# EPR
## Electron Paramagnetic Resonance

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**About the student:** Jitavati Das is a student at Ashok Hall Girls' Higher Secondary School, Kolkata, India.This paper was prepared by Jitavati as a part of her course work for LS102-07 Introduction to College Level Research course at Allegheny College during summer 2022.

## SUMMARY:

### ABSTRACT

Electron paramagnetic resonance (EPR) spectroscopy or Electron spin resonance (ESR) spectroscopy is a versatile, non-destructive analytical technique which can be used for a variety of applications including: oxidation and reduction processes, bi-radicals and triplet state molecules, reaction kinetics, as well as numerous additional applications in biology, medicine and physics. However, this technique can only be applied to samples having one or more unpaired electrons, it is performed in different states and temperature.

In Allegheny College at Professor Petasis's Lab, the EPR spectral analysis of DPPH (at room temperature) and $MNCL_2$ were recorded. In this paper, the same has been analysed.

### INTRODUCTION

Electron paramagnetic resonance spectroscopy (EPR) is a tool for investigating paramagnetic species, including organic radicals, inorganic radicals, and triplet states. The basic principles behind EPR are very similar to the more ubiquitous nuclear magnetic resonance spectroscopy (NMR), except that EPR focuses on the interaction of an external magnetic field with the unpaired electrons in a molecule, rather than the nuclei of individual atoms. EPR has been used to investigate kinetics, mechanisms, and structures of paramagnetic species and along with general chemistry and physics, has applications in biochemistry, polymer science, and geosciences.

EPR provides information about the paramagnetic ions of a sample, additionally, provides us with the following:

- The identity, oxidation and spin state of the paramagnetic ions

- The nature of the ligands surrounding the paramagnetic ions

- The interactions of the paramagnetic ions with the lattice.

DPPH & MNCL[2]

DPPH is a common abbreviation for the organic chemical compound 2,2-diphenyl-1-picrylhydrazyl. It is a dark-coloured crystalline powder composed of stable free radical molecules. DPPH has several crystalline forms which differ by the lattice symmetry and melting point. DPPH is a well-known radical and a trap ("scavenger") for other radicals. Therefore, rate reduction of a chemical reaction upon addition of DPPH is used as an indicator of the radical nature of that reaction.

DPPH has two major applications, both in laboratory research: one is a monitor of chemical reactions involving radicals, most notably it is a common antioxidant assay, and another is a standard of the position and intensity of electron paramagnetic resonance signals.

MnCl2 is an inorganic chemical existing in the anhydrous form, as well as the dihydrate & tetrahydrate, with the tetrahydrate being the most common form. It is a paramagnetic salt and has characteristic of transition metal complexes with high spin d5 configurations.

# BACKGROUND THEORY

The Electron paramagnetic resonance spectroscopy technique is based on the interaction of an external magnetic field with spin magnetic moment of unpaired electrons, that is the Zeeman effect (the splitting of a spectral line into two or more components of slightly different frequency when the light source is placed in a magnetic field).

This interaction produces a splitting of the degenerate Ms spin energy levels. An electron on the lower energy level can absorb electromagnetic radiation and make a transition to the excited state giving rise to the EPR phenomenon.
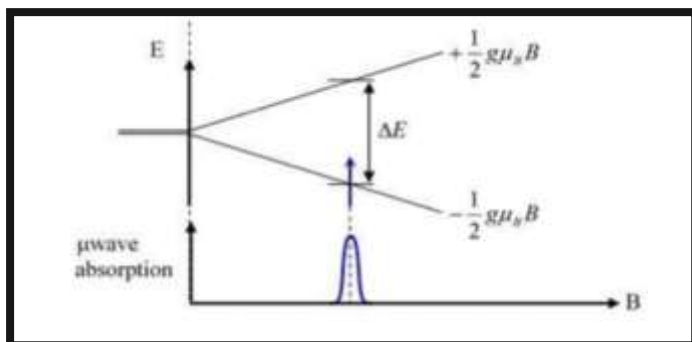


**Figure 1.** *Zeeman splitting of the degenerate electronic spin states for an S= 1 2 / system. An electron can absorb energy to make a transition to the excited state resulting in an EPR absorption line.*
(Dr. Petasis handout)

The degeneracy of the electron spin states is lifted when an unpaired electron is placed in a magnetic field, creating two spin states, $m_s = \pm \frac{1}{2}$, where $m_s = -\frac{1}{2}$, the lower energy state, is aligned with the magnetic field. The spin state on the electron can flip when electromagnetic radiation is applied. In the case of electron spin transitions, this corresponds to radiation in the microwave range.

