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NUCLEAR MAGNETIC RESONANCE STUDY OF THE
TRANSVERSE RELAXATION OF OXYGEN 17 IN
AQUEOUS SOLUTIONS OF TITANOUS ION

Herbert L. Charles, Jr.
(Ph.D. Thesis)

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ABSTRACT

Oxygen-17 NMR has been used to study the solvation of Ti(III) in aqueous solution. The temperature and frequency dependence of the bulk water line width, $1/T_2$, of the O^{17} NMR signal in aqueous solutions of titanous ion has been studied in the range 0°C to ca. 70°C at 1.999, 4.337, 6.086, and 8.134 MHz. The temperature dependence of the bound water linewidth, $1/T_2$, was studied in the range $+2$ to -30°C at 8.134 MHz. The chemical shifts of both the bulk and bound waters were measured as a function of temperature at 8.134 MHz. The former was studied in the range 0 to 70°C and the latter in the range $+2$ to -30°C .

Below 12°C , at 8.134 MHz, the broadening becomes increasingly controlled by the lifetime of the water molecules in the first coordination sphere of Ti(III). In this region the enthalpy and entropy of activation for the water-water exchange of this system have been calculated to be 7.7 kcal/mole and -9 eu respectively. Above 12°C the broadening is primarily controlled by the rate of transverse relaxation within the first coordination sphere. An investigation of the frequency dependence of $\frac{1}{T_{2p}}$ and the temperature dependence of $1/T_{2m}$ at 8.134 MHz indicates that the relaxation is a consequence of both scalar coupling and $\Delta\omega$ mechanisms. The negative temperature dependence of T_{2m} has been interpreted in terms of a scalar coupling interaction

interrupted by T_{1e} of the electron where the electron is probably being relaxed by the Van Vleck-Raman process.

The scalar coupling constant was determined from the chemical shift measurements which were made on both the bulk and bound waters. In spite of the known tetragonal distortion the results of these studies, on the time scale determined by NMR absorption, are consistent with six equivalent waters composing the first coordination sphere of Ti^{3+} over the temperature range covered.

Evidence is also presented in this work for the existence of three species previously thought to exist in aqueous solutions of $Ti(III)$ i.e., $Ti_x(OH)_y^{3x-y}$, $Ti(H_2O)_6^{3+}$ and also some TiO^{2+} from oxidation.

I. INTRODUCTION

A. Background

Nuclear magnetic resonance can be used for the investigation of very rapid reactions in solution.¹⁻³ This technique, NMR, uses the broadening of the nuclear magnetic resonance line as a measure of exchange rates between two or more sites. In aqueous solutions of titanous ion there are specific interactions between the electron of the paramagnetic metal ion and the first coordination sphere O^{17} nuclei which produce this broadening. By observing the oxygen-17 nuclear magnetic resonance, as opposed to the proton nuclear magnetic resonance, one is able to investigate the exchange of the entire H_2O^{17} molecules instead of the chemical exchange of protons which may or may not exchange independently of the oxygens.⁴

The experimentally observed quantity is the width of the resonance line of the bulk water. This quantity is expressed in units of radians per second and is equal to $\frac{1}{T_2}$, the rate of transverse relaxation. The quantity representing the broadening, or the enhancement in the transverse relaxation rate due to interaction between the paramagnetic metal ion and the O^{17} nuclei, is $\frac{1}{T_{2p}}$. This quantity, $\frac{1}{T_{2p}}$, is the difference between the rate of relaxation in the presence of the paramagnetic ion and the rate in the absence of the paramagnetic ion, i.e.,

$$\frac{1}{T_{2p}} = \frac{1}{T_2} - \frac{1}{T_{2H_2O}}$$

The broadening is controlled by either of two factors: 1) the lifetime of the water molecule in the first coordination sphere of the paramagnetic metal ion (chemical exchange controlled region) or 2) the rate of transverse relaxation within the first coordination sphere of the paramagnetic ion (relaxation controlled region). In the first situation

the waters spend sufficient time in the first coordination sphere such that the O^{17} nuclei are fully relaxed before returning to the solvent waters. In this case the broadening is dependent on the exchange rate and shows an Arrhenius type temperature dependence. In the second situation the waters are exchanging too rapidly to experience the full effect of the metal ion before they exchange, and only the rate of transverse relaxation can be measured. In this case a determination of the actual exchange rate depends upon the correct interpretations of the specific interactions and interruptions causing the relaxation. In any event, it is usually necessary to study the temperature dependence of the line-broadening in order to ascertain which region and what relaxation mechanism is being observed.

The purpose of this work is to determine the kinetic parameters for the water-water exchange between the bulk solution and the first coordination sphere of Ti(III) ion and to make a study of the exchange process involved in this system. The experiments mentioned in the abstract were performed in order to achieve this purpose.

B. Titanous Ion

Titanous ion, Ti(III) belongs to the first transition series and has the electronic structure $(A)3d^1$ where (A) represents a closed argon configuration. Ti^{3+} forms octahedral complexes and in aqueous solution the $Ti(H_2O)_6^{3+}$ ion has a crystal field absorption band⁵ at $20,300\text{ cm}^{-1}$ with a shoulder at $17,400\text{ cm}^{-1}$. The absorption band is interpreted as a ${}^2T_{2g} \rightarrow {}^2E_g$ transition with the double peak being the result of a Jahn-Teller effect in the excited 2E_g state.⁶ The ground state, ${}^2T_{2g}$, is only slightly split under a Jahn-Teller distortion⁷ and, consequently, the hydrated ion having a T_{2g} electron is only slightly distorted. Because of the slowness of the distortion, and or, rapid inversion an

inequivalence of the of the hyperfine coupling constant and of the lability of the coordinated waters is not to be observed.

An important consequence of the smallness of the distortion is the introduction of a nonrotational electron spin relaxation mechanism (eff) in explaining the NMR observations presented in this work. Most mechanisms⁸ of electron spin relaxation result from anisotropic g tensors and hyperfine interactions both of which involve the rotational or tumbling motion of the molecules. In the electric field-fluctuation (eff) process the intermolecular potentials are modulated by molecular vibrations. Van vleck was the first to discuss properly the eff mechanisms for crystals.⁹ Kivelson has extended this with a theoretical investigation of these processes in liquids.¹⁰

Because of the relative smallness of the trigonal field splitting parameter it is believed that one of the eff mechanisms¹¹ (Van Vleck-Raman process) could be important in solutions of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. Evidence of such a process is provided in the present work.

II. THEORY

A. General Comments

As mentioned earlier, the experimentally observed quantity is the width of the resonance line which, when expressed in units of radians per second, is equal to $\frac{1}{T_2}$, the rate of transverse relaxation. This quantity is the rate at which the component of nuclear magnetization perpendicular to the external field loses its precessional coherence. It was Felix Bloch¹² who first proposed a set of phenomenological equations for the variation of the components of the total nuclear magnetic moment of nuclei when placed in an external magnetic field. For liquid samples, the equations give, in most cases, a correct quantitative description of the phenomena.

For the experimental conditions used in this work, i.e., steady state under conditions of slow passage with sideband detection of the first sideband, the observed NMR signal has the form¹³

$$S = \frac{\pm \frac{2}{\beta} [J_1(\beta)]^2 \gamma H_1 T_2 M_0}{1 + (\Delta\omega_{\pm} T_2)^2 + (\gamma H_1)^2 T_1 T_2 [J_1(\beta)]^2} \quad (1)$$

$$\beta = \frac{\gamma H_m}{\omega_m}; \quad \omega_{\pm} = \omega_0 - \omega \pm \omega_m$$

where

S is the observed signal

J_1 is the first Bessel function of the first kind

γ is the magnetogyric ratio of the nucleus

H_1 is one half the amplitude in gauss of the radiofrequency field

T_2 is the transverse relaxation time

M_0 is the equilibrium magnetization of the sample

ω_0 is the precessional frequency of the nuclei

ω is the frequency of the radiofrequency in radians per second

ω_m is the frequency of the modulation field in radians per second

T_1 is the longitudinal relaxation time

In the present work H_1 is small such that $(\gamma H_1)^2 T_1 T_2 T_1 [J_1(\beta)]^2 \ll 1$.

This is the condition of negligible saturation which reduces Eq. (1) to

$$S = \frac{\pm \frac{2}{\beta} [J_1(\beta)]^2 \gamma H_1 T_2 M_0}{1 + (\Delta\omega \pm T_2)^2} \quad (2)$$

S will pass through a maximum when $\Delta\omega_{\pm} = 0$ and these two maxima will be separated by twice $\Delta\omega_m$. On the other hand, when $(\Delta\omega_{\pm} T_2)^2 = 1$ these two signals will be at half maximum and

$$\frac{1}{T_2} = \frac{\delta\omega}{2} \quad (3)$$

where $\delta\omega$ is the full width at half maximum. Equation (2) is valid only under the condition that $\Delta\omega_m \gg \frac{1}{T_2}$. If $\Delta\omega_m \ll \frac{1}{T_2}$ the derivative of the absorption is observed. Under this condition the peak to peak separation of δ is related to $\frac{1}{T_2}$ by

$$\frac{1}{T_2} = \sqrt{3}/2 \delta\omega' \quad (4)$$

where $\delta\omega'$ is the peak to peak separation expressed in radians per second.

B. T_2 in the Presence of Chemical Exchange

The above expressions for $\frac{1}{T_2}$ were derived under the assumption that chemical exchange did not take place between different magnetic environments. McConnell¹⁴ has modified the Bloch equations to account for the possibility of chemical exchange and Swift and Connick⁴ have extended this treatment for the special case of a dilute solution of a paramagnetic ion. The steady state solution of the modified equation

has the following form

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

where

$\frac{1}{T_{2p}}$ represents the broadening of the bulk water linewidths due to the presence of the paramagnetic ion

$\frac{1}{T_{2H_2O}}$ is the rate of transverse relaxation in the absence of the paramagnetic ion

τ_{H_2O} is the lifetime of a water molecule in the bulk solution

τ_m is the lifetime of a water molecule in the first coordination sphere of the paramagnetic ion

$\Delta\omega_m$ is the difference in precessional frequencies between the bulk and bound waters.

