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Polarization dependence of two-photon absorption and electronic Raman scattering intensities in crystals

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A formalism using the properties of the irreducible representation of the scattering tensors has been developed to predict up to the third order the polarization-dependent behavior of the electronic Raman-scattering intensities and the two-photon absorption intensities of transitions between Stark levels. The polarization behavior of ions in crystals are tabulated for the 32 crystallographic point groups. The theory provides a stringent test for the Judd-Ofelt-Axe theory for two-photon intensities between Stark levels. [S0163-1829(97)04609-2]

I. INTRODUCTION

Two-photon spectroscopy has emerged as an important tool in the study of electronic states of ions in crystals. There are two types of two-photon spectroscopy. The first type is two-photon absorption (TPA), in which both photons are simultaneously absorbed by the ion. The second type is electronic Raman scattering (ERS), in which a photon is inelastically scattered from an ion such that the ion is excited to a different electronic state. Both types of spectroscopy are considered complementary to linear spectroscopy. TPA has provided access to higher-energy absorption bands than single-photon absorption, and ERS has been used to probe low-energy levels near the ground state. Since the selection rules for two-photon processes are different from those for single-photon processes, transitions that are forbidden in linear absorption may be explored by TPA. The freedom to independently vary each of the two polarizations in two-photon processes has provided a powerful tool to study the symmetries of the initial and final states in a transition. Among the important applications of two-photon spectroscopy one may include the study of phonons, polaritons, excitons, and intra- and interconfigurational electronic transitions in a wide variety of solids.[1–4]

The theory of two-photon processes owes much of its origin to the theory of one-photon processes. The quantitative theory of single-photon transition intensities within an f^N configuration was developed by Judd[2] and Ofelt[3] in 1962. By introducing the so-called ''Judd-Ofelt closure approximation'' Judd and Ofelt were able to derive an expression in which the oscillator strengths of the one-photon transitions of rare-earth (RE) ions in host lattice crystals are described in terms of a radial factor, which can be estimated for a particular rare earth, and only three parameters. The values of these so-called Judd-Ofelt parameters are usually determined by fitting experimental oscillator strengths. Typically, a single set of Judd-Ofelt parameters are used to fit all observed oscillator strengths of a particular RE ion in a given host crystal or solution. The phenomenological treatment has successfully accounted for the intensities of a majority of transitions for each RE ion. The most extensive work has been done by Carnall *et al.*[5,6] on the aqueous solutions of trivalent RE's. References on analyses of RE oscillator strengths can be found in review papers such as that of Peacock.[7]

The quantitative study of two-photon processes began when Axe,[4] using the Judd-Ofelt closure approximation, derived an expression for the second-order two-photon line strength, in a manner analogous to Judd and Ofelt's formula for single-photon line strength. The expression for TPA line strength, however, generally contains only one parameter, instead of three, as in the one-photon expression. As a result, the ratio of the line strengths of two-photon transitions can be computed without the need for phenomenological parameters. Experimental measurements of line strength ratios and the polarization dependence of line strengths therefore provide rigorous tests of the second-order theory of TPA. Axe's theory, however, is traditionally applied to intraconfigurational transitions from one multiplet to another, with the polarization of the excitation photons being either parallel or perpendicular to the z axis of the lanthanide complex, where the z axis is the highest symmetry.[4,8–13]

The overwhelming success of the Judd-Ofelt theory when applied to RE materials has been the motivation for the intensive study of two-photon intensities using Judd-Ofelt-Axe's theory. Strong disagreement, however, was found when Axe's theory was applied to Gd^{3+} ions in a number of RE hosts. In particular, the experimental results in Gd^{3+}:LaF, reported by Dagenais, Downer, Neumann, and Bloembergen[9] showed that two-photon transitions from the ground level $^8S_{7/2}$ of Gd^{3+} to the first three excited levels, $^6P_{7/2}$, $^6P_{5/2}$, and $^6P_{3/2}$, were anomalously strong with respect to the predictions of a second-order theory, and that the angular momentum selection rule $\Delta J \leqslant 2$ broke down in several transitions ($^8S_{7/2} \rightarrow {}^6I_{13/2,15/2,17/2}, {}^6D_{1/2}$). In order to account for the anomalous intensity observed for $^8S_{7/2} \rightarrow {}^6P_{7/2}$ in Gd^{3+}, Judd and Pooler expanded Axe's second-order theory of TPA to include third-order terms involving the spin-orbit interaction.[10] Downer and co-workers[11,12] later showed that the inclusion of third-order terms involving the crystal-field interaction among intermediate states could explain the anomalous intensity of the $^8S_{7/2} \rightarrow {}^6I_J$ lines in Gd^{3+}. A fuller analysis of the experimental results for the integrated and

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crystal component intensities for the $^8S \rightarrow ^6I$ transitions in the Gd^{3+} ion using expressions which include up to the fourth-order contributions involving spin-orbit and/or crystal-field interactions was given by Downer *et al.*[12,13] Ceulemans and Vandenberghe later presented a more general expression which can be applied to any RE ion.[14]

Other third-order mechanisms in two-photon processes were also investigated by several workers. Reid and Richardson,[15] for example, estimated the ligand-polarization contribution in two-photon processes. Sztucki and Strek,[16–19] expanding Reid and Richardson's idea, proposed the third-order contributions to the two-photon processes from the static and dynamic coupling mechanisms developed within the independent systems model. Smentek-Mielczarek *et al.*[20–24] examined the third-order electron-correlation and crystal-field contributions to the two-photon amplitude within the framework of double perturbation theory.[25,26]

All of the mechanisms mentioned above have been applied to intraconfigurational two-photon transitions, where the initial and final states both belong to the f^N configurations and the two-photon processes are therefore allowed because of the parity rule. TPA transitions from the $4f^N$ to the $4f^{N-1}5d$ have also been observed for Ce^{3+} ions in various crystals.[27–31] These transitions are parity forbidden in the second order within the electric-dipole approximation scheme and thus can be treated as a third-order process. A theoretical description of the cross section of the two-photon f-d transitions based on the perturbation coming from the rank-one component of the crystal field was first proposed by Gayen *et al.*[29] Their calculated polarization anisotropy for the zero-phonon transition in Ce^{3+}:CaF_2, however, were far from the observed values. Leavitt[32] later derived the static and dynamic contributions to the TPA cross section and applied the results to the lowest $4f \rightarrow 5d$ two-photon transition in Ce^{3+}:CaF_2. Leavitt's calculated values were closer to the experiment, compared with Gayen *et al.*'s value, but were still not satisfactory. Expanding the TPA cross-section theory to include arbitrary polarizations in spherical polar coordinates, Makhanek *et al.*,[33,34] showed that good agreement between calculated and observed values for the polarization anisotropy might be obtained if the third-rank component of the crystal field were the dominant term. Sztucki and Strek,[18] using the independent systems model to describe the influence of crystal field and ligand polarization on the f-d two-photon transitions, obtained a cross-section value of the same magnitude as the experimental one, if the value of the magnitude of the crystal-field component $B_0^{(1)}$ was properly chosen. From the values obtained for the polarization anisotropy, they concluded that the first-rank component of the crystal field should be the dominant term, in contradiction to the Makhanek *et al.*'s result. Finally, using the symmetry adaptation technique developed by Kibler,[35,36] Daoud and Kibler developed a formalism to determine the intensity of interconfigurational two-photon transitions. The model was then applied to the case of the Ce^{3+} ion in CaF_2 and $LuPO_4$ with reasonable agreement with observed data.[37]

Two-photon absorption processes in which one photon is absorbed by a magnetic dipole transition and the other by electric dipole transition have also been investigated by Frohlich *et al.*[38] and Daoud and Kibler[39] as possible mechanisms contributing to interconfigurational excitonic transitions observed in RbI, NaI, and NaBr. Daoud and Kibler's prediction using symmetry adaptation technique,[39] however, disagreed with Frohlich *et al.*'s assignments of the observed transitions.[38]

Except the derivations proposed by Makhanek *et al.*[33,34] and Daoud *et al.*,[37,39] all of two-photon studies up to the fourth order mentioned above have been applied in the framework of the Cartesian coordinates or circular polar coordinates. The general study of polarization dependence behavior of the thirty two crystallographic point groups was initiated by Inoue and Toyozawa.[40] Bader and Gold[41] later revised the theory and tabulated the results for TPA transitions between Stark levels. These are the most general polarization dependence formulas for two-photon intensities, in which the polarization vectors are described in the spherical polar coordinates. The major disadvantage of the Bader and Gold formalism is the presence of a number of phenomenological parameters, which in some cases weaken the predictive power.

