A new contribution to spin-forbidden rare earth optical transition intensities: Analysis of all trivalent lanthanides

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We expand upon recent quantitative calculations which show that numerous parity- and spin-forbidden linear optical transitions observed in trivalent rare earth ions acquire a major fraction of their intensity from hitherto neglected contributions involving spin-orbit linkages within excited configurations. Extending our revised analysis of observed linear absorption intensities for Gd$^{3+}$ and Eu$^{3+}$ to the other nine trivalent lanthanides with visible wavelength transitions, we find that the new contributions are at least as important in these other lanthanides, and are often comparable to standard contributions. We also show that spin-forbidden $\Delta S = 1$ transitions are selectively modified over the spin-allowed $\Delta S = 0$ transitions. In addition, we examine contributions from linkages with $g$ orbital excited states in the light of recent electronic Raman scattering data for lanthanide phosphates, and show that these long neglected terms may actually dominate the transition intensity. With substantial modification of previously fitted phenomenological parameters, however, the good fit with observed intensities is retained.

I. INTRODUCTION

In a recent paper, 1 subsequently referred to as I, we demonstrated that the intensity analysis of spin-forbidden one-photon transitions in Gd$^{3+}$ and Eu$^{3+}$ is substantially revised when new contributions involving spin-orbit interactions in the excited $4f^{N-5}d^5$ configuration are taken into account. Our introduction and quantitative evaluation of these new terms in one-photon absorption has been motivated by the demonstrated importance of analogous contributions in the two-photon absorption spectroscopy of Gd$^{3+}$ and the isoelectronic Eu$^{2+}$, both of which contain a half-filled ($4f^7$) shell. It is now widely accepted that such "third-order" terms dominate two-photon line strengths within the $4f^7$ shell; our previous paper has shown that they also contribute significantly to one-photon transitions with $4f^7$. The standard second-order contribution in $4f^7$ is small not only because all the observed transitions are spin forbidden in $LS$ coupling, but also because of a separate, unique characteristic of half-filled shells, namely that all diagonal reduced matrix elements $\langle 2S+1L \mid U^{(k)} \mid 2S+1L \rangle$, vanish. This latter fact sometimes tends to reduce the value of intermediate coupled reduced matrix elements $\langle \langle 2S+1L \mid U^{(k)} \rangle \langle 2S+1L \mid \rangle$, connecting states of differing spin, when the initial and final states share common $LS$ coupled admixtures, compared to analogous matrix elements in other configurations. 6 This general consideration, however, can easily lead to the conclusion that third-order contributions are unique to spin-forbidden transitions in $4f^7$. Indeed, one recent study showed that third-order terms do not contribute significantly to the spin-forbidden two-photon transition $7F_0 \rightarrow 7D_0$ in Sm$^{2+}$-7. On the other hand, examination of the two-photon transition $3H_4 \rightarrow 5S_0$ in Pr$^{3+}$-8 as well as our recent study of various one-photon transitions (particularly $7F_0 \rightarrow 5D_0$ in Eu$^{3+}$-1 have shown that higher-order terms are important in selected transitions within other lanthanide $4f^{N-5}$ configurations. Thus, there is no systematic support, either theoretical or experimental, for concluding that third-order terms involving spin-orbit mixing in excited configurations contribute proportionally more line strength to $4f^7$ transitions, whether one photon or two photon, than to spin-forbidden transitions in other configurations.

This paper extends our previous analysis of spin-forbidden one-photon transitions in Gd$^{3+}$ and Eu$^{3+}$ to all of the remaining trivalent lanthanides with visible wavelength transitions. A general result of this extended analysis is that large third-order contributions are not a unique feature of $4f^7$. On the contrary, we find that third-order spin-orbit contributions are proportionately larger in Sm$^{2+}$, Tb$^{3+}$, and Ho$^{3+}$ for examined spin-forbidden transitions than in Gd$^{3+}$. In addition, individual transitions in each of the other lanthanide ions have important third order contributions. The theoretical framework for incorporating third order linkages into a revised intensity analysis has been described in detail in I. A central feature of this analysis is that the ratio of individual third- to second-order terms can be computed rigorously. Given the relative magnitudes of the three empirically fitted Judd–Olfet parameters, $T_2$, $T_4$, and $T_6$, the ratio of third to second order contributions then can be calculated for each transition. In presenting our results, we emphasize the value of this contribution ratio as a gauge of the relative importance of third-order terms for each transition. In addition, revised fits to the very complete experimental data compiled by Carnall et al. 9 for aqueous solutions are performed.

