EPR Spectrum Analysis of DPPH and MnCl$_2$

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Abstract

This paper presents the findings of electron paramagnetic resonance (EPR) spectroscopy experiments conducted on two different samples: 2,2-diphenyl-1-picrylhydrazyl (DPPH) and Manganese Chloride (MnCl$_2$) dissolved in H$_2$O. EPR spectroscopy is used to study the electronic and magnetic properties of paramagnetic materials, providing valuable information about their identity, oxidation and spin states, ligand environments, and interactions with the lattice.

The experiments were conducted at Dr. D. Petasis EPR lab located in Allegheny College, Meadville, PA, USA. A Varian X-Band spectrometer was utilized for the analysis of the EPR absorption spectra. The primary objective was to determine the g-values and hyperfine structure of the two samples, which can be crucial in characterizing their electronic properties. The g-values obtained for both DPPH and MnCl$_2$ were found to be remarkably close to the theoretically calculated values, suggesting the high accuracy and success of the experiments. This agreement validates the reliability of the EPR measurements and demonstrates the precision of the instruments and experimental procedures employed. For the MnCl$_2$ sample, a hyperfine structure with 6 visible EPR lines was observed. By analyzing the number of EPR lines, the nuclear spin of the Mn(II) ion was determined to be I = 5/2, consistent with the expected value for Mn(II). The hyperfine constant (A) was also calculated from the field position differences between adjacent lines, providing further insights into the sample's magnetic properties.

Comparisons were made between the obtained g-values and hyperfine constant with the expected values for Mn(II) in the literature, confirming the accuracy of the measurements and reinforcing the credibility of the experimental data. Overall, the EPR spectroscopy experiments conducted on DPPH and MnCl$_2$ in H2O have provided valuable information about the electronic and magnetic properties of these paramagnetic materials. The results demonstrate the effectiveness of EPR spectroscopy as a powerful experimental technique for investigating various bio-chemical samples and understanding the effects of solvents on the EPR spectra of compounds. The close agreement between the experimental and theoretical values for the g-factors and hyperfine constants reinforces the reliability of the data obtained from the EPR experiments. These findings contribute to a deeper understanding of the studied compounds and can serve as a foundation for further research in the field of EPR spectroscopy and its applications in various scientific disciplines.

1.Introduction

Electron Paramagnetic Resonance (EPR) spectroscopy is a highly valuable analytical method widely employed in chemistry and materials science to investigate paramagnetic species. These compounds possess unpaired electrons, granting them unique electronic and magnetic properties that make them captivating subjects of study. EPR combined with magnetic susceptibility experiments provide valuable insights into various magnetic properties of samples. This includes determining the identity, oxidation,

and spin states of paramagnetic ions, understanding the ligands surrounding the paramagnetic ions, and investigating the interactions between paramagnetic ions and the lattice of the sample.

This research paper focuses on conducting a comparative analysis of the EPR spectra of two specific paramagnetic compounds: 2,2-diphenyl-1-picrylhydrazyl (DPPH) and manganese chloride ($MnCl_2$). The data was graphed on an X-Y plotter and analyzed to extract g-values and other pertinent parameters. The objectives of our experiments are twofold: firstly, to investigate and interpret the EPR spectra of DPPH and $MnCl_2$, with the aim of comprehending their electronic and magnetic properties. Secondly, to compare the obtained EPR spectra of these compounds, elucidating their differences and similarities.

The experimental outcomes offer valuable insights into the electronic structures and magnetic properties of both DPPH and $MnCl_2$ and have a profound understanding of their unpaired electron characteristics, and hyperfine interactions.

2.Background Theory

Electron Paramagnetic Resonance (EPR) is a spectroscopic technique used to analyze complex systems containing unpaired electrons, providing valuable information about the nature of ligands, interactions of paramagnetic ions with the lattice, and other properties such as the identity, oxidation, and spin states of the paramagnetic ions.