Under conditions of exchange equilibrium

$$\frac{1}{\tau_m} n[M^{+p}] = \frac{1}{\tau_{H_2O}} [H_2O]_{bulk} \quad (6)$$

where n is the number of coordinated waters and $[H_2O]_{bulk}$ and $n[M^{+p}]$ are the concentrations of water molecules in the bulk and bound environments respectively. Defining

$$P_m = \frac{n[M^{+p}]}{[H_2O]_{bulk}} \quad (7)$$

Equation (5) yields

$$\frac{1}{T_{2p}} = \frac{P_m}{\tau_m} \left[\frac{\frac{1}{T_{2m}^2} + \frac{1}{T_{2m}\tau_m} + \Delta\omega_m^2}{\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m}\right)^2 + \Delta\omega_m^2} \right] \quad (8)$$

In the exchange controlled region a water molecule is relaxed every time it enters the metal ion's first coordination sphere and the line broadening is determined by the rate of chemical exchange. For this region $\frac{1}{\tau_m} \ll \frac{1}{T_{2m}} + |\Delta\omega_m|$ and Eq. (8) reduces to

$$\frac{1}{T_{2p}} = \frac{1}{\tau_{H_2O}} = \frac{P_m}{\tau_m} \quad (9)$$

Since

$$\tau_m = \frac{h}{kT} \exp(\Delta H^\ddagger/RT - \Delta S^\ddagger/R) \quad (10)$$

a plot of T_{2p} vs $\frac{1}{T}$ gives $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

In the relaxation controlled region exchange is so rapid that the H_2O^{17} molecules do not spend sufficient time in the first coordination sphere to be completely relaxed. $\frac{1}{T_{2p}}$ now becomes dependent on the rate of relaxation and will exhibit the temperature dependence of the mechanisms which are responsible for relaxation. For the relaxation controlled region $\frac{1}{\tau_m} \gg \frac{1}{T_{2m}} + |\Delta\omega_m|$. Equation (8) now reduces to

$$\frac{1}{T_{2p}} = \frac{P_m}{T_{2m}} + P_m \tau_m \Delta\omega_m^2 \quad (11)$$

C. Transverse Relaxation Mechanisms

In the presence of chemical exchange two different types of relaxation mechanisms may contribute to $\frac{1}{T_{2p}}$. From Eqs. (8) and (11) these mechanisms are seen to be the T_{2m} and $\Delta\omega_m$ mechanisms. The $\Delta\omega_m$ or chemical shift mechanism is a direct consequence of the exchange process and occurs if the magnetic moment of the nucleus originally in the bulk solution has experienced an appreciable shift in phase due to exchange into an environment which has a significantly different precessional frequency. In the relaxation controlled region the $\Delta\omega_m$ mechanism

contributes to $\frac{1}{T_{2p}}$ through the $P_m \Delta\omega_m^2 \tau_m$ term in Eq. (11). According to Bloembergen¹⁵

$$(|\Delta\omega_m| + |\Delta\omega_{H_2O}|)/\omega_o = \frac{S(S+1) A \frac{\gamma_S}{\gamma_I}}{3kT} \quad (12)$$

where

S is the spin angular momentum of the paramagnetic ion

A is the scalar coupling constant

γ_S is the magnetogyric ratio for the electron

γ_I is the magnetogyric ratio for the nucleus

k is Boltzman's constant

T is the absolute temperature

ω_m and ω_o have been defined previously

The interruption mechanism for $\Delta\omega_m$ relaxation is the chemical exchange process itself.

T_{2m} relaxation can occur as a result of the following interactions:

(a) dipole-dipole, (b) quadrupole, (c) anisotropic chemical shift and (d) scalar coupling. The contributions of these interactions to $\frac{1}{T_{2p}}$ will be given in their respective order. Reference 16 gives a more complete explanation of the theory describing the various interactions.

(a) Dipole-Dipole

This interaction results from the coupling between the magnetic moments of the O^{17} nucleus and of the paramagnetic ion. The interruption of this interaction occurs by means of chemical exchange, tumbling or electron spin relaxation. The analytical expression for this interaction's contribute to $\frac{1}{T_{2p}}$ is given by

$$\frac{1}{T_{2p}} = \frac{S(S+1)\gamma_I^2 \gamma_S^2 \hbar^2}{15 r^6} P_m \left[4\tau_1 + \frac{\tau_2}{1 + (\omega_I - \omega_S)^2 \tau_2^2} + \frac{3\tau_1}{1 + \omega_I^2 \tau_1^2} + \frac{6\tau_2}{1 + \omega_S^2 \tau_2^2} + \frac{6\tau_2}{1 + (\omega_I + \omega_S)^2 \tau_2^2} \right] \quad (13)$$

where r is the dipole-dipole distance. The following definitions are employed for τ_1 and τ_2

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

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

τ_r is the tumbling time for a sphere of radius a tumbling in a medium of viscosity η . It is given approximately by Stoke's formula:¹⁷

$$\tau_r = \frac{4\pi\eta a^3}{3kT} \quad (14)$$

T_{1e} and T_{2e} are the longitudinal and transverse relaxation times respectively and ω_I and ω_S are the precessional frequencies of the O^{17} nucleus and the paramagnetic electron respectively. In the present work $\omega_S \gg \omega_I$ and $\omega_I \tau_1 \ll 1$. Under these conditions Eq. (13) reduces to

$$\frac{1}{T_{2p}} = \frac{S(S+1)\gamma_I^2 \gamma_S^2 \hbar^2}{15 r^6} P_m \left[7\tau_1 + \frac{13 \tau_2}{1 + \omega_S^2 \tau_2^2} \right] \quad (15)$$

(b) Quadrupole

This coupling arises from the interaction of the nuclear quadrupole moment with the fluctuating electronic field gradients. The interruption of this interaction is governed either by chemical exchange or by

tumbling. For the condition $\omega_o \tau_d \gg 1$ the quadrupole coupling's contribution to $\frac{1}{T_{2p}}$ is given by

$$\frac{1}{T_{2p}} = \frac{3}{40} \frac{(2I+3)}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3} \left(\frac{eqQ}{h} \right)^2 P_m \tau_d \right) \quad (16)$$

where

$$\frac{1}{\tau_d} = \frac{1}{\tau_m} + \frac{1}{\tau_r}$$

and

I is the nuclear spin angular momentum quantum number

η is a measure of the axial symmetry of the electric field gradient

Q is the quadrupole moment of the nucleus

eq is the z component of the electric field gradient

(c) Anisotropic chemical shift

This process represents the interaction of the nucleus with its surrounding magnetic field. Again, the interruption is provided either by tumbling or by chemical exchange. For the condition $\omega^2 \tau^2 \ll 1$ the anisotropic chemical shift's contribution to $\frac{1}{T_{2p}}$ is

$$\frac{1}{T_{2p}} = \frac{14}{40} \omega_o^2 \delta_{zz}^3 \left(1 + \frac{\eta^2}{3} \right) P_m \tau_d \quad (17)$$

where

δ_{zz} is the z component of the traceless tensor for the interaction

η is given by $\frac{\delta_{xx} - \delta_{yy}}{\delta_{zz}}$

The anisotropic chemical shift's contribution to $\frac{1}{T_{2p}}$ is usually negligible with respect to the other interactions considered.

(d) Scalar Coupling

This coupling may occur if the wave function for the electron has a nonvanishing value at the position of the nucleus I. It can be interrupted by relaxation of the electron spin or by chemical exchange. The correlation time for scalar coupling, as well as the other mechanisms, will always be dominated by the fastest interruption process.

Noting that A is the scalar coupling constant and employing the condition $\omega_I \tau_2 \ll 1$ the contribution to $\frac{1}{T_{2p}}$ is represented by

$$\frac{1}{T_{2p}} = \frac{S(S+1)}{3} \left(\frac{A}{\hbar} \right)^2 P_m \left[\tau_1 + \frac{\tau_2}{1 + \omega_s^2 \tau_2^2} \right] \quad (18)$$

where

$$\frac{1}{\tau_1} = \frac{1}{\tau_m} + \frac{1}{T_{1e}}$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_m} + \frac{1}{T_{2e}}$$

This process and the $\Delta\omega_m$ mechanism have been found to provide the major contribution to O^{17} relaxation in dilute aqueous solutions of $Tl(III)$ ion.

III. EXPERIMENTAL

A. Sample Preparation

A 20% standardized solution of TiCl_3 was the source of Ti^{3+} in the preparation of all samples for the bulk water experiments. A higher concentration of Ti^{3+} was required for the bound water experiments, consequently anhydrous TiCl_3 was used as starting material. The 20% solution of TiCl_3 (Lot No. 1904) was purchased from LaMotte Chemical Company in Chestertown, Maryland. The total titanium was analyzed by oxidizing an aliquot of the 20% solution with nitric acid. The oxidized product was then ignited and the resulting TiO_2 was weighed to determine the total titanium. The concentration of Ti(III) ion was determined by adding an aliquot of the 20% TiCl_3 solution to a solution containing excess ferric ion. The ferrous ion produced by the reaction was then titrated with KMnO_4 to give the Ti(III) ion concentration. Both the 20% standardized solution and the anhydrous TiCl_3 gave a spectral-chemical analysis of less than 2 PPM manganese impurity.

The perchlorate salt would have been an ideal choice for the sample preparation since the perchlorate¹⁸ forms a very weak complex with Ti^{3+} . However, $\text{Ti}(\text{ClO}_4)_3$ is stable¹⁹ only below 0°C and can not be used for temperature investigation above that temperature. As a result, all NMR investigations were made on the TiCl_3 system.

The samples were prepared by adding a known volume of the 20% solution to a weighed amount of O^{17} enriched water. The acidity of all samples was adjusted to ca 0.1 M with the addition of concentrated HCl . All preparations were done in a nitrogen atmosphere since the TiCl_3 is sensitive to air oxidation.²⁰ The O^{17} enriched water (ca. 1,10 and 20 atom percent enrichment) was also degassed to remove dissolved oxygen. The O^{17} water was obtained from the Oak Ridge National Laboratory and was normalized in deuterium.

B. Instrumentation

The O^{17} resonance signals were observed with a Varian model V4311 high resolution NMR spectrometer or with a Varian model V4200 wide line NMR spectrometer. The high resolution spectrometer is a fixed frequency unit operating at 8.134 MHz whereas the wide line spectrometer is a variable frequency unit operating at 6.085, 4.337 and 1.999 MHz. The signals were detected using the sideband technique for linewidths less than 2000 cps. Accordingly, the gross magnetic field was modulated with frequencies of ca. 300, 400 and 500 cps depending upon the linewidth. Phase sensitive detection and modulation were performed by a Princeton Applied Research (PAR) model Jb-8 lock-in amplifier. A Bogen model CHA-10 audio amplifier was used to amplify the reference output of the PAR. The amplified modulation signal was then applied to the sweep coils in the probe.

The fixed frequency unit was used to observe chemical shifts and linewidths of both the bulk and bound waters as a function of temperature. The variable frequency unit was used to study bulk water linewidths as a function of temperature and frequency. All experiments were performed under conditions of slow passage and negligible saturation, with the gross magnetic field being swept at rates which depended upon the linewidth of the resonance signal. These rates varied from ca. 300 milligauss/min. to 1000 milligauss/min. The detected signal was filtered with a time constant from 0.0 to 0.6 sec. depending upon experimental conditions.

The derivative method of detection was used for the bound water observations. This was necessary because of the very large modulation frequency which would have been required to observe the signal by the sideband technique. Also, because of the weakness in signal intensity

and the low signal to noise ratio, a Varian Associates model 1024 time averaging computer was used to provide signal averaging for the bound water experiments. The super stabilizer was removed from the system and the internal ramp of the computer was fitted directly to the sweep input of the power supply. The computer was used to record both linewidth and chemical shift measurements of the bound waters.

The bulk water samples for T_2 measurements were contained in 10 mm O.D. pyrex tubes. The chemical shift samples were contained in 8 mm O.D. ampules. These ampules fitted snugly in a 10 mm O.D., 8 mm I.D. pyrex tube that had the receiver coil wound directly around it. The bound water samples were contained in 13 mm O.D. tubes. The part of the tube having the sample had been drawn out to thin the wall. The increased size and thin wall improved the filling factor and, hence, the signal.

The temperature of the sample above room temperature was controlled by a Varian EPR temperature control unit. Below room temperature a split flow gas system was used with liquid nitrogen or dry ice and acetone as the cold bath. The temperature was measured with two copper-constantan thermocouples. One of these was placed below the sample and the other above. The temperature difference of the two thermocouples never varied more than 1.0°C . The temperature of the sample was taken as the average of the two thermocouples. This temperature was controlled within 0.5°C at all times.