The energy difference between the two spin states is given by the equation

$$\Delta E = E+ - E- = h\nu = g\mu_B B_0$$
$$\text{Or, } g = 0.71449\ \nu(GHz)/\ B_0\ (kG)$$

where h is Planck's constant ($6.626 \times 10^{-34}$ J s-1), $\nu$ is the frequency of radiation, ß is the Bohr magneton ($9.274 \times 10^{-24}$ J T-1), B is the strength of the magnetic field in Tesla, and g is known as the g-factor. The g-factor is a unit less measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.002. The value of g can vary, however, and can be calculated by rearrangement of the above equation.

An electronic transition is possible when: $h\nu = \Delta E = g\mu_B B$

HYPERFINELINE
The nuclei of the atoms in a molecule or complex usually have their own fine magnetic moments. Such magnetic moments occurrence can produce a local magnetic field intense enough to affect the electron. Such interaction between the electron and the nuclei produced local magnetic field is called the hyperfine interaction. Then the energy level of the electron can be expressed as:

$$E = g m_B\ B_0\ M_S + A\ M_s\ m_I$$

with A as the hyperfine coupling constant, mI is the nuclear spin quantum number.

Many transition series ions have nuclei with spin that interact with unpaired spins and produce splittings in the EPR spectra. These electron-nuclear interactions give rise to hyperfine structure. A nucleus with spin I interacting with an electron with spin S produces splittings in the $m_s$ electronic levels.

The multiplicity of these levels is given by (2I+1) and each level is labelled by the quantum number m; Transitions are now allowed between the mi levels obeying the selection rules: Δms = +1 and ΔmI = 0.



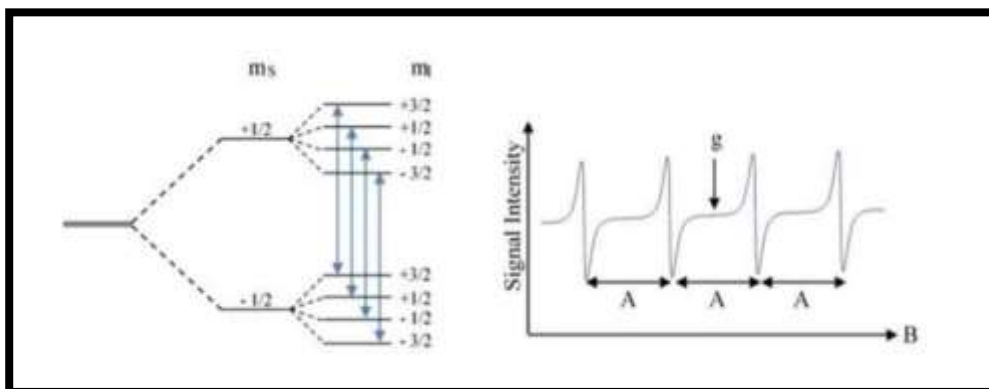**Figure 2.** *Hyperfine splitting's in a system with S = 1/2 and I = 3/2 . Allowed transitions between the nuclear levels obey the selection rule Δms = ±1 and Δmi = 0 and are indicated by the arrows. On the right hand side figure, ideal EPR hyperfine spectrum for a species with I = 3/2*

These transitions give rise to (2I+1) equally spaced EPR lines of equal intensity. The magnetic field separation of the hyperfine lines is called the hyperfine constant A and it is characteristic of the particular ion. Typical transition series ions with nuclear spin are $Cu^{2+}$ (I = 3/2), $Mn^{2+}$ (I = 5/2) and $Co^{2+}$ (I = 7/2).

LIGAND

Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom. A metal ion in solution does not exist in isolation, but in combination with ligands, giving rise to complex ions or coordination compounds.
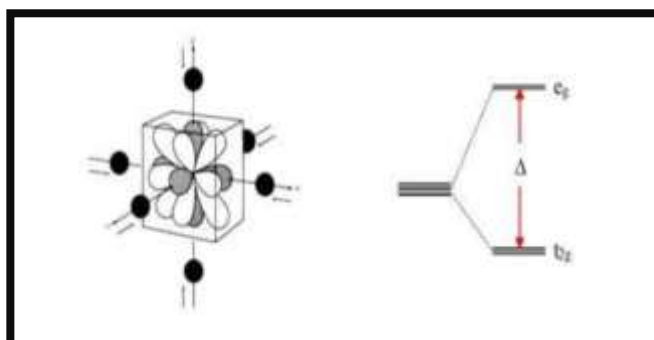


