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Summary and References:

ALLEGHENY COLLEGE

EPR Investigations of DPPH and Manganese Chloride

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Prof. Petasis
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ABSTRACT:

EPR investigations on DPPH and Manganese Chloride were successful and matched the theory concerning EPR and ESR that is currently accepted. There were some anomalies but there were similarities between the accepted values and the experimental values. The g-values calculation was much more concrete and simple with the help of the simplified formula, using only the microwave frequency and the centre field, and the scalar constant. The instrument used for the experiment was complex, combining many uses to give readings relevant to EPR spectroscopy. The g-values for both the DPPH and the $MnCl_2$ experiments were quite close to the theoretically calculated g-values, which hence proves that the experiment was accurate and successful.

INTRODUCTION:

EPR(Electron Paramagnetic Resonance) and ESR(Electron Spin Resonance) are spectroscopic techniques used to examine and analyse complex systems with unpaired electrons providing a variety of information such as nature of ligands, interactions of paramagnetic ions with the lattice and various other knowledge which includes but not exhaustive to identity, oxidation and spin states of the paramagnetic ions. It also provides a plethora of knowledge about magnetic properties of materials, primarily EPR requires the presence of an external magnetic field, involving the interaction between microwave radiation and these paramagnetic ions(which include spin magnetic moments of unpaired electrons), this interaction is known as the Zeeman effect, as shown below.

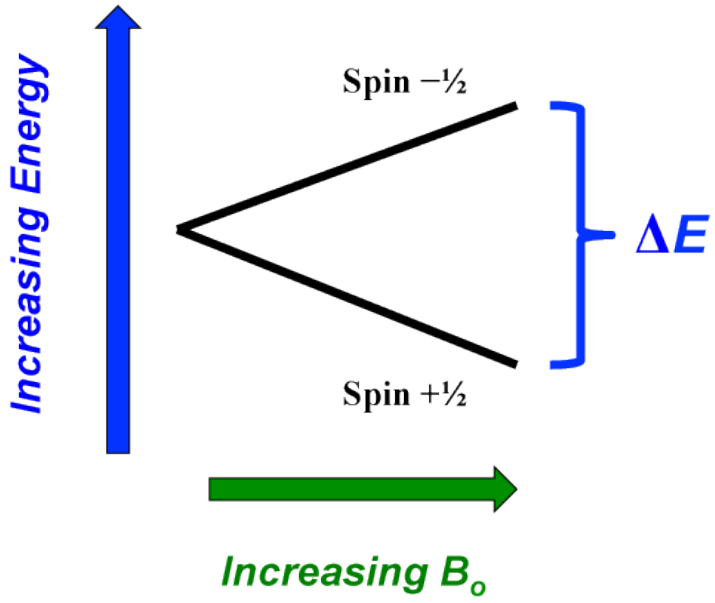

Figure 1 above shows the positive, direct correlation between the magnetic field and energy.

This interaction of the external magnetic field and the paramagnetic ions causes a splitting of the degenerate m_s energy levels. When an electron on the lower energy level absorbs electromagnetic radiation and moves to the excited state, which is the higher energy level, it gives rise to a phenomenon known as the EPR phenomenon. This electron transition between different energy levels is possible under certain rules and conditions, given by the equation:

$$\mathbf{h\nu = \Delta E = \mu_B B}$$

In this equation, h is Planck constant, v is the frequency of the electromagnetic radiation that the electron absorbs, g is the electronic g-value, μ_B is the Bohr Magneton, and B is the applied/external magnetic field, and this is the equation scientifically called as the EPR resonance condition. The EPR spectrophotometer measures the small but significant changes in the electron energy level transition. The independent variable here is the magnetic field while the frequency remains constant. The electronic g-value is simply the ratio between the two energy levels in the electron transition. In this paper, through the spectrophotometer, the g values can be determined for DPPH and Manganese Chloride, and with further analysis, a comparison will be made with the accepted g-values and the experimental g-values.

THEORY:

BASIC EPR SPECTROSCOPY THEORY:

EPR experiments and EPR spectroscopy can be performed on various types of chemical compounds, in this paper, I am going to explore the various aspects of DPPH and Manganese Chloride. These typical EPR experiment, a klystron: a linear beam vacuum tube produces microwave radiation at a constant frequency and the magnetic field has a sweep range. When the magnetic field value satisfies the resonance condition, the microwave energy is absorbed, hence showing a curve in the microwave power spectrum, and this curve is known as the EPR resonance line.

