HIGH-FREQUENCY ELECTRON PARAMAGNETIC RESONANCE STUDY OF GADOLINIUM(III) COMPLEXES IN AQUEOUS SOLUTIONS

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Introduction

Gadolinium(III) complexes are routinely used as contrast agents for medical Magnetic Resonance Imaging (MRI). The paramagnetic gadolinium(III) ions accelerate the magnetic relaxation of water protons observed in MRI, which improves the picture quality.

Many factors influence the efficiency of the gadolinium(III) complexes for this application. Among other things, the electron spin relaxation rates in solution can play an important role. In order to design novel contrast agents with optimized properties, understanding the relationship between the molecular structure and the electron spin relaxation would be extremely useful. However, the physical bases of that phenomenon are not yet completely clear. Using electron paramagnetic resonance (EPR) at variable temperature (273-373 K) in aqueous solutions, we can directly probe the electron spin dynamics. The commonly available X- and Q-band instruments (~9 and ~35 GHz respectively) are not sufficient for an exhaustive relaxation study, so we turned to very high-frequency EPR.

Experimental

We recorded continuous wave EPR spectra of 18 different gadolinium(III) complexes in liquid solutions (water and dimethyl sulfoxide; gadolinium concentrations 0.5-50 mM), at temperatures from 275 to 325 K. The experiments were performed on the spectrometers available at the NHMFL EMR facility. A commercial Bruker Elexsys E-680 spectrometer was used for W-band (94 GHz) measurements (275-320 K). We used the homodyne quasi-optical spectrometer for measurements at 217 and 325 GHz (17 Tesla magnet; 275-295 K), and the heterodyne quasi-optical spectrometer (9 T magnet; 275-320 K) at 240 GHz.

Results and Discussion

More than 270 spectra were recorded, and their treatment is still under way. The peak-to-peak width and central field dependence on the temperature and EPR frequency will be analyzed in order to extract the mathematical parameters that describe our physical model of the electron spin relaxation (modulation of the zero-field splitting acting on the S = 7/2 electron spin of gadolinium(III) through molecular tumbling and collisions with the solvent).

At this very early stage of the project, we can already observe some general results and trends. The observed g-factors are slightly frequency-dependent, but consistent with an effective $g_{\text{eff}} = 1.99-1.995$. The observed spectra were generally single lines, but shoulders attributed to a partially resolved $^{155/157}\text{Gd}$ hyperfine coupling are visible in several 217 and 325 GHz spectra. The line width of the various complexes decreases dramatically between X-band (typically 100-1000 G) and 325 GHz (5-20 G). However, the W-band width is already significantly less than at X- and Q-band, and the change between 217 and 325 GHz is much smaller.

Conclusions

Thanks to the unique equipment found at the NHMFL EMR facility, we were able to collect a wealth of EPR spectra from several interesting gadolinium(III) complexes in liquid solutions. Since such experiments are very scarce in the literature, the availability of such data is already a quantum leap. When combined with conventional X- and Q-band measurements in Lausanne, these spectra will give us new insights into the relaxation mechanisms.

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