**Figure 3.** *The orientation of the d-orbitals relative to the ligands in an octahedral symmetry shown on the left. The splitting of the degenerate orbital states is shown on the right* (Dr. Petasis handout)

Paramagnetic ions are part of a lattice and interact with the various ligands in the lattice. This effect is due to the interaction of the d-orbitals of the metal ion with the electrostatic field created by the ligands. The ligand geometry is responsible for the nature and strength of the interactions. The most common symmetry is octahedral where the paramagnetic ion is at the origin of coordinates and the eight ligands are symmetrically arranged about it, forming pairs along the coordinate axe. The octahedral ligands interact more strongly with the $e_g$ orbitals ($dz^2$ and $d x^2-y^2$) than with the $t_{2g}$ orbitals ($d_{xy}$, $dyz$, and $d_{xz}$) resulting in a splitting of the degenerate orbital states. The consequence of this splitting is that we can now have different spin states for a particular valence state of an ion, depending on the strength of the interactions between transition series ion and the ligands.

## EXPERIMENT

The instrument we are using is a Varian E-3 X-band EPR spectrometer with a liquid nitrogen flow cryostat. This spectrometer operates in the frequency range 8.5–12 GHz and in the temperature range from about 80 K to room temperature. It utilizes a microwave bypass arm to bias a diode detector for increased sensitivity. The signal from the detector is processed by an electronics console and is plotted on an X-Y plotter. We have access to a scanner and a computer in the lab that allows us to digitize the spectra and convert them into electronic copies.



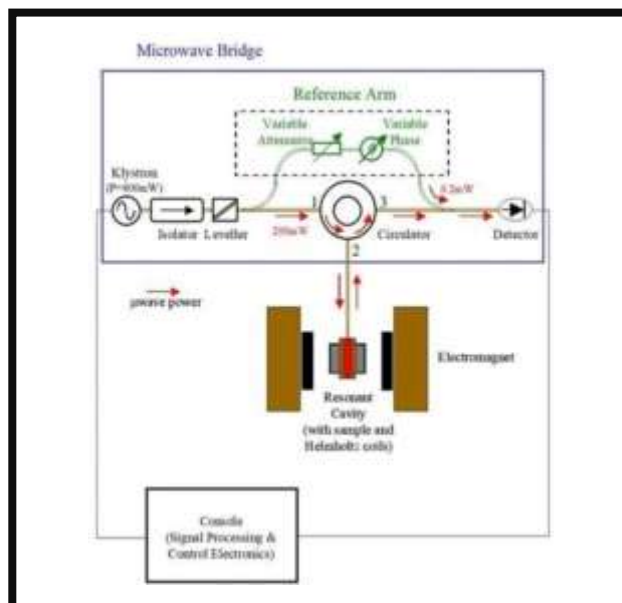**Figure 4.** *Setup of the Varian E-3 spectrometer*
(Dr. Petasis handout)



**Figure 5.** *Schematic diagram of the EPR spectrometer*

(Dr. Petasis handout)

## STEPS TO FOLLOW

- When doing a room temperature scan, the spectrometer and the universal counter needs to be turned on.

- The temperature controller can remain off.

- The frequency channel must be set to channel three to get an accurate reading.

- Next, the intensity of the oscilloscope (arrow fourteen) must be turned all the way to the right.



**Figure 6.** *Control board for Varian E-3 spectrometer* (Dr. Petasis handout)

- Once a signal is seen, a sample can then be placed within the cavity and the mode knob must be turned to tune.

- There should be a dip displayed on the oscilloscope. The horizontal position of the dip is controlled by the frequency knob and the vertical position of the dip is controlled by the power attenuation knob. We need to adjust the horizontal position of the dip until it lines up with the black line present on the oscilloscope.

- The bottom of the dip is controlled by the coupling iris, which is controlled by the Teflon rod, the black rod located behind the cavity. Turn this rod clockwise or counter clockwise until the dip bottoms out.

- Once the dip is in the proper position, the mode knob can be turned to operate. Now, the recorder switch can be turned on.

- The frequency and power attenuation knobs must be adjusted to ensure that the frequency error and detector current are in the proper positions.

