DYNAMIC NUCLEAR-POLARIZATION STUDIES OF PARAMAGNETIC
SPECIES IN SOLUTION

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Contents

Abstract	v
I. Introduction	1
II. Electron Spin Relaxation in Liquids	4
A. Mechanisms for $S = 1/2$	4
B. Mechanisms for $S \geq 1$	11
III. Theory of Dynamic Nuclear Polarization	15
A. DNP in Solution	15
B. DNP in the Presence of Chemical Exchange	26
C. Measuring Spin Lattice Relaxation Times	30
IV. Flow Spectrometer	36
A. Introduction	36
B. Spectrometer	39
V. Flow Spectrometer Results	48
A. Vanadyl Ion	48
B. Copper Ethylenediamine	64
C. Manganous Ion	78
VI. Moving Sample Spectrometer	89
A. Introduction	89
B. Sample Arrangement	90
C. Microwave Power	93
D. NMR Spectrometer	94
E. Experimental Timing	96
F. Estimates of $\langle H_1^2 \rangle_s$	99

VII. Moving Sample Tube Results	104
A. Hexacyano-Chromium (III) Ion	104
B. $\text{Cu}(\text{H}_2\text{O})_6^{2+}$	112
References	135
Acknowledgments	140

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ABSTRACT

Dynamic Nuclear Polarization (DNP) was used to measure the electron spin lattice relaxation times, T_1 , of transition metal ions in aqueous solution. Saturation which is induced in the electron spin system is transferred to the solvent proton spins by dipole-dipole interactions. The change in the polarization of the proton spins is much larger than it is in the electron spins. The change in proton polarization is easily measured by proton Nuclear Magnetic Resonance (NMR).

In one experimental arrangement the sample solution was continuously flowed through a microwave cavity to the NMR coil. The NMR was observed with a continuous wave NMR spectrometer. In a second arrangement the whole sample tube was moved from within the microwave cavity to the NMR coil in less than 40 ms by a blast of compressed air. The NMR was then observed with a pulse-Fourier-transform spectrometer. With the second arrangement a mean-square microwave magnetic field at the sample of more than 10 G^2 is obtainable with 14 W of microwave power.

Measurements of DNP at 9 GHz were made on aqueous solutions of VO^{2+} , Mn^{2+} , $\text{Cr}(\text{CN})_6^{3-}$, Cu^{2+} and $\text{Cu}(\text{ethylenediamine})_2(\text{H}_2\text{O})_2^{2+}$ ions from $3-60^\circ\text{C}$. It was also possible to observe DNP on resolved proton resonances from mixed water-acetonitrile solutions of VO^{2+} and $\text{Cr}(\text{CN})_6^{3-}$ ions.

I. Introduction

Magnetic resonance spectroscopy has proven to be a valuable tool in the solution of physical, chemical, and biological problems. New applications of magnetic resonance are constantly being found and new instruments are being built to increase the generality of its use. Magnetic resonance, however, is more than a tool; it has been the object of intensive study in its own right. The desire to understand the number, position, intensity, and shapes of magnetic resonance signals has provided ample opportunity for the development of theories describing the interactions of paramagnetic species with their physical and chemical environments. In this work, one magnetic resonance phenomenon, Dynamic Nuclear Polarization (DNP), has been used as a tool to investigate another magnetic resonance phenomenon, electron spin relaxation in solution.

DNP is a process whereby the polarization which is induced in an electronic spin system is transferred to a nuclear spin system. The electron polarization is induced by the application of a strong microwave field at the resonance frequency of the Electron Paramagnetic Resonance (EPR) transition.

In this work, DNP is used to aid in the measurement of electron spin relaxation rates which are difficult or impossible to measure by other means. Other uses of DNP can include Nuclear Magnetic Resonance (NMR) sensitivity enhancement and studies of molecular motion in solutions.

Bloch (1946) characterized the relaxation of a spin system with two relaxation times. The first, which he called T_1 , the spin-lattice

relaxation time, is the time constant for the return to equilibrium of the z component of the magnetization after it has been perturbed away from thermal equilibrium. It describes the time dependence of the population of the spin states. The second relaxation time, T_2 , the spin-spin relaxation time, is the time constant for the disappearance of magnetization which has been induced in the x-y plane. It describes the disappearance of phase coherence in the ensemble of spins. In EPR spectroscopy, T_2 for well-resolved lines is easily determined from the widths of the lines. The determination of T_1 is usually much more difficult.

Two things are required for paramagnetic relaxation in solution. The first is a perturbation which can operate on the spin wavefunctions of the system. The second requirement is a motion which generates small oscillating magnetic fields to make this perturbation time-dependent and allows the flipping or dephasing of the spins. By studying the magnitude and temperature dependence of the relaxation rates, it is possible to learn something about the nature of both the perturbation and the motion which are responsible for the relaxation.

The pioneering work on relaxation in solution was that of Bloembergen, Purcell, and Pound (1948). They found that the motion responsible for the time dependence of the dipole-dipole interaction which was responsible for the relaxation of protons in water could be treated by using classical theories of diffusion which involved correlation functions for the random motion which decayed exponentially with respect to time. Measurement of the relaxation times could thus

yield correlation times which are indicative of the speed and type of motion responsible for relaxation.

We are interested in the electron spin relaxation times of transition metal ions in solution. Understanding of the mechanisms of relaxation of these ions can yield information about their electronic structure in solution and their interaction with the solvent. The magnitudes of the relaxation times are also useful to other workers who are interested in the effect of paramagnetic ions on the relaxation times of nuclei in the solution. Many measurements of T_2 have been made on transition metal ions in solution, but often T_1 is the relaxation time of interest to those investigating nuclear relaxation. In addition, knowledge of both T_1 and T_2 is useful in determining the mechanisms responsible for relaxing the electron spin, since many interactions do not contribute equally to T_1 and T_2 .

The present work was undertaken in order to measure T_1 values for some transition metal ions for which the relaxation mechanisms were not completely understood, with the hope of aiding in the understanding of the electron spin relaxation of these ions. Some ions for which the relaxation mechanisms are reasonably well understood were also studied. This was done to test the applicability of using DNP to measure T_1 , since this method is not in general use.

II. Electron Spin Relaxation in Liquids

A large number of theories have been proposed to describe electron spin relaxation in liquids, but only a few of them have been verified experimentally. Those theories which seem to have applicability to the ions studied in this work are discussed in this section. Only a simple description of the mechanism and the results of the theoretical calculations will be given here. The original papers should be consulted for details.

The electron spin relaxation of transition metal ions is dominated by the influence of the spin-orbit coupling. Spin orbit coupling produces magnetic anisotropies, which can cause relaxation when they are modulated by molecular motion. Also, perturbation of the electronic orbital wavefunctions caused by interactions with the surrounding molecules can be transferred to the electron spins through the spin-orbit coupling to cause spin relaxation. The dominant relaxation mechanisms for transition metal ions with electronic spin, $S \geq 1$, involve the zero-field splitting terms which are largely the result of spin-orbit coupling. In this section the relaxation mechanisms for ions with $S = 1/2$ are discussed separately from those for which $S \geq 1$.

A. Mechanisms for $S = 1/2$

1. Anisotropic g and A Tensors

One of the most widely observed electron spin relaxation mechanisms in liquids is the "microcrystalline tumbling" mechanism proposed by McConnell (1956). In McConnell's model the metal ion and its associated ligands were proposed to tumble as a whole. If the g values

and electron-nuclear hyperfine constant, A , of the complex were anisotropic, then tumbling of the complex would modulate the energy of the EPR transition and cause relaxation. What is most interesting about this mechanism is that it predicts relaxation rates which depend on the nuclear spin quantum number, M_I , of the transition being observed. Kivelson (1960) used the linear response theory of Kubo and Tomita (1954) to calculate the relaxation rates from this mechanism. He found that the relaxation from this mechanism could be divided into nonsecular terms, which contribute to both T_1 and T_2 , and secular terms, which contribute only to T_2 . There are also pseudosecular terms, which directly contribute only to T_2 , but which affect the saturation behavior of the EPR transitions. Later, Wilson and Kivelson (1966a) repeated the calculation using a more accurate static Hamiltonian. They found

$$\frac{1}{T_2} = \alpha + 8M_I + \gamma M_I^2 + 8M_I^3, \quad (2.1)$$

where

$$\begin{aligned} \frac{\alpha}{T_R} = & \frac{4}{45} (\Delta\gamma B_0)^2 + \frac{3}{40} b^2 I(I+1) \\ & - \frac{1}{30} b \left(\frac{a}{\omega_0} \right) \Delta\gamma B_0 I(I+1) + u \left[\frac{1}{15} (\Delta\gamma B_0)^2 + \frac{7}{40} b^2 I(I+1) \right. \\ & \left. - \frac{1}{30} b \left(\frac{a}{\omega_0} \right) \Delta\gamma B_0 I(I+1) - \frac{5}{40} b^2 \left(\frac{a}{\omega_0} \right) I(I+1) f \right] \end{aligned} \quad (2.2)$$

$$\begin{aligned}
\frac{\beta}{\tau_R} = & \frac{4}{15} b \Delta \gamma B_0 - \frac{8}{45} (\Delta \gamma B_0)^2 \left(\frac{a}{\omega_0} \right) \\
& - b^2 \left(\frac{a}{\omega_0} \right) \left[\frac{1}{20} I(I+1) + \frac{3}{40} \right] + u \left[\frac{1}{5} b \Delta \gamma B_0 - \frac{2}{15} (\Delta \gamma B_0)^2 \left(\frac{a}{\omega_0} \right) (1+f) \right] \\
& - \frac{1}{20} b^2 \left(\frac{a}{\omega_0} \right) u [I(I+1) + 7I(I+1)f] \quad , \quad (2.3)
\end{aligned}$$

$$\begin{aligned}
\frac{\gamma}{\tau_R} = & \frac{1}{8} b^2 - \frac{7}{30} b \left(\frac{a}{\omega_0} \right) \Delta \gamma B_0 \\
& - u \left[\frac{1}{40} b^2 + \frac{1}{6} b \left(\frac{a}{\omega_0} \right) \Delta \gamma B_0 + \left(\frac{2}{5} b \Delta \gamma B_0 - \frac{5}{40} \right) b^2 \left(\frac{a}{\omega_0} \right) f \right] \quad , \quad (2.4)
\end{aligned}$$

$$\frac{\epsilon}{\tau_R} = \frac{1}{20} b^2 \left(\frac{a}{\omega_0} \right) + \frac{1}{20} b^2 \left(\frac{a}{\omega_0} \right) u(1+f) \quad , \quad (2.5)$$

where

$$a = 1/3(2A_{\perp} + A_{\parallel}) \quad ,$$

$$b = 2/3(A_{\parallel} - A_{\perp}) \quad ,$$

$$\Delta g = g_{\parallel} - g_{\perp} \quad ,$$

$$\Delta \gamma = \beta_0 \Delta g / \hbar \quad ,$$

$$B_0 = \hbar \omega_0 / g \beta_0 \quad ,$$

$$g = 1/3(2g_{\perp} + g_{\parallel}) \quad ,$$

$$u = 1/(1 + \omega_0^2 \tau_R^2) \quad ,$$

$$f = \omega_0^2 \tau_R^2 u \quad ,$$

ω_0 is 2π times the observing frequency, and β_0 is the Bohr magneton. The tumbling correlation time, τ_R is given by the Stokes-Einstein relation,

$$\tau_R = \frac{4\pi a^3}{3kT} \eta \quad , \quad (2.6)$$

where η is the viscosity of the liquid, a is the hydrodynamic radius of the complex, k is Boltzman's constant, and T is the absolute temperature. The definition of the correlation time treats the complex as a tumbling sphere. This relaxation mechanism is strongly field dependent. Its contribution to T_1 is detailed in a later section.

2. Spin-Rotation

The spin-rotation relaxation mechanism is due to the interaction of the spin magnetic moment with the rotational magnetic moment of the molecule. The rotational magnetic moment arises because the electrons do not follow the motion of the nuclei rigidly. A charge imbalance is created which generates a magnetic field as the molecule rotates. The energy of interaction of the magnetic field with the spin is given by

$$\mathcal{H}_{SR} = \underline{\underline{J}} \cdot \underline{\underline{C}} \cdot \underline{\underline{S}} \quad ,$$

where $\underline{\underline{J}}$ is the rotational angular momentum, $\underline{\underline{C}}$ is the spin-rotational coupling tensor, and $\underline{\underline{S}}$ is the spin angular momentum. Relaxation can occur when $\underline{\underline{J}}$ is modulated by collisions or $\underline{\underline{C}}$ is modulated by reorientation of the molecule. In liquids the modulation of $\underline{\underline{J}}$ is usually

much faster than the modulation of $\underline{C}$. Under these conditions, Hubbard (1963) found for molecules with cylindrical symmetry, in the extreme narrowing limit,

$$\frac{1}{T_2} = \frac{1}{T_1} = \frac{2IT\tau_\omega}{3h^2} (2C_\perp^2 + C_\parallel^2) \quad , \quad (2.7)$$

where I is the molecular moment of inertia, T is the absolute temperature, $C_\parallel$ and $C_\perp$ are the components of $\underline{C}$ along the molecular axis and perpendicular to it, respectively, and τ_ω is the angular momentum correlation time. The components of $\underline{C}$ are seldom known, but Curl (1965), and Atkins and Kevelson (1966) were able to relate the spin-rotation tensor to the g tensor. If use is made of Hubbard's relation

$$\tau_\omega \tau_R = I/6kT \quad ,$$

a useful expression for the spin-rotational contribution to relaxation is

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{9\tau_R} [(g_\parallel - g_e)^2 + 2(g_\perp - g_e)^2] \quad , \quad (2.8)$$

where g_e is the free electron g value. Equation (2.8) is the result of second-order perturbation theory and is most accurate for transition metal ions when the spin-orbit coupling is small compared to the crystal field splitting. Note that Eqs. (2.8) and (2.6) predict that

for this mechanism, $\frac{1}{T_1}$ is proportional to T/η and is independent of the magnetic field.

3. Electric Field Fluctuations

Kivelson (1966) considered three relaxation mechanisms for which the modulation of the intermolecular potentials by molecular motion contribute through the spin-orbit coupling to the electron spin relaxation. Two of these mechanisms were first proposed by Van Vleck (1940) to explain electron spin relaxation in crystals. The third is due to Orbach (1961).

The first mechanism Kivelson considered is called the Van Vleck-direct, because an electron spin is flipped by the direct interaction with a single phonon from the lattice. The contribution to T_1 from this mechanism is

$$\frac{1}{T_1} = \frac{1}{T_2} = 64 \left(\frac{\lambda}{\Delta} \right)^2 \left(\frac{\phi q_0}{\Delta r_0} \right)^2 \frac{(\omega_0 \tau_c)^2 \tau_c^{-1}}{1 + \omega_0^2 \tau_c^2} \quad (2.9)$$

where λ is the spin orbit coupling constant, Δ is the energy separation between the ground state and the first excited state connected to it by spin-orbit coupling, ϕ is the magnitude of the time dependent potential, q_0 is the root-mean-square amplitude of intermolecular oscillations, r_0 is the characteristic intermolecular distance, and τ_c is the correlation time.

The second process Kivelson considered is called the Van Vleck Raman process, because the spin is relaxed by a two-phonon process. The contribution to T_1 from this mechanism is

$$\frac{1}{T_1} = 32 \left(\frac{\lambda}{\Delta}\right)^2 \left(\frac{\phi q_0}{\Delta r_0}\right)^4 \tau_c^{-1} \quad , \quad (2.10)$$

when $\omega_0^2 \tau_c^2 \ll 1$. Kivelson concluded that both the Van Vleck direct and Raman processes are negligible for liquids unless there is a low lying excited state connected to the ground state by spin-orbit coupling. However, if there is such a low lying state, relaxation can be very fast indeed.

The final process considered by Kivelson was the Orbach mechanism. In this mechanism an interaction with a phonon from the lattice causes a simultaneous electronic excitation and spin flip. The contribution of this mechanism to the relaxation rate is

$$\frac{1}{T_1} = 16 \left(\frac{\lambda}{\Delta}\right)^2 \left(\frac{\phi q_0}{\Delta r_0}\right)^2 \left(\frac{\Delta}{\delta_{on}}\right)^2 \frac{\lambda^{-1} \tau_c^{-1}}{\left[\exp\left(\frac{\hbar \delta_{on}}{kT}\right) - 1\right]} \quad (2.11)$$

where δ_{on} is the transition energy to the lowest orbitally excited state. This expression is correct only for $\delta_{on}^2 \tau_c^2 \leq 1$. Kivelson concludes that the Orbach process could be important for liquids if δ_{on} is sufficiently small.

The correlation time, τ_c , for these three mechanisms should be characteristic of the translational fluctuations of the molecules in the liquid. Kivelson used $\tau_c = 10^{-12}$ sec in his estimation of the importance of these mechanisms.

B. Mechanisms for $S \geq 1$

Transition metal ions with $S \geq 1$ have in their spin-Hamiltonian a term which is given by

$$\mathcal{H}_{\text{ZFS}} = D \left[S_z^2 - \frac{1}{2} S(S+1) \right] + E(S_x^2 - S_y^2) \quad ,$$

where D and E are the components of the zero-field-splitting (ZFS) tensor. Modulation of this term is a powerful relaxation mechanism for ions with $S \geq 1$. The term involving E vanishes for axial symmetry, and the ZFS interaction vanishes completely for cubic symmetry. McGarvey (1957), and Carrington and Luckhurst (1964) considered relaxation by rotational modulation of the ZFS interaction, but the complexes studied in this work have cubic symmetry and should thus have a vanishing static ZFS. Bloembergen and Morgan (1961) suggested that dynamic fluctuations in the ZFS caused by distortions of the complex could be the cause of spin relaxation for cubic complexes with $S \geq 1$.

Most calculations of the magnitude of the relaxation rates from the modulation of a dynamic ZFS have employed the relaxation theory of Redfield (1957). The use of this theory involves the calculation of the elements of the relaxation matrix R , which are given by

$$R_{\kappa\kappa',\lambda\lambda'} = 2J_{\kappa\lambda\kappa',\lambda'}(\kappa - \lambda) - \sum_{\gamma} \delta_{\kappa',\lambda'} J_{\gamma\lambda\gamma\kappa}(\gamma - \lambda) \\ - \sum_{\gamma} \delta_{\kappa\lambda} J_{\gamma\lambda',\gamma\kappa'}(\gamma - \lambda') \quad , \quad (2.12)$$

where the J 's are spectral densities, and δ is a Kronecker delta function. The form of the spectral densities depends on the nature of the perturbation and the type of motion involved in the relaxation mechanism.

Rubinstein, Barum, and Luz (1971) used the Redfield approach to calculate relaxation times from modulation of the ZFS. They assumed that the fluctuations only changed the direction of the principal components of the ZFS tensor, and not their magnitudes. In this work we are interested in ions with $S = 3/2$ and $S = 5/2$. For $S = 3/2$, Rubinstein, Barum, and Luz found that there are two transverse relaxation times and two longitudinal relaxation times. The two transverse times are given by

$$\frac{1}{T_{2e}(I)} = \frac{6}{5} \Delta^2 [j(\omega) + j(2\omega)] \quad (2.13)$$

and

$$\frac{1}{T_{2e}(II)} = \frac{6}{5} \Delta^2 [j(0) + j(2\omega)] \quad . \quad (2.14)$$

The longitudinal times are

$$\frac{1}{T_{1e}(I)} = \frac{12}{5} \Delta^2 j(\omega) \quad , \quad (2.15)$$

and

$$\frac{1}{T_{1e}(II)} = \frac{12}{5} \Delta^2 j(2\omega) \quad , \quad (2.16)$$

where,

$$\Delta^2 = \frac{2}{3} D^2 + E^2 \quad , \quad (2.17)$$

and

$$j(n\omega) = \frac{\tau}{1 + n^2 \omega^2 \tau^2} \quad .$$

These results are the same as those obtained by Carrington and Luckhurst (1964) for rotational modulation of a static ZFS, except that in this case

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{n}{n-1} \frac{1}{\tau_C} \quad (2.18)$$

where τ_R is the correlation time for rotational diffusion and τ_C is the correlation time for distortions of the complex along n equivalent axes. The intensity of the EPR transition which is labeled I, is 1.5 times the intensity of the transition labeled II.

