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# RATE OF ELIMINATION OF WATER MOLECULES FROM THE FIRST COORDINATION SPHERE OF PARAMAGNETIC CATIONS AS DETERMINED BY NUCLEAR MAGNETIC RESONANCE MEASUREMENTS OF $O^{17}$

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## ABSTRACT

The $O^{17}$ nuclear magnetic resonance spectra of solutions with various concentrations of paramagnetic ions have been studied. Values for the transverse relaxation time, $T_2$, have been calculated from the line-width broadening. Chromic ion is much less effective than the other cations in shortening $T_2$, which is consistent with the theory that relaxation occurs in the first coordination sphere of all the cations studied except with chromic ion.

Lower limits for the rates of exchange of bulk water molecules with those in the first coordination sphere of the cations are calculated. The order of decreasing first-order rate constants is $Mn^{++} > Cu^{++} > Co^{++} > Ni^{++} > Fe^{+++}$.

Saturation experiments on various solutions of paramagnetic ions indicate that $T_1$ increases with increasing concentration of paramagnetic cation in some cases.

A study of the effect of pH on $T_2$ values shows that within experimental accuracy there exists no dependence on pH over the range 0.9 to 10.5.

# I. INTRODUCTION

When a nucleus with spin I possessing angular momentum $I\hbar$ and magnetic moment $\mu$ is placed in a magnetic field ($H_o$), the normally degenerate (2I + 1) quantized Zeeman energy levels are distributed at equilibrium according to the Boltzmann factor. If we picture the nuclei as small bar magnets which attempt to align themselves with the magnetic field -- each nucleus having two possible orientations -- then the ratio of the population in each orientation is given by

$$\frac{N_{(+1/2)}}{N_{(-1/2)}} = \frac{\exp\left[-U_{(1/2)}/kT\right]}{\exp\left[-U_{(-1/2)}/kT\right]} \cong 1 + 2\mu\,\frac{H_o}{kT}\,, \qquad (1)$$

where $U_{(1/2)}$ is the energy of the nuclei in the lowest energy state, k is Boltzmann's constant, and T is the equilibrium temperature. We can see that there will be a slight excess of nuclei in the lower state, giving a net nuclear magnetization. Alignment of the nuclei is opposed by thermal agitation. The system of nuclei will, however, gradually come to equilibrium by interacting with the surroundings or "lattice," i.e., by transferring energy to it. The time taken for this "relaxation" is called the spin-lattice or longitudinal relaxation time, $T_1$.[1]

Nuclei, when subjected to a large magnetic field, will precess around the field axis with frequency $\omega_o$. If a smaller oscillating field $H_1$ is introduced perpendicularly to the larger stationary field so that a magnetic field vector rotates with angular velocity $\omega_o$, there will be a magnetic torque exerted on the precessing nuclei. This will tend to flip the nuclei from one orientation to another, thus transferring energy. Measurement of the absorption of energy can be used to detect the nuclei.

The width of the observed resonance is determined by the lifetime of the coherence of the observed signal in the plane perpendicular to the strong magnetic field. This lifetime, $T_2$, is controlled by a variety of processes such as spin-spin exchange, quadrupole coupling, and variations in the local magnetic field.[2] For the nucleus of interest in the present work, $O^{17}$, having a nuclear spin of 5/2, the quadrupole coupling effect is probably responsible for the observed $T_1$ and $T_2$ relaxation times when the $O^{17}$ is present in pure water.

Bloch[1] has derived the equation for the absorption signal on the assumption that the transverse components of magnetization in the absence of an external influence decay exponentially with a decay constant $T_2$. The result is given by

$$\text{Absorption} \propto \frac{\gamma H_1 T_2}{1 + (\Delta\omega T_2)^2 + (\gamma H_1)^2 T_1 T_2} , \qquad (2)$$

where $\Delta\omega = \omega_o - \omega$. For low values of $H_1$, it may be shown that the half-width at half-maximum intensity occurs when $T_2(\omega_o - \omega) = 1$.

The addition of paramagnetic ions to an aqueous solution will alter the effective magnetic field, thus affecting the relaxation of nuclei already in the solution.

The effect of paramagnetic ions on the transverse relaxation time has been used by McConnell and Berger[3] to predict the reaction rate for certain fast chemical reactions involving both paramagnetic and diamagnetic species of a given nucleus. Under certain conditions, the rate of the reaction

$$D + P^* \rightleftharpoons P + D^*$$

may be found from

$$k = \frac{1}{(P)} \left[ \frac{1}{(T_2)_{DP}} - \frac{1}{(T_2)_D} \right] \tag{3}$$

where D and P are the diamagnetic and paramagnetic species respectively, k is the bimolecular rate constant, $(T_2)_{DP}$ is the transverse nuclear relaxation time in a mixture containing D and P, $(T_2)_D$ is the transverse nuclear relaxation time of the diamagnetic species for (P) = 0, and (P) is the concentration of paramagnetic species.

The sufficient conditions for the validity of this equation are: (a) $\tau_D \gg \tau_P$, (b) $(\delta\omega\tau/2)^2 \gg 1$, and (c) $(T_2)_D \gtrsim \tau_D$, where $\tau_D$ and $\tau_P$ are the average lifetimes in the diamagnetic and paramagnetic environments, respectively, $\tau$ is the lifetime of a particular paramagnetic state, and $\hbar\,\delta\,\omega$ is the energy of the magnetic hyperfine interaction between the paramagnetic species and the observed nucleus. As noted by Connick and Poulson,[4] the second condition is more rigid than necessary and may be replaced by $(\delta\omega^2\tau\tau_P)/4 \gg 1$. If the broadening arises from a $T_1$ effect, the necessary condition (b) is replaced by $2(T_1)_P \ll \tau_P$.[3,4]

In the present experiment, we may consider the paramagnetic species to be that in which the water molecule is next to the paramagnetic ion, and the diamagnetic species to be the free water molecules in the bulk of the solution. Thus from a measurement of $T_2$ values we may calculate the rate of exchange of water molecules near paramagnetic ions provided the above conditions can be fulfilled. However, since in this case $\delta\omega$, $\tau$, and $\tau_P$ are not known, we may calculate only a lower limit for the rate constant.[4]

