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RESEARCH ARTICLE

EPR INVESTIGATIONS OF DPPH AND MN(II)CL2/H2O

Rajnandini Dey[1] and Prof. Doros Petasis[2]
1. IB1, Calcutta International School, Anandapur, Kolkata, India-700107.
2. Department of Physics, Allegheny College, Meadville, PA-16335, USA.

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Abstract

EPR (Electron paramagnetic resonance) spectroscopies of DPPH (DiPhenylPicrylHydrazyl) and Mn(II)Cl2/H2O were carried out at different temperatures and the spectra were analyzed using EPR theory and spectroscopic techniques. The g-values and hyperfine constants were determinedfrom the spectra and were compared to previously established data in other experiments in this field and thus analyzed.

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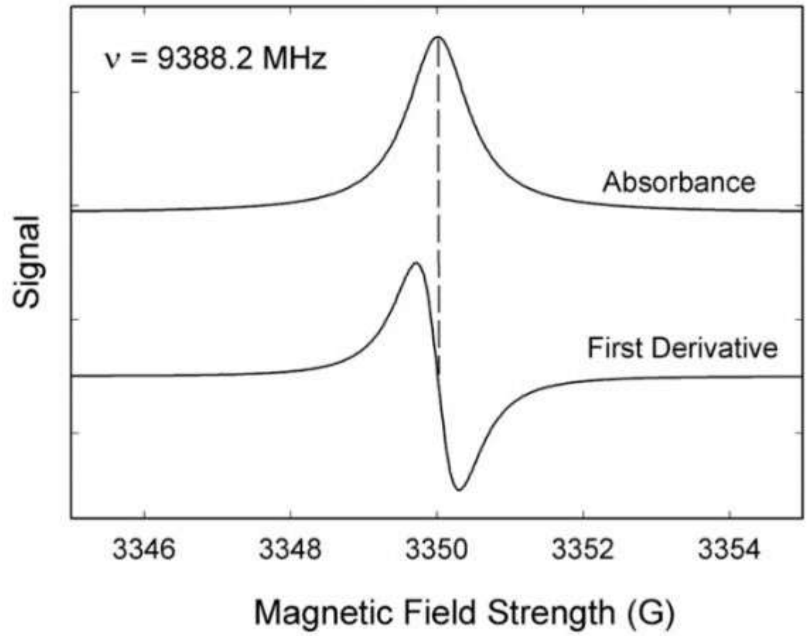
Introduction:-

EPR spectroscopy is a technique, based on absorption of electromagnetic radiation, that is used to investigate materials with one or more unpaired electrons, which are usually paramagnetic or ferromagnetic species. The electromagnetic radiation used in ESR instruments are usually microwaves in a frequency range of 10^9 Hz and higher. When the material absorbs these microwaves, and thus energy, its electrons move to a higher energy state. However, rather than changing the frequency of the microwaves in order to analyze the absorption spectrum of the material, the magnetic field is changed while keeping the frequency constant. Hence, in EPR spectrum diagrams, the absorption of microwave frequency radiation is plotted against the magnetic field intensity. When recording these EPR spectra, there are two methods that are used: continuous wave (CW) method and the pulsed EPR method. The actual EPR spectrum however, when using the continuous wave method, is the derivative of the absorption curve, as shown in Figure 1.

Corresponding Author:- Rajnandini Dey
Address:- IB1, Calcutta International School, Anandapur, Kolkata, India-700107.

Figure 1:- Since the continuous wave (CW) method is used, the absorption signal is shown as thefirst derivative of the absorbance.



The main components of an EPR spectrometer include the microwave resonator, the microwave bridge, the magnet system, and the control electronics. The microwave resonator is responsible for generating an adequate microwave magnetic field at the sample position and for converting the sample response into a microwave signal that can be detected by the circulator.

