Electron Spin Resonance (ESR) Spectroscopy

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ABSTRACT

The primary objective of this experiment is to understand the method of Electron Paramagnetic Resonance (ESR)spectroscopy by finding the a Landé g-factor of two well known free radicals: Tetracyanoquinodimethane (TCNQ) and Diphenyl Picylhydrazyl (DPPH). We observe how different frequencies of EM Waves bombarding the sample under a magnetic field ($\vec{B}$) shifts the graph of absorption of energy by the electron and its first derivative or line widths from TCNQ and DPPH.

1 Introduction

ESR Spectroscopy emerged as a product of a large number of scientific experiments leftover from World War II. ESR was discovered shortly after Purcell and Bloch's discovery of NMR in 1944 using paraffin wax at Stanford University. The first ESR spectrum was found by Yevgeny Zavoisky in 1945 using $CuCl_2 \cdot 2H_2O$ at 4.76 mT and a magnetic field of 133 MHz at the Kazan Institute of Physics. ESR essentially relies on the observation of the energy level of spins of unpaired electrons in atoms or molecules. The energy required to excite spins is in the form of electromagnetic waves, easily absorbed by unpaired electrons. Unpaired electrons can be found in several materials including semiconductors, polymers and free radical. ESR is primarily based on the concept of magnetically induced splitting of electronic spin states[1].

In ESR, a sample of material is immersed in a homogenous, static magnetic field of sufficient magnitude and exposed to an orthogonal low-amplitude, high-frequency field of photons. These spins interact among themselves and with the crystal lattice of our sample to give a large set of magnetic states. For relatively isolated spins, the magnetic moment is proportional to the spin by the gyromagnetic ratio, and the energy of the moment is expressed below

$$\Delta E = g\mu_b B_0 \tag{1}$$

where g is the Lande g-factor, μ_B is Bohr magneton, and B_0 is the initial magnetic field.

As in NMR, ESR has its own chemical shift commonly referred to as the g-factor. Where different materials have their own unique resonance frequencies that characterize the chemical species of the material. Unlike NMR, ESR is about 1000 times more sensitive because the spin states will not only absorb the applied magnetic field but also the magnetic moments of surrounding atoms or ions. The amount of quantum energy absorbed by the excited electron spin is far greater than an excited nucleus in a magnetic field. Even the slightest perturbations can cause a discrepancy in data collection.

2 Experimental Setup

This experiment setup includes a NMR/ESR spectrometer, a Helmholtz coil, and probehead (See Figure 2). The program used to collect the signal works with the spectrometer to record the peak absorbance of energy into the electron under a range of magnetic field strengths. First, we slide the sample into the coils from the side and check the coils are connected to spectrometer. Next, we start the "CW NMR/ ESR Spectrometer" program (See Figure 2) and use the the parameters from Figure 3 as the initial settings. We can adjust "Gain," "Phase," and "B0" to obtain similar signals to what we would like to analyze. After successfully obtaining the signal, we increment the frequency "F" in 0.1 MHz intervals between 49 MHz and 50.5 MHz. For each interval we determine the magnetic field value where the signal shows peak absorbance and record the value in Gauss units. Similarly to what we did with the TCNQ sample, we set the parameters from Figure 3 as our initial settings and then adjust them to obtain the signal we want. We follow the same process of incriminating the frequency of bombarding photons between 49 MHz and 50.5 MHz and recording each $\vec{B}$ value where there is peak absorbance.

