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# $g$-VALUES OF TRIGONALLY DISTORTED OCTAHEDRAL $d^1$ SYSTEMS: THE $Ti(H_2O)_6^{3+}$ COMPLEX ION IN FROZEN AQUEOUS SOLUTIONS

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MO expressions for the $g$-values of octahedral $d^1$ system with a relatively strong trigonal distortion, $D_{3d'}$, $D_3$ and $C_{3v}$ symmetries, are derived in terms of a $d_{z^2}$ ground state neglecting the contributions of charge-transfer terms. For the $Ti(H_2O)_6^{3+}$ complex ions in frozen aqueous solutions, where we assume that the metal-ligand bonding is rather ionic, this MO treatment is shown to be equivalent to that of the crystal field and offers a plausible interpretation for the recently published ESR $g$-values. This is demonstrated within the point-charge formalism by correlating theoretical $g_\perp$–values with the angular distortion parameter $\theta$.

## INTRODUCTION

ESR studies of paramagnetic transition-metal complexes yield information about the distribution of the unpaired electrons and hence about the nature of the bonding between the metal ion and its ligands. There have been many reports concerning the application of ESR to trigonally distorted octahedral compounds of Ti(III), and of the interpretations of the ESR parameters in terms of crystal field parameters and the covalency of the metal-ligand bonding. Shifts of $g$-values from the free electron value as a measure of spin-orbit mixing of antibonding states into the ground state varies remarkably from compound to compound, for example, the $g$-values of titanium (III) acetylacetonate approach the free electron value while those of cesium titanium (III) alum show appreciable deviation from that value. The spin-lattice relaxation time also varies considerably from one system to another. In some cases the ESR could be observed only at liquid helium temperature, e.g. cesium titanium (III) alum while that of titanium (III) acetyl acetonate is readily observed at room temperature.

The ground state of a $3d^1$ ion such as Ti (III) is $^2D$, separated in the free ion by a rather large energy, 80378 $cm^{-1}$ from the first excited state (the $3d^1-4s^1$) transition.[1] An ideal octahedral crystal field, $O_h$ symmetry, splits the $^2D$ state into a low lying $^2T_{2g}$ state and an upper $^2E_g$ state.

[1] C. E. Moore, "Atomc Energy Levels", US Bur. Stand. Circ. No. 467, 1964.

If the octahedron is distorted along the trigonal axes, the symmetry of the complex molecule is lowered from $O_h$ to $D_{3d}$, $D_3$ or $C_{3v}$ ; in all three cases the threefold degenerate level $T_{2g}$ in $O_h$ splits into one single and one twofold degenerate level. The twofold level $E_g$, in $O_h$, however, remains degenerate. The correlation diagram for $d^1$ ion in the trigonal crystal field is given in Figure 1.

The crystal field expressions for the $g$-values of octahedral Ti (III) complexes with some trigonal distortion have been discussed by Bleaney,[2] Jarrett,[3] Gladney and Swalen[4] and McGarvey[5] in terms of a $d_z^2(=d_0)$ ground state. Ray[6] also considered this problem and derived expressions for the $g$-values in the presence of a crystal field of trigonal symmetry and covalent bonding. He expressed the $g$-values as a function of two parameters ($P$ and $Q$ in his terminology) in such a fashion that the quantitative estimates of the relative importance of the crystal-field parameters and the influence of covalent bonding are difficult to make. Interpretation of $g$-values in terms of these parameters does little to further chemical insight. McGarvey[7] presents equations for the $g$-values which are only an extension of the work of Ray and which include the effects of covalent bonding on the second order terms.

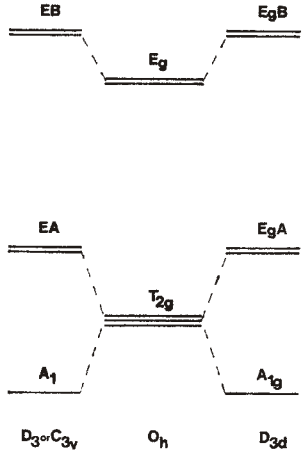


Fig. 1. — Splittings under trigonal distortion.

In the first part of this paper, we derive expressions for the $g$-tensor in terms of MO expansion coefficients for octahedral $d^1$ systems with a relatively strong trigonal distortion which have charge transfer bands at much higher energy than $d-d$ bands. This is done in order to illustrate the importance of certain terms which have usually been neglected in the past. In the second part, we attempt to show the sensitivity of the $g_\perp$-values to small angular departures from octahedral symmetry in trigonal systems. As an example we use the $Ti(H_2O)_6^{3+}$ complex ion in frozen aqueous solutions in which we assume that the covalency plays a minor role. In this case the MO formula for the $g_\perp$-value developed in the first part reduces to a relatively simple expression. Employing this expression and the point-charge calculation of Gerloch and coworkers,[8] theoretical $g_\perp$-values are obtained for this system. The following abbreviations will be used : CF = crystal field, PC = point-charge, and CT = charge transfer.

[2] B. Bleaney, *Proc. Phys. Soc.* (*London*), **A63**, 407 (1950).
[3] B. H. S. Jarrett, *J. Chem. Phys.*, **42**, 1999 (1965).
[4] B. H. S. Gladney and J. D. Swalen, *J. Chem. Phys.*, **42**, 199 (1965).
[5] B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).
[6] D. K. Ray, "Soviet Phys.-Solid State", **3**, 1838 (1962). See also *Nuovo Cimento*, **21**, 1 (1961).
[7] B. R. McGarvey, *J. Chem. Phys.*, **38**, 388 (1963).
[8] M. Gerloch, J. Lewis, G. G. Philips and P. N. Quested, *J. Chem. Soc.* (*A*), **(1970)**, 1941.

## THE PRINCIPAL COMPONENTS OF THE g-TENSOR IN A TRIGONAL $d^1$ SYSTEM *

We shall consider a one electron-system, with the electron in the $d_z^2$ orbital, so that the ground state is $A_{1g}^*$. Only states of $E_g$ symmetry can mix with ground state under perturbation of the angular momentum operator so that we need consider only MO's belonging to the representation $a_{1g}$ and $e_g$. The coordinate axis system is shown in Figure 2. The $z$ axis is chosen as the threefold axis. If the angle $\theta$ is defined as the angle between any bond and the principal rotation axis $z$, then a trigonal squash occurs when $\theta > 54.75°$ ($= \theta_{oct}$, the angle in $O_h$ symmetry) and a trigonal elongation when $\theta < 54.75°$. The relevant antibonding MO's can be written down as:

$$a_{1g} = \alpha_1^* d_z^2 - \alpha_2^* \Phi(a_{1g}) \quad (1)$$

$$e_g 1A = a_1 d_{x^2-y^2} - b_1 d_{xz} - \beta_2^* \Phi(e_g 1A) \quad (2)$$

$$e_g 2A = a_2 d_{xy} + b_2 d_{yz} - \gamma_2^* \Phi(e_g 2A) \quad (3)$$

$$e_g 1B = b_3 d_{x^2-y^2} + a_3 d_{xz} - \delta_2^* \Phi(e_g 1B) \quad (4)$$

$$e_g 2B = b_4 d_{xy} - a_4 d_{yz} - \varepsilon_2^* \Phi(e_g 2B) \quad (5)$$

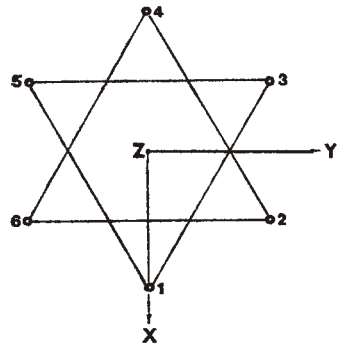


Fig. 2. — Definition of axes.

where the metal orbitals are the usual $d$ functions, and the ligand functions, $\Phi$, are group orbitals (or set of group orbitals) of appropriate symmetry.**

Notice that Ray[6] preferred to use as the metal orbitals the linear combinations

| *Symmetry* | *Metal Orbital* |
|---|---|
| $a^1{}_g$ | $d_0$ |
| $e_g A$ | $ad_2 - bd_{-1}$ |
| | $ad_{-2} + bd_1$ |
| $e_g B$ | $bd_2 + ad_{-1}$ |
| | $bd_{-2} - ad_1$ |

with the orthonormality condition $a^2 + b^2 = 1$. However, metal orbitals given by expressions (1) — (5) are found to be particularly convenient and simple here since matrix elements such as $<d|H_{1s}|d>$ and $<d|\hat{l}_x|d>$ can be more readily evaluated using table A.1. in Appendix A. Clearly, the two ways of writing the metal orbitals are equivalent and supplementary to each other.

