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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF THE RELAXATION OF COPPER (II), TITANIUM (III) and VANADYL IONS IN SOLUTION

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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF THE RELAXATION OF COPPER (II), TITANIUM (III) AND VANADYL IONS IN SOLUTION

Contents

Experiments at S-band (3 GHz) confirm the assignment of the relaxation processes involved. The variation of the isotropic g and A values with temperature is discussed. Extension of the results to the similar problem of $Cu(H_2O)_6^{2+}$ in water were made. A tentative assignment of the relaxation processes were made in which relaxation is due to spin-rotation interaction, tumbling, a dynamic Jahn-Teller effect, and a Van Vleck Raman process.

The EPR spectra of acidified aqueous solutions of Ti (III) were observed both above and below the freezing point. In the frozen glass, an axial spin Hamiltonian was found for the $Ti(H_2O)_6^{3+}$ complex with $g_{\parallel} = 1.988 \pm 0.002$ and $g_{\perp} = 1.892 \pm 0.002$. When warmed above -50°C, broadening occurs which follows $T_2^{-1} = 2.90 \times 10^{14} e^{-\Delta E/kT}$ sec^{-1}, where $\Delta E = 1850 \pm 50$ cm^{-1}. This same broadening is followed for both the solution and frozen glass. The g values are explained assuming that the 1850 cm^{-1} value is the first excited orbital state energy, and the relaxation is explained as an Orbach process.

I. INTRODUCTION

Electron paramagnetic resonance (EPR) has established itself as a sensitive probe of molecular environment. For transition metal ions both the energy splittings and the relaxation of the spin system are sensitive to changes in the immediately surrounding molecules. Substitution of different molecules or even small changes in the symmetry of molecules surrounding the transition metal ion can make the difference between a readily observable resonance signal and a signal so broad as to be undetectable.

The EPR of transition metal ions, either as impurities in other lattices or as single crystals, has several advantages. Dealing with a set of ions fixed in the lattice, the energy splittings and relaxation behavior, as a function of orientation in an external magnetic field, can usually be readily determined. The relaxation processes in solids are well known and their vastly different temperature dependences make assignment of the relaxation mechanism unambiguous in most cases. The symmetry about the transition metal ion can be determined by X-ray diffraction measurements. The problem with solid state systems comes in trying to study the effects of the ligands bound to the metal ion on the energy levels of the metal ion. The symmetry and relaxation properties of the transition metal complex are so intertwined with the lattice that separability into lattice effects and ligand effects is not always possible.

In liquids the situation is somewhat different. For solvated ions or, in those complexes in which there are ligands other than solvent molecules, where the rate of exchange of ligands for solvent molecules is slow, the transition metal is influenced only by the few molecules immediately surrounding it. With the simplicity of isolating ligand effects come problems. The simplicity of an ordered system of well characterized symmetry is lost. The relaxation is complicated by complex molecular motion and the task of uniting a well defined quantum mechanical system with a complex, semi-classical description of the motion is formidable. Many of the theories of electron spin relaxation in liquids give little more than the correct temperature dependence. It is for these reasons that liquid relaxation has been much less thoroughly examined than solid state relaxation.

The present work was undertaken to study the g values, symmetry, and relaxation behavior of three spin 1/2 transition metal complexes in solution. Vanadyl acetlyacetonate (VOAA), $VO(CH_3COCH\,C\,OCH_3)_2$, has long been considered the prime example of the validity of the Kivelson tumbling mechanism (Wilson and Kivelson, 1966a). The relaxation of VOAA in liquid ammonia allows probing viscosity ranges not explored in previous studies in organic solvents. VOAA in liquid ammonia also provides a test of the effects of a hydrogen bonding solvent on the relaxation behavior.

The solution EPR of copper (II) ions has been one of the most studied and most puzzling problems in the field. Lack of resolution of the hyperfine quartet of hexaquocopper (II) has been the major cause of difficulty in assignment of the relaxation processes involved. The hexamminecopper (II) complex was chosen for this work because its larger hyperfine splitting, combined with the smaller viscosity of liquid ammonia, allows resolution of the individual hyperfine lines. It was particularly hoped that a thorough understanding of the relaxation of hexamminecopper (II) would cast some light upon the mechanisms involved in hexaquocopper (II) relaxation.

The EPR spectrum of hexaquotitanium (III) has long been thought to be too broad to be observed. Only recently (Charles, 1971) has the room temperature EPR been reported. This work is the first study of the solution EPR of hexaquotitanium (III) and the relaxation process involved.

In the relaxation studies the quantity measured is the peak-to-peak linewidth of the derivative presentation. This can be related to the theoretically calculable quantity T_2, the spin-spin relaxation time. The spin lattice relaxation time, T_1, was not measured and unless otherwise stated is assumed to equal T_2.

II. RELAXATION OF SPIN 1/2 SYSTEMS IN SOLUTION

The EPR relaxation behavior of systems with one unpaired electron have been the subject of extensive theoretical treatment. In this section these theories shall be presented. Systems with spin greater than 1/2 have additional relaxation mechanisms due to modulation of the zero-field splitting and will not be discussed here. The results are not derived in detail. The reader is referred to the original papers for further information.

The first major effort to explain spin relaxation in solution was the pioneering work of Bloembergen, Purcell, and Pound (1948), hereafter referred to as BPP. Although derived for nuclear spin relaxation, their method is also applicable to electron spin relaxation. BPP considered the relaxation of protons in water. They assumed the perturbation causing relaxation to be the result of modulation of the magnetic dipole-dipole interaction between the protons by random thermal motions of the molecules. Using time dependent perturbation theory, they computed transition probabilities which could be related to relaxation times. Since the perturbation is random, they used the correlation function methods of Brownian motion to derive spectral densities and hence relaxation times. By making the usual assumption that the autocorrelation function of the perturbed system returns to equilibrium in an exponential fashion governed by a characteristic time, τ_c, the correlation time, they arrived at a formulation of the problem closely related to the problem of dielectric dispersion in polar liquids considered by Debye (1945). Following Debye's assumptions of a sphere embedded in a continuous, viscous liquid, they found that the correlation time, τ_c, is given by the Stokes-Einstein relation,

$$\tau_c = 4\pi\eta a^3/3kT, \qquad (2.1)$$

where η is the bulk viscosity of the liquid, a the hydrodynamic radius of the sphere, k Boltzmann's constant, and T the absolute temperature.

Since the time of BPP, more elegant methods of calculating relaxation times have been developed. The two most widely used methods are the relaxation matrix theory of Redfield (1965) and Wangsness and Bloch (Wangsness and Bloch, 1953; Bloch, 1956, 1957), and the linear response theory of Kubo and Tomita (1954). All of these theories assume that the perturbation is small, ie., that the state of the system changes by a small amount during the collisions which cause relaxation.

Several excellent reviews of relaxation in liquids have appeared in the literature. Of particular note are those by Luckhurst and Hudson (1969), Luckhurst (1969), Carrington and Luckhurst (1968), Atkins (1972), and Muus and Atkins (1972).

A. MAGNETIC PERTURBATIONS

1. Anisotropic g and A Tensors

One of the most important models for explaining the linewidths of transition metal ions in solution was the "microcrystalline" model proposed by McConnell (1956). He proposed that the metal ion, in solution, be treated as a rigid microcrystal having the same magnetic properties as an identical unit in a single crystal would have. Thus the g and A tensors would have the anisotropies measured in single crystals. As the microcrystal tumbled in solution due to Brownian motion, the Zeeman interaction with an external magnetic field would be modulated by the changing orientation of the molecule with respect to the external field. Following the method of BPP, for the case of axial symmetry, McConnell derived the following result,

$$\frac{1}{T_1} \approx \frac{8\pi^2}{15h^2} (\Delta g \beta H_0 - bm_I)^2 \frac{\tau_R}{1+4\pi^2\nu_o^2\tau_R^2} , \qquad (2.2)$$

where

$$\Delta g = g_{\parallel} - g_{\perp}$$
$$b = A_{\parallel} - A_{\perp} , \qquad (2.3)$$

H_o is the magnetic field, m_I the nuclear spin quantum number, ν_o the Larmor frequency, and τ_R is given by the Stokes-Einstein relation, eq. 2.1. Examination of eq. 2.2 shows that there are three types of terms; a term caused by anisotropy of the g tensor and independent of m_I, a term caused by anisotropy of the A tensor and quadratic in m_I, and a cross term between the two tensors linear in m_I.

The "microcrystalline" model was reexamined by Kivelson (1960, 1964) using the formalism of Kubo and Tomita (1954). He obtained essentially the same result as McConnell.

To explain the linewidths of Vanadyl acetylacetonate in solution, Wilson and Kivelson (1966a, 1966b) did a more extensive calculation retaining cross terms neglected previously. They concluded that the linewidth could be expressed by

$$\Delta H_{m_I} = (\alpha' + \alpha'') + \beta m_I + \gamma m_I^2 + \delta m_I^3, \tag{2.4}$$

where α" is the contribution from all mechanisms other than reorientational tumbling. The coefficients in eq. 2.4 are given by

$$\begin{aligned} \frac{\alpha'}{\tau_R} = {} & \frac{4}{45}(\Delta\gamma B_o)^2 + \frac{4}{15}(\delta\gamma B_o)^2 + \frac{3}{40}b^2 I(I+1) \\ & + \frac{2}{5}c^2 I(I+1) - \frac{1}{30}b\frac{a}{\omega_o}\Delta\gamma B_o I(I+1) \\ & + u\Big[\frac{1}{15}(\Delta\gamma B_o)^2 + \frac{1}{5}(\delta\gamma B_o)^2 + \frac{7}{40}b^2 I(I+1) \\ & + \frac{14}{15}c^2 I(I+1) - \frac{1}{30}b\frac{a}{\omega_o}\Delta\gamma B_o I(I+1) \\ & - \frac{5}{40}b^2\frac{a}{\omega_o}I(I+1)f\Big], \end{aligned} \tag{2.5}$$

$$\frac{\beta}{\tau_R} = \frac{4}{15}\, b\Delta\gamma B_o - \frac{8}{45}\,(\Delta\gamma B_o)^2\,\frac{a}{\omega_o} + \frac{16}{15}\, c\delta\gamma B_o$$
$$-b^2\,\frac{a}{\omega_o}\left[\frac{1}{20}\,I(I+1) + \frac{3}{40}\right] + u\left[\frac{1}{5}\, b\Delta\gamma B_o\right.$$
$$\left. + \frac{4}{5}\, c\delta\gamma B_o - \frac{2}{15}\,(\Delta\gamma B_o)\frac{a}{\omega_o}\,(1+f)\right]$$
$$- \frac{1}{20}\, b^2\,\frac{a}{\omega_o}\, u\left[I(I+1) + 7I(I+1)f\right], \qquad (2.6)$$

$$\frac{\gamma}{\tau_R} = \frac{1}{8}\, b^2 - \frac{7}{30}\, b\,\frac{a}{\omega_o}\Delta\gamma B_o + \frac{2}{3}\, c^2 - u\left[\frac{1}{40}\, b^2\right.$$
$$+ \frac{1}{6}\, b\,\frac{a}{\omega_o}\Delta\gamma B_o - \frac{2}{15}\, c^2 + (\frac{2}{5}\, b\,\frac{a}{\omega_o}\Delta\gamma B_o$$
$$\left.- \frac{5}{40}\, b^2\,\frac{a}{\omega_o})\, f\right], \qquad (2.7)$$

$$\frac{\delta}{\tau_R} = \frac{1}{20}\, b^2\,\frac{a}{\omega_o} + \frac{1}{20}\, b^2\,\frac{a}{\omega_o}\, u\,(1+f), \qquad (2.8)$$

where

$$a = \frac{1}{3}\,(A_x + A_y + A_z),$$
$$b = \frac{2}{3}\left[A_z - \frac{1}{2}(A_x + A_y)\right],$$
$$c = \frac{1}{4}\,(A_x - A_y),$$
$$g = \frac{1}{3}\,(g_x + g_y + g_z),$$
$$\Delta g = g_z - \frac{1}{2}(g_x + g_y),$$
$$\delta g = \frac{1}{2}(g_x - g_y),$$
$$\Delta\gamma = \beta\Delta g/\hbar,$$
$$\delta\gamma = \beta\delta g/\hbar,$$

$$B_o = \hbar\omega_o/g\beta,$$

$$u = 1/(1+\omega_o{}^2 R^2), \qquad (2.9)$$

$$f = \omega_o{}^2 \tau_R{}^2 \, u.$$

For the case of axial symmetry,

$$c = \delta g = \delta\gamma = 0,$$

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

$$b = \frac{2}{3}(A_{\parallel} - A_{\perp}). \qquad (2.10)$$

The Kivelson tumbling theory has the same general properties as McConnell's original model, eq. 2.2. The major characteristics of tumbling relaxation are a strong dependence of the linewidth on m_I and a strong frequency dependence.

2. Pseudo-Reorientation

Spencer (1965) considered pseudo-reorientation in complexes of high symmetry, particularly $Cu(H_2O)_6{}^{2+}$. In an octahedral field, the complex should distort due to the Jahn-Teller Theorem. In copper complexes, in solids, a tetragonal distortion is most often found. A tetragonal distortion is the only axial distortion which will remove the degeneracy of the ground state. A distortion along either the x, y, or z axes of the complex should be equivalent. Spencer considered the complex "jumping" from a configuration with the distortion along one axis to an equivalent configuration with the distortion along a different axis of the complex. Defining his Hamiltonian in terms of delta functions, specifying the axis of distortion, he performed a McConnell type calculation and derived the result that

$$T_2^{-1} = \frac{32\pi}{9h2} (\Delta g\beta H_o + b\ m_I)^2 \tau_i. \qquad (2.11)$$

Assuming that the correlation time for pseudo-reorientation, τ_i, is equal to the correlation time for tumbling, pseudo-reorientation should give 2 1/2 times the contribution to the linewidth that tumbling gives. Of course, as Spencer points out, since neither mechanism exists without the other, and since both mechanisms give the same functional form, experimentally it is difficult to distinguish the contributions of each mechanism separately. The pseudo-reorientation mechanism introduces no spin-lattice relaxation, thus measurement of T_1 can distinguish the relative contribution of each mechanism.

Spencer gave no temperature dependence, but it would be expected to show an η/T dependence.

Hudson (1965, 1966) treated the pseudo-reorientation process in a more elegant manner. He considered the case of an octahedral complex with a distortion axis hopping between three equivalent orientations. As the hopping frequency increases, the spectral anisotropies are averaged in a manner analogous to the familiar two state problem (Kubo, 1954, 1957; Sack, 1958). Averaging over all angles to account for the random orientations of the molecules in a liquid yields the standard result of tumbling theory, although, of course, with the hopping correlation time in the place of the reorientation tumbling correlation time.

Rubenstein, et al. (1971) and Noack, et al. (1971) have shown that consideration of both tumbling and pseudo-reorientation simultaneously yields the standard result of tumbling theory, but with an apparent correlation time given by $1/\tau = 1/\tau_R + 1/\tau_I$, where τ_R and τ_I are the reorientational and pseudo-reorientational correlation times, respectively.

3. Spin-Rotation Interaction

When a molecule rotates, the nucleus and the electron cloud do not rotate rigidly as a unit. If there are unpaired electrons, a magnetic field can be generated by the motion and energy can be exchanged between the electrons and the nucleus. This interaction has the effect of coupling the spin angular momentum to the rotational angular momentum of the molecule. The interaction can be represented by a Hamiltonian of the form

$$\mathcal{H}_{SR} = \underset{\sim}{J} \cdot \underset{\sim}{C} \cdot \underset{\sim}{S}, \tag{2.12}$$

where $\underset{\sim}{J}$ is the rotational angular momentum in units of $\hbar$, $\underset{\sim}{S}$ the spin in units of $\hbar$, and $\underset{\sim}{C}$ the spin-rotational interaction tensor.

The problem has been treated, for nuclear relaxation, by many workers (Ramsey, 1950; Oppenheim and Bloom, 1959; Powles and Mosley, 1960; Johnson and Waugh, 1962; Brown, Gutowsky and Shimomura, 1963; Freed, 1964) and most notably by Hubbard (1963).

For cylindrical molecules in liquids Hubbard found that

$$T_1^{-1} = T_2^{-1} = (2IkT\tau_\omega/3\hbar^2)\ (2C_\perp^{\ 2} + C_\parallel^{\ 2}), \tag{2.13}$$

where I is the molecular moment of inertia, $C_\parallel$ and $C_\perp$ the diagonalized components of C along the unique molecular axis and perpendicular to it, respectively, and τ_ω the rotational angular momentum correlation time.

In this model, it is clear that τ_ω is proportional to η^{-1} since angular momentum is decelerated more rapidly in viscous media and τ_R is proportional to η since reorientation is more difficult in viscous media.

Furthermore, Hubbard found that for the special case of liquids following the Stokes-Einstein relation

$$\tau_\omega \tau_R = I/6kT. \tag{2.14}$$

Curl (1965) showed the relationship between the electron spin-rotational coupling tensor and the g-tensor. He found that

$$g_{ij} = g_e \delta_{ij} - \hbar^2 \sum_k C_{ik} I_{kj}, \tag{2.15}$$

where g_e is the free electron g value, δ_{ij} is a delta function, and I_{kj} is the inertial tensor component.

Atkins and Kivelson (1966) obtained the same expression as Curl had and calculated the linewidth due to spin-rotation interaction to be

$$T_2^{-1} = (12\pi r^3)^{-1} \left(\Delta g_{\parallel}^{\,2} + 2\Delta g_{\perp}^{\,2}\right) kT/\eta, \tag{2.16}$$

where

$$\begin{aligned} \Delta g_{\parallel} &= g_{\parallel} - g_e, \\ \Delta g_{\perp} &= g_{\perp} - g_e, \end{aligned} \tag{2.17}$$

and r is the hydrodynamic radius of the molecule.

The spin-rotation linewidth is independent of the applied magnetic field.

More general theories, removing restrictions on the asymmetry of the molecule have been developed by Nyberg (1967) and Atkins (1967).

Hoel and Kivelson (1975b) have considered anisotropy in the rotational motion and the effect it would have on the relaxation. They have found that, for an oblate spheroid,

$$T_2^{-1}{}_{\text{anis}} = \frac{\hbar k}{6\sqrt{3}\,\pi g_o \beta} \left[(\Delta g_x)^2 + (\Delta g_y)^2 + (\Delta g_z)^2 (1+\chi)\right] \frac{T}{\eta \kappa_\perp r^3}, \tag{2.18}$$

where

$$\chi = \frac{[\lambda-(1-\lambda^2)\ \tan^{-1}\lambda]\ [2+\lambda^2]}{[(1-\lambda^2)\ \tan^{-1}\lambda-\lambda]\ [1+\lambda]}\ \frac{\kappa_\perp}{\kappa_\parallel} - 1,$$

$$\lambda^2 = (\ r_x{}^2 - r_z{}^2)/r_z{}^2, \tag{2.19}$$

r_x and r_z are the semiaxis of the oblate spheroid, and $K_\perp$ and $K_\parallel$ are the anisotropic interaction parameters, discussed in the next section, perpendicular and parallel to the unique axis.

4. Modifications to the Stokes-Einstein Relation

All of the theories discussed thus far assume that the appropriate correlation time is obtainable from the Stokes-Einstein expression, eq. 2.1, and the temperature dependence of the experimentally observed linewidth for each mechanism shows this to be a good assumption. However, the Stokes-Einstein expression was derived for translational diffusion of a spherical particle in a uniform, sticky, viscous medium. The equating of the translational correlation time with the reorientational correlation time would be expected to cause some problems with the theory, and it does. Since the first thorough treatment of liquid relaxation (Wilson and Kivelson, 1966a), the hydrodynamic radius, r, has always been smaller than the molecular radius measured by X-ray crystallography, translational diffusion experiments, and other methods. It would be expected that the hydrodynamic radius should be greater in solution, since, presumably, the molecule is more or less bound to a sphere of solvent molecules which should contribute to the effective radius. It was thus something of a surprise to find the hydrodynamic radius always to be smaller than expected and sometimes by quite a large amount.

This problem led McClung and Kivelson (1968) to propose that the Stokes-Einstein expression be written using the effective radius, a, which is related to the actual radius, r, of the molecule by,

$$a = \kappa^{1/3} r, \tag{2.20}$$

where κ is an empirical parameter, $0 \leq \kappa \leq 1$. κ is usually independent of temperature and is only dependent on the nature of the solvent.

Hwang, Kivelson and Plachy (1973) considered the problem of molecules of less than spherical symmetry, in which case κ, now called the anisotropic interaction parameter, is a tensor. They found that κ can often be approximated by

$$\kappa_{ii} = (3/4r^2) \left(\langle T_i^2 \rangle / \langle F^2 \rangle \right), \tag{2.21}$$

where T_i represents the intermolecular torque around the i^{th} molecular axis and F_i the intermolecular force on the paramagnetic solute molecule. The angle brackets indicate an equilibrium ensemble average. κ is expected to increase with decreasing solvent size.

If κ is anisotropic, the value of κ for reorientation may differ from the value for spin-rotation. These two parameters are different averages of the κ tensor, the reorientational motion favoring the higher components and the spin-rotational motion favoring the lower components (Hoel and Kivelson, 1975b). Thus $a_{(\text{reorient})} \geqslant a_{(\text{SR})}$.

All of these derivations,of course, depend upon the validity of Debye's assumption of stick boundary conditions, ie., that the tangential velocity of the spheroid and the liquid are equal at the spheroid's surface. Hu and Zwanzig (1974) have carried out hydrodynamic calculations with slip boundary conditions, ie., where the tangential velocity of the liquid is zero at the spheroid's surface. In this case, $K = \Xi$ where Ξ is the ratio of the effectiveness of torques under slip conditions to those under stick conditions (Hoel and Kivelson, 1975b). The value of Ξ is dependent only on geometric factors and has been tabulated (Hu and Zwanzig, 1974).

Hoel and Kivelson (1975a) have proposed an empirical "stickiness" parameter, s, to describe intermediate conditions where neither slip nor stick conditions hold. The "stickiness" paramater is given by

$$s = \frac{K - \Xi}{1 - \Xi} \tag{2.22}$$

with s=1 for stick and s=0 for slip. This would give eq. 2.1 the form,

$$\tau_R = \frac{4\pi\eta r^3}{3kT}\left[s\left(1-\Xi\right)+\Xi\right]. \tag{2.23}$$

Bauer _et al_. (1974) indicate that there should be a viscosity independent term added to the right side of eq. 2.1. This term should be of the order of the free rotational period. None of the data we will report is precise enough to determine such a small additive term.

B. ELECTRIC FIELD FLUCTUATIONS

Electric field fluctuations (EFF) are the liquid analog of phonons in solids. The EFF mechanisms of interest in liquids may be divided into four main catagories. The first mechanism, proposed by Van Vleck (1940) for relaxation in solids, is the direct process in which the spin relaxes within the ground orbital state by the emission of a phonon. The second mechanism, also proposed by Van Vleck (1940), is a two phonon, or Raman process, involving relaxation through a virtual excited state. The third mechanism, due to Orbach (1961), is a two phonon process involving a real excited state. The fourth mechanism, described by Kivelson (1966) as a "vibrational process", involves the spin's relaxation being accompanied by the simultaneous excitation of a discrete, localized molecular vibrational state. This is effectively an Orbach process within the orbital ground state. These mechanisms are illustrated in Fig. 1.

1. Al'tschuler and Valiev Mechanism.

One of the first mechanisms utilizing fluctuations in the electric field of a transition metal ion was derived by Al'tshuler and Valiev (1959). They considered the normal modes of vibration of the complex to be perturbed by the Brownian motion of the surrounding particles. As a result, the electric field of the ligands acting on the paramagnetic ion becomes a random function of time. The variations in the electric field are communicated to the unpaired spin of the ion by spin-orbit coupling. Following the derivation of Van Vleck (1939), they expanded the perturbation Hamiltonian in terms of the normal coordinates of the complex,

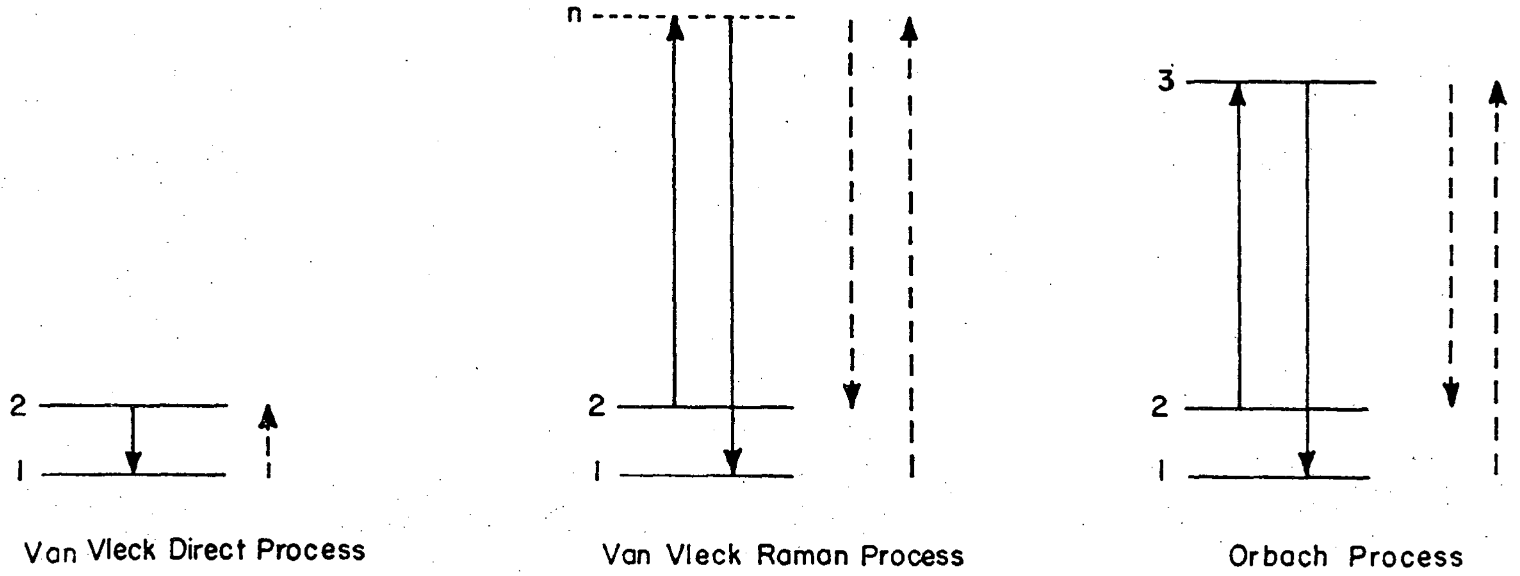

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Fig. 1. Electric field fluctuation mechanisms for relaxation between levels 1 and 2. Solid arrows represent electron transitions and the dashed arrows represent the corresponding lattice transitions. State n is a virtual excited state.

$$\mathcal{H} = \sum_{i=2}^{6} V^{(i)} Q_i, \tag{2.24}$$

where Q_i is the i^{th} normal coordinate and $V^{(i)}$ is the partial derivative of the ligand field potential with respect to Q_i.