In addition to the second-order theory of polarization dependence of TPA cross sections developed by Makhanek,[33,34] Kibler, Gâcon, and co-workers[42–48] have reported a number of results in which the observed intraconfigurational two-photon transition intensities were compared with a polarization dependence theory which made use of the symmetry adaptation technique and of the Judd-Ofelt approximation. The Makhanek's and Gâcon-Kibler's formalisms are generally more useful than that of Bader-Gold's formalism, since in the former cases the two-photon intensities between Stark levels and their corresponding polarization dependence expressions for a particular system contain only one or two parameters, which in turn can be further evaluated if the radial factors are known. Their polarization dependence expressions are in good agreement with the more general forms given by Bader and Gold, once the parameters' values in the latter's expression are appropriately assigned. The major disadvantage of the Gâcon-Kibler theory is that its computation appears to be complicated. As a consequence, the theory has been applied to only a few particular systems, rather than being tabulated for the 32 crystallographic point groups as did Bader and Gold.

In this paper another formalism for obtaining the polarization dependent behavior of two-photon intensities between the Stark levels is developed. The general expressions for the polarization dependent two-photon intensities are tabulated for the 32 point groups, whose parameters can be calculated explicitly when applied to a particular system. The proposed theory is derived from a formalism in which the two-photon scattering tensors in polar coordinates are expressed in terms of the irreducible representation of the scattering tensors. The explicit expressions for the irreducible scattering tensors can be obtained by applying the second-order theory of Axe for the TPA processes within the framework of the electric-dipole-interaction perturbation theory[49–51] and/or by expanding perturbation theories which include higher-order mechanisms.[10–24] Since Axe's theory is based on the Judd-Ofelt approximation, the theory provides a stringent test for the Judd-Ofelt theory. When applied to a given system, the expressions for the polarization dependent behavior of the TPA transition intensities are identical to those of Gâcon *et al.*[46] The calculation using this proposed method is, however, more straightforward than that of Gâcon *et al.*[46] The second-order intensity calculations using this new method are given in the ERS framework, but can be applied to the TPA with little modification.

Intensity calculations involving the irreducible scattering tensors in the proposed theory are straightforward and have been routinely practiced in ERS work. When explicit forms for the irreducible scattering tensors are not available, such as in the case of Raman phonon scattering, the table of the polarization dependent behavior for two-photon intensities are particularly useful, since this table was derived using the group-theoretical selection rules for two photon transitions and the special properties of the second-rank irreducible tensors without eliciting its explicit forms for a particular transition.

By use of the irreducible representation of the scattering tensors, the proposed polarization dependence theory can be readily extended to include higher-order interactions contributing to two-photon transition intensities. Using the standard tensor coupling technique, the explicit polarization dependence formulas for the third- or higher-order contributions to the second-order two-photon intensities are obtained for the first time. The third-order contributions including the spin-orbit interaction, crystal-field interaction are discussed. In addition the polarization dependence expressions for interconfigurational two-photon transition intensities are given.

II. THEORETICAL ANALYSIS

A. Second-order theory

We employ the conventional set up for the two-photon processes. In the ERS experiment, one beam is incident on the crystal, and the scattered light is collected at 90° with respect to the incident beam. In the TPA experiment, two light beams are incident on the crystal. The z axis is assumed to be parallel to the z axis of the center ion. For a uniaxial crystal, the z axis is the crystallographic c axis. In the TPA case we define by $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ the polarization unit vectors of the first and second beams, respectively. In the ERS case we use the commonly employed notation[49–53] in which $\hat{\mathbf{e}}_1$ denotes the polarization of the incident beam and $\hat{\mathbf{e}}_2$ the polarization of the scattered light.

The ERS amplitude for a transition from state $|i\rangle$ to state $|f\rangle$ is given by[54]

$$(\alpha_{21})_{if} = -\sum_j \left[\frac{\langle i|\hat{\mathbf{e}}_2\cdot\mathbf{D}|j\rangle\langle j|\hat{\mathbf{e}}_1\cdot\mathbf{D}|f\rangle}{\hbar\omega_j - \hbar\omega_1} + \frac{\langle i|\hat{\mathbf{e}}_1\cdot\mathbf{D}|j\rangle\langle j|\hat{\mathbf{e}}_2\cdot\mathbf{D}|f\rangle}{\hbar\omega_j + \hbar\omega_2} \right], \tag{1}$$

where i, j, and f are the respective initial, intermediate, and final Stark levels of the two-photon transition, 1 and 2 represent the polarizations of the incident and scattered photons,[55] $\hat{\mathbf{e}}_i\cdot\mathbf{D}$ is the electric dipole operator of the ith polarization vector, $\hbar\omega_1$, $\hbar\omega_2$ are the energies of the incident and scattered photons, and $\hbar\omega_j$ are the energies of the intermediate Stark levels.

The TPA amplitude is the same as the ERS amplitude, with a change of sign for $\hbar\omega_2$ in the denominator of the second term of expression (1). Applying the Judd-Ofeft-Axe approximation[2–4] the expression for the ERS amplitude can be recast in the tensorial form:[50,52,56]

$$\alpha_{21} = \sum_t (-1)^t F_t (\mathbf{e}_2\mathbf{e}_1)^{(t)} \cdot \mathbf{U}^{(t)}, \tag{2}$$

where

$$F_t = (-1)^t \sum_{nf^{N-1}n'l'} 7(2l'+1) \begin{pmatrix} 3 & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \langle nf|r|n'l'\rangle^2 \times (2t+1)^{1/2} \begin{Bmatrix} 1 & 3 & l' \\ 3 & 1 & t \end{Bmatrix} \left[\frac{1}{E_{n'l'} - \hbar\omega_1} + \frac{(-1)^t}{E_{n'l'} + \hbar\omega_2} \right]. \tag{3}$$

In Eqs. (2) and (3), t can be 0, 1, or 2, $\mathbf{U}^{(t)}$ is the unit tensor of rank t, and $(\mathbf{e}_2\mathbf{e}_1)^{(t)}$ is the coupled form of the polarization unit vectors of the incoming and scattered light.

The F_t parameter, first introduced by Koningstein and Mortensen,[49] can be treated as a phenomenological constant, which is dependent only on the energy of the $n'l'$ configurations and the radial overlap between the $n'l'$ and nl configurations. For TPA transitions the expression for F_t is the same as in Eq. (3), with the minus sign in front of $\hbar\omega_2$.

The irreducible representation of the Raman-scattering tensor has the simple form[57]

$$\alpha_q^{(t)} = F_t U_q^{(t)}. \tag{4}$$

If we define the initial and final intermediate coupling states as

$$|i\rangle = \sum_{\alpha SLJJ_z} a(i;nf^N\alpha SLJJ_z)|nf^N\alpha SLJJ_z\rangle \tag{5}$$

and

$$|f\rangle = \sum_{\alpha' S'L'J'J'_z} a'(f;nf^N\alpha' S'L'J'J'_z)|nf^N\alpha' S'L'J'J'_z\rangle, \tag{6}$$

the scattering amplitude for the ERS transition between states $|i\rangle$ and $|f\rangle$ is given by

$$\langle i|\alpha_q^{(t)}|f\rangle = F_t \sum_{\alpha SLJJ_z} \sum_{\alpha' S'L'J'J'_z} a(i;nf^N\mu SLJJ_z) \times a'(f;nf^N\mu' S'L'J'J'_z) \times (-1)^{2J+S+L'+t-J_z}[(2J'+1)(2J+1)]^{1/2} \times \begin{pmatrix} J & t & J' \\ -J_z & q & J'_z \end{pmatrix} \begin{Bmatrix} L & J & S \\ J' & L' & t \end{Bmatrix} \times \langle SL|||\mathbf{U}_q^{(t)}|||SL'\rangle \delta(S,S'). \tag{7}$$

We can now express the scattering amplitude in polar coordinates and obtain the polarization dependent forms for TPA and ERS intensities. Consider the general case in which both polarization unit vectors are oriented in an arbitrary direction and independent of each other. In spherical coordinates a unit polarization vector is written

$$\hat{e} = l\hat{x} + m\hat{y} + n\hat{z}, \tag{8}$$

where we have used the same notation as given in Inoue and Toyozawa,[40] in which

$$(l,m,n)=(\sin\theta\ \cos\varphi,\sin\theta\ \sin\varphi,\cos\theta). \tag{9}$$

