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Review Article

A Review of Electron Paramagnetic Resonance Spectroscopy

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ABSTRACT

Electron paramagnetic resonance (EPR) spectroscopy, also called electron spin resonance (ESR) or electron magnetic resonance (EMR) measures the absorption of microwaves by paramagnetic centers with one or more unpaired electrons. In the presence of a magnetic field the degeneracy is lifted, and transitions can be caused to occur by supplying energy. When the energy of the microwave photons equals the separation between the spin energy levels, the system is said to be at "resonance," and there is absorption of energy by the sample. Materials with unpaired electrons are investigated. It is concerned with microwave radiation. Electron paramagnetic resonance spectroscopy is a type of spectroscopy that is used to detect and identify free radicals in solid, liquid, or gaseous states, as well as in paramagnetic centers such as F centers.

Keywords: Electron Spin Resonance Spectroscopy, Electrons, klystron oscillator, Magnet, Cavities, Resonance of electron spin.

INTRODUCTION

Electron paramagnetic resonance spectroscopy [EPR] is an absorption-based spectroscopy. EPR is another name for electron spin resonance. The technique for determine the spinning properties of electrons in resonance. It is used to investigate materials with unpaired electrons. Electron paramagnetic resonance spectroscopy is an extremely flexible and nondestructive analytical method. Electron Paramagnetic Spectroscopy instrument can be as in fig:1.

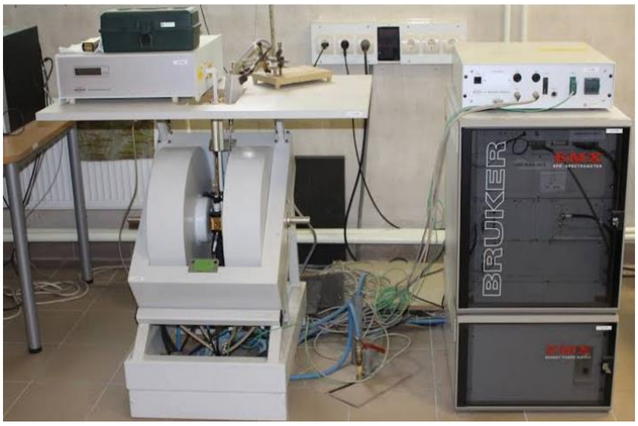

Figure 1: Instrument of electron paramagnetic resonance spectroscopy

It is a molecule and every molecule has an atom and every atom has nucleus. Every nucleus contains neutron and proton. Overall nucleus is charged with positive and i. e, proton. Nucleus is positively charged body. Around nucleus negatively charged electron are present. Electron has property to rotate around nucleus and its own axis also.

When charged body rotates it behaves like magnet and generate magnetic field. When electrons rotate around its own axis it acts as magnet. There are 2 types of magnetic properties by an electron. They are diamagnetic and paramagnetic. Molecules contain paired electrons. Both are negatively charged. One rotates in clockwise direction then its magnetic field is denoted as an arrow pointing upward while another rotates in anti-clock wise direction then its magnetic field is denoted as an arrow pointing downward. when two electrons which has opposite rotation and anti-parallel magnetic field due to parallel magnetic field, the magnetic field generated by two electrons. They cancel each other magnetic field. So, we can say there is self cancellation of magnetic field by two electrons in anti-parallel direction. To explain the rotation of an electron around its own axis, we use a special term to explain it and i.e, is electron spin quantum number which is represented by Ms.

$$Ms = +1/2 \text{ or } -1/2$$

The electrons which rotate in clockwise direction show +1/2 and have diamagnetic properties due to self cancellation of electrons, whereas the electrons which move in anti-clockwise direction show -1/2 and show paramagnetic properties due to no self cancellation of electrons.

PRINCIPLE OF EPR SPECTROSCOPY:

It is a subfield of magnetic resonance spectroscopy in which microwave radiation is used to explore species with unpaired electrons, such as free radicals and electrons in the triplet state. Absorption of microwaves can be explained as in fig:2.

Electron particle and acts as a tiny bar magnet as its spins around its own axis. Static magnetic fields and charged microwaves are used to study the behaviour of paramagnetic electrons in a sample.