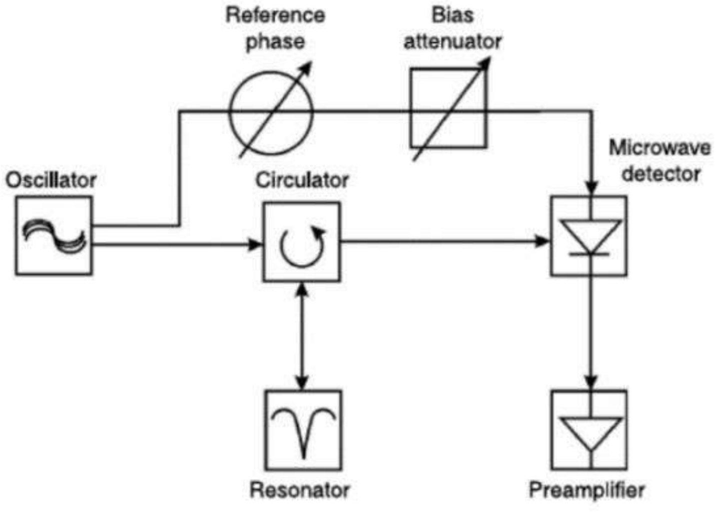


Figure 2:- Components of a microwave bridge. The microwave detector receives input from the circulator, as well as the reference phase and bias attenuator. The circulator also redirects the powerreceived from the oscillator to the sample through the resonator [1].

One of the main components of a microwave bridge, as shown in Figure 2, is the oscillator. The oscillator generates and supplies microwave power in an EPR spectrometer, which is absorbed by the resonator. The reference arm supplies a specific amount of power in order to shift the detector into its linear response regime. The bias attenuator adjusts the bias induced by the powerthat is supplied by the reference arm. The conversion of the microwave into a zero-frequency voltage is done by the detector. The magnet system in an EPR spectrometer consists of a power supply, a magnet, a field sensor and a field regulator. In the EPR system, the magnetic field is swept over a range based on the microwave frequency and sample's properties in order to detect the EPR spectrum.

Background Theory

The key properties of an electron that are fundamental to EPR spectroscopy are the spin of an electron and its associated magnetic moment. Microwave absorption occurs when the magnetic field is changed in a limited range around a central value B_O (applied magnetic field). In B_O, the electron has two different energies for its two possible spin states due to the Zeeman effect, as can be seen in Figure 3. This difference in energies only occurs when there is an applied magnetic force, B_O, and the increase in energy difference between the two spin states is directly proportional to the increase in the strength of B_O.

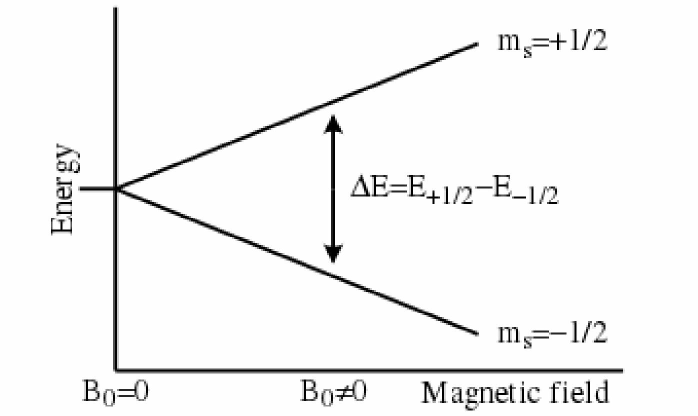


Figure 3:- Energy levels for the electron's two spin states in B_O. Where the magnetic moment (μ) is oriented against the magnetic field (B_O), the higher energy level of the electron spin quantum number m_s = $\frac{1}{2}$ occurs. Where the magnetic moment (μ) is aligned with the magnetic field (B_O), the lower energy level of m_s = $\frac{1}{2}$ occurs [2].

The difference in the two energy levels for the electron's two spin states, ΔE, is given by ΔE = hν where h is Planck's constant and ν is the frequency of the microwave radiation. E = gμBBOMS = ±1/2 gμBBO where g is the proportionality factor (Landé factor), μB is the Bohr magneton (a constant for the magnetic moment of an electron), and BO is the applied magnetic field. Since μB < 0 [1], E may also be written as E = g|μB|BOMS = ±1/2 g|μB|BO. When the microwave radiation is absorbed, an electron that is in the lower energy state moves to the higher energy state. An electron in a higher energy state cannot absorb radiation since there no possible states for the electron at a higher energy level. Since we change the magnetic field while keepingthe radiation constant, for this absorption of radiation to take place, the magnetic field must alignthe two spin states of the electron such that the difference in their energies, E, is equal to the radiation. This is true for all isolated electrons.