- The magnetic field mid-range and scan range can be set, and the scan button can be pushed to the right to begin a room temperature EPR run.
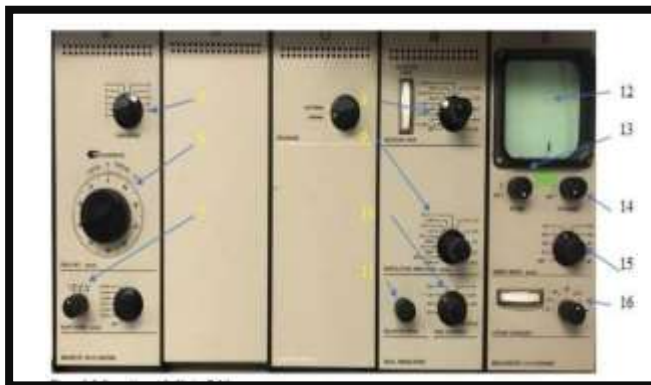
INSTRUMENTAL PARAMETERS

Microwave frequency = 9.139 GHz

Microwave power = 3.2 mW

Center Field = 3.2 kG

Sweep range = ±250 G

Modulation field = 20 G

Modulation frequency = 100 kHz

Scan time = 4 min

Gain = $10 \times 10^2$

T = room temperature (approx. 298K)


## FOR MNCl$_2$/ H$_2$O


## STEPS TO FOLLOW

- When conducting a low temperature (or, MNCl$^2$) EPR run with the Varian E-3 Spectrometer, the temperature controller needs to be turned on after coolant water is turned on.
- The main valve on the nitrogen tank, located behind the spectrometer, needs to be opened.
- The nitrogen flow should have a pressure around 25 or 30 psi.
- Insert liquid nitrogen into the dewar
- Once liquid nitrogen is in the dewar, the sample being tested needs to be slowly lowered into a separate dewar which contains liquid nitrogen.
- Once the sample is cooled, it can then be placed into the cavity.
- Now, steps similar to the DPPH sample or room temperature sample must be conducted.

INSTRUMENTAL PARAMETERS

Microwave frequency = 9.144 GHz

Microwave power = 5 mW

Center Field = 3 kG

Sweep range = ±2500 G

Modulation field = 40 G

Modulation frequency = 100 kHz

Scan time = 2 min
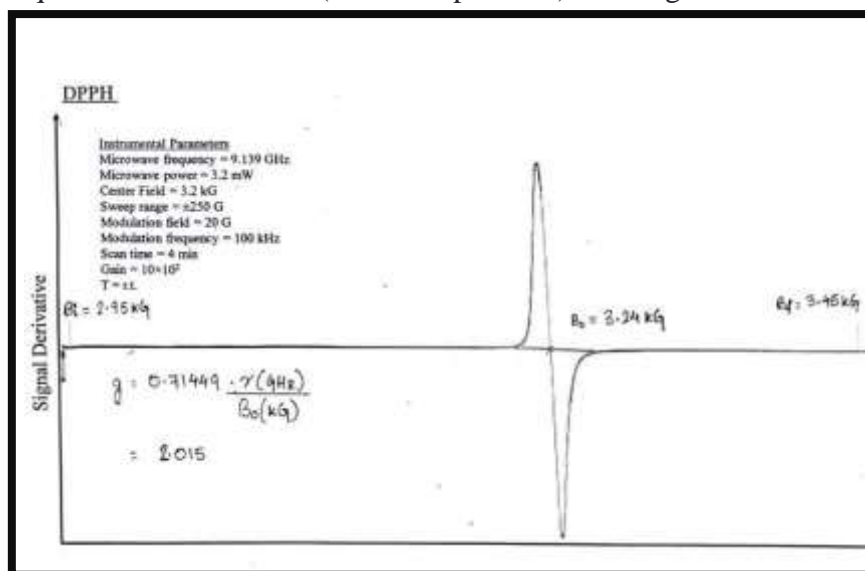
Gain = $5 \times 10^3$

T = 104 K

# RESULTS & DISCUSSION

From the EPR spectrum and the resonance condition we can determine the g-value of our spin system. The g-value gives us information on the different interactions that the spin system experiences such as spin-orbit coupling (g=2.002 for free electrons, g $\neq$ 2.002 for bound electrons), hyperfine interactions (present when nuclear spin is not zero: (2I+1) EPR lines where I, is the nuclear spin), ligand symmetry (high spin and low spin states), interactions with ligands and other paramagnetic ions (eg: exchange and dipolar interactions).

