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Analysis of $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ two-photon absorption spectra of Cs_2NaYF_6:Eu^{3+}

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Abstract
The direct calculation of transition line strengths and relative intensities is presented for two intraconfigurational two-photon absorption (TPA) transitions of Eu^{3+} in the cubic Cs_2NaYF_6 host. Crystal field wavefunctions were utilized for the initial and final f^N-electron states and various approaches were used in constructing all the $4f^{N-1}\,5d^1$ intermediate-state wavefunctions. The calculated relative intensities of the $(^7F_0)\ \Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} TPA transitions are in reasonable agreement with experiment. The neglect of J-mixing in the initial state has only a small effect upon the calculation, whereas the neglect of spin–orbit couplings within the initial and terminal states drastically reduces the calculated transition linestrengths, but does not markedly change the intensity ratios. In the case of the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ transitions, serious discrepancies between experiment and theory are found if the intermediate states are constructed from a $4f^5$ core comprising free ion states and the $5d^1$ crystal field states. Satisfactory agreement is, however, found when the $4f^5$ crystal field states are utilized in constructing the intermediate states. The contributions to the transition moment have been evaluated for various Hamiltonian terms and the results are discussed.

1. Introduction

Two-photon absorption (TPA) spectroscopy has emerged as a complementary spectroscopic technique to conventional one-photon spectroscopy in the study of electronic states of rare-earth (RE) ions in crystals. This technique can provide access to higher-energy electronic

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states than one-photon absorption. TPA can also explore transitions that are forbidden in one-photon absorption, since the selection rules for two-photon processes are different from those for one-photon processes.

Analyses of intraconfigurational $4f^N$–$4f^N$ TPA transitions of RE ions in various host crystals have generated much theoretical interest since the standard second-order theory of Judd, Ofelt and Axe (JOA) [1–3] has been proven inadequate to explain many of the observed relative intensities of transitions. Judd and Pooler [4], and Downer and co-workers [5–7], showed that higher orders of perturbation theory (up to fourth order) were able to provide contributions to the TPA intensities that could then fit the experimental data. For example, in the case of Gd^{3+}, the third- and fourth-order contributions were found to be important, including spin–orbit (SO) and crystal field (CF) interactions within the $4f^6 5d$ configuration [6], which is of opposite parity to the $4f^7$ ground configuration and provides the most important virtual intermediate states in the TPA theory.

The direct evaluation of two-photon transition intensities was first put forward by Xia *et al* [8], who performed a direct calculation of the electronic Raman scattering (ERS) intensities of $TmPO_4$, including the detailed energy level structure of the intermediate excited configuration $4f^{11}5d$. Most of the calculated scattering intensities were improved when compared with the standard JOA calculations. Later, Reid and co-workers [9] used a simplified four-state system to demonstrate the equivalence of the direct and the Judd–Pooler-type perturbation calculations in calculating TPA transition intensities, provided that the appropriate eigenstates and eigenvalues were employed. Later, Chua and Tanner [10, 11] employed direct calculation methods to investigate the $(^7F_6)\Gamma_{1g} \rightarrow (^5D_4)\Gamma_{1g}$ TPA transition of Tb^{3+}, and the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_0)\Gamma_{1g}$ TPA transition of Sm^{2+}, with both lanthanide ions being situated at octahedral symmetry sites. It was proposed that the $(^7F_6)\Gamma_{1g} \rightarrow (^5D_4)\Gamma_{1g}$ TPA transition of Tb^{3+} with $\Delta J \neq 0$ is actually a third-order process rather than a fourth-order process. The calculated line strength was found to be sensitive to the location of the intermediate-state energy levels [10]. The dominant pathway of the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_0)\Gamma_{1g}$ transition of Sm^{2+} with $\Delta J = 0$ involves the $4f^{N-1}5d$ intermediate core state ^6H, and the Judd–Pooler calculation became closer in agreement with the direct calculation as the energy barycentre of the $4f^{N-1}5d$ configuration increased [11]. In these direct calculations [10, 11], the pure Russell–Saunders multiplets for the ground- and final-state wavefunctions were employed, thereby neglecting the J-admixtures and SL-admixtures caused by the CF and SO interactions respectively within the ground $4f^N$ configuration. Furthermore, only the lowest-energy intermediate states of the $4f^{N-1}5d$ configuration were considered as intermediate states.