* Although we are dealing in our treatment with the $D_{3d}$ system, the results are applicable for the $D_3$ and $C_{3v}$ systems. Note that in these cases the proper notation ought to be used (Figure 1).

** The wavefunctions (1)—(5), which describe MO's, will represent the states (denoted by capital letters) arising from the occupancy by the $d^1$ electron.

We now proceed to derive expressions for the principal $g_{\|}$ and $g_{\perp}$ components of the $g$-tensor in our trigonal $d^1$ system. To first order, the two ground-state spin functions in the presence of spin-orbit interaction will be

$$a_{1g}^{+} = A_{1g}^{+} - \frac{\langle E_g^{-}\, 1A \,|\, H_{ls} \,|\, A_{1g}^{+}\rangle}{\Delta E(A_{1g} \to E_g\, A)}\, E_g^{-}\, 1A - \frac{\langle E_g^{-} 1B \,|\, H_{ls} \,|\, A_{1g}^{+}\rangle}{\Delta E(A_{1g} \to E_g B)}\, E_g^{-}\, 1B -$$

$$- \frac{\langle E_g^{-}\, 2A \,|\, H_{ls} \,|\, A_{1g}^{+}\rangle}{\Delta E(A_{1g} \to E_g\, A)}\, E_g^{-}\, 2A - \frac{\langle E_g^{-}\, 2B \,|\, H_{ls} \,|\, A_{1g}^{+}\rangle}{\Delta E(A_{1g} \to E_g\, B)}\, E_g^{-}\, 2B \tag{6}$$

$$a_{1g}^{-} = A_{1g}^{-} - \frac{\langle E_g^{+}\, 1A \,|\, H_{ls} \,|\, A_{1g}^{-}\rangle}{\Delta E(A_{1g} \to E_g A)}\, E_g^{+} 1A - \frac{\langle E_g^{+}\, 1B \,|\, H_{ls}\, A_{1g}^{-}\rangle}{\Delta E(A_{1g} \to E_g B}\, E_g^{+}\, 1B -$$

$$- \frac{\langle E_g^{+}\, 2A \,|\, H_{ls} \,|\, A_{1g}^{-}\rangle}{\Delta E(A_{1g} \to E_g\, A)}\, E_g^{+} 2A - \frac{\langle E_g^{+}\, 2B \,|\, H_{ls} \,|\, A_{1g}^{-}\rangle}{\Delta E(A_{1g} \to E_g B)}\, E_g^{+}\, 2B \tag{7}$$

where $\Delta E(A_{1g} \to E_g A)$ and $\Delta E(A_{1g} \to E_g\, B)$ are the energies of the $E_g A$ and $E_g\, B\, d - d$ excited states. Before proceeding any further, it is useful to calculate the matrix elements in expressions (6) and (7).

The most general expression for the spin-orbit coupling operator, $H_{ls}$, in the one-electron case is

$$H_{ls} = \lambda_M(r_M)\, \hat{l}_M \hat{s} + \sum_{L=1}^{6} \lambda_L(r_L)\, \hat{l}_L\, \hat{s} \tag{8}$$

where $r_k$ is the distance of the unpaired electron from the nucleus $k = M$, $L(=1 - 6)$, where the subscripts $M$ and $L$ denote the metal and the appropriate ligand atom, respectively; $\hat{l}_k$ is the orbital angular momentum operator for the unpaired electron centred on nucleus $k$; and $\lambda_k(r_k)$ is the atomic spin-orbit coupling constant for the appropriate orbital of atom $k$.

The operator $\hat{l} \cdot \hat{l}$ is written as

$$\hat{l} \cdot \hat{s} = \hat{l}_x\, \hat{s}_x + \hat{l}_y\, \hat{s}_y + \hat{l}_z\, \hat{s}_z \tag{9}$$

The functions obtained by the operation of the $\hat{l} \cdot \hat{s}$ operator are given in table A.1 (Appendix A).

Now we are in position to evaluate the various matrix elements in expression (6). Consider first the integral $\langle E_g^{-}\, 1A \,|H_{ls}\,|\, A_{1g}^{+}\rangle$, where the $E_g^{-} 1A$ is a $d-d$ excited state with the electron in the $e_g\, 1A$ antibonding MO as given by (2). Writing this integral out *in extenso*, we have

$$\langle a_1\, d_{x^2-y^2}^{-} - b_1 d_{xz}^{-} - \beta_2^{*}\, \Phi^{-}(e_g\, 1A) \,|\, H_{ls} \,|\, \alpha_1^{*}\, d_{z^2}^{2} - \alpha_2^{*} \Phi^{+}(a_{1g}) \rangle \tag{10}$$

Since $\lambda_k$ is proportional to $r_k^{-3}$ for hydrogen-like wavefunctions it seems reasonable to suppose that only one-center integrals of the type

$\langle\psi|\lambda_k(r_k)\,\hat{l}_k\hat{s}\,|\,\psi\rangle$ are significantly different from zero. There are only two terms to consider, given by (11) and (12).

$$-b_1\alpha_1^*\langle d_{xz}^-\,|\,\lambda_M(r_M)\,\hat{l}_M\,\hat{s}\,|\,d_{z^2}^+\rangle \tag{11}$$

$$\alpha_2^*\,\beta_2^*\langle\,\Phi^-(e_g\,1A)\;|\;\lambda_L(r_L)\,\hat{l}_L\cdot\hat{s}\,|\,\Phi^+(a_{1g})\,\rangle \tag{12}$$

The first of these (11) is simply equal to

$\frac{\sqrt{3}}{2}b_1\alpha_1^*\lambda_M$. Equation (12), after expansion of the ligand group orbitals,*

is found to be zero.

We thus end up

$$-\langle\,E_g^-\,1A\,|\,H_{ls}\,|\,A_{1g}^+\,\rangle=-\frac{\sqrt{3}}{2}b_1\,\alpha_1^*\,\lambda_M \tag{13}$$

Similarly, we evaluate the rest of the integrals in equations (6) and (7) and the solutions are

$$-\langle\,E_g^-\,1B\,|\,H_{ls}\,|\,A_{1g}^+\,\rangle=\frac{\sqrt{3}}{2}\,a_3\,\alpha_1^*\,\lambda_M \tag{14}$$

$$-\langle\,E_g^-\,2A\,|\,H_{ls}\,|\,A_{1g}^+\,\rangle=\frac{\sqrt{3}}{2}\,\mathrm{i}b_2\,\alpha_1^*\,\lambda_M \tag{15}$$

$$-\langle\,E_g^-\,2B\,|\,H_{ls}\,|\,A_{1g}^+\,\rangle=-\frac{\sqrt{3}}{2}\,\mathrm{i}a_4\,\alpha_1^*\,\lambda_M \tag{16}$$

$$-\langle\,E_g^+\,1A\,|\,H_{ls}\,|\,A_{1g}^-\,\rangle=\frac{\sqrt{3}}{2}\,b_1\,\alpha_1^*\,\lambda_M \tag{17}$$

$$-\langle\,E_g^+\,1B\,|\,H_{ls}\,|\,A_{1g}^-\,\rangle=-\frac{\sqrt{3}}{2}\,a_3\,\alpha_1^*\,\lambda_M \tag{18}$$

$$-\langle\,E_{1g}^+\,2A\,|\,H_{ls}\,|\,A_{1g}^-\,\rangle=\frac{\sqrt{3}}{2}\,\mathrm{i}b_2\,\alpha_1^*\,\lambda_M \tag{19}$$

$$-\langle\,E_g^+\,2B\,|\,H_{ls}|\,A_{1g}^-\rangle=-\frac{\sqrt{3}}{2}\,\mathrm{i}a_4\alpha_1^*\,\lambda_M \tag{20}$$

* These are obtained from the standard projection operator method.

