HIGH SCHOOL EDITION
Journal of Student Research

Volume 11 Issue 4 (2022)

Analysis of DPPH and $MnCl_2$ Using Electron Paramagnetic Resonance (EPR) Spectroscopy

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ABSTRACT

EPR spectroscopy, in a constant-frequency field-swept experiment, was used to determine the resonant magnetic field, g-factor, line width, and hyperfine constant for diphenyl picrylhydrazyl at room temperature and manganese (II) chloride at cryogenic temperatures (using liquid nitrogen). Diphenyl picrylhydrazyl was determined to be a free radical, indicated by a g-factor of 2.022, with a resonant magnetic field of 3.23 kG at a microwave frequency of 9.14 GHz. The manganese (II) chloride was found to have six signal peaks, indicating hyperfine interaction of a nucleus with non-zero spin with unpaired electrons (spin was determined to be 5/2).

Introduction

In this paper, the EPR spectroscopy technique will be applied to the molecule diphenyl picrylhydrazyl (DPPH) and $MnCl_2$/Water solution in order to derive information regarding its electron structure. DPPH is often used in spectroscopy due to the stability of its free radical—that is, the free electron. This spectroscopy technique is often employed in biophysics to determine information about free radicals, but the technique can be used to study any paramagnetic sample. Aerobic organisms, for instance, use oxygen for metabolic processes which then generates reactive oxygen species (ROS) and reactive nitrogen species (RNS) which may lead to tissue damage. Such molecules can be analysed through EPR spectroscopy.

This study also aims to corroborate findings regarding analyses on DPPH and MnCL2 molecules with EPR. In addition, it provides insight into possible sources of error and how the phenomena observed can be explained with theory.

Background Theory

Electron paramagnetic resonance (EPR) is a technique that allows for the analysis of the magnetic characteristics of materials. This is achieved by observing the absorption of microwave radiation in materials—which occurs due to the radiation's interactions with the spin magnetic moment of unpaired electrons.

The energy levels an electron can occupy are quantized—they can only occupy certain discrete states. In understanding the energy states (in particular, differences between the energy states) of these electrons, attributes of the atom, such as its structure and identity, can be observed. Since the electron energy states are discrete, an electron can only be excited to the next state if the energy of the radiation is equivalent to the energy difference of the states—the event in which the energy is indeed absorbed by the electron is termed *resonance*. This is represented by the resonance condition:

$$hv = g\mu_B B$$

where hv is the energy of the photon, μ_B is the Bohr magneton constant, and B is the external magnetic field. The $g\mu_B B$ term is the difference between the energy states, ΔE.

In an external magnetic field, the spin energy state of unpaired electrons split (the Zeeman effect), leading to low and high energy levels. This is because the energy of interaction of an unpaired electron is given by

$$E = m_s g_e \mu_B B$$

and, in a magnetic field for a spin state of ½, m_s can assume values of + ½ or – ½ based on the alignment of the spin with the field, leading to two energy states.

This can be illustrated with an energy level diagram:

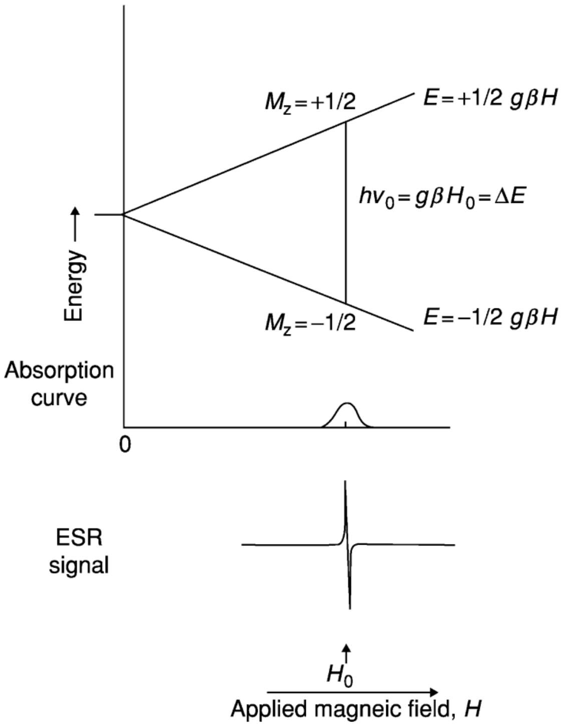

Figure 1. Energy states of an unpaired electron with an I of ½ diverge according to the Zeeman effect. At a certain magnetic field, resonance occurs, leading to absorption of the radiation and an ESR signal. Adapted from [6].

As seen in the figure, the energy levels diverge as the magnetic field increases and at the point where the magnetic field causes an energy difference between the states such that the energy of the photon matches the difference, absorption occurs and an ESR signal is detected.

