# TUNABLE-FREQUENCY HIGH-FIELD EPR OF FERRIC PHTHALOCYANINE CHLORIDE

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## Introduction

Porphyrinic complexes of iron are relevant both as model compounds for the active sites of heme proteins and as building blocks for molecular materials. Iron(III) phthalocyanine complexes have especially interesting electronic structure in that the spin ground state for the Fe(III) ion ($3d^5$) can be high-spin ($S$ = 5/2), low-spin ($S$ = 1/2), or intermediate-spin ($S$ = 3/2).[1] Furthermore, a spin-admixed state is also possible in which, e.g., spin sextet and quartet states are very close in energy. Such systems have been studied by X-band EPR and Mössbauer spectroscopy, but not by HFEPR. Ferric phthalocyanine chloride, Fe(Pc)Cl, is proposed to be a spin-admixed system,[1] which we have initially selected for investigation into such behavior.

## Experimental

The Mm and Sub-mm Wave Spectroscopy Facility and the 25-T "Keck" magnet were used to study polycrystalline Fe(Pc)Cl.

## Results and Discussion

Simulations of field-frequency dependences of resonances using $S$ = 3/2 (Figure 1) were more successful than those with $S$ = 5/2. The positive sign of $D$ could be determined from single-frequency powder spectra (Figure 2).

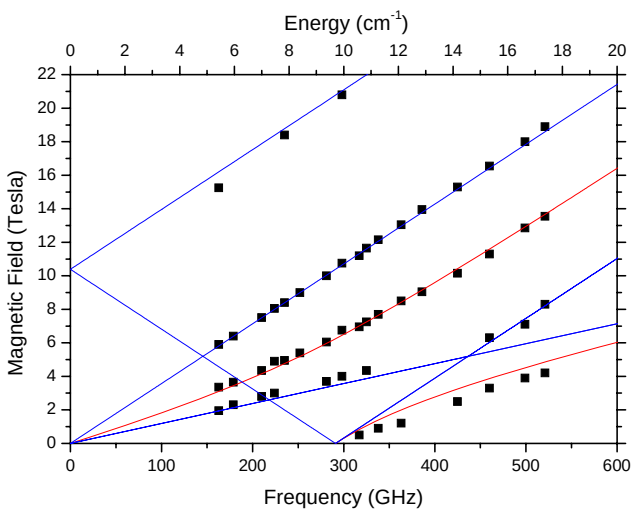


**Figure 1.** A 2-D map of resonances vs. frequency or energy. Squares are experimental points; curves were simulated: $S$ = 3/2 and $|D|$ = 4.85 cm$^{-1}$, $|E|$ = 0, $g_{iso}$ = 2.0. Red curves are perpendicular, and blue – parallel transitions.

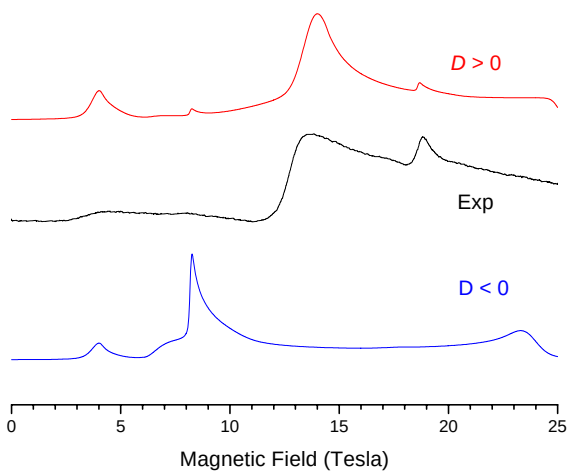


**Figure 2.** Experimental (black trace) and simulated (colored) single-frequency (521 GHz) spectra at 4.2 K using same parameters as in Figure 1 with positive, and negative $D$.

## Conclusions

Based on HFEPR data we can tentatively claim that the ground spin state of the complex is a quartet ($S$ = 3/2), although some peculiarities of the spectra point to spin mixing. Our technique can thus provide insight into the ground state of spin-admixed systems. Future studies will employ variable temperatures to track changes in ground state behavior.

## Acknowledgements

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## References

[1] Kennedy, B.J., *et al.* Inorg. Chem., **25**, 2539-2545 (1986).