Making the standard assumption of exponential recovery, they found the correlation function of Q_i to be given by

$$\langle Q_i(t), Q_i(0) \rangle = \langle \left[Q_i(0)\right]^2 \rangle \exp(-|t|\tau_c). \tag{2.25}$$

For a transition between levels 1 and k they found the transition probability to be

$$A_{1k} = \frac{\overline{Q^2}}{\hbar^2} \sum_i |V_{1k}^{(i)}|^2 \frac{\tau_c}{1+\omega_{1k}^2 \tau_c^2}, \tag{2.26}$$

where ω_{1k} is the frequency separating levels 1 and k and $\overline{Q^2}$ an average over all the normal coordinates assumed to be given by

$$\overline{Q^2} = (\hbar/2m\omega_o) \coth (\hbar \omega_o/2kT), \tag{2.27}$$

where m is close to the mass of the complex and ω_o is an average frequency. They also assume that the correlation time, τ_c, is inversely proportional to the square-root of the temperature.

Thus for $\tau_c^2 \omega_{\ell k}^2 \ll 1$,

$$A_{1k} \approx T^{-1/2} \coth (\hbar\omega_o/2kT) \tag{2.28}$$

and for $\tau_c^2 \omega_{\ell k}^2 \gg |$,

$$A_{1k} \approx T^{1/2} \coth (\hbar\omega_o/2kT). \tag{2.29}$$

Hayes (1961) examined the Al'tshuler and Valiev mechanism and found several faulty assumptions. The most critical faults were that the spectral density is not normalized and that $\overline{Q^2}$ is correct only for frequencies far removed from resonance.

Hayes rederived the transition probability for this mechanism and found that it should be directly proportional to temperature.

The theory was extended by Valiev and Zaripov (1962) to include quadratic terms in the normal coordinate expansion. The quadratic terms were expected to be more effective than the linear terms in producing relaxation (Alexsandrov and Zhidomirov, 1961). Valiev and Zaripov derived a temperature dependence given by

$$T_1^{-1} \approx \coth^2(\hbar\omega_o/2kT)\,\frac{\tau_c}{1+\omega_{1k}^2\tau_c^2}\,. \qquad (2.30)$$

In this form the theory corrects the problems pointed out by Hayes in the original theory. The temperature dependence of the linewidth is silmilar to the temperature dependence of McConnell's theory as long as $T \ll \hbar\omega_o/2k$.

2. Kivelson EFF Mechanism

Kivelson (1966) considered the most important nonrotational relaxation mechanisms in liquids. The electric fields of the paramagnetic complex were modulated by molecular vibrations and by collisions with surrounding diamagnetic molecules. The electric field fluctuations are then transmitted to the spin by the spin-orbit coupling. These processes were originally called "second order statistical processes" by

Lloyd and Pake (1954) and vibrational spin-orbit processes by Kivelson and Collins (1963).

Kivelson (1966) found that, in liquids, the contribution to the relaxation from the vibrational process is negligible. The contribution from the Van Vleck direct process is given by

$$T_1^{-1} = T_2^{-1} = 64\left(\frac{\lambda}{\Delta}\right)^2\left(\frac{\phi q_o}{\Delta r_o}\right)^2 \frac{(\omega_o\tau_c)^2\,\tau_c^{-1}}{1+\omega_o^2\,\tau_c^2}\,, \qquad (2.31)$$

where λ is the spin-orbit coupling constant, Δ the energy separation between the ground state and the first excited state coupled to it by the spin-orbit interaction, ϕ the magnitude of the time dependent potential, q_o the lattice or liquid modes, r_o the characteristic intermolecular distance, and ω_o the Larmor frequency. If $\omega_o^2\tau_c^{\,2} \ll 1$, the linewidth is proportional to the applied field squared, whereas if $\omega_o^2\tau_o^{\,2} \gg 1$, the linewidth is independant of the applied field. In general this mechanism causes only a small relaxation contribution and is usually ignored.

Kivelson also calculated the contributions from both the first and second order Van Vleck Raman processes. The second order process is much more important than the first order process in causing relaxation. For $\omega_o^2\tau_c^{\,2} \ll 1$, as is usually the case,

$$T_1^{-1} = T_2^{-1} = 32\left(\frac{\lambda}{\Delta}\right)^2\left(\frac{\phi q_o}{\Delta r_o}\right)^4 \tau_c^{-1}. \qquad (2.32)$$

This process is independent of the applied field.

The Orbach process gives

$$T_1^{-1} = T_2^{-1} = 16\left(\frac{\lambda}{\Delta}\right)^2\left(\frac{\phi q_o}{\Delta r_o}\right)^2\left(\frac{\Delta}{\delta_{o\eta}}\right)^2 \frac{\tau_i^{-1}}{[\exp(\hbar\delta_{o\eta}/kT)-1]}\,, \qquad (2.33)$$

if $\delta^2_{o\eta}\,\tau_c^2 \geq 1$, where $\delta_{o\eta}$ is the energy separating the ground state and the n^{th} excited orbital state. The Orbach process is also magnetic field independent.

Kivelson and Collins (1962) also considered the rotational spin-orbit process. This is not to be confused with the spin-rotation interaction discussed earlier, which does not involve relaxation through an excited state. The spin-orbit interaction is $\lambda \underset{\sim}{S}.\underset{\sim}{L}$. The spin $\underset{\sim}{S}$ is quantized along the applied field, while the rotational angular momentum $\underset{\sim}{L}$ is evaluated in a molecular framework. As the molecule rotates, the angle between $\underset{\sim}{S}$ and $\underset{\sim}{L}$ changes. Relaxation can occur only if the system undergoes a simultaneous spin and electronic transition. The contribution to the relaxation for this process is given by

$$T_2^{-1} = \frac{3}{2}\,(g - g_e)^2\tau_r^{-1}/\Sigma_\eta\Sigma_\alpha|\langle 0|\underset{\sim}{L}_\alpha|\eta\rangle|^2, \qquad (2.34)$$

where g is the isotropic g value, g_e the free electron g value, τ_r the correlation time for rotation, the matrix elements are between the ground state and the n^{th} electronic state and are summed all over states ($\eta \neq 0$) and all orientations of the molecule (α = x, y, z).

In general, vibrational spin-orbit processes are expected to be more important than rotational spin-orbit processes, especially for symmetric complexes with nearly degenerate states where $\langle 0|\underset{\sim}{L}_\alpha|\eta\rangle$ is very small.

Kivelson (1966) has found that, in the absence of low lying excited states, the EFF mechanisms are all negligible. Only the Orbach mechanism is expected to be significant, and then only if $h\delta_{o1}/kT$ is not too large.

3. Modulation of the Hyperfine Interaction Tensor

Atkins (1967) has considered the process in which collisions with diamagnetic solvent molecules excite the paramagnetic system to a higher vibrational or orbital level in which the hyperfine interaction tensor differs from that in the ground state. The unpaired spin is then subject to a fluctuating field, the amplitude of which corresponds to the difference in the hyperfine interaction field in the two states and with a correlation time which is, approximately, the inverse of the collision frequency.

The Raman process may be ignored, since no change in hyperfine interaction occurs. Atkins considered the direct vibrational process in which a real excitation occurs, but the excitation remains in the orbital ground state. For such a process, in liquids, Atkins obtained transition probabilities of the form,

$$W_D' \approx \frac{4\,(A_0^{01})^2\,\hbar\, f(I,s\pm1,\mp m_I)^2(\phi q/r_o)^2}{\omega_\nu^3\,\tau_c\omega_o^2\,M_k r_o^2[\exp(h\omega_\nu/kT)-1]}, \qquad (2.35)$$

where

$$A_n^{\nu\nu'} = \langle n\nu|A|n\nu\rangle - \langle n\nu'|A|n\nu'\rangle,$$
$$f(I,s\pm1,\mp m_I) = [I(I+1)-m_I(m_I\mp 1)]^{1/2}, \qquad (2.36)$$

A is the isotropic hyperfine coupling constant, ω_ν the molecular vibration frequency, M_k the reduced mass of the k^{th} vibrational mode, ω_o the Larmor frequency, τ_c the correlation time for collision, ϕ, q, and r_o are defined as in the Kivelson EFF mechanisms.

For what Atkins calls the Orbach process (Type I), which leaves the vibrational state of the molecule unchanged, he obtained

$$W_0' \approx \frac{4\,A_{on}^2\, f(I,s\pm1,\mp m_I)^2(\phi q/r_o)^2}{\omega_o^2\Omega_{on}^2\,\tau_c\,[\exp(\hbar\Omega_{on}/kT)-1]}, \qquad (2.37)$$

where,

$$A_{nn'} = \langle n'|A|n'\rangle - \langle n|A|n\rangle, \qquad (2.38)$$

and Ω_{on} is the excitation energy from the ground state to the n^{th} excited state.

Atkins also considered what he called the Orbach process (Type II), in which the final state includes a molecular vibration excitation. This process is less significant than the Orbach process (Type I) and may be neglected.

Atkins compared the Orbach process (Type I) with the Kivelson result for Orbach relaxation through the spin-orbit coupling and found that

$$\frac{W_K}{W_0'} \approx \frac{\omega_o^2\lambda^2}{A_{on}^2\Delta^2} \approx (\omega_o\Delta g/A_{on})^2, \qquad (2.39)$$

where $\Delta g = g - g_e$. Thus, at sufficiently low microwave frequency, the Orbach process (Type I) will dominate in those molecules possessing hyperfine interaction, while at higher frequencies the Kivelson Orbach process will always dominate.

III. EXPERIMENTAL METHODS

A. SAMPLE PREPARATION

1. Vanadyl acetylacetonate (VOAA).

The vanadyl acetylacetonate was purchased from K & K laboratories. The EPR spectrum showed no paramagnetic impurities and further purification was considered unnecessary. All solvents were at least reagent grade and were degassed on a vacuum line before use.

Samples were prepared in the following manner. The solid VOAA was placed in a 3 mm diameter pyrex tube, sealed at one end. The tube was then joined to the vacuum line and evacuated. Prolonged pumping seemed to cause spectral changes, so pumping time was kept to a minimum. Ammonia was then distilled into the sample tube and frozen by immersion of the tube in liquid nitrogen. Excess ammonia was removed by gentle pumping and the tube was sealed with a torch. Since the room temperature vapor pressure of ammonia is of the order of ten atmospheres, great care was taken during the warming of the sample to room temperature. Failures were relatively rare when using 3 mm diameter tubing, but became more common with larger tube sizes.

The 50%NH_3/50%THF glass samples were similarly prepared. The THF was distilled into the sample tube before the ammonia.

The rate of exchange of the acetylacetonate ligands is very slow, but samples older than 24 hours began to show changes in the EPR spectrum. Because of this fresh samples were prepared and run immediately in all experiments. All samples used were sufficiently dilute that no broadening due to concentration was observed.

2. Copper (II).

The copper experiments were performed using isotopically enriched ^{63}CuO (99.62%) obtained from Oak Ridge National Laboratories. The oxide was dissolved in 0.15 M perchloric acid. A small quantity of this solution was placed in the sample tube and the water was slowly pumped out on the vacuum line. Ammonia was distilled into the sample tube dissolving the copper. The ammonia was then pumped off. This was repeated to reduce the number of water molecules bound to the copper ions. Sample preparation continued from this point in a manner analogous to the VOAA preparation.

Since glycerine, in the glass samples, could not be distilled into the sample tube, the preparation was changed slightly. After pumping off the water and ammoniating the sample several times, the sample tube was removed from the vacuum line and the mixture of equal parts glycerine and absolute ethanol was added. The sample tube was then reattached to the vacuum line and the sample was degassed using the freeze-pump-thaw method. Ammonia was then distilled into the tube and the tube was sealed off.

The X-band measurements were carried out in 3 mm diameter pyrex tubes. The S-band measurements required 5 mm diameter pyrex tubes in order to improve the filling factor of the cavity. All samples were sufficiently dilute that the linewidth was independent of the copper concentration.

3. Titanium (III).

Titanium (III) was obtained from Alfa Inorganic in the form $TiCl_3$, and from Sargent Chemical Company as a 1 M solution of $Ti_2(SO_4)_3$. The concentrations of the samples varied from 0.5 M to 3 M. Comparison of the data obtained at high Ti (III) concentrations with that for low concentrations showed negligible effects from Ti-Ti interactions. All samples were approximately 1 M in acid to prevent formation of $Ti(H_2O)_5OH^{2+}$ which becomes significant as the pH approaches 4 (Pecsok and Fletcher, 1962).

The samples were contained in a Varian E-248-1 aqueous solution sample cell. K-band spectra were obtained with the sample sealed in a 10 mm by 3 mm diameter quartz tube. In all cases a nitrogen atmosphere was used to minimize oxidation of the titanous ion.

B. SPECTROMETERS

Field measurements were made using a Harvey-Wells NMR Precision Gaussmeter, Model 0-502, with the proton resonance frequency measured by either a Hewlett-Packard Model 5245L frequency counter or a General Radio Model 1192-B frequency counter.

The klystron frequency, at S-band and X-band, was measured by a Hewlett-Packard Model 5245L frequency counter equipped with a 5255A frequency converter plugin. At K-band the frequency was measured by observing the beating of the klystron frequency with the frequency of a Polarad Model 1207 3.8-8.2 GHz Signal Source. The Polarad frequency was then measured as described above.

The sample temperature was controlled in two ways. For the titanium samples a Varian V-4557 Variable Temperature Accessory with a quartz dewar insert and a Varian V-4540 Temperature Controller were used. For the vanadyl and copper samples, nitrogen gas, boiling from a dewar of liquid nitrogen, was used as a coolent. The rate of boiling was controlled by a Variac supplying current to a resistor immersed in the liquid nitrogen. For temperatures close to room temperature, nitrogen gas at room temperature was mixed with the cold nitrogen gas stream to ensure adequate gas flow past the sample.

The temperature was measured using a copper-constantan thermocouple with one junction immediately outside the cavity and the reference junction at 273 K. The voltage was measured using either a Digitec Model 268 DC millivoltmeter or a Keithley Model 160B digital multimeter. The voltage was converted to temperature using Omega Engineering Inc., 1971 conversion table IV (see N.B.S. Circular #561). The thermocouple was calibrated at 77 K and 373 K. The precision of the temperatures measured was thought to be ±0.5°.

The viscosity of ammonia was obtained using the results of Hutchison and O'Reilly (1970).

1. S-band.

The S-band spectrometer was constructed in this laboratory and is of conventional design. A block diagram of the system is shown in Fig. 2. The cavity was designed by James Chang and operates at 3.27 GHz with the quartz dewar insert installed. The modulation frequency was 100kHz.

2. X-band.

The X-band spectrometer used was a Varian V4502 EPR spectrometer, equipped with field dial, a 9 inch magnet, and a Hewlett-Packard Model 7004b X-Y recorder. The cavity was a Varian Model V-4531 multipurpose rectangular cavity resonating at 9.2 GHz with the quartz dewar insert installed. The modulation frequency was 100 kHz.

3. K-band.

K-band measurements were carried out at 23.9 GHz using an OKI Model 24V10A klystron and a bridge constructed in this laboratory. A block diagram of the system is shown in Fig. 3. The rectangular cavity was fabricated from brass waveguide and silver plated. The modulation frequency was 800 Hz.

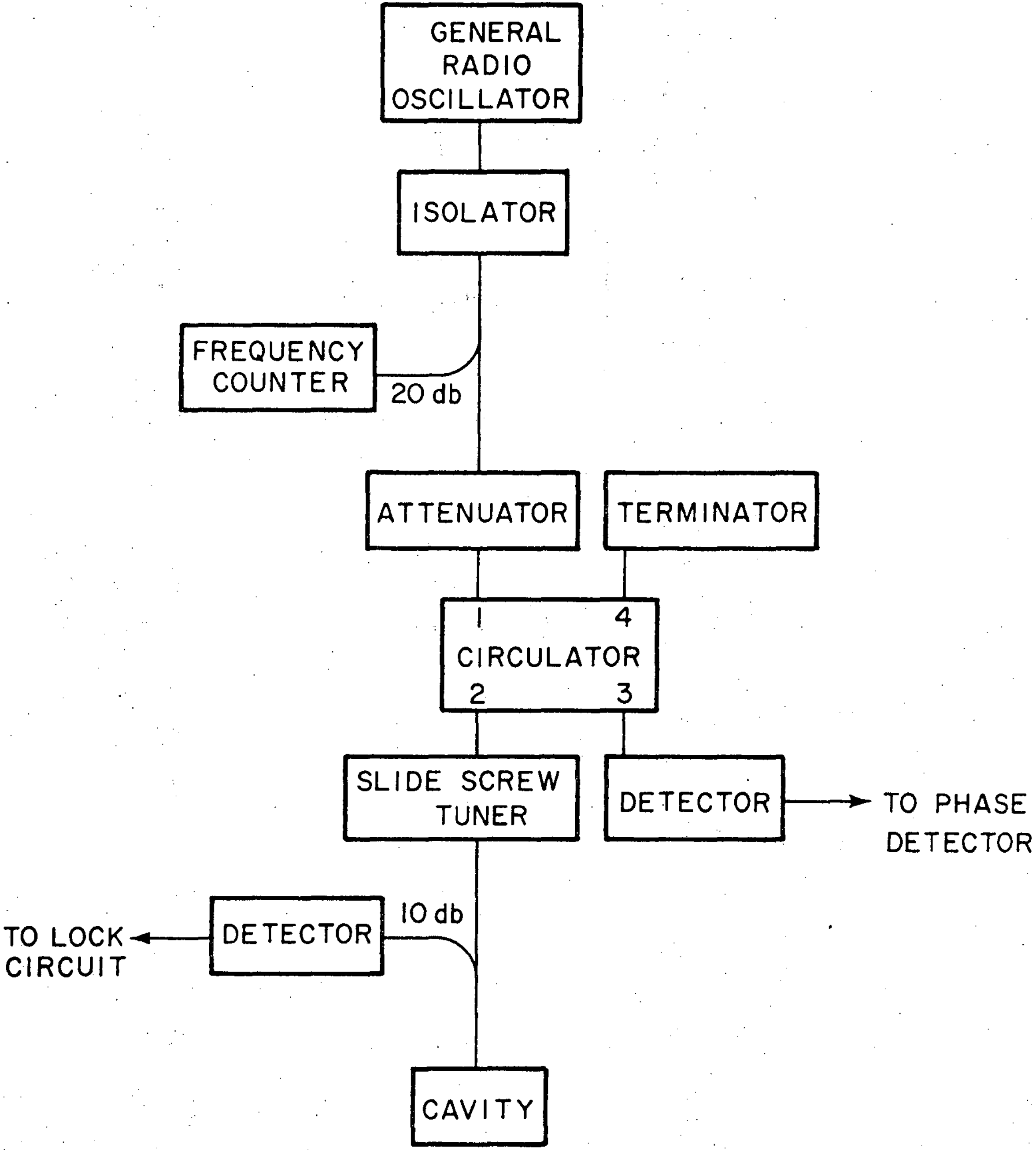

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Fig. 2. Block diagram of the S-band spectrometer.

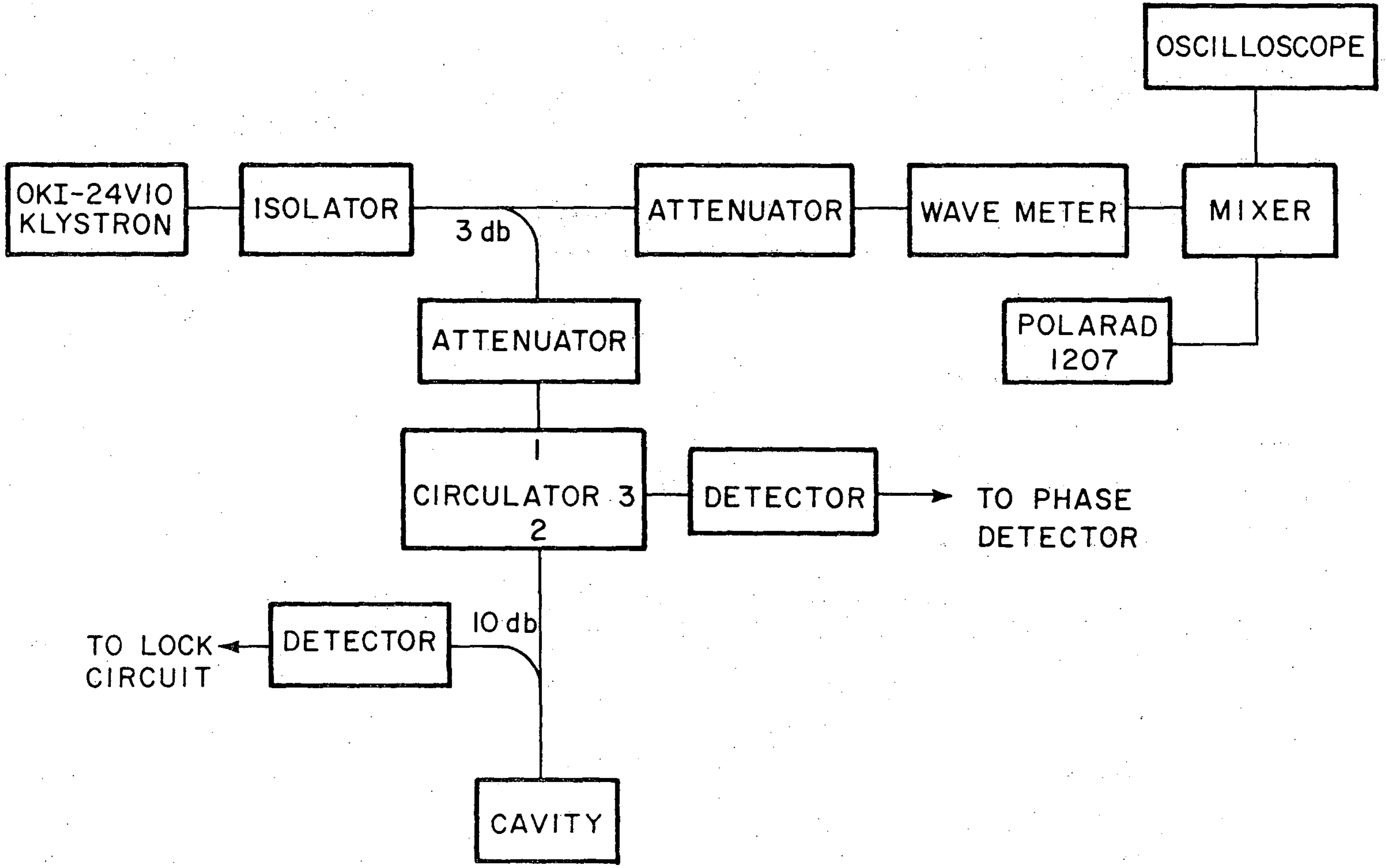

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Fig. 3. Block diagram of the K-band spectrometer.

IV. VANADYL ACETYLACETONATE

A. INTRODUCTION

The EPR linewidths of vanadyl ion (VO^{2+}), in solution, have been of interest for many years. The spectrum was first reported by Garif'yanov and Kozyrev (1954) and by Pake and Sands (1955).

The vanadyl ion is the most common of the transition metal oxy-cations and has relatively simple magnetic properties. It has only a single 3d electron and the strength of the V-O bond creates a strong axial field which has been well characterized structurally (Dodge, Templeton, and Zalkin, 1961). The ^{51}V nucleus is in nearly 100 percent natural abundance. Its spin of 7/2, interacting with the electron spin of 1/2, gives eight well resolved lines with marked differences in the linewidths.

Kivelson anisotropic g and A value theory has been used to explain the linewidths of many vanadyl complexes with great success. The vanadyl system is now considered to be a prime example of the success of Kivelson theory.

Before embarking upon the much more ambitious problem of explaining the relaxation of copper (II) ions in solution, it was decided to use the vanadyl system to determine whether solvent effects in liquid ammonia might cast doubt upon the validity of the conclusions drawn from the copper experiments. Liquid ammonia also enables one to observe the vanadyl relaxation in viscosity ranges not previously explored.

