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OXYGEN-17 NUCLEAR MAGNETIC RESONANCE STUDIES OF THE SECOND COORDINATION SPHERE OF CHROMIUM (III) IN AQUEOUS SOLUTION

William Lee Earl
(Ph. D. thesis)

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Contents

Abstract iii

I. Introduction 1

II. Theory 5

A. Measurement of Relaxation Times 5

B. Relaxation in the Presence of Chemical Exchange 10

C. Relaxation Mechanisms 15

D. Chemical Shifts 22

III. Experimental 26

A. Sample Preparation 26

B. Continuous Wave Saturation Measurements of T_1 29

C. Measurement of T_2 31

D. Measurement of Chemical Shifts 34

E. Pulsed T_1 Measurements 35

F. Computer Curve Fitting Programs 36

IV. Results and Discussion 39

A. Discussion of Electronic Relaxation Times 39

B. Chemical Shifts 41

C. Interactions Responsible for Chemical Exchange 50

1. Spin Rotation 50

2. Anisotropic Chemical Shift 50

3. Quadrupole Coupling 51

4. Dipole-Dipole Coupling 55

5. Scalar Coupling 56

D. Pulsed Measurements of T_1 64

E. Discussion. 68

Acknowledgments 75

Appendix. Experimental Data. 76

Figure Caption. 83

References. 86

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OXYGEN-17 NUCLEAR MAGNETIC RESONANCE STUDIES OF THE SECOND COORDINATION SPHERE OF CHROMIUM (III) IN AQUEOUS SOLUTION

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ABSTRACT

The oxygen-17 bulk water relaxation times and chemical shifts have been measured at 8 MHz on several aqueous solutions of $Cr(H_2O)_6^{3+}$ and on a solution of $CrF(H_2O)_5^{2+}$. Analysis of the NMR data has yielded the average lifetime of water molecules in the second coordination sphere. Further, the data have been analyzed to yield the relative contributions of each NMR relaxation mechanism to the overall relaxation.

The average lifetime of water molecules in the second coordination sphere of $Cr(H_2O)_6^{3+}$ has been calculated at 298°K to be 1.0×10^{-10} sec. The activation parameters are: $\Delta H^{\ddagger} = 2.8$ kcal and $\Delta S^{\ddagger} = -0.8$ eu.

A few measurements were made on a sample of $CrF(H_2O)_5^{2+}$. From these data it was concluded that the average lifetime for water molecules in the second coordination sphere of $CrF(H_2O)_5^{2+}$ is not greatly different from the lifetime of water in the second coordination sphere of $Cr(H_2O)_6^{3+}$.

These lifetimes are longer than the calculated lifetime for self diffusion in water and consequently are thought to reflect the electrostatic attraction between the charge on the Cr(III) and the dipole of the water molecules.

I. INTRODUCTION

Nuclear magnetic resonance has long been used as a tool for the study of solvent exchange reactions in solution.[1,2] In studies of the exchange rate of solvent molecules from the first coordination sphere of paramagnetic metal ions, several researchers have encountered broadening of the NMR resonance at low temperatures where such behavior is unexpected.[3-5] This residual broadening has been attributed to interactions between the paramagnetism of the metal ion and solvent molecules in the second coordination sphere. More recently there has been an interest in establishing a more detailed model for the structure and dynamics of molecules in the second sphere.[6,7]

Ligand exchange reactions have been discussed in a manner that assumed the formation of outer sphere complexes and subsequent interchange of the ligand between the outer and inner sphere.[8,9] In a dilute solution it is reasonable to assume that any given complex will be surrounded by solvent molecules and additionally there may be some outer sphere association with any free ligands present including the counterion. It is implicitly assumed that the electrostatic interactions into the second sphere coupled with the structure of the first sphere are sufficient to impose order upon the second sphere other than the solvent structure.

It is the intent of the following work to measure the dynamical parameters of solvent exchange from the second coordination sphere of hexa-aquochromium (III) ion. The reasons for undertaking this

work are: First, to quantify the extent of the interaction between a transition metal and its second coordination sphere in aqueous solution and second, to obtain the average lifetime of a water molecule in the second sphere.

Hexa-aquochromium (III) ion is a well characterized species in aqueous solution. Through isotopic dilution experiments it has been shown that there are six water molecules in the first coordination sphere and that they are substitution inert on any NMR time scale.[10-12] In fact the half life of a water molecule in the first coordination sphere of $Cr(H_2O)_6^{3+}$ is on the order of 40 hours at room temperature. The hydrolytic behavior of the Cr^{3+} monomer has been studied by van Meyenburg, et.al.[13] and the equilibrium constants for the hydrolytic dimer and trimer are reported by Thompson.[14]

Connick and co-workers observed that the linewidth of the ^{17}O NMR resonance signal in aqueous solutions of chromic salts is significantly greater than the linewidth of pure water.[15,16] In light of the known inertness of the first coordination sphere, this increase in linewidth can be assumed to be due to interactions between the unpaired electrons of the Cr (III) ions and water molecules in the second coordination sphere of $Cr(H_2O)_6^{3+}$.

Alei measured the chemical shift of the ^{17}O NMR resonance of both H_2O and ClO_4^- in aqueous solutions of $Cr(ClO_4)_3$.[17] Alei's work is especially significant to this thesis since he measured the chemical shift as a function of perchlorate concentration, thereby

making it possible to calculate the ratio of H_2O to ClO_4^- in the second sphere. Furthermore, the existence of a chemical shift for the bulk waters implies that there is scalar coupling between the second sphere waters and the unpaired electrons since the high symmetry of the $Cr(H_2O)_6^{3+}$ ground state ($^4A_{2g}$)[18] virtually excludes pseudocontact shift as the mechanism of the shift.[19] As will be shown below, scalar coupling is a particularly tractable relaxation mechanism for obtaining the average lifetime.

Several research groups have studied the ^1H NMR of chromic ion in aqueous solution, the most recent and most complete study was done by Melton and Pollak.[20] The results of their work have led to a thorough understanding of the magnetic behavior of the paramagnetic electrons of hexa-aquochromic ion but yielded no information on the dynamics of the second coordination sphere. Olson, Kanazawa and Taube studied the ^{17}O NMR of aqueous solutions of the isoelectronic species V(II) and Cr(III).[21] Their data are sufficient to give an upper limit of 3×10^{-10} sec for the lifetime of water molecules in the second coordination sphere of the hexa-aquo ions. The work in this thesis was commenced before Olson's results were known.

From the above arguments it was concluded that an ^{17}O NMR investigation of $Cr(H_2O)_6^{3+}$ had a very good chance of yielding exchange lifetimes for the second coordination sphere as well as the other NMR parameters in the relaxation equations.

Only one resonance signal is observed for the aqueous solution of $Cr(ClO_4)_3$ because the waters in the first coordination sphere

are shifted and broadened beyond detection by the methods used in this work. Further, the exchange rate between the second coordination sphere and the bulk is so great that these positions are effectively averaged. The difference between the transverse and longitudinal relaxation rates should be very close in magnitude to the scalar coupling contribution to the transverse relaxation rate. (The proof of this is shown in the Results and Discussion). The interruption of the scalar coupling can only be due to the relaxation of the paramagnetic electrons or chemical exchange from the second coordination sphere.

Measurements of the relaxation times of various solutions of $Cr(H_2O)_6^{3+}$ as a function of temperature allow calculation of the enthalpy and entropy of activation for the exchange of waters from the second coordination sphere of hexa-aquochromic ion. The techniques which have been used to study the second coordination sphere of $Cr(H_2O)_6^{3+}$ can be applied to other paramagnetic metal ions under favorable conditions, i.e. an inert first coordination sphere and electronic relaxation times which are not much shorter than the lifetime of solvent moleculed in the second sphere. An example of such systems would be substituted Cr(III) complexes.

II. THEORY

A. Measurement of Relaxation Times

In 1946, Bloch proposed a set of phenomenological equations to describe the behavior of nuclei when placed in an external magnetic field.[22] The "Bloch Equations" have been modified and solved to encompass virtually every condition of interest to the NMR spectroscopist. Of immediate concern is the modification to include audio modulation of the external field. With the above modification, the steady-state solution (slow-passage conditions) to the Bloch equations can be obtained.[23,24] The experimental conditions used in this work, i.e. r.f detection 90° out of phase followed by audio detection, yield a series of sidebands. The equation describing the signal can be written:

$$S = \sum_{n=-\infty}^{\infty} \frac{2n}{\beta} \frac{J_n^2(\beta)\,|\gamma|\,H_1 T_2 M_o}{1 + T_2^2(\Delta\omega + n\omega_m)^2 + (\gamma H_1)^2 T_1 T_2 J_n^2(\beta)}, \qquad (1)$$

where:

n = a dummy index which numbers the sideband being observed,

$J_n(\beta)$ = the n th Bessel function of the first kind,

$\beta = \frac{\gamma H_m}{\omega_m}$,

H_m = the strength of the audio modulation field in gauss,

ω_m = the frequency of the audio modulation field,

γ = the magnetogyric ratio of the nucleus being observed,

H_1 = one half the strength of the radio frequency field, in gauss,

$\Delta\omega = \omega - \omega_o$, where ω_o is the Larmor precession frequency,

ω = the frequency of the rf field,

M_o = the equilibrium value of the magnetization, in the absence of H_1,

T_1 = the longitudinal relaxation time,

T_2 = the transverse relaxation time.

Under conditions of negligible saturation where H_1 is small enough that $(\gamma H_1)^2 T_1 T_2 J_1^2(\beta) << 1$, the equation for the signal of the first sideband becomes:

$$S = \frac{2}{\beta} \frac{J_1^2(\beta)|\gamma| H_1 T_2 M_o}{1 + T_2^2(\Delta\omega + \omega_m)^2} \tag{2}$$

Under the usual experimental conditions of scanning the rf frequency, ω, or the external field, which corresponds to scanning ω_o, the above equation describes a Lorentz line with half width at half height (measured in radians per second) equal to $\frac{1}{T_2}$, if the inhomogeneity in H_o is small compared to $\frac{1}{T_2}$.[25]

The signal given by Eq. 1 reaches a maximum when $\Delta\omega + \omega_m = 0$, and the height of the signal is given by:

$$h = \frac{2}{\beta} \frac{J_1^2(\beta)|\gamma| H_1 T_2 M_o}{1 + (\gamma H_1)^2 T_1 T_2 J_1^2(\beta)} . \tag{3}$$

It is possible to vary the magnitude of the H_1 field and measure the peak height as a function of γH_1. The functional form of the peak height vs rf power is

$$y = \frac{Ax}{1 + Bx^2}$$

where:

y = peak height,

x = r.f. power, γH_1, measured in radians per second,

A = a normalization constant and is of no interest,

$B = T_1 T_2 J^2_1(\beta)$.

Details of the curve fitting procedure are discussed in the experimental section. The value of T_2 is measured from the half width at half height under non-saturation conditions. From Eq. 1 it is clear that the ratio of the peak heights of the first and the second sidebands, when there is negligible saturation is:

$$\frac{h_1}{h_2} = \frac{J_1^2(\beta)}{2J_2^2(\beta)} .$$

The properties of Bessel functions are well known so $J_1^2(\beta)$ can be determined from the ratio of the peak heights of the first and second sidebands.

Consequently, by measurement of the peak height as a function of r.f. power, measurement of the linewidth, and determination of $J_1(\beta)$ from the ratio of the first to second sideband, T_1 can be determined with reasonable accuracy.

Pulsed techniques[26] and Fourier transform NMR[27] have made it possible to measure relaxation times in a time domain rather than the frequency domain as above. Hahn's original spin echo experiment allowed measurement of T_2.[26] Carr and Purcell[28] and later Meiboom and Gill[29] modified the original pulse sequence to eliminate many

instrumental problems, nevertheless there are still difficulties in obtaining an accurate measurement of T_2.[30] In the systems studied in this work the ^{17}O electric quadrupole provides a reasonably efficient relaxation mechanism so the value of $1/T_2$ is never smaller than 25 sec^{-1}. It is possible to adjust the magnet homogeneity such that the resolution is better than 4 sec^{-1}. Therefore, measurement of T_2 from the halfwidth of the absorption signal is as accurate as a complicated pulse sequence and it is considerably easier. All T_2's reported are the result of the half width of the absorption signal.

Pulse measurement of T_1 is faster and in principle more accurate than the continuous wave power saturation technique described above. The pulsed "progressive saturation" technique developed by Freeman and Hill[31] was never attempted since it is known to be a difficult technique to apply in systems with short relaxation times.

The inversion recovery technique has been used to measure T_1's.[32] In this technique a 180°, τ, 90° pulse sequence is used. The 180° pulse inverts the magnetization, M, so that it points along the -Z axis. During the time τ the longitudinal relaxation time causes -M to increase. Then the application of the 90° pulse allows measurement of the z component by detection of the free induction signal. The initial height of the free induction signal is proportional to the magnitude of M_τ, the value of the z component at the end of the time interval τ. Measurement of the initial height or equivalently, Fourier transformation of the free

induction decay and measurement of the area under the resulting absorption signal, as a function of τ yields T_1.

This pulse sequence measures the decay of M_z with $M_x = M_y = 0$, from which the applicable Bloch equation can be written:

$$\frac{dM_z}{d\tau} = -\frac{(M_z - M_o)}{T_1} . \tag{4}$$

Integration of Eq. 4 with the boundary condition $M_z = -M_o$ at $\tau = 0$ gives:

$$M_z = M_o(1-2e^{-\tau/T_1}). \tag{5}$$

With the amplitude, A, proportional to M, Eq. 5 can be rewritten in the usual notation

$$\ell n(A_\infty - A_\tau) = \ell n 2A_\infty - \frac{\tau}{T_1} \tag{6}$$

Where A_τ is the amplitude of the signal following the 90° pulse at time τ, and A_∞ is the amplitude of the signal for a very long value of τ so that the magnetization has returned to its equilibrium value. The value of T_1 is determined from the slope of the line obtained when $\ell n(\frac{A_\infty - A_\tau}{2A_\infty})$ is plotted versus τ.

Longitudinal relaxation times have also been measured by a pulsed saturation recovery technique developed by Markley, et.al.[33] and then modified by McDonald and Leigh.[34] The technique as described by Markley, consists of applying a burst of nonselective pulses to

saturate the system, then waiting a variable time, τ , applying a 90° pulse and measuring the magnetization. The disadvantage with this technique is that the saturating pulse must be at high power and must have a time duration of several T_1's. This situation can cause heating in the sample which is inconvenient when temperature control is critical. The method used by McDonald and Leigh consists of applying a 90° pulse followed by a pulsed field gradient along the z axis to reduce the effective magnetization to zero (homospoil), then waiting a variable time τ followed by another 90° pulse to sample the magnetization. Conceptually this technique is equivalent to the inversion recovery technique except that the boundary condition at $\tau = 0$ is $M_z = 0$. The equation describing the behavior of the magnetization is:

$$\ell n(A_\infty - A_\tau) = \ell n A_\infty - \frac{\tau}{T_1} , \qquad (6a)$$

and T_1 is determined from the slope of the line obtained when $\ell n(\frac{A_\infty - A_\tau}{A_\infty})$ is plotted vs. τ. The pulsed saturation recovery technique has the advantage of being relatively insensitive to H_1 inhomogeneities and to deviations of the pulse widths from exactly 90°.[35]

B. Relaxation in the Presence of Chemical Exchange

The Bloch equations originally applied to a system of nuclei in one magnetic environment. The system under study here involves two distinct magnetic environments with chemical exchange of the nuclei between the two sites. McConnell modified the Bloch equations

to include the possibility of chemical exchange.[36] Swift and Connick treated the possibility of chemical exchange, applying several limiting conditions.[1] Swift and Weinberger have applied slightly different limiting conditions.[37] These treatments arrive at a set of equations which describe the shape of the NMR line as a function of the NMR parameters of both sites and the rate of exchange between the two sites.

Leigh has solved the modified Bloch equations in terms of two generalized relaxation rates $\frac{1}{T_1}$ and $\frac{1}{T_2}$.[38] This results in exact solutions to the set of differential equations given by the modified Bloch equations. It is then possible to apply whatever limiting conditions one might desire to the exact solutions. McLaughlin and Leigh have applied limiting conditions to the exact solutions to make the equations more tractable, but they have not imposed the conditions of one site being in much lower concentration than the other.[39] Therefore their equations are useful for the conditions used in this work.

At this point it is necessary to estimate approximate values for the parameters used in the modified Bloch equations. Using these approximate values, one can simplify the exact solutions to the Bloch equations and verify the validity of the approximate solutions when the final NMR data are discussed. The notation used follows McLaughlin and Leigh.

The system under study is a Cr(III) ion with a first coordination sphere which is inert on the NMR time scale. The waters in the first coordination sphere will have a resonance so broad

that they will be beyond detection by normal means; so for the purposes of this experiment these waters are non-existent. The ^{17}O resonance is considered to be the result of a two site chemical exchange process. Site A is the bulk water, i.e. water outside the second coordination sphere of the Cr(III) ions. Site B is the second coordination sphere waters. For the present it is not necessary to define the second coordination sphere rigorously, only to state that it will contain n water molecules, whose ^{17}O nuclei interact strongly enough with the unpaired electrons of the Cr(III) ion to increase the efficiency of their relaxation and to produce a contact shift.

At this point, approximate values for the relaxation and exchange parameters will be guessed at, the intent being to simplify the solutions to the Bloch equations given by McLaughlin and Leigh. Since the bonding between the Cr^{3+} and the second sphere waters is very weak, the lifetime of the second sphere waters will be short. Olson's data indicate that $\tau_b \approx 3\times10^{-10}$ sec,[21] which implies that for an approximately 1 M solution of Cr(III) $\tau_a \approx 3\times10^{-9}$ sec, where τ_a is the average lifetime of a water molecule in Site A or alternatively $1/\tau_a$ is the first order rate constant for water exchanging from Site A to Site B. From chemical shift experiments made by Alei[17] $\Delta\omega_{ab} \approx 2\times10^4$ sec, where $\Delta\omega_{ab}$ is the shift of the resonance position of Site B from pure water, measured in radians per second. The relaxation times for the bulk water, Site A, will be assumed to be the same as for pure acidified water

i.e. $\frac{1}{T_{2A}} = \frac{1}{T_{1A}} = 1.6\ 10^2\ \text{sec}^{-1}$.