Introducing (13) — (16) and (17) — (20) into expressions (6) and (7), respectively, we get

$$a_{1g}^{+} = A_{1g}^{+} - \frac{\sqrt{3}\alpha_1^{*}\lambda_M}{2\Delta E(A_{1g} \to E_g A)} (b_1 E_g^{-}\, 1A - \mathrm{i} b_2 E_g^{-}\, 2A) +$$

$$+ \frac{\sqrt{3}\alpha_1^{*}\lambda_M}{2\Delta E(A_{1g} \to E_g B)} (a_3 E_g^{-}\, 1B - \mathrm{i} a_4 E_g^{-}\, 2B) \tag{21}$$

$$a_{1g}^{-} = A_{1g}^{-} + \frac{\sqrt{3}\alpha_1^{*}\lambda_M}{2\Delta E(A_{1g} \to E_g A)} (b_1 E_g^{+}\, 1A + \mathrm{i} b_2 E_g^{-}\, 2A) -$$

$$- \frac{\sqrt{3}\alpha_1^{*}\lambda_M}{\Delta E(A_{1g} \to E_g B)} (a_3 E_g^{+}\, 1B + \mathrm{i} a_4 E_g^{-}\, 2B) \tag{22}$$

Throughout this paper we shall look at the case where the effective spin-orbit coupling constant $\lambda_M$ of the $d^1$ complex ion in an octahedral ligand field of trigonal symmetry is much smaller than $\Delta E(A_{1g} \to E_g A)$. We shall consider this approximation valid for every system in which $\Delta E(A_{1g} \to E_g B) > 10\lambda_M$.

The basic theory of the Zeeman splitting in a trigonal $d^1$ system is given in Appendix B, expressions (23) and (24) being obtained for $g_{\|}$ and $g_{\perp}$.

$$g_{\|} = 2.0023 \tag{23}$$

$$g_{\perp} = 2 \cdot 0023 - 2\sqrt{3}\, \mathrm{i}\alpha_1^{*}\, \lambda_M \left( \frac{b_2 \langle e_g\, 2A \,|\, \hat{l}_x \,|\, a_{1g} \rangle}{\Delta E(A_{1g} \to E_g A)} - \frac{a_4 \langle e_g\, 2B \,|\, \hat{l}_x \,|\, a_{1g} \rangle}{\Delta E(A_{1g} \to E_g B)} \right) \tag{24}$$

We are now in position to derive the expressions for the $g$-values in terms of the CF model. In contrast to MO model, the CF approach supposes that partly-filled shells are pure d-orbitals. In this regard the expansion of the integrals $\langle e_g \,|\, \hat{l}_x \,|\, a_{1g} \rangle$* is rather simple and yields

$$\langle e_g\, 2A \,|\, \hat{l}_x \,|\, a_{1g} \rangle = -\mathrm{i}\sqrt{3} b_2 \tag{25}$$

$$\langle e_g\, 2B \,|\, \hat{l}_x \,|\, a_{1g} \rangle = \mathrm{i}\sqrt{3} a_4 \tag{26}$$

Since $\alpha_1^{*} = 1$ in CF model we can write

$$g_{\|} = 2.0023 \tag{27}$$

$$g_{\perp} = 2.0023 - \frac{6 b_2^2\, \lambda_M}{\Delta E(A_{1g} \to E_g A)} - \frac{6 a_4^2\, \lambda_M}{\Delta E(A_{1g} \to E_g B)} \tag{28}$$

* The functions obtained by the operation of $\hat{l}_x$ are given in table A.2 (Appendix A).

If the six ligand donor atoms to the $d^1$ ion are arranged in a nearly octahedral arrangement, then the symmetry is approximately octahedral in which case common approximation is to assume that $a_4 = a \sim \sqrt{\frac{2}{3}}$ and $b_2 = b \sim \sqrt{\frac{1^*}{3}}$ and we arrive at

$$q_{\parallel} = 2.0023 \tag{29}$$

$$q_{\perp} = 2.0023 - \frac{2\lambda_M}{\Delta E(A_{1g} \to E_g A)} - \frac{4\lambda_M}{\Delta E(A_{1g} \to E_g B)} \tag{30}$$

These are the so-called CF expressions for the principal components of the $g$-tensor of the $d^1$ metal ion in the CF of the octahedral symmetry with a strong trigonal distortion.

We proceed now to calculate the $g$-values in terms of the MO model. We shall calculate some of the matrix elements in detail in order to illustrate some interesting points. Consider first the integral $\langle e_g\, 2A | \hat{l}_x | a_{1g} \rangle$ wh ch occurs in expression (24). We want to evaluate (31).

$$\langle a_2\, d_{xy} + b_2\, d_{yz} - \gamma_2^* \Phi(e_g\, 2A) | \hat{l}_x | \alpha_1^*\, d_{z^2} - \alpha_2^* \Phi(a_{1g}) \rangle \tag{31}$$

This is expanded as the sum of 6 terms. Integrals of the type $\langle d | \hat{l}_x | d \rangle$ are straightforward

$$a_2 \alpha_1^* \langle d_{xy} | \hat{l}_x | d_{z^2} \rangle = 0 \tag{32}$$

$$b_2 \alpha_1^* \langle d_{yz} | \hat{l}_x | d_{z^2} \rangle = -i\sqrt{3} b_2 \alpha_1^* \tag{33}$$

That of the type $\langle \Phi | \hat{l}_x | d \rangle$ is also straightforward and leads to metal-ligand group overlap integral

$$-\alpha_1^* \gamma_2^* \langle \Phi(e_g\, 2A) | \hat{l}_x | d_{z^2} \rangle = i\sqrt{3} \alpha_1^* \gamma_2^* S(d_{yz'},\ e_g\, 2A) \tag{34}$$

Integrals of the type $\langle d | \hat{l}_x | \Phi \rangle$ can be easily calculated using the Hermitian property of $\hat{l}_x$, which may be defined by

$$\int \Phi^* \hat{l}_x\, \psi d\tau = \int \psi \hat{l}_x^* \Phi^*\, d\tau \tag{35}$$

Since in our case all $\Phi$ and $\psi$ orbitals are real and $\hat{l}_x^* = -\hat{l}_x$, we have identity

$$\int \Phi^* \hat{l}_x\, \psi d\tau = -\int \psi\, \hat{l}_x\, \Phi d\tau \tag{36}$$

* The correctness of these assumed values will be discussed in detail under "Modification of the Lower $E_g$ Wavefunctions and the $g$-Values" (See also Ref.[6]).

Terms of these types arising from the expansion of the integral $\langle e_g\, 2A\,|\hat{l}_x|\, a_{1g}\rangle$ are given

$$-a_2\,\alpha_2^*\,\langle d_{xy}\,|\,\hat{l}_x\,|\,\Phi(a_{1g})\rangle = \mathrm{i}a_2\alpha_2^*\,S(d_{xz},\ a_{1g}) \tag{37}$$

$$-b_2\alpha_2^*\,\langle d_{yz}\,|\,\hat{l}_x\,|\,\Phi(a_{1g})\rangle = \mathrm{i}b_2\alpha_2^*\,[S(d_{x^2-y^2},\ a_{1g}) + \sqrt{3}S(d_{z^2},\ a_{1g})] \tag{38}$$

The remaining term arising from the expansion of (32) is the sum of the matrix elements between ligand group orbitals and can be presented in a more convenient form

$$a_2^*\,\gamma_2^*\,\langle\,\Phi(e_g\,2A)\,|\,\hat{l}_x\,|\,\Phi(a_{1g})\rangle = \alpha_2^*\,\gamma_2^*\,R(e_g\,2A,\ a_{1g}) \tag{39}$$

where $R(e_g\,2A,\ a_{1g}) = \langle\,\Phi(e_g\,2A)\,|\,\hat{l}_x\,|\,\Phi(a_{1g})\,\rangle$.