In the present study, a direct TPA calculation has been undertaken by using the exact wavefunctions for the ground and final states of $4f^N$ configuration, and almost exact wavefunctions for the intermediate states of the whole $4f^{N-1}5d$ configuration. Moreover, we are unaware of previous direct calculations of $\Delta S = 1$, ΔL, $\Delta J \geqslant 2$ TPA transition intensities, with the exception of Downer's study [6] of the $^8S \rightarrow {}^6I$ transitions of Gd^{3+} using the method of second quantization. Hence, this stimulated us to investigate this type of transition, and to use it as a test of our calculation methods.

The electronic ground state of Eu^{3+} diluted into the cubic host lattice Cs_2NaYF_6 is $(^7F_0)\Gamma_{1g}$. The detailed energy level scheme has been given in [12]. We have chosen the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ transitions of Eu^{3+} in Cs_2NaYF_6 for our investigation, since the one-colour two-photon excitation (OCTPE) spectra of these two groups of transitions have recently been measured, in the spectral region between 21 000 and 25 000 cm^{-1} [12]. The relative transition intensities between the individual CF levels, in the polarizations of $\theta = 0°$ and $\theta = 45°$ (where θ is the angle between the [100] crystal axis and the unit electric vector of the excitation beam propagating along the [001] crystal

axis), have been determined by integration of the 70 K spectra. The major errors in these experimental intensity ratios result from polarization leakage, and from the choice of baseline for markedly tailing spectral features.

Following the approach used by Xia *et al* [8], we present herein the second-order direct calculations of the above TPA transitions, using the 'exact' eigenfunctions (i.e. including SL-admixtures and J-admixtures) and energies of the states within the ground $4f^6$ configuration, and almost exact eigenfunctions and energies of the intermediate states within the whole intermediate $4f^5 5d$ configuration. This calculation formalism implicitly includes the third-order and even the fourth-order etc calculation as explained in the following section.

2. Theory

TPA transitions within a $4f^N$ configuration involve intermediate states belonging to opposite-parity configurations, i.e. the $4f^{N-1}5d$, $4f^{N+1}4d^9$ and $4f^{N-1}5g$ configurations etc. Since the $4f^{N-1}5d$ configuration lies at a much lower energy than any other opposite-parity configuration, we only consider this configuration in the calculation. Bassani *et al* [13, 14] have discussed the choice of the gauge in two-photon intensity calculations, i.e. whether the 'length' form $(-e\boldsymbol{E}\cdot\boldsymbol{r})$ or the 'velocity' form $(-e(mc)^{-1}\boldsymbol{A}\cdot\boldsymbol{p})$ of the electric dipole interaction Hamiltonian is utilized to calculate the transition rate when only a limited number of intermediate states can be taken into account. Also, Wilse Robinson [15] presented a modified equation in which a unique average-frequency approximation and a sum rule based upon the gauge invariance were used. In the case of the f^N–f^N TPA transitions of RE ions, the electronic states (especially the single-electron 4f orbitals of RE ions in crystals) are localized. Thus, with $\boldsymbol{A}$ and $\boldsymbol{E}$ along the molecular z axis, and with $n'l' = 5d, 5g, 6d, 6g, \ldots$, until the energy continuum, the single-electron radial matrix elements $\langle n'l'|r|4f\rangle$, and therefore the elements $\langle n'l'm'|r_z|4fm\rangle$, converge more rapidly than the elements $\langle n'l'm'|p_z|4fm\rangle$. This is because the localized orbitals, especially the $|4fm\rangle$, contain many momentum eigenfunctions with very different eigenvalues p_z. Therefore, in this paper we choose the 'length' form to perform the calculation, as is usually the case for RE ions, and just as Bassani *et al* [13] chose for the 1s–2s two-photon transition in atomic hydrogen.

