Analysing EPR Spectra: DPPH Free Radical and $MnCl_2$ in H_2O

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Abstract

Electron Spin Resonance is a spectroscopy technique which helps determine electronic structures and ligand interactions of materials with unpaired electrons. Broad in every respect, EPR experiments range from simple to highly complicated, their results are applicable is a multitude of fields from chemistry to medicine.

This research paper briefly walks you through the basic theory and set up of this spectroscopy experiment. The primary aim was to examine the EPR spectra of DPPH and $MnCl_2$ samples and thereby determining their g-factor (an important quantity in deducing the nature of a paramagnetic material) along with other spectral terms. The study concludes with an elementary error analysis and hypothesis of how these are evolved.

Introduction

Electron Spin Resonance is a spectroscopy technique that produces signal derivatives through the interaction of microwave radiation with the spin magnetic moment of paramagnetic chemical species. The interaction induces the resonance effect between to quantized/discrete magnetic energy levels through absorption of photon energy.

The purpose of this experiment is to use EPR to investigate two paramagnetic samples namely DPPH (2,2-diphenyl-1-picryl-hydrayl-hydrate) and $MnCl_2$ solution with water. Upon obtaining the spectra, we can determine the g – value of the observed system using the resonance condition. The primary purpose of this spectroscopic splitting factor is to understand the properties and determine the electronic structure of the paramagnetic sample.

The value of the g – factor varies according to the orientations of the molecule in an external magnetic field. In addition to considering the total magnetic dipole moment of a paramagnetic species, the g-value takes into account the local environment of the spin system. The existence of local magnetic fields produced by other paramagnetic species, magnetic nuclei, ligand fields can alter the effective magnetic field that the electron experiences. Thus, the g-factor vital to understand the characteristic interactions of the paramagnetic system such as spin orbit coupling, hyperfine interactions, and ligand symmetry.

Today, EPR is widely applied in varied scientific fields to distinguish magnetic properties of species, like in research of biological free radicals for the quantitative and qualitative analyses of reactive oxygen – and nitrogen – species. Given the sensitivity of the EPR technique, it is crucial to gain an in-depth understanding of the physics principles, experimental procedure, and spectra analysis.

Background Theory

Electron Paramagnetic Resonance (EPR) is a spectroscopic technique that gives us an insight into systems with unpaired electrons. EPR provides us a wealth of information about the paramagnetic ion samples, such as:

-   Their identity, oxidation, and spin state of the paramagnetic ion(s).

- Identification of free radicals in different states of matter, while gaining an understanding of the ligands surrounding the paramagnetic ions.
- Determination of the electronic structure and understanding of its interactions with the lattice.

Underlying Principles:

1) **ZEEMAN EFFECT:** The basis of EPR lies in the interaction of an external magnetic field with paramagnetic spin moment known as the Zeeman Effect. With the splitting of degenerate energy fields upon this interaction, electrons from lower ground state transitions to higher excited states. Jumping of electrons to a higher energy state by absorption only occurs when the following resonance condition is satisfied,

$$h\nu = \Delta E = g\mu_B B$$

Such that energy of the photon is exactly equal to the energy of separation between the two quantized spin levels. (Refer Fig. 1)

Here, in the above equation,

- ν is frequency of the microwave radiation,
- g is the electronic splitting factor,
- μ_B is the Bohr magneton,
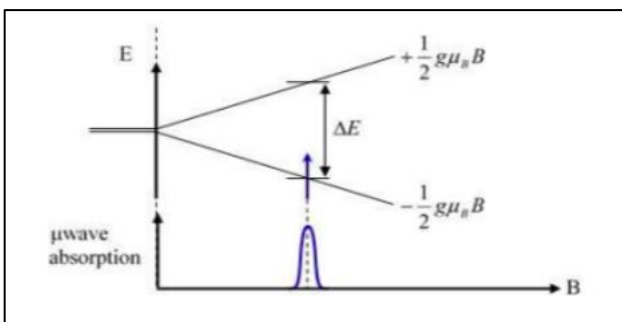- B is the applied magnetic field

Fig 1. Zeeman splitting of discrete electronic spin states and the resultant EPR absorption line spectrum
D. Petasis, EPR Handout 1, Accessed August 2022

In the experiment, the microwave source (klystron) emits radiation at a constant frequency while the external magnetic field is swept over a range. The radiation is

absorbed when the magnetic field value satisfies the resonance condition. At this point, a Gaussian graph (a bell-shaped curve) represents absorption whose 1st derivative is plotted.

