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PROTON AND ELECTRON SPIN RELAXATION IN AQUEOUS SOLUTIONS OF NICKEL(II) AND COBALT(II) IONS

Thomas Michael Hynes
(Ph.D. thesis)

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PROTON AND ELECTRON SPIN RELAXATION IN AQUEOUS SOLUTIONS OF NICKEL(II) AND COBALT(II) IONS

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PROTON AND ELECTRON SPIN RELAXATION IN AQUEOUS SOLUTIONS OF NICKEL(II) AND COBALT(II) IONS

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ABSTRACT

Measurements were made of the NMR linewidths of bulk water protons in aqueous solutions of nickel(II) ions, at magnetic fields of 14.1, 23.5 and 51.7 kilogauss and temperatures from -50°C to +155°C. Proton relaxation was caused by dipolar interaction with the magnetic moment of the nickel ion, interrupted by longitudinal and transverse relaxation of the electron spin. Other sources of proton relaxation were found to be negligible. Rapid proton exchange, catalyzed by added acid, was used to avoid the condition in which relaxation of the bulk protons is rate limited by chemical exchange of protons. Below room temperature, T_{1e} and T_{2e} were not equal. The absolute magnitudes of T_{1e} were in reasonable agreement with results of ^{17}O studies. T_{1e} increased with decreasing temperature and with increasing magnetic field, reaching a value of 3.5×10^{-11} sec at -45°C and 51.7 kG. The temperature dependence of T_{1e} was noticeably less than that of the viscosity of water. Relaxation of the spin of the nickel was attributed to random fluctuations of the zero field splitting. Other mechanisms were considered and found to be ineffective in comparison. T_{1e} was significantly less dependent upon magnetic field than predicted. This discrepancy was tentatively attributed to violation of the requirement, common to theories of relaxation, that the relaxation rate be slow

compared to the precessional frequency and to the frequencies of the motions which cause the relaxation. With the aim of extending the valid range of theory, a different method of accounting for the spectrum of motional frequencies was developed. This calculation was successful in explaining the observed magnetic field dependence, but unsuccessful in explaining the observed temperature dependence.

Measurements were also made of the NMR linewidths of bulk water protons in aqueous solutions of cobalt(II) ions, at temperatures from -50°C to +158°C and magnetic fields of 14.1, 23.5 and 51.7 kilogauss. Proton T_1 measurements were made at 51.7 kG at temperatures from -3°C to +148°C. Proton longitudinal relaxation was caused by dipolar interaction with the magnetic moment of the cobalt ion, interrupted by relaxation of the electron spin. Proton transverse relaxation was caused by this dipolar coupling and also by the $\Delta\omega$ mechanism. This mechanism was sufficiently strong to make the proton T_2 at 51.7 kG and 0°C a full order of magnitude shorter than either T_1 under the same conditions, or T_2 at fields below 8 kG. The exchange rate of whole water molecules appeared to be the same as the exchange rate for protons, provided the pH was above 2. The electron T_{1e} was found to be extremely short, independent of magnetic field, and almost independent of temperature. Due to the shortness of T_{2e}, it was not possible to determine if T_{1e} and T_{2e} were different. If $T_{1e} = T_{2e}$, then at 5°C, $T_{1e} = 2.4\times10^{-13}$ sec, and at 130°C, $T_{1e} = 1.2\times10^{-13}$ sec. These times are shorter by a factor of five than those derived from ^{17}O measurements, yet are consistent with earlier proton studies. The discrepancy has not been explained. All observed characteristics of the electron relaxation may be explained by the resonant relaxation mechanism of Orbach.

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SYMBOLS

A	scalar coupling constant in ergs
A_∞, A_τ	amplitudes of FID signal after 90° pulse at times $t = \infty$ and $t = \tau$ in a 180°, τ, 90° experiment
a	molecular radius
b	anisotropic hyperfine interaction constant; see Eq. (3-22)
$C_\parallel, C_\perp$	spin rotation constants parallel and perpendicular to the symmetry axis
D	axial ZFS constant
d	distance
d (as subscript)	due to dipolar coupling
E_n	energy of state n
g	Lande g factor
$g_\parallel, g_\perp$	g values parallel and perpendicular to the symmetry axis
Δg	$g_\parallel - g_\perp$
$\Delta g_\parallel$	$g_\parallel - 2.0023$
$\Delta g_\perp$	$g_\perp - 2.0023$
H, H_o	external magnetic field
H_m	amplitude of magnetic field modulation
H_1	half the amplitude of the radio frequency field
$[H^+]$	hydrogen in concentration
h	Plank's constant
$\mathcal{H}_1(t)$	time dependent perturbation
$\Delta H^\ddagger$	enthalpy of activation
I	nuclear spin quantum number
I_z	z component of the nuclear spin
I	moment of inertia

$J_1(x)$	first Bessel function of the first kind
$J(\omega)$	spectral density at frequency ω; see Eq. (5-20)
$\bar{J}(\omega_o)$	frequency averaged spectral density about a center frequency ω_o; see Eq. (5-21)
k	Boltzmann's constant
k_2	constant in Eq. (2-16a)
k_3	constant in Eq. (5-19)
M	molarity
M_z	magnetization along the magnetic field axis
M_o	equilibrium value of M_z
N	Avagadro's number
n	number of ions per unit volume
^{17}O	oxygen seventeen nucleus
P_m	fraction of nuclei coordinated to metal ion
R	1.987 cal deg^{-1} $mole^{-1}$
r	distance from proton to electron
S	spin quantum number of the electron; signal height
$\Delta S^{\ddagger}$	entropy of activation
sc (as subscript)	due to scalar coupling
T	temperature
T_D	Debye temperature
T_{pd}	phonon temperature
T_1	longitudinal relaxation time
T_2	transverse relaxation time
T_{1e}	longitudinal relaxation time of the electron
T_{2e}	transverse relaxation time of the electron

T_{1m}	T_1 of nuclei bound to metal ion
T_{2m}	T_2 of nuclei bound to metal ion
T_{1H_2O}	T_1 of nuclei in bulk solution (in absence of chemical exchange to metal ions)
T_{2H_2O}	T_2 of nuclei in bulk solution (in absence of chemical exchange to metal ions)
T_{1p}^{-1}	contribution to nuclear T_1 arising from paramagnetic ions
T_{2p}^{-1}	contribution to nuclear T_2 arising from paramagnetic ions
V	volume
$V(0),V(1),V(2)$	terms in crystal field potential expansion; see Eq. (3-2)
v	velocity of sound
W_{12}	transition rate between states 1 and 2
β	Bohr magneton
γ	magnetogyric ratio
γ_I	magnetogyric ratio of the nucleus
γ_S	magnetogyric ratio of the electron
Δ	rms value of the ZFS constant in solution; an unspecified crystal field splitting
$\Delta\nu$	full width of absorption signal at half height, in H_z
$\Delta\omega_{H_2O}$	difference in resonance frequency between the sample and pure water
$\Delta\omega_m$	the difference between the resonance frequency of nuclei in the first coordination sphere (without exchange) and the actual resonance frequency of the sample
$\Delta\omega_\pm$	see Eq. (2-1)
ε	strain constant
η	viscosity
μ_{eff}	effective magnetic moment

ν_o	vibrational frequency
ρ_{ph}	phonon density per unit volume
τ	time between radio frequency pulses in 180° - τ - 90° sequence
τ, τ_c	unspecified correlation times
τ_D	translational diffusion correlation time
τ_1	see Eq. (2-19)
τ_2	see Eq. (2-20)
τ_3	see Eq. (2-23)
τ_4	see Eq. (2-24)
τ_m	time a nucleus spends bound to a metal ion before exchanging to the bulk
τ_{mH_2O}	time a water molecule spends bound to a metal ion before exchanging to the bulk
τ_r	rotational correlation time: see Eq. (3-23)
τ_ω	angular momentum correlation time
ω_I	nuclear Larmor precession frequency
ω_m	frequency of the magnetic field modulation
ω_{max}	see Eq. (3-6)
ω_o	Larmor procession frequency
ω_S	Larmor precession frequency of the electron
ω_{12}	frequency separation of energy levels 1 and 2

<u>Abbreviations</u>

EFF	electric field fluctuation
EPR	electron paramagnetic resonance
FID	free induction decay
kG	kilogauss

rf	radio frequency
ZFS	zero field splitting
$\Delta\omega$ mechanism	see Eq. (2-26)
90°,180° pulses	rf fields which rotate the nuclear magnetization 90° and 180°, respectively

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I. INTRODUCTION

This thesis is a nuclear magnetic resonance study of the longitudinal and transverse relaxation times of protons and unpaired electrons in aqueous solutions of Ni(II) and Co(II) ions. These relaxation times indicate the rates at which the properties of a spin system approach their equilibrium values.

When a collection of nuclear or electron spins is placed in a magnetic field, it exhibits a new magnetic moment along the field axis. This results from a Boltzmann distribution of spins among the allowed energy levels. If the system is disturbed from equilibrium, the magnetization along the field axis will return to its equilibrium value with a time constant T_1, or longitudinal relaxation time. At equilibrium, there is no net magnetization perpendicular to the magnetic field axis due to the random phases of the precessing spins. If a transverse magnetization is created, as by applied microwave or radio frequency radiation, this magnetization will return to zero with a time constant T_2, or transverse relaxation time. Studies of these relaxation rates assumed an important role early in the history of magnetic resonance spectroscopy because of the observational difficulties which arise when these relaxation times are inconveniently short or long (Bloch, Hansen and Packard, 1946; Bloembergen, Purcell and Pound, 1948).

Relaxation studies have come to yield a great deal of physical and chemical information about liquids. This includes translational and rotational correlation times of molecules, rates of conformational changes and chemical exchange rates of molecules, electrons and protons.

Such information can be deduced from relaxation measurements because these molecular motions give rise to the time independent local fields which are responsible for the relaxation.

Electron spin relaxation in liquids is on the whole, less well understood than nuclear relaxation. The first reason for this is that electron spin relaxation can be caused by a greater number of interactions than can nuclear relaxation. While both nuclear and electron spins are affected by magnetic fields, electron spins are also influenced by electric fields. This is due to the coupling of the orbital and spin angular moments of the electron. This spin orbit coupling can allow the spin of a transition metal ion to interact with the static and time dependent crystalline electric fields caused by liquids surrounding the ion. The second reason that electron spin relaxation is less well understood is that the relaxation times are often so short that direct measurement is difficult or impossible. Whereas nuclear relaxation times are usually in the range of 10^{-5} sec to 10 sec, electron spin relaxation times of transition metal ions in solution are often in the range of 10^{-9} sec to 10^{-12} sec. All techniques for directly measuring longitudinal relaxation times have fundamental limitations that make it impossible to work at time scales this short. These methods and difficulties have been discussed by McCain (1966), and by Standley and Vaughan (1969). The method of continuous power saturation cannot measure longitudinal relaxation times shorter than 10^{-9} sec because not enough noise free microwave power can be produced and applied to the sample to achieve saturation. The method of spin echoes (Hahn, 1950) fails due to the difficulties of producing a microwave pulse of length less than

10^{-9} sec. The method of pulse saturation followed by monitored recovery of the magnetization encounters similar difficulties. McCain (1966) has described a dynamic nuclear polarization technique for measuring relaxation times as short as 10^{-10} sec. This, however, seems to be about the present limit of the ability to measure short longitudinal relaxation times of the electron.

The transverse relaxation time of the electron is less difficult to measure. T_2 may be obtained by measuring the linewidth of the resonance signal in a conventional EPR spectrometer. Then

$$T_2 = \frac{h}{\pi \sqrt{3} g \beta (\Delta H_{pp})} , \qquad (1\text{-}1)$$

where g is the Lande g factor, β is the Bohr magneton, and ΔH_{pp} is the peak to peak linewidth of the first derivative of the absorption signal. Instrumental limitations make it impossible to detect and measure signals that are much wider than 2000 gauss. A signal this wide has a T_2 of 3.3×10^{-11} sec, which is the lower limit of relaxation times that can be measured with EPR techniques.

In contrast, NMR methods are available for determining even the shortest of electron spin relaxation times in solution. The most direct of these methods is the measurement of the relaxation rates of nuclei in water molecules coordinated to metal ions. In this case, the relaxation times of the electron spin can be calculated using well known equations describing nuclear relaxation caused by dipolar and scalar coupling with electron spins. This method has the limitation that the nucleus must, on the average, stay bound to the metal ion for a time longer

than the nuclear relaxation time. For aqueous solutions, this condition usually limits the applicability of the method to temperatures below 0°C or even -30°C. This is a rather restricted temperature region in which to study relaxation mechanisms.

A similar procedure can be used over a much wider temperature range. If certain limiting conditions, to be detailed later, are satisfied, the relaxation times of the nuclei in the bulk of the solution are related in a simple manner to the relaxation times of the electron spin. One of these conditions is that the electron spin relaxation must be the fastest of the processes which can interrupt the magnetic coupling of the nucleus and electron. This in turn usually limits the technique to the study of just those metal ions which cannot be studied by EPR techniques. Such measurements of the relaxation times of bulk protons in aqueous solutions of nickel and cobalt ions are the experimental part of this thesis.

Nickel(II) and cobalt(II) ions were chosen for this study because their relaxation in solution is extremely fast. Early proton NMR studies of aqueous nickel ion (Hausser and Laukien, 1959; Morgan and Nolle, 1959) and of cobalt ion (Nolle and Morgan, 1957; Hausser and Laukien, 1959; Bernheim, et al., 1959) were primarily concerned with the nuclear relaxation, and conditions were never adjusted so as to learn a maximum amount about the electron spin relaxation. Later NMR studies of aqueous nickel (Connick and Fiat, 1966; Chmelnick and Fiat, 1971; Neely and Connick, 1972) and of Cobalt (Chmelnick and Fiat, 1967; Fiat, Luz and Oliver, 1968; Natwiyoff and Darley, 1968; Zeltman, Matwiyoff and Morgan, 1969) have still left unanswered basic questions

regarding the causes of the electron spin relaxation.

Neither ion has an aqueous chemistry complicated enough to be a source of difficulty in the interpretation of the present results. Hydrolysis can be prevented if the pH is kept below about four. Both ions are known to have six water molecules in the first coordination sphere. Evidence for this has been given by various NMR studies of nickel at temperatures ranging from -30°C to +200°C (Swift and Weinberger, 1968; Chmelnick and Fiat, 1971), and for cobalt at temperatures from -63°C to +183°C (Matwiyoff and Darley, 1968; Chmelnick and Fiat, 1967).

Nickel(II) has a d^8 configuration, with S = 1. In an octahedral crystal field the ground state is an orbital singlet. The threefold spin degeneracy of this state may be lifted by the combined effects of spin orbit coupling and deviations from perfect octahedral symmetry. The time dependence of this direction dependent splitting has previously been considered the only important cause of the relaxation of Ni(II) ion in solution (McLaughlin, 1964; Lewis and Morgan, 1968), despite the scarcity of data regarding the magnetic field dependence of the relaxation.

Cobalt(II) has a d^7 configuration, with S = 3/2. In an octahedral crystal field, three orbital states lie lowest, but they are split apart by spin orbit coupling. As a result, the ground state is a spin doublet, separated from the nearest excited state by some 300 cm^{-1}. Relaxation of the electron spin in the solid is attributed to transitions between the ground state and nearby excited states, and this process is usually presumed to operate in solution as well.

II. THEORY OF NMR RELAXATION

A. Introduction

This chapter will consider macroscopic quantities and then work backwards to the relevant molecular processes. First, the time dependence of bulk magnetization will be related to T_1 and T_2 of the protons in the solutions studied. Then T_1 and T_2 will be related to T_{1m} and T_{2m}, the relaxation rates the protons would have if they remained in water molecules bound to the paramagnetic ion, and also to rates of proton exchange between the bound and unbound (i.e., bulk) environments. Then these relaxation rates will in turn be related to the rates of electron spin relaxation, whose elucidation is a major aim of this work.

Unsurprisingly, classical physics suffices to explain much of the behavior of bulk magnetization, while quantum mechanics becomes more and more necessary as our focus becomes microscopic.

The phenomenological equations of Bloch (1946a,b) provide a helpful physical picture of magnetic resonance. As we shall see, they can be extended to treat such conditions as chemical exchange and magnetic field modulation. The origins of nuclear relaxation theory are more varied. The typical theoretical procedure, however, is to treat the spin system quantum mechanically, while describing the relevant molecular motions classically. It is often helpful to consider a relaxation rate as a product of two factors: the first being the square of an interaction energy, and the second being a function of the time scale of the molecular motions which interrupt the interaction. Two excellent general discussions of relaxation theory are found in the books by Slichter (1963) and Abragam (1961).

B. Measurement of Nuclear T_2 and T_1

A nuclear transverse relaxation time, T_2, may be measured by observing the resonance signal with a continuous wave spectrometer. The Bloch equations for the conditions of continuous rf irradiation have been previously discussed (e.g., by Pople, Schneider and Bernstein, 1959). Effects caused by field modulation and detection methods are described by Acrivos (1962) and by Haworth and Richards (1966). When the modulation frequency exceeds $(T_2)^{-1}$, sidebands are produced. When either of the first sidebands (following phase detection) is observed, and saturation and rapid passage effects are negligible, the signal height, as given by Acrivos, is

$$S = \frac{(2/x)[J_1(x)]^2 \gamma H_1 T_2 M_o}{1 + (T_2 \Delta\omega_\pm)^2} \qquad (2\text{-}1)$$

where

$$x = \frac{\gamma H_m}{\omega_m}, \quad \Delta\omega_\pm = \omega_o \pm \omega_m - \omega$$

and S is the observed signal height

J_1 is the first Bessel function of the first kind

H_m is the amplitude of the field modulation

H_1 is half the amplitude of the radio frequency field

γ is the magnetogyric ratio of the detected nucleus

T_2 is the nuclear transverse relaxation time

M_o is the equilibrium magnetization of the detected nucleus

ω is the radio frequency

ω_m is the frequency of the field modulation

ω_o is the Larmor precessional frequency of the detected nucleus in a static field H_o

$\omega_o \pm \omega_m$ are the first sideband resonance frequencies in the presence of field modulation

The signal S will have a maximum at $\omega_o = \gamma H_o = -(\pm\omega_m - \omega)$, whether ω or H_o is swept. In either case, $\Delta\omega_\pm$ is a variable, and Eq. (1) is seen to be Lorentz in shape. S will be at half maximum when $(T_2\Delta\omega_\pm)^2 = 1$. Therefore,

$$\frac{1}{T_2} = \Delta\omega_\pm = \frac{\Delta\omega}{2} = \pi\Delta\nu \quad , \tag{2-2}$$

where $\Delta\omega$ is the full width (in radians sec^{-1}) at half height for either of the two signals.

A nuclear longitudinal relaxation time, T_1, may be measured by changing M_z, the magnitude of the z component of magnetization, and monitoring its return to M_o, its equilibrium value. In practice this may be done by a $180° - \tau - 90°$ pulse sequence (Carr and Purcell, 1954; Farrar and Becker, 1971). The 180° pulse is a strong radio frequency field, of strength and length just sufficient to invert the z magnetization. Then M_z begins to return to M_o. After a time delay τ, a 90° pulse is applied, and the resulting free induction decay is observed. The initial amplitude of this free induction decay is proportional to the value of M_z at time τ. A series of such sequences finds M_z as a function of τ. Solution of the Bloch equations yields

$$M_z(\tau) = M_o\{1 - 2\exp(-\tau/T_1)\} \quad . \tag{2-3}$$

Rearrangement of Eq. (3) gives

$$\ln\{M_o - M_z(\tau)\} = \ln(2M_o) - \tau/T_1 \quad , \tag{2-4}$$

an equation which may be used to find T_1.

If more than one resonance signal contributes to the free induction decay, measurement of the separate T_1 values is more difficult (Vold, Waugh, Klein and Phelps, 1968).

C. Relaxation in the Presence of Chemical Exchange

McConnell (1958) modified the Bloch equations to include the possibility of chemical exchange of detected nuclei. Swift and Connick (1962) considered the case of an aqueous solution of paramagnetic ions dilute enough so that the nuclei spend a small fraction of their time in the coordination spheres of the ions (i.e., bound), and the detected resonance is that of the bulk nuclei. When rapid passage and saturation effects are negligible, they showed that the contribution to nuclear transverse relaxation arising from the paramagnetic ions is given by

$$\frac{1}{T_{2p}} = \frac{1}{T_2} - \frac{1}{T_{2H_2O}} = \frac{P_m}{\tau_m}\left[\frac{(1/T_{2m})(1/T_{2m}+1/\tau_m)+\Delta\omega_m^2}{(1/T_{2m}+1/\tau_m)^2+\Delta\omega_m^2}\right] \tag{2-5}$$

where T_2 is the measured transverse relaxation time

T_{2H_2O} is the transverse relaxation time for protons in the bulk solution (in the absence of chemical exchange to paramagnetic ions)

T_{2m} is the transverse relaxation time for protons in the first coordination sphere (in the absence of chemical exchange)

τ_m is the time a proton spends bound to a metal ion before exchanging to the bulk

$\Delta\omega_m$ is the difference between the resonance frequency of protons in the first coordination sphere (without exchange) and the actual resonance frequency of the sample.

The quantity P_m is the ratio of the number of protons in first coordination spheres of ions to the total number of protons in the solution (Lee, 1970). The quantity T_{2H_2O} includes the effects of inhomogeneous magnetic fields and of relaxation occurring outside the first coordination sphere of the metal ion. It is common to plot $P_m T_{2p}$ in order to compare solutions of different metal ion concentrations.

Equation (5) may be simplified for certain conditions realized in this study. If

$$\frac{1}{\tau_m} << \frac{1}{T_{2m}} \quad , \tag{2-6}$$

then

$$\frac{1}{T_{2p}} = \frac{P_m}{\tau_m} \quad , \tag{2-7}$$

and relaxation is controlled by the rate of chemical exchange. This condition was found at lowered temperatures for nickel solutions low in acid.

If

$$\frac{1}{\tau_m} >> \frac{1}{T_{2m}} \text{ and } \frac{1}{\tau_m^2} >> \Delta\omega_m^2 \quad , \tag{2-8}$$

then

$$\frac{1}{T_{2p}} = P_m\left[\frac{1}{T_{2m}} + \Delta\omega_m^2\tau_m\right] \quad , \tag{2-9}$$

and relaxation is controlled both by relaxation in the first coordination sphere and by the $\Delta\omega$ mechanism. The later is a mechanism, not effective for T_1 whereby nuclei in the bulk solution lose precessional phase coherence by exchanging between the magnetically dissimilar bulk and bound environments. Equation (9) was used to treat the linewidth data for the cobalt solutions.

If

$$\frac{1}{\tau_m} >> \frac{1}{T_{2m}} \quad \text{and} \quad \frac{1}{(T_{2m}\tau_m)} >> \Delta\omega_m^2 \quad , \tag{2-10}$$

then

$$\frac{1}{T_{2p}} = \frac{P_m}{T_{2m}} \quad , \tag{2-11}$$

and relaxation is controlled solely by the rate of relaxation in the first coordination sphere. This condition was found to hold at all temperatures for the nickel solution high in acid, but was not obtainable for cobalt solutions. This condition was sought in this study, since well known equations for dipolar and scalar coupling (see Section D-1 of this chapter) relate T_{2m} to T_{1e} and T_{2e}.

The quantity $\Delta\omega_m$ is related to the observed chemical shift for the system relative to pure water, $\Delta\omega_{H_2O}$, by a relation due to Swift and Connick (1962):

$$\Delta\omega_{H_2O} = \frac{-P_m\Delta\omega_m}{(\tau_m/T_{2m} + 1)^2 + \Delta\omega_m^2\tau_m^2} \quad . \tag{2-12}$$

In the case where $\frac{1}{\tau_m} >> \frac{1}{T_{2m}}$ and $\frac{1}{\tau_m} >> \Delta\omega_m^2 \tau_m$, Eq. (12) yields

$$\Delta\omega_{H_2O} = -P_m \Delta\omega_m \quad . \tag{2-13}$$

Thus chemical shift measurements may be used to help interpret relaxation measurements.

The analogous equation for longitudinal relaxation in the presence of chemical exchange was first given by Bloembergen and Morgan (1961), and first derived by Luz and Meiboom (1964c). The relaxation due to the paramagnetic ion is given by

$$\frac{1}{T_{1p}} = \frac{1}{T_1} - \frac{1}{T_{1H_2O}} = \frac{P_m}{T_{1m} + \tau_m} \quad , \tag{2-14}$$

where T_1 is the measured quantity, T_{1m} is the longitudinal relaxation time for protons in the first coordination sphere in the absence of chemical exchange, and T_{1H_2O} is the longitudinal relaxation time for protons in the bulk solution (in the absence of chemical exchange to paramagnetic ions). For the T_1 measurements made in this study, $T_{1m} >> \tau_m$, so that

$$\frac{1}{T_{1p}} = \frac{P_m}{T_{1m}} \quad . \tag{2-15}$$

The temperature dependence of T_{1p} and T_{2p} will often indicate which terms in Eqs. (5) and (14) may be neglected. The temperature dependence of τ_{mH_2O}, the exchange lifetime of whole water molecules, is expected to follow the equation of Eyring (1935),

$$\tau_{mH_2O} = \frac{h}{kT} \exp\left[\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}\right] \quad , \qquad (2\text{-}16)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation for water exchange. Values for $\Delta H^{\ddagger}$ are usually in the range of 8-12 kcal mole^{-1} for first row transition metals (Swift and Connick, 1962). This temperature dependence exceeds that expected for molecular rotation or for electron spin relaxation in solution. If Eqs. (6) and (7) are valid, T_{2p} will rapidly become longer as the temperature drops. If Eqs. (8) and (9) are valid, and $\Delta\omega_m^2\tau_m > \frac{1}{T_{2m}}$, then T_{2p} will have exactly the opposite temperature dependence. If Eqs. (10), (11) and (15) are valid, the temperature dependences of T_{1p} and T_{2p} are expected to be smaller. If acid is present in the solution, protons may exchange between the bulk and bound environments by an acid catalyzed mechanism which differs from the mechanism for whole water exchange, as discussed by Swift, Stephenson, and Stein (1967). In this case τ_m is given by

$$\frac{1}{\tau_m} = \frac{1}{\tau_{mH_2O}} + k_2[H^+] \quad . \qquad (2\text{-}16a)$$

The $k_2[H^+]$ term seems to have little temperature dependence in aqueous solutions of metal ions (Swift and Stephenson, 1966). For some ions, the presence of acid is sufficient to change the system from condition (6) to condition (10). This is the case for aqueous Ni(II) below room temperature.

D. Expressions for Nuclear Relaxation

This section will describe all mechanisms which may affect the measured T_1 and T_2. Mechanisms that may affect both T_{1m} and T_{2m} are dipolar coupling between the proton and the electronic spin, scalar coupling with the electronic spin, nuclear spin rotation interaction, and anisotropic chemical shift. The previously mentioned $\Delta\omega$ mechanism only affects T_{2p}. Nuclei in the bulk solution may be relaxed by long range dipolar coupling with the electronic spin, and by several mechanisms which are independent of the presence of paramagnetic ions.

1. Mechanisms for T_{1m} and T_{2m} Relaxation

a. Dipolar Coupling. Early work on relaxation caused by dipolar coupling between two spins was that of Solomon (1955) and of Solomon and Bloembergen (1956). Other important discussions of nuclear relaxation caused by time dependent dipolar coupling to electronic spins are those of Bloembergen and Morgan (1961), Abragam (1961, p. 289ff), and Connick and Fiat (1966). The relaxation rates of a nuclear spin I at a fixed distance r from an electronic spin S are given by

$$\left(\frac{1}{T_{1m}}\right)_d = \frac{S(S+1)\,\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left[6\tau_1 + \frac{14\tau_2}{1+\omega_S^2\tau_2^2}\right] \qquad (2\text{-}17)$$

and

$$\left(\frac{1}{T_{2m}}\right)_d = \frac{S(S+1)\,\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left[7\tau_1 + \frac{13\tau_2}{1+\omega_S^2\tau_2^2}\right] \qquad (2\text{-}18)$$

where we have already assumed that $\omega_I^2\tau_1^2 \ll 1$ and that $\omega_I \ll \omega_S$. Here γ_I and γ_S are the magnetogyric ratios of the protons and electrons,

respectively, and ω_I and ω_S are the respective Larmor precessional frequencies. These two equations are correct only for paramagnetic ions having no orbital contribution to the magnetism. For other ions the quantity $\gamma_S^2 \hbar^2 S(S + 1)$ must be replaced by the mean square of the magnetic moment (Abragam, 1961, p. 303). The quantities τ_1 and τ_2 are defined by

$$\frac{1}{\tau_1} = \frac{1}{\tau_m} + \frac{1}{\tau_r} + \frac{1}{T_{1e}} \tag{2-19}$$

and

$$\frac{1}{\tau_2} = \frac{1}{\tau_m} + \frac{1}{\tau_r} + \frac{1}{T_{2e}} \quad , \tag{2-20}$$

where T_{1e} and T_{2e} are the longitudinal and transverse relaxation times of the electron, and τ_r is the rotational correlation time for the complex. More precisely, the τ_r used in this work will be the rotational correlation time for spherical harmonics of order two, a time equal to one third the time characteristic of dielectric relaxation (Abragam, 1961, p. 300).

Dipolar coupling will later be shown to be virtually the sole mode of relaxation for protons bound to nickel or cobalt ions in aqueous solution.

b. Scalar Coupling. A nuclear spin I may couple with an electronic spin S through a scalar interaction. The corresponding term in the Hamiltonian is $A\bar{I}\cdot\bar{S}$. Solomon and Bloembergen (1956) and Bloembergen (1957a) first proposed this scalar coupling as a mechanism for nuclear relaxation, and the subject has been discussed in detail by Abragam (1961, p. 306ff). The relaxation rates of a nucleus in this case are

$$\left(\frac{1}{T_{1m}}\right)_{sc} = \frac{S(S+1)}{3} (A/\hbar)^2 \frac{2\tau_4}{1 + \omega_S^2\tau_4^2} \tag{2-21}$$

and

$$\left(\frac{1}{T_{2m}}\right)_{sc} = \frac{S(S+1)}{3} (A/\hbar)^2 \left[\tau_3 + \frac{\tau_4}{1 + \omega_S^2\tau_4^2}\right] \tag{2-22}$$

where we have assumed that $\omega_I << \omega_S$, that $1/\tau_3 >> A/\hbar$, and that $1/\tau_4 >> A/\hbar$. The quantities τ_3 and τ_4 are defined by

$$\frac{1}{\tau_3} = \frac{1}{\tau_m} + \frac{1}{T_{1e}} \tag{2-23}$$

and

$$\frac{1}{\tau_4} = \frac{1}{\tau_m} + \frac{1}{T_{2e}} \quad . \tag{2-24}$$

The symbols A and $A/\hbar$ represent the scalar coupling constant, expressed in ergs and in radians sec^{-1}, respectively. The magnitude of A may be obtained through chemical shift measurements. An equation of Bloembergen (1957b) gives the chemical shift of the bound protons relative to pure water as

$$|\Delta\omega_m| + |\Delta\omega_{H_2O}| = \omega_I S(S+1) \frac{\gamma_S}{\gamma_I} \frac{A}{3kT} \quad . \tag{2-25}$$

where $\Delta\omega_m >> \Delta\omega_{H_2O}$ for dilute solutions. This equation is only approximately correct for ions whose magnetic susceptibility deviates significantly from the Curie law. The more general case is discussed by Golding (1964) and by Kurland and McGarvey (1970). The shift $\Delta\omega_m$ is related to the observed chemical shift through Eq. (12). Relaxation through scalar coupling can be important for protons when the electronic

relaxation times are relatively long. However, it will be shown to be quite unimportant in this study, since the transition metal ions used were specifically chosen to have very short electron relaxation times.

c. Other Mechanisms. Three other conceivable mechanisms for T_{1m} and T_{2m} relaxation are mentioned here for completeness. Each will be quickly dismissed as being negligible in the present work.

