Electron Paramagnetic Resonance Spectroscopy of Charge Carrier in Solids

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ABSTRACT

A form of magnetic resonance spectroscopy, Electron Paramagnetic Resonance (EPR), or Electron Spin Resonance (ESR), uses microwave radiation to probe unpaired electrons, such as radicals, radical cations and triplets in the presence of an externally induced static magnetic field. There are significant similarities between EPR and NMR in terms of their physical characteristics (NMR). Electron spin characteristics are directly measured in EPR, as opposed to nuclear spins, in NMR, the most noticeable distinction. As long as you have unpaired electron spins, EPR spectroscopy may be used in a number of ways, from examining extremely reactive radical intermediates to finding out how paramagnetic metal clusters interact with bioenzymes. EPR may also be employed in the semiconductor sector to analyse materials containing conducting electrons. Biological applications of electron paramagnetic resonance (EPR) spectroscopy include radicals and transition metal ion complexes having one or more unpaired electrons. Understanding the fundamental phenomena of spectroscopy, such as electronic Zeeman interaction, resonance, anisotropy, saturation, hyperfine interaction and zero-field interactions is covered in this chapter. Spectral powder pattern from randomly oriented samples is discussed, and a simulation method based on unit-sphere walking is presented. Spin counting or quantitative EPR is also discussed in connection to the concept of effective spins, which are physiologically important.

INTRODUCTION

Using EPR spectroscopy, we will examine a range of paramagnetic materials. We evaluate the EPR signals and use the resonance condition to determine the g-factor of the paramagnetic sample's unpaired electrons. When electrons contain both orbital and spin angular momentum, the gfactor EPR is typically employed to analyse these systems, which requires a scaling factor to account for the connection between the two momenta. The g-factor is utilised in the same way as chemical shift is used in NMR, and it has a similar usefulness. Molecular orientation in an external magnetic field affects the g-factor, which might change its value.

In order to completely comprehend the electronic structure of a particular paramagnetic ion sample, the g-value is crucially important. As a result, values are meticulously determined.

EPR has a wide range of applications in many different industries, therefore it's crucial to know how it works and what critical observations might help us make significant inferences.

THEORY

Electrons are negatively charged particles with two primary types of movement. Orbital magnetic moment is brought about by the first one, which spins around the nucleus The other is "spinning" around its own axis, causing a magnetic spin moment to occur. The spin magnetic moment of an unpaired electron is the primary source of the molecule's magnetic moment. It acts like a miniature bar magnet because it rotates around its axis. The spin of an unpaired electron may align in two distinct directions when it is put in a strong magnetic field, generating two states of spin- $m_s = \pm \frac{1}{2}$.

For a lower energy state, it is possible to align in the same direction as the magnetic field (parallel)- $m_s = -\frac{1}{2}$ and in the opposite direction of the applied magnetic field - $m_s = +\frac{1}{2}$

The degeneracy of the electron spin states is reduced by the differing energies of the two alignments. The energy difference is given by:

$$\Delta E = E_+ - E_- = h\nu = gm\text{ß}B$$

Where,

h = Planck's constant (6.626×10^{-34} J s^{-1})

ν = the frequency of radiation

ß = Bohr magneton (9.274×10^{-24} J T^{-1}) B = strength of the magnetic field in Tesla

g = the g-factor which is a unit less measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023.

When a photon of energy hv of an unpaired electron is absorbed or emitted, it moves between the two energy levels in accordance with the resonance condition, hv = ΔE EPR, spectroscopy's fundamental equation. When an external magnetic field interacts with unpaired electrons' spin magnetic moments, the EPR method is used (the Zeeman effect). This interaction, as shown in class, causes a splitting of the degenerate m5 spin energy levels, as seen in Fig. As a result of the EPR phenomenon, electrons on lower energy levels are capable of absorbing electromagnetic radiation and transitioning to an excited state.
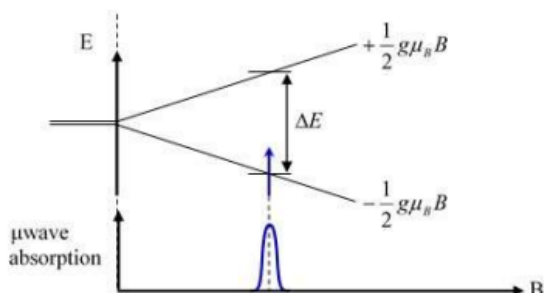

Fig. 1   Zeeman splitting of the degenerate electronic spin states for an S = ½ system. An electron can absorb energy to make a transition to the excited state resulting in an EPR absorption line.

