

Electron Spin Resonance (ESR) Spectroscopy

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Electron spin resonance (ESR)

- Electron paramagnetic resonance (EPR) or Electron Magnetic Resonance (EMR) or otherwise known as electron spin resonance (ESR) spectroscopy is the resonant absorption of microwave radiation by an unpaired electron of an atom or molecule (paramagnetic species) when placed in a strong magnetic field.
- ESR is built on the idea that molecules, ions, atoms or molecular fragments with an odd amount of electrons have distinctive magnetic properties.
- The electron is spin-dependent and as a result of spin, there is a magnetic moment.
- In 1944 when it was discovered by E.K. Zavoisky, EPR spectroscopy has been utilized as a highly precise and useful technique to study different types of paramagnetic species found in liquid and solid states.

- It is a powerful technique used to study:
- **Free Radicals:** Atoms, molecules or ions containing one unpaired electron either in the Solid, Liquid or Gaseous Phases
- **Transition Ions Including Actinide Ions:** These routinely may have up to five or seven unpaired electrons
- **Various 'Point' Defects in solids:** Localized Imperfections
- **Systems with More than One Unpaired Electron:** Triplets state systems, biradicals and multiradicals
- **Systems with Conducting Electrons:** Semiconductors and metals

Principle of Electron Spin Resonance (ESR)

- The phenomenon of electron spin resonance (ESR) is based on the fact that an electron is a charged particle.
- It spins around its axis and this causes it to act like a tiny bar magnet.
- Every electron has a magnetic moment and spin quantum number $s = 1/2$ with magnetic components $m_s = + 1/2$ or $m_s = -1/2$.
- When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align in two different ways creating two spin states $m_s = \pm 1/2$.
- The alignment can either be along the direction (parallel) to the magnetic field which corresponds to the lower energy state $m_s = - 1/2$
Opposite (antiparallel) to the direction of the applied magnetic field $m_s = + 1/2$

...Principle

- The two alignments have different energies and this difference in energy lifts the degeneracy of the electron spin states. The energy difference is given by:

$$\Delta E = E_{+1/2} - E_{-1/2} = h\nu = g\beta B$$

Where,

- h = Planck's constant ($6.626 \times 10^{-34} \text{ J s}^{-1}$)
- ν = the frequency of radiation
- β = Bohr magneton ($9.274 \times 10^{-24} \text{ J T}^{-1}$)
- B = strength of the magnetic field in Tesla
- g = the g-factor which is a unit less measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023.
- An unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy $h\nu$ such that the resonance condition, $h\nu = \Delta E$, is obeyed.
- This leads to the fundamental equation of EPR spectroscopy.

Working of Electron Spin Resonance (ESR)

- Although the equation permits a large combination of frequency and magnetic field values, the great majority of EPR measurements are made with microwaves in the 9000–10000 MHz (9–10 GHz) region.
- EPR spectra can be generated mostly by keeping the photon frequency fixed while varying the magnetic field incident on a sample.
- A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency.
- By increasing an external magnetic field, the gap between the energy states is widened until it matches the energy of the microwaves.
- At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, there is a net absorption of energy.
- It is this absorption that is monitored and converted into a spectrum.

Instrumentation of Electron Spin Resonance (ESR)

KLYSTRONS

- Klystron tube acts as the source of radiation.
- It is stabilized against temperature fluctuation by immersion in an oil bath or by forced air cooling.
- The frequency of the monochromatic radiation is determined by the voltage applied to klystron.
- It is kept a fixed frequency by an automatic control circuit and provides a power output of about 300 milli watts.

WAVE GUIDE OR WAVEMETER

- The wave meter is put in between the oscillator and attenuator.
- To know the frequency of microwaves produced by klystron oscillator.
- The wave meter is usually calibrated in frequency unit (megahertz) instead of wavelength.
- Wave guide is a hollow, rectangular brass tube. It is used to convey the wave radiation to the sample and crystal.

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ATTENUATORS

- The power propagated down the wave guide may be continuously decreased by inserting a piece of resistive material into the wave guide. This piece is called variable attenuator.
- It is used in varying the power of the sample from the full power of klystron to one attenuated by a factor 100 or more.

ISOLATORS

- It's device which minimizes vibrations in the frequency of microwaves produced by klystron oscillator.
- Isolators are used to prevent the reflection of microwave power back into the radiation source.
- It is a strip of ferrite material which allows micro waves in one direction only.
- It also stabilizes the frequency of the klystron.

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SAMPLE CAVITIES

- The heart of the ESR spectrometer is the resonant cavity containing the sample.
- Rectangular TE₁₂₀ cavity and cylindrical TE₀₁₁ cavity have widely been used.
- In most of the ESR spectrometers, dual sample cavities are generally used. This is done for simultaneous observation of a sample and a reference material.
- Since magnetic field interacts with the sample to cause spin resonance, the sample is placed where the intensity of magnetic field is greatest.

COUPLERS AND MATCHING SCREWS

- The various components of the micro wave assembly to be coupled together by making use of irises or slots of various sizes.

CRYSTAL DETECTORS

- Silicon crystal detectors, which converts the radiation in D.C has widely been used as a detector of microwave radiation.