Relaxation through spin rotation interaction arises from the coupling of spins with magnetic moments generated by molecular rotation. The time scale for the interaction is the time between interruptions of the molecular rotation, a time usually quite short compared to the rotational correlation time. This spin rotation interaction has been discussed as a weak relaxation mechanism for nuclei in diamagnetic molecules (Hubbard, 1963), and for electrons in paramagnetic complexes (Atkins and Kivelson, 1966; Nyberg, 1967). In the later case, the interaction strength was related to the amount of orbital angular momentum in the complex. In principle, nuclear spin rotation relaxation should be much more effective in paramagnetic complexes having orbital angular momentum than it is in diamagnetic molecules. In the absence of a quantitative treatment, it may nevertheless be seen why nuclear spin rotation relaxation may be neglected in the presence of dipolar coupling with an electronic spin. First, since dipolar coupling includes contributions from both electron spin and orbital angular momentum, it is expected to be a stronger interaction than spin rotation, which has no contribution from electron spin angular momentum. Second, the correlation time for dipolar coupling will be longer than the time scale for spin rotation interaction, even in the presence of rapid

electron spin relaxation (Atkins and Kivelson, 1966).

Relaxation through anisotropic chemical shift has been described by Abragam (1961). This is an extremely weak mechanism, and is rarely observed (Farrar and Becker, 1971, p. 60). An order of magnitude calculation by Lee (1970, p. 45) shows that it may always be neglected for nuclei coupled to paramagnetic ions.

Relaxation through quadrupole coupling has been described by Abragam (1961). However, protons cannot relax by this means, since nuclei of spin one-half do not couple with electric field gradients.

2. Other Mechanisms for T_{1p} and T_{2p} Relaxation

a. $\Delta\omega$ Mechanism. This mechanism has been discussed by McConnell and Berger (1957) and by Swift and Connick (1962). It was shown in Section C that when chemical exchange of protons is fast enough,

$$\frac{1}{T_{2p}} = P_m\left[\frac{1}{T_{2m}} + \Delta\omega_m^2\tau_m\right] \quad . \tag{2-26}$$

The contribution from the $\Delta\omega$ mechanism is then just $P_m\Delta\omega_m^2\tau_m$. The magnitude of $\Delta\omega_m$ may be obtained from chemical shift measurements, according to Eq. (12). This mechanism was important for cobalt solutions, especially at high fields and low temperatures, but negligible for the nickel solutions.

b. Second Coordination Sphere Relaxation. Nuclei in the bulk water may be relaxed through dipolar coupling with paramagnetic ions. Equations (17) and (18) may be used to describe the relaxation if proper modifications are made. The interaction is no longer interrupted by rotation of the complex, and τ_m must be replaced by a translational

diffusion correlation time τ_D for solvent molecules which may be a function of r (Bloembergen, Purcell and Pound, 1948). Since r^{-6} and τ_D are not constants, the whole expression must be integrated over all possible values of r. Following Abragam (1961, p. 304), Wüthrich and Connick (1967) gave the result when the interruption by translational diffusion is faster than the interruption by electron spin relaxation. Luz and Meiboom (1964c) gave the result when electron spin relaxation is faster than translational diffusion, but made the assumption that $T_{1e} = T_{2e}$. Pfeifer (1961) gave the result when both modes of interruption must be considered simultaneously. If we use the integration procedure of Luz and Meiboom, and assume that $T_{1e} << \tau_D$ and that $T_{2e} << \tau_D$, we find that the contribution of second coordination sphere relaxation to the total relaxation is given by

$$\frac{1}{T_{1p}} = \frac{4\pi nS(S+1)\,\gamma_I^2\gamma_S^2\hbar^2}{45d^3}\left[6T_{1e} + \frac{14T_{2e}}{1+\omega_S^2T_{2e}^2}\right] \qquad (2\text{-}27)$$

and

$$\frac{1}{T_{2p}} = \frac{4\pi nS(S+1)\,\gamma_I^2\gamma_S^2\hbar^2}{45d^3}\left[7T_{1e} + \frac{13T_{2e}}{1+\omega_S^2T_{2e}^2}\right] . \qquad (2\text{-}28)$$

Here d is the distance of closest approach of bulk protons to the paramagnetic ion. The quantity n is the number of paramagnetic ions per unit volume of solution, given by NM, where N is Avogadro's number and M is the molar concentration of the metal ions. As discussed following Eq. (18), the expression $\gamma_S^2\hbar^2S(S+1)$ is strictly correct only for ions which have no orbital magnetism. This contribution

to the overall relaxation is much smaller than that of relaxation in the first coordination sphere, but it cannot always be neglected.

c. Mechanisms Independent of Paramagnetic Ions. Relaxation of protons in water has contributions from dipolar coupling with other protons (BPP, 1948), spin-spin interaction with natural abundance oxygen 17 (Meiboom, 1961), and spin rotation (Smith and Powles, 1966). This subject has been reviewed by Krynicki (1966). Dissolved diamagnetic salts may lengthen or shorten proton relaxation rates by changing the correlation time of the proton-proton dipolar coupling (Hertz, 1967 p. 216). Dissolved oxygen, being paramagnetic, will relax nuclei in water (Chiarotti and Giulotto, 1954). These effects are all small, and magnetic field inhomogeneity will usually have a greater effect on measured T_2 than any of the relaxation mechanisms mentioned, even in a carefully tuned magnet.

There are two reasons why none of these interactions need be considered in detail here. First, their effects are small compared to those of dissolved paramagnetic ions. Second, it is easy to correct for their effects by making duplicate relaxation measurements on similar solutions which lack the paramagnetic ions.

III. THEORY OF ELECTRON SPIN RELAXATION

A. Introduction

It has been shown how nuclear magnetic relaxation times are related to electron spin relaxation times. This chapter, in turn, will show how electron spin relaxation is related to fundamental properties such as crystal fields, orbital angular momentum, and molecular motions.

In general, electron spins relax much more rapidly than do nuclear spins. Their larger magnetic moments enable them to respond more rapidly to fluctuating magnetic fields. In addition, spin orbit coupling allows electrons to be relaxed through the effects of fluctuating electric fields.

Mechanisms for electron spin relaxation of transition metal ions in solution may be divided into two general classes: those that are important in solids as well as in liquids, and those that are important only in liquids. The principal mechanisms belonging to the first class are the Van Vleck direct, the Van Vleck Raman, and the Orbach process. The principal mechanisms belonging to the second class are: modulation of zero field splitting, anisotropic hyperfine interaction, anisotropic Zeeman interaction, and spin rotation interaction. The general theoretical approaches of the two classes are quite different.

Mechanisms of electron spin relaxation in the solid state act through the combined effects of fluctuating electric fields and spin orbit interaction. Just as the static electric field produced by the ligands in a complex produces a crystal field splitting of the orbital

levels, so can fluctuations of the ligand field occurring at the proper frequency induce transitions between the levels. The spins are affected to the extent that spin orbit coupling mixes orbital and spin functions together. The matrix elements to be calculated are those of electric field potentials. This is in contrast to the usual theory of relaxation in liquids, which calculates matrix elements of the spin operators found in the spin Hamiltonian of the system. As spins flip, the crystal lattice loses or gains energy in the form of quantized lattice vibrations, or phonons. Relaxation rates in solids are strongly dependent upon the existence of sufficient phonons having the proper frequency. These same electric field fluctuation (EFF) mechanisms also operate in liquids. Here, however, the concept of phonons loses its simplicity, and alternate concepts are needed to describe the motions in liquids.

Most mechanisms of electron spin relaxation which are effective only in liquids act by making time dependent those interactions already present in solids and described by terms in the spin Hamiltonian. Relaxation through spin rotation interaction is an exception. The strengths of these interactions, which can be expressed in magnetic field units, can often be estimated by making measurements of shifts and splitting of EPR signals of hydrated metal ions in single crystals or glasses. For example, suppose that the slow rotation of such a crystal in an external magnetic field produces an EPR signal shift of 10 gauss. Then if that crystal is dissolved in water, and the symmetry of the ligand field at the ion is not changed, we may guess that the rotating ion is now seeing an oscillating magnetic field of the order of 10 gauss. The

motions in liquid which are important to relaxation are usually treated classically. The common model of rotation, for example, is that of Debye (1929), who pictured a molecule as a sphere in a viscous medium, subject to many small random changes of angle. Theories of EPR relaxation in liquids, like those for NMR relaxation, have been developed along the lines of first order perturbation theory, since the fluctuating magnetic fields are usually very much smaller than the external magnetic field. An expression for a relaxation rate may usually be thought of as the product of the square of an interaction energy, and a function of the time scale for the molecular motion.

It should be mentioned that if a crystal or a solution has a high concentration of paramagnetic ions, the ions can interact with each other via dipolar coupling or spin exchange. Both effects can influence relaxation times, but can be eliminated by keeping the concentration of the paramagnetic ion low enough. There is no reason to expect either of these interactions to be present in the particular solutions used in this study, and so neither effect will be considered further.

As we saw earlier, an ion with an EPR signal too wide to observe has a $T_{2e} < 3.3 \times 10^{-11}$ sec, and therefore a relaxation rate $(T_{2e})^{-1} > 3 \times 10^{10}$ sec^{-1}. Therefore as we consider each mechanism for electron spin relaxation, we may neglect any mechanism that does not seem capable of producing $(T_{2e})^{-1} = 3\times10^{10}$ sec^{-1} for Ni(II) or Co(II).

B. Mechanisms Effective in Solids and Liquids

1. Relaxation in Solids

Theory for electron spin relaxation in solids reflects the fact that it was developed to explain EPR measurements made upon ions, usually of effective spin one half, in crystalline solids, usually below 20°K. Fairly good description has been made of the observed temperature and field dependences of relaxation, although calculations of absolute values of relaxation rates are rarely good to better than an order of magnitude. We shall see that the successes of existent theory are due in large measure to an adequate description of the crystalline lattice rather than to a detailed understanding of the method of energy transfer between spin and lattice. Thus it is only with difficulty that equations describing relaxation in solids may be adapted for the liquid case.

The most important contributions to the subject of electron spin relaxation in solids have been those of Van Vleck (1940) and of Orbach (1961). General discussions of relaxation in solids are those of Stevens (1967), Orton (1969), Abragam and Bleaney (1970), and Abragam (1961, pp. 401-8). Standley and Vaughan (1969) give a compilation of experimental results.

Since relaxation depends upon energy transfer between the spin system and the lattice, careful consideration must be made of the manner in which thermal energy appears in crystalline lattices. This lattice energy is quantized as phonons. These are energy carrying waves of lattice vibration, whose frequencies are

related to such crystal properties as interatomic spacings and force constants (Kittel, 1966). The phonon distribution is known in detail for only a few simple solids. In the absence of accurate knowledge of a particular crystal, it is typical to make the Debye, or continuum, approximation to the phonon spectrum. This approximation was utilized at an early date to explain the thermal properties of solids (see, e.g. Kittel, 1966, Ch. 6). If the difference between transverse and longitudinal wave velocities is neglected, the phonon density per unit volume in the frequency range ω to $\omega + d\omega$ may be approximated as

$$\rho_p d\omega = \left\{ \frac{3\omega^2 d\omega}{2\pi^2 v^3} \right\} \left\{ \frac{1}{\exp(\hbar\omega/kT_{ph})-1} \right\} \tag{3-1}$$

where v is the velocity of sound and T_{ph} is the phonon temperature. At temperatures below about 5°K, the spin system may transfer energy to the phonons faster than the phonons can transfer energy to the bath surrounding the crystal. This situation, known as the phonon bottleneck, leads to $T_{ph} > T$. Expression (1), shown in Fig. 1, may be seen as a product of the number of phonon modes, $(3\omega^2 d\omega/2\pi^2 v^3)$, times the number of phonons per mode. For temperatures above a few degrees Kelvin, most phonons have frequencies far exceeding a typical Larmor frequency. As we shall see, this leads to the rather striking temperature dependences often observed for electron relaxation in solids.

The phonons play their role in relaxation by introducing a time dependence into the crystal field potential seen by the central metal ion. Following Orbach (1961), it has become common to expand the crystal field potential V in powers of the strain ε:

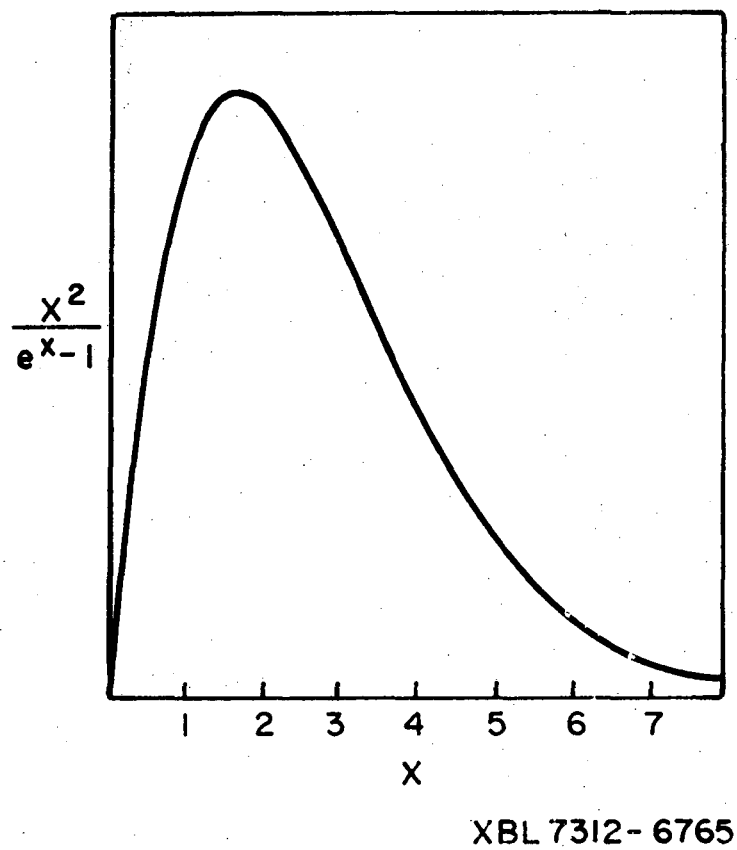

Fig. 1. Usual continuum approximation of the phonon density in crystalline solids as a function of phonon frequency. Here $x = \hbar\omega/kT$.

$$V = V(0) + \varepsilon V(1) + \varepsilon^2 V(2). \qquad (3\text{-}2)$$

Here V(0) is just the static field potential, and the other terms represent the additional potential generated by the alteration of the crystal field caused by phonons. Of course, each term in Eq. (2) actually represents a small sum of terms of different symmetries. The unitless strain constant ε may be thought of as a fractional change of distance of the ligands. Scott and Jeffries (1962) and others have obtained order of magnitude correspondence between theory and experiment by introducing the simplification that V(0) = V(1) = V(2).

Waller (1932) considered processes in which phonons modulated the magnetic dipolar coupling between paramagnetic ions. These processes were found to be too weak by many orders of magnitude, and will not be considered here.

Since Eq. (2) gives the time dependent operator, we see that the matrix elements to be calculated will follow the selection rules for electric field induced transitions. The most important of these rules is that there are no allowed matrix elements of an electric perturbation between a pair of Kramers conjugate states. This is just a restatement of Kramers' rule. It means that, to first order, a fluctuating electric field cannot induce transitions between the two levels of a spin doublet. This transition will be allowed, however, to the extent that an external magnetic field mixes excited states into the ground state (Abragam and Bleaney, 1970, p. 558). This admixture is of order $(\hbar\omega/\Delta)$, where Δ is a crystal field splitting, and therefore depends upon the strength of the external magnetic field. Ions with even spin

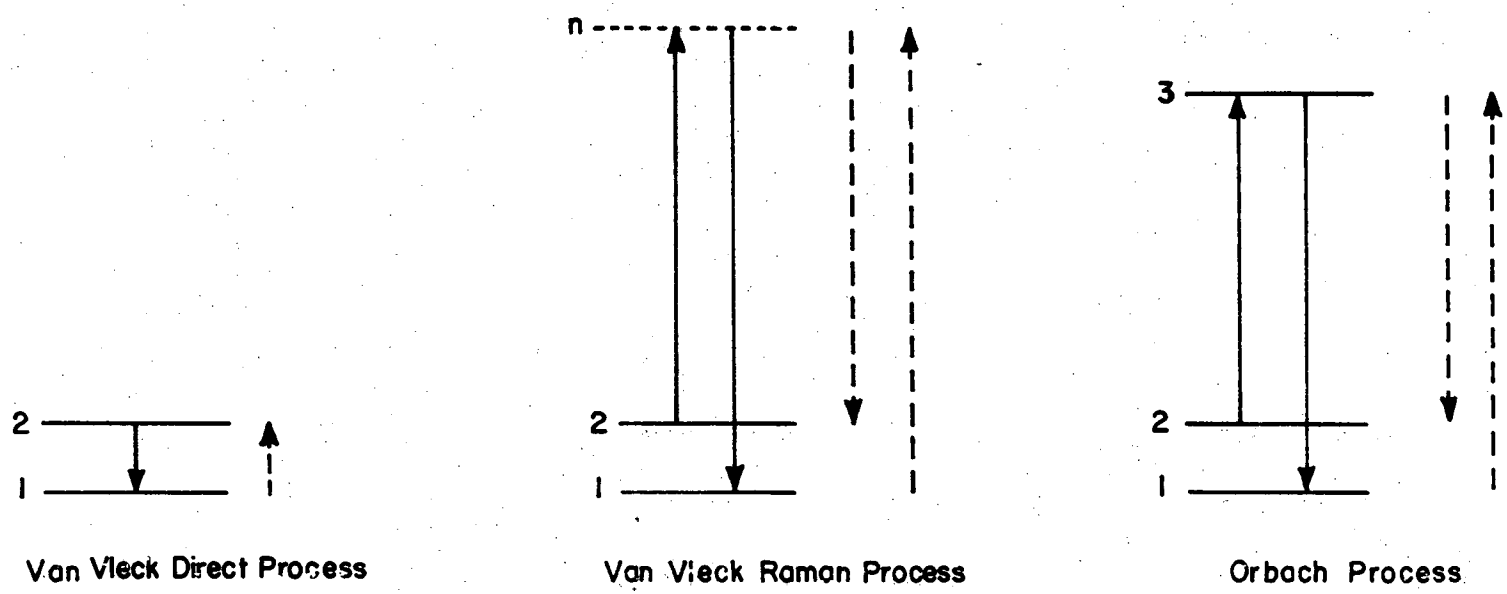

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Fig. 2. Electric field fluctuation mechanisms for electron spin relaxation between levels 1 and 2. Solid lines represent electron transitions. Dotted lines represent lattice transitions. The Van Vleck process utilizes a virtual excited state n.

are not limited by this selection rule difficulty, and show relaxation behavior somewhat different from that of Kramers' ions.

The strain constant is also considered an operator. It acts upon the phonon states, and has matrix elements analogous to those of a harmonic oscillator (Orton, 1969, p. 160). These elements are independent of field and vary with the square root of the frequency.

We may now consider the three important mechanisms for electron spin relaxation in the solid state. All three concern themselves only with the longitudinal relaxation time T_{1e}, which is the inverse of the transition rate W_{12} between the two spin states. The transverse relaxation time in solids is often determined by dipolar broadening, and frequently T_{1e} is much longer than T_{2e}. The first of these three mechanisms, the Van Vleck process, is illustrated in Fig. 2a. This is a mechanism in which a spin flips through the simultaneous creation or annihilation of a phonon of equal energy. The relaxation rate W_{12} between levels 1 and 2 may be represented by

$$W_{12} \propto |\langle \psi_1 | V(1) | \psi_2 \rangle|^2 |\langle \phi_1 | \varepsilon | \phi_2 \rangle|^2 \rho_{ph} \qquad (3\text{-}3)$$

where ψ_1 and ψ_2 represent the electron energy states, ϕ_1 and ϕ_2 represent the lattice states, and the other symbols have been defined in Eqs. (1) and (2). In crystalline solids this process is limited in effectiveness because most phonons have frequencies above the Larmor frequency, and are therefore ineffective in causing relaxation. If kT greatly exceeds $\hbar\omega_{12}$, the energy separation of the spin states, then

$$W_{12} \propto H^2 T \text{ for non-Kramers ions} \tag{3-4a}$$

and

$$W_{12} \propto H^4 T \text{ for Kramers ions,} \tag{3-4b}$$

where H is the external magnetic field.

The Van Vleck Raman process, shown in Fig. 2b, is one in which a transition occurs through the simultaneous creation of one phonon and annihilation of another. The energy difference of the two phonons is equal to the energy separation of the ground states 1 and 2. This process is usually pictured as an excitation to a virtual intermediate state. The Raman process usually dominates the direct process in solids above about 5°K, since it can make use of phonons of all avaialable frequencies. The relaxation rate, as calculated by second order perturbation theory, may be expressed as

$$W_{12} \propto \int_0^{\omega_{max}} \frac{|\langle \psi_1 | V(1) | \psi_n \rangle \langle \psi_n | V(1) | \psi_2 \rangle|^2 \langle \varepsilon \rangle^2}{(E_n)^2} \rho_{ph}^2 \, d\omega \tag{3-5}$$

where $\langle \varepsilon \rangle = |\langle \phi_1 | \varepsilon | \phi_n \rangle \langle \phi_n | \varepsilon | \phi_2 \rangle|$, and E_n is the energy separation of the virtual state ψ_n and the ground state. The frequency ω_{max} is given by

$$\omega_{max} = v \left\{\frac{6\pi^2 N}{V}\right\}^{1/3} \tag{3-6}$$

where v is the velocity of sound, N is the number of atoms in the crystal, and V is the volume of the crystal. The Debye temperature, T_D, may be defined by the relation

$$T_D = \frac{\hbar}{k}\,\omega_{max} \tag{3-7}$$

A typical ω_{max} is perhaps 2×10^{13} sec^{-1}, corresponding to a Debye temperature of a few hundred degrees Kelvin. The necessity for imposing a maximum on the phonon frequency is somewhat artificial. It arises from the assumed distribution (1), and the requirement that the number of phonon modes not exceed three times the number of atoms.

Equation (5) contains an integral of the form

$$W_{12} \propto \int_0^{\omega_{max}} \frac{\exp(\hbar\omega/kT)}{\{\exp(\hbar\omega/kT) - 1\}^2}\,\omega^6\,d\omega \tag{3-8}$$

whose integration is discussed by Abragam and Bleaney (1970, p. 563). At temperatures far below the Debye temperature, where $kT \ll \hbar\omega_{max}$, the upper limit of the integral may be extended to infinity, and the integral is then proportional to T^7. This leads to

$$W_{12} \propto H^0T^7 \quad \text{for non-Kramers ions at low temperature} \tag{3-9a}$$

and

$$W_{12} \propto H^0T^9 \quad \text{for Kramers ions at low temperature.} \tag{3-9b}$$

Abragam and Bleaney (1970, p. 563), discuss the so called "Van Vleck cancellation", which introduces the additional temperature dependence into the relaxation rate for Kramers ions. At temperatures above the Debye temperature, $kT \gg \hbar\omega$, and

$$W_{12} \propto H^0T^2 \quad \text{for all ions at high temperatures.} \tag{3-10}$$

At temperatures comparable to the Debye temperature, the temperature dependence of the Raman process is less simple.

The Raman process we have described is more properly called the second order Van Vleck Raman process. A first order Raman process exists, in which the crystal field potential V(2) has allowed matrix elements between the relevant spin states. In this case the transition rate may be written as

$$W_{12} \propto |\langle \psi_1 | V(2) | \psi_2 \rangle|^2 \; |\langle \phi_1 | \varepsilon^2 | \phi_2 \rangle|^2 \; \rho_{ph} \; . \tag{3-11}$$

This first order Raman process is usually considered to be weaker than the second order Raman process, and will not be considered further.

Orbach and Blume (1962) discuss Van Vleck Raman relaxation for ions with spins greater than one half. Here the intermediate state can be one of the spin states within the ground multiplet. In this case the relaxation rate varies with T^5 at very low temperatures and with T^2 at very high temperatures.

Orbach (1961) described a two phonon, two step process involving a real excited state (Fig. 2c). First the ion goes to an excited electronic state with the simultaneous annihilation of a phonon. Then the ion drops back to the ground state with the emission of another phonon. Each of the two steps is actually a Van Vleck direct process, describable by Eq. (3). If the excited state is separated from the ground state by an energy E_3 exceeding kT, then the rate limiting step will be the one involving the transition to the excited state. Since the energy separation of the excited and ground states is little affected by the external magnetic field, the magnetic field dependence largely disappears. The transition rate is then

$$W_{13} \propto (E_3)^3 \{\exp(E_3/kT) - 1\}^{-1} . \qquad (3\text{-}12)$$

The temperature dependence arises entirely from the temperature dependence of phonons of energy E_3. When a low lying excited state exists, the Orbach process usually is the dominant relaxation mechanism above 20-50°K. For ions having a spin greater than one half, a spin state within the ground multiplet may serve as the intermediate state (Orton, 1969).

2. Relaxation in Liquids

Relaxation of electron spins in solids through EFF mechanisms seems moderately well understood. However, the extension of the theory of these processes to liquids has drawn little attention. This is due in large part to the lack of experimental data. Ions which have relatively low lying excited states, such as the hexaquo complexes of Ti(III), Fe(II), or Co(II), are subject to rapid relaxation via the Orbach process, with the result that the EPR resonances cannot usually be detected in the temperature range of ordinary liquids. Some information about T_{1e} values is available from NMR relaxation measurements made upon nuclei bound to paramagnetic ions in solution. However, these measurements cannot in general be made over a very wide temperature range, and workers have been hesitant about assigning mechanisms to the electron relaxation. On the other hand, ions which have relatively sharp EPR signals in crystals at room temperature usually exhibit much wider lines in solution. This is usually interpreted to mean that the EFF mechanisms for these ions are significantly weaker in solution than are the magnetic field fluctuation mechanisms to be described in section

C of this chapter. The implicit assumption is that the EFF mechanisms are no more effective in solution than they are in solids.

The extension of the EFF mechanisms to liquids is hampered also by the difficulties of describing the relevant molecular motions. Concepts such as the Debye temperature, phonon bottleneck, and Debye approximation to the phonon distribution now lose their simplicity.

Theoretical work in this area has been done by Al'tshuler and Valiev (1959), Hayes (1961), Valiev and Zaripov (1962), and Kivelson (1966). Unfortunately the treatments are generally restricted to ions with spin of one half. Each of these treatments of EFF mechanisms in solution should be regarded with a healthy skepticism until it is possible to make comparisons with a reasonable body of experimental data.

Al'tshuler and Valiev (1959) adapted the Van Vleck direct process to liquids. Their mechanism actually is more similar to the Orbach process, since they usually ignored transitions within the ground multiplet. They pictured the vibrations of the complex to be affected in a random way by the Brownian motions of the surrounding molecules. They wrote the relaxation rate between levels 1 and 2 as

$$W_{12} \propto \overline{Q^2}\, |\langle \psi_1 | V(1) | \psi_2 \rangle|^2 \frac{\tau_c}{1 + \omega_{12}^2 \tau_c^2} \tag{3-13}$$

where ω_{12}, the frequency separation of the two levels, need not be the resonance frequency. Here $\overline{Q^2}$ is a kind of average amplitude of the vibrations of the complex, having the form

$$\overline{Q^2} \propto \left(\frac{1}{v_o}\right) \coth x = \left(\frac{1}{v_o}\right) \frac{e^x + e^{-x}}{e^x - e^{-x}} \tag{3-14}$$

where $x = \frac{h\nu_o}{2kT}$, and ν_o is a vibrational frequency for the complex. The value of ν_o varies with the nature of the ligand (Kobayashi and Fujita, 1955), but for hexahydrates of the transition metals it is generally between 200 and 300 cm^{-1}. (Schultz, 1942). Hence, near room temperature, where 2kT is about 400 cm^{-1}, the function coth x cannot readily be simplified to the low temperature form, $\coth \frac{h\nu_o}{2kT} = 1$, nor to the high temperature form, $\coth \frac{h\nu_o}{2kT} = \frac{2kT}{h\nu_o}$. The correlation time τ_c was thought to be inversely proportional to the square root of the absolute temperature. They inferred this relation from the temperature dependence of the linewidths of the infrared spectra of rare earth ions in crystals. The functions ψ_1 and ψ_2 and the sum of potentials V(1) have the same meaning as in Eqs. (2) and (3). Thus if relaxation takes place through an excited state, such that $\omega_{12}^2\tau_c^2 >> 1$, then

$$W_{12} \propto (T)^{1/2} \coth\left(\frac{h\nu_o}{2kT}\right) \tag{3-15}$$

if

$$\omega_{12}^2\tau_c^2 << 1, \text{ then}$$

$$W_{12} \propto (T)^{-1/2} \coth\left(\frac{h\nu_o}{2kT}\right) \tag{3-16}$$

Hayes (1961) has criticized the theory of Al'tschuler and Valiev on two counts. He disagreed with the functional form they assigned to $\overline{Q^2}$. He also considered the spectral density $\tau_c(1 + \omega_{12}^2\tau_c^2)^{-1}$ they used to be improperly normalized for the model of relaxation they proposed. He stated that if $\hbar\omega_{12} << kT$, the spectral density of the relevant

molecular motion at the frequency ω_{12} should be proportional to the absolute temperature. He concluded that if there were no temperature dependence to the coupling between the solvent motions and the vibrations of the complex, the relaxation rate should be directly proportional to the temperature.