An electronic transition is possible only when

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

where g is the electronic g-factor (or g-value), IAB is the Bohr magneton, and B is the applied magnetic field, v is the frequency of the electromagnetic radiation. The EPR resonance condition is the name given to this kind of expression. The electromagnetic radiation has frequencies in the GHz range, with magnetic fields ranging from 0 to 1 Tesla. For example, EPR signals are generated by transition series and rare earth ions.

An EPR experiment often involves using a klystron, which emits microwave radiation at a fixed frequency while varying the magnetic field by several kilogauss (IT = 104 G). When the magnetic field reaches a value that meets the resonance criterion, microwave radiation is absorbed. Because of this, when we look at the microwave power spectrum, we see an absorption curve with a bell-shaped form. Figure 2 shows the first derivative of a "EPR resonance line," which we can plot with the help of a spectrometer.
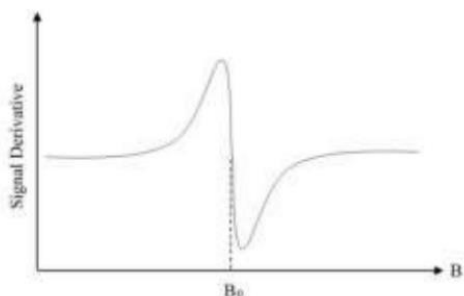
Fig. 2　Typical EPR resonance line for an S = ½ system.　The point where the line crosses the baseline determines the resonance magnetic field B_0 which allows us to calculate the g-value for the system.

The g-value of our spin system may be calculated using the EPR spectrum and resonance state. In addition to the spin-orbit coupling (g=2.002 for free electrons, g2.002 for bound electrons), hyperfine interactions (present when nuclear spin is not zero: (2I+1) EPR lines where I is the nuclear spin), ligand symmetry (high spin and low spin states), interactions with other paramagnetic ions (e.g. exchange and dipolar interactions), etc., the g-value provides information on the various interactions that the spin system experiences.

In Fig. 2, an isotropic spectrum is shown by the EPR line. When all the other atoms in the lattice establish cubic symmetry at the position of the paramagnetic ion, this happens. G-values are equal in all directions around the ion, which means that g., = g. = g,,. = g. Due to the fact that two directions of space are equal, we may get two distinct g-values for an axially symmetric system: g_z = Gi and g_x = GY = Gl when symmetry is just one way. Because there are no corresponding spatial axes for symmetry with rhombic symmetry, three g-values g_x g_y g_z result.
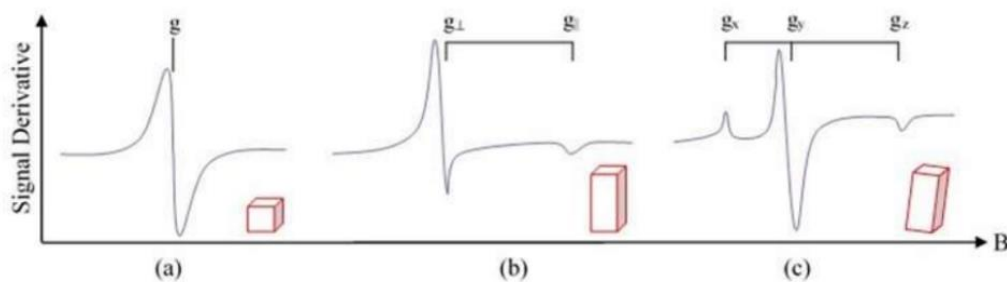

Fig. 3　Typical EPR powder (polycrystalline) spectra for various point symmetries at the paramagnetic ion: (a) isotropic spectrum (cubic symmetry), (b) axial spectrum (hexagonal symmetry), (c) rhombic spectrum (orthorhombic symmetry).

