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### Ligand polarization contributions to two-photon absorption in lanthanide ions

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A third-order process involving ligand excited states is discussed. We estimate that for two-photon absorption within the  $f^7$  configuration of  $\text{Gd}^{3+}:\text{CaF}_2$  this mechanism makes a contribution comparable to the third-order crystal-field process which has been used previously to explain the experimentally observed intensity distributions in that system.

Recent measurements of  $4f \rightarrow 4f$  two-photon absorption (TPA) spectra in  $\text{Gd}^{3+}:\text{LaF}_3$  (Refs. 1–3) and  $\text{Eu}^{2+}:\text{CaF}_2$  (Ref. 4) have prompted a reexamination of the TPA theory of lanthanide  $4f \rightarrow 4f$  transitions. For certain transitions in the  $\text{Gd}^{3+}:\text{LaF}_3$  system, the TPA results have been found to conform to the predictions of the simple second-order TPA theory developed by Axe.<sup>5</sup> However, for other transitions this theory fails to account for the observed integrated intensities, intensity distributions among Stark components, and line polarizations.<sup>1–4</sup> Judd and Pooler<sup>6</sup> introduced third-order terms involving spin-orbit interactions among levels of the intermediate configurations (such as  $f^6d$  and  $f^6g$ ) to explain the experimental results reported by Dagenais, Downer, Neumann, and Bloembergen.<sup>1</sup> However, further TPA measurements obtained by Downer and co-workers<sup>2,3</sup> gave results that could not be explained by either the Axe theory<sup>5</sup> or the third-order mechanism proposed by Judd and Pooler.<sup>6</sup> Downer and co-workers<sup>2–4</sup> found it necessary to invoke both third- and fourth-order terms involving spin-orbit and/or crystal-field interactions among levels of the  $4f^65d$  intermediate configuration to rationalize their TPA intensity and polarization results. The higher-order terms in their analysis play the crucial role of breaking down the  $\Delta S$ ,  $\Delta L$ , and  $\Delta J$  selection rules left intact by lower-order terms.

One of the central features in the third- and fourth-order TPA analysis presented by Downer and Bivas<sup>3</sup> for  $\text{Gd}^{3+}:\text{LaF}_3$  is the use of crystal-field perturbations to overcome the  $\Delta L, \Delta J \leq 2$  selection rules inherent to the second-order theory of Axe.<sup>5</sup> It is clear from the relative line intensities and the polarization dependence of the intensity distributions observed within certain multiplet-to-multiplet transitions that these selection rules are violated. Inclusion of crystal-field perturbations, along with spin-orbit interactions, operating within the  $4f^7$  and  $4f^65d$  configurational manifolds led Downer and Bivas<sup>3</sup> to a quite successful rationalization of the  $\text{Gd}^{3+}:\text{LaF}_3$  TPA results.

Given the apparently essential role of crystal-field perturbations in determining the TPA line strengths and polarizations, it is reasonable to ask whether there may be other ligand-dependent effects capable of making significant con-

tributions to the TPA line strengths. One obvious candidate is radiation-induced ligand polarization leading to  $f \rightarrow d$  virtual excitations on the lanthanide ion via an odd-multipole(lanthanide)–dipole(ligand) interaction mechanism, followed by  $d \rightarrow f'$  deexcitations induced by a direct radiative coupling mechanism. In this case, one photon of the radiation field acts on the electronic charge distributions of the ligands and the other photon acts on the lanthanide ion. Two different sets of intermediate states are involved in these processes; one consists of ligand excited states and the other consists of  $4f^{N-15d}$  lanthanide states. In contrast, both the second-order theory of Axe<sup>5</sup> and the higher-order theory of Downer and Bivas<sup>3</sup> restrict radiative coupling to the lanthanide ion, and the intermediate states involved in the TPA process are constructed from electronic configurations localized on the lanthanide. The crystal-field perturbations introduced by Downer and co-workers<sup>2,3</sup> reflect only the ground-state charge distributions of the ligands (presumed to be unaffected by the radiation field), and they act only *within* either the  $4f^N$  or  $4f^{N-15d}$  lanthanide configurations.

