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ABSTRACT

To date no satisfactory agreement has been obtained between theory and experiment for $4f \rightarrow 4f$ transitions for Tm (IV) ($4f^{12}$). It is clear from the considerations that have appeared so far in the literature that intermediate coupling is important in the case of Tm (IV). We have taken the pure electrostatic equations as given by Condon and Shortley and have evaluated them as a constant times $F_2$. The ratios $F_4/F_2$ and $F_6/F_2$ used were in agreement with those given by Elliott, Judd, and Runciman. Crystal field interaction was also considered. After the electrostatic levels were put into the secular equations for Tm (IV), each term in the equations was divided by $F_2$ and the variable $X = + \frac{5}{F_2}$ introduced. Our experimental data give an excellent fit to a plot of $E/F_2$ vs $X$ for $X = 3$ and $F_2 = 450$ cm$^{-1}$. From such an approach one obtains $\delta = 1350$ cm$^{-1}$. The polarization and Zeeman data of Johnsen are in complete agreement with this treatment.
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INTRODUCTION

Experimental investigations together with the theoretical considerations of Van Vleck and Bethe indicate that the sharp absorption lines of the rare earth ions in the visible and near infrared spectra are due to \(4f \rightarrow 4f\) transitions. The case of Tm IV (Tm\(^{3+}\) ion) should yield to complete theoretical treatment, since it is the relatively simple problem of 12 \(f\) electrons. To date there have been many papers dealing with the absorption spectrum of Tm IV. Spedding has made the intermediate field calculations for Tm IV using the ratios of \(F_{4}/F_{2}\) and \(F_{6}/F_{2}\) as derived from La II. The disagreement between Spedding's calculated and observed values averages about 1500 cm\(^{-1}\). Jørgensen, who has made similar calculations, disagrees with Spedding on the assignments of the \(3F_{2}, 1I_{6}\), and \(3P_{2}\) levels. It would seem reasonable that better agreement should exist, particularly since very good agreement between theory and experiment has been obtained for Pr IV. This paper is the first in a series in which we intend to describe the absorption and fluorescence spectra of Tm IV and to present a theoretical interpretation of these results.

A. GENERAL

The electronic configuration of Tm IV in the ground state is sometimes written as [Xe Core] \(4f^{12}\) where there are essentially two "holes" in the \(4f\) shell. It is easily seen that Tm IV spectroscopically is quite similar to Pr IV which has only two electrons in the \(4f\) shell. According to the Pauli equivalence theorem, both ions should have the same number of electronic states. The only difference, as described by Hund's rules, would be that the multiplets are inverted. The calculations for pure electrostatic interactions for Tm IV (\(f^{12}\)) are the same as for Pr IV (\(f^{2}\)), but the secular equations will differ by a change in sign in front of each \(\xi\), the spin-orbit interaction function.
The Hamiltonian for Tm IV must include terms which represent the magnetic interactions of the electronic orbits and spins, and terms which represent the Coulomb repulsion of the two "holes." Since we shall be considering Tm IV in the solid state either as a pure single crystal of TmCl$_3$, or the ethyl-sulfate, or diluted in some matrix, it will be necessary to add a perturbation which essentially describes the interaction of the internal crystal field with the Tm IV electrons. We may write the Hamiltonian as

$$H = \sum_{i=1}^{N} \left[ \frac{1}{2m} \sum_{i}^{N} \frac{\kappa^{2}}{r_{i}^{2}} - Ze^{2}/r_{i} + \xi \left( r_{i} \right) \left( \hat{L}_{i} \cdot \hat{S}_{i} \right) \right] + \sum_{i>j=1}^{N} \frac{e^{2}}{r_{ij}} + K \quad (1)$$

The subscripts 1, 2 \ldots N distinguish the number of different electrons or "holes", $r_{i}$ is the distance of the ith electron from the nucleus, $r_{ij}$ is the mutual distance of the ith and jth electrons, and $K$ is the crystal field potential which is experienced by the $4f$ electrons when Tm IV is placed in a solid matrix.

