# Molecular spectroscopy (NMR and ESR)

## Magnetic Resonance spectroscopy:-

Molecular spectroscopy ~~inbt~~ including rotational or microwave spectra, vibrational and vibration-rotational spectra, Raman spectra and electronic (visible and ~~ER~~ UV) spectra have been studied so much.

There are some of the application of magnetic spectroscopy:-

1) NMR is an indispensible tools in the hands of organic chemist for synthetic investigations.

2) ESR tells us about the transience of extremely short lived free radicals.

3) NQR and NRF are useful in determining the strong electric field gradients (EFGs) found in metal and alloys.

4) PES helps us in verifying quantum mechanical calculations on atoms and molecules and determination of ionization potentials.

## NMR Spectroscopy:-

→ Independently discovered in 1946 by the American physicists : F. Bloch (1905 - 1983) and E.M. Purcell (1912-1997).

→ First applications was made in 1951 for the recording of ethanol spectrum.

→ All atomic nuclei possess nuclear spin, I, which may be integral (i.e. 1, 2, 3, etc.) or half-integral (i.e. 1/2, 3/2, 5/2, 7/2, etc.). the proton and neutron has spin 1/2. since a nucleus contains nucleons (protons and neutrons), the spin of the nucleus can be considered as the resultant of the spins of the protons and neutrons comprising it.

→ For the deuteron nucleus, $^2D$, containing one proton and neutron. If the spins of proton and neutron and neutron are aligned parallel (↑↑) or anti-parallel (↑↓), the deuteron is expected to have spin of 1 or 0. It has been found that in ground state the spin of deuteron has been found to be 1, which means the proton and neutron spins are aligned parallel to each other.

→ The following rules are useful to predict the nuclear spin:-

i) If the mass number A is odd, nuclear spin I is half integral. Thus in case of $^1H$, $^{15}N$, $^{19}F$, $^{31}P$ and their I = 1/2 and in case of $^{11}B$, I = 3/2.

ii) If the mass number A and the atomic number Z are both even, the spin is zero. Thus, in the case of $^4_2He$, $^{12}_6C$, $^{16}_8O$, I = 0.

iii) If the mass number A is even but the atomic number Z is odd, the spin is integral. Thus, the spin of $^2_1H$, and $^{14}_7N$ is 1 while that of $^{10}_5B$ is 3.

since a nucleus possesses an electric charge, the spinning nucleus gives rise to a magnetic field whose axis coincides with the axis of spin.

→ Thus, each nucleus can be said to be equivalent to a minute magnet having a magnetic moment $\mu$. Each nucleus with $I > 0$ has magnetic moment. However $^{12}_{6}C$ and $^{16}_{8}O$ having $I = 0$ do not possess a magnetic moment, i.e. they are non-magnetic.

→ Nuclei possessing $I \geq 1$ have also a nuclear electric quadrupole moment, Q, which is a measure of the deviation of the nuclear charge distribution from spherical symmetry.

→ The nuclear quadrupole moments exists with the electric field gradient (EFG) created ~~by~~ at the nucleus by the bonding and non-bonding electrons in a molecule. The quantity $e^2Qq$ (where e is the electronic charge and q the EFG) is known as <u>nuclear quadrupole coupling constant</u>.

→ Nuclear quadrupole spoils their own NMR spectra but also the NMR spectra of nuclei attached to them in the molecule. The NMR spectra of the quadrupolar nuclei are generated very broadly and not all are sharp.

→ when a magnetic nucleus is placed in a uniform magnetic field, the magnetic dipole associated with the magnetic moment assumes a discrete set of orientations.

→ Assuming that a nucleus with spin 2I+1 orientations with the direction of ~~electric field~~ applied magnetic field. Suppose that a nucleus with spin I is placed in an external magnetic field $B_z$, applied along the z-direction. As a result of quantization of spin, the observable component $m_I$ of the spin I along the direction of the field is given by:-

(i) $m_I = I, I-1, I-2, \ldots\ldots 0, -(I-2), -(I-1), -I$
(for integral spins).

(ii) $m_I = I, I-1, I-2, \ldots\ldots I/2, -1/2, \ldots\ldots, -I$
(for half-integral spins)

In such cases, there are $(2I+1)$ values of $m_I$,

A nucleus with spin has associated with it a magnetic dipole moment (or simply magnetic moment) $\vec{\mu}$ that is proportional to the angular momentum $\vec{I}$ given by $[(I(I+1)]^{1/2}\hbar$. Thus,

$$\vec{\mu} = g_N \mu_N \vec{I}$$

where $g_N$ is called the nuclear g-factor and $\mu_N$ is the nuclear magneton defined as $\mu_N = e\hbar/2m_p$, where e is the electronic charge, $m_p$ is the mass of the proton. On substituting the values

$$\mu_N = \frac{(1.602 \times 10^{-19}\,C) \times (1.055 \times 10^{-34}\,Js)}{(2) \times 1.673 \times 10^{-27}\,kg} = 5.05 \times 10^{-27}\,JT^{-1}$$

The magnitude of the nuclear magnetic moment is thus given by

$$\mu = g_N \mu_N [I(I+1)]^{1/2}$$

since, the magnetic moment and the angular momentum can be parallel or antiparallel vectors, $g_N$ can have a positive or a negative value.

The value of the electron g-factor, $g_e$ has been accurately calculated to be equal to 2.0023, the value of nuclear g-factor, $g_N$, can be only obtained from experiment and is different for different nuclei.

Q: calculate the nuclear spin angular momentum and the magnetic moment for a proton, given that $I = 1/2$, $g_N$ for proton is 5.585 and $\mu_N = 5.05 \times 10^{-27} JT^{-1}$.

The nuclear spin angular momentum

$$= [I(I+1)]^{1/2}\hbar = \left[\frac{1}{2}\left(\frac{1}{2}+1\right)\right]^{1/2} \times (1.054 \times 10^{-34} Js)$$

$$= 0.866 \times 1.055 \times 10^{-34} Js$$

$$= 0.914 \times 10^{-34} Js$$

The nuclear ~~moment~~ magnetic moment is given by

$$\mu = g_N \mu_N [I(I+1)]^{1/2}$$

$$= (5.585) \times (5.05 \times 10^{-27} JT^{-1}) \left[\frac{1}{2}\left(\frac{1}{2}+1\right)\right]^{1/2}$$

$$= 2.44 \times 10^{-26} JT^{-1}$$