Figure 1. EPR Spectroscopy setup (1) software, (2) spectrometer, (3) helmholtz coil and probehead/ sample holder

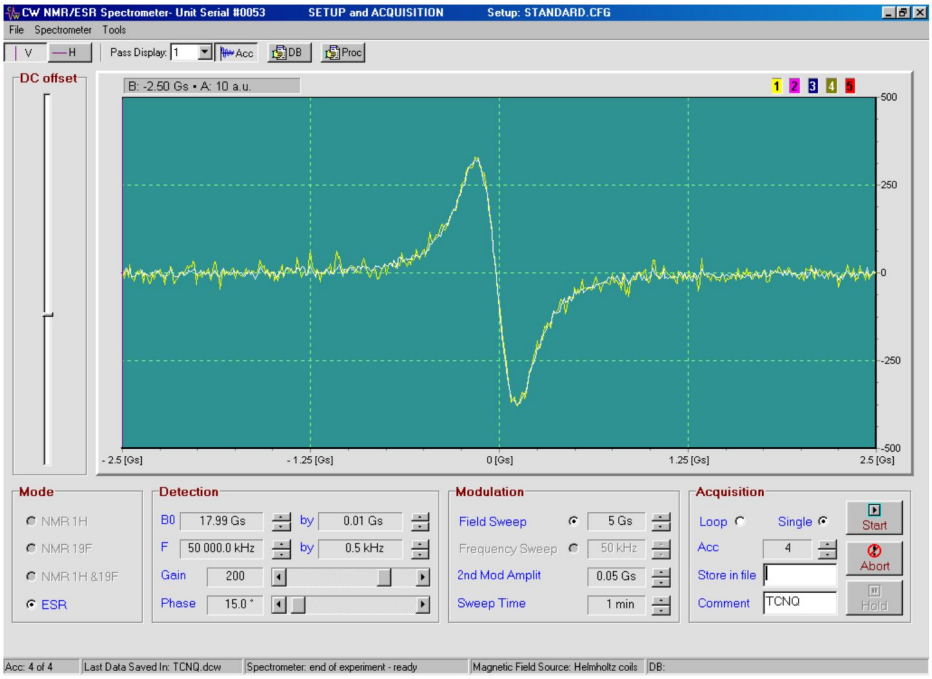


Figure 2. The above initial parameter should be used for TCNQ sample to set up the experiment.

3 Result

Graphing the change in $\vec{B}$ for each frequency measured and have obtained the following data sets, which tells us how deviations from the original 49MHz offsets magnetic field at which peak absorbance happens. There is a clear linear relationship between the changing frequency of the photons we send to the molecule and the amount that

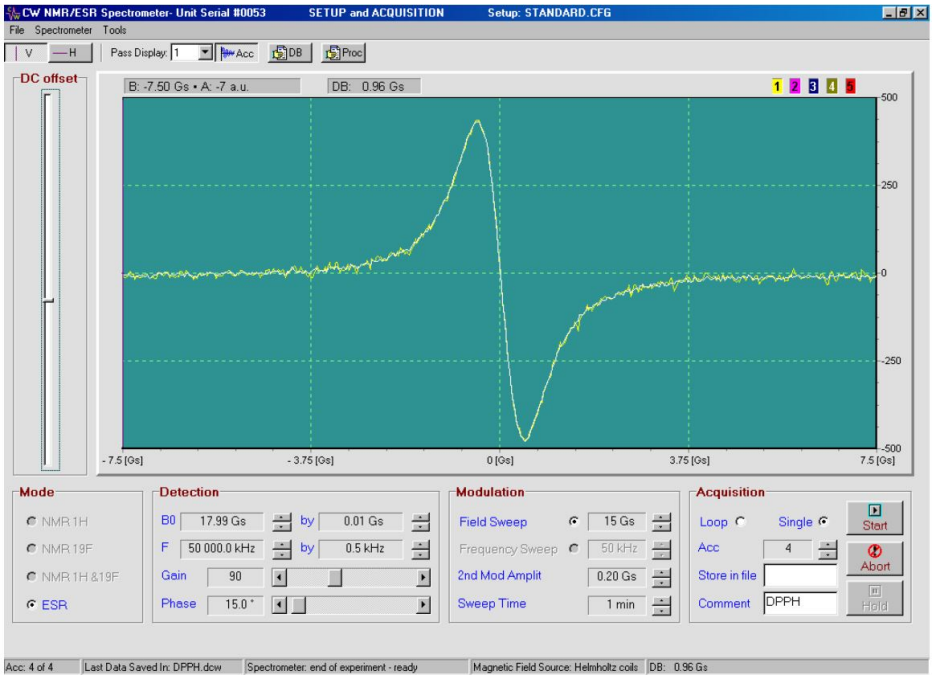
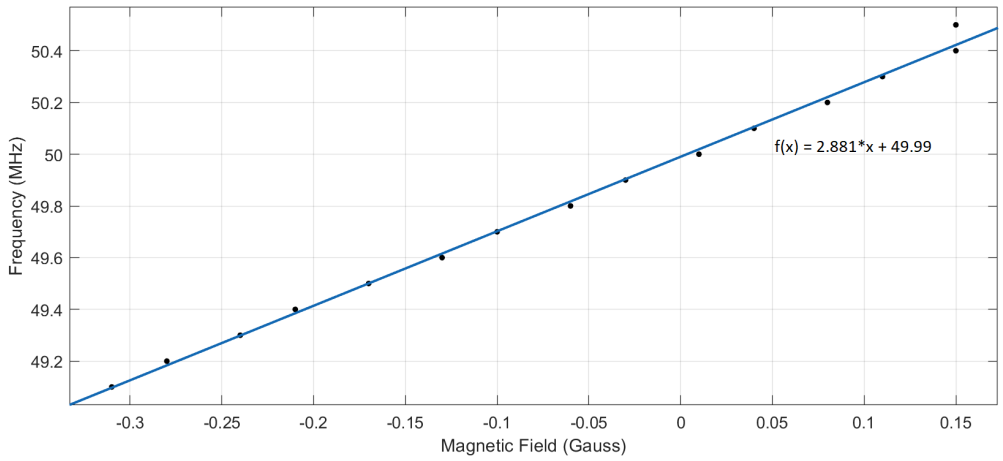