## DPPH\

The EPR spectrum obtained from DPPH sample shows that it is a free radical with a g factor equal to 2.015 at 298K (room temperature). The signal at $B_0$ = 3.24 kG depicts a very narrow line width, that is a small $\Delta B$ value due to the highly concentrated crystalline used. The g value for DPPH is supposed to be 2.002 while the value obtained from the given sample is 2.015, having an error of only 0.6%.



**Figure 7.** *EPR absorption spectrum of DPPH*

## MNCl₂/ H₂O

The EPR spectrum obtained for MnCl2/H2O shows six hyperfine lines due to coupling for the S = 1/2 electron spin with the I = 5/2 nuclear spin for the $Mn^2$+ion. The $g_{avg}$ of the six hyperfine lines is 1.6 while the g-factor at B0= 2715G is 2.4.

The hyperfine coupling constant A is taken to be 90 G. Upon manually obtaining the hyperfine constant A from the given sample a value of 80.41G (finding the average of the differences between adjacent lines) has been obtained.
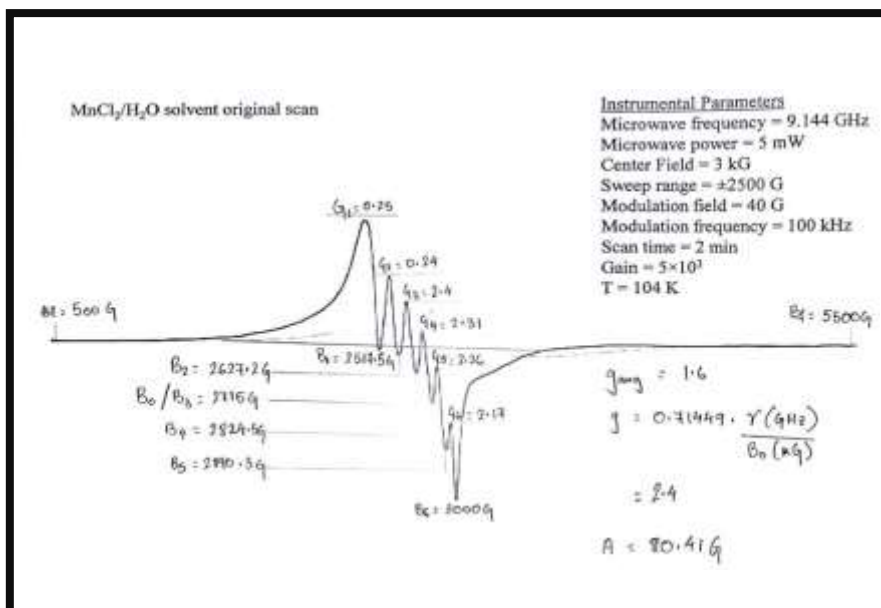
Therefore, obtaining an error of 11.1%. The simplest explanation of the reduced value of A in the complex is that the unpaired electrons are delocalized on to the chloride ions of the complex and result in decreased interaction with the Mn nucleus.

**Figure 8.** *EPR absorption spectrum for Mncl₂ in water*

Thus, the Mn hyperfine spacing is less than would be expected for no electron delocalization. Plus, there are two other possible explanation that are source of error in field range and determination of the field position not being accurate.

## CONCLUSION

| SAMPLE | SPECTRUM DETAILS |
|---|---|
| **DPPH** | g factor= 2.015 & $B_0$ = 3.24 kG, error%= 0.6% |
| **MNCl₂/ H₂O** | 6 hyperfine lines, $g_{avg}$= 1.6, $B_0$= 2715G, g factor= 2.4, $g_{avg}$ & g factor= 0.33…, A= 80.41G, ΔA= 11.1%, Δg = 1.9%, |

**CHART 1.** *It shows the sample and its details obtained from the Varian E-3 X-band EPR spectrometer*

## REFERENCE

- (James R. Bard, Joe T. Holman, and James 0. Wear, "An Electron Paramagnetic Resonance Study of Mn (II)-Chloro Complex Formation in N, N-Dimethylformamide" Zeitschrift für Naturforschung B, vol. 24, no. 8, 1969, pp. 989-993)
- (Pavan M.V. Raja & Andrew R. Barron, "Physical Methods in Chemistry and Nano Science")
- ("Supplemental Modules: Physical and Theoretical Chemistry", under chemistry LibreTexts)
- Handouts by Prof. Petasis