

University of Babylon
College of Science
Department of Chemistry
Course No. Chsc 424



Undergraduate Studies
Physical chemistry
Fourth year - Semester 2
Credit Hour: 3 hrs.
Scholar units: three units

Lectures of Molecular Spectroscopy
Second Semester, Scholar year 2021-2022
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Lecture No. Eight: Electron Spin Resonance Spectroscopy

1-Introduction:

- Electron spin resonance is technique for studying a chemical species that have one or more unpaired electrons, such as organic, inorganic free radicals or inorganic complexes possessing a transition metal ion.
- Study of the radicals produced by such radiation gives information about the locations and mechanisms of radiation damage.
- The method of ESR is very selective method of free radical identifications (neutral and negative radicals generally) due to the ability for detection at short life time of radicals (0.1 microsecond) and very low concentration approximately 10^{-10} molar concentrations.

Q// What are chemical species can be detect by ESR ((the types and kinds))?

ESR can detect the chemical species as follow:

- Transition metal ions and complexes Mn^{2+} , Cu^{2+} , Gd^{3+} etc.
- Simple inorganic compounds: O_2 , NO , NO_2

- Short-lived intermediate radicals *OH, *H, *F etc. in kinetics study.
- Defects in crystals.
- Electrons trapped in radiation damaged sites.
- Stable organic radicals.
- Triplet states.

Q// What are the Biological applications of ESR?

The biological application of ESR are:-

- i- Paramagnetic cofactors: iron sulfur, copper proteins.
- ii- Free radicals of biological origin and their spin-trapping products.
- iii- Spin-labeling.

2- Physical concepts of ESR:

- The electron spins that are excited, since the molecules of a solid exhibit Para magnetism because of the unpaired electron spins, transitions can induced between spin states by applying a magnetic field and then supplying electromagnetic energy, usually in the microwave range of frequencies. The resulting absorption spectra are described as electron spin resonance (ESR).
- The interaction of an external magnetic field with an electron spin depends upon the magnetic moment associated with the spin, and the nature of an isolated electron spin is such that two and only two orientations are possible.
- The application of the magnetic field then provides a magnetic potential energy that splits the spin states by an amount proportional to the magnetic field (Zeeman Effect), and then radio frequency

radiation of the appropriate frequency can cause a transition from one spin state to the other.

- The energy associated with the transition is expressed in terms of the applied magnetic field B , the electron spin g -factor g , and the constant μ_B which is called the Bohr magneton.

The difference between the energies of two possible spin states of a free electron in a magnetic field of flux density B_0 is

For a molecule with one unpaired electron – In the presence of a magnetic field, the two electron spin energy levels are:

$$E = g\mu_B B_0 M_S$$

g = proportionality factor μ_B = Bohr magneton

M_S = electron spin B_0 = Magnetic field

quantum number

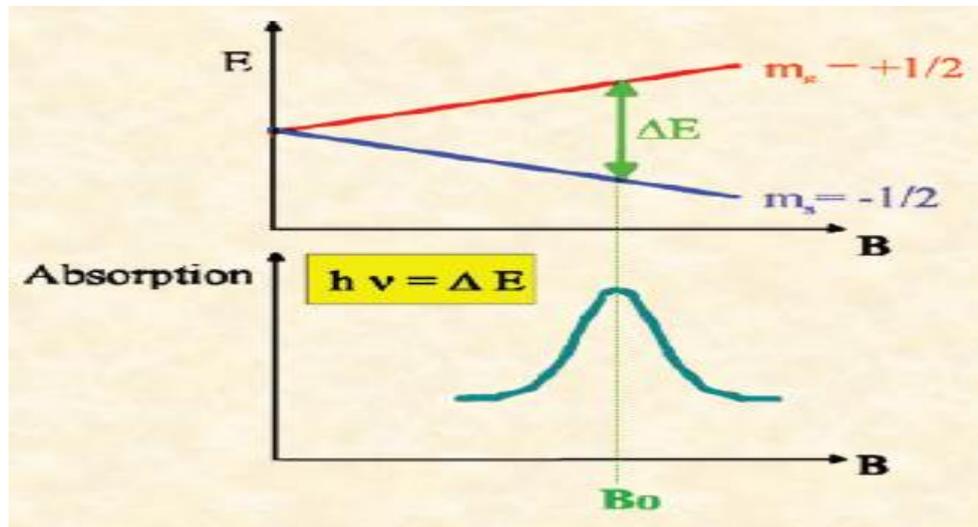
($+1/2$ or $-1/2$)