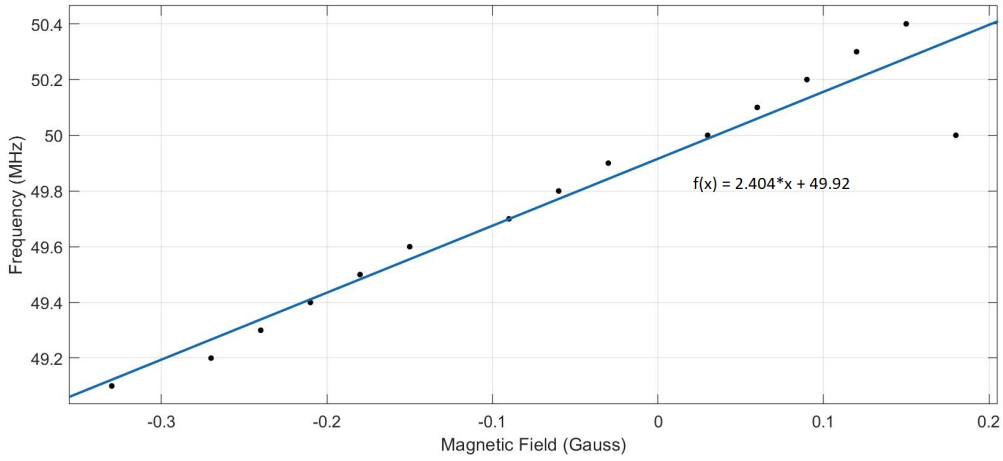
Figure 3. The above initial parameter should be used for DPPH sample to set up the experiment.

the peak absorption $\vec{B}$ value is offset from the origin we had set. This essentially means that the frequency of the light linearly affects the ideal $\vec{B}$ of absorption for the electron. From Figure 4, we determined from the slope of the equation that g-factor for TCNQ is equal to 2.881. Similarly, we also obtained that the g-factor for DPPH is 2.404.