The transverse relaxation time for the bound waters can be estimated from preliminary measurements, and it is well known that $T_1 \geq T_2$ so:

$$\frac{1}{T_{1B}} \leq \frac{1}{T_{2B}} \approx 8\times10^2\ \text{sec}^{-1}.$$

From the above values. for the system being studied, it is easy to verify that the conditions are the ones which McLaughlin and Leigh refer to as fast exchange, exchange narrowing. Mathematically the conditions are:

$$\frac{1}{\tau_{ab}} >> \left|\frac{1}{T_{1A}} + \frac{1}{T_{1B}}\right|$$

$$\frac{1}{\tau_{ab}} >> \left|\frac{1}{T_{2A}} + \frac{1}{T_{2B}}\right| \qquad (7)$$

$$\frac{1}{\tau_{ab}} >> \Delta\omega_{ab}$$

where $1/\tau_{ab} = 1/\tau_a + 1/\tau_b$.

Although others have used these conditions to derive the equations which follow, it is convenient to use the formalism of McLaughlin and Leigh. Their solutions to the modified Bloch equations are given by their Eqs. (9), (10) and (14).

There will be one resonance at a frequency:

$$\omega = \omega_a f_A + \omega_b f_B, \tag{8}$$

with transverse relaxation time:

$$\frac{1}{T_2} = \frac{f_A}{T_{2A}} + \frac{f_B}{T_{2B}} + f_A f_B \tau_{ab} \Delta\omega_{ab}^2 \tag{9}$$

and longitudinal relaxation time

$$\frac{1}{T_1} = \frac{f_A}{T_{1A}} + \frac{f_B}{T_{2B}} . \tag{10a}$$

Where f_A is the fraction of time that a nucleus spends in Site A, i.e. $f_A = \frac{\tau_a}{\tau_a + \tau_b}$. It is easy to verify that under the conditions of this work, Eq. 9 may be further simplified since:

$$f_A f_B \tau_{ab} \Delta\omega_{ab}^2 << \frac{f_A}{T_{2A}} , \frac{f_B}{T_{2B}} .$$

We write:

$$\frac{1}{T_2} = \frac{f_A}{T_{2A}} + \frac{f_B}{T_{2B}} \tag{10b}$$

There are five common relaxation mechanisms which operate in liquids.[41] The relaxation times; T_{1A}, T_{1B}, T_{2A} and T_{2B}; will be given by the sum of the contributions from all of the mechanisms, added as reciprocals, i.e.

$$\frac{1}{T_{1A}} = \frac{1}{T_{1A}^{DD}} + \frac{1}{T_{1A}^{S}} + \frac{1}{T_{1A}^{Q}} + \frac{1}{T_{1A}^{CSA}} + \frac{1}{T_{1A}^{SR}}, \tag{11}$$

where DD = Dipole-dipole coupling,

S = Scalar coupling,

Q = Quadrupole coupling,

CSA = Relaxation through chemical shift anisotropy,

SR = Relaxation through spin rotation.

C. Relaxation Mechanisms

Each relaxation mechanism will now be treated independently. An attempt will be made to describe the form of the interaction and the resultant relaxation equations will be given.

The dipole-dipole coupling is the result of through-space coupling between the magnetic dipole of the ^{17}O nucleus and the magnetic dipole of the unpaired electrons on the Cr(III) ion. In principle there would be coupling to any nuclear dipoles in the system, but the magnetic dipoles of the electrons are so large that they overshadow any other interaction. The equations for the relaxation times are given:

$$\frac{1}{T_1^{DD}} = \frac{S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left\{\frac{2\tau_2}{1+(\omega_I-\omega_S)^2\tau_2^2} + \frac{6\tau_1}{1+\omega_I^2\tau_1^2} + \frac{12\tau_2}{1+(\omega_I+\omega_S)^2\tau_2^2}\right\},$$

$$\frac{1}{T_2^{DD}} = \frac{S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left\{4\tau_1 + \frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2^2} + \frac{3\tau_1}{1+\omega_I^2\tau_1^2} + \frac{6\tau_2}{1+\omega_S^2\tau_2^2} + \frac{6\tau_2}{1+(\omega_I+\omega_S)^2\tau_2^2}\right\},$$

where the terms used are defined as follows:

S = electron spin, 3/2 for Cr(III),

γ_I = magnetogyric ratio of ^{17}O in radians sec^{-1} $Gauss^{-1}$,

γ_S = magnetogyric ratio for the unpaired electrons = $\frac{g\beta}{\hbar}$,

r = distance of separation of I and S, generally taken to be the metal-oxygen internuclear distance,

ω_I = resonance frequency of ^{17}O in radians sec^{-1},

ω_S = resonance frequency of the electrons,

$$\frac{1}{\tau_1} = \frac{1}{T_{1S}} + \frac{1}{\tau_r} + \frac{1}{\tau_b},$$

$$\frac{1}{\tau_2} = \frac{1}{T_{2S}} + \frac{1}{\tau_r} + \frac{1}{\tau_b},$$

τ_r = rotational correlation time for the Cr-O entity,

τ_b = exchange lifetime of the bound water,

T_{1S} = longitudinal relaxation time of the electrons,

T_{2S} = transverse relaxation time of the electrons.

Since $\omega_S >> \omega_I$ and $\omega_I \tau_1 << 1$, the above equations can be simplified.

$$\frac{1}{T_1^{DD}} = \frac{S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left\{6\tau_1 + \frac{14\tau_2}{1+\omega_S^2\tau_2^2}\right\}$$

$$\frac{1}{T_2^{DD}} = \frac{S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left\{7\tau_1 + \frac{13\tau_2}{1+\omega_S^2\tau_2^2}\right\} \qquad (12)$$

Scalar coupling results from the coupling between the unpaired electrons of the Cr(III) ion and the ^{17}O nucleus through the electronic interaction between them. This interaction may be due to the non-vanishing probability of finding one of the unpaired electrons at the ^{17}O nucleus or through the polarization of the ^{17}O orbitals by "back bonding" into the Cr(III) half filled orbitals. Since the interaction is not orientation dependent, it is not interrupted by molecular tumbling. The equations describing the relaxation are:[42]

$$\frac{1}{T_1^S} = \frac{S(S+1)}{3}\left(\frac{A}{\hbar}\right)^2 \frac{2\tau_{c2}}{1+(\omega_I-\omega_S)^2\tau_{c2}^2},$$

$$\frac{1}{T_2^S} = \frac{S(S+1)}{3}\left(\frac{A}{\hbar}\right)^2 \left[\tau_{c1} + \frac{\tau_{c2}}{1+(\omega_I-\omega_S)^2\tau_{c2}^2}\right] \qquad (13)$$

where A = Scalar coupling constant, measured in ergs. This quantity can be measured from the chemical shift and will be discussed below.

$$\frac{1}{\tau_{c1}} = \frac{1}{\tau_b} + \frac{1}{T_{1S}}$$

$$\frac{1}{\tau_{c2}} = \frac{1}{\tau_b} + \frac{1}{T_{2S}}$$

Quadrupole coupling arises from the existence of an electric quadrupole moment in nuclei with $I>\frac{1}{2}$. When such a nucleus is placed in an electric field with symmetry lower than cubic, there

are energetically preferred orientations of the electric quadrupole relative to the electric field gradient. Many nuclei in molecules are in an electronic field of low symmetry due to the electrons in the bonds. The tumbling of the molecule modulates the quadrupole interaction, providing a fairly efficient mode of relaxation, the equations for which are:[43]

$$\frac{1}{T_1^Q} = \frac{1}{T_2^Q} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\,(1+\frac{\eta^2}{3})\,(\frac{e^2qQ}{\hbar})^2\,\tau c, \qquad (14)$$

where: eQ = Quadrupole coupling constant of the nucleus,

eq = the largest component of the electric field gradient tensor, measured in the principle axis system of the molecule,

η = the asymmetry parameter, which is a measure of the deviation of the electric field gradient from axial symmetry,

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau_b}$$

The above equation is derived for the extreme narrowing case, i.e. $\omega_I^2\tau_c^2 \ll 1$. If the extreme narrowing condition is not met, it is likely that the relaxation will be non-expontial and the assumptions underlying the Bloch equations will be violated.[44]

The quadrupole and field gradient parameters, $(\frac{e^2qQ}{\hbar})$ and η, can sometimes be measured by nuclear quadrupole resonance experiments. Unfortunately, quadrupole resonance experiments have not been done

in metal-$H_2{}^{17}O$ systems so we have no independent measure of these parameters.

The theory for chemical shifts in fluids has been developed by Ramsey.[45] Formally, the interaction is given as a bilinear coupling between the external field, $\vec{H}_o$, and the spin, $\vec{I}$, through a chemical shift tensor. The physical interaction can be thought of as arising from the external field causing the electrons to "circulate" which in turn produces a magnetic field at the nucleus. The magnetic field felt by the nucleus will be the vector sum of the external field and the induced field. In principle this interaction will be asymmetric since the circulation of the electrons will be different if $\vec{H}_o$ is orientated along a bond axis or perpendicular to a bond axis. The trace of the chemical shift tensor produces a shift in energy and thus, the chemical shift. The off diagonal elements of the tensor will produce relaxation as the molecule rotates relative to $\vec{H}_o$. The resultant equations for the relaxation are:

$$\frac{1}{T_1^{CSA}} = \frac{12}{40}\gamma^2 H_o^2 \delta_z^2 (1 + \frac{\eta_S^2}{3}) \frac{\tau_c}{1 + \omega_I^2 \tau_c^2} ,$$

$$\frac{1}{T_2^{CSA}} = \frac{2}{40}\gamma^2 H_o^2 \delta_z^2 (1 + \frac{\eta_S^2}{3}) \left\{ 4\tau_c + \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} \right\} . \tag{15}$$

Where: H_o = the external magnetic field strength,

δ_z = the largest component of the chemical shift tensor in a molecular principle axis system,

η_S = the chemical shift asymmetry parameter which measures the deviation of the chemical shift tensor from cylindrical symmetry.

It is possible to obtain the values for the components of the chemical shift tensor by NMR of oriented systems, specifically in crystals. These experiments have not been done by the system under study here; but approximations for the ^{17}O asymmetry will be made by analogy to ^{13}C experiments.

Using an analogy to gases, several authors have discussed and derived equations for spin rotation relaxation.[47-51] Formally this interaction is a tensor coupling between the spin, $\vec{I}$, and the rotational angular momentum of the molecule, $\vec{J}$. Physically, one considers the molecule as a rigid rotator. The asymmetry of distribution of electric charge under rotation is analogous to an electric current in a closed loop, resulting in a magnetic field. Also one considers that the electrons are not rigidly fixed to the molecular framework so they will "slip" upon rotation of the molecule. This slippage results in the electrons having a smaller velocity than the nuclei. The magnetic field generated by the moving positive charges is not quantitatively cancelled by the field of the moving negative charges. The coupling between $\vec{I}$ and $\vec{J}$ is modulated by collisions which can produce a change in the orientation of $\vec{J}$ without changing the molecular angular momentum (Gordon has called this M-diffusion)[50] or the collisions might randomize the orientation of J and change the magnitude of $\vec{J}$ (Gordon's J-diffusion).

Unfortunately the general physical model, in which the molecule has three components to the moment of inertia and in which collisions completely randomize $\vec{J}$, results in a set of equations which are difficult to solve. The equations for spin rotation relaxation have been derived in several limiting cases. The most commonly used form of the equation is:[51]

$$\frac{1}{T_1^{SR}} = \frac{1}{T_2^{SR}} = \left(\frac{I_r kT}{\hbar^2}\right) C_{eff}^2 \tau_J. \tag{16}$$

Where: C_{eff} = a function of the components of the spin rotation coupling tensor,

τ_J = the angular momentum correlation frunction,

I_r = the moment of inertia of the molecule.

This equation has been derived for the extreme narrowing case, for a symmetric top molecule where there are only two independent components of the spin rotation coupling tensor. The extreme narrowing condition, $\omega_I^2 \tau_J^2 << 1$, is almost certainly met in all conditions where the model is applicable. The symmetric top condition probably introduces only a small error in most conditions of interest. McClung has shown that for liquids, not too close to their boiling point,

$$\tau_r \tau_J = \frac{I_r}{6kT} \Rightarrow \tau_J = \frac{I_r}{6kT\tau_r}$$

and τ_J becomes longer as the temperature increases.[48] (Note: this is not the same as the condition which obtains when $\omega_I^2\tau_J^2 >> 1$.)

Finally there is a relaxation mechanism known as the "$\Delta\omega$ mechanism" which operates in chemically exchanging systems. This is only a method of T_2 relaxation. It arises because the nucleus being observed exchanges between different environments having different precessional frequencies so that an exchange produces a dephasing of the moment of the exchanged nucleus relative to the other nuclei in the original environment. This mechanism is formally derived in the modified solutions to the Bloch equations for chemical exchange.[1] For the rapid exchange expected in this work and the relatively small shift of the ^{17}O resonance in the second sphere with respect to the bulk $H_2{}^{17}O$ resonance, this mechanism does not contribute appreciably. This can be seen from Eq. 9 where the third term, $f_A f_B \tau_{AB}^2 \Delta\omega_{AB}^2$ is the "$\Delta\omega$ contribution" to $1/T_2$ and the approximation used to derive Eq. 10b is the necessary approximation to exclude "$\Delta\omega$ mechanism".

D. Chemical Shift

The theory of chemical shifts has been treated in many different ways, depending upon the application. For the purpose of this work we will use the equation for chemical shifts in paramagnetic systems developed by Bloembergen.[52] This is a semi-empirical equation relating the chemical shift to the scalar coupling constant, A, which is used in the scalar relaxation equation (Eq. 13). Bloembergen gives:

$$\frac{\Delta\omega}{\omega} = \frac{\gamma_S}{\gamma_I} \frac{S(S+1)}{3kT} A \frac{n[M]}{[H_2O]} \tag{17}$$

Where: A = the scalar coupling constant,

n = the number of coordination sites on the metal ion,

[M] = the concentration of the metal ion,

$[H_2O]$ = the concentration of labile water molecules, i.e. all water outside of the first coordination sphere,

$\Delta\omega$ = the chemical shift, the difference in resonance frequency between pure H_2O and the solution of Cr(III),

ω = the resonance frequency of $H_2{}^{17}O$.

The quantity $\frac{\Delta\omega}{\omega} \times 10^6$ is the chemical shift of the bulk water resonance in a solution of a paramagnetic ion relative to pure H_2O, measured in parts per million. Equation 17 describes the Fermi contact interaction. It is assumed that there is no pseudo-contact or other interaction causing the chemical shift.

Alei has measured the ^{17}O chemical shift of the bulk waters in solutions of $Cr(H_2O)_6^{3+}$ and ClO_4^- at various concentrations.[17] He considers the possibility of the anion, ClO_4^-, occupying some of the sites in the second sphere, thus excluding H_2O and thereby reducing the effective coordination number of the second sphere. Equation 17 may be modified to include this possibility as follows:

$$\frac{\Delta\omega}{\omega} = \frac{\gamma_S}{\gamma_I} \frac{S(S+1)}{3kT} A \frac{y\ m_{Cr}}{m_{H_2O}} . \tag{18}$$

Where: m_{Cr} = the number of millimoles of Cr(III) in the sample,

m_{H_2O} = the number of millimoles of labile H_2O in the sample,

y = the number of sites in the second sphere which are occupied by water molecules.

Alei gives data on the chemical shift as a function of ClO_4^- concentration; from this it is possible to extrapolate to zero perchlorate concentration, thus obtaining the scalar coupling constant with no complications due to ClO_4^- in the second sphere.

We define a quantity $\Delta\omega°$, the chemical shift at zero perchlorate concentration. The chemical shift will obey Eq. 17 at zero perchlorate since there will be no perchlorate in the second sphere to exclude water from any of the n sites available. Then taking the ratio of the chemical shift at some finite perchlorate concentration to the extrapolated value at zero perchlorate concentration, one obtains:

$$\frac{\Delta\omega}{\Delta\omega°} = \frac{y}{n} \tag{19}$$

Thus from the measured chemical shift, $\Delta\omega$, the extrapolated shift at zero perchlorate concentration, and assuming a coordination number for the second sphere, n; a value of y, the number of sites in the second sphere occupied by water is obtained. The quantity y is needed to calculate f_B used in the relaxation equations (Eq. 10). From the principle of microscopic reversability,

$$[A]\frac{1}{\tau_a} = [B]\frac{1}{\tau_b},$$

and from the definition of f_B,

$$f_B = \frac{\tau_b}{\tau_a + \tau_b},$$

it is easy to show that

$$f_B = \frac{\text{number of millimoles of Site B}}{\text{number of millimoles of Site A + number of millimoles of Site B}}. \tag{20}$$

Where the number of millimoles of Site B = $y\ m_{Cr}$.

The quantity f_B is the mole fraction of water molecules in the second coordination sphere and consequently it is a function of n, the coordination number of the second sphere. There are no available measurements of the coordination number of the second sphere, so at this point f_B will be defined in terms of the undetermined quantity, n.

III. EXPERIMENTAL

A. Sample Preparation

High purity $Cr(ClO_4)_3 \cdot xH_2O$ was prepared by reducing reagent grade CrO_3 (Mallinckrodt) using 30% H_2O_2 in a 5 M solution of $HClO_4$. The resulting solution was put on a Dowex 50W-X8 ion exchange column. The $Cr(H_2O)_6^{3+}$ was forced off the column with 1 M $Ba(ClO_4)_2$. This procedure separates the $Cr(H_2O)_6^{3+}$ from any hydrolytic polymers, which adhere to the column more strongly. The resulting solution of $Cr(ClO_4)_3$ was then put on a vacuum line at room temperature to remove H_2O. After there was considerable crystallization, the crystals were filtered and stored in a dessicator over P_2O_5.