By using the EPR signal, we can deduce B_0, the value at which for a particular frequency of radiation, resonance occurs and the electron jumps to an excited state. This allows us to solve for the g-value in the resonance equation, which is indicative of the nature of the electrons in the sample. For instance, a g-factor of approximately 2.00 indicates that the sample is a free radical while a g-factor diverging from this indicates that the electron is not delocalised.

A hyperfine structure, where the energy states of an electron again diverge, arises due to the fact that some nuclei can have a magnetic moment. If the nucleus has a spin of ½, it can have two orientations relative to the external magnetic field (with or against). This causes the energy states to again split, leading to two possible energy jumps. The hyperfine constant, A, is defined as the field separation between the hyperfine peaks in the ESR signal.

Experimental Procedure

The samples of BPPH and MnCl2/H_2O were placed in EPR tubes. For the low temperature EPR with MnCl2, the temperature controller was also turned on to be able to monitor the temperature. The valve on the nitrogen tank was then opened and the liquid nitrogen was placed into the dewar.

Note: the sample must be lowered slowly into the liquid nitrogen to ensure it does not break due to sudden temperature change.

A *Varian E-3* spectrometer, operating at a frequency between 9 and 12 GHz, was used to make the measurements. The anatomy of the spectrometer, in essence, comprises of waveguides to ensure the radiation reaches the sample and a metallic cavity concentrates the microwave radiation (and is surrounded by an electromagnet). The radiation then passes through another waveguide where it finally reaches the detector for analysis.

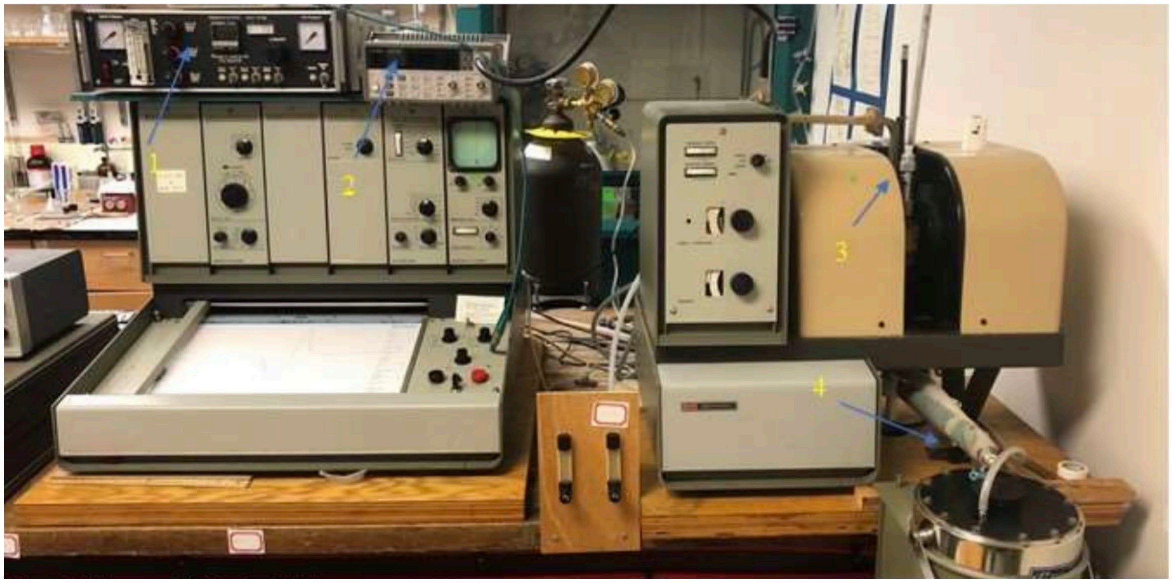

Figure 2. The Varian E-3 spectrometer employed for spectroscopy. Source: Doros Petasis's.

Broadly, the equipment used (labelled in *Fig. 2.*) are as follows:

1) Temperature controller
2) Frequency counter
3) Cavity for sample
4) Dewar for liquid nitrogen

The instrumental parameters, including the microwave power and center field, are set by modifying the knobs on the spectrometer. The radiation goes through the iris, shining into the cavity and reflecting back. Upon resonance, however, the microwave power reflected dips to zero—indicating no power is reflected from cavity and is instead absorbed by the electrons.

Results and Discussion

DPPH Sample

For the DPPH sample, the following instrumental parameters were used:

Table 1. Basic instrumental parameters for DPPH spectroscopy

Radiation Frequency	**Center Field**	**Sweep Range**	**Temperature**
9.139 GHz	3.2 kG	± 0.25 kG	R. T.