An approximate allowance for the spin-orbit interaction is made by including for each electron a term of the form $\xi \left( r_{i} \right) \hat{L}_{i} \cdot \hat{S}_{i}$ which describes the magnetic interactions of the electronic orbits and spins. It is found that terms expressing the mutual repulsion of electrons prevent the separation of variables. These terms cannot be considered as small and therefore treated by perturbation theory, because on summation their total effect is comparable with the interaction between the electrons and the nucleus. The usual calculation, however, is based on the idea of screening, according to which the greatest part of the mutual repulsion terms are taken into account in the approximate solution upon which a perturbation-theory treatment is based.

Let us now rewrite Eq. (1) as

$$H = H_{0} + K, \quad (2)$$

where $H_{0}$ is the Hamiltonian for the free atom and $K$ is the perturbation due to the crystal field. Here $H_{0}$ is invariant to all rotations of the coordinate system in which the origin at Tm IV remains the same, to an inversion through the origin, and to reflections in all planes through the origin. The perturbation $K$, and therefore $H$, is invariant only to the finite number of rotations and reflections contained in the point symmetry of the atom in the crystal lattice. Let us write for the free atom

$$H_{0} \psi_{JM} = H_{J} \psi_{JM} \quad (3)$$
where only states with \( M = J, J-1, \ldots -J \) belong to the same eigenvalue \( W_J \). Then the crystal states \( \Phi_1 \) in

\[
H \Phi_1 = (H_0 + K) \Phi_1 = W_1 \Phi_1
\]

are linear combinations of \( \Phi_1 = \sum J M \psi_{J M} a_{J M} \). According to Pauli the degenerate states belonging to a given eigenvalue, \( W \), transform linearly among each other under a coordinate transformation which leaves \( H \) invariant. Therefore, a state in the crystal belongs to a nondegenerate eigenvalue when it transforms into itself under all symmetry operations, except for a constant factor which may be taken as unity for reasons of normalization. K. H. Hellwege elaborates on this by saying that a state in the crystal belongs to a doubly-degenerate eigenvalue when there exists a second linearly independent state such that these two states transform into each other, etc.

The problem is to construct states \( \Phi_1 \) which go over into themselves under all operations of point symmetry. We follow the theoretical considerations of Hellwege by allowing the field about Tm IV in the solid to vanish but without changing the symmetry. Therefore \( \Phi_1 \) is reduced to a linear combination of only \( 2J + 1 \) degenerate levels belonging to the eigenvalue \( W_J \) of the free atom,

\[
\Phi_1 = \sum_{M} \psi_{M} a_{M} (J = \text{constant})
\]

A given level of the free Tm IV will be split into less than \( 2J + 1 \) components in the crystal. In order to see how the zeroth-order states consisting of \( \psi_{M} \) transforms in the crystal, one must determine the transformation properties of the \( \psi_{M} \)'s themselves. We shall discuss this for Tm IV in a later paper under the heading of crystal-field calculations.

We shall be interested only in the \( \hbar f \rightarrow \hbar f \) transitions. Direct dipole transitions within the \( \hbar f \) shell are forbidden as long as the \( \hbar f \) electrons are subject to an electric field symmetrical with respect to inversion at the Tm IV nucleus. However, forced electric-dipole transitions are possible when caused by a natural lack of symmetry of the crystalline field. Magnetic-dipole transitions are also possible, but the question of the multipolarity can be answered by a study of polarization spectra.
B. PURE ELECTROSTATIC INTERACTIONS

Following the coupling scheme of Russell and Saunders, we may couple two equivalent \( f \) electrons to obtain,

\[
1_s \ 3_p \ 1_d \ 3_f \ 1_g \ 3_h \ 1_i.
\]

To calculate an energy value for each of these levels, taking \( 3_H \) to be the ground state, we must expand that part of the Hamiltonian in which \( \Sigma e^{2/r_{ij}} \) appeared. Of the nonvanishing elements \( H_{AB} \), only certain of the diagonal ones need to be evaluated in order to calculate the energy levels.