The relevant second- (i.e. the lowest-), third- and fourth-order terms for the TPA transition elements $M_{\Gamma_i\gamma_i\to\Gamma_f\gamma_f}$ between the ground state $\Gamma_i\gamma_i$ and the final state $\Gamma_f\gamma_f$ (where γ_i is a component of the irreducible representation Γ_i of the site point group of the RE ion) are as follows, respectively [3–6]:

$$-\sum_n\left[\frac{\langle\Gamma_f\gamma_f|\varepsilon_1\cdot\boldsymbol{D}|n\rangle\langle n|\varepsilon_2\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar(\omega_n-\omega_2)}+\frac{\langle\Gamma_f\gamma_f|\varepsilon_2\cdot\boldsymbol{D}|n\rangle\langle n|\varepsilon_1\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar(\omega_n-\omega_1)}\right] \tag{1}$$

$$\sum_{m,n}\left[\frac{\langle\Gamma_f\gamma_f|\varepsilon_1\cdot\boldsymbol{D}|m\rangle\langle m|V'|n\rangle\langle n|\varepsilon_2\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar^2(\omega_m-\omega_2)(\omega_n-\omega_2)}+\frac{\langle\Gamma_f\gamma_f|\varepsilon_2\cdot\boldsymbol{D}|m\rangle\langle m|V'|n\rangle\langle n|\varepsilon_1\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar^2(\omega_m-\omega_1)(\omega_n-\omega_1)}\right] \tag{2}$$

$$-\sum_{l,m,n}\left[\begin{array}{l}\dfrac{\langle\Gamma_f\gamma_f|\varepsilon_1\cdot\boldsymbol{D}|l\rangle\langle l|V''|m\rangle\langle m|V'|n\rangle\langle n|\varepsilon_2\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar^3(\omega_l-\omega_2)(\omega_m-\omega_2)(\omega_n-\omega_2)}\\ +\dfrac{\langle\Gamma_f\gamma_f|\varepsilon_2\cdot\boldsymbol{D}|l\rangle\langle l|V''|m\rangle\langle m|V'|n\rangle\langle n|\varepsilon_1\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar^3(\omega_l-\omega_1)(\omega_m-\omega_1)(\omega_n-\omega_1)}\\ +\dfrac{\langle\Gamma_f\gamma_f|\varepsilon_1\cdot\boldsymbol{D}|l\rangle\langle l|V'|m\rangle\langle m|V''|n\rangle\langle n|\varepsilon_2\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar^3(\omega_l-\omega_2)(\omega_m-\omega_2)(\omega_n-\omega_2)}\\ +\dfrac{\langle\Gamma_f\gamma_f|\varepsilon_2\cdot\boldsymbol{D}|l\rangle\langle l|V'|m\rangle\langle m|V''|n\rangle\langle n|\varepsilon_1\cdot\boldsymbol{D}|\Gamma_i\gamma_i\rangle}{\hbar^3(\omega_l-\omega_1)(\omega_m-\omega_1)(\omega_n-\omega_1)}\end{array}\right]. \tag{3}$$

In these expressions, $|l\rangle$, $|m\rangle$ and $|n\rangle$ refer to intermediate states within the $4f^{N-1}5d$ configuration; $\hbar\omega_l, \hbar\omega_m$ and $\hbar\omega_n$ are the energies of the corresponding intermediate states above the ground-state energy and $\hbar\omega_1$ and $\hbar\omega_2$ are the photon energies. $V'$and V'' can be the SO or the CF operator, acting between intermediate states. $\varepsilon \cdot \boldsymbol{D}$ is the scalar product of the polarization vector ε of the photon and the electric dipole operator $\boldsymbol{D}$ of the RE ion.

The states and energies in equations (1)–(3) can be eigenstates and eigenvalues of different Hamiltonians in a stationary perturbation treatment, in which the almost complete Hamiltonian is

$$H = H_0 + V \tag{4}$$

where H_0 includes the central field Hamiltonian and the Coulomb interaction between the 4f electrons, whilst the interaction between the $(N-1)$ 4f electrons and the 5d electron for the intermediate configuration $4f^{N-1}5d^1$ should also be included, but is, as usual, ignored in our calculation; and V is the perturbation Hamiltonian, which includes the SO interaction and the CF interaction. The Judd–Pooler-type perturbation calculation [4] (equations (1), (2)) and Judd–Pooler–Downer- (JPD-) type perturbation calculation [6] (equations (1)–(3)) both use eigenstates of the Hamiltonian H within the $4f^N$configuration (like the direct calculation). However, these approaches use eigenstates of only the zeroth-order Hamiltonian within the $4f^{N-1}5d$ configuration, H_0, whilst the relevant energies are approximately taken to be degenerate, by using the closure approximation. By contrast, in the direct calculation, the eigenstates and eigenvalues of the almost complete Hamiltonian, H, are used within the $4f^{N-1}5d$ configuration, as well as within the $4f^N$ configuration, and only the second-order expression of equation (1) needs to be evaluated.