The vanadyl complex chosen for this work was vanadyl acetylacetonate (VOAA). This complex was chosen for several reasons. Its relaxation has been explained in a number of solvents (Gersmann and Swalen, 1962; Wilson and Kivelson, 1966a; Atkins and Kivelson, 1966; Wilson and Kivelson, 1966b; Hwang, Kivelson, and Plachy, 1973; Hoel and Kivelson, 1975a, 1975b; Kivelson and Lee, 1964). It is stable over the range of temperatures studied. It is also soluble in liquid ammonia and the rate of ligand exchange is not very fast.

The EPR spectrum of VOAA is known to be sensitive to changes in the solvent (Bernal and Rieger, 1963; Wilson and Kivelson, 1966b; Kivelson and Lee, 1964; Hoel and Kivelson, 1975a, 1975b). The solvent dependence of the EPR spectrum is thought to arise from the structure of VOAA. The two acetylacetonate ligands are bidentate, forming a plane perpendicular to the axis of the V-O bond. Solvent molecules can be coordinated in the sixth position, opposite the oxygen atom. Since the EPR spectrum of vanadyl complexes are dominated by the strength of the V-O bond, any effect the solvent molecule has upon the axial molecular orbital will have a large effect on the spectra. Thus VOAA should be a sensitive test of any unusual solvent effects caused by liquid ammonia.

B. SPECTRA

Before embarking upon a proper treatment of the linewidths, the anisotropic spin Hamiltonian parameters must be known. Solution spectra yield only the isotropic values of these parameters, and thus solid state measurements must be used. Measurements on magnetically dilute, single crystals should give the best values for the anisotropic parameters, however, there are often drawbacks to the use of single crystal measurements. Often a suitable crystal lattice cannot be found. Also, there often occur distortions in a crystal lattice which do not correspond to the distortions present in solution.

In the case of VOAA in ammonia, we have, for lack of a better source, obtained the anisotropic parameters from frozen glass spectra. This method, originally used by Sands (1955), has been shown, in many cases, to yield the anisotropic parameters (Blinder, 1960; Kneubuhl, 1960; Neiman and Kivelson, 1961; Ibers and Swalen, 1962; Gersmann and Swalen, 1962; Weil and Hecht, 1963; Vanngard and Aasa, 1963; Taylor and Bray, 1970).

In a glass or polycrystalline sample, the spectrum observed is the envelope of spectra from ions of all possible orientations. For a simple, axial anisotropy of the g tensor, the values of $g_{\parallel}$ and $g_{\perp}$ may be readily measured from the extrema of the absorption. The addition of hyperfine anisotropy quickly results in complicated spectra. Simulation of the spectrum by digital computer is often the only way to extract the magnetic parameters from a complicated spectrum. The spectral parameters can then be adjusted until satisfactory agreement between the calculated and experimental spectrum is reached.

The glass used was developed by Spencer (1965) and consisted of equal parts ammonia and tetrahydrofuran. Liquid ammonia alone tends to crystalize as it freezes and broadens the resulting spectrum. The observed spectrum was simulated using the method of Vanngard and Aasa (1963). The program used to simulate the spectrum is described by Chang (1971). The observed and calculated spectra are shown in Fig. 4.

For comparison with other solvents, the magnetic parameters of VOAA in a variety of representative solvents are presented in Table I. For

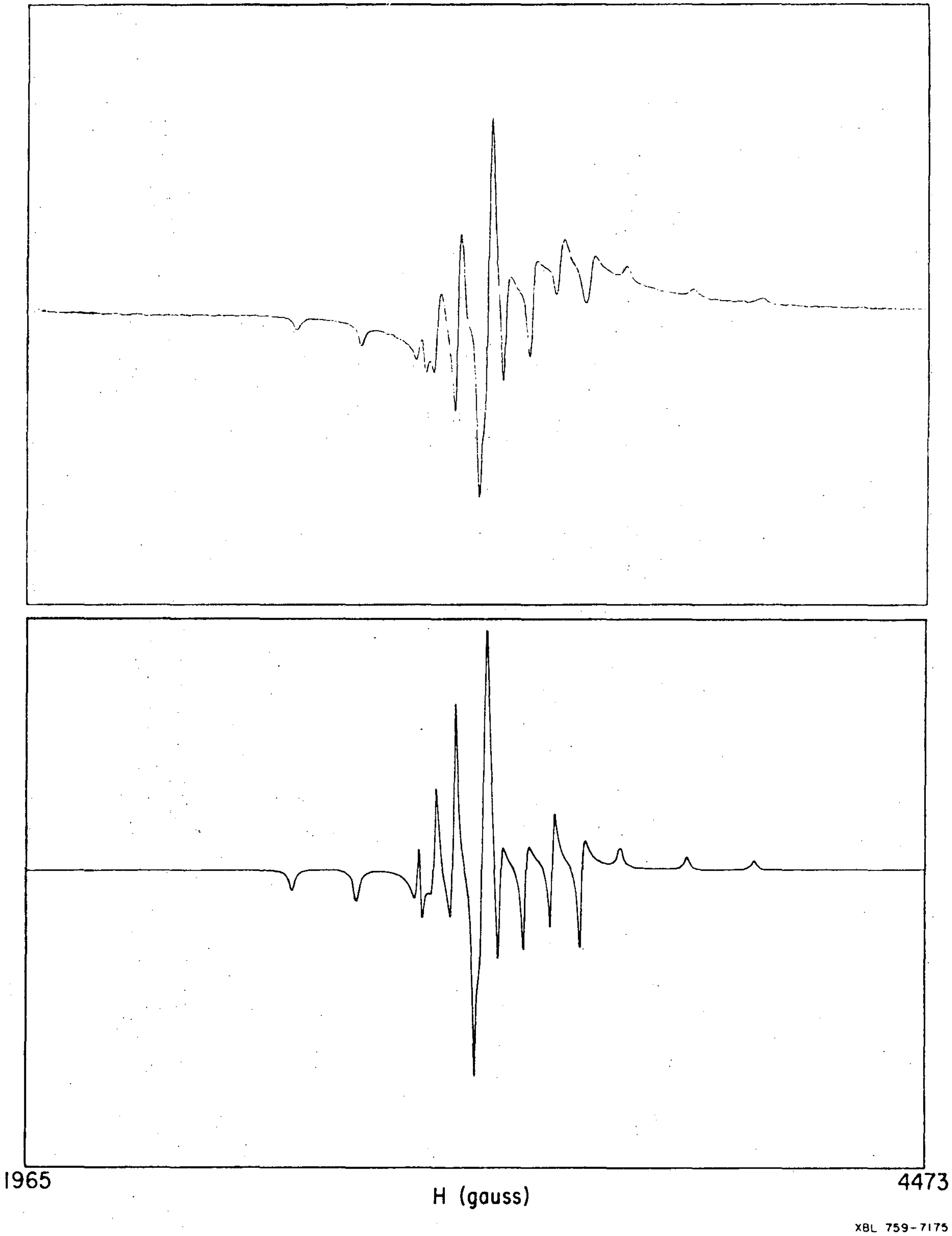


Fig. 4. Glass spectrum of VOAA in NH_3/THF. The upper curve is experimental and the lower curve is a simulation.

TABLE I. Magnetic Parameters of VOAA

solvent	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle^{a}$	$A_{\parallel}^{b}$	$A_{\perp}^{b}$	$\langle A \rangle^{a,b}$	Reference
toluene	1.943	1.979[c] 1.985	1.969	-169.2	-63.0[c] -59.1	-97.6	Wilson and Kivelson, 1966a.
diphenylmethane	1.945	1.984	1.971	-172.4	-61.2	-98.3	Wilson and Kivelson, 1966b.
CS_2			1.968[d]			-99.5	Kivelson and Lee, 1964.
THF	1.945	(1.981)[e]	1.969	(-169.0)[e]	-61.8	-97.5	Kivelson and Lee, 1964.
NH_3	1.945	(1.979)[e]	1.968	(-165.0)[e]	-59.9	-95.0	Kivelson and Lee, 1964.
CH_3OH	(1.944)[f]	(1.983)[f]	1.968[d]			-94.0[d]	Bernal and Rieger, 1963.
toluene-$CHCl_3$	1.944	1.996	1.979	-173.5	-63.5	-100.2	Gersmann and Swalen, 1962.
NH_3/THF	1.945	1.980	1.968	-170.0	-59.7	-96.5	This work.

a. $\langle g \rangle = (g_{\parallel} + 2g_{\perp}) /3$; $\langle A \rangle = (A_{\parallel} + 2A_{\perp})/3$.

b. Hyperfine coupling constants are assumed to be negative (Myers, 1973) and are given in units of 10^{-4} cm^{-1}.

c. The values given are g_x and g_y respectively, and similarly for A_x and A_y.

d. Values given are measured in solution.

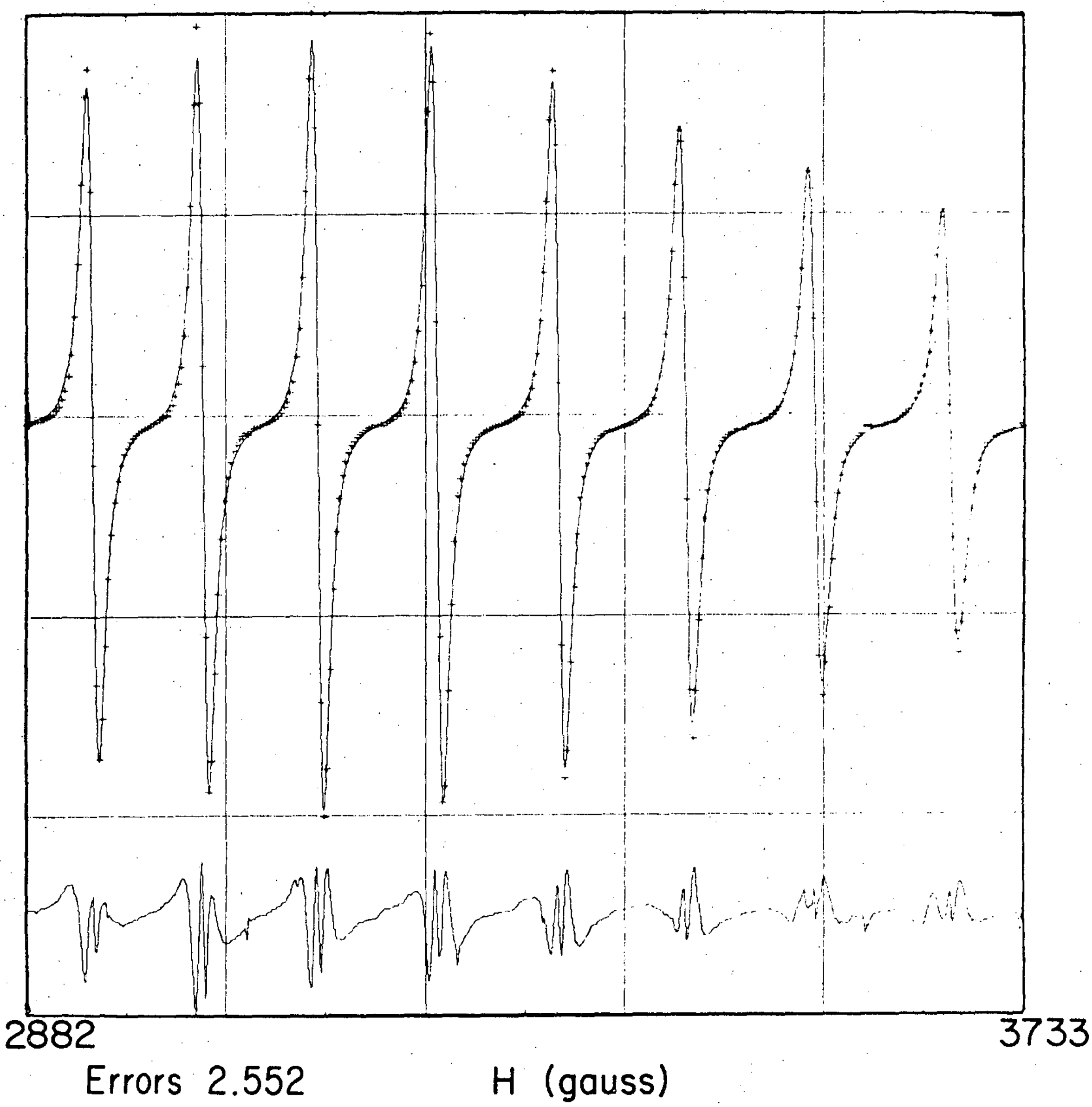
e. Values given are calculated from the other magnetic parameters.

f. Values given are calculated from optical data.

a more extensive tabulation see Kivelson and Lee (1964). As can be seen from Table I, our g values are in excellent agreement with those found in other solvents, particularly NH_3 and THF. Solvent effects show the greatest effect in the A values. Our value of the isotropic hyperfine interaction, ⟨A⟩, obtained from the frozen glass measurements, does not appear to agree with the value obtained in NH_3. This discrepancy may be due to crystallinity in the pure ammonia glass. The difference in any case is not great and will have little effect on the calculations to follow.

No superhyperfine interaction was resolved in the glass spectra. This is to be expected since the unpaired electron is almost completely localized on the vanadium ion in a d_{xy} atomic orbital (Ballhausen and Gray, 1962), although polarization of filled orbitals is expected to give a small contribution to the linewidth (Kivelson and Lee, 1964).

The X-band EPR spectra of VOAA in ammonia were measured between -72° C and 23° C in order to determine the linewidths and isotropic spin Hamiltonian parameters. The spectra were digitized using the apparatus described by Chang (1971). The digitized spectra were analyzed using a least squares fitting procedure described elsewhere (Bauder and Myers, 1968; Chang, 1971). However, we used a fitting method involving eight separate lines instead of the second-order Hamiltonian used by Chang. An example of the fit obtained is shown in Fig. 5. The experimental curve is represented by the crosses, and the solid curve represents the fitted values. The error curve, at the bottom, represents the difference between the two curves expanded by the scale factor shown. The A value was extracted from the eight line positions by calculating the average



XBL 759-7191

Fig. 5. Example of the fit of the solution spectrum of VOAA in liquid ammonia. The crosses are the experimental points and the continuous curve is the theoretical fit of the data. The lower curve is the difference between the experimental curve and the theoretical curve and is expanded by a factor of 2.552.

value obtained from the outer three pairs of lines. This value was then used in a second-order Hamiltonian to calculate the g value. The g value is also the average of the values obtained from the outer three pairs.

It has been observed previously that the isotropic g and A values of VOAA vary as a function of temperature (Wilson and Kivelson, 1966a). This has been explained as being caused by changes in solvation and bonding (Kivelson and Neiman, 1961; Wilson and Kivelson, 1966a). The values obtained in this work are shown in Figs. 6 and 7. As expected from bonding theory, the isotropic g and A values have opposite temperature dependences.

The variation of the isotropic g and A values place a limitation upon the accuracy of the relaxation results, but the variation is not great enough to seriously affect the results. The values chosen to use in the relaxation calculations were $\langle g \rangle = 1.968$ and $\langle A \rangle = -103.7$ gauss. Small changes in these parameters do not cause marked changes in the results obtained.

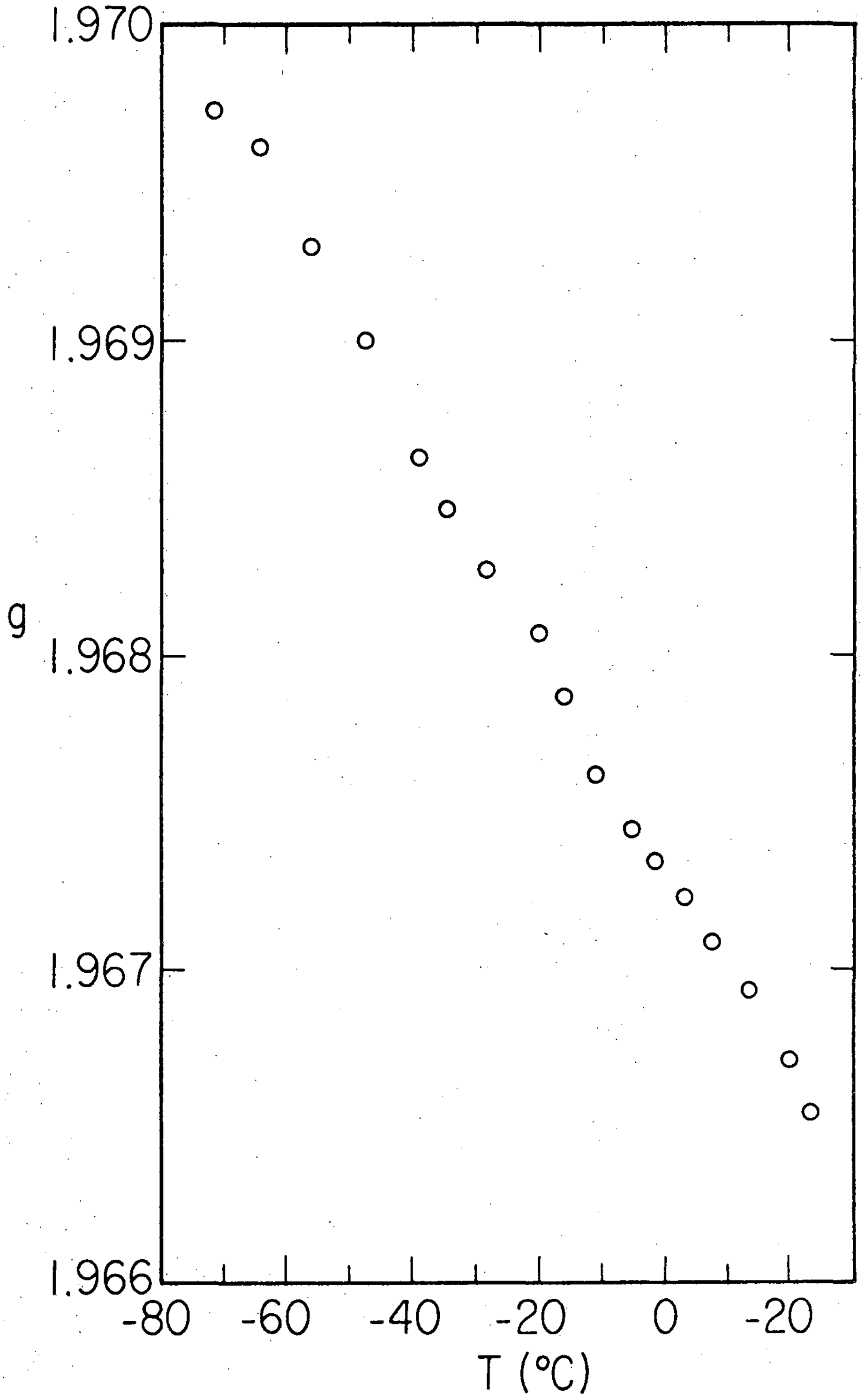


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Fig. 6. g vs T for VOAA in liquid ammonia.

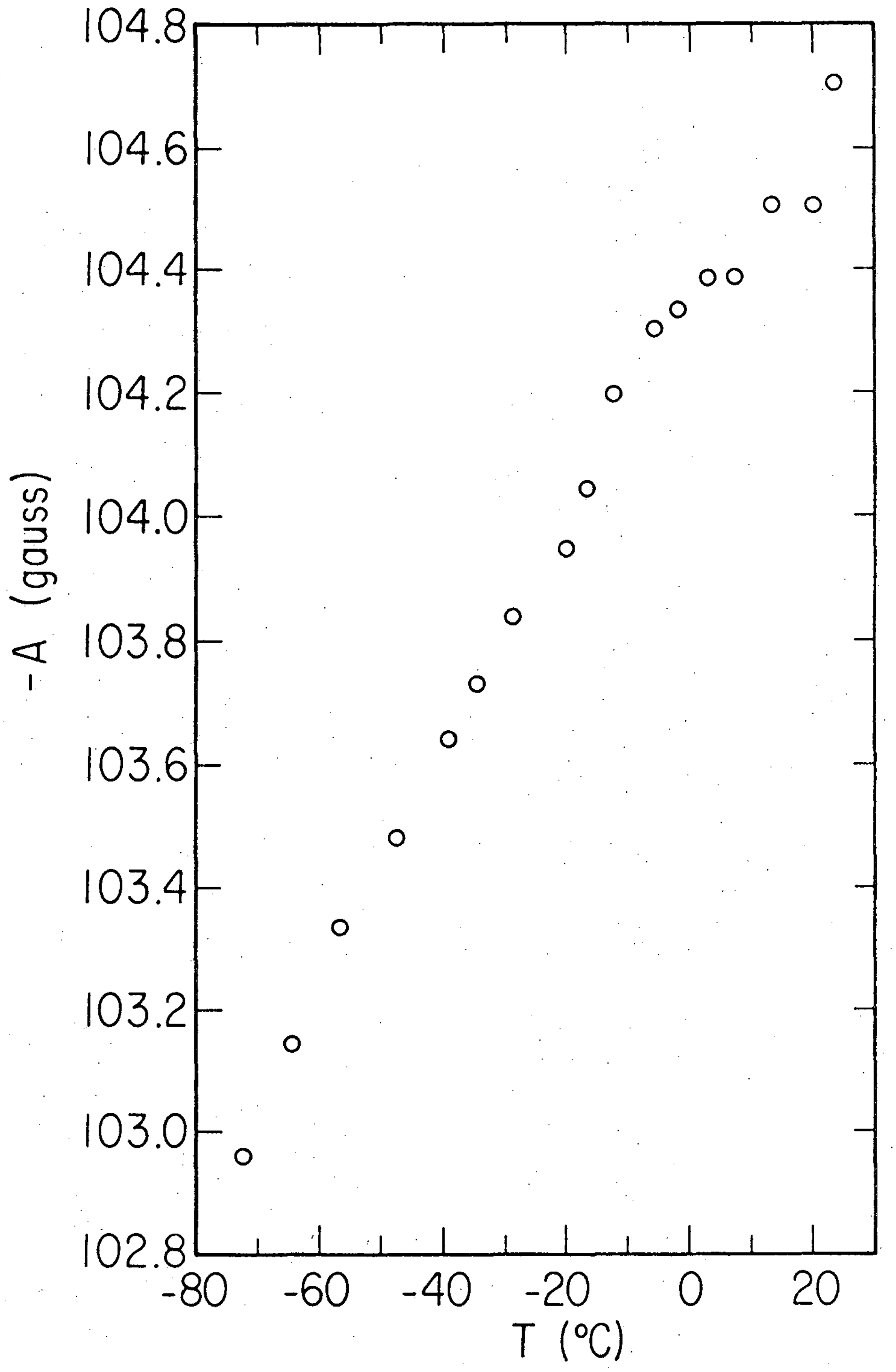

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Fig. 7. -A vs T for VOAA in liquid ammonia.

C. RESULTS AND DISCUSSION

Wilson and Kivelson (1966a) have shown that the linewidths of VOAA can be well represented by

$$\Delta H = \alpha+\beta m_I + \gamma m_I^2 + \delta m_I^3, \tag{4.1}$$

where $\alpha = (\alpha'+\alpha'')$, and α', β, γ, and δ are given by Kivelson tumbling theory. α'' includes the effects of all other mechanisms which do not depend on the nuclear magnetic quantum number.

Since, experimentally, we obtain eight linewidths for each temperature and have only four parameters (α, β, γ, and δ) to fit, the system is overdetermined. A least squares fitting procedure was used to extract the parameters at each temperature. From the beta curve it is possible to calculate a hydrodynamic radius (Chang, 1971). For the data obtained in liquid ammonia the radius calculated is 3.53 A.

At this point it is instructive to consider whether the assumptions of the rotational diffusion model are valid. From eqs. 2.1 and 2.20 we obtain

$$\tau = \frac{4\eta\pi r_o^3}{3\ k\ T}\,\kappa, \tag{4.2}$$

where in this case

$$\kappa^{1/3} r_o = 3.53\ \text{A}. \tag{4.3}$$

The hydrodynamic radius for VOAA in benzene, r_T, has been measured for translational diffusion (Hwang, Kivelson, and Plachy, 1973). The translational diffusion experiments measured the diffusion constant, D, which is related to the hydrodynamic radius by

$$D = kT/6\pi\eta r_T. \tag{4.4}$$

The hydrodynamic radius obtained was 3.8 A. Although D was measured at only one temperature and in only one solvent, similar measurements indicate that r_T is independent of solvent and temperature. For VOAA, $r_o=r_T$. Thus eq. 4.3 gives $\kappa = 0.93$. The stickiness parameter, s, can be calculated from eq. 2.22 using a value of 0.3 for Ξ (Hoel and Kivelson, 1975a). Such a calculation gives a value of 0.90 for the stickiness parameter. Recalling that s=1 is the pure stick condition assumed in the derivation of the rotational diffusion model, a value of 0.90 indicates that the theory should be a good approximation of the actual behavior.

From the magnetic parameters and the effective hydrodynamic radius, the contributions to the relaxation caused by anisotropies in the g and A tensors can be calculated. The results of these calculations and the experimental values of α, β, and γ as a function of η/T are presented in Figs. 8, 9, and 10 respectively. The values of δ determined from the experimental linewidths were very small and the errors relatively large and are not presented. As can be seen from Fig. 9 and 10, the values of β and γ as a function of η/T are in good agreement with the theoretical curves. Figure 8 shows that $\alpha \neq \alpha'$ and that there is another mechanism responsible for this residual linewidth.

