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DYNAMIC NUCLEAR POLARIZATION AS A MEANS OF DETERMINING ELECTRONIC SPIN-LATTICE RELAXATION TIMES IN AQUEOUS SOLUTIONS OF Cr^{3+}, Cu^{2+} and Gd^{3+}

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While the electronic spin-spin relaxation times (T_{2e}) for paramagnetic ions in solution are very small, they can often be directly obtained by observing the line widths of an electron paramagnetic resonance (EPR) spectrum [1]. The corresponding electron spin-lattice relaxation times (T_{1e}) are much more difficult to measure. Direct power saturation studies become very difficult when T_{1e} drops below about 10^{-8} s. For transition-metal ions in solution one usually finds $T_{1e} < 10^{-8}$ s. It is sometimes possible to utilize NMR broadening to make indirect determinations of T_{2e} and T_{1e}, but this often calls for a delicate balance between the rates of chemical exchange and the rates of electron spin relaxation [2]. In aqueous solution Cr^{3+}, Cu^{2+}, and Gd^{3+} all have observable EPR spectra, but little is known about their T_{1e} values.

Dynamic nuclear polarization (DNP)[3] offers a method for extending power saturation techniques so that T_{1e} values as short as 10^{-10} s can be measured. It should be able to fill any gap between NMR and direct power saturation and this paper reports a preliminary DNP study on Cr^{3+}, Cu^{2+}, and Gd^{3+}. In this work we used the basic DNP apparatus previously described [4]. In this apparatus the aqueous solution flows first through a microwave cavity excited by about 100 watts of power at 3 GHz and then through the coil of a simple NMR spectrometer operating in the same magnetic field. At any given field, B, we can measure the enhancement factor, E_B, of the proton NMR of the solution shortly after EPR has taken place. A plot of E_B versus B constitutes the DNP spectrum of the paramagnetic ion in solution.

Without hyperfine structure the DNP spectrum should be nearly Lorentzian in shape with a width equal to the EPR line width and with an amplitude which depends upon T_{1e} and the nature of the interaction between the protons and the paramagnetic ion [4,5]. Since the amplitude is dependent upon a number of experimental factors, DNP is best used to determine the relative T_{1e} values of two ions. In our work we have used VO^{2+} in water as a reference [4].

The EPR spectrum of $Cr(H_2O)_6^{3+}$ in aqueous solution consists of three superimposed transitions with a nearly Lorentzian line shape. At 9 GHz line widths of 190 and 160 gauss have been reported [1] and we found at 3.1 GHz and 28°C a derivative width of 188 gauss. This corresponds to $T_{2e} = 3.5 \times 10^{-10}$ s. At low magnetic fields where $\omega_e \tau_c << 1$, one expects that $T_{1e} = T_{2e}$. Since $\tau_c \approx 10^{-12}$ s this condition should be well-satisfied at 3 GHz. In a DNP experiment we found for 0.0013 M Cr^{3+} and $E_B = 0.038$

at line center. Calibration with VO^{2+} gave $T_{1e} = 3.5 \times 10^{-10}$ s for Cr^{3+} in aqueous solution. Within our experimental error we find $T_{1e} = T_{2e}$ at our low field.

The EPR spectrum of Gd^{3+} in aqueous solution consists of a single broad line. Ruben [6] reports a line width of 400 gauss at 9 GHz and 200 gauss at 24 GHz. At 3.1 GHz and 27°C we find a line width of 407 gauss and $T_{2e} = 1.6 \times 10^{-10}$, s for 3.6×10^{-4} M Gd^{3+} in 10^{-3} M $HClO_4$. These data suggest that $T_{1e} = T_{2e}$ at the lower fields and our DNP spectrum gave $E_B = 0.008 \pm 0.002$ at line center. Calibration with VO^{2+} gives $T_{1e}/T_{2e} = 1.2 \pm 0.3$. The small E_B value shows that $T_{1e} = 10^{-10}$ s is close to the limit of our present apparatus.

Since $Cu(H_2O)_6^{2+}$ has unresolved hyperfine structure in its EPR spectrum it is a difficult case, and its relaxation mechanisms are under considerable debate [7,8] In our DNP experiment we used solutions containing both 6.67×10^{-3} M $Cu(ClO_4)_2$, 3.33×10^{-3} M $VOSO_4$ and 10^{-3} M $HClO_4$. We ran DNP spectra at 5°, 30°, and 60°C and used the VO^{2+} as an internal standard. The individual hyperfine widths at 9 GHz have been accurately determined by Chang [8] and he also gives sufficient data to extrapolate these widths to 3.1 GHz. If we follow the procedures previously established [9], our DNP results give average values of $1/T_{1e}$ for the four hyperfine levels as 3×10^8, 6×10^8, and 14×10^8 s^{-1} at 5°, 30°, and 60°C, respectively. While the 30°C value agrees well with the estimate for $1/T_{1e}$ made from NMR by Poupko and Luz [7] at 1.4 T, our values all indicate that $T_{1e} > T_{2e}$ even at our low field of 0.1 T. At 5°C these data require that $T_{1e} \approx 2T_{2e}$,

but T_{1e} approaches T_{2e} at the highest temperature. More accurate DNP data would have allowed us to determine the spread in T_{1e} among the four hyperfine states.

While our low field DNP results show only small deviations for water solutions of these ions from $T_{1e} = T_{2e}$, similar work at higher fields should be very valuable for deciding between proposed relaxation mechanisms. In water solutions DNP measurements become more difficult as the microwave frequency is raised, but our simple flow technique should be usuable even above 9 GHz.

Acknowledgement:

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