

EPR Investigations of DPPH and MnCl₂

Summary by : Divij Butte
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Professor : Prof. Doros Petasis

About the Student : Divij Butte is a student at Smt. Sulochanadevi Singhanian School, India. This paper was prepared by Divij as a part of his course work for LS190 - Introduction to College Level Research course at Allegheny College during summer 2021.

Summary:

Abstract

In this paper, I give a brief overview of the Electron Paramagnetic Resonance (EPR) spectroscopy method, and detail some of the essential background theory, such as the Zeeman effect. A detailed description of the experimental procedure to operate a Varian E-3 spectrometer is included, and a subsequent analysis of two EPR scans is shown along with a discussion of their results. The samples taken for spectral analysis were DPPH (2,2-diphenyl-1-picrylhydrazyl) and MnCl₂/H₂O (manganese (II) chloride in frozen water). The experiments were conducted at Dr. D. Petasis' EPR lab located in Allegheny College, Meadville, PA, USA.

Introduction

Spectroscopy is the measurement and interpretation of the energy differences between different atomic or molecular states. Electron Paramagnetic Resonance (EPR) is a spectroscopic technique that allows the study of systems with unpaired electrons, such as free radicals and transition metal ions. It deals with the interaction of microwave radiation with the spin magnetic moment of unpaired electrons in atoms (paramagnetic ions), and is thus ideal for detecting the magnetic properties of individual atoms and the interactions between individual magnetic moments at the atomic scale. EPR along with magnetic susceptibility experiments yield a wealth of information about the different magnetic properties of samples, including the identity, oxidation and spin states of paramagnetic ions, natures of ligands surrounding the paramagnetic ions, and the interactions of paramagnetic ions with the lattice of the sample.

Theory

An atom or molecule has discrete energy states, each with a corresponding energy. The energy differences between two states give us a lot of insight into the identity, structure and dynamics of the sample being studied.

The EPR technique is based on the Zeeman effect – the splitting of a spectral line into multiple equally spaced components under the influence of an external magnetic field. The interaction with the external magnetic field produces a splitting of degenerate electronic spin energy states. An electron on the lower energy level can absorb the supplied electromagnetic radiation and transition to the excited state, causing microwave absorption and giving rise to the EPR phenomenon.

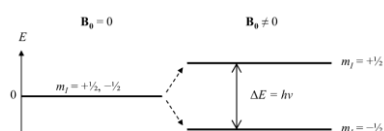


Figure 1. Demonstration of the Zeeman effect. When the magnetic field is 0 ($B_0 = 0$), both spin states of the electron have the same energy. Once an external magnetic field is introduced ($B_0 \neq 0$), the energy levels split into two separate electron spin states: spin down ($-1/2$) and spin up ($1/2$).

The phenomenon of EPR takes place because of the Zeeman effect wherein an electron jumps from the spin down energy state to the spin up energy state by absorbing microwave radiation. This electronic transition is, however, *only* possible when:

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

where, ν is the frequency of radiation, h is Planck's constant (6.626×10^{-34} Js) and E is the energy difference between two energy states ($E_2 - E_1$, shown in Fig. 2). g is the g-factor (or g-value), μ_B is the Bohr magneton (9.274×10^{-24} JT⁻¹) and B_0 is the externally applied magnetic field. This expression thus shows when EPR resonance takes place. The frequencies of electromagnetic radiation are in the GHz region of the spectrum, with magnetic fields ranging from 0-1T.

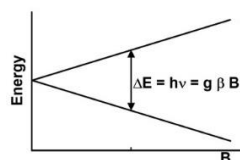


Figure 2. E_2 represents the higher energy state and E_1 represents the lower energy state. The energy difference between the two states is given by the expression shown above.

In the presence of a magnetic field \vec{B} , an electron has two possible energies: $-\frac{1}{2}g\mu_B B_0$ or $\frac{1}{2}g\mu_B B_0$. Electromagnetic radiation will be absorbed and the electron will jump to the higher energy state if the radiation energy exactly matches the energy difference between two states. This condition is known as the EPR resonance condition. The final goal of an EPR experiment is to determine the g-value, which gives a lot of information about the sample in question, such as the different interactions that the spin system experiences, hyperfine interactions, ligand symmetry, interactions with ligands and other paramagnetic ions, etc. The value of g tells us about the electrons in the sample that produced an EPR signal. A g-value of 2.002 ($g = 2.002$) implies that the sample is a free radical, and deviation from ~ 2.00 ($g \neq 2.002$) shows that the electrons are bound to atoms (presence of spin-orbit coupling). In this case, it is necessary to use appropriate analysis to determine which species gave rise to the EPR spectrum. The g-value is determined using the expression given below:

$$g = \frac{hv}{\mu_B B_0}$$

This expression can be further simplified by combining constants h and μ_B into a single numerical constant and written as:

$$g = 0.71449 \frac{v(\text{GHz})}{B_0(\text{kG})}$$

In a typical EPR experiment, a klystron produces microwave radiation of a constant frequency, while the magnetic field is varied (swept) through a range of a few kilogauss ($1\text{T} = 10^4 \text{ G}/10 \text{ kG}$). The electromagnetic radiation is absorbed when the magnetic field goes through the exact value that satisfies the EPR resonance condition and this appears as a parabola in the resultant spectrum. This is called an “EPR resonance line” and the spectrometer plots the first derivative of this line. During the experiment, the intensity of the microwave radiation is constantly monitored and the integrated intensity gives the number of spins of the system.

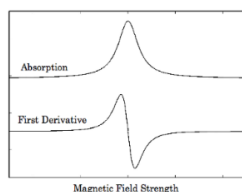


Figure 3. Typical EPR absorption and first derivative spectra for $S = \frac{1}{2}$ systems. The point at which the first derivative line crosses the baseline determines the resonance magnetic field B_0 which allows us to calculate the g-value.

Many transition series ions have nuclei with spin that interact with the spin of unpaired electrons and produce splitting in the EPR spectra. These electron-nuclear interactions give rise to *hyperfine structure*. Hyperfine interactions can be used to provide information such as number and identity of nuclei and their distances from unpaired electrons. The nuclei possess a magnetic moment μ_1 which interacts with the magnetic moment of electrons. The total magnetic field experienced by the electrons is then the sum of external magnetic field \vec{B} and the field due to μ_1 . A nucleus with nuclear spin I will give rise to $(2I + 1)$ orientations for μ_1 and thus $(2I + 1)$ EPR lines. For example, a nucleus with $I = \frac{3}{2}$ will produce $(\frac{3}{2} * 2 + 1) = 4$ EPR lines. These EPR lines are equally spaced and have equal intensity. The magnetic field separation of hyperfine lines is called the hyperfine constant A and it is characteristic to particular ions. It is measured as the distance between the centers of two consecutive EPR signals.

A nucleus with spin I interacting with an electron with spin S produce splitting in the m_s electronic levels. The multiplicity of these different levels is given by $(2I + 1)$ and each level is labeled by the quantum number m_I and transitions can now take place between m_I levels obeying certain selection rules: $\Delta m_S = \pm 1$ and $\Delta m_I = 0$. Transition ions with nuclear spin include Cu^{2+} ($I = 3/2$), Mn^{2+} ($I = 5/2$) and Co^{2+} ($I = 7/2$).

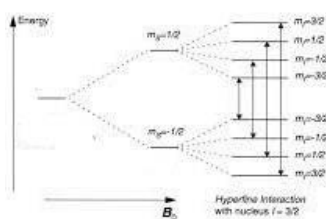


Figure 4. Hyperfine interaction for a nucleus with spin $I = 3/2$. Transition between electronic levels show that they obey selection rules ($\Delta m_S = \pm 1$ and $\Delta m_I = 0$).

Experimental Procedure and Instrumentation

The instrument used for the experiment is a 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 the temperature range 80K to room temperature (~300K). 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. A scanner and a computer in the laboratory allow us to digitize the spectra and convert them into electronic copies for analysis.

The klystron produces the microwave radiation necessary for the experiment, and the radiation travels down through a series of waveguides to the sample present in the resonant cavity. When the magnetic field is swept through resonance, microwave power is absorbed by the sample in the cavity and an EPR signal is reflected back to the detector from the cavity, which then travels to the electronics console for processing.

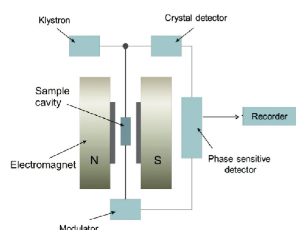


Figure 5. A simple schematic diagram demonstrating an EPR spectrometer and its parts. The signal received from the detector goes to the electronics console for processing and plotting.

Upon switching the spectrometer ON, the sample placed in the cavity and the microwave bridge is set on TUNE, the microwave power spectrum is visible on the oscilloscope screen. A dip in power is seen due to absorption of power by the cavity and the sample is placed close to the center of the mode, and the iris is adjusted until the bottom of the dip touches the baseline. Once this happens, the instrument is fully tuned and ready for use as no power is being reflected to the detector. It is then necessary to switch to OPERATE to proceed with the experiment and begin gathering data. During the course of the experiment, the liquid nitrogen flow cryostat directs cold dry nitrogen (from the valve mentioned earlier) into the cryostat cold finger so that it flows around the sample tube maintaining the low temperature.