Electron Spin and Magnetic Moment:

In atoms and molecules, electrons possess intrinsic angular momentum, known as spin. The spin of an electron can take on two values: +1/2 or -1/2, referred to as "spin up" and "spin down," respectively. This spin property results in the generation of a magnetic moment associated with the electron's spin.
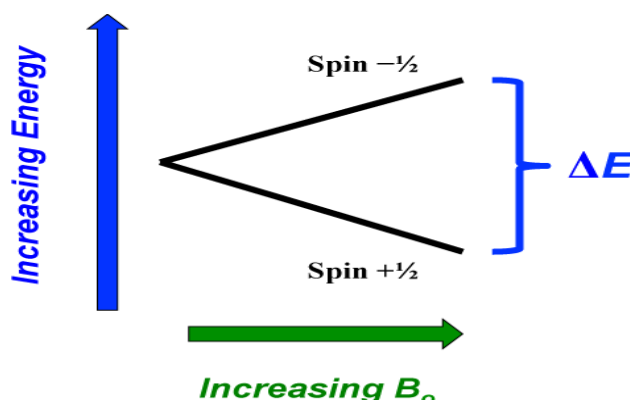

Figure 1 shows the positive, direct correlation between the magnetic field andenergy.[1]

Paramagnetic materials are those that contain unpaired electrons, leading to a non-zero magnetic moment even in the absence of an external magnetic field. The magnetic susceptibility, χ, quantifies the material's response to an applied magnetic field and is directly related to the number of unpaired electrons present in the system.

Energy Levels in Magnetic Fields:

When a paramagnetic species is placed in an external magnetic field, the magnetic moments of its unpaired electrons align with or against the field. The energy difference between these levels is directly proportional to the applied magnetic field strength.

The Zeeman Effect:

The interaction of the electron's magnetic moment with the external magnetic field results in the splitting of energy levels, known as Zeeman splitting and involves the interaction between microwave radiation and paramagnetic ions, which possess spin magnetic moments due to their unpaired electrons. When an electron transitions from a lower state to an excited state due to the absorption of electromagnetic radiation, the EPR phenomenon is observed.
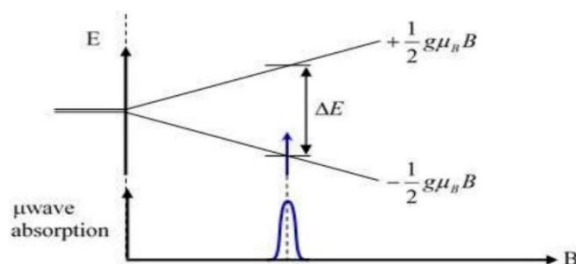

Figure 2: Zeeman splitting of the degenerate electron spin states for an S=1/2 system.[1]

When an electron in the lower energy level absorbs electromagnetic radiation and transitions to the excited state (higher energy level), it gives rise to the EPR phenomenon. As the magnetic field (B) increases, typically ranging between 0 to 1 Tesla, certain microwave frequencies (hv) are continuously emitted. However, the electron can only absorb this energy and transition to an excited spin state when the resonance condition is met.

$$h\nu = \Delta E = g\mu_B B_0$$

where h is Planck's constant (6.626×10^{-34}Js), ν is the frequency of absorbed electromagnetic radiation, g is the electronic g-value, μ_B is the Bohr magneton, and B is the applied/external magnetic field.

The g- value:

The g value, also known as the spectroscopic splitting factor, quantifies the ratio of the magnetic moment to the angular momentum of an electron. It plays a crucial role in interpreting EPR spectra, as it determines the relationship between the magnetic field strength and the resonance frequency of the EPR signal. The g value is influenced by various factors, including the electronic structure of the paramagnetic species and its local environment.
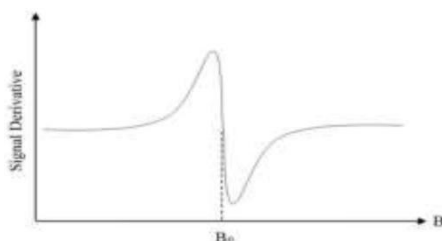