IV. RESULTS AND DISCUSSION

A. Preliminary Investigations

From preliminary O^{17} NMR linebroadening experiments performed on the aqueous $TiCl_3$ system at 8.13 MHz it was found that the exchange controlled region was accessible in the temperature region below $12^\circ C$. In Fig. 1, the temperature dependence of $P_m T_{2p}$ is shown for an aqueous solution that is 0.1 M in Ti^{3+} and 0.1 M in H^+ . The temperature dependence of the linewidth indicates that $\frac{1}{P_m T_{2p}}$ increases with increasing temperature from below $0^\circ C$ to ca. $12^\circ C$. This means that the O^{17} water molecules are effectively relaxed in this region and that the linebroadening is controlled primarily by the rate of chemical exchange of O^{17} waters into the first coordination sphere of $Ti(III)$. Above $12^\circ C$ $\frac{1}{P_m T_{2p}}$ decreases with increasing temperature. This indicates that the O^{17} waters are exchanging too rapidly to be completely relaxed by the titanous ion before exchange, and that the broadening of the linewidth is being controlled primarily by the rate of transverse relaxation within the first coordination sphere of the paramagnetic ion. In order to ascertain which relaxation process might be operative in the temperature region above $12^\circ C$ it is necessary to examine Fig. 1 in more detail. An initial fit of the data indicates that the slopes of the two fitted lines describing the exchange and relaxation controlled region are equal in magnitude and opposite in sign. This means that the $\Delta\omega$ relaxation mechanism and the lifetime of the O^{17} waters in the first coordination sphere of $Ti(III)$ ion are responsible for the line broadening above and below $12^\circ C$ respectively. To demonstrate this it is instructive to recall the complete Swift and Connick⁴ equation.

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

If it is assumed that there is no contribution from T_{2m} relaxation processes, i.e., $\frac{1}{T_{2m}} = 0$, Eq. (5) reduces to

$$\frac{1}{P_m T_{2p}} = \frac{\Delta \omega_m^2}{\frac{1}{\tau_m} + \tau_m \Delta \omega_m^2}$$

and

$$T_{2p} P_m = \tau_m + \frac{1}{\tau_m \Delta \omega_m^2} \quad (19)$$

Since the temperature dependence of $\Delta \omega_m$ (from Eq. (12.)) is linear and since the temperature dependence of τ_m (Eq. (10)) is exponential it is reasonable to expect the major temperature effect to arise from the τ_m factor. Accordingly, Eq. (19) demonstrates that the two terms contributing to $T_{2p} P_m$, neglecting the $\Delta \omega_m$ temperature dependence, should be approximately equal in magnitude and opposite in sign.

This preliminary line broadening experiment at 8MHz provides useful information about the state of affairs of the system. First it shows that the $\Delta \omega$ mechanism should exist as a means of relaxation of the O^{17} nucleus. Secondly, the data allow evaluations of the scalar coupling constant. It also allows evaluations of τ the correlation time for scalar relaxation. τ is defined in relation to Eq. (18) as

$$\tau = \left[\tau_1 + \frac{\tau_2}{1 + \omega_s^2 \tau_2^2} \right] \quad (20)$$

τ_1 and τ_2 which were defined earlier, can be used in connection with other assumptions and information to evaluate the contributions of T_{2m} when T_{2m} is dipole-dipole, quadrupole and anisotropic chemical shift relaxation. With the information from Fig. (1), and sources to be referred to, preliminary calculations are now carried out to determine the contribution from the T_{2m} processes listed above.

1. Dipole-Dipole

Equation (15) is used to estimate the dipole-dipole contribution to $\frac{1}{T_{2p}}$. If it is assumed that the contribution from τ_m is negligible for the proton and oxygen atom in the water molecule such that $(\tau_1)_0 = (\tau_1)_H$ and $(\tau_2)_0 = (\tau_2)_H$ the following result is obtained, in terms of Eq. (15), for the ratio of the oxygen-17 to proton dipole-dipole contributions to $\frac{1}{T_{2p}}$ for an aqueous solution of Ti(III) ion.

$$\frac{\left(\frac{1}{T_{2p}}\right)_{DD}^O}{\left(\frac{1}{T_{2p}}\right)_{DD}^H} = \left(\frac{\gamma_O}{\gamma_H}\right)^2 \left(\frac{r_H}{r_O}\right)^6 \quad (21)$$

The above assumption, $(\tau_i)_{O17} = (\tau_i)_H$ etc., is good since T_{le} , $\tau_r \ll \tau_{mO17}$ and $T_{le}, \tau_r \ll \tau_{mH}$. To demonstrate the latter inequality consider

where

$$K_f = \frac{1}{\tau_{mH}} +$$

and

$$K_H = \frac{K_f}{K_r}$$

For $(K_H = 6.31 \times 10^{-11})^{18}$ and $K_R = 10^{+11}$ (assuming K_r is diffusion controlled)

$$K_f \cong 10^9 = \frac{1}{\tau_{mH}} \ll \frac{1}{\tau_r}, \frac{1}{T_{le}}$$

where $\tau_r = 4.68 \times 10^{-11}$ and $T_{le} = 1.99 \times 10^{-11}$ at 25° (see section following Eq. (23) for evaluation of T_{le}).

The value for r_o is taken as the sum of the ionic radii of Ti(III) and O^{2-} . The TiOH bond angle for the coordinated state is taken as the tetrahedral angle, $109^\circ 25'$, and the OH bond distance for a coordinated water molecule is taken equal to $0.96^\circ \text{ \AA}$. From these values r_H is found to be $2.82 \text{ \AA}$. Substituting these values into Eq. (21) yields

$$\left(\frac{1}{T_{2p}}\right)_{DD}^0 = (.092) \left(\frac{1}{T_{2p}}\right)_{DD}^H$$

Hausser and Laukin²¹ observed the proton transverse relaxation time in an aqueous solution of Ti(III). Correcting their value for $\frac{1}{T_{2p}}$ with respect to the concentration of the present system yields, from Eq. (21),

$$\left(\frac{1}{T_{2p}}\right)_{DD}^0 = (.092)(16 \text{ sec.}^{-1}) = 1.47 \text{ sec.}^{-1} \quad \text{at } 20^\circ\text{C}$$

This value is found to be negligibly small compared to the observed $\frac{1}{T_{2p}}$ value of 285 sec.^{-1} at 20°C . As a result, the dipole-dipole contribution to $\frac{1}{T_{2p}}$ is assumed to be completely negligible.

Another means of estimating the dipole-dipole relaxation from Eq. (15) makes use of the assumption $\tau_1 = \tau_2$ which in turn implies that $T_{1e} = T_{2e}$. T_{1e} and T_{2e} may be estimated from the 8 MHz linewidth data. Scalar relaxation of the coordinated O^{17} waters is given by

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3} \left(\frac{A}{h}\right)^2 \tau \quad (22)$$

where the assumption has been made that $T_{1e} = T_{2e}$ and that

$$\tau = T_{1e} + \frac{T_{1e}}{1 + \omega_s^2 T_{1e}^2} \quad (23)$$

τ is evaluated by computer fitting the 8 MHz linewidth data where the temperature dependence of $\frac{1}{T_{2m}}$ in Eq. (22) is assumed to be completely negligible (zero activation energy). The fit gives a value of 2.07×10^{-11}

sec.⁻¹ for τ . Substituting this value into Eq. (23) yields a value of 1.99×10^{-11} sec. for T_{1e} . This value must be compared with the rotational correlation time τ_r in Eq. (13) since the shortest interruption will dominate. Recalling Eq. (14) and assuming a value of 3.56 Å for a and 1.0025 centipose for the viscosity η , τ_r is calculated to be 4.68×10^{-11} sec.⁻¹ at 20°C. A comparison of the values for τ_r and T_{1e} indicates that the interaction is primarily interrupted by T_{1e} . For [Ti(III)] = .1M, Eq. (15) yields

$$\left(\frac{1}{T_{2p}}\right)_{DD} = 0.91 \text{ sec.}^{-1}.$$

This estimation is not as good as the first because of the assumptions and approximations, however, it does support the finding that relaxation through dipolar coupling is completely negligible.

2. Quadrupole

The quadrupole contribution to $\frac{1}{T_{2p}}$ is evaluated by recalling the analytical expression for quadrupole coupling and noting that $I = 5/2$ in the present system. Equation (16) reduces for $I = 5/2$ to

$$\frac{1}{T_{2p}} = \frac{3}{125} \frac{eqQ^2}{h} (1 + \eta^2/3) P_m \tau_d \quad (24)$$

$\frac{eqQ}{h}$ is not known for a water molecule bound to Ti(III), however, in this evaluation, $\frac{eqQ}{h}$ is assumed to be the same for a coordinated and uncoordinated water molecule. This value has been determined by Verhoven, Dymanus and Bluyssen.²² They investigated the hyperfine structure of HD¹⁷O by beam-laser spectroscopy and found for the components X_{jj} of the quadrupole coupling tensor in the principle axis for the HDO molecule the values 10.175, (-) 8.63 and (-) 1.283 MHz for X_{xx} , X_{yy} and X_{zz} respectively. Taking eqQ as X_{zz} , η is found from

$$\eta = \frac{X_{xx} - X_{yy}}{X_{zz}}$$

to be 14.859. Substituting their values in Eq. (24) gives

$$\frac{1}{T_{2p}} = (4.76)(10^3)P_m \quad (24)$$

For $[Ti^{3+}] = 0.1 \text{ M}$

$$\frac{1}{T_{2p}} = 50 \text{ sec}^{-1}$$

This value represents approximately 20% of the linewidth at 25°C and would be a significant contribution if the above estimation is valid. Another estimation of the quadrupole contribution may be made by taking the ratio for quadrupole relaxation in the presence of titanous ion to that in pure water. The following result is obtained in terms of Eq.(24):

$$\frac{\left(\frac{1}{T_{2p}}\right)_{Ti(III)}^Q}{\left(\frac{1}{T_2}\right)_{H_2O}^Q} = \frac{P_m \tau_r}{\tau_{rH_2O}} \quad (25)$$

where eqQ and n are assumed to be the same for the coordinated and uncoordinated water molecules. Using the known values for $\left(\frac{1}{T_2}\right)_{H_2O}^Q$, τ_{rH_2O} and τ_r in Eq. (25) gives

$$\left(\frac{1}{T_{2p}}\right)_{Ti(III)}^Q = (2.54)(10^3) P_m \quad \text{at } 25^\circ\text{C}$$

for $[Ti(III)] = 0.1\text{M}$

$$\left(\frac{1}{T_{2p}}\right)_{Ti(III)}^Q \equiv 25 \text{ sec}^{-1}$$

This represents 10% of the observed linewidth and differs by a factor of 2 from the first estimation. The values for eqQ and η were determined by assuming that the coordinated water molecules do not rotate around the oxygen-metal bond. If the waters are allowed to rotate rapidly the averages of the components X_{xx} and X_{yy} must be used to determine η and eqQ. In this case X_{zz} is not affected by rotation and is

equal to (-) 1.283 such that eqQ retains its initial value. On the other hand $X_{xx} = X_{yy} = 0.642$ and η is now equal to zero. Accordingly, Eq. (24) gives, for the same conditions of temperature and concentration,

$$\left(\frac{1}{T_{2p}}\right)_{\text{Ti(III)}}^Q = .689 \text{ sec}^{-1}$$

This indicates that the quadrupole contribution is completely negligible. It is reasonable to think that some averaging would occur, however, the magnitude would be difficult to estimate with the present information. This problem will be dealt with again in Part 4.