The usual explanation of the residual linewidth in VOAA is a spin-rotation relaxation mechanism (Atkins and Kivelson, 1966; Wilson and Kivelson, 1966b). Figure 11 shows the residual linewidth as a function of T/η. As expected from eq. 2.16, the residual linewidth is a linear function of T/η, indicating a spin-rotation interaction. The solid line in Fig. 11 is the result of a least-squares fit of the residual linewidth

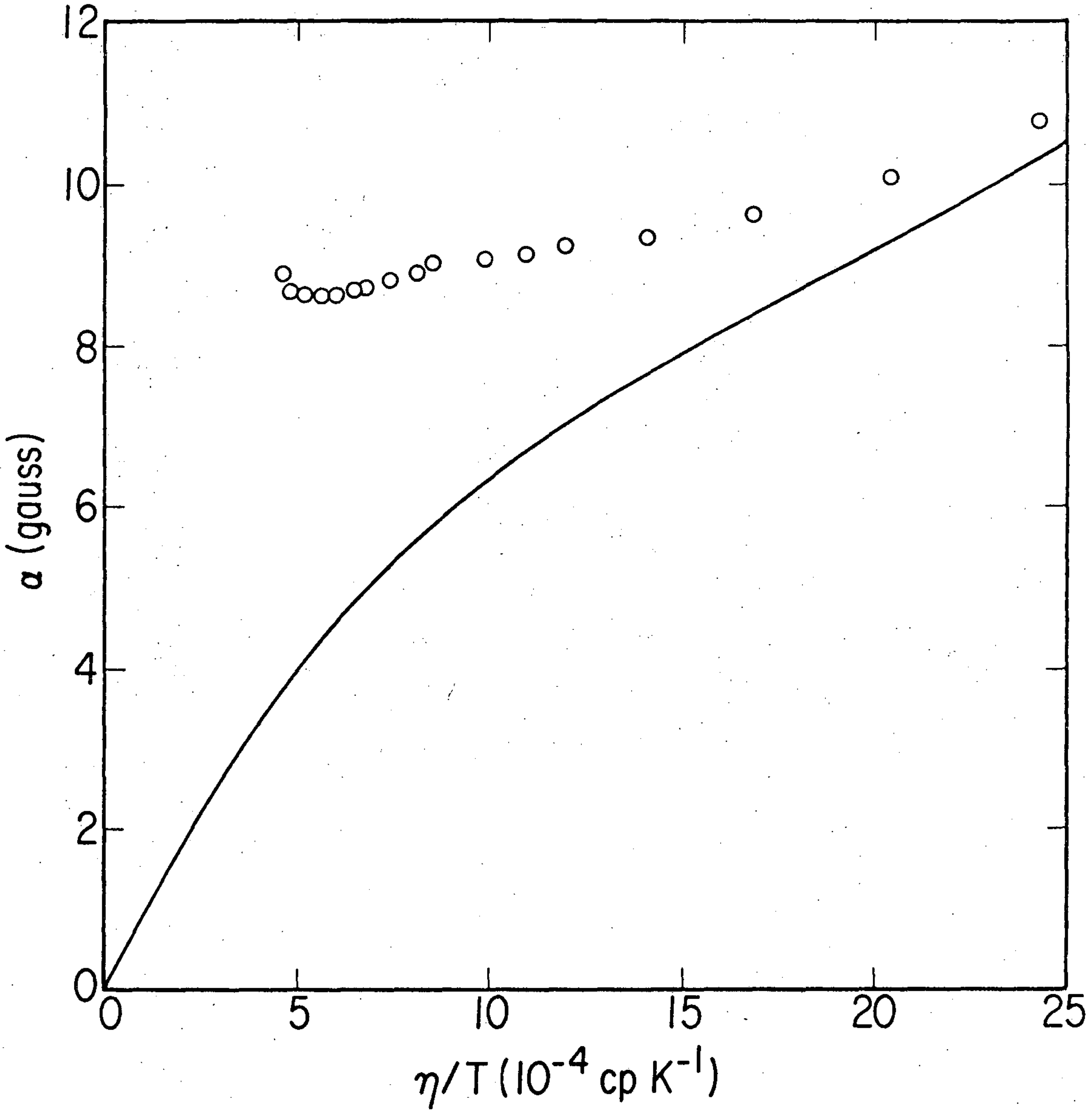

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Fig. 8. Alpha parameter vs η/T for VOAA in liquid ammonia. The curve is theoretical.

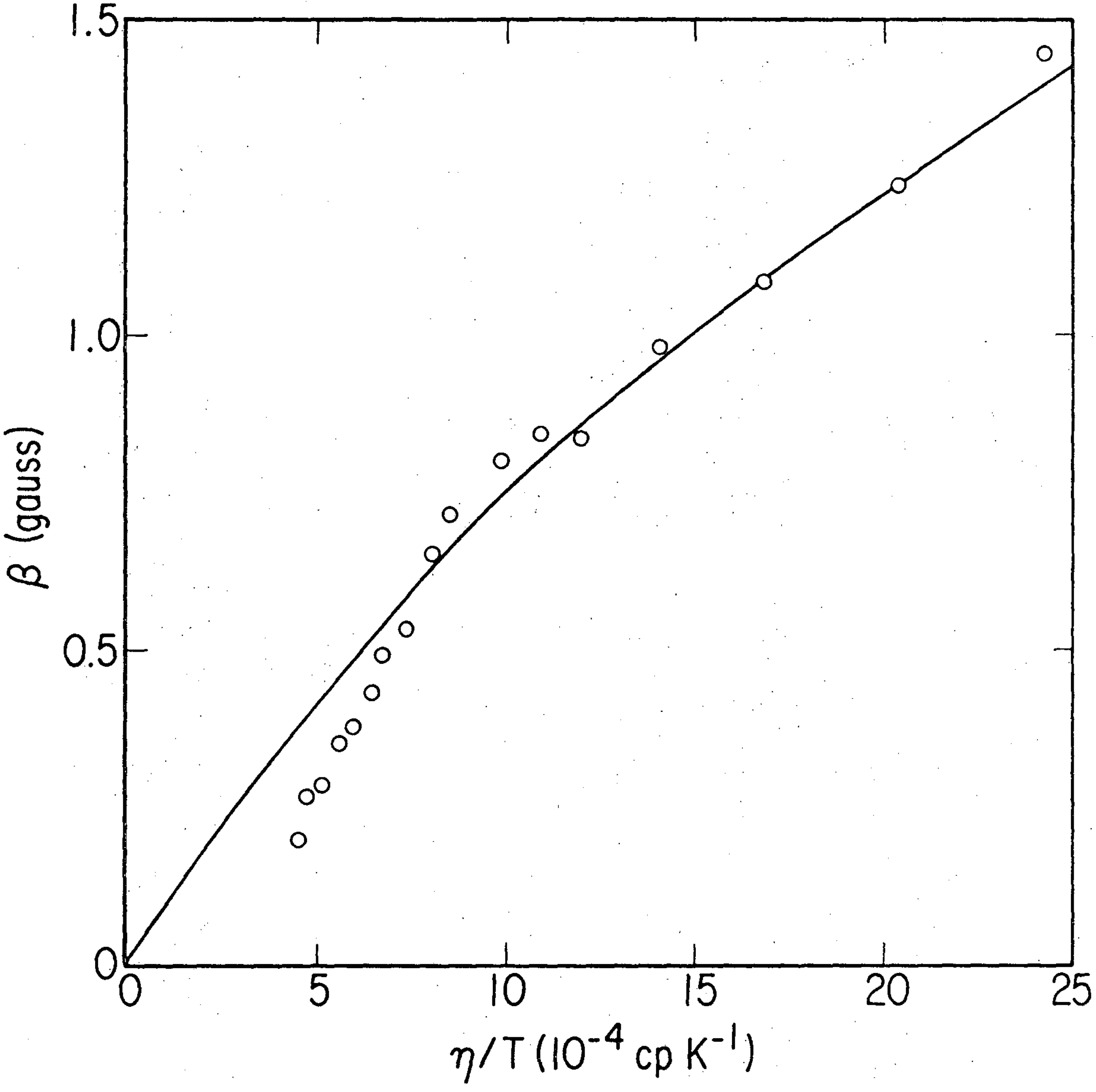

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Fig. 9. Beta parameter vs η/T for VOAA in liquid ammonia. The curve is theoretical.

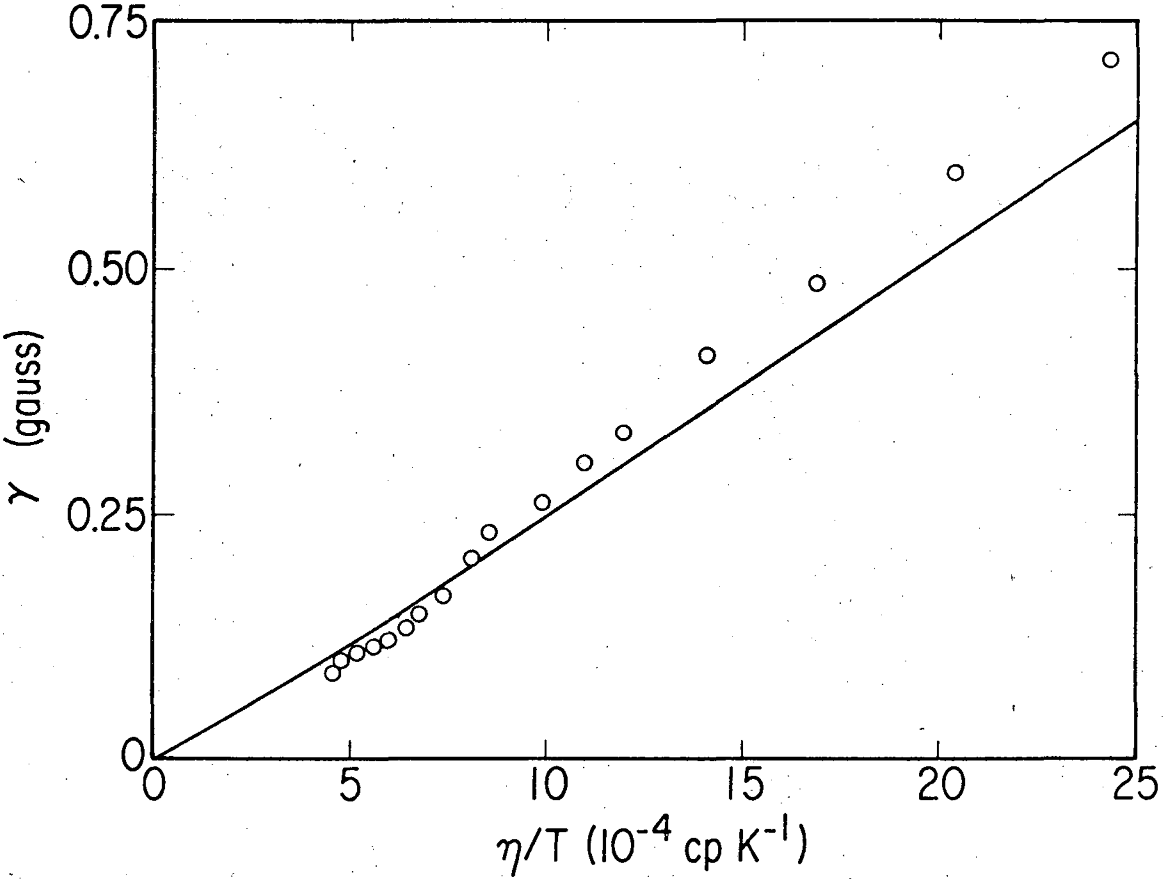

Fig. 10. Gamma parameter vs η/T for VOAA in liquid ammonia. The curve is theoretical.

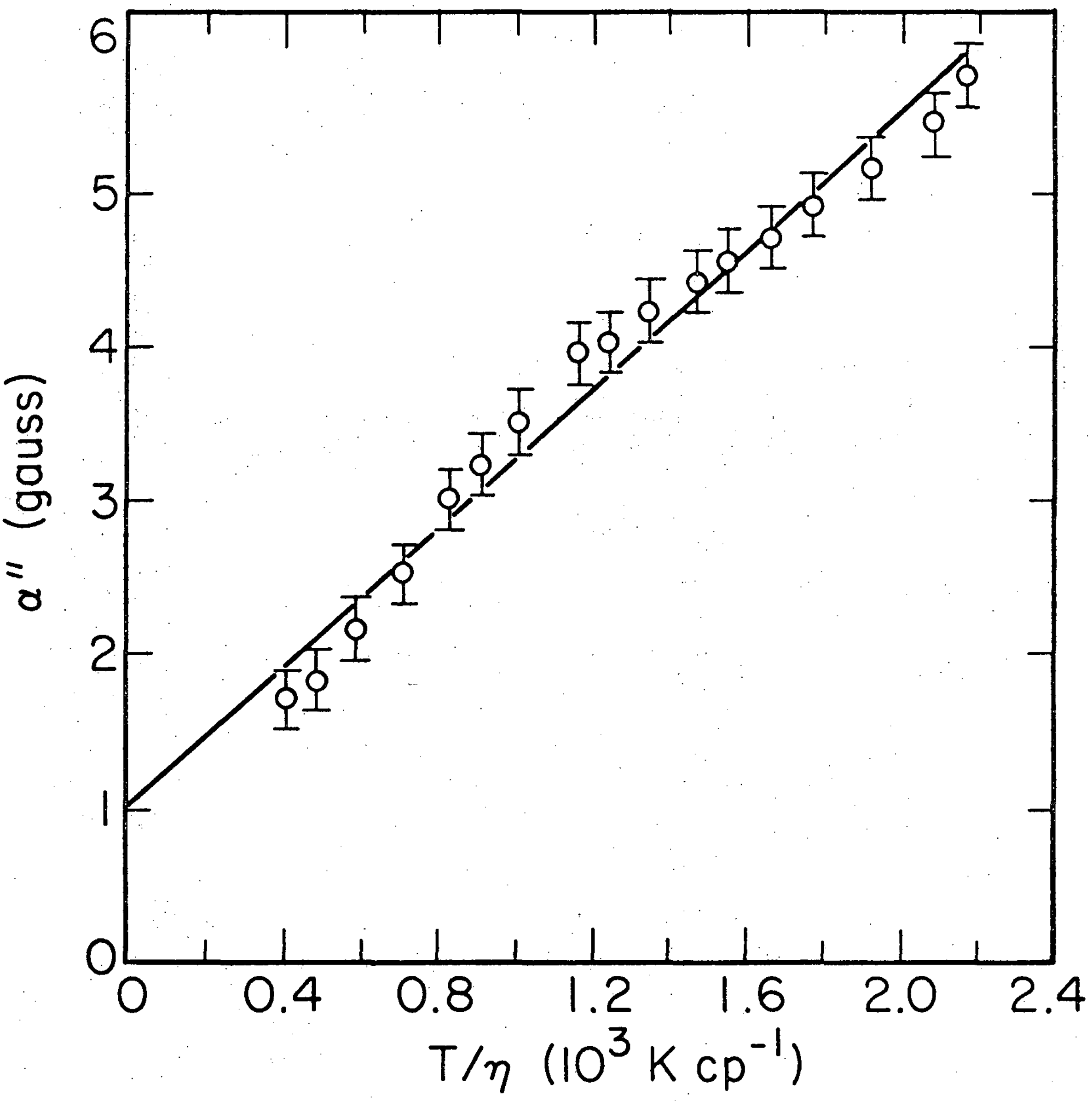

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Fig. 11. Residual linewidth, α", vs T/η for VOAA in liquid ammonia. The straight line is a least-squares fit of the data.

to a straight line. As expected for a system in which the rotational diffusion model is a good approximation, the hydrodynamic radius calculated from the residual linewidth is in exact agreement with the radius calculated fom Kivelson tumbling theory.

The intercept in Fig. 11 of 1 gauss is probably due to unresolved, isotropic ^{14}N superhyperfine interaction. For vanadyl in porphyrin systems, ^{14}N superhyperfine structure has been observed (O'Reilly, 1958; Kivelson, 1960; Kivelson and Lee, 1964). The porphyrin nitrogens form a plane perpendicular to the V-O bond and have a nearly isotropic coupling constant of 2.8 gauss. In our system, we have only one nitrogen contributing to the hyper hyperfine structure and it is situated directly opposite the V-O bond. Since the free electron is in a d_{xy} orbital on the vanadium atom, there are nodes in the wavefunction at the nitrogen nuclei in both the porphyrins and in our case. To explain the porphrin ^{14}N superhyperfine structure, Kivelson and Lee, (1964) did a configuration interaction calculation. Their calculation gave a reasonable explanation of the porphyrin system. Our system has approximately the same symmetry as the porphyrin and the calculation should be approximately valid. The calculation indicated a contribution of about a gauss for the d_{z^2} orbital directed at a nitrogen atom, and the interaction should be isotropic. This appears to be a reasonable explanation of the intercept in Fig. 11.

If the relaxation of VOAA in liquid ammonia is actually a combination of reorientational tumbling and spin-rotation interaction, the linewidths at any frequency can be readily calculated. The spin-rotation interaction has no frequency dependence and the reorientational tumbling frequency dependence is given in eqs. 2.5-2.8. The linewidth parameters calculated for S-band (3.5 GHz) as well as the experimental values are presented in Table II. The agreement between the theory and experiment is very good, confirming the analysis of the relaxation mechanisms. A typical, room temperature spectrum of VOAA in ammonia at S-band is shown in Fig. 12.

TABLE II. S-band Linewidth Parameters for VOAA

	Calculated from X-band data	Experimental S-band values
α'	3.25	3.13
α''	(5.64)[a]	(5.64)[a]
β	.222	.234
γ	.0861	.0903
δ	-.00686	-.0134

a. Assumed to be field independent.
All values are given in gauss.

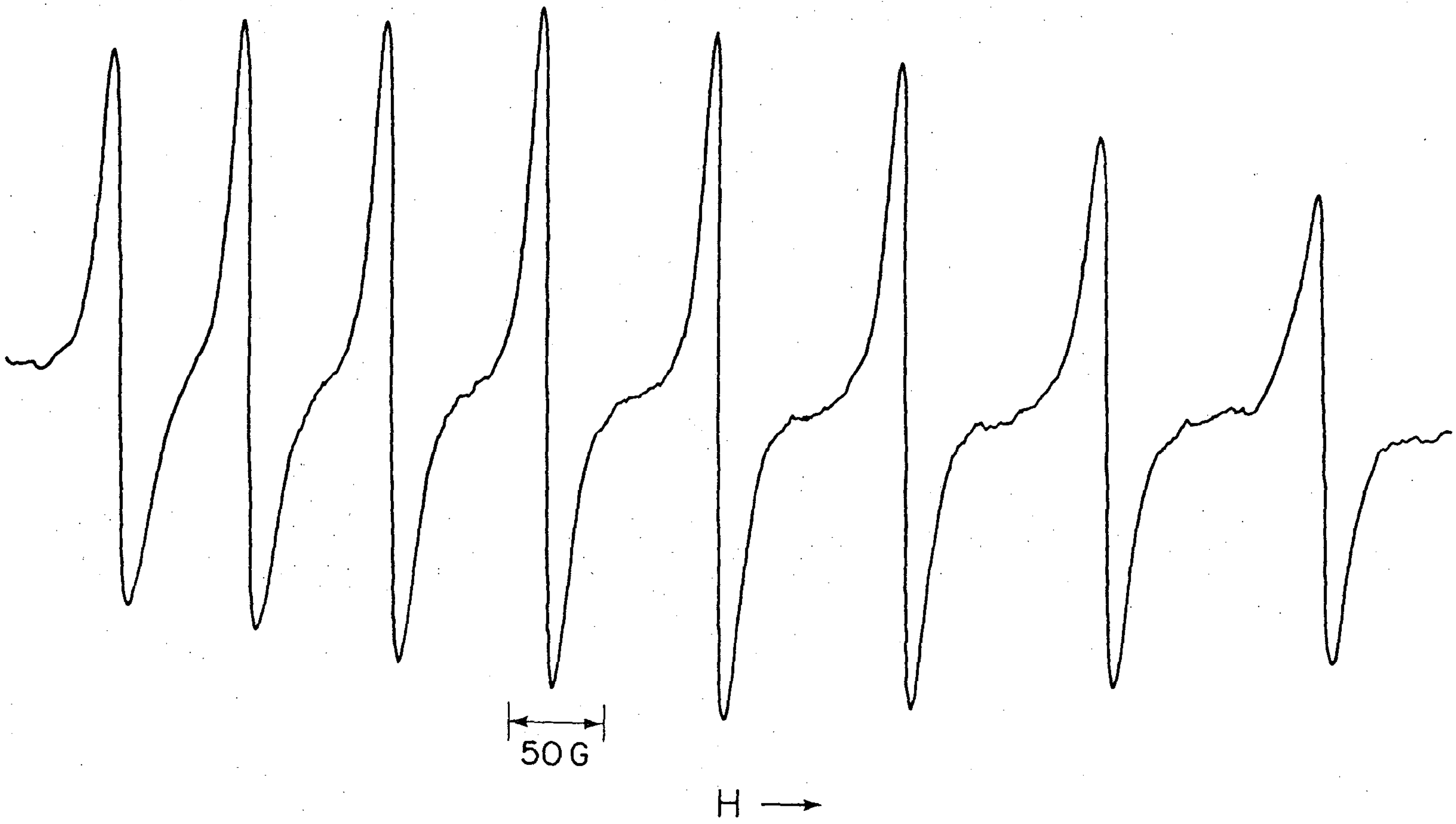

Fig. 12. Room temperature spectrum of VOAA in liquid ammonia at 3.27 GHz.

XBL 759-7182

V. COPPER

A. INTRODUCTION

Copper (II) is a d^9 system. In a field of octahedral symmetry the five-fold orbitally degenerate free ion energy levels split as shown in Fig. 13a. The lowest level being doubly degenerate, the complex will spontaneously distort due to the Jahn-Teller theorum. A trigonal distortion of the octahedral field will not remove the degeneracy of the ground state, therefore most copper complexes tend to elongate tetragonally along one of the four-fold axes of the octahedron. The energy levels for a tetragonal distortion are shown in Fig. 13b. In some cases the distortion is large enough that the complex may be considered to be square planar in symmetry. The molecular orbital treatment of Kivelson and Neiman (1961) gives the symmetry labeling of the orbitals shown in Fig. 13. The B_{1g} orbital is assumed to be the ground state. If the A_{1g} orbital were the ground state it would require that $g_{\|}$ would be the free electron value, and this is not found experimentally.

The A_{1g} orbital is expected to be a low lying excited state in square planar and octahedral complexes (Kivelson and Keiman, 1961). From single crystal relaxation measurements, Stoneham (1965) estimated the energy splitting between the B_{1g} and A_{1g} orbitals to be over 7000 cm^{-1}. In solution the splitting has been estimated by Valiev and Zaripov (1966) to be of the order of 1500 cm^{-1} and by Kivelson (1966) and by Lewis and Morgan (1968) to be of the order of 1000 cm^{-1}.

The EPR spectra of copper (II) complexes has been one of the most studied problems in magnetic resonance. The earliest EPR studies of

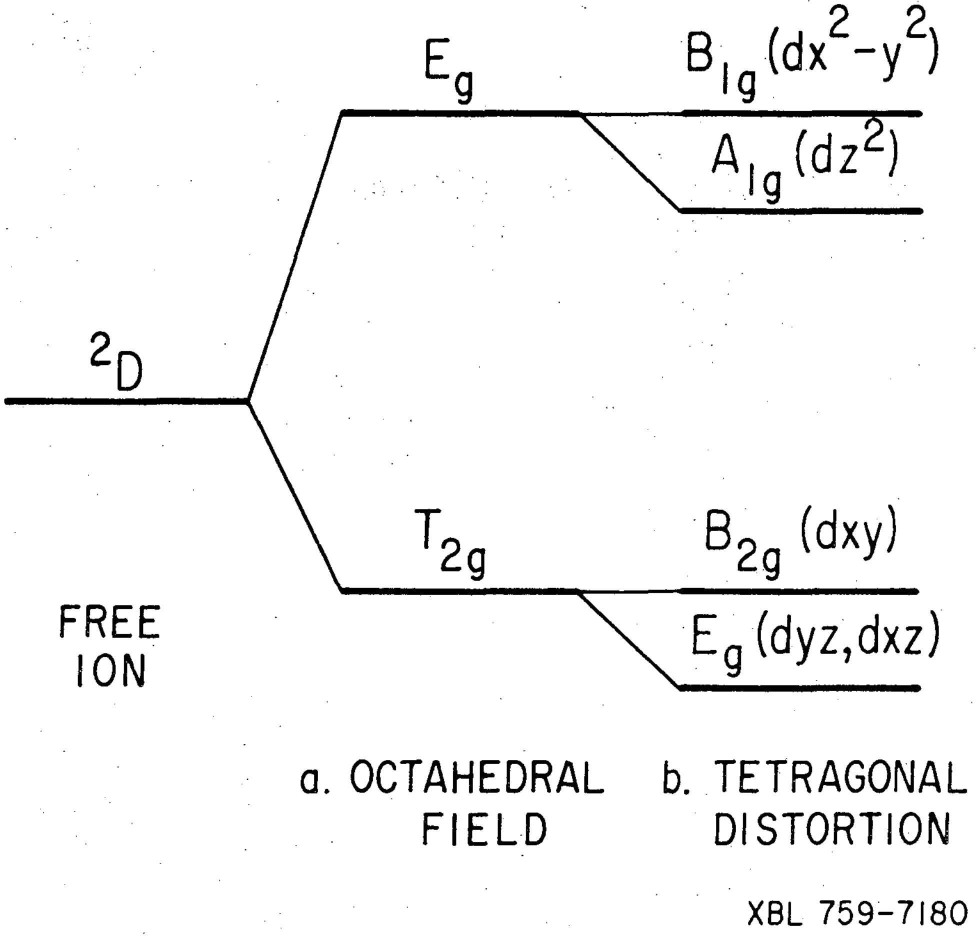

Fig. 13. Energy levels of a d^9 system.