## A. Sideband Technique for the Measurement of Relaxation Times

The theory of the sideband technique has been developed and used in high-resolution nuclear magnetic resonance (NMR) spectroscopy by Primas[5] and Vladimirski.[6] Recently the theory has been adapted and applied to the lower resolution studies of wide-line NMR spectra.[7] Solving the Bloch macroscopic equations of motion by integration and expansion in Fourier series gives an equation for the resonance signal of the $n^{th}$ harmonic of the induction signal:

$$F_n(t) = \frac{-|\gamma| H_1 M_o (T_2 - i\, T_2^2\, \Delta_n\omega)\left(\frac{2n}{\beta} J_n^2(\beta) e^{-i\omega_m t} + 2iJ_n(\beta) J_{n-1}(\beta) \sin \omega_m t\right)}{1 + T_2^2\, (\Delta_n\omega)^2 + \gamma^2 T_1 T_2\, J_n^2\, (\beta)\, H_1^2} \qquad (4)$$

where standard notation of NMR induction literature has been used and $\omega_m$ and $H_m$ are the modulation frequency and amplitude respectively. Here $\Delta_n\omega = \Delta\omega + n\omega_m$, $\Delta\omega = |\gamma|\, H_o - \omega$, $\beta = \frac{|\gamma|\, H_m}{\omega_m}$, and $J_n$ and $J_{n-1}$ are Bessel functions of the first class generated upon Fourier expansion of the induction signal.

When this signal is mixed in the lock-in detector with a reference signal, and the phase of the reference signal is adjusted to zero, we see the first sidebands (i.e., n = 1):

$$F_{\pm 1}(0) = \mp 2\, \frac{J_1^2\, (\beta)}{\beta} \cdot A \cdot \frac{|\gamma|\, H_1\, M_o\, (T_2 - i\, T_2^2\, \Delta_{\pm 1}\omega)}{1 + T_2^2\, (\Delta_{\pm 1}\omega)^2 + \gamma^2 H_1^2 T_1 T_2 J_1^2(\beta)}\,, \qquad (5)$$

where A is a constant depending on the machine characteristics. It can be shown[7] that the sideband method gives a somewhat more favorable signal to noise ratio than the derivative method under similar operating conditions.

## B. Measurement of $T_1$

Under slow passage conditions, the usual expression for the absorption-resonance signal may be modified to:

$$\text{absorption} = \text{constant } N \left( \frac{I+1}{I} \right) \left( \frac{\mu^2 H_o^2}{3kT} \right) \left( \frac{\gamma^2 H_1 J_1^2(\beta) T_2 \beta^{-1}}{1 + T_2^2(\Delta_{\pm 1}\omega)^2 + \gamma^2 H_1^2 J_1^2(\beta) T_1 T_2} \right) \tag{6}$$

where N is the number of nuclei in the active volume of the receiver coil, and $(\Delta_{\pm 1}\omega)$ is the angular frequency displacement from the resonance peak. As $H_1$ increases, the absorption first increases and then decreases. Thus for large values of $H_1$, at the absorption peak (i.e., when $\Delta_{\pm 1}\omega = 0$), the term $\gamma^2 H_1^2 J_1^2 (\beta) T_1 T_2$ is dominant and we have absorption = constant $1/H_1 \beta T_1$. The maximum value of the absorption peak occurs when $\gamma^2 H_1^2 J_1^2 (\beta) T_1 T_2$ is unity. For this condition, one need know only $T_2$ and the $H_1$ field to calculate $T_1$. This value of $H_1$ may be determined by recording spectra at various radiofrequency powers until the amplitude of the absorption peak has reached a maximum and begun to decline. Then, by measuring these amplitudes and the sideband separation, the effective $H_1$ field in each case can be determined, since:[8]

$$\Delta = 2(\omega_m^2 - \gamma^2 H_1^2)^{1/2} , \tag{7}$$

where $\Delta$ is the sideband sepration, $\omega_m$ is the modulation frequency (400 cps), $\gamma$ is the magneto-gyric ratio, and $H_1$ is the measured $H_1$ field.

Although the relative effectiveness of paramagnetic ions in producing relaxation of protons[2] and chlorides[9] has been reported, little work has been done in similar studies of $O^{17}$. For paramagnetic cations, the observation of $O^{17}$ resonance assures that water molecules are entering

and leaving the first coordination sphere, whereas proton relaxation may involve the exchange of protons as well as water molecules. This study was undertaken to clarify and extend those begun on the exchange rates of water molecules in solutions of paramagnetic ions[4] and to gain more insight into the relaxation of $O^{17}$ in these solutions.

# II. EXPERIMENTAL

## A. The Nuclear Magnetic Resonance Spectrometer and Methods of Measuring Relaxation Times

For all resonance measurements, a wide-line nuclear magnetic resonance (variable frequency) spectrometer (Varian Associates model V-4200) was used with a 12-inch electromagnet. The operating frequency for all but the final cobalt experiments was set at 5.77 Mc corresponding to a field approximating 10 kgauss for the $O^{17}$ nuclear resonance. For the final cobalt experiments, a frequency of 5.44 Mc was used, corresponding to a field approximating 9.4 kgauss.

The frequency of the sweep oscillator was 400 cps and the sweep amplitude was approximately 0.9 gauss. For the saturation experiments, the radio-frequency power was increased from the non-saturating value of around 0.05 gauss to about 0.25 gauss.

The sideband technique was used in all measurements, and the phasing of the audio-amplified voltage delivered to the synchroverter phase detector was carefully tuned so that only the first sidebands were detected.

The time constant of the integrating filter was set at 0.64 sec, and the polarizing magnetic field ($H_o$) was scanned at a sweep speed of 1 rpm.

In all resonance measurements the sample holders were 15-by 125-mm pyrex tubes, fitted with ground-glass jointed caps. Sample tubes were held firmly in place in the sample holder by a Teflon adapter. The sample size used was 4 ml.

Samples were prepared by weighing the enriched water sample, adding a small volume of concentrated stock solution whose specific gravity had been measured, and reweighing the sample. In the earlier measurements the

samples were then degassed on a high-vacuum line and the sample tube refilled with $N_2$ in an effort to prevent dissolved oxygen in the water from broadening the resonance. However, it was later found that any additional oxygen present was not enough to cause measurable broadening, and the degassing technique was abandoned.

The $T_2$ measurements were all taken at the same rf power setting, where no saturation was occurring. The saturation measurements were made by increasing the rf power until the spectrum peak height reached a maximum and began to decrease.

