High-Field EPR Observation of the Light-Induced Excited Spin State Trapping

A. Ozarowski (NHMFL)

Introduction

The 'Spin-Crossover' in iron(II) complexes is a thermally-driven change of the spin state.[1] Compounds that are high-spin (S=2) at room temperature undergo an abrupt and complete transition to the diamagnetic low-spin state with S=0, when cooled (typically at temperatures 120-180 K). The spin state transition is often accompanied by a color change. Irradiation by green light of a sample in its low-spin state at 50 K or less causes transition to the high-spin state which is then stable at low temperatures for essentially unlimited time. This phenomenon, called Light Induced Excited Spin State Trapping, or LIESST, has been studied by means of magnetic susceptibility measurements, Mössbauer spectroscopy and electronic spectroscopy.[1] High-spin Fe^{2+} ion cannot be directly observed in standard EPR because of very large zero-field splitting in its S=2 spin state. EPR studies on iron(II) 'crossover' complexes doped with Mn^{2+} have been reported.[2]
This research was undertaken in a hope that direct EPR observation of high-spin Fe^{2+} in the LIESST state may be possible with high microwave frequencies and magnetic fields available at the NHMFL.[3]

Experimental

High-field and frequency EPR spectra of single crystal and powder samples of the 'crossover' complex $Fe(PTZ)_6(BF_4)_2$ (PTZ = 1-propyl-tetrazole) were recorded on the transmission EPR instrument of the NHMFL EMR facility at frequencies 96-632 GHz at the liquid helium temperatures. The LIESST state was achieved by green light irradiation of the sample kept inside the EPR spectrometer at 10K or below.

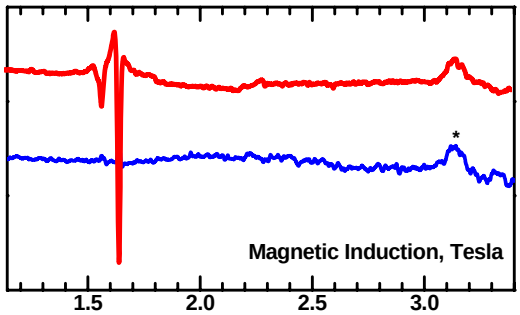

Fig. 1. Single-crystal EPR spectrum of $Fe(PTZ)_6(BF_4)_2$ at 216 GHz, 10 K. Blue trace: sample kept in its diamagnetic state. Red trace: spectrum of the S=2 state after sample irradiation with green light. The asterisk indicates a resonance due to frozen oxygen.

Results and Discussion

The green-light irradiation of samples kept at 4-10K caused a new resonance line to appear (signal at 1.6 T in Fig. 1). The position of that signal was measured as a function of microwave frequency over the range 9.6 to 632 GHz. The slope of that dependence indicates an effective g value of 9.2 which allows to identify this signal as a $\Delta M_S=4$ transition in the S=2 spin state of Fe^{2+} ions whose intrinsic g_z value equals 2.3. The absence of the 'allowed', i.e. $\Delta M_S=1$ resonances indicates that the zero-field splitting in this system is very large, with the zfs parameter D possibly larger than 50 cm^{-1}. The $\Delta M_S=4$ EPR transition can be observed because the zfs parameter E is small compared to D: the $M_S=2$ and $M_S=-2$ states are split by $3E^2/D$ while other M_S states within S=2 are split by much larger energies.

Conclusions

The spin Hamiltonian parameters D and E could not be determined – the available evidence only indicates that both D and E are large compared to the microwave quantum energy and that E is small compared to D. Nevertheless, this work represents the first direct EPR observation of the LIESST.

Acknowledgements

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References

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[3] Ozarowski, A. *et al*., J. Am. Chem. Soc., **126,** 6574, (2004)