The $Cr(H_2O)_6^{3+}$ samples were prepared by weighing the crystals of $Cr(ClO_4)_3 \cdot xH_2O$ into a special flask, followed by weighed addition of $H_2{}^{17}O$, enriched to 6 to 12 atom percent in ^{17}O. At the same time a sample of the $Cr(ClO_4)_3$ crystals was weighed for analysis of the percent Cr.

The percent Cr was determined by oxidation to CrO_4^{2-} in alkaline H_2O_2 and spectrophotometric determination of CrO_4^{2-} using a Cary model 14 spectrophotometer. This procedure is necessary due to the uncertainty in the amount of water in the crystals.

The $Al(H_2O)_6^{3+}$ sample was prepared from reagent $Al(ClO_4)_3 \cdot xH_2O$ (Alfa). The $Al(ClO_4)_3$ solid is very hygroscopic so the sample was prepared by weighing the solid into a tared flask in a glove bag, the flask was then stoppered, removed from the glove bag and weighed, then the enriched water was added and weighed, and finally, standardized $HC\ell O_4$ was weighed into the flask.

The $CrF(H_2O)_5^{2+}$ sample was prepared using a modification of a technique described by Swaddle and King.[53] A solution of high purity $Cr(H_2O)_6^{3+}$ was prepared as described above. To this solution was added reagent grade KF (Mallinckrodt) followed by refluxing for 6 hours. The resulting solution was filtered to remove $KClO_4$ and then put on a Dowex 50W-X8 Ion exchange column. It was found that there were three prominent bands on the column which proved to be: $Cr(H_2O)_6^{3+}$, $CrF(H_2O)_5^{2+}$ and $CrF_2(H_2O)_4^{+}$. These three bands were easily separated by forcing them off the column using 1 M $Ba(ClO_4)_2$. The $CrF(H_2O)_5^{2+}$ band was collected and found to be 0.5 M in $CrF(H_2O)_5^{2+}$. Various attempts were made to crystallize the $CrF(H_2O)_5(ClO_4)_2$ salt, all of which were unsuccessful. A concentrated stock solution (2.9 M in Cr) was prepared by putting the dilute solution of CrF^{2+} on an ion exchange column and forcing it off with a saturated solution of $Ba(ClO_4)_2$. This resulted in a solution which was 1.2 M in CrF^{2+}. This solution was then evacuated and pumped on for several hours at about minus 5° C resulting in a final solution which was 2.9 M in CrF^{2+}. The final solution was diluted with an equal volume of $H_2{}^{17}O$, ca. 10% in ^{17}O.

The compositions of the samples which were used for the NMR experiments were:

	Sample 1	Sample 2	Sample 3
millimoles $Cr(H_2O)_6^{3+}$	1.04	1.77	1.92
millimoles H^+	3.06	5.01	3.26
millimoles ClO_4^-	6.19	10.33	9.02
millimoles labile H_2O	68.88	99.55	85.39

Sample Al^{3+}	Sample CrF^{2+}
1.08 millimoles $Al(H_2O)_6^{3+}$	2.07 millimoles $CrF(H_2O)_5^{2+}$
3.16 millimoles H^+	0.27 millimoles H^+
6.28 millimoles ClO_4^-	4.40 millimoles ClO_4^-
70.06 millimoles labile H_2O	59.46 millimoles labile H_2O

The term "labile H_2O" as used above includes all water in the system except that in the first coordination sphere of the metal ions.

The samples described above were put in NMR sample tubes, frozen, evacuated and sealed. The sample tubes for T_1 and T_2 measurement were 11 mm o.d. cylindrical tubes (∿2 ml volume) constructed with a thermocouple well immersed in the solution for temperature measurement in the NMR experiments. The sample tubes for chemical shift measurement were spheres, 11 mm o.d. with a 4 mm neck for filling. They were filled to the neck and sealed. Care was taken to minimize the amount of solution in the neck. The spherical sample shape eliminates making shift corrections for the bulk susceptibility of the solutions which is a large correction for concentrated solutions of paramagnetic compounds.

B. Continuous Wave Saturation Measurements of T_1

All saturation measurements were made using an NMR spectrometer comprised of a Varian V-4021A Electromagnet operated at 14 kGauss, using a Varian flux stabilizer-slow scan unit for field sweep. A Varian V-4311 fixed frequency rf unit and V-4331A probe operated at 8.134 MHz provided the rf detection. Audio modulation and phase detection were carried out with by a Princeton Applied Research model HR-8 lock in amplifier. The right hand portion of Fig. 1. shows a block diagram of the 8 MHz spectrometer as used in these experiments.

Temperature regulation was accomplished by using a dewared insert in the probe, through which heated or cooled nitrogen gas was forced. The temperature was measured above and below the sample, before and after each saturation experiment and the four readings averaged. The deviation between the top and the bottom of the sample ranged from 0° at ambient temperature to 5° at about 100°C. The temperature stability (between the outset and completion of a power saturation series) was better than 2° at 100°C over approximately 3 hours.

The saturation measurement of T_1 requires accurate knowledge of the rf field strength, γH_1. The rms output voltage from V4311 rf transmitter was measured with a Hewlett-Packard Model 411AR rf millivoltmeter. The millivoltmeter was standardized by repeatedly power saturating a sample of acidified $H_2{}^{17}O$ where it is well known that $T_1 = T_2$.[54, 55] From these power saturations a proportionality constant between volts rms and γH_1 in radians

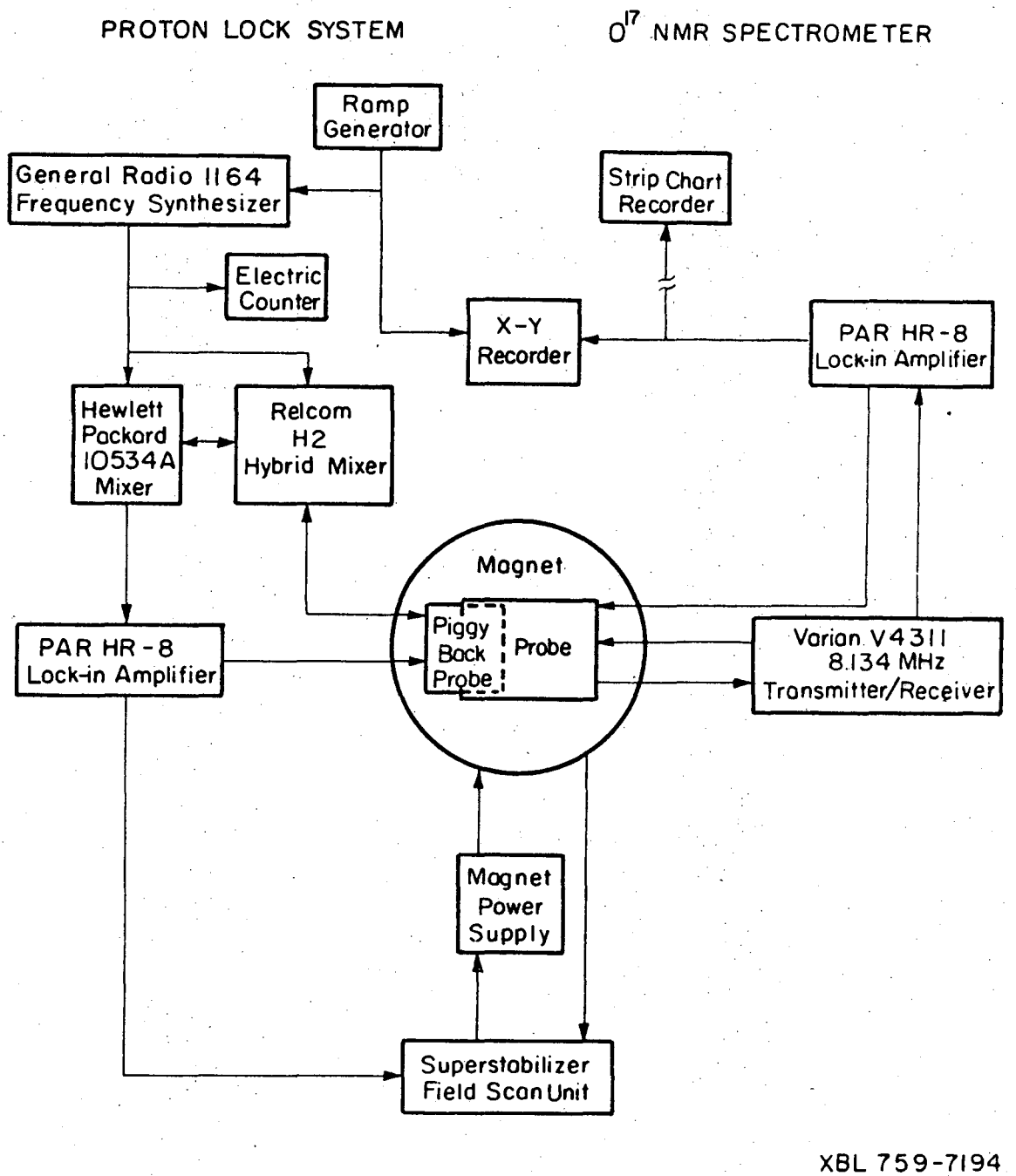
PROTON LOCK SYSTEM
O17 NMR SPECTROMETER
Ramp Generator
General Radio 1164 Frequency Synthesizer
Strip Chart Recorder
Electric Counter
X-Y Recorder
PAR HR-8 Lock-in Amplifier
Hewlett Packard 10534A Mixer
Relcom H2 Hybrid Mixer
Magnet
Piggy Back Probe
Probe
PAR HR-8 Lock-in Amplifier
Varian V4311 8.134 MHz Transmitter/Receiver
Magnet Power Supply
Superstabilizer Field Scan Unit
XBL 759-7194

Fig. 1.

sec^{-1} was established.

As shown in the theory section, the power saturation experiment is accomplished by measuring the peak height of the resonance signal as a function of rf power. The peak height was measured by repetitively scanning through both the upfield and downfield first sideband absorption signals a minimum of 4 times. This gives at least 8 measurements of the peak height and the baseline can be accurately measured between the two peaks (see Fig. 2). During each power saturation experiment, the peak height of the second sideband was measured by repetitively scanning through the second sideband at least 8 times. From Eq. 3, it can be seen that twice the ratio of the first sideband to the second sideband yields the ratio of the squares of the Bessel functions, $J_1(\beta)/J_2(\beta)$. From an accurate plot of $J_1(\beta)$ versus $J_1(\beta)/J_2(\beta)$, the value of $J_1(\beta)$ was determined. A non-linear curve fitting computer program was used to fit the peak height vs rf voltage. Knowing the proportionality constant between rf voltage and H_1, $J_1(\beta)$, and T_2; T_1 was determined. Figure 3 shows the results of such a computer fit, where the points are the measured peak heights and the solid line descibes the best fit to the data. The details of the curve fitting program are described below.

C. Measurement of T_2

It was shown earlier that T_2 can be measured from the half width at half height of the absorption signal. The NMR instrument was set up in exactly the same configuration as described above

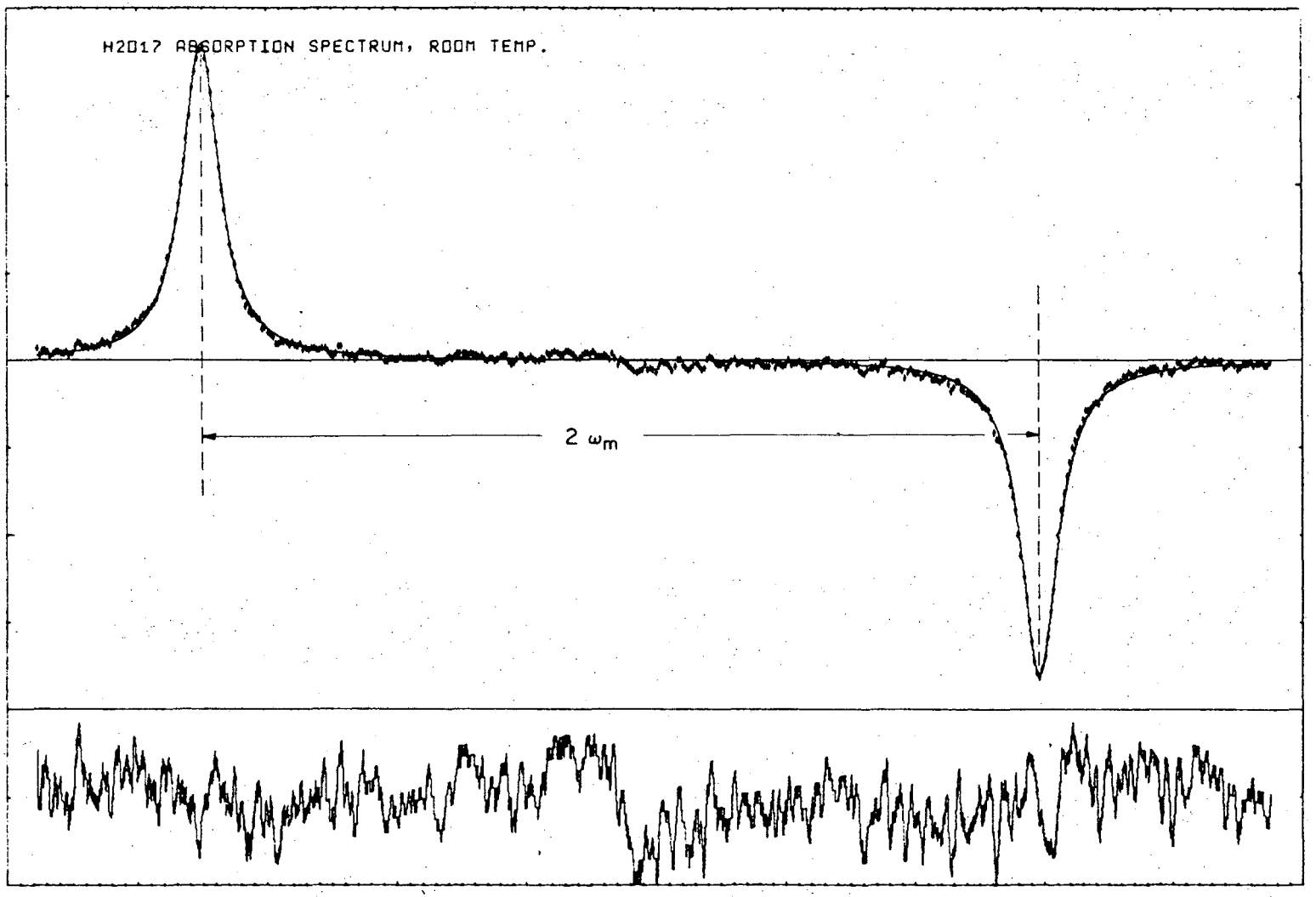

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Fig. 2.

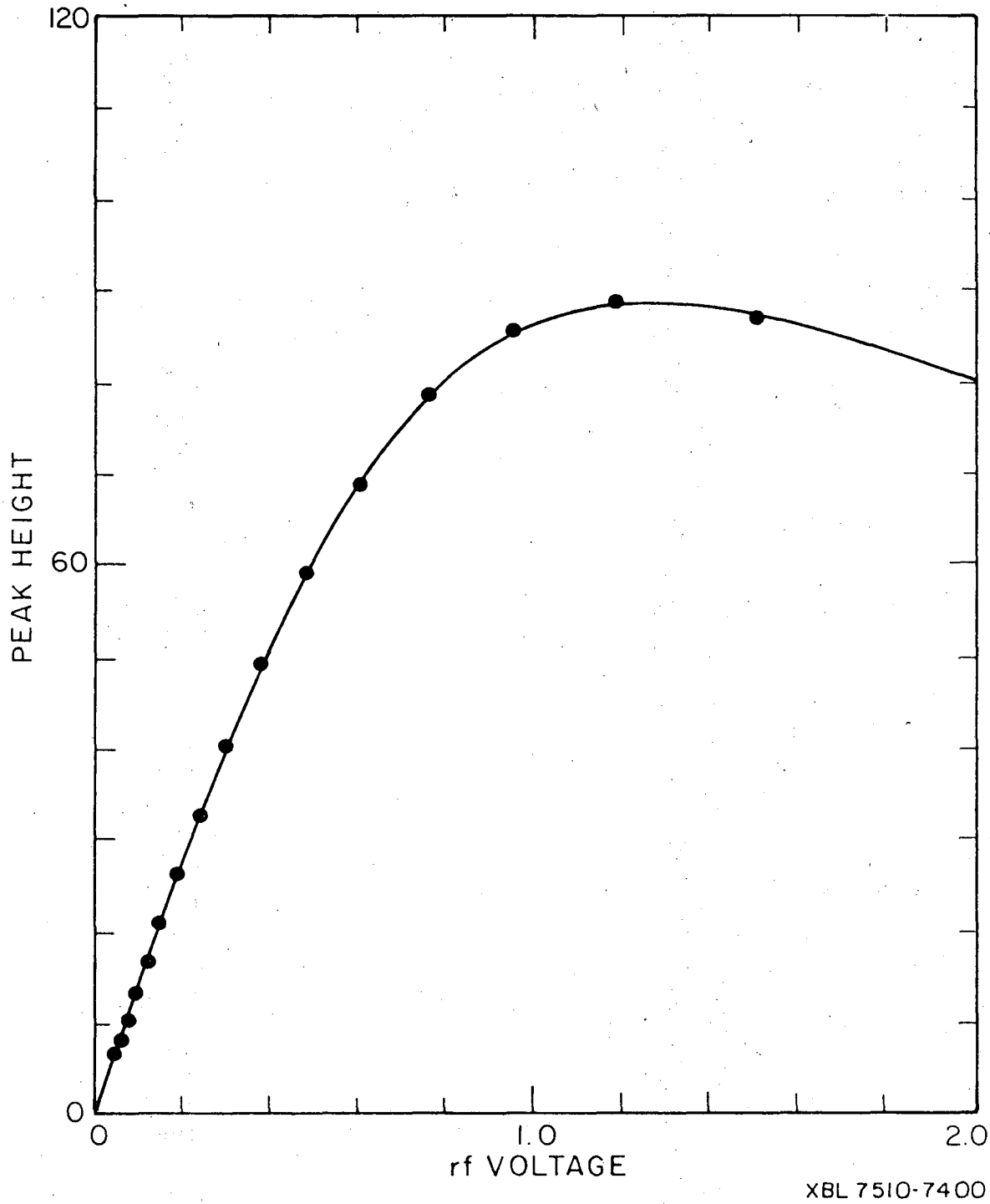

Fig. 3.