3. Anisotropic Chemical Shift

It was stated earlier that there is little experimental evidence for the observation of the anisotropic chemical shift relaxation mechanism. An upper limit to it's contribution to the present system is estimated by setting $\delta_{zz} = \frac{\Delta \omega}{\omega_o P_m}$ where $\frac{\Delta \omega}{\omega}$ is the observed chemical shift of the bulk water molecules. If the shift has, or can not be measured, it can be estimated from the parameters of the 8 MHz linewidth data (Fig. 1) and the following equation²³ for the shift of the bulk waters resonance in the presence of a paramagnetic ion.

$$\Delta \omega_{\text{H}_2\text{O}} = \frac{P_m \Delta \omega_m}{\tau_m \left[\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m} \right)^2 + \Delta \omega_m^2 \right]} \quad (26)$$

All of the above parameters have been defined earlier. Substituting the values for these parameters at 20°C and 0.1 M Ti(III) ion in Eq. (26) gives $\Delta \omega_{\text{H}_2\text{O}} = 4.05 \times 10^2 \text{ rad/sec}$. Assuming then $\eta = 1$ reduces Eq. (17) to

$$\left(\frac{1}{T_{2p}}\right)^{\text{A.C.S.}} = \frac{14}{40} \frac{\Delta \omega^2}{P_m} \tau_r \quad (27)$$

and, upon insertion of the known parameters gives

$$\left(\frac{1}{T_{2p}}\right)^{\text{A.C.S.}} = 3.3 \times 10^{-4} \text{ sec}^{-1}$$

which is seen to be a completely negligible contribution.

4. Scalar Coupling

The contribution to $\frac{1}{T_{2p}}$ from scalar relaxation is given by

$$\frac{1}{T_{2p}} = \frac{S(S+1)}{3} \left(\frac{A}{h}\right)^2 P_m \tau \quad (28)$$

τ , defined by Eq. (20), and A , the scalar coupling constant are equal to $2.07 \times 10^{-11} \text{ sec}^{-1}$ and 5.47 MHz respectively. As pointed out earlier this information was provided by curve fitting the 8 MHz T_{2p} data. Insertion of these values into Eq. (28) yields the following at 25°C

$$\frac{1}{T_{2p}} = 6.1 \times 10^{-3} \text{ sec}^{-1} P_m$$

For $[\text{Ti(III)}] = 0.2_m$, $P_m = 1.08 \times 10^{-2}$ and

$$\frac{1}{T_{2p}} = 65.0 \text{ sec}^{-1}$$

This represents approximately 23% of the linewidth and is indeed a sizeable contribution. Also, there is much less uncertainty in this estimation than in the one for quadrupole relaxation. Fitting the data with the scalar coupling and $\Delta\omega$ mechanisms when theory might or might not allow for quadrupole coupling is some indication that the water molecules are rotating.

B. Chemical Shift Measurements

The various experiments performed in this study are now examined in detail in order to ascertain the validity of the assumptions and approximations used in the preliminary investigations. One of the important parameters used in these preliminary calculations was the scalar coupling constant. This parameter, which was determined by computer curve fitting the 8 MHz linewidth data, is very important since both the scalar coupling and $\Delta \omega$ mechanism contain it. Chemical shift measurements of the bulk waters with respect to pure water was investigated over the temperature range of 0°C to ca 70°C to provide a check for the value of the scalar coupling constant which was determined by curve fitting the 8 MHz T_{2p} data. Because of the smallness of the shift, the solution was made 0.3255 M in Ti(III) ion in order to observe a sizeable shift. In Fig. 2 the log of the chemical shift of the bulk waters is plotted vs $\frac{1}{T}$. Above 50°C the log of the chemical shift is seen to have a $\frac{1}{T}$ temperature dependence. This is explainable by considering Eq. (26) under certain limiting conditions. In the limit where chemical exchange is rapid, i.e., where

$$\frac{1}{\tau_m} \gg \frac{1}{T_{2m}} + |\Delta \omega_m|$$

Equation (26) reduces to

$$\Delta \omega_{H_2O} = P_m \Delta \omega_m \quad (30)$$

and since

$$\Delta \omega_m = \frac{S(S+1)}{3kT} A \left(\frac{\gamma_S}{\gamma_I} \right) \omega_o \quad (12)$$

the $\frac{1}{T}$ temperature dependence is obvious upon substitution of $\Delta \omega_m$ from Eq. (12) into the expression given by Eq. (30). In the limit where chemical exchange is rapid Eq. (30) gives

$$\Delta \omega_{H_2O} = \frac{S(S+1) A \left(\frac{\gamma_S}{\gamma_I} \right)}{3kT} \omega_{O^p_m} \quad (31)$$

Putting in the value for the observed chemical shift, $(\Delta \omega_{H_2O})$, at a given temperature, and all the known parameters yields

$$\frac{A}{h} = 5.58 \times 10^6 \text{ sec}^{-1}$$

as compared to $\frac{A}{h} = 5.47 \times 10^6 \text{ sec}^{-1}$ as determined from curve fitting the 8 MGz T_{2p} data. It should be noted that the experimental error in the shift measurements is significant to the extent of ca 5% in the high temperature region and more in the low temperature region.

Consequently, the computer fit, utilizing the entire Swift and Connick expression for T_{2p} , gives a more accurate evaluation of the coupling constant. The scalar coupling constant determined by the computer fit was used to calculate the reference points in Fig. 2. The agreement between the calculated points and the experimental points is quite good. In fact, scalar relaxation becomes more significant at higher temperatures and lower magnetic fields. This effect can be seen immediately from the expressions for $\Delta \omega$ and T_{2m} when T_{2m} is scalar relaxation. From Eq. (12) the frequency dependence of $\Delta \omega$ is seen to occur through ω_o . The smaller the field the smaller the $\Delta \omega_m$ contribution to $\frac{1}{T_{2p}}$ in Eq. (11). In other words, this term becomes much smaller with respect to the T_{2m} term in Eq. (11) at lower magnetic fields if T_{1e} and T_{2e} of the electron are not frequency dependent. More will be said of this

later in the determination of T_{2m} .

Both the chemical shifts and T_{2p} measurements were investigated by means of bulk water resonances. From Eq. (6) the relation between the bulk and bound water lifetimes occurs through the P_m factor and, accordingly, all such experimental information for the bulk waters will be in error to the extent that this quantity is uncertain. The error in the P_m factor, according to Eq. (7) arises in the coordination number since the concentration of a given sample is known accurately through preparation and analysis. This problem is apparent in the analysis of the above bulk water experiments since the P_m factor does enter into the scalar coupling and linewidth expressions even though the coordination number of Ti(III) has not been determined and has to be assumed. This problem does not manifest itself, however, in the evaluation of the scalar coupling constant from the shift of the pure H_2O^{17} with respect to the bound waters since the P_m factor does not enter the shift expression for bound waters (see Eq. (12)). The same is true in the expression for the observation of the linewidth of the waters in the solvation shell. This means, then, that a direct observation of the solvated waters would yield linewidths and shifts that are independent of coordination number. This is important since the information from bound and bulk water shifts allows an indirect determination of the coordination number. This is seen by considering the following expression for the chemical shift of the bound waters relative to pure water. Writing the complete expression for Eq. (12) gives, according to Bloombergen¹⁵,

$$|\Delta \omega_m| + |\Delta \omega_{H_2O}| = \omega_o S(S+1) \frac{\gamma_S}{\gamma_I} \frac{A}{3kT} \quad (12)$$

where $\Delta\omega_{H_2O}$ is completely negligible at the low temperature used in this study. Figure 3 shows a plot of $\log \Delta\omega_m$ vs $\frac{1}{T}$ over the temperature range of (-) 30°C to (+) 2°C. The experimental error which resulted from the presence of the titanyl signal made it impossible to determine a precise value of the scalar coupling constant. However, the parameter yielded by this observation is within 8% of the value of A/h which was evaluated by the computer analysis of the 8MHz T_{2p} data and the maximum deviation of the experimental values from the average was 8%. Again the agreement between the solid line calculated from the $\frac{A}{h}$ value obtained from the bulk water shift and the experimental points is quite good considering the intrinsic experimental problem of measuring very broad lines that have low signal to noise ratios. If the scalar coupling parameter could have been accurately determined from the bound water observation it would have been simple to evaluate $\Delta\omega_m$ in Eq. (12) and then to substitute this value into the following expression for bulk water shifts in the limit of rapid chemical exchange, i.e.,

$$\Delta\omega_{H_2O} = \Delta\omega_m \frac{n [Ti(III)]}{55.5}$$

which allows n , the coordination number of Ti(III), to be determined upon substitution of the known parameters. Because of the uncertainty in A/h from the bound water shifts a definite value can not be given for the coordination number, however, choosing six for the coordination number of Ti(III) is consistent with the experimental data. If n is calculated from the experimental data the values for n range from ca. 5.6 to 6.4.

It should be pointed out that the value of the scalar coupling constant determined by the bulk water chemical shift observations in this work is not consistent with the value determined by Chmelnick and Fiat, i.e., their value of A/h was lower by 20% than the value reported in this work. Now, it was just observed that NMR observations made on the bulk

solution can be in error to the extent that the P_m factor and, hence, concentration is in error. It is also known that Ti(III) is sensitive to oxidation in aqueous solution but Chmelnick and Fiat give no indication that they analyzed their solutions at the conclusion of their observations. Consequently, it is possible that their actual concentrations of Ti(III) were smaller than they believed. This is consistent since the smallness of their scalar coupling constant corresponds to a smaller Ti(III) concentration.

The water exchange rate reported by Chmelnick and Fiat also differs by 20% from the rate reported in this work. The value of their rate is smaller by 20% which again corresponds to less Ti(III) ion in solution i.e., the smaller the Ti(III) concentration, the less effective the relaxation and therefore, the smaller the rate. Thus, both their rate fit and chemical shift fit can be reconciled with the present work by assuming the same discrepancy in concentration. (This does not account for the experimental points, T_{2mp} , since their fitted τ_m is not correct.)

The same concentration error, 20% does not account for their bulk water linewidth measurements in the relaxation controlled region. Since they do not attempt to completely resolve their experimental data and since they do not discuss the relaxation processes responsible for the linebroadening in this region it is difficult to interpret their findings in this region. On the other hand, it was found by the present investigator that both the scalar coupling and $\Delta\omega$ mechanisms are responsible for relaxation in this region and that complete resolution of the experimental curve is consistent with these findings.

C. Determination of T_{2m}

Experimental

Investigations of the transverse relaxation time of the bound O^{17}

waters and of the frequency dependence of the bulk O^{17} -waters were performed as a function of temperature in order to determine the actual activation energy for the T_{2m} curve hypothesized in Fig. 1. As stated earlier, the transverse relaxation of the bound O^{17} -waters in an aqueous solution of $Ti(III)$ ion is due to scalar coupling being interrupted by T_{1e} and T_{2e} of the paramagnetic electron. Consequently, the temperature dependence of T_{2m} should be small since the activation energies of the processes responsible for T_{1e} and T_{2e} relaxation (i.e., tumbling, molecular vibrations and distortions) are small. Consequently the activation energy for T_{2m} in Fig. 1 was a priori assumed to be zero since the sign of the T_{2m} slope also was not known. The sign of the slope is very important and will be discussed later in this section.

