TUNABLE-FREQUENCY ELECTRON PARAMAGNETIC RESONANCE OF THE HIGH-SPIN COBALT(III) ION


Introduction

An ongoing research project at NHMFL is to investigate the electronic structure of high-spin (HS), transition metal ion complexes by high–frequency and–field electron paramagnetic resonance (HFEPR). These efforts have led to successful studies of a variety of complexes, including integer spin (non-Kramers) ions such as V(III) (3d², S = 1),1 Mn(III) (3d⁴, S = 2),2 Ni(II) (3d⁸, S = 1),3 and Kramers ions such as Co(II) (3d⁷, S = 3/2).4 We continually seek to expand the range of systems that can be investigated by HFEPR.

Among the many transition metal ions, Cobalt(III) (3d⁶) occupies a unique place in coordination chemistry: the hexaaqua ion, [Co(H₂O)₆]³⁺, is low-spin (S = 0), rather than high-spin (S = 2),5 which is the case for iso-electronic [Fe(H₂O)₆]²⁺. There is, however, a single well-documented example of HS Co(III): [CoF₆]³⁻. This complex was reported many years ago, but has not been characterized by modern spectroscopic techniques. The pale-blue, highly reactive solid was synthesized from elemental fluorine as a potassium salt and has now been characterized by vibrational (IR and Raman) spectroscopy and by HFEPR. Computational studies on the vibrational and electronic absorption spectroscopic results are in progress.

Experimental

K₃[CoF₆] was investigated using the mm and sub-mm spectroscopy facility at the NHMFL and the 25 T Keck magnet, in the 150-700 GHz frequency range, at 4.2 K.

Results and Discussion

Figure 1 shows a plot of EPR resonances versus applied sub-THz energy for polycrystalline K₃[CoF₆]. Multiple transitions are detected throughout the whole range of frequencies, which fall into well-distinguishable branches. Most interestingly, at least three zero-field transitions at ca. 7.5, 13, and 17 cm⁻¹ are observed. Although this octahedral, homoleptic complex would be expected to have no zero-field splitting due to its high symmetry, this is clearly not the case. The number of transitions observed indicates that the complex has rhombic symmetry, which is likely the consequence of static Jahn-Teller distortion. An analysis of the dataset is currently in progress to determine the values of the spin Hamiltonian parameters for this interesting system.

References