Valiev and Zaripov (1962) extended the work of Al'tshuler and Valiev. They considered those terms in the perturbation Hamiltonian which were quadratic in the coordinates. They wrote complex expressions for the spectral densities of the perturbing energy in terms of the rotational times and also of the frequencies of the various vibrational modes. They expressed the temperature dependence of the relaxation rate as

$$\frac{1}{T_{1e}} \propto \coth^2\left(\frac{h\nu_o}{2kT}\right)\frac{\tau}{1 + \omega_{12}^2\tau^2} \tag{3-17}$$

where τ is apparently a rotational correlation time.

Kivelson (1966) investigated all the EFF mechanisms. He discussed their absolute strengths and relative importances in solution. He guessed that the correlation function for the amplitudes q_i of electric polarization induced by solvent motions was of the form

$$q_i(0)q_i(\tau) = (q_i)^2\exp(-|\tau|/\tau_c) \ . \tag{3-18}$$

Upon integration over time, this correlation function yields the sort of spectral density seen in Eq. (13). This correlation time τ_c was said to be similar in nature and magnitude to the correlation time that enters into expressions for infrared and Raman vibrational relaxation.

Its temperature dependence was not made explicit.

In reporting Kivelson's equations, we shall write only those factors which have a field or temperature dependence, and neglect the constants, some of which are admitted by him to be "difficult to estimate". For the Van Vleck direct process he found that

$$W_{12} \propto \frac{\omega_{12}^2 \tau_c}{1+\omega_{12}^2 \tau_c^2} \tag{3-19}$$

Thus there is a field dependence when the molecular motions are fast enough to make $\omega_{12}^2 \tau_c^2 < 1$. This arises because the levels 1 and 2 are supposed equal in energy in the absence of an external magnetic field. For the second order Van Vleck Raman process, in the case where $\omega_{12}^2 \tau_c^2 \ll 1$,

$$W_{12} \propto \frac{1}{\tau_c} \quad . \tag{3-20}$$

For the Orbach process, he concluded that

$$W_{12} \propto \frac{(\tau_c)^{-1}}{\exp(E_3/kT)-1} \tag{3-21}$$

where, as in Fig. 2c and Eq. (12), E_3 is the energy of the excited intermediate state. Equation (21) is valid only if $(E_3\tau_c/\hbar)^2 \geqslant 1$, which means that E_3 must exceed about 10 cm^{-1}. Kivelson also considered the first order Van Vleck Raman process and a so called direct vibrational process, and found them both unimportant.

Equation (19) for the Van Vleck direct process may be compared to Eq. (4b) for the case of solids. Equation (20) for the Van Vleck Raman process may be compared to Eq. (10). Equation (21) for the

Orbach process may be compared with Eq. (12). The Bose-Einstein factor appearing in Eq. (21) was said by Kivelson to account for the populations of liquid "lattice states". This interpretation seems odd in view of his correlation function approach to the solvent motions.

Kivelson concluded that in liquids, just as in solids, the Orbach process will dominate the other EFF mechanisms if a low lying electronic level is present such that E_3 is less than about 6kT.

It will be suggested later that the Orbach mechanism is primarily responsible for the relaxation of Co(II) in aqueous solution. Although $Co(H_2O)_6^{2+}$ has a spin of 3/2, its relaxation may be treated by theory derived for the case of S = 1/2. Under the influence of an octahedral crystal field, Co(II) has a Kramers spin doublet ground state of effective spin one half which is separated from the lowest excited state by a few hundred cm^{-1} (Abragam and Bleaney, 1970, p. 446).

Ni(II), of course, has a spin of one. However, EFF mechanisms are probably unimportant for its relaxation in solution. An upper limit for the strength of the EFF mechanisms can be estimated from EPR linewidths of Ni(II) ions in octahedral coordination in diamagnetic crystal lattices. If we take a representative EPR line width of a Ni(II) sample at room temperature to be perhaps 200 gauss, we see that the EFF mechanisms can do no better than produce a relaxation rate of $(T_{2e})^{-1} = 3\times10^9\ sec^{-1}$. This is small compared to the relaxation rate of Ni(II) in solution. This assumes that the EFF mechanisms for the relaxation of Ni(II) are no more effective in liquids than in solids. This assumption is reasonable, but rather difficult to verify.

C. Mechanisms Effective Only in Liquids

The principle mechanisms for electron spin relaxation effective only in liquids are: anisotropic Zeeman interaction, anisotropic hyperfine interaction, spin rotation interaction, and modulation of zero field splitting. This last mechanism, which exists only for ions of spin greater than one half, is the only one of these mechanisms which appears powerful enough to produce a T_{1e} as short as 3×10^{-11} sec.

Lewis and Morgan (1968) have extensively reviewed the subject of paramagnetic relaxation in solutions. The formalism of relaxation theory has been well discussed by Slichter (1963), Abragam (1961), Redfield (1965), and Wangness and Bloch (1953). Treatments of EPR relaxation in general are given by Hudson and Luckhurst (1969a) and by McLachlan (1964).

1. Anisotropic Zeeman and Hyperfine Interactions

In EPR measurements of single crystals, the resonance line position will be affected by the strengths of the Zeeman interaction and the hyperfine interaction with any nuclear spin present. If these interactions are anisotropic, rotation of the crystal produces resonance line shifts. In solution, random tumbling of the complex will produce oscillating magnetic fields at the ion. These oscillating fields will produce relaxation to the extent that the oscillations have frequency components at the Larmor frequency. McConnell (1956) considered these interactions for relaxation of ions having axial symmetry. Kivelson (1960) and Wilson and Kivelson (1966a) have extended the theory by removing the requirement of axial symmetry and by retaining small terms previously neglected. Their complicated equations have been discussed by Chang (1971). However, for the present discussion, the equation of McConnell shall suffice.

He wrote the relaxation rate due to these anisotropic terms as

$$\frac{1}{T_{1e}} = \frac{2}{15\hbar^2} [(g_{\parallel} - g_{\perp})\beta^4 + bI_z]^2 \frac{\tau_r}{1 + \omega_s^2 \tau_r^2} \tag{3-22}$$

where $b = A_{\parallel} - A_{\perp}$, ω_s is the Larmor frequency, and β is the Bohr magneton. The coupling constant A was encountered earlier in the discussion of nuclear relaxation via scalar coupling with electrons. The rotational correlation time τ_r is given by the Stokes-Einstein equation,

$$\tau_r = \frac{4\pi\eta a^3}{3kT} \tag{3-23}$$

where η is the viscosity, a is the radius of the complex, k is Boltzmann's constant, and T is the absolute temperature. The Zeeman contribution is expected to dominate the hyperfine contribution if the external field H_o becomes large enough. Values for $g_{\parallel} - g_{\perp}$ and b can be obtained from EPR spectra of glasses. Use of such values in Eq. (22) generally produces good correspondence with measured solution linewidths for ions not subject to relaxation via other mechanisms. These linewidths are often from one to fifty gauss in an external field of 3300 gauss. For the case where the anisotropy of the hyperfine interaction is small compared to the anisotropy of the Zeeman interaction, the field and temperature dependence of Eq. (22) may be ascertained. If $\omega_o^2 \tau_r^2 << 1$, then

$$\frac{1}{T_{1e}} \propto \frac{H_o^2 \eta}{T} \tag{3-24}$$

If $\omega_o^2 \tau_r^2 << 1$, and b is still negligible, then

$$\frac{1}{T_{1e}} \propto \frac{T}{\eta} \tag{3-25}$$

2. Spin Rotation Interaction

As a molecule rotates in a gas or liquid, the rotation of the electrons creates a magnetic field which interacts with any nuclear or electron spins in the molecule. This interaction has been considered as a mechanism for nuclear relaxation by several people, notably Hubbard (1963), who found for molecules with cylindrical symmetry that

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{2IkT\tau_\omega}{3\hbar^2}\{2(C_\perp)^2 + (C_\parallel)^2\} \tag{3-26}$$

where $C_\perp$ and $C_\parallel$ are the spin rotation interaction constants, and I is the moment of inertia.

The angular momentum correlation time τ_ω, which is a mean time between interruptions of the molecular rotation, is given by

$$\tau_\omega = \frac{1}{8\pi a^3 \eta} \tag{3-27}$$

where a and η retain their same meanings. By comparison with Eq. (23), the relation between τ_r, the rotational correlation time, and τ_ω is given by

$$\tau_\omega \tau_r = \frac{I}{6kT} \tag{3-28}$$

Using Eq. (27), we find

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{I^2 k}{12\pi\hbar^2 a^3}\left(\frac{T}{\eta}\right)\left\{(C_\parallel)^2 + 2(C_\perp)^2\right\} \tag{3-29}$$

The evaluation of the spin rotation constants $C_\parallel$ and $C_\perp$ from first principles is quite difficult.

Spin rotation as a mechanism for electron relaxation has been considered by Nyberg (1967), and by Atkins and Kivelson (1966). Both papers show that the electron spin rotation constants of a molecule may be directly related to its g values. The Atkins and Kivelson result may be expressed quite simply as

$$\frac{1}{T_{1e}} = \frac{1}{T_{2e}} = \frac{k}{12\pi a^3}\left(\frac{T}{\eta}\right)\left\{(\Delta g_{\parallel})^2 + 2(\Delta g_{\perp})^2\right\} \tag{3-30}$$

where $\Delta g_{\parallel} = g_{\parallel} - 2.0023$ and $\Delta g_{\perp} = g_{\perp} - 2.0023$. This equation is valid only when $\Delta g/g$ is small. This mechanism is seen to be linearly dependent upon temperature, in contrast with most other relaxation mechanisms operating in solution, and independent of the external magnetic field. It is not dependent upon any anisotropy of the Zeeman interaction. Spin rotation relaxation is in principle dependent upon the magnetic field. However the usual values for τ_{ω} are so short that $\omega^2\tau_{\omega}^2$ is always negligible compared to unity, and the more general forms of Eqs. (26), (29), and (30) are rarely written. In Eq. (30), the only adjustable parameter is the molecular radius. Spin rotation relaxation was used by Wilson and Kivelson (1966a) to account for some of the relaxation of vanadyl acetylacetonate in toluene, and by Wilson and Kivelson (1966b) to account for some of the relaxation of copper acetylacetonate in toluene and chloroform. Excellent agreement with experiment was found in both studies. Nyberg (1967) has indicated that Eq. (30) should be valid without modification for ions of spin greater than one half.

3. Modulation of Zero Field Splitting

Transition metal ions with spin greater than one half generally exhibit, in the absence of an external magnetic field, a lifting of at least some of the degeneracy of the spin multiplet. This zero field splitting (or ZFS) arises largely from the combined effects of spin orbit coupling and a deviation of the complex from octahedral symmetry (McGravey, 1966). This effect adds a term to the spin Hamiltonian of the form $D\{S_z^2 - S(S + 1)\} + E(S_x^2 - S_y^2)$. Values of D can always be defined to be larger than those for E, which vanishes if the distortion is axial. The zero field splitting may be rather large, in some cases exceeding the Zeeman splitting. When this happens, EPR signals from a single crystal can be shifted thousands of gauss by rotation of the crystal with respect to the magnetic field (see, e.g., McGarvey, 1966, p. 132). Clearly, if the ZFS becomes time dependent through molecular motion, it will be an extremely powerful means for relaxing an electron spin in solution. In fact, with the exception of the Orbach process, it is usually the only mechanism considered important for the relaxation of ions of spin greater than one half in solution.

A great deal of experimental and theoretical work has been done on relaxation caused by modulation of the ZFS. Much of this work was done on ions having S = 5/2. McGarvey (1957) first attributed the relaxation of aqueous Cr(III), Mn(II), Fe(III), and Ni(II) to rotational modulation of the ZFS. In an important paper, Bloembergen and Morgan (1961) found from proton relaxation measurements that the correlation times for the electron spin relaxation of Mn(II) and V(II) were too short to be associated with molecular rotation. They therefore proposed that the

was due to distortions of the hydrated complex caused by collisions with solvent molecules. This proposal has become more or less accepted. They also were able to explain the rates of the electron relaxation by assuming that the instantaneous values of the distortion of the complex had the same order of magnitude as the static distortions measured in crystals. EPR studies of aqueous Mn(II) have been made by Hayes and Myers (1961), Nolle and Morgan (1962), Garrett and Morgan (1966), and others.

McLachlan (1964) considered the theory of a number of relaxation processes in solution. For the case of relaxation of an ion with S = 1 through modulation of the ZFS he obtained

$$\frac{1}{T_{1e}} = \frac{\Delta^2}{10}\left[\frac{2\tau_c}{1+\omega_S^2\tau_c^2} + \frac{8\tau_c}{1+4\omega_S^2\tau_c^2}\right] \tag{3-31}$$

and

$$\frac{1}{T_{2e}} = \frac{\Delta^2}{20}\left[6\tau_c + \frac{10\tau_c}{1+\omega_S^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_S^2\tau_c^2}\right] \tag{3-32}$$

where Δ is the root mean square value of the zero field splitting in solution, and τ_c is the correlation time for whatever motion makes the ZFS time dependent. Ions of S > 1 may have more than one T_{1e} and more than one T_{2e}. These complications will not be discussed here. At the start of this present study, it was believed that these two equations were sufficient to explain the relaxation of Ni(II) in aqueous solution.

Other theoretical investigations of relaxation through modulation of the zero field splitting have been made by Carrington and Luckhurst (1964), Hudson and Luckhurst (1969b), and Luckhurst and Pedulli (1971).

These studies support the form of Eqs. (31) and (32).

Levanon, Stein, and Luz (1970) made EPR linewidth and intensity measurements upon aqueous Fe(III) at X band and Q band. They found that the correlation time for the relaxation was 5×10^{-12} sec at room temperature, again too fast to be associated with molecular rotation. Levanon, Charbinsky, and Luz (1970) measured the EPR linewidths and intensities at X and Q band for Cr(III) and Fe(III) in water-glycerol mixtures. Rubinstein, Baram, and Luz (1971) compared EPR and NMR measurements in aqueous solutions of Cr(III), Fe(III), and Mn(II). They assumed that the time dependence of the ZFS involved only fluctuations of its direction and not its magnitude.

Most experimental data, notably the work of Luz and coworkers, supports the Bloembergen and Morgan conclusion that the correlation time for the modulation of the zero field splitting is too fast to be that for molecular rotation. No consensus regarding the model of the motion has emerged. For example, while Rubinstein, Baram and Luz (1971) assumed that τ_c in Eqs. (31) and (32) was a mean time between solvent collisions, Hudson and Luckhurst (1969b) assumed that τ_c was a lifetime of a collision-induced distortion. No investigator seems to have explored the possibility of ascribing a temperature dependence to the magnitude of the zero field splitting.

IV. EXPERIMENTAL

A. Solutions

$Co(ClO_4)_2 \cdot 6H_2O$ and $Ni(ClO_4)_2 \cdot 6H_2O$ were purchased from Alfa Inorganics. These salts contained 1 to 2% excess water, which was driven off by heating them to constant weight at 55°C. Solutions of known concentration were prepared by weighing the dried salts as the hexahydrates and diluting to known volume. All metal solutions had pH values of 3 or lower in order to prevent hydrolysis. Some solutions were made 5.27 molar in $HClO_4$ in order to promote rapid chemical exchange of protons, and to prevent freezing at low temperatures. Concentrations of stock acid solutions were determined by volumetric titration. Calcium perchlorate was present in some low acid solutions to inhibit freezing. The concentration of the stock calcium perchlorate solution was determined by adding a portion of it to a column filled with cation exchange resin in the hydrogen form, and titrating the eluted acid (Samuelson, 1963). The perchlorate ion, chosen for its low complexing ability, was the only anion present in any solution.

The bottles of nickel and cobalt perchlorate were checked for the presence of other paramagnetic ions. EPR spectra were carefully run on 0.05 M solutions of each ion, but no signals were seen from impurity ions. A Mn^{2+} impurity would be the most troublesome, because it can be as much as 100 times more effective than Co^{2+} in reducing the T_2 of bulk water protons (Bernheim, et al., 1959). However, the EPR results showed that the concentration of Mn^{2+} was sufficiently low to be neglected in this work.

Application of the Swift and Connick equation (Swift and Connick, 1962) requires that the ratio of bound to total nuclei (here protons) be small compared to unity. In this work, that ratio did not exceed 0.045 for any solution. Samples for linewidth measurements were not deoxygenated.

B. Spectrometers and Measurements

1. T_2 Measurements

Linewidths of bulk water proton signals were measured using conventional NMR spectrometers. Care was taken to minimize line broadening arising from inhomogeneous magnetic fields at the sample. Each sample tube was spun. The field gradient along the sample tube axis was readjusted for each sample. This was necessary in particular for solutions containing more than about 1/10 mole per liter of metal ions. The explanation is this. Unless a sample is spherical, the magnetic field in the sample will depend upon the geometry of the sample and its magnetic susceptibility (Bothner-By and Glick, 1957; Mulay and Haverbusch, 1964). In the samples of higher metal ion concentration, the paramagnetism of the metal would cancel out the diamagnetism of the solvent water, so that the magnetic susceptibility of each sample was different.

Few measurements were made above 65°C using 5 mm tubes. At elevated temperatures, sample tubes with a large air space will allow refluxing of water in the tube. This causes a concentration gradient, with the result that the metal ion concentration in the receiver coil is increased by an unknown amount. The problem may be solved by using a two-tube arrangement, as was done for work at 220 MHz. It

was not done, however, for the measurements at 60 MHz and 100 MHz.

Resonances were swept under conditions minimizing saturation and rapid passage effects. All three spectrometers used modulation frequencies of at least 4 kHz, a value far exceeding any detected linewidths in the present study. Since each spectrometer was tuned to detect the first sideband of the out of phase component of magnetization, proper phasing yielded signals of normal absorption lineshape (Acrivos, 1962; Haworth and Richards, 1966). Linewidths were measured from chart paper, using compass and straightedge. Generally, five or six measurements were averaged. Each resonance linewidth was corrected by subtracting the width of a blank, namely, a sample similar in chemical composition but lacking the paramagnetic ion. The linewidths of the blanks were generally 0.6 Hz to 1.5 Hz, but approached 3 Hz below -30°C. These blank widths were mainly due to magnetic field inhomogeneity and to relaxation caused by the paramagnetism of dissolved oxygen (Chiarotti and Giulotto, 1954). Uncertainties in the blank correction were not a major source of error, since most samples of interest had linewidths exceeding 10 Hz. After the blank correction, the nuclear T_2 for a line was computed from the full width at half height, $\Delta\nu$, expressed in Hz, by the relation $T_2 = (\pi\Delta\nu)^{-1}$.

a. <u>60 MHz</u>. Linewidth measurements at 60 MHz were made on a conventional Varian A-60, operating at 14.1 kG. Field sweeps were calibrated in the following manner. An additional low frequency modulation was applied to the field modulation coils, producing sidebands on a detected signal. The sideband separation was then measured in frequency by a counter and in distance on the chart paper,

thereby yielding the calibration. Sample tubes were standard commercial 5 mm OD glass tubes.

b. 100 MHz. Measurements at 100 MHz were made on a JEOL MH-100, operating at 23.5 kG. The machine was run using a swept frequency and an external proton lock. Sweep widths were calibrated by directly counting the swept audio frequency at which the 100 MHz was modulated. For some reason, narrow (therefore strong) water signals were usually distorted unless observed under low rf power. Commercial 5 mm OD sample tubes were used.

c. 220 MHz. Measurements at 220 MHz were made on a Varian HR-220, operating at 51.7 kG. The magnetic field was produced by a superconducting solenoid, and needed no lock for stability. Sweep calibrations were performed as they were at 60 MHz.

It was not found possible to achieve desired field homogeneity (i.e., resolution under 1 Hz) using 5 mm tubes. Samples were, therefore, sealed into 1 mm ID glass capillaries (Fig. 3), which were held coaxially in the 5 mm tubes. Construction of the capillary tubes is described in detail by McCain (1966). Perfluorokerosene-H obtained from P. C. R. Incorporated was used as a virtually protonless heat conducting medium between the inner and outer tubes. With this arrangement, linewidths of 0.6 Hz to 0.8 Hz were routinely achieved on water samples. The signal to noise ratio was not a problem with the reduced sample size, and the spinning sidebands did not interfere with the linewidth measurements. In fact, the sidebands were surprisingly small in view of the fact that the capillaries were made from tubing that would

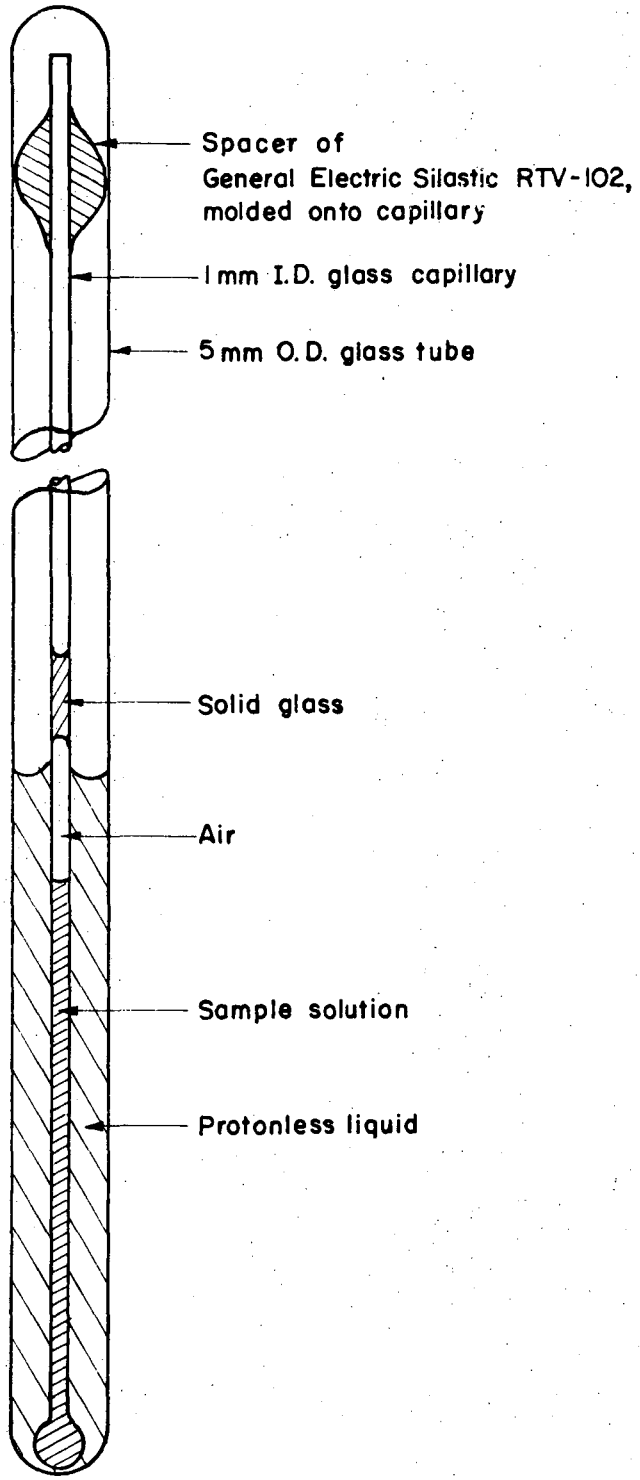

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Fig. 3. NMR sample tube arrangement used at 220 MHz.

barely roll on a flat surface. Prior to the measurements at elevated temperatures, the outer tube was sealed, and the assembly tested for leaks in a 175°C oven.

2. T_1 Measurements at 220 MHz

The T_1 measurements were made using the same capillary tube arrangement used for the T_2 measurements. The cobalt sample used at temperatures below 85°C was prepared by degassing the cobalt solution by the standard freeze-pump-thaw technique, and transferring it to a capillary under a nitrogen atmosphere before sealing. A second cobalt sample, used at elevated temperatures, was not degassed, nor was the nickel sample.

The usual 180°-τ-90° pulse sequence (Carr and Purcell, 1954) was employed, using pulse equipment at the Chemical Biodynamics Laboratory of the Lawrence Berkeley Laboratory. The 90° pulse length was generally 4×10^{-5} sec, shorter than the shortest T_1 measured by a factor of 400. It was never possible to completely invert the magnetization by the 180° pulse. This was possibly due to the fact that the sample was longer than the receiver and transmitter coils, a situation which can lead to an rf field which is not homogeneous over the sample. This situation does not affect the accuracy of the T_1 measurement when the data is treated properly (Farrar and Becker, 1971, p. 43). The radio frequency was always set at least 800 Hz off resonance, so that the free induction decay (or FID), had a rapid oscillatory behavior, much like a "ringing" pattern (Farrar and Becker, 1971, p. 20). This insured that the initial amplitude of the FID was insensitive to field shifts.

For each value of τ, the pulse sequence was usually repeated four times, while a small computor digitized and summed the free induction decays which followed the 90° pulses. The FID sum was presented on a storage oscilloscope, and its initial amplitude was measured. The process was usually repeated for 30-35 different values of τ. The proton T_1 at that temperature was then determined from the slope of a plot of $\ln(A_\infty - A_\tau)$ vs τ, where A_∞ is the initial amplitude of the FID at $\tau = \infty$ (Farrar and Becker, 1971).

No blank corrections were made for T_1 measurements. Upper limits for proper corrections for the undeoxygenated samples were calculated from the linewidths of the blank samples mentioned previously. (The limits were certainly too high, since inhomogeneous magnetic fields made $T_1 > T_2$ for these narrow resonances.) These upper limits were found never to exceed the 5-8% uncertainty in each T_1 determination. The deoxygenated samples, of course, would need even smaller blank corrections. Accordingly, such corrections were ignored.

C. Temperature Measurement and Control

1. Temperature Control

Both Varian spectrometers employed the usual Varian variable temperature system. Nitrogen gas passed over a heating coil, then a coil of fine platinum wire, then the sample tube. Resistance changes of the platinum were used to regulate the current going to the heater. For low temperature operation, the incoming nitrogen was precooled.

The JEOL MH-100 used a nitrogen flow system for operation above room temperature. Nitrogen gas passed over a heater, then a thermocouple, then the sample tube. Temperature changes at the thermocouple were used

to regulate the voltage across the heater. For low temperature operation, liquid nitrogen was boiled off from a dewar by a submerged heating coil, and immediately passed over the sample. The temperature at the thermocouple was used to regulate the boiling rate. Faster boiling produced more cold nitrogen gas and lower sample temperatures. Intermediate sample temperatures were achieved using a constant liquid nitrogen boiling rate plus a regulated heating of the resulting nitrogen gas. The small dewar supplied with the spectrometer was replaced by a 25 liter round dewar, and the submerged heating coil was replaced by a 75 ohm, 25 watt resistor.

All three control systems were able to limit slow temperature drift to a degree per hour at maximum.

2. Temperature Measurement

For the work at 60 MHz, temperatures were determined by measuring the chemical shifts of sealed Varian samples of methanol or ethylene glycol. These shifts were converted to temperatures by means of the calibrations performed by Van Geet (Van Geet, 1968a, 1970). He found that the calibration charts published by Varian were in error by as much as four degrees. However, even the calibrations of Van Geet do not seem above suspicion. For example, near 35°, where both methanol and ethylene glycol shifts could be used as thermometers, temperatures differing by two degrees were obtained.

In view of these difficulties, temperature measurements at 60 MHz may have systematic errors as large as 2°.

Temperature measurements at 100 MHz were begun using the identical methanol and ethylene glycol samples and the calibrations

of Van Geet, adjusted for the larger field. However, this measurement procedure now gave temperatures that seemed too low. For example, when the methanol sample gave a chemical shift indicative of a temperature of 22°C, it was slightly warm to the touch upon removal from the probe, and when room temperature nitrogen was passed over the sample, it gave a shift indicative of 16°C. In order that comparison measurements could be made, a copper-constantan thermocouple was made, and one junction placed in a liquid-containing NMR tube. Room temperature nitrogen was passed through the probe. The chemical shift of the methanol indicated 15°C using the Van Geet calibration and 14°C using the Varian calibration, while the thermocouple gave a voltage indicative of 22°C, the expected result. The temperature of the probe was raised and the three methods yielded 23°C, 22°C and 30°C. At a higher temperature the three methods yielded 65°C, 62°C and 69°C. The thermocouple was then tested in freezing water and condensing steam, and found to be accurate within half a degree. The thermocouple measurements were presumed to be the correct ones, and the chemical shift method for temperature measurement was abandoned. The reason for the discrepancies is unknown. It seemed possible that the chemical shift measurements were in error, but the sweep calibrations were redone, and found to be consistent with the earlier calibrations and with the calibrated chart paper supplied with the spectrometer.

The thermocouple used on the Varian HR-220, also made of copper-constantan, was of necessity made of fine wire. On this spectrometer, the probe is cylindrical, and is inserted into the solenoid from the bottom. Since the solenoid had no opening to the top, the wires emerging

from the top of the probe had to travel down the very small space between the probe and the solenoid. Number 34 copper wire was used with "Advance" wire, of similar size, made by Driver-Harris. The junctions were made by twisting the bared ends together and soldering the connection. Since this thermocouple was used for high temperature work, one junction was introduced into a partially constricted 5 mm sample tube, which was then sealed with General Electric Silastic RTV-102. The tube contained mineral oil as a heat transfer liquid. This thermocouple was likewise tested for accuracy. It had been observed that many of the spools of "Advance" wire were unsuitable as thermocouple wire, giving temperatures erroneous by as much as 3° at 100°C. Presumably, the chemical composition varies somewhat from spool to spool.

V. RESULTS FOR NICKEL SOLUTIONS

A. NMR Relaxation

Extensive measurements were made of proton linewidths in various nickel solutions. The data, along with that for a few proton T_1 measurements, are listed in Appendix I. The solutions low in acid have a chemical exchange controlled region, and therefore, yielded information about electron spin relaxation over a limited temperature region. The solution 5.27 M in $HClO_4$ was much more useful in this regard, and was, therefore, studied at magnetic fields from 14.1 kG to 51.7 kG, and at temperatures from -50°C to +155°C. The proton data for this solution will be considered separately from that for the solutions low in acid. There are many common features, however, and these will be discussed in the following section.

1. General

Considerations that apply equally to all the nickel solutions are: the magnitudes of the constants in the dipolar coupling equation, the relative rates of the processes which interrupt the dipolar coupling, the relative importance of relaxation in the first and in the second coordination sphere, and the relative effectiveness of dipolar and scalar coupling between the protons and the nickel.

The equations for relaxation through dipolar coupling, Eqs. (2-17), (2-18), (2-27) and (2-28), all contain the expression $\gamma_S^2\hbar^2 S(S + 1)$, often written as $g^2\beta^2 S(S + 1)$. As pointed out by Abragam (1961, p. 303), this expression must be replaced by the mean square of the effective magnetic moment for those ions having appreciable orbital contribution to the paramagnetism. This value for Ni(II) in aqueous solution is

3.22β (Myers, 1973). This may be seen to be numerically equivalent to setting g = 2.28 or $\gamma_S = 2.003\times10^7$ $sec^{-1}gauss^{-1}$.