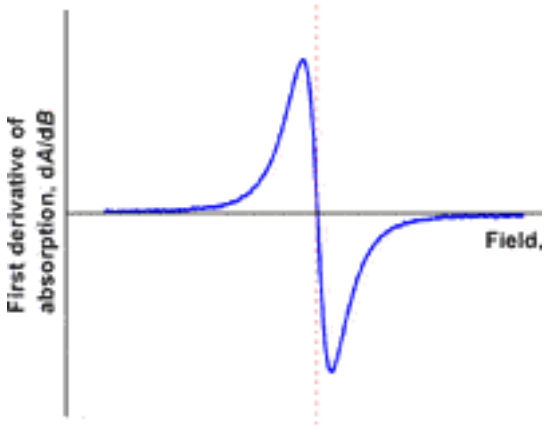

Figure 2 above shows the EPR resonance line for S=1/2 system.

The diagram shown above and physical quantities, magnetic field, microwave frequency helps us calculate the g-value of the spin system which further provides more complex information about the spin system such as the ligand interactions and ligand symmetry, about the interactions with other paramagnetic ions, spin orbit coupling, hyperfine interactions. The symmetry also has some certain specifications: if the symmetry is axial, the reading shows only two distinct g-values as one axis in space is unique, while if the system symmetry is rhombic, then three different g-values will be obtained.

LIGAND INTERACTIONS:

The paramagnetic ions interact very frequently with the several ligands in a lattice. The ligand interactions is caused by the d-subshell orbital in the cation, along with the strong electrostatic field created by the ligands. The electrostatic field created by the ligands and hence the interactions with the paramagnetic ions depend on the ligand geometry. Ligand geometry is if several types, but here in EPR experiments and spectroscopy, the most common is the octahedral structure but these geometric structures in the lattice, interact with greater strength with the d_{z^2} and $d_{x^2-y^2}$ than the d_{xy},d_{xz} and d_{yz} orbitals, thus causing the splitting of the degenerate orbital states. Apart from the normal ligand interactions, there is zero field splitting. Excluding the external magnetic fields, other local, already existing magnetic fields created by atoms in the lattice cause partial degeneration of the S-state which ultimately results in zero field splitting of the spin states.

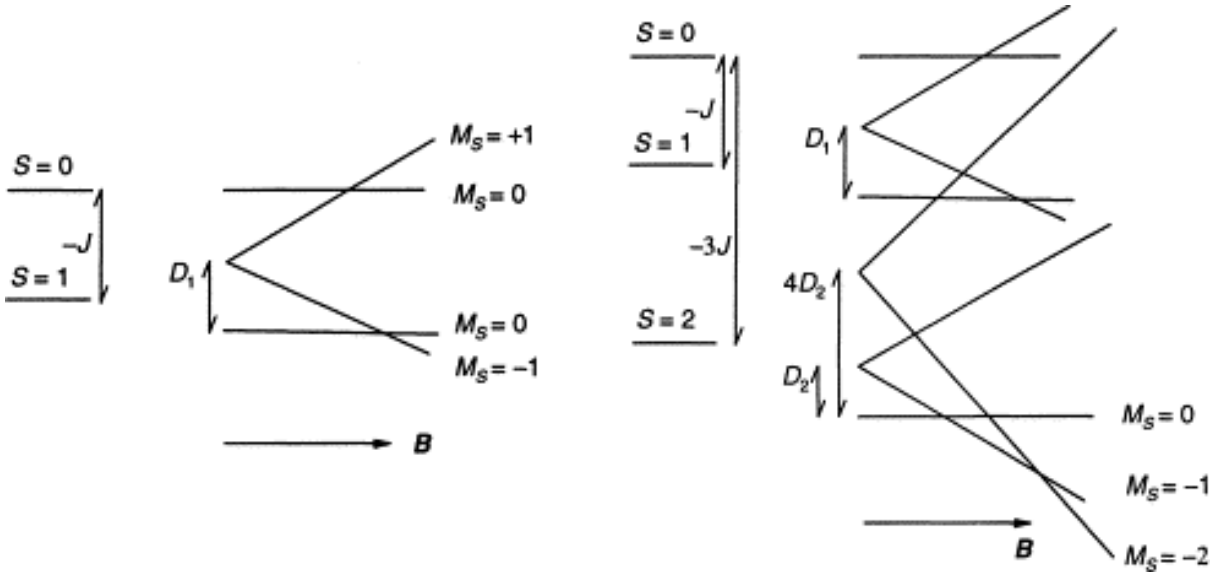

Figure 3 above shows the zero field splitting(ZFS) in metal complexes.

The formula to calculate the g-value in the experiments can be further simplified and can be expressed as:

$$\mathbf{g = \frac{0.71449v(GHz)}{B(kG)}}$$

By this formula it becomes much simpler to calculate the g-values with the microwave frequency in GHz and the magnetic field in kilo-gauss.

