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Electron Spin Resonance and its Applications

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ABSTRACT :

The vast majority of magnetic Resonance spectroscopic investigations make use of Nuclear Magnetic Resonance (NMR) which is based on the interaction of atomic nuclei with applied static and Radio frequency magnetic fields. There exists another important Magnetic Resonance called Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR)- which can also provide extremely useful information in the study of free radicals, Inorganic compounds, biological and biomedical applications.ESR relies on interactions with electron spins, specifically unpaired electron spin, usually located in free radical molecules. Like NMR, ESR can be used in both spectroscopic and imaging modes.

Keywords :

ESR , Bohr magneton, NMR , g- factor , Planck's constant; gyro magnetic Radio, X-band spectrometer , L- band spectrometer, Q- band spectrometer , Relaxation timer, klystron oscillator, Phase Sensitive Detector (PSD)

The Phenomenon of Electron Spin Resonance (ESR) is based on the fact that an electron is a charged particle which spins around its axis and this causes it to act like a tiny bar magnet, (i.e) it has a magnetic moment, the value of which is called the Bohr Magneton

If an external magnetic field Bo is impressed on the system, the electron will align itself with the direction of this field and process around this axis. This behavior is analogous to that of a spinning top in the earth's gravitational field. Increasing the applied magnetic field will include the electron to process faster and acquire more energy of motion called Kinetic energy.

An unpaired electron has a quantum mechanical spin of ½ So, like the proton can occupy one of two possible orientations relative to an applied magnetic field. These correspond to a low energy state, with electron spin aligned parallel to the applied magnetic field Bo and a high energy state in which the electron spin is aligned against the applied magnetic field. The energy difference between these state, ΔE , is given by

$$\Delta E = g \beta Bo \qquad (1)$$

Where g is termed the " g-factor " and is approximately 2. β is a physical constant known as Bohr Magneton.

Resonance occurs when electromagnetic radiation with photon energy equal to ΔE is applied to the sample, the frequency , ν_o , of this radiation can be predicted through the " Bohr relationship "

$\Delta E = h \nu_o$, where h is the plank's constant. Therefore the frequency is given by

$$\nu_o = \Delta E / h = g \beta Bo / h \qquad (2)$$

$$\text{or} \qquad Bo = \nu_o h / g\beta \qquad (3)$$

Equation (2) is analogous to the equation $\nu_o = (r / 2 \Pi) \beta o$ from NMR, In the case of ESR the gyro magnetic ratio in frequency units (r / 2 Π) is replaced by g β / h , the value of which is equivalent to 659 times the proton gyro magnetic ratio, (i.e) 28 GHz/T In a manner exactly analogous to the basic NMR experiment, The basic concept of ESR is to apply electromagnetic radiation at the correct frequency to promote electron spins from the low to the high energy state, then the detect the radiation emitted when electrons return to the low energy state .

Difference between NMR and ESR:

Resonant Frequency:

One important difference between NMR and ESR is that in ESR. The resonant frequencies tend to be much higher 659 times higher gyro magnetic ratio of an unpaired electron relative to proton. A typical magnetic field strength used in ESR spectrometer is 0.35 T, with a corresponding resonant frequency of about 9.8 GHz. This frequency range is known as "X-band" and the spectrometer as an " X-band ESR spectrometer" such spectrometer are used to study small solid samples, Non-aqueous solutions up to a few hundred μL in volume. They cannot be used for biological samples, because of the strong non-resonant absorption of microwaves of 9.8 GHz. ESR spectrometer constructed to operate at lower magnetic fields and correspondingly lower frequencies (about 40 mT and 1 GHz) are L-band spectrometer. Spectrometer operating higher magnetic fields (about 1-3 T and 35 GHz) are called Q-band spectrometer.

