

1 Electron Spin Resonance

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4 ABSTRACT

5 Electron spin resonance (ESR) spectrometry measures how much electromagnetic radiation is absorbed by a compound when
the free electrons in the compound undergo spin-flip. ESR spectrometry can determine a compound's g-factor, a constant
measuring their absorption of electromagnetic radiation in an ESR spectroscopy experiment. We obtain several pairs of
resonance frequency and magnetic field strength for each compound, which are correlated to the g-factor according to the
Zeeman effect. We apply linear regression to our data and find the g-factors to be 2.0626 for TCNQ and 1.8514 for DPPH.
These measured values differ from the accepted values by 2.97% for TCNQ and 7.59% for DPPH.

6 1 Introduction

7 In 1921, Otto Stern and Walther Gerlach experimentally determined that electrons have the quantum spin value $s = 1/2$, which
8 allows for magnetic moment values $m_s = \pm 1/2$ ¹. In their experiment, Stern and Gerlach sent a beam of silver atoms through a
9 deflecting magnet and observed that the beam split into two paths as shown in Fig. 1. Based on this result, they determined that
10 the magnetic moment of the silver atoms in the beam was equivalent to one Bohr magneton, $\mu_B = \frac{e\hbar}{2m_e}$, where e is the electron
11 charge, \hbar is the reduced Planck constant, and m_e is the electron mass.

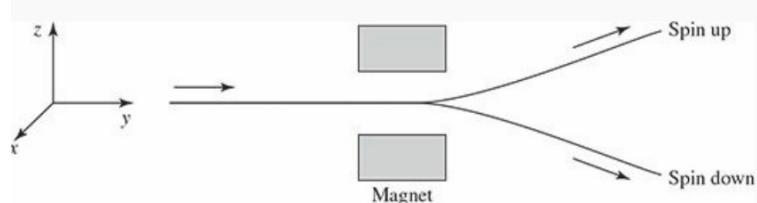


Figure 1. Diagram of the Stern-Gerlach Experiment². It shows the beam passing through the magnets and orienting up or down according to electron spin.

12 For a particle with spin value s , there are $2s + 1$ possible energy levels. For electrons, $s = 1/2$, so there are two possible
13 energies corresponding to the two different m_s values (often called "spin-up" for $m_s = 1/2$ and "spin-down" for $m_s = -1/2$).
14 The difference in the energies of these states is described by the Zeeman effect³:

$$\Delta E = g\mu_B B_0, \quad (1)$$

15 where g is the g-factor, μ_B is the Bohr magneton, and B_0 is the applied field. ΔE represents the energy needed to change an
16 electron's state from spin-down to spin-up or vice versa (this change is often called "spin-flip").

17 The g-factor is an intrinsic quantity of an atom that describes its magnetic moment. Our experiment focuses on determining
18 the g-factor for two compounds, 1,1-diphenyl-2-picrylhydrazyl (DPPH) and 7,7,8,8-tetracyanoquinodimethane (TCNQ),
19 through the use of electron spin resonance (ESR) spectrometry. These compounds are widely used for ESR because of their
20 paramagnetic properties. DPPH is a free radical with an unpaired electron on one of the Nitrogens, shown in Fig. 2. TCNQ
21 also has free electrons on the Nitrogens, giving it paramagnetic properties.

22 ESR spectrometry measures the relative amount of free electrons that undergo spin-flip in a sample compound when the
23 sample is placed in an external field and exposed to electromagnetic radiation. The static external field is produced by a
24 Helmholtz coil, and the radiation is supplied by an oscillating magnetic field perpendicular to the field produced by the coil.
25 The energy of this radiation is given by $E = h\nu$, where h is Planck's constant and ν is the frequency of the oscillating field.
26 When the energy of the radiation is equal to the energy gap described in Eq. (1), free electrons in the compound absorb the
27 radiation and undergo spin-flip. This phenomenon is known as resonance. The resonance frequency is thus given by