In our previous analysis, introduction of third-order contributions required revisions in the value of the three em-
Empirically fitted Judd–Ofelt parameters, $T_g$, $T_d$, and $T_o$ but did not require that any additional parameters be introduced. In extending this analysis to other trivalent lanthanides, it is necessary to comment on the possible role of third-order operators of rank 3 and 5, not occurring in second order, which would necessitate inclusion of two additional parameters. Such operators are included in the final term of the general expression (4b) in I, and written out explicitly, take the form,

$$+ \frac{1}{2} T_A \frac{1}{2} E_{2g} \frac{1}{2} E_{2g} (E^{(4)B_4}^{(3)B_4} (i)(W^{(3)B_4})) \langle f |$$

and

$$- T_A \frac{1}{2} E_{2g} \frac{1}{2} E_{2g} (E^{(4)B_4}^{(5)B_4} (i)(W^{(5)B_4})) \langle f |.$$  

(1a)

Our calculations, however, show that the magnitudes of contributions from these operators are consistently much less than 1% of those from corresponding even rank operators. Thus we can neglect these $t = 3, 5$ terms, and continue using the line strength expression

$$P = \nu(2J + 1) \sum_{\lambda = A, B} T_{\lambda} \left[ \left( \frac{i}{i} \right) (U^{(2)} \langle f | \langle f | (i)(O_3^{(2)}) \langle f | + (i)(O_3^{(2)}) \langle f |) \right]^2$$

(2)

which contains only the three Judd–Ofelt parameters, $T_g$, $T_d$, and $T_o$, revised in magnitude to accommodate third-order contributions.

In Sec. II, we reanalyze observed intensity data for the entire lanthanide series, comparing the experimental results and second-order calculations of Carrell et al. with our new third-order calculations. Then in Sec. III, we discuss the importance of g-orbital contributions through a detailed examination of second-order g-orbital terms for ErPO$_4$ and TmPO$_4$.

II. RESULTS AND DISCUSSION

As we showed explicitly in Eq. (5) of I, third-order contributions to the line strength are dependent upon the ratios of spin-orbit parameters $\xi_f$ and $\xi_d$ to the average energy denominator $E_{df}$. Our estimates of these parameters for each triply charged lanthanide ion in aqueous solution are given in Table I.

Empirical Judd–Ofelt parameters used in the fitting process throughout the lanthanide series are presented in Table II. As shown in this table, very substantial modifications of these empirical parameters are necessitated by inclusion of third-order terms. Thus for Pr$^{3+}$, for example, $T_g$ is reduced from 42.0 $\times 10^{-10}$ cm$^{-1}$ in our second-order fitting, to 22.2 $\times 10^{-10}$ cm in our third-order fitting. Similarly, $T_d$ is decreased from 7.40 $\times 10^{-10}$ to 7.10 $\times 10^{-10}$ cm and $T_o$ is decreased from 41.2 $\times 10^{-9}$ to 38.3 $\times 10^{-9}$ cm. Once these revisions are made, many of the calculated oscillator strengths change very little. However, they are now comprised of comparable second- and third-order contributions, rather than only second-order terms.

A comparison of standard deviations of the calculated fitting of oscillator strengths to experiment are presented in Fig. 1. As shown in this figure, the typical change in the standard deviation from the second- to third-order fitting is about 20%, with half of the fits better and half worse by about this amount. Thus inclusion of these third-order terms does not significantly affect the overall degree of fit for the entire series. However, new insight can be gained for some individual transitions, as described in more detail below.

A. Praseodymium$^{3+}$

Calculated and experimental results for Pr$^{3+}$ are presented in Fig. 2. The first panel shows the ratio of the third-order contribution,

$$\nu(2J + 1) \sum_{\lambda = A, B} T_{\lambda} \left[ 2 \cdot (i)(U^{(2)} \langle f | \langle f | (i)(O_3^{(2)}) \langle f | + (i)(O_3^{(2)}) \langle f |) \right]^2$$

(3a)

TABLE I. Empirical Judd–Ofelt parameters used in lanthanide fitting. The first column gives the individual trivalent lanthanide ion, while the next three columns present present parameters $T_g$, $T_d$, and $T_o$ used for the second-order fitting (Ref. 9). The last three columns present respective Judd–Ofelt parameters for our new third-order fitting.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$T_{2g}$</th>
<th>$T_{4i}$</th>
<th>$T_{15}$</th>
<th>$T_{2g}$</th>
<th>$T_{4i}$</th>
<th>$T_{15}$</th>
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<td>Pr$^{3+}$</td>
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<td>1.81</td>
<td>4.73</td>
<td>10.03</td>
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<td>5.32</td>
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<td>4.83</td>
<td>3.32</td>
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<td>Eu$^{3+}$</td>
<td>1.88</td>
<td>8.59</td>
<td>6.96</td>
<td>3.74</td>
<td>10.23</td>
<td>6.22</td>
</tr>
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<td>6.1</td>
<td>2.50</td>
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<td>4.46</td>
<td>8.50</td>
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<tr>
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<td>2.40</td>
<td>0.93</td>
<td>2.59</td>
<td>2.37</td>
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</table>

$^a$All parameters in units of $10^{-9}$ cm.
to the second-order contribution,
\[ \nu(2J + 1) \sum_{k \in \mathbb{A}} T_A \cdot |\langle i|U^{(4)}|f\rangle|^2, \]
(3b)

where \( i \) is the ground state \( ^3H_{4s} \), and the final state \( f \) is listed at the bottom of each column. For each transition listed in this panel, the second-order contribution has been scaled to a value of one. For the \( ^3H_{4s} \rightarrow ^1G_{4s} \) transition, the third-order contribution is actually negative in sign. This is allowed since the third-order contribution includes cross terms between second- and third-order matrix elements as well as squares of the third-order matrix elements. Three of the four spin-forbidden triplet to singlet transitions shown in this panel have third-order contributions greater than 20% of the second-order contributions, whereas none of the spin-allowed triplet to triplet transitions have third-order contributions greater than 10% of respective second-order terms.