Figure 3: Typical EPR resonance line for S=1/2 system. The point where the line crosses the baseline gives the resonance magnetic field B_0 used to calculate g value.[1]

The g-valueisdeterminedusingthe expressiongiven below: $g = h\nu / \mu_B B_0$. The g value can be calculated using the relation $g = 0.71449 * \nu(GHz) / B_0(kG)$. This simplified formula enables straightforward determination of g-values using the microwave frequency in gigahertz (GHz) and the magnetic field in kilogauss (kG). For free radicals, the g-value is approximately 2.002. Deviation from

this value indicates electron binding to an atom.

Hyperfine Interactions:

Paramagnetic species can exhibit hyperfine interactions, which arise from the interaction of the unpaired electron's magnetic moment with nearby nuclear spins. Hyperfine interactions lead to further splitting of EPR spectral lines, providing valuable information about the nuclear spins and the electronic environment of the paramagnetic species.

If a nucleus with spin I, which interacts with an electron of spin S, the multiplicity for the hyper fine splitting is given as $(2I + 1)$. The hyper-fine splitting as discussed above is represented in Figure 5, where A represents the hyper-fine constant and it's the characteristic of a particular ion. In the figure a sample with a hyperfine multiplicity of 3 can be observed, based on which the nuclear spin(I) can be calculated to be $I = 3/2$.
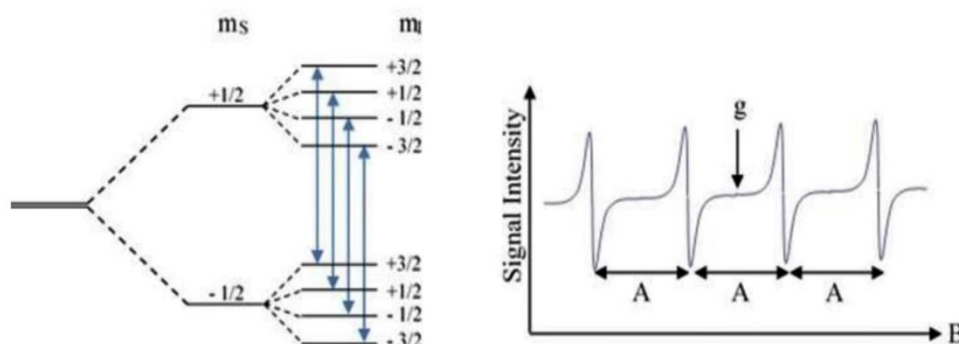

Figure 4: Hyper-fine splittings in a system with ms $=1/2$ and $m_I = 3/2$. On right is a typical hyper-fine spectrum of a species with $I = 3/2$[1]

3.Experimental Procedure:

The experimental setup employed a Varian E-3 X-band spectrometer with a liquid nitrogen flow cryostat, capable of operating within a temperature range of 80K to approximately 293K and a frequency range of 8.5-12 GHz. The spectrometer incorporated a microwave bypass arm to enhance sensitivity by biasing a diode detector. The generated electric signals were then processed on an electronics console and plotted in a two-dimensional graph.

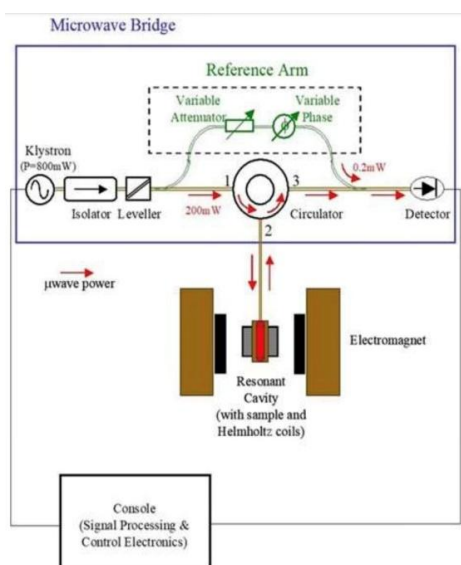Figure 5: Varian E 3 X band Spectrometer equipped with liquid N_2 cryostat. [1]