For the L-S representation, all the nondiagonal elements are zero. For an \( \Sigma^2 \) system with the two "holes" having parallel spin, we have

\[
H_{AB} = \int \overline{u}_A (i) \overline{u}_B (j) [\ell^2/r_{ij}] u_A (i) u_B (j) \, d\tau_i \, d\tau_j. \tag{7}
\]

The orthogonality of the \( u \)'s restricts the permutation \( P \) in Eq. (7) to \( P = 1 \) and \( P = (ij) \), the identity operation and the interchange of \( i \) and \( j \) respectively.\(^{15}\)

The first choice of \( P \) will contribute the terms

\[
\Sigma_{i,j>1} \int \overline{u}_A (i) \overline{u}_B (j) [\ell^2/r_{ij}] u_A (i) u_B (j) \, d\tau_i \, d\tau_j = \Sigma_{i,j>1} J_{ij}, \tag{8}
\]

while the second yields

\[
-\Sigma_{i,j>1} \int \overline{u}_A (i) \overline{u}_B (j) [\ell^2/r_{ij}] u_A (i) u_B (j) \, d\tau_i \, d\tau_j = -\Sigma_{i,j>1} K_{ij}. \tag{9}
\]

The integral \( K_{ij} \) vanishes unless the spins of \( u_A (i) \) and \( u_B (j) \) are parallel. The functions \( J_{ij} \) and \( K_{ij} \) may be evaluated by the use of the expansion for \( 1/r_{ij} \),

\[
1/r_{ij} = \Sigma \frac{(k-m)(k+m)}{(k+|m|)} \left[ \frac{r_a^{k}}{r_b^{k+1}} \right] P_k (\cos \theta_i) P_k (\cos \theta_j) e^{im(\varphi_i - \varphi_j)}. \tag{10}
\]

Here \( P_k (\cos \theta) \) is an associated Legendre function; \( r_a \) is the smaller of \( r_i \) and \( r_j \), and \( r_b \) is the greater, and \( k \) itself represents a series term in the expansion. For \( J_{ij} \) and \( \varphi_i \) part of the integral has the form

\[
\int_0^{2\pi} e^{im\varphi} \, d\varphi, \tag{11}
\]
which vanishes unless \( m = 0 \). We may rewrite \( J_{ij} \) as,

\[
J_{ij} = \sum_{k} a^{k}(\ell m; \ell' m') F^{k}(n\ell; n'\ell'), \tag{12}
\]

where

\[
a^{k}(\ell m; \ell' m') = \frac{(2\ell+1)(\ell - |m|)!}{2(\ell + |m|)!} \frac{(2\ell'+1)(\ell' - |m'|)!}{2(\ell' + |m'|)!}, \tag{13}
\]

\[
\int_0^\pi \left| m \right| P_{\ell}^{m} \left( \cos \theta_{i} \right)^{2} P_{\ell'}^{m} \left( \cos \theta_{i} \right) \sin \theta_{i} \sin \theta_{j} \sin \theta_{j} \sin \theta_{j} \ dx_{i} \sin \theta_{i} \sin \theta_{j} \sin \theta_{j} \sin \theta_{j} \ dx_{j}, \tag{14}
\]

\[
F^{k}(n\ell; n'\ell') = 4^{2} \int_{0}^{\infty} \int_{0}^{\infty} R_{n\ell}^{2} \left( r_{i} \right) R_{n'\ell'}^{2} \left( r_{j} \right) [x_{a}/r_{b}^{k+1}] r_{i}^{2} r_{j}^{2} dr_{i} dr_{j}. \tag{15}
\]

One may obtain the values for the \( a^{k} \)'s from the angular parts of the wave functions, which are the same as for the hydrogen atom. To avoid the occurrence of fractional coefficients for the \( F \)'s in evaluation \( J_{ij} \), we define \( F_{k} = F^{k}/D_{k} \) where \( D_{k} \) is the denominator given by Condon and Shortley.\(^{16}\)

The results of such calculations give us the formulae for \( \ell^{2} = \ell_{12}^{2} \) which appear in Table I.

