An Analysis of ESR Programs

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Abstract

Isotropic and Anisotropic programs were studied to examine their capabilities with experimental data extracted from an electron spin resonance (ESR) instrument. The programs were used to analyze and simulate spectra. The mechanics of the instrument were studied and were used to find information related to parameters on the programs which allowed simulation of paramagnetic species to be conducted.

Introduction

ESR spectroscopy deals with resonant absorption of microwave radiation by electrons on a paramagnetic species under the presence of a magnetic field[1]. When a species with unpaired electrons is studied under conditions of a strong magnetic field, the spin of an electron can be oriented in two different way giving a plus or minus ½ charge[1]. When ESR studies occur, spectrometer magnetic fields are swept linearly to excite electrons in low and high energy fields[1]. Certain magnetic field strengths can change the spin of the electron[1], which is measured by the ESR spectrometer to determine properties of the species.

In a typical ESR experiment the sample is placed in between a magnet so that the optimal amount of the sample reacts with the magnetic fields as the sample’s absorbance of microwave radiation is measured in real time. The 9.5 Ghz range is of importance because this region is representative of the transitions between the microwave region of electromagnetic radiation[2].

The Zeeman effect is also an important principle to understand because it helps explain certain phenomena in ESR spectra including hyperfine coupling. The Zeeman effect represents the splitting of electronic spin state in presence of external magnetic field[2]. The hyperfine coupling between electron spins and a nucleus consists of two components: the exchange interaction and dipolar interaction[3]. Typically, the exchange interaction is said to be isotropic, while the dipolar said to be anisotropic[3].

The new Hampden-Sydney College owned ESR spectrometer software included two programs which are intended to analyze and simulate isotropic and anisotropic ESR spectra. The goal of my project was to examine the capabilities of these programs. Hyperfine coupling remained important for the understanding of the programs studied. Hyperfine and super hyperfine coupling constants had to be calculated, either through literature search or computer programs. Anisotropic systems were direction dependent, while isotropic systems were not directionally dependent.

Results and Discussion

<u>Isotropic Simulation</u>:

First the isotropic simulation program was studied to understand the capabilities of the program when compared to experimental data. A spectrum of biphenylene was produced using the ESR spectrometer for comparison with the simulated spectrum. (Figure 1)

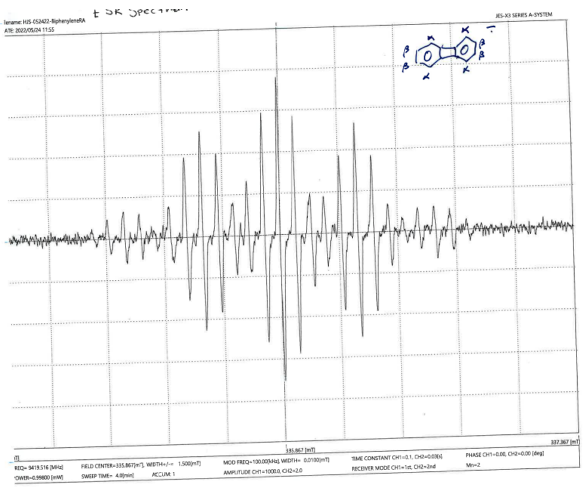


***Figure 1**: Experimental Biphenylene Spectrum*

Once the g-value, the hyperfine coupling constants and line width were determined, a simulated ESR spectrum of biphenylene was produced using the isotropic program. The simulated spectrum for biphenylene appeared accurate when compared to experimental data. (Figure 2)