(Saturation measurement of T_1). In fact, the linewidth was measured at the same time each power saturation was accomplished, since T_2 is a parameter in the T_1 curve fitting. At some power setting, below saturation, the halfwidth of the sidebands was measured. The separation between the sidebands is exactly twice the modulation frequency which was counted on an electronic counter; from this the linewidth in Hz was easily calculated. Figure 2 shows the results of collecting a continuous scan through both first sidebands in a Fabritek Model 1074 computer of average transients, then transferring the data to a CDC 7000 series computer and performing a non-linear curve fit on the data. The points are the raw data, the solid curve is the best fit to the data and the lower curve is a plot of the difference between the measured points and the calculated value for the points, plotted on a greatly expanded scale. Figure 2 shows a trace of dispersion in the center of the spectrum, probably due to a slight mismatch in the audio phase detector. In spite of this slight error, it can be seen that the data conform very closely to the Lorentzian function used in the curve fitting routine. Normally the data were not taken in digital form but rather taken in analog form on a strip chart recorder and the linewidth was measured with a ruler.

D. Measurement of Chemical Shifts

All chemical shift measurements were made relative to the resonance of an acidified sample of pure water. The shift was measured using the same spectrometer as was used for the saturation

measurements of T_1 and the linewidth measurements, with the addition of an external proton lock system, used for both locking and scanning the external field. The left half of Fig. 1 shows a block diagram of the locking system which consists of a General Radio model 1164 frequency synthesizer as a scannable rf source, a passive rf phase detection system and a PAR model HR-8 lock in amplifier providing audio modulation and phase detection; all coupled to a Varian "piggy back" probe.

The synthesizer was operated at 60 MHz, which frequency was continuously scanned by driving the synthesizer with a ramp voltage. The result of changing the proton rf frequency was to cause the superstabilizer to scan the external field. Calibration of the magnetic field was accomplished by counting the proton rf frequency, with an electronic counter, at the beginning and end of each scan.

The shift was measured by a minimum of four scans through the resonance of the sample, replacement of the sample by a pure $H_2{}^{17}O$ sample followed by four scans through the pure water resonance. The total of eight scans, at each temperature were averaged to give a single data point.

E. Pulse T_1 Measurements

The spectrometer used to attempt pulse measurement of ^{17}O T_1's was a "home built" pulsed spectrometer using a superconducting solenoid magnet with the ^{17}O resonance at 14.4 MHz. The spectrometer is described in detail by Pines, Chang and Griffin.[56] The 90° pulse width was approximately 8×10^{-6} sec, which corresponds to an rf field strength of 54 Gauss. The data were collected as free

induction decays in a PDP 8/e minicomputer and then transferred to a CDC 7600 computer where a non-linear curve fitting program was used to fit the free induction decay, yielding the amplitude of the magnetization as a parameter in the fitting routine.

The pulse sequence used was the pulsed saturation recovery technique described earlier. In this technique the amplitude of the magnetization is measured as a function of a variable delay time, τ. These data were then fitted to the appropriate exponential function using a non-linear curve fitting program.

The saturating pulse length was approximately 35 milliseconds and a delay of 4 sec was inserted between each repetition of the pulse sequence in order to keep the duty cycle low, thereby minimizing the rf heating of the sample. To improve signal to noise, each free induction decay consisted of 20 to 50 transients summed in the PDP 8/e.

F. Computer Curve Fitting Programs

All computer fitting was accomplished using the Oak Ridge General Least Squares (ORGLS) computer program[57] or modifications of that program which only changed the input and output formats.

The power saturation data consisted of peak heights versus rf output voltage. The equation to which the data were fitted is:

$$h = \frac{P_1 v}{1+P_2 v^2} ,$$

where h is the peak height and v the rf output voltage. The variable parameters, P_1 and P_2, were obtained as the results of the fitting. The parameter P_2 implicitly contains T_1, as was described earlier. The peak heights were weighted by the average deviation in the measurement of eight peak heights. Convergence was assumed to have been obtained when the value of T_1 was the same to four significant figures on two successive cycles of the least squares iteration.

The free induction decays consisted of 1024 data points representing the signal amplitude as a function of time. The points were equally weighted in the fitting program. The equation fitted was:

$$A = P_3 \cos(P_4 t + P_5) \exp(-P_6 t) + P_7,$$

where A is the signal amplitude and t is the time. The fitting parameters describe the free induction decay for a single Lorentz line with:

P_3 proportional to the initial amplitude of the magnetization, M,

P_4 proportional to the heterodyne frequency in the detector, i.e. the difference between the resonance frequency and the spectrometer rf frequency,

P_6 proportional to $1/T_2^*$, the half width of the line,

P_5 and P_7 are the phase shift and the baseline corrections and are of no particular interest.

The exponential behavior of the pulse saturation recovery data

was treated by fitting the quantity M, which is parameter P_3 obtained above, versus the variable delay time, τ. The equation fitted was:

$$M_\tau = P_8 (1-e^{-P_9 \tau}) ,$$

where P_8 is proportional to the equilibrium value of the magnetization, M_o, and $P_9=1/T_1$.

IV. RESULTS AND DISCUSSION

A. Discussion of Electronic Relaxation Times

In the analysis of the ^{17}O NMR data, it will be necessary to use the magnetic relaxation times of the paramagnetic electrons in $Cr(H_2O)_6^{3+}$. These relaxation times have been measured by Melton and Pollak[20] in a ^1H NMR experiment. Their experiment involved measuring the ^1H NMR relaxation times as a function of field strength and temperature and curve fitting the results to a five parameter relaxation function. They analyzed their results in terms of a model developed by Bloembergen and Morgan[58] where collisions between the complex metal ion and bulk water molecules produce a modulation of the quadratic crystalline field splitting which then causes the electronic relaxation. The equation for the relaxation is:

$$\frac{1}{T_{1S}} = C\left[\frac{\tau_V}{1+\omega_S^2\tau_V^2} + \frac{4\tau_V}{1+4\omega_S^2\tau_V^2}\right] , \qquad (21)$$

where τ_V = the characteristic correlation time for the relaxation,

C = a constant related to the deformability of the crystal field around the Cr(III) ion.

Melton and Pollak give the values for the parameters in the above equation:

$$\tau_V = 9.3\times10^{-14} \exp(2.1 \text{ kcal/RT}),$$

$$C = 1.3\times10^{20} \text{ sec}^{-2}$$

In the relaxation equations for the ^{17}O nuclear magnetic resonance, there exist terms involving T_{2S}. In the following sections it will be shown that these terms are unimportant relative to the terms involving T_{1S}, so the transverse electronic relaxation will not be considered.

In the following discussions of the ^{17}O NMR relaxation data, preliminary studies of the fluorochromic ion, $CrF(H_2O)_5^{2+}$, were undertaken and compared to the data on hexa-aquochromic ion. The electronic relaxation time, T_{1S}, for the fluorochromic ion is needed to analyze this system. Unfortunately there are no available data on the electronic relaxation of CrF^{2+}. As a point of reference, the value of T_{1S} for CrF^{2+} will be taken to be equal to T_{1S} for $Cr(H_2O)_6^{3+}$. This approximation is undoubtably not rigorous since the quantity C in Eq. 21 is related to the dynamic deformability of the crystal field around the Cr(III) ion and it is possible that this quantity will be different for CrF^{2+} than for $Cr(H_2O)_6^{3+}$. Further, the F^- ion will undoubtably distort the crystal field around the Cr(III) ion, providing zero field splitting of the electron spin energy levels which is anisotropic and will be modulated by rotation of the $CrF(H_2O)_6^{3+}$ complex. This additional electronic relaxation mechanism will have a relaxation time with a form essentially the same as Eq. 21 but with different values for the parameters C and τ_C.[59] The zero field splitting should act to shorten the relaxation time of the CrF^{2+} relative to $Cr(H_2O)_6^{3+}$ but the exact relaxation times are not known.

To the extent that F^- ion is a similar ligand to H_2O, the approximation of similarity between CrF^{2+} and $Cr(H_2O)_6^{3+}$ may not be too bad and almost certainly $1/T_{1S}$ for $Cr(H_2O)_6^{3+}$ is a lower limit to the value of $1/T_{1S}$ for $CrF(H_2O)_5^{2+}$.

B. Chemical Shifts

Alei[17] measured the ^{17}O chemical shift of perchlorate ion and labile water in aqueous solutions of $Cr(ClO_4)_3$ at 20°C. He analyzes his data in terms of Bloembergen's equation for chemical shifts in paramagnetic systems (Eq. 17).[52] Bloembergen's model is developed for paramagnetic metal ions with a well defined first coordination sphere but it can equally well be applied to the second coordination sphere of paramagnetic metal ions.

Alei found that the chemical shift of the $H_2{}^{17}O$ resonance is not proportional to the concentration of chromic perchlorate as is predicted by Eq. 17. The reason for the deviation is thought to be the complexation by ClO_4^- in the second sphere of $Cr(H_2O)_6^{3+}$. Alei also reports the chemical shift of ClO_4^- in the aqueous solutions. This shift is further evidence for the complexation of ClO_4^- ion in the second sphere. Unfortunately there is not enough information available in these experiments to determine both the number of second sphere water sites occupied by each ClO_4^- ion, $n_{ClO_4^-}$, and the relative affinity of ClO_4^- for the second coordination sphere, Q, where Q is defined as the ratio of the moles of ClO_4^- to moles of water in the second coordination sphere divided by the ratio of total moles of ClO_4^- to total moles of water.

Alei concludes that the product $Qn_{ClO_4^-} = 2$, which might be taken to mean that Q=1, i.e. the ratio of ClO_4^-/H_2O is the same in the second sphere as in the bulk and $n_{ClO_4^-} = 2$, i.e. each ClO_4^- ion occupies two second sphere water sites; or perhaps each ClO_4^- ion occupies only one water site ($n_{ClO_4^-} = 1$) and the second sphere is twice as concentrated in ClO_4^- as the bulk; or some other combination which gives a product $Qn_{ClO_4^-} = 2$.

In terms of this thesis, the most immediately useful datum to be obtained from Alei's experiment is the chemical shift of $H_2{}^{17}O$ at zero perchlorate concentration, ω^o. As was stated in the theory section, the chemical shift at zero perchlorate concentration is used to obtain the average number of water molecules in the second coordination sphere of $Cr(H_2O)_6^{3+}$. Additionally, ω^o is necessary to determine the value of the scalar coupling constant, A, which is a parameter in the scalar coupling relaxation equations (Eq. 13).

The data in Alei's Table I have been plotted as $\frac{\Delta\omega}{\omega}\frac{m_{H_2O}}{m_{Cr}}$ versus $\frac{m_{ClO_4}}{m_{H_2O}}$ where the quantity m_{H_2O} used in this work is the quantity which Alei calls N, i.e. the number of millimoles of labile water in the solution, and m_{Cr} and m_{ClO_4} are the mollimoles of the species indicated. Figure 4 shows the plot of Alei's data as stated above. A linear least squares fit to the data gives an intercept of 2.84 10^3. Using Eq. 17 and the intercept, values of $\Delta\omega^o \frac{m_{H_2O}}{m_{Cr}} = 1.45\times10^5$ radians/sec and $An=1.89\times10^{-20}$ ergs are calculated.

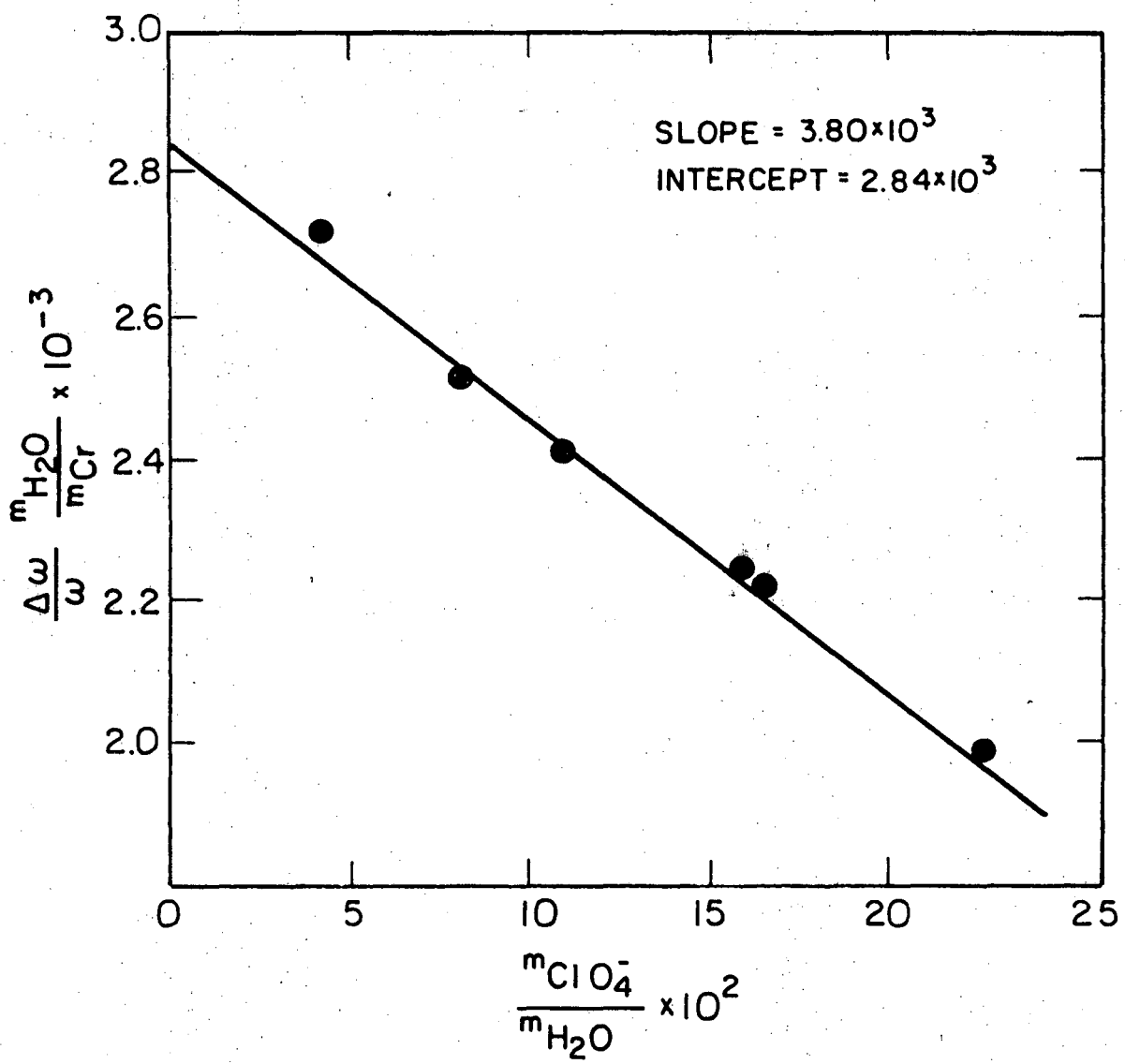

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Fig. 4.

At this point it is not necessary to assume a value for the number of water coordination sites in the second coordination sphere, n, but rather it will be carried along as an undetermined parameter.

The above treatment of the chemical shift, to a first approximation, corresponds to considering the Cr(III) solution as a two phase system with the second sphere being one phase and the bulk solution being the other phase. There is an internal inconsistency in fitting the chemical shift data with a straight line. A more detailed treatment of the chemical shift as a function of $m_{ClO_4^-}/m_{H_2O}$ shows that the data should have a slight curvature (concave upwards) as the concentration of ClO_4^- increases. This inconsistency in the above treatment of the data means that the value of $\Delta\omega^o$ reported above is somewhat smaller than would be obtained using a more consistent treatment. The comparison between samples 1 through 3 does not suffer greatly due to this inconsistency since all three samples have similar concentrations of perchlorate. A more accurate model than the two phase distribution used above would be to treat the data using successive equilibrium constants for second sphere complexation, but the equilibrium constant model introduces too many variables. Treatment of the data by the straight line, two phase model, probably introduces no large error and is justified by the crudeness of all of these models.

The chemical shift of the three chromic samples used in the relaxation experiments, was measured as a function of temperature. As was shown in the section on the theory of chemical shifts (Eq. 19), the ratio of the measured chemical shift to $\Delta\omega^o$ can be used to calculate the ratio of second sphere sites occupied

by water molecules to the total number of sites in the second sphere. In the derivation of Eq. 19 it was assumed that both $\Delta\omega$ and $\Delta\omega^{o}$ were measured at the same temperature and concentration. The correction to Eq. 19 for $\Delta\omega$ measured at some arbitrary temperature, T, and $\Delta\omega^{o}$ measured at 298°K is:

$$\frac{\Delta\omega T\left(\frac{m_{H_2O}}{m_{Cr}}\right)}{298(1.45\ 10^{5}\ \text{rad/sec})} = \frac{y}{n}\ , \qquad (22)$$

where $\frac{m_{Cr}}{m_{H_2O}}$ = the mole ratio of Cr^{3+} to labile H_2O, and 1.45×10^{5} = the normalized value of $\Delta\omega^{o}$ as determined above.