The present study concerns linearly polarized radiation, with polarization vector ε incident upon a single crystal. The TPA transition line strength can be expressed as [16]

$$S_{\Gamma_i \to \Gamma_f} = \sum_{\gamma_i, \gamma_f} |M_{\Gamma_i \gamma_i \to \Gamma_f \gamma_f}|^2. \tag{5}$$

In O_h point group symmetry the electric dipole operator transforms as Γ_{4u} [16]. Since TPA is a second-order process, the allowed TPA transitions from a Γ_{1g} initial CF energy level are to those terminal CF levels which are contained in the direct product $\Gamma_{4u} \otimes \Gamma_{4u}$, i.e. to Γ_{1g}, Γ_{3g}, Γ_{4g} and Γ_{5g} states. A $\Gamma_{1g} \to \Gamma_{2g}$ TPA transition is therefore symmetry forbidden. The Γ_{4g} irrep belongs to the antisymmetric direct product representation of $\Gamma_{4u} \otimes \Gamma_{4u}$, and a $\Gamma_{1g} \to \Gamma_{4g}$ transition has zero intensity when using two photons from a single beam in the present case since the polarization dependence is $(\varepsilon \times \varepsilon)^2$ [17].

2.1. Energies and wavefunctions of the $4f^6$ electron system

The $4f^6$ configuration is shielded from the external influence of the crystal environment by the outer closed shells $5s^2 5p^6$, and the SO coupling effect acting upon a 4f electron is stronger than the CF effect. The energies and wavefunctions of Eu^{3+} ($4f^6$) used in this work are reproduced using the f-shell empirical programs developed by Reid and the fitted parameters reported by Thorne *et al* [12]. The wavefunctions can be expressed in terms of Russell–Saunders coupled wavefunctions:

$$|4f^6[\alpha_i S_i L_i J_i]\Gamma_i \gamma_i\rangle = \sum_{\alpha SLJJ_z} a_{\Gamma_i \gamma_i}(\alpha SLJJ_z)|4f^6 \alpha SLJJ_z\rangle \tag{6}$$

$$|4f^6[\alpha_f S_f L_f J_f]\Gamma_f \gamma_f\rangle = \sum_{\alpha SLJJ_z} a_{\Gamma_f \gamma_f}(\alpha SLJJ_z)|4f^6 \alpha SLJJ_z\rangle. \tag{7}$$

The symbol α in the above expressions represents any other quantum numbers that are needed when the set $SLJJ_z$ fails to define the states uniquely. Since the electric dipole operator

Table 1. Eigenstates and eigenfunctions for the $5d^1$ configuration of Ce^{3+} in the elpasolite host lattice.