The final result for the matrix element $\langle e_g\,2A\,|\,\hat{l}_x\,|\,a_{1g}\,\rangle$ is given by

$$\begin{aligned}\langle\,E_g\,2A\,|\,\hat{l}_x\,|\,A_{1g}\rangle = -\mathrm{i}\sqrt{3}b_2\,\alpha_1^*\Big\{1 - \frac{\gamma_2^*}{b_2}\,S(d_{yz}\ e_g\,2A) - \\ - \frac{a_2\alpha_2^*}{\sqrt{3}b_2\alpha_1^*}\,S(d_{xz},\ a_{1g}) - \frac{\alpha_2^*}{\sqrt{3}\alpha_1^*}\,[S(d_{x^2-y^2},\ a_{1g}) + \\ + \sqrt{3}S(d_{z^2},\ a_{1g})] + \alpha_2^*\,\gamma_2^*\,R(e_g\,2A,\ a_{1g})\Big\}\end{aligned} \tag{40}$$

The expansion of $\langle e_g\,2B\,|\hat{l}_x\,|a_{1g}\rangle$ presents no additional complication and turns out to be

$$\begin{aligned}\langle e_g\,2B\,|\,\hat{l}_x\,|a_{1g}\,\rangle = \mathrm{i}\sqrt{3}a_4\alpha_1^*\Big\{1 + \frac{\varepsilon_2^*}{\sqrt{3}a_4}\,S(d_{yz},\ e_g\ 2B) + \\ + \frac{b_4\alpha_2^*}{\sqrt{3}a_4\alpha_1^*}\,S(d_{xz}\ e_g\ 2B) - \frac{\alpha_2^*}{\sqrt{3}\alpha_1^*}\,[S(d_{x^2-y^2},\ a_{1g}) + \\ + \sqrt{3}S(d_{z^2},a_{1g})] + \alpha_2^*\,\varepsilon_2^*\,R(e_g\,2B,\ a_{1g})\Big\}\end{aligned} \tag{41}$$

where $R(e_g\,2B,\ a_{1g}) = \langle\,\Phi(e_g\,2B)\,|\,\hat{l}_x\,|\,\Phi(a_{1g})\rangle$.

We are now in position to write down final expressions for the $g_{\parallel}$ and $g_{\perp}$ principal components of the $g$-tensor. These are

$$g_{\parallel} = 2.0023 \tag{42}$$

$$g_\perp = 2.0023 - \frac{6b_2^2\,\alpha_1^{*2}\lambda_M}{\Delta E(A_{1g} \to E_g A)} \left\{ 1 - \frac{\gamma_2^*}{b_2} S(d_{yz},\ e_g\,2A) - \right.$$

$$- \frac{a_2\alpha_2^*}{\sqrt{3}b_2\,\alpha_1^*} S(d_{xz},\ a_{1g}) - \frac{\alpha_2^*}{\sqrt{3}\alpha_1^*} [S(d_{x^2-y^2},\ a_{1g}) +$$

$$\left. + \sqrt{3}S(d_{z^2}, a_{1g})] \right\} - \frac{6a_4^2\,\alpha_1^*\,\lambda_M}{\Delta E(A_{1g} \to E_g B)} \left\{ 1 + \frac{\varepsilon_2^*}{\sqrt{3}a_4} S(d_{yz}, e_g\,2B) + \right. \tag{43}$$

$$\left. + \frac{b_4\alpha_2^*}{\sqrt{3}\alpha_1^*} S(d_{xz},\ e_g\,2B) - \frac{\alpha_2^*}{\sqrt{3}\alpha_1^*} [S(d_{x^2-y^2}, a_{1g}) + \sqrt{3}S(d_{z^2},\ a_{1g})] \right\} -$$

$$- 2\sqrt{3}\,\mathrm{i}\alpha_1^*\,\lambda_M[\alpha_2^*\,\gamma_2^*\,R(e_g\,2A, a_{1g}) + \alpha_2^*\,\varepsilon_2^*\,R(e_g\,2B, a_{1g})]$$

Note that the expressions (42) and (43) are deficient in that they do not contain CT terms. Kon and Sharpless [9] showed that such terms could be important in the $d^1$ systems. However, many titanium (III) compounds to which our discussion is applicable exhibit CT bands at relatively high energies ($>$ 50000 cm$^{-1}$), so these CT terms are of minor importance. We shall later discuss such a system : the $Ti(H_2O)_6^{3+}$ complex ions in frozen aqueous solution.

## DISCUSSION

Our expression (43) for the $g_\perp$ component is rather complicated. It seems therefore more instructive for our subsequent discussion to simplify this expression as follows :

$$g_\perp = 2.0023 - \frac{6b_2^2\,\alpha_1^{*2}\,\lambda_M}{\Delta E(A_{1g} \to E_g A)} f_1 - \frac{6a_4^2\,\alpha_2^{*2}\,\lambda_M}{\Delta E(A_{1g} \to E_g B)} f_2 - C \tag{44}$$

where $f_1$ and $f_2$ are

$$f_1 = 1 - \frac{\gamma_2^*}{b_2} S(d_{yz},\ e_g\,2A) - \frac{a_2\alpha_2^*}{\sqrt{3}b_2\alpha_1^*} S(d_{xz}, a_{1g}) -$$

$$- \frac{\alpha_2^*}{\sqrt{3}\alpha_1^*} [S(d_{x^2-y^2},\ a_{1g}) - \sqrt{3}S(d_{z^2},\ a_{1g})] \tag{45}$$

$$f_2 = 1 + \frac{\varepsilon_2^*}{\sqrt{3}a_4} S(d_{yz},\ e_g\,2B) - \frac{b_4\alpha_2^*}{\sqrt{3}a_4\alpha_1} S(d_{xz},\ e_g\,2B) -$$

$$- \frac{\alpha_2^*}{\sqrt{3}\alpha_1^*} [S(d_{x^2-y^2},\ a_{1g}) + \sqrt{3}S(d_{z^2}, a_{1g})] \tag{46}$$

[9] a. H. Kon and N. E. Sharpless, *J. Chem. Phys.*, **42**, 906 (1965).
b. H. Kon and N. E. Sharpless, *J. Chem. Phys.*, **43**, 1081 (1965).

and $C$ is

$$C = 2\sqrt{3}i\alpha_1^* \lambda_M[\alpha_2^* \gamma_2^* R(e_g\, 2A,\ a_{1g}) + \alpha_2^* \varepsilon_2^* R(e_g\, 2B,\ a_{1g})] \tag{47}$$

In order to discuss the relative importance of the parameters $f_1$, $f_2$ and $C$ in expression (44) we should have available the appropriate MO expansion coefficients and various overlap integrals. Unfortunately, it is not possible from the present experimental and theoretical data to give good numerical values either for the MO parameters describing the chemical bonding or for the overlap integrals. While detailed theoretical calculation of the parameters $f_1$, $f_2$ and $C$, i.e. the $g_\perp$ values, for an individual complex species will not be attempted here we shall try to use the simpler formula and content ourselves with the $Ti(H_2O)_6^{3+}$ complex ion in a frozen aqueous solution for which such formula is applicable.

## TITANIUM (III) HEXA-AQUO COMPLEX IONS IN FROZEN AQUEOUS SOLUTIONS

The titanium (III) halides and titanium (III) sulphate have been studied both chemically and spectroscopically and are believed to contain only octahedrally solvated ions, Ti $(H_2O)_6^{3+}$.[10]

The broad weak band in the optical spectrum of the $Ti(H_2O)_9^{3+}$ complex ion is assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition.[10a] One interesting feature of the spectrum is the asymmetric character of the visible absorption band. This band consists of a broad maximum at $\sim$ 20300 cm$^{-1}$ with a pronounced shoulder at $\sim$17000 cm$^{-1}$. The splitting is considered to arise from a nuclear configurational instability in the excited state, i.e. from the Jahn-Teller effect. The perfect octahedral ion $Ti(H_2O)_6^{3+}$ cannot be stable because of the threefold degeneracy of the $^2T_{2g}$ ground state and a tetragonal distortion is required so that a nondegenerate ground state exists, i.e. ($^2B_{2g}$). However, the theoretical background of the Jahn-Teller effect gives no direct information concerning the magnitude of the deviation from octahedral symmetry, or a choice between a static and a dynamic equilibrium between limiting structures. It is, however, expected that the splitting of the $^2T_{2g}$ ground state will be smaller than that of the excited $^2E_g$ state.