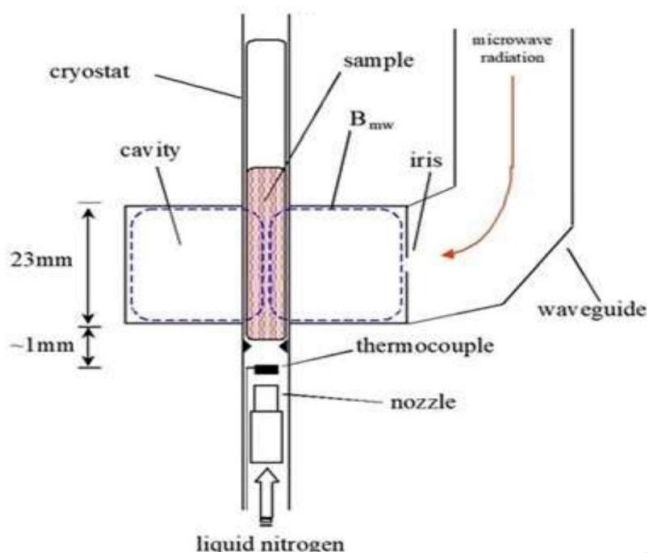Figure 6: Schematic diagram of EPR Spectrometer[1]

Figure 7: Resonant cavity with sample and cryostat[1]

The schematic representation in Figure 6 illustrates the configuration of the ESR spectrometer, showcasing the interaction between the microwave energy from the Klystron, the resonant cavity housing the samples, and the reflected absorption signal detected and processed by the electronics console.

To initiate the experiment, the spectrometer was switched on, and the samples, namely DPPH and Manganese Chloride, were placed inside the resonant cavity of the spectrometer. The microwave bridge was set to TUNE mode, and the spectrometer was tuned to achieve optimal performance. In TUNE mode, no power was detected by the diode detector, confirming proper calibration. Subsequently, the spectrometer was set to OPERATE mode for data collection and further analysis.

During the experiment, the external magnetic field was continuously swept through the resonance range. As the magnetic field reached the resonance condition, the samples started absorbing microwave radiation, generating detectable signals in the form of absorption curves. The liquid nitrogen flow cryostat, specifically designed for EPR experiments, was used to cool down the samples during data

collection at a temperature of 104K for Manganese Chloride and room temperature (approximately 293K) for DPPH.

The EPR spectra obtained through this setup were recorded and analyzed to extract valuable information about the electronic and magnetic properties of the samples. The data was plotted on an X-Y plotter and interpreted to determine g-values and other relevant parameters.

4.Results and Discussions:

The EPR absorption spectra of both DPPH and Manganese Chloride ($MnCl_2$) were recorded and analyzed to determine their respective g-values and compare them with the expected theoretical values.

4.1 EPR analysis for DPPH

The results from the EPR analysis for DPPH were consistent with what was expected for a free radical, showing a typical EPR line. The narrow linewidth indicated a high concentration of the dry polycrystalline sample.

The EPR analysis was performed at room temperature for a duration of 4 minutes. The microwave radiation frequency remained constant at 9.139 GHz, with a power of 3.2 mW (3.2×10^{-3} W). The spectrometer provided a center field value of 3.2 kG, and the sweep range was ± 250 G (2.5×10^{-4} kG), indicating that the magnetic field at the beginning of the experiment was 2.95 kG and 3.45 kG at the end.

The value of B_o, which represents the point where the EPR line crosses the baseline, was determined to be 3255.04 G (3255.04×10^{-3} kG). Using the provided relation from the Theory section, the calculated g-value was approximately 2.00603498 or ~2.006.