EXPERIMENTAL PROCEDURE :

The spectrometer used for the experiment is the Varian E-3 X-band spectrometer consisting a liquid nitrogen flow cryostat. The spectrometer operates at a temperature range from 80K to about 293K, while its frequency range is from 8.5-12GHz. By the use of the microwave bypass arm it biases a diode detector for increasing its sensitivity. The electric generated is then passed and processed on an electronics console and its results is plotted in a two dimensional graph. After switching on the spectrometer, the sample, here DPPH and Manganese Chloride is put on the cavity of the spectrometer while the microwave bridge is set on **TUNE**. After the spectrometer is tuned, no power is observed or detected by the detector and hence **OPERATE** can be turned on for data collection and then further analysis. When the external magnetic field is swept through the resonance(through its sweep range), sample will start to absorb microwave radiation, and again small amounts of power will be detected by the detector in the form of signals. The cryostat, specifically for liquid nitrogen, cools down nitrogen vapour and sends it into the cold finger of the liquid nitrogen cryostat. Here, in this experiment the DPPH sample experiment was conducted at room temperature(293 K) and Manganese Chloride at 104K.

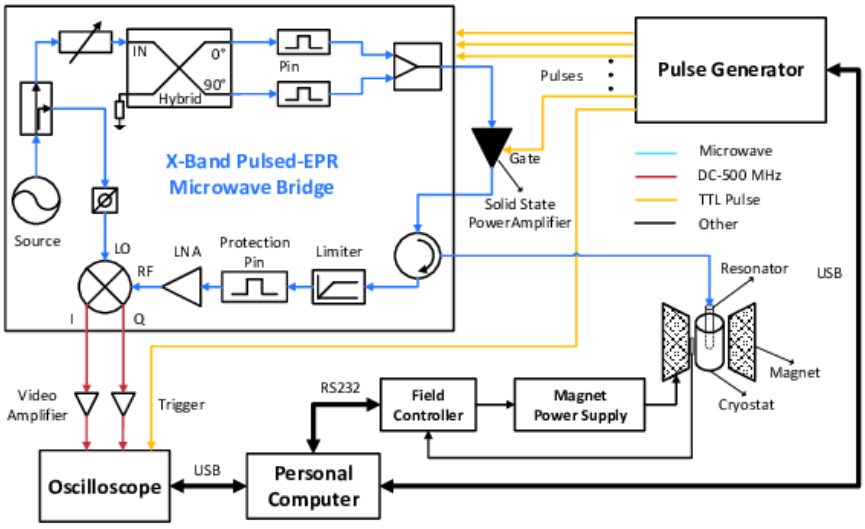

Figure 4 above showing the simple flowchart of how the EPR spectrometer works

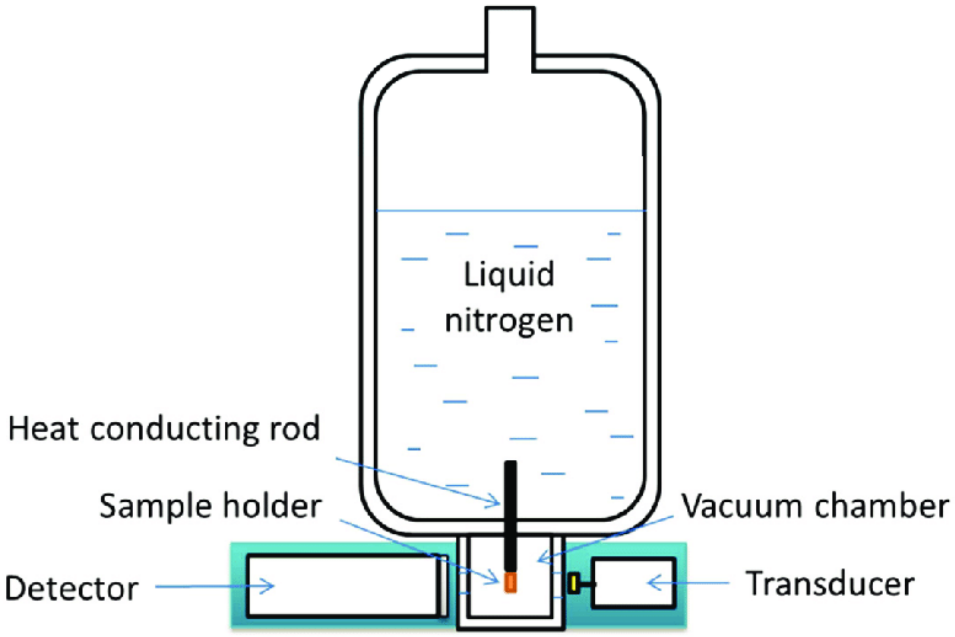

Figure 5 above showing the basic mechanism of a liquid nitrogen cryostat, similar to the one used for EPR experiments.