For $S = 5/2$, a closed form solution to the relaxation problem is not possible except when $\omega^2 \tau^2 \ll 1$. In that case

$$\frac{1}{\tau_{1e}} = \frac{1}{\tau_{2e}} = \frac{32}{5} \Delta^2 \tau \quad . \quad (2.19)$$

The correlation time, τ_c , for the fluctuations responsible for the instantaneous distortions of the complex should be in the same range as those for the electric field fluctuation mechanism for $S \approx 1/2$, about 10^{-12} sec.

III. Theory of Dynamic Nuclear Polarization

A. DNP in Solution

The existence of dynamic nuclear polarization as a consequence of the relaxation processes in coupled systems of electron and nuclear spins was first predicted by Overhauser (1953). The theory and some early experimental results are discussed extensively by Abragam (1961). Some of the important theoretical and experimental aspects of DNP applied to liquids are reviewed by Hausser and Stehlik (1968). The portions of the theory necessary for understanding the experimental results of this work are discussed in this section.

Many of the results of DNP experiments can be understood by considering some simple kinetic models. A treatment of a two spin system was given by Solomon (1955). It will be useful to review this treatment in some detail.

The energy levels of a system of two spins of spin 1/2, labeled I and S, are shown schematically in Fig. 1, along with the possible transitions between them. The rates of change of the populations of the levels can be written down in a straightforward manner as

$$\frac{dP}{dt} ++ = -(w_1 + w_1' + w_2) P_{++} + w_1' P_{+-} + w_1 P_{-+} + w_2 P_{--} \quad , \quad (3.1a)$$

$$\frac{dP}{dt} +- = -(w_0 + w_1 + w_1') P_{+-} + w_0 P_{-+} + w_1 P_{--} + w_1' P_{++} \quad , \quad (3.1b)$$

$$\frac{dP}{dt} -+ = -(w_0 + w_1 + w_1') P_{-+} + w_1 P_{++} + w_0 P_{+-} + w_1' P_{--} \quad , \quad (3.1c)$$

$$\frac{dP}{dt} -- = -(w_1 + w_1' + w_2) P_{--} + w_2 P_{++} + w_1 P_{+-} + w_1' P_{-+} \quad , \quad (3.1d)$$

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Fig. 1. Relaxation in a system of two spins.

where the P's are the populations of the respective levels and the w's are transitions between the levels, as designated in Fig. 1. The measurable quantities, the magnetizations $\langle S_z \rangle$ and $\langle I_z \rangle$ are related to the populations of the individual levels by

$$K\langle I_z \rangle = (P_{++} + P_{+-}) - (P_{-+} + P_{--}) \quad ,$$

and

$$K\langle S_z \rangle = (P_{++} + P_{-+}) - (P_{+-} + P_{--}) \quad ,$$

where K is a proportionality constant. When combined with equations 3.1a-d, this definition yields the pair of coupled equations:

$$\frac{d\langle I_z \rangle}{dt} = -(w_0 + 2w_1 + w_2)(\langle I_z \rangle - I_0) - (w_2 - w_0)(\langle S_z \rangle - S_0) \quad (3.2a)$$

and

$$\frac{d\langle S_z \rangle}{dt} = -(w_2 - w_0)(\langle I_z \rangle - I_0) - (w_0 - 2w_1 + w_2)(\langle S_z \rangle - S_0) \quad (3.2b)$$

Because interactions with the lattice tend to bring the system to thermal equilibrium, the quantities $\langle I_z \rangle$ and $\langle S_z \rangle$ are replaced by the differences from their respective equilibrium values I_0 and S_0 . If the S spin is an electronic spin and the I spin a nuclear spin, the system of equations is simplified. Mechanisms other than its interactions with the I spin are usually responsible for the rapid relaxation of the S spin. Equation 3.2b can thus be disregarded. Equation 3.2a solved in steady state gives

$$\langle I_z \rangle - I_0 = - \frac{(w_2 - w_0)(\langle S_z \rangle - S_0)}{(w_0 + 2w_1 + w_2)} = - \frac{\sigma}{\rho} (\langle S_z \rangle - S_0) ,$$

where $\sigma = (w_2 - w_0)$ and $\rho = (w_0 + 2w_1 + w_2)$. The specific enhancement, E can be defined

$$E \equiv 1 - \frac{\langle I_z \rangle}{I_0} , \quad (3.3)$$

so

$$E = \frac{\sigma(\langle S_z \rangle - S_0)}{\rho I_0} . \quad (3.4)$$

Saturation of the S spin would lead to

$$E = - \frac{\sigma S_0}{\rho I_0} . \quad (3.5)$$

A slightly more complicated situation arises when the electronic spin is coupled to a third spin, K, resulting in hyperfine splitting of the EPR spectrum. The number of levels to consider in a kinetic model grows from 4 to $4 \times (2K + 1)$. However, transitions which involve a change of the state of the K spin do not contribute to the relaxation of I, because we assume that there is no direct coupling between the I and K spin. This makes it possible to treat this system as $2K + 1$ separate two spin systems, each with equations of motion

$$\frac{d\langle I_z \rangle_m}{dt} = -\rho_m(\langle I_z \rangle_m - I_{0m}) - \sigma_m(\langle S_z \rangle_m - S_{0m}) \quad , \quad (3.6)$$

where $m = M_K$. Only the total $I_z = \sum_m \langle I_z \rangle_m$ is measurable, however, so

$$\frac{d\langle I_z \rangle}{dt} = \sum_{m=-K}^K -\rho_m(\langle I_z \rangle - I_{0m}) - \sigma_m(\langle S_z \rangle_m - S_{0m}) \quad . \quad (3.7)$$

When hyperfine lines are well resolved, it is usually possible to get appreciable saturation in only one line. If this is the case, only one of the $2K + 1$ systems is affected. The rest remain at their equilibrium values. When the m 'th line is saturated, in steady state, Eq. (3.7) becomes

$$\langle I_z \rangle_m - I_{0m} = \frac{\sigma_m}{\rho_m} S_{0m} \quad . \quad (3.8)$$

The observable $\langle I_z \rangle = \langle I_z \rangle_m + \sum_{n \neq m} I_{0n}$, so

$$\langle I_z \rangle - I_0 = \frac{\sigma_m}{\rho_m} S_{0m} \quad . \quad (3.9)$$

Since $S_{0m} \approx S_0/(2K + 1)$, the amount of enhancement observable will be decreased by a factor of $2K + 1$.

If the hyperfine lines are not well resolved, Eq. (3.7) can only be collapsed under certain circumstances. If the hyperfine splitting constant is small compared to the static field, all of the ρ_m 's can be considered to be approximately equal. Then

$$E = \frac{-1}{\rho_{I0}} \sum_{m=-K}^K \sigma_m (\langle S_z \rangle_m - S_{0m}) \quad , \quad (3.8)$$

where $\rho = \rho_{-K} = \rho_{-K+1} \dots = \rho_K$.

The use of kinetic models to describe DNP becomes increasingly difficult as one tries to apply them to systems with I or S greater than one-half. Also one eventually has to be more specific about what the rates w_0 , w_1 , and w_2 actually are in order to properly evaluate the frequency and temperature dependence of the DNP.

The semiclassical density matrix formulation of Abragam (1961) can be used to calculate the relaxation rates of a spin subject to a time dependent Hamiltonian, $\mathcal{H}'(t)$. For DNP

$$\mathcal{H}'(t) = A \vec{I} \cdot \vec{S} + \frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^5} - \frac{\vec{I} \cdot \vec{S}}{r^3} \quad ;$$

where $\vec{r}$ is the distance vector between the two spins. $\vec{I}$ and $\vec{S}$ are the nuclear and electronic spin operators respectively. The first term is the Fermi-contact interaction between the nucleus and the electron. The second two terms are the electron-nuclear dipolar interaction. The dipolar interaction can be rewritten as

$$\mathcal{H}'(\text{dipolar}) = \sum_{q=-2}^2 F^{(q)} A^{(q)} \quad , \quad (3.10)$$

where

$$F^{(1)} = \sin\theta \cos\theta e^{i\phi}/r^3, \quad (3.10a)$$

$$F^{(2)} = \sin^2\theta e^{2i\phi}/r^3, \quad (3.10b)$$

$$F^{(0)} = 1 - 3 \cos^2\theta/r^3, \quad (3.10c)$$

and the angles θ and ϕ give the orientation of r with respect to the static magnetic field. For $A^{(q)}$ we have,

$$A^{(0)} = \alpha \left[-\frac{2}{3} I_z S_z + \frac{1}{6} (I_+ S_- + I_- S_+) \right],$$

$$A^{(1)} = \alpha [I_z S_+ + S_z I_+],$$

$$A^{(2)} = \frac{\alpha}{2} [I_+ S_+],$$

where

$$\alpha = -\frac{3}{2} \gamma_I \gamma_S,$$

$$S_+ = S_x + i S_y, \quad I_+ = I_x + i S_y,$$

$$S_- = S_x - i S_y, \quad I_- = I_x - i S_y,$$

and,

$$F^{(q)} = F^{-q*},$$

$$A^{-(q)} = A^q.$$

The time dependence comes either from variations of r or θ and ϕ from translation or rotation in the system containing I and S, or from modulation of the S spin due to electron spin relaxation. The time dependence of the scalar interaction, $AS \cdot I$ can come from modulation of A by chemical exchange or from modulation of S from electron spin relaxation.

Using the semiclassical density matrix approach, Abragam finds

$$\frac{d\langle I_z \rangle}{dt} = -\rho[\langle I_z \rangle - I_0] - \sigma[\langle S_z \rangle - S_0] \quad , \quad (3.12)$$

where

$$\rho = \frac{\gamma_I^2 \gamma_S^2}{10r^6} (6J(\omega_I + \omega_S) + J(\omega_I - \omega_S) + 3J(\omega_I)) \quad ,$$

and

$$\sigma = (6J(\omega_I + \omega_S) - J(\omega_I - \omega_S)) \quad .$$

Note that this is the same form as obtained by the use of the kinetic models. In this case σ and ρ are given in terms of the spectral density functions $J_q(\omega)$, where

$$J_q(\omega) = \int_{-\infty}^{\infty} \overline{\langle F^q(t) F^q(t + \tau) \rangle} e^{-i\omega\tau} d\tau$$

and

$$\langle F^{(q)}(t) F^{(q)}(t + \tau) \rangle$$

is the autocorrelation, function of the random force $F^{(q)}$. Equation (3.12) is exact for both spins 1/2, and is correct for spins greater than 1/2 within the accuracy of the high temperature approximation (Abragam, 1961, p. 201).

The experimental work discussed in later chapters concerns the DNP of solvent molecules in a solution of paramagnetic ions or molecules. The paramagnetic species often form complexes with the solvent that have an average lifetime, τ_h , which is longer than the correlation time for the interaction responsible for the relaxation of the nuclear spin. If this is the case, a treatment of the motion as classical rotational diffusion leads to

$$\rho = \frac{\gamma_I^2 \gamma_S^2 S(S+1)}{15 r^6} \left[6\tau_c + \frac{14\tau_c}{1 + \omega_e^2 \tau_c^2} \right] + \frac{2S(S+1) A^2}{3} \left[\frac{\tau_x}{1 + \omega_e^2 \tau_x^2} \right] \quad , \quad (3.13)$$

$$\sigma = \frac{I(I+1) \gamma_I^2 \gamma_S^2}{15 r^6} \left[\frac{10 \tau_c}{1 + \omega_e^2 \tau_c^2} \right] - \frac{2I(I+1) A^2}{3} \left[\frac{\tau_x}{1 + \omega_e^2 \tau_x^2} \right] \quad , \quad (3.14)$$

where

$$\frac{1}{\tau_c} = \frac{1}{\tau_h} + \frac{1}{\tau_R} + \frac{1}{\tau_{le}} \quad ,$$

$$\frac{1}{\tau_x} = \frac{1}{\tau_h} + \frac{1}{\tau_{le}} \quad ,$$

and τ_R is correlation time for rotational diffusion and T_{1e} is the electron spin relaxation time. We have assumed that $\omega_I \ll \omega_S$ and $\omega_I^2 \tau_C^2 \ll 1$. For the ions studied in this work $T_{1e} \geq 10^{-10}$ sec and $\tau_h \geq 10^{-10}$ sec. At the magnetic field used for these experiments $\omega_e^2 \tau_x^2 \gg 1$, making the effect of scalar coupling small compared to that of the dipolar interaction in both σ and ρ .

There is evidence for some radicals and paramagnetic ions that long-lived complexes are not formed (Pfeifer, 1961, Günter and Pfeifer, 1964). In this case DNP is governed by the translational diffusion of the paramagnetic species. For translation the calculation of the spectral densities is more complicated. Abragam finds

$$\frac{\sigma}{\rho} = \frac{6J(\omega_I + \omega_S) - J(\omega_I - \omega_S)}{6J(\omega_I + \omega_S) + 3J(\omega_I) + J(\omega_I - \omega_S)} \frac{I(I+1)}{S(S+1)}, \quad (3.16)$$

where for pure translational motion

$$J(\omega) = \frac{\tau_L I(x)}{d^3},$$

and

$$I(x) = x^{-5} \left\{ x^2 - 2 + e^{-x} [(x^2 - 2) \sin x - (x^2 + 4x + 2) \cos x] \right\}, \quad (3.17)$$

with

$$x = (2\omega_S \tau_t)^{1/2}$$

and

$$\tau_t = \frac{d^2}{D_I + D_S} \quad .$$

D_I and D_S are the translational diffusion coefficients of the molecules containing the nuclear and electronic spins respectively, and d is the distance of closest approach of the two molecules.

The dependence of the quotient σ/ρ on frequency and temperature for translational motion is somewhat different from rotational motion, particularly in the region where $\omega_e^2 \tau^2 \geq 1$. Both functions approach zero as $\omega_e^2 \tau^2$ gets large, but in the translational case the approach is much more gradual. As $\omega_e^2 \tau^2$ gets small both functions approach $\frac{1}{2} \frac{I(I+1)}{S(S+1)}$. For small $\omega_e^2 \tau^2$,

$$E = -\frac{1}{2} \frac{S_0}{T_0} \approx 330 \quad . \quad (3.18)$$

This means that the NMR signal when the EPR line is saturated is roughly 330 times as intense and in the opposite direction of the NMR signal without DNP. If the electron experiences hyperfine coupling from another nucleus of spin K , this enhancement is reduced by a factor of $2K + 1$, as was explained by the kinetic model. This is because electrons which are not affected by the saturating field because they are out of resonance still contribute to the relaxation of the spin I .

The enhancement will also be reduced from its theoretical maximum by the existence of any relaxation mechanism for the nuclear spin other than interaction with the electron spin. An extra term must be added to ρ to account for this independent relaxation; it is usually referred to as the "leakage" term. In solutions of paramagnetic ions it is usually possible to keep the leakage term relatively small by making the solution sufficiently concentrated in the paramagnetic species.

B. DNP in the Presence of Chemical Exchange

The model previously discussed only treats a pair of isolated interacting spins. In a dilute solution of paramagnetic ions only a small fraction of the nuclei are in close contact with the paramagnetic ion at any particular instant. If DNP is to be observed in the bulk nuclei there must be chemical exchange between the paramagnetic complex and the bulk.

McConnell (1958) gives modified Bloch (1946) equations for two site chemical exchange. The equations can be modified further to include steady state polarization of the minority species. For the z components of the magnetization one has

$$\frac{dM_z^A}{dt} = \frac{M_0^A}{T_{1A}} - \frac{M_z^A}{T_{1A}} - \frac{M_z^A}{\tau_A} + \frac{M_z^m}{\tau_m} \quad , \quad (3.19a)$$

$$\frac{dM_z^m}{dt} = \frac{M_0^m}{T_{1m}} + \frac{\delta M}{T_{1m}} - \frac{M_z^m}{T_{1m}} - \frac{M_z^m}{\tau_m} + \frac{M_z^A}{\tau_A} \quad , \quad (3.19b)$$

where

M_Z^A = bulk magnetization,

M_Z^m = magnetization for paramagnetic complex,

T_{1A} = spin lattice relaxation time in the bulk,

T_{1m} = spin lattice relaxation time on the complex,

τ_A = lifetime in the bulk,

τ_m = lifetime in the paramagnetic complex,

δM = the effect of DNP pulling the m spins away from equilibrium.

The modified Bloch equations have been solved in steady state with an r.f. field present (Swift and Connick, 1962) and as differential equations (Leigh, 1971) to determine the apparent relaxation rates of the bulk magnetization, but these calculations have not been extended to determine the magnetization itself. The system of Eqs. (3.19a) and (3.19b) can be manipulated to yield a single second order differential equation,

$$\tau_m \frac{d^2 M_Z^A}{dt^2} + \left(\frac{\tau_m}{\tau_{1m}} + \frac{\tau_m}{\tau_{1A}} \right) \frac{dM_Z^A}{dt} + \left(\frac{\tau_m}{\tau_{1m} \tau_{1A}} - \frac{1}{\tau_A} \right) M_Z^A = \frac{M_O^m + \delta M}{T_{1m}} + \frac{\tau_m M_O^A}{\tau_{1m} \tau_{1A}} \quad (3.20)$$

where using McConnell's notation,

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A} \quad ,$$

and

$$\frac{1}{\tau_{1m}} = \frac{1}{\tau_{1m}} + \frac{1}{\tau_m} .$$

At $t = 0$ both magnetizations are at their equilibrium values. The electron spins are then irradiated, activating the $\delta M/\tau_{1m}$ term. The magnetizations are allowed to propagate according to Eq. (3.20). Under these conditions the solution to Eq. (3.20) is

$$M_z^A = c_+ e^{r_+ t} + c_- e^{r_- t} + M_\infty , \quad (3.21)$$

where $r_\pm$ is the same as determined by Leigh,

$$2\tau_m r_\pm = -\frac{\tau_m}{\tau_{1m}} + \frac{\tau_m}{\tau_{1A}} \pm \sqrt{\left(\frac{\tau_m}{\tau_{1m}} + \frac{\tau_m}{\tau_{1A}}\right)^2 - 4\tau_m\left(\frac{\tau_m}{\tau_{1A}\tau_{1m}} - \frac{1}{\tau_A}\right)} ,$$

and m_∞ is the solution as t approaches infinity, the steady state solution.