The samples used for the experiment were DPPH (2,2-diphenyl-1-picrylhydrazyl) and manganese chloride with water as the solvent ($\text{MnCl}_2/\text{H}_2\text{O}$). DPPH is a deep purple, crystalline powder while $\text{MnCl}_2/\text{H}_2\text{O}$ appears as a pink crystalline solid. For DPPH, a small amount of vacuum grease was placed inside an EPR tube and then into the resonance cavity of the spectrometer. The sample of DPPH was placed on the grease spot and the scan was conducted at room temperature. For $\text{MnCl}_2/\text{H}_2\text{O}$, the sample was slowly cooled down with the help of liquid nitrogen in a dewar and it was then carefully placed in the cavity. The scan was conducted at a temperature of 104K.

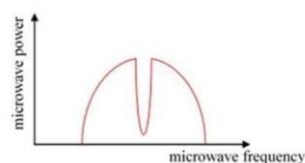


Figure 6. Power spectrum of the klystron, displayed on the oscilloscope screen. The dip in power is due to absorption by the sample in the cavity. The instrument is tuned until the tip of the dip touches the baseline for accurate results.



Figure 7. The Varian E-3 X-band spectrometer in Dr. Petasis' lab at Allegheny College. 1 corresponds to the temperature controller which displays the temperature and controls dry nitrogen flow, 2 is the universal counter that displays the microwave radiation parameters, 3 is the cavity where samples are placed and 4 is the liquid nitrogen dewar for supplying liquid nitrogen to the sample cavity during low temperature EPR scans.

Results

DPPH

The spectrum obtained upon EPR analysis matched expectations for how a typical EPR line would look like for a free radical. The particularly narrow linewidth is an indication of the highly concentrated dry polycrystalline sample. The EPR line was an isotropic spectrum, suggesting the symmetry produced by the other atoms in the lattice around the paramagnetic

ion was cubic. The scan was conducted for 4 minutes at room temperature. The frequency of the microwave radiation was kept constant at 9.139 GHz and the power was 3.2 mW ($3.2 \times 10^{-3}\text{ W}$). The center field value during the experiment, as obtained from the spectrometer, was 3.2 kG and the sweep range was $\pm 250\text{ G}$ ($2.5 \times 10^{-4}\text{ kG}$), implying that the magnetic field at the start of the experiment was 2.95 kG and 3.45 kG at the end of the experiment. The value of B_0 (the point where the EPR line crosses the baseline) was found to be 3255.04 G ($3255.04 \times 10^{-3}\text{ kG}$). The g -value is hence calculated to be 2.00603498 , or ~ 2.006 . (using the relation given in the *Theory* section). The linewidth (ΔB) of the EPR line was measured to be 14.90827 G ($14.90827 \times 10^{-3}\text{ kG}$), using the EPR resonance condition for finding the field positions of the positive and negative peaks and then obtaining the difference.

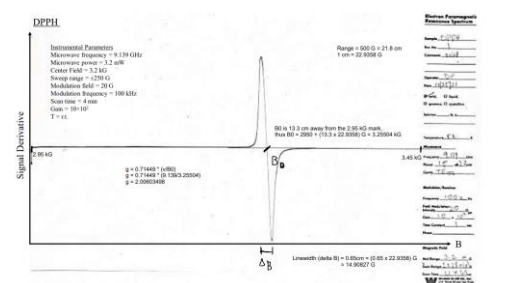


Figure 7. EPR spectrum of DPPH (2,2-diphenyl-1-picrylhydrazyl), along with calculations.

$MnCl_2/H_2O$

The EPR spectra of manganese (II) chloride showed a hyperfine structure with 6 EPR lines visible. The nuclear spin of the Mn^{2+} ion can then be easily found using the relation $(2I + 1)$ for the number of EPR lines and it is calculated that $I = 5/2$, which agrees with the expected nuclear spin value for the Mn (II) ion. The intensities and separations of the signals were approximately equal. The scan was conducted for 2 minutes at a temperature of 104 K, achieved with the help of the liquid nitrogen cooling procedure mentioned earlier. The microwave radiation frequency was set to 9.144 GHz and the power was 5 mW ($5 \times 10^{-3}\text{ W}$). The center field value was 3 kG , with a sweep range of $\pm 2500\text{ G}$ (2.5 kG), implying that the magnetic field at that beginning of the experiment was 0.5 kG (500 G) and at the end of the experiment was 5.5 kG (5500 G). The B_0 value was taken at a point where the positive and negative parts of the EPR line were roughly equal, at almost the centre of all 6 EPR lines and was found to be 2729.4371 G ($2729.4371 \times 10^{-3}\text{ kG}$) and the g_0 value calculated subsequently yielded 2.39364247 , or ~ 2.3936 .