However, the electrons and their spins are not isolated and are affected by their environment and by other electrons. For instance, many nuclei of atoms also have a magnetic moment. This magnetic moment causes an interaction between the nucleus of an atom and the electron, called a hyperfine interaction, because it produces a local magnetic field at the electron.This means that the magnetic field of the electron consists of the applied magnetic field, BO, as well as the magnetic field produced due to the hyperfine interaction. The equation E = gμBBOMS thus changes to E = gμBBOMS + aMSmI where a is the hyperfine coupling constant and mI is the nuclear spin quantum number.

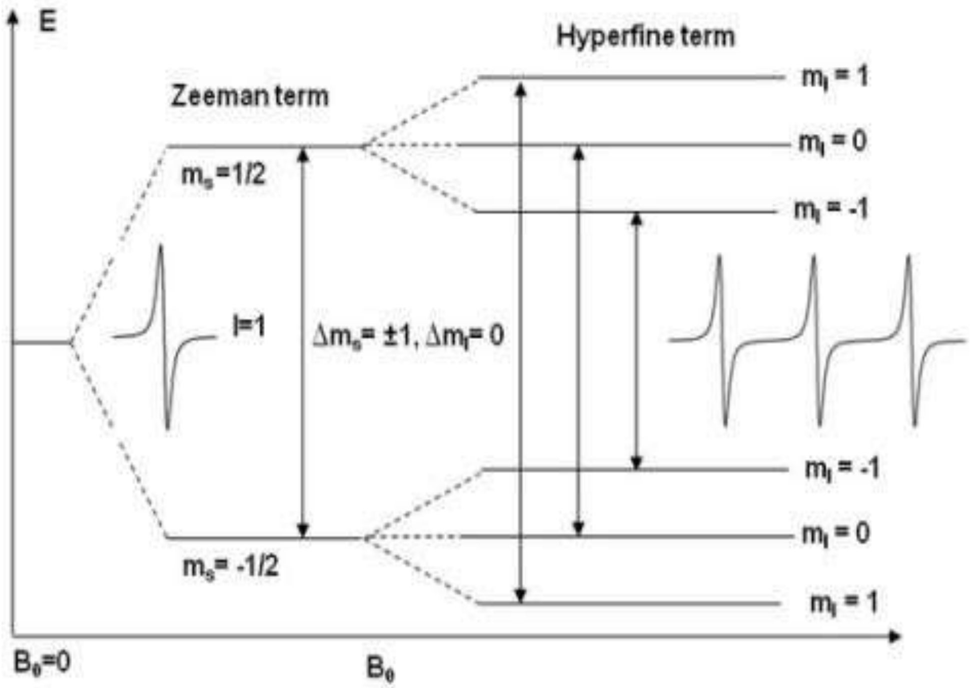


Figure 4:- Energy levels for electrons produced due to hyperfine interaction in B_O. The inset tracesshow the corresponding electron paramagnetic resonance (EPR) spectrum in the absence and presence of a 14N (I = 1) hyperfine interaction [3].

These hyperfine interactions cause each of the two energy levels of the electron to split into two and hence produce a new EPR spectrum with more lines as shown in Figure 4. The number of lines that are formed because of this hyperfine coupling is given by 2NI + 1 where N is equal to the number of equivalent nuclei, and I is the nuclear spin.

Experimental Procedure

DPPH: The sample was placed in the cavity and the microwave bridge was set on tune. The iris was adjusted so that the bottom of the dip touched the baseline and liquid nitrogen cryostat was used. EPR measurements were carried out with a Varian E-3 X-band EPR spectrometer at room temperature for a scan time of 4 minutes. The instrumental parameters used were a microwave frequency of 9.139 GHz, microwave power of 3.2 mW, center field of 3.2 kG, sweep range of ±250 G, modulation field of 20 G and a modulation frequency of 100 kHz.

