

# **ABSTRACT:**

**Progress was made on a transmission probe for electron paramagnetic** resonance spectroscopy at high frequencies. The probe is intended for use over a broad frequency range up to 1 THz, where the cavity resonance technique is not efficient.

The probe was successfully tested by analyzing two previously studied samples: 1,3-bisdiphenylene-2-phenylallyl (BDPA) and PPN[VSalen(CN)<sub>2</sub>] using the frequency ranges 95-139 GHz and 80-225GHz respectively. (PPN = bistriphenylphosphinoimine, Salen = N,N'-Ethylenebis(salicylimine)) BDPA analysis was performed in the PPMS (7T) magnet. PPN[VSalen(CN)<sub>2</sub>] analysis was performed in both the PPMS and Oxford (15T) magnets.

# **ELECTRON PARAMAGNETIC RESONANCE:**

Electron paramagnetic resonance (EPR) uses microwave radiation to excite electronic energy level transitions in molecules within a magnetic field.<sup>4</sup> In a magnetic field, the Zeeman effect results in a splitting of the energy levels.<sup>4</sup> Further splitting occurs due to the geometry of the molecule and the interactions between the electrons and nuclei, known as zero-field and hyperfine splitting respectively.<sup>4</sup>



Figure 1: The above figure depicts possible EPR transitions for spin systems with zerofield splitting and hyperfine splitting respectively. (image credit: reference 3)

# The simplest Hamiltonian that describes single molecule magnets can be written as:

$$\hat{H} = \hat{H}_{Zeeman} + \hat{H}_{ZFS} + \hat{H}_{HF}$$
$$\hat{H}_{Zeeman} = \mu_B \vec{B}g\hat{S}$$
$$\hat{H}_{ZFS} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$$
$$\hat{H}_{HF} = A\hat{I}\hat{S}$$

where  $\mu_{\rm B}$  is the Bohr magneton, B is the magnetic field, S is the electronic spin, and g, D, E, and A are constants.

Via EPR one can observe a molecule's intrinsic energy level transitions.

# **PROBE DESIGN:**

extender

port for valve and vacuum pump attachment

e pin-connecto

clamps used to attach source and detector to transmission pipes





transmission pipes

Figure 2: (top) Probe head and (bottom) base with critical parts labeled.

# **Electron Paramagnetic Resonance Transmission Probe Design and Testing**

Lauren Paladino<sup>\*</sup>, Komalavalli Thirunavukkuarasu<sup>#</sup>, Stephen Hill<sup>#</sup> \*Physics Department, University of South Florida, Tampa, Florida <sup>#</sup>National High Magnetic Field Laboratory (NHMFL), Tallahassee, Florida

There are three sections of brass transmission pipes, the middle of which may be added or removed depending on the magnet to be used: the shorter configuration for the PPMS, the longer for the Oxford. An extender is attached to the probe head when used in the PPMS so the sample is in the field center. When the Oxford is used, a jacket is attached and a Pyrex spacer ensures the sample is in the field center.

### **SAMPLES:**

#### **BDPA**:

- Relatively isotropic ( $D \approx E \approx 0$ )
- g-value close to that of free electron  $(g_{BDPA} = 2.00264)^1$
- $(g_e = 2.0023193)^5$

• Could use large amount of sample without considering orientation





#### **PPN[VSalen(CN)<sub>2</sub>]:**

- Two inequivalent vanadium sites ... two sets of resonances
- Anisotropic g-value (similar to most materials investigated in group)
- Sample aligned such that magnetic field oriented parallel to long axis
- Studied comprehensively in NHMFL EMR group Figure 4: aligned PPN[VSalen(CN)<sub>2</sub>] crystal

# **RESULTS & DISCUSSION:**



Figure 5: EPR scan at 130GHz with the magnetic field varying at a rate of 86 Oe/s, performed at 5.5K on BDPA.

The slope in figure 6 is the g-value of BDPA found, with the intercept forced to be the origin.



Figure 6: Plot of peak locations for 5 EPR scans of BDPA where the slope is the g-value, 2.00212.

Comparing the experimentally determined value of 2.00212 with the value found by Dane et. al., 2.00264, results in a percent difference less than 0.03%.



**EPR** measurements of the **PPN[VSalen(CN)**<sub>2</sub>] sample were performed in the Oxford magnet for the frequency range from 80 GHz to 225 GHz. The sample was aligned roughly parallel to the magnetic field. The wavy features are a result of helium gas flow within the sample chamber and are absent when a jacket is used.

Figure 7: EPR scans of PPN[VSalen(CN)<sub>2</sub>], performed at a scan rate of 1T/min at 1.4K without jacket, are shown for a few selected frequencies.



Figure 3: BDPA structure <sup>1</sup>

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The frequency dependence of the resonance peaks were simulated using the spin Hamiltonian with the help of the ediff program. The simulation results shown as lines were obtained for easy-axis gvalue of 1.95, hard plane gvalues of 2.00, D = 114 GHz, and E = 0. The solid line is

The dashed line is with  $\Theta$ equal to 57°. The data and fit agree reasonably well.

Figure 8: Peak locations (blue squares) of PPN[VSalen(CN)<sub>2</sub>] EPR scans in Oxford magnet at approximately 1.4K plotted together with the simulation results.

**Results obtained here are** consistent with those obtained from recent EPR studies of the same sample (figure 9). The data could be fit with the same D and **E** parameters. Θ differs because of differing sample orientations.



Figure 9: The PPN[VSalen(CN)<sub>2</sub>] EPR peak locations (blue squares) plotted on chart of recent field-modulated EPR data with previous fit results for  $\Theta = 0^{\circ}$  and 55°.

# **CONCLUSION:**

Analysis performed on the BDPA and PPN[VSalen(CN)<sub>2</sub>] samples confirm the transmission probe's functionality and sensitivity. However, before the probe may be used for high-field EPR, an additional support system for the source and detector must be designed. In addition, a secondary temperature sensor may be incorporated at the probe base, which could require a new vacuum jacket with a larger diameter.

# **ACKNOWLEDGEMENTS:**

I would like to thank the members of the EMR group for their instruction, assistance, and patience, and Sanhita Gosh for initiating the probe design. I would also like to thank Jose Sanchez and Roxanne Hughes. This project was sponsored by NSF DMR1157490.

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