In the present system there are two methods by which the transverse relaxation time of the bound O^{17} -waters might be determined. The first method utilizes the direct observation of the O^{17} -resonance signal of the bound O^{17} -waters in the first coordination sphere of $Ti(III)$ ion. In this case, the observed linewidth is directly related to the rate of O^{17} transverse relaxation in the first coordination sphere, i.e., to T_{2m} . The second method entails going to such low magnetic fields and high temperatures that the T_{2m} term is dominant in Eq. (11) and, as a result, the bulk water broadening is related to T_{2m} through the P_m factor, i.e.,

$$\frac{1}{T_{2p}} \cong \frac{P_m}{T_{2m}} \quad (32)$$

Because of decomposition above $60^\circ C$, the present system is limited to a fixed temperature range. At $60^\circ C$ the system is just on the threshold of the region where Eq. (32) is valid.

Figure 4 shows a plot of T_{2p} at various frequencies vs. $10^3/T$. The frequency dependence of T_{2p} is in the right direction since $\frac{1}{\rho_m T_{2p}}$ becomes smaller at lower frequencies. This can be seen by considering the following expression which was taken from Eqs. (11) and (12)

$$\frac{1}{\rho_m T_{2p}} = \tau_m \left[\omega_o \frac{\gamma_S}{\gamma_I} \frac{S(S+1)}{3kT} A \right]^2 + \frac{1}{T_{2m}} \quad (33)$$

The frequency dependence of the linewidth also supports the initial finding that the $\Delta \omega$ mechanism provides a major path of relaxation for the transverse relaxation of the bulk O^{17} water molecules. Below 6 MHz it is interesting to note that the log of the linewidths deviates from the $\frac{1}{T}$ temperature dependence as prescribed by Eq. (19) which assumes no T_{2m} contribution to the linewidth. This is evidence that, in the present system, scalar relaxation becomes more important at lower fields. From the shape of the linewidth curve above 50°C at 2 MHz the system appears to be just on the threshold of the region where relaxation of the O^{17} water molecules is due solely to scalar coupling. As a result, much higher temperatures would be required in order to determine T_{2m} explicitly by this method. Also, there is quite a bit of scatter in the experimental points observed at 2 MHz. This is due to the difficulty in making experimental observations at this frequency. The intensity of the observed signal is proportional to the strength of the magnetic field H_o and at 2 MHz, the observed signal has a very low signal to noise ratio and is easily saturated. In spite of the experimental uncertainties the data do indicate that the slope of the linewidth curve above 50°C is changing very slightly which means, as implied above, that the experimental points above 50°C will begin to define a limiting value for T_{2m} at 8MHz, if T_{2m} is frequency independent. This would

imply that $T_{1e} = T_{2e}$ and that $\omega_s^2 T_{1e}^2 \ll 1$ at all frequencies considered. Assuming for the moment that the above assumptions are true there are, nevertheless, still too few data points to determine the sign of the slope of the T_{2m} curve.

In order to define a limiting value for T_{2m} in the low temperature region (ca. $+2^\circ$ to -30°C) measurements of the bound water linewidths were made. The analytical expression for the linewidth of the bound waters is derived from the equations which McConnell proposed in dealing with the possibility of chemical exchange between two or more sites where no assumptions are made such that one site is much more populated than the other sites. Formulating these equations for the linewidth of the bound waters gives the following expression²⁴ for ν_b , the out of phase component of the signal

$$\nu_b = -\omega_1 \left(\frac{\left[M_O^b + \frac{M_O^a}{\tau_{ab}} \times \frac{\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}}{\left(\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\right)^2 + \Delta\omega_a^2} \right] \left[\frac{1}{T_{2b}} + \frac{\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}}{\left(\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\right)^2 + \Delta\omega_a^2} \right] + \left[M_O^b + \frac{M_O^a}{\tau_{ab}} \times \frac{\frac{1}{T_{2a}}}{\left(\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\right)^2 + \Delta\omega_a^2} \right] \left[\frac{M_O^a \Delta\omega_a \Delta\omega_b}{\tau_{ab} \left\{ \left(\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\right)^2 + \Delta\omega_a^2 \right\}} \right]}{\left[\frac{1}{T_{2b}} + \frac{1}{\tau_{ba}} \frac{\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}}{\left(\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\right)^2 + \Delta\omega_a^2} \right]^2 + \left[\Delta\omega_b + \frac{\Delta\omega_a}{\tau_{ba} \tau_{ab} \left\{ \left(\frac{1}{T_{2a}} + \frac{1}{\tau_{ab}}\right)^2 + \Delta\omega_a^2 \right\}} \right]} \right) \quad (34)$$

There are two limiting conditions under which Eq. (34) can be simplified. The first condition arises if the bulk water resonances are shifted sufficiently far away from the bound water resonance such that their respective signals do not overlap. If this condition prevails $\Delta\omega_a$ is large with respect to the other parameters and causes the expressions which contain it to vanish. For $\tau_{ba} = \tau_m$ and $T_{2b} = T_{2m}$ Eq. (34) reduces to

$$V_b = \frac{\frac{1}{T_2} \omega_i M_o^b}{\frac{1}{T_2} + \Delta\omega^2} \quad (35)$$

where
$$\frac{1}{T_{2m}} = \frac{1}{T_2} - \frac{1}{\tau_m} \quad (35')$$

when solving for $\frac{1}{T_{2m}} \cdot \frac{1}{\tau_m}$ is known from the bulk water measurements and $\frac{1}{T_2}$ is the observed bound water linewidth.

The coordination number can be determined directly in this case, i.e., when bound and bulk water signals are observable and do not overlap. This is accomplished by integrating the area under the bound water resonance and comparing this value with the results obtained by integrating the area under the bulk water resonance. The area under the curve is proportional to the magnetization which in turn is proportional to the number of H_2O^{17} molecules. Unfortunately, it was not possible to determine the coordination number directly in the present system since the temperature region could not be reached where the bulk and bound water signals do not overlap. Also, due to the overlapping of signals, the linewidth of the bound water and, hence, T_{2m} could not be determined in this situation.

The other condition under which Eq. (34) can be simplified arises if the bulk water signal is completely broadened²⁵ or shifted through

experimental techniques such that the bound water signal might be observed. The broadening technique is utilized in the present system. This is accomplished by adding manganous ion. The manganous ion relaxes the bulk waters so effectively that $\frac{1}{T_{2a}}$ becomes very large in comparison to the other parameters in Eq. (34). As a result, the expressions containing this term become completely negligible. In this situation Eq. (34) reduces to Eq. (35').

Figure 5 shows the experimental points for T_{2m} over the temperature range $+2^{\circ}\text{C}$ to -30°C . It was not possible to determine the linewidth of the bound water signal above $+2^{\circ}\text{C}$ since the signal began to become asymmetric at temperatures above ca. $+2^{\circ}\text{C}$. This asymmetry resulted from the overlapping of the bound water O^{17} signal and a second signal which was attributed to titanyl ion (See App. 1). In the temperature region below $+2^{\circ}\text{C}$ the O^{17} resonance signal becomes sufficiently narrow to separate out the effects of the titanyl ion and to allow for fairly accurate linewidth measurements. Accordingly, the low temperature values for T_{2m} are determined by these observations even though the experimental error, in this case, is relatively large (ca. 8%). The experimental error is a result of linewidth measurement of signals that are broad with weak intensity and a low signal to noise ratio.

Figure 5 shows a plot of T_{2m} vs $10^3/T$. The solid line representing T_{2m} in Fig. 5 was determined by substituting the necessary parameters from the bulk water linewidth data and from the chemical shift measurements into Eq. (5) and solving for T_{2m} by successive approximations. The values of T_{2m} have reliability only in the high temperature region above 25°C . The experimental points in Fig. 5 were measured over the temperature range $+2^{\circ}\text{C}$ to ca. -30°C . The extension of the solid line to low temperatures, representing the calculated T_{2m} curve from the bulk

water NMR observations, agrees remarkably with the bound water data.

T_{2m} can also be evaluated at 6 and 4 MHz with information from the 8 MHz data. T_{2p} is experimentally observable at any frequency and τ_m , which is frequency independent, is known from the 8MHz bulkwater linewidth data. The scalar coupling constant, which was determined from the chemical shift measurements of both the bulk and bound waters at 8MHz, is frequency independent and allows $\Delta\omega_m$ to be evaluated irrespective of the frequency (see Eq. 12). T_{2m} is then found by successive approximations. Figure 6 shows a plot of T_{2m} at various frequencies vs $10^3/T$. As is evident from the plot, there appears to be no noticeable difference between the T_{2m} curves which were evaluated at 8, 6 and 4 MHz, however there is a relatively large difference when considering the 2 MHz data. This difference lies beyond the limit of experimental error (ca 8% for the 2 MHz linewidth data) and does not appear to be an artifact. This would mean that T_{2m} is frequency dependent.

The frequency dependence of T_{2m} can occur through the longitudinal and transverse electronic relaxation times, T_{1e} and T_{2e} , and through the ω_s factor in the denominator of Eq. (18). If it occurs through the electron relaxation times T_{1e} will not equal T_{2e} and many of the evaluations which were performed earlier in this work will not be valid. This inequality would occur since T_{1e} and T_{2e} can have different frequency dependencies; in fact $T_{1e} \geq T_{2m}$. The T_{2m} frequency dependence arising through the ω_s factor can be determined by recalling Eqs. (22) and (23) where

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3} \left(\frac{A}{\hbar} \right)^2 \tau \quad (22)$$

and

$$\tau = T_{1e} + \frac{T_{1e}}{1 + \omega_s^2 T_{1e}} \quad (23)$$

From the 2MHz linewidth data at 333.33°K, $\frac{1}{T_{2m}} = 7.6 \times 10^3$ (see Fig. 6). Substituting this value and the values of the other known parameters into Eq. (22) gives $\tau = 2.07 \times 10^{-11}$ sec. To be consistent with earlier calculations T_{2e} in Eq. (23) was assumed to be equal to T_{1e} such that a value of $T_{1e} = 1.99 \times 10^{-11}$ is found upon solving Eq. (23) for T_{1e} at 2MHz. (At 2MHz $\omega_s = (2\pi)(2.8)(10^6)(3.402)(10^3) = 6.05 \times 10^{10}$. Now, if the frequency dependence of T_{2m} arises solely through the ω_s factor the value for $T_{1e} = T_{2e}$ at 2MHz should equal the value for $T_{1e} = T_{2e}$ at 8MHz. This can be verified by inserting the value for ω_s at 8MHz and the value for $T_{1e} = T_{2e}$ from the 2MHz data into Eq. (23) and solving for τ at 8MHz. If this calculated value for τ at 8MHz (using 2MHz $T_{1e} = T_{2e}$) equals the original value for τ found by curve fitting the 8MHz data it can be concluded that $T_{1e} \text{ 8MHz} = T_{1e} \text{ 2MHz}$. Inserting the value for ω_s at 8MHz [$\omega_s = (2\pi)(2.8)(10^6)(1.4)(10^4) = (2.46)(10^{11})$] and the value for $T_{1e} = T_{2e}$ at 2MHz into Eq. (23) gives $\tau = 2.07 \times 10^{-11}$ sec. This is in fortuitous agreement with the value obtained by curve fitting the 8MHz data which also give $\tau = 2.07 \times 10^{-11} \text{ sec}^{-1}$. This means that the T_{2m} frequency dependence can be accounted for through the ω_s factor and that the assumption for $(T_{1e} = T_{2e})_{8\text{MHz}} = (T_{1e} = T_{2e})_{2\text{MHz}}$ is consistent with this interpretation. The frequency dependence of T_{2m} is also in the right direction since $\frac{1}{T_{2m}} \propto \frac{1}{1 + \omega_s^2 T_{2e}^2}$ and the larger the frequency the larger T_{2m} (See Fig. 6). Theoretically, the 8, 6, and 4 MHz T_{2m} 's are also frequency dependent, however the differences were within experimental error and therefore not observable.

