= \frac{14.5695 \times 10^{-40}}{1.138 \times 10^{-23}} cm^2$$

$$= 12.8027 \times 10^{-17}\ cm^2$$

$$= 1.28 \times 10^{-16}\ cm^2$$

$$R^2 = 1.31 \times 10^{-8}\, cm$$

$$R = 1.31\, A^\circ$$

The effect of isotopic substitution:

An isotope is an element identical in every way except its mass. When a particular atom is replaced by its isotope, there is no change chemically. Particularly, there is no appreciable change in internuclear distance. there is, however, exchange in mass and thus a change in moment of inertia and rotational constant ‘B’ of the molecule.

In the example of carbon monoxide, on replacing $^{12}C^{16}O$ with $^{13}C^{16}O$, there is an increase in mass and hence a decrease in ‘B’ Value. This implies that the heavier isotopes will have a smaller separation between the rotational energy levels. (2B’ if we denote the heavier isotopes with a prime) than the lighter one (2B).

Observation of this decreased separation has helped in calculation of precise atomic mass. Experimental values of rotational constants were found to be B = 1.92118 cm^{-1} and B'= 1.83669 cm^{-1} respectively where B' refers to the rotational constant of the heavier molecule ($^{13}C^{16}O$).

From the ratio of the B: B' value the precise mass of the heavier isotope can be calculated. In such a study, the precise atomic mass of 13 C isotope was found to be 13.0007 amu.

In addition, microwave studies can give an estimate of abundance of isotopes, by comparison of absorption intensities.

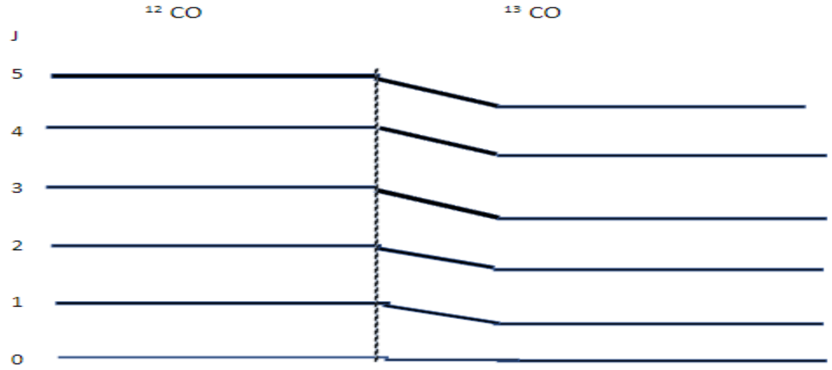


Fig. Effect of isotopic substitution on this energy level and rotational spectrum of a diatomic molecule like CO or HCl.

The B' value can be used for precise calculation of atomic mass of the isotope

<u>Applications of microwave spectroscopy:</u>

To sum up, following are the applications of microwave spectroscopy.

1) At lower rotational quantum levels, the lines in microwave spectrum are equidistant. This distance has been utilised in the calculation of moment of inertia and bond length of the molecule.
2) Microwave spectroscopy has been used to calculate precise value of atomic masses of isotopes.
3) Microwave spectroscopy has been used to calculate the relative abundance of isotopes from the rotational spectrum of a mixed sample of isotopes.

Problems:

1. Which of the following will show pure rotational Spectra?

a) NaCl b) NH_4Cl

c) NH_3 . d) H_2

2. Selection rule for rotational Spectra is?

a) $\Delta J=\pm1$. b) $\Delta J=+1$

c) $\Delta J=-1$ d) $\Delta J=0$

3. The reduced mass of diatomic rigid rotator is given by?

a) $\frac{1}{m_1}+\frac{1}{m_2}$ b) $\frac{m_1+m_2}{m_1m_2}$

c) $\frac{m_1m_2}{m_1+m_2}$ d) m_1+m_2

4. What is <u>correct</u>? If isotope of heavier mass is introduced in rotational spectroscopy?

a) it makes smaller value of B b) $B \propto 1/\mu$

c) it makes smaller separation between spectral line d) all are correct.

5. The relation among frequency(ν), velocity(c) and wave number($\bar{\nu}$) is?

a) $\bar{\nu}=c/\nu$ b) $\nu=h/\bar{\nu}$

c) $\nu=c\bar{\nu}$ d) $\bar{\nu}=c\nu$

References:

1.Fundamentals of Molecular Spectroscopy by C N Banwell