A comparison between calculated and experimental oscillator strengths for this ion is presented in the second panel of Fig. 2, with transition line intensities given in units of \( P \times 10^3 \), where \( P \) is the probability of transition. The large discrepancy between theoretical and experimental transition line strengths for some transitions in this ion is well known, although not fully understood. Following the convention of Carnall et al., we have not used the \( ^3H_{4s} \rightarrow ^3F_{4s} \) transition in our parameter fitting. Although this allows a much closer fit to the other transitions, second-order calculations still overestimate the \( ^1H_{4s} \rightarrow ^1G_{4s} \) transition by a factor of 4. As illustrated in this figure, the large negative third-order contribution, along with the reduction of relevant Judd–Ofelt parameters, presented in Table II, does reduce the calculated oscillator strength for this transition, but only by about 20%, allowing some improvement in the fit. Inclusion of third-order terms in the other observed transitions reduces the experimental discrepancy in every case, allowing a 25% better fit between calculation and experiment. Thus these new terms partially account for the large experimental discrepancy found in this ion.

### B. Neodymium\(^{3+}\)

Calculated and experimental results for Nd\(^{3+}\) are presented in Fig. 3. The first panel presents the ratios of third- to second-order terms for observed transitions from the ground state \( ^4I_{15/2} \). Third-order contributions for the spin-allowed quartet to quartet transitions have small positive values between 5% and 13% of respective second-order terms and have been omitted from this panel. In contrast, third-order contributions for many of the spin-forbidden quartet to doublet transitions shown in this panel have magnitudes greater than 30% of the corresponding second-order contribution. The largest relative third-order contribution comes from the \( ^4I_{15/2} \rightarrow ^2F_{4s} \) transition, where the third-order term is 88% of the magnitude of the second-order term. This greatly improves the calculated fit to experiment, as shown by the last column of the second panel. Whereas second-order calculations underestimate this transition by a factor of 2, our third-order results only underestimate this transition by 22%. The third-order fit for this transition would actually be closer, except for the modifications to the Judd–Ofelt pa-
parameters (shown in Table II) necessary to fit the other transitions.

C. Promethium\textsuperscript{3+}

Figure 4 presents the relative second- and third-order electric dipole contributions and absolute oscillator strengths for Pm\textsuperscript{3+} in the same format as Fig. 3. As shown in the first panel of this figure, no spin-allowed quintet to quintet transition has a third-order contribution greater than 11\% of the corresponding second-order term. In contrast, the spin-forbidden transitions \( ^5I_4 \rightarrow ^7K_{\pi} \), \(^7K_{\pi} \), \(^5K_0 \), and \(^5H_5 \), have third order intensities 52\%, 45\%, 32\%, and 23\% the magnitude of respective second-order contributions. However, these large third-order contributions are hidden in the experimental observations, since each observed peak, illustrated in the second panel of this figure, is dominated by at least one spin-allowed transition.

D. Samarium\textsuperscript{3+}

Third-order electric dipole contributions for Sm\textsuperscript{3+} are compared with second order and magnetic dipole contributions in the top panel of Fig. 5. The largest second-order contribution, whether magnetic or electric dipole, is scaled to a value of one in this panel. All spin-allowed \(^5H_{11/2} \rightarrow ^7H_{15/2} \), \(^7F_2 \) transitions are very low lying, with more than a 7000 cm\(^{-1} \) energy band gap between the highest \(^7F_2 \) state and the lowest spin-forbidden state. These spin-allowed transitions have small positive third-order contributions of between 5\% and 12\% of corresponding second-order terms, and have been omitted from both panels of Fig. 5. Selected sextet to quartet transitions of Sm\textsuperscript{3+} have the largest third-order contributions of any trivalent lanthanide. To take a few examples, the \(^5H_{11/2} \rightarrow ^7H_{15/2} \), \(^5H_{9/2} \), and \(^5H_{7/2} \) transitions have third-order contributions of 65\%, 160\%, and 130\% of respective second-order terms. Although the last two of these transitions have not been experimentally resolved from the larger \(^6H_{15/2} \rightarrow ^8D_{11/2} \) transition (transition E in the second panel), a marked improvement in the \(^6H_{15/2} \rightarrow ^8H_{11/2} \) transition is shown in the second to last column of the second panel. Whereas second-order calculations underestimate this transition by more than a factor of 2, with inclusion of third-order terms this transition is only underestimated by 30\%. The only other transition with a third-order contribution larger than the corresponding second-order term is the \(^6H_{15/2} \rightarrow ^8F_{5/2} \) transition, with a third-order contribution of 123\%. Second-order theory underestimates this transition.
FIG. 5. Relative magnetic and second- and third-order electric dipole contributions and absolute oscillator strengths for ground state transitions of Sm$^{3+}$. The first panel gives relative magnetic dipole along with second- and third-order electric dipole contributions for indicated transitions from the ground state. The largest second-order term, either electric or magnetic dipole, is scaled to 1.0 for each transition. Crosshatching indicates partial cancellation of the second-order term by a negative third-order term. Low-lying $^2H_{11/2}$, $^4H_{15/2}$, $^6F_2$ transitions have been left off of both panels of this figure. Experimentally measured absolute oscillator strengths for indicated transitions from the ground state are compared with calculated values in the second panel, using the same notation as Fig. 2. Unresolved transitions to more than two states, given by a single capital letter, are defined as follows:

- $A = ^4H_{11/2}$, $^2H_{13/2}$, $^4F_{11/2}$, $^4G_{11/2}$, $^4G_{13/2}$, $^4F_{13/2}$, $^4F_{15/2}$, $^2H_{15/2}$, $^4F_{17/2}$, $^2H_{17/2}$, $^4F_{19/2}$, $^2H_{19/2}$, $^4F_{21/2}$, $^2H_{21/2}$
- $B = ^2H_{11/2}$, $^4H_{13/2}$, $^4G_{11/2}$, $^4G_{13/2}$, $^4F_{11/2}$, $^2H_{13/2}$, $^4H_{15/2}$, $^4F_{13/2}$, $^2H_{15/2}$, $^4F_{15/2}$, $^2H_{17/2}$, $^4F_{17/2}$, $^2H_{19/2}$, $^4F_{19/2}$, $^2H_{21/2}$, $^4F_{21/2}$
- $C = ^2H_{11/2}$, $^4H_{13/2}$, $^4G_{11/2}$, $^4G_{13/2}$, $^4F_{11/2}$, $^2H_{13/2}$, $^4H_{15/2}$, $^4F_{13/2}$, $^2H_{15/2}$, $^4F_{15/2}$, $^2H_{17/2}$, $^4F_{17/2}$, $^2H_{19/2}$, $^4F_{19/2}$, $^2H_{21/2}$, $^4F_{21/2}$
- $D = ^2H_{11/2}$, $^4H_{13/2}$, $^4G_{11/2}$, $^4G_{13/2}$, $^4F_{11/2}$, $^2H_{13/2}$, $^4H_{15/2}$, $^4F_{13/2}$, $^2H_{15/2}$, $^4F_{15/2}$, $^2H_{17/2}$, $^4F_{17/2}$, $^2H_{19/2}$, $^4F_{19/2}$, $^2H_{21/2}$, $^4F_{21/2}$

The transition $^2H_{11/2} \rightarrow ^2D_{1/2}$ has been reduced by a factor of 2 in this panel while the $^2H_{11/2} \rightarrow ^4F_{13/2}$ and $^2H_{11/2} \rightarrow ^4H_{15/2}$ transitions have been increased by factors of 100 and 10, respectively.

by a factor of 9. Thus, with inclusion of this large third-order contribution, this transition is still underestimated by a factor of 4. Even more interesting is the $^5H_{11/2} \rightarrow ^4D_{1/2}$ transition, in which the negative third-order contribution cancels 98% of the second-order term. However, the large closely lying $^3H_{5/2} \rightarrow ^2F_{5/2}$ transition (transition D) hides any experimental confirmation of this extremely large cancellation.

E. Europium$^{3+}$

Calculated relative second- and third-order electric dipole contributions for Eu$^{3+}$ are presented in the first panel of Fig. 6. As illustrated in this panel, large negative third-order contributions cancel out 50% and 29% of corresponding second-order terms for the $^7F_{0} \rightarrow ^5D_2$ and $^5I_4$ transitions. Also, large positive third-order contributions add 42%, 46%, and 33% to respective second-order terms for the $^7F_{0} \rightarrow ^5G_4$, $^5G_6$, $^5F_2$, and $^5F_4$ transitions. Third-order values for these transitions have been slightly modified from results in I due to inclusion of extra intermediate coupled $U^{1/2}W^{1/2}$ terms. Thus, for the $^7F_{0} \rightarrow ^5D_2$ transition, in I we included only the dominant $\langle 7F_0|U^{1/2}|F_2 \rangle \langle F_2|W^{1/2}\rangle \langle 5D_2 \rangle$ connection, whereas in this study, we also included smaller terms, such as $\langle 7F_0|U^{2}|5D_2 \rangle \langle 5D_2|W^{1/2}\rangle \langle 5D_2 \rangle$, which are nonzero only in intermediate coupling.

The first transition shown in Fig. 6 is the $^7F_{0} \rightarrow ^5D_2$ transition. Since this is the only transition used in fitting empirical parameter $T_2$, an exact fit between calculation and experiment can be guaranteed. Third-order results for this transition are interesting because the third-order term is 50% of the magnitude of the second-order term and of opposite sign. Thus the Judd–Ofelt parameter $T_2$ must be dramatically increased over its second-order value to counteract this cancellation. This is shown in Table II, where $T_2$ is increased from a value of $1.88 \times 10^{-3}$ to $3.74 \times 10^{-9}$ cm.

F. Gadolinium$^{3+}$

Second- and third-order electric dipole as well as magnetic dipole contributions to the oscillator line strengths for
Gd$^{3+}$ are examined in the first panel of Fig. 7. Our third-order analysis of this ion is again somewhat modified from our analysis in I due to inclusion of extra third-order terms and the use of intermediate-coupled, rather than LS coupled, final state wave functions.