Energy difference is given by,

Δ E = E+ - E- = hv = gm ß b

Where as,

H = Planck's constant (6.626x10-34Js-A)

V = the frequency of radiation

ß = Bohr magneton (9.274 x 10-24 J T-1)

B = strength of the magnetic field in tesla

G = the g- factor

Two samples oriented at different orientations in our sample cavity, if we have a sample i. e perpendicular to the applied field, then magnetic response shifts towards lower field. But, when our sample oriented parallel to our applied field then signal shifts towards higher fields which describe about magnetic field of our sample.

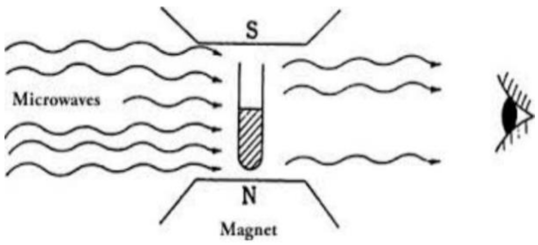

Figure 2: Absorption of microwaves

WORKING OF EPR SPECTROSCOPY:

As EPR Spectroscopy is an absorption spectroscopy, sample absorbs microwave radiations from bar magnet and therefore we get detailed information about our sample. when we put a molecule that contains unpaired electrons and its rotating in anti-clockwise direction. So, when we generate applied magnetic field then the electrons move downwards. So, thereby these electrons rotating and generate magnetic field.

So, in the presence of an applied magnetic field, these leads to adjustment of magnetic field of the revolving electron it means after adjustment the direction of an applied magnetic field and magnetic field caused by the revolving of the electrons will be alongside. Thus, this condition is known as alpha state. Alpha state is always a parallel state and has lowest energy.

So, when we provide some energy to the electrons present in alpha state, the energy provided in the form of radiation, the radiation we use in ESR is microwave. When microwave radiation is incident on these electrons (alpha state) then these electrons are able to resist the direction of an applied magnetic field and now it changes spin and shifts its position and after shifting its position it changes to opposite direction of an applied magnetic field.

After absorbing the radiofrequency, these electrons change its spin and it will be in anti-parallel direction in applied magnetic field. Magnetic field caused by the revolving of electrons will be upward direction and direction of an applied magnetic field generated by magnet of an ESR is downward. So now both the magnetic field is in opposite direction in such condition known as beta state. Beta state is an anti-parallel state and always has higher energy state.

Due to the changing of the spin/ changing the direction of spinning electrons is known as resonance. Resonance is shown by an electron and it is spinning. So, it is known to be electron spin resonance. That technique used to study it is known as electron spin resonance spectroscopy.

When we block microwave radiation the electrons present in beta state, it again come back in alpha state means the magnetic field of applied and generated are in same direction.[1-7]

EPR Vs NMR:

Difference between EPR & NMR are discussed in the table 1.

Table 1: EPR & NMR differences

Variants	EPR	NMR
1.Spin probes	Free radicals, transition metal complexes	Tissue protons
2. Sensitivity	More sensitive	Less sensitive
3.Relaxation time	Order of 0.1-1sec	Order of 0.1-1sec
4.Field	Radiofrequency constant Magnetic field vary	Radiofrequency Vary Magnetic field constant
5. Line width	0.1M Hz	Hz - KHz
6.Position expression	In terms of g-value	In terms of chemical shift

Instrumentation:

EPR Spectroscopy includes source, electromagnet, sample cavity, crystal detector, auto amplifier, and recorder or oscilloscope as shown in fig 3.

Source:

The source to produce microwave radiation is klystron oscillator. Klystron oscillator normally operates at 9500 mHz and produce monochromatic microwave radiation. Klystrons are high power microwave vacuum tubes. They are used in radars as amplifiers or oscillators due to velocity-modulator tube. Kinetic energy is used in klystron for the amplification of a high-frequency signal. Working of klystron oscillator was shown in fig 4.