To measure the linewidth (ΔB) of the EPR line, the EPR resonance condition was used to find the field positions of the positive and negative peaks, and the difference between them was determined to be 14.90827 G (14.90827×10^{-3} kG).
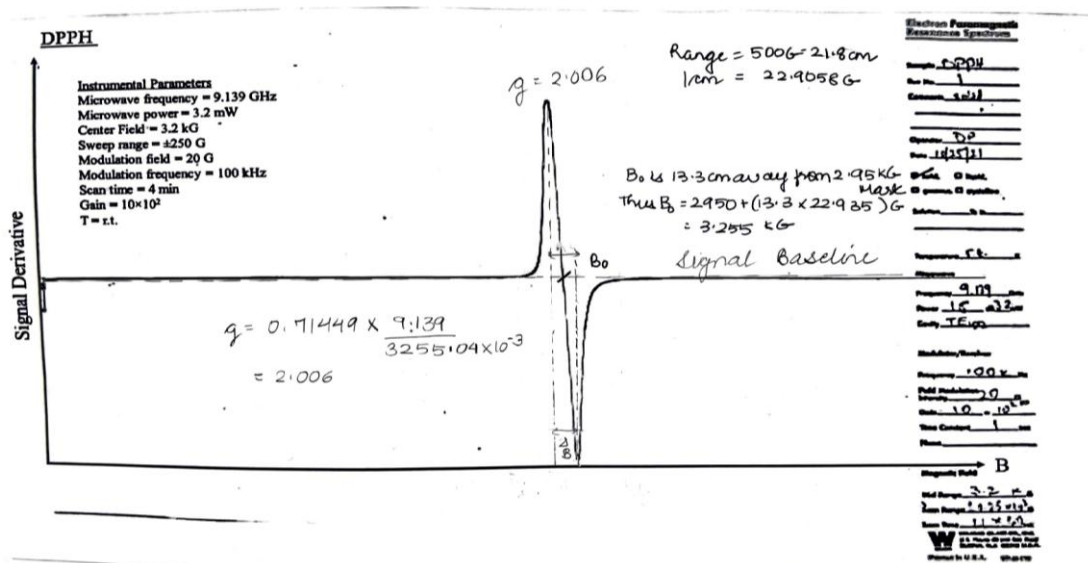

Figure 8: Illustration of the EPR absorption spectrum of DPPH with calculations.

Data analysis compares the experimental g-values with their respective theoretical values for DPPH. The obtained g-value for DPPH was found to be 2.006, while the theoretical g-value is expected to be 2.00. The slight discrepancy between the experimental and theoretical g-values suggests the presence of instrumental error within the experiment. The results confirm that DPPH is a free radical.

Sources of experimental uncertainty in EPR measurements include instrument calibration, sample purity, sample homogeneity, instrument resolution, and data processing methods etc.

4.2 EPR analysis of Manganese Chloride (MnCl₂)

The EPR spectra of Manganese Chloride ($MnCl_2$) dissolved in H_2O exhibited a hyperfine structure with six visible EPR lines. The number of EPR lines corresponds to the nuclear spin of the Mn^{2+} ion, which was found to be $I = 5/2$, in agreement with the expected value for the Mn (II) ion. The intensities and separations of the signals were approximately equal. The experiment was conducted at a temperature of 104 K using liquid nitrogen cooling for a duration of 2 minutes. The microwave radiation frequency used was 9.144 GHz, and the power was 5 mW.

To determine the values of B and g for the six EPR lines, the magnetic field positions and g-values were calculated. The average value of the separation between hyperfine lines (A) is determined as well.
Upon comparing the values of gave and g_o, the difference Δg is approximately 0.136%, and when comparing B_{avg} and B_0, the difference ΔB is approximately 0.264%.