INSTRUMENTATION

When conducting EPR spectroscopy, the frequency and magnetic field may be varied independently of each other, or both can be varied simultaneously (as is the case for NMR spectroscopy). In contrast to NMR spectrometers, commercial EPR spectrometers frequently alter the magnetic field while maintaining a fixed frequency. However, there are several EPR spectrometers that operate at lower and higher frequencies than the general 8-10 GHz (X-band) - 1-2 GHz (L-band) and 2-4 GHz (S-band), 35 GHz (Q-band) and 95 GHz (W-band).
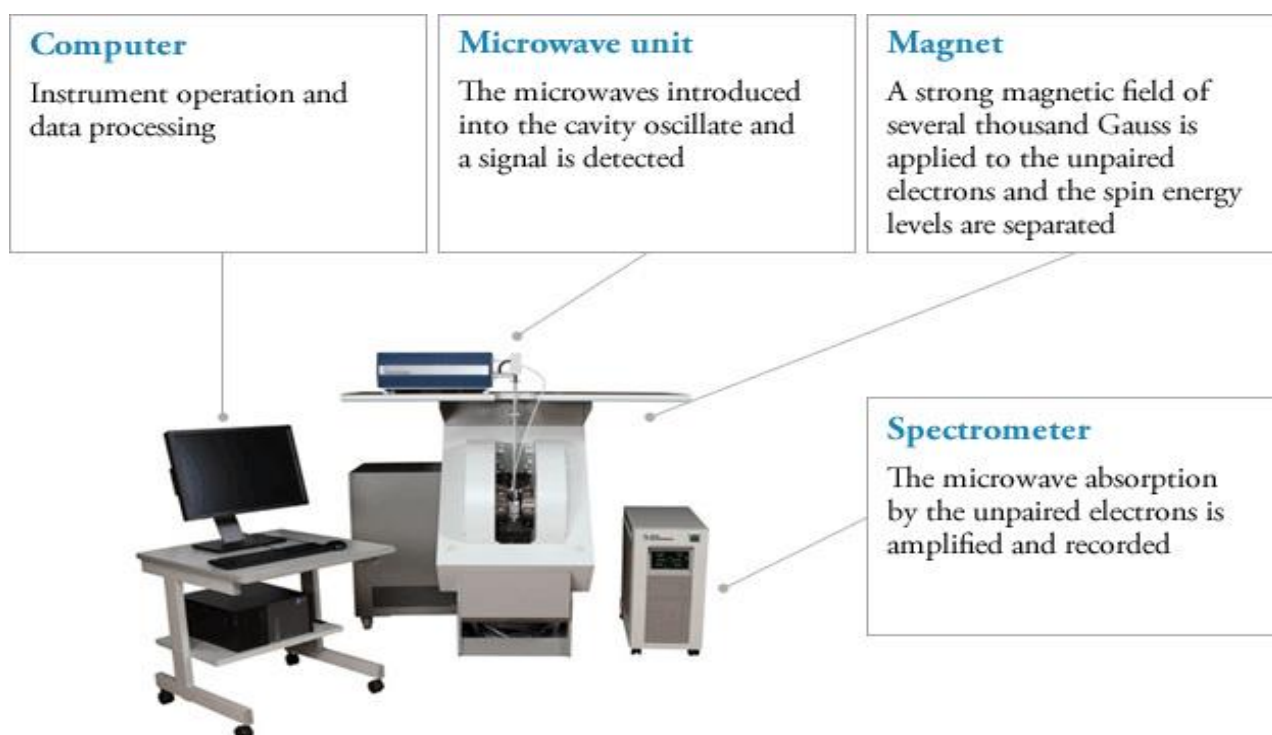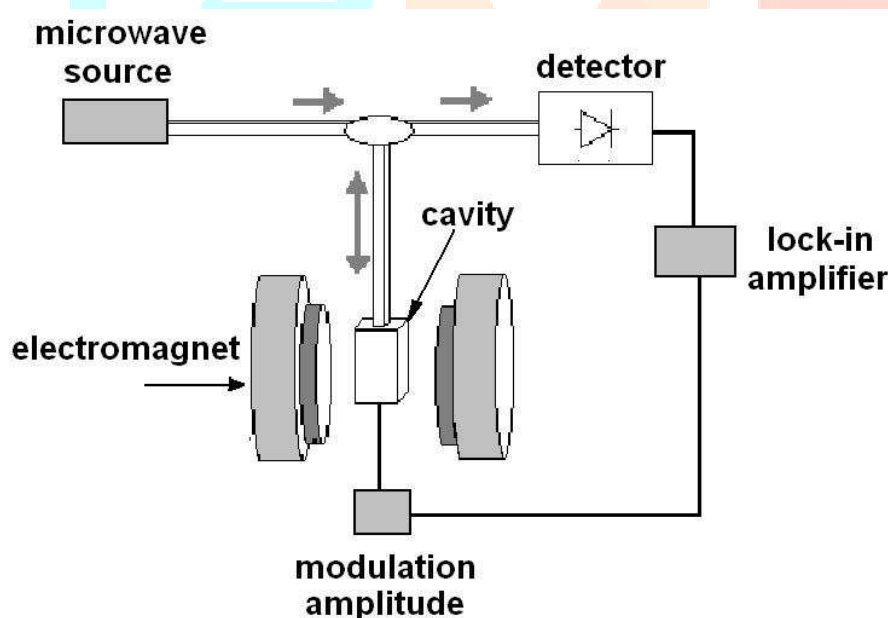
FIG.3a ESR instrument composition

FIGURE.3b

Block diagram of a typical EPR spectrometer.