Recently, Glebov[11] and Premovič and West[12] have reported that rapidly frozen (77 K) strongly acidic aqueous solutions of titanium (III) chloride, bromide, iodide or sulfate provide an identical spectrum from each sample with $g_{||} = 1.99$ and $g_\perp = 1.89$. Premovič and West's [12] analysis indicates

[10] a. F. E. Ilse and H. Hartmann, *Z. phys. Chem.*, (*Leipzig*), **197**, 239 (1951).
b. H. Hartmann, H. L. Schläfer and K. H. Hansen, *Z. Anorg. Chem.*, **284**, 153 (1964).

[11] a. V. A. Glebov, *Zhur. strukt. Khim.*, **11**, 809 (1970).
b. V. A. Glebov, *Doklady Akad. Nauk S.S.S.R.*, **190**, 1378 (1970).

[12] P. I. Premovic and P. R. West, *Canad. J. Chem.*, **53**, 1630 (1975).

that the local symmetry of the Ti (III) ions providing the signal is trigonal. It was proposed that these ions are $Ti(H_2O)_6^{3+}$ species * located in sites in the ice structure subject to strong crystal package forces.

ESR and spectroscopic studies [13] and hexaquo complex ions of the transition metals of the iron group have convincingly demonstrated that chemical bonding between the central metal ion and water ligands is rather ionic. It is reasonable to suppose an analogous situation for the Ti $(H_2O)_6^{3+}$ complex ion. Moreover, another argument against the existence of covalent bonding in the Ti $(H_2O)_6^{3+}$ complex ion is the position of water in the neuphelauxetic series.[14] Those ligands which are known to form strong covalent bonds, such as $Br^-$ and $I^-$ have high positions in this series. Ligands which give rise to rather weak covalency in chemical bonding, such as $F^-$, have unusually low position in the series. Water, however, has a position very close to that of the fluoride ion, and this fact indicates that covalency of the chemical bonding between central metal ion and water ligands is likely to be rather weak. Since ionic bonding in the Ti $(H_2O)_6^{3+}$ complex ion implies that $\alpha_1^*$, $f_1$ and $f_2$ are close to unity, $C$ is close to zero, $a_4 = a$ and $b_2 = b$. The expressions (42) and (43) can be written

$$g_{\parallel} = 2.00 \tag{48}$$

$$g_{\perp} = 2.00 - \frac{6b^2\,\lambda_M}{\Delta E(A_{1g} \rightarrow E_g A)} - \frac{6a^2\,\lambda_M}{\Delta E(A_{1g} \rightarrow E_g B)} \tag{49}$$

These expressions are, of course, equivalent to the CF expressions (27) and (28).

Throughout this discussion, it has been assumed the ground-term splitting $\Delta E(A_{1g} \rightarrow E_g A) > 10\lambda_M$. Gladney and Swalen[4] have examined in detail ESR $g$-values calculated from a $^2D$ term perturbed by a CF$-D_3$ potential and spin-orbit coupling. They found that for $g$-values close to 2, the ratio $\lambda_M/\Delta E(A_{1g} \rightarrow E_g A) < 0.1 (\lambda_M/\delta < 0.1)$ in their terminology. Although their calculation suffers from all the deficiencies inherent in their CF approach, which neglects the relative importance of excited state admixture CF, we may reasonably suppose that this value for the ratio $\lambda_M/\Delta E(A_{1g} \rightarrow E_g A)$ is realistic and can meaningfully be used in our discussion.

As we stated above, very common device in order to reduce the number of unknowns either in the MO or CF expressions for the $g_{\parallel}$

* Although Ti(III) usually enters compounds into a site of local point symmetry $C_3^4$, the problem can frequently be discussed as one with $D_{3d}$ point symmetry if the CF in the vicinity of Ti(III) is determined primarily by the charges in the six oxygen atoms of water ligands.

[13] a. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
b. R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960).
c. K. Dearmond, B. B. Garrett and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1964).
d. M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).

[14] J. E. Huheey, "Inorganic Chemistry", Harper and Row, New York, 1972, p. 349.

and $g_{\perp}$ in a trigonal $d^1$ system is to regard the symmetry of this system approximately octahedral in which case $a \sim \sqrt{\frac{2}{3}}$ and $b \sim \sqrt{\frac{1}{3}}$*. However such an assumption is questionable.

Recently, Gerloch and coworkers,[8] in their paper dealing with the magnetic properties of trigonally distorted iron (II) complexes, have pointed out the sensitivity of the magnetic properties to small angular departures from regular octahedral symmetry in trigonal systems. They emphasized that the analysis of magnetic data based on a constant geometry of the complex ion in different lattice environments is dangerous, in the trigonal case in particular, because of peculiarities of the angular functions with which the magnetic properties are associated. It therefore seems timely to reconsider the relationship between the $a$ and $b$ coefficients and features of structure of trigonal $d^1$ systems in the light of recent developments mentioned above.

## MODIFICATION OF THE LOWER $E_g$ WAVEFUNCTIONS AND THE $g$-VALUES

In trigonal symmetry the total CF potential may be represented by

$$V_{D_{3d}} \quad AY_2^0 + BY_4^0 + C(Y_4^3 \quad Y_4^{-3}) \qquad 50)$$

for $d$ orbitals, where $A$, $B$, and $C$ are independent parameters. We may relate these parameters to features of structure and metal ion wavefunctions *via* the PC model. Instead of a potential parameterized by coefficients $A$, $B$, and $C$ as in expression (50), this only involves the final matrix elements parameterized by $Dq$, $Cp$ and $\theta$. $Dq$ and $Cp$ are fourth-and second order radial parameters which do not involve the angular distortion parameter $\theta$. Thus, the PC model separates distortion and radial parameters and allows a correlation with geometry of the complex ion.

Although it is inappropriate here to review the PC formalism developed by Gerloch and coworkers[8] it is instructive, however, to emphasize one aspect of their definitions, particularly $Dq$. Their definition of 10 $Dq$, which we use consistently throughout this paper, is identical, practically, with the $E_g - T_{2g}$ energy splitting, in octahedral symmetry. For our calculation we used for the cubic splitting 10 $Dq$ a value of 20 300 cm$^{-1}$ according to Hartmann and Schläfer.[10]

Initially, we do not know which value $Cp$ parameter might take but Gerloch and coworkers[8] suggested that $5\ Dq \geqslant Cp \geqslant 2Dq$. However, their detailed analysis did not yield unambiguous results. In our case it is likely that $Cp$ is at least greater than 4060 cm$^{-1}$ ($2Dq$) so we ought to include in our calculation a range of values for this parameter, from 4060 cm$^{-1}$ to 10150 cm$^{-1}$ ($5Dq$).

* I.e., using a basis set of orbitals restricted to the cubic $^2T_{2g}$ and $^2E_g$ states.[15]

[15] C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962, p. 68.