In order to verify the value of $T_{2e} = 1.99 \times 10^{-11}$ sec, an attempt

was made to see the EPR signal (at 9,500 MHz) of hexaquo Ti(III) in aqueous/HCl at room temperature (see Appendix 1-B). A sample which was 0.5M in Ti(III) and 1.1M in H^+ ion gave a relatively broad signal. The width of the signal measured 2400 ± 200 gauss from peak to peak which corresponds to $T_{2e} \approx 2.2 \times 10^{-11}$ sec. This value of T_{2e} is in good agreement with the value of T_{2e} that was found from the 2MHz and 8MHz work. This signal is believed to be the hexahydrate since the linewidth and hence, T_{2e} , is the same as that which is predicted by the NMR results. Also, the width and intensity of the signal indicated that more than 90% of the Ti(III) ions are responsible for the signal. This is further evidence that the hexahydrate is being observed since the major species in aqueous solutions of $TiCl_3$ is $[Ti(H_2O)_6]^{3+}$.^{5, 26}

Theory

In order to understand the temperature dependence of T_{2m} , and, hence, T_{1e} , processes of electron spin relaxation in magnetically dilute liquids must be considered. The theoretical evaluations of electron spin relaxation times have been centered on treatments where the anisotropy of the g tensor and the nuclear hyperfine tensors provide the dominant cause of relaxation.^{27, 28} (Both of these processes involve the rotation or tumbling motion of the molecules). Regardless of whether the relaxation originates through the anisotropy in the g tensor or through hyperfine interactions the treatments developed by Carrington and Lockhurst,²⁹ Bloombergen and Morgan³⁰ and McLachlan³¹ give identical results, i.e., the various theories for electron relaxation times have identical forms for correlation times and frequency dependencies for electrons in a given spin state.

The various treatments give the following results for a spin when the dominant cause of relaxation occurs by means of the anisotropy of the g tensor

$$\frac{1}{T_{1e}} \propto \frac{2\tau_c}{1 + \omega_s^2 \tau_c^2} \quad (38)$$

$$\frac{1}{T_{2e}} \propto \tau_c + \frac{\tau_c}{1 + \omega_s^2 \tau_c^2} \quad (39)$$

The conditions under which these formulas are valid is

$$\tau_c \ll T_{1e}, T_{2e}$$

Now the temperature dependence of the electron relaxation times arises through the correlation time τ_c . To establish T_{2m} 's temperature dependence from Eqs. (38) and (39) consider the previous assumption that $T_{1e} = T_{2e}$ in which case $\omega_s^2 \tau_c^2 \ll 1$ and

$$T_{2m} \propto \frac{1}{T_{1e}} \propto \tau_c \quad (40)$$

Since the interactions responsible for relaxation are modulated by the rotation or tumbling motion of the molecule the correlation time τ_c should have an n/T temperature dependence. This means that the molecules will tumble more slowly at lower temperatures. Accordingly, this corresponds to a longer τ_c and, hence, a shorter electron relaxation time. The opposite is true at higher temperatures. In any event, T_{2m} should have a positive slope since T_{2m} is directly proportional to τ_c . Actually, the opposite temperature dependence for T_{2m} was found to occur in the present work. The only way this temperature dependence can be explained using the treatment developed by Bloombergen and Morgan etc. would be to assume that T_{1e} and T_{2e} are frequency dependent.

However, previous calculations indicate that this is not the case in the present system. Consequently, other electron spin relaxation mechanisms will now be considered in order to account for the temperature dependence of T_{2m} .

Kivelson has found that some of the theories of electron spin relaxation for crystals, are applicable, after some modification, to spin relaxation in liquids. The mechanisms that are of interest in this work are the so called 'electric-field-fluctuation (eff) mechanisms. Van Vleck was the first to properly discuss the eff mechanisms for crystals. In magnetically dilute crystals the dominant spin relaxation mechanism occurs via the spin orbit coupling. In describing these relaxation processes Van Vleck considered the coupling of the spins with the normal modes in a complex where these modes are modulated by the Debye waves of the crystalline lattice, i.e., the electron spin is relaxed by the lattice vibrations which produce a fluctuating electric field. The electron spin senses this variation in electric field through spin orbit coupling. In liquids the fluctuating electric fields, associated with lattice vibrations in crystals, are provided by modulation of molecular vibrations and by collisions with surrounding diamagnetic molecules. The electric fields constitute the crystal fields and the spin senses the variation in field by means of the spin orbit interaction.

Kivelson¹⁰ has theoretically investigated three different eff mechanisms, however, only the Van Vleck-Raman process will be presented in this work since it has been found to be the only process applicable to the present system, i.e., to $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. In this work only the basic outline of Kivelson's treatment for the Raman process will be presented. The original paper is recommended for the complete

theoretical treatment of all the eff processes. The notation in this work is essentially the same as in the original paper.

The following treatment is provided in order to explain the temperature dependence of T_{2m} and to establish an analytical expression for $T_{1e} = T_{2e}$ which is proportional to an electronic correlation function τ_c . It is assumed that the system under study has an electron spin $S = \frac{1}{2}$ and that the ground electronic (orbital) state is non-degenerate. This is the case for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $S = \frac{1}{2}$ and Δ is positive which means that the orbital singlet lies lower. (Δ , the tetragonal distortion, (see Fig. 7) measures the splitting of the T_{2g} state due to distortion of the complex from octahedral symmetry). This means that for Ti(III) ion, the ground-state orbital term is 2D which describes a five-fold degeneracy. When the ion is subjected to the electric field, which is produced by the surrounding octahedron of H_2O molecules, the 2D ground-state splits into a lower orbital triplet (T_{2g}) and an excited doublet, E_g . The distortion, Δ , further splits the three-fold level, T_{2g} , into an orbitally two-fold degenerate level, E_g , and an orbitally nondegenerate level, B_{2g} , with the B_{2g} level lying lowest. The sign of the distortion parameter corresponds to a tetragonal environment with D_{4h} symmetry. Finally, the spin orbit interaction leaves three Kramer's doublets in the ground manifold and two in the upper manifold. (see Fig. 7).

In this treatment $|S\rangle$, $|N\rangle$ and $|V\rangle$ represent the spin state, electronic (orbital) state and the lattice and localized vibrational states respectively; $N = 0\rangle$ is the ground electronic state and the lattice refers to the diamagnetic surrounding of the paramagnetic molecules. The Hamiltonian for this system is taken as

$$H = H_0 + \epsilon H_1 + V(t) \quad (41)$$

and

$$H_1 = \tau_l \cdot S + \beta_0 l \cdot H \quad (42)$$

where ϵ is a perturbation parameter, H_1 is a time-independent term, $V(t)$ is a time-dependent perturbation representing the lattice-orbit interaction, $\tau_l \cdot S$ is the spin orbit interaction, $\beta_0 l \cdot H$ is the orbital Zeeman term where β_0 is the Bohr magneton and H is the applied magnetic field. The perturbation scheme used in this evaluation is due to Orbach³². He suggested that only the time-dependent V terms be treated as perturbations and that the stationary states be solved with H_1 in the zeroth order Hamiltonian, i.e., the Hamiltonian is transformed into a form for which the wavefunctions are eigen-functions to second order in H_1 . This transformation also alters the time dependent perturbations which, in turn, induce transitions between $|NSV\rangle$ states. H is transformed³³ by means of a unitary transformation into a new Hamiltonian G where

$$G = \exp(i\epsilon T) H \exp(-i\epsilon T) \quad (43)$$

and T has the form

$$\langle a | T | a' \rangle = i \frac{\langle a | H_1 | a' \rangle}{\Delta \mu_{a'a}} \quad (44)$$

where

$$\Delta \mu_{a'a} = \langle a' | H_0 | a \rangle - \langle a | H_0 | a \rangle \quad (45)$$

for $a' \neq a$. The time dependent part of G is μ where

$$\exp(i\epsilon T) V \exp(-i\epsilon T) = \mu = \mu_0 + \epsilon \mu_1 + \epsilon^2 \mu_2 \quad (46)$$

to second order ϵ . The matrix elements of these time dependent perturbations are then used to compute the transition probability per unit time, i.e., according to second order time dependent transition probability theory³⁴

$$W'' = (a|a') = 2\pi \sum_{a''} \int \left| \frac{\langle a|\mu|a'' \rangle \langle a''|\mu|a' \rangle}{\Delta \mu a'' a} \right|^2 \exp(\mu a a') d\mu a a' \quad (47)$$

where ρ is the spectral density of final states and the expression is to be averaged over the comonomical ensemble. The time dependent terms, V , are the crystal field terms that are linearly dependent upon the lattice mode fluctuation q_i , i.e.,

$$V = \phi \sum a_i \left(\frac{q_i}{r_0} \right) + \phi \sum b_{ik} \left(\frac{q_i}{r_0} \right) \left(\frac{Q_k}{r_0} \right) \quad (48)$$

where a_i and b_{ik} are dimensionless coefficients which are of order unity or smaller; the Q_k 's are molecular (localized) normal coordinates, and the q_i 's are liquid modes which are associated with the fluctuation of intermolecular coordinates in liquid, r_0 is a characteristic intermolecular distance and ϕ is the approximate magnitude of the time-dependent interaction.

$$\phi = \sum_i \left| \left(\frac{\partial V_{\text{cry}}}{\partial q_i} \right)_{r_0} \right| \quad (49)$$

where V_{cry} is the crystal field.

The Raman process depends upon perturbation terms of the form

$$\begin{aligned} \langle 0SV|U_1|OS \pm 1, V' \rangle = \sum_{V''} \left(\frac{\langle 0SV|U_1|N'' S \pm 1, V'' \rangle \langle N''V''|U_0|OV' \rangle}{\Delta\mu_{N''O} \pm \omega_0 + \omega_{V''V}} \right. \\ \left. + \frac{\langle 0V|U_0|N''V'' \rangle \langle N''SV''|U_1|OS \pm 1, V' \rangle}{\Delta\mu_{N''O} + \omega_{V''V}} \right) \end{aligned} \quad (50)$$

where $\omega_{V''V} = \mu_{V''V} \Delta$ (51)

The matrix elements for μ_0 and μ_1 result from operating on V with the unitary transformation, i.e., upon expanding $\exp(i\epsilon T)$

$$\left(1 + i\epsilon T + \frac{(i\epsilon T)^2}{2} \right) V \left(1 - i\epsilon T + \frac{(i\epsilon T)^2}{2} \right) = U \quad (52)$$

where $\langle a|U_0|a' \rangle = \langle a|V|a' \rangle$ (53)

and $\langle a|U_1|a' \rangle = -\Delta^{-1} \sum_{a''} \left(\frac{\langle a|H_1|a'' \rangle \langle a''|V|a' \rangle}{\mu_{a''a}} \right.$ (54)

$$\left. - \frac{\langle a|V|a'' \rangle \langle a''|H_1|a' \rangle}{\mu_{a'a''}} \right)$$