The first three transitions given in this panel are for $^8S_{7/2} \rightarrow ^6P_{1/2}$, $^6P_{3/2}$ transitions, third-order terms are 60% and 113% of the magnitude of respective second-order terms. However, third-order contributions have small effects upon predicted intensities of these two lines since about 3/4 of their strength is due to the magnetic dipole term. For $^6P_{3/2}$, on the other hand, there is no magnetic dipole contribution, so the large third-order term dominates. The oscillator strength measured by Carnall et al. for $^6P_{3/2}$ is an order of magnitude greater than predicted by second-order theory. However, as shown in the second panel of this figure, inclusion of the large third-order term, 848% larger than the second-order term, accounts for the strength of this previously unexplained transition.

For the $^8S_{7/2} \rightarrow ^6I_7$ transitions shown in this figure, third-order terms contribute between 22% and 23% of respective oscillator strengths. Since these are the only transitions with a dominant sixth rank component, a 23% reduction in the Judd–Ofelt parameter $T_6$ compensates almost exactly for these third-order contributions. Our reanalysis of Gd$^{3+}$ is also remarkably successful in predicting the $^8S_{7/2} \rightarrow ^6D_J$ transitions.

**G. Terbium$^{3+}$**

Second- and third-order line strength contributions for Tb$^{3+}$ transitions are compared in the first panel of Fig. 8. Most remarkable is the extreme cancellation by third-order terms of second-order electric dipole terms for the $^7F_6 \rightarrow ^7D_J$ transitions. Third-order terms cancel 66%, 76%, and 80% of the second-order term for $^7F_6 \rightarrow ^7D_{4,3,2}$ transitions, respectively, and cancel out over 98% of the second-order term for the $^7F_6 \rightarrow ^7D_{1,0}$ transitions. For the two experimentally resolved $^7F_6 \rightarrow ^7D_J$ transitions, shown in the second panel of Fig. 8, second-order contributions are already too small by factors of 2.5 for the $^7F_6 \rightarrow ^7D_4$ transition, and 12 for the $^7F_6 \rightarrow ^7D_4$ transition. Thus neither the second- nor third-order theory can account for the observation of these transitions.

**H. Dysprosium$^{3+}$**

Third-order electric dipole contributions for Dy$^{3+}$ are compared with second-order electric and magnetic dipole contributions in the first panel of Fig. 9. As was the case for Sm$^{3+}$, all spin-allowed $^6H_{15/2} \rightarrow ^6H_J, ^6F_J$ transitions are very

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**FIG. 7.** Relative magnetic and second- and third-order electric dipole contributions and absolute oscillator strengths for ground state transitions of Gd$^{3+}$. Notation used is the same as Fig. 5. Unresolved transitions to more than two states, given by a single capital letter in the second panel, are defined as follows: $A = ^8S_{7/2} \rightarrow ^4I_{15/2}, ^4I_{13/2}, ^4I_{11/2}, ^4I_{9/2}, ^4I_{7/2}$; $B = ^5I_{15/2}, ^5I_{13/2}, ^5I_{11/2}, ^5I_{9/2}$; $C = ^8S_{7/2} \rightarrow ^6G_{4,3,2,1,0,1/2,3/2}$. Transition $A$ has been reduced by a factor of 2 in this panel while the $^8S_{7/2} \rightarrow ^6P_{3/2}$ transition has been increased by a factor of 100.

**FIG. 8.** Relative second- and third-order electric dipole contributions and absolute oscillator strengths for ground state transitions of Tb$^{3+}$. Notation used is the same as Fig. 2. Unresolved transitions to more than two states, given by a single capital letter in the second panel, as defined are follows: $A = ^7F_6 \rightarrow ^7D_{4}, ^7G_6 \rightarrow ^7I_{15/2}$; $B = ^7F_6 \rightarrow ^7G_4, ^7D_5, ^7G_6 \rightarrow ^7I_{13/2}, ^7I_{11/2}$; $C = ^7F_6 \rightarrow ^7G_6 \rightarrow ^7I_{11/2}$, ^7I_{9/2}$; $D = ^7F_6 \rightarrow ^7H_{4,3,2} \rightarrow ^7I_{11/2}$, ^7I_{9/2}$, ^7I_{7/2}$.
FIG. 9. Relative magnetic and second- and third-order electric dipole contributions and absolute oscillator strengths for ground state transitions of Dy$^{3+}$. Notation used is the same as Fig. 5. Low-lying $^9H_{15/2}$→$^7H_{15/2}$, $^9F_7$, transitions have been left off of both panels of this figure. Unresolved transitions, given by a single capital letter in the second panel, are defined as follows: $A = ^9H_{11/2}$→$^9F_{11/2}$, $^9I_{11/2}$→$^9M_{11/2}$, $^9K_{11/2}$; $B = ^9H_{11/2}$→$^9M_{11/2}$, $^9P_{11/2}$, $^9P_{11/2}$, $^9I_{11/2}$, $^9M_{11/2}$; $C = ^9H_{11/2}$→$^9M_{11/2}$, $^9F_{11/2}$, $^9S_{11/2}$, $^9K_{11/2}$, $^9E$; $E = ^9H_{11/2}$→$^9H_{13/2}$, $^9S_{11/2}$, $^9P_{11/2}$, $^9I_{11/2}$, $^9M_{11/2}$, $^9G_{0/2}$, $^9G_{1/2}$; $F = ^9E$→$^9L_{1/2}$.