2) **HYPERFINE INTERACTIONS:** In addition to the splitting of the energy fields, majority of the transition elements possess spinning nuclei. Thus, the electron-nuclear interactions give rise to hyperfine structure with multiplicity given by a factor of $(2I + 1)$, labeled by the quantum number m_I.

Within these, the electronic transitions follow the selection thumb rule,

$$\Delta m_s = \pm 1, \Delta m_I = 0$$

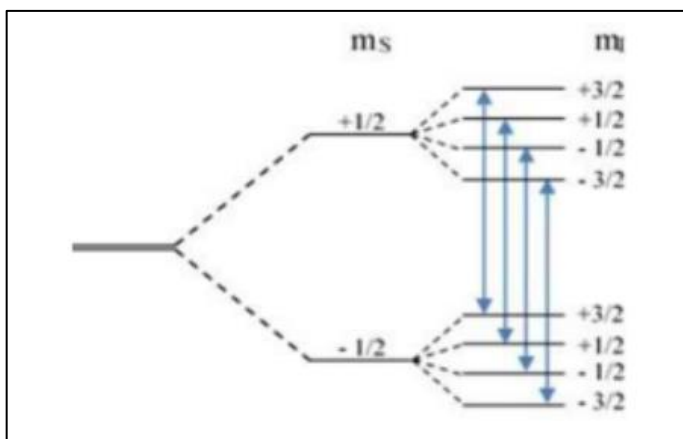This results in a regularly spaced EPR lines of equal intensity. (As shown in Fig. 2)

Fig. 2: Hyperfine line splitting, Schematic representation of the selection rule
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The magnetic field separation of the hyperfine lines is called the hyperfine coupling constant, denoted by A. In the typical case of Cu^{2+} ion with the nuclear spin I=3/2, a spectrum as shown in Fig. 3 is obtained.
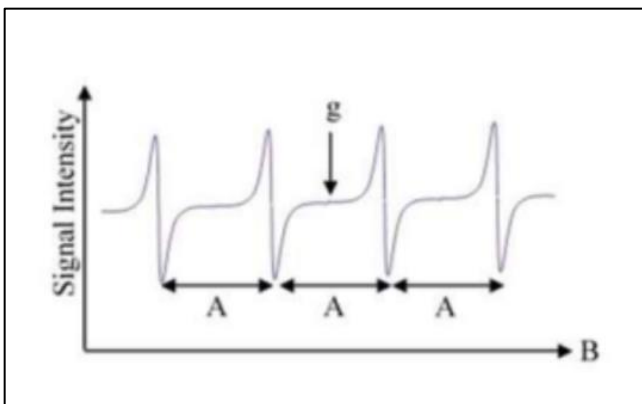
Fig. 3 A typical spectrum of Cu^{2+} ion, with a characteristic nuclear spin I=3/2 and hyperfine constant A
D. Petasis, EPR Handout 1, Accessed August 2022

Experimental Procedure

Spectrometer Used: Varian E-3 X-Band EPR spectrometer with a liquid nitrogen flow cryostat. It operates in the frequency range 8.5 – 12 GHz and in temperature range from about 80 K to room temperature. It utilizes a microwave bypass arm to bias a diode detector for increased sensitivity as shown in Fig. 4.
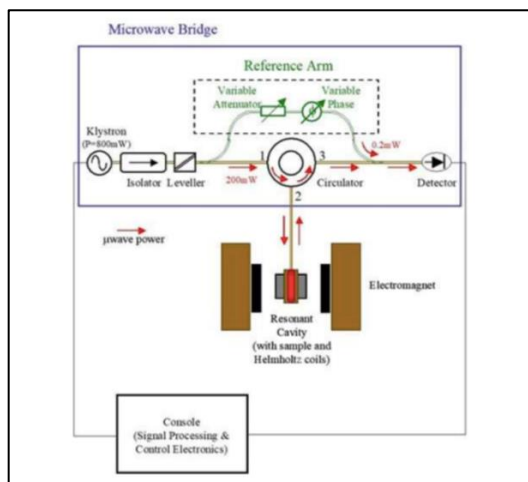