The possible importance of ligand-polarization effects in the TPA processes of lanthanide ions is suggested by their demonstrated importance in contributing to *one-photon*  $4f \rightarrow 4f$  transition intensities.<sup>7–11</sup> In the latter case, radiation-induced ligand polarization serves to enhance  $4f \rightarrow 4f$  multipolar transition probabilities via multipole(lanthanide)–dipole(ligand) interaction mechanisms.<sup>8</sup> This mechanism for one-photon  $4f \rightarrow 4f$  transition intensities is often referred to as the *dynamic-coupling* mechanism, reflecting the dynamic response of the ligands to the radiation field. The dynamic ligand-polarization contributions to TPA intensities and polarizations would be modulated by the dynamic dipolar polarizabilities and polarizability anisotropies of the ligands surrounding the lanthanide ion. These ligand properties are not represented in the *static* crystal-field perturbations introduced by Downer and co-workers.<sup>2,3</sup> Variations in these ligand properties versus variations in the static crystal field may be expected to be quite different in going, for example, from a fluoride to an oxide or a chloride host material.

In this Communication we examine just one of several terms that dynamic ligand-polarization effects may contribute to a third- or fourth-order TPA intensity analysis. Our primary aim is to demonstrate that the magnitude of the ligand polarization terms will, in general, be comparable to those associated with static crystal-field perturbations, and that ligand polarizability may be an important property to consider in designing materials for TPA applications.

$$\sum_{\chi, \chi'} \Delta_{\chi}^{-1} \Delta_{\psi'}^{-1} [\langle \psi | \chi | \bar{E} \cdot \bar{D} | \psi' \rangle \langle \psi' | \chi' | \hat{V} | \psi'' \rangle \langle \psi'' | \chi | \bar{E} \cdot \bar{D} | \psi' \rangle + \langle \psi | \chi | \bar{E} \cdot \bar{D} | \psi'' \rangle \langle \psi'' | \chi' | \hat{V} | \psi' \rangle \langle \psi' | \chi | \bar{E} \cdot \bar{D} | \psi' \rangle] , \quad (1)$$

where  $\chi$  and  $\chi'$  denote ligand ground and excited (electronic) states, respectively,  $\psi''$  denotes a lanthanide electronic state of opposite parity to the  $\psi$  and  $\psi'$   $4f^N$  states,  $\bar{E}$  is the radiation vector,  $\bar{D}$  is the electric dipole moment operator, and the  $\Delta$  are (average) energy denominators. The interaction between lanthanide and ligand electrons,  $\hat{V}$  ( $=e^2/r_{ij}$ ), couples the  $\chi \rightarrow \chi'$  ligand transitions to  $\psi \rightarrow \psi''$  or  $\psi' \rightarrow \psi''$  lanthanide transitions.

In evaluating the matrix elements of  $\hat{V}$  we shall ignore orbital overlap and consider only dipolar  $\chi \rightarrow \chi'$  virtual excita-

The term we consider makes a third-order contribution to the TPA line strength, and it involves one photon interacting directly with the lanthanide ion and the other photon polarizing the charge distributions on the ligands ( $L$ ). Each photon-system interaction is assumed to be electric dipolar in character. For a two-photon  $4f \rightarrow 4f$  transition,  $\psi \rightarrow \psi'$ , our third-order term may be written as

tions. Following the procedures used previously<sup>8-10</sup> in formulating the dynamic-coupling mechanism for one-photon  $4f \rightarrow 4f$  transition intensities, the first term in (1) may be simplified to yield

$$\sum_{\psi''} \Delta_{\psi''}^{-1} [\langle \psi | \hat{D}_{\text{eff}} | \psi'' \rangle \langle \psi'' | \bar{E} \cdot \bar{D} | \psi' \rangle + \langle \psi | \bar{E} \cdot \bar{D} | \psi'' \rangle \langle \psi'' | \hat{D}_{\text{eff}} | \psi' \rangle] , \quad (2)$$

where  $\hat{D}_{\text{eff}}$  is an "effective" operator, which acts only on lanthanide electrons:

$$\hat{D}_{\text{eff}} = \sum_L \bar{\alpha}_L \sum_k (-1)^k r_i^{k-1} R_L^{-(k+1)} [k(2k+1)]^{1/2} [C^k(L) E^1]^{k-1} \cdot C^{k-1}(i) . \quad (3)$$