In terms of the irreducible spherical scattering tensors

$$\alpha_{21}=\sum_{l=0}^{2}\ \sum_{q=-1}^{t}\ \lambda_q^t\alpha_q^{(t)}, \tag{10}$$

where the polarization dependent coefficients λ_q^t's are defined by

$$\lambda_0^0=-\frac{1}{\sqrt{3}}\,[n_2n_1+m_2m_1+l_2l_1],$$

$$\lambda_{-1}^1=\frac{1}{2}\,[(-m_2n_1+n_2m_1)i+(n_2l_1-l_2n_1)],$$

$$\lambda_0^1=\frac{i}{\sqrt{2}}\,[m_2l_1-l_2m_1],$$

$$\lambda_1^1=\frac{1}{2}\,[(m_2n_1-n_2m_1)i+(n_2l_1-l_2n_1)],$$

$$\lambda_{-2}^2=\frac{1}{2}\,[(l_2l_1-m_2m_1)+(l_2m_1+m_2l_1)i],$$

$$\lambda_{-1}^2=\frac{1}{2}\,[(n_2m_1+m_2n_1)i+(n_2l_1+l_2n_1)],$$

$$\lambda_0^2=\frac{1}{\sqrt{6}}\,[2n_2n_1-m_2m_1-l_2l_1],$$

$$\lambda_1^2=\frac{1}{2}\,[(n_2m_1+m_2n_1)i-(n_2l_1+l_2n_1)],$$

$$\lambda_2^2=\frac{1}{2}\,[(l_2l_1-m_2m_1)-(l_2m_1+m_2l_1)i]. \tag{11}$$

Putting Eq. (4) into Eq. (10) we obtain the polarization dependence expression for second-order two-photon transition intensities

$$(\alpha_{21})^{2\mathrm{nd}}=\sum_{t=0}^{2}\ \sum_{q=-t}^{t}\ \lambda_q^tF_t\mathbf{U}_q^{(t)}. \tag{12}$$

Equation (10) is the most general polarization dependence expression of two-photon transition intensities between Stark levels. For clarity purpose we will use the symbol α_q^t to denote the matrix element of the irreducible scattering tensor $\alpha_q^{(t)}$. For a particular transition between Stark levels only certain α_q^t are nonzero, according to the Raman activity of the group corresponding to the Stark levels.[58,59] In particular, the following comments apply. First, since $\alpha_0^{(0)}$ is proportional to $\mathbf{U}_0^{(0)}$ in the second-order approximation, where $\mathbf{U}_0^{(0)}$ is a number operator proportional to $-N/(14)^{1/2}$ for the f^N configuration, α_0^0 is exactly zero for different initial and final states used in Raman transitions. We therefore will omit all α_0^0's for second-order calculations. Secondly, in the case of TPA where the two beams come from the same source, the $\alpha_q^{(1)}$ terms vanish.

Table I gives the angular dependence functions for ERS and TPA transitions for all 32 crystallographic point groups. In Table I, we have labeled the irreducible representations by the usual symbols for molecular representations, in order to facilitate comparison with Bader and Gold.[41] In RE intensity calculations, however, the irreducible representations of a point group G often appear[60] as Γ_i, where i denotes the ith representation of group G. Only transitions of the type $\Gamma_1\leftrightarrow\Gamma_j$, where Γ_1 is the totally symmetric representation and Γ_j any irreducible representation, are considered. Other transitions can be calculated using the fact that the triple product $\Gamma_{\psi_i^*}\otimes\Gamma_{\alpha_{21}}\otimes\Gamma_{\psi_f}$ of any of the 32 point groups must contain the totally symmetric representation. The three terms appearing in the triple product are the irreducible representations of the initial state, the Raman tensor, and the final state. For a transition to an n fold degenerate level the total intensity is proportional to the sum of the squares of each scattering amplitude corresponding to each degenerate state. In Table I only contributions from one of the degenerate levels is listed. The total contribution is the sum of each contribution coming from one of the **n** fold degenerate levels. If the states of these levels are Kramers states, the two-photon contribution from an initial Kramers state (Ψ_i) to a final Kramers state (Ψ_f) is different from the two-photon contribution from (Ψ_i) to the Kramers conjugate state of the final state (Ψ_f^K), i.e., $|\alpha_{21}(\Psi_i\rightarrow\Psi_f)|^2\neq|\alpha_{21}(\Psi_i\rightarrow\Psi_f^K)|^2$; the two-photon contribution from Ψ_i to Ψ_f is, however, exactly equal to the two-photon contribution from Ψ_i^K to Ψ_f^K, i.e., $|\alpha_{21}(\Psi_i\rightarrow\Psi_f)|^2=|\alpha_{21}(\Psi_i^K\rightarrow\Psi_f^K)|^2$. For transitions between non-Kramers state, the TPA contributions from a singlet (Ψ_i) to each state of a doubly degenerate level (Ψ_{fx} or Ψ_{fy}) are equal,[61] i.e., $|\alpha_{21}(\Psi_i\rightarrow\Psi_{fx})|^2=|\alpha_{21}(\Psi_i\rightarrow\Psi_{fy})|^2$.

It can be noted that Table I agrees with Bader and Gold,[41] since the expression for the polarization dependence of the intensities of transitions between Stark levels only depends on the Cartesian Raman tensors and their corresponding irreducible spherical tensors whose nonzero values are predicted by group theory. No approximation has been required to derive the relationship between the intensities and the general form of the irreducible spherical Raman tensors $\alpha_q^{(t)}$, which replace the parameters λ_i's in Bader and Gold's theory. The explicit second-order expressions for $\alpha_q^{(t)}$ in Eq. (12), in terms of F_t and $\mathbf{U}_q^{(t)}$, however, are derived using the Judd-Ofelt-Axe theory. Since $\mathbf{U}_q^{(t)}$ can be calculated for a particular transition, the expression for the intensities for two photon processes in terms of F_1 provides a stringent test for the Axe theory. In the case of TPA from the same source only F_2 would appear in the expression for intensities. Thus relative intensities between Stark levels can be calculated and compared with experimental values. For a single two-photon transition the polarization dependence of the intensities on θ and φ can be directly compared with experimental data.

Another test for the second-order theory of Axe may come from the ratio F_1/F_2, as first demonstrated by Becker *et al.* in the case of $TmPO_4$ and $ErPO_4$.[53] Using Cartesian coordinates it is common to obtain ERS intensities corresponding to at most four polarization states. Asymmetry[50]

TABLE I. Angular-dependence functions for RE ERS and TPA transitions. The symbols are defined in the text.