Fig. 4: Diagrammatic Representation of ESR Spectrometer used
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Working of the Spectrometer: The microwave power is produced by the klystron, which is a high-power microwave vacuum tube. It is velocity modulated and uses the kinetic energy of an

electron beam to amplify the signals. The power travels through a series of waveguides as directed by the red arrows in Fig. 4.

The first step in operating the spectrometer is to turn on the coolant water that prevents overheating of the electromagnets. After placing EPR tube with the sample in the cavity, we can tune the instrument by observing the microwave power spectrum on the oscilloscope. To achieve the perfect reflection, we must ensure that the dip in the otherwise inverted U-curved graph touches the X axis. Alongside, the iris of the instrument should be regulated, such that when away from the resonance condition no radiation leaks out.

When conducting low temperature experiments, the main valve of the nitrogen tank is required to be opened and liquid nitrogen should be allowed to flow. Once liquid nitrogen is in the dewar, the testing sample needs to be lowered in the dewar slowly. The speed here is imperative, for if we so too fast, the sample tube will break. Using the temperature controller, reach the desired cooling for the specimen.

On OPERATE Mode, data is collected and when the magnetic field satisfies the resonance condition, the sample absorbs the radiations, and a small signal is reflected to the detector. The signal from the detector is processed by an electronics console and is plotted on an X – Y plotter. A scanner along with a computer is used to digitize the spectra and convert them into electronic copies.

Results and Discussions

Samples Taken for the Experiment:

1) **DPPH** – DPPH is a stable free radical with wide applications in plant biochemistry. The DPPH experiment is conducted at room temperature i.e., 300 K. The theoretical value of its electronic g-factor is 2.0036.
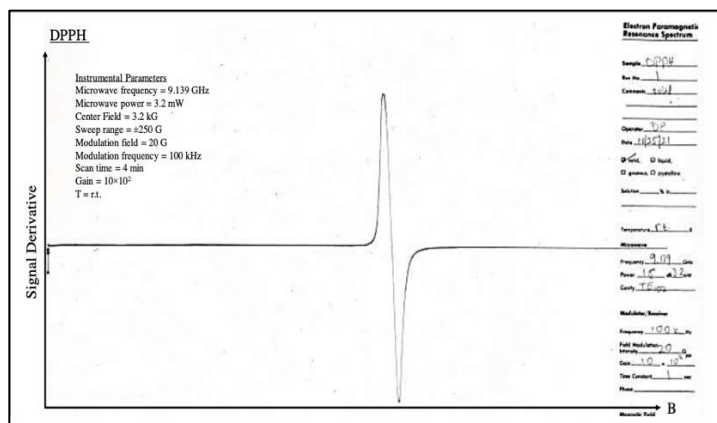
   Spectrum Obtained:

Fig. 5: Scan of the DPPH Spectrum Obtained

Results:

S. No	Measured Quantity	Value	Formula Used
1	B_S and B_E respectively	2950, 3450 (kG)	Central Field $\pm$ Sweep Range
2	Spectral Width (w_s)	23.7 cm	By inspection
3	Resonance Magnetic Field (B_0)	3.2284 (kG)	Dividing the X axis according to the w_s obtained and applying unitary method.
4	g-factor	2.0225	$0.71449 \dfrac{v(GHz)}{B(kG)}$
5	Linewidth	0.0148 (kG)	Finding the Magnetic field at peaks and subsequently calculating the change

Table 1: Analysis of DPPH Free Radical Spectra

Inference: The difference between the theoretical and the experimental value of DPPH is 0.0189 which leads to an error of 0.94%. Though, this is not insignificant, the value could be off due to experimental inaccuracies and human error. One of the major sources of error could be the fact that we determined certain quantities through inspection and a meter scale (with a least count of 1 mm).

