Varying Experimental Cases of Electron Spin Resonance (ESR)

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Summary:

Electron spin resonance otherwise known as ESR is a method is a spectroscopy technique that is used to derive certain properties in materials that specifically tend to have unpaired electrons. By using an apparatus found in the lab of Dr. Petasis we were able to investigate the different g-values of certain samples which were tested in various states and various different conditions. The paper below attempts to observe each of these changes and why they have occurred (on the ESR spectra graphs) and what their significance is. In addition, the paper concludes with some fading thoughts on the future of electron spin resonance and as well as a final analysis to each sample that was tested along with suitable calculations (formulas provided).

Abstract:

In this experimental paper we investigate the resonance magnetic field required to fulfill the resonance condition for DPPH, MNCL2, dry Myoglobin, Myoglobin in water, and Myoglobin in glycerol. In doing so we calculate the g-values of all of these compounds and through the analysis of EPR spectra graphs. In addition, we discuss some of the primary reasons why there was a difference in EPR spectra and resonance magnetic field in the myoglobin samples that were placed in different conditions.

Introduction:

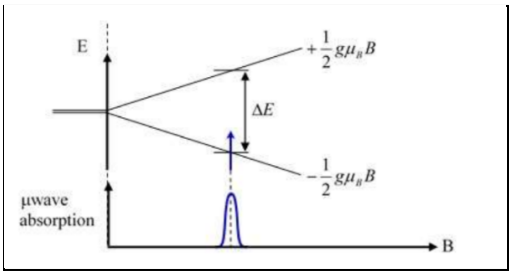
The world being a vast and unknown place, discovery and research is not only needed but encouraged. Whether it be the works of Aristotle in the philosophical realm or the work of Newton in his shaping of the physics world, this quest for knowledge will forever remain unrelinquished. Thus leading us to the overall usage and requirement for such a study known as electron spin resonance. This phenomenon is a spectroscopy based procedure that allows scientists and researchers to understand further information about elements and compounds with unpaired electrons. Through the usage of this technique and the collection of various values known as g-values, the science world is able to collect information regarding certain systems' oxidation states, complex ions that may be bonded to them, as well as their spin state, and how given ions interact within the lattice of cations and delocalised electrons. This is all thanks to Yevgeny Zavoisky who introduced ESR analysis/probing to the science world in 1945. Through his instrumental first report that was published, paired with the development of the study into the worlds of quantum chemistry from 1960 to 1970, and finally the usage of ESR in the medical and pharmaceutical industry ESR was able to go from a small seemingly useless analysis technique to that of the biggest points of research in the modern science world today. The significance of this method lies in the fact that we are able to interact with that of microscopic electrons and atoms on a macroscopic scale using our given ESR apparatus. This magic-like feat takes advantage of the fact that these materials are paramagnetic and possess that of unpaired electrons, which allows scientists to exploit the electron spin resonance method to gain a deeper understanding of how specific compounds are composed and why they may exhibit certain properties. All in all, this leads us back to the main agenda and motivation of using such a study and even writing this paper, in which we will conduct electron spin resonance experiments upon samples such as DPPH, manganese chloride, and more with a primary purpose of understanding their unique properties. Hence, through the use of our apparatus we aim to define and calculate certain g-values for different compounds, similar compounds in different solvents, as well as detect the presence of certain unique structures based on the magnitude of resonance magnetic field and the shape of the EPR spectra first-derivative and original curve..

Background Knowledge:

Some things to comprehend before delving into the paper first include the idea of a physicist known as Pieter Zeeman in an effect regarded as the 'Zeeman effect'. In this phenomenon, we

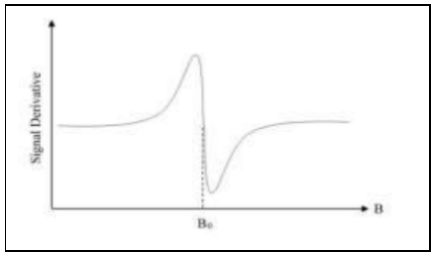
can observe a splitting of atomic orbitals as a result of an external magnetic field applied on the given substance's atoms and electrons. This splitting of the orbitals can be seen in Figure 1.1 below.