We have for the steady state solution,

$$M_\infty = \frac{\frac{M_0^m + \delta M}{\tau_{1m}} + \frac{\tau_m M_0^A}{\tau_{1m}\tau_{1A}}}{\frac{\tau_m}{\tau_{1m}\tau_{1A}} - \frac{1}{\tau_A}} . \quad (3.22)$$

The coefficients are given by

$$c_+ = \frac{(M_0^A - M_\infty) r_-}{r_- - r_+} \quad (3.24)$$

and

$$c_- = \frac{(M_0^A - M_\infty) r_+}{r_- - r_+} \quad f$$

In a dilute solution

$$\frac{1}{f} \equiv \frac{M_0^A}{M_0^m} = \frac{\tau_A}{\tau_m} \gg 1 \quad .$$

Also usually we have $f T_{1A} \gg T_{1m}$. With these approximations Leigh finds

$$r_+ = - \frac{f}{(T_{1m} + \tau_m)} = - \frac{1}{T_{1p}} \quad . \quad (3.25)$$

This result was also found by Luz and Meiboom (1964) under slightly different approximations. Within the same degree of approximation

$$r_- = - \left(\frac{1}{\tau_m} + \frac{1}{T_{1m}} \right) \quad . \quad (3.26)$$

With these approximations and the additional assumption of fast exchange ($\tau_m \ll T_{1m}$)

$$M_z^A(t) = (M_0^A - M) e^{-t/T_{1p}} + M_\infty, \quad (3.27)$$

and

$$M_\infty = \frac{1}{F} (M_0^m + \delta M) \quad (3.28)$$

Equations (3.27) and (3.28) show that the steady state magnetization of the bulk species does reflect the magnetization of the paramagnetic complex under the previously stated conditions. If exchange is not fast, the bulk magnetization will not accurately reflect the polarization in the complex. The polarization of the complex will also not be accurately reflected in the bulk if T_{1m} is not much smaller than fT_{1A} , even if exchange is fast. Corrections must be made to the observed polarization in cases of intermediate exchange very and dilute solutions. The only ion studied in this work for which slow exchange might be a problem is the VO^{2+} ion. The application of Eq. (3.22) using parameters from the work of Wüthrich and Connick (1968) shows that the bulk polarization accurately reflects the polarization of protons bound to the metal ion for 0.05 M VO^{2+} solution, but that a 0.005 M solution would result in inaccuracies.

C. Measuring Spin Lattice Relaxation Times

The classical method for measuring spin-lattice relaxation times is to measure the absorption spectrum with increasing amounts of incident power. If the system obeys the Bloch (1946) equations, then

when the absorption reaches its maximum as a function of power, $H_1^2 \gamma^2 T_1 T_2 = 1$, where H_1 is the magnitude of the irradiating field, γ is the gyromagnetic ratio of the spin and T_2 is the spin-spin relaxation time. This is often referred to as "half saturating" the signal since s , the saturation parameter, which is defined as

$$s = 1 / (1 + \gamma^2 H_1^2 T_1 T_2) \quad , \quad (3.29)$$

equals 1/2. In EPR spectroscopy the first derivative of the absorption is usually measured. When the first derivative is maximum, $s = 2/3$. T_2 and γ can be determined from the low power spectrum. H_1^2 is proportional to the incident power and is in principle calculable, but this proves difficult in practice. Usually a sample of known T_1 must be used to determine H_1^2 for a given experimental arrangement.

The direct saturation method becomes difficult for the broad lines common to transition metal ions. A line 10 G wide has $T_2 = 6.5 \times 10^{-9}$ sec. If $T_1 = T_2$, then to half saturate the line requires $H_1^2 = 75 \text{ G}^2$. Microwave fields of this size are beyond the range of conventional EPR spectrometers using conventional cavities and klystrons. Microwave sources with a larger power output than small klystrons, such as traveling wave tubes and magnetrons, are available, but the detection of absorption signals with these high power sources is difficult due to the inherent noisiness of the high power sources and the lack of sensitive detectors which can operate in a high power environment (McCain, 1966). Furthermore, many interesting EPR systems

have linewidths considerably larger than 10 G. Since the power necessary to half saturate a line goes up roughly with the square of the linewidth, if $T_1 = T_2$, power requirements escalate rapidly.

It is of course not necessary to half saturate a line to measure its T_1 . Since

$$\frac{1}{S} = 1 + \gamma^2 H_1^2 T_1 T_2 = [\lim_{H_1 \rightarrow 0} (v'/H_1) / (v'/H_1)]^2 / 3 \quad (3.30)$$

where v' is the peak to peak amplitude of the derivative of absorption (Poole and Farrach, 1971), a plot of the right hand side of Eq. (3.30) vs H_1^2 would have a slope $\gamma^2 T_1 T_2$. For transition metal ions the power necessary to make the ratio

$$\frac{(\lim_{H_1 \rightarrow 0} v'/H_1) / (v'/H_1)}{H_1 \rightarrow 0}$$

measurably different from unity is larger than that available from conventional spectrometers, so this approach would suffer from the previously discussed problems with a high power spectrometer.

Dynamic Nuclear Polarization can be used to determine the saturation parameter. If the electronic spin obeys the Bloch equations, at resonance

$$\langle S_z \rangle = \frac{S_0}{1 + \gamma_e^2 H_1^2 T_{1e} T_{2e}} \quad . \quad (3.31)$$

Substitution of this relation into Eq. (3.5) yields

$$E = - \frac{\sigma S_0 \gamma_e^2 H_1^2 T_{1e} T_{2e}}{\rho I_0 (1 + \gamma_e^2 H_1^2 T_{1e} T_{2e})} \quad . \quad (3.32)$$

A plot of $1/E$ vs $1/H_1^2$ would be linear with a slope of $1/\gamma_e^2 T_{1e} T_{2e}$ (Haupt and Muller-Warmuth, 1962; Richards and White, 1964). DNP has been used to measure electron T_{1e} 's at 15 G (Muller-Warmuth, 1963), and to measure the electron T_1 of free radicals at 3300 G (Kramer, Muller-Warmuth, and Schindler, 1965).

McCain and Myers (1967, 1974) used DNP to measure T_{1e} of transition metal ions. Because of the short relaxation times involved and the limited power of their spectrometer they found $H_1^2 \gamma_e^2 T_{1e} T_{2e} \ll 1$. This condition simplifies Eq. (3.32) to

$$E = - \frac{\sigma S_0 \gamma_e^2 H_1^2 T_{1e} T_{2e}}{\rho I_0} \quad , \quad (3.33)$$

where H_1^2 is proportional to the incident power, P , and I_0 is proportional to the static field, H . Taking into account the possibility of being off-resonance, and the additional complication of hyperfine structure yields

$$E \propto \frac{P}{\rho H} \sum_m \frac{a_m T_{1em} T_{2em}}{1 + (\omega - \omega_{em}) T_{2e}^2} \quad . \quad (3.34)$$

Because the ratio S_0/I_0 is large (~ 660 in the case of protons), a small and most likely immeasurable saturation of the electron spins of a few hundredths of a percent results in an enhancement of a few percent or more, which is easily measured. Equation 3.33 can be used to obtain the relative T_{1e} of two species, where one of the species is a standard with a known T_{1e} .

The comparison of enhancements of different paramagnetic species is complicated because σ/ρ is in general different for different species. The differences are particularly pronounced at the microwave frequency used in this work. A plot of σ/ρ vs. τ at X-band (9 GHz) is shown in Fig. 2. This plot assumes rotational modulation of the dipolar interaction as the interaction responsible for DNP. Some species will have DNP determined by translational modulation. Fortunately the behavior of σ/ρ can usually be determined from measurement of nuclear magnetic relaxation times of the solvent. Hauser and Stehlik (1968) discuss a method for doing this, but often it is more convenient to fit the nuclear relaxation to a diffusional model and use the correlation times determined from nuclear relaxation measurements in Eqns. (3.13) and (3.14) or (3.16). This is often necessary because nuclear relaxation measurements are not always available at all of the frequencies and temperatures desired.

XBL 827-5965

Fig. 2. σ/ρ calculated from the dipolar parts of equations 3.13 and 3.14 for $\omega_e = 5.56 \times 10^{10} \text{ sec}^{-1}$

IV. Flow Spectrometer

A. Introduction

A major limitation to the observation of DNP in aqueous solutions is the large dielectric loss of water at microwave frequencies. This limitation is particularly severe for transition metal ion solutions. Because of their short relaxation times, the level of microwave power necessary to cause a measurable amount of DNP would also cause severe dielectric heating of the solution.

Another problem inherent in the observation of DNP is the inconvenience of irradiating the sample at both the EPR and NMR frequencies. The simplest experimental configuration, which would consist of simply placing the NMR coil within the microwave cavity is unsatisfactory because the presence of the coil in the microwave field will both lower the Q of the cavity and shield the sample from the field, resulting in inefficient use of the saturating power. Several solutions to this problem are discussed by Hausser and Stehlik (1968).

McCain and Myers (1967) solved both the dielectric heating and the coil geometry problems by placing the NMR coil just outside the cavity and flowing the solution through the cavity and then into the NMR coil. They were able to observe the DNP of transition metal ions at S-band (3 GHz) without excessive heating of the solutions. An X-band (9 GHz) spectrometer based on the same principle is described in the next section.

The use of the flow system adds additional complications to the interpretation of the measured enhancements. Because the solution is

exposed to the microwave field for a limited time and because it takes time for the solution to reach the NMR coil, the observed enhancements will depend on the spin lattice relaxation time of the nucleus being observed. Also, the microwave field is in general not uniform along the flow path through the cavity.

One can model the build-up of enhancement by combining the definition of enhancement with the Bloch (1946) equations for the z component of the magnetization. We get

$$\frac{dE}{dt} = - \frac{E - E_{ss}}{T_1} \quad , \quad (4.1)$$

where E_{ss} is the steady-state value of the enhancement. Because the microwave field is non-uniform within the cavity we find that

$$E_{ss} = kH_1^2(z) \approx kH_1^2(vt) \quad , \quad (4.2)$$

where v is the flow velocity, t is the time spent in the cavity and k is determined from Eq. (3.33). For a narrow sample tube placed along the axis of a cylindrical cavity only the field components in the direction of the cavity axis contribute significantly to H_1^2 over the sample. For the TE_{011} , mode

$$H_z = H_{\max} \sin\left(\frac{\pi z}{d}\right) \quad , \quad (4.3)$$

where d is the length of the cavity (Poole, 1967). For this mode

$$H_1^2(vt) = H_{\max}^2 \sin^2 \left(\frac{\pi vt}{d} \right) \quad (4.4)$$

The solution of Eq. (4.1) yields

$$E = \frac{kH_{\max}^2 (1 - e^{-d/vT_1})}{2 + \frac{1}{2} \left(\frac{d}{\pi v} \right)^2 / T_1^2} \quad (4.5)$$

for solution emerging from the cavity. For this field distribution the mean square field over the sample, $\langle H_1^2 \rangle$, is just half of the maximum field. Defining

$$E_{AV} \equiv k \langle H_1^2 \rangle = \frac{kH_{\max}^2}{2},$$

we have

$$E\left(\frac{d}{v}\right) = \frac{E_{AV} (1 - e^{-d/vT_1})}{1 + \left(\frac{d}{2\pi v} \right)^2 / T_1^2} \quad (4.6)$$

Once the solution leaves the cavity the enhancement is expected to decay to zero exponentially, yielding

$$E(v, d, a) = \frac{E_{AV} (1 - e^{-d/vT_1}) e^{(-a/vT_1)}}{1 + \left(\frac{d}{2\pi v} \right)^2 / T_1^2} \quad (4.7)$$

where a is the distance from the cavity to the coil. This expression is plotted as a function of flow velocity in Fig. 3. Note that flowing the solution rapidly samples the average value of the microwave field, and loses a factor of two in enhancement compared to a static sample located at the maximum of the microwave field. The plot in Fig. 3 can be considered as E vs. v for constant T_{1n} or E vs. T_{1n} for constant v . It is obvious that in order to compare the enhancements of two different solutions they should have roughly the same T_{1n} . However, if one operates on the gently sloping portion of the curve small differences in T_{1n} will not have a large effect on the relative enhancements. The plot of measured enhancement versus flow rate in Fig. 4 shows qualitative agreement with this model. The points at the lowest rates probably show too much enhancement because the heating of the solution at those rates was not negligible.

B. Spectrometer

A simplified block diagram of the flowing sample DNP spectrometer is shown in Fig. 5. The solution being studied is pumped through Tygon tubing to a 1mm i.d. quartz tube which passes through the axis of the cylindrical microwave cavity. Also in the flow path are thermometers to measure the temperature of the solution before and after it passes through the cavity, a flowmeter to measure the flow rate, and a heat exchanger which can be immersed in a water bath to control the temperature. The solution is pumped through the flow path with a magnetically coupled gear pump, the Paragon model 3316-2. A typical flow rate is 150 cc/min. At this flow rate the temperature

XBL 827-5966

Fig. 3. A plot of Eq. 4.7 vs flow velocity with $d = 7$ cm, $a = 1$ cm, and $T_{1n} = 40$ msec.

XBL 827-5967

Fig. 4. Enhancement vs flow rate for 0.031 M VOSO_4 .

XBL 827-5968

Fig. 5. Block diagram of the flowing sample DNP spectrometer.

rise of the solution upon passing through this cavity is less than 1.5°C for 15 W of incident power.

The microwave cavity is a Varian V-4535 large sample cylindrical cavity. The main virtue of this cavity appears to be its length along the cylindrical axis. Because the enhancement is expected to build up as in Eq. (4.7), the larger the cavity length d , is, the more enhancement there will be for a given flow rate and $\langle H_1^2 \rangle$. Enhancements in this cavity, with a 6.9 cm length and a 4.1 cm diameter were generally a factor of two larger than for a cavity 2.9 cm in length and 4.9 cm diameter. This was true even though the smaller cavity would be expected to have a larger value of $\langle H_1^2 \rangle$. The larger cavity can be operated in either the TE_{012} or the TE_{011} mode. The resonant frequency of the TE_{011} mode with the sample in place is 9.0 GHz. The loaded Q is approximately 2000.

The initial source of X-band radiation is a Varian V-58C klystron. Power from the klystron can be switched to the cavity directly for tuning purposes or amplified by a Varian VA-618M travelling wave tube (TWT). The TWT is capable of supplying 20 W of continuous power. Power from the tube is leveled by controlling the input power with an HP 8735B P.I.N. modulator and the leveling circuit shown in Fig. 6. The klystron is not locked to the cavity. Reflected power is monitored with a crystal. The klystron reflector voltage can be adjusted by hand to keep the microwaves at the cavity resonance frequency. Klystron drift is not a serious problem for measurements on broad EPR lines.

XBL 827-5969

Fig. 6. Leveling circuit.

The NMR spectrometer is a continuous wave field modulated spectrometer. The NMR coil is located in the end cap of the cavity, as close to the interior of the cavity as possible in order to observe the induced polarization before it can decay away. Radio frequency radiation from a General Radio 1164-A frequency synthesizer is applied to the coil through a hybrid tee (Relcom Hybrid H2) and a network of tuning and matching capacitors. The capacitors are adjusted until no reflected power is observed from the third port of the tee when it is terminated with 50 Ω . The spectrometer is tunable to operate from 11.5 - 17 MHz. The frequency of the synthesizer can be swept by the application of a voltage from a ramp generator (Datatron 2600-102). The NMR signal from the probe is taken from the third port of the tee and pre-amplified by two Watkins-Johnson thin film amplifiers. This setup supplies 30 db of gain. The amplified signal is mixed with some of the original r.f. from the synthesizer in an HP10534 mixer. The magnetic field is modulated at 1 KHZ. One of the 1 KHZ sidband signals from the mixer is amplified and phase detected with a Princeton Applied Research 124A lock-in amplifier.

Experiments are done under the control of a PDP-8I computer, which is equipped with the AX08 lab peripheral. The microwaves can be turned on and off by the computer through a solid state relay and the leveling circuit. The ramp generator was modified to begin sweeps on computer command. The output signal from the lock-in amplifier is digitized and the intensities are calculated by the computer.

The magnetic field is supplied by a Pacific Electric Motors 12A-LI-EC, current stabilized electromagnet. The stability of the

magnet is just barely adequate for these experiments. The amount of field drift makes averaging of individual NMR spectra impossible, but it is slow enough that intensities can be measured and averaged for several minutes without having to readjust the field. Homogeneity at the NMR coil is adjusted by a Varian VK-3532 homogeneity controller.

A typical run would consist of taking several scans of the NMR spectrum, both with the microwave power on and off. The computer averages the intensities and calculates the enhancements. The enhancement can be printed on a teletype and stored on magnetic tape for later manipulations. Typically, the enhancement as a function of magnetic field over the EPR line, the enhancement spectrum, is desired. For each point in the spectrum, before the enhancement can be measured, the NMR frequency must be set, the probe tuned, and the NMR signal found by adjustment of the magnetic field. This can be quite tedious. It takes from one to several hours to obtain the enhancement spectrum with acceptable signal to noise. Figure 7 shows the enhancement spectrum of the $M_I = -1/2$ line of VO^{2+} , which was taken in this manner. Each point is the result of averaging 50 NMR spectra.

XBL827-5970

Fig. 7, DNP enhancement spectrum of the $M_I = -1/2$ line of VO^{2+} .

V. Flow Spectrometer Results

A. Vanadyl Ion

1. Introduction

The EPR spectrum of VO^{2+} (vanadyl) ion in aqueous solution was first reported by Garif'ianov and Kozyrev (1954) and Pake and Sands (1955). Pake and Sands noted the appearance of eight lines due to hyperfine coupling to the Vanadium-51 nucleus ($I = 7/2$; natural abundance 99.8 per-cent) and also commented that each of the eight lines had a different width. This variation of the widths of the hyperfine lines has been the subject of a significant amount of experimental and theoretical interest.

VO^{2+} ion has a single unpaired electron in a 3d orbital. Because of the strong influence of the V-O bond there is expected to be a strong tetragonal distortion to the aquated ion, $\text{VO}(\text{H}_2\text{O})_5^{2+}$. This results in a non-degenerate ${}^2\text{B}_2$ ground state and an EPR spectrum with lines narrow enough to be easily observed at room temperature.

The variation of the linewidths with M_I suggests a relaxation mechanism involving tumbling modulation of the anisotropic spin-Hamiltonian parameters first predicted by McConnell (1956) and then refined by Kivelson (1960). Wilson and Kivelson (1966a) refined the theory even further and applied it to linewidth measurements on the neutral acetylacetonate complex of VO^{2+} in toluene and chloroform. They were able to explain the linewidths satisfactorily with the tumbling theory and a small, but predictable contribution from a spin-rotation mechanism.

Rogers and Pake (1960) measured the linewidths of the aqueous VO^{2+} ion at X-band (9.25 GHz) and K-band (24.3 GHz). They were able to fit the observed X-band linewidths to a polynomial in M_I and, using a version of the Kivelson (1960) theory, predict the K-band linewidths with moderate accuracy.

McCain and Myers (1967) observed aqueous VO^{2+} at S-band (3 GHz) and X-band. They also measured the anisotropic spin-Hamiltonian parameters $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ of VO^{2+} in a perchloric acid glass to make a more direct use of the theory. The anisotropic parameters of the aquated ion cannot be determined from measurements on the liquid solution. They chose to measure the anisotropic parameters in perchloric acid glass to take advantage of the non-complexing properties of the perchlorate ion. It was hoped that the environment of the VO^{2+} ion in the glass did not differ significantly from that of the aquated ion in liquid solution. They used the measured anisotropic parameters in Eqs. (2.1)–(2.5). Assuming a tumbling correlation time of 3.5×10^{-11} sec at 30°C, they found that the combination of the Kivelson theory and spin-rotation underestimated the M_I independent component of the linewidth by 3.1 G out of 12.7 G at X-band and 5.9 G out of 21.3 G at S-band. They felt that perhaps the difference between the residual widths could be due to terms in the theory proportional to $(a/\omega)^2$ which were discarded by Kivelson. These terms would be much more important at S-band. Since the lines at S-band are considerably wider than those at X-band, and since partial overlap of the lines would make accurate determination of the linewidths more difficult, the X-band data should be considered more reliable.