Using a PC—CF model, as developed by Gerloch and coworkers[8], energy levels were calculated as functions of $Cp \geqslant 4060$ cm$^{-1}$ and θ (and $Dq = 2030$ cm$^{-1}$).* Some typical results are shown in Figure 3. Analogous to the iron (II) case the behaviour of CF splittings for trigonal Ti (III) systems varies markedly with the magnitude of $Cp$. We observed that regardless of the magnitude of $Cp$ coefficient a lowest-lying $A_{1g}$ term is associated with a compressed octahedron ($\theta > 54.75°$), similarly a lowest-lying $E_g$ term with an elongated octahedral system ($\theta < 54.75°$). Since our

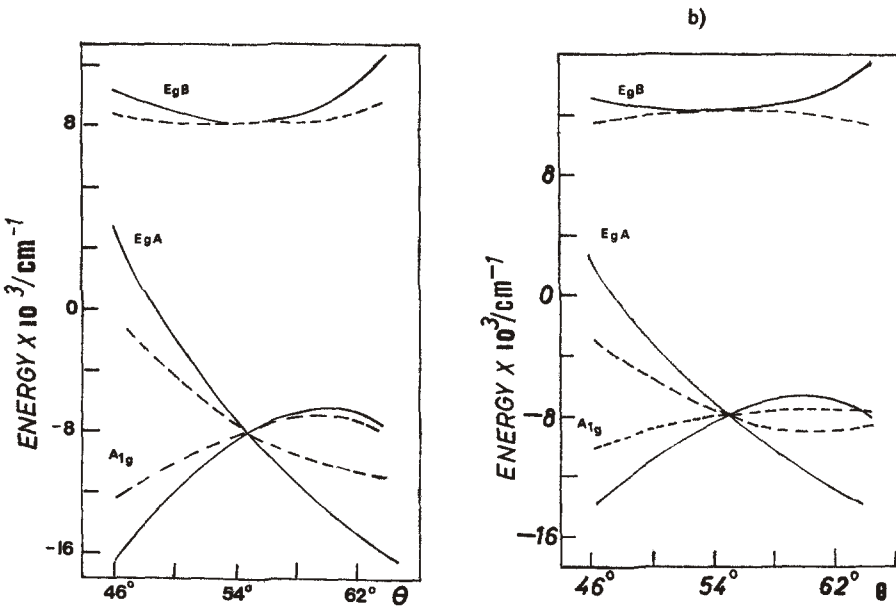


Fig. 3. — Energy levels in trigonal symmetry: $Cp$ values are: a) ——— 10150 cm$^{-1}$; – – – 6090 cm$^{-1}$; and (b) ——— 8120 cm$^{-1}$; – – – 4060 cm$^{-1}$.

experimental $g$-values are only consistent with an $A_{1g}$ ground state we conclude that the octahedron of the $Ti(H_2O)_6^{3+}$ complex ion in frozen aqueous solutions is trigonally compressed!

Moreover, for a compressed octahedron the ground-term splitting $\Delta E(A_{1g} \rightarrow E_gA) < 1540$ cm$^{-1}$ ($10\lambda_M$) either for $Cp = 2Dq$ throughout angular range (Figure 3b) or for $\theta \leqslant$ ca. 56° regardless that $Cp$ may be as high as $5Dq$ (Figure 3a). We note here that our calculation of the splitting $^2T_{2g}$ cubic-field ground term showed that when $Cp \sim Dq$ an $E_g$ ground term persists throughout the angular range irrespective of the sense of distortion. These facts confirm our initial assumption that $Cp \geqslant 2Dq$. On the other hand, since we supposed that the ground-term splitting $\Delta E(A_{1g} \rightarrow E_gA) > 1540$ cm$^{1-}$ ($10\lambda_M$) in the $Ti(H_2O)_6^{3+}$ complex ion in frozen aqueous solutions, we shall consider in our $g_\perp$ — calculation only the cases where this requirement is fulfilled.

*In this calculation we have assumed that there are equal and constant bond lengths.

Perhaps the most important point in our treatment of the $g_\perp$-values of the octahedral $d^1$ systems with a relatively strong trigonal distortion is the inclusion of the higher $E_g$ into the lower $E_g$ wavefunctions *via* trigonal field mixing. The coefficient $a$ may be used as an indicator for the character of the lower $E_g$ functions.

Simple perturbation theory suggests that the mixing coefficient $m$ is given by

$$e_g = t_{2g}^{\pm} - m e_g^{\pm} \tag{51}$$

where

$$t_{2g}^{+} = \frac{\sqrt{2}}{3} d_2 - \frac{\sqrt{1}}{3} d_{-1} \tag{52}$$

$$t_{2g}^{-} = \frac{\sqrt{2}}{3} d_{-2} + \frac{\sqrt{1}}{3} d_1 \tag{53}$$

$$e_g^{+} = \frac{\sqrt{1}}{3} d_2 + \frac{\sqrt{2}}{3} d_{-1} \tag{54}$$

$$e_g^{-} = \frac{\sqrt{1}}{3} d_{-2} - \frac{\sqrt{2}}{3} d_1 \tag{55}$$

are cubic-field quantized basis eigenfunctions[15]; and, $m$ is

$$m = \frac{\langle t_{2g}^{\pm} | V_{D3d} | e_g^{\pm} \rangle}{\Delta E(t_{2g}^{\pm} \rightarrow e_g^{\pm})} \tag{56}$$

Figure 4 shows $a^2$ plotted as a function of $\theta$ for various $Cp$ values ($Cp \geqslant 3090$ cm$^{-1}$). Analogous to the iron (II) case, all curves intersect at $\theta_{oct}$ when $a^2 = \frac{\sqrt{2}}{3}$ (cf. cubic quantized basis eigenfunctions given by expressions (52) — (55)) as a result of the orthogonality of $E_g$ and $T_{2g}$ in ideal octahedral symmetry. Note that when $Cp$ is $5Dq$, a compression of the octahedron by 5° causes $a^2$ to decrease by ca. 55% and $b^2$ (calculated using the orthonormality condition $a^2 + b^2 = 1$) to increase by ca. 52%! Such a change in geometry, of course, would cause the same changes in the contributions to the $g_\perp$-value of the first (quadratic in $b$) and the second (quadratic in $a$) terms in expression (49). However, it should be noted that the first term is several times greater than the second term, since $\Delta E(A_{1g} \rightarrow E_g B) > \Delta E(A_{1g} \rightarrow E_g A)$ (Figure 3) and its contribution

dominates the $g$-anisotropy. Consequently, a calculation of the energy levels (usually the $\Delta E(A_{1g} \rightarrow E_g A)$ transition) from experimental $g_\perp$-values based on the CF expression (30) would be, of course, irreconcilable with the optical or other data (magnetic relaxation, etc.). It has been customary to rationalize such discrepancies by introducing covalent bonding. This generally is done with Stevens'[16] orbital reduction factors * in the sense that it is possible to fit any ESR results without difficulty but not uniquely as the following idealized treatment shows.

The theoretical behaviour of $g_\perp$ values ** for the $Ti(H_2O)^{3+}$ complex ion as functions of $\theta$ ($\geqslant 56°$) for three representative values of $Cp$ ($\geqslant 3Dq$), is shown in Figure 5. The $g_\perp$ values are clearly dependent on $Cp$. Notice

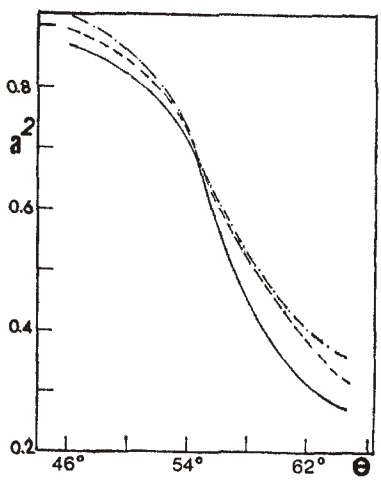


Fig. 4. — Angular variation of the coefficient $a^2$:

$Cp$ values are: —— 10150 cm$^{-1}$; - - - 8120 cm$^{-1}$; and —.—.—. 6090 cm$^{1}$.

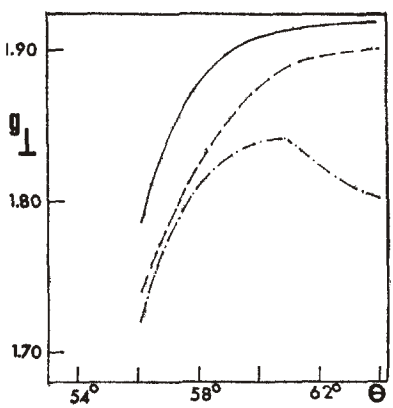


Fig. 5. — Angular variation of the $g_\perp$:

$Cp$ values are: —— 10150 cm$^{-1}$; - - - 8120 cm$^{-1}$; and —.—. 6090 cm$^{-1}$.

particularly, for ca. $56° \leqslant \theta \leqslant 60°$ $g_\perp$ values vary rapidly. For example, with $Cp = 5Dq$, $g_\perp$, value increases from ca. 1.79 to ca. 1.91 as $\theta$ increases by only 4° from $\theta = 56°$. It is just this behaviour which is considered responsible for the $g$-anisotropy. Thus $g_\perp$ in this system can be significantly affected by small angular distortions, provided $Cp$ is a large quan-

[16] For a discussion of the significance of orbital reduction parameters in metal complexes see Ref. 13d.