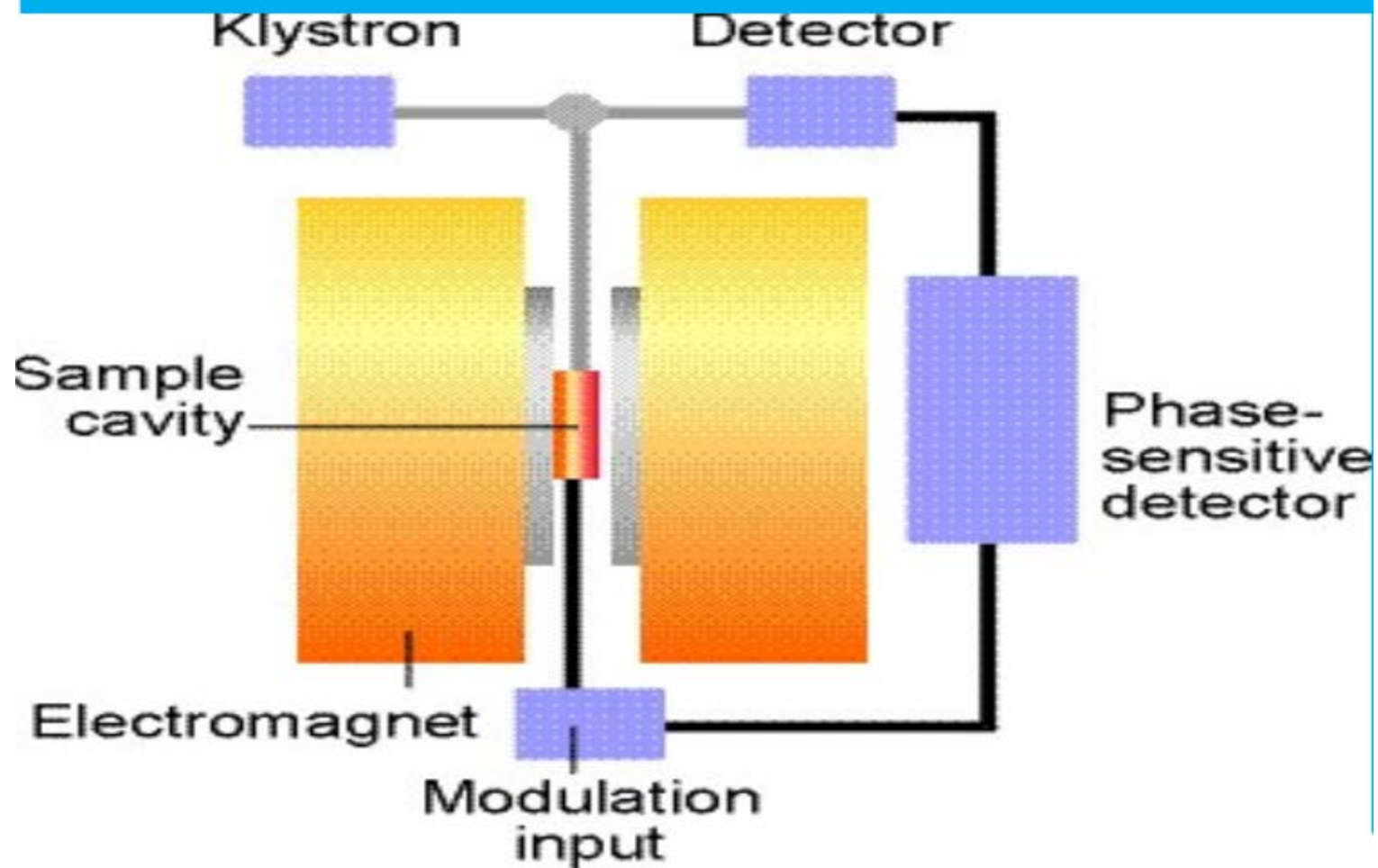
MAGNET SYSTEM

- The resonant cavity is placed between the poles pieces of an electromagnet.
- The field should be stable and uniform over the sample volume.
- The stability of field is achieved by energizing the magnet with a highly regulated power supply.
- The ESR spectrum is recorded by slowly varying the magnetic field through the resonance condense by sweeping the current supplied to the magnet by the power supply.

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- **MODULATION COIL**
- The modulation of the signal at a frequency consistent with good signal noise ratio in the crystal detector is accomplished by a small alternating variation of the magnetic field.
- The variation is produced by supplying an A.C. signal to modulation coil oriented with respect the sample in the same direction as the magnetic field.
- **DISPLAY DEVICES**
- In order to observe the signal a system is connected different devices can be used.

ESR Spectrometer:



Applications of Electron Spin Resonance (ESR)

- ESR spectrometry is one of the main methods to study transition metal containing metalloproteins.
- To determine the rate of catalysis.
- To know about the active site geometry.
- To study denaturation and protein folding.
- In studies relating to enzyme-ligand interaction.
- In Biological Systems
- Study of Free Radicals
- Spin Labels
- Study of Inorganic Compounds
- Reaction Velocities & Mechanisms
- Study of naturally occurring substances such as minerals with transition elements, minerals with defects (e.g; quartz), Hemoglobin (Fe), Petroleum, Coal, Rubber etc.
- Conducting Electrons