Resonance shifts were measured by calibrating various positions of the scanning helipot at different points between the two first sideband peaks for a pure enriched water sample, and then comparing these with the scanning helipot positions for the solution containing the paramagnetic ion.

Since the supply of enriched water was not large, the solutions containing the paramagnetic ions were distilled on a high-vacuum line in the following manner. The sample to be distilled (A in Fig. 1) was frozen with liquid nitrogen. The whole system was then pumped down to several microns pressure and the sample was allowed to melt at room temperature. A small vacuum flask was placed under tube B and filled with liquid nitrogen until its level was just below the narrow evacuation tube. The sample in A then distilled into tube B while tube A was kept at room temperature. Tube A was warmed by placing a beaker of lukewarm water beneath it. When most of the liquid had distilled (97.5%), the liquid-nitrogen flask was removed and the distilled ice melted. At this point in earlier distillations, dried nitrogen was allowed into the system through valve C. This later proved unnecessary, so the pressure in the system was then increased by merely opening stopcock C to the air slowly.

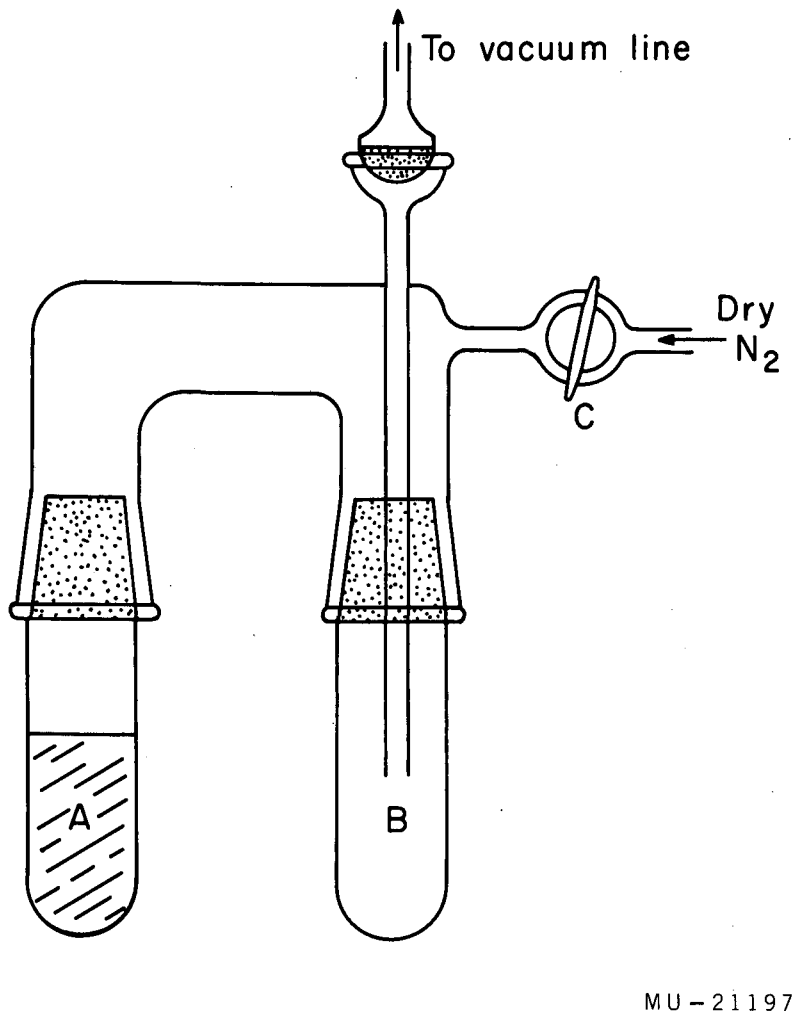


Fig. 1. Apparatus for distillation of enriched water sample.

## B. Chemical Reagents and Analyses

The preparations and analyses of the stock solutions are given below. G. Frederick Smith reagent-grade chemicals were used unless otherwise stated.

### Enriched Water

Ten milliliters of water were obtained from the Weizmann Institute of Science. The sample containing 0.7% $O^{17}$ and enriched in $D_2O$ was distilled on a high-vacuum line. To 4 ml of this water enough $HClO_4$ was added to make the solution 0.1 M in acid. The remainder of the sample was used to make up the solutions of paramagnetic ions. In every case, except for chromic perchlorate, the $O^{17}$ enriched samples of paramagnetic salts contained 0.1 M $HClO_4$.

### $HClO_4$

Mallinckrodt 70-72% reagent grade acid was used.

### $Co(ClO_4)_2$

The $Co(ClO_4)_2 \cdot 6H_2O$ was dissolved in distilled water to make an approximately 2 M stock solution. Part of this solution was then diluted to give a second stock solution of approximately 1.6 M. These solutions were then analyzed colorimetrically by comparing their spectra with a standard $CoCl_2$ solution. The concentration of chloride ion was made equal in both the standard and perchlorate solutions, and the perchlorate-ion concentration was made as nearly equal as possible.

### $Ni(ClO_4)_2$

The $Ni(ClO_4)_2 \cdot 6H_2O$ was used to prepare a saturated solution. Its exact concentration was determined colorimetrically by comparing its spectrum with that of a standard $Ni(NO_3)_2$ solution prepared by dissolving

a weighed amount of reagent grade $Ni(NO_3)_2$. Again, the nitrate and perchlorate ion concentrations were as nearly equalized as possible.

$Mn(ClO_4)_2$

An approximately 0.4 M stock solution was prepared by dissolving $Mn(ClO_4)_2 \cdot 6H_2O$ in 0.1 M $HClO_4$. Part of this was then diluted twice more to make stock solutions of approximately 0.04 M and 0.004 M. These solutions were analyzed colorimetrically. A standard solution was prepared by reducing a weighed amount of pure $KMnO_4$ with sulfite in sulfuric acid. The standard and stock solutions were then oxidized to permanganate by the persulfate method.[10] The peak heights at 525 mμ were compared.

$Fe(ClO_4)_3$

The $Fe(ClO_4)_3 \cdot 6H_2O$ was dissolved in 0.1 M $HClO_4$ to make stock solutions which were approximately 0.6 M and 0.3 M. The stock solutions were analyzed colorimetrically by the thiocyanate method.[11] An iron standard was made by dissolving analytical iron wire in $HNO_3$. Acetone was also added to the solutions to increase color intensity and stability. The peak heights at 485 mμ were compared.