In order to calculate the electrostatic energy levels, it is necessary to consider what radial-wave equations should be put into the Slater integrals, \( F_{k} \). There is no reason to expect that the HF hydrogenic wave functions will describe very satisfactorily the \( \ell \) electrons in the Tm ion. A self-consistent field approximation would be necessary in order to obtain better radial functions. However, the ratio of \( F_{k} \) integrals is reasonably insensitive to the choice of the actual radial distribution function. One of the members of our group (John D. Axe) has calculated \( F_{4}/F_{2} \) and \( F_{6}/F_{2} \) ratios for the unlikely "squares" radial distribution of \( \ell \) electrons and has obtained values which are not far from those obtained by Elliott, Judd, and Runciman\(^{17}\) for hydrogenic distribution.
We have calculated the ratios, $F_1/F_2$ and $F_3/F_2$, using hydrogenic wave functions by straight integration methods (see Appendix) and have obtained values identical with those of Judd. When the electrostatic equations in terms of $F_2$ were normalized to $^3\text{H}$ as the ground state, the results were found to be in complete agreement with those obtained by Elliott, Judd, and Runciman.
<table>
<thead>
<tr>
<th>Level</th>
<th>Electrostatic equations in terms of Slater integrals</th>
<th>Electrostatic equations in terms of $F_2$ (a)</th>
<th>Energy levels normalized to $3^3_H = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3^3_H$</td>
<td>$F_0 - 25F_2 - 51F_4 - 13F_6$</td>
<td>$F_0 - 32.3F_2$</td>
<td>0.00 $F_2$</td>
</tr>
<tr>
<td>$3^3_F$</td>
<td>$F_0 - 10F_2 - 33F_4 - 286F_6$</td>
<td>$F_0 - 18.9F_2$</td>
<td>13.4 $F_2$</td>
</tr>
<tr>
<td>$1^1_G$</td>
<td>$F_0 - 30F_2 + 97F_4 + 78F_6$</td>
<td>$F_0 - 15.5F_2$</td>
<td>16.8 $F_2$</td>
</tr>
<tr>
<td>$1^1_D$</td>
<td>$F_0 + 19F_2 - 99F_4 + 715F_6$</td>
<td>$F_0 + 16.3F_2$</td>
<td>43.4 $F_2$</td>
</tr>
<tr>
<td>$1^1_I$</td>
<td>$F_0 + 25F_2 + 9F_4 + F_6$</td>
<td>$F_0 + 26.3F_2$</td>
<td>58.6 $F_2$</td>
</tr>
<tr>
<td>$3^3_P$</td>
<td>$F_0 + 45F_2 + 33F_4 - 1287F_6$</td>
<td>$F_0 + 30.3F_2$</td>
<td>62.6 $F_2$</td>
</tr>
<tr>
<td>$1^1_S$</td>
<td>$F_0 + 69F_2 + 193F_4 + 1716F_6$</td>
<td>$F_0 + 113.2F_2$</td>
<td>145.5 $F_2$</td>
</tr>
</tbody>
</table>

(a) $F_4 = 0.138 F_2$, and $F_6 = 0.0151 F_2$. 

Table I

Pure Electrostatic Energy Levels - $1^{12}$ Configuration
C. SPIN-ORBIT INTERACTION AND SECULAR EQUATIONS

It has been found for many of the +3 rare earth ions that intermediate coupling is important. Qualitatively the L-S coupling scheme may predict the proper order of levels from the ground state in some cases where one is not too far out into intermediate coupling. In the case of Tm IV certain levels such as \( ^1G_{4}\) and \( ^3F_2 \) are greatly affected by other levels of the same \( J \) value. In the crystal lattice, levels having the same crystal quantum numbers of levels related to one another by crystal quantum selection rules will also be affected to a smaller extent. It is therefore necessary to introduce the spin-orbit interaction term (\( i \)) into the secular equations. The addition of the crystal field interaction to the secular equations will be considered in a later paper.

Spedding has given the secular equations for \( F_2^6 \). For the \( F_2^{12} \) configuration one need only change the sign in front of each \( \xi \) value. Now let us divide each term and \( \xi \) value in these equations by \( F_2 \) and introduce the variable \( \chi = \xi / F_2 \). The results of such modification will give the following secular equations:
\begin{align*}
\text{For } J = 6 & \quad \begin{bmatrix}
1_{I_6} \\
1_{I_6} \\
3_{H_6}
\end{bmatrix} \\
& \begin{bmatrix}
\text{I/F}_2 & -\sqrt{6x} \\
-\sqrt{6x} & (\text{H/F}_2)-5x
\end{bmatrix}
\end{align*}

\begin{align*}
J = 5 & \quad \begin{bmatrix}
3_{I_6} \\
3_{I_6}
\end{bmatrix} \\
& \begin{bmatrix}
\text{I/F}_2 + x
\end{bmatrix}
\end{align*}