$C_1 \quad C_i$	
$A\leftrightarrow A \;\; A_g\leftrightarrow A_g$	$\Big\|\Big(-\frac{1}{\sqrt{3}}\Big)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\Big(-\frac{1}{\sqrt{6}}\Big)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2 + \tfrac{1}{2}[(n_2m_1+m_2n_1)i-(n_2l_1+l_2n_1)]\alpha_1^2+\tfrac{1}{2}[(n_2m_1+m_2n_1)i+(n_2l_1+l_2n_1)]\alpha_{-1}^2 + \tfrac{1}{2}[(l_2l_1-m_2m_1)-(l_2m_1+m_2l_1)i]\alpha_2^2+\tfrac{1}{2}[(l_2l_1-m_2m_1)+(l_2m_1+m_2l_1)i]\alpha_{-2}^2 + \frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1+\tfrac{1}{2}[(m_2n_1-n_2m_1)i+(n_2l_1-l_2n_1)]\alpha_1^1 + \tfrac{1}{2}[(-m_2n_1+n_2m_1)i+(n_2l_1-l_2n_1)]\alpha_{-1}^1\Big\|^2$
$C_2 \quad C_s \quad C_{2h}$	
$A\leftrightarrow A \;\; A\leftrightarrow A \;\; A_g\leftrightarrow A_g$	$\Big\|\Big(-\frac{1}{\sqrt{3}}\Big)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\Big(-\frac{1}{\sqrt{6}}\Big)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2 + \frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1+\tfrac{1}{2}[(l_2m_1+m_2l_1)i](\alpha_{-2}^2-\alpha_2^2)+\tfrac{1}{2}[l_2l_1+m_2m_1](\alpha_{-2}^2+\alpha_2^2)\Big\|^2$
$A\leftrightarrow B \;\; A'\leftrightarrow A'' \;\; A_g\leftrightarrow B_g$	$\Big\|n_2m_1\Big(\frac{\alpha_1^2-\alpha_1^1}{2}\Big)+m_2n_1\Big(\frac{\alpha_1^2+\alpha_1^1}{2}\Big)\Big\|^2+\Big\|n_2l_1\Big(\frac{\alpha_1^2-\alpha_1^1}{2}\Big)+l_2n_1\Big(\frac{\alpha_1^2+\alpha_1^1}{2}\Big)\Big\|^2 + \Big\|n_2m_1\Big(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\Big)+m_2n_1\Big(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\Big)\Big\|^2+\Big\|n_2l_1\Big(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\Big)+l_2n_1\Big(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\Big)\Big\|^2$
C_3, C_{3i}	
$A\leftrightarrow A$	$\Big\|-\Big(\frac{1}{\sqrt{3}}\Big)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\Big(-\frac{1}{\sqrt{6}}\Big)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2+\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1\Big\|^2$
$A\leftrightarrow E$	$\|\tfrac{1}{2}[n_2l_1-l_2n_1](\alpha_{-1}^1+\alpha_1^1)+\tfrac{1}{2}[\dot{n}_2l_1+l_2n_1](\alpha_{-1}^2-\alpha_1^2) + \tfrac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\|^2+\|\tfrac{1}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_{-2}^2) + \tfrac{1}{2}[n_2m_1-m_2n_1](\alpha_{-1}^1-\alpha_1^1)+\tfrac{1}{2}[n_2m_1+m_2n_1](\alpha_1^2+\alpha_{-1}^2)\|^2$
C_4, C_{4h}, S_4	
$A\rightarrow A$	$\Big\|\Big(-\frac{1}{\sqrt{3}}\Big)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\Big(-\frac{1}{\sqrt{6}}\Big)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2+\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1\Big\|^2$
$A\leftrightarrow B$	$\|\tfrac{1}{2}[(l_2l_1-m_2m_1)-(l_2m_1+m_2l_1)i]\alpha_2^2+\tfrac{1}{2}[(l_2l_1-m_2m_1)+(l_2m_1+m_2l_1)i]\alpha_{-2}^2\|^2$
$A\leftrightarrow E$	$\Big\|n_2m_1\Big(\frac{\alpha_1^2-\alpha_1^1}{2}\Big)+m_2n_1\Big(\frac{\alpha_1^2+\alpha_1^1}{2}\Big)\Big\|^2+\Big\|n_2l_1\Big(\frac{\alpha_1^2-\alpha_1^1}{2}\Big)+l_2n_1\Big(\frac{\alpha_1^2+\alpha_1^1}{2}\Big)\Big\|^2 + \Big\|n_2m_1\Big(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\Big)+m_2n_1\Big(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\Big)\Big\|^2+\Big\|n_2l_1\Big(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\Big)+l_2n_1\Big(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\Big)\Big\|^2$
$C_{3h} \;\; C_6(C_{6h})$	
$A'\leftrightarrow A' \;\; A\leftrightarrow A$	$\Big\|\Big(-\frac{1}{\sqrt{3}}\Big)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\Big(-\frac{1}{\sqrt{6}}\Big)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2+\frac{i}{2}[m_2l_1-l_2m_1\alpha_0^1\|^2$
$A'\leftrightarrow E' \;\; A\leftrightarrow E_1$	$\|\tfrac{1}{2}(l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\|^2+\|\tfrac{1}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_2^2)\|^2$
$A'\leftrightarrow E' \;\; A\leftrightarrow E_2$	$\Big\|n_2m_1\Big(\frac{\alpha_1^2-\alpha_1^1}{2}\Big)+m_2n_1\Big(\frac{\alpha_1^2+\alpha_1^1}{2}\Big)\Big\|^2+\Big\|n_2l_1\Big(\frac{\alpha_1^2-\alpha_1^1}{2}\Big)+l_2n_1\Big(\frac{\alpha_1^2+\alpha_1^1}{2}\Big)\Big\|^2 + \Big\|n_2m_1\Big(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\Big)+m_2n_1\Big(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\Big)\Big\|^2+\Big\|n_2l_1\Big(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\Big)+l_2n_1\Big(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\Big)\Big\|^2$

TABLE I. (*Continued*).

$C_{2\nu}$ D_2 $D_{2h}(D_{2h}=D_2xC_i)$	
$A_1\leftrightarrow A_1$ $A\leftrightarrow A$	$\left\lvert\left(-\frac{1}{\sqrt{3}}\right)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\left(-\frac{1}{\sqrt{6}}\right)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2\right.$ $\left.+\tfrac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\right\rvert^2$
$A_1\leftrightarrow A_2$ $A\leftrightarrow B_1$	$\lvert\tfrac{1}{2}[m_2l_1-l_2m_1]\alpha_0^1+\tfrac{1}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_2^2)\rvert^2$
$A_1\leftrightarrow B_1$ $A\leftrightarrow B_2$	$\lvert\tfrac{1}{2}[n_2l_1+l_2n_1](\alpha_{-1}^2-\alpha_1^2)+\tfrac{1}{2}[n_2l_1-l_2n_1](\alpha_1^1+\alpha_{-1}^1)\rvert^2$
$A_1\leftrightarrow B_2$ $A\leftrightarrow B_3$	$\lvert-\tfrac{1}{2}[n_2m_1+m_2n_1](\alpha_1^2+\alpha_{-1}^2)+\tfrac{1}{2}[m_2n_1-n_2m_1](\alpha_1^1-\alpha_{-1}^1)\rvert^2$
D_3, $C_{3\nu}$, $D_{3d}(D_{3d}=D_2xC_i)$	
$A_1\leftrightarrow A_1$	$\left\lvert\left(-\frac{1}{\sqrt{3}}\right)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\left(-\frac{1}{\sqrt{6}}\right)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2\right\rvert^2$
$A_1\leftrightarrow A_2$	$\left\lvert\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1\right\rvert^2$
$A_1\leftrightarrow E$	$\lvert\tfrac{1}{2}[n_2l_1-l_2n_1](\alpha_{-1}^1+\alpha_1^1)+\tfrac{1}{2}[n_2l_1+l_2n_1](\alpha_{-1}^2-\alpha_1^2)$ $+\tfrac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\rvert^2+\lvert\tfrac{1}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_2^2)$ $+\tfrac{1}{2}[n_2m_1-m_2n_1](\alpha_{-1}^1-\alpha_1^1)+\tfrac{1}{2}[n_2m_1+m_2n_1](\alpha_1^2+\alpha_{-1}^2)\rvert^2$
$D_4, C_{4\nu}, D_{2d}$, $D_{4h}(D_{4h}=D_4xC_i)$	
$A_1\leftrightarrow A_1$	$\left\lvert\left(-\frac{1}{\sqrt{3}}\right)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\left(-\frac{1}{\sqrt{6}}\right)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2\right\rvert^2$
$A_1\leftrightarrow A_2$	$\left\lvert\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1\right\rvert^2$
$A_1\leftrightarrow B_1$	$\lvert\tfrac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\rvert^2$
$A_1\leftrightarrow B_2$	$\lvert-\frac{i}{2}[l_2m_1+m_2l_1](\alpha_2^2-\alpha_{-2}^2)\rvert^2$
$A_1\leftrightarrow E$	$\left\lvert n_2m_1\left(\frac{\alpha_1^2-\alpha_1^1}{2}\right)+m_2n_1\left(\frac{\alpha_1^2+\alpha_1^1}{2}\right)\right\rvert^2+\left\lvert n_2l_1\left(\frac{\alpha_1^2-\alpha_1^1}{2}\right)+l_2n_1\left(\frac{\alpha_1^2+\alpha_1^1}{2}\right)\right\rvert^2$ $+\left\lvert n_2m_1\left(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\right)+m_2n_1\left(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\right)\right\rvert^2+\left\lvert n_2l_1\left(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\right)+l_2n_1\left(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\right)\right\rvert^2$
$D_5, C_{5\nu}$ $D_{5h}(D_{5h}=D_5xC_i)$, $D_6, C_{6\nu}$ D_{3h} $D_{6h}(D_{6h}=D_6xC_i)$ D_{4d}	
$A_1\leftrightarrow A_1$ $A_1'\leftrightarrow A_1'$ $A_1\leftrightarrow A_1$	$\left\lvert\left(-\frac{1}{\sqrt{3}}\right)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0+\left(-\frac{1}{\sqrt{6}}\right)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2\right\rvert^2$
$A_1\leftrightarrow A_2$ $A_1'\leftrightarrow A_2'$ $A_1\leftrightarrow A_2$	$\left\lvert\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1\right\rvert^2$
$A_1\leftrightarrow E_1$ $A_1\leftrightarrow E'$ $A_1'\leftrightarrow E_3$	$\left\lvert n_2m_1\left(\frac{\alpha_1^2-\alpha_1^1}{2}\right)+m_2n_1\left(\frac{\alpha_1^2+\alpha_1^1}{2}\right)\right\rvert^2+\left\lvert n_2l_1\left(\frac{\alpha_1^2-\alpha_1^1}{2}\right)+l_2n_1\left(\frac{\alpha_1^2+\alpha_1^1}{2}\right)\right\rvert^2$ $+\left\lvert n_2m_1\left(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\right)+m_2n_1\left(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\right)\right\rvert^2+\left\lvert n_2l_1\left(\frac{\alpha_{-1}^2+\alpha_{-1}^1}{2}\right)+l_2n_1\left(\frac{\alpha_{-1}^2-\alpha_{-1}^1}{2}\right)\right\rvert^2$

TABLE I. (*Continued*).

