Submitted to the Journal of Molecular Physics

RECEIVED
LAWRENCE
RADIATION LABORATORY

JUN 19 1974

LIBRARY AND
DOCUMENTS SECTION

LBL-2751
Preprint c.2

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

Douglas C. McCain and Rollie J. Myers

May 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-2751
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

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

by

Douglas C. McCain

Department of Chemistry, University of Southern Mississippi
Southern Station, Box 5281, Hattiesburg, Mississippi 39401

and

Rollie J. Myers

Department of Chemistry, and Inorganic Materials Research Division of
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

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:

This work was conducted under the auspices of the U.S. Atomic Energy Commission.

References

1. W. B. Lewis and L. O. Morgan, "Transition Metal Chemistry," Vol. 4, (R. L. Carlin, ed.,), pp. 33-112, Marcel Dekker, Inc., New York (1968).
2. T. J. Swift, "NMR of Paramagnetic Molecules," (G. N. La Mar et al., eds.), pp. 53-83, Academic Press, New York (1973).
3. J. Potenza, Advan. Mol. Relaxation Processes, 4, 229 (1972).
4. D. C. McCain and R. J. Myers, J. Phys. Chem., 71, 192 (1967).
5. A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London (1961).
6. J. Ruben, J. Phys. Chem., 75, 3164 (1971).
7. R. Poupko and Z. Luz, J. Chem. Phys., 57, 3311 (1972); M. Noack, G. F. Kokoszka and G. Gordon, J. Chem. Phys., 54, 1342 (1971).
8. J. J. Chang, Ph.D. Thesis, Lawrence Radiation Laboratory Report, UCRL 19691, University of California, Berkeley (1971).
9. For the details of correcting DNP results see: D. C. McCain, Ph.D. Thesis, Lawrence Radiation Laboratory Report UCRL-17064, University of California, Berkeley (1966).

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720