The estimation of the r^6 factor in the equations for dipolar coupling is difficult. Common estimates of the distance r between a first row transition ion and a water proton generally run from 2.4Å to 2.8Å. This uncertainty becomes considerable when raised to the sixth power. For example, if r is changed from 2.4Å to 2.6Å, r^6 increases by a factor of $(2.6/2.4)^6 = 1.62$. This difficulty will hamper attempts at exact determination of electron relaxation times through these equations. The admittedly somewhat arbitrary choice of r = 2.6Å will be made in order to interpret the data.

The correlation time for the interruption of the dipolar coupling must be determined. According to Eqs. (2-19) and (2-20),

$$\frac{1}{\tau_1} = \frac{1}{\tau_m} + \frac{1}{\tau_r} + \frac{1}{T_{1e}} \tag{5-1}$$

and

$$\frac{1}{\tau_2} = \frac{1}{\tau_m} + \frac{1}{\tau_r} + \frac{1}{T_{2e}} \tag{5-2}$$

In general, T_{1e} and T_{2e} will be the shortest of the possible correlation times for the nickel solutions. From the work of Connick and Fiat (1966) and Neely and Connick (1972), T_{1e} is expected to be of the order of 5×10^{-12} sec at room temperature. Connick and Fiat found the exchange time for whole water molecules to be about 3.3×10^{-5} sec. Using Eq. (2-16) and the Connick and Fiat value of 10.8 kcal $mole^{-1}$ for $\Delta H^{\ddagger}$, τ_{mH_2O} may be estimated to be about 10^{-7} sec near 150°C. This is

still much longer than T_{1e}. The acid-catalyzed proton exchange mechanism discussed by Swift and Stephenson (1966) could produce a τ_m for protons of 10^{-7} sec at room temperature if the acid concentration is about 5 molar. However, this mechanism appears to have little or no temperature dependence. Therefore, the $(\tau_m)^{-1}$ term in Eqs. (5-1) and (5-2) is always completely negligible for nickel solutions.

The rotational correlation time τ_r is also smaller than T_{1e} and T_{2e}, but not by such a large margin. The Stokes-Einstein equation gives τ_r as

$$\tau_r = \frac{4\pi\eta a^3}{3kT} \quad . \tag{5-3}$$

It is difficult to assign an accurate value to a, the effective molecular radius, since water molecules in the second coordination sphere may tumble along with the first coordination sphere. NMR evidence for such a second sphere of coordinated water molecules has been given for Cr(III) by Alei (1964) and Earl (1968). If we set η = 1 cp, and T = 20°C, and guess that a = 3Å, we obtain $\tau_r = 2.7\times10^{-11}$ sec. It is probably safer, however, to use experimental values for τ_r. From NMR measurements of Bloembergen and Morgan (1961) and of Hausser and Noack (1964), Hertz (1967) determined room temperature values of τ_r for many hexahydrates of transition metals. For the ions Mn(II), V(II), Cr(III), and Cu(II), the lowest value was 2×10^{-11} sec and the highest was 8×10^{-11} sec. Assuming that τ_r for $Ni(H_2O)_6^{2+}$ is within this range, we expect $(\tau_r)^{-1}$ to be an order of magnitude smaller than $(T_{1e})^{-1}$ or $(T_{2e})^{-1}$ at room temperature. However, as the temperature rises, τ_r

will decrease, and may eventually approach T_{1e} in magnitude. For example, if a = 3Å, τ_r may be calculated to be 1.4×10^{-11} sec at 50°C, 6.2×10^{-12} sec at 100°C, and 3.9×10^{-12} sec at 140°C. Thus, at elevated temperatures, the effects of τ_r must be taken into consideration.

Equations (2-27) and (2-28), which describe relaxation occurring beyond the first coordination sphere, have been written with the assumption that T_{1e} and T_{2e} are much shorter than τ_D, the translational diffusion time for the solvent nuclei. This should hold at most temperatures for aqueous solutions of Ni(II). Abragam (1961, p. 302) showed by general arguments that the relationship of τ_D and τ_r for a molecule is expected to be $\tau_D = 9\tau_r$. Hertz (1967) gives, from the work of Krynicki (1966), τ_r for H_2O molecules as a function of temperature. For example, τ_r equals 3.0×10^{-12} sec at 20°C, 1.2×10^{-12} sec at 70°C, and 0.8×10^{-12} sec at 100°C. Abragam's relationship then predicts $\tau_D = 2.7\times10^{-11}$ sec at 20°C, 1.1×10^{-11} sec at 70°C, and 7×10^{-12} sec at 100°C. These times, although approximate, are similar to the rotational correlation times for the hydrated nickel ion. This suggests that the two inequalities, $T_{1e}<\tau_D$ and $T_{1e}<\tau_r$, will be valid over the same temperature range. In other words, the effects of translational diffusion upon the outer sphere relaxation rate should be minor at or below room temperature.

The proton relaxation caused by scalar coupling between the protons and the nickel can be neglected in comparison to the relaxation caused by the dipolar coupling. The equations of importance here are Eqs. (2-18) and (2-22). For the sake of comparison, these may be simplified by setting T_{1e}, $T_{2e}<<\tau_r$, τ_m. Then

$$\left(\frac{1}{T_{2m}}\right)_d = \frac{\gamma_I^2(\mu_{eff})^2}{15r^6}\left[7T_{1e} + \frac{13T_{2e}}{1 + \omega_S^2T_{2e}^2}\right] \tag{5-4}$$

and

$$\left(\frac{1}{T_{2m}}\right)_{sc} = \frac{S(S+1)}{3}(A/\hbar)^2\left[T_{1e} + \frac{T_{2e}}{1 + \omega_S^2T_{2e}^2}\right]. \tag{5-5}$$

If we assume for the moment that $\omega_S^2T_{2e}^2 \ll 1$, and that $T_{2e} = T_{1e}$, we find that the ratio of the two expressions is

$$\frac{(T_{2m})_d^{-1}}{(T_{2m})_{sc}^{-1}} = \frac{2\gamma_I^2(\mu_{eff})^2}{r^6S(S+1)(A/\hbar)^2} \quad . \tag{5-6}$$

If we take $\gamma_I = 2.675\times10^4$ $sec^{-1}gauss^{-1}$, $\mu_{eff} = 3.22\ \beta$, $r = 2.6$Å, $S = 1$, and the Luz and Shulman (1965) value of $A/h = 2\times10^5$ Hz, this ratio is 1.3×10^3. The ratio is still 6×10^2 if the rather large value of 3Å is given for r. If $\omega_S^2T_{2e}^2 \gg 1$, or if $T_{1e} \gg T_{2e}$, then the ratio is still 900 or 400, depending upon the estimate of r. We may safely conclude that the effect of the scalar coupling is completely negligible compared to that of the dipolar coupling.

The contribution of relaxation in the second coordination sphere, given by Eq. (2-28), must be estimated. The ratio of relaxation in the first coordination sphere to relaxation in the second sphere may be found by putting Eq. (5-4) into Eq. (2-11) and dividing the result by Eq. (2-28). Assuming for simplicity that T_{1e}, $T_{2e} \ll \tau_r$, τ_D, we obtain

$$\frac{(T_{2p})^{-1}(\text{first sphere})}{(T_{2p})^{-1}(\text{second sphere})} = \frac{3d^3P_m}{4\pi r^6 n} \quad . \tag{5-7}$$

We have assumed that the relaxation is not controlled by the rate of chemical exchange. Here, n, the concentration of ions, is given by NM, where N is Avagadro's number and M is the molar concentration of the metal ions. For dilute solutions of hexaquo complexes, P_m, the fraction of nuclei coordinated, is equal to 6M/55.5 moles liter^{-1}. Then, n and P_m are related by $n = (55.5\ NP_m/6)$, and Eq. (5-7) becomes

$$\frac{(T_{2p})^{-1}(\text{first})}{(T_{2p})^{-1}(\text{second})} = \frac{4.30\times10^{-23}\text{cm}^3 d^3}{r^6} \quad . \qquad (5\text{-}8)$$

This ratio is highly dependent upon the values given for r and for d, the distance of closest approach of second sphere nuclei. Lee (1970) considered relaxation in the second coordination sphere. He assigned a value of 4.1Å for d, based upon molecular models and Van der Waals radii. If we let $d = 4.1\times10^{-8}$ cm and $r = 2.6\times10^{-8}$ cm, then

$$\frac{(T_{2p})^{-1}(\text{first})}{(T_{2p})^{-1}(\text{second})} = 9.6 \quad .$$

Thus we see that relaxation in the second coordination sphere may be about 1/10 as important as relaxation in the first sphere. This ratio of 9.6 is highly uncertain, of course. We may obtain a ratio as low as 4.5 by assuming that r = 2.8Å and d = 3.7Å, or a ratio as high as 18 by letting r = 2.4Å and d = 4.3Å. These estimates show that proton relaxation occurring beyond the first coordination sphere may be expected to provide from 5 to 20% of the total relaxation when scalar coupling and the $\Delta\omega$ mechanism can be neglected.

We note that the form of Eq. (5-4) is similar to Eq. (2-28), and that they depend upon T_{1e}, T_{2e} and magnetic field in the same way. Hence, if proton exchange is fast enough to make $P_m T_{2p}$ dependent upon T_{2m}, as shown in Eqs. (2-8) and (2-9), the ratio of the contributions of first and second sphere relaxation will be constant. Therefore, relaxation outside the first coordination sphere may be completely neglected if the temperature or field dependence of T_{1e} and T_{2e} is sought from nuclear relaxation measurements. If absolute values of T_{1e} and T_{2e} are desired, then in principle a correction for the contribution of second sphere relaxation should be made. Such a correction will be ignored here, since it is so much smaller than the uncertainty caused by the difficulty of evaluating the sixth power of r. Of course, when chemical exchange of protons is slow enough, conditions of Eqs. (2-6) and (2-7) apply, and relaxation in the first coordination sphere is not the rate limiting step in determining T_{2p}. In this case, relaxation in the second coordination sphere does contribute to the temperature dependence of the observed proton linewidth. This has been observed in aqueous Ni(II) solutions here and also by Swift and Weinberger (1968). The data are consistant with the calculated value of ten for the relative importance of relaxation in the first and second coordination spheres.

It may be useful to summarize the conclusions reached so far. The contribution to proton relaxation that arises from the scalar coupling between the protons and the electron spin is entirely negligible compared to that arising from the dipolar coupling. The relaxation of the spin of the nickel is expected to be the fastest process interrupting the dipolar coupling, although rotation of the hydrated complex may be

nearly as rapid at elevated temperatures. Proton relaxation occurring outside the first coordination sphere is expected to be a small correction. It may be neglected here in view of the larger uncertainty which arises from the difficulty of evaluating the r^6 factor. Neither source of uncertainty affects conclusions regarding temperature or magnetic field effects.

2. Solutions Low in Acid

Proton linewidth data at 60 MHz and 100 MHz for nickel solutions are shown in Figs. 4 and 5. It may be noted that the different solutions do not show identical proton relaxation rates at elevated temperatures. The explanation is unknown. Measurements and calculations to be described shortly indicate that changes in viscosity should not affect P_mT_{2p}. Part of the effect could be due to the high concentration of perchlorate ions. If perchlorate ions successfully compete with water molecules in the coordination spheres around the metal ion, then fewer protons are close enough to be relaxed, and P_mT_{2p} rises.

It has been established that scalar coupling may be ignored, and that second coordination sphere effects are small. The next task is to assign magnitudes to quantities appearing in Eq. (2-5), the Swift and Connick equation. From the rise of P_mT_{2p} as the temperature is lowered from room temperature, it is clear that the system is in the chemical exchange controlled region. Here, as Eqs. (2-6) and (2-7) specify, $\tau_m >> T_{2m}$, and $P_mT_{2p} = \tau_m$. However, P_mT_{2p} does not rise in a continuous steep manner as has been observed in the ^{17}O experiments. Swift and Connick (1962) found a value of 11.6 kcal mole^{-1} for the $\Delta H^{\ddagger}$ for the exchange of whole water molecules, Connick and Fiat (1966) found a

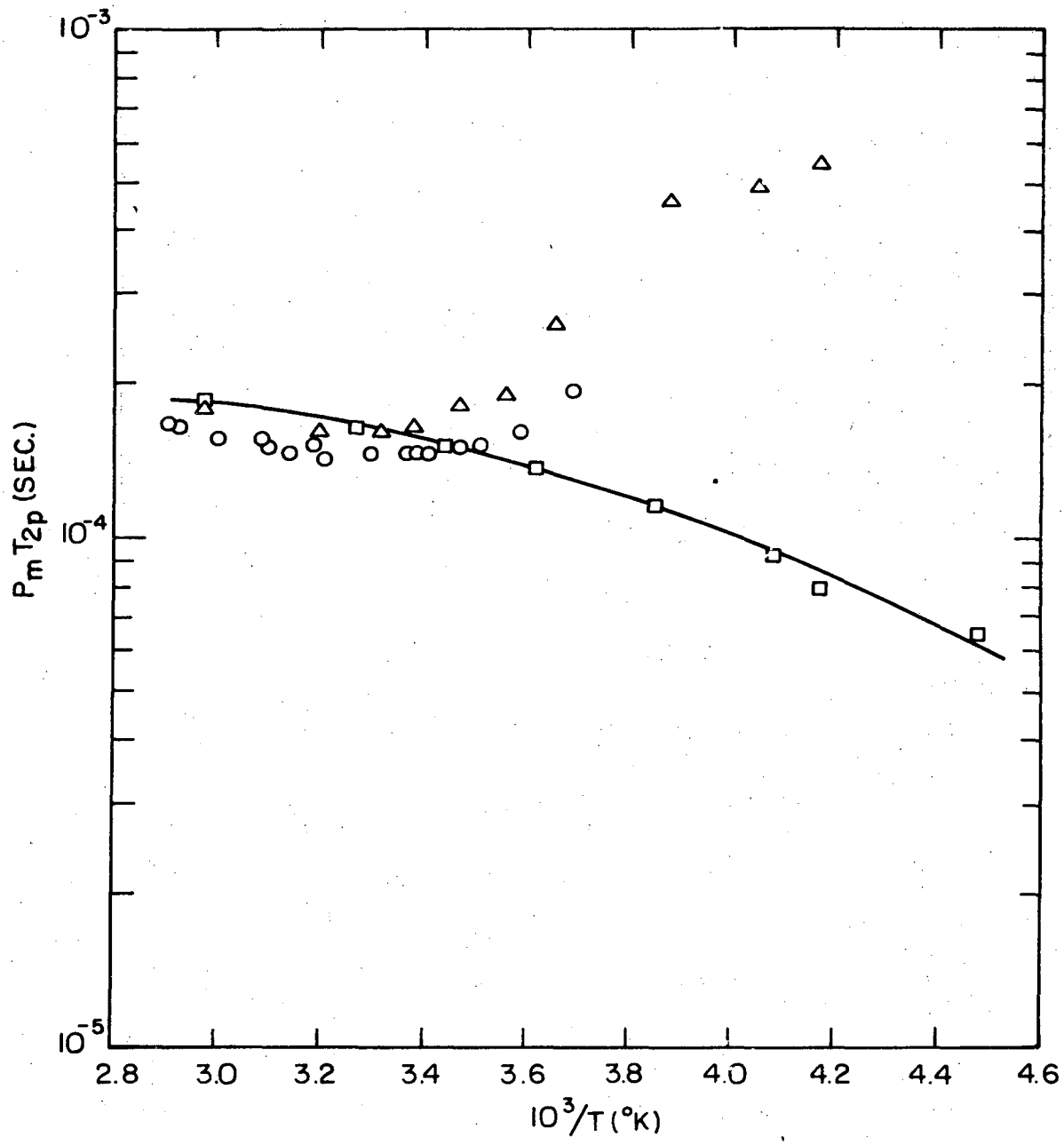

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Fig. 4. $P_m T_{2p}$ of protons in aqueous Ni(II) solutions at 60 MHz as a function of temperature. The solution represented by circles contained 0.003 M $HClO_4$. The solution represented by triangles also contained 2.46 M $Ca(ClO_4)_2$. The solution represented by squares contained 5.27 M $HClO_4$.

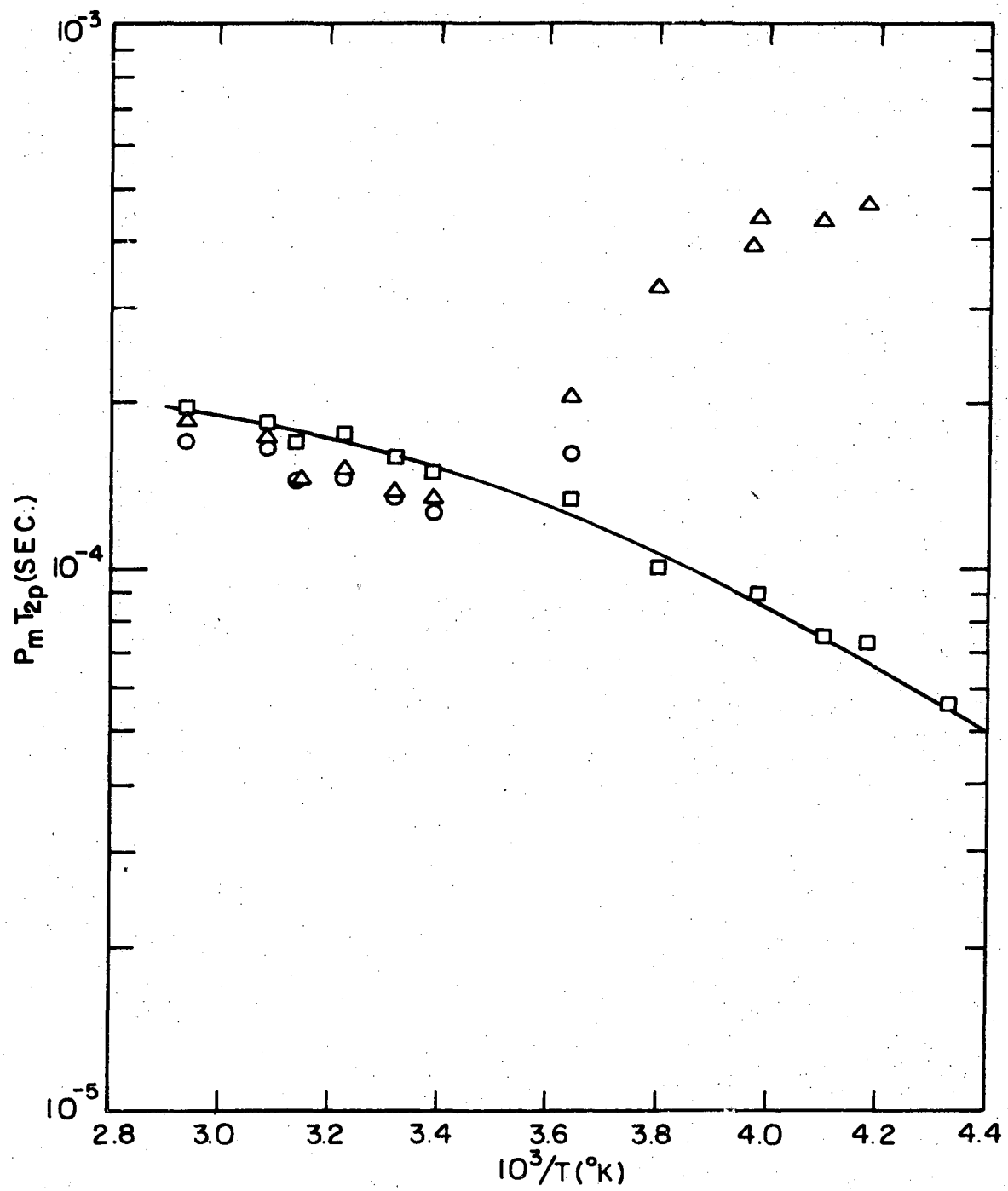

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Fig. 5. $P_m T_{2p}$ of protons in aqueous Ni(II) solutions at 100 MHz as a function of temperature. Symbols are the same as in Fig. 4.

value of 10.8±0.5 kcal mole^{-1}, and Neely and Connick found 13.9 kcal mole^{-1}. There are two reasons for the difference. The first reason is that the effects of relaxation in the second coordination sphere tend to flatten out the steepness. This reason was advanced by Swift and Weinberger (1968) to explain their similar observations. This effect was absent from the ^{17}O work for the following reason. Nickelous ion relaxes ^{17}O primarily through scalar coupling in the first coordination sphere. Scalar coupling effects drop off rapidly with distance, and are weak beyond the first coordination sphere. In comparison, dipolar coupling operates over long distances, and the effect of the nickel ions upon protons drops off slowly enough that it is appreciable in the second coordination sphere. The second reason that P_mT_{2p} does not continue to rise sharply is the presence here of about 10^{-3} M acid. Any acid present serves to cause proton exchange, and has the effect of putting a minimum value on τ_m, as shown by Eq. (2-16a). Swift and Stephenson (1966) found a value of 1.3×10^6 $M^{-1}sec^{-1}$ for the proton exchange rate constant k_2. If this value does not change much with temperature, the exchange rates of protons and whole water molecules can be compared. For this acid concentration, the proton exchange rate is expected to be faster at temperatures below perhaps -20°C. In this region, τ_m and, therefore, P_mT_{2p} are not expected to show a strong temperature dependence. Again, this is an effect that would not appear in the ^{17}O work.

The low temperature results for the low acid solutions give little information about electron relaxation, so we will proceed to consider the data above room temperature. As shown in Eq. (2-9), relaxation

in the bulk solution has contributions from the $\Delta\omega$ mechanism and from relaxation occurring in the first coordination sphere. We can show that the $\Delta\omega_m^2\tau_m$ term is generally smaller than the $(T_{2m})^{-1}$ term. First, the data do not show the rapid rise in $P_m T_{2p}$ with rising temperature that would be expected if the $\Delta\omega_m^2\tau_m$ term were dominant. Second, we may calculate both terms in Eq. (2-9). At room temperature, $\tau_m = 3.3\times10^{-5}$ sec, as determined both by proton NMR (Swift and Weinberger, 1968), and by ^{17}O NMR (Connick and Fiat, 1966). $(T_{2m})^{-1}$ is 6×10^3 sec^{-1} at 60 MHz and 100 MHz, as determined by measurements, to be described later, upon nickel solutions high in acid. This value is in agreement with the results of Swift and Weinberger at 60 MHz. Finally, $\Delta\omega_m$ is needed. Swift and Weinberger use the room temperature shift measurements of Wayland and Rice (1966), which indicate a scalar coupling constant of 0.9×10^5 Hz. However, Luz and Shulman (1965) made more extensive shift measurements, and they obtained $A/h = 2\times10^5$ Hz. Using this value with Eq. (2-25), we obtain $\Delta\omega_m = 6.0\times10^3$ sec^{-1} at room temperature and 60 MHz, and 10.0×10^3 sec^{-1} at 100 MHz. Now the terms in Eq. (2-9) are known, and we see that at 60 MHz,

$$6\times10^3 \text{ sec}^{-1} = (T_{2m})^{-1} > \Delta\omega_m^2\tau_m = 1.2\times10^3 \text{ sec}^{-1} \quad .$$

Thus the $\Delta\omega$ mechanism is found to be somewhat more important than estimated by Swift and Weinberger. The term $\Delta\omega_m^2\tau_m$ would be equal to to 3.3×10^3 sec^{-1} at 100 MHz. Since both $\Delta\omega_m$ and τ_m drop with rising temperature, the $\Delta\omega$ mechanism will quickly lose importance. For example, at 60 MHz, $\Delta\omega_m^2\tau_m$ falls to 430 sec^{-1} at 40°C and 230 sec^{-1} at 50°C, while $(T_{2m})^{-1}$ changes only slightly with temperature.

Unfortunately, a narrow temperature range of useful data is left, since none of the low acid measurements were made above 85°C. We shall be content for the present with a calculation of the magnitudes of T_{1e} and T_{2e} at one temperature. At 60 MHz and 40°C, where $10^3/T = 3.19$, $P_m T_{2p} = 1.5\times10^{-4}$ sec. Neglecting the $\Delta\omega$ mechanism allows us to set $P_m T_{2p} = T_{2m}$. Neglecting rotation of the complex allows us to use Eq. (5-4). Setting r = 2.6Å, we obtain

$$7T_{1e} + \frac{13T_{2e}}{1 + \omega_S^2 T_{2e}^2} = 4.84\times10^{-11} \text{ sec} \quad . \tag{5-9}$$

In the limit $T_{1e} \gg T_{2e}$, $T_{1e} = 6.9\times10^{-12}$ sec. If $T_{1e} = T_{2e}$, then $T_{1e} = 3.6\times10^{-12}$ sec. The actual ratio of T_{1e} and T_{2e} at 60 MHz may be estimated from Eqs. (3-31) and (3-32), if we assume that modulation of the zero field splitting is the only contribution to the electron spin relaxation. If we set $\omega_S = \gamma_S H_0 = 2.82\times10^{11}$ sec^{-1}, and assume $\tau_c = 4\times10^{-12}$ sec, we obtain $T_{1e}/T_{2e} = 2.43$. Use of this ratio in Eq. (5-9) gives $T_{2e} = 1.8\times10^{-12}$ sec and $T_{1e} = 4.4\times10^{-12}$ sec. These values are in essential agreement with the ^{17}O work of Connick and Fiat (1966) and Neely and Connick (1972).

3. <u>Solutions High in Acid</u>

Proton linewidth data for a nickel solution 5.27 molar in $HClO_4$ are presented in Fig. 6. The data are in agreement with the room temperature measurements of Neely and Connick (1972) at 60 MHz and 100 MHz, made upon unacidified solutions, but are in disagreement at 220 MHz. Analysis of the data is simplified by the rapid proton exchange. Conditions in Eq. (2-10) are easily satisfied, and $P_m T_{2p} = T_{2m}$ over the

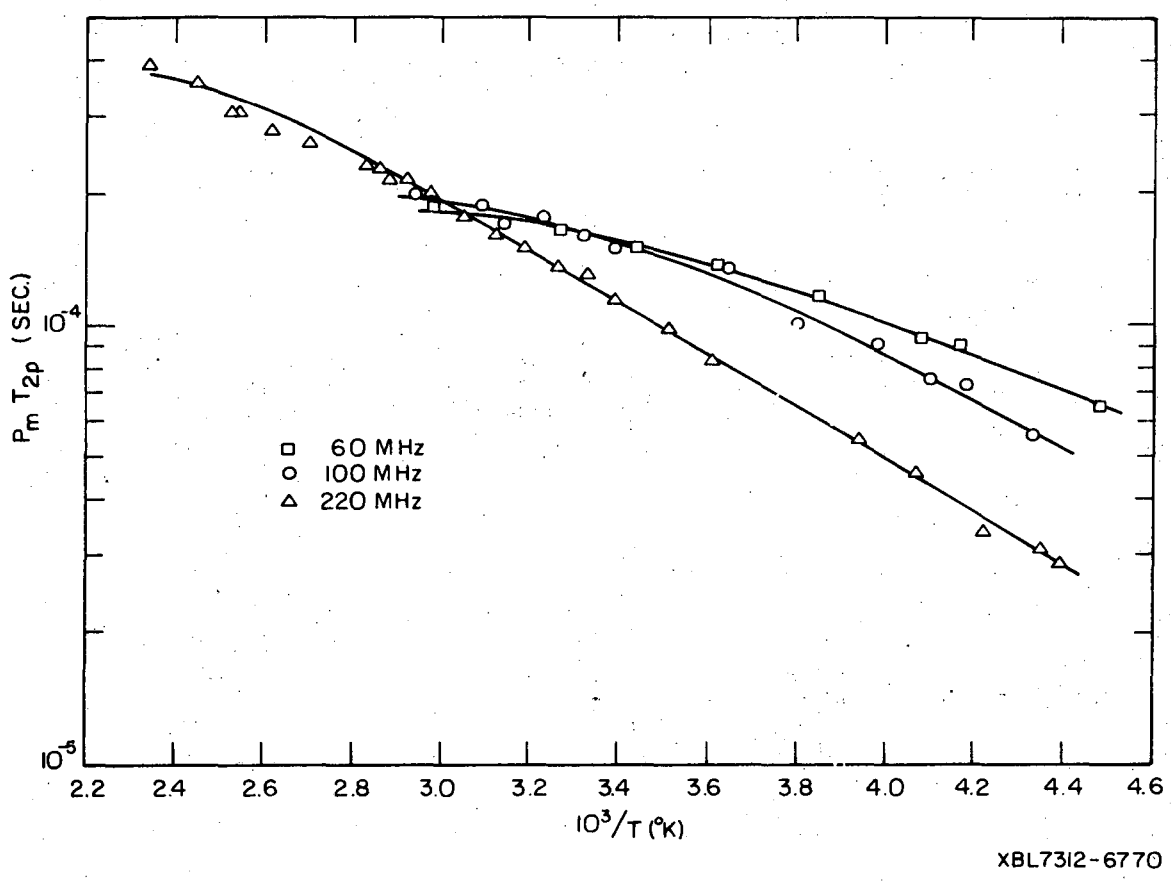

Fig. 6. $P_m T_{2p}$ of protons in an aqueous Ni(II) solution as a function of temperature and frequency. The $HClO_4$ concentration was 5.27 M.

entire temperature range. This can be shown by calculation and by experiment. Swift and Stephenson (1966) give a room temperature value of $1.3\pm0.2\times10^{6}\ M^{-1}sec^{-1}$ for the constant k_2 appearing in Eq. (2-16a). If $[H^+] = 5.27$ M, then $\tau_m = 1.46\times10^{-7}$ sec. Then at 60 MHz near room temperature,

$$6.9\times10^{6}\ sec^{-1} = (\tau_m)^{-1} >> (T_{2m})^{-1} = 6\times10^{3}\ sec^{-1}$$

and

$$4.1\times10^{10}\ sec^{-2} = (T_{2m}\tau_m)^{-1} >> (\Delta\omega_m)^2 = 3.6\times10^{7}\ sec^{-2} \quad .$$

At 220 MHz, $(\Delta\omega_m)^2$ will become $4.8\times10^{8}\ sec^{-2}$, but this will scarcely affect the inequality.

The experimental proof of the relation $P_mT_{2p} = T_{2m}$ for this acid solution consisted of measuring P_mT_{2p} in solutions of different acid strength. The experiment was done under conditions where τ_m and $\Delta\omega_m$ are largest, namely, minimum temperature and maximum field. Proton linewidths were measured for solutions of acid concentration from 1 M to 5.27 M at -45°C and 220 MHz, which is a magnetic field of 51.7 kG. P_mT_{2p} was observed to be constant. This showed that a nickel solution that is one molar in protons has a τ_m short enough to eliminate the chemical exchange controlled region, and to eliminate the effectiveness of the $\Delta\omega$ mechanism.