Angerman and Jordan (1971), and Chang (1971) measured the linewidths of aqueous VO^{2+} ion as a function of temperature at X-band. Angerman and Jordan found a residual width which decreased with increasing temperature. They used the experimentally determined γ parameter to estimate the correlation time. This correlation time was then used in Eqs. (2.1)-(2.5) to calculate the theoretical linewidth. Chang's results were qualitatively similar, and they showed a residual width which decreased with increasing temperature, although the residual width was smaller with a less pronounced temperature dependence. Chang determined his linewidths by fitting the observed spectra to a lineshape function composed of the sum of derivatives of Lorentzians. This method is expected to avoid errors due to partial overlap of the lines. Angerman and Jordan measured the peak to peak separations directly from their spectra. Perhaps this explains the difference between the two sets of data, especially at low temperatures where overlap is more severe.

At 20°C, Chang found that 2.2 G of the linewidth was unexplained by tumbling theory plus spin-rotation. Lewis and Morgan (1968) suggested that the residual width was due to unresolved proton superhyperfine coupling. Chang measured spectra in D_2O and found residual widths similar to the normal aqueous system. If the residual width were due to superhyperfine it should have been considerably reduced in D_2O .

Reuben and Fiat (1969) determined the VO^{2+} -proton superhyperfine constant from the chemical shift of the proton NMR spectrum. They determined a superhyperfine constant of 1.1 G. Ianuzzi, Kubiak, and Rieger (1976) measured the linewidths of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ in 1 M $\text{Na}(\text{ClO}_4)_2$ solution as a function of temperature. They also did computer simulations to determine the effect of proton superhyperfine on the observed linewidths. They found that a 1 G superhyperfine contribution from eight equivalent protons would only contribute 0.3 G to the average linewidths. When they corrected for this superhyperfine interaction this left them with a residual linewidth of 3.0 G. They also measured linewidths of VOCl_2 solutions in D_2O and H_2O , finding a 0.4 G larger residual width for the protonated species, in close agreement to their expected excess of 0.3 G.

Some of the residual widths observed seem to depend on the concentrations and types of anions used in the measurements. Yet, in the dilute chloride solutions used by Ianuzzi, Kubiak and Rieger, and the dilute perchlorate solutions examined by Chang, there remains a residual width which cannot be accounted for by the presence of excessive concentrations of anions or unresolved proton superhyperfine coupling.

McCain and Myers (1967) used DNP to measure the relative T_{1e} of the eight VO^{2+} hyperfine lines and they compared them to the T_{1e} calculated from the nonsecular terms of the theory derived by Wilson and Kivelson (1966a). These terms yield

$$\frac{1}{T_1} = a_1 + b_1 M_I + c_1 M_I^2 + d_1 M_I^3 \quad , \quad (5.1)$$

with,

$$\begin{aligned} \frac{\alpha_1}{\tau_R} = & \frac{1}{15} (\Delta\gamma B_0)^2 u + \frac{1}{40} I(I+1) b^2 u \left(1 + f\left(\frac{a}{\omega_0}\right)\right) \\ & + \frac{3}{20} I(I+1) b^2 u \left(1 - f\left(\frac{a}{\omega_0}\right)\right) - \frac{1}{30} b \Delta\gamma B_0 I(I+1) \left(\frac{a}{\omega_0}\right) u \quad (5.2) \end{aligned}$$

$$\begin{aligned} \frac{\beta_1}{\tau_R} = & \frac{1}{5} b \Delta\gamma B_0 u - \frac{2}{15} (\Delta\gamma B_0)^2 \left(\frac{a}{\omega_0}\right) u (1 + f) \\ & - b^2 I(I+1) u \left[\frac{7}{20} \left(\frac{a}{\omega_0}\right) f + \frac{3}{20} \left(\frac{a}{\omega_0}\right) \right] \\ & + \frac{1}{20} b^2 [2I(I+1) - 1] \left(\frac{a}{\omega_0}\right) u \quad , \quad (5.3) \end{aligned}$$

$$\frac{\gamma}{\tau_R} = -\frac{1}{40} b^2 u - b \Delta\gamma B_0 u \left[\frac{2}{15} \left(\frac{a}{\omega_0}\right) + \left(\frac{2}{5}\right) f\left(\frac{a}{\omega_0}\right) + \frac{3}{20} b^2 u f\left(\frac{a}{\omega_0}\right) \right] \quad , \quad (5.4)$$

$$\delta/\tau_R = \frac{1}{20} b^2 u \left(\frac{a}{\omega_0}\right) (1 + f) \quad (5.5)$$

where the meaning of the variables in the expressions are given following Eq. (2.5). These expressions assume axial symmetry of the paramagnetic complex. In their analysis, McCain and Myers assumed all of the residual linewidth was a T_1 process. When they assumed that $\alpha_1(\text{measured}) = \alpha(\text{theoretical})$, the measured values of γ_1 and δ_1 agreed well with the theory. However, there was a large discrepancy in β_1 . There are of course no grounds for expecting $\alpha_1(\text{measured})$ to be the

same as the theoretical α_1 . A discrepancy in the α 's would most likely show up as a discrepancy in the β 's when this comparison method is used. As in the case of the linewidth measurements the difference between theory and experiment was ascribed to the neglect of terms in $(a/\omega_0)^2$ in the theory.

There are many reasons to measure the DNP of VO^{2+} ion at X-band. The use of DNP to measure absolute T_{1e} requires a standard with a known T_{1e} . Because the linewidths of the VO^{2+} EPR spectrum are well explained by theory (with the exception of a small residual width), it may be possible to compare other ions with VO^{2+} . The theoretical value of T_{1e} could serve as the absolute guidepost. The terms in $(a/\omega_0)^2$ which were neglected in the theory are less important at X-band than at S-band. Measurements of the relative T_{1e} values of the eight VO^{2+} hyperfine lines would serve to reinforce confidence in the theory. Since at X-band $\omega_e \tau_c \geq 1$, the non-secular contributions to the linewidth are smaller than the secular contributions. If the residual width were a T_1 process it should contribute a larger fraction to T_{1e} . It would have a large effect on the relative T_{1e} 's and should be easy to detect. A superhyperfine contribution would not affect T_{1e} , so relative T_{1e} measurements could shed some light on the residual width question for $\text{VO}(\text{H}_2\text{O})_5^{2+}$.

2. Experimental Methods

$\text{VO}(\text{ClO}_4)_2$ solutions were prepared from VOSO_4 (Eastman) by the ion exchange method described by Chang (1971). Solutions were analyzed

for VO^{2+} by monitoring the absorbance at 765 nm. The molar extinction coefficient ϵ , was taken as 16.98 (Santini, Hazel, and McNabb, 1952).

DNP measurements were made with the apparatus described in Chapter IV. The microwave power level was 10 W. The flow rate was 150 cc/min. The temperature was not controlled, but it did not deviate from the room temperature, 23°C, by more than 1°C during the course of the experiment.

3. Results and Discussion

Figure 8 shows the DNP spectra of the $M_I = -7/2$ line and $M_I = 7/2$ line of VO^{2+} . Spectra of this sort were taken for all eight hyperfine lines. This was done primarily to accurately determine the linecenters, because a second-order perturbation treatment does not predict the linecenters of the outer lines correctly. The enhancement data for each line were fitted to a function of the form

$$E = \frac{E_0 H_0}{H(1 + (H - H_0)^2/\delta^2)} \quad , \quad (5.6)$$

where E_0 is the enhancement at line centers, H_0 is the linecenter and δ is the half-width at half height. The fitted half-widths were always slightly larger than the equivalent widths measured from the EPR spectrum. This was most likely due to overlap from adjacent lines. Once the linecenters were determined more data were taken for each line at the linecenter field. The uncertainty in each of the measured enhancements was less than $\pm .005$.

Fig. 8a. The DNP enhancement spectrum of the $M_I = 7/2$ line of VO_2^+

XBL 827-5971

Fig. 8b. The enhancement spectrum of the $M_I = -7/2$ line of VO_2^+ . Both spectra in this figure were taken with 10 W of microwave power.

The measured enhancements were corrected for overlap by solving eight equations in eight unknowns of the form

$$E_{M_I}(\text{measured}) = \sum_{M_I = -\frac{7}{2}}^{\frac{7}{2}} \frac{E_{M_I}(\text{actual})}{\left(1 + \frac{(H - H_{M_I}^0)^2}{\delta_{M_I}^2}\right)} \quad (5.7)$$

where δ_M and H_M^0 are the half-width and linecenter of the M_I 'th hyperfine line, and H is the field of the measured enhancement, E_M (measured). The unknowns are the E_M (actual)'s. The overlap corrections are small and can be calculated nearly as accurately by only considering the effect of lines adjacent to the line of interest.

Numbers proportional to T_{1e} can be obtained by multiplying the overlap corrected enhancement by the linewidth and linecenter of the line. The numbers are then normalized with respect to the line having the largest T_{1e} . These ratios are given in Table I. The linewidths used in Table I are interpolated from EPR measurements by Chang (1971). The linewidths from EPR measurements are presumed to be more accurate than those obtained from the DNP fits.

The calculated values of T_{1e} shown in Table I are determined from Eqs. (5.1)–(5.4) and (2.8) using spin-Hamiltonian parameters determined by Chang. The correlation time used in these calculations was 4.6×10^{-11} sec. It was calculated using Eq. (2.6) and the hydrodynamic radius determined by Chang. The residual width was

Table I. DNP Parameters for VO_2^+

M_I	H_O (G)	ΔH (G)	Normalized T_1 (Measured)	Normalized T_1 (Calculated)
-7/2	2860.4	16.48	0.78	1.00
-5/2	2963.7	12.98	0.92	0.93
-3/2	3071.3	11.55	0.87	0.86
-1/2	3182.5	11.92	0.84	0.80
1/2	3299.1	13.83	0.81	0.75
3/2	3419.2	17.36	0.80	0.71
5/2	3583.6	22.31	0.79	0.68
7/2	3671.3	28.99	0.78	0.66

included as a contribution to T_{1e} in the calculation made here. The residual width measured by Chang at 23°C would contribute $2.7 \times 10^7 \text{ sec}^{-1}$ to $1/T_{1e}$ if its contribution to T_{1e} and T_{2e} were equal. The calculated contribution to $1/T_{1e}$ from spin-rotation is $1.5 \times 10^7 \text{ sec}^{-1}$. The calculated contribution from tumbling to $1/T_{1e}$ for the $M_I = -7/2$ line is $1.9 \times 10^7 \text{ sec}^{-1}$. If the residual width does contribute equally to T_{1e} and T_{2e} , then its contribution to the total T_{1e} would be quite significant.

Comparison of the measured and calculated T_{1e} ratios shows reasonable qualitative agreement, since T_{1e} is seen to decrease monotonically with increasing M_I for both the measured and calculated values. However, one can see that the spread of the measured T_{1e} ratios is less than that given by the theory. Since the residual width contributed equally to the calculated T_{1e} value for each M_I , diminishing its contribution would only make the quantitative agreement between the measured and calculated ratios worse. This disagreement is larger than expected from the experimental uncertainty and seems to be systematic, since the measured T_{1e} ratios appear consistently low. This is similar to the results reported by McCain and Myers (1967). They also had a smaller spread of the T_{1e} ratios for the experimentally determined numbers. This may point to a flaw in the tumbling theory, but there are also complications in the interpretation of the experimental results.

The experimental interpretation is complicated by cross relaxation among the VO^{2+} EPR hyperfine lines. The tumbling modulation of g

and A anisotropy leads to terms in the relaxation proportional to $S_{\pm} I_z$, $S_{\pm} I_{\pm}$ and $S_{\pm} I_{\mp}$, where I refers to the spin of the Vanadium-51 nucleus. These terms cause a leakage of polarization out of an irradiated line. There is in fact not a single T_{1e} for each line, but there are several. A steady state saturation experiment cannot measure these relaxation times separately. What is actually measured is a quantity called the saturation parameter, which is a function of all the processes which resist saturation of an irradiated line. The DNP experiment is somewhat different. It measures $\langle S_z \rangle - S_0$. Because of cross relaxation, the irradiation of one set of spins as represented by a hyperfine line can cause a polarization change in a non-irradiated line, making $\langle S_z \rangle - S_0$ non-zero for the nonirradiated spins. The DNP enhancement is proportional to all of the electron spin polarization. The assignment of relaxation times, or more precisely, saturation parameters, to individual lines on the basis of DNP results requires a more careful consideration of the cross relaxation process.

Freed (1965, 1972) considered saturation and double resonance experiments in the presence of cross relaxation. Figure 9a shows a schematic level diagram for an electron coupled to a single nucleus of spin 1/2. The possible electron spin relaxation transitions are indicated by the arrows. Note that W_N only involves a nuclear spin flip, W_e only an electron spin flip, and W_x , and W_x involve flips of both. If the 2 to 1 transition is saturated, and the absorption of the 3-4 transition is measured using low power, Freed (1972) finds that the percentage reduction of the absorption signal, R is given by

XBL 827-5972

Fig. 9.

$$R = \frac{100 (W_N^2 - W_{x_1} W_{x_2})}{W_e (2W_N + W_{x_1} + W_{x_2}) + (W_N + W_{x_1})(W_N + W_{x_2})} \quad (5.8)$$

If $W_N \gg W_{x_1}, W_{x_2}$, then saturating the 2 to 1 transition also saturates the 3-4 transition, resulting in a decrease in signal intensity. If $W_{x_1}, W_{x_2} \gg W_N$ saturating the 1-2 transition results in an increase of signal in the 3-4 transition.

The rates W_N, W_{x_1} and W_{x_2} can be calculated for VO^{2+} from the theory (Wilson and Kivelson, 1966a, p. 164). At X-band we have $\omega_e^2 \tau_R^2 = 7$. The rate, W_N , which only requires a nuclear spin flip, is about eight times larger than W_{x_1} and W_{x_2} , which are proportional to $1/(1 + \omega_e^2 \tau_R^2)$. Thus saturation of one VO^{2+} line will lead to saturation in adjacent lines. In the DNP experiment microwave power is limited and only partial saturation is possible. It is necessary to consider the effect of partial saturation on total $\langle S_z \rangle \sim S_0$.

Consider the four level system in Fig. 9b, which now neglects W_{x_1} and W_{x_2} , but has a different W_e for each hyperfine transition. It can be shown (Freed, 1972) that

$$(\langle S_z \rangle - S_0)_{\Omega} = \frac{-S_0(\Omega_p + \Omega_{op}) \tau_{2p} d^2}{2(1 + d^2 \tau_{2p} \Omega_p)} \quad (5.9)$$

when one of the transitions is partially saturated at resonance by an oscillating field of magnitude H_1 . Here $d = (1/2)\gamma_e H_1$, Ω_p is the saturation parameter of the pumped resonance, Ω_{op} is a cross-saturation

parameter and T_{2p} is the spin-spin relaxation time. In the case of Fig. 9b,

$$\Omega_0 = \frac{2(W_N + 2W_{34})}{2W_{12}W_{34} + W_N(W_{12} + W_{34})} \quad (5.10)$$

and

$$\Omega_{op} = \frac{2W_N}{2(W_{12}W_{34}) + W_N(W_{12} + W_{34})} \quad (5.11)$$

Because of the limited power in our DNP experiment $d^2 T_{2p} \Omega_p \ll 1$ so

$$(\langle S_z \rangle - S_0)_{\text{total}} = \frac{-S_0(\Omega_p + \Omega_{op}) T_{2p} d^2}{2} \quad (5.12)$$

If $W_N = 0$ (no cross relaxation), then

$$\langle S_z \rangle - S_0 = \frac{-S_0}{W_{12}} T_{2p} d^2 \quad (5.13)$$

This reduces to the familiar result

$$(\langle S_z \rangle - S_0)_{\text{total}} = \frac{-S_0 \gamma^2 \hbar^2 T_{1p} T_{2p}}{2} \quad ,$$

if we made the identification $T_{1p} = 1/2W_{12}$. If we now allow cross relaxation, $W_N \neq 0$, but make $W_{12} = W_{34}$, then

$$(\langle S_z \rangle - S_0)_{\text{total}} = \frac{-S_0^2(2W_N + 2W_{12}) T_{2p} d^2}{4 W_{12}(W_{12} + W_N)} = \frac{-S_0 T_{2p} d^2}{W_{12}} .$$

This is the same result as if there were no cross relaxation. When the saturating power is limited, the opening of a new pathway for saturation by cross relaxation does not necessarily result in more saturation being observed. In this case, where $W_{12} = W_{34}$, the same total saturation is observed, only it is shared between the two spin systems. As W_N increases, the amount of saturation in the spin system which is not being pumped increases, but the total amount of saturation in the two spin systems remains the same. A final interesting limiting case is that of $W_N \gg W_{34}, W_{12}$. Here we have

$$(\langle S_z \rangle - S_0)_{\text{total}} = \frac{-S_0^2 T_{2p} d^2}{(W_{12} + W_{34})} . \quad (5.15)$$

In this limit cross relaxation leads to the measurement of an apparent spin lattice relaxation rate which is an average of the rates of the two transitions involved.

The VO^{2+} case with eight lines is of course more complicated than the four level system, but the effect of cross relaxation on the experimental results can be understood qualitatively on the basis of this model. Cross relaxation makes the measured enhancements reflect a weighted average of the spin lattice relaxation rates of all the lines. The weighting of the average depends on the size of W_N compared to the spin-lattice rates. Clearly if W_N were totally

dominant, the same apparent spin-lattice relaxation rate would be measured no matter which line was saturated. Our measurements do not support this result. Using the pseudo-secular terms of the tumbling theory (Wilson and Kivelson 1966, p. 164), W_N can be calculated. For the $M_I = 1/2$ line $W_N = 1 \times 10^8$. If the residual width and spin-rotation effects are included, W_e for this line is 8×10^7 . In this case cross relaxation is significant, but not overly dominant. Only averaging of relaxation rates with adjacent lines would be significant. W_N becomes even less significant for the outer lines of the VO^{2+} spectrum. The net result is that the spread of the observed T_{1e} 's should be smaller than is predicted by theory. This is qualitatively what is observed.

Cross relaxation should not hinder the use of VO^{2+} as a DNP standard too severely, since the spin-lattice relaxation rates of adjacent lines are very similar. The results of these relative relaxation measurements give enough confidence in the theory to make our use of VO^{2+} as a DNP standard quite reasonable.

8. Copper Ethylenediamine

1. Introduction

Another system for which the EPR linewidths are reasonably well understood is the ethylenediamine complex of copper, $Cu(en)_2(H_2O)_2^{2+}$. DNP measurements on this ion should serve as a good test of the experimental technique. In particular, these measurements should test the usefulness of VO^{2+} as a T_{1e} standard.

$\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ is a d^9 , $S = 1/2$ ion. The abundant isotopes of copper, ^{63}Cu (69 percent natural abundance), and ^{65}Cu (31 percent natural abundance) both have nuclear spin $I = 3/2$. The gyromagnetic ratios of the two isotopes are sufficiently similar that the difference in the hyperfine coupling constants between ^{63}Cu and ^{65}Cu can be neglected for the interpretation of our $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ spectra. Lewis, Alei, and Morgan (1966b) measured the EPR spectra of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ from -10°C to 100°C . The ^{63}Cu hyperfine coupling constant is -87.5 G. The spectrum appears as a partially resolved quartet over this temperature range. The individual hyperfine lines have different widths, suggesting a contribution to the linewidth from the tumbling mechanism proposed by McConnell (1956). The g values differ significantly from the free electron value, so spin-rotation should also contribute substantially to the relaxation. There is also a nitrogen-14 superhyperfine coupling of 11.6 G which cannot be neglected in the interpretation of the spectrum.