* In our case, the orbital reduction factors are: $k_1 = \sqrt{f_1} \cdot \alpha_1^*$ and $k_2 = \sqrt{f_2}\,\alpha_1^*$.

** These are calculated using the expression (49).

tity. Assuming that the octahedron may only be *slightly* compressed, say $\theta - \theta_{oct} \leqslant 5°$, then it can be seen (Figure 5) that only $Cp = 5Dq$ may be compatible with experimental $g_\perp$ value of 1.89.[12] If the value is as large as 10150 $cm^{-1}$ (i.e. $5Dq$) then the effective distortion angle $\theta$ can be as low as ca. 58.5° and the ground term splitting can be as high as ca. 5000 $cm^{-1}$ (Figure 3b).

Gerloch and coworkers,[8] using the appropriate PC definitions, predicted, on the basis of the theoretical calculations of Ballhausen[17] and of Ballhausen and Acomon,[18] that $Cp \approx 5Dq$. In the light of this prediction and the findings in the present work a high value of $Cp$ seems reasonable. Moreover, observation of the relatively sharp ESR spectra of the randomly oriented samples of the $Ti(H_2O)^{3+}$ complex ion in frozen aqueous solutions at 77 K would, also, indicate an excited state of a few thousand cm above the ground state.[12]

In spite of the unpaired electron that is present, no ESR signal is observed for the $Ti(H_2O)_6^{3+}$ complex ions in acidic aqueous solutions at room temperature. Such an observation is fully consistent with the octahedral CF symmetry of the ion. In the orbitally degenerate ground state, $^2T_{2g}$, the spin angular momentum is cancelled by the residual orbital angular momentum, leading to the expectation that $g \approx 0$.[19] Although small distortion (for instance, as a result of the Jahn-Teller effect) can partially "quench" the orbital angular momentum, spin-lattice relaxation time is too short providing extremely broad resonance line. However, in the frozen solution (77 K), the crystal package forces (or similar effects) may cause a small departure from the regular (or nearly regular) octahedral symmetry in trigonal system* so that the $Ti(H_2O)_6^{3+}$ species will have now a well-separated orbital singlet leading to the requisite long spin-lattice relaxation time for the observation of the spectrum. Clearly, then we are not dealing with a hypothetical temperature dependent process of the $Ti(H_2O_6)^{3+}$ complex ion that would render its spectrum observable at 77 K!

The variations of the energy levels (Figure 3), the coefficients $a^2$ (Figure 4) and the $g_\perp$ values (Figure 5) are shown for the $Ti(H_2O)_6^{3+}$ complex ion assuming that $\alpha_1^* \sim 1$, $f_1 = f_2 \sim 1$, and $C \sim O$; the departures from these conditions likely to be found in this complex ion would not change the overall patterns of the graphs and the qualitative and quantitative analyses must be similar.

[17] C. J. Ballhausen, *Mat. Fys. Medd. Dan. Vid. Selsk.*, **29**, 4 (1954).

[18] C. J. Ballhausen and E. M. Acomon, *Mat. Fys. Medd. Dan. Vid. Selsk.*, **31**, 2 (1958).

[19] A. Carington and A. D. McLachland, "Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics", Harper and Row, New York, 1967, Chapt.10.

* This point emphasizes the danger of a ready comparison of data involving the complex ions in the same solutions in liquid and frozen states.

## APPENDIX A

*Table A.1*

**Functions obtained by the operation of the $\hat{l}\cdot\hat{s}$ operator on relevant atomic orbitals**

| | $\|x^2-y^2,+\rangle$ | $\|xy,+\rangle$ | $\|yz,+\rangle$ | $\|xz,+\rangle$ | $\|z^2,+\rangle$ | $\|x^2-y^2,-\rangle$ | $\|xy,-\rangle$ | $\|yz,-\rangle$ | $\|xz,-\rangle$ | $\|z^2,-\rangle$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\langle x^2-y^2,+\|$ | 0 | $-i$ | 0 | 0 | 0 | 0 | 0 | $+1/2$ | $+1/2$ | 0 |
| $\langle xy,+\|$ | $+i$ | 0 | 0 | 0 | 0 | 0 | 0 | $+1/2$ | $-1/2$ | 0 |
| $\langle yz,+\|$ | 0 | 0 | 0 | $i/2$ | 0 | $-1/2$ | $-1/2$ | 0 | 0 | $-i\sqrt{3}/2$ |
| $\langle xz,+\|$ | 0 | 0 | $-i/2$ | 0 | 0 | $-1/2$ | $+i/2$ | 0 | 0 | $+\sqrt{3}/2$ |
| $\langle z^2,+\|$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $+i\sqrt{3}/2$ | $-\sqrt{3}/2$ | 0 |
| $\langle x^2-y^2,-\|$ | 0 | 0 | $+i/2$ | $-1/2$ | 0 | 0 | $+i$ | 0 | 0 | 0 |
| $\langle xy,-\|$ | 0 | 0 | $-1/2$ | $-i/2$ | 0 | $-i$ | 0 | 0 | 0 | 0 |
| $\langle xz,-\|$ | $-i/2$ | $+i/2$ | 0 | 0 | $-i\sqrt{3}/2$ | 0 | 0 | 0 | $-i/2$ | 0 |
| $\langle xz,-\|$ | $+1/2$ | $+i/2$ | 0 | 0 | $-\sqrt{3}/2$ | 0 | 0 | $+i/2$ | 0 | 0 |
| $\langle z^2,-\|$ | 0 | 0 | $+i\sqrt{3/2}$ | $+\sqrt{3}/2$ | 0 | 0 | 0 | 0 | 0 | 0 |

*Table A.2*

**Functions obtained by the operation of $\hat{l}_x$ on relevant atomic orbitals**

| $\|d_{x^2-y^2}\rangle$ | $\|d_{xy}\rangle$ | $\|d_{yz}\rangle$ | $\|d_{xz}\rangle$ | $\|d_{z^2}\rangle$ |
|---|---|---|---|---|
| $\hat{l}_x - i\|d_{yz}\rangle$ | $i\|d_{xz}\rangle$ | $i[\|d_{x^2-y^2}\rangle + \|d_{z^2}\rangle]$ | $i\|d_{xy}\rangle$ | $-i\sqrt{3}\|d_{yz}\rangle$ |

## APPENDIX B

We wish to find the effect of applying a magnetic field upon the doubly degenerate ground state of $d^1$ in a trigonal field of $D_{3d}$, $D_3$ and $C_{3v}$ symmetries. The perturbation operator for this is given by

$$H_{\text{Zeeman}} = \beta_e(\hat{l} + 2.0023)\cdot\vec{H} = \beta_e\,(\hat{l}_z + 2.0023\,\hat{s}_z)H_z +$$

$$+\frac{1}{2}\,\beta_e\,[(\hat{l}_+ + 2.0023\,\hat{s}_+)\,H_- + (\hat{l}_- + 2.0023\,\hat{s}_-)\,H_+] \qquad \text{(B1)}$$

where $\beta_e$ is so called the Bohr magneton; $\hat{l}_\pm = \hat{l}_x \pm i\hat{l}_y$ and $\hat{s}_\pm = \hat{s}_x \pm i\hat{s}_y$ are the appropriate 'ladder' operators; and $H_\pm = H_x \pm iH_y$.

