

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 2018-2019  
Prof. Dr. Abbas A-Ali Draea

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**Lecture No. Eight: Electron Spin Resonance Spectroscopy**

- 1-Introduction.
- 2- Physical concepts of ESR.
- 3- Hyperfine interactions.
- 4-Applications.

**1-Introduction:**

Electron spin resonance spectroscopy (**ESR**) or electron paramagnetic resonance (**EPR**) is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion.

The radicals typically produce an unpaired spin on the molecule from which an electron is removed. Particularly the ESR spectra of radicals has been produced as radiation damage from ionizing radiation. 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 for free radical identifications (neutral and negative radicals generally) because due the ability for detection a short life radicals (0.1

microsecond) and very low concentration approximately  $10^{-10}$  molar concentrations.

Chemical species can be detecting by ESR are represented as follow:

- Transition metal ions and complexes  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Gd}^{3+}$  etc.
- Simple inorganic compounds:  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$  ....
- Short-lived intermediate radicals  $\cdot\text{OH}$ ,  $\cdot\text{H}$ ,  $\cdot\text{F}$  etc. in kinetics study.
- Defects in crystals.
- Electrons trapped in radiation damaged sites.
- Stable organic radicals.
- Triplet states.
- *Biological applications:*
- Paramagnetic cofactors: iron sulfur, copper proteins.
- Free radicals of biological origin and their spin-trapping products.
- Spin-labeling.

Therefore this technique finds application in physics, chemistry, biology and medicine.

## **2- Physical concepts of ESR:**

The basic physical concepts of EPR are analogous to those of nuclear magnetic resonance (NMR), but it is electron spins that are excited instead of spins of atomic nuclei.

When the molecules of a solid exhibit Para magnetism as a result of the unpaired electron spins, transitions can be 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) or electron paramagnetic resonance (EPR). 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 which 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  $\mu_B$  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

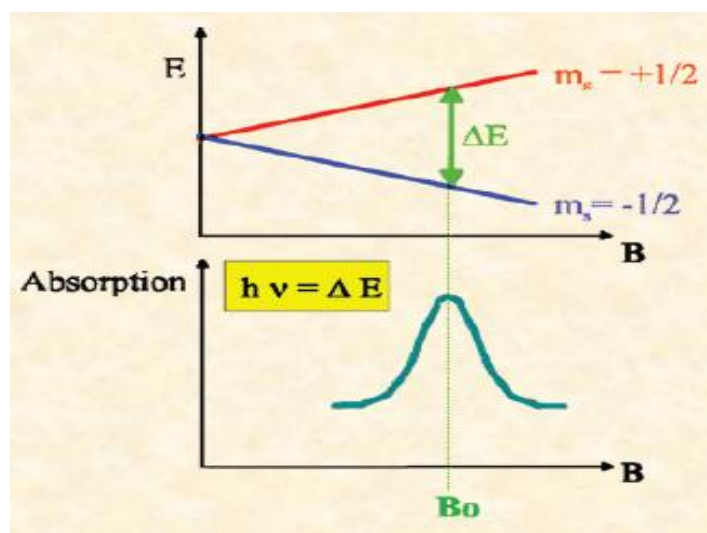
$$\Delta E = \mu_B \cdot g \cdot B_0 \text{-----1}$$