$A_1\leftrightarrow E_2$ $A_1\leftrightarrow E'$ $A_1'\leftrightarrow E_2$	$\lvert\frac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\rvert^2+\frac{1}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_2^2)\rvert^2$
$O,Td\,,\quad Oh(Oh=OxCi)$	
$A_1\leftrightarrow A_1$	$\left\lvert\left(-\frac{1}{\sqrt{3}}\right)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0\right\rvert^2$
$A_1\leftrightarrow E$	$\left\lvert\left(-\frac{1}{\sqrt{6}}\right)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2+\frac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\right\rvert^2$
$A_1\leftrightarrow T_1$	$\left\lvert\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1+\frac{i}{2}[m_2n_1-n_2m_1](\alpha_1^1-\alpha_{-1}^1)\right\rvert^2+\lvert\frac{1}{2}[n_2l_1-l_2n_1](\alpha_1^1+\alpha_{-1}^1)\rvert^2$
$A_1\leftrightarrow T_2$	$\left\lvert\frac{i}{2}[n_2m_1+m_2n_1](\alpha_1^2+\alpha_{-1}^2)+\frac{i}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_2^2)\right\rvert^2+\lvert\frac{1}{2}[-(n_2l_1+l_2n_1)](\alpha_1^2-\alpha_{-1}^2)\rvert^2$
T,Th	
$A\leftrightarrow A$	$\left\lvert\left(-\frac{1}{\sqrt{3}}\right)[n_2n_1+m_2m_1+l_2l_1]\alpha_0^0\right\rvert^2$
$A_1\leftrightarrow E$	$\left\lvert\left(-\frac{1}{\sqrt{6}}\right)[-2n_2n_1+m_2m_1+l_2l_1]\alpha_0^2+\frac{1}{2}[l_2l_1-m_2m_1](\alpha_2^2+\alpha_{-2}^2)\right\rvert^2$
$A_1\leftrightarrow T^b$	$\left\lvert\frac{i}{2}[m_2l_1-l_2m_1]\alpha_0^1+\frac{i}{2}[m_2n_1-n_2m_1](\alpha_1^1-\alpha_{-1}^1)\right\rvert^2+\lvert\frac{1}{2}[n_2l_1-l_2n_1](\alpha_1^1+\alpha_{-1}^1)\rvert^2$
$A_1\leftrightarrow T^a$	$\left\lvert\frac{i}{2}[n_2m_1+m_2n_1](\alpha_1^2+\alpha_{-1}^2)+\frac{i}{2}[l_2m_1+m_2l_1](\alpha_{-2}^2-\alpha_2^2)\right\rvert^2+\lvert\frac{1}{2}[-(n_2l_1+l_2n_1)](\alpha_1^2-\alpha_{-1}^2)\rvert^2$

can be measured by the ratio of two of these intensities, I_{XZ} (or I_{YZ}) and I_{ZX} (or I_{ZY}), from which the value of F_1/F_2 can be obtained. From the Raman-scattering intensities of light with incident and scattered polarizations being arbitrarily varied, a better fit for the ratio F_1/F_2 may be obtained. Thus this analysis method should provide a more reliable value for the ratio F_1/F_2.

In general the two-photon scattering tensor α_{21} is related to the irreducible representation of the scattering tensor $\alpha_q^{(t)}$ by the relation

$$(\alpha_{21})=\sum_{t=0}^{2}\sum_{q=-t}^{t}(-1)^{t+q}(\mathbf{e}_2\mathbf{e}_1)_{-q}^{t}(\alpha_q^{(t)}), \tag{13}$$

where $(\mathbf{e}_2\mathbf{e}_1)_{-q}^{t}$ is the coupled form of the polarization unit vectors. Equation (13) can be derived by the use of the standard method of tensor operators.[61]

B. Third-order contribution to intraconfigurational two-photon transition intensities

The line strength of a two-photon transition from an initial state $|i\rangle$ to a final state $|f\rangle$ shown up to the third-order is proportional to

$$\left|-\sum_{i}\frac{(i|\mathbf{E}\cdot\mathbf{D}|j)(j|\mathbf{E}\cdot\mathbf{D}|f)}{E_j}+\sum_{j,k}\frac{(i|\mathbf{V}_1|j)(j|\mathbf{V}_2|k)(k|\mathbf{V}_3|f)}{E_jE_k}-\cdots\right|^2, \tag{14}$$

where E_j and E_k are the average energy of the excited j and k configurations.

Depending on the specific details of the interaction $\mathbf{V}_i$ ($i=1$, 2, or 3) and the initial and final states, expression (14) represents different third-order contributions to the two-photon intensities. If the initial and final states are crystal field states belonging to the $4f^N$ configuration, $\mathbf{V}_1=\mathbf{V}_3=\mathbf{E}\cdot\mathbf{D}$, and $\mathbf{V}_2=\mathbf{H}_{SO}$, expression (14) represents the third-order spin-orbit contribution. If $\mathbf{V}_2=\mathbf{H}_{\mathrm{CF}}$, however, the third-order contribution comes from the interaction between intermediate configurations via the crystal-field potential. When the wave functions i, j, k, and f are products of lanthanide and ligand wave functions, and $\mathbf{V}_2=\mathbf{H}_C$, where $\mathbf{H}_C$ is the Coulomb interaction between the electrons in the lanthanide ion and the ligand excited states, expression (14) represents the ligand-polarization third-order contribution.[15–19] This ion-ligand excitation mechanism is called the dynamic mechanism to distinguish it from the static mechanism as it involves ligand excited states. Finally, a third-order contribution can come from electron correlation, if $\mathbf{V}_2 = \mathbf{V}_c^{\text{noncentral}}$, where $\mathbf{V}_c^{\text{noncentral}}$ denotes the noncentral part of the Coulomb interaction:

$$\mathbf{V}_c^{\text{noncentral}} = \mathbf{V}_C - \mathbf{U}, \tag{15}$$

where $\mathbf{U}$ stands for the potential of the central field approximation.

In the independent systems model[15–19] and in the double perturbation model,[20–26] the third-order terms in which $\mathbf{V}_2$ is interchanged with $\mathbf{V}_1$ or $\mathbf{V}_3$ also arise, and the electric dipole operator $\mathbf{E}\cdot\mathbf{D}$ may represent the light-central ion or light-ligand interaction.