Mn(II)Cl2/H2O solvent: The sample was placed in the cavity and the microwave bridge was set on tune. The iris was adjusted so that the bottom of the dip touched the baseline and liquid nitrogen cryostat was used. The liquid nitrogen cryostat is used in this sample to cool it in order to reduce thermal energy but also in order to minimize the interference of water with the absorbance measured since ice hardly absorbs microwaves, unlike water. EPR measurements were carried out with a Varian E-3 X-band EPR spectrometer at 104 K for a scan time of 2 minutes. The instrumental parameters used were a microwave frequency of 9.144 GHz, microwave power of 5 mW, center field of 3 kG, sweep range of ±2500 G, modulation field of 40G and a modulation frequency of 100 kHz.

Results And Discussion:-

DPPH: As shown in Figure 5, the EPR spectrum for the DPPH sample shows that it has a g- value of ≈ 2.03, calculated using the formula g = 0.71449 $^{\nu(GHz)}$, which denotes that the sample
$B_O(kG)$ is a free radical taking into account the sweep range. The accepted g-value for DPPH is 2.0036. The calculated g-value of the sample is very close to 2.0036 when account~~ing for~~ the uncertainty of measurement and calculation. The linewidth of the spectrum is calculated to be ~141.18 G.

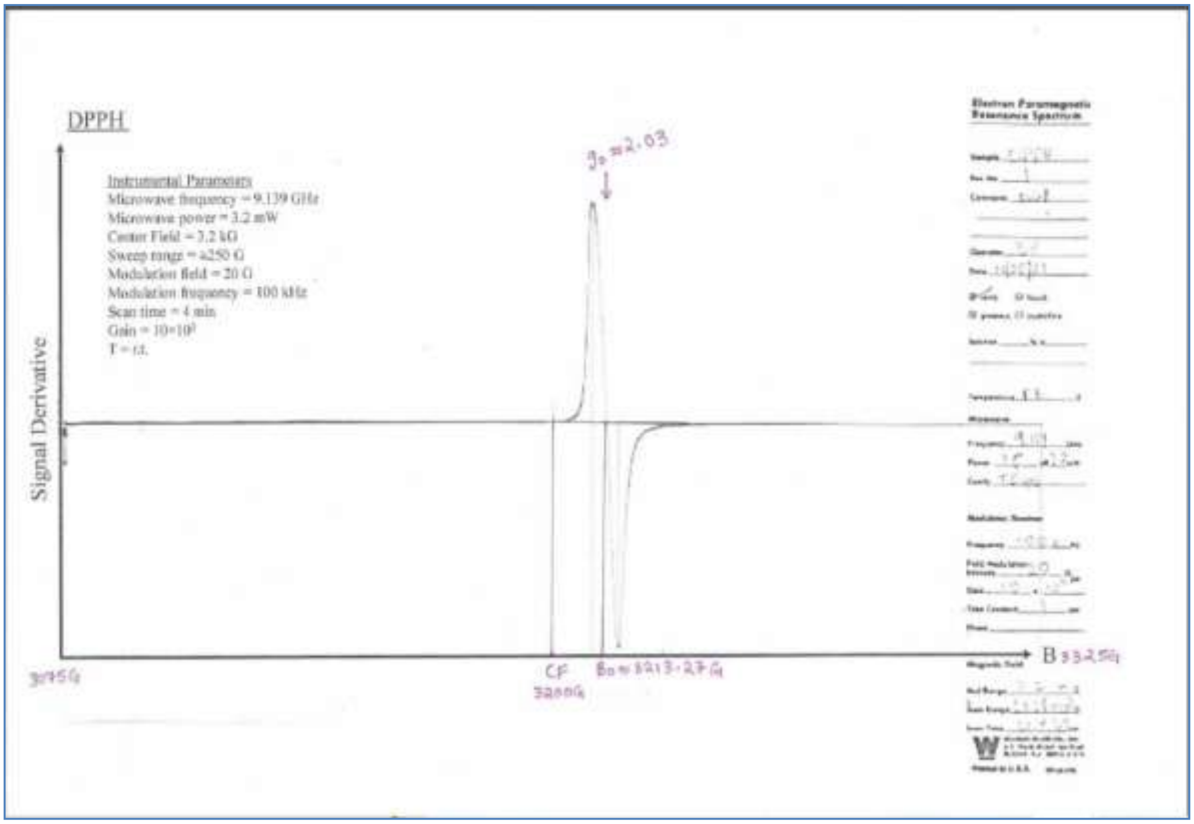


Figure 5:- EPR spectrum of the DPPH sample.