Figure 1.1



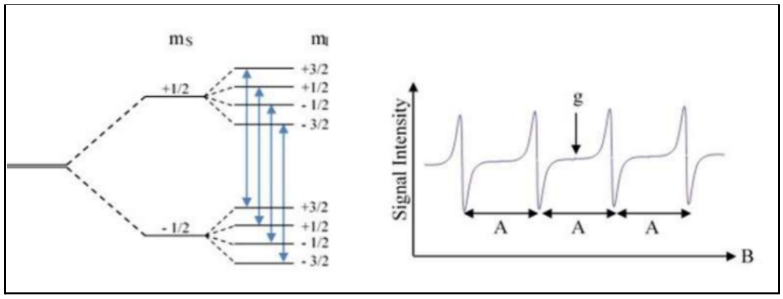
In this diagram we can observe a graph with axes of energy (y-axis) and external magnetic field (x-axis) that shows us that as the external magnetic field is increased there is a splitting of the energy levels that occurs. This splitting in energy levels allows electrons from the lower ground state to be able to transition to a higher excited state if and when they are supplied a given amount of energy. In our experiment, we will be utilizing a Klystron to produce microwave radiation that can be absorbed by the sample being tested. This sample will be able to absorb the radiation and go to an excited state only if the external magnetic field that is applied to it goes through a certain value specific to its characteristics and properties that we call a resonance condition. We can use this frequency value along with the external magnetic field that fulfilled the resonance condition to solve for this aforementioned unitless value 'g' using the expression on the right ($h\nu = \Delta E = g\mu_b B_0$) or ($g = 0.71449\frac{\nu}{B_0}$) known as the EPR resonance condition expression. However, in order to find this magnetic field value B_0 we must procure a graph of what is called an EPR resonance line which can be seen in Figure 1.2 below.

Figure 1.2



Without the use of a spectrometer (on our machine) we would receive a 'bell-shaped' curve that displays the absorption signal as a function of the external magnetic field applied. However, when we use this spectrometer, it supplies us with a first-derivative graph that gives the required value, B_0, by marking the magnetic field value for which the signal derivative crosses the baseline value that it began with. On these graphs there are two types of EPR spectra that can occur, the first being an isotropic curve (Figure 1.2) which has equivalent g-values for all the different orientations in space, and the second being an axial which creates different width size curves that correspond to different g-values for different orientations (g_x , g_y ,etc.). In addition to this, structures that have additional splitting after the separation caused by the external magnetic field as a result of interaction of the nuclei with unpaired electron spins are known as hyperfine structures. This additional splitting has a sort of pattern which can be modelled by the equation (2I + 1) where I is the spin of the nuclei interacting with that of the electron spins, which creates an array of energy levels for the given compound as can be seen in Figure 1.3 below.

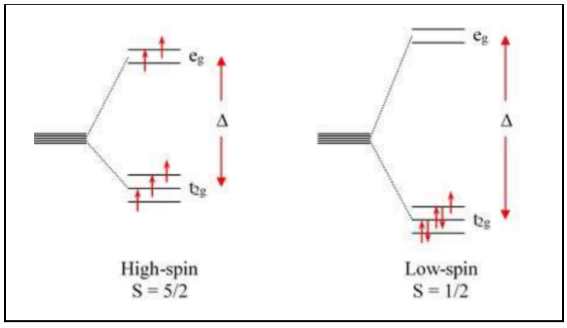
Figure 1.3



These energy levels are a direct result of the increased amount of transitions available from the ground state (bottom) to the excited state (top) (when modelling such transitions one must keep in mind that a change in m_s is 1 and the net change in m_1 is 0 as can be seen on the graph above). This rise in equanimous available transitions causes the absorption derivative-external magnetic

field graph to have more EPR lines of equal g-values but with a separation known as ‘A’ more commonly called the hyperfine constant. An additional factor that changes the overall shape of the EPR spectra as well as the orbital splitting include that of the nature of a complex ion’s ligands and the total spin state of the compound. Complex ions are paramagnetic metal ions that are covalently bonded (coordinate bonds) to that of groups with a lone pair of electrons. The electrostatic field created by the ligands causes interactions between the metal ions depending upon the geometry and number of ligands attached to the paramagnetic ion. This interaction will be higher for one set of orbitals than the other and hence create a splitting. The size of this splitting as seen in Figure 1.4 is defined by the total spin state of the specific compound at hand.