Figure 5 shows the results of calculating y/n from the chemical shifts of the Cr(III) samples as a function of temperature, where y is the number of water molecules in the second coordination sphere and n is the number of available sites in the second sphere. Therefore $(y/n)10^{2}$ is the percent of the second sphere occupied by water and $(1.0-y/n)\times100$ is the percent of the second sphere occupied by perchlorate ions. The data are plotted in this manner to investigate the possibility of a temperature dependence for the equilibrium between ClO_4^- in the bulk and ClO_4^- in the second coordination sphere. Although the data may have a slight positive slope, the scatter in the points percludes drawing any definite conclusions. If there exists a temperature dependence, it is so slight that over the temperatures used in this study it will be assumed that y/n is a constant. The data in Table 1 give the

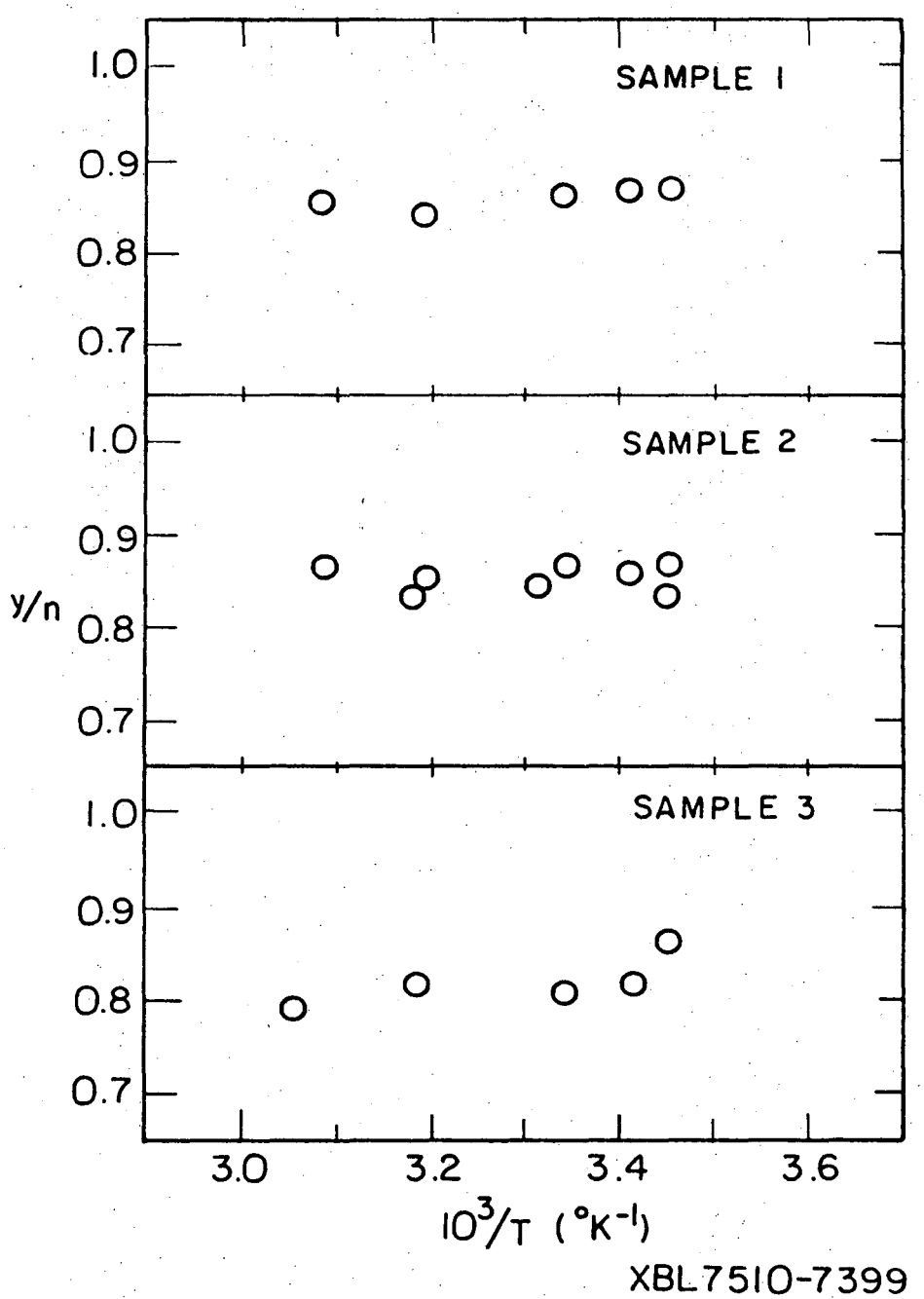

SAMPLE 1
SAMPLE 2
SAMPLE 3
y/n
1.0
0.9
0.8
0.7
3.0
3.2
3.4
3.6
$10^3/T$ (°K^{-1})
XBL7510-7399

Fig. 5.

Table 1. The ratio of water molecules in the second sphere to sites in the second sphere and the mole fraction of second sphere waters for the $Cr(H_2O)_6^{3+}$ samples used in this work.

	y/n	$f_B\ 10^2$
Sample 1	0.856	1.298 n
Sample 2	0.849	1.514 n
Sample 3	0.817	1.837 n

Note: The mole fraction is given above in terms of the total number of sites in the second sphere, n.

average y/n for each sample and the value of f_B in terms of the number of coordination sites in the second sphere (Eq. 20).

A comparison has been made between Alei's chemical shifts and the shifts measured in this work. Alei measured his chemical shifts at 20°C which corresponds to $10^3/T=3.41$. The chemical shifts of samples 1 through 3 have been interpolated at that temperature and the quantity $\frac{m_{Cr}}{m_{H_2O}} \frac{\omega}{\Delta\omega} \times 10^{-4}$ calculated for each sample. This quantity is the one plotted on Alei's Fig. 1. The corresponding values predicted from Alei's data were calculated from his slope and intercept by inserting the values of $\frac{m_{ClO_4}}{m_{H_2O}}$ for samples 1 through 3. The comparison is:

	Alei	This Work	Percent Difference
Sample 1	4.02×10^{-2}	4.05×10^{-2}	1%
Sample 2	4.12×10^{-2}	4.13×10^{-2}	0.5%
Sample 3	4.13×10^{-2}	4.24×10^{-2}	3%

The agreement is better than the scatter in the measurement of the shift might indicate.

Olson, et. al.[21] report a comparison to Alei's data. They use different units but the result is that their shift is 4% lower than predicted by Alei's shift data. Again, the agreement is very good, considering the experimental accuracy.

The chemical shift of a sample of $CrF(H_2O)_5^{2+}$ was measured at ambient temperature (28°C). From the measured chemical shift and

the known concentrations of CrF^{2+} and H_2O in the solution, y/n = 0.695 and $f_B = 2.42\times10^{-2}n$ can be calculated as above. This calculation requires the assumption that $\Delta\omega^o$ is the same for CrF^{2+} as for $Cr(H_2O)_6^{3+}$. The calculated value of y/n above is surprisingly low, since the concentration of ClO_4^- in the CrF^{2+} sample was relatively lower than in the $Cr(H_2O)_6^{3+}$ samples. This low value of y/n indicates that the second sphere of CrF^{2+} has a higher affinity for ClO_4^- than does the second sphere of $Cr(H_2O)_6^{3+}$, if the assumption about $\Delta\omega^o$ is correct.

The behavior of the second coordination sphere is undoubtably governed by the electrostatic attractions between the charge on the metal ion and the dipole of water or charge on ClO_4^-. To a first approximation, the charge on CrF^{2+} is reduced by one, relative to $Cr(H_2O)_6^{3+}$ so one would expect that the attraction between CrF^{2+} and ClO_4^- would be weaker than in hexa-aquochromic ion. In fact, the rationale in studying the relaxation behavior of CrF^{2+} was primarily to investigate the possibility of an increased rate of water exchange from the second sphere.

Without performing a detailed study on the CrF^{2+} system, it is impossible to give a quantitative estimate of the extent to which the second sphere of CrF^{2+} is similar to the second sphere of $Cr(H_2O)_6^{3+}$. We have chosen to assume that the value of the scalar coupling constant, A, is the same for the two ions and this assumption with the chemical shift measured leads to the indication that the second sphere of CrF^{2+} has a greater affinity for ClO_4^- than the second sphere of $Cr(H_2O)_6^{3+}$. This result seems unlikely and

therefore calls into question the above assumption, that A is equal for the second spheres of $Cr(H_2O)_6^{3+}$ and CrF^{2+}.

C. Interactions Responsible for Relaxation

1. Spin Rotation

The spin rotation relaxation arises from the generation of a magnetic moment by the rotation of the molecule in solution. Systems which have small, symmetric molecules frequently exhibit significant spin rotation relaxation but usually it is neglected as a relaxation mechanism in aqueous systems because the extensive hydrogen bonding precludes free rotation of water molecules or hydrated ions. Maryott, et. al.[60] have measured the extent of spin rotation relaxation in the ^{19}F NMR of liquid ClO_3F, where they were able to evaluate the spin rotation coupling constant and the angular momentum correlation time. Hindman, et. al.[61] showed a significant spin rotational contribution to the proton relaxation time in water at temperatures approaching the critical temperature. They report T_1^{SR} on the order of 30 sec at approximately 280°C. As the temperature is lowered, spin rotation is expected to become a less effective relaxation mechanism. As a result of the above discussion, spin rotation will be neglected as a significant contribution to the ^{17}O relaxation.

2. Anisotropic Chemical Shift

The anisotropic chemical shift relaxation arises from modulation of the off diagonal elements of the chemical shift tensor by molecular reorientation. The equations for the relaxation are given by Eq. 15 in the theory section. In ^{13}C relaxation studies it has been found that the off diagonal elements of the chemical shift

tensor may be approximately the same size as the diagonal elements.[62] This implies that the term δ_z in Eq. 15 may be several hundred parts per million.[63] In order to estimate the anisotropic chemical shift contribution to the relaxation, a value of $\delta_z = 1\times10^{-3}$ will be assumed. The asymmetry parameter, η_S, ranges between zero and one so it will be assumed to be one to obtain an upper limit to $1/T_1^{CSA}$. Finally, a value of 1×10^{-12} will be assumed for τ_c, the molecular orientation correlation function. With the above assumptions, a value of $1/T_1^{CSA} = 1\ sec^{-1}$ is obtained. This number is an upper limit to the contribution due to chemical shift anisotropy. The real contribution is probably smaller than this since in ^{13}C relaxation studies the chemical shift anisotropy relaxation time is usually on the order of a few hundred seconds.[64] It can be concluded that the chemical shift anisotropy will make only an insignificant contribution to the ^{17}O relaxation discussed below.

3. Quadrupole Coupling

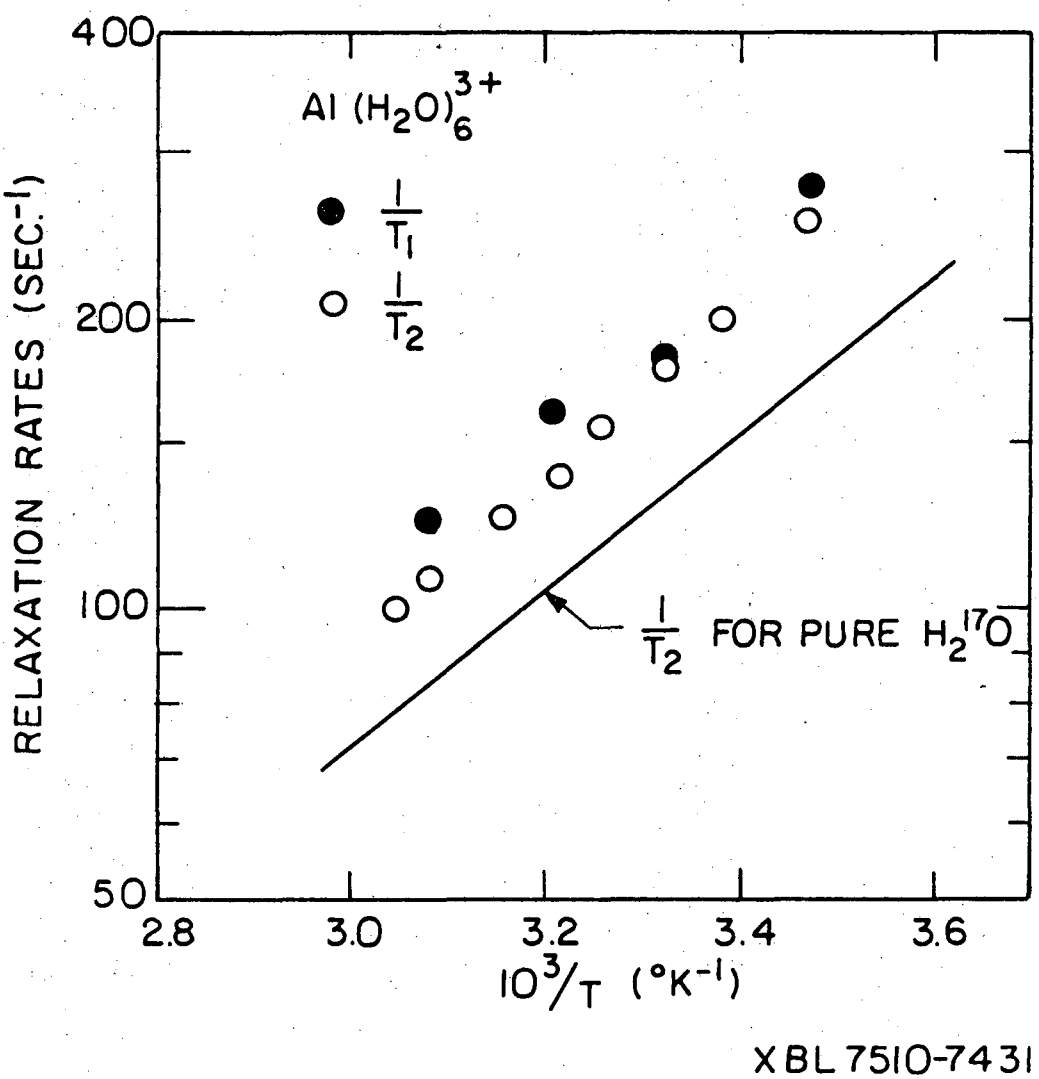
Nuclei with electric quadrupole moments frequently exhibit NMR relaxation times which are dominated by the quadrupole coupling relaxation mechanism. This interaction is modulated by changes in the molecular orientation and by chemical exchange. Unless the exchange lifetime for water molecules in the second coordination sphere is extremely short, the molecular reorientation correlation time will provide the interruption to the interaction.

An exact evaluation of the ^{17}O quadrupole relaxation for the $Cr(H_2O)_6^{3+}$ system would be extremely difficult. Although quadrupole

coupling constants and asymmetry parameters for $H_2{}^{17}O$ have been measured in ice[65] and water vapor,[66] there is no independent measurement of these parameters in liquid water. Additionally, the electrostatic effect of the metal ion may appreciably change the values of the components of the quadrupole coupling tensor for water molecules in the second coordination sphere.

It was thought possible to measure the relaxation times of a concentrated solution of $Al(ClO_4)_3$ at temperatures near room temperature, where it is known that the first coordination sphere of $Al(H_2O)_6^{3+}$ is substitution inert on the NMR time scale.[67] It can be assumed that the $Al(H_2O)_6^{3+}$ ion will affect water molecules in its second sphere the same way that $Cr(H_2O)_6^{3+}$ affects its second sphere, and that $Al(H_2O)_6^{3+}$ affects the microscopic viscosity of the bulk water like $Cr(H_2O)_6^{3+}$. Then the value of T_2 for $Al(H_2O)_6^{3+}$ can be used as an approximation to T_2^Q for $Cr(H_2O)_6^{3+}$.

Figure 6 is a plot of $1/T_2$ for the sample of $Al(ClO_4)_3$ described earlier. Several measurements were made of T_1 for the same sample and are also plotted. Within the experimental accuracy, $T_1=T_2$ as is predicted by Eqs. 14. The fact that $1/T_1$ is consistently larger than $1/T_2$, when in an isotropic solution $1/T_2 \geq 1/T_1$, may reflect a small systematic error in the measurement of T_1. The solid line of Fig. 6 represents a line drawn through some measured values for $1/T_1$ and $1/T_2$ for a sample of pure, acidic $H_2{}^{17}O$ A comparison between the linewidth of acidic H_2O and the $Al(H_2O)_6^{3+}$ solution indicates that there is an increase in the relaxation rate



XBL 7510-7431

Fig. 6.

due to addition of $Al(ClO_4)_3$.

The relaxation can be treated as a two site problem, i.e. the waters in the second sphere of $Al(H_2O)_6^{3+}$ and the bulk, for which Eq. 10b applies:

$$\frac{1}{T_2} = \frac{f_A}{T_{2A}} + \frac{f_B}{T_{2B}}$$

Site A will be taken to be the bulk waters and Site B, those in the second coordination sphere of $Al(H_2O)_6^{3+}$. Since the viscosity of the $Al(ClO_4)_3$ solution is greater than pure water, the pure water relaxation rate will be corrected for the viscosity difference using the Stokes-Einstein equation: $\tau_r = \frac{4\pi a^3 \eta_v}{3kT}$ where a is the radius of the rotating species and η_v is the macroscopic viscosity. Using the equations for quadrupole coupling (Eq. 14) and the Stokes-Einstein equation, the relaxation rate of a simple tumbling molecule at a given temperature is proportional to viscosity, i.e. $1/T_2^Q \alpha \eta_v$. Correcting the bulk relaxation for the viscosity increase: $\frac{1}{T_{2A}} \approx \frac{\eta_v(Al^{3+}soln)}{\eta_v(H_2O)} \frac{1}{T_2}(H_2O)$. The viscosity of the Al^{3+} solution has been interpolated from viscosity measurements made by Fiat[67] and by Neely[70] at higher concentrations of $Al(ClO_4)_3$, from which: $\eta_v(Al^{3+}soln) = 0.0135$ poise and $\eta_n\ (H_2O)=0.01$ poise, $1/T_2(H_2O) = 150\ sec^{-1}$; all at 25°C. Then a value of $1/T_{2A} = 203\ sec^{-1}$ is calculated. The quantity f_B in Eq. 10b can be calculated from the concentration of Al^{3+} in the solution and $f_A = f_B - 1 = 0.89$. Applying Eq. 10b; $\frac{f_B}{T_{2B}} = \frac{1}{T_2} - \frac{f_A}{T_{2A}} = 195 - 181 = 14\ sec^{-1}$.