Where μ_B is Bohr's magnetron and g the Landé factor (almost exactly equal to 2 for a free electron) or Zeeman Effect. The absorption of electromagnetic radiation at the resonance frequency

$$\nu = \Delta E/h \text{-----} 2$$

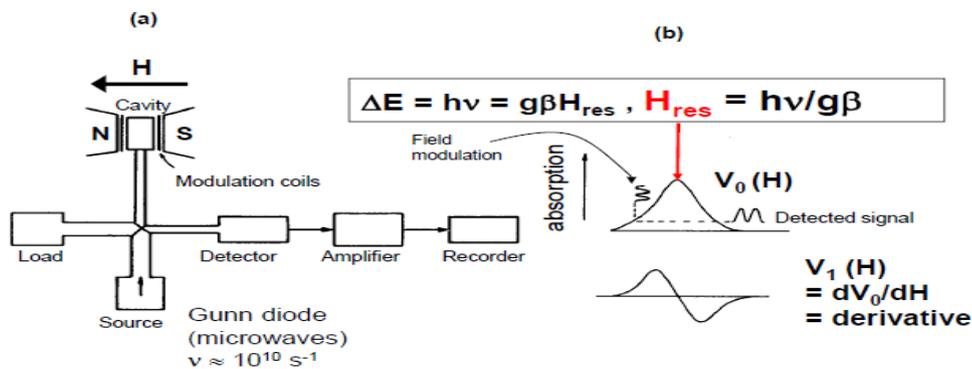
Equation 2 represent the Induces transitions from the low-energy level to the higher level. The numerical equation value is $\nu = 2.8026 \cdot 10^{10} \cdot B_0$ (Hz / T). Due to the interaction between spin and lattice, the occupation of the higher level is again reduced. The absorbed energy is dissipated (radiated) to the environment in the form of heat. The resonance is determined by linearly varying the flux density B of the magnetic field over a small interval approximately the resonance value B_0 and by recording the

variation of the absorbed energy with B as the signal of a so-called ESR spectrometer. Following figure represented the mechanism and signal of ESR.



A

Measurement of EPR spectrum: Keep ν constant, vary H , determine H_{res}



B

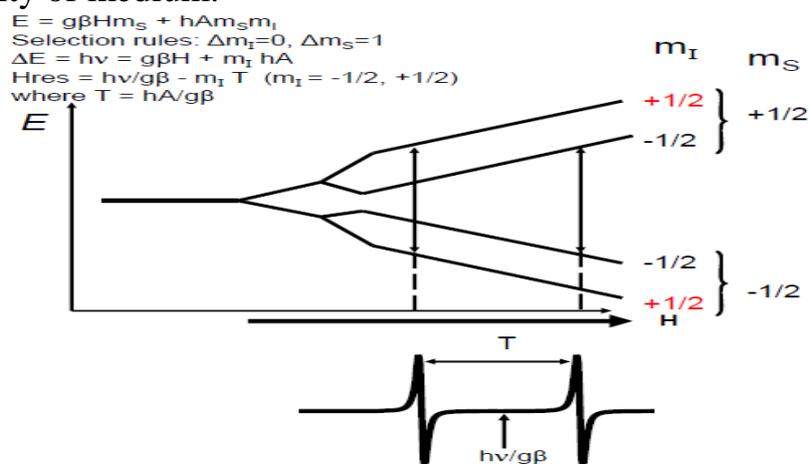
Figure (A). The essentials of the EPR instrument. (B) Absorption curve and its first derivative obtained by field modulation (small amplitude H_m) and phase-sensitive detection at the modulation frequency, which decreases noise and flattens the baseline.

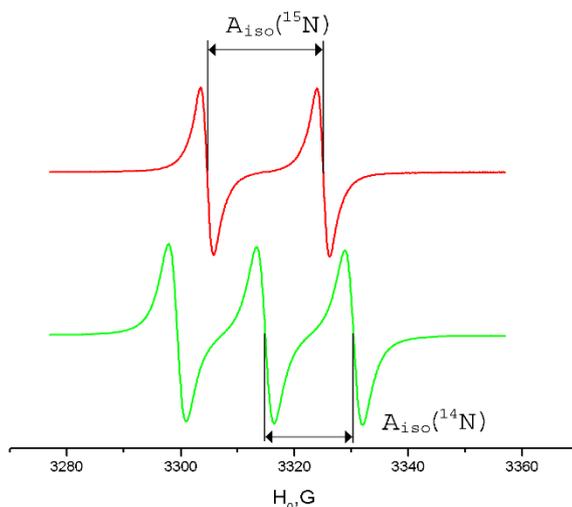
3-Hyperfine interactions:

The unpaired electron, which gives us the EPR spectrum, is very sensitive to local fields in its surroundings. Local fields arising from magnetic nuclei are permanent and independent of H. Interaction with neighboring nuclear magnetic dipoles gives the nuclear hyperfine interaction and hyperfine splitting a corresponds to the NMR coupling constant J. A splitting are independent of the external field. For several equivalent nuclei n, $(2n_M I_M + 1)$ transitions are observed for a nucleus M with a spin I. The relative intensities are given by Pascal's triangle for $I = 1/2$. As in following rule:

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1
1 7 21 35 35 21 7 1

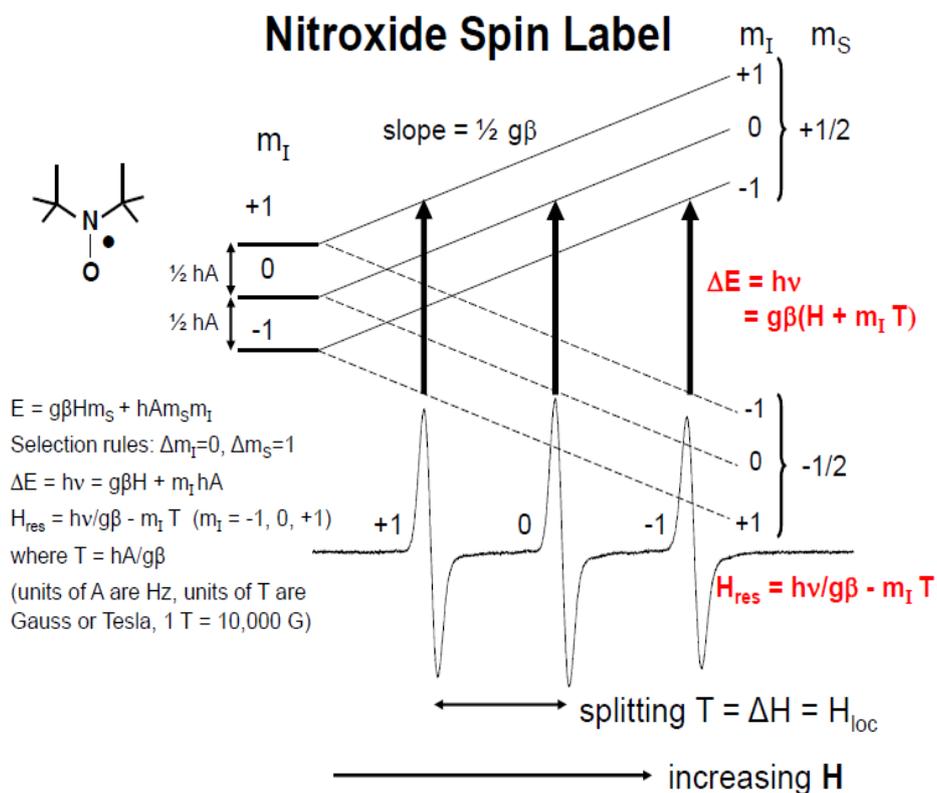
Following figure, show this phenomenon. The phenomena depend also on the polarity of medium.





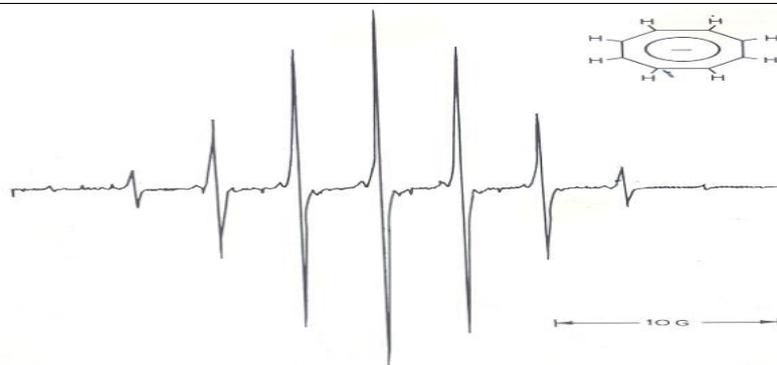
Hyperfine Splitting T Increases with Polarity of Medium, as example:

The nitro oxide group is in equilibrium (resonance) between two structures, having the unpaired e^- on the O (left, no hyperfine interaction) or N (right, hyperfine interaction). A polar medium stabilizes the latter (**electron is present on nitrogen atom**) and thus increases the hyperfine splitting T .

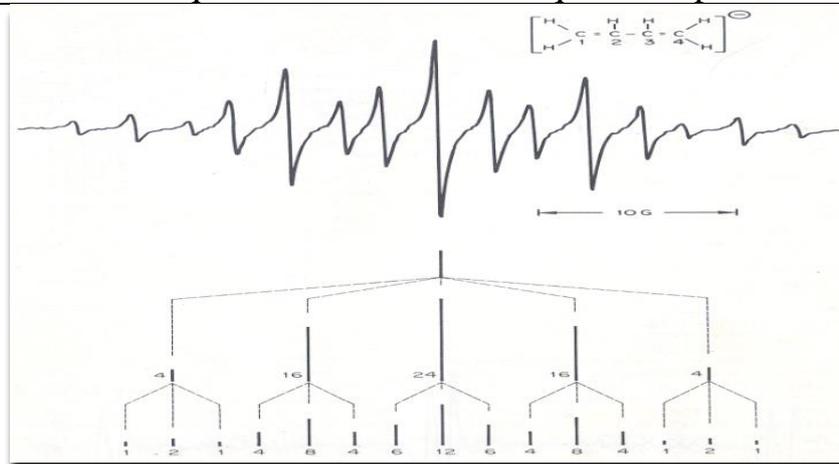


4-Applications:

1-Cyclooctatetraen anion: Observation of the spectrum shows that eight protons are equivalent 1:8:28:56:70:56:28:8:1.



2-Butadien ion in liquid NH_3 : Two sets of equivalent protons: 2 and 4.



3-Pyrazine anion: two state with two different spectrum.

First with Na^+ is the counter ion, second with K^+ is the counter ion.