In (3),  $L$  labels ligands,  $i$  labels the lanthanide optical electrons,  $R_L$  is the lanthanide- $L$  distance,  $r_i$  is an electron radial coordinate, and  $\bar{\alpha}_L$  is the polarizability of ligand  $L$  (here assumed to be isotropic). The spherical tensors  $C^k(L)$  and  $C^{k-1}(i)$  are functions of ligand and lanthanide-electron coordinates, respectively. Since  $\hat{D}_{\text{eff}}$  connects states with  $\Delta l$  odd,  $k-1$  must be odd in (3) [in contrast to the one-photon dynamic-coupling mechanism where this expression acts between  $f^N$  states—Ref. 10, Eq. (22)].

Expression (2) is similar to the standard Judd-Ofelt<sup>12,13</sup> crystal-field expression for one-photon absorption (with  $\hat{D}_{\text{eff}}$  taking the place of the odd-parity crystal field). By analogy to Eq. (4) of Judd,<sup>8</sup> we obtain an effective operator which acts between the  $f^N$  states,  $\psi$  and  $\psi'$ , in (2):

$$\sum_L \bar{\alpha}_L \sum_{k,\lambda} R_L^{-(k+1)} [k(2k+1)(2\lambda+1)]^{1/2} \Xi(k-1, \lambda) \{E^1 [C^k(L) E^1]^{k-1}\}^\lambda \cdot U^\lambda . \quad (4)$$

In order to compare our third-order ligand-polarization expression (4) with the third-order crystal-field expression [Ref. 3, expression (6a)], the latter must be multiplied by  $\langle f|r|d \rangle^2$ , and the  $\Xi$  parameters in (4) must be those associated with  $4f^N-4f^{N-1}5d$  interconfigurational mixings (Downer and Bivas<sup>3</sup> ignore  $4f^{N-1}g$  configurations). Note that both  $k$  and  $\lambda$  must be even in (4), and when we sum over the ligands,  $C^k(L)$  will be subject to the same symmetry restrictions as the crystal-field parameters appearing in expression (6a) of Downer and Bivas.<sup>3</sup> Therefore, no new spectral polarization effects would be introduced by (4).

In comparing our expression (4) with (6a) of Downer and Bivas,<sup>3</sup> we shall consider a  $\Delta J=6$  transition in the  $\text{Gd}^{3+}:\text{LaF}_3$  system. In this case, we require  $k=\lambda=6$ . To calculate  $\Xi(5,6)$ , we interpolate the  $f-d$  integrals tabulated by Krupke<sup>14</sup> for  $\text{Gd}^{3+}$  and take the energy of the  $4f^{65}d$  configuration to be  $10^5 \text{ cm}^{-1}$  above  $4f^7$ . Setting  $\bar{\alpha}_L=1 \text{ \AA}^3$  for  $F^-$  and  $R_L=2.5 \text{ \AA}$ , we obtain

$$-1.39 \times 10^{-23} \{E^1 [C^6(L) E^1]^5\}^6 \cdot U^6 \text{ cm}^3 \quad (5)$$

for expression (4), considering just a single ligand. To evaluate (6a) of Downer and Bivas,<sup>3</sup> we require the  $k=6$ ,  $t=5$  term. Downer and Bivas estimated  $B_0^{(4)}$  for the  $5d$

electron in  $4f^{65}d$  to  $30000 \text{ cm}^{-1}$ . To facilitate our comparison, we replace the  $B^{(4)}$  in their expression (6a) by  $C^4 \times 30000 \text{ cm}^{-1}$ , again take the energy of  $4f^{65}d$  to be  $10^5 \text{ cm}^{-1}$ , and multiply their expression by  $\langle f|r|d \rangle^2$  (from Krupke<sup>14</sup>). This gives

$$-2.03 \times 10^{-23} \{E^1 [C^4 E^1]^5\}^6 \cdot U^6 \text{ cm}^3 . \quad (6)$$