Where  $\mu_B$  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

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

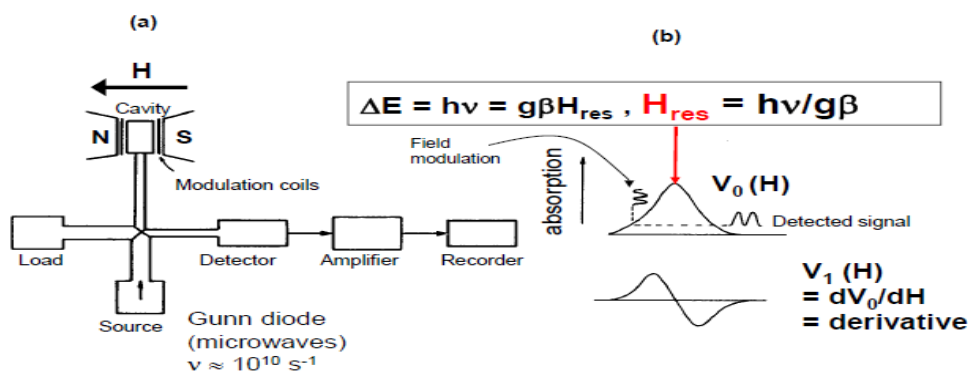
Equation 2 represent the Induces transitions from the low-energy level to the higher level. The numerical value equation is  $\nu = 2.8026 \cdot 10^{10} \cdot B_0$  (Hz / T), i.e. for a magnetic field of about 0.35 T the resonance frequency lies in the so-called X-band between 9 and 10 GHz. Due to the interaction between spin and lattice, the occupation of the higher level is again reduced, i.e. 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 in the

vicinity of 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  $\nu$  constant, vary  $H$ , determine  $H_{\text{res}}$



B

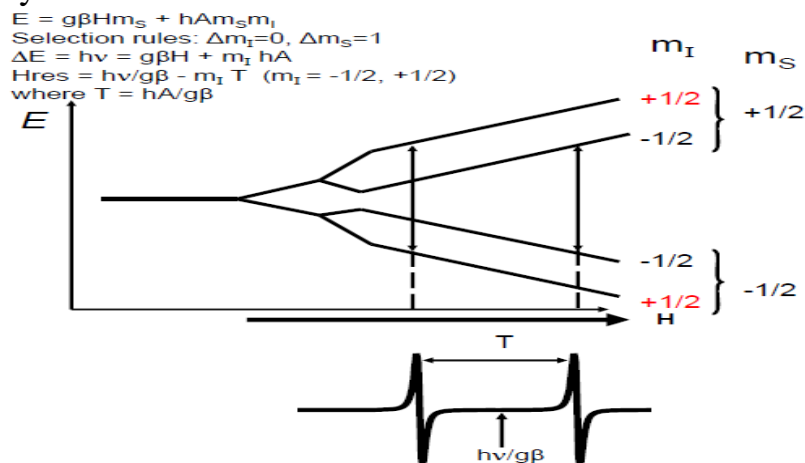
Figure (A). The essentials of the EPR instrument. (B) Absorption curve and its first derivative obtained by field modulation (small amplitude  $H_m$ ) and phase-sensitive detection at the modulation frequency, which decreases noise and flattens the baseline.

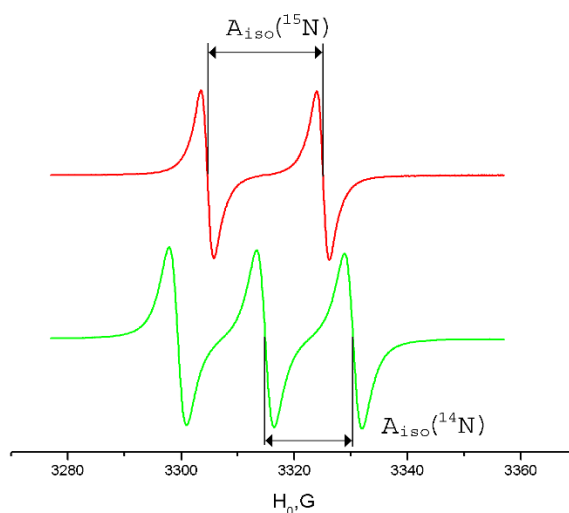
### 3-Hyperfine interactions:

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  $I = \frac{1}{2}$ . 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