EPR spectrometers work by generating microwaves from a source (typically a klystron), sending them through an attenuator, and passing them on to the sample, which is located in a microwave cavity. Microwaves reflected back from the cavity are routed to the detector diode, and the signal comes out as a decrease in current at the detector analogous to absorption of microwaves by the sample. Samples for EPR can be gases, single crystals, solutions, powders, and frozen solutions. For solutions, solvents with high dielectric constants are not advisable, as they will absorb microwaves. For frozen solutions, solvents that

will form glass when frozen are preferable. Good glasses are formed from solvents with low symmetry and solvents that do not hydrogen bond. Drago provides an extensive list of solvents that form good glasses.

EPR spectra are generally presented as the first derivative of the absorption spectra for ease of interpretation. An example is given in Figure.
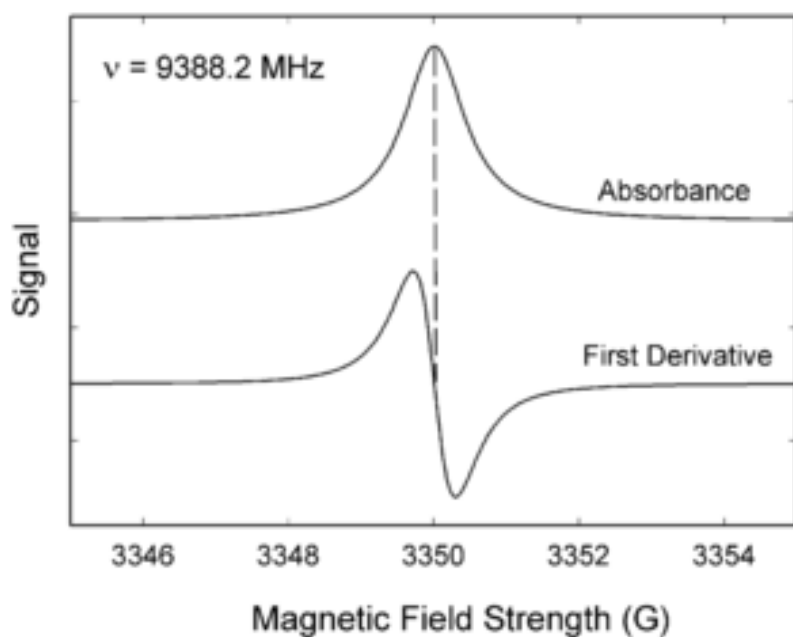

Figure 4. An example of the first and second derivative EPR spectrum.

Magnetic field strength is generally reported in units of Gauss or mTesla. Often EPR spectra are very complicated, and analysis of spectra through the use of computer programs is usual. There are computer programs that will predict the EPR spectra of compounds with the input of a few parameters.

Experimental Procedures

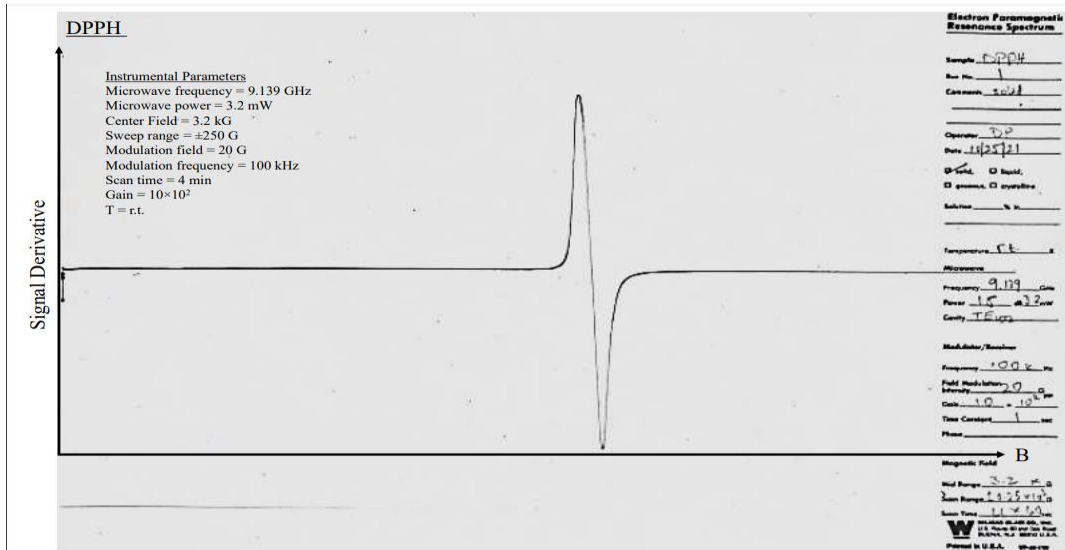Figure 5 Instrument Setup Varian E-3 X-band Spectrometer. D.Petasis Lab, Allegheny College