low lying, with a 21 000 cm$^{-1}$ energy band gap between the highest $^9F_j$ state and the lowest spin-forbidden state. These low-lying spin-allowed transitions have small positive third-order contributions of between 4% and 9% of corresponding second-order terms. For clarity, these transitions have been omitted from Fig. 9. As shown in the first panel, the $^9H_{15/2}$→$^9M_{11/2}$ transition has the largest relative third-order contribution, which is 89% of the respective second-order term. However, the large, close-lying $^9H_{15/2}$→$^9P_{3/2}$ transition (transition D in the second panel), completely overwhelms any experimental confirmation of this contribution. Large third-order cancellations of 46%, 50%, and 65% occur in the $^9H_{15/2}$→$^9G_{1/2}$, $^9G_{11/2}$, and $^9M_{11/2}$ transitions, respectively. However, none of these transitions are resolved from nearby larger transitions in aqueous solution. Thus these large individual effects are not observable in the fit to experiment presented in the second panel.

I. Holmium$^{3+}$

Calculated and experimental results for Ho$^{3+}$ are presented in Fig. 10. The first panel presents ratios of third- to second-order terms for observed transitions from the ground state. Low lying $^5I_6$→$^5I_{15/2}$, $^5F_7$, $^5S_{7/2}$, and $^5G_7$ transitions are dominated by second-order terms, and have been left off of both panels for clarity. In contrast, third-order contributions for many of the spin-forbidden quintet to triplet transitions, shown in the top panel, have magnitudes greater than 50% of the corresponding second-order contribution. The largest relative third-order contribution comes from the $^5I_6$→$^5D_3$ transition, where the third-order term is 116% of the magnitude of the second-order term. This transition is already well explained by second-order terms, however, and inclusion of this large third-order term causes an overestimation by a factor of 2 in the predicted intensity. Other transitions, such as $^5I_6$→$^5F_{4/2}$, $^5F_{5/2}$, $^5I_6$, and $^5L_6$, all have third-order terms greater than 50% of respective second-order terms. However, these transitions either are not observed, or are hidden by close lying dominant transitions.

J. Erbiium$^{3+}$

Calculated and experimental results for Er$^{3+}$ are presented in Fig. 11. The first panel gives the ratios of third- to second-order terms for observed transitions from the ground state $^4I_{15/2}$. This is the only ion in which the largest third-order contribution comes from a spin-allowed transition. As
shown in the first panel, the \( ^1I_{5/2} \rightarrow ^4G_{5/2} \) transition has a third-order contribution of 39\%, whereas no spin-forbidden transition has a third-order contribution greater than 25\%.

**K. Thulium\(^{3+}\)**

Calculated and experimental results for Tm\(^{3+}\) are presented in Fig. 12. The first panel presents the ratios of third-to second-order terms for observed transitions from the ground state \(^3H_{6}\). The largest relative third-order contribution comes from the unobserved \(^3H_{6} \rightarrow ^5S_{2}\) transition, where the third-order term is 65\% of the magnitude of the second-order term. The spin-allowed \(^3H_{6} \rightarrow ^3P_{2}\) transition also has a significant (26\%) third-order contribution. As shown in the second to last column of the second panel, second-order calculations underestimate this transition by 31\%. However, when the third-order contribution is included, this transition is only underestimated by 17\%.

**III. \(g\)-ORBITAL CONTRIBUTIONS**

Our analysis so far has followed the conventional approximation that only intermediate states of \(4f^{N-5d}\) character are important in lanthanide transitions, since \(4f^{N-15d}\) is by far the lowest energy excited configuration in the free ions. However, as pointed out by Becker et al.,\(^{14}\) linear combinations of ligand orbitals can transform like components of \(g\)-electron wave functions. Thus, low-lying states of \(g\) character can be formed from these ligand orbitals, and the energy denominators for \(d\)- and \(g\)-orbital excited configurations may be similar. The importance of \(g\)-orbital electrons in lanthanide transitions has long been suspected. In their early attempts to calculate the \(T_g\) parameters, both Judd\(^{15}\) and Krupke\(^{15}\) concluded that \(g\)-orbital electron configurations make a substantial or even a dominant contribution to the parameters. Axe,\(^{16}\) in his analysis of europium ethylsulphate, similarly concluded that \(4f^{N-1g}\) configurations make important contribution to the electric dipole transition line strengths. However, neither they nor subsequent investigators have included these configurations into a quantitative Judd–Ofelt analysis of lanthanide transitions.

The successes of the Judd–Ofelt formalism in predicting lanthanide transition line strengths has been a major contributing factor in the neglect of these terms. In this formalism, the crystal field terms and radial integrals are included in the empirically fitted Judd–Ofelt parameters. Since the second order \(U^{(2)}\) matrix elements act solely between initial and final states within the \(4f^N\) ground configuration, inclusion of the \(g\)-orbital excited configuration does not change the individual second-order matrix elements, but merely changes their common multipliers. Thus appropriate scaling of the fitted parameters can exactly cancel any second-order
g-orbital contribution. However, recent observations of an anomalous absence of asymmetry in certain electronic Rac- man transitions in lanthanide phosphates \(^4,18\) not only have provided strong evidence that intermediate states of \(4f^{N-1}g\) character are comparable in importance to \(4f^{N-2}d\) states in lanthanide radiative processes, but also have given us a quantitative way to establish the magnitude of the g-orbital contribution.