Because of the partially resolved nature of the ^{63}Cu hyperfine lines and the existence of the ^{14}N coupling it is not possible to measure the linewidths directly from the spectrum. Lewis, Alei and Morgan extracted the linewidths by comparing the experimental spectra with computer simulations. They also measured the anisotropic spin-Hamiltonian parameters for the complex in frozen glass. They found that the temperature dependence of the difference between the width of the $M_I = -3/2$ line and the $M_I = 3/2$ line could be adequately explained by the tumbling theory if a correlation time of 1.7×10^{-11} sec at

25°C was assumed. After the contribution to the linewidth from tumbling was subtracted, they found that the remaining width could be accounted for by spin-rotation. The application of Eq. (2.8) using their measured values of $g_{\parallel} = 2.209$ and $g_{\perp} = 2.047$ yielded a value for τ_R of 1.4×10^{-11} sec. The temperature dependence of this remaining width was found to be somewhat less than the T/η dependence predicted by Eqs. (2.6) and (2.8). These correlation times estimated from tumbling and spin rotation were in fair agreement with the correlation time determined from the frequency dependence of proton NMR relaxation rates, 2×10^{-11} sec (Morgan, Murphy, and Cox, 1959).

2. Experimental Methods

Solutions of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ were prepared by dissolving weighed amounts of $\text{Cu(en)}_3\text{SO}_4$ (Alfa-Ventron) in distilled water. Both the first and second association constants for Cu^{2+} with ethylenediamine are large ($\log K_1 = 10.72$, $\log K_2 = 9.31$), while the third is small ($\log K_3 = -0.90$) (Bjerrum and Nielson, 1948), so only the $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ species is expected to be present in solution.

DNP of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ was observed in the flowing sample spectrometer described previously. Enhancements were compared with measurements on separate solutions of $\text{VO}(\text{ClO}_4)_2$ at the same temperature and flow rate. Concentrations were adjusted to give approximately the same nuclear spin-lattice relaxation times according to measurements in the literature (Morgan, Murphy and Cox, 1959; Hausser and Laukien (1959)).

3. Results and Discussion

DNP enhancement spectra were determined for $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ at 3, 23, 41 and 59°C. Figures 10 and 11 show these spectra. In order to make use of the data, linecenter enhancements must be extracted. This was done by fitting each spectrum to a function of the form

$$E(H) = \sum_{I=-3/2}^{3/2} \sum_{j=-4}^4 \frac{g(j) T_I}{H \delta_I \left(1 + \frac{(H - H_{0I} - jA)^2}{\delta_I^2} \right)} \quad (5.16)$$

The summation is over the four ^{63}Cu hyperfine lines which are each in turn split into nine superhyperfine lines by the scalar interaction with four equivalent ^{14}N nuclei. H is the magnetic field, and δ_I is the halfwidth at half height of the I th ^{63}Cu line. H_{0I} is the line-center of the I th hyperfine line and A is the ^{14}N superhyperfine coupling constant. All of these parameters are available or calculable from information given by Lewis, Alei and Morgan (1966b). The factor $g(j)$ reflects the intensity of the j th superhyperfine line. The relative intensities for $j = -4$ to 4 are 1/81, 4/81, 10/81, 16/81, 19/81, 16/81, 10/81, 4/81, 1/81. T_I is the number proportional to T_{1e} of the I th hyperfine line. T_I is determined by linear least squares. The fitted functions are the dotted lines in the figures. The fitted values of T_I are turned into enhancements by dividing by $H_0 \delta_I$. Enhancements ranged from 0.19 to 0.06. Uncertainties in these values estimated from the standard deviation of the fit and the inverse normal equation matrix (Shoemaker, Garland and Steinfeld, 1974)

Fig. 10a. DNP spectrum of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ at 3°C .

XBL 827-5973

Fig. 10b. DNP spectrum of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ at 23°C .

Fig. 11a. DNP spectrum of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ at 23°C .

XBL827-5974

Fig. 11b. DNP spectrum of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ at 59°C .

ranged from 0.007 for the largest enhancements to 0.004 for the smallest. Absolute T_{1e} 's were calculated from the relation

$$T_{1e_{\text{meas}}} = \frac{4E_{\text{Cu}}H_{\text{Cu}}\Delta H_{\text{Cu}}\left(\frac{\rho}{\sigma}\right)_{\text{Cu}} T_{1e_{\text{ref}}}}{E_{\text{ref}}H_{\text{ref}}\Delta H_{\text{ref}}\left(\frac{\rho}{\sigma}\right)_{\text{ref}} (2K + 1)}, \quad (5.17)$$

where E_{Cu} , H_{Cu} and ΔH_{Cu} are the linecenter enhancement, linecenter, and linewidth of the 63 Cu hyperfine line. K is the nuclear spin of the reference species. E_{ref} , H_{ref} and ΔH_{ref} are the enhancement, linecenter and linewidth of the reference species. When VO^{2+} is used as a reference $T_{1_{\text{ref}}}$ is calculated from theory using Eqs. (5.1)-(5.5) and (2.8), and spin-Hamiltonian parameters determined by Chang (1971). The parameters σ and ρ were calculated for each species using Eqs. (3.13) and (3.14). The room temperature correlation time for VO^{2+} , which was determined by Chang (1971) from EPR linewidth measurements, 4.6×10^{-11} sec, was used in Eqs. (3.13) and (3.14). The value for $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ determined from NMR relaxation measurements, 2×10^{-11} sec, was used. The correlation times were assumed to vary with viscosity and temperature according to Eq. (2.6).

Figures 12 and 13 compare T_{1e} 's determined in this manner with the T_{2e} measured by Lewis, Alei and Morgan (1968). At room temperature and above T_{1e} is very nearly equal to T_{2e} , with essentially the same temperature dependence. This is reasonable since spin-rotation is expected to dominate the relaxation at these temperatures. Also τ_R for the tumbling interaction is short enough that the tumbling contribution to T_{1e} is close to its limiting value of $7/6 T_{2e}$.

XBL 827-5975

Fig. 12. T_1 and T_2 for the $M_I = 3/2$ line of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$.
 Circles- T_1 determined using VO^{2+} as a standard.
 Squares- T_2 from linewidth measurements of Lewis, Alei
 and Morgan (1966b).

XBL 827-5976

Fig. 13. T_1 and T_2 for the $M_I = -3/2$ line of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$.
 Circles- T_1 determined using VO^{2+} as a standard.
 Squares- T_2 from linewidth measurements of Lewis, Alei and Morgan (1966b).

The measurements at 3°C are disappointing since this is where T_{1e} is expected to differ from T_{2e} , especially for the $M_I = -3/2$ line. For both the $M_I = -3/2$ and $M_I = 3/2$ line the measured T_{1e} is less than T_{2e} by much more than experimental uncertainty. This is of course impossible. This discrepancy is surely due to a systematic error. It is partially due to improper matching of the nuclear spin-lattice relaxation times of the VO^{2+} and $Cu(en)_2(H_2O)_2^{2+}$ solutions, but it is unlikely that this is the only source of this large error. As a check, $Cr(CN)_6^{3-}$ ion was also tried as a standard. The relaxation of $Cr(CN)_6^{3-}$ is discussed in detail later in this work. For $Cr(CN)_6^{3-}$ it proves reasonable to assume $T_{1e} = T_{2e}$ at X-band. Line-width measurements for $Cr(CN)_6^{3-}$ were made by Hayes (1961). The T_{1e} 's using $Cr(CN)_6^{3-}$ as a standard are compared with the T_{2e} 's in Figs. 14 and 15. These measurements compare favorably with those using VO^{2+} as a standard at room temperature and above. These 3° measurements are more in line with theoretical predictions and the linewidth data of Lewis, Alei and Morgan. Within experimental error $T_{1e} = T_{2e}$ for the $M_I = 3/2$ line, while T_{1e} is clearly greater than T_{2e} by more than the experimental uncertainty for the $M_I = -3/2$ line. At 3° the tumbling mechanism contributes much more to T_{2e} than to T_{1e} for the $M_I = -3/2$ line.

Figure 16 shows a plot of $1/T_{1e}$ vs T/n , after $1/T_{1e}$ has been corrected for tumbling. If spin-rotation were the only remaining relaxation mechanism, this plot should extrapolate to zero at $T/n = 0$. This is not the case. If the slope of the line drawn through the

XBL 827-5977

Fig. 14. T_1 and T_2 for the $M_I = 3/2$ line of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$.
 Circles- T_1 determined using Cr(CN)_6^{3-} as a standard.
 Squares- T_2 as in Fig. 12.

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Fig. 15. T_1 and T_2 for the $M_1 = -3/2$ line of $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$.
 Circles- T_1 determined using Cr(CN)_6^{3-} as a standard.
 Squares- T_2 as in Fig. 13.

XBL 827-5979

Fig. 16. $1/T_1$ vs T/η for $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$.

points is used to calculate a hydrodynamic radius the resulting tumbling correlation time at 25°C is found to be 2.1×10^{-11} sec. This agrees better with the correlation time determined from proton relaxation measurements (Morgan, Murphy and Cox, 1959) than if all of the relaxation were considered to be from spin rotation. Obtaining the hydrodynamic radius in this manner is probably not correct, however. The non-zero intercept indicates that there is another relaxation mechanism in operation besides spin-rotation. Surely this mechanism is not temperature independent, so a proper determination of the hydrodynamic radius would require subtracting the effects of this mechanism first. Lewis, Alei and Morgan did not consider any other relaxation mechanisms for this ion, but in similar work on $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ they (Lewis, Alei and Morgan, 1966a) suggested that an additional mechanism could be a Van Vleck Raman relaxation process. Calculations by Kivelson (1966) however, indicate that this mechanism should be negligible in liquids. Elucidation of the additional mechanism or mechanisms might be possible with the aid of more precise linewidth measurements.

The results of the DNP measurements are in reasonable agreement with what would be predicted from theory and the linewidth measurements. The agreement is not, however, as good as would be expected considering the precision with which the DNP enhancements were measured. It does appear that roughly one significant figure can be obtained from DNP T_{1e} measurements. The agreement can be improved by making small corrections in the correlation times used in the σ/ρ

correlations. It seems that the σ/ρ correction is a large contributor to the uncertainty in the T_{1e} values determined from DNP measurements.

C. Manganous Ion

1. Introduction

Manganous ion, Mn^{2+} is a $(3d)^5$ ion. In a weak octahedral crystal field the ground state is the totally symmetric ${}^6A_{1g}$ state. Because of the absence of low lying orbitally excited states ${}^6A_{1g}$ ions usually have observable EPR spectra in solution. Tinkham, Weinstein, and Kip (1951) were the first to observe the EPR spectrum of $Mn(H_2O)_6^{2+}$ in solutions dilute enough to resolve the six ${}^{55}Mn$ ($I = 5/2$, 100 percent abundant) hyperfine lines. The six lines have different widths. At first this would suggest a McConnell (1956) tumbling contribution to the linewidth. However, both the g and A tensors are isotropic for the ${}^6A_{1g}$ state. This rules out such a tumbling mechanism for this ion.

The spectrum of the $S = 5/2$, $I = 5/2$ ion should consist of thirty transitions allowed by the $\Delta M_S = 1$, $\Delta M_I = 0$ selection rule. The Hamiltonian for the system in solution is $\mathcal{H} = gBH_S_z + AS I$. To first-order the energy of each of the five $\Delta M_S = 1$ transitions is $gBH + AM_I$, which is independent of M_S . Thus each hyperfine line would consist of a sum of five lines at the same field, one for each $\Delta M_S = 1$ transition. In second and higher orders, however, the hyperfine interaction splits apart the $\Delta M_S = 1$ transitions. Each of the six $\Delta M_I = 0$ hyperfine lines consists of five $\Delta M_S = 1$ transitions which are split by the higher order hyperfine interaction. They are un-

resolved because the splitting is less than the linewidths of the lines. The amount of splitting depends on M_I , therefore each of the hyperfine lines experiences a different amount of inhomogeneous broadening. This situation tends to complicate both the experimental and theoretical interpretation of the relaxation of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$.

Most models of relaxation for Mn^{2+} in solution consider the dominant mechanism to be fluctuations in an instantaneous quadratic zero-field splitting. Most other mechanisms can be neglected. Tunneling has already been discounted. The g value for Mn^{2+} is very close to the free electron value, so spin-rotation is not likely as a source of relaxation. The octahedral $S = 5/2$ ions have quartic zero-field terms in their spin Hamiltonian which are given by (Coster and Statz, 1959)

$$\mathcal{H} = \frac{a}{6} \left[S_a^4 + S_b^4 + S_c^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1) \right] \quad .$$

S_a , S_b , and S_c represent spin operators in a molecular coordinate system. The fine structure parameter, a , is a function of the crystal field potential. Rotational modulation of this Hamiltonian can induce relaxation, but Luckhurst (1972) has calculated that its contribution should be negligible for Mn^{2+} . This leaves fluctuations of the quadratic zero-field splitting as the most likely mechanism of relaxation.

Much of the theoretical and experimental work pertaining to Mn^{2+} has been reviewed by Burlamacchi et al. (1978). A few examples of

previous work will be discussed here to provide a proper background for the discussion of DNP measurements on $\text{Mn}(\text{H}_2\text{O})_6^{2+}$.

Garrett and Morgan (1966) used Redfield (1957) theory to calculate linewidths for Mn^{2+} . They assumed that relaxation was due to instantaneous fluctuations in the quadratic zero-field splitting. They calculated relaxation coefficients $R_{\kappa\kappa',\lambda\lambda'}$ according to Eq. (2.12). They neglected off-diagonal elements in the relaxation matrix. This treatment led to the conclusion that there were three distinct T_{1e} 's and three T_{2e} 's for Mn^{2+} , even in the case of extreme narrowing. They found that in the case of extreme narrowing

$$\left[\frac{1}{T_2} \right]_{3/2,5/2} = \left[\frac{1}{T_2} \right]_{-5/2,-3/2} = 2.14 Z(0)$$

$$\left[\frac{1}{T_2} \right]_{1/2,3/2} = \left[\frac{1}{T_2} \right]_{-3/2,-1/2} = 1.89 Z(0)$$

$$\left[\frac{1}{T_2} \right]_{-1/2,1/2} = 1.53 Z(0)$$

where

$$Z(0) = \frac{32}{5} \langle D^2 \rangle ,$$

and where $\langle D^2 \rangle$ is the average of the square of the ZFS tensor.

Using line positions calculated from perturbation theory (Hurd, Sachs, and Hershberger, 1954) and the relative linewidth information, they were able to simulate the experimental lineshape with moderate success.

Levanan and Luz (1968) found that it was not possible to fit the most inhomogeneously broadened lines of Mn^{2+} using the methods of Garrett and Morgan. They felt that this was due to the separated line approximation used by Garrett and Morgan in developing their theory. Rubinstein, Barum and Luz (1971) did the relaxation calculation assuming that each hyperfine line consisted of five superimposed lines. Under these conditions it is permissible to diagonalize the relaxation matrix formed from Eq. (2.12). They found that only a single T_{1e} and T_{2e} were important over a wide range of ω_{TC} . From a consideration of proton spin-spin and spin-lattice relaxation times measured from 10-100 MHz, T_{1e} could be determined and Δ^2 and τ could be estimated. The parameter Δ is given by Eq. (2.17). They found $\tau = 3.2 \times 10^{-12}$ s at 30°C and $\Delta = 0.014 \text{ cm}^{-1}$. However, when these numbers were used to calculate the X-band linewidth, the value calculated was found to underestimate the linewidth by a factor of two.

Luckhurst and Pedulli (1971) felt that the failure of Garrett and Morgan and Rubinstein, Barum and Luz to properly predict lineshapes of Mn^{2+} spectra was due to improper treatment of the overlapping lines. Since the five transitions of each Mn^{2+} hyperfine line were neither superimposed nor well separated, they felt an intermediate treatment of the problem was necessary. Luckhurst and Pedulli used a more general theory of magnetic resonance lineshapes (Binch, 1968) to simulate Mn^{2+} spectra. This method involves calculation of the lineshape function, $L(\omega)$, where

$$L(\omega) = -\text{Re}[\sum_{\alpha} \underline{M}_0^{-1} \underline{\sigma}]$$

$\underline{S}_-$ is the vector composed of matrix elements $\langle \kappa | S_- | \kappa' \rangle$, of S_- and σ is given by

$$\sigma \approx \langle \kappa | S_- | \kappa' \rangle (\rho_{\kappa\kappa} - \rho_{\kappa'\kappa'})$$

where $\rho_{\kappa\kappa} - \rho_{\kappa'\kappa'}$ are the difference in the diagonal elements of the density matrix for the system. The matrix M_0 is given by

$$M_{0\kappa\kappa',\lambda\lambda'} = i(\omega_{\kappa\kappa'} - \omega) \delta_{\kappa\lambda} \delta_{\kappa'\lambda'} + R_{\kappa\kappa',\lambda\lambda'},$$

where $R_{\kappa\kappa',\lambda\lambda'}$ is an element of the relaxation matrix calculated from Eq. (2.12) and $\omega_{\kappa\kappa'}$ is the resonant frequency for the transition from $\kappa' \rightarrow \kappa$. When all the $\omega_{\kappa\kappa'}$'s are equal this method is equivalent to that employed by Rubinstein, Borum and Luz (1971). When the lines are well separated it reduces to the method used by Garrett and Morgan (1966). Luckhurst and Pedulli calculated the relaxation matrix for fluctuations in the quadratic term of the zero-field splitting. They were able to simulate the spectrum of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ at 90°C with excellent agreement using $\Delta \approx 690$ MHz and $\tau = 1.18 \times 10^{-12}$ s. They also determined the resonant frequencies by numerical diagonalization of the static Hamiltonian matrix, which probably aided in the excellent agreement between experiment and simulation. They felt that this agreement confirmed that the major relaxation process for Mn^{2+} is fluctuation in the quadratic zero-field splitting terms.

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$$L(\omega) = -\text{Re}[S_{\underline{M}_0}^{-1}g] \quad .$$

$\underline{S}_-$ is the vector composed of matrix elements $\langle \kappa | S_- | \kappa' \rangle$, of S_- and σ is given by

$$\underline{g} = \langle \kappa | S_- | \kappa' \rangle (\rho_{\kappa\kappa} - \rho_{\kappa'\kappa'})$$

where $\rho_{\kappa\kappa} - \rho_{\kappa'\kappa'}$ are the difference in the diagonal elements of the density matrix for the system. The matrix M_0 is given by

$$M_{0\kappa\kappa',\lambda\lambda} = i(\omega_{\kappa\kappa'} - \omega) \delta_{\kappa\lambda} \delta_{\kappa'\lambda} + R_{\kappa\kappa',\lambda\lambda},$$

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Mn^{2+} ion was also the subject of early DNP work. Measurements in a field of 5 G on an aqueous solution of $MnCl_2$ (Codrington and Bloembergen, 1958) showed an increase in the intensity of the proton NMR signal when the electronic transition was saturated. This was an indication of the dominance of the scalar contribution to the spin lattice relaxation time of the protons at 5 G. Kul'bada (1964) measured the temperature dependence of the DNP of aqueous Mn^{2+} at 80 G. He found that the sign of the enhancement changed at $60^\circ C$, indicating a switch in the importance of the electron-nuclear coupling from dipolar to scalar.

At the magnetic field used in this work, DNP is dominated by the dipolar interaction. Proper treatment of DNP data should lead to reasonable estimates of T_{1e} for $Mn(H_2O)_6^{2+}$. Since previous work on the lineshape of Mn^{2+} seems to confirm that the dominant mechanism of relaxation is fluctuations in the quadratic zero-field splitting, measurements of T_{1e} are not likely to contribute a great deal more to the understanding of the mechanism. However, T_{1e} measurements should confirm that relaxation occurs through a mechanism with a correlation time short enough that $\omega\tau_c \ll 1$. If τ_c is $\sim 10^{-12}$ sec then at X-band with $\omega_e \sim 6 \times 10^{10}$ it should be found that $T_{1e} = T_{2e}$. The DNP results should also be interesting as a direct measurement of T_{1e} to compare with the results of NMR relaxation measurements on aqueous Mn^{2+} solutions.