For the two samples at the highest concentrations, the salt was added directly to the sample and the concentration determined by removing an aliquot and analyzing as above.

$Cu(ClO_4)_2$

The $Cu(ClO_4)_2 \cdot 6H_2O$ was used to prepare a stock solution which was approximately 0.40 M. This was diluted twice more to make stock solutions which were analyzed colorimetrically by extracting them with dithizone[12] and measuring the peak-height at 550 mμ. A standard copper solution was

made for comparison by dissolving pure copper wire in $HNO_3$. Again, the nitrate and perchlorate ion concentrations were made as nearly equal as possible in the stock and standard solutions.

$\underline{Cr(ClO_4)_3}$

The $Cr(ClO_4)_3 \cdot 6H_2O$ was weighed directly into the enriched water sample tubes since such a high concentration was desired. After the NMR spectra had been run, small aliquots were removed and analyzed by oxidizing the chromic ion to chromate with peroxide in basic solution, and comparing the peak-height at 370 mμ with that of a standard chromate solution made by dissolving $Na_2CrO_4$ in distilled water.

The specific gravity of all the stock solutions was determined and appropriate amounts of each added to enriched water to make up the various solutions of paramagnetic ions.

In Table I, a summary of analyses and specific gravity is given.

Table I

| Solution | Concentration (moles/liter) | Specific Gravity (g/ml) |
|---|---|---|
| $Co(ClO_4)_2$ | 2.12 M | 1.369 |
| | 1.60 | 1.305 |
| $Ni(ClO_4)_2$ | 3.00 | 1.565 |
| $Mn(ClO_4)_2$ | 0.376 | 1.071 |
| | 0.0376 | 1.007 |
| | 0.00376 | 1.001 |
| $Fe(ClO_4)_3$ | 0.58 | 1.172 |
| | 0.32 | 1.087 |
| $Cu(ClO_4)_2$ | 0.340 | 1.079 |
| | 0.136 | 1.032 |
| | 0.034 | 1.008 |

## III. RESULTS AND DISCUSSION

### A. Line-width Broadening at Various Concentrations of Paramagnetic Ions

The line widths (i.e., half widths at half height) and transverse relaxation times found for the various solutions used are given in Table II. Agreement was found with the results of Connick and Poulson[4] that chromic perchlorate was the least effective in producing relaxation.

A plot of the dependence of line-width on concentration of paramagnetic ion is shown in Fig. 2. The spectra were all taken at a temperature of approximately 26° C. The curves were broadened considerably for some of the more concentrated solutions, making accurate measurement of line-width difficult. This accounts at least in part, for the scatter.

### B. Rates of Elimination of Water Molecules

It was hypothesized earlier that the $T_2$ effect of $Cr^{+3}$ represents the magnitude of interactions arising outside the first coordination sphere and that therefore the appreciably larger effects observed with other ions must arise within the first coordination sphere.[4] If the transverse relaxation of the $O^{17}$ nucleus is due to an alteration of the effective magnetic field by paramagnetic ions, so that the phase relationships between perturbed and unperturbed nuclei are disturbed, then a lower limit for the rate constant for the exchange of water molecules may calculated from $T_2$ values. Taking

$$\frac{1}{(T_2)_P} + \frac{1}{(T_2)_D} = \frac{1}{(T_2)_{DP}} , \qquad (8)$$

we may calculate $(T_2)_P$, the contribution due to the presence of paramagnetic

Table II

Transverse Relaxation Times at Room Temperature

| Solution | Molar concentration | Line width (ppm)[a] | $T_2 \times 10^3$ (sec) |
|---|---|---|---|
| $Cu(ClO_4)_2$ | $1.10 \times 10^{-4}$ | 6.2 | 4.5 |
| | $5.25 \times 10^{-4}$ | 10.2 | 2.7 |
| | $1.28 \times 10^{-3}$ | 19.4 | 1.4 |
| $Cr(ClO_4)_3$ | 0.088 | 5.1 | 5.5 |
| | 0.36 | 5.34 | 5.2 |
| | 0.67 | 6.4 | 4.3 |
| $Fe(ClO_4)_3$ | $4.44 \times 10^{-3}$ | 5.29 | 5.2 |
| | $1.14 \times 10^{-2}$ | 6.30 | 4.4 |
| | $5.57 \times 10^{-2}$ | 9.33 | 3.0 |
| | $8.32 \times 10^{-2}$ | 11.0 | 2.5 |
| $Mn(ClO_4)_2$ | $6.24 \times 10^{-5}$ | 8.74 | 3.2 |
| | $1.43 \times 10^{-4}$ | 14.3 | 1.9 |
| $Ni(ClO_4)_2$ | $1.19 \times 10^{-2}$ | 6.34 | 4.3 |
| | $5.17 \times 10^{-2}$ | 9.89 | 2.8 |
| | $9.44 \times 10^{-2}$ | 14.4 | 2.1 |
| $Co(ClO_4)_2$[b] | $3.28 \times 10^{-3}$ | 8.58 | 3.4 |
| | $6.70 \times 10^{-3}$ | 12.1 | 2.2 |
| | $1.41 \times 10^{-2}$ | 19.0 | 1.5 |
| $H_2O^{17}$ | - - - - - - | $5.20 \pm 0.37$ | $5.3 \pm 0.3$[c] |

[a]Field inhomogeneity was less than 0.5 ppm.

[b]Measured at $5.44 \times 10^6$ cps. All others measured at $5.77 \times 10^6$ cps.

[c]Average of 8 different spectra.