Cu(II) in solution were reported by Kozyrev (1955, 1957) and McGarvey (1956, 1957). They observed a single, broad line, approximately 150 gauss wide. Since the two naturally occurring copper isotopes, ^{63}Cu and ^{65}Cu, both have a nuclear spin of 3/2, the lack of a hyperfine quartet was somewhat surprising.

Kozyrev (1955) attributed the lack of hyperfine structure to the formation of copper dimers in solution. He based his conclusion on early data and later work with dilute solutions showed that the lack of hyperfine structure persisted even when the formation of copper dimers was highly unlikely.

McGarvey (1957) proposed that the hyperfine structure was broadened through interaction with a low lying excited state. A combination of broadening caused by slow tumbling of the hydrated ion and broadening caused by interaction with the low lying excited state accounted for the observed linewidth.

Al'tshuler and Valiev (1959) explained the observed broadening of the line with increasing temperature in terms of a vibrational modulation of the crystal field.

All of these early workers assumed that the lack of resolvable hyperfine structure indicated that the observed absorption could be treated as a single line. Thus, the linewidth could be taken as the peak-to-peak separation of the derivative presentation. Hays (1961) and Rivkind (1961) showed that this was not true. Hays observed hyperfine structure in hexaquocopper (II) at 0°C. The hyperfine splitting of 38 gauss indicated that the overall linewidth was largely caused by unresolved hyperfine structure. Rivkind reported that the linewidths of the hyperfine components showed a dependance on m_I, in agreement with McConnell theory, but they became sharper as the viscosity of the solution was raised instead of narrower as required by McConnell theory.

Spencer (1965) measured the EPR spectra of hexaquocopper (II) and hexamminecopper (II) over a wide range of temperatures. Using an aquo-complex hyperfine coupling constant of 53×10^{-4} cm^{-1}, he made crude corrections to the linewidths for overlap of the lines. Although no definate conclusion was drawn, Spencer felt that the relaxation was caused by a combination of the McConnell tumbling mechanism, Jahn-Teller inversion (pseudo-reorientation) and possibly even chemical exchange.

Fujiwara and Hayashi (1965) measured the overall linewidth of the overlapped hyperfine quartet of $Cu(H_2O)_6^{2+}$ as a function of concentration, temperature, and magnetic field. They concluded, from their data, that the predominate relaxation mechanism must be an Orbach spin-orbit process.

Valiev and Zaripov (1966) proposed a mechanism specific to aqueous solutions of copper (II) ions. In their theory, broadening was caused by transitions between the ground state and excited states. They assumed a separation of 1500 cm^{-1} between the ground state and the first excited state. Using this value they obtained reasonable agreement with the experimental work of Avvakumov, Garif'yanov, Kozyrev, and Tishkov (1959). An interesting aspect of their theory is that there is no contribution to T_1.

Lewis, Alei, and Morgan (1966) made an attempt to measure the linewidths of the individual hyperfine components of hexaquocopper (II) by reconstructing the EPR spectrum from four Lorentzian lines. They concluded that the relaxation is a combination of the Kivelson tumbling mechanism, spin-rotation interaction and a Van Vleck Raman process. Their expression for the linewidth, exclusive of the tumbling mechanism, was

$$T_2^{-1} = T_1^{-1} = 2.04 \times 10^4 \left[(T/\eta) + 0.23\, T^2\right], \qquad (5.1)$$

where η is the viscosity of the solution and T the absolute temperature. Kivelson (1966) has indicated that this Raman process in solution is not expected to make such a large contribution to the relaxation.

Wilson and Kivelson (1966c) studied copper acetylacetonate in a variety of organic solvents. The acetylacetonate complex has sufficiently narrow lines that direct measurement of the linewidths could be made. They found that, although only an approximation for copper, Kivelson tumbling theory provided an adequate explanation of the observed m_I dependence of the linewidths of the hyperfine components. The residual width, after subtraction of the tumbling contribution, was explained as being due to spin-rotation interaction.

Nyberg (1969) studied the relaxation of copper (II) in a 2 M solution of ammonia. In such a solution there are four ammonia molecules and two water molecules bounded to the copper ion. He concluded that the linewidths were caused by a combination of tumbling, spin-rotation interaction, and unresolved nitrogen hyperfine structure. The poor agreement of some of the calculated contributions from tumbling theory he postulated could be due to ligand exchange.

In this laboratory Chang (1971) measured the linewidths of hexaquocopper (II) by a least-squares fitting procedure. By fitting four Lorentzian lines, whose positions were determined by a second-order spin Hamiltonian, to the unresolved spectra, he was able to determine the linewidths to a precision of from 0.5% to a few percent over a temperature range from -10°C to 80°C. He demonstrated the fallacy of using the temperature dependence of the overall linewidth to explain the relaxation mechanism. He accounted for some of the m_I dependence of the hyperfine linewidths as being caused by anisotropy in the g and A tensors. The hydrodynamic radius necessary to fit the data, $r_o = 1.71$ A, seemed much too small for the copper complex. The residual linewidth was approximately fit to a spin-rotation interaction. The hydrodynamic radius calculated for this process was much more reasonable, $r_o = 3.08$ A. There also appeared to be a third mechanism, since the residual linewidth did not extrapolate to zero at zero temperature. Also, the temperature variation of the isotropic g and A values were not consistant with theories of covalency (Kivelson and Neiman, 1961). Chang concluded that the linewidths were due to a spin-rotation interaction, a tumbling mechanism, and a third mechanism, possibly Jahn-Teller inversion, that interrupts the tumbling mechanism, causing the small hydrodynamic radius.

Noack, et al. (1971) studied the relaxation of 2, 2'- dipyridine complexes of copper (II). They found that the asymmetric $\left[\mathrm{Cu(dipy)(OH_2)_4}\right]^{2+}$ complex followed the temperature behavior expected from a combination of Kivelson tumbling theory, spin-rotation interaction and superhyperfine contributions from nitrogens on the ligands and that the relaxation gave a reasonable value for the hydrodynamic radius. The symmetric $\left[\mathrm{Cu(dipy)_3}\right]^{2+}$ complex, on the other hand, exhibited the same behavior, but gave a hydrodynamic radius much too small for such a large complex. They interpreted the difference in the two complexes as being caused by a dynamic Jahn-Teller effect in the symmetric complex which was not possible in the asymmetric case. They introduced a pseudo-reorientational Jahn-Teller correlation time, τ_{J-T}, and concluded that in a system in which a dynamic Jahn-Teller distortion is possible, the experimentally observed correlation time, τ_c, for reorientation is given by

$$\frac{1}{\tau_c} = \frac{1}{\tau_R} + \frac{1}{\tau_{J-T}} \tag{5.2}$$

where τ_R is the correlation time from hydrodynamic theory. Introduction of the dynamic Jahn-Teller effect in this manner, as a pseudo-reorientational process, produces no change in Kivelson tumbling theory except to reduce the value of the correlation time, which, in turn, produces a smaller value of the hydrodynamic radius than would be expected.

Poupko and Luz (1972) studied the relaxation of $Cu(ClO_4)_2$ in solutions of methanol and water at X- and Q-bands (9 and 35 GHz). They considered only spin-rotation and anisotropy in the g tensor as relaxation processes. Because of the lack of resolution of the hyperfine structure, particularly at Q-band, they only measured the overall linewidth of the four overlapped lines.

It was at this point in the understanding of copper (II) relaxation in solution that the present work was started. There were numerous explanations, each fitting some of the data, and each with some discrepancy, but no unifying picture of the processes involved. It was thought that a clearer perspective on the problem could be gained by reconsideration of the hexamminecopper (II) system. The lines are both narrower and spread further apart, due to the larger hyperfine splitting, than in aqueous solution. If the $Cu(NH_3)_6^{2+}$ system could be understood, there would be some additional groundwork for a generalized picture of copper relaxation in solution.

B. SPECTRA

Before proceeding to an analysis of the linewidths of copper (II) in solution, the magnetic parameters must be obtained. Values for hexamminecopper (II) and hexaquocopper (II) are presented in Table III.

Spencer's work on the NH_3-THF glass system was repeated using isotopically enriched ^{63}Cu. The spectra obtained were similar to Spencer's. Although slightly better resolution was obtained, the structure in the perpendicular resonance could only be estimated even through the use of computer simulation. Experiments were conducted on a variety of other glasses. It was found that a significant narrowing of the resonance lines could be obtained using a glass composed of ammonia, glycerol, and absolute ethanol (AGE) in the proportions 2:1:1. A typical spectrum along with a computer simulation are shown in Fig. 14. Of particular interest is the superhyperfine pattern visible in Fig. 14. The spectrum was simulated using a program supplied by H. A. Kuska of the University of Akron. The superhyperfine structure results from the interaction between the ^{14}N nuclei of the ammonia molecules and the unpaired spin of the copper (II) ion. The interaction is expected to be isotropic (Maki and McGarvey, 1958; Kivelson and Neiman, 1961) and consequently cannot cause relaxation, but it could yield an inhomogenously broadened line. The superhyperfine splitting in Fig. 14 is 11 gauss, in good agreement with the values of 11-15 gauss obtained from other copper complexes containing ^{14}N nuclei bound to the copper (Lewis and Morgan, 1968).

The simulated spectrum in Fig. 14 was calculated using the contributions from the four equatorial ^{14}N atoms. Inclusion of the two

Table III. Magnetic parameters of Cu (II).

Solute/Solvent	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle^a$	$A_{\parallel}{}^b$	$A_{\perp}{}^b$	$\langle A \rangle^{a,b}$	Reference
<u>NH_3</u>							
$Cu(ClO_4)_2/NH_3$-THF	2.228	2.055	2.124	-192	$(-3)^c$	-69	Spencer, 1965
$Cu(ClO_4)_2$/AGE[d]	2.242	2.053	2.121	-180.0	-11.5	-67.7	This work
<u>H_2O</u>							
$Cu(ClO_4)_2$/5.3 F $HClO_4$	2.379	2.066	2.170	-155	$(-7)^c$	$(-58)^c$	Spencer, 1965
$Cu(NO_3)_2$/glycerol	2.400	2.099	2.199	-127.8	-12.6	-51.0	Lewis, <u>et</u> <u>al</u>., 1966
$Cu(ClO_4)_2$/5.3 F $HClO_4$	2.387	2.072	2.177	-153	-5	-54.3	Chang, 1971.
$Cu(ClO_4)_2$/dil. $HClO_4$	2.387	2.070	2.176	-142.0	-15.8	-57.9	Poupko and Luz, 1971

[a] $\langle g \rangle = (g_{\parallel} + 2g_{\perp})/3$; $\langle A \rangle = (A_{\parallel} + 2A_{\perp})/3$.

[b] Hyperfine coupling constants are assumed to be negative and are given in units of 10^{-4} cm^{-1}.

[c] Estimated values.

[d] AGE = 50% NH_3, 25% glycerol and 25% ethanol.

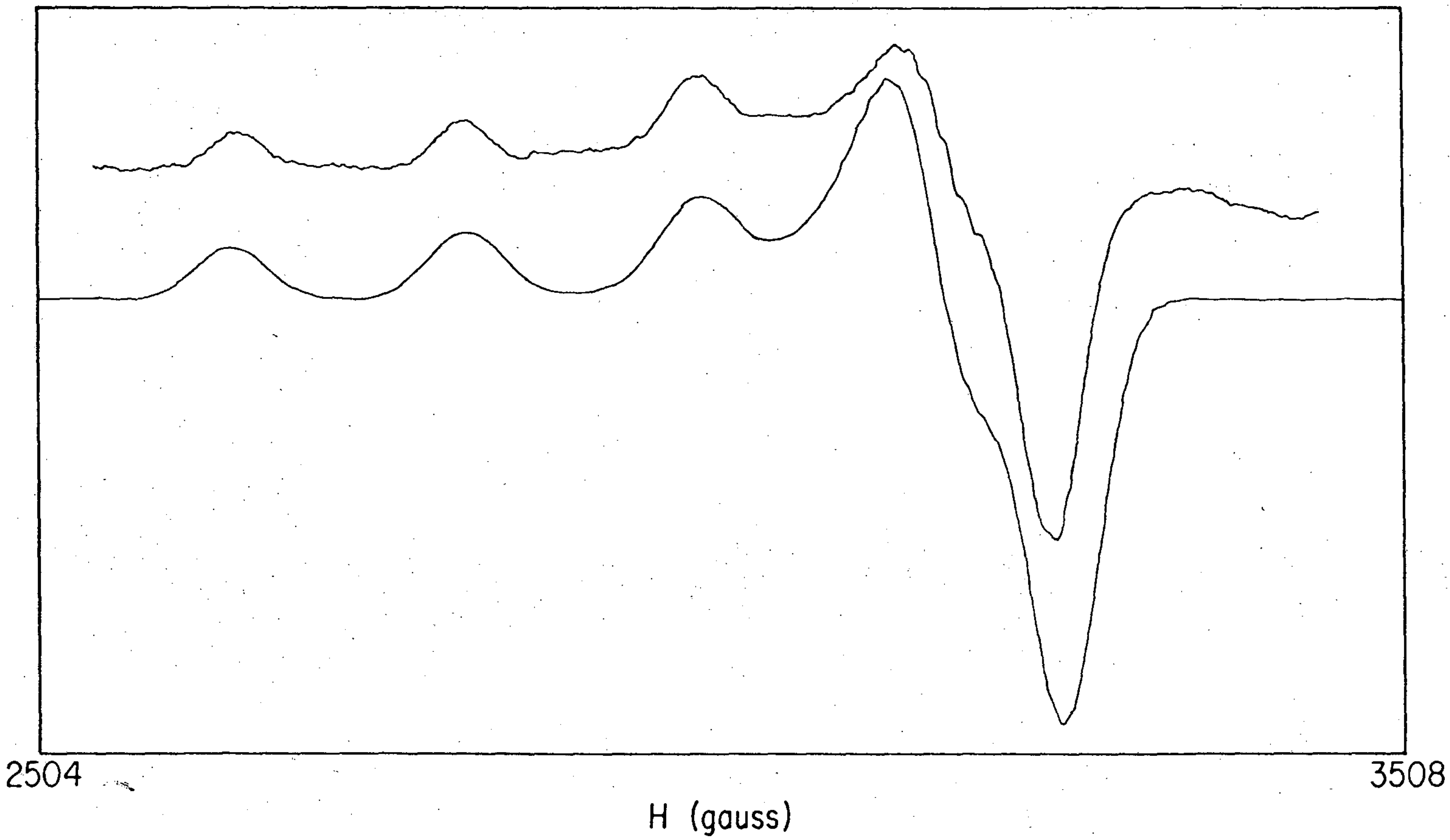

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Fig. 14. Glass spectrum of $Cu(NH_3)_6^{2+}$ in AGE. The upper curve is experimental and the lower curve is a simulation.

axial ligands into the calculation gives a superhyperfine pattern which is not in agreement with experiment. This is consistant with the usual tetragonal distortion of copper (II) complexes. For a tetragonal elongation of an octahedral d^9 system, the unpaired spin is in a $d_{x^2-y^2}$ atomic orbital. In such an orbital, interaction between the unpaired spin and the equitorial ligands is at a maximum and there is no interaction with the axial ligands.

For comparison with the frozen solution data, the magnetic parameters obtained from single crystal studies are presented in Table IV. In the first two rows, the copper (II) ion is complexed to four ammonia molecules, forming a plane. The structure is nearly square planar with water molecules occupying the fifth and sixth coorination positions (Mazzi, 1955). No hyperfine structure could be resolved due to exchange in the undiluted crystals. In the last two rows, the copper (II) ion is surrounded by a roughly octahedral arrangement of water molecules (Webb, et al., 1965; Montgomery and Lingafelter, 1966).

The EPR spectra of $^{63}Cu^{2+}$ in liquid ammonia were measured between -75°C and 23°C. The spectra were digitized and analyzed in a manner similar to that used on VOAA in liquid ammonia except that a second-order Hamiltonian was used to calculate the line positions. A typical spectrum near room temperature is shown in Fig. 15. As the temperature is lowered the linewidths narrow. The spectrum near zero degrees, shown in Fig. 16, exhibits approximately the same resolution of the hyperfine quartet as can be seen in hexaquocopper (II) at the same temperature. This is approximately the best resolution attainable for Cu^{2+} in H_2O. At still lower temperatures the individual lines in ammonia become well

Table IV. Magnetic parameters of Cu(II) in single crystals.

System	g_x	g_y	g_z	A_x	A_y	Az	Reference
$Cu(NH_3)_4SO_4 \cdot H_2O$	2.05_3	2.05_2	2.22_2				Carlson and Spence, 1956
$Cu(NH_3)_4SO_4 \cdot H_2O$ undiluted	2.05_5	2.05_5	2.22_2				Abe and Ono, 1956
$Cu(NH_4)_2SO_4 \cdot 6H_2O$ in $Zn(NH_4)_2SO_4 \cdot 6H_2O$	2.02	2.05	2.46	25±5	35±5	130±5	Bleaney, <u>et</u> <u>al</u>., 1955
Cu^{+2} in $ZnSeO_4 \cdot 6H_2O$	2.0963	2.0963	2.4289	10.3	10.3	119.7	Jindo, 1971

Hyperfine coupling constants are in units of 10^{-4} cm^{-1}. No hyperfine structure could be observed in the undiluted crystals.

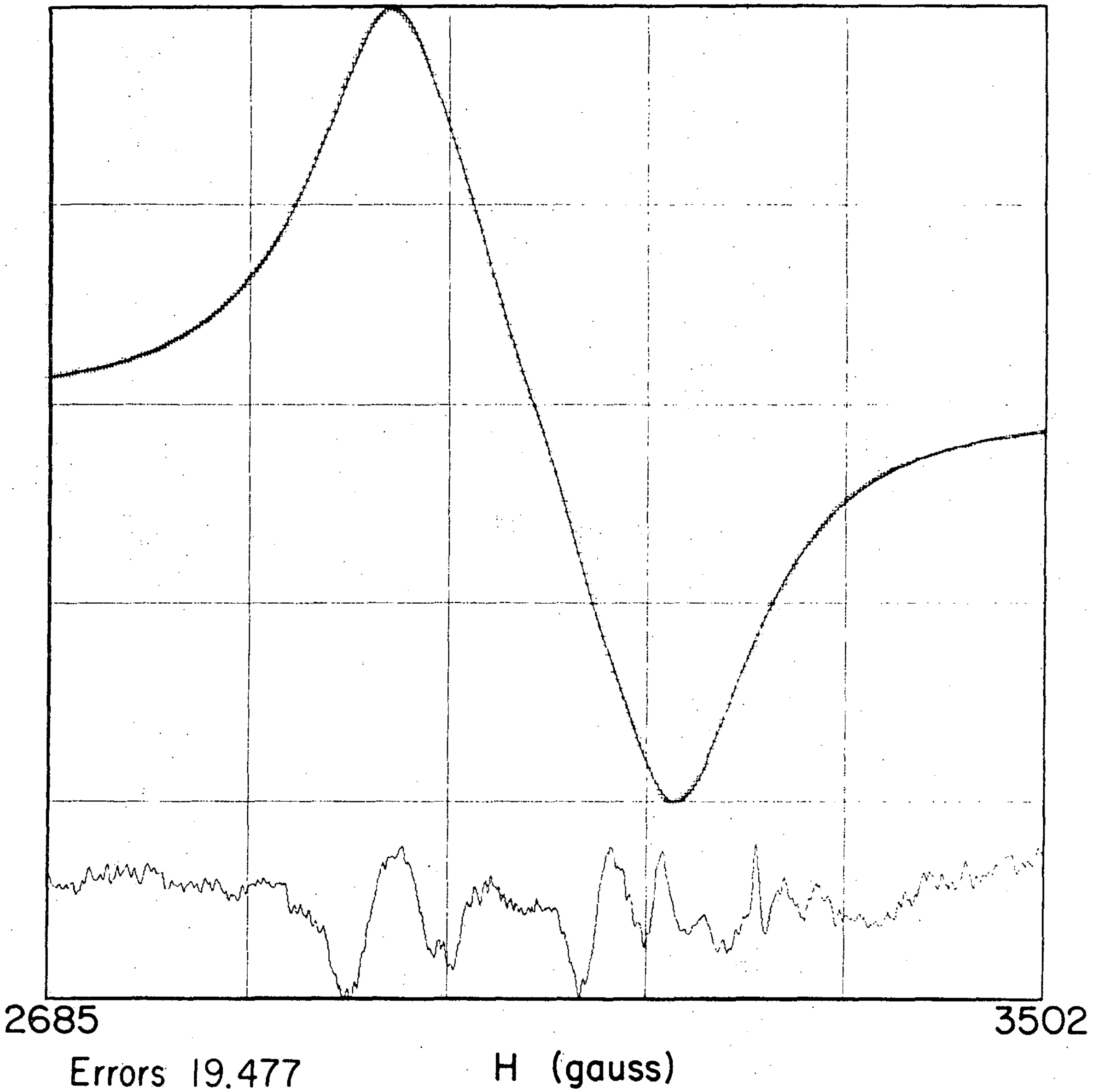

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Fig. 15. Fit of $Cu(NH_3)_6^{2+}$ spectrum at room temperature.

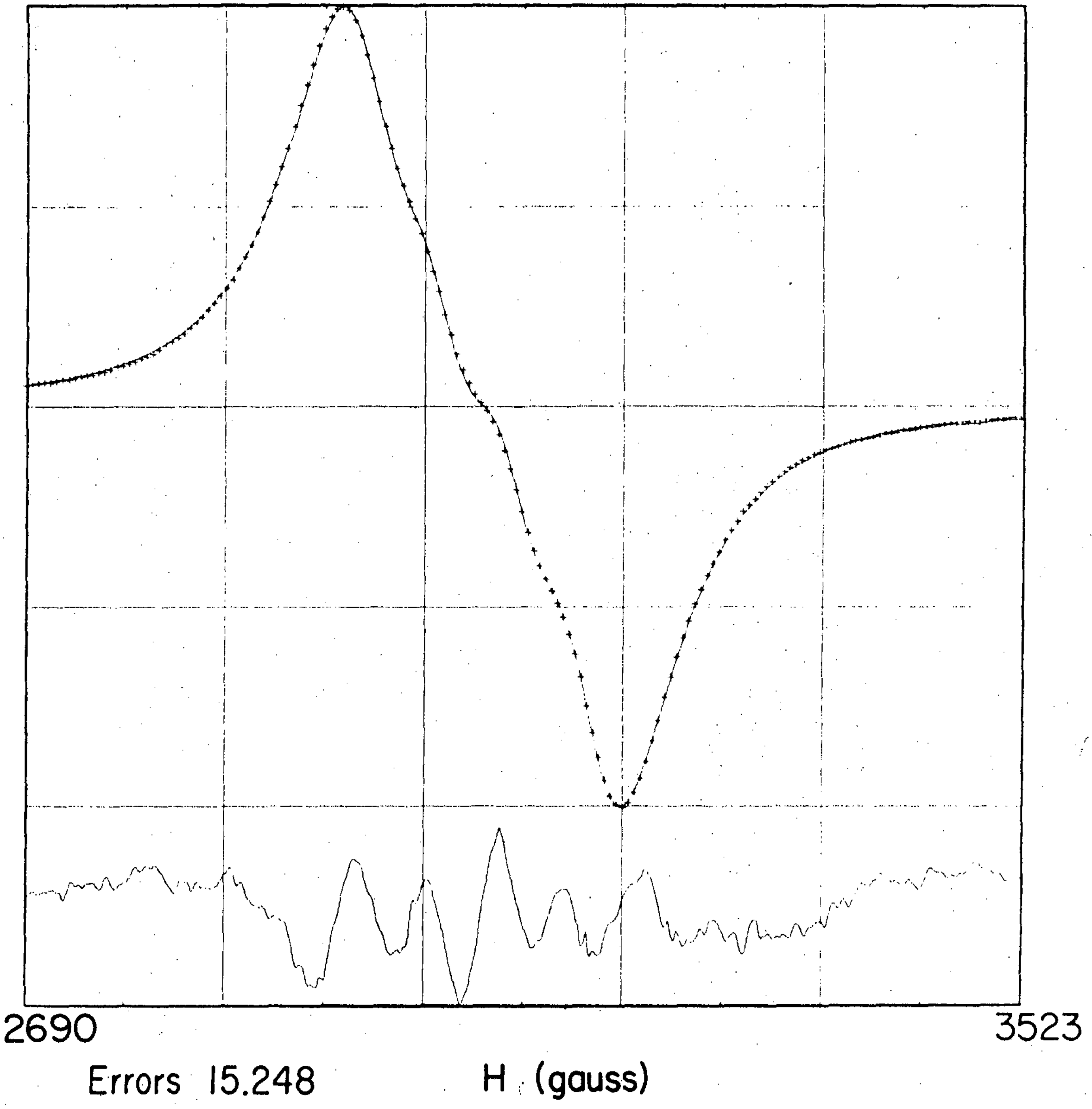

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Fig. 16. Fit of $Cu(NH_3)_6^{2+}$ spectrum at 0 C.

resolved. A spectrum at -49°C is shown in Fig. 17.