We have, then, what was sought: values for T_{2m}, the relaxation time of protons in the first coordination sphere of aqueous Ni(II), over a wide range of experimental conditions. The field strengths run from 14.1 kG to 51.7 kG, and the temperatures from -50°C to +155°C. These T_{2m} values are related to the electron spin relaxation times

through Eq. (2-18). Combining that equation with Eq. (2-11), we obtain

$$\frac{1}{P_m T_{2p}} = \frac{\gamma_I^2 (\mu_{eff})^2}{15 r^6} \left[7\tau_1 + \frac{13\tau_2}{1 + \omega_S^2 \tau_2^2} \right] \tag{5-10a}$$

$$= 1.38 \times 10^{14} \text{ sec}^{-2} \left[7\tau_1 + \frac{13\tau_2}{1 + \omega_S^2 \tau_2^2} \right] \tag{5-10b}$$

where we have used the values adopted previously for the various constants. Here τ_1 and τ_2 are given the restricted definitions

$$\frac{1}{\tau_1} = \frac{1}{\tau_r} + \frac{1}{T_{1e}} \tag{5-11}$$

and

$$\frac{1}{\tau_2} = \frac{1}{\tau_r} + \frac{1}{T_{2e}} \quad . \tag{5-12}$$

Equation (5-10) should accurately describe the proton linewidth data in the highly acidic nickel solution at all fields and all temperatures. Based upon the estimates mentioned, we expect $T_{1e} \ll \tau_r$ for $10^3/T \geq 3.2$, $T_{1e} < \tau_r$ for $2.6 < 10^3/T < 3.2$, and $T_{1e} \sim \tau_r$ for $10^3/T < 2.6$. Calculations of rotational correlation times have been made using the viscosity of pure water, even though the solution under consideration is about 41% $HClO_4$ by weight. This was done for convenience, since the viscosities of concentrated $HClO_4$ solutions at temperatures above 50°C did not seem to be readily available. Brickwedde (1949) has shown that the viscosity of 40% $HClO_4$ is similar to that of pure water, the ratio being 1.5 at 50°C, 1.3 at 15°C, and 1.1 at -5°C. However, errors of 50% in the estimation of rotational correlation times are not large enough to be of concern

here, since at most temperatures the rate of rotation of the complex has little effect upon the proton relaxation rate. For temperatures below about 30°C, we expect that

$$\frac{1}{P_m T_{2p}} = 1.38\times10^{14}\ \text{sec}^{-2} \left[7T_{1e} + \frac{13T_{2e}}{1 + \omega_S^2 T_{2e}^2} \right] . \qquad (5\text{-}13)$$

Values for T_{1e} and T_{2e} may now be calculated using experimental data. The term $\omega_S^2 T_{2e}^2$ is a minor complication, because at these high fields, it is never completely negligible compared to unity. Also, the ratio of T_{1e} to T_{2e} is available only if we assume we know the details of the electron spin relaxation. However, at low temperatures and 220 MHz, the $\omega_S^2 T_{2e}^2$ term is so large that the expression in brackets in Eq. (5-13) simplifies to $7T_{1e}$. We may easily find T_{1e} values then. For example, at -45°C, $T_{1e} = 3.5\times10^{-11}$ sec. At -21°C, $T_{1e} = 2.1\times10^{-11}$ sec. At -5°C, $T_{1e} = 1.5\times10^{-11}$ sec. At +15°C, $T_{1e} = 1.0\times10^{-11}$ sec. These are the longest relaxation times ever reported for aqueous Ni(II). The respective values at lower fields are shorter by about a factor of two, as can qualitatively be seen from the larger $P_m T_{2p}$.

The considerable length of these relaxation times at 220 MHz raises the question of the importance of the rotation of the complex as an interruption of the dipolar coupling. If T_{1e} were almost as long as τ_r, then the values of T_{1e} as calculated from Eq. (5-13) would be somewhat shorter than the actual T_{1e} values.

It can be shown that τ_r is still longer than T_{1e}. Hallett (1963) has given the viscosities of water below 0°C. Use of his values with Eq. (5-3) gives τ_r for metal complexes as 7.9×10^{-11} sec at -9°C and

1.4×10^{-10} sec at -20°C. This is still about five times the 220 MHz values for T_{1e} at the respective temperatures, and so Eqs. (5-4) and (5-13) are still expected to be fairly accurate. At lower fields, T_{1e} is shorter, and τ_r should be about ten times T_{1e}. Frankel (1968) performed a simple experiment which seemed to show that $\tau_r \gg T_{1e}$ for nickel solutions, at least at 60 MHz at one temperature. He observed water proton linewidths at 60 MHz in Cu(II), Co(II), and Ni(II) solutions at 40°C as a function of viscosity. At this temperature for Ni(II), the bulk proton linewidth is determined by the relaxation rate in the first coordination sphere. The viscosity was varied from 1 to 9 cp by the addition of glycerin, and the $P_m T_{2p}$ of the nickel solution was constant as a function of viscosity. In comparison, $P_m T_{2p}$ of the copper solution changed by a factor of five or six under the same conditions. This experiment seems to prove that the interruption rate of the dipolar coupling between the protons and the nickel is not affected by the viscosity. If τ_r greatly exceeds T_{1e} at 40°C, it should exceed it at all lower temperatures, because of their similar temperature dependence. It would be useful to repeat Frankel's experiment at higher fields and at other temperatures.

These results may be compared with other determinations of T_{1e} at 14.1 kG. Connick and Fiat (1966) observed the ^{17}O resonance of water molecules bound to Ni(II). They found, at temperatures between 0°C and 40°C, $T_{1e} = 6.4\times10^{-12}$ sec, assuming $T_{1e} \gg T_{2e}$, or $T_{1e} = 4.3\times10^{-12}$ sec, assuming $T_{1e} = T_{2e}$. Chmelnick and Fiat (1971), in a similar experiment, found at -30°C, $T_{1e} = 7.6\times10^{-12}$ sec or 5.7×10^{-12} sec, using the same assumptions. The present measurements at 14.1 kG and -30°C indicate

that $T_{1e} = 1.1\times10^{-11}$ sec, assuming that $T_{1e} \gg T_{2e}$, or 6.3×10^{-12} sec, assuming that $T_{1e} = T_{2e}$. The field dependence of T_{1e} observed by Neely and Connick (1972) is confirmed by the present linewidth measurements below room temperature. The field dependence in this region is largely due to the field dependence of T_{1e}, and not due to the explicit field dependence of Eq. (5-13). From the form of Eqs. (3-31) and (3-32), we see that the existence of a field dependence of T_{1e} means that $T_{1e} > T_{2e}$. Then the present value of $T_{1e} \cong 1\times10^{-11}$ sec at -30°C and 60 MHz is seen to be in fair agreement with the ^{17}O work.

A very few proton T_1 measurements were made at 220 MHz. These are illustrated in Fig. 7. It is not possible to give a precise value for the ratio of T_1 to T_2. A ratio of 7/6 is to be expected when $\omega_S^2 T_{2e}^2 \gg 1$, as shown by Eqs. (2-17) and (2-18). However, the experimental accuracy is not sufficient to verify this. The most that can be said with certainty is that the T_1 measurements do not conflict with the interpretation given to the T_2 measurements.

B. Electron Spin Relaxation

It had been previously expected (Lewis and Morgan, 1968; Neely and Connick, 1972) that the electron spin relaxation of aqueous Ni(II) could be satisfactorily described solely in terms of the time dependence of the zero field splitting, as written by McLachlan (1964) and others. This mechanism seened by far the strongest of the available mechanisms, and it does provide for a magnetic field dependence of T_{1e}, as observed. However, Eqs. (3-31) and (3-32) do not accurately describe the data: the observed field dependence of the proton linewidths is much less than expected. This can most easily be shown using the results at very

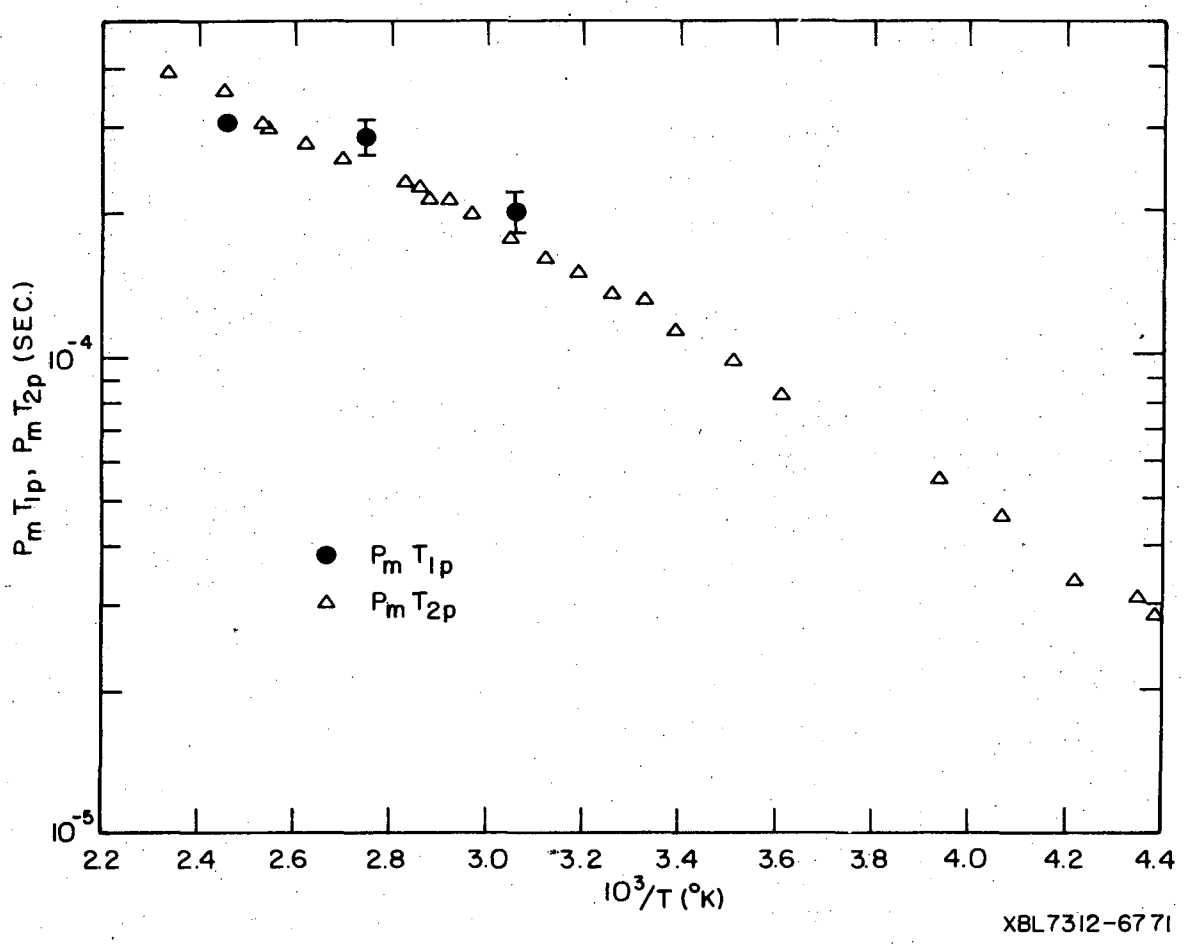

Fig. 7. $P_m T_{1p}$ of protons in an aqueous Ni(II) solution as a function of temperature. The $HClO_4$ concentration was 5.27 M. $P_m T_{2p}$ is included for comparison.

low temperatures, where T_{1e} exceeds 10^{-11} sec. If $T_{1e} = T_{2e}$, then $\omega_S^2 T_{2e}^2 >> 1$, and $7T_{1e} > 13T_{2e}(1 + \omega_S^2 T_{2e}^2)^{-1}$, and Eq. (5-13) shows that $P_m T_{2p}$ is proportional to $(T_{1e})^{-1}$. On the other hand, if $T_{1e} >> T_{2e}$, then $7T_{1e} > 13T_{2e}$, and again $P_m T_{2p}$ is proportional to $(T_{1e})^{-1}$. Therefore, at temperatures below about -35°C, the ratio of $P_m T_{2p}$ at two fields will be equal to the ratio of the respective values of $(T_{1e})^{-1}$. This ratio in turn is expected to be equal to the inverse square of the ratio of the resonant frequencies when $\omega_S^2 \tau_c^2 >> 1$, as can be seen from Eq. (3-31). Then at low enough temperatures we expect the limiting ratio of $P_m T_{2p}$ at 60 MHz to $P_m T_{2p}$ at 220 MHz to be $(220/60)^2 = 13.4$. Or if we make the conservative estimate that τ_c at, for example, -45°C is at least twice the room temperature value of about 4×10^{-12} sec, we still expect the value of this ratio to be at least 11. In contrast, the observed ratio of the $P_m T_{2p}$ values at -45°C is only 6.4. The inescapable conclusion is that T_{1e} for aqueous Ni(II) has significantly less field dependence than Eq. (3-31) predicts. We must, therefore, consider the other mechanisms which can contribute to the electron spin relaxation.

We may omit consideration of anisotropic hyperfine interaction, since only 1% of nickel nuclei have spin. Then the McConnell equation for anisotropic interactions, Eq. (3-22), becomes

$$\frac{1}{T_{1e}} = \frac{2}{15\hbar^2} [(g_{\parallel} - g_{\perp}) \beta H_o]^2 \frac{\tau_r}{1 + \omega_S^2 \tau_r^2} \quad . \qquad (5\text{-}14)$$

Nickel in general has very isotropic g values. McGarvey (1966) lists g values for nickel(II) in 14 host crystals, and the largest value of $(g_{\parallel} - g_{\perp})$ listed is 0.1. Using this value in Eq. (5-14), with a

magnetic field of 51.7 kG, and a room temperature τ_r of 3×10^{-11} sec, we obtain $(T_{1e})^{-1} = 10^6$ sec^{-1}. This upper limit for the effectiveness of the anisotropic Zeeman interaction mechanism falls short of being significant by several orders of magnitude at 220 MHz. This mechanism will be no more effective at lower magnetic fields, and we shall not consider it further.

Spin rotation interaction may likewise be shown to be too small. The Atkins and Kivelson equation is

$$\frac{1}{T_{1e}} = \frac{1}{T_{2e}} = \frac{k}{12\pi a^3} \frac{T}{\eta} [(\Delta g_{\parallel})^2 + 2(\Delta g_{\perp})^2] \quad . \qquad (5\text{-}15)$$

If we let a = 3Å and $\Delta g_{\parallel} = \Delta g_{\perp} = 0.28$, we obtain $(T_{1e})^{-1} = 4.9\times10^8$ sec^{-1} at 0°C, 1.9×10^9 sec^{-1} at 50°C, and 7.5×10^9 sec^{-1} at 150°C. Therefore, spin rotation interaction is also too weak to have a significant effect upon the electron spin relaxation of aqueous nickel.

There is also experimental evidence of the relative unimportance of anisotropic Zeeman interaction and of spin rotation interaction. Equations (5-14) and (5-15) show that both mechanisms depend upon the viscosity of the solution. In the case where $\omega_S^2\tau_r^2 >> 1$, both equations predict that T_{1e} will increase when viscosity increases. Yet the variable viscosity experiment of Frankel (1968), described in Section A-3 of this chapter, indicated that the relaxation rate of nickel was not affected by a tenfold change in viscosity. That proton NMR experiment was done at 40°C and 14.1 kG, conditions where $\omega_S^2\tau_r^2 >> 1$.

In contrast with other mechanisms, the modulation of the zero field splitting can be shown to be a sufficiently powerful mechanism

to explain the rate of relaxation of the aqueous Ni(II) ion. We may rewrite Eq. (3-31) here:

$$\frac{1}{T_{1e}} = \frac{\Delta^2}{10}\left[\frac{2\tau_c}{1 + \omega_S^2\tau_c^2} + \frac{8\tau_c}{1 + 4\omega_S^2\tau_c^2}\right] \quad . \tag{5-16}$$

At room temperature we expect τ_c to be about 4×10^{-12} sec, a value supported by the EPR work of Luz and co-workers, as explained in Chapter III. If, in accord with observation at 60 MHz, we set $T_{1e} = 5\times10^{-12}$, we find that Δ, the root mean square value of the zero field splitting in solution, is equal to 2.3 $cm^{-1} = 4.4\times10^{11}$ sec^{-1}. This value, although not unreasonable, is surprisingly large: roughly equal to half the size of the largest zero field splittings observed for nickel in single crystals (McGarvey, 1966). As pointed out by Bloembergen and Morgan (1961) and Lewis and Morgan (1968), the relaxation times of ions such as Cr(III), Fe(III), and Mn(II) in solution can be explained by the ZFS mechanism if the Δ parameter in liquids is assumed equal to a typical value found in single crystal work.

An initial attempt was made to fit the proton linewidth data using the equations developed. This is shown in Fig. 8. Equation (5-10b) was used to calculate $P_m T_{2p}$ at each frequency. Rotation of the complex was explicitly considered. The rotational correlation time was calculated as

$$\tau_r = 9.0\times10^{-12} \text{ sec } (T)^{-1} \exp(E/RT) \quad , \tag{5-17}$$

where E = 4 kcal $mole^{-1}$, R = 1.987 cal $deg^{-1}mole^{-1}$, and the temperature T is in degrees Kelvin. This activation energy was chosen so that

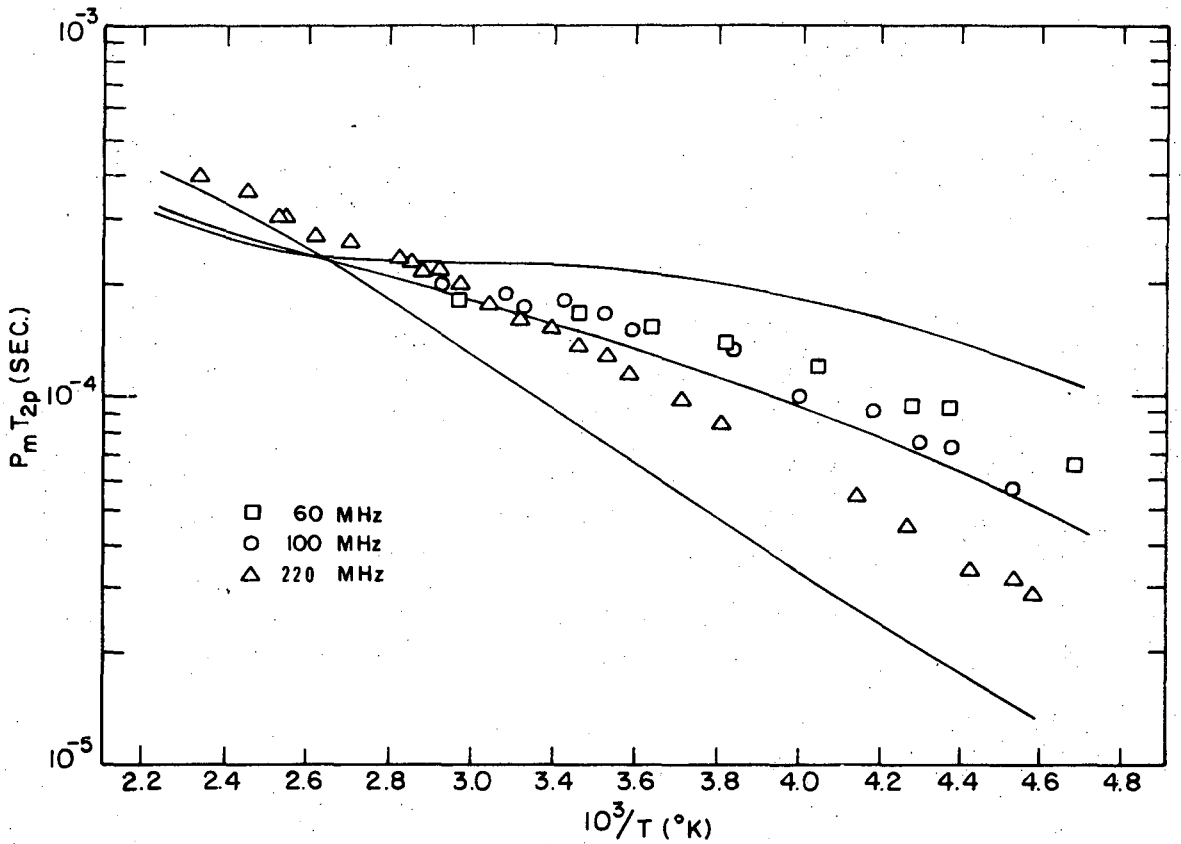

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Fig. 8. Initial attempt to fit protons $P_m T_{2p}$ data for aqueous nickel solution 5.27 M in $HClO_4$, using conventional theory. See text for parameters used.

Eq. (5-17) would simulate the temperature dependence of the viscosity of water divided by temperature. This function gives values of τ_r that do not differ by more than 30% from those previously calculated from Eq. (5-3) over a temperature range from -20°C to +140°C. The electron spin relaxation times were calculated using Eqs. (3-31) and (3-32). The correlation time τ_c for the electron spin relaxation was calculated as

$$\tau_c = 4.8\times10^{-11} \text{ sec } (T)^{-1} \exp(E/RT) \quad . \qquad (5\text{-}18)$$

Here E was set equal to 2 kcal $\text{deg}^{-1}\text{mole}^{-1}$ in order to approximate the temperature dependence of the data, and the pre-exponential factor was adjusted to give $\tau_c = 5\times10^{-12}$ sec at room temperature. The zero field splitting parameter Δ was set equal to 3.1 $\text{cm}^{-1} = 5.8\times10^{11}\ \text{sec}^{-1}$ in order to obtain a gross correspondence with the experimental results. The fit is terrible: the observed magnetic field dependence is much less than predicted. The only parameter used here that can be varied in order to reduce the amount of calculated field dependence is the rotational correlation time. However, in order to reduce the calculated field dependence enough, it would be necessary to reduce the rotational correlation times by a factor of five to eight. Even a factor of three is insufficient. The rotational correlation time for hydrated Ni(II) ion at room temperature would have to be between 3×10^{-12} sec and 5×10^{-12} sec in order to explain the data. It seemed impossible that the nickel ion could rotate so much faster than the other first row transition ions, and so this explanation was rejected. The calculation also fails to account for the rather curious fact that the proton relaxation times at

60 MHz and 100 MHz are so similar.

The crossing of the curves at elevated temperatures has a simple explanation. Equation (5-10) shows that when T_{2e} becomes short enough to make $\omega_S^2 T_{2e}^2$ comparable to unity, then $(P_m T_{2p})^{-1}$ has an explicit field dependence. This behavior only becomes manifest at high temperatures.

The experimental results are hard to explain. There are at least three sorts of alternative ways to approach the problem. The first alternative is to postulate the presence of another mechanism for electron spin relaxation, equal in strength to the ZFS mechanism, but having either the opposite field dependence or none at all. It is difficult to argue that one of the so called electric field fluctuation mechanisms could be responsible here, for it would have to be at least an order of magnitude more effective in solution than in the solid. One could perhaps envision a mechanism dependent upon the deviation of the g value from 2.0023. However, if there were such a mechanism strong enough, it should have been observed for Cu(II), whose rotationally averaged g value is almost as large as that of Ni(II).

It was found that the temperature and field dependence of the proton data could be roughly simulated if it were assumed that the spin of the nickel is subject to an additional relaxation process whose strength is independent of field and weakly dependent upon temperature. Figure 9 shows an attempt to fit the data using such a hypothetical mechanism. Equation (5-10b) was used to calculate $P_m T_{2p}$ at each frequency. The relaxation rates of the electron spin were written as

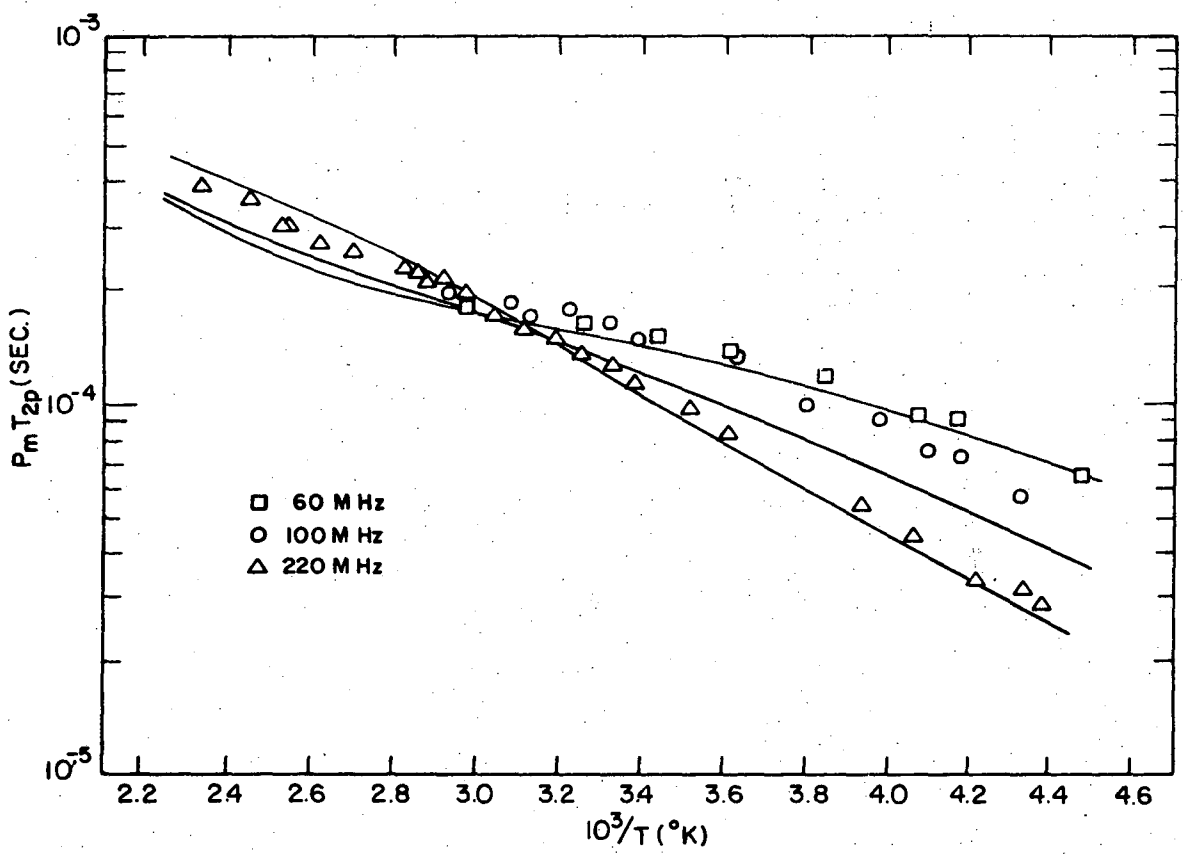

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Fig. 9. Second attempt to fit proton $P_m T_{2p}$ data for aqueous nickel solution 5.27 M in $HClO_4$. Equations (5-19) and (5-20) were used to describe the electron spin relaxation.

$$\frac{1}{T_{1e}} = \frac{\Delta^2}{10}\left[\frac{2\tau_c}{1 + \omega_S^2\tau_c^2} + \frac{8\tau_c}{1 + 4\omega_S^2\tau_C^2}\right] + \frac{k_3}{\tau_c} \tag{5-19}$$

and

$$\frac{1}{T_{2e}} = \frac{\Delta^2}{20}\left[6\tau_c + \frac{10\tau_c}{1 + \omega_S^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_S^2\tau_c^2}\right] + \frac{k_3}{\tau_c} \quad , \tag{5-20}$$

where Δ was set equal to 3.92×10^{11} sec^{-1} = 2.09 cm^{-1}, and the constant k_3 was set equal to 0.3. As before, the correlation time τ_c was given by Eq. (5-18), and the rotational correlation time τ_r was given by Eq. (5-17). This hypothetical mechanism has to be quite strong in order to explain the reduced field dependence of the proton relaxation. In fact, at 100 MHz the two terms in Eq. (5-19) are equal in magnitude within 20% over a temperature range from -30°C to +60°C. No suggestion is made concerning the existence or nature of such a hypothetical mechanism. It may be noted that relaxation through spin rotation interaction is of a similar form. However, there seems to be no reason why spin rotation interaction for nickel would be more than an order of magnitude greater than predicted.

A second possible alternative way to explain the data is to assume that the theory for relaxation via modulation of the zero field splitting has basic inadequacies. A seeming inadequacy is that the time averaged value of the zero field splitting has previously been assumed to be independent of temperature. The very existence of such splitting in solution has customarily been attributed to collisions with solvent molecules, and it is entirely reasonable to suppose that the strength

of these collisions varies with temperature. An investigation should be made of the temperature dependence of the strength of the collision-induced distortions, perhaps along the lines of the work of Valiev (Al'tshuler and Valiev, 1959; Valiev and Zaripov, 1962). However, what was sought was a way to alter the predicted field dependence rather than the temperature dependence. Therefore, such considerations were not pursued. Another possible inadequacy is that the equations for relaxation via the ZFS mechanism use, without proper justification, the spectral density functions which were developed to describe molecular rotation and translation. Nevertheless, EPR linewidths of a number of transition ions appear to obey Eq. (3-32) and similar equations derived for the case of S>1. There is no a priori reason to expect that Ni(II) will be less well behaved, excepting the extreme shortness of its relaxation times.

It is conceivable that somehow, perhaps on geometric grounds, one could divide the solvent collisions into two types. The first type would consist of all those weak collisions whose combined effects could be described by Eq. (5-16). The second type would consist of those collisions which were so effective that they would cause spin relaxation every time they occurred. The effects of these collisions would be described by the second term in Eq. (5-19), where τ_c/k_3 is now interpreted as the average time between such favored collisions. This is similar to the "pulse process" described by McConnell (1961). He argued that if a type of process in solution were strong enough and acted for a long enough time, it could cause spin relaxation every time it occurred, with no field dependence. Since we have seen that $(T_{2e})^{-1} \cong (\tau_c)^{-1}$ for aqueous

Ni(II), it is clear that the random fluctuations are that effective in relaxing the electron spin. Even if we cannot divide the molecular motions into two separate classes, it is not unreasonable to expect some reduction in the observed magnetic field dependence.

A third alternative, one having more theoretical justification than the first two, is to assume that the conditions for rigorous application of Eqs. (3-31) and (3-32) do not apply for aqueous Ni(II). The theory of Redfield (1965) applies without modification only when the correlation time is short compared to T_2. This condition is violated for the relaxation of aqueous Ni(II). For example, at 60 MHz, T_{1e} is approximately equal to the correlation time calculated by Eq. (5-18) at all temperatures below room temperature. Abragam (1961, p. 283) stated that his formulation of relaxation theory is correct only when $\mathcal{H}_1(t)\ \tau_c$, the product of the time dependent interaction and the correlation time for that interaction, is small compared to unity. This condition is also clearly violated here. For example, if we take $\mathcal{H}_1(t)$ to be equal to 2 cm^{-1} = 3.8×10^{11} sec^{-1}, and $\tau_c = 5\times10^{-12}$ sec, we obtain $\mathcal{H}_1(t)\ \tau_c = 1.9$. It may be noted in passing that Redfield's condition, $\tau_c \ll T_2$, and Abragam's condition, $\mathcal{H}_1\tau_c \ll 1$, are equivalent if $(T_2)^{-1}$ is set equal to $(\mathcal{H}_1)^2\ \tau_c$.