Relaxation Times:

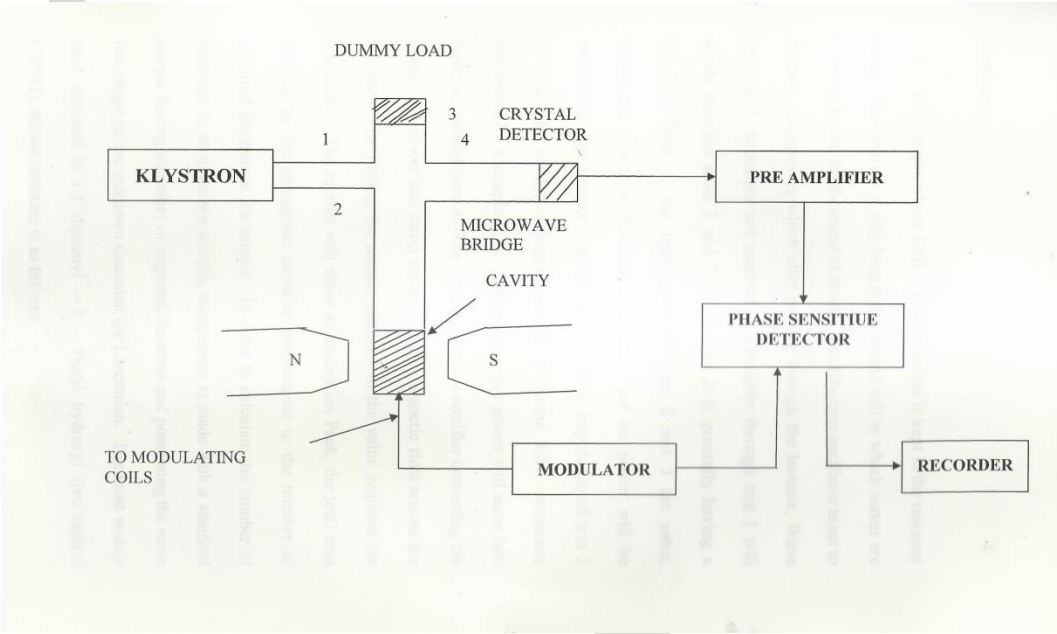
The second important difference between NMR and ESR is the typical relaxation times encountered. In bio-medical proton NMR the relaxation times T1 and T2 are typically of the order of 0.1 to 1 sec. In biomedical ESR the equivalent electron relaxation times are million times shorter, (i.e) 0.1 to 1 μ sec. The extremely short relaxation times have important implications on the way in which ESR measurements are carried out.

Instrumentation of ESR Spectrometer:

Electron Spin Resonance provides a powerful tool for studying the unpaired electrons in condensed matter systems. In fields of a few kiloguass, the two magnetic substates of an electron differ in frequency by an amount on the order of the frequency of microwave radiation, when an incident microwave has a frequency equal to the difference frequency of two states, resonance absorption of the microwave occurs. The exact frequency of absorption is determined not only

by external magnetic field but by interactions with magnetic moments in the system, which can generate local fields comparable to the external field.

A sample block diagram of an ESR spectrometer is shown in the Figure



The source of radiation is a klystron oscillator which produces monochromatic radiation of the required frequency. The radiation from the source is transmitted to the sample cavity through a microwave impedance bridge. The rectangular microwave cavity which contains the sample is kept between the pole piles of the electromagnet. A dummy load is kept in the third arm and a semiconducting crystal in the fourth arm of the microwave bridge. The radiations that arrive in the fourth arm are detected by the crystal. It is item amplified and fed to the suitable recorder. Phase sensitive detectors are usually used to detect ESR signals and represented as absorption or first derivative curve. When the bridge is in a balanced position, microwave power flows only in the two arms the one to cavity and the other to the dummy load. There will not be any power in the fourth arm. Power in the fourth arm will be there only when the bridge is not balanced. Thus if balance exists initially no signal appears at the detector and when the sample absorbs, the balance of the bridge is last and power appears in the fourth arm. The width of ESR lines is fairly large and hence the spectrum is recorded.