Figure 1.4



Setup/Procedure:

The apparatus used in the experiment consists of a Varian E-3 X Band EPR Spectrometer which can be seen with labels in the image below. It functions with a frequency range of 8.5 - 12 GHZ and with a temperature range from 80 Kelvin all the way till room temperature. To understand the process of operating the Varian E-3 for room and low temperature refer to Figure 1.6 below accompanied by Table 1.1 and a short description of low temperature trial procedure.

Figure 1.6

Table 1.1 (Room Temperature Trial)

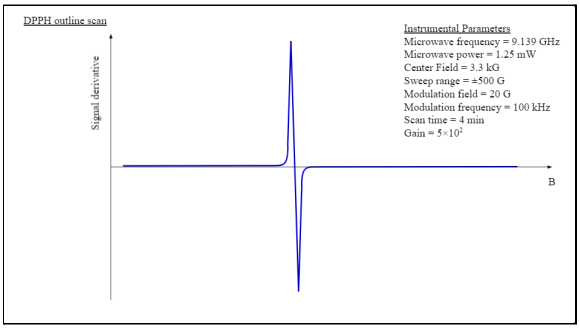
Step Number	Part of Apparatus	Location (Number)	Procedure
1	Fume Hood	N/A	Switch on the coolant water to make sure that the magnet being used does not overheat.
2	Spectrometer	N/A	Can both be turned on for a room temperature scan.
	Universal Counter	(1)	
3	Frequency Knob	(2)	Set to channel three.
4	Intensity Knob	(3)	The intensity of the oscilloscope must be shifted all the way rightward such that a signal shows up.
5	Cavity	(4)	Place a sample inside (after the signal shows up on the screen).
6	Mode Knob	(5)	Must be turned to TUNE.
7	Frequency Knob	(2)	Adjust the position of the dip such that it is in line with the black line of the oscilloscope.
8	Coupling Iris/Teflon Rod	(6)	Turn the Teflon rod (which controls the position of the coupling iris) clockwise or anticlockwise until the dip reaches the baseline.

9	Mode Knob	(5)	Must be turned to OPERATE.
10	Recorder Switch	(7)	Can be turned ON.
11	Frequency Knob	(2)	Must be adjusted such that frequency error and detector current are at a suitable level.
	Power Attenuation Knob	(8)	
12	Magnetic Field Mid Range	(9)	Both can be set to a suitable level and finally the scan button can be pressed.
	Scan Range	(10)	

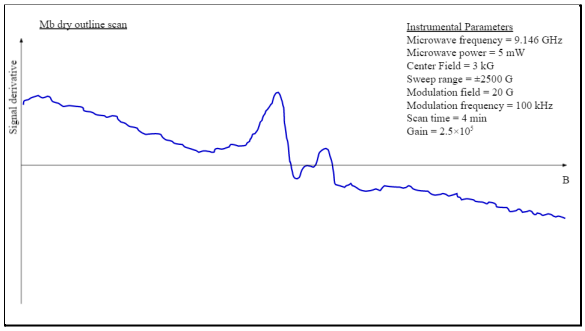
Some of the variances in procedure when conducting a low temperature trial include the fact that after the coolant is switched on from the fume hood the temperature controller will also be flicked on (as opposed to the initial steps in a room temp. trial). Next, the nitrogen valve located behind the spectrometer should be turned on and have a nitrogen flow with pressure of around 25 - 30 psi. Once liquid nitrogen is placed into the bin looking container in the bottom left of the image (a dewar) the sample that is being tested must be lowered extremely slowly into another separate dewar containing more liquid nitrogen. After this sample has cooled to an apt temperature the sample can be placed into the cavity and the same steps used in a room temperature trial can be used now to finish off the low temperature trial.