The influence of \(4f^{N-1}g\) states enters in second order as well as third order. Although third-order g-orbital revisions are not insignificant, the importance of these g-orbital states can be demonstrated by considering only second-order revisions. Expanding expression (4a) of \(I\) for \(d\) and \(g\) electrons with cancellation of common terms, we can explicitly derive the ratios of g- to d-orbital contributions. The second and sixth rank terms are calculated to be

\[
U^{(2)}_g = \frac{5}{2} \frac{E_{df} (4f^d|g|4f^d|g)}{E_{df} (4f^d|r|d)(4f^d|r|d)},
\]

\[
U^{(6)}_g = \frac{1}{13} \frac{E_{df} (4f^d|g|4f^d|g)}{E_{df} (4f^d|r|d)(4f^d|r|d)},
\]

where \(U^{(2)}_g\) are the second-order g-orbital terms, scaled so that \(U^{(2)}_g + U^{(4)}_g\). For fourth rank terms, however, calculation is more complicated, and the ratio between crystal field terms \((E^{(3)}_{df})^{(4)}\) and \((E^{(3)}_{df})^{(5)}\) must be known. Considering three cases, (a) the first term predominates, (b) the two terms are equal, and (c) the second term dominates, we get, respectively,

\[
U^{(4)}_g = \frac{3}{11} \frac{E_{df} (4f^g|g|4f^g|g)}{E_{df} (4f^g|r|d)(4f^g|r|d)},
\]

\[
U^{(4)}_g \approx \frac{15}{14} \frac{E_{df} (4f^g|g|4f^g|g)}{E_{df} (4f^g|r|d)(4f^g|r|d)},
\]

\[
U^{(4)}_g = \frac{6}{E_{df} (4f^g|r|d)(4f^g|r|d)},
\]

However, the magnitudes of these crystal field terms will not change for different transitions from the same ion site. Thus, in second-order calculations, the effect of these g-orbital contributions can be completely masked by a modification of the \(T_\alpha\) appropriate multipliers.

Radial integrals \((4f^g|r|l')\) are normally included in the \(T_\alpha\) parameters. However, in order to calculate the relative importance of g-orbital contributions to d-orbital terms, the ratios of these radial integrals must be estimated. From the Raman asymmetry data of Ref. 18, the value of \(E_{df}/E_{df} (4f^d|g|4f^g|r|d)\) can be determined rigorously, and is calculated to be 0.91 for ErPO\(_4\) and 1.09 for TmPO\(_4\). Since these ratios are close to one, we make the further assumption that \(4f^g|r|d = 4f^g|r|d\) for \(k = 3.5\). Table III gives the resultant scaling in the fitted Judd–Ofelt parameters \(T_\alpha\) when g-orbital effects are included for these two cases. As shown in this table, \(T_\alpha\) is decreased by more than an order of magnitude: to only 9.4% of its original value for Er\(^{3+}\) and to 7.2% for Tm\(^{3+}\). There is a factor of 30 uncertainty in \(T_\alpha\) due to uncertainty in the ratio between crystal

<table>
<thead>
<tr>
<th>g/d orbital contribution ratio</th>
<th>Standard theory</th>
<th>New theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_2)</td>
<td>1.0</td>
<td>0.91</td>
</tr>
<tr>
<td>(T_4)</td>
<td>1.0</td>
<td>0.094</td>
</tr>
<tr>
<td>(T_6)</td>
<td>1.0</td>
<td>0.64</td>
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<tr>
<td>(T_8)</td>
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<td>(T_{10})</td>
<td>1.0</td>
<td>0.024</td>
</tr>
<tr>
<td>(T_{12})</td>
<td>1.0</td>
<td>0.87</td>
</tr>
<tr>
<td>(T_{14})</td>
<td>1.0</td>
<td>0.85</td>
</tr>
</tbody>
</table>

TABLE III. Modification of Judd–Ofelt parameters due to inclusion of g orbitals. The first row gives the ratio between g- and d-orbital contributions taken from the Raman asymmetry data of Ref. 18. The second row presents the modification in the Judd–Ofelt parameter \(T_\alpha\) from an arbitrarily scaled value of 1.0 in the standard theory. Remaining rows present modification of \(T_\alpha\) for the three cases mentioned in the text, and of \(T_{\chi\alpha}\) each also from a scaled value of 1.0 in the standard theory.

field parameters \((E^{(3)}_{df})^{(4)}\) and \((E^{(3)}_{df})^{(5)}\). Thus \(T_\alpha\) is reduced to between 2.4% and 64% of its original value for Er\(^{3+}\), depending upon this ratio. Similarly, for Tm\(^{3+}\), parameter \(T_\chi\) must be reduced to between 1.7% and 59% of its original value. The smallest change occurs in \(T_{\chi\alpha}\), in which the new value is 87% and 85% of its original value for Er\(^{3+}\) and Tm\(^{3+}\), respectively.