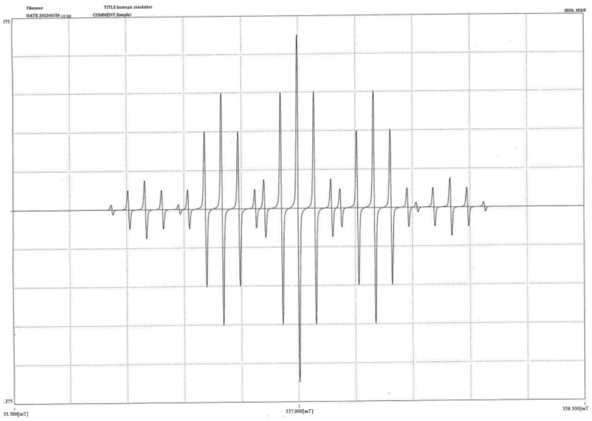


Figure 2: Simulated Biphenylene Spectrum

There were however some issues with the first simulation of fluoranthene as the parameters were incorrect. (Fig. 3)

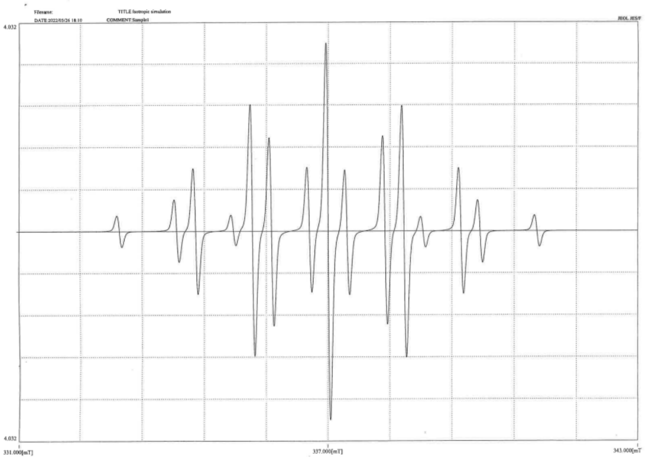


Figure 3: Simulated Fluoranthene Spectrum

This simulation contained negative coupling constants, which altered the shape of the spectrum.

Pictured below is a simulated spectrum with the same simulation parameters, but with positive coupling constants instead of negative coupling constants, as the simulation program was unlikely to consider negative constants.

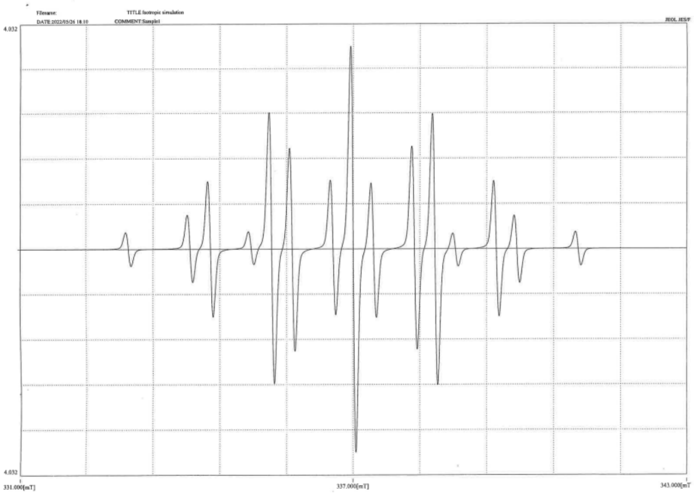
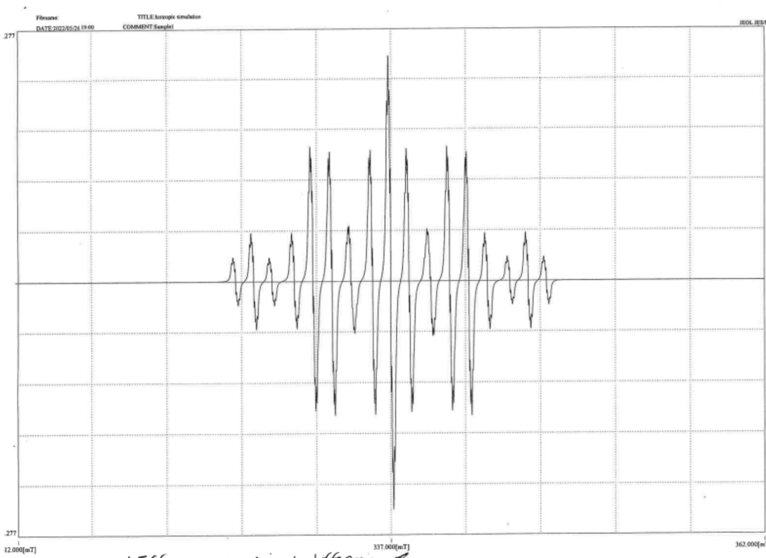


