An Approach to the Free Radical Organic BDPA using Electron Paramagnetic Resonance

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ABSTRACT:

Studies were performed to the 1,3-bis diphenylene-2-phenyl allyl (BDPA) using the Millimeter Vector Network Analyzer (MVNA) as a source and receptor. With the spectra collected from the MVNA, a signal was detected in the region of 3.4 Tesla. Several trials were made at a fixed frequency with varying power and magnetic field modulation in order to increase the signal-to-noise ratio. Also, a new 95 GHz non rotating copper cavity was designed to be tested with the same sample.

INTRODUCTION:

EPR Spectroscopy

Many techniques have been adapted for the study of chemical species. Electron Paramagnetic Resonance (EPR) is used for studying chemical species that have unpaired electrons such as organic free radicals and complexes with metal ions. Therefore, EPR is a very specific technique since ordinary molecules are not shown in EPR spectra. The EPR spectra are generated by unpaired electrons that can move between different energy levels by either absorbing or emitting electromagnetic radiation.

1, 3-bis diphenylene-2-phenyl allyl (BDPA)

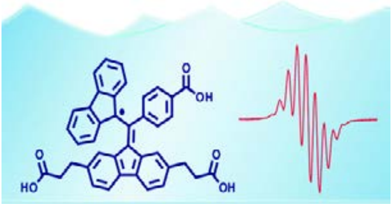
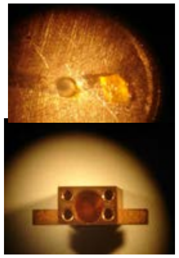


Figure 1. Molecular structure of a water soluble BDPA radical. A 9 GHz EPR spectrum in glycerol/water is shown.

In this experiment, we chose to study a system that is well known from conventional ESR experiments. It is an organic molecule [1, 3-bis diphenylene-2-phenyl allyl (BDPA)] that contains free radicals. These free radicals give rise to a strong spin signal, which makes it an ideal candidate for test experiments. For example, the BDPA radical's resonance generates a narrow peak in high-field EPR because it is highly delocalized.



This air-stable, carbon-centered radical is unique among organic radicals in the extent of delocalization of its unpaired electron. The unpaired electron is usually located at the 1- and 3-positions of the allyl compound, but it is more stable by delocalization into the two biphenyl rings attached at those positions. Also, its geometry protects the radical from potential reaction partners.

Figure 2. A sample of BDPA is placed in a rotating cavity as shown above for testing in the MVNA-8-350. Below, a 95 GHz non rotating cavity is shown.

Millimeter Vector Network Analyzer MVNA-8-350

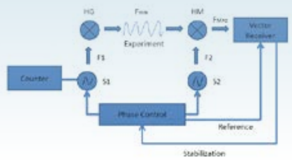


Figure 3. MVNA-8-350 diagram for EPR

The MVNA works by generating microwave signals that come from the harmonic generator at an initial frequency. Detection is then achieved by mixing this wave signal with the signal from a second source at a second diode called harmonic mixer. The beat frequency, which preserves the phase and amplitude of the wave signal relative to the second source oscillator, is then sent to a vector receiver. Finally, the magnetic field is swept at fixed temperature and frequency obtaining a spectrum of inverted peaks which means that the microwave signal was successfully transmitted through the sample.

Magnetic Field Modulation

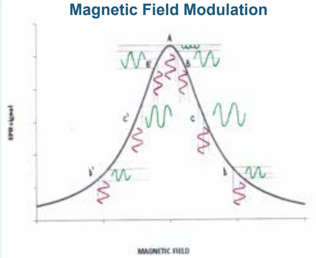


Figure 4. EPR signal produced in a magnetic field modulated spectrometer

Most electron spin spectrometers incorporate magnetic field modulation. The mechanism whereby the magnetic field is transformed to microwave power modulation is shown in Figure 4. Basically, the field modulated sine wave is converted in a complex signal by superposition of the frequency and a large number of harmonics.

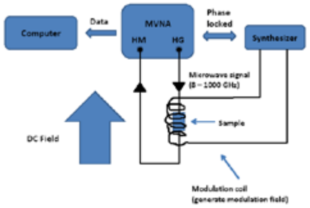


Figure 5

- Microwave signal is generated and received by the MVNA
- Modulation coil is driven by the sinthesizer which is phase locked with the MVNA to reduce noise The modulation frequency is 15 KHz
- When field modulation is used a sideband signal is detected in the MVNA
- The final signal is sent from the MVNA to the computer for storage. DC field is also controlled by the computer.

RESULTS AND DISCUSSION:

Figure 6 shows an EPR spectrum of BDPA without applying magnetic field modulation. A small absorption peak of BDPA is observed at 3.4 T. However, even when the BDPA is a free radical, the signal is relatively small due to the small signal to noise ratio. Indeed, we can hardly see the absorption peak at high temperature because the signal is not strong compared to noises

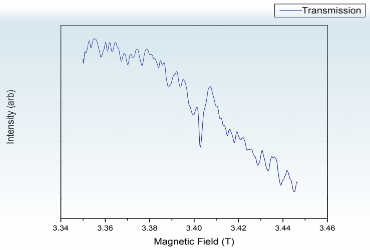


Figure 6. EPR spectrum of BDPA at a frequency of 95 GHz without magnetic field modulation.

The magnetic field modulation method is much sensitive to signal changes. Figure 7 shows a plot of an EPR spectrum applying magnetic field modulation. The derivative absorption signal is now clearly observed at 3.4 T with a frequency of 95 GHz. The field modulation method provides a derivative signal, not raw signal. As a comparison with Figure 6, one can see the significant improvement of the signal to noise ratio.

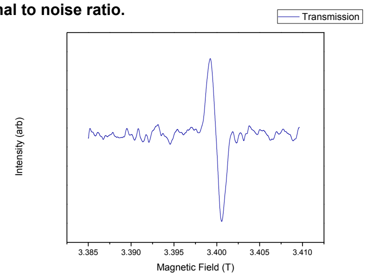


Figure 7. Plot of the derivative of the peak absorption spectrum at a frequency of 95 GHz now using magnetic field modulation

CONCLUSIONS:

EPR is a well employed spectroscopy technique because of its high spin sensitivity and no other method can offer more precise information about the spatial location of the spin center in the sample. Magnetic field modulation can increase our sensitivity when working at low frequencies.

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REFERENCES:

AB Millimetre. Introduction to the Millimeter Vector Network Analyzer MVNA-8-350. http://www.abmillimetre.com/Introduction.htm#i4 (accessed July 2010).

Dane, E.L.;Swager, T.M. Synthesis of a Water-Soluble 1, 3-Bis (diphenylene)-2-phenylallyl Radical. *J. Org. Chem.*, [Online] 2010, *75 (10)*, 3533–3536.

Lawrence, Jon. Comprehensive High Frequency Electron Paramagnetic Resonance Studies of Single Molecule Magnets. PhD Thesis, December, 2007.

Mola, Monty. Superconducting Mixed State Phase Diagram of κ-(BEDT-TTF)2Cu(NCS)2. PhD Thesis, Montana State University, 2001.