Eigenstates $\lvert\Gamma_l\Gamma_s\Gamma_d\gamma_d\rangle$	Eigenfunctions
$\lvert[\Gamma_5\Gamma_6]\Gamma_8\lambda\rangle$	$0.0513\lvert 20\frac{1}{2}\frac{1}{2}\rangle - 0.9988\lvert 21\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_5\Gamma_6]\Gamma_8\kappa\rangle$	$0.5767\lvert 21\frac{1}{2}\frac{1}{2}\rangle - 0.6129\lvert 21\frac{1}{2}-\frac{1}{2}\rangle + 0.5404\lvert 2-2\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_5\Gamma_6]\Gamma_8\mu\rangle$	$0.9988\lvert 2-1\frac{1}{2}\frac{1}{2}\rangle - 0.0513\lvert 20\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_5\Gamma_6]\Gamma_8\upsilon\rangle$	$-0.5404\lvert 22\frac{1}{2}\frac{1}{2}\rangle + 0.6129\lvert 2-2\frac{1}{2}\frac{1}{2}\rangle - 0.5767\lvert 2-1\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert\Gamma_5\Gamma_6\Gamma_7\alpha\rangle$	$0.4083\lvert 22\frac{1}{2}\frac{1}{2}\rangle - 0.4083\lvert 2-2\frac{1}{2}\frac{1}{2}\rangle - 0.8165\lvert 2-1\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert\Gamma_5\Gamma_6\Gamma_7\beta\rangle$	$-0.8165\lvert 21\frac{1}{2}\frac{1}{2}\rangle - 0.4083\lvert 22\frac{1}{2}-\frac{1}{2}\rangle + 0.4083\lvert 2-2\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_3\Gamma_6]\Gamma_8\lambda\rangle$	$-0.9988\lvert 20\frac{1}{2}\frac{1}{2}\rangle - 0.0513\lvert 21\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_3\Gamma_6]\Gamma_8\kappa\rangle$	$0.0296\lvert 21\frac{1}{2}\frac{1}{2}\rangle + 0.6766\lvert 22\frac{1}{2}-\frac{1}{2}\rangle + 0.7359\lvert 2-2\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_3\Gamma_6]\Gamma_8\mu\rangle$	$0.0513\lvert 2-1\frac{1}{2}\frac{1}{2}\rangle + 0.9988\lvert 20\frac{1}{2}-\frac{1}{2}\rangle$
$\lvert[\Gamma_3\Gamma_6]\Gamma_8\upsilon\rangle$	$-0.7359\lvert 22\frac{1}{2}\frac{1}{2}\rangle - 0.6766\lvert 2-2\frac{1}{2}\frac{1}{2}\rangle - 0.0296\lvert 2-1\frac{1}{2}-\frac{1}{2}\rangle$

$\boldsymbol{D}$ is a single-electron-type operator, $|4f^6\alpha SLJJ_z\rangle$ is expressed in terms of a core state and a single f-electron state as follows:

$$\begin{aligned}|4f^6\alpha SLJJ_z\rangle &= \sum_{M_SM_L}\langle SM_SLM_L|JJ_z\rangle 4f^6\alpha SM_SLM_L\rangle \\ &= \sum_{\substack{M_SM_L\alpha'S'L' \\ M_{S'}M_{L'}m_{sf}m_{lf}}}\langle SM_SLM_L|JJ_z\rangle\langle S'M_{S'}\tfrac{1}{2}m_{sf}|SM_S\rangle\langle L'M_{L'}3m_{lf}|LM_L\rangle \\ &\quad\times\langle 4f^5\alpha'S'L'|\}4f^6\alpha SL\rangle|4f^5\alpha'S'L'M_{S'}M_{L'}\rangle|4f^1\tfrac{1}{2}m_{sf}3m_{lf}\rangle. \qquad (8)\end{aligned}$$

The values of the Clebsch–Gordan coefficients and the coefficients of fractional parentage are available in [18, 19].

2.2. *$4f^5 5d$ energy-level structure and wavefunction representations*

The $4f^5 5d$ intermediate configuration results from the combination of the $4f^5$ states and the single-5d-electron states. The energy levels and wavefunctions of $4f^5$ states were assumed to be the same as those obtained by diagonalizing the energy matrix for $Sm^{3+}(4f^5)$ in the same elpasolite host [20], and for simplicity, in most calculations of this paper, the CF interaction for $4f^5$ is ignored (i.e. setting B_0^4, B_0^6 etc to be zero). Energy levels and wavefunctions for the $5d^1$electron states were obtained from the analysis of the excited $5d^1$ configuration of Ce^{3+} in the elpasolite host [21], and can be expressed in terms of $|2m_{ld}\frac{1}{2}m_{sd}\rangle$:

$$|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle = \sum_{\gamma_l\gamma_s m_{sd}m_{ld}}\langle\Gamma_l\gamma_l\Gamma_s\gamma_s|\Gamma_d\gamma_d\rangle\langle 2m_{ld}|\Gamma_l\gamma_l\rangle\langle\tfrac{1}{2}m_{sd}|\Gamma_s\gamma_s\rangle|5d2m_{ld}\tfrac{1}{2}m_{sd}\rangle \qquad (9)$$

where the irreducible representations Γ_l, Γ_s and Γ_d describing the 5d electron refer to orbit, spin and SO-coupled states, respectively. The $5d^1$ wavefunctions are shown in table 1.