Results and Discussion:

DPPH Sample

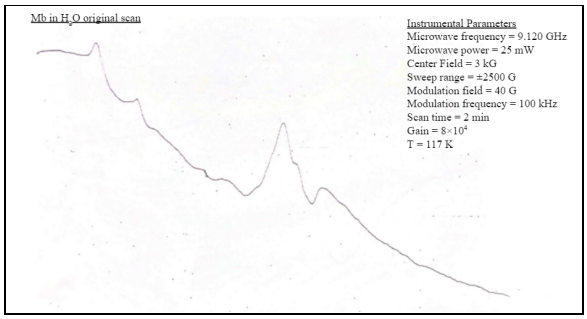


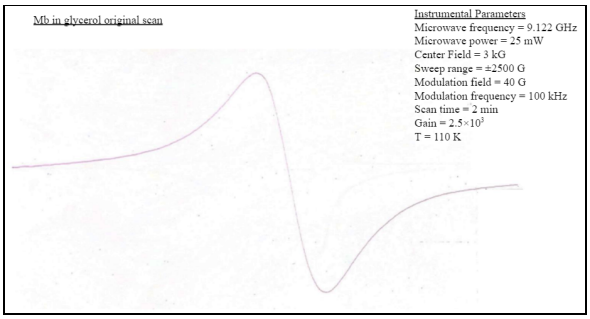
Dry Myoglobin Sample



Myoglobin in Water Sample

Myoglobin in Glycerol Sample





Manganese Chloride in Water Sample

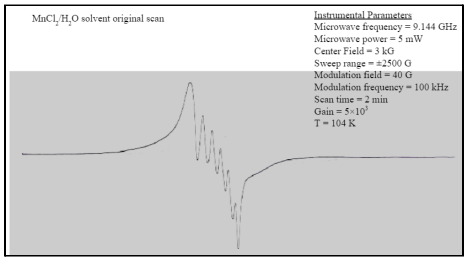


Table 1.2 (Results)

Sample	**Starting Field (B_s) (G)**	**Ending Field (B_e) (G)**	**Spectra Width (w_s) (cm)**	**External Magnetic Field (B_0) (G) (using formula below)**
DPPH	2800	3800	19	3236.821
Dry Mb	500	5500	26.1	3124.526
Mb in Water	500	5500	21.8	3412.8
Mb in Glycerol	500	5500	23.2	3215.5
MnCl2 in Water	500	5500	22.5	2811.111

Formula: $B_0 = (((B_e - B_s) \div w_s) \times w_{rmf}) + B_s$ (w_{rmf} - width of the resonance magnetic field)

Sample	**Frequency (v) (GHz)**	**Resonance Magnetic Field (B_0)(kG)**	**G-Value (g) (Unitless)**	**Additional Notes**
DPPH	9.139	3.2368	2.0173	Identified as an isotropic curve. The literature g-value is at 2.0037 for DPPH.
Dry Mb	9.146	3.1245	2.0914	Took resonance field as the point where positive

				part of derivative line was equal to negative.
Mb in Water	9.120	3.4128	1.9093	N/A
Mb in Glycerol	9.122	3.2155	2.0269	Had wide split so measured linewidth as 3cm or 647G
MnCl2 in Water	9.144	2.8111	2.3241	Took resonance field as the point where positive part of derivative line was equal to negative.