1. Spin-orbit interaction

The polarization dependence of the two-photon scattering amplitude can be expressed in third order:

$$(\alpha_{21})^{3\text{rd}} = \sum_{t=0}^{2} \sum_{q=-t}^{t} \lambda_q^t (\alpha_q^{(t)})^{3\text{rd}}, \tag{16}$$

The explicit tensor form for the third-order spin orbit interaction has been given by Judd and Pooler,[10] Downer and Bivas,[11] and Ceulemans and Vandenberghe.[14] Its corresponding irreducible tensor form is given by

$$(\alpha_q^{(t)})^{3\text{rd}} = H(t)(\mathbf{a}^\dagger\mathbf{a})_q^{(0t)t}(\mathbf{a}^\dagger\mathbf{a})^{(11)0} + \sum_{\lambda} G(t,\lambda)(\mathbf{a}^\dagger\mathbf{a})_q^{(1\lambda)t}, \tag{17}$$

where $\mathbf{a}^\dagger,\mathbf{a}$ represent creation and annihilation tensors, and $H(t)$ and $G(t,\lambda)$ are defined by

$$H(t) = 3(-1)^l[l(l+1)(2l+1)]^{1/2} \times \frac{\zeta_l(nl|r|nl')^2}{E_{l'l}^2} \begin{Bmatrix} 1 & l & l' \\ l & 1 & t \end{Bmatrix} \tag{18}$$

and

$$\begin{aligned} G(t,\lambda) = & -3(-1)'[l(l+1)(l+1/2)]^{1/2} \frac{\zeta_l(nl|r|nl')^2}{E_{l'l}^2} \\ & \times(-1)^{\lambda+1}(2\lambda+1)^{1/2} \begin{Bmatrix} 1 & l & l \\ l & 1 & \lambda \end{Bmatrix} \begin{Bmatrix} 1 & l & l' \\ l & 1 & t \end{Bmatrix}, \\ & -3(-1)^t[l'(l'+1)(l'+1/2)]^{1/2} \frac{\zeta_{l'}(nl|r|nl')^2}{E_{l'l}^2} \\ & \times(-1)^{\lambda+1}(2\lambda+1)^{1/2} \begin{Bmatrix} 1 & l & l' \\ 1 & l & l' \\ t & \lambda & 1 \end{Bmatrix}. \end{aligned} \tag{19}$$

In expressions (17)–(19) the only nonvanishing terms occur for $t=0$, 1, and 2 and for $\lambda=1$, 2, and 3, and ζ_l, $\zeta_{l'}$ are the spin-orbit coupling constants for l and l' electrons, respectively.

Since the third order spin-orbit contribution to two-photon intensities can be expressed in terms of the second rank irreducible tensor form, with the same polarization dependent coefficients as the second-order contribution, one can just add the results for α_q^t calculated in the third order into the second-order results in Eq. (12) and square the resulting total amplitude $(\alpha_{21})^{\text{total}}$ to obtain the TPA transition intensities calculated up to the third order involving spin-orbit coupling. Note from expression (17), because of the presence of the operator $(\mathbf{a}^\dagger\mathbf{a})^{(11)0}$, the scattering tensor $\alpha_0^{(0)}$ is not a scalar, and its corresponding matrix elements are no longer identically zero for distinct initial and final states as in the case of the second order theory. One must include the $\alpha_0^{(0)}$ term in the third-order calculation in order to obtain meaningful results.

2. Crystal-field interaction

The original expression for the third-order TPA tensor operator involving crystal-field interaction has been developed by Downer and co-workers[12,13] and is given by

$$\begin{aligned} & -(-1)^{l+l'}[(2l+1)(2l'+1)^2] \frac{(nl|r|nl')^2}{\sqrt{2}E_{l'l}^2} \\ & \times\begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{t,k,h} (-1)^k(2k+1)^{1/2}(2t+1)^{1/2} \\ & \times\begin{pmatrix} l' & h & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l & 1 & l' \\ h & l' & k \end{Bmatrix} \begin{Bmatrix} 1 & l & l' \\ l & k & t \end{Bmatrix} \\ & \times[\mathbf{e}_2^{(1)}(B^{(h)}\mathbf{e}_1^{(1)})^{(k)}]^{(t)}\cdot(\mathbf{U})^{(t)}, \end{aligned} \tag{20}$$

where h,k,t are tensor ranks and $B^{(h)}$ is the crystal field tensor corresponding to the third-order crystal field interaction acting between excited configurations $|j\rangle$ and $|k\rangle$ in expressions (14).

As can be seen from expression (20); the crystal field tensor operator $B^{(h)}$ is coupled to the electric field vectors. By further recoupling the electric field tensors, Ceulemans and Vandenberghe have obtained an expression in which the electric field tensors are directly coupled and all the $6-j$ symbols are combined into a single $9-j$ symbol.[14] We will, however, consider only the special case of Downer's expression in which the only crystal-field term appearing in Eq. (20) is the fourth rank crystal field term $B_0^{(4)}$. Putting $k=5$, $t=6$, $h=4$, $l=3$, and $l'=2$, the polarization dependent form for the crystal-field third-order contribution is given by

$$\begin{aligned} & B_0^{(4)} \frac{1}{3\sqrt{11}} \{\sqrt{14}\lambda_{-2}^2\mathbf{U}_{-2}^{(6)} + \sqrt{35}\lambda_{-1}^2\mathbf{U}_{-1}^{(6)} + 3\sqrt{5}\lambda_0^2\mathbf{U}_0^{(6)} \\ & + \sqrt{35}\lambda_1^2\mathbf{U}_1^{(6)} + \sqrt{14}\lambda_2^2\mathbf{U}_2^{(6)}\}, \end{aligned} \tag{21}$$

where λ_q^t's are defined in Eq. (11).

The crystal-field third-order contribution is proportional to $(10/33)^{1/2}\langle i|\mathbf{U}_0^{(6)}|f\rangle$ and $(14/99)^{1/2}\langle i|\mathbf{U}_{-2}^{(6)}|f\rangle$ for parallel and circular polarization, respectively. For the ${}^8S_{7/2}\rightarrow{}^6I_J$ transitions in Gd^{3+}:LaF_3, the ratio of the integrated two-photon line strength corresponding to parallel polarization to that corresponding to circular polarization is 15/7, in exact agreement with Downer *et al.*[13]

C. Third-order contribution to interconfigurational two-photon absorption transition intensities

The theory of static and dynamic contributions to the two-photon f-d transitions has been developed by Leavitt,[32] Daoud and Kibler,[37,39] and Sztucki and Strek.[18] Their polarization dependent expressions can be derived by using methods described in the previous section. Applications of Leavitt's and Sztucki and Strek's theories in the case of $4f\rightarrow 5d$ two-photon transition in Ce^{3+}:CaF_2 are given in the examples section.

D. Relative magnitude of higher-order contributions to second-order contribution

We finally consider the relative magnitude of the third- (or higher) order contribution to the second-order contribution. Using the intermediate coupling states we have

$$\frac{\langle\Psi|(\alpha_q^{(t)})^{n\mathrm{th}}|\Psi'\rangle}{\langle\Psi|(\alpha_q^{(t)})^{2\mathrm{nd}}|\Psi'\rangle}=\frac{\Sigma_{SLJ,S'L'J'}a(SLJM)a'(S'L'J'M')\begin{pmatrix} J & t & J'\\ -M & q & M'\end{pmatrix}(-1)^{(J-M)}\langle SLJ\|(\alpha^{(t)})^{n\mathrm{th}}\|S'L'J'\rangle}{\Sigma_{SLJ,S'L'J'}a(SLJM)a'(S'L'J'M')\begin{pmatrix} J & t & J'\\ -M & q & M'\end{pmatrix}(-1)^{(J-M)}\langle SLJ\|(\alpha^{(t)})^{2\mathrm{nd}}\|S'L'J'\rangle},\tag{22}$$

where nth can be 3rd, 4th, or any higher order contribution taken into account.

If the SLJ mixing are negligible for the states Ψ and Ψ' the coefficients $a(SLJM)$ and $a'(S'L'J'M')$ are functions of J and M, i.e., $a(SLJM)=a(JM)$, $a'(S'L'J'M')=a'(J'M')$. We then have

$$\begin{aligned}\frac{\langle\Psi|(\alpha_q^{(t)})^{n\mathrm{th}}|\Psi'\rangle}{\langle\Psi|(\alpha_q^{(t)})^{2\mathrm{nd}}|\Psi'\rangle}&=\frac{\langle SLJ\|(\alpha^{(t)})^{n\mathrm{th}}\|S'L'J'\rangle\Sigma_{SLJ,S'L'J'}a(JM)a'(J'M')\begin{pmatrix} J & t & J'\\ -M & q & M'\end{pmatrix}(-1)^{(J-M)}}{\langle SLJ\|(\alpha^{(t)})^{2\mathrm{nd}}\|S'L'J'\rangle\Sigma_{SLJ,S'L'J'}a(JM)a'(J'M')\begin{pmatrix} J & t & J'\\ -M & q & M'\end{pmatrix}(-1)^{(J-M)}}\\&=\frac{\langle SLJ\|(\alpha^{(t)})^{n\mathrm{th}}\|S'L'J'\rangle}{\langle SLJ\|(\alpha^{(t)})^{2\mathrm{nd}}\|S'L'J'\rangle},\end{aligned}\tag{23}$$

which is independent of q. For a TPA process with a single laser excitation wavelength, $\alpha_q^{(1)}$ vanishes, and $\alpha_0^{(0)}$ also vanishes if J' is different from J. In this case the polarization dependence and relative amplitudes of TPA Stark intensities, which now depend only on α_q^2, would not change when higher order contribution were included. We now apply the polarization dependence theory into a number of cases including intra- and interconfigurational TPA.