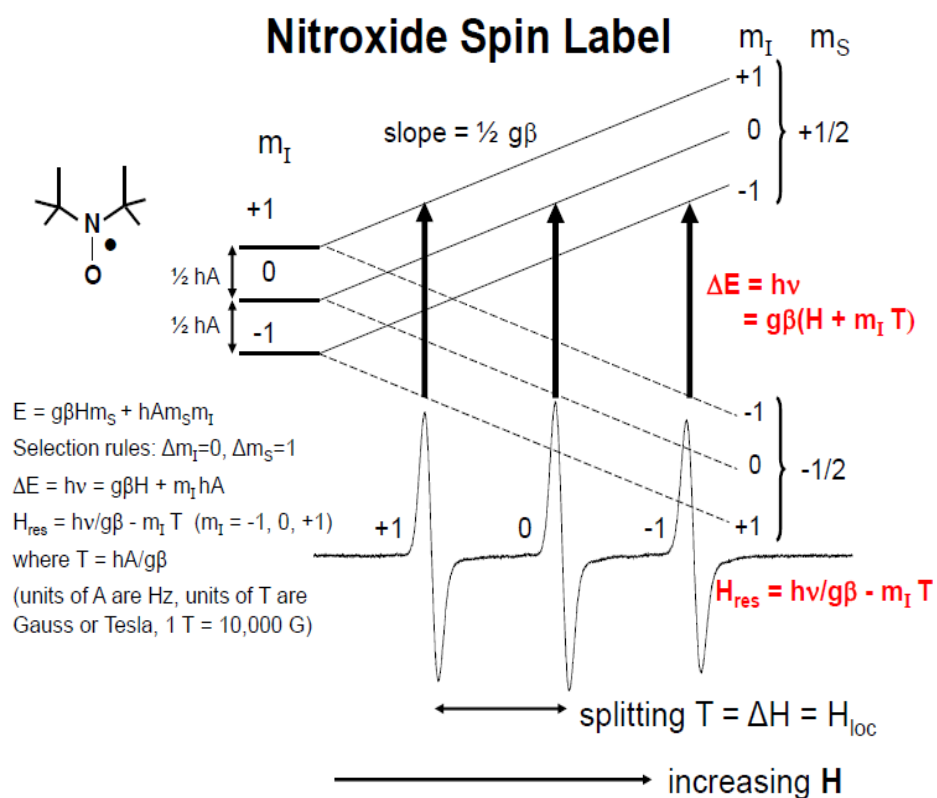
Following figure show this phenomena. The phenomena depend also on the polarity of medium.





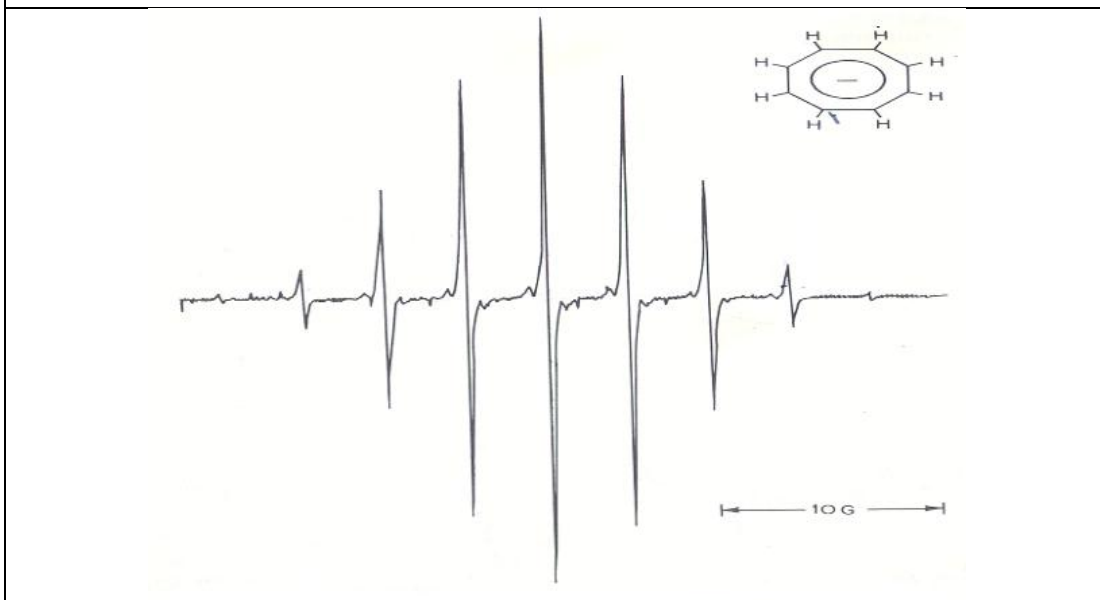
Hyperfine Splitting  $T$  Increases with Polarity of Medium, as example:

The nitroxide 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 and thus increases the hyperfine splitting  $T$ .

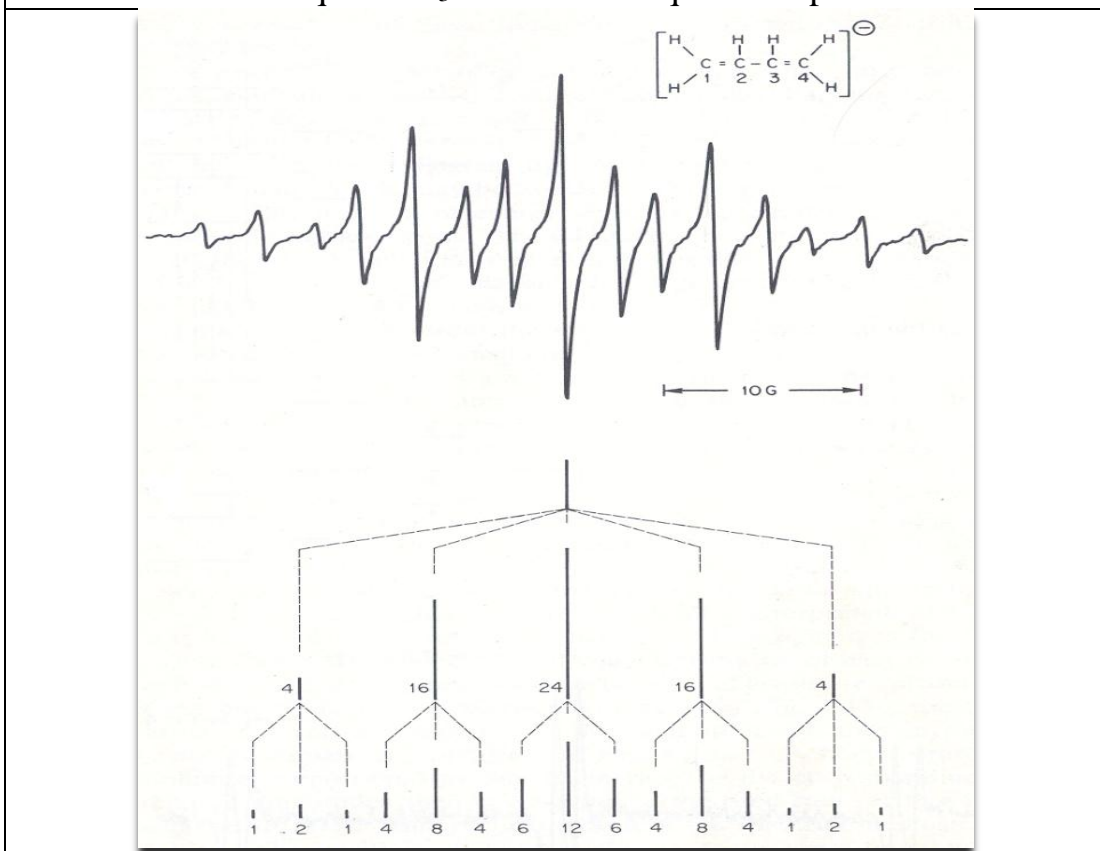


#### 4-Applications:

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  $\text{NH}_3$ : Two sets of equivalent protons: 2 and 4.



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

First with  $\text{Na}^+$  is the counter ion, second with  $\text{K}^+$  is the counter ion.