These parameter revisions are larger than those brought about by a third-order analysis restricted to \(4f^{N-1}5d\) intermediate states. Although second-order g-orbital contributions can be incorporated into existing calculations without affecting previously calculated oscillator strengths, revisions of this magnitude will strongly affect any calculations which attempt to relate the magnitude of the Judd–Ofelt parameters to the underlying structure of the crystal field, such as in Refs. 16 and 19. Assessment of the importance of g orbitals for lanthanides in other host materials will need to await further measurements of Raman asymmetry, which have a unique capability to evaluate their importance.

We would also expect third-order g-orbital contributions to be similar in importance to third-order d-orbital terms. However, to determine the exact significance of these new terms, we will need sufficient experimentally determined oscillator strengths to provide a fitting for the empirical parameters \(T_\alpha\). This is in direct contrast to the second-order g-orbital contributions, which can be determined directly from Raman asymmetry data.

IV. CONCLUSIONS

This paper has presented the role of third-order contributions involving excited state spin–orbit intensities throughout the trivalent lanthanide series. Their importance for each transition has been determined relative to the conventional second-order terms. We have found that third-order terms contribute substantially, either constructively or destructively, to a majority of spin-forbidden trivalent lanthanide transitions, with typical magnitudes greater than 20% of the second-order electric dipole contribution to which conventional Judd–Ofelt analysis is confined. In selected cases, these third-order terms are actually greater than their respective second-order terms. This is in sharp contrast to
the spin-allowed transitions, in which third-order contributions are seldom greater than 15% of corresponding second-order terms, and only Ho\(^{3+}\), Er\(^{3+}\), and Tm\(^{3+}\) have spin-allowed transitions with significant third-order contributions. In those lanthanides where states of differing spin lie close together, the larger spin-allowed transitions tend to dominate the experimental data, and thus hide any otherwise significant third-order contributions to individual spin-forbidden transitions. Although systematic higher resolution one-photon intensity data in crystalline samples will be necessary to confirm the importance of third-order terms in these cases, inclusion of third-order terms necessitates revision of the Judd–Ofelt parameters even in these aqueous solution experiments. Since the magnitude of the third-order contribution is inversely proportional to the energy gap between the ground and excited configurations, we expect these contributions to be increased in host media with low energy charge transfer bands. We also expect these terms to be more pronounced in actinide transitions, since they have systematically lower charge transfer bands than corresponding lanthanides.

Inclusion of these new third-order contributions does not produce a systematic improvement or worsening in fitting line strengths. However, new insight has been gained into selected transitions with a dominant third-order contribution, such as the \(F_{9/2} \rightarrow 2F_{5/2}\) transition of Nd\(^{3+}\) and the \(5S_{3/2} \rightarrow 6P_{3/2}\) transition of Gd\(^{3+}\). The Eu\(^{3+}:F_{7/2} \rightarrow \Delta D_0\) transition has received particular attention in recent optical storage experiments, as well as calcium europium oxyapatite studies, where this transition dominates the fluorescence. As we showed in I, this Eu\(^{3+}\) transition, which is strictly forbidden in second order, can be explained through inclusion of the third-order term. Other transitions, however, such as the \(F_9 \rightarrow D_1\) transitions of Tb\(^{3+}\), which are not explained by second-order theory, actually have a worsened fit to experiment when third-order terms are included, raising further questions as to the source of these transitions.

We have also examined the role in one-photon transitions of g-orbital contributions, required to explain the Ramman asymmetry data of Becker and co-workers. Second-order g-orbital terms have been shown to dominate in the case of selected rare earth phosphates, and we would expect this to be true in other media as well. Although these terms do not affect the fitting of individual line strengths, they do necessitate major revisions in the Judd–Ofelt parameters, which will strongly affect any calculations which attempt to relate the magnitude of these Judd–Ofelt parameters to the underlying structure of the crystal field. In those case which allow a large second-order g-orbital contribution, we would expect there to be a significant third-order g-orbital contribution as well.

The results clearly demonstrate that both of these contributions play a major role in lanthanide transition intensities. At the same time, these terms in themselves do not bring about a systematic improvement in the fitting of intensities across the lanthanide series. This fact suggests that spin–orbit mixing in intermediate states, though important, is only one part of a more comprehensive lanthanide intensity analysis. Parallel work by other groups now reveals other pieces which contribute to the complete puzzle. Third-order electron-correlation effects have been found to be significant by Smentek-Mieleczarek and co-workers for both one-photon and two-photon transitions. Recent one- and two-photon calculations by Reid and Nţ confirm that ligand polarization effects are also important. However, more complete Raman and two-photon absorption data will be necessary before a complete understanding of lanthanide transitions can be achieved.

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10A divisor of \((2J+1)\) in this expression, necessary to correlate our Judd–Ofelt parameters with those of Ref. 9, was omitted through typographical error in Eq. (6) of I. Also, we have included an estimate of the contribution of the remainder term \(E^{\text{R}}\) in expression (5) of I to the third order term \(O^{(4)}\) by setting \((E^{\text{B}})^{\text{B}}\) equal to \((E^{\text{B}})^{\text{B}}\) in the expression for \(R^{(4)}\).
25M. F. Reid and B. Ng, Mol. Phys. (in press).