This quantity is so small that one is forced to conclude that the rate of relaxation in the second sphere is nearly equal to the rate of relaxation in the bulk. Wuthrich[69] and Neely[70] have both observed that water molecules in the first coordination sphere of metal ions have quadrupole relaxation rates considerably smaller than would be predicted by the quadrupole coupling constant and the tumbling of the hydrated metal ion. Their conclusions were that there is internal rotation of the water in the first sphere. It is reasonable to assume that the water molecules in the second sphere will have even more freedom of motion than those in the first sphere, which makes reasonable the conclusion that there is no great difference between the quadrupole relaxation in the second sphere and in the bulk.

4. Dipole-Dipole Coupling

The rates of relaxation for dipole-dipole coupling are given by Eqs. 12. In these equations, there are only two quantities which are not known independently; the radius, r and the correlation times. Inserting all of the known parameters into Eqs. 12, the dipole-dipole relaxation rates can be written:

$$\frac{1}{T_1^{DD}} = \frac{1.13\times10^{-33}}{r^6}\left\{6\tau_1 + \frac{14\tau_2}{1+\omega_S^2\tau_2^2}\right\} \tag{23}$$

$$\frac{1}{T_2^{DD}} = \frac{1.13\times10^{-33}}{r^6}\left\{7\tau_1 + \frac{13\tau_2}{1+\omega_S^2\tau_2^2}\right\}, \tag{24}$$

where r is the distance from the paramagnetic electrons to the ^{17}O nuclei in the second sphere, measured in cm.

It is necessary to verify that $T_1^{DD} \approx T_2^{DD}$ in the $Cr(H_2O)_6^{3+}$ system in order to give validity to Eq. 25 used in the discussion of scalar coupling. First we assume that $\tau_1 = \tau_2$ since the electronic relaxation times are very long and either chemical exchange or molecular tumbling will dominate τ_1 and τ_2. Then the limiting conditions for Eq. 23 and 24 are: $\tau_2^2 \omega_S^2 << 1$ and $\frac{1}{T_1^{DD}} = \frac{1}{T_2^{DD}} = \frac{1.13 \times 10^{-33}}{r^6} \{20\tau_1\}$ or $\tau_2^2\ \omega_S^2 >> 1$ and $1/T_1 = 6/7\ 1/T_2$. In either case $T_1^{DD} \approx T_2^{DD}$.

At the end of the discussion of scalar coupling below, an estimate of the dipole-dipole contribution to the transverse relaxation rate, $1/T_2$, is made.

5. Scalar Coupling

Scalar coupling between the paramagnetic electrons and the ^{17}O nuclei can be a source of relaxation in transition metal solutions. The interruption of the scalar coupling interaction is either the electronic relaxation or chemical exchange. The electronic relaxation times for $Cr(H_2O)_6^{3+}$ are relatively long,[20] so it was thought that an analysis of the scalar coupling relaxation of the ^{17}O would yield an exchange rate for the second coordination sphere.

The equations for scalar coupling are given by Eqs. 13, which can be written functionally as:

$$\frac{1}{T_1^S} = \text{fcn}(A)\ \{\frac{2\tau_{c2}}{1+(\omega_I-\omega_S)^2\tau_{c2}^2}\}$$

$$\frac{1}{T_2^S} = \text{fcn}(A)\ \{\tau_{c1} + \frac{\tau_{c2}}{1+(\omega_I-\omega_S)^2\tau_{c2}^2}\}$$

Inserting the following values into the above equations in order to estimate the relative magnitude of the two relaxation terms: $(\omega_I-\omega_S)^2 = 6.2\times10^{22}$, $1/T_{1S} = 7.3\times10^8\ \text{sec}^{-1}$ at 298°K (from Eq. 21), and $1/\tau_b = 1\times10^{10}$, the scalar relaxation times can be calculated as $1/T_1^S \cong \text{fcn}(A)\ 3.2\times10^{-13}$ and $1/T_2^S \cong \text{fcn}(A)\ 1\times10^{-10}$. From the above approximation it is clear that $\frac{1}{T_2^S} - \frac{1}{T_1^S} \approx \frac{1}{T_2^S}$.

If it is assumed that water molecules in the bulk, Site A, exhibit relaxation behavior analogous to pure, acidified water, this implies that $T_{1A} = T_{2A}$. From Eqs. 10:

$$\frac{1}{T_2} - \frac{1}{T_1} = f_A[\frac{1}{T_{2A}} - \frac{1}{T_{1A}}] + f_B[\frac{1}{T_{2B}} - \frac{1}{T_{1B}}] = f_B[\frac{1}{T_{2B}} - \frac{1}{T_{1B}}]$$

It was shown that the chemical shift anisotropy and spin rotation relaxation mechanisms make negligible contributions to $1/T_{1B}$ and $1/T_{2B}$. From the above discussions on quadrupole coupling $(1/T_1^Q = 1/T_2^Q)$ and dipole-dipole coupling $(1/T_1^{DD} \approx 1/T_2^{DD})$, we conclude that:

$$f_B[\frac{1}{T_{2B}} - \frac{1}{T_{1B}}] = \frac{1}{T_2} - \frac{1}{T_1} \approx \frac{f_B}{T_2^S}\ . \qquad (25)$$

The relaxation times, T_1 and T_2, have been measured for three separate samples of $Cr(H_2O)_6^{3+}$ as a function of temperature. Figures 6 through 8 are semi-logarithmic plots of the relaxation rates, $1/T_1$ and $1/T_2$, for these samples as a function of $10^3/T$. The slopes for all of the relaxation rates are nearly the same which implies that the processes interrupting the relaxation interaction have similar activation energies. The difference between the absolute values of the relaxation rates reflects the different compositions of the samples, f_B.

Figure 9 is a plot of $(\frac{1}{T_2} - \frac{1}{T_1}) \frac{n}{f_B}$ for all three samples with $10^3/T$ as the abcissa. The data in Fig. 10 correspond to: $(\frac{1}{T_2} - \frac{1}{T_1}) \frac{n}{f_B} = \frac{n}{T_2^S}$. From Eq. 13 in the theory section and the approximations made above, the second term in the brackets for $1/T_2^S$ is negligible and Eq. 13 can be rewritten:

$$\frac{n}{T_2^S} = n \frac{S(S+1)}{3} (\frac{A}{\hbar})^2 \tau_{cl} \tag{26}$$

The quantity $A/\hbar$ is not known by itself; it can only be evaluated to within a factor of n, i.e. $A/\hbar = 1.79\times10^7/n$ rad sec^{-1}. Inserting the values for the appropriate constants, Eq. 26 is rewritten:

$$\frac{n}{T_2^S} = \frac{4.02\ 10^{14}}{n} \tau_{cl} \tag{27}$$

Since τ_{cl} is the inverse of first order rate constant, it can be assumed to follow an exponential function of the form:

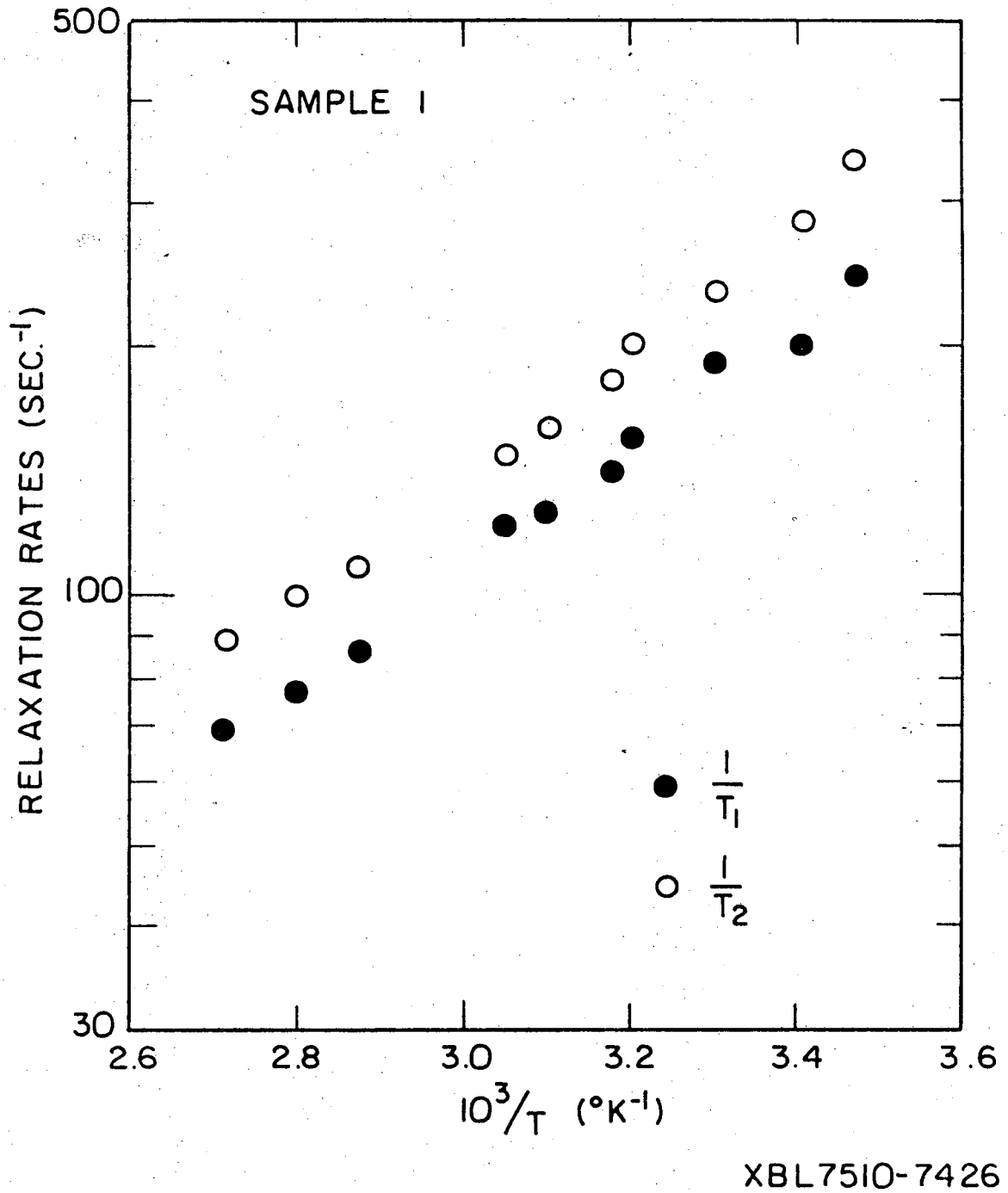

SAMPLE I
500
100
30
RELAXATION RATES (SEC.$^{-1}$)
2.6
2.8
3.0
3.2
3.4
3.6
$10^3/T$ (°K^{-1})
$\frac{1}{T_1}$
$\frac{1}{T_2}$
XBL7510-7426

Fig. 7.

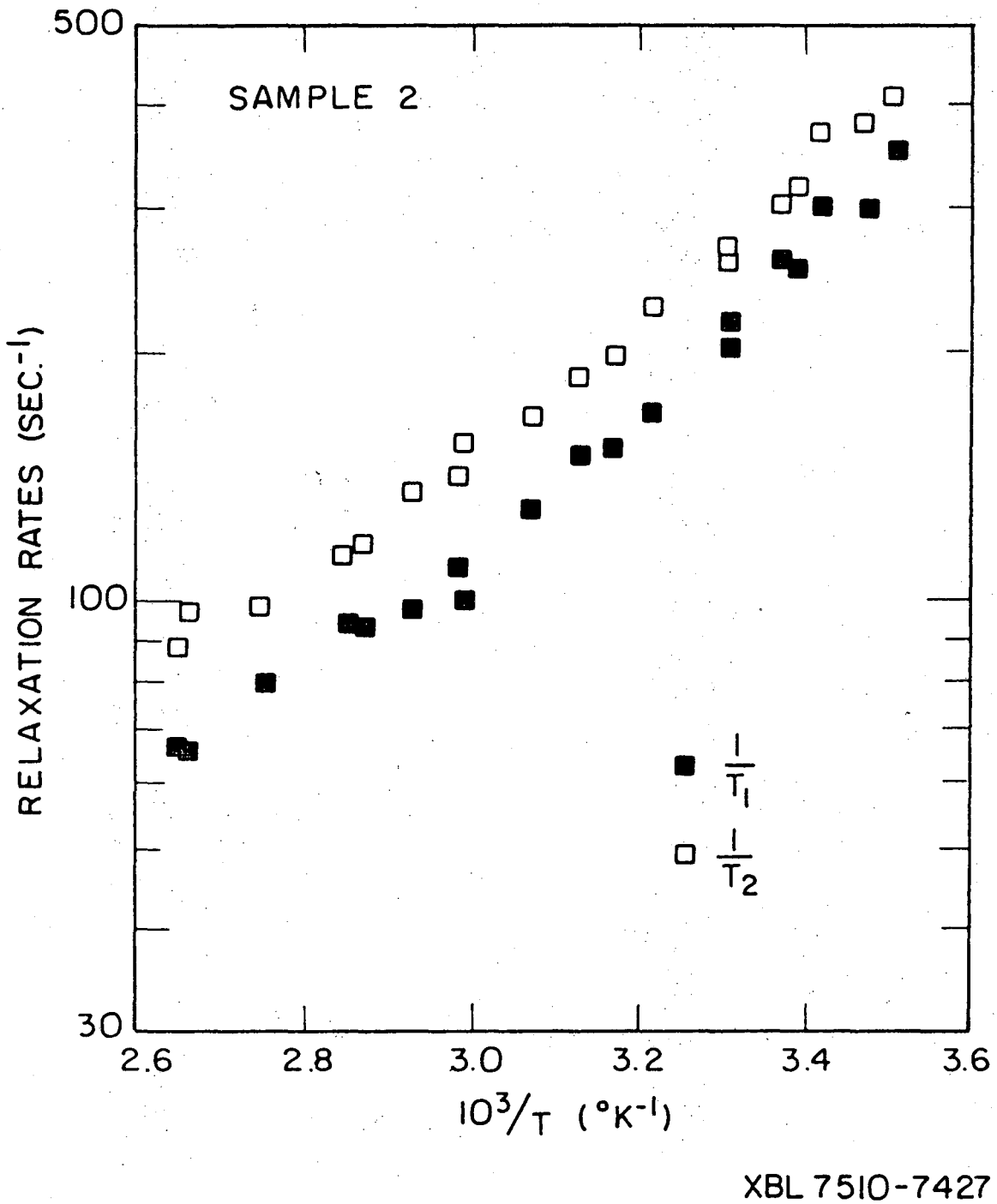


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Fig. 8.

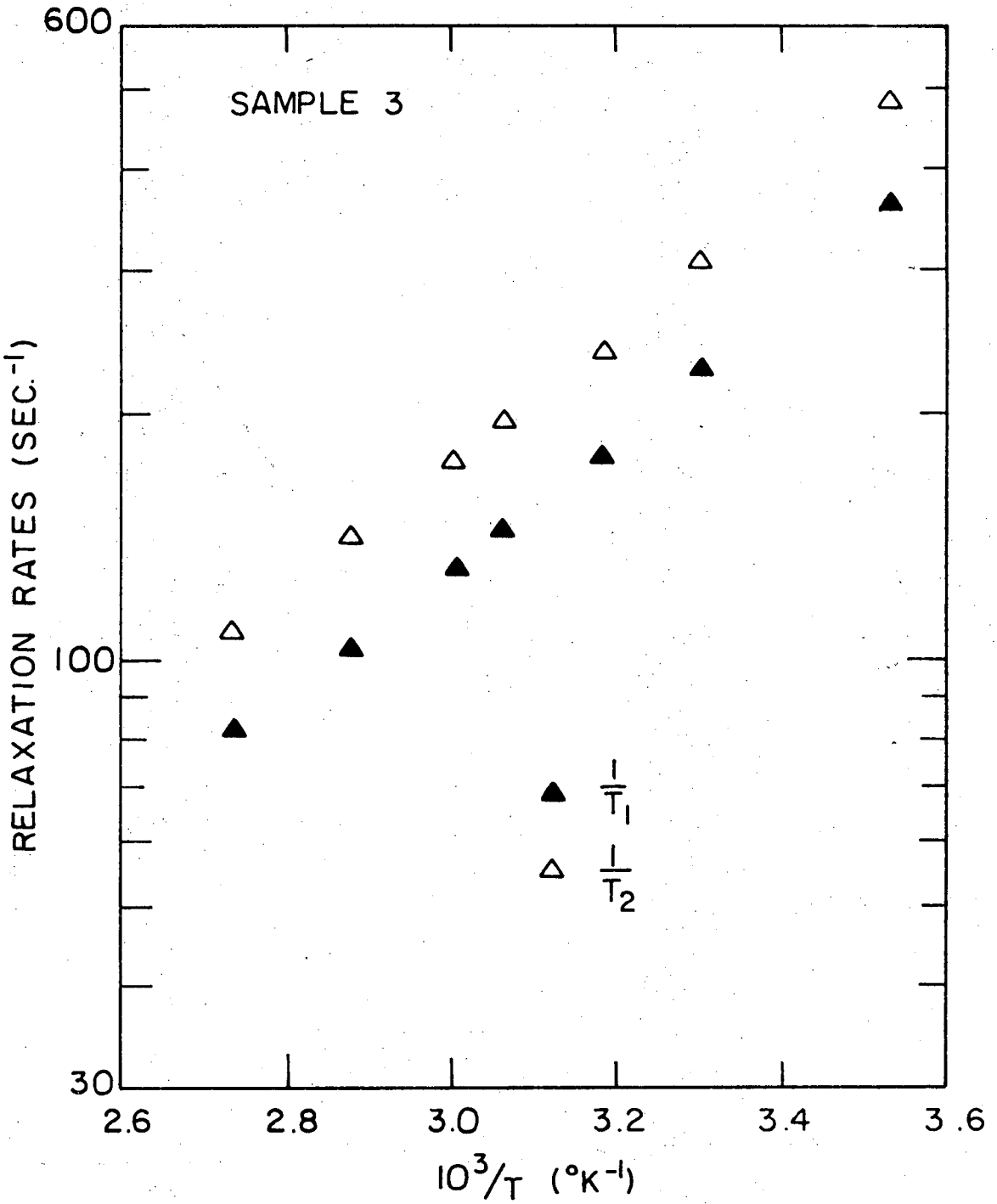

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Fig. 9.

