CONCENTRATION SENSITIVITY OF Cu^{II} COMPLEX SOLUTIONS AT DIFFERENT EPR FREQUENCIES

J. Krzystek, S. Nellutla (NHMFL); S. Youngme (Khon Kaen U., Thailand, Chemistry)

Introduction

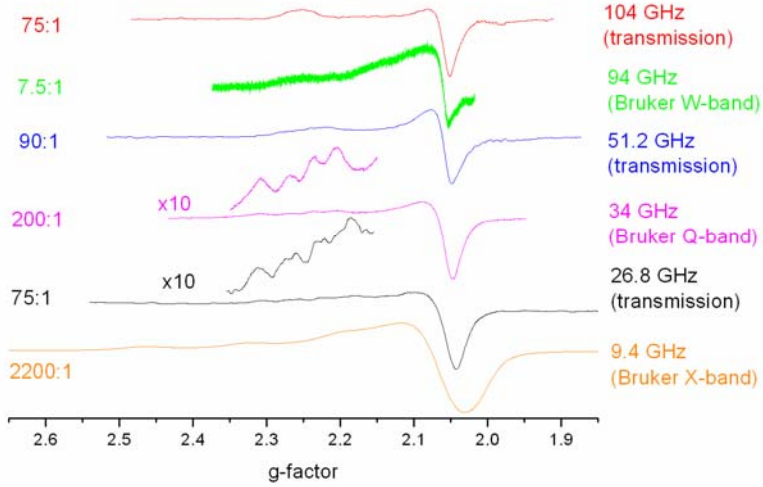
Concentration sensitivity, defined in electron paramagnetic resonance (EPR) as the minimum concentration yielding a 1:1 signal-to-noise (S/N) ratio for the given solution, has been often neglected in considerations of the choice of frequency for the EPR experiment. Instead, such considerations have more often than not given priority to absolute sensitivity, defined as the minimum number of unpaired spins detectable with a similar 1:1 S/N ratio. We will show below that absolute sensitivity bears little relevance to the suitability of EPR frequency for a given experiment if the sample is not volume-limited. As an object of our study we chose the complex $[Cu(dpyam)_2(NCO)][BPh_4]$ where dpyam = di-2-pyridylamine and Ph = phenyl (complex **1**), which is a simple $S = 1/2$ system with an axial g-anisotropy.

Experimental

EPR experiments were performed on a 5 mM solution of complex **1** in dimethylsulfoxide (DMSO) at T = 77 K using the Bruker ElexSys spectrometers at NHMFL and FSU for X-, Q- and W-band measurements, and the transmission instrument of the EMR facility for K-, V- and D-band (>100 GHz) measurements. The Bruker spectrometers are equipped with single-mode resonators; the transmission instrument operates without a resonator.

Results and Discussion

The resulting EPR spectra are collected in Figure 1 (right) in which the X-axis is normalized with respect to the g-value, and the Y-axis approximately normalized with respect to the amplitude of the perpendicular component of the axial g-tensor. The numbers on the left indicate the S/N ratio at the given frequency. The S/N ratio was defined by the amplitude of the perpendicular component of the g-tensor related to noise amplitude. The parallel g-tensor component was magnified 10 times in the K- and Q-band spectra to show the hyperfine structure due to the nuclear $I = 3/2$ spin of copper.



Conclusions

The concentration sensitivity for a typical Cu^{II} complex solution goes up (worsens) approximately by a factor of 10 with the EPR frequency increasing by a factor of 3 for the resonator-equipped spectrometers, with X-band offering the best S/N ratio for the given Cu concentration. This is a reverse of the trend in *absolute* sensitivity, which *improves* with increasing frequency. Concentration sensitivity remains approximately constant for all frequencies offered by the transmission spectrometer, and is ca. 3 times higher (worse) than that at Q-band, but still ca. 10 times lower (better) than that offered by the Bruker W-band spectrometer. At the same time, while the resolution of the parallel and perpendicular components of the g-tensor increases with increasing frequency, the resolution of hyperfine components of the parallel turning point *decreases* with increasing frequency due to A-strain. For the case presented here, i.e. axial $S = 1/2$ and $I = 3/2$ complex in solution, we find the optimum frequency at Q-band (34 GHz). For other type of experiments performed on different spin systems, concentration sensitivity should be carefully evaluated, and compared to advantages offered by high frequencies.