Applications:

All application of ESR is based on three aspects, which are,

1. Study of free radicals,
2. Investigation of molecules in the triple state, and
3. Study of inorganic compounds.

Study of free radicals

Even in very low concentration of sample ESR can study via free radicals. It is also applied in determination of structure of organics and inorganics free radicals. The intensity of ESR signal is directly proportional to the no. of free radicals present. Hence using ESR we can measure relative concentration of free radicals.

Investigation of molecules in the triple state

A triple state molecule has a total spin S=1 so that, its multiplicity can be given as 2S+1=3. While free radicals with S=½ has an odd no. of unpaired electrons. A triple state molecule has an even no. of electrons two of them unpaired. In triple state molecule the unpaired electrons must interact whereas in diradical, the unpaired electrons do not interact for they are a great distance apart.

Study of inorganic compounds

ESR is very successful in the study of inorganic compounds. The ESR studies may be used in knowing the exact structures of solvated metal ions. ESR is used in the study of catalysts. ESR is used in the determination of oxidation state of metal. eg. Copper is found to be divalent in copper protein complexes whereas it is found to be monovalent in some biologically active copper complexes. The information of unpaired electrons is very useful in various aspects in applications of ESR. Like, Spin labels, Structural determination, and Reaction velocities and reaction mechanisms.

Spin labels:

Groups with unpaired electron can be attracted to macromolecules such as protein and membranes to obtain a great deal of information obtain their structure. The *nitroxide molecules* bound to macromolecules are called spin labels. This spin labels are stable molecules that possessing an unpaired 2p electrons. A commonly used

TEMPOL (2,2,6,6-tetramethyl piperidinol-n-oxyl. The hyperfine structure of an ESR spectrum is a kind of fingerprint that helps to identify the free radicals presents in the sample. Spin labels give very useful information about the molecules to which they are bound.

Also, we get information like, The rate of motion of macromolecules to which they are bound, or the amount of thermal motion in a membrane in which they have been inserted. The spin label can give information about the polarity of its environments.

Structural determination

The ESR technique cannot be applied to determine molecular structure because the information obtained from the superfine structure is mostly about the extent of delocalization and Fermi contact interaction. It does not tell us about the arrangement of the atoms in the molecule although the symmetry of the molecule can be sometimes deduced from the sets of equivalent nuclei. In certain cases ESR is able to provide useful information about the shape of the radicals.

Reaction velocities and reaction mechanisms:

A large no of organic reactions are known which proceed by a radical mechanism. Most of the radicals formed during organic reaction are not stable but are very reactive. The ESR spectroscopy can be used to study very rapid electron exchange reactions.

The various applications of ESR spectroscopy are grouped in to two categories.

1.Analytical applications

2.Biological applications

Analytical applications:

$Mn+^{2}$ ions can be measured and detected even when present in trace quantities. The method is very rapid and can be measured in aqueous solution over the range from 10-6 M to 0.1M. ESR method has proved to be a rapid and convenient method for determination of Vanadium in petroleum products. ESR can also be used to estimate Cu(II), Cr(II), Gadolinium(III), Fe(III) and Ti(III). The ESR spectroscopy has been used to estimate polynuclear hydrocarbons, which are first, converted in to radical cations and then absorbed in the surface of an activated silica-alumina catalyst.

Biological systems:

From the ESR studies of variety of biological system such as, leaves, seeds, and tissue preparation, it is found that a definite, correlation exists between the concentration of *free radicals* and the metabolic activity of the plant material. ESR has studied the presence of *free radicals* in healthy and diseased tissues. Most of the oxidative enzymes function via one electron redox reaction involving the production of either enzyme bound *free radicals* or by a change in the valence state of transition metal ion. This has been conformed by ESR studies. Much of the ESR work on photosynthesis has been carried out with photosynthetic bacteria. The oxidation of bacteriochlorophyll in vitro produces an ESR signal.