Mn(II)Cl_2/H_2O solvent: As shown in Figure 6, the EPR spectrum for the Mn(II)Cl_2/H_2O solvent sample shows that it has a g-value of ~ 2.28. This g_0 value of ~2.28 is almost the same as g_{ave}, the calculated average value of g_1, g_2, … and g_6, which is ~ 2.27. The hyperfine constant A can be calculated to be ~ 50.42 G. The expected g-value for Mn(II) is 2.0023 and the expected hyperfine constant A is ~ 90 G. This discrepancy between the calculated and expected values may be, in part, due to uncertainty in measurements and calculation. Furthermore, the presence of water in the sample, despite it being in its solid state and thus having very low absorbance of microwaves and very low dielectric losses, may still result in minute differences in the calculated and expected values as there is still a very small amount that is absorbed. These differences in the calculated and expected values may also stem from the changes that take place in a sample upon freezing. As stated in [1], "Cells can be ruptured and membranes shredded by formation of ice crystals upon freezing. It is well known that proteins can be partially denatured by freezing." These factors can all affect the EPR signal and thus the values of g and A.

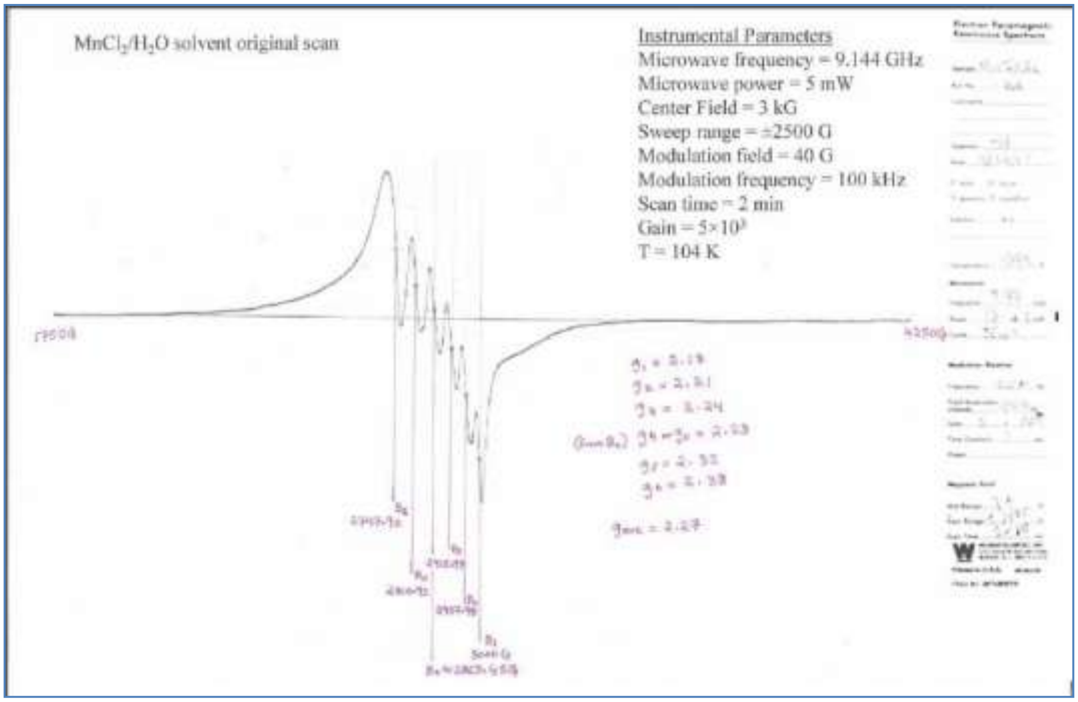


Figure 6:- EPR spectrum of the Mn(II)Cl$_2$/H$_2$O solvent.

Conclusion:-

The EPR spectra collected from the EPR spectroscopy of DPPH and Mn(II)Cl2/H2O were studied using the values of g, B0, and hyperfine constants and these values were analyzed and interpreted using EPR theory. While the results from the DPPH spectrum correlated with established studies of EPR spectroscopy of DPPH, the results for Mn(II)Cl2/H2O differed from the expected values, and the possible causes behind this were speculated to be the uncertainty in measurement and calculation, and/or the presence of water in the sample.

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