HFEPR Studies of Iron Porphyrin Biomimetic Models

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Introduction

Two five-coordinate iron(III) porphyrin complexes, planar Fe^{III}(TPP)Cl and saddle-shaped Fe^{III}(OETPP)Cl, had been characterized as a pure S = 5/2 or admixed (S = 3/2, 5/2) spin state, respectively. The saddle deformation-induced fine-tuning in the spin state has been regarded as a heme model of cytochrome c'.[1] However, the accurate magnetic parameters of these two iron(III) porphyrinate complexes remain yet to be determined. For Fe(TPP)Cl, its zero-field splitting (zfs) parameter $|D|$ was found to vary in the 3.2 – 12.9 cm^{-1} range depending on a technique, reviewed by Hunter *et al.*[2] We thus employed high-frequency and -field EPR (HFEPR), which has an outstanding ability to investigate both Kramers and non-Kramers spin systems with large zfs (D),[3] in an attempt to accurately determine the zfs in these two model complexes as a way to explore the structural environment of heme-related enzymes.

Experimental

Fe^{III}(TPP)Cl (TPP = dianion of 5,10,15,20- tetraphenyl porphyrin) and Fe^{III}OETPPCl (OETPP = dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20- tetraphenyl porphyrin) were synthesized by literature methods.[4] HFEPR spectra were recorded at the NHMFL using a variety of sub-THz wave sources, including backward wave oscillators (BWOs) in conjunction with a 15/17 T superconducting magnet.

Results and Discussion

The HFEPR spectra were simulated using a spin Hamiltonian for S = 5/2 in both systems composed of Zeeman and zero-field splitting (zfs) terms:

$$H = \beta_e B \cdot g \cdot \hat{S} + D(\hat{S}_z^2 - S(S+1)/3) + E(\hat{S}_x^2 - \hat{S}_y^2) \qquad [1]$$

The spin Hamiltonian parameters for Fe(TPP)Cl are: D = +6.46(1) cm^{-1}; E = 0.013(2) cm^{-1}; $g_\perp$ = 2.004(3), $g_{||}$ = 2.022(3) (Fig. 1). This stands in excellent agreement with a very recent Inelastic Neutron Scattering study ($|D|$ = 6.33 cm^{-1}).[2] For Fe(OETPP)Cl, an S = 5/2 spin also adequately describes the HFEPR spectra; however, we found two spin species, differing by about 0.9 cm^{-1} in the magnitude of D, that are simultaneously observed. They can be simulated using the spin Hamiltonian parameters: D = +12.0 cm^{-1}, $|E|$ = 0.3 cm^{-1}, g_{iso} = 2.00, and S = 5/2, D = +12.9 cm^{-1}, $|E|$ = 0.3 cm^{-1}, g_{iso} = 1.95, respectively.

Conclusions

From planar to saddled iron(III) porphyrins, their zfs parameters are first time characterized with high accuracy by HFEPR, and may serve as references in understanding the relevant heme structures in diverse hemoproteins. In addition, Fe(OETPP)Cl is confirmed by the HFEPR to be a high-spin (S = 5/2) species, but the appearance of two distinct spin species in this non-planar system remains yet to be understood.

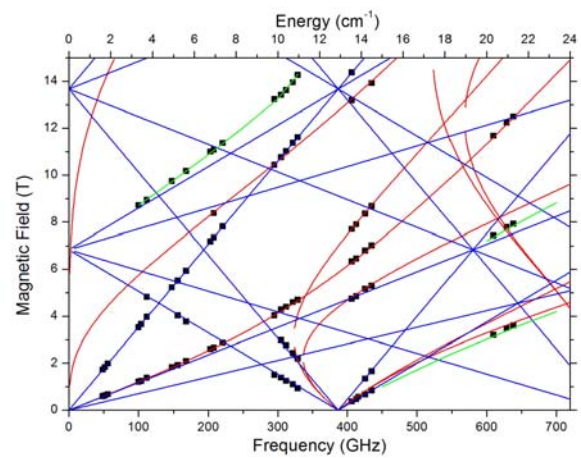

Fig.1 A field/frequency (or quantum energy) map of HFEPR turning points in powdered Fe(TPP)Cl at low temperatures (5 – 10 K). Squares are experimental points while lines are simulations using spin Hamiltonian parameters as in text. Blue: parallel, red: perpendicular, green: off-axis turning points.

Acknowledgements

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. Department of Energy. This work was supported by the National Science Council of Republic of China, Grant No. NSC102-2113-M-005-005 and NSC88-2113-M005-014.

References

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