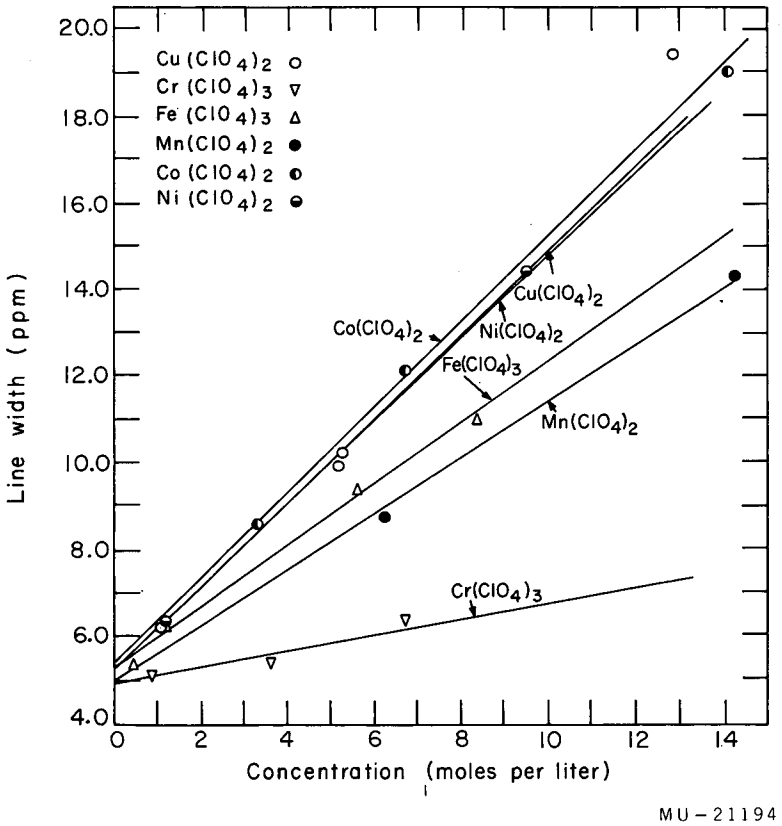


Fig. 2. Variation of line width with concentration. Concentrations of perchlorate solutions are X $10^4$ for Cu, X 10 for Cr, X $10^2$ for Fe, X $10^5$ for Mn, X $10^2$ for Ni, and X $10^3$ for Co.

ions, from a knowledge of $(T_2)_D$, obtained from the line-width in the absence of paramagnetic ions, and $(T_2)_{DP}$, the measured relaxation time for the solution.

The quantity $(T_2)_P$ is related to the bimolecular rate constant of Eq. (3):

$$k(P) = \frac{1}{\tau_D} \geqq \frac{1}{(T_2)_P} \qquad (9)$$

With $1.14 \times 10^{-2}$ M $Fe(ClO_4)_3$ solution as an example, $(T_2)_P$ was calculated to be $2.9 \times 10^{-2}$ sec. Rather than to calculate the bimolecular rate constant k, it is more instructive to determine the lower limit of the lifetime of a water molecule in the first coordination sphere of the metal ion, i.e., the first-order rate constant, $k_1$, for the loss of a particular water molecule from the metal ion according to the reaction

$$M(H_2O^*)^{+3} + H_2O \rightleftharpoons M(H_2O)^{+3} + H_2O^*$$

The lifetime of a water molecule in the paramagnetic environment is related to that in the diamagnetic environment by the ratio of the populations:

$$\tau_P = \tau_D \times \frac{n(P)}{55.5} \qquad (10)$$

where it is assumed that the metal ion is n-fold coordinated. Then for the above iron case, assuming n = 6, we have

$$k_1 = \frac{1}{\tau_P} \geqq \frac{55.5}{6 \times 1.14 \times 10^{-2} \times 2.9 \times 10^{-2}} = 2.8 \times 10^4 \text{ sec}^{-1} . \qquad (11)$$

Since several data are available for each salt, it is convenient to average by using the slopes of the lines drawn in Fig. 2. Designating

the slope by s, one finds

$$s = \frac{10^6}{(P)(T_2)_p \ \omega_o} \qquad (12)$$

From this and the previously developed equations, the lower limits for the values of $k_1$ shown in Table III were calculated.

The results obtained for the rate constants of the solutions containing $Mn^{++}$, $Ni^{++}$ and $Co^{++}$ compare favorably with the results obtained by Connick and Poulson.[4] There is a slight discrepancy in comparison of $Cu^{++}$ results and a much larger discrepancy in $Fe^{+++}$ results. The source of these discrepancies is unknown. It may be noted, however, that the experimental conditions necessitated by observation of the derivative curve at low sweep frequencies, such as those used by Connick and Poulson, produce appreciable experimental errors in the measurement of the true line width.

Table III

Calculated Lower Limits for First-Order Rate Constants for Water Exchange

| Solution | Slope (s) | $k_1(sec^{-1})$ | $k_1(sec^{-1})$ from Connick and Poulson[4] |
|---|---|---|---|
| $Cu(ClO_4)_2$ | $9.8 \times 10^3$ | $3.3 \times 10^6$ | $6 \times 10^5$ |
| $Cr(ClO_4)_3$ | 1.8 | a | |
| $Fe(ClO_4)_3$ | $7.15 \times 10$ | $2.4 \times 10^4$ | $1.1 \times 10^6$ |
| $Mn(ClO_4)_2$ | $6.45 \times 10^4$ | $2.2 \times 10^7$ | $1 \times 10^7$ |
| $Ni(ClO_4)_2$ | $9.5 \times 10$ | $3.2 \times 10^4$ | $4 \times 10^4$ |
| $Co(ClO_4)_2$ | $9.85 \times 10^2$ | $3.1 \times 10^5$ | $2 \times 10^5$ |

[a]Since the relaxation is not occurring in the first coordination sphere for $Cr^{+++}$, no value for $k_1$ is calculated.

## C. Saturation Experiments and $T_1$ Values

While measuring the $T_2$ values for the various paramagnetic solutions, it was also of interest to determine the corresponding $T_1$ values where possible. No attempt is made to attach significance to the results at this time.

The values for peak amplitude, sideband separation, and $H_1$ field are given in Table IV. The peak amplitudes and sideband separations were measured from the spectra. The value of $\beta$ was known from a measurement of the ratio of the first and second harmonics.[7] In each case the highest value for $H_1$ was calculated from the sideband separation, using Eq. (7). An attenuation ratio from a calibration of the instrument was applied to the high $H_1$ value to obtain the lower values. When the plot is made of peak amplitude vs field strength, curves result similar to the one in Fig. 3. A summary of the $T_1$ values obtained by this method is given in Table V. The term $H_1$ at max. max. refers to the maximum value of $H_1$ at a point where the peak amplitude is at its maximum. With the equipment available it was impossible to obtain good saturation curves for some of the more concentrated solutions. The dependence of $T_1$ on concentration is plotted in Fig. 4. Bloembergen, Purcell, and Pound[2] in their work on the effect of paramagnetic ions on the $T_1$ relaxation of protons, found that the relaxation time varied inversely as the concentration for high concentrations of paramagnetic ion. However, they also found a deviation from this relationship at low concentrations. From Fig. 4, a direct dependence can be seen for cupric and cobaltic ions, and an inverse dependence for ferric and chromic ions.