\begin{align*}
J = 4 & \quad \begin{bmatrix}
3_{I_4} \\
1_{O_4} \\
3_{F_4}
\end{bmatrix} \\
& \begin{bmatrix}
\text{I/F}_2 + 6x & \sqrt{40/3}x & 0 \\
\sqrt{40/3}x & (\text{O/F}_2) - \sqrt{44/3}x & 0 \\
0 & -\sqrt{44/3}x & (\text{F/F}_2)-3x
\end{bmatrix}
\end{align*}

\begin{align*}
J = 3 & \quad \begin{bmatrix}
3_{F_3} \\
\end{bmatrix} \\
& \begin{bmatrix}
\text{F/F}_2 + x
\end{bmatrix}
\end{align*}

\begin{align*}
J = 2 & \quad \begin{bmatrix}
3_{F_2} \\
1_{D_2} \\
3_{P_2}
\end{bmatrix} \\
& \begin{bmatrix}
\text{F/F}_2 + 4x & \sqrt{24}x & 0 \\
\sqrt{24}x & (\text{D/F}_2) - \sqrt{18}x & 0 \\
0 & -\sqrt{18}x & (\text{P/F}_2)-x
\end{bmatrix}
\end{align*}

\begin{align*}
J = 1 & \quad \begin{bmatrix}
3_{P_1} \\
\end{bmatrix} \\
& \begin{bmatrix}
\text{P/F}_2 + x
\end{bmatrix}
\end{align*}

\begin{align*}
J = 0 & \quad \begin{bmatrix}
3_{P_0} \\
1_{S_0}
\end{bmatrix} \\
& \begin{bmatrix}
\text{P/F}_2 + 2x & \sqrt{48}x \\
\sqrt{48}x & (\text{S/F}_2)
\end{bmatrix}
\end{align*}
The secular equations may be solved for $\text{energy}/F_2$ as a function of $X$. Since all equations were solved by hand except the three-by-three's, it is possible to give the following complete analytical expressions (see Table II).

The values for the three-by-three equations were obtained from an IBM-650 program. The results of the calculations appear in Figure 1.

D. PRELIMINARY COMPARISON OF THEORY WITH EXPERIMENT

Johnsen$^9$ has studied the polarization and Zeeman spectra of Tm IV in ethyl sulfate and has assigned values to the $^3F_2, ^3F_3, ^3F_4,$ and $^1G_4$ energy levels. If one divides his values by $F_2 = 450 \text{ cm}^{-1}$ and fits them to our curve at $X = 3$ as a preliminary fit, one obtains good agreement between experiment and theory.

Since $X = \xi/F_2$, we find that $\xi$ for this selection of parameters gives $1350 \text{ cm}^{-1}$. Table III lists Johnsen's values together with the solution data of Stewart.$^8$

We are at present making a complete experimental investigation of the spectra, using single crystals of the ethyl sulfate and pure chloride grown from the melt.

A posteriori evidence that crystal field interaction is small is given by the agreement between theory and experiment. Preliminary first-order perturbation calculations for levels $J = 1, 3,$ and 5 show that unsplit levels are shifted from the present values plotted on the order of $7 \text{ cm}^{-1}, 5 \text{ cm}^{-1},$ and $8 \text{ cm}^{-1}$ at $X = 3$. Such small perturbations therefore need not be added to the Hamiltonian since they represent shifts within the error of the calculations (3 significant figures). Crystal field splitting for levels $J = 1, 3,$ and 5 by the use of modified form of Judd's parameters for Pr$^{3+}$ gives a total splitting of $35 \text{ cm}^{-1}, 90 \text{ cm}^{-1},$ and $190 \text{ cm}^{-1}$, respectively. These results are by no means definitive, but they do represent first-order approximations. We hope in the future to give a more detailed consideration of crystal field splitting.