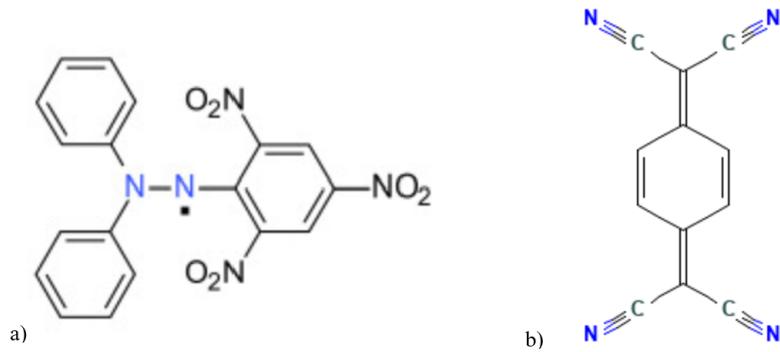


Figure 2. a) Diagram of DPPH chemical structure, with the black dot representing the free electron⁴. b) Diagram of TCNQ chemical structure⁵

$$h\nu = g\mu_B B_0. \quad (2)$$

By measuring the transmittance of radiation through the sample, we can determine the parameters required for resonance. In our experiment, we sweep through values of magnetic field strength while keeping the frequency of the radiation constant. We record the magnetic field strength that corresponds to resonance for ten different frequencies. We use our data to model a relationship between ΔE and B_0 according to Eq. (1) from which we determine the g-factor for each compound.

In the following sections, we will go over the experimental set up, our significant results, and conclude with applications of ESR.

2 Experimental Setup

Our experimental setup is shown in Fig. 3. The DPPH and TCNQ samples are prepared in a small acrylic tube. The ESR probehead holds the tube between the Helmholtz coils through a small hole shown in Fig. 4. The Helmholtz coil and probehead receive power from the spectrometer unit. The Helmholtz coil produces a static magnetic field B_0 oriented perpendicular to the plane of the coil loops and varies the strength of the field through a range of values specified by the data acquisition software. The oscillating magnetic field is applied along the axis of the probehead, supplying electromagnetic radiation to the sample. The frequency of the oscillation is set by the software (between 49MHz to 51MHz).

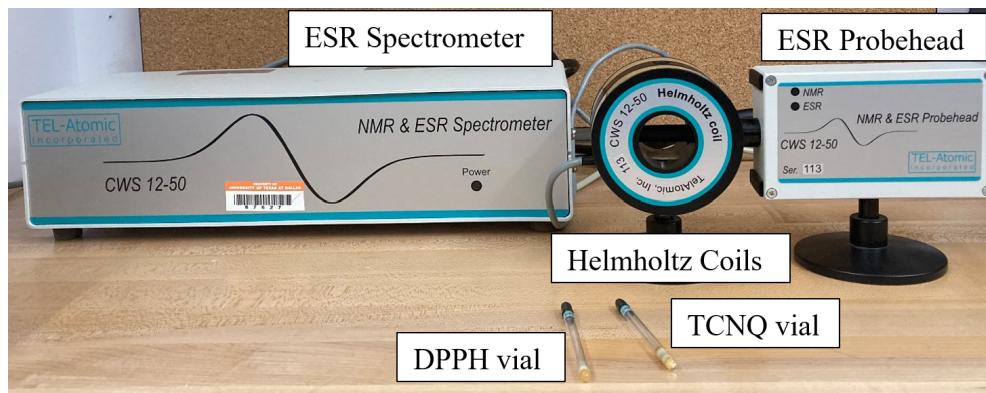


Figure 3. All components of our experimental apparatus.