Figure 4: Second Simulated Fluoranthene Spectrum

Switching the coupling constants negative sign to positive affected the spectrum but did not produce the correct simulation for fluoranthene. Once the correct coupling constants were found, the correct simulation was produced and superimposed upon an experimental fluoranthene spectrum.



* Shaped points HFCC made the biggest difference

try to see about converting file so we can open up existing spectrum into simulation

Figure 5: Experimental Fluoranthene Spectrum

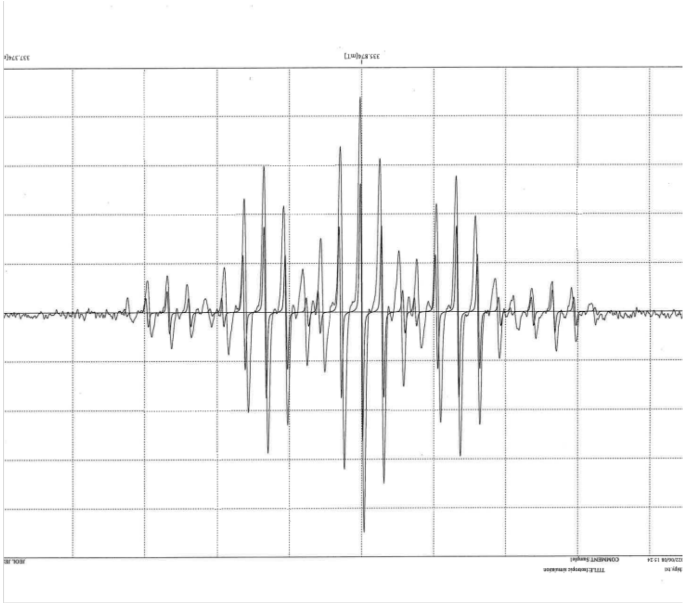


***Figure 6**: Superimposed Simulated Fluoranthene Spectrum and Experimental Fluoranthene spectrum*

The superimposed spectrum (Fig. 6) proved the capability of the program to properly simulate a spectrum that matched the experimental spectrum. Adjustments were then made to the simulated spectrum in order to scale it closer to the experimental spectrum in terms of intensity.

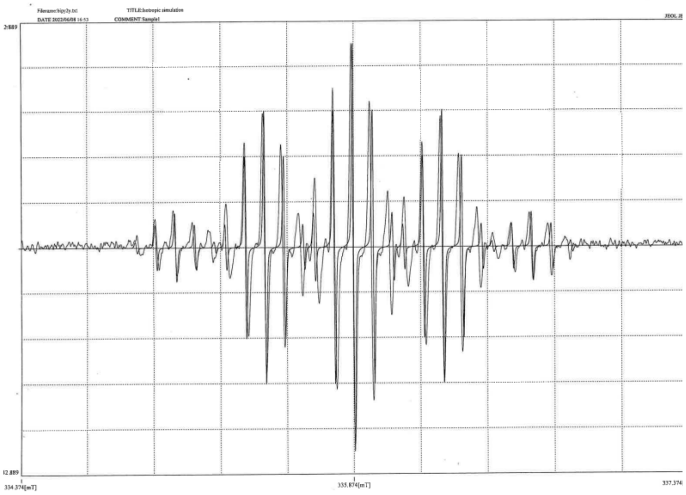


***Figure 7**: Adjusted Superimposed Spectra*

Anisotropic simulation:
The anisotropic simulation program had different parameters. We focused on the axial mode rather than the rhombic. There were important parameters such as the a-value, the g-value, and the y-value. Another important parameter consisted of theta step degree and phi step degree. It was found that axial was more accurate for anisotropic simulation purposes unless one dealt with super hyperfine coupling constants. Pictured below was the first simulation that displayed anisotropic properties.