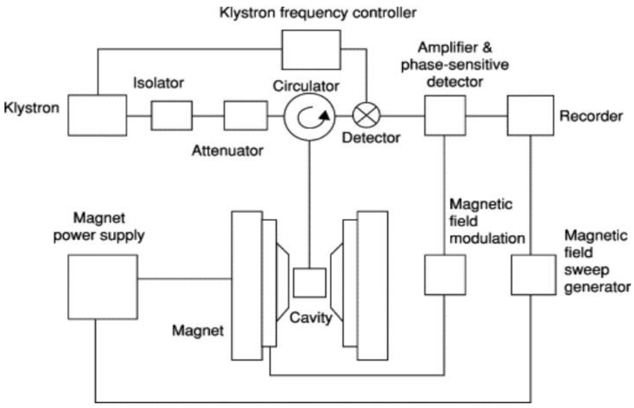

Figure 3: Instrumentation of ESR

Working on klystron oscillator:

As klystron, contains electron emitter which is associated to negative terminal whereas positive terminal is associated with cavity. As we give electric pressure to electron emitter, electrons are produced and generated in the vertical direction. So here produced electron goes towards same direction and composed in the cavity.

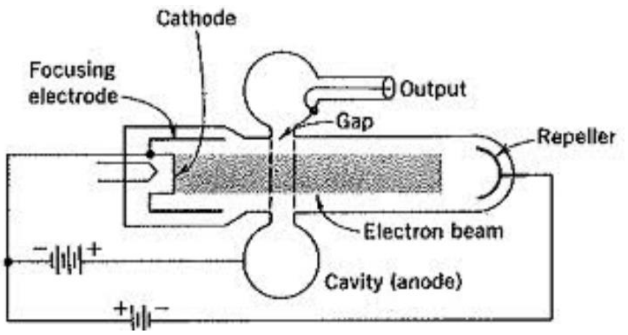

Figure 4: Working of klystron Oscillator

Electrons cross cavity and space between the cavity to repeller electrode is repeller space. Electrons in repeller space are repelled by electrode.

Due to the repulsive force of repeller electrode, the electrons change its direction and recollected by having bouncing from repeller and they will go into anode cavity. Electrons are continuously generated in which some are early electrons, reference electrons, and late electrons. But the case is that we want to have bunching of electron so how we can bunch electron.

Early electrons which will be having more time to travel in this space, so there will be less amount of repulsive force which will be there because of this repeller electrode and because of less force acceleration coefficient is less thereby its velocity is less.

The electrons which are late electron they will be having higher amount of accelerating force which is happening by this electrode so they will be moving in this anode cavity electron higher velocity.

So ultimately at the end what happens is those electrons are getting collected as a bunch in this cavity and at this cavity we are connecting RF output coaxial cable. So, there will be a bunch of electrons with some periodic time feed here. So that we can have generation of microwave oscillation with a fixed reference time barrier and this is what we are keeps on repeating continuously, so will be having continuous bunching of electrons which is happening in this cavity. So ultimately basic operation is here electron gun is generating electrons that is actually moving in this anode cavity but some electrons are drifting towards repeller space and they are again repelled by this repeller electrode and the reason is negative terminal of battery is been connected to repeller electrode. So now gain they will further move in opposite direction because of repulsive force and they will be collected over but that collection of those electrons should be in bunch and that is what happening as for velocity modulation which is happening over repeller space.

Velocity modulation means those electrons which are early they are provided with lesser velocity and those electrons which are late they provided with higher velocity. So, after fixed time failure all electrons getting bunched at a fixed position and to understand that we need to see a per gate diagram of this reflex.

Early electrons velocity is denoted as Ve, reference electrons velocity is denoted as Vr and late electrons velocity is denoted as Vl. Ve<Vr<Vl then after fixed time interval it is possible that it can bunch the electrons at one position the reason is the electrons (early electrons) will move slow. Late electrons will move fast so ultimately when it reaches anode cavity all those electrons will be there in bunch. So, this is what velocity modulation which is happening inside of klystron supply.

If you connect reflux klystron supply and vary another voltage and repeller, we can observe signal transformation is happening in rectangular wave guide and some repeller voltage and anode voltage. So those some anode voltage and repeller voltage transformation of signal that could be there with respect to these zones.

Electromagnet:

Strong electromagnets that are mounted on the sides of the resonant cavity produce a linear magnetic field by modulating the magnetic field. By giving an a.c. signal to modulation coils directed towards the sample in the same direction as the magnetic field, the variation is created. The coils can also be installed on the magnet pole components for low frequency modulations (400 cycles per second or less). Since metal cannot be efficiently penetrated by high modulated frequencies (1KV or more), either the modulation coils must be positioned inside the resonant cavity, or cavities made of non-metallic materials (such as quartz with a thin silver plating) must be used.

Wave guide:

It is located between the isolator and the attenuator. The microwave frequency emitted by the klystron is known.