Table IV

Results of Saturation Experiments

| Solution | Concentration (moles/liter) | Peak Amplitude (cm) | Side-band Separation (cps) | $H_1$ (gauss) |
|---|---|---|---|---|
| $Cu(ClO_4)_2$ | $1.10 \times 10^{-4}$ | 4.30 | 752 | 0.239 |
| | | 4.47 | 773 | 0.222 |
| | | 4.57 | 780 | 0.203 |
| | | 4.51 | 785 | 0.179 |
| | | 4.61 | 787 | 0.148 |
| | | 4.58 | 790 | 0.124 |
| | | 4.19 | 810 | 0.105 |
| | | 3.69 | 800 | 0.091 |
| | | 2.93 | 815 | 0.076 |
| | $5.25 \times 10^{-4}$ | 2.77 | 763 | 0.212 |
| | | 2.80 | 770 | 0.197 |
| | | 2.82 | 775 | 0.180 |
| | | 2.71 | 781 | 0.159 |
| | | 2.69 | 784 | 0.132 |
| | | 2.54 | 785 | 0.110 |
| | | 2.24 | 789 | 0.093 |
| | | 1.84 | 805 | 0.081 |
| | | 1.46 | 797 | 0.068 |
| $Cr(ClO_4)_3$ | 0.088 | 4.24 | 752 | 0.239 |
| | | 4.36 | 759 | 0.222 |
| | | 4.47 | 769 | 0.203 |
| | | 4.57 | 772 | 0.179 |
| | | 4.54 | 773 | 0.148 |
| | | 4.45 | 790 | 0.124 |
| | | 4.21 | 795 | 0.105 |
| | | 3.64 | 792 | 0.091 |
| | | 2.97 | 800 | 0.076 |
| | | 2.04 | 802 | 0.054 |
| | 0.36 | 3.86 | 756 | 0.232 |
| | | 4.02 | 756 | 0.216 |
| | | 3.99 | 770 | 0.197 |
| | | 3.97 | 775 | 0.174 |
| | | 3.93 | 778 | 0.144 |
| | | 3.85 | 784 | 0.121 |
| | | 3.46 | 784 | 0.102 |
| | | 2.93 | 790 | 0.088 |
| | | 2.39 | 795 | 0.074 |
| | | 1.73 | 802 | 0.052 |

Table IV
(Page 2)

Results of Saturation Experiments

| Solution | Concentration (moles/liter) | Peak Amplitude (cm) | Side-band Separation (cps) | $H_1$ (gauss) |
|---|---|---|---|---|
| $Fe(ClO_4)_3$ | $4.44 \times 10^{-3}$ | 4.72 | 758 | 0.221 |
| | | 4.76 | 767 | 0.206 |
| | | 4.89 | 771 | 0.188 |
| | | 4.90 | 782 | 0.166 |
| | | 4.87 | 785 | 0.137 |
| | | 4.80 | 791 | 0.115 |
| | | 4.41 | 794 | 0.097 |
| | | 3.87 | 794 | 0.084 |
| | | 3.15 | 800 | 0.071 |
| | | 2.31 | 796 | 0.050 |
| | $1.14 \times 10^{-2}$ | 4.30 | 745 | 0.254 |
| | | 4.46 | 762 | 0.236 |
| | | 4.50 | 766 | 0.216 |
| | | 4.56 | 768 | 0.191 |
| | | 4.53 | 775 | 0.158 |
| | | 4.31 | 776 | 0.132 |
| | | 3.91 | 795 | 0.112 |
| | | 3.35 | 795 | 0.096 |
| | | 2.78 | 800 | 0.081 |
| | | 1.95 | 795 | 0.057 |
| $Mn(ClO_4)_2$ | $6.24 \times 10^{-5}$ | 3.35 | 737 | 0.270 |
| | | 3.41 | 761 | 0.251 |
| | | 3.43 | 773 | 0.230 |
| | | 3.48 | 766 | 0.202 |
| | | 3.35 | 778 | 0.167 |
| | | 3.13 | 789 | 0.140 |
| | | 2.81 | 787 | 0.119 |
| | | 2.31 | 795 | 0.103 |
| | | 1.90 | 797 | 0.086 |
| | | 1.35 | 800 | 0.061 |
| $Ni(ClO_4)_2$ | $1.19 \times 10^{-2}$ | 4.59 | 758 | 0.219 |
| | | 4.66 | 755 | 0.204 |
| | | 4.71 | 773 | 0.186 |
| | | 4.61 | 764 | 0.164 |
| | | 4.59 | 780 | 0.136 |
| | | 4.37 | 779 | 0.114 |
| | | 3.83 | 792 | 0.096 |
| | | 3.26 | 793 | 0.083 |

Table IV
(Page 3)

Results of Saturation Experiments

| Solution | Concentration (moles/liter) | Peak Amplitude (cm) | Side-band Separation (cps) | $H_1$ (gauss) |
|---|---|---|---|---|
| $Ni(ClO_4)_2$ | $1.19 \times 10^{-2}$ | 2.53 | 803 | 0.070 |
| | | 1.69 | 800 | 0.049 |
| $Co(ClO_4)_2$ | $3.28 \times 10^{-3}$ | 2.06 | 737 | 0.268 |
| | | 2.13 | 744 | 0.249 |
| | | 2.33 | 753 | 0.228 |
| | | 2.43 | 757 | 0.201 |
| | | 2.49 | 760 | 0.166 |
| | | 2.52 | 770 | 0.139 |
| | | 2.57 | 785 | 0.118 |
| | | 2.46 | 786 | 0.102 |
| | | 2.18 | 784 | 0.086 |
| | | 1.58 | 800 | 0.060 |
| | $6.70 \times 10^{-3}$ | 2.08 | 746 | 0.251 |
| | | 2.23 | 760 | 0.234 |
| | | 2.30 | 771 | 0.213 |
| | | 2.32 | 790 | 0.188 |
| | | 2.35 | 780 | 0.156 |
| | | 2.29 | 775 | 0.131 |
| | | 2.20 | 795 | 0.110 |
| | | 1.98 | 796 | 0.095 |
| | | 1.61 | 805 | 0.080 |
| | | 1.09 | 803 | 0.056 |
| $H_2O^{17}$-Run A | | 4.69 | 755 | 0.232 |
| | | 4.80 | 760 | 0.216 |
| | | 4.95 | 768 | 0.197 |
| | | 5.12 | 774 | 0.174 |
| | | 5.13 | 780 | 0.144 |
| | | 5.05 | 785 | 0.121 |
| | | 4.69 | 790 | 0.102 |
| | | 4.11 | 792 | 0.088 |
| | | 3.47 | 795 | 0.074 |
| | | 2.53 | 800 | 0.052 |