2. Experimental

Solutions of Mn^{2+} ions were prepared from $Mn(ClO_4)_2 \cdot 6H_2O$ (G. Frederic Smith). The perchlorate salt was used to avoid large

anion effects on the Mn^{2+} relaxation (Hayes and Myers, 1964). The concentration was adjusted according to proton T_1 measurements (Morgan and Nolle, 1959) to insure that nuclear T_1 values of the Mn^{2+} solution were approximately the same as the nuclear T_1 values of the VO^{2+} reference solution. DNP measurements were made in the flowing sample spectrometer described earlier with 15 W of incident microwave power.

3. Results and Discussion

Linecenter enhancements were measured for the $M_I = 1/2$ line of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ at 3, 23, 41, and 59°C. These enhancements are listed in Table II. The values given have been corrected for overlap of adjacent hyperfine lines. The values of T_{je} calculated from these enhancements are also given in Table II. The calculation was made according to Eq. (5.17) with the proper correction factor for the number of Mn^{2+} hyperfine lines. The correlation time for the σ/ρ corrections were based on the value from proton NMR relaxation measurements (Morgan and Nolle, 1959), 3.1×10^{-11} sec at 27°C. Linewidths for Mn^{2+} were interpolated from measurements by Hayes (1961). This treatment of the data assumes that the $M_I = 1/2$ line is a single lorentzian, which the preceding discussion made clear is not quite the case. However, for this line perturbation theory predicts that the largest separation between linecenters of the unresolved lines is 5.4 G. Even at 59°C the peak-to-peak linewidth is 12.2 G., more than twice the splitting. At lower temperatures the linewidths are larger. There is little to be gained from simulating lineshapes of enhancement

Table II. DNP Results for Mn^{2+}

$T^{\circ}\text{C}$	E	ΔH_{pp}^a (G)	T_{1e}^b (sec)
3°	0.049	35	1.7×10^{-9}
23	0.136	22.2	2.8×10^{-9}
41	0.464	16.6	5.0×10^{-9}
59	0.909	12.2	5.9×10^{-9}

^a From Hayes (1961)^b From DNP (this work)

spectra at these temperatures. The experimental precision does not permit the assignment of separate T_{1e} 's for lines which are this poorly resolved. The treatment of the $M_I = 1/2$ line as a single line is the best that can be done with the data at hand.

The calculated T_{1e} values are compared in Fig. 17 with T_{2e} values which were calculated from the linewidth under the same assumption of a single lorentzian line. The values of T_{1e} and T_{2e} agree reasonably well with each other. This is not surprising since they were determined using the same assumptions, and at X-band $\omega\tau = 0.03$ for $\tau = 3.2 \times 10^{-12}$ sec (Rubinstein, Barum, and Luz, 1971).

The measured T_{1e} at 23°, which is 2.8×10^{-9} sec, does not agree well with the value, 9.4×10^{-9} sec determined by Rubinstein, Barum and Luz (1971) from proton relaxation data at 30°C. There is reasonable agreement between the value measured from DNP and the value determined from best fits to temperature dependent relaxation data for protons, 3.5×10^{-9} sec (Bloembergen and Morgan, 1961) and 170 , 3.8×10^{-9} sec (Swift and Connick, 1962). The value determined by Rubinstein et al. is based on a measurement of the scalar coupling constant between the electrons and protons from the chemical shift of the protons in Mn^{2+} solution (Luz and Shulman, 1965). The value for the superhyperfine coupling constant which they used, 6.2×10^5 Hz, is less than the values determined from best fits to temperature dependences of proton relaxation in Mn^{2+} solution (1×10^6 Hz by Bloembergen and Morgan, 1961 and $0.70 \pm 0.03 \times 10^6$ Hz by Sprinz, 1967). Electron-nuclear double resonance measurements on crystals of $La_2(Mg, Mn)_3(NO_3)_{12} \cdot 24 H_2O$ (Van Ormondt, et al. 1969), which contains

XBL 827-5980

Fig. 17. T_1 and T_2 for Mn^{2+} . Circles- T_1 from DNP. Squares- T_2 from linewidth measurements (Hayes, 1961).

the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ entity, give a superhyperfine coupling constant of 0.80×10^6 Hz. T_{1e} was determined by Rubinstein et al. from the expression

$$\frac{1}{T_{2c}} = \frac{A^2 S(S+1) \tau_e}{3}$$

where T_{2c} is the proton spin-spin relaxation time corrected for the dipolar contribution. A is the electron-proton superhyperfine coupling constant and S is the total electronic spin. The electron spin-exchange correlation time, τ_e is given by

$$\frac{1}{\tau_e} = \frac{1}{\tau_h} + \frac{1}{T_{1e}},$$

where τ_h is the lifetime of a proton in the first coordination sphere of Mn^{2+} . The measured value of T_{1e} determined from this method varies with A^{-2} . If the value of A were 0.80×10^6 Hz then the value of T_{1e} calculated in this manner would be 4.0×10^{-9} sec, which is much closer to the value determined from direct linewidth measurements and the DNP measurements of this work. Thus, if allowance for possible uncertainty in the value of A is made, the values of T_{1e} determined from NMR measurements do not differ too significantly from those using DNP and treating the $M_I = 1/2$ line as a single line. It appears that the more sophisticated lineshape treatment employed by Luckhurst and Pedulli (1971) is not necessary except at high temperatures where the inhomogeneities contribute a significant portion to the linewidth of the $M_I = 1/2$ line.

VI. Moving Sample Spectrometer

A. Introduction

The flowing sample DNP spectrometer described earlier has a number of drawbacks to its operation. Most importantly, the flow system requires 150–200 ml of solution, which makes sample preparation inconvenient at best and impossible for expensive chemicals or isotopically substituted material. Also, the requirement that enhancements can only be compared between solutions of approximately the same T_{1n} makes sample preparation and analysis important and occasionally makes it necessary to extrapolate T_{1n} information from theory when measured values at the desired frequency and temperature are not available from the literature. Finally, the resolution of the NMR spectrometer is limited by the lifetime of the flowing sample in the coil. This is important if DNP on solvents with more than one type of proton is to be observed.

These drawbacks can be overcome by changing to a moving sample spectrometer. The NMR coil is still located outside of the microwave cavity, but in this case after DNP is induced by a pulse of microwave power, the entire sample tube is moved by a pulse of compressed air. Polarized nuclei from within the cavity are moved to the NMR coil rapidly enough to allow observation of the enhancement before it can decay away. Less than 0.2 ml of solution is required for this experimental arrangement, allowing DNP experiments on a wider range of materials. The details of the moving sample spectrometer are described in this section.

B. Sample Arrangement

A diagram of the sample arrangement is shown in Fig. 18. The samples are sealed in standard melting point tubes of 1.5-1.8 mm o.d. Sealing can be accomplished a number of ways. If high temperatures are not reached a simple paraffin plug is acceptable. For higher temperature work tubes can be sealed by inserting a nylon plug which is coated with epoxy. Tubes can also be sealed by inserting a low viscosity potting resin, Ecosseal W-19 (Emerson and Cuming Inc., Technical Bulletin 2-2-7) with a syringe. All of the sealing methods leave the exterior of the sample tube unchanged in order to allow unimpeded motion of the tube. The sample tube fits inside of a 3 mm o.d. standard glass tube which runs through a cylindrical TE₀₁₁ X-band microwave cavity. This tube arrangement is surrounded by a quartz Dewar through which a temperature controlled gas can be flowed. Temperature is controlled by the feedback system shown in Fig. 19. Temperature can be monitored by a thermocouple placed down the dewar near the sample. The outer glass tube is sealed to an aluminum tube which is threaded to accept a screw containing the upper stop wire. The lower stop wire is supported by the tee which also serves as the inlet for the compressed air. The NMR coil is wrapped around the 3 mm tube just outside the microwave cavity. The stops are positioned to enable the portion of the sample from the center of the cavity to move inside of the NMR coil when the compressed air is turned on. Since the important part of the microwave magnetic field distribution is given by Eq. (4.3), H_1^2 is the largest at the center of the cavity. Errors in positioning the stops would result in less

XBL 827-5981

Fig. 18. The cavity arrangement for the moving sample tube spectrometer.

XBL 827-5982

Fig. 19. A simple temperature controller.

than optimum enhancements. After the NMR spectrum is acquired, the compressed air is turned off and the sample tube is allowed to drop by gravity.

The compressed air is controlled by a small commercial 120V, 60 Hz two way solenoid valve from Allied Control Company. The valve is opened and closed on computer command through an International Rectifier D1210 solid state relay. The valve vents to the room when it is off, allowing the sample to drop to the lower stop when the compressed air is turned off. The sample tube reaches the upper stop within 40 ms after the move command is given, when the driving air pressure is 35 psig. About one half of the 40 ms is due to switching delay in the relay and solenoid, and a pressure propagation delay from the solenoid valve to the sample. The rest of the 40 ms is spent in the actual motion of the sample tube.

C. Microwave Power

The microwave power system is essentially the same as the one used for the flowing sample spectrometer. The V-58C klystron provides drive for the Varian VA-618M traveling wave tube. The microwaves are pulsed on and off under computer control by the Hewlett-Packard 8735B PIN modulator. The microwave frequency and power level can be adjusted by observing incident and reflected power with crystals while the microwaves are pulsed on and off at a low duty cycle to avoid heating the sample excessively.

The cavity is a right circular cylinder of length 2.9 cm and diameter 4.9 cm. These dimensions allow a 9 cm capillary to rest with solution simultaneously in the microwave cavity and the NMR coil.

This makes simultaneous tuning of the microwave and NMR system possible without having to move the sample with the compressed air.

D. NMR Spectrometer

The requirement that the NMR polarization be measured as soon as possible after the microwaves are turned off makes a pulse spectrometer necessary for this experimental arrangement. The block diagram of the spectrometer constructed for this purpose is shown in Fig. 20.

Radio frequency pulses are generated by switching the output from a General Radio GR-1164A synthesizer using two mini-circuits SRA-1 double-balanced mixers in series. The switching pulses are provided from an Intercontinental Instruments PG-2 pulse generator on computer command. The r.f. pulses are amplified by a Boonton 230 power amplifier. The receiving coil is made of 10 turns of #28 wire wrapped around the 3 mm tube. A set of tuning and matching capacitors allows operation from 11-17 MHz. The pre-amp is protected by a set of crossed IN914B diodes to ground following a quarter wavelength cable. The pre-amp is isolated from the transmitter by 5 pairs of IN 914B crossed diodes in series. The radio frequency amplification of the signal is provided by two Watkins-Johnson thin film amplifiers, followed by a Motorola MWA 320 and an Anzac AM-105. This collection delivers 61 dB of gain. The signal is mixed with some of the r.f. from the synthesizer in an Hewlett-Packard 10534A mixer. The signal from the mixer is amplified by a LH0044C to give a few volts of signal with a bandwidth of about 1 KHz. Free induction decays are acquired by an Analog Devices ADC1002 12 bit analog to digital converter, which is interfaced to a PDP-8I computer.

XBL 827-5983

Fig. 20. Block diagram of the pulse NMR spectrometer used in moving sample tube DNP measurements.

The Fourier transforms of the free induction decays are desired to discriminate between signals from non-equivalent nuclei and to preserve phase information in order to tell if enhancements are positive or negative. Software was written to support a commercially available Fast Fourier Transform subroutine (Digital Equipment Corporation Users Society, 8-143) for the PDP-8I. Transformed spectra are displayed on a Tektronix 611 storage oscilloscope. The computer is used to calculate and average intensities as was done in the case of the CW spectrometer described previously.

The magnetic field is supplied by the same equipment as the CW spectrometer. The instability of the magnetic field precludes the averaging of free induction decays, but it is small enough to allow averaging of intensities of successive transformed spectra.

E. Experimental Timing

Timing for a DNP experiment is controlled by the PDP 8I. The timing for a typical experiment is shown in Fig. 21.

First, the microwaves are turned on. Because it is at least 20 ms after the move command is given before the sample begins to move, the move command is given 20 ms before the microwaves are turned off. A delay of at least 20 ms more is taken to allow the sample to travel to the upper position. After this delay the radio frequency pulse is applied and the free induction decay is acquired.

After the NMR is acquired the air is turned off and the sample falls back to its initial position. The computer then computes the Fourier Transform and signal intensities, and displays the spectrum. This cycle is repeated with the microwaves alternately on and off.

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Fig. 21. Timing diagram for a typical moving sample tube DNP experiment.

The microwave pulse length is limited to control the temperature rise, but a 70 ms pulse still results in approximately 1.5°C of temperature rise. The computing time between cycles (3-4 sec to transform and phase 1000 points) allows for some thermal recovery of the sample, but successive cycles are usually limited to five to prevent a large cumulative temperature rise.

Using the definition of specific enhancement given in Eq. (3.3), the enhancement observed by this technique is

$$E_{\text{observed}} = E_{\infty} (1 - e^{-t_m/T_{1n}}) e^{-t_d/T_{1n}}, \quad (6.1)$$

where E_{∞} is the enhancement for an infinitely long microwave pulse with no delay before NMR measurement, t_m is the length of the microwave pulse and t_d is the delay before observation of the NMR. Since the length of the microwave pulse is limited by heating effects and the delay is limited by the transit time of the sample, T_{1n} must be adjusted favorably for enhancement to be observed. Usually T_{1n} can be adjusted by changing the concentration of the paramagnetic species. For $t_m \approx 70$ ms and $t_d \approx 20$ ms a T_{1n} of 45 ms is optimum. By holding the microwave pulse length constant and varying the delay time, T_{1n} may be measured, since then

$$E_{\text{observed}} = E_{\text{no delay}} e^{-t_d/T_{1n}}.$$

An example of such a measurement is shown in Fig. 22a. When T_{1n} is known, Eq. (6.1) can be used to calculate E . Thus as long as enhancement can be observed with sufficient signal to noise to measure T_{1n} , matching T_{1n} 's between samples is not necessary, and neither are extrapolations of T_{1n} 's from the literature. Alternatively, the delay time could be held constant and the microwave pulse length varied, to give

$$E_{\text{observed}} = E_{\text{delay}}(1 - e^{-t_m/T_{1n}})$$

as shown in Fig. 22b, but this is less practical since the data from long pulse lengths are likely to be inaccurate from heating effects.

F. Estimates of $\langle H_1^2 \rangle_s$

One of the primary reasons to have a moving sample spectrometer is to keep the NMR coil outside of the microwave cavity in order to maximize $\langle H_1^2 \rangle_s$. It is interesting to make some estimates of $\langle H_1^2 \rangle_s$ for this experimental arrangement.

Poole (1967) gives expressions for $\langle H_1^2 \rangle_s$ as a function of a number of experimental parameters. Assuming that the only effect of placing the sample in the cavity is to lower the quality factor, Q , of the cavity, Poole finds

$$\langle H_1^2 \rangle_s = 2 \times 10^{-3} P_{\omega} Q_L n(V_{\omega}/V_L) \quad (6.2)$$

where P_{ω} is the incident power in watts and Q_L is the quality factor of the loaded cavity. V_{ω} is the volume of the section of

Fig. 22a. Enhancement vs delay time for 0.05 M $\text{Cr}(\text{CN})_6^{3-}$. The dotted line is a fit to $E = E_0 e^{-(t_d/T_{1n})}$ with $T_{1n} = 27.1 \pm 0.5$ msec.

XBL 827-5985

Fig. 22b. Enhancement vs microwave pulse length for methyl protons of CH_3OD doped with Cu^{2+} . The dotted line is a fit of the form $E = E_\infty(1 - e^{-(t_m/T_{1n})})$.

waveguide one guide wavelength long, and V_s is the volume of the sample. The filling factor η is defined

$$\eta = \frac{\int_{\text{sample}} H_1^2 dV}{\int_{\text{cavity}} H_1^2 dV} .$$

For this cavity and sample geometry

$$\eta = \frac{12.33}{1 + (0.82a/d)^2} \frac{V_s}{V_c} , \quad (6.3)$$

where a is the cavity radius and d is its length. V_c is the volume of the cavity. Q_L for a sample at room temperature is approximately 800. V_w is 10.6 cm^3 at 9.1 GHz. The effective volume of the sample is that portion which the NMR coil would enclose. Since the length of the coil is 0.5 cm, $V_s \approx 8.8 \times 10^{-3} \text{ cm}^3$. Insertion of these values and the cavity dimension into Eqs. (6.2) and (5.3) yields $\langle H_1^2 \rangle_s = 38 \text{ G}^2$ for 14 W of incident power which is critically coupled to the cavity.

Figure 23 shows an enhancement spectrum of a $<9 \times 10^{-3} \text{ M}$ solution of peroxyamine disulphonate dianion in 10 percent Na_2CO_3 solution which was taken with 14 W of power. Peroxyamine disulphonate gives rise to a well known EPR triplet with relatively narrow linewidths. The peak to peak derivative linewidth of this solution was measured to be 0.5 G on a Varian V4502 X-Band EPR spectrometer. The width of the

XBL 827-5966

Fig. 23. The enhancement spectrum of peroxylamine disulphonate dianion taken with 14 W of microwave power. The dotted line is a simulation according to Eq. (5.4) with $\gamma^2 H_1^2 T_1 T_2 = 65$.

lines in the enhancement spectrum are considerably larger because of the high degree of saturation. According to Eq. (3.32)

$$E = -\frac{\sigma S_0}{\sigma I_0} \sum_{I=-1}^1 \frac{\gamma_e^2 H_1^2 T_{1e} T_{2e}}{1 + (\omega - \omega_I) T_{2e}^2 + \gamma_e^2 H_1^2 T_{1e} T_{2e}} .$$

Using the value of T_{2e} from the low power EPR spectrum the data can be fitted to a reasonable extent with $\gamma_e^2 H_1^2 T_{1e} T_{2e} = 65$. If it is assumed $T_{1e} = T_{2e}$ an upper bound for $\langle H_1^2 \rangle_s$ can be calculated to be 12.4 G^2 . This compares to $\langle H_1^2 \rangle_s = 0.16 \text{ G}^2$ for 6 W of incident power for an X-band DNP spectrometer described by Kramer, Mueller-Warmouth and Schindler (1965), which had the NMR coil inside of the cavity.

The agreement between the calculated and measured value of $\langle H_1^2 \rangle_s$ is about as good as can be expected considering that the theory neglected the effects of the sample on the field and the fact that the experiment was not done under conditions of a perfect match of the cavity to the waveguide.

If we accept the measured estimate of $\langle H_1^2 \rangle_s = 12.4 \text{ G}$, and 0.01 as the smallest enhancement which can be reliably measured, then it is possible to calculate the minimum possible T_{1e} which can be detected with this apparatus. Using Eq. (3.33) and assuming $T_{1e} = T_{2e}$ and $\sigma/\rho = 1/2$, we find that the minimum detectable T_{1e} would be $9 \times 10^{-11} \text{ sec}$. In practice this value should be increased by a factor of two, because with standard experimental values of $t_m = 70 \text{ ms}$, $t_d = 20 \text{ ms}$ and $T_{1n} = 45 \text{ ms}$, Eq. (6.1) gives $E_{(\text{observed})} \approx E/2$.

VII. Moving Sample Tube Results

A. Hexacyano-Chromium (III) Ion1. Introduction

Hexacyano-chromium (III) ion, $\text{Cr}(\text{CN})_6^{3-}$, is one of the many cubic complexes of Cr^{3+} which has an easily observable EPR spectrum at room temperature in aqueous solution. Of these complexes, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{CN})_6^{3-}$ have received the most experimental attention.