How then are we to describe the relaxation caused by time dependent perturbations if the commonly used equations are no longer correct? A suggested correction to the usual relaxation equations has been developed: a derivation is presented in Appendix II. Use was made of the fact that the Larmor precession of the spin of the nickel ion does not occur at one sharp resonance frequency, but rather at a spread of frequencies,

describable through the transverse relaxation time T_{2e}. Instead of calculating the spectral density of molecular motions having exactly the resonance frequency, a calculation was made of the spectral density of motions occurring over a range of frequencies. This range was described by $(T_{2e})^{-1}$ and the distribution was assumed to be Lorentz. The result was that spectral densities of the form

$$J(n\omega_o) = \frac{2\tau_c}{1 + n^2\omega_o^2\tau_c^2} \tag{5-20}$$

were replaced by averaged spectral densities of the form

$$\bar{J}(n\omega_o) = 2\tau_c + \left[\frac{2T_2 - 2\tau_c(1 + n^2\omega_o^2T_2^2) - \left\{\dfrac{4\tau_e n^2\omega_o^2T_2^4}{\tau_c^2 + T_2^2(n^2\omega_o^2\tau_c^2 - 1)}\right\}}{1 + T_2^2(n^2\omega_o^2 - 1/\tau_c^2) + \left\{\dfrac{4n^2\omega_o^2T_2^4}{\tau_c^2 + T_2^2(n^2\omega_o^2\tau_c^2 - 1)}\right\}}\right]. \tag{5-21}$$

These two functions are equal in value when $(n\omega_o)^{-1} \ll T_2$, but diverge when $(n\omega_c)^{-1}$ approaches T_2. Under the conditions common in magnetic resonance, namely, $\tau_c \ll T_2$, $(n\omega_o)^{-1} \ll T_2$, and $n\omega_o\tau_c \ll 1$, we find that $J(n\omega_o) = \bar{J}(n\omega_o) = 2\tau_c$. The magnetic field dependences of Eqs. (5-20) and (5-21) differ when τ_c is not short compared to T_2. If we let $n = 1$ for ease of comparison and set $T_2 = \tau_c$, we find that

$$\frac{J(\omega_1)}{J(\omega_2)} = \frac{1 + \omega_2^2\tau_c^2}{1 + \omega_1^2\tau_c^2} \tag{5-22}$$

while

$$\frac{\bar{J}(\omega_1)}{\bar{J}(\omega_2)} = \frac{1 + (1/4)(\omega_2^2\tau_c^2)}{1 + (1/4)(\omega_1^2\tau_c^2)} \quad . \tag{5-23}$$

We see that the modified spectral densities predict a reduced magnetic field dependence in the region where $\omega_1^2\tau_c^2$ and $\omega_2^2\tau_c^2$ are comparable to unity.

An attempt was made to fit the proton relaxation data using these modified spectral densities. This is shown in Fig. 10. Equations (3-31) and (3-32) describing relaxation through time modulation of the zero field splitting were rewritten as

$$\frac{1}{T_{1e}} = \frac{\Delta^2}{10}\,[\bar{J}(\omega_S) + 4\bar{J}(2\omega_S)] \tag{5-24}$$

and

$$\frac{1}{T_{2e}} = \frac{\Delta^2}{20}\,[3\bar{J}(0) + 5\bar{J}(\omega_S) + 2\bar{J}(2\omega_S)] \quad . \tag{5-25}$$

The parameter T_2 appearing in Eq. (5-21) was set equal to 3×10^{-12} sec, and Δ was again set equal to 5.8×10^{11} sec^{-1}. Other parameters, such as the rotational correlation time, were identical to those used for the previous two figures. The fit is poor: the temperature dependence was completely altered at temperatures below room temperature. However, one feature appeared in the calculated curves which had not been encountered before. For the first time a calculation supported the observation that the proton relaxation times are almost equal at 60 MHz and 100 MHz.

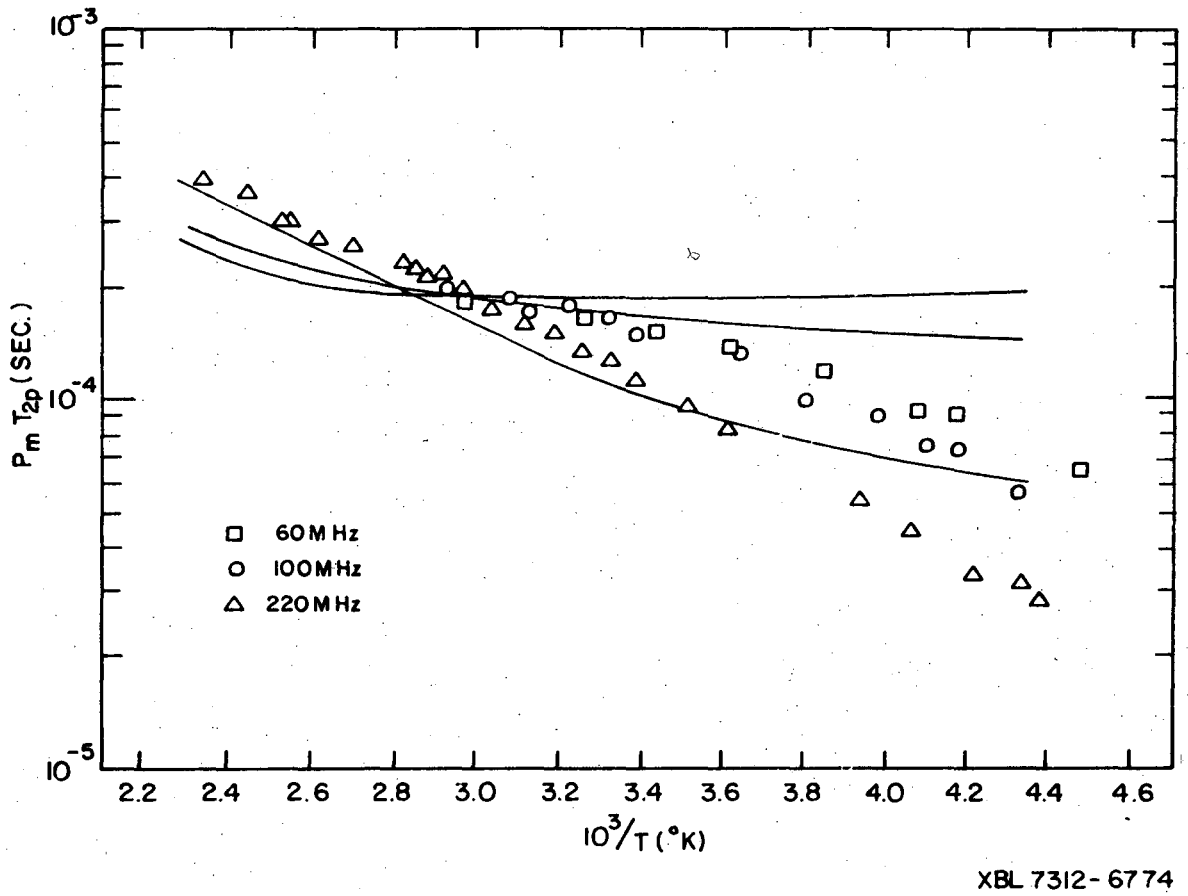

Fig. 10. Attempt to fit proton $P_m T_{2p}$ data for aqueous nickel solution 5.27 M in $HClO_4$ using modified spectral density functions. See text for parameters used.

None of the three alternative ways to explain the proton relaxation data has proven satisfactory. No additional relaxation processes were visualized which would be highly effective for nickel yet ineffective for other ions. Proposed alterations of the ZFS mechanism have the burden of being compatible with the considerable body of relaxation data that has been gathered for ions which relax via this mechanism. The third alternative, a generalization of relaxation theory for the case of very rapid transverse relaxation appeared the most fruitful. This was because such a generalization for the case of Ni(II) seemed to be demanded by general considerations, and because it would not necessarily affect the theory of the relaxation of other ions having sufficiently long T_{2e} values. However, the specific generalization considered here gave an incorrect description of the observed temperature effects.

It may be noted that proton relaxation studies of nickel in non-aqueous solvents indicate similar weak temperature and magnetic field dependences for the electron spin relaxation. Studies of Luz and Meiboom upon bulk and bound methanol protons in Ni(II) solutions (1964 bc) indicate very little temperature dependence for the electron spin relaxation. Experiments with ammonia (Van Geet, 1968b) and with dimethyl formamide (Matwiyoff, 1966) also support the notion that the relaxation of Ni(II) in solution has significantly less temperature dependence than does the viscosity of the solvent. A search of the literature failed to find examples to the contrary. Blackstaffe and Dwek (1968) measured T_1 and T_2 of protons in dimethyl sulfoxide solutions

of Ni(II) ions at 20, 35 and 90 MHz. They saw no magnetic field dependence whatsoever for the T_1 of the bulk protons. No explanation was given for this surprising result. Campbell, et al. (1971) made similar measurements in acetonitrile solutions at 20, 35 and 60 MHz. Their T_1 data showed a weak field dependence, different in appearance from that of the linewidth data of the present work. Apparently in the acetonitrile solution the "crossover" point, where $\omega_S^2 T_{2e}^2 \cong 1$, falls below room temperature.

One may conclude from all available evidence that there exists a discrepancy between theory and experiment for the electron spin relaxation of Ni(II) ion in solution.

VI. RESULTS FOR COBALT SOLUTIONS

A. NMR Relaxation

Proton linewidths in aqueous solutions of cobalt ions were measured at 60 MHz, 100 MHz, and 220 MHz. Proton T_1 measurements were made at 220 MHz. The data are listed in the first six tables of Appendix I. Analysis of the data is simplified by the extreme shortness of the electron spin relaxation time. Transverse relaxation caused by the $\Delta\omega$ mechanism was found to be quite significant at low temperatures, exceeding the relaxation taking place in the first coordination sphere of the cobalt ion. Only that part of the transverse relaxation rate of the protons which is caused by dipolar coupling is directly proportional to T_{1e} of the cobalt. The longitudinal relaxation rate of the protons is directly proportional under all conditions to T_{1e} of the cobalt. The results show that the electron spin relaxation is extremely fast, independent of magnetic field, and almost independent of temperature.

The linewidth measurements will be considered separately from the T_1 measurements. However, the features common to both sets of measurements will be treated now.

1. General

In the chapter on proton relaxation in nickel solutions, it was concluded that relaxation occurring outside the first coordination sphere could be neglected relative to relaxation occurring in the first coordination sphere. This same assumption will be used in order to interpret the results for cobalt solutions. We will now proceed to consider the dipolar coupling between protons and the spin of the cobalt.

The effective magnetic moment of cobalt will be set equal to 5.04 β, a typical value obtained from magnetic susceptibility measurements in liquids (Myers, 1973). For computing the strength of the dipolar coupling, this is numerically equivalent to setting g = 2.60 or $\gamma_S = 2.29\times10^7$ sec^{-1} $gauss^{-1}$. As before, r will be set equal to 2.6 Å.

Due to the shortness of the electron spin relaxation time, determination of the correlation time for the interruption of the dipolar coupling is rather straightforward. As can be seen from Eqs. (2-17) through (2-20), the dipolar coupling may be interrupted by electron spin relaxation, rotation of the complex, or chemical exchange. These rates may all be estimated. From their ^{17}O measurements, Chmelnick and Fiat (1967) found T_{1e} for aqueous cobalt to be 1.7×10^{-12} sec at -10°C and 4.6×10^{-13} sec at 183°C, assuming in both instances that $T_{1e} = T_{2e}$. In Chapter 5, rotational correlation times for aqueous complexes of transition metal ions were estimated to be about 8×10^{-11} sec at -10°C and 4×10^{-12} sec at 140°C. These times are an order of magnitude longer than the expected relaxation times of the cobalt. The chemical exchange time for whole water molecules bound to Co(II) is 4.2×10^{-7} sec at 27°C and 1.4×10^{-7} sec at 158°C (Chmelnick and Fiat, 1967). These times are longer still. Therefore, the correlation times τ_1 and τ_2 appearing in Eqs. (2-17) and (2-18) may be set equal to T_{1e} and T_{2e}, respectively, for all conditions studied in this work.

Making the explicit assumptions r = 2.6 Å, $\mu_{eff} = 5.04\,\beta$, $\gamma_I = 2.675\times10^4$ $sec^{-1}gauss^{-1}$, $\tau_1 = T_{1e}$, and $\tau_2 = T_{2e}$, the Eqs. (2-17) and (2-18) become

$$\left(\frac{1}{T_{1m}}\right)_d = (3.37\times10^{14}\ \mathrm{sec}^{-2}) \left[6T_{1e} + \frac{14T_{2e}}{1+\omega_S^2T_{2e}^2}\right] \tag{6-1}$$

and

$$\left(\frac{1}{T_{2m}}\right)_d = (3.37\times10^{14}\ \mathrm{sec}^{-2}) \left[7T_{1e} + \frac{13T_{2e}}{1+\omega_S^2T_{2e}^2}\right] \tag{6-2}$$

These equations will simplify further, since we expect $\omega_S^2T_{2e}^2 << 1$ under most conditions. This further simplification is a mixed blessing, since it is accompanied by the loss of the ability to experimentally detect a difference between T_{1e} and T_{2e}.

As with the solutions containing Ni(II) ion, we may compare the importance of dipolar coupling with that of scalar coupling. Equation (5-6) was derived using the conditions that $T_{1e} = T_{2e}$, that $\omega_S^2T_{2e}^2 << 1$, and that T_{1e}, $T_{2e} << \tau_r$, τ_m. It shows that the ratio of the transverse relaxation caused by dipolar coupling compared to that caused by scalar coupling is

$$\frac{(T_{2m})_d^{-1}}{(T_{2m})_{sc}^{-1}} = \frac{2\ \gamma_I^2\ (\mu_{eff})^2}{r^6\ S(S+1)(A/\hbar)^2} \tag{6-3}$$

Use of the same limiting conditions yields an identical expression for the longitudinal nuclear relaxation rates. If we use the value of $A/h = 3.7\times10^5$ Hz from the proton chemical shift work of Matwiyoff and Darley (1968), set S = 3/2, and use the previously quoted values of

the other constants, we find this ratio equal to 500. Scalar coupling, then, can be completely ignored relative to the dipolar coupling.

We conclude that the longitudinal and transverse relaxation rates of protons of water molecules in the first coordination sphere of Co(II) are entirely controlled by dipolar coupling as described by Eqs. (1) and (2). As in the case with nickel, we expect the largest source of error in determining the absolute magnitudes of T_{1e} and T_{2e} to be due to the uncertainty in evaluating the r^6 factor.

2. Linewidth Measurements

Results of proton linewidth measurements at 60 MHz, 100 MHz, and 220 MHz are shown in Figs. 11, 12, and 13. Temperatures below -5°C were achieved by using solutions either 5.27 molar in $HClO_4$ or 2.46 molar in $Ca(ClO_4)_2$. Measurements for the $Ca(ClO_4)_2$ solutions agree with those for the dilute aqueous solution at temperatures between -5°C and about 30°C, but diverge somewhat at higher temperatures. This unexplained divergence was also seen in similar solutions of Ni(II). In Fig. 13, the data below -5°C are from the solutions containing $Ca(ClO_4)_2$, and above -5°C are from dilute aqueous solutions.

The solutions low in acid show the importance of the $\Delta\omega$ mechanism at temperatures below room temperature. This mechanism was not seen in the earlier proton work of Hausser and Laukien (1959), done at 26.5 MHz, or of Bernheim, Brown, Gutowsky, and Woessner (1959), done at 20 MHz. This is perhaps not surprising, since the strength of the $\Delta\omega$ mechanism increases with the square of the external field. If the relaxation occurring in the first coordination sphere could be completely neglected

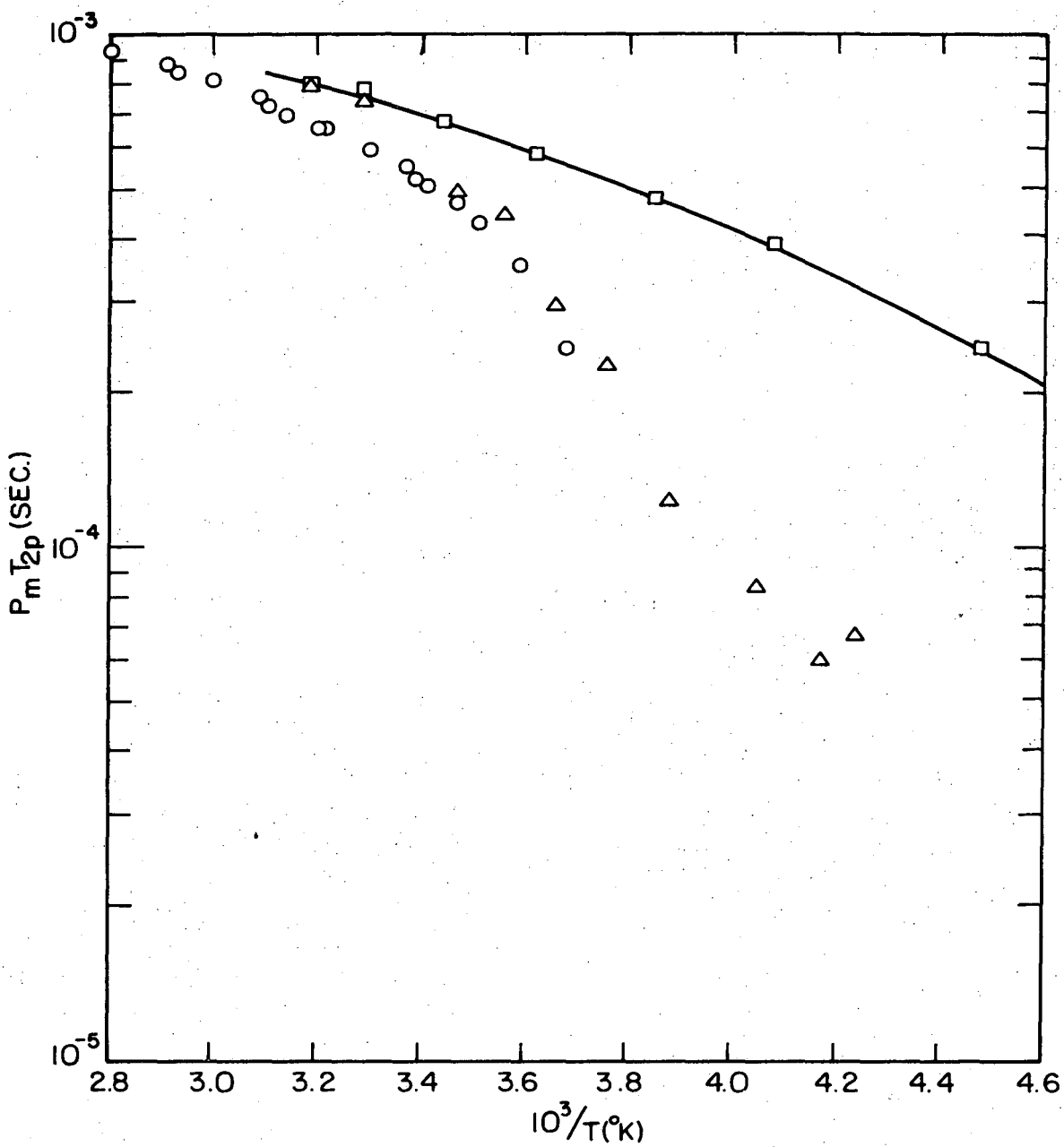

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Fig. 11. $P_m T_{2p}$ of protons in aqueous Co(II) solutions at 60 MHz as a function of temperature. The solutions represented by circles contained about 10^{-3} M $HClO_4$. The solution represented by triangles also contained 2.46 M $Ca(ClO_4)_2$. The solution represented by squares contained 5.27 M $HClO_4$. The smooth curve was drawn by eye.

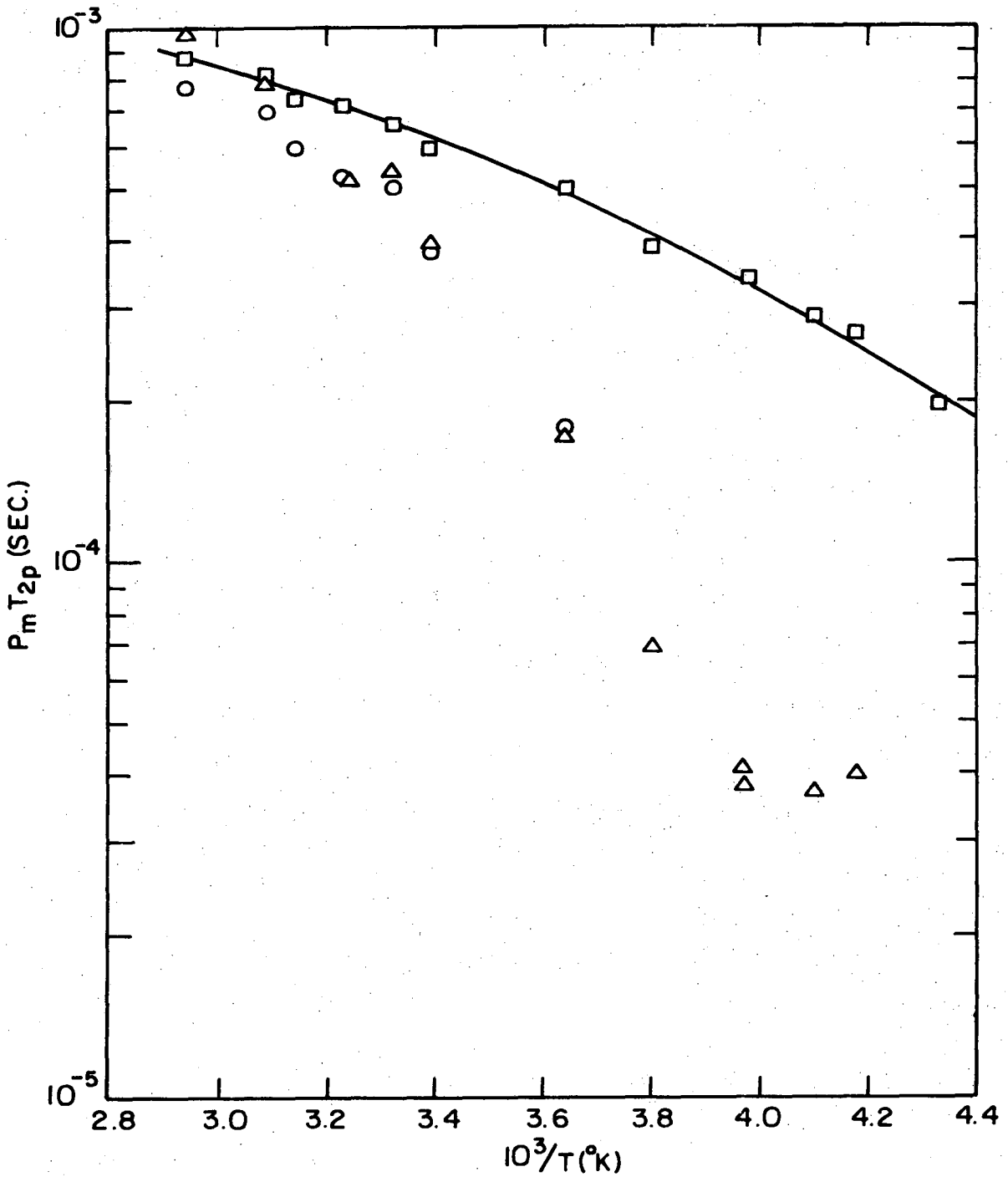

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Fig. 12. $P_m T_{2p}$ of protons in aqueous Co(II) solutions at 100 MHz as a function of temperature. Symbols are the same as in Fig. 11. The smooth curve was drawn by eye.

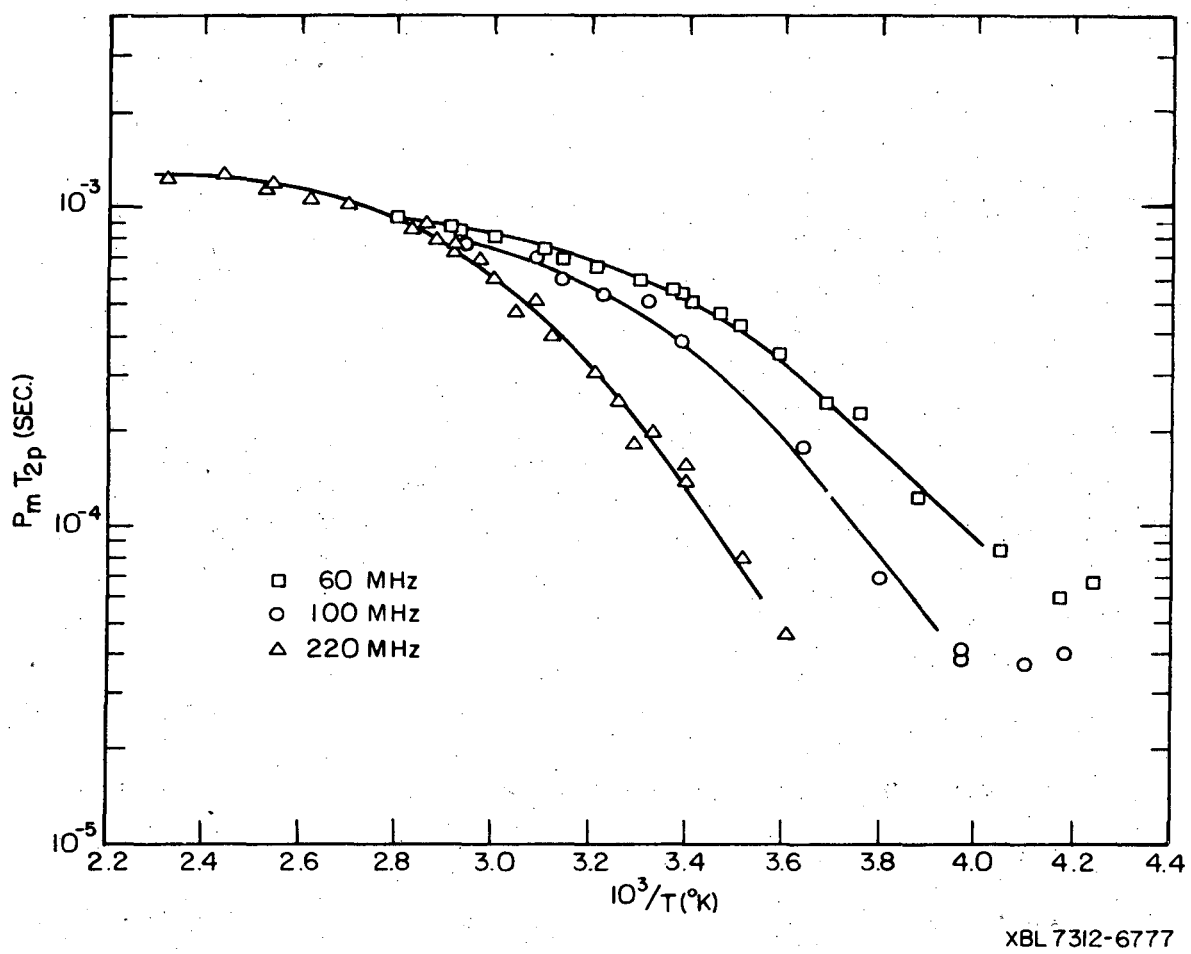

Fig. 13. $P_m T_{2p}$ of protons in Co(II) solutions low in acid as a function of temperature and frequency. The smooth curves were drawn by eye.

in comparison with that resulting from the $\Delta\omega$ mechanism, then $P_m T_{2p}$ would vary inversely with the square of the magnetic field. This situation was approached but not reached at the lowest temperatures studied. For example, at 4°C the ratio of $P_m T_{2p}$ at 100 MHz to that at 220 MHz was approximately 3.7, whereas $(220/100)^2 = 4.84$.

Comparison of the present data with that of the two earlier studies just mentioned shows that the ability of cobalt to relax bulk protons can be a full order of magnitude greater at 52 kG than it is below 7 kG. This surprisingly great ability to relax protons could perhaps find cobalt a role as an agent for the study of proton and water mobilities in biological systems. Equations (2-6) through (2-9) show that τ_m for protons can be obtained from proton linewidth measurements under any circumstances where $\Delta\omega_m^2 \tau_m >> (T_{2m})^{-1}$. Cobalt(II) in octahedral symmetry has been regarded as extremely ineffective for relaxing protons (Dwek, 1972) on the grounds that its relaxation time is so short that it could have little effect on the relaxation times of protons in the system. The effectiveness of the $\Delta\omega$ mechanism, of course, is not hindered by the shortness of T_{1e}. In fact, T_{1e} must be quite short in order for T_{2m} to be long enough to satisfy the condition $\Delta\omega_m^2 >> (T_{2m})^{-1}$. As NMR spectrometers with higher magnetic fields become available, Co(II) can become even more effective in affecting proton linewidths.

In the region below about -20°C, $P_m T_{2p}$ stops falling and begins to rise. This is due to the onset of the chemical exchange controlled region, a region in which $P_m T_{2p} = \tau_m$. It was not a major aim of this work to study the exchange rates of protons, and so this low temperature region was not explored in any detail. One conclusion that can be drawn,

however, is that in solutions low in acid, the exchange time of the protons seems to be the same as the exchange time of whole water molecules. This is seen by considering the conditions at which P_mT_{2p} is a minimum. As shown in Chapter 2, $P_mT_{2p} = \tau_m$ at temperatures below the minimum point, and $P_mT_{2p} = \Delta\omega_m^2 \tau_m + (T_{2m})^{-1}$ at temperatures above. At the minimum, $\Delta\omega_m^2 \tau_m >> (T_{2m})^{-1}$, so that $\Delta\omega_m^2 \tau_m = (\tau_m)^{-1}$. Now it can be predicted where the minima should occur. Values of τ_m for whole water molecules in cobalt solutions are given by an equation due to Chmelnick and Fiat (1967)

$$\tau_m = (4.8\times10^{-11}\ \text{sec})(T)^{-1} \exp\left(\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}\right) \qquad (6\text{-}4)$$

where $\Delta H^{\ddagger} = 10.4$ kcal mole^{-1} and $\Delta S^{\ddagger} = 5.3$ e.u. Values for $\Delta\omega_m$ at 100 MHz are given by Matwiyoff and Darley (1968). The conditions for which $\Delta\omega_m = (\tau_m)^{-1}$ are $10^3/T = 4.11$ at 60 MHz and $10^3/T = 4.02$ at 100 MHz. These values are not inconsistent with the observed minima in the P_mT_{2p} curves in Fig. 13. It may be concluded that Eq. (4) describes the exchange rate of protons in cobalt solutions low in acid.