Table IV
(Page 4)

| Solution | Concentration (moles/liter) | Peak Amplitude (cm) | Side-band Separation (cps) | $H_1$ (gauss) |
|---|---|---|---|---|
| $H_2O^{17}$-Run B | | 4.76 | 732 | 0.280 |
| | | 4.90 | 741 | 0.260 |
| | | 5.00 | 760 | 0.238 |
| | | 5.07 | 765 | 0.210 |
| | | 4.93 | 770 | 0.174 |
| | | 4.81 | 774 | 0.146 |
| | | 4.36 | 782 | 0.123 |
| | | 3.85 | 793 | 0.107 |
| | | 3.00 | 793 | 0.090 |
| | | 2.19 | 800 | 0.063 |
| Run C | | 4.78 | 753 | 0.234 |
| | | 5.02 | 758 | 0.218 |
| | | 5.03 | 770 | 0.199 |
| | | 5.05 | 772 | 0.176 |
| | | 5.00 | 787 | 0.145 |
| | | 4.89 | 784 | 0.122 |
| | | 4.51 | 787 | 0.103 |
| | | 3.88 | 791 | 0.089 |
| | | 3.07 | 796 | 0.075 |
| | | 2.23 | 800 | 0.052 |
| Run D | | 4.75 | 742 | 0.259 |
| | | 5.00 | 752 | 0.241 |
| | | 5.05 | 768 | 0.220 |
| | | 5.09 | 766 | 0.194 |
| | | 5.00 | 776 | 0.161 |
| | | 4.91 | 783 | 0.135 |
| | | 4.46 | 792 | 0.114 |
| | | 3.84 | 794 | 0.098 |
| | | 3.23 | 795 | 0.083 |
| | | 2.05 | 800 | 0.058 |

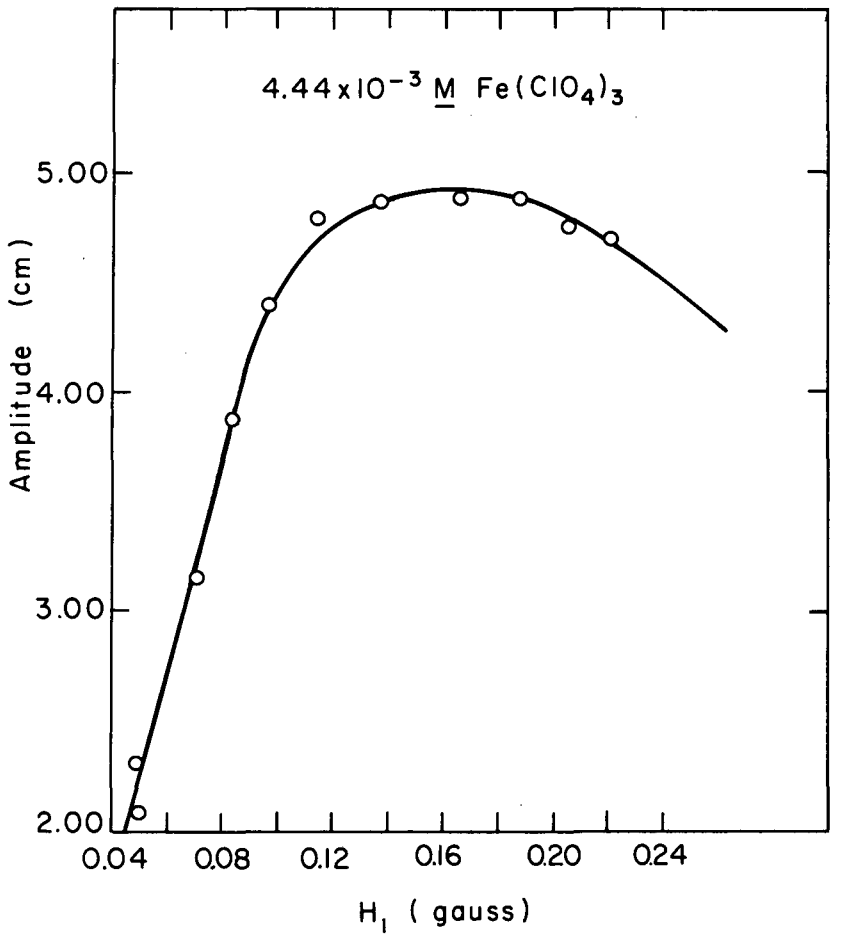


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Fig. 3. A typical saturation curve.

Table V

| Longitudinal Relaxation Times | | | |
|---|---|---|---|
| Solution | Concentration (moles per liter) | $H_1$ (gauss) at max.max. | $T_1 \times 10^3$ (sec) |
| $Cu(ClO_4)_2$ | $1.10 \times 10^{-4}$ | 0.169 | 4.8 |
| | $5.26 \times 10^{-4}$ | 0.176 | 7.9 |
| $Cr(ClO_4)_3$ | 0.088 | 0.160 | 4.7 |
| | 0.36 | 0.174 | 4.2 |
| $Fe(ClO_4)_3$ | $4.44 \times 10^{-3}$ | 0.160 | 4.9 |
| | $1.14 \times 10^{-2}$ | 0.183 | 4.5 |
| $Mn(ClO_4)_2$ | $6.24 \times 10^{-5}$ | 0.214 | 4.5 |
| $Ni(ClO_4)_2$ | $1.19 \times 10^{-2}$ | 0.173 | 5.1 |
| $Co(ClO_4)_2$ | $3.28 \times 10^{-3}$ | 0.139 | 9.9 |
| | $6.70 \times 10^{-3}$ | 0.169 | 10.4 |
| $H_2O^{17}$ | - - - | 0.178 | 4.1 |