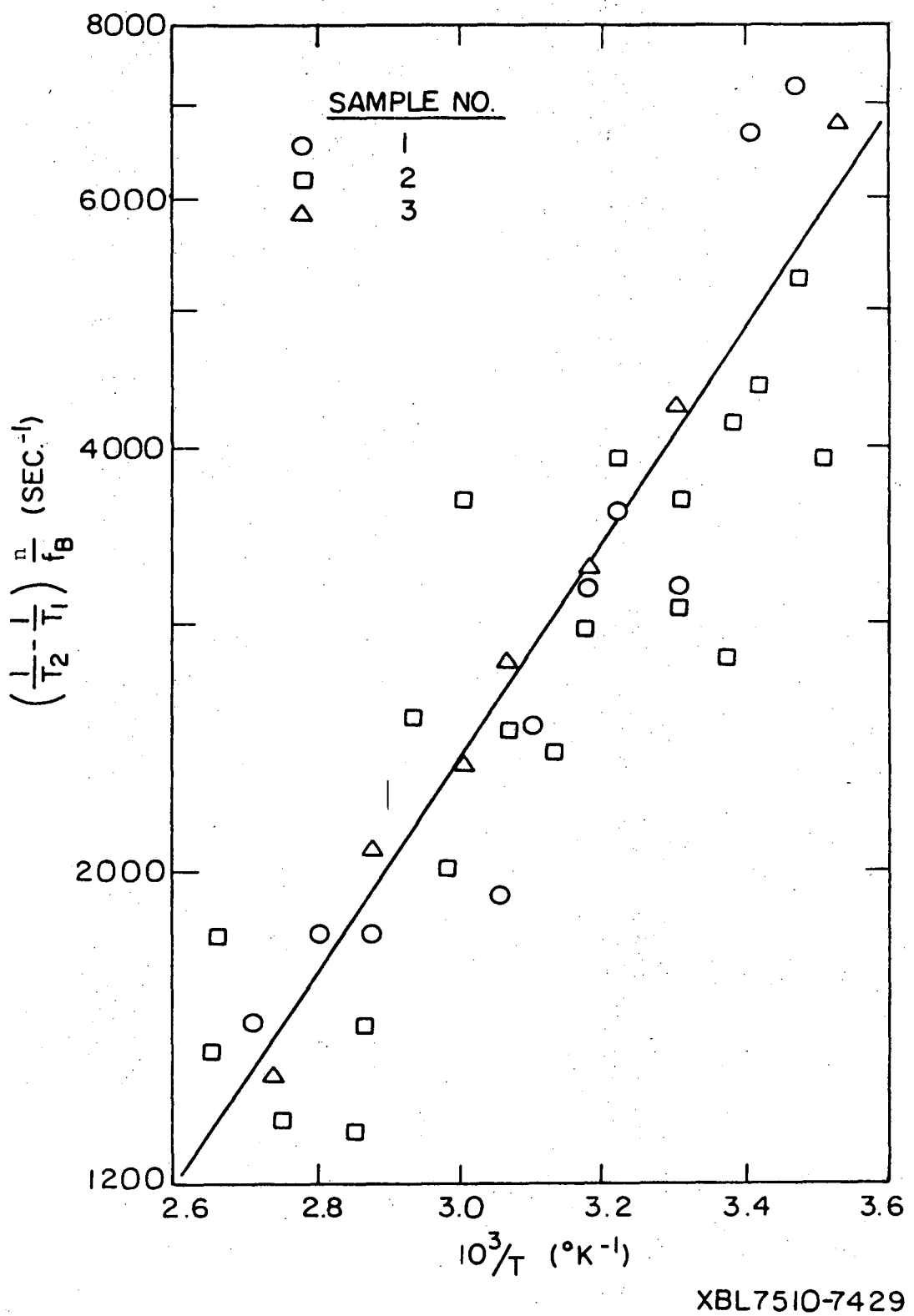
SAMPLE NO.
1
2
3
8000
6000
4000
2000
1200
2.6
2.8
3.0
3.2
3.4
3.6
$10^3/T$ (°K^{-1})
$\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{n}{f_B}$ (SEC.$^{-1}$)
XBL7510-7429

Fig. 10.

$$\tau_{c1} = \frac{h}{kT} e^{-\Delta S^{\ddagger}/R} e^{\Delta H^{\ddagger}/RT} \tag{28}$$

Where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation for second sphere exchange of water molecules with the bulk water.

The solid line through the data in Fig. 9 corresponds to the best fit of the data to the function:

$$y = P_1 \; x \; \exp(P_2 x) \tag{28}$$

where $y = (\frac{1}{T_2} - \frac{1}{T_1}) \frac{n}{f_B}$,

$x = 1/T$,

$P_1 = \frac{4.02 \; 10^{14}}{n} \; \frac{h}{k} \; e^{-\Delta S^{\ddagger}/R}$

$P_2 = \frac{\Delta H^{\ddagger}}{R}$.

In this fitting routine, the data from sample 3 were weighted three times as heavily as the data from samples 1 and 2. The heavier weighting of sample 3 is rationalized as follows: Sample 3 was more highly enriched in ^{17}O than the others so the signal to noise was better, f_B for sample 3 is greater so the absolute difference $(1/T_2 - 1/T_1)$ is greater, the scatter in the data from sample 3 is smaller than the data from the other samples due to refinement of experimental technqiue. The results of the curve fitting are: $P_1 = 1.16\times10^4$ and $P_2 = 1.42\times10^3$. Using the equations above, a value of $\frac{\tau_{c1}}{n}$ at 25°C can be calculated, $\tau_{c1}/n = 1.14\times10^{11}$ sec. At this point it will be assumed that n=8; a discussion of this assumption will be deferred until later. This implies that

$\tau_{c1} = 9.1\times10^{-11}$ sec and $1/\tau_{c1} = 1.1\times10^{10}$ sec^{-1}. (This value is consistent with the estimated value of 1×10^{10} which was used in making the approximation that $1/T_2^S - 1/T_1^S \cong 1/T_2^S$.)

From the definition of τ_{c1} in the section on theory, $\frac{1}{\tau_{c1}} = \frac{1}{\tau_b} + \frac{1}{T_{1S}}$. Using Eq. 21 above, the electronic relaxation at 25°C can be calculated to be $1/T_{1S} = 7.3\times10^8$ sec^{-1}. By difference $1/\tau_b = 1.0\times10^{10}$ sec^{-1}, consequently the electronic relaxation makes only a minor contribution to the correlation time, τ_{c1}. Thus, τ_b the average lifetime of water molecules in the second coordination sphere of $Cr(H_2O)$ is 1.0×10^{-10} sec.

The relaxation times, T_1 and T_2, were also measured for a sample of $CrF(H_2O)_5^{2+}$. The data are shown plotted in Fig. 10, where the upper plot is $1/T_1$ and $1/T_2$ versus $10^3/T$ and the lower plot is $(1/T_2-1/T_1)$ vs. $10^3/T$. The straight line in the lower plot is drawn only to estimate a value of $1/T_2-1/T_1$ at 25°C, which estimate is: 1.9×10^2 sec^{-1}. Using Eq. 25, a value of $\tau_{c1}/n = 2.0\times10^{-11}$ sec is obtained. This value is somewhat longer than the value of the same parameter for $Cr(H_2O)_6^{3+}$, but the difference is probably not significant, given the scatter in the data. A more detailed discussion of the exchange rates follows below.

D. Pulsed Measurements of T_1

An attempt was made to measure T_1 for the samples in this study by pulsed techniques. In order to insure that the NMR spectrometer was working properly, the T_1 of a sample of pure, acidified $H_2{}^{17}O$ was measured since $T_1=T_2$. The first attempt at measuring T_1 was

0 0 0 0 4 3 0 2 2 1 6

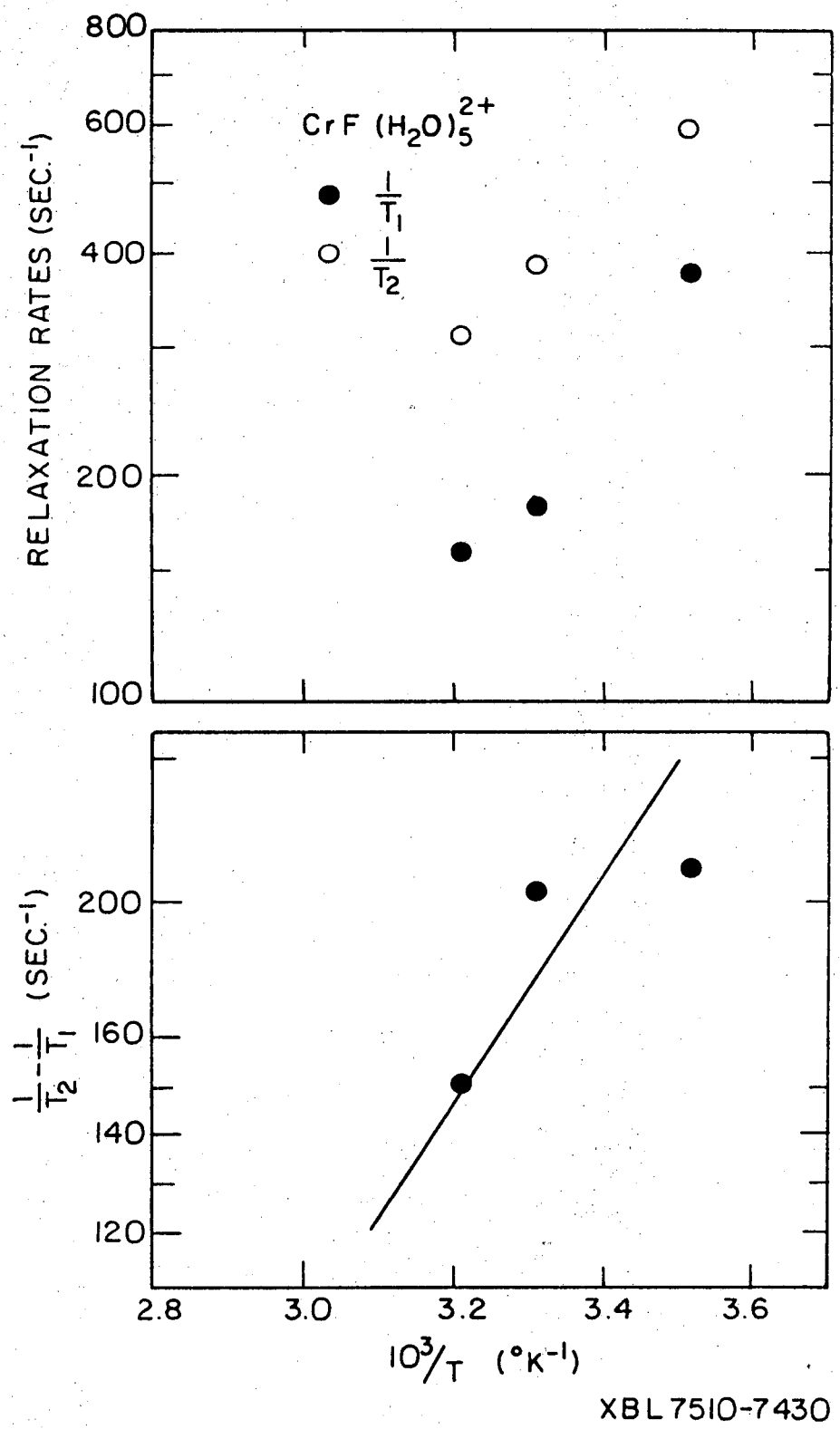

Fig. 11.

done using the inversion recovery technique.[32] The results obtained gave a value of $T_1 < T_2$. It was thought that this error could arise from inaccuracy in the pulse lengths. If the 180° pulse, in the inversion recovery, is not very nearly 180° it will lead to a component of magnetization in the X-Y plane which will interfere with the magnetization after the 90° pulse. In order to obviate this problem the pulsed saturation recovery technique described by McDonald and Leigh was tried.[34] The short relaxation times of the ^{17}O resonance require that the homogeneity spoiling pulse have a very high field gradient in order to destroy the X-Y component of magnetization in a time, short compared to T_1. This proved to be difficult to accomplish so the technique was discarded in favor of the saturation technique described by Markley, et. al.[33] The data obtained were first treated by a non-linear least squares curve fit to the free induction decays, giving values of the magnetization, M_τ, as a function of the variable delay, τ. Then M_τ versus τ was curve fitted to the appropriate exponential function. It was found that the measured magnetization as a function of τ was not exponentially approaching the measured value of M_o. In fact, the measured values of M_τ went through a maximum and slowly approached M_o. Figure 12 shows a plot of the data taken in one of the saturation recovery experiments. The solid curve represents the best fit of the equation:

$$M_\tau = M_o \, (1-e^{-\tau/T_1})$$

0 0 0 0 4 3 0 2 2 1 7

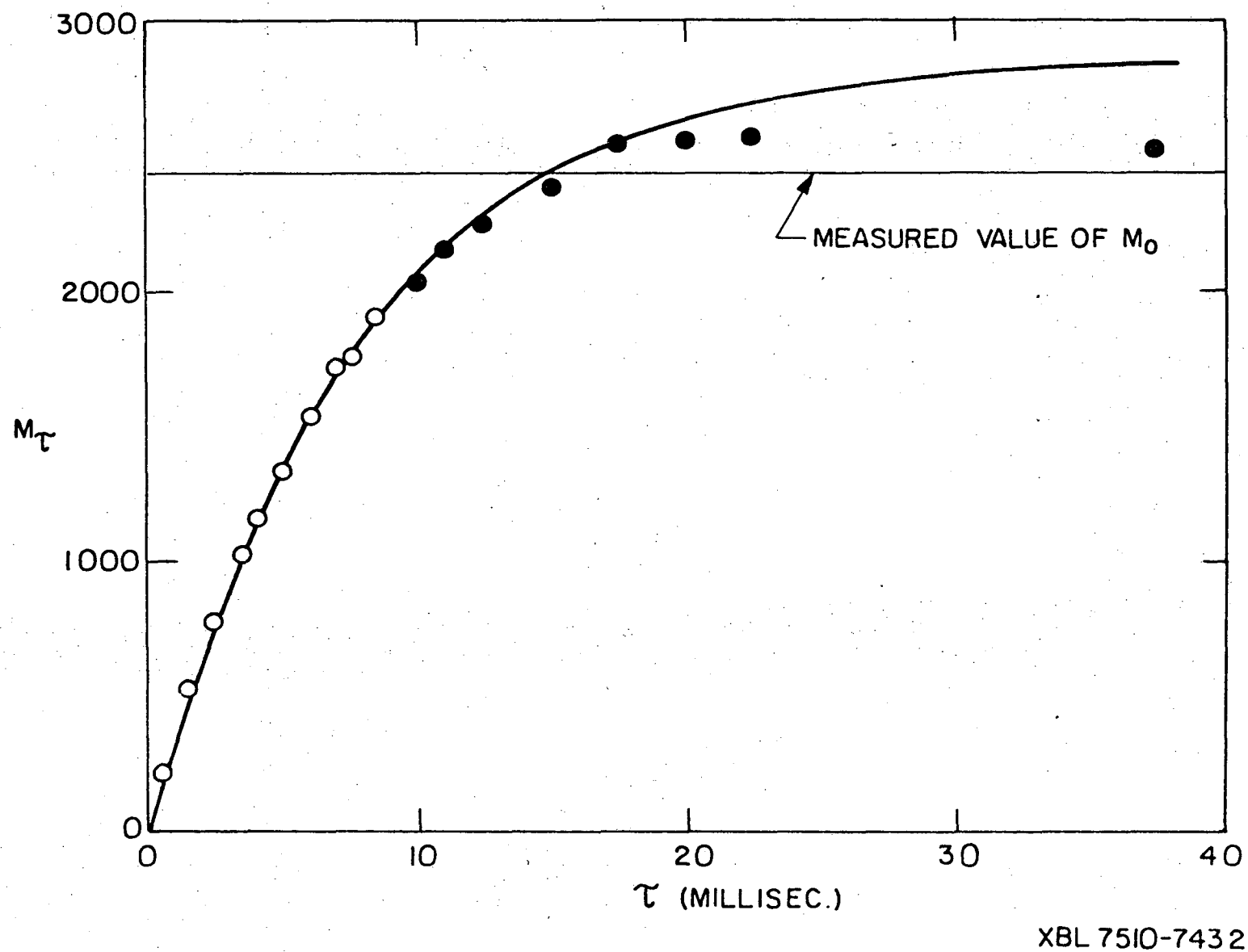

Fig. 12.

to the points which are shown as open circles. The solid circles represent values of M_τ which were measured in the same experiment but were not included in the curve fitting program. The horizontal line represents M_o as measured by five measurements of M_τ with τ= 250 millisec $\approx$ 30 T_1. Since the data are non-exponential and since the calculated value of T_1 was often close but never equal to T_2, it was decided not to attempt measurements of T_1 on the Cr^{3+} and Al^{3+} samples by pulsed technqiues.