It was observed by Chang (1971) that the isotropic g and A values of hexaquocopper (II) both decreased in magnitude as the temperature was increased. Chang could not arrive at an adequate explanation of the effect. The isotropic g and A values of hexamminecopper (II) are shown in Figs. 18 and 19. Although the change in the g value as the temperature is increased is relatively small, there is a definate trend toward lower values. The values used in the analysis of the linewidths were $\langle g \rangle = 2.121$ and $\langle A \rangle = -60.5$ gauss.

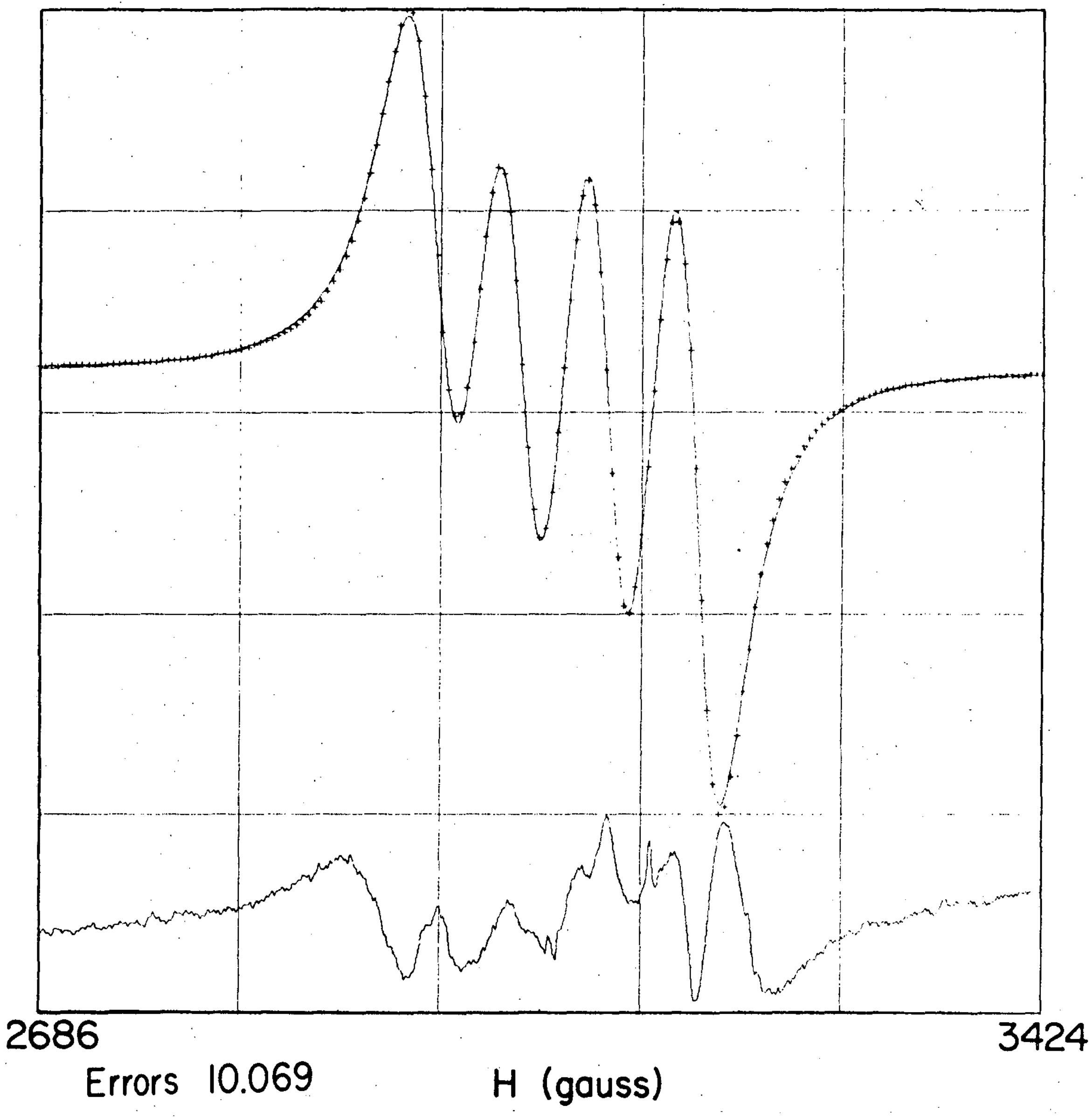

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Fig. 17. Fit of $Cu(NH_3)_6^{2+}$ spectrum at -49 C.

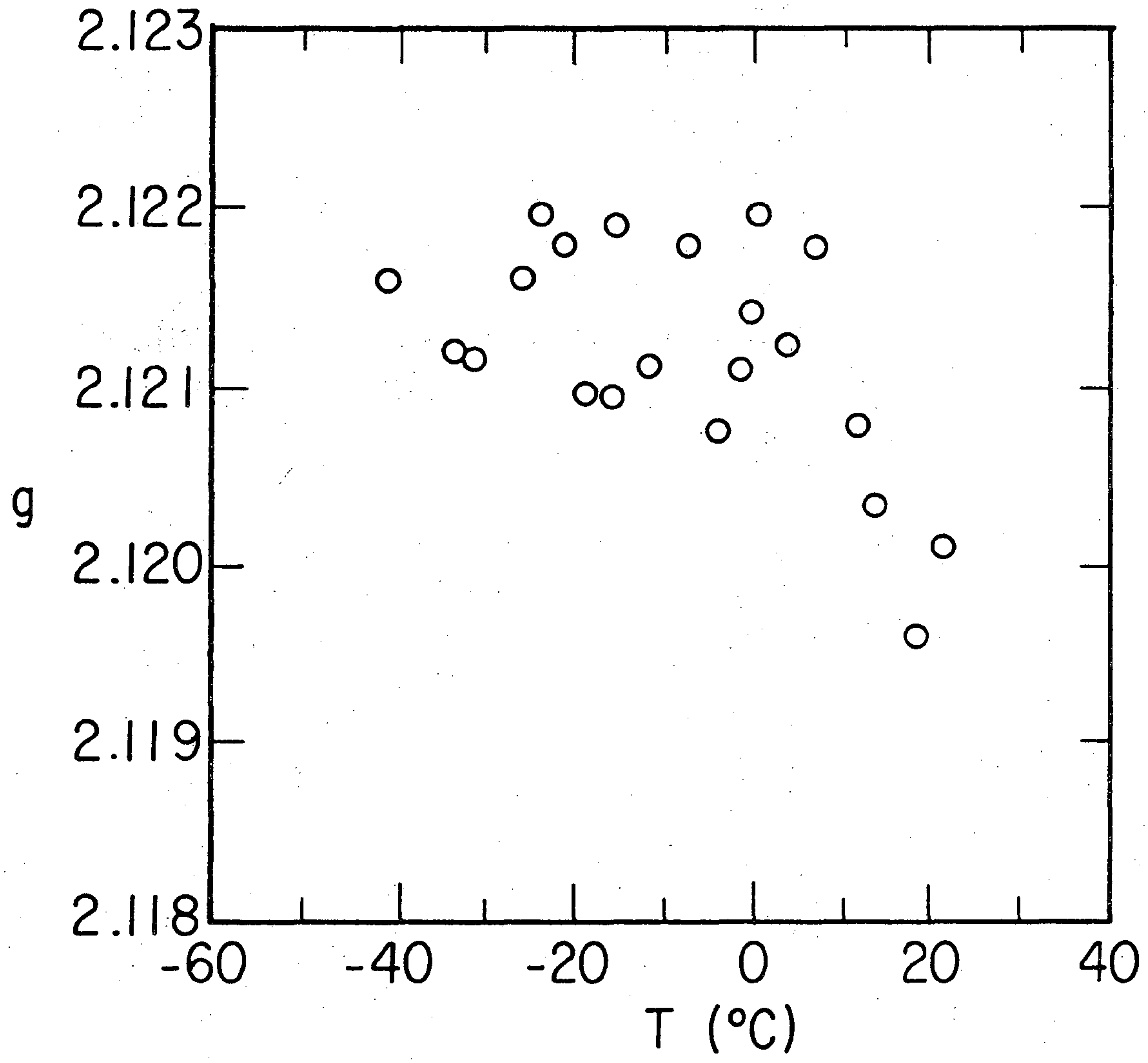

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Fig. 18. g vs T for $Cu(NH_3)_6^{2+}$.

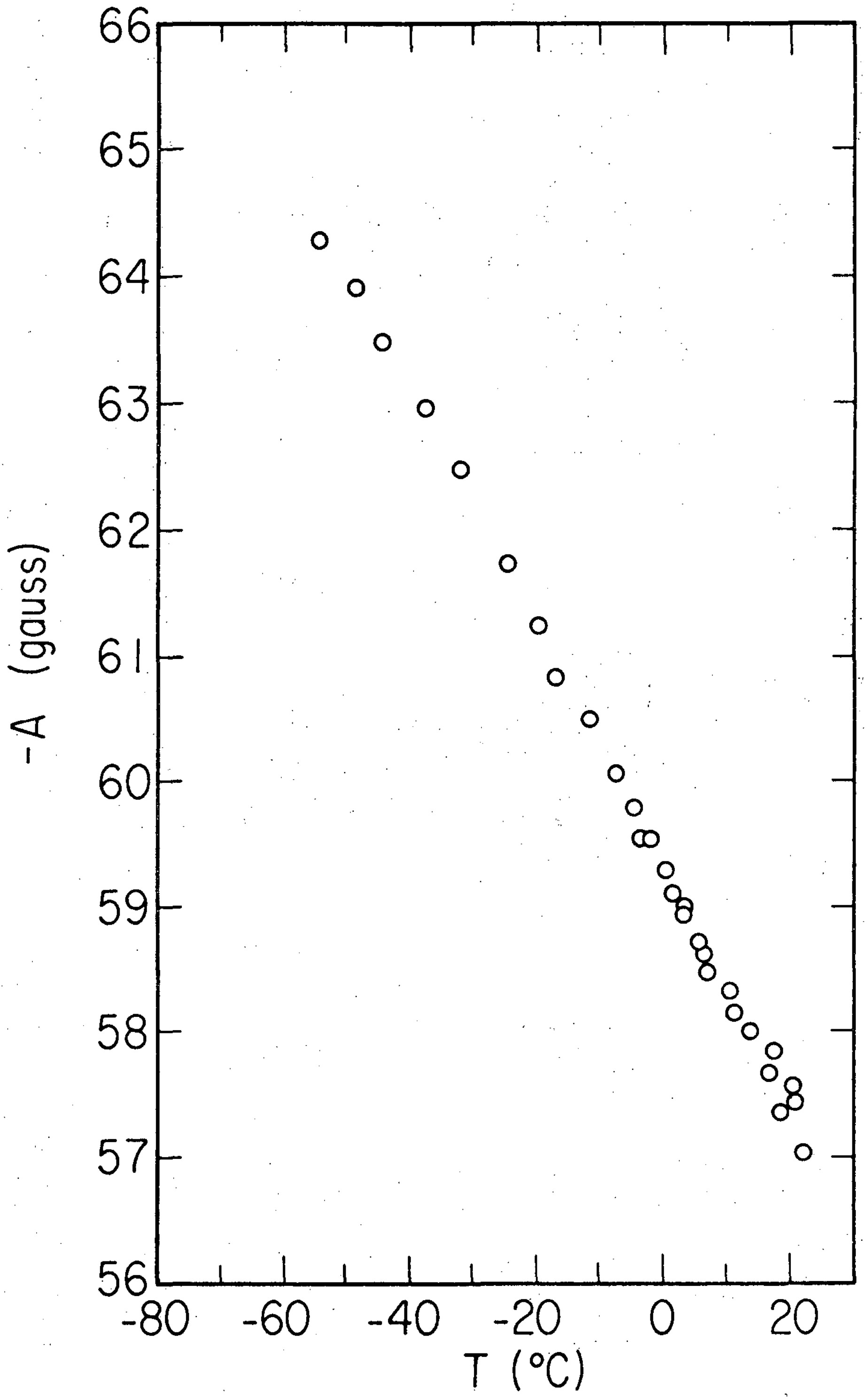

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Fig. 19. -A vs T for $Cu(NH_3)_6^{2+}$.

C. RESULTS AND DISCUSSION

As is readily apparent from Figs. 16 and 17, there is a marked dependence of the linewidth on m_I. A Kivelson tumbling mechanism is immediately suggested. As in the case of VOAA, the beta term was used to determine the hydrodynamic radius. The experimental and calculated beta parameters are shown in Fig. 20. The beta term is used, in this case, since it is the only term with the proper η/T dependence as can be seen from Figs. 21 and 22. The agreement in the beta term is reasonable, especially at lower temperatures where the lines are well resolved. The calculated hydrodynamic radius was 2.34A, rather small for $Cu(NH_3)_6^{2+}$. This result was not completely unexpected since Chang (1971) and the data of Lewis, et al. (1966) gave values of 1.71 A and 1.83 A, respectively, for the hexaquocopper (II) complex.

The small value of the hydrodynamic radius may be caused by a dynamic Jahn-Teller effect combined with tumbling reorientation. As Noack, et al. (1971) pointed out, for highly symmetric copper (II) complexes the dynamic Jahn-Teller effect is expected to cause pseudo-reorientation. In such a case the apparent correlation time is given by eq. 5.2. Consideration of eq. 5.2 shows that τ is always less than τ_R if pseudo-reorientation is present. From eq. 2.1 it can be seen that a smaller value of τ will yield a smaller value of the hydrodynamic radius. From the X-ray diffraction results of Mazzi (1955), an estimate of 3.5 A for the radius of a hexamminecopper (II) ion can be obtained. Substitution into eq. 2.1 yields $\tau_R = 6.08 \times 10^{-10}$ sec. at 20°C. Experimentally, $\tau = 1.82 \times 10^{-10}$ sec. at 20°C. Using these values in eq. 5.2 yields a pseudo-reorientation correlation time of 2.6×10^{-10} sec. Using 3.5 A as the radius of the

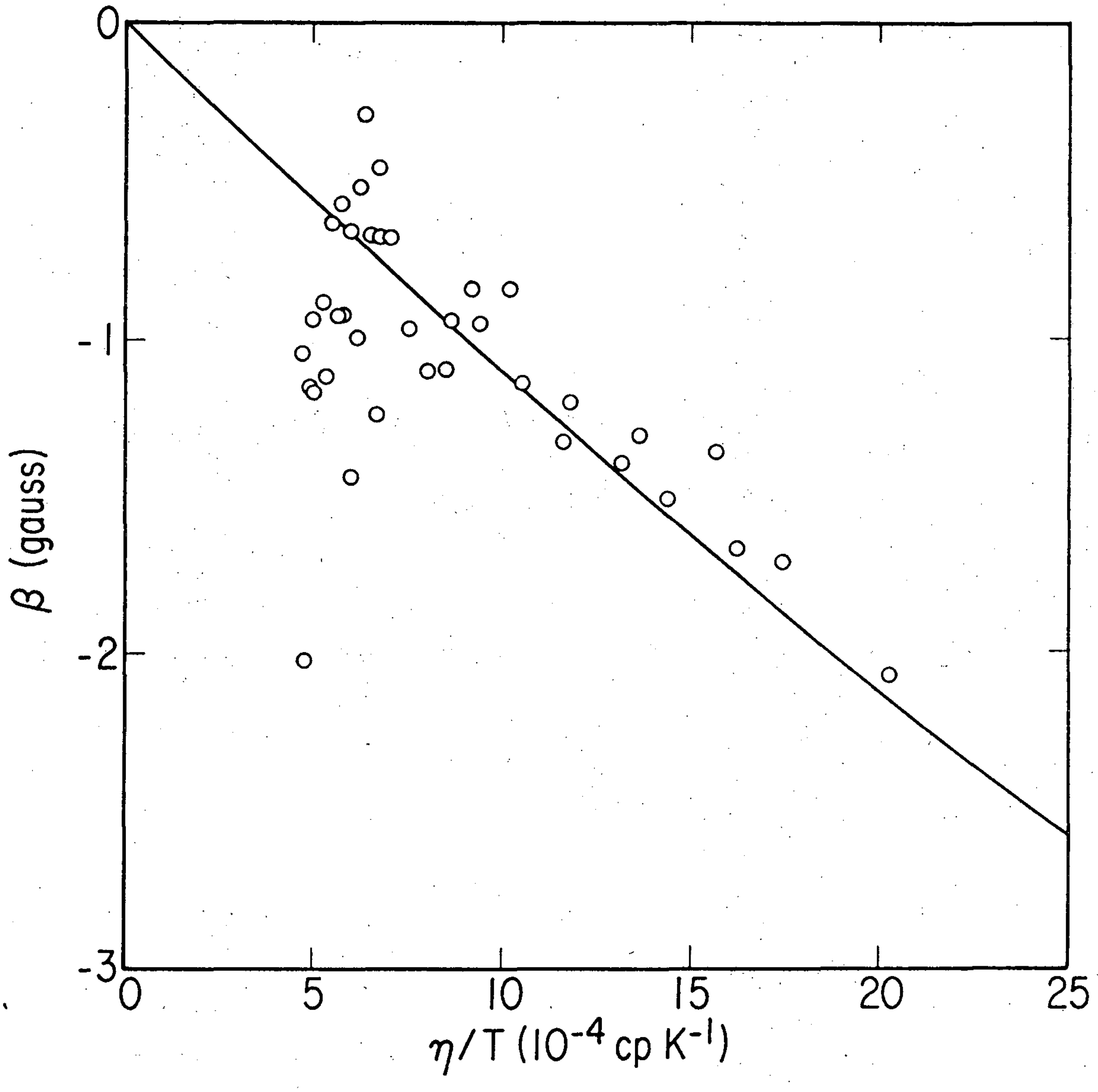

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Fig. 20. Beta parameter vs η/T for $Cu(NH_3)_6^{2+}$. The curve is theoretical.

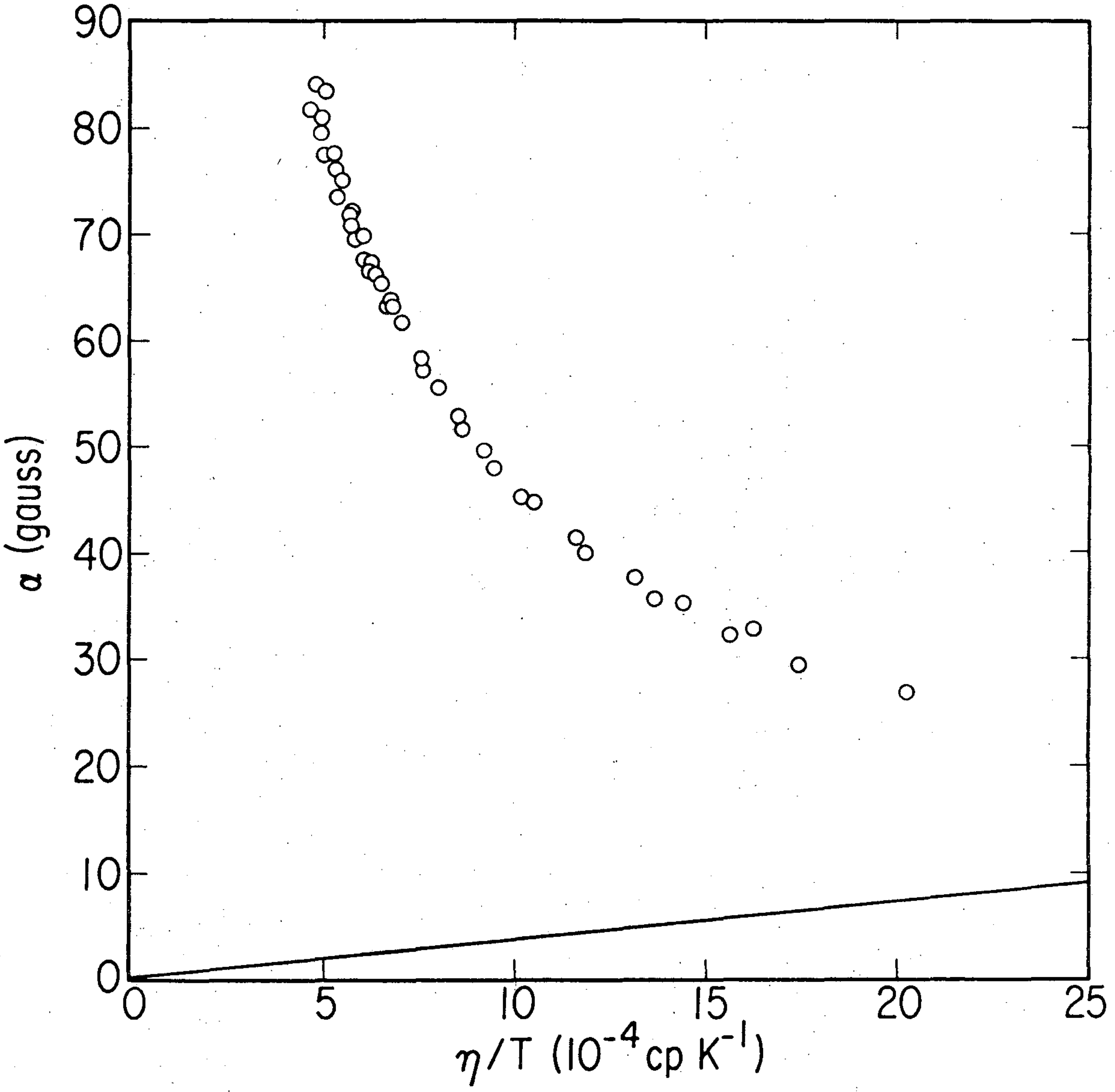

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Fig. 21. Alpha parameter vs η/T for $Cu(NH_3)_6^{2+}$. The curve is theoretical.

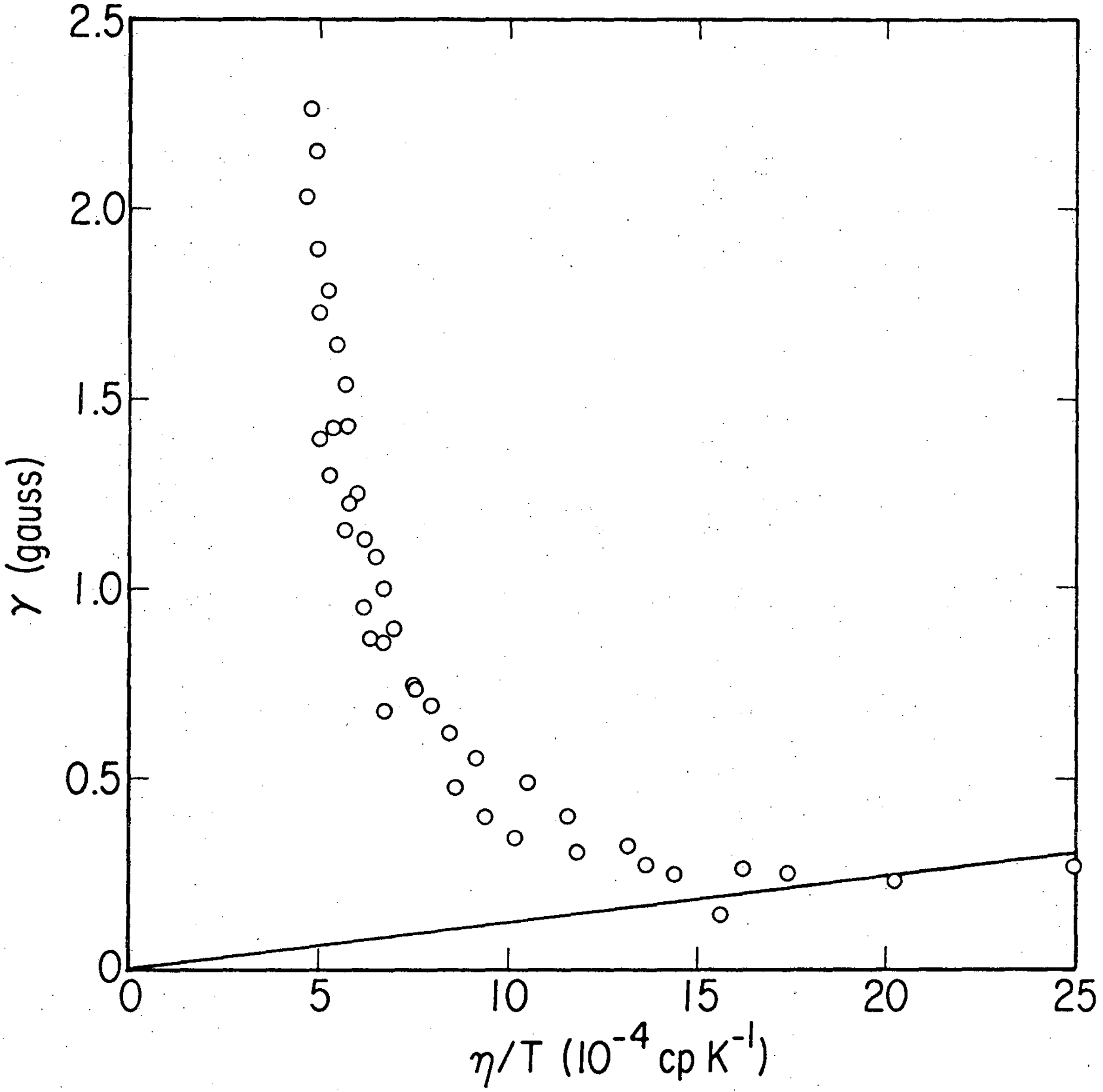

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Fig. 22. Gamma parameter vs η/T for $Cu(NH_3)_6^{2+}$. The curve is theoretical.

complex and Chang's value for the hydrodynamic radius yields a pseudo-reorientation correlation time of 5.9×10^{-10} sec. for the hexaquo complex at 20°C.