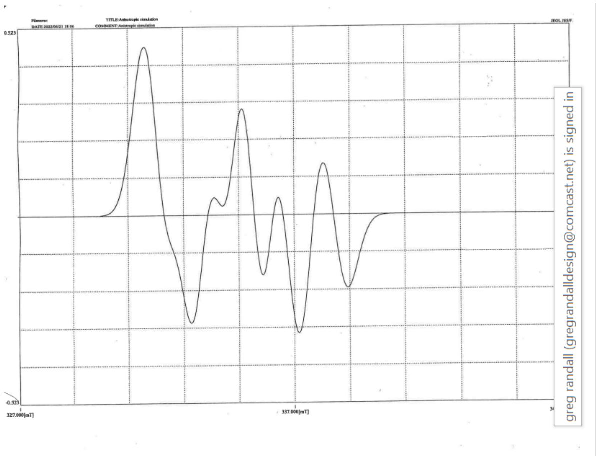


***Figure 8**: Anisotropic Simulation*

We produced an experimental anisotropic spectrum using Frémy's salt for comparison with its simulated spectrum

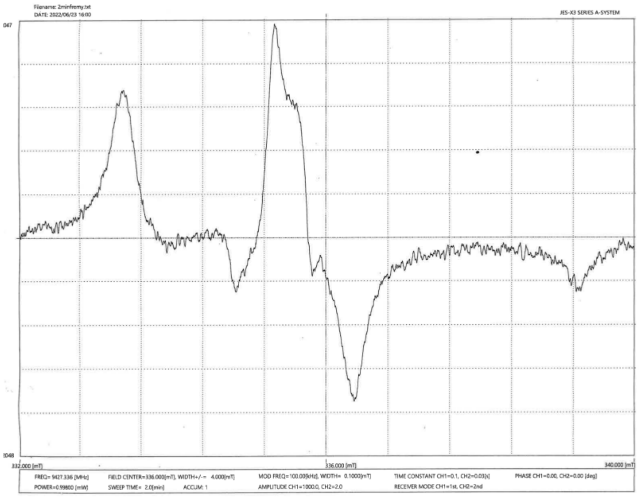


***Figure 9**: Experimental Spectrum of Frémy's Salt*

Experimental and simulated spectra of Frémy's salt proved similar demonstrating the accuracy of the program in anisotropic simulation.

Conclusion

Both the Isotropic and Anisotropic simulation programs show promising capabilities. One can simulate a spectrum with the correct parameters in both programs and superimpose simulated and experimental spectra (although only demonstrated in the isotropic program). Going forwards, Hampden-

Sydney College students will be able to use these programs to confirm the accuracy of their ESR spectra for years to come.

References

1. Principles of Electron Paramagnetic Resonance Spectroscopy (Introduction) : Absorption spectroscopy : Biotechnology and Biomedical Engineering : Amrita Vishwa Vidyapeetham Virtual Lab https://vlab.amrita.edu/?sub=3&brch=206&sim=583&cnt=999 (accessed 2022 -08 -22).
2. Basics of ESR Spectroscopy https://www.rdchemistry.com/2019/11/basics-of-esr-spectroscopy.html.
3. Hyperfine Coupling - an overview | ScienceDirect Topics https://www.sciencedirect.com/topics/chemistry/hyperfine-coupling (accessed 2022 -08 -14).