Since we neglect the CF interaction within the $4f^5$ configuration and the electrostatic interaction between $4f^5$ core and the 5d electron as in [8], the wavefunctions of $4f^5 5d$ states can be written in terms of uncoupled antisymmetric wavefunctions as $|4f^5[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}_z\rangle$; $|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle_A$, where '$A$' means antisymmetric with respect to electron exchange. This approximation makes the energy structure of the $4f^5 5d$ intermediate states of Eu^{3+} very simple. Each of the $[\bar{\alpha}\bar{S}\bar{L}]\bar{J}$ levels for $4f^5$ is combined with the three CF levels $a\Gamma_8$, Γ_7 and $b\Gamma_8$ of $5d^1$. The energy difference between the lowest level of the $4f^5 5d$ configuration and the ground CF level of the $4f^6$ configuration is estimated to be 65 000 cm^{-1} [22].

2.3. Two-photon transition matrix element

The fundamental matrix element in equation (1) is

$$\begin{aligned}\langle\Gamma_f\gamma_f|D_q^1|n\rangle &= {}_A\langle 4f^6[\alpha_f S_f L_f J_f]\Gamma_f\gamma_f|\sum_i r_i C_q^1(i)||4f^5[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}_z\rangle;\,|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle\rangle_A \\ &= 6\,{}_A\langle 4f^6[\alpha_f S_f L_f J_f]\Gamma_f\gamma_f|r_N C_q^1(N)||4f^5[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}_z\rangle;\,|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle\rangle_A \\ &= \frac{6}{\sqrt{6}}\,{}_A\langle 4f^6[\alpha_f S_f L_f J_f]\Gamma_f\gamma_f|r_N C_q^1(N)||4f^5[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}_z\rangle_A;\,|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle_N\rangle\end{aligned} \tag{10}$$

where the electric dipole operator D_q^1 is expressed in terms of the spherical tensor operator $C_q^1(N)$ acting on the state $|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle_N$ of the Nth electron as in equation (9). The factor $1/\sqrt{6}$ in the last step relates to the probability that the Nth electron occupies the $5d^1$ state while the other $(N-1)$ electrons occupy the $4f^5$ states [23, 24]. The antisymmetric wavefunctions of the core $4f^5$ are expanded as

$$\begin{aligned}|4f^5[\bar{\alpha}\bar{S}\bar{L}]\bar{J}\bar{J}_z\rangle_A &= \sum_v C_v|4f^5\bar{\alpha}_v\bar{S}_v\bar{L}_v\bar{J}\bar{J}_z\rangle \\ &= \sum_{v\bar{M}_S\bar{M}_L} C_v\langle\bar{S}_v\bar{M}_S\bar{L}_v\bar{M}_L|\bar{J}\bar{J}_z\rangle|4f^5\bar{\alpha}_v\bar{S}_v\bar{M}_S\bar{L}_v\bar{M}_L\rangle\end{aligned} \tag{11}$$

where the coefficients C_v are obtained from [20] by setting all $B_q^k = 0$ as mentioned earlier.