Evidence for the existance of the pseudo-reorientation mechanism is given by the bahavior of spectra just below the freezing point of the solution. We have observed, as was also reported by Spencer (1965), that, upon freezing, the lines suddenly became much broader but still exhibited isotropic behavior indicating that some mechanism is still operative averaging the anisotropies. As the temperature is lowered further, the lines broaden and eventually the usual anisotropic spectrum is observed. Such behavior has been observed in single crystals doped with copper (II) impurities (Bleaney, Bowers, and Trenam, 1955; Bijl and Rose-Innes, 1953) and has been ascribed to a dynamic Jahn-Teller distortion. This also appears to be the case in hexamminecopper (II). Notice that when the solution freezes, $1/\tau_R$ in eq. 5.2 equals zero and thus $\tau = \tau_{J-T}$. The broadening upon freezing occurs since $\tau < \tau_{J-T}$ so long as $1/\tau_R \neq 0$.

The contribution to the linewidth from anisotropy in the g and A tensors and the experimental values of α and γ for $Cu(NH_3)_6^{2+}$ are shown in Figs. 21 and 22. The failure of tumbling theory to adequately explain the α term is not unusual since a large spin-rotational contribution is expected (Lewis, et al., 1966; Wilson and Kivelson, 1966c; Chang, 1971). The discrepency in the γ term is surprising, however. Even though Kivelson tumbling theory is only an approximation for Cu (II) (Kivelson, 1960), the discrepency is much too large.

The γ term is expected to be the term least sensitive to experimental error (Angerman and Jordan, 1971). The data we have obtained certainly do not have errors of the order of one to two gauss and the fact that the experimental points follow a smooth curve as a function of temperature implies that some mechanism, other than tumbling and spin-rotation, is operative. A nuclear spin dependent spin-rotation mechanism (Nyberg, 1967) gives much too small a contribution.

The only other mechanism which has a dependence on m_I^2 is the modulation of the hyperfine interaction tensor (Atkins, 1967). Eq. 2.37 predicts an exponential dependence of the residual γ term, γ^*, with the inverse temperature. In Fig. 23 is shown γ^* versus 1/T. The straight line is a least-squares fit of the data to a straight line of the form,

$$\frac{1}{T_2} = \frac{A}{\omega^2} \exp\left(-\Delta/kT\right) \quad , \tag{5.3}$$

Where ω is the microwave frequency and $A = 3.30 \times 10^{26}\ \mathrm{sec}^{-1}$ and $\Delta = 1840\ \mathrm{cm}^{-1}$ (5.25 kcal) the energy separation between the ground state and the first excited state.

The value of A_{on} in eq. 2.37 is not known experimentally, but it can be calculated using the equations of McGarvey (1967). This relatively simple calculation yields a value of $-7 \times 10^{-4}\ \mathrm{cm}^{-1}$ for A_{on}. The quantity $(\phi q/r_o)^2$ may be estimated from Kivelson (1966). Substitution into eq. 2.37 yields $\tau_c = 1.6 \times 10^{-13}$ sec. This is in good agreement with the usual estimation of $\tau_c = 10^{-12}$ sec. (Al'tshuler and Valiev, 1959).

Consideration of the optical spectra of Bjerrum, et al. (1954) and simple crystal field theory (see Orton, 1968 and Holmes, 1955), lead to

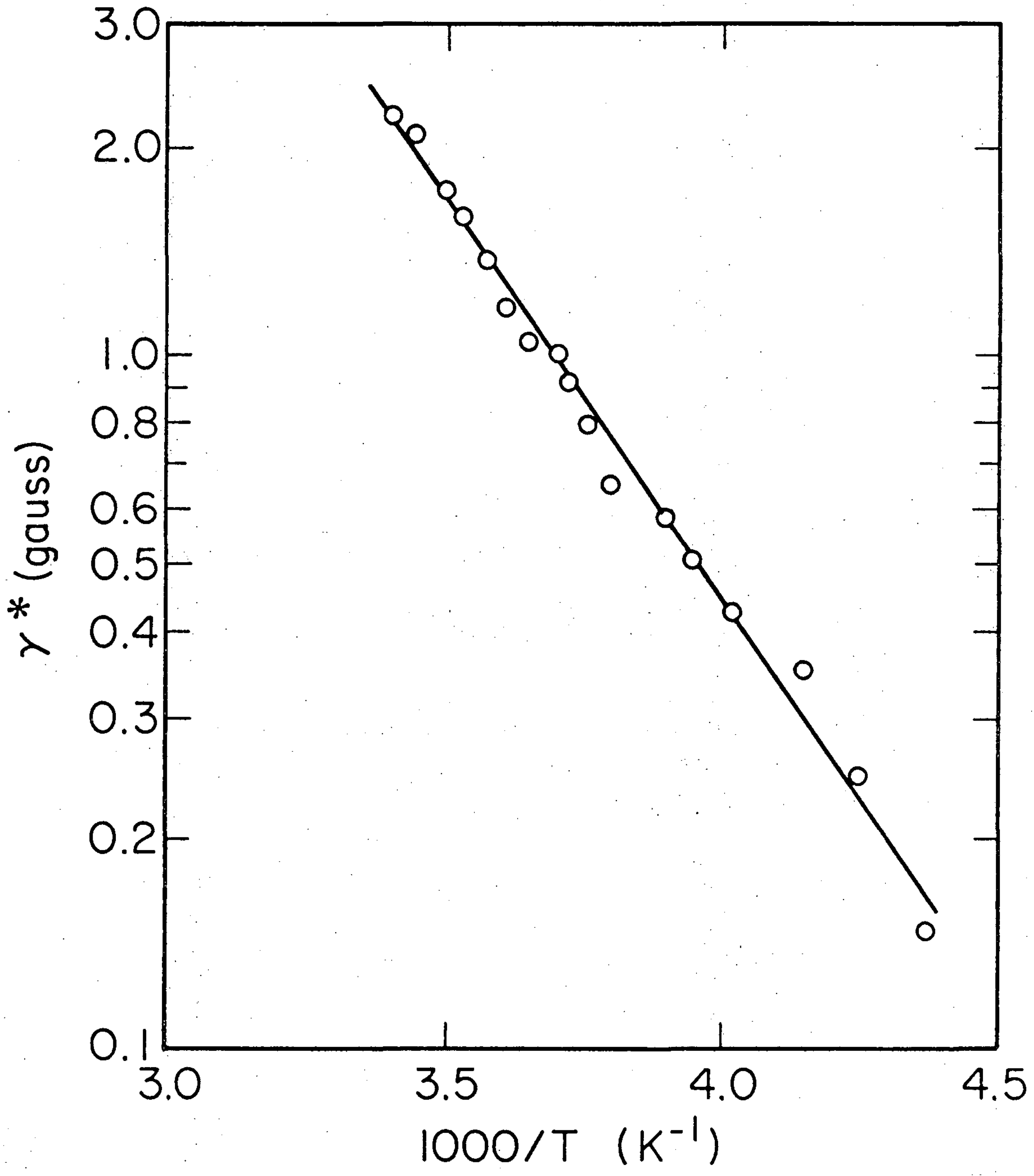

Fig. 23. Residual gamma parameter, γ*, vs 1000/T. The straight line is a least-squares fit of the data.

a splitting of 1440 cm^{-1} between the B_{1g} and A_{1g} states in $Cu(H_2O)_6^{2+}$. For the hexammine complex the value should be slightly higher, in agreement with the value of 1840 cm_{-1} obtained in this work. It should be noted that eq. 2.37 was derived for a doublet free radical system and that terms in $\lambda \underset{\sim}{L}\cdot\underset{\sim}{S}$ have been ignored. The theory is valid in this case since there is no spin-orbit coupling between the B_{1g} and A_{1g} states.

Although there is no direct EPR evidence to eliminate the direct vibrational relaxation mechanism, eq. 2.34, other pieces of experimental evidence seem to indicate that the process involved is the Orbach process. Solution Raman spectroscopy of $Cu(NH_3)_4^{2+}$ show a vibrational mode at 415 cm^{-1} (Schultz, 1942). Other transition metals (Ni^{2+}, Cr^{3+}, and Co^{3+}) when coordinated to six ammonia molecules show infrared active vibrations in the range of 680-830 cm^{-1} with the other metal-ligand vibrations at lower energy. The internal vibrations of the ammonia molecules occur below 1600 cm^{-1} and above 3000 cm^{-1} (Kobayshi and Fujita, 1955). Thus, there appear to be no vibrations of the complex in the right energy range to be causing the relaxation observed.

Additionally, the dependence of the isotropic g and A values on temperature can now be explained. The trend of both toward lower magnitudes as the temperature is increased was thoroughly discussed by Chang (1971). He could find no definate explanation for the effect using a variety of mechanisms including changes in solvation and bonding (Kivelson and Neiman, 1961), demagnetization effects (Van Gervan, Talpe, and van Itterbeck, 1967), nonsecular shifts (Kivelson, 1960), thermal vibrations of the ligands (Benedek, Engleman, and Armstrong, 1963), changes in delocalization of the unpaired electron (Soos, 1968), and configurational interactions caused by a dynamic phonon-induced field (Simanek and Orvach, 1966; Calvo and Orbach, 1967). Chang concluded that temperature dependent mixing of excited state configurations with the ground state was a possible explanation of the g and A value variation. In the light of our experimental evidence, this explanation is even more likely.

As pointed out previously, the hyperfine interaction in the first excited state is 7×10^{-4} cm^{-1} smaller than the hyperfine interaction in the ground state. As the temperature is raised a larger proportion of time is spent in the excited state. Since the hyperfine interaction is smaller in the excited state, the isotropic A value will appear to decrease exponentially toward the lower value as the temperature is raised. A simple crystal field calculation will show that a similar argument will not account for the g value variation since the isotropic g value is the same in the ground and first excited states. The g value variation is probably due to changes in solvation and bonding (Kivelson and Neiman, 1961) as was the case in VOAA. The corresponding increase in the A value would be masked by the larger decrease caused by interaction with the excited state, and would explain why the expected exponential dependence on temperature is not observed.

The usual method of obtaining the spin-rotation interaction contribution to the linewidth is to subtract the contribution of Kivelson tumbling theory from the experimental α term (Atkins and Kivelson 1966). This residual linewidth is then plotted as a function of η/T. Such a plot for hexamminecopper (II) is shown in Fig. 24. The straight line is obtained through a least-squares fit of the data. The major problem in Fig. 24 is that the intercept at zero degrees is significantly greater than zero. In the hexaquo system the deviation from zero is almost an order of magnitude greater (Chang, 1971). Obviously, the spin-rotation interaction is inadequate to account for the observed residual linewidth. Using eq. 2.37, it is possible to calculate the contribution to α from the Atkins-Orbach process. In Fig. 25 contributions from both the Kivelson tumbling process and the Atkins-Orbach process have been taken into account to obtain a plot of the spin-rotation contribution, α''. The straight line in Fig. 25 is again obtained through a least-squares fit of the data. The intercept now passes through zero and the hydrodynamic radius calculated from Fig. 25 and eq. 2.16 is 3.47 A, in good agreement with the estimate of 3.5 A obtained from the X-ray work of Mazzi (1955).

The lack of any indication of unresolved superhyperfine broadening in Fig. 25 is probably due to a change in electron density at the nitrogen nuclei during excitation to the A_{1g} state. The A_{1g} state has less electron density at the nitrogen nuclei (Kivelson and Neiman, 1961). For the very fast Orbach relaxation, averaging of the superhyperfine interaction would be expected. Exchange of the ammonia ligands does not appear to be rapid enough to average the superhyperfine interaction (Rowland, 1975).

Lowering the microwave frequency is expected to have a large effect on the linewidth. As can be seen from eq. 2.37, the Atkins-Orbach mechanism is expected to have a $1/\omega_o^2$ dependence. By changing to S-band, the contribution from the Atkins mechanism is expected to increase by about a factor of nine.

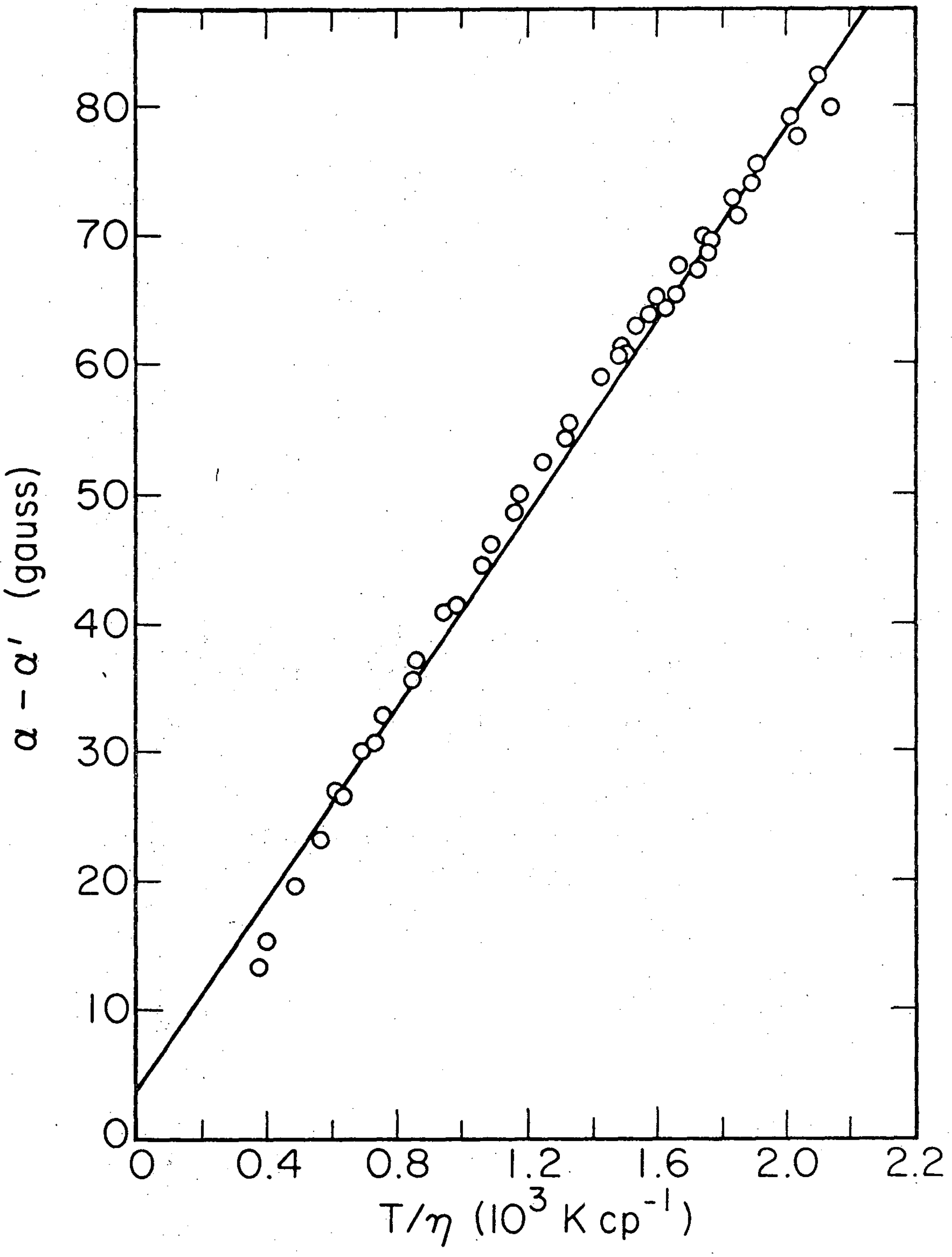

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Fig. 24. Alpha parameter minus correction for tumbling vs T/η. The straight line is a least-squares fit of the data.

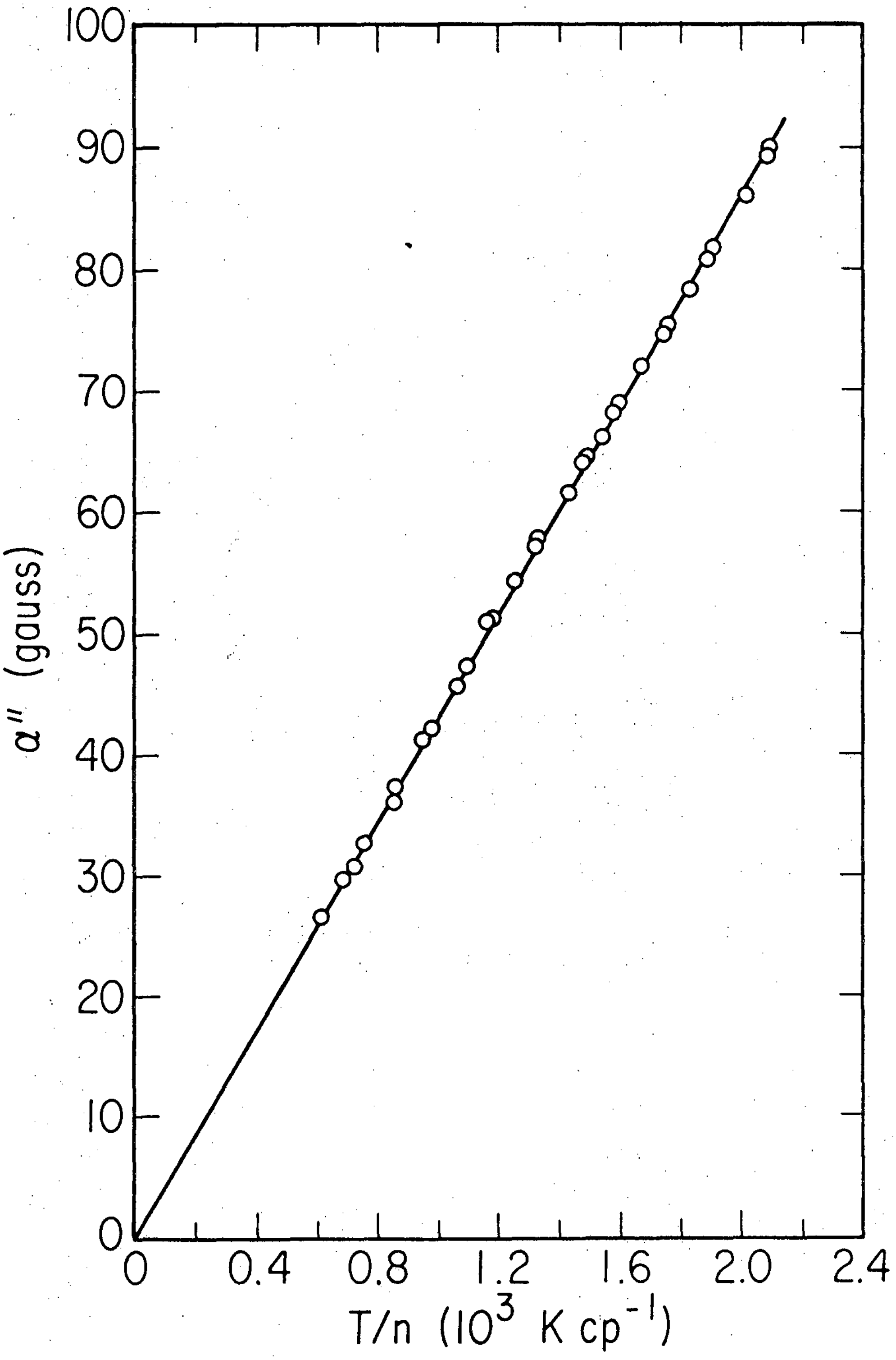

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Fig. 25. Spin-rotation contribution to the alpha parameter vs T/η. The straight line is a least-squares fit of the data.

Because of the rather poor signal-to-noise ratio in our S-band spectrometer and the broadening of the lines at lower microwave frequency, rather low temperatures were required before meaningful fits of the linewidths could be obtained. The values of α, β, and γ obtained from the S-band data at -32°C along with the values, calculated from the X-band data, for the Kivelson tumbling contribution (α', β', γ'), the spin-rotation interaction contribution (α''), which is assumed to be frequency independent, and the Atkins-Orbach contribution (α^*, γ^*) are presented in Table V. The values are in reasonable agreement. The disagreement in the beta term can be traced to the uncertainty of ± 0.7 gauss in the fitted linewidths and the approximate nature of tumbling theory for copper (II) at low microwave frequencies.

The relaxation of hexamminecopper (II) thus appears to be fairly well established. The predominate relaxation process is the spin-rotation interaction, with smaller contributions from the Atkins-Orbach process, the Kivelson tumbling mechanism, and pseudo-reorientation.

The relaxation of hexaquocopper (II) would be expected to be similar. The major differences are the smaller A value and larger deviation of the g value from the free electron value in the hexaquo complex. The differences in the g and A values will make the Atkins-Orbach process less important and the Kivelson-Orbach process much more important as can be seen from eq. 2.39.

To determine the relaxation behavior of hexaquocopper (II) in solution, we have made use of the linewidth measurements of Chang (1971). Using Chang's value of 1.71 A for the hydrodynamic radius, the contribution due to tumbling combined with pseudo-reorientation can be calculated.

Table V. S-band linewidth parameters of $Cu(NH_3)_6^{2+}$.

	Calculated from X-Band Data	S-Band Results
α'	15.3	
α''	43.5	
α^*	-13.4	
α_{total}	45.8	44.99
β	-0.50	-0.893
γ'	0.13	
γ^*	3.17	
γ_{total}	3.30	3.27

All values are given in gauss, α'' is assumed to be frequency independent.

The reduction of the hydrodynamic radius has already been discussed. The linewidths above room temperature become so broad that meaningful computer fits to the data are increasingly difficult to obtain and excessive scatter becomes evident in both the beta and gamma parameters. This limits the usable data to temperatures below 20°C. The gamma parameter shows no evidence of any contribution from the Atkins mechanism. In fact, throughout the temperature range studied, the gamma term is very nearly zero, within the experimental error. The beta term, as expected, agrees with tumbling theory.

That leaves the alpha term. After subtraction of the tumbling contribution from the experimental alpha term, the residual linewidth can be well fit to an exponential in T^{-1} with an activation energy of 1205 cm^{-1}(3.4 kcal). This is the same behavior observed vy Lewis, Alei, and Morgan (1966). Although the activation energy is of the right magnitude for an Orbach process, this approach must be rejected since it ignores the major relaxation process, spin-rotation. Rapid relaxation can, at best, only produce an isotropic g value. So long as the isotropic g value differs from the free electron value, spin-rotation will cause relaxation. The large deviation of the isotropic g value of hexaquocopper (II) from the free electron value, should make spin-rotation the dominate mechanism of relaxation.

Using a suitable radius, the spin-rotation contribution can be calculated and subtracted from the residual alpha value. Since the remainder is appreciable, particularly at low temperatures, the temperature dependence of the remainder can be used to determine the remaining relaxation processes. This approach can be criticized as yielding almost any relaxation mechanism desired. Small changes in the hydrodynamic radius used in the spin-rotation calculation can yield most any temperature dependence.

The relaxation mechanism, as well as having a suitable temperature dependence, must also explain the frequency dependence of the linewidths and the differences between the relaxation of hexaquocopper (II) and hexamminecopper (II). It has been observed that, after correcting for tumbling, the linewidths of hexaquocopper (II) are virtually frequency independent (Kozyrev, 1957; Fujiwara and Hayshi, 1965; chang, 1971; Poupko and Luz, 1972). Since spin-rotation is frequency independent, whatever mechanism is responsible for the remaining alpha term must also be frequency independent. This immediately narrows the field of possible mechanisms. The only frequency independent mechanism left are the Van Vleck Raman process, eq. 2.32, the Kivelson-Orbach process, eq. 2.33, and the rotational spin-orbit process, eq. 2.34. The Kivelson-Orbach process can be discarded because the activation energy of the remaining alpha term, after tumbling and spin-rotation corrections, is only a few hundred wavenumbers, much too small to be an orbital excited state energy. The rotational spin-orbit process may also be dismissed since the deviations of the isotropic g values from the free electron value would predict only a two-fold increase in the hexaquo complex as compared to the hexammine complex. Such a small increase means that there should be deviations of the order of 10 to 20 gauss in the analysis of the alpha term of $Cu(NH_3)_6^{2+}$, which is not the case.

The remaining mechanism is the Van Vleck Raman process. The dependence on Δ^{-6} makes the Van Vleck Raman process more than an order of magnitude larger in hexaquocopper (II) than in hexamminecopper (II). Thus, the deviations of the order of 20 to 40 gauss observed in hexaquocopper (II) would be only of the order of 1 to 2 gauss in hexamminecopper (II). Such small deviations would not be detectable. Using the standard assumption that $\tau_c \propto T^{-1/2}$, the Raman process is expected to have a $T^{1/2}$ dependence. A spin-rotation radius of 3.47Å, by coincidence the same radius as hexamminecopper (II), will yield an alpha term which varies as $T^{1/2}$ after tumbling and spin-rotation corrections. This, by no means, confirms the assignment of the Raman process, but the Raman process seems a reasonable explanation of the remaining alpha term.

In summary, the proposed relaxation mechanisms of hexaquocopper (II) are not as well established as the mechanisms in the hexammine case. The predominate relaxation process is the spin-rotation interaction, with smaller contributions from the Van Vleck Raman process, tumbling, and pseudo-reorientation.