2) **MnCl$_2$ in H$_2$O** – An experiment with a sample of MnCl$_2$ in water is conducted at 104 K using liquid nitrogen. MnCl$_2$ contains the Mn^{2+} paramagnetic ion resulting in hyperfine structure.
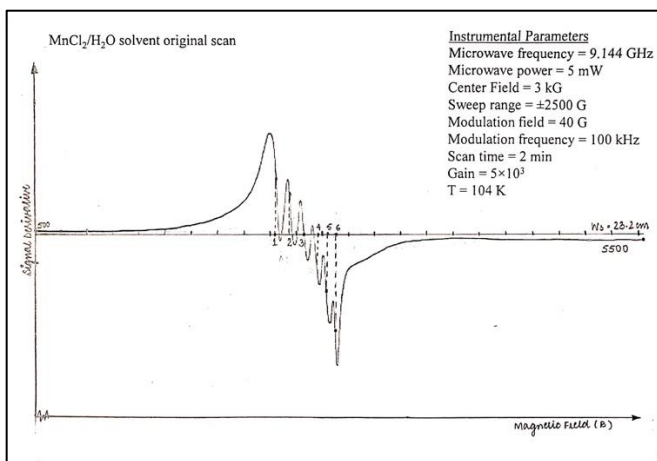
Spectrum and Results Obtained:

Fig. 6: Scan of MnCl₂ Spectrum Obtained

Dividing the X axis, according to sweep range and the spectral width, we get the following values for magnetic fields (in kG) at individual points:

$B_1 = 2.4827$, $B_2 = 2.5905$, $B_3 = 2.7198$, $B_4 = 2.8275$, $B_5 = 2.8922$, $B_6 = 2.9784$

Using the resonance condition, we calculate the g-factors at the 6 marked points:

$g_1 = 2.6315$, $g_2 = 2.5220$, $g_3 = 2.4021$, $g_4 = 2.31063$, $g_5 = 2.2589$, $g_6 = 2.1936$

Thus, $g_{avg} = 2.3864$.

Similarly, for the coupling constant (A): $A_{2-1} = 0.1708$, $A_{3-2} = 0.1293$, $A_{4-3} = 0.1077$, $A_{5-4} = 0.0647$, $A_{6-5} = 0.0862$.

Thus, $A_{avg} = 0.09904$ kG

To find the g value directly from the resonance magnetic field, we have B_0 coinciding with $B_3 = 2.7198$ kG.

Thus, $g_0 = 2.4021$.

Inference: Between g_{avg} and g_0, there is a minute difference of 0.0157. However, for high spin Mn^{2+} ions, the theoretical value of the Lande factor (g) = 2.0 and for the hyperfine coupling constant (A), it is 90 G. For A, the error adds to a whooping 10.0444% whereas for the g-factor, the average error is 19.713%. One of the plausible reasons for the inaccuracy could be the temperature dependence of the technique. Even though, the experiments were conducted at 104 K and the sample with water was frozen (lower Dielectric constant), there would still be thermal kinetic energy of electrons causing disturbances in the system.

Seeing the hyperfine structure with a multiplicity of 6, we can conclude that the nuclear spin I = 5/2 (Using ***2I + 1 = No. of Hyperfine lines***).

Conclusion

In conclusion,

S. No	Derived Quantity	DPPH Free Radical	$MnCl_2$ in H_2O
1	Resonance Magnetic Field	3.2284 kG	2.7198 kG
2	g-Factor	2.0225	2.4021
3	% Error in g-Factor	0.94%	19.713%
4	Linewidth	0.0148	-
5	Hyperfine Constant	-	9.904 G

Table 2: Brief Overview of Results obtained

The experiment analysis could have improved to minimize errors. For calculation of the g-factor, we used inspection to pinpoint the location for the resonance magnetic field which could entail human errors.

Given the wide applications of the EPR spectroscopy technique, the research in this field would surely continue to grow. Fresh approaches in deriving electronic structures are trending towards detection of free radicals and their characteristic features with applications in varied fields. Advancements in the technology itself, such as to include higher magnetic fields and higher frequencies experiments, speak to developing phase of this spectroscopy technique. In the end, I firmly believe that this technique will continue to foster to give us detailed accounts of structures, and ligand interactions with the crystal lattice.

References

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