III. EXAMPLES

A. Intraconfigurational TPA—application to Sm^{2+} in BaClF

In the second-order approximation the polarization dependence functions of the TPA intensities are expressed in terms of $\alpha_q^{(t)}$'s, which can be further evaluated in terms of the parameters F_t's when one applies equations (5)–(9) to a particular TPA transition. The final polarization dependence functions are thus expressed in terms of the parameter F_t's and can be compared directly with observed data. We now apply formulae (8) and (9) to the transition ${}^7F_0\rightarrow{}^5D_2$ for Sm^{2+} in BaClF (C_{4v} site symmetry). Using the crystal-field parameters given by Gâcon *et al.*,[46] we can obtain the crystal-field wave functions and coefficients for the initial and final states.

The initial state, which is the ground state, can be expressed as[62]

$$|\Gamma_1\rangle=0.97\ {}^7F(0,0)-0.17\ {}^5D1(0,0),\tag{24}$$

where we have used the ${}^{2S+1}\mathrm{Li}(J,J_z)$ notation.

The final states are

$$\begin{aligned}|\Gamma_1\rangle&=-0.74[{}^5D3(2,0)]+0.6[{}^5D1(2,0)],\\|\Gamma_3\rangle&=-0.74\left[\frac{1}{\sqrt{2}}\,{}^5D3(2,2)+\frac{1}{\sqrt{2}}\,{}^5D3(2,-2)\right]\\&\quad+0.6\left[\frac{1}{\sqrt{2}}\,{}^5D1(2,2)+\frac{1}{\sqrt{2}}\,{}^5D1(2,-2)\right],\\|\Gamma_4\rangle&=-0.74\left[-\frac{1}{\sqrt{2}}\,{}^5D3(2,2)+\frac{1}{\sqrt{2}}\,{}^5D3(2,-2)\right]\\&\quad+0.6\left[-\frac{1}{\sqrt{2}}\,{}^5D1(2,2)+\frac{1}{\sqrt{2}}\,{}^5D1(2,-2)\right],\\|\Gamma_{5x}\rangle&=-0.74[-{}^5D3(2,1)]+0.6[-{}^5D1(2,1)]\\|\Gamma_{5y}\rangle&=-0.74[-{}^5D3(2,-1)]+0.6[-{}^5D1(2,-1)],\end{aligned}\tag{25}$$

where Γ_{5x} and Γ_{5y} are the two components of the doubly degenerate Γ_5 states.

For $\mathrm{Sm}^{2+}(4f^6)$ the nonzero values of α_q^t are given by

$$\langle\Gamma_1|\alpha_0^{(2)}|\Gamma_1\rangle=\frac{0.079}{5}F_2,$$

$$\langle \Gamma_1 | \alpha^{(2)}_{\pm 2} | \Gamma_3 \rangle = \frac{0.079}{5\sqrt{2}} F_2,$$

$$\langle \Gamma_1 | \Gamma^{(2)}_{\pm 2} | \Gamma_4 \rangle = \mp \frac{0.079}{5\sqrt{2}} F_2,$$

$$\langle \Gamma_1 | \alpha^{(2)}_{1} | \Gamma_{5x} \rangle = \langle \Gamma_1 | \alpha^{(2)}_{-1} | \Gamma_{5y} \rangle = -\frac{0.079}{5} F_2. \qquad (26)$$

Equation (14) can be rewritten for the case of TPA from the same source:

$$\alpha_{21}^{\mathrm{TPA}} = \left(\frac{3\cos^2\theta - 1}{\sqrt{6}} \right) \alpha_0^{(2)} - \left(\frac{e^{-i\varphi}}{2} \sin 2\theta \right) \alpha_1^{(2)} + \left(\frac{e^{i\varphi}}{2} \sin 2\theta \right) \alpha_{-1}^{(2)} + \left(\frac{e^{-2i\varphi}}{2} \sin^2\theta \right) \alpha_2^{(2)} + \left(\frac{e^{2i\varphi}}{2} \sin^2\theta \right) \alpha_{-2}^{(2)}, \qquad (27)$$

$$\langle \Gamma_1 | \alpha_{21} | \Gamma_1 \rangle = \frac{a_2}{\sqrt{3}} (3\cos^2\theta - 1),$$

$$\langle \Gamma_1 | \alpha_{21} | \Gamma_3 \rangle = a_2 \sin^2\theta \cos 2\varphi,$$

$$\langle \Gamma_1 | \alpha_{21} | \Gamma_4 \rangle = i a_2 \sin^2\theta \sin 2\varphi,$$

$$\langle \Gamma_1 | \alpha_{21} | \Gamma_{5x} \rangle = \frac{a_2}{\sqrt{2}} (\sin 2\theta) e^{-i\varphi},$$

$$\langle \Gamma_1 | \alpha_{21} | \Gamma_{5y} \rangle = -\frac{a_2}{\sqrt{2}} (\sin 2\theta) e^{i\varphi}, \qquad (28)$$

$$\text{where } a_2 = \frac{0.079}{5\sqrt{2}} F_2. \qquad (29)$$

The angular dependence of the TPA line strengths can be expressed in terms of the overall strength S_0 of the ${}^7F_0 \rightarrow {}^5D_2$ two-photon transition,

$$S(\Gamma_1 \rightarrow \Gamma_1) = \tfrac{1}{3} S_0 (3\cos^2\theta - 1)^2$$

$$S(\Gamma_1 \rightarrow \Gamma_3) = S_0 \sin^4\theta \cos^2 2\varphi$$

$$S(\Gamma_1 \rightarrow \Gamma_4) = S_0 \sin^4\theta \sin^2 2\varphi$$

$$S(\Gamma_1 \rightarrow \Gamma_5) = S(\Gamma_1 \rightarrow \Gamma_{5x}) + S(\Gamma_1 \rightarrow \Gamma_{5y}) = S_0 \sin^4 2\theta. \qquad (30)$$

Note that we can equivalently obtain Eq. (30) by using Table I for the case of C_{4v} and substitute the nonvanishing values of $\alpha_q^{(t)}$ given in Eq. (26) into the polarization functions for each two-photon transition. Table I is particularly useful when the intermediate coupling coefficients of the wavefunctions for the initial and final states are unknown. Once these coefficients are obtained, and the corresponding $\alpha_q^{(t)}$'s are determined, the master formula (10) can be used instead. The results in Eq. (30) are identical with those of Gâcon *et al.*,[46] which were shown to agree well with experiment. As pointed out by Gâcon *et al.*, the results given in Eq. (30) agree with the results of Bader and Gold and, furthermore, complete their results.

B. Interconfigurational TPA—application to Ce^{3+}:CaF_2

Table I and Eq. (10) can be used to calculate the dependence of the TPA cross section on the directions of the electric field vector $\hat{\mathbf{e}}$ and the wave vector $\mathbf{k}$ of the incident laser beam. For the Ce^{3+} ion in CaF_2 with site symmetry C_{4v}, only α_0^0, α_0^2, and α_1^2 (or α_{-1}^2) are nonzero for a TPA transition from the $4f$ ground state (Γ_7) to the lowest $5d$ state (Γ_7). The TPA cross section σ for the corresponding zero-phonon transition is proportional to

$$\left[-\frac{1}{\sqrt{3}} \alpha_0^0 + \left(\frac{3\cos^2\theta - 1}{\sqrt{6}} \right) \alpha_0^2 \right]^2 + \left[\left(\frac{e^{-i\varphi}}{2} \sin 2\theta \right) \alpha_1^2 \right]^2. \qquad (31)$$

For the case where $\mathbf{k} \| [100]$ and $\hat{\mathbf{e}} \| [010]$ we have

$$\sigma \propto 1 + C \sin^2 2\theta, \qquad (32)$$

$$\text{where } C = (2b - 1/2)/(3a^2 - 2a + 1), \qquad (33)$$

$$\text{with } a = \frac{1}{3} + \frac{\sqrt{2}}{3} \frac{\alpha_0^0}{\alpha_0^2} \quad \text{and } b = \frac{1}{6} \left(\frac{\alpha_1^2}{\alpha_0^2} \right)^2. \qquad (34)$$

Similarly, we obtain

$$\sigma \propto 1 + \frac{3C}{4} \sin^2 2\theta + C \sin^2\theta \quad \text{for the case where } \mathbf{k} \| [110] \text{ and } \hat{\mathbf{e}} \| [001], \qquad (35)$$

and

$$\sigma \propto 1 + C \quad \text{for the case where } \mathbf{k} \| [111] \text{ and } \hat{\mathbf{e}} \| [110]. \qquad (36)$$

The fitted curves for Eqs. (32), (35), and (36) are shown in Fig. 1. The best fit for C is found to be 1.774. The polarization anisotropy for the case where $\mathbf{k} \| [100]$ and $\hat{\mathbf{e}} \| [010]$ is

$$A = \frac{\sigma(45°) - \sigma(0°)}{\sigma(45°) + \sigma(0°)} = \frac{C}{2 + C}, \qquad (37)$$

is 0.47, in good agreement with the observed value, which is 0.5 in this case.