DPPH

Instrumental Parameters
Microwave frequency = 9.139 GHz
Microwave power = 3.2 mW
Center Field = 3.2 kG
Sweep range = ±250 G
Modulation field = 20 G
Modulation frequency = 100 kHz
Scan time = 4 min
Gain = 10×10^2
T = r.t.

Figure 6

Mb dry

Instrumental Parameters
Microwave frequency = 9.147 GHz
Microwave power = 8 mW
Center Field = 3.0 kG
Sweep range = ±250 G
Modulation field = 20 G
Modulation frequency = 100 kHz
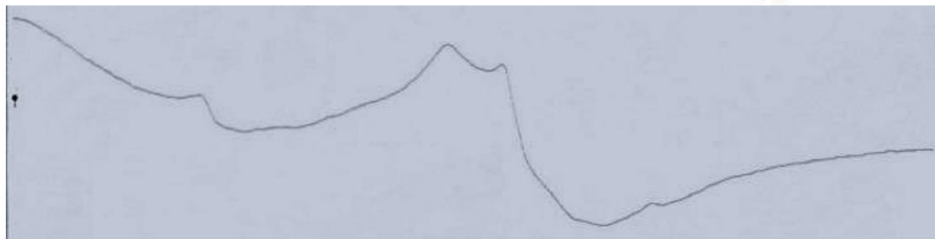Scan time = 4 min
Gain = 5×10^4
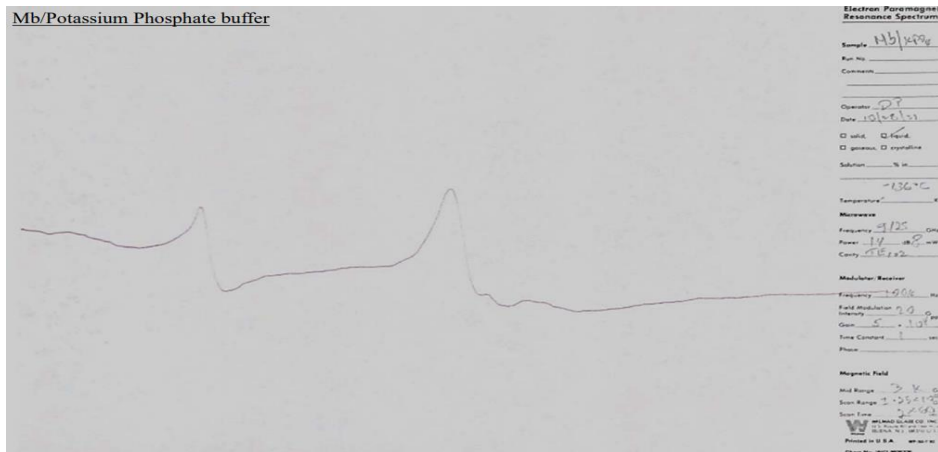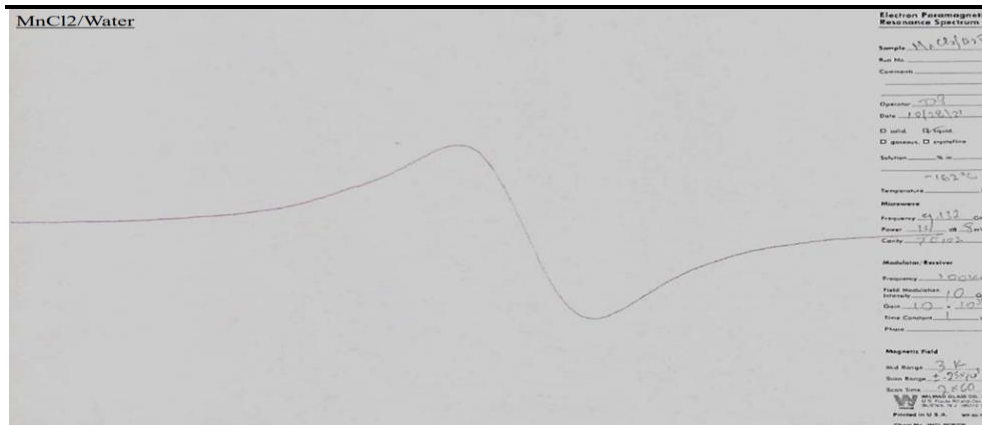T = r.t.