Since the determination of T_{2m} was the immediate goal, an attempt was made to eliminate the contribution of the $\Delta\omega$ mechanism by making the rate of proton exchange sufficiently great. This effect can be seen by reconsidering Eq. (2-9) here:

$$\frac{1}{P_mT_{2p}} = \frac{1}{T_{2m}} + \Delta\omega_m^2 \tau_m \qquad (6\text{-}5)$$

This equation is valid when $\tau_m << T_{2m}$, and $(\tau_m)^{-1} >> \Delta\omega_m$, and should be accurate above about 0°C for cobalt solutions. If τ_m decreases due to acid-catalyzed proton exchange, then the contribution of the $\Delta\omega$

mechanism decreases. The presence of 5.27 M $HClO_4$ did have a dramatic effect, as Figs. 11 and 12 show. However, the contribution of the $\Delta\omega$ mechanism could not be made negligible at all temperatures. This was shown by an experiment whose results appear in Table 5. Five cobalt solutions were prepared, of acid concentration from 10^{-3} M to 5.27 M. Linewidth measurements of each were made at 60 MHz at -33°C, a temperature where the $\Delta\omega$ mechanism is very important. The quantity $P_m T_{2p}$ rose with increasing acid concentration, but never became constant. Since the linewidth measurements in the 5.27 M $HClO_4$ solution were affected to an unknown extent by the $\Delta\omega$ mechanism, it was decided not to try to extract from them any information about the electron spin relaxation of the cobalt.

It is not surprising that the use of a perchloric acid eutectic was sufficient to suppress proton exchange effects in the nickel solutions but not in the cobalt solutions. The exchange rate for whole water molecules from the first coordination sphere of Co(II) is about two orders of magnitude greater than it is for Ni(II). Therefore, it is difficult for the acid catalyzed exchange process to increase this exchange rate much further.

Therefore, measurements made upon solutions low in acid were used to calculate T_{2m}. The equation of Swift and Connick,

$$\frac{1}{P_m T_{2p}} = \frac{1}{\tau_m}\left[\frac{\frac{1}{T_{2m}}\left(\frac{1}{T_{2m}}+\frac{1}{\tau_m}\right)+\Delta\omega_m^2}{\left(\frac{1}{T_{2m}}+\frac{1}{\tau_m}\right)^2+\Delta\omega_m^2}\right] \qquad (6\text{-}6)$$

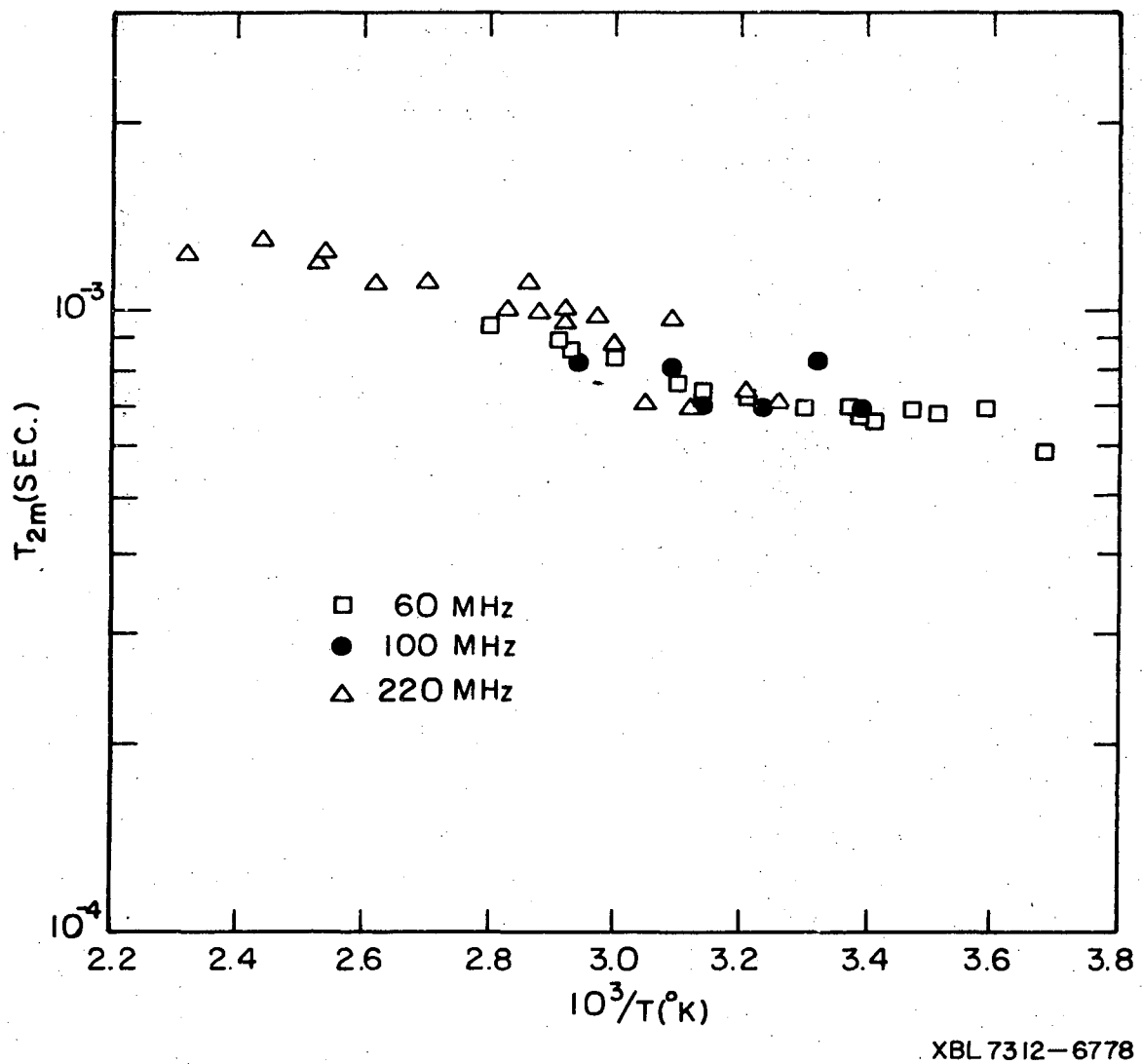

Fig. 14. T_{2m} for protons in aqueous Co(II) solutions as a function of temperature and frequency. Calculations were done using the data of Fig. 13, as explained in the text.

relates T_{2m} to known quantities. $P_m T_{2p}$ has been measured at three magnetic field strengths and a range of temperatures, as shown in Fig. 13. Values for τ_m were obtained from Eq. (4). Values for $\Delta\omega_m$ at 100 MHz were computed as

$$\Delta\omega_m = (1.272\times10^7 \text{ sec}^{-1})(T)^{-1} + 0.24\times10^4 \text{ sec}^{-1} \qquad (6\text{-}7)$$

This equation was obtained by fitting a straight line equation to values of $\Delta\omega_m$ read from the graph of Matwiyoff and Darley (1968). Values of $\Delta\omega_m$ at 60 MHz and 220 MHz were then obtained by multiplying by 0.6 and 2.2. Equation (6) was solved for T_{2m}, and the $P_m T_{2p}$ values displayed in Fig. 13 were used to calculate the points shown in Fig. 14. At each magnetic field, T_{2m} was computed only for temperatures at or above the temperature at which $\Delta\omega_m^2\tau_m = (T_{2m})^{-1}$. This is the point at which the $\Delta\omega$ mechanism is equal in effectiveness to relaxation occurring in the first coordination sphere through dipolar coupling.

Two features are immediately apparent. Transverse relaxation of the proton occurring in the first coordination sphere of the cobalt ion has no measurable magnetic field dependence. It also has almost no temperature dependence. For example, at 130°C, T_{2m} has only twice the value it has at 5°C.

The longitudinal relaxation time of the cobalt ion was then calculated by use of Eq. (2). It was assumed that $T_{1e} = T_{2e}$, and that $\omega_S^2 T_{2e}^2 << 1$. At 130°C, $T_{2m} = 1.25\times10^{-3}$ sec, so that $T_{1e} = 1.2\times10^{-13}$ sec. At 5°C, $T_{2m} = 6.1\times10^{-4}$ sec, so that $T_{1e} = 2.4\times10^{-13}$ sec. The assumption about the frequency independence is seen to be valid, since at the highest field strength reached,

$$\omega_S^2 T_{2e}^2 = (1.18\times10^{12}\ \mathrm{sec}^{-1})^2 (2.4\times10^{-13}\ \mathrm{sec})^2 = 0.08.$$

These values for T_{1e} are about a factor of five shorter than those obtained from ^{17}O measurements (Chmelnick and Fiat, 1967; Fiat, Luz, and Silver, 1968; Zeltmann, Matwiyoff, and Morgan, 1969). The discrepancy is far too large to be attributed to an incorrect value for the distance r. In order to increase the calculated value of T_{1e} by a factor of 5, r would have to be increased from 2.6 Å to 3.4 Å. Such an increase in r was felt to be unjustified, especially in view of the comparatively good agreement reached between the proton and ^{17}O work for the case of Ni(II) using a value of 2.6 Å. Neither can the discrepancy be due to an inaccurate correction for the relaxation caused by the $\Delta\omega$ mechanism, for this correction is small above room temperature. For example, at 60 MHz the $\Delta\omega$ mechanism contributes less than 10 percent of the total proton relaxation at temperatures above 40°C. On the other hand, the values for T_{2m} obtained here are consistent with the experimental work of Matwiyoff and Darley (1968). They directly observed the resonance of protons of water molecules in the first coordination sphere of Co(II) at very low temperatures. In the region from -56°C to -64°C, they obtained $T_{2m} = 2.2\times10^{-4}$ sec, which corresponds well with an extrapolation of the data in Fig. 14 to a temperature at which $10^3/T = 4.7\pm0.1$. The T_{2m} values calculated here are also in good agreement with the T_{1m} values obtained from the proton T_1 measurements to be discussed in section B of this chapter.

No explanation is advanced here for the fact that the ^{17}O measurements give a much longer value for T_{1e} of cobalt than do the proton

studies. The ^{17}O nucleus is relaxed via scalar coupling to the cobalt, and in principle there are difficulties in determining the scalar coupling constant A. In practice, this constant is evaluated from the observed chemical shift of the bulk nuclei by use of Eq. (2-12) in conjunction with Eq. (2-25). This last equation, first written by Bloembergen, states that for dilute solutions,

$$|\Delta\omega_m| = \omega_I S(S+1) \frac{\gamma_S}{\gamma_I} \frac{A}{3kT} \tag{6-8}$$

As discussed in chapter 2, this relationship is expected to be less accurate for solutions of ions, such as cobalt, which do not follow the Curie law. Yet the chemical shifts of protons (Matwiyoff and Darley, 1968) and of ^{17}O (Chmelnick and Fiat, 1967) in cobalt solutions indicate that the Bloembergen equation is obeyed if a proper value for γ_S is used. Thus it seems highly unlikely that the discrepancy between the proton and the ^{17}O results could be due to errors in determining the scalar coupling constant.

3. T_1 Measurements

Measurements were made of the longitudinal relaxation time of protons in a dilute aqueous cobalt solution at 220 MHz. The results are shown in Fig. 15, and cover a temperature range from -3°C to +148°C. The interpretation is simple. Equation (2-14) shows that in the general case, $P_m T_{1p} = T_{1m} + \tau_m$. Using Eq. (4), we find that at temperatures above -3°C, τ_m is never longer than 3×10^{-6} sec. On the other hand, the measured $P_m T_{1p}$ is never less than 7×10^{-4} sec. Thus $T_{1m} >> \tau_m$ and

$$P_m T_{1p} = T_{1m} \tag{6-9}$$

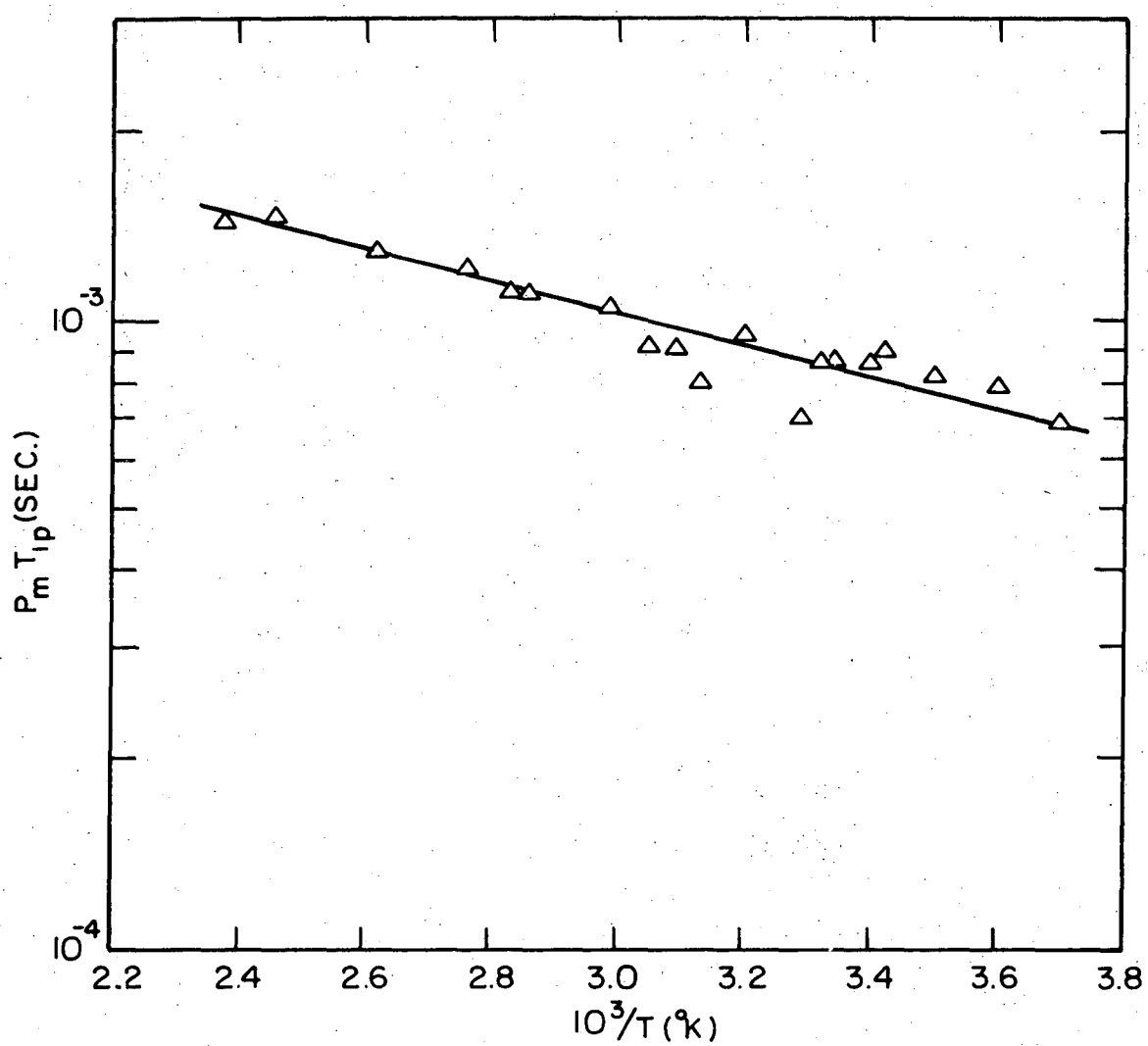

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Fig. 15. $P_m T_{1p}$ for protons in an aqueous Co(II) solution at 220 MHz as a function of temperature. A straight line was drawn through points at -3°C and +109°C.

at all temperatures in this study. These T_{1m} values show the same small temperature dependence that the T_{2m} values do. For some reason, T_{1m} is longer than T_{2m} by about 15 percent at all temperatures. This behavior was also seen in the earlier work of Bernheim, et al. (1959). The reason is not known, but the effect could be due in part to systematic experimental error. A T_1/T_2 ratio of 1.17 may be expected when $T_{1e} >> T_{2e}$. However, this situation seems highly unlikely in view of the already remarkably short value of T_{1e}.

Since $P_m T_{1p} = T_{1m}$, Eq. (1) was used to calculate T_{1e}. It was again assumed that $\omega_S^2 T_{2e}^2 << 1$, so that

$$\frac{1}{P_m T_{1p}} = \frac{1}{T_{1m}} = (3.37\times10^{14}\text{sec}^{-2})(20T_{1e}) \qquad (6\text{-}10)$$

The T_{1e} values calculated are similar to those calculated from the linewidth data. For example, at -3°C, $T_{1e} = 2.2\times10^{-13}$ sec, and at +109°C, $T_{1e} = 1.15\times10^{-13}$ sec. The temperature dependence of T_{1e} can be expressed as

$$T_{1e} = 5.2\times10^{-14}\text{sec}\ \{\exp(E/kT) - 1\} \qquad (6\text{-}11)$$

where $E = 310\pm80\ \text{cm}^{-1}$. This equation was fit using only the two T_{1e} values mentioned, and the error limits were obtained by assuming a 10 percent error in one of the two values. This temperature dependence is quite small, but is consistent with the Orbach mechanism, as we shall see.

B. Electron Spin Relaxation

The Orbach process is the dominant mechanism for the longitudinal relaxation of cobalt(II) in solids at all temperatures above about 10°K (Zverev and Petelina, 1962; Zverex and Prokhorov, 1963; Pryce, 1965). It is likewise expected to be the dominant mechanism in solution. This is largely due to the inability of any other mechanism to explain the extreme shortness of the relaxation time. All the results of the present study are consistent with the assumption that the Orbach process is the only important relaxation mechanism for cobalt in solution. These results include the magnitude of the electron spin relaxation time, the absence of a magnetic field dependence, and the very weak temperature dependence. Before considering this Orbach process in any detail, we shall briefly consider the strengths of the other mechanisms which could in principle contribute to the electron spin relaxation.

Relaxation through spin rotation interaction is dependent upon the presence of orbital angular momentum, and therefore might be expected to be appreciable for cobalt. The relaxation rate due to this mechanism is usually expressed in terms of the difference between the actual g value and the g value of the free electron, as shown by Eq. (3-30), given by Atkins and Kivelson (1966). The observed g value for the lowest doublet of Co(II) in an octahedral environment in a crystal at low temperature is typically near 4.3. However, this is a misleading indicator of the strength of spin rotation interaction in aqueous solution, where other levels are populated. It is more nearly correct to use experimental results obtained from solutions near room temperature. However, since the EPR resonance signal is unobservable under such

conditions, the only way to estimate the amount of orbital angular momentum for the solvated cobalt ion appears to be by magnetic susceptibility measurements. It was shown earlier that such measurements are compatible with an average g value of 2.6 for cobalt in solution. If such a g value is used with the Atkins and Kivelson expression, relaxation rates of $(T_{1e})^{-1} = 8\times10^{9}$ sec^{-1} at 50°C and 3×10^{10} sec^{-1} at 150°C are obtained. These rates are appreciable, and indicate that cobalt is subject to more relaxation through spin rotation interaction than other transition metal ions. However, the mechanism falls short of explaining the observed relaxation rate of cobalt by two orders of magnitude. Even if, without justification, the calculation is repeated using a g value of 4.3, the largest $(T_{1e})^{-1}$ that can be obtained is 5×10^{11} sec^{-1} at 150°C, a rate still less than observed.

Relaxation through anisotropic Zeeman interaction is likewise expected to be too weak, since there is no reason to expect a permanent anisotropy for the complex in solution. Although the root mean square anisotropy of g in solution cannot be determined, we may, merely for convenience of estimation, set $g_{\parallel} - g_{\perp} = 4$ as an extreme upper limit. This corresponds to the largest g value anisotropies measured for Co(II) in distorted octahedral symmetry in crystalline solids. Then Eq. (5-14), together with the rotational correlation times discussed in chapter 5, show that the anisotropic Zeeman interaction cannot produce a $(T_{1e})^{-1}$ greater than 8×10^{10} sec^{-1} at any field or temperature.

Relaxation through anisotropic hyperfine interaction is even weaker. If $A_{\parallel} - A_{\perp}$ is set equal to 2.4×10^{-3} cm^{-1}, the largest hyperfine anisotropy found in the eleven octahedral environments listed

by McGarvey (1966), then Eq. (3-22) predicts that $(T_{1e})^{-1}$ is only about 10^7 sec^{-1}.

There is also experimental evidence of the relative unimportance of spin rotation interaction, anisotropic Zeeman interaction, and anisotropic hyperfine interaction. All three mechanisms depend upon the rotational correlation time of the complex, and hence upon the viscosity. Yet an experiment of Frankel (1968) seemed to show that the relaxation of Co(II) is independent of viscosity. He measured water proton linewidths at 60 MHz in solutions of Co(II) ions at 40°C as a function of viscosity. Although the viscosity was varied from 1 to 9 cp by the addition of glycerin, the $P_m T_{2p}$ of the cobalt solution remained constant. At this temperature and field, the bulk proton relaxation rate in the first coordination sphere. This rate, in turn, is directly proportional to the relaxation time of the cobalt. Therefore, since $P_m T_{2p}$ is independent of viscosity, T_{1e} is likewise independent, and any relaxation mechanisms dependent upon viscosity must be negligible.

By process of elimination, it is apparent that in solution cobalt must relax by one of the processes that are available to it in solids. It is not possible to make accurate estimates of the expected strengths of each of the electric field fluctuation mechanisms in solution. However, their relative strengths may be estimated. Kivelson (1966) has done such a calculation of the relative strengths of all known EFF mechanisms in solution. His comparison procedure showed that the Orbach process will dominate the other mechanisms if the lowest excited state having proper symmetry is separated from the ground state by no

more than about 6kT. For aqueous Co(II) this separation never exceeds 2kT, and is therefore small enough to ensure that the Orbach process is at least an order of magnitude stronger than any of the other EFF mechanisms.

It now remains to be shown that the Orbach process can explain the three major features of the relaxation of Co(II) in solution. The lack of a magnetic field dependence is the easiest observation to explain. Whereas most relaxation mechanisms require the lattice to supply a motional frequency equal to the Larmor precession frequency, the Orbach process requires the lattice to supply an energy equal to the energy of an excited electronic state. In the case of cobalt(II), this is several hundred cm^{-1}. When the magnetic field is changed, this level separation does not change, and the relaxation rate is not altered.

The small temperature dependence of the relaxation in solution likewise has a simple explanation. The relaxation time will depend upon the quantity $\{\exp(E_3/kT) - 1\}$, where E_3 should be close to the 254 cm^{-1} that is expected for the separation of the first excited state in the case of octahedral symmetry (Abragam and Bleaney, 1971, p. 405). The value of this expression varies rapidly with temperature when kT is small, but is almost constant with temperature when kT becomes comparable to E_3. The observed temperature dependence of T_{1e}, shown in Eq. (11) is acceptably close to the expected result.

The Orbach mechanism may also be shown to give a rough estimate of the absolute magnitude of the relaxation rate of cobalt in solution. In order to make such an estimate, it is necessary to assume that the

cobalt relaxation is relatively insensitive to whether the ion is in the liquid or the solid state. Such an assumption is plausible if the relaxation process is visualized as the exchange of energy between the ion and the motions of its coordinate ligands, since these motions may be little changed upon going from the solid to solution. The concept of a localized phonon is well established theoretically (see, e.g., Kittel, 1968), and it is not necessary to visualize the whole crystal or solution as the immediate recipient of the energy exchanged with the spin.

This estimate of T_{1e} in solution involves the extrapolation of T_{1e} measurements in low temperature crystalline solids up to room temperature. The measurements to be quoted were made in the range from 7°K to 70°K, where T_{1e} was always longer than about 10^{-9} sec, so the extrapolation is a long one. Unfortunately, the available data are from measurements made using metallic oxide host crystals, where the cobalt ion was surrounded by six oxygen atoms rather than six water molecules. Despite this difficulty, the comparison is still fruitful.

Zverev and Petelina (1962) measured T_{1e} of cobalt in Al_2O_3, a crystal in which cobalt exists in two non-equivalent sites. Cobalt ions in the first site had a T_{1e} equal to 1.6×10^{-11}sec $\exp(\frac{110\pm15\text{cm}^{-1}}{kT})$ at temperatures from 9°K to 30°K. Ions in the second site had a T_{1e} equal to 10^{-12}sec $\exp(\frac{185\pm20\text{cm}^{-1}}{kT})$ from 14°K to 26°K. At room temperature, these equations give T_{1e} equal to 3×10^{-11}sec and 3×10^{-12}sec, respectively. Pryce (1965) measured relaxation times for cobalt in MgO. At temperatures from 50°K to 70°K, the relaxation was described by the equation

$T_{1e} = 2.4\times10^{-12}\text{sec}\ \exp(\frac{310\pm10\text{cm}^{-1}}{kT})$. At room temperature, this gives T_{1e} equal to 1×10^{-11}sec. Zverev and Prokhorov (1963) measured relaxation times for cobalt in TiO_2. In the region from 7°K to 23°K, T_{1e} was equal to $5.9\times10^{-12}\text{sec}\ \exp(\frac{102\pm5\text{cm}^{-1}}{kT})$. At room temperature this gives T_{1e} equal to 1×10^{-11} sec. These four expression actually give values of room temperature T_{1e} shorter in each case by a factor of two or three when the original data are fitted by expressions having the factor $\{\exp(E/kT) - 1\}$. The difference is negligible, of course, at low temperatures where $kT < E$. These four expressions then predict room temperature values for T_{1e} in the range from 1×10^{-12}sec to 1×10^{-11}sec. These extrapolations serve to establish the Orbach process as the strongest of the available relaxation mechanisms.

Even though the calculated and measured values of T_{1e} at room temperature still differ by about an order of magnitude, this correspondence must be considered close. Not only have expressions originally covering a range of T_{1e} values from about 10^{-4} sec to about 10^{-9} sec been extrapolated some three orders of magnitude, but they have also been expected to apply equally well to coordination by water molecules and by oxygen atoms.

The suggestion that the Orbach process is insensitive to whether the metal ion is in a solid or in a liquid has other experimental support. Wilson and Myers (1974) have measured the EPR linewidths of hexaquo titanium(III) in liquid solution and in the glass, at temperatures from room temperature to -45°C. The very broad EPR lines exhibited the exponential type of temperature dependence characteristic

of the Orbach process, and indicated a low lying excited state about 1800 cm^{-1} removed from the ground state. The striking observation was that there was no discontinuity of the relaxation behavior as the solution cooled and became a glass. One straight line fit the plot of log T_{2e} vs $10^3/T$ both above and below the freezing point.

Unfortunately, no such direct EPR experiment can be done for a cobalt sample both above and below the freezing point, owing to the extremely short T_{1e}. In principle, a comparable NMR experiment could be done by measuring proton T_1 values in an aqueous glass containing cobalt(II) ions. If sufficient protons were present to make $\tau_m < T_{1m}$, then measurements of T_{1p} could be compared with the measurements reported here.

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APPENDIX I. EXPERIMENTAL DATA

Table I-1. P_mT_{2p} for protons as a function of temperature. Solution was 0.337 M $Co(ClO_4)_2$ and 5.27 M $HClO_4$. P_m was 0.0448.

$\frac{10^3}{T(°K)}$	T(°C)	Linewidth*(Hz)	$P_mT_{2p}\times10^4$ (sec)
		At 60 MHz	
4.48	-50	58.8±2.7	2.42±0.11
4.08	-28	36.9±1.1	3.86±0.10
3.85	-13	30.1±0.5	4.74±0.08
3.62	3	24.7±0.6	5.78±0.14
3.44	18	21.4±0.5	6.67±0.15
3.29	31	18.3±0.3	7.79±0.13
3.19	40	17.9±0.3	7.96±0.13
		At 100 MHz	
4.33	-42	72.9±0.8	1.96±0.03
4.18	-34	53.4±0.6	2.67±0.03
4.10	-29	49.8±0.9	2.86±0.05
3.98	-22	42.3±0.9	3.37±0.07
3.80	-10	37.2±0.4	3.84±0.05
3.64	3	28.7±0.3	4.97±0.05
3.39	22	24.2±0.4	5.90±0.10
3.32	28	21.6±0.3	6.60±0.10
3.23	37	19.9±0.3	7.17±0.11
3.14	45	19.5±0.7	7.32±0.25
3.09	51	17.3±0.4	8.24±0.18
2.94	67	16.2±0.4	8.80±0.20

*All linewidths reported in this Appendix refer to the whole width at half intensity, expressed in Hz, and are the average of 3-7 measurements. Corrections for blanks have already been subtracted.

Table I-2. P_mT_{2p} for protons as a function of temperature. Solution was 0.337 M $Co(ClO_4)_2$ and 10^{-3} M $HClO_4$. P_m was 0.0364.

At 60 MHz			
$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)
3.69	-2	47.6±0.6	2.43±0.03
3.68	-1	47.8±2.1	2.42±0.10
3.59	6	3.33±0.5	3.48±0.05
3.51	12	27.3±0.5	4.24±0.07
3.47	15	24.9±0.7	4.66±0.13
3.41	20	23.0±0.7	5.03±0.14
3.39	22	22.3±0.7	5.19±0.16
3.37	24	21.1±0.5	5.49±0.13
3.30	30	19.4±0.8	5.97±0.12
3.30	30	19.9±0.5	5.82±0.15
3.21	39	17.8±0.5	6.50±0.17
3.20	39	17.8±0.7	6.5 ±0.25
3.14	44	16.7±0.5	6.9 ±0.2
3.10	50	16.1±0.3	7.20±1.14
3.09	51	15.5±0.4	7.5 ±0.2
3.00	60	14.3±0.4	8.1 ±0.2
2.93	68	13.8±0.3	8.4 ±0.2
2.91	71	13.3±0.5	8.7 ±0.3
2.80	84	12.5±0.4	9.3 ±0.3
At 100 MHz			
3.64	3	66.0±1.0	1.76±0.03
3.39	22	30.6±0.6	3.78±0.08
3.32	28	23.0±0.3	5.03±0.07
3.23	37	22.0±0.3	5.27±0.08
3.14	45	19.6±0.3	5.91±0.09
3.09	51	16.7±0.3	6.94±0.12
2.94	67	15.0±0.2	7.73±0.08

Table I-3. $P_m T_{2p}$ for protons as a function of temperature. Solution was 0.253 M $Co(ClO_4)_2$ and 10^{-3} M $HClO_4$. P_m was 0.0287.