VI. TITANIUM

Titanium (III) has a single unpaired electron in a 3d orbital giving a ^2D state for the free ion. A crystal field of octahedral symmetry will split this five-fold degenerate state into an orbital doublet, ^2E_g, and an orbital triplet, $^2T_{2g}$, with the triplet lower in energy. An axial distortion will split the $^2T_{2g}$ ground state into an orbital singlet, $^2A_1$, and an orbital doublet, ^2E. Depending upon the sign of the distortion, either the singlet or the doublet may be lowest in energy.

The optical spectra of most hexacoordinate Ti (III) complexes show a broad, weak absorption with a maximum absorption between 15,000 and 22,000 cm^{-1} and a shoulder about 2000 cm^{-1} lower in energy (Hartmann and Schlafer, 1951; Hartmann, Schlafer and Hansen, 1956; Gardner, 1967). This absorption has been assigned by Ilse and Hartmann (1951) to the $^2T_{2g} \rightarrow {}^2E_g$ transition. The splitting of the band has been considered to be the result of a Jahn-Teller distortion of the excited state. This has been discussed at length by Liehr (1962). The splitting, δ, between the ground state and the first excited state has been estimated to be of the order of 1000 cm^{-1} in complexes in which the Ti (III) ion is surrounded by an octahedron of water molecules (Van Vleck, 1940; Lewis and Morgan, 1968).

There have been several reports of EPR studies of Ti (III) ions in solution (McGarvey, 1957, 1963; Waters and Maki, 1962; Watanabe and Fujiwara, 1970; Premovic and West, 1974, 1975; Avvakumov, Garif'yanov and Semenova, 1960; Glebov, 1970a; Johnson, Murchison and Bolton, 1970; Charles, 1971). In most cases the Ti(III) ion is complexed in such a way that the symmetry of the ligands is much less than octahedral, resulting in sharp EPR lines with linewidths less than 100 gauss. Most attempts to study more symmetric Ti(III) complexes result in broad lines which are generally undetectable. In particular, hexaquotitanium (III) has long been considered to be undetectable at room temperature using standard EPR techniques. Failure to observe the resonance of $Ti(H_2O)_6^{3+}$ has been ascribed to extremely fast relaxation through the low-lying excited state. Charles (1971) has reported a spectrum consisting of a single-line centered at a g value slightly less than 2 with a peak-to-peak linewidth of 2400±200 gauss at room temperature in acidic, aqueous solutions of $Ti_2(SO_4)_3$. In dilute, acidic solutions of Ti (III), the predominate species is expected to be $Ti(H_2O)_6^{3+}$ (Hartmann and Sclafer, 1951; Ilse and Hartmann, 1951; Pecsok and Fletcher, 1962). Charles observed no dependence on the concentration of any of the starting materials used to prepare the samples and concluded that the resonance was due to hexaquotitanium (III). Further work in this laboratory, by Hynes (1971), confirmed Charles conclusion and indicated an extremely fast relaxation mechanism was present.

The purpose of this work was to determine the magnetic properties of $Ti(H_2O)_6^{3+}$ and to investigate the relaxation process involved.

A. SPECTRA

A rapidly frozen solution of $TiCl_3$ in 1 M H_2SO_4 at K-band (∿24 GHz) gives the spectrum shown in Fig. 26. The spectrum was assigned using computer simulation. The g values obtained are presented in Table VI along with the other reported g values. The g values obtained in this work are in good agreement with the g values obtained by Glebov (1970b). The g values of Premovic and West (1975) require some explanation. From the figures they present, the value of $g_\perp$ was taken to be the high field maximum of the derivative presentation. While such a method introduces little error in the case of narrow linewidths, for these broad lines simulation of the spectrum is required to obtain the magnetic parameters (Ibers and Swalen, 1962). As can be seen from Fig. 26, there is quite a difference between the position of $g_\perp$ calculated by simulation and the position chosen by Premovic and West. There also appears to be a compensating error in their measurements resulting in reasonable agreement in $g_\perp$ and a discrepency in $g_\parallel$. Premovic and West measured their values relative to diphenyldipicrylhydrazyl (DPPH) in a Varian dual sample cavity in a 6 in. magnet. A dual sample cavity always has some field difference between the two samples which must be taken into account to get meaningful data. In a 6 in. magnet field differences of the order of 1% are usual. From the g values they obtained, it would appear that there is a difference of approximately 10 gauss that has not been corrected for in their calculations. Choosing $g_\perp$ at the appropriate position and properly correcting the the field difference gives values in good agreement with the values we obtained. In no instance was there any evidence of less than axial symmetry.

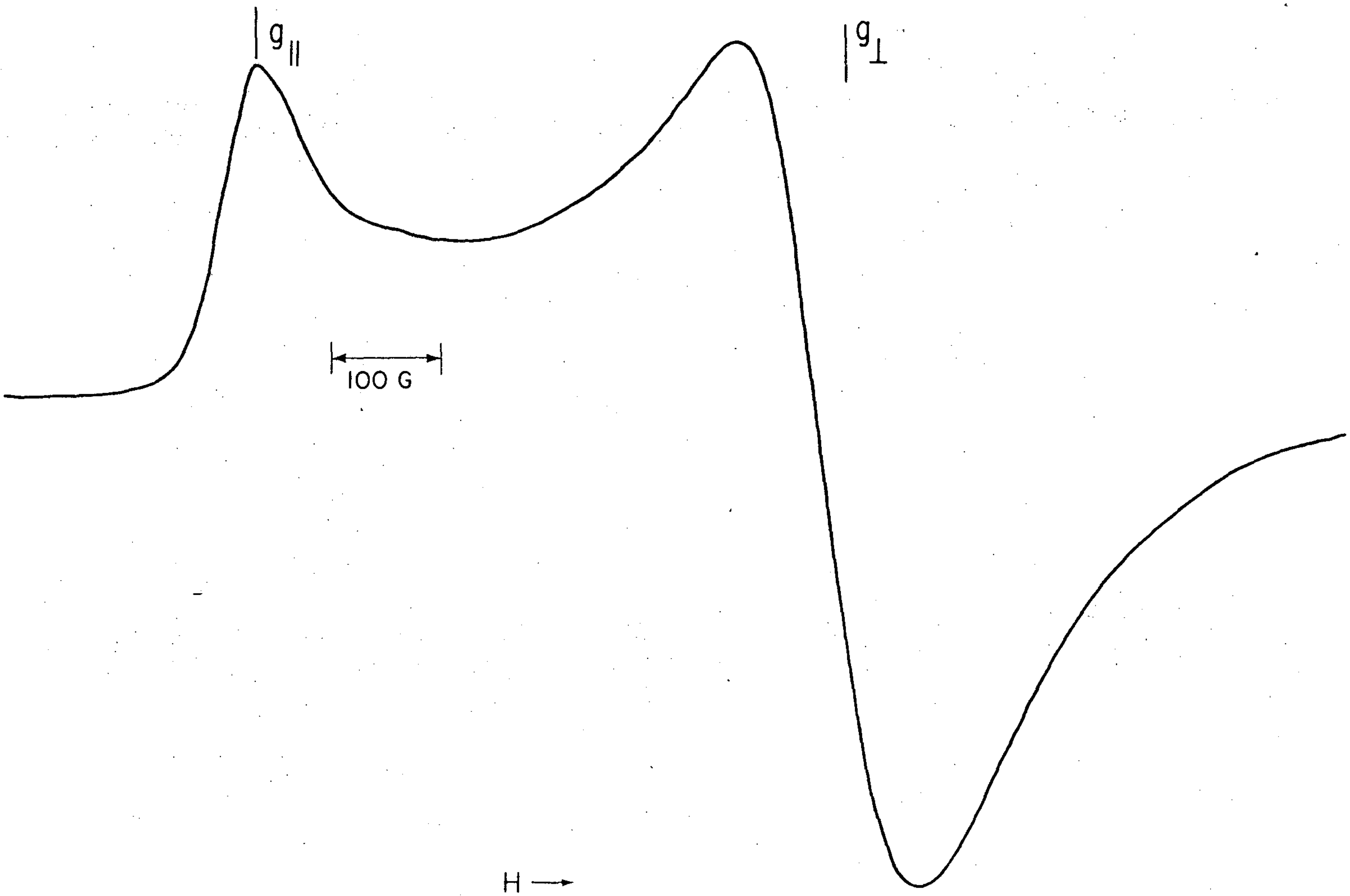

Fig. 26. Glass spectrum of $TiCl_3$ in 1 M H_2SO_4 at 24 GHz. The indicated positions for the g values are based upon computer simulations.

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Table VI. Magnetic parameters of hexaquotitanium (III).

Solute/Solvent	$g_{\parallel}$	$g_{\perp}$	Reference
$TiCl_3$/1 M HCl	1.98	1.89	Glebov, 1970b
$TiCl_3$/2 M HCl	1.994±0.001	1.896±0.001	Premovic and West, 1975
$TiCl_3$/1 M H_2SO_4	1.988±0.002	1.892±0.002	This work

The linewidth of $Ti(H_2O)_6^{3+}$ was measured at X-band (∿9 GHz) in the temperature range from 20°C to -50°C. Above -40°C the line remained a symmetric, Lorentzian line. Below -40°C the linewidth becomes asymmetric and at still lower temperatures a glass spectrum is observed. The linewidth as a function of reciprocal temperature for 1 M $TiCl_3$ in 1 M HCl is shown in Fig. 27. A least-squares fit of the data gave an activation energy of 1850±50 cm^{-1}. It is interesting to note that no discontinuity occurs when the solution freezes.

To determine the effect of the anion on the linewidth behavior, experiments were conducted using $TiCl_3$, and $Ti_2(SO_4)_3$ as sources of titanium ions and HCl, H_2SO_4, and CF_3SO_3H as acids. CF_3SO_3H is a large, non-complexing monoprotic acid. All combinations of the reagents gave the same temperature dependence of the linewidth indicating that anion effects may be neglected. This is an agreement with the conclusion of Charles (1971). The nature of the anion has also been found to have no effect on glasses of Ti (III) ions (Premovic and West, 1975).

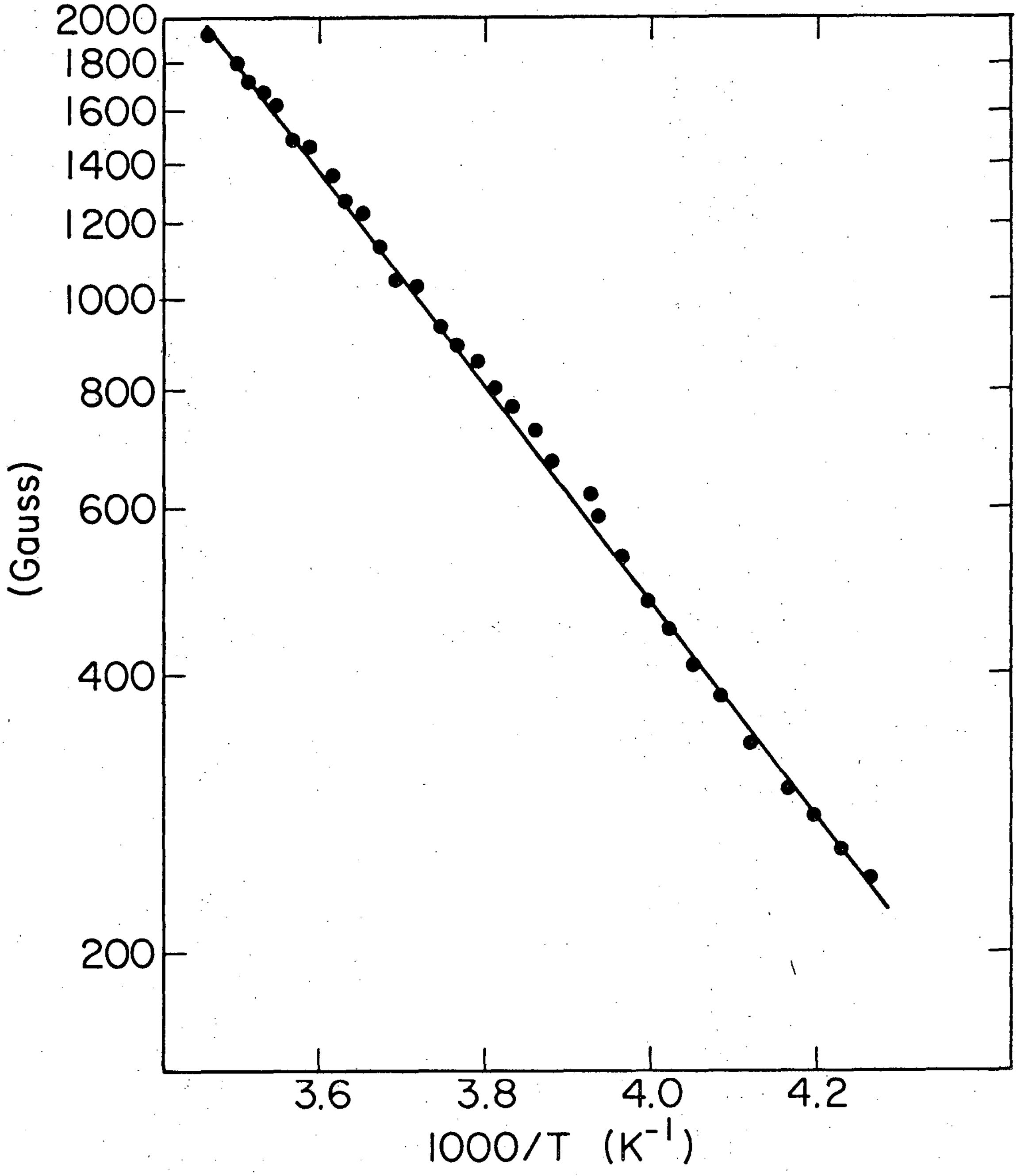

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Fig. 27. First derivative linewidth for $Ti(H_2O)_6^{2+}$ vs 1000/T. The linewidths greater than 1,000 G are for liquid solutions.

B. RESULTS AND DISCUSSION

1. g Values

The g values of Ti (III) in frozen glasses give information about the local symmetry of the complex and the degree of bonding to the ligands. An axial distortion of the octahedral symmetry of the complex is evident from the glass spectrum shown in Fig. 26. In the presence of either a trigonal or tetragonal distortion the T_{2g} level will split into a singlet A_1 and a doublet E state. From the g values the singlet A_1 state is the ground state since the E state would give g values close to zero.

It has long been known that simple crystal field calculations of the g values of a $3d^1$ system in an axially distorted, octahedral field can only approximate the observed g values (Bleaney, 1950; Gladney and Swallen, 1965). Generally, inclusion of effects from the upper E_g state (Bleaney, et al., 1955) and introduction of a covalence factor, k, first suggested by Stevens (1953), must be included to obtain adequate agreement with experiment. The covalency factor accounts for the effects of bonding to the ligands by effectively reducing the matrix elements of orbital momentum and is in the range $0 \leqslant k \leqslant 1$. A value of k = 1 implies no covalent bonding. From the g values alone it is impossible to determine whether the reduction of the orbital momentum is caused by covalent bonding or a dynamic Jahn-Teller effect (Ham, 1965), but generally it is assumed that if $k \approx 1$, the reduction is probably due to covalency. There are two reduction factors, $k_{\pi\pi}$ and $k_{\sigma\sigma}$, corresponding to bonding in a π manner and bonding in a σ manner respectively. For a $3d^1$ system only π-bonding is present to first order and $k_{\sigma\sigma}$ enters only in higher order terms.

Relatively simple crystal field calculations indicate that a tetragonal distortion is not consistant with $g_{\|}$ being so close to the free electron value. To first order and neglecting covalency terms, the value, for a tetragonal distortion should be given by

$$g_{\|} = 2.0023 - 8\lambda/\Delta \quad , \tag{6.1}$$

where λ is the spin-orbit coupling constant, and Δ is the octahedral field splitting. The spin-orbit coupling is usually between 100 cm^{-1} and 154 cm^{-1} in titanium (III) complexes, and Δ has been found to be 20,300 cm^{-1} for $Ti(H_2O)_6^{3+}$ from optical measurements (Hartmann and Schlafer, 1951). Substitution of these values in eq. 6.1 yields $g_{\|} = 1.96$. Second order terms only make $g_{\|}$ smaller (Ray, 1961). Only by invoking abnormally large covalent effects can eq. 6.1 be made to agree with the experimental value of $g_{\|}$. On this basis a tetragonal distortion is rejected. This is an agreement with the conclusion of Premovic and West (1975).

A great deal of work has been done on the g values of titanium (III) in a trigonally distorted octahedral field. In those crystals in which titanium (III) has been successfully introduced as a magnetic impurity, the titanium ion is usually found to reside in a predominately octahedral field with a small trigonal distortion.

For a small trigonal distortion, McGarvey (1963), expanding on the work of Ray (1971), obtained

$$g_{\|} = 2.0023 - 2(2.0023+k_{\pi\pi}) \cos^2\alpha + \frac{4\lambda\, k_{\pi\pi}k_{\sigma\sigma}(\cos^2\alpha + \sqrt{2}\,\sin\alpha\cos\alpha)}{\Delta} \tag{6.2}$$

$$g_{\perp} = 2.0023 - 2.0023\,\cos^2\alpha - 2\sqrt{2}\,k_{\pi\pi}\sin\alpha\cos\alpha - \frac{2\lambda k_{\pi\pi}k_{\sigma\sigma}(2\,\sin^2\alpha + \sqrt{2}\,\sin\alpha\cos\alpha)}{\Delta}\ , \tag{6.3}$$

where

$$\tan\alpha = \left[\delta + \lambda_1/2 + \left(\delta^2 + \lambda_1\delta + 9\lambda_1{}^2/4\right)^{1/2}\right]/\sqrt{2}\,\lambda_1\ , \tag{6.4}$$

$$\lambda_1 = k_{\pi\pi}\lambda\ ,$$

λ is the free ion spin-orbit coupling constant, δ the energy separating the ground A_1 state from the first E state (the trigonal field splitting), and Δ the octahedral field splitting. Assuming that the relaxation behavior exhibited in Fig. 27 is caused by an Orbach process, then $\delta = 1850\ \text{cm}^{-1}$. Substitution into eqs. 6.2 through 6.4 yields values of $k_{\pi\pi} = 0.96\pm0.12$ and $k_{\sigma\sigma} = 1\pm0.7$. The value of $k_{\pi\pi}$ is reasonable when compared to the larger amounts of covalency needed to explain the g values of chelated Ti (III) ions where more covalency is expected. As McGarvey found, the g values are not very sensitive to the value of $k_{\sigma\sigma}$ and little significance can be placed on its value save that it is of the right order of magnitude.

The g values of $Ti(H_2O)_6{}^{3+}$ are thus consistant with the assumption of octahedral symmetry with a small trigonal distortion and the presence of an excited state $1850\ \text{cm}^{-1}$ above the ground A_1 state. It is perhaps worthwhile to note that, for the acetyacetonate, McGarvey found that $\delta = 3\pm1\times10^3\ \mathrm{cm}^{-1}$. Since his g values are closer to 2 than the hexaquo complex, the energy splitting should be slightly less in the hexaquo case, in line with the assignment of $\delta = 1850\ \mathrm{cm}^{-1}$.

2. Relaxation

The linewidth behavior shown in Fig. 27 can be fit to an equation of the form

$$T_2^{-1} = \frac{\sqrt{3}g\beta}{2\hbar}\ \Delta H_{p-p} \exp(-\delta/kT) \quad , \tag{6.5}$$

where ΔH_{p-p} is the peak-to-peak linewidth of the derivative presentation and $\delta = 1850\ 50\ \mathrm{cm}^{-1}$. The pre-exponential factor has a value of $2.6\times10^{14}\ \mathrm{sec}^{-1}$. The form of eq. 6.5 strongly indicates an Orbach mechanism. Substitution of our values into eq. 2.33 and making the approximations discussed by Kivelson (1966) yields a physically unreasonable value of τ_c. The problem is due, in large part, to the independence of the relaxation on whether the solution is frozen or not. The assumptions Kivelson (1966) used to derive eq. 2.33 are no longer valid once the solution freezes. Approaching the problem from the other side, Orbach (1961) found that for Kramer's ions in solids

$$T_1^{-1} = T_2^{-1} = A\delta^3 \exp[\delta/4\,kT - 1]^{-1} \quad . \tag{6.6}$$

For $\delta > kT$ the last term may be approximated by $\exp(-\delta/kT)$. If δ is measured in degrees Kelvin, comparison with experimental results (Stanley and Vaughan, 1969) shows that eq. 6.6 can be approximated by

$$T_1^{-1} = T_2^{-1} = A\delta^3 \exp(-\delta/T) \quad , \tag{6.7}$$

where A is in the range 10^3-10^5. Equation 6.7 holds very well for a large variety of transition metal ions including Ni^{3+}, V^{2+} and Co^{2+}. For V^{4+}, which is isoelectronic with Ti^{3+}, A is almost exactly 10^4. Using this value and $\delta = 1850\ cm^{-1}$ in eq. 6.7 gives a pre-exponential factor of $2\times10^{14}\ sec^{-1}$, in excellent agreement with the experimental value of $2.6\times10^{14}\ sec^{-1}$.

Experiments conducted at S-band showed no change in the relaxation behavior on changing the frequency. This is further confirmation of the Orbach process, since it is expected to have no frequency dependence.

Possible contributions to the linewidth from other mechanisms can be quickly shown to be negligible. The predominate isotope is ^{48}Ti, which has no nuclear spin. Therefore, all mechanisms utilizing the hyperfine coupling are necessarily zero. In titanium (III) complexes having linewidths narrow enough to allow observation of the hyperfine lines from the ^{47}Ti and ^{49}Ti nuclei, there is a dependence of the linewidth upon m_I. This suggests that the tumbling mechanism may have an appreciable contribution to the overall linewidth. Using 2.04 Å for the interatomic distance of Ti-H_2O (Yalsimirshii and Volchenskova, 1967), an estimate of the molecular radius can be made. Using 3Å, the contribution from the anisotropy of the g tensor is 4.8 gauss at room temperature. This contribution is expected to increase as the temperature is decreased, but, since the relaxation is dependent on random reorientation of the molecule with respect to the applied magnetic field, this mechanism will not cause relaxation once the solution freezes. Relaxation caused by the anisotropy in the g tensor may therefore be neglected except above the freezing point. The contribution from this mechanism never exceeds 1% of the total linewidth. Spin-rotation interaction is also operative only above the freezing point since it is dependent upon the complex rotating with respect to the applied magnetic field. The contribution from this mechanism is 0.04 gauss at room temperature. This contribution is expected to decrease as the temperature is lowered and may be neglected. The rotational spin-orbit mechanism also gives an extremely small contribution and is also neglected. Unresolved portion hyperfine splittings are expected to give a contribution of about 2 gauss (Luz and Shulman, 1965; Lewis and Morgan, 1968). Thus there is no significant contribution from any mechanism other than the Orbach process.

Watanabe and Fujiwara (1970) have reported Orbach relaxation in the solution EPR of Ti (III) chelated with organic ligands. They concluded that δ is less than 7000 cm^{-1}. There appears to be no EPR evidence to support the supposition of Charles (1971) that the relaxation mechanism is a Van Vleck-Raman process.

Linewidth measurements of $TiCl_3$ in D_2O were also made as a function of temperature. A value of 1820±50 cm^{-1} was obtained, well within the experimental error of the value obtained in H_2O and indicating that the relaxation is not dependent on internal vibrations of the water ligands. The probable source of energy needed to cause an excitation of 1850 cm^{-1} appears to be vibrations of the octahedral complex. This could explain the independence of the relaxation upon whether the solution is frozen or liquid.

3. The Jahn-Teller Effect

Both the g values and the relaxation of hexaquotitanium (III) are consistent with the assignment of a trigonally distorted octahedral complex with a trigonal splitting of 1850 cm^{-1}. The source of the distortion is most probably the consequence of the theory of Jahn and Teller (1937). The symmetric, octahedral complex possesses a triply degenerate orbital ground state. The Jahn-Teller theorem states that the complex will spontaneously distort to a configuration of lower energy with a non-degenerate ground state. The magnitude of the Jahn-Teller distortion has been calculated by Van Vleck (1939a) to be of the order of 1000 cm^{-1}. The experimental splitting of 1850 cm^{-1} is thus seen to be an extremely reasonable value considering the usually approximate agreement of calculated Jahn-Teller splittings with experiment. From the size of the Jahn-Teller distortion and the nearness of the covalency factors in eqs. 6.2 and 6.3 to unity, a static Jahn-Teller distortion appears to be present.

For titanium (III) ions substituted into CsAl alum, the titanium atom is located in an octahedron of water molecules trigonally distorted by the effects of more distant atoms in the crystal. Thus, even before invoking any Jahn-Teller stabliization, the ground state of the titanium (III) ion is split, with the singlet state lowest in energy. The fixed trigonal distortion caused by the alum lattice inhibits the Jahn-Teller effect. Instead of the large, static Jahn-Teller splitting observed in the hexaquotitanium (III) complex, Shing and Walsh (1974) have observed a rapid, dynamic Jahn-Teller distortion in the alum. From the EPR spectrum and the extremely fast Orbach relaxation observed they conclude that the dynamic Jahn-Teller effect results in an orbital reduction factor of sufficient magnitude to nearly cancel the trigonal field of the lattice. Thus instead of a trigonal splitting of the order of 1000 cm^{-1} (Van Vleck, 1940), their experiments show a splitting of 6 cm^{-1}. This results in extremely fast relaxation and resonance can only be observed at liquid helium temperatures. The much larger splitting in aqueous solution slows the relaxation and allows observation of the resonance at room temperature.

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