Upon making the appropriate substitution for $|a \rangle$, V and H_1 Eqs. (53) and (54) may be written as

$$\langle N, V|U_0|N', V' \rangle = \phi \sum_i \langle N|a_i|N' \rangle \langle V|\frac{qi}{r_0}|V' \rangle \quad (55)$$

and

$$\begin{aligned}
 \langle NSV | U_1 | N', S \pm 1, V' \rangle &= \frac{\lambda}{\Delta} \phi \sum \langle V | \frac{a_i}{r_0} | V' \rangle \\
 &\times \left[\frac{\langle NS | 1.S | N'' S \pm 1 \rangle \langle N'' | a_i | N' \rangle}{\mu_{N''N} + \mu_{S \pm 1, S}} \right. \\
 &\left. - \frac{\langle N | a_i | N'' \rangle \langle N'' | 1.S | N'' S \pm 1 \rangle}{\mu_{N'N''} + \mu_{S \pm 1, S}} \right] \quad (56)
 \end{aligned}$$

Substituting these matrix elements into Eq. (50) while making use of the following relations and definitions ($\langle NS | 1.S | N' S \pm 1 \rangle = -\langle N'S | 1.S | NS \pm 1 \rangle$; $\langle N | a_i | N' \rangle = \langle N' | a_i | N \rangle$; $|V\rangle = |V_i V_j\rangle$; $|V'\rangle = |V_i + 1, V_j - 1\rangle$; $|V''\rangle = |V_i + 1, V_j\rangle$ or $|V''\rangle = |V_i, V_j - 1\rangle$; where $\omega_{V''V} = \omega_i$ or $\omega_{V''V} = -\omega_j$) yields

$$\begin{aligned}
 \langle 0 S | U_1 | 0, S \pm 1 \rangle &= \frac{\lambda \phi^2}{\Delta^3} \langle V_i | \frac{a_i}{r_0} | V_i + 1 \rangle \langle V_i | \frac{a_i}{r_0} | V_j - 1 \rangle \\
 &\times \left[\left(D^{(\pm ij)} - D^{(\pm ji)} \right) (\omega_i + \omega_j) \pm \left(D^{(\pm ij)} \right. \right. \\
 &\left. \left. + D^{(\pm ji)} \right) \omega_0 \right]
 \end{aligned}$$

where

$$\begin{aligned}
 D^{(\pm ij)} &= \sum_{N', N''} \left[\frac{\langle 0S | 1.S | N'S \pm 1 \rangle \langle N' | a_i | N'' \rangle \langle N'' | a_j | 0 \rangle}{\mu_{N'0} \mu_{N''0}^2} \right. \\
 &\left. + \frac{\langle 0 | a_i | N' \rangle \langle N'S | 1.S | N''S \pm 1 \rangle \langle N'' | a_j | 0 \rangle}{\mu_{N'N''} \mu_{N''0}^3} \right]
 \end{aligned}$$

The transition probability for the Raman process can now be evaluated with the aid of Eqs. (47) and (57) however, something must first be said about the spectral density function in Eq. (47). The approach of a neighboring molecule in liquids give rise to polarization effects which cause changes in the electric field within the paramagnetic molecule. The polarization is determined by the time dependent q_i 's which in turn depend upon the translational fluctuations of the molecules in the liquid. It is assumed, therefore, that the correlation function $\langle q_i(t) q_i(0) \rangle$ is of the form

$$\langle q_i(t) q_i(0) \rangle = q_o^2 \exp - \left(\frac{|t|}{\tau_e} \right) \quad (59)$$

where τ_c is a correlation time and q_o is a typical root-mean-square value of q_i . The spectral density is obtained by taking the Fourier transform of the correlation function and dividing by q_o^2 . The results yield

$$\rho(\omega) = \left(\frac{2}{\pi} \right) \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} \right] \quad (60)$$

In liquids the Raman process is negligible compared to the other processes unless $\omega_o^2 \tau_c^2 \ll 1$. Utilizing this information and the expression for $\rho(\omega)$ along with Eqs. (47) and (57) yields

$$\frac{1}{T_{1e}} = \frac{1}{T_{2e}} = W = 32 \left(\frac{\lambda}{\Delta} \right)^2 \left(\frac{\phi q_o}{\Delta r_o} \right)^4 \tau_c^{-1} \quad (61)$$

where the sum over D^2 in Eq.(58) has been set equal to unity. For comparison the expressions for the other eff mechanisms are presented.

The Van Vleck direct process is given by

$$W = 64 \left(\frac{\tau}{\Delta} \right)^2 \left(\frac{\phi_{q_o}}{\Delta r_o} \right)^2 \left[\frac{(\omega_o \tau_c)^2 \tau_c^{-1}}{H_{\omega_o}^2 \tau_c^2} \right] \quad (62)$$

and the Orbach process is given by

$$W = 16 \left(\frac{\tau}{\Delta} \right)^2 \left(\frac{\phi_{q_o}}{\Delta r_o} \right)^2 \left(\frac{\Delta}{\delta_{on}} \right)^2 \left[\frac{\tau_c^{-1}}{\left[\exp \frac{k \delta_{on}}{kt} - 1 \right]} \right] \quad (63)$$

where λ is the spin orbit coupling constant; Δ is the energy of the lowest excited orbital state coupled to the orbital ground state by the spin orbit coupling interaction; $-\frac{\phi_{q_o}}{r_o}$ is the amplitude of the time-dependent electric field potential; δ_{on} is the energy of the lowest excited electronic state above the ground state and τ_c is a mean correlation time for intermolecular fluctuation.

As was said earlier, the Van Vleck Raman process is appreciable only if $\omega_o^2 \tau_c^2 \ll 1$. In this case the Van Vleck Direct process can be ruled out as a possible relaxation mechanism since Eq. (64) is field dependent if $\omega_o^2 \tau_c^2 \ll 1$. The experimental data for the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ system indicates that $T_{1e} = T_{2e}$ is not field dependent. The Orbach process is also ruled out for the present system because of its large temperature dependence relative to the Van Vleck-Raman process. In the Direct process a spin is flipped by a phonon of equivalent energy. The Raman process describes the process of phonon induced spin flipping by a phonon of arbitrary energy provided a second phonon of higher or lower energy than the first is emitted so that the total energy including that of spin is conserved. The Orbach process is similar to the Direct process except that the spin flip is accompanied by the

simultaneous excitation of the electronic state.^{32, 35}

Equations (61)(62) and (63) can't be used quantitatively because of the difficulty in the evaluation of certain parameters. (e.g. the electronic correlation time for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ remain unknown due to the inability to evaluate the amplitude of the time-dependent electric field potential, $\frac{\phi_0}{r_0}$). Kivelson expects $\frac{\phi_0}{r_0}$ to be of the order of observed solvent induced shifts in the visible spectra. He also suggests that τ_c can be related to the correlation time that enters into expressions for infrared and Raman vibrational relaxation, however, this is all highly theoretical and no real information is to be obtained from these relations. On the other hand, Eqs. (61)(62) and (63) can be used to provide qualitative information concerning the magnitude of the eff effects and definite information concerning the frequency and temperature dependencies of the various processes.

The value estimated for T_{1e} from Eq. (61), the Raman expression, is of the same order of magnitude as the values which were estimated from the NMR and EPR experiments. From the EPR and NMR experiment it was concluded that $T_{1e} \approx 2.0 \times 10^{-11}$. Therefore, τ_c can safely be assured to be on the order of 10^{-13} since $\tau_c \ll T_{1e}, T_{2e}$. This would mean that $\omega_0^2 \tau_c^2 \ll 1$, which is the condition of validity for the Raman process relative to the other eff processes. The most important information, for the present work, resulting from the Raman process is the temperature dependence of T_{1c} . All the mechanisms of electron spin relaxation involving the rotational or tumbling motion of the molecular yields

$$T_{2m} \propto \frac{1}{T_{1e}} \propto \tau_c \propto \frac{\eta}{T}$$

which means that T_{2m} should have a positive slope when plotted vs $\frac{\eta}{T}$.

The opposite temperature dependence was observed experimentally in the present system and the opposite temperature dependence is predicted by the Raman process, i.e.,

$$T_{2m} \propto \frac{1}{T_{le}} \propto \frac{1}{\tau_c}$$

The T_{2m} slope (See Fig. 6) is not as steep as an $\frac{\eta}{T}$ plot would predict. This is further evidence that τ_c is not a rotational correlation time.

The temperature dependence and the order of magnitude estimates for T_{le} imply that the Raman process is appreciable for electronic relaxation in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. Morgan and Lewis³⁶ also felt that the Raman process might be important for the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ system. They felt that due to the inverse sixth power dependence on Δ (see Eq. (61)) the Raman process could be important in solutions of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and similar ions where Δ approximately equals 10^3 cm^{-1} . It should be pointed out that the present work provides the first reported experimental evidence for the Van Vleck-Raman process in solution.

D. Summary

The NMR experimental curve in Fig. 1 can now be successfully resolved since the temperature dependence of T_{2m} can be accounted for by means of the Van Vleck-Raman process. Resolution of the experimental curve gives three straight lines as shown in Fig. 8. This information along with the bulk and bound water chemical shift measurements give the kinetic parameters presented in Table 1. The value of the first order rate constant, k_f , is consistent with the correlation of exchanging waters made by Connick and Neely³⁷. Their correlation is based on an electrostatic model which relates the first order rate constant for the water-water exchange to the charge and ionic radii of

the metal ion. The temperature dependent bulk and bound water chemical shift measurements yield a value of six for the coordination number of Ti(III) over the temperature range covered.

In the low temperature region, the bulk water NMR observations indicate that the linebroadening is being controlled by the lifetime of the water molecules in the first coordination sphere of Ti(III) whereas in the high temperature region, the data indicate that the broadening is being controlled by the rate of transverse relaxation. Experimental evidence shows that the transverse relaxation is a consequence of both scalar coupling and $\Delta \omega$ mechanism. The scalar coupling interaction is interpreted as being interrupted by T_{1e} of the paramagnetic electron where the electron is being relaxed by the Van Vleck-Raman process, an electric field fluctuation, eff, mechanism.

Besides determining the kinetic parameters for the water-water exchange this work also indicates that NMR observation of the frequency and temperature dependence of the bound water linewidth can be used for evaluation and separation of the various eff mechanism relative to other electronic relaxation mechanism involving the rotational or tumbling motions of the molecules. Evidence is also presented in this work for the observation of three species which were previously thought to exist in aqueous solutions of Ti(III) i.e., the hydrous oxide $Ti_2O_3 \cdot n H_2O$ ³⁸ (See Appendix 1-A), the titanyl ion³⁹ and the hexahydrate.⁴⁰

APPENDIX

A. Titanyl ion

The instrumentation for the O^{17} NMR investigation described below is given in Section III part B. Oxygen 17 NMR experiments which were performed on an aqueous system that was 1M in $TiCl_3$ containing some $Ti(IV)$ and ca. 5M in HCl gave partially resolved assymetric signals in the temperature region (+) $2^\circ C$ to (-) $30^\circ C$ (See Section IV part C and Fig. 9). The modulation amplitude was lowered by a factor of 100 in order to further separate out the effect of the smaller signal which is obviously saturated at any power which might be required to observe the bound water signal.