At 220 MHz			
$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_m T_{2p} \times 10^4$ (sec)
3.61	4	196 ± 2.5	0.465±0.006
3.52	11	114 ± 2	0.80 ±0.01
3.40	21	58.0±2	1.57 ±0.06
3.40	21	65.7±0.6	1.39 ±0.02
3.33	27	46.3±0.3	1.97 ±0.01
3.29	31	50.5±0.7	1.81 ±0.03
3.26	34	36.7±0.3	2.49 ±0.02
3.21	39	30.0±0.3	3.05 ±0.03
3.12	47	23.2±0.2	3.94 ±0.04
3.09	51	17.9±0.25	5.12 ±0.07
3.05	55	19.5±0.3	4.69 ±0.07
3.00	60	15.3±0.25	6.00 ±0.10
2.97	64	13.4±0.2	6.85 ±0.10
2.92	69	11.9±0.5	7.7 ±0.3
2.92	69	12.5±0.25	7.33 ±0.14
2.88	74	11.5±0.15	7.95 ±0.10
2.86	77	10.3±0.15	8.87 ±0.12
2.83	80	10.7±0.25	8.53 ±0.20
2.70	98	9.00±0.3	10.15 ±0.33
2.62	108	8.66±0.13	10.55 ±0.15
2.54	120	7.66±0.25	11.9 ±0.4
2.53	123	7.97±0.16	11.5 ±0.25
2.44	137	7.2 ±0.3	12.7 ±0.5
2.32	158	7.5 ±0.5	12.2 ±0.8

Table I-4. P_mT_{2p} for protons as a function of temperature. Solution A was 0.0565 M $Co(ClO_4)_2$ and 2.46 M $Ca(ClO_4)_2$, with P_m=0.00769. Solution B was 0.0171 M $Co(ClO_4)_2$ and 2.46 M $Ca(ClO_4)_2$, with P_m=0.00233.

$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)	Solution
At 60 MHz				
4.24	-37	11.0±0.4	0.67±0.03	B
4.17	-33	12.3±0.25	0.60±0.02	B
4.05	-26	8.8±0.5	0.84±0.05	B
3.88	-15	19.9±0.5	1.23±0.03	A
3.76	-7	3.35±0.17	2.22±0.11	B
3.76	-7	10.7±0.5	2.29±0.11	A
3.66	0	8.3±0.2	2.95±0.07	A
3.56	8	5.6±0.3	4.4 ±0.2	A
3.47	15	5.0±0.2	4.9 ±0.2	A
3.29	31	3.3±0.15	7.4 ±0.3	A
3.19	40	3.1±0.15	7.9 ±0.4	A
At 100 MHz				
4.18	-34	18.4±0.4	0.40±0.01	B
4.10	-29	19.9±0.5	0.37±0.01	B
3.97	-21	64.3±1.0	0.38±0.01	A
3.97	-21	18.0±0.6	0.41±0.01	B
3.80	-10	36.1±0.7	0.68±0.02	A
3.80	-10	10.8±0.1	0.69±0.01	B
3.64	+3	14.4±0.2	1.70±0.03	A
3.39	22	6.2±0.4	3.95±0.25	A
3.32	28	4.58±0.15	5.35±0.2	A
3.24	36	4.72±0.14	5.20±0.17	A
3.09	51	3.1 ±0.2	7.9 ±0.5	A
2.94	67	2.5 ±0.2	9.8 ±0.6	A

Table I-5. P_mT_{2p} for protons in Co(II) solutions as a function of acid concentration. The temperature was -33°C. The perchlorate ion was the only anion. All concentrations are in moles per liter.

At 60 MHz					
$[Ca^{2+}]$	$[Co^{2+}]$	P_m	$[H^+]$	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)
2.46	0.0171	0.00233	0.001	14.0±0.3	0.53±0.01
2.05	0.0704	0.00941	0.878	27.9±0.5	1.08±0.02
1.12	0.191	0.0254	2.88	36.4±0.5	2.22±0.03
0.82	0.230	0.0306	3.52	40.1±0.6	2.44±0.04
0.0	0.337	0.0448	5.27	48.3±0.6	2.95±0.04

Table I-6. P_mT_{1p} for protons as a function of temperature. Solution was 0.253 M $Co(ClO_4)_2$ and 10^{-3} M $HClO_4$. P_m was 0.0287. All measurements except last four were made upon degassed samples.

At 220 MHz			
$\frac{10^3}{T(°K)}$	T(°C)	$T_1 \times 10^3$ (sec)	$P_mT_{1p} \times 10^4$ (sec)
3.70	-3	24.1±1.6	6.9±0.4
3.60	+5	27.6±1.7	7.9±0.5
3.50	13	28.5±2.0	8.2±0.6
3.42	19	31.3±2.1	9.0±0.6
3.40	21	30.0±2.0	8.65±0.6
3.34	26	30.5±1.9	8.7±0.5
3.32	28	30.1±2.1	8.65±0.6
3.29	31	24.4±2.2	7.0±0.6
3.20	39	33.4±1.6	9.6±0.5
3.13	46	27.5±2.7	8.0±0.8
3.09	51	31.7±1.7	9.1±0.5
3.05	55	32.0±1.5	9.2±0.4
2.99	61	37.1±1.9	10.6±0.5
2.86	76	38.8±2.5	11.1±0.7
2.83	80	39.0±2.1	11.2±0.6
2.76	89	42.5±2.5	12.2±0.7
2.62	109	45.0±2.4	13.0±0.8
2.46	133	51.0±2.5	14.7±0.8
2.38	148	50.0±2.5	14.3±0.8

Table I-7. P_mT_{2p} for protons as a function of temperature. Solution was 0.101 M $Ni(ClO_4)_2$ and 5.27 M $HClO_4$. P_m was 0.0133.

$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)
		At 60 MHz	
4.48	-50	65 ± 2	0.65±0.02
4.17	-33	47.2±0.9	0.90±0.02
4.08	-28	45.3±1.1	0.93±0.02
3.85	-13	36.5±1.1	1.16±0.03
3.62	3	31.1±0.5	1.36±0.02
3.44	18	27.9 0.7	1.51 0.03
3.27	33	26.0±0.5	1.63±0.03
2.98	63	23.1±0.5	1.83±0.04
		At 100 MHz	
4.33	-42	76.0±1.0	0.56±0.01
4.18	-34	58.0±1.1	0.73±0.02
4.10	-29	56.0±1.0	0.75±0.02
3.98	-22	47.0±1.4	0.90±0.03
3.80	-10	42.0±0.6	1.01±0.02
3.64	3	31.8±0.4	1.33±0.02
3.39	22	28.3±0.4	1.49±0.02
3.32	28	26.6±0.2	1.59±0.02
3.23	37	24.1±0.3	1.76±0.02
3.14	45	25.0±0.4	1.69±0.03
3.09	51	22.7±0.4	1.86±0.03
2.94	67	21.5±0.3	1.97±0.02

Table I-8. P_mT_{2p} for protons as a function of temperature. Solution was 0.101 M $Ni(ClO_4)_2$ and 5.27 M $HClO_4$. P_m was 0.0133.

At 220 MHz			
$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)
4.39	-45	148±1.5	0.286±0.003
4.35	-43	136.5±2	0.310±0.005
4.22	-36	125.9±0.8	0.336±0.003
4.07	-27	91.3±1.0	0.46 ±0.005
3.94	-19	77.1±0.5	0.55 ±0.01
3.61	+4	50.8±0.7	0.83 ±0.01
3.51	12	43.3±0.4	0.98 ±0.01
3.39	22	37.5±0.4	1.13 ±0.01
3.33	27	32.6±0.3	1.30 ±0.01
3.26	34	31.6±0.2	1.34 ±0.01
3.19	40	28.4±0.2	1.49 ±0.01
3.12	47	26.6±0.4	1.59 ±0.02
3.05	55	24.2±0.3	1.75 ±0.02
2.97	64	21.4±0.3	1.98 ±0.03
2.92	69	20.0±0.4	2.12 ±0.04
2.88	74	20.0±0.25	2.12 ±0.03
2.86	77	18.7±0.15	2.26 ±0.03
2.83	80	18.4±0.3	2.30 ±0.04
2.70	98	16.4±0.3	2.58 ±0.05
2.62	108	15.4±0.13	2.75 ±0.03
2.54	120	14.1±0.35	3.01 ±0.06
2.53	123	13.95±0.17	3.03 ±0.03
2.45	135	11.9±0.25	3.55 ±0.07
2.34	155	10.8±0.35	3.92 ±0.13

Table I-9. P_mT_{2p} for protons as a function of temperature. Solution was 0.10 M $Ni(ClO_4)_2$ and 0.003 M $HClO_4$. P_m was 0.0108.

At 60 MHz			
$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)
3.69	-2	17.7±0.3	1.94±0.03
3.68	-1	17.8±0.6	1.93±0.06
3.59	6	21.2±0.4	1.62±0.03
3.51	12	22.7±0.3	1.52±0.02
3.47	15	22.8±0.7	1.51±0.05
3.41	20	23.7±1.1	1.45±0.06
3.39	22	23.5±0.6	1.46±0.03
3.37	24	23.5±0.8	1.46±0.05
3.30	30	23.2±0.8	1.48±0.05
3.30	30	24.1±1.1	1.43±0.06
3.21	39	24.2±0.5	1.42±0.03
3.19	40	22.7±1.1	1.51±0.06
3.14	44	23.7±0.5	1.45±0.03
3.10	50	22.9±0.9	1.50±0.05
3.09	51	22.1±0.6	1.56±0.05
3.00	60	22.1±0.8	1.56±0.06
2.93	68	21.0±0.6	1.64±0.05
2.91	71	20.6±1.1	1.67±0.09
2.80	84	20.3±0.5	1.69±0.04
At 100 MHz			
3.64	3	21.3±0.3	1.61±0.02
3.39	22	27.1±0.4	1.27±0.02
3.32	28	25.8±0.2	1.33±0.01
3.23	37	23.5±0.3	1.46±0.02
3.14	45	23.7±0.6	1.45±0.04
3.09	51	20.8±0.3	1.65±0.02
2.94	67	20.1±0.2	1.71±0.02

Table I-10. $P_m T_{2p}$ for protons as a function of temperature. Solution was 0.103 M $Ni(ClO_4)_2$ and 2.46 M $Ca(ClO_4)_2$. P_m was 0.0140.

$\frac{10^3}{T(°K)}$	T(°C)	Linewidth (Hz)	$P_m T_{2p} \times 10^4$ (sec)
At 60 MHz			
4.17	-33	8.2±0.25	5.45±0.15
4.05	-26	9.1±0.5	4.9 ±0.3
3.88	-15	9.7±0.2	4.60±0.10
3.66	0	17.0±0.4	2.62±0.07
3.56	8	23.6±0.8	1.89±0.06
3.47	15	24.7±0.4	1.81±0.03
3.38	23	27.2±0.6	1.64±0.04
3.32	28	27.7±0.5	1.61±0.03
3.20	39	27.6±0.7	1.61±0.04
2.98	63	25.1±0.8	1.78±0.06
At 100 MHz			
4.18	-34	9.5±0.4	4.7±0.2
4.10	-29	10.2±0.4	4.37±0.15
3.98	-22	10.1±0.7	4.4±0.3
3.97	-21	11.4±0.5	3.9±0.15
3.80	-10	13.6±0.2	3.28±0.06
3.64	3	21.6±0.3	2.06±0.03
3.39	22	33.2±0.6	1.34±0.03
3.32	28	32.3±0.4	1.38±0.02
3.23	37	29.3±0.3	1.52±0.02
3.15	44	30.8±0.7	1.45±0.03
3.09	51	25.8±0.4	1.73±0.02
2.94	67	23.9±0.3	1.87±0.02

Table I-11. P_mT_{2p} for protons in Ni(II) solutions as a function of acid concentration. The temperature was -45°C. The perchlorate ion was the only anion. All concentrations are in moles per liter.

At 220 MHz					
$[Ca^{2+}]$	$[Ni^{2+}]$	P_m	$[H^+]$	Linewidth (Hz)	$P_mT_{2p}\times10^4$ (sec)
1.97	0.102	0.0139	1.05	156±2	0.283±0.004
1.23	0.102	0.0137	2.64	156±2	0.280±0.004
0	0.101	0.0133	5.27	148±2	0.286±0.004

Table I-12. $P_m T_{1p}$ for protons as a function of temperature. Solution was 0.101 M $Ni(ClO_4)_2$ and 5.27 M $HClO_4$. The sample was not degassed. P_m was 0.0133.

At 220 MHz			
$\frac{10^3}{T(°K)}$	T(°C)	$T_1 \times 10^3$ (sec)	$P_m T_{1p} \times 10^4$ (sec)
3.06	54	15.5±1.5	2.0±0.2
2.75	90	21.5±2.0	2.85±0.25
2.46	134	23.0±1.0	3.05±0.15

APPENDIX II. THE THEORY OF FREQUENCY AVERAGED SPECTRAL DENSITY FUNCTIONS

The usual theory of magnetic spin relaxation in liquids finds that relaxation rates are proportional to spectral density functions (Abragam, 1961; Slichter, 1963). These are functions that express the frequency distribution of the random molecular motions which give rise to the relaxation. The importance of such functions is apparent, since only those motions having frequency components near the Larmor precession frequency will be effective in causing longitudinal relaxation. The value of the spectral density $J(\omega)$ at a frequency ω_S may be expressed as the Fourier transform of a correlation function, $G(t)$:

$$J(\omega_S) = \int_{-\infty}^{\infty} G(t) \exp(-i\omega_S t)\, dt \quad . \qquad \text{(II-1)}$$

For many physical processes, such as molecular rotation and translation in liquids, $G(t)$ has the form

$$G(t) = \exp(-|t|/\tau_c) \quad . \qquad \text{(II-2)}$$

Here, τ_c is a time constant, dependent upon temperature, which is characteristic of the molecular motion. A short correlation time indicates that the molecular property under consideration, such as orientation in space, is changing rapidly. Equation (II-1) expresses the density of molecular motions occurring at the precession frequency ω_S. It may be integrated to yield

$$J(\omega_S) = \int_{-\infty}^{\infty} \exp(-|t|/\tau_c)\, \exp(-i\omega_S t)\, dt = \tag{II-3}$$

$$\int_0^{\infty} \exp\{(-1/\tau_c - i\omega_S)\, t\}\, dt + \int_{-\infty}^{0} \exp\{(1/\tau_c - i\omega_S)t\}\, dt =$$

$$\frac{1}{1/\tau_c + i\omega_S} + \frac{1}{1/\tau_c - i\omega_S} = \frac{2\tau_c}{1 + \omega_S^2\tau_c^2} \quad .$$

If τ_c is held constant, and ω_S is varied, $J(\omega_S)$ is seen to be Lorentz in shape. If ω_S is held constant, and τ_c varied, $J(\omega_S)$ has a maximum at $\tau_c = (\omega_S)^{-1}$. When $\omega_S^2\tau_c^2 \ll 1$, $J(\omega_S)$ is independent of frequency. These properties have been extensively verified by relaxation measurements.

The integration procedure in Eq. (II-3) assumed that ω_S is a frequency sufficiently sharp that its uncertainty may be neglected. This assumption may not be valid for the case of electron spins that relax extremely rapidly. If the uncertainty in ω_S becomes comparable to ω_S or to $(\tau_c)^{-1}$, Eq. (II-3) is not expected to be valid. It is of interest to calculate a modified spectral density that explicitly takes into account a spread in ω_S.

We shall now calculate a frequency averaged spectral density function $\bar{J}(\omega_o)$, where ω_o is the center of the resonance line. The frequency ω_S now becomes a variable. We shall assume that the spread of frequencies about the center is Lorentz in nature, a shape predicted from the general theory of the magnetic resonance of isolated spins. We shall account for this spread about ω_o by introducing a weighting factor

$$g(\omega_S) = \left(\frac{1}{\pi}\right) \frac{T_2}{1 + T_2^2(\omega_S - \omega_o)^2} \quad , \tag{II-4}$$

which is normalized so that

$$\int_{-\infty}^{\infty} g(\omega_S)\, d\omega_S = 1 \quad .$$

Here T_2 is the phenomenological transverse relaxation time, defined by the linewidth of the absorption signal. We now proceed to calculate the modified spectral density

$$\bar{J}(\omega_o) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g(\omega_S)\, \exp(-|t|/\tau_c)\, \exp(-i\omega_S t)\, dt d\omega_S \quad .$$

Since $g(\omega_S)$ is independent of t, the integral over dt is solved as before, yielding

$$\bar{J}(\omega_o) = \int_{-\infty}^{\infty} g(\omega_S) \left(\frac{2\tau_c}{1 + \omega_S^2\tau_c^2}\right) d\omega_S \quad . \tag{II-5}$$

We may note that if T_2 is sufficiently long, $g(\omega_S)$ acts like a delta function, and $\bar{J}(\omega_o) = J(\omega_o) = 2\tau_c(1 + \omega_o^2\tau_c^2)^{-1}$, as before. Equation (II-5) may be rewritten as

$$\bar{J}(\omega_o) = \frac{2\tau_c T_2}{\pi} \int_{-\infty}^{\infty} \left(\frac{1}{1 + T_2^2(\omega_S - \omega_o)^2}\right) \left(\frac{1}{1 + \omega_S^2\tau_c^2}\right) d\omega_S \quad .$$

The integration may be accomplished by the method of partial fractions. The integrand is set equal to

$$\left(\frac{1}{1 + T_2^2(\omega_S - \omega_o)^2}\right)\left(\frac{1}{1 + \omega_S^2\tau_c^2}\right) =$$

$$\left(\frac{A\omega_S + B}{1 + T_2^2(\omega_S - \omega_o)^2}\right) + \left(\frac{C\omega_S + D}{1 + \omega_S^2\tau_c^2}\right) \quad .$$

Tedious algebra reveals that

$$D = \left\{1 + T_2^2(\omega_o^2 - 1/\tau_c^2) + \frac{4T_2^2\omega_o^2}{\tau_c^2 + T_2^2(\omega_o^2\tau_c^2 - 1)}\right\}^{-1} \quad , \qquad \text{(II-6a)}$$

$$A = \frac{-2DT_2^4\omega_o}{\tau_c^2 + T_2^2(\omega_o^2\tau_c^2 - 1)} \quad , \qquad \text{(II-6b)}$$

$$B = 1 - D(1 + T_2^2\omega_o^2) \quad , \qquad \text{(II-6c)}$$

and

$$C = \frac{2DT_2^2\omega_o}{1 + T_2^2(\omega_o^2 - 1/\tau_c^2)} \quad . \qquad \text{(II-6d)}$$

Now

$$\bar{J}(\omega_o) = \frac{2\tau_c T_2}{\pi}(I_1 + I_2) \quad , \qquad \text{(II-7)}$$

where

$$I_1 = \int_{-\infty}^{\infty} \frac{A\omega_S + B}{1 + T_2^2(\omega_S - \omega_o)^2} \, d\omega_S$$

and

$$I_2 = \int_{-\infty}^{\infty} \frac{C\omega_S + D}{1 + \omega_S^2\tau_c^2} \, d\omega_S \quad .$$

Integration yields

$$I_1 = \frac{\pi}{T_2}(A\omega_o + B) \quad \text{and} \quad I_2 = \frac{D\pi}{\tau_c} \quad .$$

Now

$$\bar{J}(\omega_o) = 2\tau_c(A\omega_o + B) + 2T_2 D \quad , \tag{II-8}$$

or using Eq. (II-6),

$$\bar{J}(\omega_o) = 2\tau_c + \left[\frac{2T_2 - 2\tau_c(1 + T_2^2\omega_o^2) - \left\{ \dfrac{4\tau_c\omega_o^2 T_2^4}{\tau_c^2 + T_2^2(\tau_c^2\omega_o^2 - 1)} \right\}}{1 + T_2^2(\omega_o^2 - 1/\tau_c^2) + \left\{ \dfrac{4T_2^4\omega_o^2}{\tau_c^2 + T_2^2(\tau_c^2\omega_o^2 - 1)} \right\}} \right] \quad . \tag{II-9}$$

$\bar{J}(n\omega_o)$ is obtained by substituting $n\omega_o$ for ω_o. The result for $n = 0$ is simple:

$$\bar{J}(0) = \frac{2\tau_c T_2}{\tau_c + T_2} \quad . \tag{II-10}$$

Equations (II-9) and (II-10) are equal to the familiar expressions when T_2 becomes sufficiently long. For the conditions common to NMR spectroscopy, where $\tau_c \ll T_2$, $(\omega_o)^{-1} \ll T_2$, and $\omega_o\tau_c \ll 1$, we find that $\bar{J}(0) = \bar{J}(n\omega_o) = J(\omega_o) = 2\tau_c$, as expected. For the case where $\omega_o\tau_c = 1$, $\tau_c \ll T_2$ and $(\omega_o)^{-1} \ll T_2$, we find that $\bar{J}(\omega_o) = J(\omega_o) = \tau_c$, as expected.

Plots of $\bar{J}(\omega_o)$ appear in Figs. 16 and 17. The frequency ω_o was set equal to 2.48×10^{11} sec^{-1}, 4.14×10^{11} sec^{-1}, and 9.10 10^{11} sec^{-1}, corresponding to the resonance frequency of the free electron at 14.1 kG, 23.5 kG and 51.7 kG. Figure 16a shows that when $T_2 = 10^{-9}$ sec, $\bar{J}(\omega_o)$ is identical to $J(\omega_o)$ at all values of the correlation time. When T_2 is reduced to 10^{-11} sec, $\bar{J}(\omega_o)$ begins to change noticeably. When $T_2 = 5\ 10^{-12}$ sec, a not unreasonable value for aqueous Ni(II) at low temperatures, $\bar{J}(\omega_o)$ begins to lose its dependence upon τ_c for $\tau_c \geqslant (\omega_o)^{-1}$. At still shorter values of T_2, $\bar{J}(\omega_o)$ even begins to lose its magnetic field dependence when $\tau_c \geqslant (\omega_o)^{-1}$.

There is a physical explanation for this loss of temperature dependence. When the uncertainty broadening of the resonance signal starts to become comparable to the precessional frequency itself, then molecular motions of almost any frequency are equally effective in inducing relaxation. Changes in the motional frequency spectrum due to temperature changes then may have a reduced effect upon the relaxation rate, because it is no longer necessary to match motional frequencies with a sharp precessional frequency.

This treatment of relaxation theory predicts that the temperature dependence of relaxation will be reduced whenever $T_2 \leqslant \tau_c$ and $\omega_o \tau_c \geqslant 1$. These conditions should be met for the electron spin relaxation of aqueous Ni(II). It may be noted that relaxation theory in general is on less firm ground here than it is for the usual conditions where $\tau_c < T_2$ and $\omega_o \tau_c < 1$. Therefore, the present modification should be viewed as an attempt to extend the range of validity of relaxation theory.

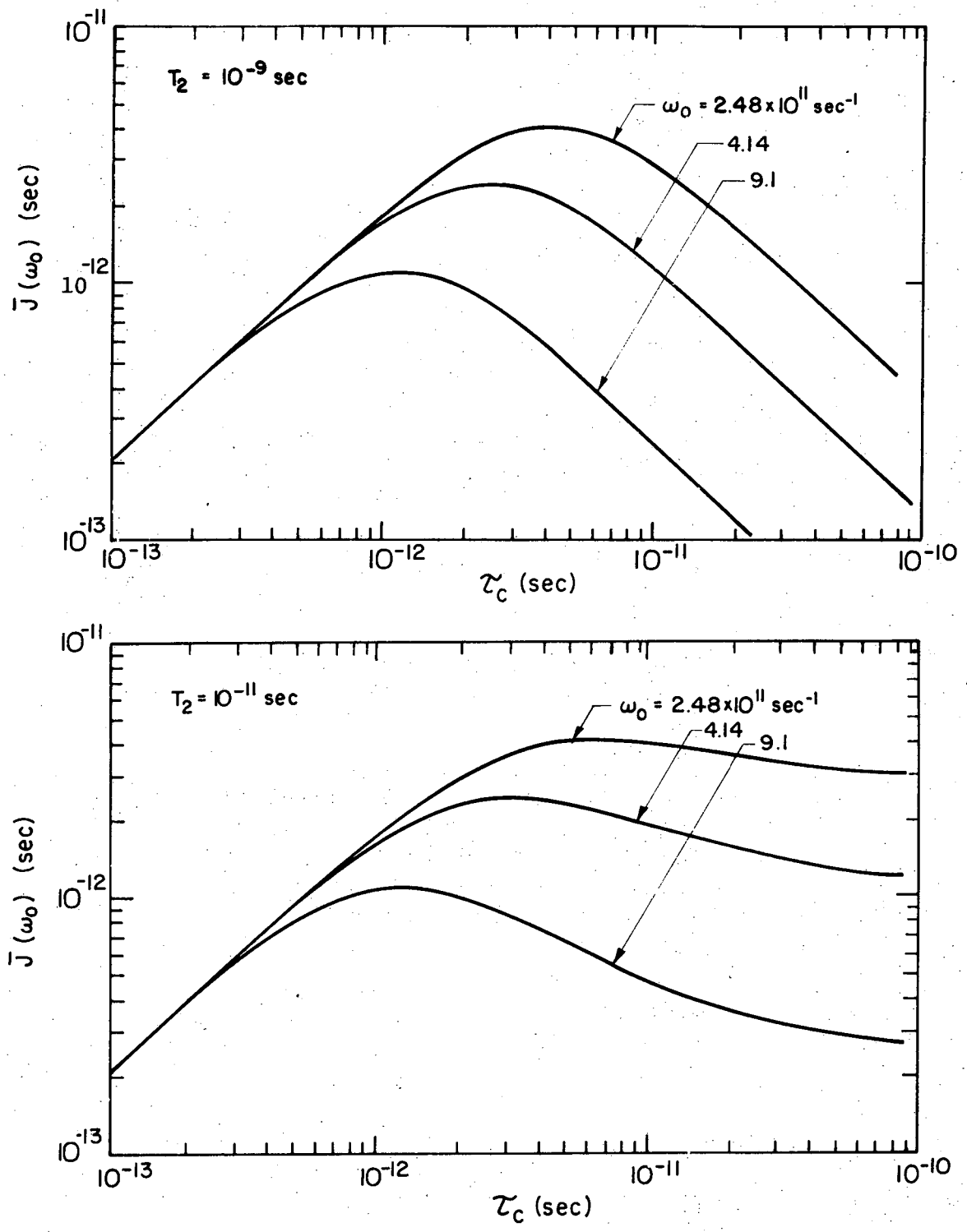

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Fig. 16. Frequency averaged spectral densities as a function of correlation time and resonant frequency. (a) Phenomenological transverse relaxation time $T_2 = 10^{-9}$ sec. (b) $T_2 = 10^{-11}$ sec.

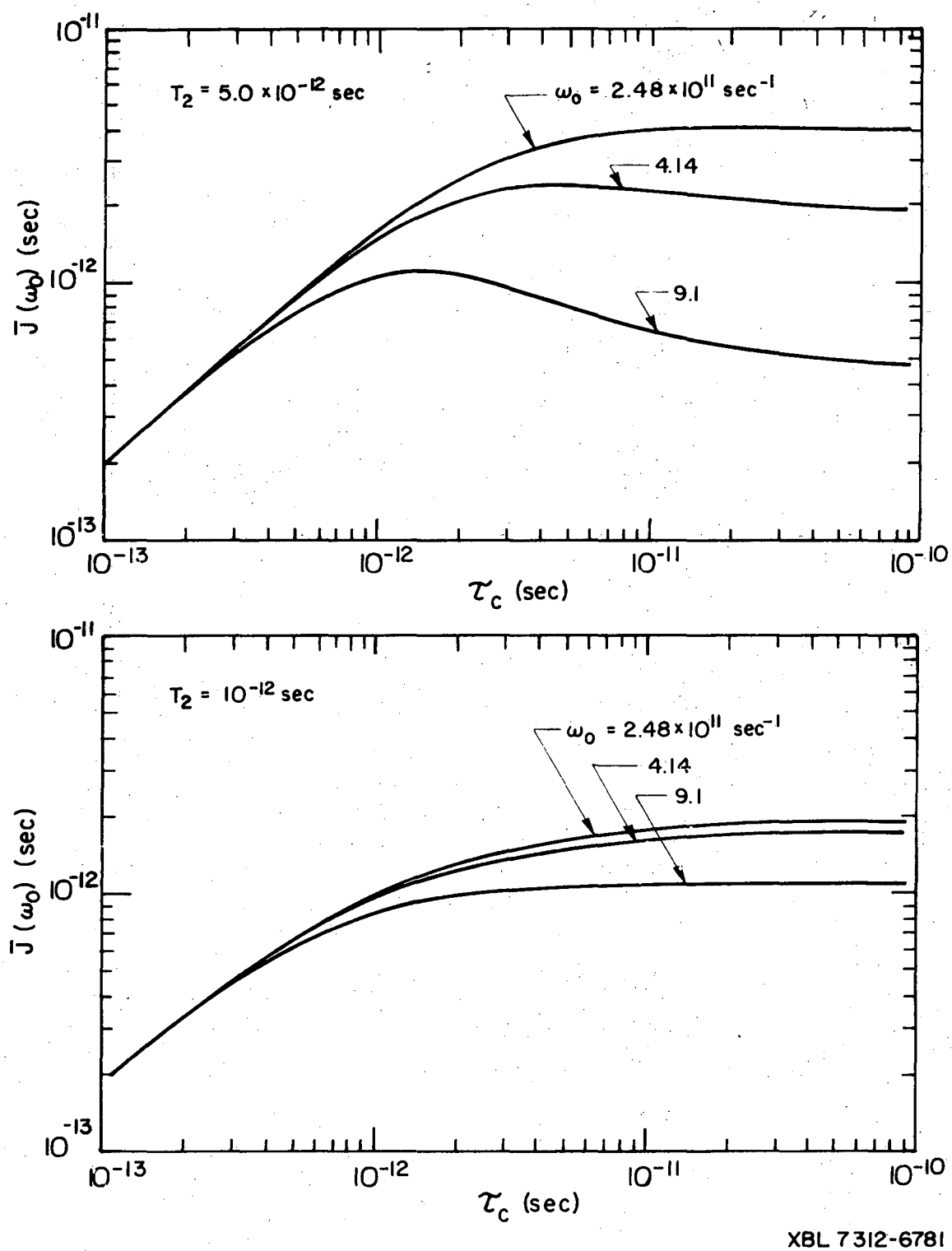

Fig. 17. Frequency averaged spectral densities as a function of correlation time and resonant frequency. (a) Phenomenological transverse relaxation time $T_2 = 5\times10^{-12}$ sec. (b) $T_2 = 10^{-12}$ sec.

In principle, relaxation of electron spins in crystalline solids should be subject to a similar effect. Relaxation rates in solids depend upon the phonon density at a frequency equal to the energy separation of the two levels. However, when the uncertainty broadening of the two levels becomes significant, corresponding to rapid electron spin relaxation, a range of phonon frequencies should be effective in connecting the levels. In this case, a proper treatment of relaxation should consider a suitable weighted spread of phonon frequencies.

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