Since $H_{\text{Zeeman}}$ is much smaller than either $\Delta E(A_{1g} \to E_gA)$ or $\lambda_M$ we can regard it as a perturbation operator acting on the two degenerate wavefunctions $a_{1g}^+$ and $a_{1g}^-$ whose matrix in the basis of wavefunctions (21) and (22) is as it is given by (B2)

$$
\begin{array}{l|l}
a_{1g}^{+} & a_{1g}^{-} \\
\begin{array}{l}
< A_{1g}^{+} - \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\Delta E\,(A_{1g}\to E_gA)}\,(b_1E_g^{-}\,1A + ib_2E_g^{-}\,2A) + \\
+ \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gB)}\,(a_3E_g^{-}\,1B + ia_4E_g^{-}\,2B)\,| \\
\mathrm{H_{Zeeman}}\,\Big|\,A_{1g}^{+} - \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gA)}\,(b_1E_g^{-}\,1A - ib_2\,E_g^{-}\,2A) + \\
+ \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gB)}\,(a_3\,E_g^{-}\,1B - ia_4\,E_g^{-}\,2\,B) > -E \\
\\
< A_{1g}^{-} + \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gA)}\,(b_1E_g^{+}\,1A - ib_2E_g^{+}\,2A) - \\
- \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gB)}\,(a_3E_g^{+}\,1B - ia_4E_g^{+}\,2B)\,| \\
\mathrm{H_{Zeeman}}\,|\,A_{1g}^{+} - \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gA)}\,(b_1\,E_g^{-}\,1A - ib_2\,E_g^{-}\,2A) + \\
+ \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gB)}\,(a_3\,E_g^{-}\,1B - ia_4\,E_g^{-}\,2\,B) >
\end{array}
&
\begin{array}{l}
< A_{1g}^{+} - \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\Delta\,E(A_{1g}\to E_gA)}\,(b_1\,E_g^{-}\,1A + ib_2E_g^{-}\,2A) + \\
+ \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\Delta\,E(A_{1g}\to E_gB)}\,(a_3\,E_g^{-}\,1B + ia_4\,E_g^{-}\,2B)\,| \\
\mathrm{H_{Zeeman}}\,|\,A_{1g}^{-} + \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\,\Delta E(A_{1g}\to E_gA)}\,(b_1E_g^{+}\,1A + ib_2\,E_g^{+}\,2A) - \\
- \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\Delta E(A_{1g}\to E_gB)}\,(a_3\,E_g^{+}\,1\,B + ia_4\,E_g^{+}\,2\,B) > \\
\\
< A_{1g}^{-} + \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\Delta E(A_{1g}\to E_gA)}\,(b_1\,E_g^{+}\,1A - ib_2\,E_g^{+}\,2\,A) + \\
+ \dfrac{\sqrt{3}\,\alpha_1^{*}\,\lambda_M}{2\Delta E(A_{1g}\to E_gB)}\,(a_3\,E_g^{+}\,1B - ia_4\,E^{+}\,2B)\,| \\
\mathrm{H_{Zeeman}}\,\Big|\,A_{1g}^{-} + \dfrac{\sqrt{3}\alpha_1^{*}\lambda_M}{2\,\Delta\,E(A_{1g}\to E_gA)}\,(b_1E_g^{+}1\,A + ib_2E_g^{+}2\,A) - \\
- \dfrac{\sqrt{3}\alpha_1^{*}\lambda_M}{2\,\Delta\,E(A_{1g}\to E_gB)}\,(a_3E_g^{+}1B - ia_4E_g^{+}2B) > -E
\end{array}
\end{array}
\qquad \text{(B2)}
$$

This matrix is diagonal when the applied external magnetic field is along the $z$ axis ($H_x = H_y = 0$). The matrix elements are given by

$$\langle a_{1g}^{+} | H_{\text{Zeeman}} | a_{1g}^{+} \rangle - E = \frac{1}{2} \cdot 2.0023 \ \beta_e H_z - E \tag{B3}$$

$$\langle a_{1g}^{-} | H_{\text{Zeeman}} | a_{1g}^{+} = 0 \tag{B4}$$

$$\langle a_{1g}^{+} | H_{\text{Zeeman}} | a_{1g}^{-} \rangle = 0 \tag{B5}$$

$$\langle a_{1g}^{-} | H_{\text{Zeeman}} | a_{1g}^{-} \rangle = -\frac{1}{2} \cdot 2.0023 \ \beta_e H_z - E \tag{B6}$$

The difference in energy of the eigenstates is then

$$\Delta E_z (= \Delta E_{\parallel}) = 2.0023 \ \beta_e H_z \tag{B7}$$

However, when the external magnetic field is along the $x$ (or $y$) axis the matrix (B2) is non-diagonal, and the matrix elements are given by

$$\langle a_{1g}^{+} | H_{\text{Zeeman}} | a_{1g}^{+} \rangle - E = -E \tag{B8}$$

$$\langle a_{1g}^{-} | H_{\text{Zeeman}} | a_{1g}^{+} \rangle = \left[ \frac{\sqrt{3} \ \alpha_1^* \lambda_M}{\Delta E(A_{1g} \to E_g A)} (b_1 \langle e_g 1A | \hat{l}_x | a_{1g} \rangle - \right.$$

$$- i b_2 \langle e_g 2A | \hat{l}_x | a_{1g} \rangle) - \frac{\sqrt{3} \ \alpha_1^* \lambda_M}{\Delta E(A_{1g} \to E_g B)} (a_3 \langle e_g 1B | \hat{l}_x | a_{1g} \rangle - \tag{B9}$$

$$\left. - i a_4 \langle e_g 2B | \hat{l}_x | a_{1g} \rangle) \right] \beta_e H_x + \frac{1}{2} \cdot 2.0023 \ \beta_e H_x$$

$$\langle a_{1g}^{+} | H_{\text{Zeeman}} | a_{1g}^{-} \rangle = \left[ \frac{-\sqrt{3} \ \alpha_1^* \lambda_M}{\Delta E(A_{1g} \to E_g A)} (b_1 \langle e_g 1A | \hat{l}_x | a_{1g} \rangle + \right.$$

$$+ i b_2 \langle e_g 2A | \hat{l}_x | A_{1g} \rangle) + \frac{\sqrt{3} \ \alpha_1^* \lambda_M}{\Delta E(A_{1g} \to E_g B)} (\langle a_3 \langle e_g 1B | l_x | a_{1g} \rangle + \tag{B10}$$

$$\left. + i a_4 \langle e_g 2B | \hat{l}_x | a_{1g} \rangle) \right] \beta_e H_x + \frac{1}{2} \cdot 2.0023 \ \beta_e H_x$$

$$\langle a_{1g}^{-} | H_{\text{Zeeman}} | a_{1g}^{-} \rangle - E = -E \tag{B11}$$

Solution of the matrix (B2) for this direction gives the energy splitting

$$\Delta E_x (= \Delta E_{\perp}) = -2\sqrt{3} i \ \alpha_1^* \lambda_M \left[ \frac{b_2 \langle e_g 2A | \hat{l}_x | a_{1g} \rangle}{\Delta E(A_{1g} \to E_g)} - \frac{a_4 \langle e_g 2B | \hat{l}_x | a_{1g} \rangle}{\Delta E(A_{1g} \to E_g} \right]$$

$$\beta_e H_x + 2.0023 \ \beta_e H_x \tag{B12}$$

Note that terms quadratic in $\lambda_M$ had been neglected since $\Delta E(A_{1g} \leftrightarrow E_g A)$, $\Delta E\,(A_{1g} \rightarrow E_g B) > \lambda_M$.

If we define $g_{||} = (g_z)$ and $g_\perp$ $(= g_x = g_y)$ as

$$g_{||} = \frac{\Delta E_z}{\beta_e H_z} \tag{B13}$$

$$g_\perp = \frac{\Delta E_x}{\beta_e H_x}$$

we end up with

$$g_{||} = 2.0023$$

$$g_\perp = 2.0023 - 2\sqrt{3}\mathrm{i}\alpha_1^* \lambda_M \left[ \frac{b_2 \langle e_g 2A | \hat{l}_x | a_{1g} \rangle}{\Delta E(A_{1g} \rightarrow E_g A)} \quad \frac{a_4 \langle e_g 2B | \hat{l}_x | a_{1g} \rangle}{\Delta E A(_{1g} \rightarrow E_g B)} \right]$$

We observe that the symmetry of the ligand field determines the axial symmetry of the $g$-tensor and, of course, the directions of its principal components. Moreover, since $\lambda_M$, $\Delta E(A_{1g} \rightarrow E_g A)$ and $\Delta E(A_{1g} \rightarrow E_g B)$ are positive, the $g_\perp$ principal component, of course, is less than the free electron value, 2.0023.

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