Attenuator:

It is situated between the wave meter and the circulator, and the attenuator adjusts the amount of microwave power landing on the sample

Circulator or magic T:

The circulator receives microwave radiation from klystron through a waveguide that is connected to an oscillating magnetic field. In the waveguide, a similar field has been put up. The most common material used to create a waveguide is hallo rectangular copper (or brass) tubing. In order to provide a flat surface that conducts electricity well, the inside of the tube is plated with silver or gold. The image(fig:5) below describes how the four-port circulator works in ESR spectroscopy.

1. Arm is exposed to microwave radiation.
2. Resonant cavity is attached to arm 2.
3. Arm 4 has a load for absorbing potential detector-reflected power.
4. Arm 4 is connected to the ESR spectrometer's detector.

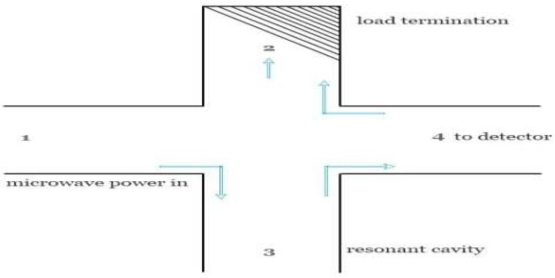

Figure 5: Circulator or magic T

Sample cavity:

These cavities are designed to create a resonant condition for the electromagnetic waves and facilitate the interaction between the sample and the applied magnetic field. Most common used sample cavities in ESR spectrometers are the rectangular TE120 cavity and the cylindrical TE011 cavity.

Due to the simultaneous observation of a sample and a reference material, dual sample cavities are employed. Sources of inaccuracies are mitigated by comparing relative signal heights when using reference material.

There is an aperture through which a little quantity of microwave can reach the material being studied when it is inserted into the cavity. Near the entrance, there is an adjustable device called iris that adjusts the "electrical size" of the opening. It is an electronic transformer. Iris is tweaked to align the cavity with the waveguide.

Choice of solvents:

ESR spectrum can be obtained for gases, powders, crystals and frozen solution. The best frozen solution results are obtained when the solvent (e.g. methyl Cyclohexane) freezes to former glass. Solvents of high dielectric constant water and alcohol should be avoided because they absorb in microwave radiation. Concentration of the sample should be about 10^{-6} m when structural determination and quantitative analysis are to be carried out.

Detectors:

A silicon crystal detector, also known as a silicon radiation detector, is a type of semiconductor detector that is used to detect ionizing radiation, such as X-rays, gamma rays, and charged particles. It is made from a single crystal of high-purity silicon, and works by exploiting the interaction between the radiation and the crystal lattice structure of the silicon.

When ionizing radiation passes through the silicon crystal, it interacts with the atoms in the crystal lattice, causing them to become ionized and generate electron-hole pairs. The electron-hole pairs can be detected as a current signal by applying a voltage across the silicon crystal and measuring the resulting electrical signal.

Silicon crystal detectors are widely used in various applications, including medical imaging, radiation monitoring, and nuclear physics research, among others. They offer high sensitivity, fast response time, and good energy resolution, making them a valuable tool for detecting and measuring ionizing radiation.

There are several types of silicon crystal detectors, including:

PIN diode: It is a type of silicon crystal detector that consists of a p-type region, an intrinsic (undoped) region, and an n-type region. The intrinsic region acts as a radiation-sensitive layer, where the ionizing radiation generates electron-hole pairs that are detected as a current signal. Fig 6 shows working of PIN diode in EPR.

Schottky diode: A Schottky diode is a type of silicon crystal detector that consists of a metal-semiconductor junction. When radiation enters the depletion region near the junction, it generates electron-hole pairs that are detected as a current signal.

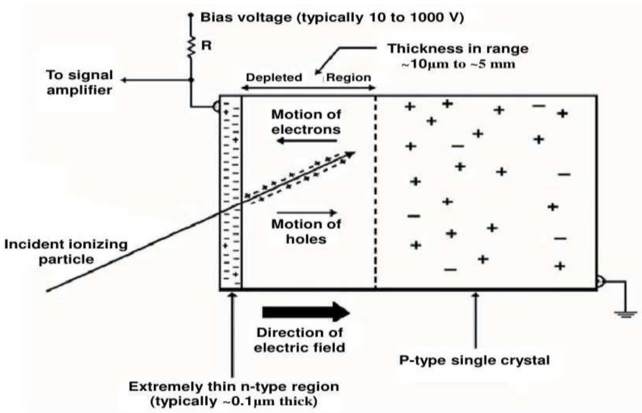

Figure 6: Working of PIN diode detector

Metal-semiconductor-metal (MSM) detector: An MSM detector is a type of silicon crystal detector that consists of two metal electrodes separated by a radiation-sensitive

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semiconductor layer. When radiation enters the semiconductor layer, it generates electron-hole pairs that are detected as a current signal between the two metal electrodes.