Moreover, from the tables below, we notice that the value of full width at half maximum (FWHM) and peak to peak separation should be constant, however, there are several variations. We believe this happens due to background fields interfering with the magnetic field during experimental process. We obtained an average value of FWHM of the absorption curve for TCNQ, which is equal to 0.303 Gs, and the average value of FWHW for DPPH is equal to 0.183 Gs from Table 1 and 2. These values allow us to further calculate the relaxation time (T_2). Besides the value of FWHM, we need peak to peak separation value to calculate the relaxation time. Thus, we obtained the average value of peak to peak separation from Table 3 and 4. For TCNQ, the calculated average value is 0.92 Gs, and 1.089 Gs is average value for DPPH. Hence, we determined that relaxation time for TCNQ is equal to 4.26 seconds. Similarly, we calculated the relaxation time for DPPH, which is equal to 1.77 seconds.



(a)



(b)

Figure 4. The above figures display the linear relationship between the Magnetic Field (Gauss) and Frequency (MHz) for two free radicals (a) TCNQ and (b) DPPH.

Frequency (MHz)	FWHM Value (Gauss)
49.0	0.31
49.1	0.30
49.2	0.31
49.3	0.31
49.4	0.31
49.5	0.31
49.6	0.32
49.7	0.31
49.8	0.31
49.9	0.30
50.0	0.31
50.1	0.31
50.2	0.20
50.3	0.32
50.4	0.31
50.5	0.30

Table 1. Yields the FWHM of the absorption curve for TCNQ (post absoprtion peak analysis) for relaxation time (T_2) calculation.

Frequency (MHz)	FWHM Value (Gauss)
49.0	1.83
49.1	1.83
49.2	1.80
49.3	1.83
49.4	1.83
49.5	1.83
49.6	1.83
49.7	1.83
49.8	1.83
49.9	1.86
50.0	1.86
50.1	1.83
50.2	1.83
50.3	1.80
50.4	1.83
50.5	1.83

Table 2. Yields the FWHM of the absorption curve for DPPH (post absoprtion peak analysis) for relaxation time (T_2) calculation.

Frequency (MHz)	Peak to Peak Separation (Gauss)
49.0	0.20
49.1	0.19
49.2	0.18
49.3	0.21
49.4	0.17
49.5	0.19
49.6	0.21
49.7	0.20
49.8	0.19
49.9	0.20
50.0	0.18
50.1	0.19
50.2	0.20
50.3	0.18
50.4	0.20
50.5	0.18

Table 3. The value of peak to peak separation (maximum to minimum) of the 1st derivative curve for TCNQ after analyzing the derivative peaks.

Frequency (MHz)	Peak to Peak Separation (Gauss)
49.0	0.99
49.1	1.17
49.2	1.11
49.3	1.23
49.4	1.17
49.5	1.08
49.6	1.17
49.7	1.02
49.8	1.14
49.9	0.96
50.0	0.99
50.1	1.11
50.2	1.14
50.3	0.99
50.4	1.08
50.5	1.08

Table 4. The value of peak to peak separation (maximum to minimum) of the 1st derivative curve for DPPH after analyzing the derivative peaks.

4 Conclusion

Using the method of ESR Spectroscopy we have successfully measured and calculated the g-factor of one of the two common free radicals of TCNQ and DPPH. The theoretical g-factor of DPPH is 2.0036 and we have measured it to be 2.404 for a 19.9% error. The theoretical g-factor of TCNQ is 2.004 and we have measured it to be 2.881 for a 43.7% error. The g-factor for TCNQ is within respectable limits of the currently accepted values. However, the g-factor the for DPPH has an error value above 20%. Assuming the purity of our sample of TCNQ is literally ideal, the following arguments could be plausible reasons for this discrepancy. Background field interference

from surrounding equipment in the laboratory is almost always a possible pitfall of collecting nearly ideal data and inevitably causes inhomogeneitys in magnetic field. Physically adjusting the sample in the magnetic field housing could easily affect the strength and/or the resolution of the signal.

References

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2. Jones, M. T. “Spin-Lattice Relaxation in Some TCNQ Ion-Radical Salts.” Stability of Plane Couette Flow of Carreau Fluids Past a Deformable Solid at Arbitrary Reynolds Numbers: Physics of Fluids: Vol 30, No 7, AIP Publishing LLC, 1 Apr. 1964.