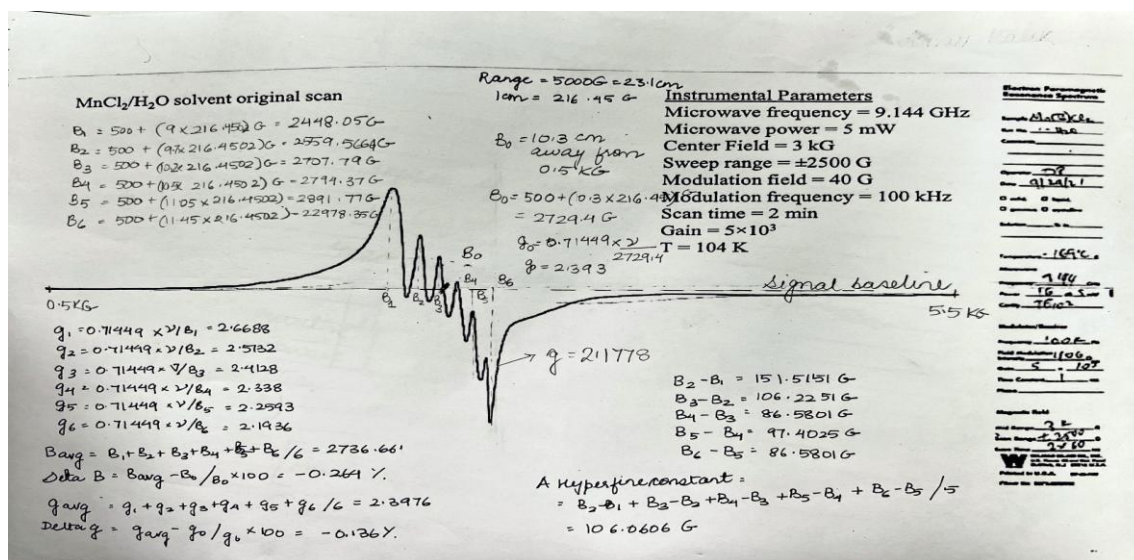| Magneticfieldpositionsof hyperfinelines	Separationbetween hyperfinelines	g-valuesofhyperfinelines
B1=2448.051G	(B2–B1)=151.515G	g1= 2.6688
B2=2599.566 G	(B3–B2)=108.225G	g2= 2.5132
B3=2707.792 G	(B4–B3)=86.580G	g3= 2.4128
B4=2794.372G	(B5–B4)=97.402G	g4= 2.3380
B5=2891.774G	(B6–B5)=86.580G	g5= 2.2593
B6=2978.354G		g6= 2.1936
Bave=2736.652G	A= 106.060G	gave=2.397

Figure 9: Illustration of the EPR spectrum for $MnCl_2/H_2O$, displaying the hyperfine structure and the calculated values for the hyperfine lines and their averages.

The g-factor in the EPR spectrum being approximately 2 indicates that the electron is a free radical, and there is no spin-orbit coupling. The presence of Mn^{2+} ions contribute to hyperfine splitting, leading to the observation of six peaks in the spectrum.

Throughout the experiments, constant monitoring of temperature, microwave frequency, and other parameters ensured greater accuracy. The data analysis and annotated graphs confirm that the experimental g-values are in close agreement with the theoretical values, validating the reliability of the experiments.

5.Conclusion

The application of EPR theory throughout the experiment, using the Varian E-3 X-band spectrometer and liquid nitrogen cryostat, resulted in successful outcomes with values closely matching the calculated ones for both DPPH and $MnCl_2$ experiments. The data collected from various EPR spectra provided valuable information about the magnetic properties of the bio-chemical samples and the influence of solvents on their EPR spectra. The calculated g-values confirmed that DPPH exhibited characteristics typical of a free radical. The EPR spectrum of $MnCl_2$ displayed a hyperfine structure with six levels, attributed to its nuclear spin, which was determined to be I = 2.5. The overall findings demonstrate the power of EPR spectroscopy as an effective experimental technique, offering valuable insights into the properties of paramagnetic samples through the calculated g-factor of each sample**.**

References

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