We then determine the six different values of B and g , along with the separation between two consecutive EPR lines, for the six different EPR lines. The formulae for calculating these remain the same as discussed in the *Theory* section. The values are shown in the table given below:

Magnetic field positions of hyperfine lines	g -values of hyperfine lines	Separation between hyperfine lines
$B_1 = 2448.0518$ G	$g_1 = 2.6688$	$(B_2 - B_1) = 151.5151$ G
$B_2 = 2599.5669$ G	$g_2 = 2.5132$	$(B_3 - B_2) = 108.2251$ G
$B_3 = 2707.7920$ G	$g_3 = 2.4128$	$(B_4 - B_3) = 86.5801$ G
$B_4 = 2794.3721$ G	$g_4 = 2.3380$	$(B_5 - B_4) = 97.4026$ G
$B_5 = 2891.7747$ G	$g_5 = 2.2593$	$(B_6 - B_5) = 86.5801$ G
$B_6 = 2978.3548$ G	$g_6 = 2.1936$	
$B_{ave} = 2736.6521$ G	$g_{ave} = 2.3976$	$A = 106.0606$ G

Where A is the hyperfine constant and represents the average of the separation between the hyperfine lines.

When we compare g_{ave} and g_0 , we get Δg as $\frac{(g_{ave}-g_0)}{g_0} 100 = \sim 0.136\%$ and upon comparing B_{ave} and B_0 , ΔB is obtained as $\frac{(B_{ave}-B_0)}{B_0} 100 = \sim 0.264\%$.

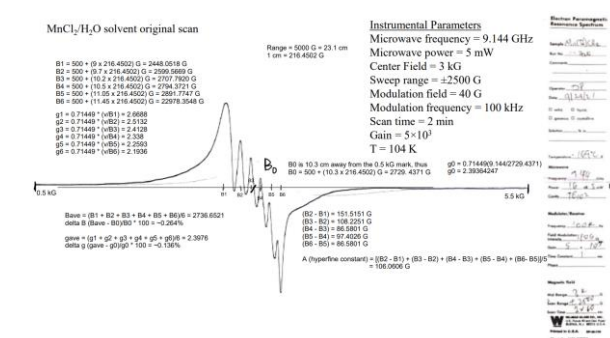


Figure 8. EPR spectrum for $\text{MnCl}_2/\text{H}_2\text{O}$ showing hyperfine structure. Six different sets of values (five for hyperfine line separation) are calculated and their averages taken as shown.

Conclusion

The EPR experiment for analysis of diphenylpicrylhydrazyl (DPPH) and manganese (II) chloride in water as the solvent showed results that were quite close to expected values and

thus could be said to have been successful. The results were in close agreement with existing theories and research in EPR. The experiment provided a detailed insight into some characteristic properties of the samples being studied and gave a lot of information that may be of great use in the future.

The EPR scan for DPPH produced a g -value of ~ 2.006 , while the theoretical g -value of DPPH is 2.0036. The deviation is calculated to be $\sim 0.12\%$, which is within the acceptable range. The linewidth was observed to be ~ 14.91 G, and DPPH's linewidth ranges from 5-15 G.

In the case of manganese (II) chloride, the percentage difference (Δg) between the average g -value (g_{ave}) and the g -value found using the central magnetic field B_0 (g_0) was found as $\sim 0.136\%$, which implies that they are quite similar and within a very small range of each other. The expected g -value for Mn(II), however was $g = 2.0$, and the g -value obtained (~ 2.3976) showed a large deviation from the expected value, of about 19.7%. This could possibly be due to the use of a polar solvent like water which may have interfered with the EPR spectrum and caused variation in the g -values and the hyperfine constant A . Another possible reason could be spin-orbit coupling – a relativistic effect that increases with larger orbitals in heavy atoms (such as the manganese ion in the sample) contributing to the singly occupied molecular orbits, and the energy gap between the higher orbital and the lower orbital increases proportionally. This causes a positive deviation in the g -value.

The hyperfine constant A , was measured to have a value of 106.0606 G, against the expected value of 90 G, a deviation of about 17.8%. This could be explained by the molecular motion and collisions in the vicinity of the paramagnetic ions, due to the presence of a solvent, that could possibly have affected the width of EPR lines and thus the value of A .

EPR is a powerful technology that helps us study chemical species with unpaired electrons. Future EPR experiments could reveal a treasure trove of valuable information that would revolutionize the way we think and work with materials. It has a wide range of applications in physics, chemistry, biology and food science. EPR helps scientists to devise new drug carrier and delivery systems, examine cosmetic substances, drugs, biochemical substances, study magnetic properties of materials and to explore many fascinating aspects of spin physics. There have been major advances in incorporating different frequency-bands into EPR scan systems, paving the way for multifrequency emission capability in single instruments.

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