Avvarakumov et al. (1960) observed the EPR spectrum of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ as a function of temperature. They found a single line of 220 G at room temperature. Similar results were found by Hayes (1961). Both workers found that the linewidth decreased with increasing temperature. Hayes also measured the linewidth of $\text{Cr}(\text{CN})_6^{3-}$ as a function of temperature at both X-band (9 GHz) and S-band (3 GHz). The room temperature width of the $\text{Cr}(\text{CN})_6^{3-}$ line was 25 G at X-band. Since DNP enhancements are proportional to the $T_{1e}T_{2e}$ product, the enhancement from $\text{Cr}(\text{CN})_6^{3-}$ would be nearly two orders of magnitude larger than that from $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ if the relative T_{1e} of the two ions were similar to the relative T_{2e} . Indeed, the enhancement expected from a line the width of the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ line begins to approach the limits of detectability with the present DNP apparatus. Consequently DNP measurements were made only on $\text{Cr}(\text{CN})_6^{3-}$.

The electronic spin relaxation for $\text{Cr}(\text{CN})_6^{3-}$ and all of the cubic Cr^{3+} complexes has generally been attributed to fluctuations in the quadratic zero-field splitting. For $S = 3/2$ ions such as these, this mechanism yields the results of Eqs. (3.13)-(3.16) for the

appropriate relaxation times. In the limit $\omega^2 \tau_c^2 \ll 1$ these equations lead to a single lorentzian line with a single T_{1e} . When $\omega^2 \tau_c^2 \gg 1$, Eq. (2.13) predicts that one of the transitions will broaden away. In this limit the apparent intensity should reduce to 2/5 of its value when $\omega^2 \tau_c^2 \ll 1$, as the broadened line disappears into the noise.

Experimental work on both $\text{Cr}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ shows similarity in their relaxation behavior which is consistent with the above mechanism. Hayes found that the linewidths of $\text{Cr}(\text{CN})_6^{3-}$ did not change significantly on going from S-band to X-band. He also found that over the temperature range of 7–60°C the decrease in linewidth with temperature could be fit with an activation energy of 2.6 kcal/mole. The S-band linewidth of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, 188 G at 26°C (McCain, 1966) is in only moderate agreement with the room temperature X-band measurements of Kozyrev (1960) and Hayes (1961), although this difference may be due to different anions used by the various workers. McCain used $\text{Cr}(\text{ClO}_4)_3$. The room temperature X-band width of $\text{Cr}(\text{ClO}_4)_3$ solutions measured by Levanon, Charbinsky and Luz (1970) was 160 G. These workers also found that the decrease of the linewidth with temperature for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was consistent with an activation energy of about 2 kcal/mole. The small change in the linewidths of both ions on going from S-band to X-band indicates $\tau_c < 10^{-11}$ sec. This is consistent with a mechanism involving fluctuations in the second coordination sphere which would affect the instantaneous zero-field splitting.

Levanon, Charbinsky and Luz extended linewidth measurements on Cr^{3+} complexes to Q-band (35 GHz). The linewidth of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ changed

from 160 G at X-band to 72 G at Q band. This allowed them to use Eqs. (2.13) and (2.14) to estimate Δ and τ_c . They found $\tau_c = 4.9 \times 10^{-12}$ sec and $\Delta = 0.087 \text{ cm}^{-1}$. This value of Δ is of the same order of values of Δ found in solid complexes of Cr^{3+} (McGarvey, 1966). They also added glycerol to solutions of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with the intent of increasing viscosities and correlation times. They found that the apparent intensity decreased with increasing mole fraction of glycerol until it reached a limiting value of 2/5 of its original intensity. This is as predicted by Eqs. (2.13) and (2.14). Similar measurements on $\text{Cr}(\text{CN})_6^{3-}$ proved somewhat different. On going from X-band to Q-band the linewidth went from 23 G to 25 G, which is essentially no change. This implies $\tau_c < 1 \times 10^{-12}$ sec. They felt the relaxation of $\text{Cr}(\text{CN})_6^{3-}$ must be controlled by weaker and more rapid fluctuations than are operative in $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

If $\tau_c < 1 \times 10^{-12}$ sec then surely $T_{1e} = T_{2e}$ at X-band for $\text{Cr}(\text{CN})_6^{3-}$. For this reason $\text{Cr}(\text{CN})_6^{3-}$ ion is attractive as a T_{1e} standard. The abundant isotope of chromium, ^{52}Cr , has zero nuclear spin and 90.5 percent natural abundance. ^{53}Cr ($I = 3/2$) is only 9.5 abundant. The hyperfine structure from ^{53}Cr is not resolved in $\text{Cr}(\text{CN})_6^{3-}$. Its contribution to the DNP can be neglected for most purposes. Hence, in $\text{Cr}(\text{CN})_6^{3-}$ there exists a possible DNP standard which is not complicated by fine-structure or hyperfine structure. While T_{1e} for $\text{Cr}(\text{CN})_6^{3-}$ cannot be calculated from measured spin Hamiltonian parameters in the sense that the VO^{2+} T_{1e} can, T_{2e} for $\text{Cr}(\text{CN})_6^{3-}$ is available from an EPR linewidth measurement. It is likely that T_{1e} can be determined for

$\text{Cr}(\text{CN})_6^{3-}$ more accurately from linewidth measurements than T_{1e} can be calculated from theory for VO^{2+} . DNP measurements on $\text{Cr}(\text{CN})_6^{3-}$ should serve as a test of the consistency of the method.

2. Experimental

Solutions containing $\text{Cr}(\text{CN})_6^{3-}$ were made by dissolving weighed amounts of $\text{K}_3\text{Cr}(\text{CN})_6$ (Pfaltz and Bauer) in distilled water. DNP enhancements were measured in the moving sample tube spectrometer described earlier. At each temperature the enhancement of a VO^{2+} standard was also measured. Initially VOSO_4 solutions were used. Later enhancement measurements of VOSO_4 solutions vs $\text{VO}(\text{ClO}_4)_2$ solutions showed significant differences between perchlorate and sulfate solutions. Enhancements were renormalized to allow comparison of $\text{Cr}(\text{CN})_6^{3-}$ data with $\text{VO}(\text{ClO}_4)_2$ data.

Solutions for mixed solvent work were made by first preparing a solution of the paramagnetic ion in H_2O or D_2O , then diluting with the other solvent to the desired volume. Reagent grade di-methyl-sulfoxide (DMSO), acetonitrile, and methanol were used in mixed solvent studies. Linewidths for the mixed solvent studies were measured with a Varian V-4502 EPR spectrometer on samples in standard capillary tubes.

3. Results and Discussion

T_{1e} values for $\text{Cr}(\text{CN})_6^{3-}$ were calculated from measured enhancements according to an equation similar to Eq. (5.17), with the proper correction for the absence of hyperfine lines. Linewidths for $\text{Cr}(\text{CN})_6^{3-}$ were taken from measurements by Hayes (1961).

The σ/ρ corrections prove interesting for this ion. If no σ/ρ correction is made, the resulting values of T_{1e} are plotted in Fig. 24. It is found that generally $T_{1e} \neq T_{2e}$ and that the temperature dependence of T_{1e} is somewhat different from T_{2e} . This is contrary to the expectations of theory. Clearly a σ/ρ correction must be necessary. However, assumption of a rotational modulation of the dipolar interaction to make the σ/ρ correction for $\text{Cr}(\text{CN})_6^{3-}$ would require an unreasonably short rotational correlation time for $\text{Cr}(\text{CN})_6^{3-}$ in order to make the data approach theoretical expectations.

Guenther and Pfeifer (1964) found that the frequency dependence of proton spin-lattice relaxation in aqueous solutions of $\text{Cr}(\text{CN})_6^{3-}$ could be best fit by translational modulation of the dipolar interaction. Using the best fit value of τ_d from their measurements, τ_d (21°C) = 3.3×10^{-11} sec, and Eqs. (3.16) and (3.17), a proper σ/ρ correction leads to the T_{1e} values plotted in Fig. 25. With this correction, the experimentally measured T_{1e} 's and the theoretical expectation that $T_{1e} = T_{2e}$ are in reasonable agreement.

The idea that the interaction between the electrons of $\text{Cr}(\text{CN})_6^{3-}$ and the solvent protons is governed by translational motion is not too surprising. Since the paramagnetic center is completely surrounded by CN^- ligands, the only interactions possible between the solvent and paramagnetic ion are through the second and higher coordination spheres. It is reasonable to expect that the lifetime of a proton in the second coordination sphere of the chromium ion is less than the correlation time for the second sphere complex to tumble as a whole,

XBL 827-5987

Fig. 24. T_1 and T_2 for $\text{Cr}(\text{CN})_6^{3-}$. Circles- T_1 from DNP with no σ/ρ correction. Squares- T_2 from linewidth measurements (Hayes, 1961).

especially since there is no hydrogen bonding to the first sphere ligands.

The experiments on mixed solvent solutions were initially done merely to demonstrate that DNP could be done with this apparatus on systems with more than one proton resonance. These data by no means represent a complete study, but do yield some interesting qualitative information.

DNP measurements were compared between solutions of 0.055 m $\text{Cr}(\text{CN})_6^{3-}$ in 1:1 by volume mixtures of acetonitrile and H_2O , and 1:1 mixtures of acetonitrile and D_2O . The measurements were made at room temperature. The proton signals from water and acetonitrile were not completely resolved, so enhancement information from this solution was obtained from curvefitting. The curvefitting process was somewhat time consuming, so only a few spectra were averaged, resulting in poor precision. The problem was particularly severe for the acetonitrile protons because the signal from them was less intense than the H_2O protons due to the smaller concentration of CH_3CN . The solution containing D_2O was examined to obtain more precise information on the acetonitrile protons. The resulting proton T_1 values were $T_1(\text{CH}_3\text{CN}) = 25 \pm 3$ msec, $T_1(\text{H}_2\text{O}) = 33 \pm 8$ msec. The enhancements were $E_{\text{CH}_3\text{CN}} = 1.3 \pm 0.2$, $E_{\text{H}_2\text{O}} = 1.3 \pm 0.5$. The data quoted for CH_3CN were obtained from the mixed solution with D_2O . The degree of interaction with the $\text{Cr}(\text{CN})_6^{3-}$ ion seems to be roughly the same for both the acetonitrile and water protons. This is consistent with the interaction being a second sphere process, with roughly equal participation of

CH_3CN and H_2O in the second coordination sphere. (Strictly speaking, the measured T_1 and enhancement of the acetonitrile protons should be smaller than the H_2O measurements because of the slightly increased viscosity of the D_2O mixture. The precision of the measurements was not great enough to discern this difference.) Measurements on $\sim 0.02 \text{ M } \text{VO}^{2+}$ in a 1:1 by volume mixture of acetonitrile and H_2O yielded strikingly different results. It was found that $T_1(\text{CH}_3\text{CN}) = 730 \text{ msec}$ and $T_1(\text{H}_2\text{O}) = 45 \text{ msec}$. This is clearly illustrative of the difference between a second sphere interaction and a first sphere interaction. VO^{2+} apparently preferentially forms complexes with H_2O . Because of the long T_{1n} of the acetonitrile protons and the need to keep microwave pulse lengths to $\sim 100 \text{ msec}$ to avoid heating the sample excessively, accurate extrapolation of enhancement data to infinite pulse lengths was difficult. The extrapolated values were $E_{\text{CH}_3\text{CN}} = 3.1 \pm 1.7$ and $E_{\text{H}_2\text{O}} = 1.2 \pm 0.1$. Since $E_{\text{H}_2\text{O}}$ is determined by rotational modulation and $E_{\text{CH}_3\text{CN}}$ is presumably determined by translation, it is reasonable to expect the enhancements to differ, although a quantitative comparison is not possible because of the large uncertainty in the data. Qualitatively, because of the difference in σ/ρ , translational modulation would be expected to produce larger enhancements than rotational modulation at room temperature.

The results of EPR linewidth measurements on $\text{Cr}(\text{CN})_6^{3-}$ ion in mixed solvent solutions are shown in Table III. All of the mixed solvents show increased linewidths over the pure H_2O system. This is certainly not a viscosity effect, at least in a macroscopic sense, since CH_3CN

and CH_3OH are less viscous than water. One possible explanation is that the mixed solvent system has a less symmetric second coordination sphere around $\text{Cr}(\text{CN})_6^{3-}$. This would result in a larger instantaneous zero-field splitting and more efficient relaxation. It is difficult to say what the effect of a mixed solvent system would be on the correlation time. These measurements at least support the assertion that fluctuations in the second coordination sphere are important for electron spin relaxation in $\text{Cr}(\text{CN})_6^{3-}$.

The DNP measurements on $\text{Cr}(\text{CN})_6^{3-}$ in pure water indicate that it is reasonable to assume $T_{1e} = T_{2e}$ at X-band. It should indeed be possible to use $\text{Cr}(\text{CN})_6^{3-}$ as a standard for T_{1e} measurements. In some respects it seems that the more interesting experiment would have been to use $\text{Cr}(\text{CN})_6^{3-}$ as a standard for measurements of T_{1e} for each of the eight VO^{2+} lines as a function of temperature. In any case, these measurements show that the theoretical calculation of T_{1e} for VO^{2+} from measured spin-Hamiltonian parameters, and the theoretical prediction that $T_{1e} = T_{2e}$ for $\text{Cr}(\text{CN})_6^{3-}$ at X-band are consistent.

B. $\text{Cu}(\text{H}_2\text{O})_6^{2+}$

1. Introduction

Hexa-aquo copper (II) ion, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, is a $3d^9$ ion. In an octahedral crystal field the ground state would be the orbitally degenerate 2E_g . The Jahn-Teller theorem (Jahn and Teller, 1937) requires that the complex distort, in order to break this orbital degeneracy. A tetragonal distortion, an elongation along the z axis, yields an orbitally non-degenerate ${}^2B_{1g}$ ground state. This corresponds to a

Table III. Room temperature (23°C) Linewidths of $\text{Cr}(\text{CN})_6^{3-}$.

Mixture	ΔH_{pp} (G)
Pure H_2O	23
1:1 acetonitrile/ H_2O	46
1:1 acetonitrile/ D_2O	50
1:1 $\text{CH}_3\text{OH}/\text{H}_2\text{O}$	52
1:1 $\text{DMSO}/\text{H}_2\text{O}$	106

positive hole, and an unpaired electron in a $3d_{x^2-y^2}$ orbital. The $^2A_{1g}$ state, corresponding to the unpaired electron being in the $3d_{z^2}$ orbital, would be expected to be a low-lying excited state for small tetragonal distortions. The $^2A_{1g}$ state, however, is not connected to the $^2B_{1g}$ ground state by spin-orbit coupling. This makes rapid spin-lattice relaxation by the Van Vleck direct or Raman processes unlikely (Kivelson, 1966). Consequently, the EPR spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is observable at room temperature in crystals and in solution.

Early observation of the EPR spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ at room temperature by Kozyrev (1955) revealed a single line with a peak-to-peak linewidth of about 150 gauss. This was somewhat surprising, since both abundant isotopes of copper, ^{63}Cu and ^{65}Cu , have their nuclear spin, $I = 3/2$. If the hyperfine coupling constant were large compared to the linewidth one would expect to see a quartet. Kozyrev initially attributed the lack of hyperfine structure to the formation of aggregations of Cu^{2+} ions in which the hyperfine coupling was presumably exchanged away. This assertion was based on observations with rather concentrated solutions. When it became clear that the EPR spectrum was essentially the same in more dilute solutions, where the formation of aggregations was unlikely, this explanation had to be discarded. A more likely explanation was that the hyperfine lines were simply much broader than the separation between them. McGarvey (1957) suggested that the broadening was due to a combination of slow tumbling as predicted by McConnell's (1956) theory and an interaction with a low lying excited state.

It should be noted that some complexes of Cu^{2+} do have EPR spectra with resolvable ^{63}Cu hyperfine structure in aqueous solution at room temperature. The ethylenediamine complex considered earlier in this work is one such example. The $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ complex not only has narrower lines than the hexaquo complex, but also has a larger ^{63}Cu hyperfine coupling constant. Hayes (1961) was able to observe some hyperfine structure for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ near 0°C . He estimated that the hyperfine coupling constant was between -31 and -38 gauss. A more precise determination by Chang (1971) using least squares fitting of the spectrum yielded a value of -34.5 G for the isotropic coupling constant near room temperature. The isotropic ^{63}Cu coupling constant for $\text{Cu(en)}_2(\text{H}_2\text{O})_2^{2+}$ determined by Lewis, Alei and Morgan (1966b) was -85.5 G. This is quite a significant difference. Part of the difference can be explained by an indirect dipolar (pseudo-contact) interaction. This can be shown with a simple calculation. McGarvey (1967) gives a simple expression for the hyperfine coupling constant,

$$A = P(-\kappa + (g - 2.0023)) \quad ,$$

where $P \propto \langle 1/r^3 \rangle$ for the orbital containing the unpaired electron and g is the isotropic g factor. The parameter κ gives rise to the true Fermi-contact interaction and depends on the amount of polarization of s electrons induced by the presence of the unpaired d electron. For transition metal ions κ is usually positive (McGarvey, 1966). The term involving the g factor describes the pseudo-contact interaction.

A reasonable value for P is about 400 cm^{-1} (McGarvey, 1967). If values of A and g measured from frozen glasses of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ (Chang, 1971) and $\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$ (Lewis, Alci and Morgan, 1966b) are used, and P is assumed to be the same for both complexes, then the values of κ calculated for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and $\text{Cu}(\text{en})_2(\text{H}_2\text{O})_6^{2+}$ are 0.31 and 0.32 respectively. Thus the pseudo-contact interaction seems to make up most of the difference between the hyperfine coupling constants. However, the ^{63}Cu hyperfine coupling which was observed for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in the glassy state is -46.9 G , which is of considerably larger magnitude than the value observed in solution near room temperature. The hyperfine coupling constant for $\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$ observed in the glassy state, 0.0086 cm^{-1} , is not significantly different from the value observed in solution, 0.0084 cm^{-1} . Furthermore, Chang (1971) noticed that the hyperfine constant for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in solution decreased significantly with increasing temperature. Wilson (1975) observed a similar temperature dependence of the ^{63}Cu hyperfine coupling constant in the $\text{Cu}(\text{NH}_3)_6^{2+}$ complex in liquid ammonia. He attributed the effect to a temperature dependent mixing of the ground state with the A_{1g} excited state. He felt that the hyperfine coupling constant in the excited state must be smaller than in the ground state.

The mixing of the ground and first excited state is possible through a dynamic Jahn-Teller effect. This effect is discussed by O'Brien (1964). A vibrational mode can mix the ground state and the $^2A_{1g}$ excited state. In a classical sense the degree of mixing depends on the vibrational amplitude. Quantum mechanically, the electronic

and vibrational motion are not completely separable. An increase in temperature cause the occupation of higher vibronic states which contain a greater admixture of the excited electronic state.

The ^{63}Cu hyperfine coupling constant in the $^2A_{1g}$ state is expected to be of smaller magnitude than the in ground state because in tetragonal symmetry the A_{1g} state has the same symmetry as the copper s orbitals, and can mix with them. Thus the $^2A_{1g}$ state has some s character. This s character results in a direct Fermi-contact interaction of the opposite sign of that induced by spin-polarization, and thus lowers the magnitude of the hyperfine constant. Mixing of the $^2A_{1g}$ state with the ground state results in a lowered magnitude of the observed hyperfine constant in solution.