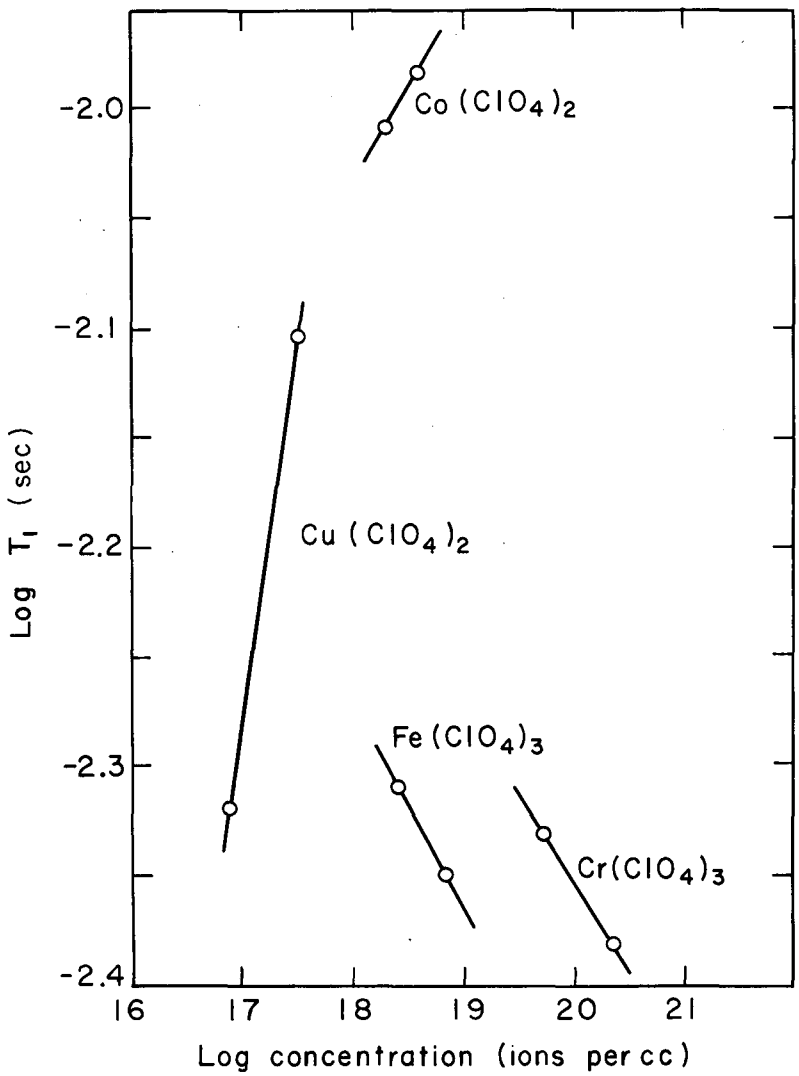


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Fig. 4. Variation of $T_1$ with concentration.

A comparison of $T_1$ and $T_2$ values shows that the ratio of $T_1$ to $T_2$ is unity or slightly less in most cases (usually $T_1 \geq T_2$). It is interesting to note that in the case of $Co(ClO_4)_2$ solution, $T_1/T_2$ is considerably greater than one. Bloembergen[13] has suggested an explanation for the existence of a longer $T_1$ value than $T_2$ for such cases. In his study of proton relaxation in paramagnetic solutions, he attributes this phenomenon to an exchange interaction between electron spin and proton spin in adjacent water molecules, whereby $T_2$ is shortened but not $T_1$.

It may be noted that the results obtained here are in marked contrast to the results of Shulman and Wyluda[14] in which the ratio $T_1/T_2$ is of the order of $10^3$ for $O^{17}$ resonance in solutions of $Gd^{+++}$.

## D. Effect of pH on $T_2$

Since Meiboom, Luz, and Gill[15] have reported a dependence of the transverse relaxation time on pH for proton relaxation, it was decided to study the effect, if any, of pH on $T_2$ for $O^{17}$ resonance. The above authors observed an increase of $T_2$ up to pH 3, after which $T_2$ decreased to a minimum at pH 7.5 and then reached a second maximum around pH 10.5. Preliminary examination of the pH dependence for $H_2O^{17}$ yielded the results shown in Table VI. The data give little evidence for any variation of $T_2$ with pH over the region studied, when it is noted that the average deviation of eight water measurements in Table II was $\pm$ 0.3 x $10^{-3}$ sec. The pH was adjusted in each case by the addition of sodium hydroxide or perchloric acid.

Table VI

Variation of $T_2$ with pH

| pH | Line-width (ppm) | $T_2$ x $10^3$ (sec) |
|---|---|---|
| 0.87 | 4.80 | 5.75 |
| 1.00 | 5.20 $\pm$ 0.37 | 5.3 $\pm$ 0.3[a] |
| 3.0 | 5.23 | 5.25 |
| 5.5 | 5.37 | 5.14 |
| 8.0 | 5.34 | 5.17 |
| 10.5 | 5.53 | 4.98 |

[a]From Table II.

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## V. BIBLIOGRAPHY


1. F. Bloch, Phys. Rev. 70, 460 (1946).
2. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
3. H. M. McConnell and S. B. Berger, J. Chem. Phys. 27, 230 (1957).
4. R. E. Connick and R. E. Poulson, J. Chem. Phys. 30, 759 (1959).
5. H. Primas, Helv. Phys. Acta 31, 17 (1958).
6. K. V. Vladimirski, Doklady Akad. Nauk. SSSR 58, 1625 (1947).
7. J. V. Acrivos, private communication, University of California, Berkeley.
8. W. Anderson, Phys. Rev. 102, 151 (1956).
9. J. E. Wertz, J. Chem. Phys. 24, 484 (1956).
10. E. B. Sandell, Colorimetric Determination of Traces of Metals, Second Edition (Interscience Publishers, Inc., New York, 1950), p. 433.
11. Ibid., p. 372.
12. Ibid., p. 303.
13. N. Bloembergen, J. Chem. Phys. 27, 572 and 595 (1957).
14. R. G. Shulman and B. J. Wyluda, J. Chem. Phys. 30, 335 (1959).
15. S. Meiboom, Z. Luz, and D. Gill, J. Chem. Phys. 27, 1411 (1957).

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