From this, we can also find the initial and final magnetic field:

Table 2. Initial and final magnetic fields for DPPH spectroscopy

Initial Magnetic Field	**Final Magnetic Field**
$3.2\text{ kG} - 0.25\text{ kG} = 2.95\text{ kG}$	$3.2\text{ kG} + 0.25\text{ kG} = 3.45\text{ kG}$

Parameters other than these are set up as follows:

Table 3. Other parameters used for DPPH spectroscopy

Microwave Power	**Modulation Field**	**Modulation Frequency**	**Scan Time**	**Gain**
3.2 mW	20 G	100 kHz	4 min	1×10^3

Running the spectroscopy yields the following plot:

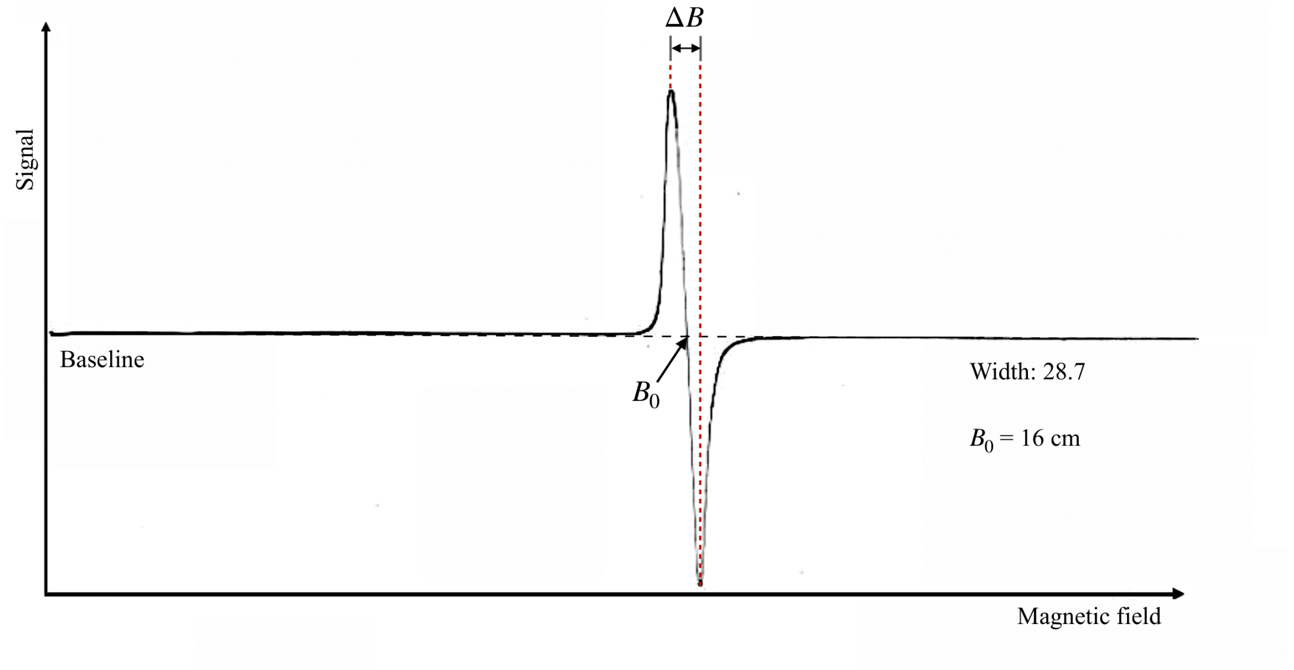

Figure 3. EPR spectra of DPPH with a constant electromagnetic radiation frequency and a varying external magnetic field.

The measured width of the reading (results were recorded on a plotter) was 28.7 cm, which corresponded to the full sweep of 0.5 kG, giving a scale of 0.0174 kG per 1 cm. The resonant magnetic field—where the signal derivative intersects the baseline and the absorption is at a maximum—was measured to occur at a distance of 16 cm from the start. This corresponds to an additional magnetic field of 0.2787 kG from the initial magnetic field of 2.95 kG, giving a B_0 of $2.95\text{ kG} + 0.2787\text{ kG} = 3.2287\text{ kG}$.

Using the resonance condition, we can find the g-factor of the sample. Rearranging the condition gives:

$$g = \frac{h}{\mu_b} \cdot \frac{v}{B_0}$$
$$\approx 7.1449 \frac{v\ (\text{GHz})}{B_0\ (\text{kG})}$$

Substituting the values used in the experiment, the g-value can be determined:

$$g = 7.1449 \frac{9.139}{3.2287}$$
$$= 2.022$$

This g-factor, approximately 2, indicates that the sample of DPPH is a free radical, containing unpaired electrons.

The accepted g-value for DPPH in literature is 2.0036. Comparing this to the observed value gives an error of

$$\frac{2.022 - 2.003}{2.003} \times 100\%$$
$$= 0.95\%.$$

Thus, the observed g-value for DPPH corroborates the value in literature, assuming some small experimental error.