The lack of resolution of the hyperfine structure forced many workers (Avvakumov, et al. 1959, Fujiwara and Hayashi, 1965) to use the peak-to-peak derivative width of the single line observed for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ as a measure of T_{2e} . Because the contribution of the unresolved hyperfine structure to the linewidth is not negligible over a large temperature range this method cannot give quantitative results. These measurements, however, produced two important qualitative observations for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. First, above room temperature, the linewidth clearly increased with temperature. Secondly, at low temperatures where some hyperfine structure was resolvable, it was apparent that the linewidth depended on M_I . This suggested that a McConnell (1956) tumbling mechanism was important at low temperatures. Since

McConnell's theory predicts a linewidth which decreases with increasing temperature, the increased linewidth at higher temperatures must be due to a different mechanism.

Spencer (1965) studied the EPR spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ as a function of temperature at X-band. He felt that some of the M_I dependent, low temperature linewidth could be ascribed to the McConnell (1956) tumbling mechanism. However, he also realized that the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex should be capable of undergoing a pseudo-rotation in which the major symmetry axis of the complex changes with respect to a space-fixed coordinate system. This pseudo-rotation, or inversion as it is sometimes called, can also cause M_I dependent relaxation. Spencer developed a simple theory to treat relaxation by the inversion mechanism, but his theory treated the tumbling process and inversion separately, which could not be correct. Later work seemed to confirm that tumbling alone could not account for the low temperature M_I dependent linewidth. Lewis, Alei and Morgan (1966a) used computer simulations to extract the individual hyperfine linewidths for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. They found that an application of Kivelson's (1960) tumbling theory to the M_I dependence of the linewidths required a room temperature rotational correlation time of 3×10^{-12} sec. This is much too short for an ion the size of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Chang (1971) used a least-squares program to determine the individual hyperfine linewidths and he came to essentially the same conclusion. The hydrodynamic radius necessary to account for the M_I dependent linewidth, $1.71\text{\AA}$ is much too small for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$.

Noack, Kokoszka and Gordon (1971) noticed a similar anomalously low tumbling correlation time for the symmetrically substituted complex of 2, 2' dipyridine, $\text{Cu}(\text{dipy})_3^{2+}$. They explained this result by concluding that symmetric complexes could undergo rapid inversion associated with a dynamic Jahn-Teller effect. They felt that the apparent correlation time, τ_c , was given by

$$\frac{1}{\tau_c} = \frac{1}{\tau_R} + \frac{1}{\tau_{J-T}}$$

where τ_R is the rotational correlation time and τ_{J-T} was the correlation time for inversion. A more complete treatment by Rubinstein, Barum and Luz (1971), showed that inversion and tumbling can be treated together with the apparent correlation time τ_c , given by

$$\frac{1}{\tau_c} = \frac{1}{\tau_R} + \frac{n}{n-1} \frac{1}{\tau_i},$$

where τ_i is the correlation time for the inversion process and n is the number of equivalent axis along which distortion can occur. In this case n is 3. Poupko and Luz (1971) measured linewidths for $\text{Cu}(\text{H}_2\text{O})_2^{2+}$ at X-band and Q band. They found τ_i (25°) = 1.2×10^{-11} sec.

Lewis, Alei and Morgan (1966a) did not interpret their data on the basis of the inversion mechanism. They felt that the apparent anomalously short correlation time was caused by the anisotropic parameters

$\Delta g = g_{\parallel} - g_{\perp}$ and $\Delta A = A_{\parallel} - A_{\perp}$ being smaller in solution than what was measured in the glassy state. They (Lewis and Morgan, 1968) based this assertion on the observation that Δg is reduced in some crystalline salts containing $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ as the temperature is raised (Baggaley and Griffiths, 1952). Linewidth measurements on $\text{Cu}(\text{NH}_3)_6^{2+}$ ion in liquid ammonia by Schmidt and Breitschwerdt (1974) support this interpretation. They were able to estimate the product $\Delta g \Delta A$ from the dependence of the β parameter of Eq. (2.3) on viscosity divided by temperature. They estimated a value of $\Delta g \Delta A$ which was 55 percent of the value determined from measurements on the $\text{Cu}(\text{NH}_3)_6^{2+}$ system in the glassy state.

Fast inversion as an explanation of the apparent short correlation time seems more attractive to us than a reduction in Δg and ΔA from their values in a glass. The apparent reduction of Δg observed in solid is probably due to a dynamic Jahn-Teller inversion which causes a reduction in Δg in the same sense that the NMR lines from a nucleus exchanging between inequivalent positions appear to move together as the exchange rate increases. If inversion were fast enough, the spectrum would be isotropic, and the linewidths would be expected to depend on the magnitudes of Δg and ΔA which existed when the motion was frozen (O'Brien, 1964). Surely the applicable values of Δg and ΔA in solution should also be those in which the motion is frozen as completely as possible. A measurement comparing the contribution of this M_I dependent mechanism to T_{1e} with its contribution to T_{2e} when $\omega_S \tau_C \geq 1$ would provide an unambiguous determination of the correlation

time for the mechanism. Unfortunately this measurement proved impossible for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ for reasons which are discussed later. However, such a measurement might be possible for $\text{Cu}(\text{NH}_3)_6^{2+}$, which has a better resolved spectrum and can be observed at temperatures where the M_I dependent contribution to T_{1e} is more significant.

The linewidth of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ above room temperature is dominated by spin-rotation. The importance of spin-rotation as a relaxation mechanism for copper complexes was demonstrated by Wilson and Kivelson (1966b) with their work on copper acetylacetonate in organic solvents. For $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, with $g_{\parallel} = 2.387$ and $g_{\perp} = 2.072$ (Chang, 1971), Eq. (2.8) predicts a linewidth contribution of 57 G for $\tau_R = 2 \times 10^{-11}$ sec. This is close to the observed linewidth at room temperature after the contribution from the low temperature tumbling or inversion mechanism is subtracted. However, Lewis Alei and Morgan (1966a) noticed that the temperature dependence of the high temperature linewidth was somewhat less than that of T/η , which would be predicted for pure spin-rotation. While Chang (1971) could draw a reasonable straight line through his plot of the M_I independent linewidth for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ vs T/η , the intercept at $T/\eta = 0$ indicated a residual linewidth of about 30 G. This is strongly suggestive that an additional relaxation mechanism besides spin-rotation and tumbling is important for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. While Eq. (2.8) is the result of perturbation theory and is thus only approximate, the residual linewidth seems much too large to be blamed on uncertainty in the theory.

On the basis of order of magnitude calculations, Kivelson (1966) suggested that the residual width might be accounted for by an Orbach process. Kivelson's estimate assumed that the energy separation between the B_{1g} ground state and the A_{1g} excited state be the order of 1000 cm^{-1} . Wilson (1975) reconsidered Chang's (1971) data. After subtracting the effect of tumbling and spin-rotation from the observed linewidth he found that the activation energy of the remaining width was only a few hundred wavenumbers. He felt that this excluded the Orbach process, since the lowest excited state should be more than a few hundred wavenumbers above the ground state. Wilson proposed that the residual width could be a solution Raman process, in spite of Kivelson's (1966) calculation that the Raman process should be less important than the Orbach process for relaxation in $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. If the energy separation between the ground and first excited electronic state, δ_{on} , were significantly larger than the 1000 cm^{-1} estimated by Kivelson, the Raman process would be more important. However, the magnitude of the Raman contribution is independent of δ_{on} . Kivelson estimated that the Raman process would only contribute $\sim 5\text{ G}$ to the linewidth of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Wilson found that if he used a hydrodynamic radius of $3.47\text{\AA}$ to calculate the spin-rotational width, the remaining width after spin rotation and tumbling were subtracted varied as $T^{1/2}$, which is expected for the Raman process.

Valiev and Zaripov (1966) developed a theory describing relaxation in $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. They felt that the primary cause of broadening of the EPR signal was transitions between the ground electronic state and the

lowest excited electronic state. These transitions proceeded without spin flipping. They were caused by vibrational modulation of the crystal field in the manner discussed by Altschuler and Valiev (1959). Valiev and Zaripov found that

$$1/T_2 \approx 1/\tau_a, \quad \text{,}$$

where τ_a was the lifetime of the molecule in the ground electronic state. Their calculations led to $\tau_a^{-1} \approx 10^9 \text{ sec}^{-1}$. These calculations cannot be correct, since they account for virtually all of the line-width of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ before spin rotation is even considered. However, they are interesting since they suggest a relaxation mechanism which does not affect T_{1e} . Perhaps the residual linewidth is not due to a spin-lattice process.

McCain and Myers (1974) made T_{1e} measurements on $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ using O NP at S-band. They found that at 5°C $T_{1e} = 2T_{2e}$, but that at 60°C T_{1e} was beginning to approach T_{2e} . The result at 5°C cannot be explained by slow tumbling modulation of anisotropic g and A values. At S band $\omega\tau_R^2 = 0.3$. If it is assumed that the appropriate correlation time for this mechanism is $2/3 \tau_i$, then $\omega\tau_C^2 < 0.05$. The T_1/T_2 ratio should be near its extreme narrowing value of $7/6$ (Poole and Farrach, 1968). Also, spin-rotation should still be more important than tumbling even at this low temperature. For spin rotation the contribution to T_{1e} and T_{2e} should be equal.

The present DNP work on $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ at X-band was undertaken with the hope of resolving some of the confusion concerning electron spin relaxation in $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Of all of the paramagnetic ions studied in this work, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is the most poorly understood and consequently has the greatest potential for providing interesting new information. Unfortunately, because of its unresolved hyperfine structure and relatively short relaxation times it is also the most difficult to study.

2. Experimental

Aqueous solutions of Cu^{2+} ion were prepared by dissolving weighed amounts of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Alfa-Ventron) in distilled water. Solutions were analyzed for Cu^{2+} by adding an excess of ethylenediamine and measuring the visible absorption at 550 nm. The molar extinction coefficient of $\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$ complex was determined by dissolving a weighed amount of copper wire in nitric acid, adding an excess of ethylenediamine and taking a visible spectrum on a Cary 14 visible spectrometer. The value of the molar extinction coefficient determined in this manner, $\epsilon = 62.5$ was in reasonable agreement with the value, $\epsilon = 65$, quoted by Pflaum and Brandt (1954). This method of analysis was sufficiently precise to allow proper matching of nuclear T_1 values for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and the VO^{2+} solutions used in the flowing sample spectrometer. Nuclear T_1 values for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ which were used in the matching process were those measured by Morgan and Nolle (1959).

DNP on Cu^{2+} was observed in both the flowing sample spectrometer and the moving sample tube spectrometer. In both cases the solutions used were ~ 0.03 M in Cu^{2+} . Measurements of enhancements for Cu^{2+} on

the moving sample tube spectrometer were compared with VO^{2+} , standards in the same manner as the $\text{Cr}(\text{CN})_6^{3-}$ measurements.

3. Results and Discussion

Enhancement spectra representative of those taken for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ with the moving sample tube spectrometer are shown in Fig. 26. Spectra which were taken with the flowing sample spectrometer were similar, although the observed enhancements were about a factor of two smaller than those which were measured with the moving sample tube spectrometer. It can be seen in Fig. 26 that there is no sign of resolved hyperfine structure, as would be expected from the appearance of the EPR spectra at these temperatures (Chang, 1971). There is no special significance to the relative amplitudes of the spectra shown in Fig. 26. Although both spectra were taken on solutions of the same Cu^{2+} concentration and at the same microwave power level, a number of parameters other than the saturation parameter which affect the enhancement are not independent of temperature. Both the cavity Q and σ/ρ increase with temperature. Also the matching of the cavity to the transmission line is not necessarily constant with temperature. Finally, the spectra shown in Fig. 26 have not been adjusted for the effects of the finite microwave pulse length and the non-zero delay before measuring the proton magnetization. This adjustment is different for each spectrum since T_{1n} is a function of temperature.

Enhancements for the individual hyperfine transitions were determined by a least squares fitting procedure similar to the one employed for $\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$. For $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ it is not necessary to include

XBL 827-5988

Fig. 25. T_1 and T_2 for $\text{Cr}(\text{CN})_6^{3-}$. Circles- T_1 from DNP using σ/ρ as described in the text. Squares- T_2 as in Fig. 24.

Fig. 26a. Enhancement spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ at 10°C . The dotted line is a fit using four enhancements.

XBL 827-5989

Fig. 26b. Enhancement spectrum of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ at 60°C . The dotted line is a simulation using only a single enhancement.

the effects of ligand superhyperfine coupling. The proton superhyperfine coupling constant of 0.03 G (Shulman and Luz, 1960) is small enough to be neglected. The results of the fitting process were disappointing, since there seemed to be no consistent pattern of M_I dependence as a function of temperature. Indeed, at 60°C the best fit required one of the hyperfine enhancements to be negative. It seems that the signal to noise was too poor, and that the hyperfine enhancements were too strongly correlated to give reliable fits. This was reinforced by the fact that above 40°C the system became so ill-conditioned that fits could not be done in 36-bit floating-point arithmetic. Extension to 48 bits was necessary to get values for the hyperfine enhancements which fit the observed spectra, and these enhancements were suspect since one of them was negative. The consequence of this is that no comment on the low temperature M_I dependent relaxation mechanism can be made from these data. In any case, it would require an exceptional signal to noise ratio to gain information on the tumbling/inversion mechanism. Estimates of the contribution of this mechanism to $1/T_{1e}$ made using Eqs. (4.1)-(4.5) indicate that it contributes only a few percent or less of $1/T_{1e}$ at X-band, even at the lowest temperatures studied.

Because of the unreliability of the fitting process only an average T_{1e} could be determined for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. All of the enhancement spectra could be simulated reasonably well using a single enhancement obtained by simply averaging together the enhancements obtained from the fitting process for each hyperfine transition. These average

enhancements were compared with enhancements measured for VO^{2+} to determine the average T_{1e} . Average linewidths and linecenters for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, which were determined from measurements by Chang (1971), were used in the comparison process. The average T_{1e} values from enhancement data taken on the moving sample tube spectrometer are plotted in Fig. 27 and are compared with average T_{2e} values. Data were taken from 10° to 60°C in 10° intervals. The data from the flowing sample spectrometer, although less extensive, are plotted for comparison in Fig. 27. The experimental error in these T_{1e} values is estimated to be as large as 20 percent, mainly because the spread in the single enhancement which could reasonably simulate the enhancement spectrum is nearly that large. The σ/ρ correction was made assuming rotational modulation of the dipolar interaction for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The hydrodynamic radius which was used in the correction, $2.8\text{\AA}$, was determined from the measurements of the frequency dependence of proton NMR relaxation in Cu^{2+} solutions by Morgan and Nolle (1959).

The results in Fig. 27 are somewhat surprising, since it appears within experimental error that T_{1e} is independent of temperature over this temperature range. Except for the spurious point at 3°C , which was explained earlier in reference to $\text{Cu}(\text{en})_2(\text{H}_2\text{O})_6^{2+}$, the T_{1e} values determined from the flowing sample spectrometer show reasonable agreement with those from the moving sample tube spectrometer. What is particularly surprising is the fact that at 60°C we find $T_{1e} \neq T_{2e}$, while T_{1e} and T_{2e} approach each other at lower temperatures. This is the opposite of the behavior which was observed by McCain and Myers (1974) at S-band.

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Fig. 27. T_1 and T_2 for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Circles- T_1 from moving sample tube DNP. Triangles- T_1 from flowing sample DNP. The σ/ρ correction is described in the text. Squares- T_2 from linewidth measurements by Chang (1971).

The apparent lack of temperature dependence of the measured T_{1e} values is difficult to reconcile with theory. In particular, a strong temperature dependent contribution to $1/T_{1e}$ is expected from the spin-rotation mechanism. One must conclude that spin-rotation is either masked by another relaxation mechanism, or that the measured T_{1e} values are incorrect due to some unforeseen experimental error or an error in interpreting the data. The agreement between the T_{1e} values measured using the two different spectrometers seems to argue against gross experimental error. The part of the data interpretation which is most subject to error is the σ/ρ correction. It is clear from the $\text{Cr}(\text{CN})_6^{3-}$ data that a proper σ/ρ correction is necessary to get a correct temperature dependence.

It has not been the policy in this work to treat σ/ρ as an adjustable parameter. The σ/ρ correction has always been made using experimentally determined correlation times. However, in this case it is interesting to investigate the changes in the temperature dependence of T_{1e} if the σ/ρ correction is changed because the hydrodynamic radius for the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex obtained from NMR relaxation measurements is considerably smaller than the value expected from structural considerations. Perhaps this is because inversion affects the proton relaxation. Proton relaxation measurements have yielded values of 2.8Å (Morgan and Nolle, 1959) and 2.3Å (Frankel, 1968) for the hydrodynamic radius, while Meredith (1965) calculated a value of 3.65Å from x-ray data on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

If the σ/ρ correction is made by assuming that $\text{VO}(\text{H}_2\text{O})_5^{2+}$ and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ have the same hydrodynamic radius, the T_{1e} values plotted in Fig. 28 result. Chang (1971) has estimated a value of $3.67\text{\AA}$ for the hydrodynamic radius of $\text{VO}(\text{H}_2\text{O})_5^{2+}$, which is near Meredith's structural value for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. This set of corrected T_{1e} values are interesting, because if $1/T_{1e}$ is plotted vs temperature divided by viscosity, the four lowest temperature points form a straight line which passes through the origin. This is the behavior expected if T_{1e} is dominated by spin rotation. Furthermore, from the slope of the line and Eqs. (2.8) and (2.5) a hydrodynamic radius of $3.5\text{\AA}$ can be estimated. While this value is not completely consistent with the σ/ρ correction, it is not in such poor agreement when one considers the approximate nature of the spin rotation theory. However, the two highest temperature points are not affected much by changes in the σ/ρ correction, and do not lie on the spin-rotation line.

No matter which σ/ρ correction is used we find $T_{1e} \neq T_{2e}$ at 60°C . It is difficult to believe that this result is due to unforeseen error, since it is easier to imagine reasons for the observed enhancement to be too small rather than too large. An additional unknown proton relaxation mechanism would cause smaller enhancements, as would relaxation by scalar coupling. It would be interesting to see if this behavior persists at higher temperatures. Higher temperature DNP measurements require technical improvements in the sealing of sample tubes to make the seals withstand the higher temperatures and pressures involved. If such improvements could be made the DNP results

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Fig. 28. T_1 and T_2 for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Circles- T_1 from moving sample tube DNP. These are the same data as in Fig. 27, but have a different σ/ρ correction, which is described in the text. Squares- T_2 as in Fig. 27.

would be most useful, since the higher temperature points are much less sensitive to the σ/ρ correction.

It is very difficult to draw definite conclusions from these $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ T_{1e} measurements. Surely the data rule out the importance of relaxation mechanisms such as those described by Al'tshuler and Valiev (1959) and Valiev and Zaripov (1964) which predict $T_{1e} \gg T_{2e}$. The lack of temperature dependence of the T_{1e} values which were calculated using NMR data to determine the σ/ρ correction seems unrealistic. The T_{1e} values calculated when the larger hydrodynamic radius estimated by Meredith (1965) is used in the σ/ρ correction are more consistent with T_{1e} being determined by a spin-rotation interaction. However, it seems inappropriate to comment on the nature of the mechanism responsible for the difference between T_{1e} and T_{2e} which these data suggest, since there is no clear justification for the use of Meredith's hydrodynamic radius for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Perhaps more useful DNP work could be done on $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ at S band where the σ/ρ correction is not so important.

The electron spin relaxation in $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ thus remains mysterious. We feel, however, that more accurate measurements of T_{1e} for this complex, whether made by DNP or some other method, can contribute to the understanding of the structure and dynamics of this ion in solution.

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