Formula: $g = 0.71449\frac{v}{B_0}$

After taking a glance at the results and calculating the respective g-values using the EPR spectra graphs that were procured from the spectrometer the first few observances include the range and meaning of some of the results. All of the first 4 results seem to permeate around the value of 2.00 thus showing similar properties to that of free electrons which have a g-value of 2.002. In the MnCl2 sample however, we observe a slightly higher g-value of 2.3. In addition to this we can observe a difference in the literature g-value of DPPH which rests at 2.0037 while our experimental value is 2.0173. I suspect that this rather minor difference is a result of a hidden variable that occurred in the experiment itself or in the period of measurement and calculation (due to a lack of precision and uncertainties). Moving on to the shape and g-value for the different types of Myoglobin samples that we had looked at, we can pinpoint upon the fact that the calculated g-value's were quite similar and that the range in values were quite small. However, I believe that the reason that different EPR spectra shapes were observed revolve around the fact that the two solvents used caused the Myoglobin sample to dissolve. Although, I don't believe that solubility of this solute and solvent was the primary factor in determining this increase in resonance magnetic field that allowed for absorption. If we investigate the bonding of both water and glycerol we can pick up on the fact that they are both hydrogen bonded and hence possess lone pairs on their atoms. Due to this fact, when they come into contact with globular proteins that are able to mesh with the solvent the formation of ligands and chelates can occur. This formation of ligands along with a subsequent change in spin state allows for a higher splitting of the degenerate orbitals. This finally acts as the reason for the higher resonance magnetic field needed to allow for this absorption. As a result, I conclude that ligand number,

ligand geometry, and spin state acted as determining factors in the resonance magnetic field magnitude for the two solvent samples of Myoglobin which hence caused a variance in that of the g-value as compared to that of the dry Myoglobin.

Conclusion:

To conclude this paper I'd like to touch upon some points of improvement in the study. To begin, I believe that the procurement of the g-value for calculation could have been made more seamless had a graph of the sensitivity of the detector against the g-value been drawn. I believe that by calculating the resonance magnetic field value by hand and visualizing the point of absorption there was room left over for human error thus resulting in the skewing of some results including that of the DPPH which ended up differing in value to that of its literature value. Next, we were able to analyze and understand the process of ESR through the calculation of characteristic g-values of compounds and elements in different solvents all with unpaired electrons. Using the formulas previously derived we were able to come up with an adequate understanding of g-values, how they are procured and what they can be used for in terms of determining the identity of a given compound. Such uses seem to be trending upward towards the future and even today in things like detection of radiation, free radicals, and even the quantification of how many free radicals may be present in something. From this we can derive things such as the compound/element that possesses these free radicals' nature and more. All in all, I firmly believe that use of ESR will exponentially grow going into the future as a direct result of its innovative methods combined with the fact that it is efficient and convenient for finding specific properties and identities of given compounds and elements in a specific area or sample.

References:

- Ann M. Schmiedekamp, M. Dominic Ryan, and Robert J. Deeth, Inorganic Chemistry 2002 41 (22), 5733-5743, DOI: 10.1021/ic0257930
- Yadav L.D.S. (2005) Electron Spin Resonance (ESR) Spectroscopy. In: Organic Spectroscopy. Springer, Dordrecht. https://doi.org/10.1007/978-1-4020-2575-4_7
- Yipin Lu, Renxiao Wang, Chao-Yie Yang, and Shaomeng Wang, Journal of Chemical Information and Modeling 2007 47 (2), 668-675, DOI: 10.1021/ci6003527

- Naumov, N.G., Tarasenko, M.S., Virovets, A.V., Kim, Y., Kim, S.-J. and Fedorov, V.E. (2006), Glycerol as Ligand: The Synthesis, Crystal Structure, and Properties of Compounds [Ln2(H2L)2(H3L)4][Re6Q8(CN)6], Ln = La, Nd, Gd, Q = S, Se. Eur. J. Inorg. Chem, 2006: 298-303. https://doi.org/10.1002/ejic.200500542
- Petasis D. 2021, EPR Handout 1 + 2
- Petasis D., McGee K., Spring 2020, EPR Spec. Details
- JEOL, Electron Spin Resonance Spectrometer (ESR), History of ESR, https://www.jeol.co.jp/en/products/esr/history.html
- Commins E. D., (2012) Annual Review of Nuclear and Particle Science, Electron Spin and Its History, Vol. 62. https://doi.org/10.1146/annurev-nucl-102711-094908
- Britannica, T. Editors of Encyclopaedia (2011, June 20). Zeeman effect. Encyclopedia Britannica. https://www.britannica.com/science/Zeeman-effect
- Stanford Environmental Health and Safety, 3.6 Fume Hood Location https://ehs.stanford.edu/manual/laboratory-standard-design-guidelines/fume-hood-location