DATA ANALYSIS:

	DPPH	**$MnCl_2$**
Expected g-value	2.0036	2.0023
Experimental g-value	2.0405	2.1777

Table 1 above shows the data obtained and the theoretical calculations of the g-values.

As we can clearly observe by the data and the annotated graphs, the experimental g-value of the DPPH experiment was 2.0405 while its theoretical value was 2.0036, thus proving that there was no major error or anomalies in the experiment. Similarly for the $MnCl_2$ experiment, the experimental g-value was 2.1777, while the theoretical value was 2.0023, therefore confirming that the experiment was successful. The temperature was monitored throughout

the experiment and to ensure greater accuracy, microwave frequency and temperature in the experiments were constantly monitored as they needed to be kept constant.

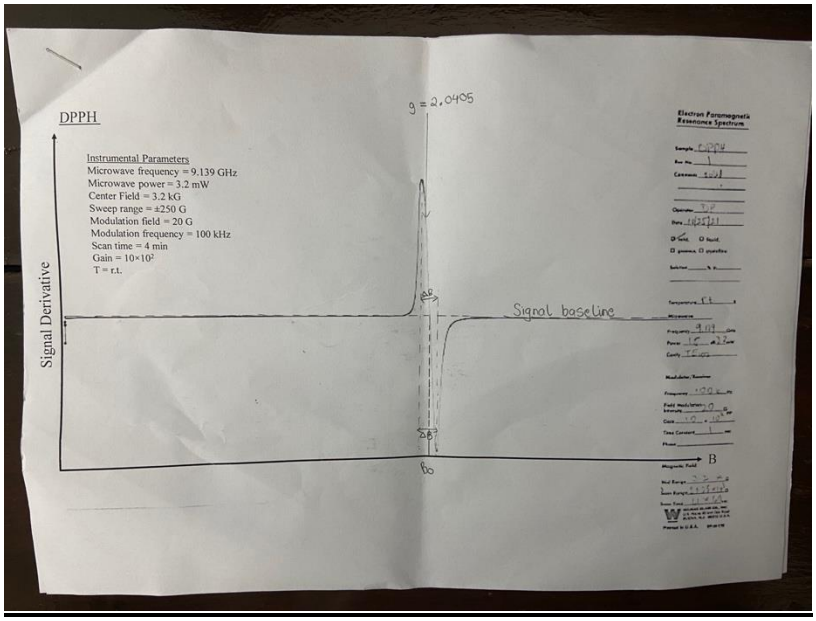

Figure 6 above shows the original scan along with analysis and calculation of DPPH.

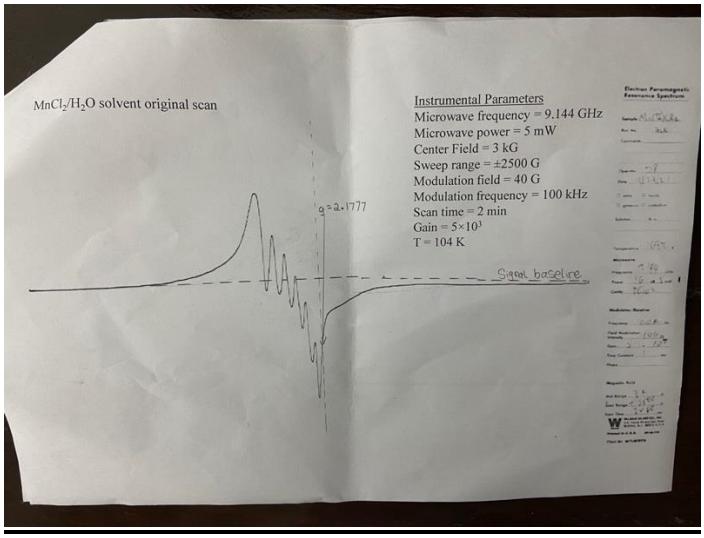

Figure 7 above shows the *original scan along with analysis and calculation of $MnCl_2$*.

CONCLUSION:

Throughout the experiment, EPR theory applications helped to carry out the experiment successfully, with the values being very close to the calculations, relying on the Varian E-3 X-band spectrometer and the liquid nitrogen cryostat. The g-values were calculated using the information already given for both the DPPH and the $MnCl_2$ experiments. Overall, the experiment was successful.

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