By combining (7)–(11), we have

$$\begin{aligned}\langle\Gamma_f\gamma_f|D_q^1|n\rangle &= \sqrt{6}\,{}_A\langle 4f^6[\alpha_f S_f L_f J_f]\Gamma_f\gamma_f|r_N C_q^1(N)||4f^5[\bar{\alpha}\overline{SL}]\overline{JJ}_z\rangle_A;\,|5d(\Gamma_l\Gamma_s\Gamma_d\gamma_d)\rangle_N\rangle \\ &= \sqrt{6}\sum_{\substack{v\alpha SLJJ_z \\ M_S M_L\bar{M}_S\bar{M}_L \\ \gamma_l\gamma_s m_{sd}m_{ld}m_{lf}}} C_v a_{\Gamma_f\gamma_f}(\alpha SLJJ_z)\langle JJ_z|SM_SLM_L\rangle\langle\bar{S}_v\bar{M}_S\bar{L}_v\bar{M}_L|\overline{JJ}_z\rangle \\ &\quad\times\langle\Gamma_l\gamma_l\Gamma_s\gamma_s|\Gamma_d\gamma_d\rangle\langle 2m_{ld}|\Gamma_l\gamma_l\rangle\langle\tfrac{1}{2}m_{sd}|\Gamma_s\gamma_s\rangle\langle 4f^6\alpha SL\{|4f^5\bar{\alpha}_v\bar{S}_v\bar{L}_v\rangle \\ &\quad\times\langle SM_S|\bar{S}_v\bar{M}_v\tfrac{1}{2}m_{sf}\rangle\langle LM_L|\bar{L}_v\bar{M}_v 3m_{lf}\rangle\langle 3m_{lf}|r_N C_q^1(N)|2m_{ld}\rangle\end{aligned} \tag{12}$$

where

$$\langle 3m_{lf}|r_N C_q^1(N)|2m_{ld}\rangle = \langle 3\|C^1\|2\rangle\langle 3m_{lf}|1q2m_{ld}\rangle\langle f|r|d\rangle/\sqrt{7}. \tag{13}$$

Similar formulae can be obtained for $\langle n|D_q^1|\Gamma_i\gamma_i\rangle$ in the same manner. By substituting equations (12) and (13) for the matrix elements $\langle\Gamma_f\gamma_f|D_q^1|n\rangle$ into the numerators, and the energies $E_n = \hbar\omega_n$ into the denominators of equation (1), the TPA transition matrix elements $M_{\Gamma_i\gamma_i\to\Gamma_f\gamma_f}$ and the transition line strengths $S_{\Gamma_i\to\Gamma_f}$ can then be calculated directly.

3. Contributions of various cross terms to the two-photon transition matrix element

The intermediate state $|n\rangle$ in equation (1) is an eigenfunction of the Hamiltonian $H_0 + H_{S_1L_1} + h_{sl} + h_{cd}$, where H_0 is the central field Hamiltonian and the Coulomb interaction between the five 4f electrons. Moreover, $H_{S_1L_1}$, h_{sl} and h_{cd} are the $4f^5$ core SO interaction, the $5d^1$ SO interaction and the $5d^1$ CF interaction respectively, which have been introduced as additional perturbation Hamiltonians to the zeroth-order Hamiltonian H_0 for the $4f^55d$ configuration in our direct calculation. By taking the states $|n\rangle$ and $\hbar\omega_n$ as eigenfunctions and eigenvalues of different Hamiltonians in the summation over $|n\rangle\langle n|/\hbar(\omega_n - \omega_2)$ etc in equation (1) (i.e. the

Table 2. Calculated and observed intensities for the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ TPA transitions of Eu^{3+} doped into the Cs_2NaYF_6 host lattice.

Final state	Transition no[a]	Energy (cm^{-1})[a]	Calculated transition line strength[b]		Relative intensities calculated (observed[a])	
			$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$
$^5D_2\Gamma_{5g}$	24	21 389	0.00	3490	0.00 (0.12)	2.96 (9.9)
Γ_{3g}	25	21 568	4670	1180	1.00 (1.00)	1.00 (1.00)
$^5L_6\Gamma_{1g}$	29	24 557	0.0154	0.0154	1.00 (1.00)	1.00 (1.00)
aΓ_{5g}	31	24 802	0.00	26.1	0.00 (0.27)	1700 (1.7)

[a] [12].
[b] In units of $(10^{-16}cm^2\langle 4f|r|5d\rangle^4/h^2c^2)$.

eigenfunctions and eigenvalues of H_0, or $H_0+H_{S_1L_1}$, or $H_0+H_{S_1L_1}+h_{sl}$, or $H_0+H_{S_1L_1}+h_{sl}+h_{cd}$), we can include or eliminate the effects of the other components of the Hamiltonian upon the calculated two-photon transition moment. The inclusion of additional components in the Hamiltonian will give rise to mixing of the corresponding 'initial' wavefunctions and change of the corresponding 'initial' energies $\hbar\omega_n$. These effects can be evaluated by the 'cross-term contributions' of this mixing in the summation over $|n\rangle\langle n|/\hbar(\omega_n - \omega_2)$ etc in equation (1), which can be separated out by performing summations over $|n\rangle\langle n|/\hbar(\omega_n - \omega_2)$ etc using different kinds of eigenfunction $|n\rangle$ and eigenvalue $\hbar\omega_n$ in equation (1) and then comparing them.