ACKNOWLEDGMENT

We wish to acknowledge the help of K. S. Pitzer, B. B. Cunningham, J. D. Axe, and R. D. McLaughlin. This work was done under the auspices of the U. S. Atomic Energy Commission.
Table II

Analytical Expressions for $E/F_2 = f(X)$

<table>
<thead>
<tr>
<th>Levels</th>
<th>$E/F_2 = f(X)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3H_5$</td>
<td>$x$</td>
</tr>
<tr>
<td>$^3P_3$</td>
<td>$13.4 + x$</td>
</tr>
<tr>
<td>$^3P_1$</td>
<td>$62.5 + x$</td>
</tr>
<tr>
<td>$^1S_0$</td>
<td>$104 + x + 1/2 \sqrt{196x^2} - 332x + 6824$</td>
</tr>
<tr>
<td>$^3P_0$</td>
<td>$104 + x - 1/2 \sqrt{196x^2} - 332x + 6824$</td>
</tr>
<tr>
<td>$^1I_6$</td>
<td>$29.3 - 2.5x + 1/2 \sqrt{49x^2} + 586x + 3440$</td>
</tr>
<tr>
<td>$^3H_6$</td>
<td>$29.3 - 2.5x - 1/2 \sqrt{49x^2} + 586x + 3440$</td>
</tr>
</tbody>
</table>
Table III

Comparison of Theory with Experiment

<table>
<thead>
<tr>
<th>Levels \</th>
<th>Theory</th>
<th>(\text{Johnsen}^9)</th>
<th>(\text{Stewart}^8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3_{H_6})</td>
<td>0.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(3_{H_4})</td>
<td>5,220</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(3_{H_5})</td>
<td>8,420</td>
<td>--</td>
<td>8,430</td>
</tr>
<tr>
<td>(3_{F_4})</td>
<td>12,630</td>
<td>12,700</td>
<td>12,800</td>
</tr>
<tr>
<td>(3_{F_3})</td>
<td>14,450</td>
<td>14,455</td>
<td>14,648</td>
</tr>
<tr>
<td>(3_{F_2})</td>
<td>14,900</td>
<td>15,080</td>
<td>15,170</td>
</tr>
<tr>
<td>(1_{G_4})</td>
<td>21,020</td>
<td>21,300</td>
<td>21,536</td>
</tr>
<tr>
<td>(1_{D_2})</td>
<td>27,990</td>
<td>--</td>
<td>28,042</td>
</tr>
<tr>
<td>(1_{I_6})</td>
<td>33,750</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(3_{P_0})</td>
<td>35,500</td>
<td>--</td>
<td>35,163</td>
</tr>
<tr>
<td>(3_{P_1})</td>
<td>36,540</td>
<td>--</td>
<td>36,552</td>
</tr>
<tr>
<td>(3_{P_2})</td>
<td>38,340</td>
<td>--</td>
<td>38,156</td>
</tr>
<tr>
<td>(1_{S_0})</td>
<td>74,930</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
APPENDIX: CALCULATION OF F_k INTEGRALS

(1) \[ F_k = \left( t^2 / K \right) \int R_1^2 \, R_2^2 \, \left( \frac{r^k}{r^{k+1}} \right) \, \frac{r^2}{r_1^2} \cdot \frac{r^2}{r_2^2} \, dr_1 \, dr_2. \]

(2) \[ F_2 = \int_0^\infty \int_0^\infty \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, r_1^2 \, r_2^2 \, dr_1 \, dr_2. \]

(3) \[ F_2 = \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1 + \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1. \]

(4) \[ F_2 = \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1 + \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1. \]

(5) We wish to put all electrostatic interaction terms in terms of \( F_2 \). Thus we need only the ratios \( F_4/F_2 \) and \( F_6/F_2 \).

(6) \[ \frac{F_4}{F_2} = \frac{\int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1 + \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1}{\int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1 + \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1}. \]

(7) \[ \frac{F_6}{F_2} = \frac{\int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1 + \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1}{\int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1 + \int_0^\infty \int_0^\infty \left[ \int_0^r \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, \frac{r_1^2}{r_2^2} \, \frac{r_2^2}{r_1^2} \, dr_2 \right] \, dr_1}. \]

(8) \[ \frac{F_4}{F_2} = 0.138 \quad \text{and} \quad \frac{F_6}{F_2} = 0.0151 \]
References

Fig. 1. Energy-level diagram for Tm IV in intermediate coupling.

The $^1S_0$ varies from 145.5 for $\chi = 0$ to 159.3 for $\chi = 5$. 
Fig. 1