Modern biotechnology:

ESR being effectively used to revealed both structure and functional information. It is very useful in modern biotechnology. There are tree branches of modern biotechnology in which ESR is applied,

a) Molecular biotechnology

b) Medical biotechnology

c) Classical biotechnology

Specific features of ESR in modern biotechnology are:

ü Selectivity

ü Specificity

ü Non-invasiveness

ü Sensitivity

ESR in molecular biotechnology :

DNA: ESR is used to investigate the nucleotide-centered free radicals in DNA, either produced by irradiation, or indirectly by other free radicals. ESR is applied to analysis of DNA hydration and the process of the hole or electron transfer from the hydration layer to DNA due to water ionization, and to the analysis of DNA repair by DNA photolyase, by detection of flavin radical formation. ESR is useful in analysis of Reverse Transcriptase (RT) inhibition by polynucleotide.

RNA: ESR was employed to structure dependent molecular dynamics of Trans Activator Responsive (TAR) RNA of HIV-1. ESR is also used to determine the map of protein-RNA interactions between RNA and ribonuclease P from E.coli.

Protein structure and dynamics: The free radical damage of proteins in the field of research is still waiting for the complete exploration. Example of the ESR investigations of the interactions between ligands and target protein is the study on the ion siderophore complex and it's binding to site directed spin labeled ferric enterobactin receptor responsible for iron uptake by enterobacteria.

Activity of enzymes: ESR can effectively screen potential inhibitors interaction with the enzymes with high speed. Now a days, ESR is used in the analysis of enzymatic activity of nitric oxide synthetase (NOS), the main enzymes delivering NO in biological systems.

Membranes: The existence of phospholipid bilayers in biological systems is confusing from the point of view of evolutionary biology. The model of Fluid Mosaic appears too simple to satisfactorily represent the details of membrane structure and the respective functions. The common view of the architecture of membrane has changed by the recent ESR evidence of the existence of structural domains stabilized by membrane proteins in the form of "rafts".

Glycobiology: Spin labeled sugars, sugar residues, and spin labeled components interacting with sugar applied in two basic fields of carbohydrate research: Sugar metabolism (degradation and transport), Structural biochemistry of glycoproteins and membranes.

o ESR is employed to analyze the process of sugar transport in bacteria.

o ESR was applied to the analysis of the influence of diabetes on the properties of erythrocytes showing the decrease in erythrocyte deformability due to the non-enzymatic glycation of hemoglobin.

oThus, structural investigation often reveals medical aspects.

ESR in medical biotechnology:

Activation and transport of drugs: ESR is useful in several pharmacological investigations like interactions between DNA binding drugs and DNA. ESR may be used to characterize some herb derived products which act by increasing the level of free radicals and other reactive species produced during light induced oxidative stress of the cell. In vivo ESR experiments revealed that multimellar liposomes enhance the topical delivery of hydrophilic compound, drugs used to be more effective when applied in liposomes then in solutions.

Imaging: ESR imaging is a valuable tool for spatially resolved redox mapping of living tissues. Redox status of tumor tissues is significant for understanding tumor physiology, and for determining the effects of chemotherapy and radiation.

ESR in classical biotechnology:

Plant biotechnology: ESR is helpful even at developing artificial photosynthesis, which is biggest biotechnological challenge for the mankind.

Food production and storage: Commercially, ESR is used to analyze shelf life of beer and wine. It is based on free radicals generated in beer or wine due to the action of light, or spontaneously during the process of storage, contribute to the degradation and flavor changes of

product. The level of free radical would depend on antioxidants presents in the solutions. Therefore antioxidant capacity of beer or wine helps to predict stability. Similar approach is applied to other food products, such as oils or milk. ESR measurement revealed also photosensitizing action of the important milk ingredient, vitamin-B_2, which may affect quality of the product. ESR also used in food science, and the field is hydration, water diffusion, and small molecule mobility in food systems, or sugar-water systems used to model much more complicated systems.

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