Phase detector:

A phase-sensitive detector (PSD) is an electronic device that extracts the phase information from a modulated signal. It works by comparing the input signal with a reference signal of the same frequency, and then extracting the phase shift between the two signals. Working of phase detector was shown in fig 7.

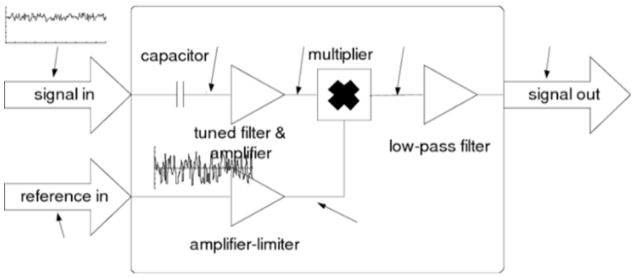

Figure 7: Working of phase detector

It is also called pulse generator circuit. This detector consists of zero crossing detector and RE differentiator. Zero crossing detector circuit basically provides output whenever the input signal crosses zero every time. Non-inverting terminal having input signal and the investing terminal is connected to ground that means in this case the V reference is equal to O as the inverting terminal is connected to ground so every time whenever the input signal crosses zero and when it becomes positive the circuit provides output as a square wave. Now and RE differentiate circuit provides positive as well as negative pulses at the output when we apply a square wave to capacitor and resistor network the diode D will allow only the positive pulse to pass through the output therefore, across load resistance we will get only positive pulses.

Sine wave is applied as input terminal of op-amp. The op-amp is used as the zero crossing detectors. It provides output as a square wave. That square wave is applied to RC differentiation network, the function of differentiator is to provide output voltage which is proportional to the differential version of input signal so when we apply square wave as input then we get positive as well as negative pulse at the output.

Further positive and negative pulses are applied to diode then they will allow only positive pulses to passes through load resistance. Phase detector which contains op-amp has as a 0% detector the output of op-amp is given to RC differentiator and further to the diode so that we can get only positive pulses as the output. [8-10]

Applications:

1. It is used to study metalloproteins, particularly those containing molybdenum, copper, iron, etc.
2. Free radicals can be studied even in very low concentrations.
3. It provides information about the shape of the radical.
4. It may be used to examine tissues, cells, biopolymers, medicines, cosmetics, botanicals, and biomaterials.
5. It is a non-invasive approach for detecting contaminants implicated in the deterioration of medicinal qualities.
6. The use of ESR in recognising and estimating irradiated goods such as meat, fruits, vegetables, spices, cereal grains, and oil seeds was examined. Finally, the potential application of the ESR method in studying microstructure change, phase transition.
7. EPR permits the direct measurement of microviscosity and micropolarity inside drug delivery systems (DDS), the detection of microacidity, phase transitions and the characterization of colloidal drug carriers.
8. EPR technique allows repeated measurements of oxygen in tissues – also in vivo and in combination with imaging techniques. The direct detection of paramagnetic species like transition metal ions by EPR allows elucidation of their specific roles in disease. [11-15]

CONCLUSION

Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful technique used to study materials with unpaired electrons. It provides detailed information about the electronic structure, local environment, and dynamics of paramagnetic species. EPR spectroscopy is widely used in chemistry, physics, biology, and materials science to investigate radicals, metal complexes, and defects in solids. Electron paramagnetic resonance (EPR) spectroscopy is a versatile technique with many applications, including natural product research, Drug delivery, radiation research, nanomaterials, protein dynamics. EPR is a sensitive to species that are paramagnetic, which means they contain one or more unpaired electrons. The recorded EPR spectrum provides information about the g-value and linewidth of the paramagnetic species, which can be used to understand the sample's electronic structure, coordination environment, and dynamics.

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