High-Field EPR of Cobalt-Catalyzed Water Oxidation

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Introduction

Nocera and coworkers have developed a cobalt-based catalyst that is able to oxidize water at ambient pH and temperature with low overpotential [1]. Electron paramagnetic resonance (EPR) has previously been employed at 9 and 34 GHz to characterize the resting state of the catalyst and has provided valuable insight into the electronic structure and mechanism for water oxidation in this system [2-4]. Important issues remain: 1) the resolution of the g-tensor at low frequencies and fields is too poor to allow unique simulation, and 2) the sample geometry of conventional EPR spectrometers necessitates film packing techniques that result in sample deadtimes of 10 minutes or more, preventing the active catalyst from being probed.

Experimental

Films were grown at 1.4V vs NHE on ITO-coated PET strips. Growing on PET allows the sample geometry to be modified according to the needs of the experiment. For these experiments, the EMR facility at NHMFL with the superconducting 15/17-T magnet was used. Films were grown on mylar strips, freeze-quenched in liquid nitrogen while under potential, and then punched into the 8mm sample disks necessary to fit into the NHMFL spectrometer probe. This method significantly reduces lag time and potentially allows it to be avoided altogether. NHMFL spectra were obtained at 156, 203, 211, 219, 295, 329, 406, and 429 GHz.

Results and Discussion

Shown below in **Figure 1**, EPR spectra obtained at higher fields and frequencies allow better resolution of the previously poorly resolved g-tensor. The newly obtained high-field spectra allow unified simulations to be performed across a broad range of frequencies (203.2 GHz data was chosen for the figure due to its high signal-to-noise ratio). Even at 203.2 GHz, a very broad spectrum is observed, indicating that there is a large amount of g-strain in these catalyst systems. Unresolved hyperfine coupling of 500 MHz, in conjunction with g-strain, was used to simulate the observed data. This is value is similar to that observed in some Co model complexes [4]. The higher frequency data also revealed the presence of a “radical-like” signal that was previously hidden in the linewidth of the spectra taken at lower frequencies. This signal is of great potential interest as it could be due to other potential intermediates in the water-oxidation reaction.

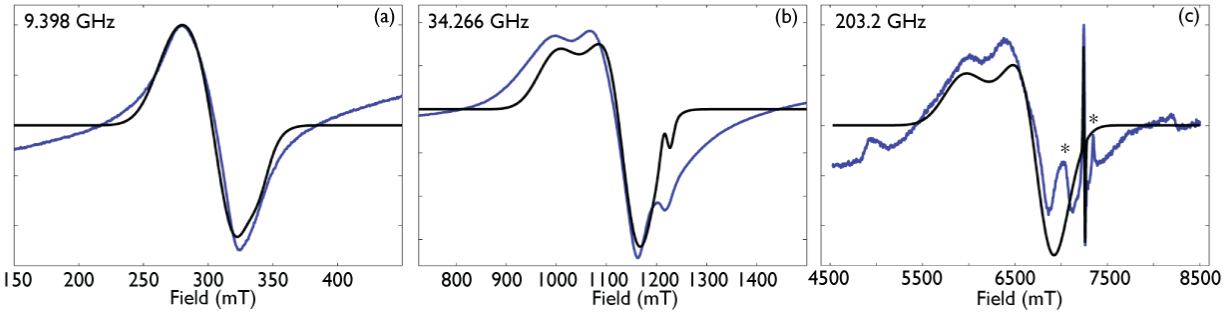

Figure 1. Unified simulations for CW spectra obtained at 9.4, 34.3, and 203.2 GHz. Spectra were simulated using two separate spin systems: a *S* = 1/2 system with g = [2.13, 2.45], and a second *S*= 1/2 “radical-like” spin system with g = 2.0023. Asterisks indicate unsimulated background signals.

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