The linewidth of the DPPH sample, ΔB, is the difference in magnetic field between the field at which the peak occurs and the field at which the trough occurs (of the signal derivative). Using the plot, the linewidth is measured to be 0.86 cm, corresponding to 0.01498 kG using the scale previously mentioned.

$MnCl_2$ Sample

The parameters for the Manganese (II) Chloride and water solution are as follows:

Table 4. Basic instrumental parameters for EPR spectroscopy of $MnCl_2$

Radiation Frequency	Center Field	Sweep Range	Temperature
9.144 GHz	3 kG	± 2.5 kG	104 K

From this, we can also derive the following:

Table 5. Initial and final magnetic field for spectroscopy of $MnCl_2$

Initial Magnetic Field	Final Magnetic Field
$3\text{ kG} - 2.5\text{ kG}$ $= 0.5\text{ kG}$	$3\text{ kG} + 2.5\text{ kG}$ $= 5.5\text{ kG}$

Other instrumental parameters are set up as follows:

Table 6. Other instrumental parameters for spectroscopy of $MnCl_2$

Microwave Power	Modulation Field	Modulation Frequency	Scan Time	Gain
5 mW	40 G	100 kHz	2 min	5×10^3

This results in the following plot:

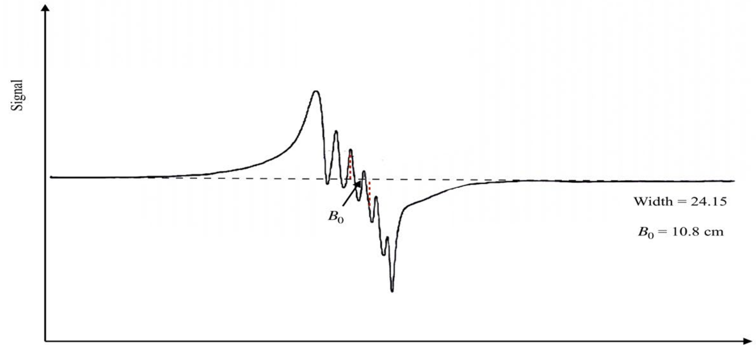

Figure 4. EPR spectra of $MnCl_2$. Some peaks and troughs of the signal derivative are either entirely above or below the baseline. In this case, B_0 was determined by finding the central magnetic field where the signal derivative is equal to 0.

On paper, the width of the spectrum has been measured to be 24.15 cm, corresponding to a magnetic field range of 5 kG. Thus, the scale of the spectrum is 24.15 cm for 5 kG or 1 cm for every 0.207 kG. Using the baseline, we find that B_0 occurs at 10.8 cm—corresponding to a magnetic field of 2.236 kG above the initial magnetic field, using the scale. Thus, $B_0 = 2.236\text{ kG} + 0.5\text{ kG} = 2.736\text{ kG}$.

Again, by rearranging the resonance condition, we can solve for the g-factor.

$$\begin{aligned} g &= 0.71449\frac{v\ (GHz)}{B_0\ (kG)} \\ &= 0.71449\frac{9.144}{2.736} \\ &= 2.84 \end{aligned}$$

The g-factor in literature for manganese (II) chloride is 2.00; hence, there is a relatively large error of $\frac{2.84-2}{2} \times 100\% = 42\%$. The higher g-value observed indicates that B_0 was incorrectly low, leading to a smaller denominator and too large a g-value. The low B_0 value indicates that there was some systematic error in the measurement, leading to all the magnetic field readings being reduced. This may be due to impurities present in the sample or test tube which affected all values measured or errors in calibration.

As seen in the plot, there are six hyperfine lines, with a hyperfine constant, A, of 0.5 cm corresponding to 0.103 kG or 103 G separating the peaks, compared to the accepted A value of 90 G. This gives a percentage error of $\frac{103-90}{90} \times 100\% = 14.4\ \%$. Using the number of hyperfine lines, we can also find the spin of the nucleus by solving for I in the following equation: $2I + 1 = 6$. This yields a nuclear spin of $\frac{5}{2}$.

Conclusion

The results from the DPPH spectroscopy largely agree with those from existing studies, indicating that a free radical is present. However, the spectroscopy from the MnCl2 study (indicating no free radical) was incongruent with previous studies—although can be explained through potential errors. The six distinct peaks, however, do agree with the literature in that they indicate hyperfine splitting due to there being some non-zero nuclear spin in the $MnCl_2$ sample which interacts with the electrons.

Future research could be conducted where the spectroscopy is done in more controlled environments or utilizing newer equipment—especially for the $MnCl_2$ sample—and results are compared. Another interesting line of research is to explore how such EPR techniques can be utilized for quantum computing—in particular, using pulse-EPR (where a sequence of microwave pulses are used) to control spin qubits.

Acknowledgments

I would like to thank my advisor for the valuable insight provided to me on this topic.

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