E. Discussion

It is possible to estimate the amount of relaxation which each mechanism contributes to the total relaxation. This estimation is best done using sample 2 because f_B for the Al^{3+} sample is closest to the value of f_B for sample 2. It was shown earlier that the spin rotation and anisotropic chemical shift mechanisms will make negligible contributions to the overall relaxation, thus:

$$\frac{1}{T_2} = \frac{1}{T_2^Q} + \frac{1}{T_2^S} + \frac{1}{T_2^{DD}} .$$

At ambient temperature (28°C) the following quantities were measured:

$$\frac{1}{T_2} = 260 \text{ sec}^{-1} \text{ (for sample 2)},$$

$$\frac{1}{T_2^S} = 56 \text{ sec}^{-1} \text{ (from } 1/T_2 - 1/T_1\text{)},$$

$$\frac{1}{T_2^Q} = 172 \text{ sec}^{-1} \text{ (From } Al^{3+} \text{ sample)}.$$

Therefore by difference:

$$\frac{1}{T_2^{DD}} = 32 \text{ sec}^{-1}.$$

The relative contributions due to each mechanism are: quadrupole coupling, 66%; scalar coupling, 22%; and dipole dipole coupling, 12%. The quadrupole contribution above is mostly due to the relaxation of pure H_2O and it is likely that the quadrupole coupling contribution will change slowly with changes in the concentration of $Cr(H_2O)_6^{3+}$ since it only reflects the viscosity change. The scalar coupling relaxation presumably results from the interaction between the waters in the second sphere and the paramagnetic electrons. The dipole dipole coupling involves the interaction between the paramagnetic electrons and waters in the second and further coordination spheres. Both of these relaxation mechanisms involve the unpaired electrons on the metal and consequently are sensitive to the concentration of the paramagnetic ion. The calculated scalar coupling constant (assuming eight waters of hydration in the second coordination sphere), 3.6×10^5 Hz, can be compared to the scalar coupling constants for water molecules in the first coordination sphere of transition metal ions which range from 1 to 4×10^7 Hz.[1] The greater than one order of magnitude decrease in the scalar coupling constant in going from the first to the second coordination sphere does not seem unreasonable.

Most of the interest in second sphere complexation has centered on studies of metal ion interaction with anions in the second sphere.[71] There have been a number of investigations of the

structure and equilibrium constants of second sphere complexation.[7] Several NMR studies have reported second sphere effects while studying other phenomena in paramagnetic systems, but at best they have arrived at approximate estimations of the rates of second sphere exchange.

The available studies on second sphere ligands, while addressing the structure of the second sphere, have dealt exclusively with complex ions, usually with complicated ligands.[7,71] As a result the systems are so different that it is impossible to infer the structure of the second coordination sphere of $Cr(H_2O)_6^{3+}$ in aqueous solution from these studies. Since the interaction between the Cr(III) and the second sphere waters is probably almost entirely electrostatic, the most tempting structure is one which places the second sphere waters on the faces of the $Cr(H_2O)_6^{3+}$ octahedron. This structure allows the water molecules the closest approach to the Cr(III) nucleus. Carrying this model one step further, one is next tempted to conclude that the third sphere is composed of waters in the interstices left by the second sphere. This implies that exchange from the second sphere to the third sphere involves motion of the water molecule through a distance somewhat shorter than one water diameter. The assumption of the second coordination sphere being composed of water molecules on the faces of an octahedron leads to a coordination number of eight for the second sphere. Olson et. al. made the same assumption.

The ultrasonic absorption spectrum of aqueous $MgSO_4$ solutions has been interpreted by Eigen and Tamm[72] to yield an average residence time of 1.7×10^{-9} sec for the SO_4^{2-} ion in the second

sphere of Mg^{2+}. Atkinson and Petrucci[73] have also investigated the ultrasonic behavior of aqueous $MgSO_4$ solutions and they arrive at an average residence time 2.4×10^{-8} sec for SO_4^{2-} in the Mg^{2+} second sphere. Although both of these values are somewhat longer than the value of 1.0×10^{-10} sec obtained for H_2O in the second sphere of Cr^{3+} in this work, this difference in not unreasonable when one considers that the Mg^{2+}--SO_4^{2-} ion pair involves two charged ions and so might have a longer lifetime than the charge-dipole interaction for Cr^{3+}--H_2O.

The work by Olson et. al.[21] involved studying the NMR line broadening by Cr^{3+} and V^{2+}. Their conclusion was that the upper limit for the lifetime of water in the second coordination sphere of $Cr(H_2O)_6^{3+}$ is 2.5×10^{-10} sec at 25°C, which conclusions is consistent with the value obtained in this work. At low temperatures, Wuthrich and Connick[4] encountered line broadening of the ^{17}O resonance in aqueous VO^{2+} solutions which they suggested might be due to second sphere effects. They estimated a lifetime of ca. 10^{-10} sec at 25°C for second sphere waters which is in agreement with the value 1.0×10^{-10} obtained in this work. The ultrasonic absorption experiments of Eigen and Tamm[72] and of Atkinson and Petrucci,[73] and the NMR experiment by Olson, et. al.[21] are the only direct measurements of second sphere exchange rates in aqueous solution known to the writer.

It is instructive to put the rate of water exchange from the second sphere in perspective with the rates of some other physical processes. Kustin and Swinehart discuss the rates of solvent

exchange and in doing so they catalogue some of the available rates.[74] Two interesting quantities are the rate of exchange from the first coordination sphere of Mn^{2+} in aqueous solution and the rate of exchange from Gd^{3+} in aqueous solution. The average lifetimes for these two processes are: 3×10^{-8} sec and 1×10^{-9} sec respectively.[1,75] These are the shortest measured times for solvent exchange from the first coordination sphere, and they are both considerably longer than the 1×10^{-10} sec obtained here.

Diffusion can be treated as a random walk process, from which a lifetime, τ, for diffusion through some distance can be calculated using the following equation:[76]

$$\overline{z^2} = 2D\tau$$

where $\overline{z^2}$ is the mean square displacement and D is the self diffusion constant. In consideration of the nature of the second sphere exchange process, it is very likely that a water molecule will only have to diffuse about 0.1 nm to enter the third coordination sphere. Using the self diffusion constant of 2.23×10^{-5} cm^2 sec^{-1} for liquid water at 25° C,[77] the calculated time for a mean square displacement of 0.1 nm is 2×10^{-12} sec. This diffusion lifetime is nearly 50 fold shorter than the value 1.0×10^{-10} sec for the lifetime of water in the second sphere of $Cr(H_2O)_6^{3+}$. Clearly the exchange process is not limited by diffusion.

The activation parameters for the exchange of water from the second coordination sphere of $Cr(H_2O)_6^{3+}$ into the bulk are:

$\Delta H^{\ddagger}$ = 2.8±0.4 kcal and $\Delta S^{\ddagger}$ = -0.8±0.5 eu. The enthalpy of activation corresponds to an Arrhenius activation energy 3.8 kcal which is very close to the Arrhenius activation energy of 4.5 kcal reported for the self diffusion of water at 25°C.[77] The very small value for the entropy of activation is not unreasonable given that the entropies of activation for water exchange from the first coordination sphere are between 3 and -4 entropy units.[1]

The fact that the measured rate for the water exchange from the second sphere of CrF^{2+} was found to be less than for $Cr(H_2O)_6^{3+}$ is somewhat surprising since it is thought that the reduction of net charge on the Cr(III) would decrease the electrostatic attraction for the second sphere waters. Apparently the situation is somewhat more complicated and specific interactions should be considered. It is possible to rationalize the somewhat longer average lifetime in CrF^{2+} in terms of hydrogen bonding of the waters near the F^- ion to the F^- but the scatter in the data do not warrant too much theorizing. The chemical shift results imply that CrF^{2+} has a stronger attraction for ClO_4^- in the second sphere than the attraction in $Cr(H_2O)_6^{3+}$, but this result depends on the assumption of equal scalar coupling constants for the second sphere of the two species. The scalar coupling constant is very sensitive to small changes in the density of unpaired electrons at the ^{17}O nucleus so it is not unreasonable that the assumption of equal scalar coupling constants be in error. If the scalar coupling constant of CrF^{2+} is smaller than the scalar coupling constant for $Cr(H_2O)_6^{3+}$ this would account for the small values calculated for y/n but a

decrease in the scalar coupling constant would cause an apparent increase in the lifetime of water molecules in the second sphere of $CrF(H_2O)_5^{2+}$, contrary to expectations. The chemical shift and relaxation data for CrF^{2+} are too few and too scattered to attempt to draw any firm conclusions about the system. It would appear however, that the rate of water exchange from the second sphere of $CrF(H_2O)_5^{2+}$ does not differ greatly from the rate for $Cr(H_2O)_6^{3+}$.

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APPENDIX

EXPERIMENTAL DATA

Table 1. Relaxation data for Sample 1. The sample composition was: 1.04 mmoles $Cr(H_2O)_6^{3+}$, 3.06 mmoles H^+, 6.19 mmoles ClO_4^-, and 75.14 mmoles total H_2O (68.88 mmoles labile H_2O).

$\frac{10^{-3}}{T}(^{0}K^{-1})$	$\frac{1}{T_2}(sec^{-1})$	$\frac{1}{T_1}(sec^{-1})$	$\frac{1}{T_2}-\frac{1}{T_1}(sec^{-1})$	$(\frac{1}{T_2}-\frac{1}{T_1})\frac{n}{f_B}\times 10^{-3}(sec^{-1})$
3.18	182.	141	41	3.2
2.71	88.3	68	20	1.8
2.80	99.1	76	23	1.8
3.05	146.	122	25	1.9
3.31	231.	191	41	3.2
3.47	334.	242	93	7.1
3.22	201.	155	46	3.6
3.10	157	125	33	2.5
3.41	285	200	86	6.6
2.87	107.	85	23	1.8

Chemical shift data for Sample 1. The sample composition is given above.

$\frac{10^3}{T}(°K^{-1})$	Chemical shift (Hz)	$\frac{y}{n}$
3.19	275	0.842
3.09	269	0.851
3.50	310	0.866
3.41	303	0.867
3.34	295	0.862

Table 2. Relaxation data for Sample 2. The sample composition was: 177 mmoles $Cr(H_2O)_6^{3+}$, 5.01 mmoles H^+, 10.33 mmoles ClO_4^-, and 110.19 mmoles total H_2O (99.55 mmoles labile H_2O).

$\frac{10^3}{T}(°K^{-1})$	$\frac{1}{T_2}(sec^{-1})$	$\frac{1}{T_1}(sec^{-1})$	$\frac{1}{T_2} - \frac{1}{T_1}(sec^{-1})$	$(\frac{1}{T_2} - \frac{1}{T_1})\frac{n}{f_B}\times 10^{-3}(sec^{-1})$
3.30	255	199	55	3.7
3.07	166	128	38	2.5
3.17	195	151	45	2.9
2.98	140	109	30	2.0
2.87	116	92	24	1.6
2.75	97.9	78	20	1.3
3.22	226	167	59	3.9
3.4]	365	299	66	4.4
3.31	261	215	46	3.1
2.66	91.8	65	27	1.8
3.13	185	149	37	2.4
2.65	87.9	66	22	1.5
2.99	155	99	55	3.7
2.93	135	97	39	2.6
3.37	298	255	43	2.8
3.47	375	296	79	5.2
2.85	113	93	20	1.3
3.50	406	347	59	3.9
3.38	314	251	63	4.1

Table 2. (continued)

Chemical shift data for Sample 2. The sample composition is given above.

$\frac{10^3}{T}$ (°K^{-1})	Chemical shift (Hz)	$\frac{y}{n}$
3.32	335	0.841
3.19	326	0.849
3.09	321	0.865
3.50	365	0.867
3.41	351	0.855
3.34	347	0.864
3.50	351	0.835

Table 3. Relaxation data for Sample 3. The sample composition was: 1.92 mmoles $Cr(H_2O)_6^{3+}$, 3.26 mmoles H^+, 9.02 mmoles ClO_4^-, and 96.91 mmoles total H_2O (85.39 mmoles labile H_2O).

$\frac{10^3}{T}$ ($°K^{-1}$)	$\frac{1}{T_2}$ (sec^{-1})	$\frac{1}{T_1}$ (sec^{-1})	$\frac{1}{T_2} - \frac{1}{T_1}$ (sec^{-1})	$(\frac{1}{T_2} - \frac{1}{T_1}) \frac{n}{f_B} \times 10^{-3}$ (sec^{-1})
3.30	300	222	79	4.3
3.06	195	143	51	2.8
3.00	172	129	44	2.4
2.89	141	103	38	2.1
3.18	236	177	60	3.3
3.53	480	356	123	6.7
2.74	108	82	26	1.4

Chemical shift data from Sample 3. The sample composition is given above.

$\frac{10^3}{T}$	Chemical Shift (Hz)	$\frac{y}{n}$
3.34	409	0.806
3.41	423	0.818
3.50	458	0.864
3.05	366	0.790
3.18	394	0.816

Table 4. Relaxation data for the CrF^{2+} sample. The sample composition was: 2.07 mmoles $CrF(H_2O)_5^{2+}$, 0.27 mmoles H^+, 4.40 mmoles ClO_4^-, and 69.78 mmoles total H_2O, (59.46 mmoles labile H_2O)

$\frac{10^3}{T}$ (°K^{-1})	$\frac{1}{T_2}$ (sec^{-1})	$\frac{1}{T_1}$ (sec^{-1})	$\frac{1}{T_2} - \frac{1}{T_1}$ (sec^{-1})
3.31	383	180	203
3.51	585	372	211
3.21	308	157	150

The chemical shift of the above sample was measured at 28°C to be 542 Hz downfield from pure $H_2{}^{17}O$. A value of y/n = 0.695 is calculated from this shift.

Table 5. Relaxation data for the Al^{3+} sample. The sample composition was: 1.08 mmoles $Al(H_2O)_6^{3+}$, 3.16 mmoles H^+, 6.28 mmoles ClO_4^-, and 76.54 mmoles total H_2O (70.06 mmoles labile H_2O).

$\frac{10^3}{T}$ ($°K^{-1}$)	$\frac{1}{T_2}$ (sec^{-1})	$\frac{1}{T_1}$ (sec^{-1})
3.47	255	276
3.26	156	
3.15	125	
3.05	102	
3.38	200	
3.32	179	182
3.08	109	124
3.21	139	161

FIGURE CAPTIONS

Fig. 1. Block diagram of the 8 MHz, ^{17}O spectrometer and ^{1}H lock system used for continuous wave NMR experiments (power saturation T_1 measurements, linewidth measurements, and chemical shift measurements).

Fig. 2. Upfield and downfield first sideband absorption spectrum of pure water. The upper curve consists of points representing the raw data and a solid line corresponding to a non-linear least squares curve fit to the data. The ordinate is the signal strength and the abcissa is the external field strength. The lower curve is the difference between the experimental and calculated points. The ordinate is expanded 7.2 times the ordinate on the upper curve.

Fig. 3. An example of the results of a power saturation measurement of T_1. The points represent the peak height versus rf voltage data and the solid line is the best fit curve obtained by a non linear least squares computer program.

Fig. 4. The dependence of the chemical shift of a series of $Cr(H_2O)_6^{3+}$ solutions on the concentration of ClO_4^- ion. The chemical shift is normalized by multiplying by m_{H_2O}/m_{Cr} and the abcissa is the mole ratio of ClO_4^- to labile H_2O. The data for this plot were taken from a paper by Alei.[17]

Fig. 5. The temperature dependence of the complexation by ClO_4^- ion of the second coordination sphere of $Cr(H_2O)_6^{3+}$ for the solutions used in this work. The quantity y/n is the ratio of the number of water molecules in the second coordination sphere to the number of water sites in the second coordination sphere, calculated from the chemical shift using Eq. 22 in the text.

Fig. 6. The relaxation data for the Al^{3+} sample plotted as a function of reciprocal temperature. The solid line is a smoothed curve through the relaxation rate for pure water ($1/T_2$), plotted to provide a point of reference from which to show the additional relaxation in the Al^{3+} sample.

Fig. 7. The quantities $\frac{1}{T_1}$ and $\frac{1}{T_2}$ for Sample 1 versus the reciprocal of the absolute temperature.

Fig. 8. The quantities $\frac{1}{T_1}$ and $\frac{1}{T_2}$ for Sample 2 versus the reciprocal of the absolute temperature.

Fig. 9. The quantities $\frac{1}{T_1}$ and $\frac{1}{T_2}$ for Sample 3 versus the reciprocal of the absolute temperature.

Fig. 10. The quantity $(\frac{1}{T_2} - \frac{1}{T_1}) \frac{n}{f_B}$ plotted versus the reciprocal of the absolute temperature.

For all three samples used, $(\frac{1}{T_2} - \frac{1}{T_1})$ gives the scalar coupling contribution to the transverse relaxation rate and $\frac{n}{f_B}$ is the normalization of the data to unit mole fraction of second coordination sphere waters. The solid line represents the best fit of the data of Eq. 27. For a discussion of the curve fitting, see the text following Eq. 27.

Fig. 11. The relaxation data for the CrF^{2+} sample versus the reciprocal of the absolute temperature. The upper plot is the raw data as measured. The lower plot is $(\frac{1}{T_2'} - \frac{1}{T_1})$ with a straight line drawn to estimate the value of $(\frac{1}{T_2} - \frac{1}{T_1})$ at room temperature.

Fig. 12. An example of the pulsed saturation recovery data. The measured value of the magnetization in arbitrary units is plotted versus the variable delay time, τ. The exponential curve is the best fit to the data shown as open circles. The closed circles are data measured in the same experiment but not included in the curve fitting. The solid, horizontal line represents the value of the equilibrium magnetization, measured for $\tau \approx 30T_1$.

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