Figure 7
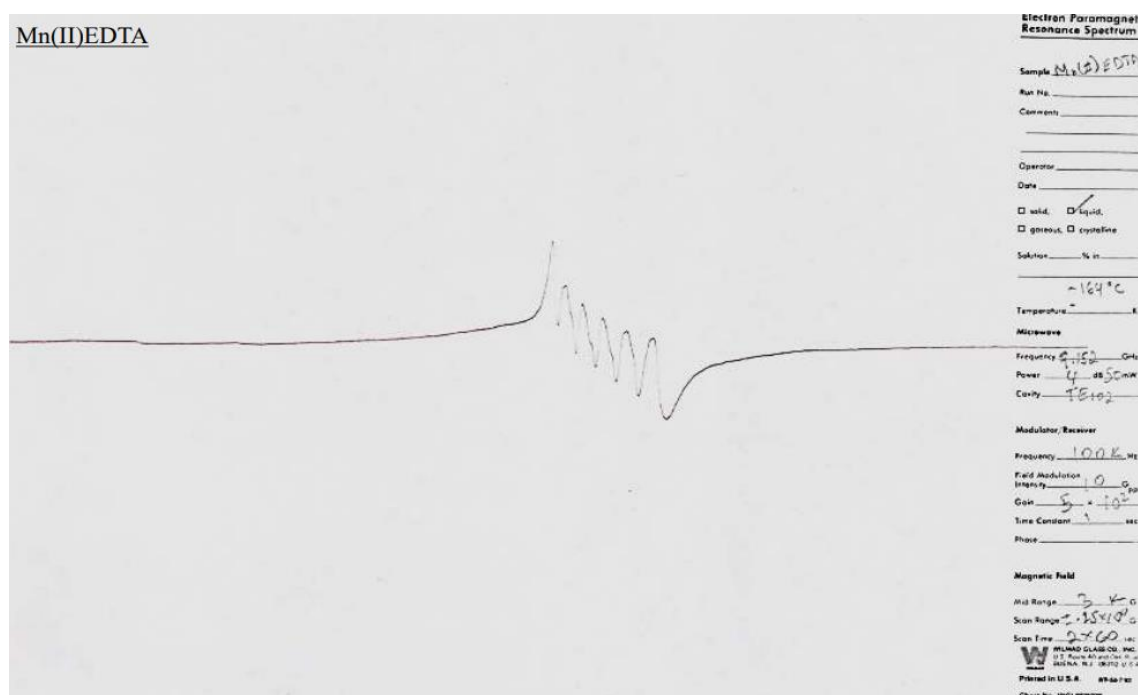

Mb/Potassium Phosphate buffer

Figure 8

Figure 9

Figure 10

Sample	Frequency (v) (GHz)	Resonance Magnetic Field (B_0)(kG)	G-Value (g) (Unitless)	Additional Notes
DPPH	9.139	3.2	2.0	Identified as an isotropic curve. The literature g-value is at 2.0037 for DPPH.
Dry Mb	9.147	3.0	2.0	Took resonance field as the point where positive part of derivative line was equal to negative.
Mb/Potassium Phosphate buffer	9.125	3.126	2.0856	N/A
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.
Mn(II)EDTA	9.152	3.045	2.1475	N/A

CONCLUSION

We were able to investigate and comprehend the process of ESR by the determination of typical g-values of compounds and elements in various solvents all containing unpaired electrons. Using the formulae previously developed we were able to come up with an appropriate grasp of g-values, how they are acquired and what they can be utilised for in terms of establishing the identification of a given molecule. Such usage appear to be increasing higher towards the future and even now in things like detection of radiation, free radicals, and even the quantification of how many free radicals may be present in anything. From this we may draw things such as the compound/element that contains 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.

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