The overlapping signals responsible for the assymetry result from first coordination sphere O^{17} waters of $Ti(III)$ and from O^{17} waters in a completely different type of environment. The symmetric part of the signal always occurs at high field and the assymetric part always occurs at lower field (these shifts are measured with respect to pure H_2O^{17} resonance, see Fig. 9). The bound water O^{17} resonance of $Ti(III)$ occurs at high fields since, after donating an electron to the paramagnetic ion, its remaining electron is aligned against the direction of the gross magnetic field. On the other hand, the other signal must result from a diamagnetic species since its resonance occurs downfield with respect to the bound water resonance. A spectrochemical analysis of the sample showed no evidence of any non-titanium species capable of producing the downfield resonance. In fact, the sample was virtually pure in titanium which indicates that the extraneous O^{17} NMR signal must be associated with a different species of titanium e.g., $Ti(IV)$. $Ti(IV)$ might produce a large shift if it is double bonded to the O^{17} nucleus, i.e., has a $Ti = O$ bond. The only established compound with a $Ti = O$ bond is

$\text{Ti O}(\text{AcAc})_2$ as there appears to be no previous proof of for the existence of a titanyl ion, TiO^{2+} .

Other investigations were carried out in order to verify the interpretation that the downfield shift is due to Ti(IV) . This verification can be made by investigating a H_2O^{17} sample which only contains Ti(IV) e.g. Ti Cl_4 . Such a sample gave two separate resonances, the bulk (not bound) water resonance and another resonance shifted $10,000 \pm 500$ CPS downfield. The downfield resonance position of the Ti(IV) and above Ti(III) samples appeared to coincide exactly when compared to the bulk water signal. Consequently, this new scalar coupling constant must correspond to a completely different environment, presumably that of the TiO^{2+} ion.

B. Hexahydrate and Hydroxy Species

All EPR spectra were taken on a Varian V-4502 X band EPR spectrometer (9.5 GHz), with a magic tee microwave bridge, a nine inch magnet, a Fieldial magnetic field regulator and 100 KHz field modulation. A standard Varian rectangular cavity was operated in the TE_{102} mode. Magnetic fields were measured using a Harvey Wells model 0-502 oscillator and a proton probe positioned in the magnet next to the EPR cavity. The microwave frequency was measured on a Hewlett-Packard electronic counter (HP 52446) with a HP 5255A plug-in (3-12.4 GHz).

A quartz flat cell containing the sample was positioned so as to obtain the highest possible cavity Q. The sample was kept at room temperature by passing a stream of air through the cavity. The ratio of the resonant frequency to the full width at half height of the cavity dip (with sample in place) was 200. The strength of the modulating field was about 20 gauss and a 250 milliwatt klystron was used

to provide the unattenuated output. The region from 0 to 10,000 gauss was swept slowly with a recorder time constant of one second. Four Ti(III) sample were investigated and appeared to have the same linewidth even though the signal to noise ratio was not high enough to locate the peaks exactly. Linewidth measurements give $\Delta H = 2400 \pm 200$ gauss (See Table II). Effects such as exchange broadening by Ti(III) and complexation by Cl^- and OH^- were ruled out since the linewidth didn't appear to be a function of these ions (See Table 2).

It should be pointed out that a second signal appeared as an artifact on the broad signal. Sensitivity considerations indicated that it arose from a minor species whose concentration was less than 1% of the major species i.e., the hexahydrate. The minor species was believed to be a hydroxy species hence, EPR investigations, using the same instrumental settings as for the hexahydrate experiment, were performed on a TiCl_3 sample whose H^+ ion had been neutralized by Na_2CO_3 (see sample E, Table 2). The sample gave a strong narrow signal, 30 ± 1 gauss wide with a g value the same as that of the minor species; the g value for the hydroxy species is $1.960 \pm .002$. This species is not important when considering the very broad signal associated with the hexahydrate.

EPR investigations, again using the same instrumental settings as for the hexahydrates, were also performed on a sample of 0.1 M $\text{Fe}(\text{ClO}_4)_3$ in order to provide an estimate for the number of titanium producing the 2400 gauss signal. The results of the $\text{Fe}(\text{ClO}_4)_3$ experiment yield a ca. 950 gauss wide signal with a signal to noise ratio of about 50. The following equation, which relates the number of spins to various parameters such as the instrumental conditions, the spin system's environment (e.g. temperature) and its characteristics (e.g.

linewidth), is used in conjunction with the information from the $\text{Fe}(\text{ClO}_4)_3$ EPR experiment.

$$\frac{N^A}{N^B} = \left(\frac{D^A}{D^B} \right) \left(\frac{g^B}{g^A} \right) \left(\frac{S^B(S^B + 1)}{S^A(S^A + 1)} \right) \left(\frac{\Delta H^A}{\Delta H^B} \right) \left(\frac{\Lambda^A}{\Lambda^B} \right) \left(\frac{H_{\text{mod}}^B}{H_{\text{mod}}^A} \right) \left(\frac{Y^A}{Y^B} \right) \quad (36)$$

where A stands for Fe^{3+} and B for Ti^{3+} . D is a multiplicity factor which takes into account hyperfine components. Since there are no hyperfine components for Fe(III) and Ti(III) the ratio $\frac{D^A}{D^B}$ will be taken as unity. g represents the gyromagnetic ratio and is equal to 2 for Fe(III). The value of 2 will also be assumed for Ti(III). S is the spin quantum number and is equal to 5/2 and 1/2 for Fe(III) and Ti(III) respectively. ΔH is the linewidth and is ca. equal to 950 gauss for the Fe(III) sample and ca. 2400 for the Ti (III) sample. Λ is the line shape and is lorentzian in both cases such that $\frac{\Lambda^A}{\Lambda^B} = 1$. H_{mod} is the modulation frequency and is the same for both experiments. Y^A is the signal to noise ratio for Fe^{3+} and is equal to 50. The signal to noise for Ti^{3+} is also about 50. N^A and N^B are the number of Fe^{3+} and Ti^{3+} ions respectively. The observed Ti(III) to Fe(III) signal amplitude ratio is ca. 1.2 where the signal height equals the gain times the signal to noise ratio. Solving Eq. (36) for the signal amplitude ratio of $\frac{\text{Ti}^{3+}}{\text{Fe}^{3+}}$ gives ca. 1.4. This indicates that approximately 90% of the the titaniums are producing the 2400 gauss signal.

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Table I. Parameters calculated from Fig. 8 for exchange of water from the first coordination sphere of Ti(III).

Quantity	Value
$k_f(\text{sec}^{-1} \text{ at } 298^\circ\text{K})$	7.92×10^{-6}
$\Delta H^\ddagger$ (K cal)	7.7
$\Delta S^\ddagger$ (eu)	-9
$\frac{A}{h}$ (CPS)	5.47×10^6
T_{1e} (sec at 298)	2.0×10^{-11}

Table II. EPR linewidths of Ti(III) solutions at 9.5 GHz

solution	[Ti ³⁺]	[H ⁺]	[Cl ⁻]	ΔH gauss
A	1.0	2.33	5.33	2400 ± 400
B	0.5	1.16	2.66	2400 ± 400
C	0.5	1.16	5.33	2400 ± 400
D	0.5	2.33	5.33	2400 ± 400
E	0.5	excess [H ⁺] neutralized	2.66	30 ± 1

Table III. $P_{m 2p} T$ as a function of temperature at 8.134 MHz

$10^3/T^{\circ}K$	$P_{m 2p} T \times 10^5$ Rad/sec
3.814	6.201
3.729	4.640
3.692	4.125
3.667	3.902
3.634	3.682
3.571	3.530
3.519	3.535
3.464	3.586
3.427	3.733
3.392	3.839
3.313	4.411
3.210	6.286
3.010	10.010

$[Ti^{3+}] = [H^+] = 1.01 \times 10^{-1} M$; Marianelli's⁴⁰ reported values for T_2 of H_2O^{17} were used as the water blank in all T_{2p} evaluations.

Table IV. P_{m2p}^T as a function of temperature at 6.085 MHz

$10^3/T^{\circ}K$	$P_{m2p}^T \times 10^5 \text{ rad/sec}$
3.646	5.232
3.599	5.149
3.528	5.375
3.501	5.589
3.454	5.924
3.407	6.221
3.280	7.818
3.205	8.920
3.133	10.020

$$[Ti^{3+}] = [H^+] = 1.01 \times 10^{-1} M$$

Table V. $P_{m2p} T$ as a function of temperature at 4.337 MHz

$10^3/T^{\circ}K$	$P_{m2p} T \times 10^5 \text{ rad/sec}$
3.643	6.421
3.592	6.891
3.531	7.322
3.451	7.960
3.392	8.579
3.370	8.946
3.295	9.732
3.224	10.67
3.103	12.32

$[Ti^{3+}] = [H^+] = 1.01 \times 10^{-1} M$

Table VI. $P_{m2p} T$ as a function of temperature at 1.999 MHz

$10^3/T^{\circ}K$	$P_{m2p} T \times 10^5 \text{ rad/sec}$
3.682	8.512
3.654	9.181
3.637	8.923
3.544	9.514
3.501	9.986
3.419	10.27
3.312	10.76
3.288	10.84
3.213	11.93
3.101	11.89
3.101	12.91
2.998	12.62
2.908	12.97
2.832	13.02

$[Ti^{3+}] = [H^+] = 1.01 \times 10^{-1} M$

Table VII. T_{2m} as a function of temperature at 8.134 MHz

$10^3/T^{\circ}K$	$T_{2m} \times 10^5 \text{ rad/sec}$
3.612	15.48
3.741	15.01
3.780	13.79
3.852	14.25
3.932	12.76
3.994	13.27
4.068	12.42
[Ti ³⁺] $\approx$ 1M; [H ⁺] $\approx$.5M	

Table VIII. $\Delta \omega_m$ as a function of temperature at 8.134 MHz

$10^3/T^{\circ}K$	$\frac{P_m T_{2p}}{2} \times 10^5 \text{ rad/sec}$
3.612	5.781
3.778	6.683
3.855	6.695
3.916	6.391
4.006	10.692

$[Ti^{3+}] \approx 1M; [H^+] = .5M$

Table IX. $\Delta \omega_{\text{H}_2\text{O}}$ as a function of temperature at 8.134 MHz

$10^3/T^\circ\text{K}$	$\Delta \omega_{\text{H}_2\text{O}} \times 10^{-2} \text{ rad/sec}$
3.009	16.51
3.101	17.24
3.182	17.14
3.268	15.73
3.379	14.29
3.452	11.02
3.521	9.22
3.589	7.33
3.660	4.31

$[\text{Ti}^{3+}] = 3.255 \times 10^{-2} \text{M}; [\text{H}^+] = 3.02 \times 10^{-1} \text{M}$

FIG.1 $P_M T_{2p}$ VS. $10^3/T$ AT 8 MHz.

XBL 715-6718

FIG. 2 CHEMICAL SHIFT OF BULK WATERS.

XBL715-6719

FIG. 3 CHEMICAL SHIFT OF BOUND WATERS.

XBL715-6720

FIG. 4 T_{2p} AT VARIOUS FREQUENCIES VS. $10^3/T$.

XBL715-6721

FIG. 5 T_{2M}' 'S TEMPERATURE DEPENDENCE AT 8 MHz.

XBL715-6722

FIG. 6 T_{2m} AT VARIOUS FREQUENCIES VS. $10^3/T$.

XBL715-6723

FIG. 7 CORRELATION DIAGRAM FOR d^1 IN A TETRAGONAL FIELD:

- (a) OCTAHEDRAL FIELD
- (b) WITH TETRAGONAL DISTORTION
- (c) AND SPIN-ORBIT COUPLING

XBL 715-6724

FIG. 8 $P_M T_{2p}$ VS. $10^3/T$ AT 8 MHz.

XBL715-6725

FIG. 9 NMR signals in Ti(III) solutions containing some Ti(IV)

XBL715-6756

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