Before we collect data, we adjust the measurement parameters of the software so that we record valid data for each compound. An example of these parameters is shown in Fig. 5. We adjusted the gain value (168 for DPPH and 45 for TCNQ) to ensure that the data did not exceed the measurable range of the software. For the DPPH trials, we sweep through B_0 values of 10.49 Gs to 25.49 Gs, and for the TCNQ trials, we sweep through values of 15.49 Gs to 20.49. The spectrometer measures the rate of absorption of the radiation and sends the data to the software, which integrates this signal to produce an absorption

46 curve seen in Fig. 6. The software also reports the value of B_0 at which the peak of the absorption curve occurs, indicating the
 47 magnetic field strength for which the compound is in maximum resonance. For both compounds, we record this field value for
 48 ten frequencies evenly spaced between 49MHz and 51MHz.

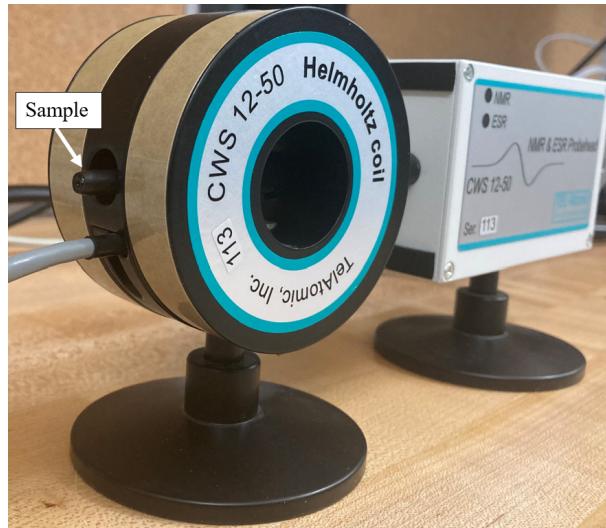


Figure 4. The probehead holds a sample tube inside the Helmholtz coil.

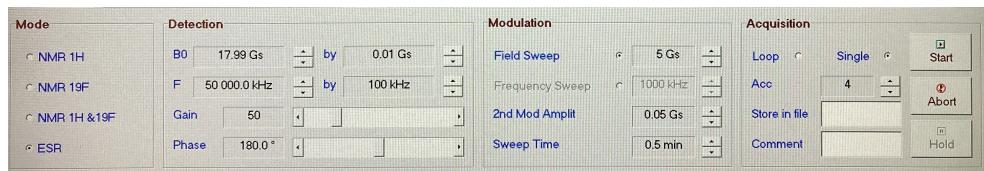


Figure 5. Data collection parameters for TCNQ trials.