Note that the fitted formulae (32), (35), and (36) can be equivalently obtained using Bader and Gold's theory.[41] Our expressions (33) and (34), however, facilitate direct calculations for the values of C and A in terms of α_q^t's, which in turn can be evaluated using existing theoretical models. The value for A calculated by Gayen *et al.*[29] is 0.076. Taking into account only the $B_0^{(3)}$ component of the crystal field and ignoring the dynamic effect, Makhanek *et al.*[33] obtained a value of 0.47. Leavitt's calculated value for A is 0.32.[32] Finally, Sztucki and Strek[18] found $A = 0.55$, 0.15, and 0.52 for the static terms proportional to $B_0^{(1)}, B_0^{(3)}$, and the dynamic

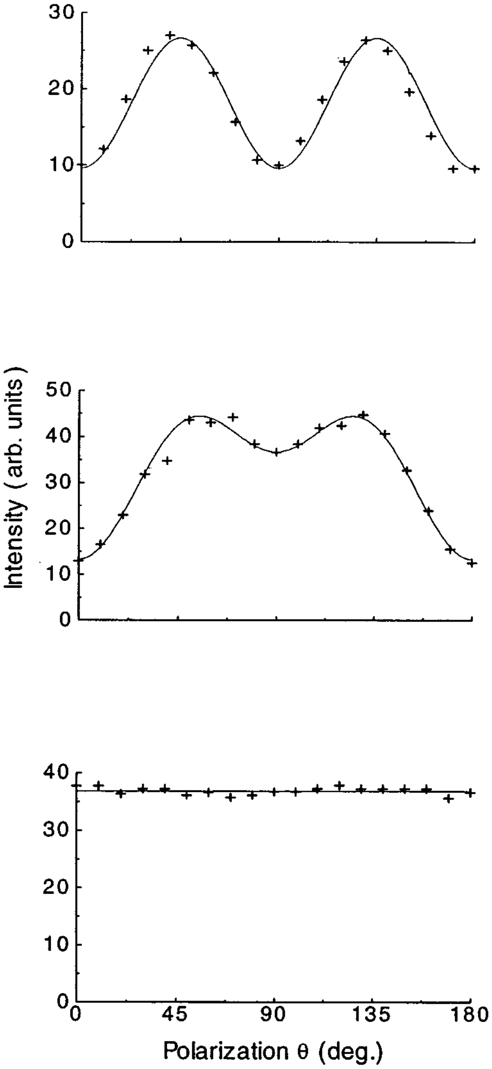

FIG. 1. Polarization dependent behavior of the two-photon cross section for the no-phonon transition of Ce^{3+}:CaF_2 at 6 K. The solid crosses represent the experimental measurements given in Ref. 29 and the solid lines are the fits to the data using the angular functions described in Eqs. (32), (35), and (36).

one, respectively. Our recalculation using Leavitt's model gives A equal to 0.17 and 0.16 for the static and dynamic contributions, respectively. The reason of the discrepancies stem from the fact that the number of α_1^2's was being overcounted in expression (13b) of Ref. 32. This is because α_1^2 and α_{-1}^2 can not be both nonzero in one TPA transition from one component of a Kramers doublet to another. We also found that Sztucki and Strek's model[18] gives A equal to 0.815, 0.51, and 0.16 for the static terms proportional to $B_0^{(1)},B_0^{(3)}$, and the dynamic one, respectively. We conclude that the third-rank component of the crystal field was in fact the dominant term in the TPA transition intensity from the $4f$ ground state to the lowest $5d$ state of the Ce^{3+} ion in CaF_2, as was claimed by Makhanek *et al.*

C. ERS and phonon Raman scattering

As in the case of two-photon absorption, the polarization dependence functions for ERS and phonon intensities are expressed in terms of the nonvanishing values of the matrix elements of the irreducible representation of the scattering tensors, α_q^t. These polarization dependence functions can be directly compared with the observed intensities, from which the fitted values of α_q^t can be obtained. In the ERS case, the more explicit expressions of α_q^t in terms of the parameters F_t, which arise in the second-order theory of Axe, can then be obtained from Eq. (4). In the second-order approximation, the final polarization dependence functions depend only on two parameters, namely, F_1 and F_2, which in general are simpler than the original polarization dependence functions expressed in terms of α_q^t. The simple expressions of the final polarization dependence thus provide a crucial test for Axe's second-order theory. Another sensitive test for Axe's theory come from the ratio F_1/F_2, which can be derived from the ratio α_q^1/α_q^2, obtained from the fit mentioned above. The ratio F_1/F_2 is predicted from the Axe theory to be approximately the same for all ERS transitions of a particular rare-earth ion. Deviation from the value of the ratio F_1/F_2 would provide insight to further revision of the second-order theory of Axe. Examples and applications of the master Eq. (10) in ERS and phonon Raman-scattering processes are given in separate communications, where all the experimental data have been obtained by our group.

IV. SUMMARY

We have proposed a theoretical framework for obtaining the polarization dependence formulae for two-photon transition intensities of rare earths doped in crystals. The theory was developed based on the properties of the irreducible representation of the scattering tensors calculated up to the third order. A table of angular dependence functions for two-photon transitions for 32 crystallographic point groups was given. Our third-order expression for the TPA scattering tensor taking into account the crystal field interaction agrees with Downer *et al.*'s expression for the case of parallel and circular polarization.[13] We have applied our second-order polarization dependence formulae to the $^7F_0\rightarrow{}^5D_2$ TPA transitions of Sm^{3+} in BaClF, and the results are identical with those given by Gacon *et al.*[46] Third-order interconfigurational two-photon absorption was also treated. Its applications in the case of Ce^{3+} in CaF_2 were given. An excellent fit to the experimental polarization dependence curves was obtained. From the fit we have calculated the polarization anisotropy using Sztucki and Strek's model, and we were able to show the dominance of the $4f-5d$ third-rank crystal field term in contributing to the $4f-5d$ TPA amplitude in the case of Ce^{3+} in CaF_2, which was in agreement with Makhanek *et al.*[33]

The properties of the irreducible scattering tensor $\alpha_q^{(t)}$, have been exploited to derive the relationship between the two-photon scattering tensor α_{21} and the coupled form of the unit polarization vectors $(e_2e_1)^{(t)}$. This relationship has been particularly useful in deriving the explicit expression for the intraconfigurational two-photon amplitude including the Judd-Ofelt-Axe's second-order term,[2–4] Judd-Pooler's third-order spin-orbit term,[10] Downer-Bivas's third-order crystal field term,[11–13] as well as the interconfigurational TPA amplitude using models given by Leavitt,[32] and Sztucki and

Strek.[18] The relative magnitude of higher order contributions to the second-order contribution was also discussed based on the properties of $\alpha_q^{(t)}$ and the Wigner-Eckart theorem.

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[57] Note the compact expression of the irreducible representation of the Raman-scattering tensor. In order to obtain this compact form, a factor $(-1)^t$ is present in the expression for F_t. Leaving out this factor in the expression for F_t has led to a sign error for the ratio F_1/F_2 in several papers written by Smentek-Mielczarek.[22–24] The derivation for expression (12) can be found in Becker's thesis,[52] in which Becker made an error in expression (3.42), which is equivalent to Eq. (8) of this paper. In (3.42), $(\mathbf{e}_2\mathbf{e}_1)^t$ was given as $(\mathbf{e}_1\mathbf{e}_2)^t$, which is a factor of $(-1)^t$ different from $(\mathbf{e}_2\mathbf{e}_1)^t$. In expression (3.57), however, Becker made another error, which accidentally cancels out the previous error be made. In expression (3.57), $(\mathbf{e}_2)_{-q}(\mathbf{e}_1)_{-q}$, was written as $(\mathbf{e}_1)_{-q}(\mathbf{e}_2)_{-q}$, where the latter is equal to the former multiplied by a factor of $(-1)^t$.

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