The coupled terms in (5) and (6) above differ by containing  $C^6(L)$  and  $C^4$ , respectively, and the former must be summed over the perturbing ligands. However, it is clear from these rough calculations that the ligand-polarization contributions are at least comparable in magnitude to the static crystal-field contributions at the third-order level of analysis.

Our third-order expression (1) is based on a mechanism in which one-photon-induced  $\chi \rightarrow \chi'$  and  $\psi$  (or  $\psi'$ )  $\rightarrow \psi''$  virtual excitations are correlated, via the  $Ln-L$  interaction operator  $\hat{V}$ , to produce a  $\psi \rightarrow \psi'$  TPA transition. One can also visualize a third-order ligand-polarization mechanism in which two ligand-localized virtual excitations are induced by the radiation field and are then coupled to the lanthanide ion to produce a  $4f \rightarrow 4f$  TPA transition. For the latter we may write

$$\sum_{\chi', \chi''} \Delta_{\chi'}^{-1} \Delta_{\chi''}^{-1} [ \langle \psi_{\chi} | \vec{E} \cdot \vec{D} | \psi_{\chi'} \rangle \langle \psi_{\chi'} | \hat{V} | \psi_{\chi''} \rangle \langle \psi_{\chi''} | \vec{E} \cdot \vec{D} | \psi_{\chi} \rangle + \langle \psi_{\chi} | \vec{E} \cdot \vec{D} | \psi_{\chi''} \rangle \langle \psi_{\chi''} | \hat{V} | \psi_{\chi'} \rangle \langle \psi_{\chi'} | \vec{E} \cdot \vec{D} | \psi_{\chi} \rangle ] \quad (7)$$

In this case, there is no direct radiative coupling to the lanthanide electrons (the photons interact only with the ligands), and the  $\hat{V}$  operator must be of even parity with respect to both the lanthanide and ligand electron coordinates. The  $\hat{V}$  matrix elements in (7) are, therefore, likely to be somewhat smaller than those in (1).

Downer and Bivas<sup>3</sup> also considered fourth-order terms involving both spin-orbit and crystal-field perturbations within the  $4f^6 5d$  intermediate configuration (of  $Gd^{3+}$ ). The contributions from these terms were estimated to be larger than those from the third-order crystal-field terms, primarily because the spin-orbit perturbations allow direct connections of the octet and sextet states via an  $S=1$  operator. As in the third-order case, fourth-order terms in which the static crystal field is replaced by dynamic ligand polarizations will give comparable contributions.

The primary objective of this study was to assess the possible importance of dynamic ligand polarizations in  $4f \rightarrow 4f$  TPA processes. Our calculations indicate that their contri-

butions to TPA line strengths will be comparable in magnitude to those arising from static crystal-field perturbations (of the type considered by Downer and Bivas<sup>3</sup>). Furthermore, considered separately, the ligand-polarization and crystal-field perturbations will produce the same sort of TPA line polarization properties. However, considering these two types of perturbations simultaneously leads to cross terms in the TPA line strength expressions which may produce different polarization properties. For example, in third order the TPA line strength would include a cross term involving expression (6a) of Downer and Bivas<sup>3</sup> and our expression (4). Finally, we point out that the ligand polarization effects will be modulated by ligand (dynamic) polarizabilities, so one may expect them to be most important for materials in which the lanthanide ion is surrounded by highly polarizable ligands (such as  $Cl^-$  or  $Br^-$ ).

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