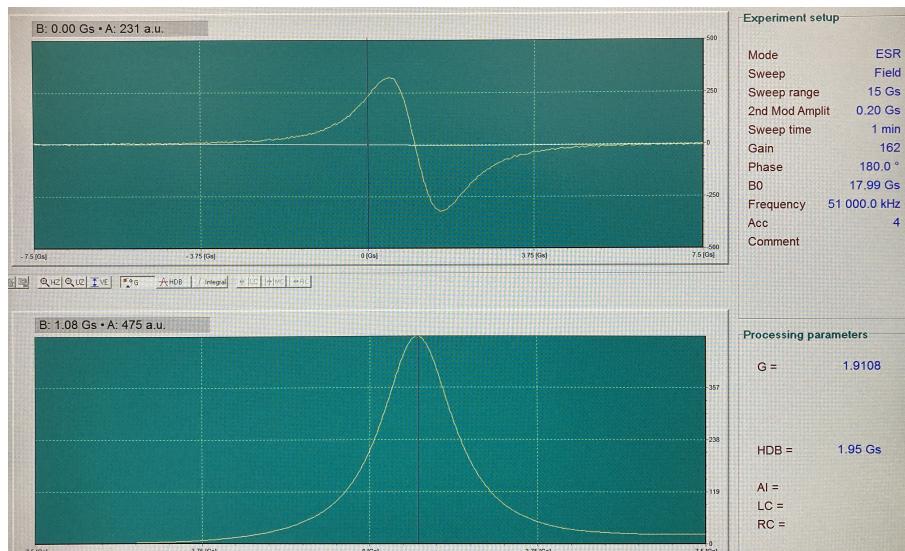
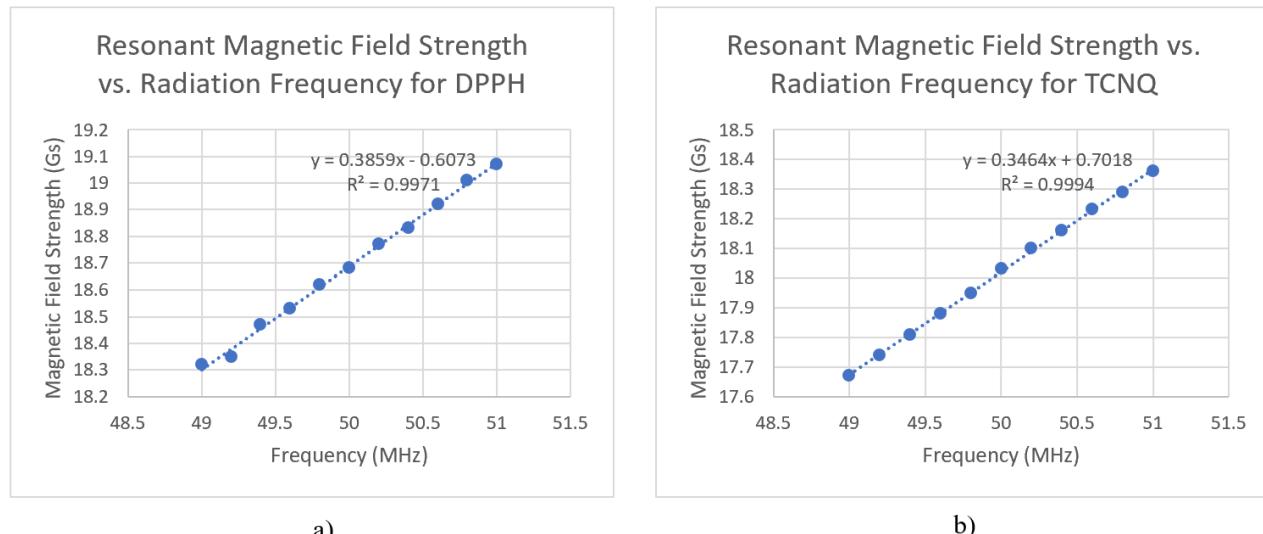


Figure 6. Software output after analysis

49 3 Results

50 Our measured data are tuples of frequency and magnetic field strengths, so we rearrange Eq. (2) to obtain a theoretical model
51 for our data. The magnetic field strength is linearly proportional to the resonance frequency by a constant in terms of the
52 g-factor. The graphs of our data for each sample are shown in Fig. 7. Comparing the slope of our data to our theoretical model
53 allows us to solve for g-factor values of 2.0626 for TCNQ and 1.8514 for DPPH.



54 **Figure 7.** a) Data for resonance of DPPH. b) Data for resonance of TCNQ.

54 4 Conclusions

55 The accepted values of g-factor are 2.0032 for TCNQ⁶ and 2.0036 for DPPH⁷. There is thus a 2.97% and 7.59% difference
56 between the accepted values and our measured values for TCNQ and DPPH respectively. Since we do not take any physical
57 measurements ourselves, the differences are attributed to systematic error within our experimental apparatus. The software
58 itself reports a g-factor for each trial, but these reported values differed from the accepted values by 1.05% for TCNQ trials and
59 4.81% for DPPH trials. Factors such as signal noise and sample container geometry can cause this systematic difference⁸.

60 Applications of ESR can be found in tracking catalytic reactions⁹. These reactions go through changes in their charged
61 states which means that electrons get exchanged during the reaction. Through ESR, we can track these electrons to see how the
62 exchange takes place and how that alters the compounds involved in the reaction.

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