4. Results and discussion

The calculated absolute transition line strengths of the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ TPA transitions are displayed in table 2. These four transitions are separated into two groups, and for each group the experimental relative intensities are compared with the theoretical ones obtained from the calculated line strengths. In addition, the effects of using alternative wavefunctions for the initial and final states (table 3) or intermediate states (table 4) have been investigated. The 'cross-term contributions' caused by Hamiltonians $H_{S_1L_1}$, h_{sl} and h_{cd} within the intermediate configuration $4f^55d$ are presented in table 5 for the four transitions with polarization $\theta = 45°$. In these tables, particular multiplets for each CF state $|[\alpha SLJ]\Gamma\gamma\rangle$ are identified by the relevant dominant Russell–Saunders component $^{2S+1}L_J$. The two groups of transitions are discussed separately in the following two subsections.

4.1. $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} *transitions*

As shown in table 2, the ratio between the TPA intensities of $\Gamma_{1g} \rightarrow \Gamma_{5g}$ and $\Gamma_{1g} \rightarrow \Gamma_{3g}$ at $\theta = 45°$ is estimated to be 2.96, which is in qualitative agreement with the experimental result. The calculated intensity ratios between $\theta = 0°$ and 45° are equal to 0.0 and 4.0 for $\Gamma_{1g} \rightarrow \Gamma_{5g}$, Γ_{3g} transitions respectively.

Quantitative calculations of Eu^{3+} CF energy levels (section 2.1) indicate that the ground level $(^7F_0)\Gamma_{1g}$ contains a small J-admixture of $^7F_4$(2%), which is caused by the CF interaction within the ground $4f^6$ configuration. When this small J-admixture is neglected, the calculated relative intensities for the two transitions are almost unchanged, as shown by the comparison between the values in rows B and A of table 3. Thus, the small J-mixing effect in the CF states of the ground configuration can be reasonably neglected for such TPA intensity calculations, just as in [10, 11].

Table 3. Calculated TPA transition intensities for the $(^7F_0)\ \Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}, \Gamma_{3g}$ transitions when using various wavefunctions for the ground state $|^7F_0, \Gamma_{1g}\rangle$ and final states $\langle^5D_2\Gamma_{5g}|, \langle^5D_2\Gamma_{3g}|$ of Eu^{3+} doped into the Cs_2NaYF_6 host lattice.

Transition		Calculated transition line strength[a]		Calculated relative transition intensities	
$\Gamma_{1g} \rightarrow$		$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$
A[b]	Γ_{5g}	0.00	3490	0.00	2.96
	Γ_{3g}	4670	1180	1.00	1.00
B[c,e]	Γ_{5g}	0.00	3480	0.00	3.08
	Γ_{3g}	4520	1130	1.00	1.00
C[d,e]	Γ_{5g}	0.00	730	0.00	3.17
	Γ_{3g}	910	230	1.00	1.00

[a] In units of $(10^{-16}\ \mathrm{cm}^2\langle 4f|r|5d\rangle^4/h^2c^2)$.
[b] The exact wavefunctions were used for the ground and final states in the calculations and the results are identical to those in table 2.
[c] The wavefunctions without J-mixing were used for the ground and final states in the calculations.
[d] The pure Russell–Saunders multiplets were used for the ground and final states in the calculations.
[e] Free-ion wavefunctions were used for the $4f^5$ core states in the intermediate $4f^55d$ configuration.

Table 4. Calculated TPA transition intensities for the $(^7F_0)\ \Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}, a\Gamma_{5g}$ transitions when using the free-ion (row A) and CF (row B) wavefunctions of $4f^5$ for the uncoupled intermediate states of the $4f^55d^1$ configuration.

Transition		Calculated transition line strength[a]		Calculated relative transition intensities
$\Gamma_{1g} \rightarrow$		$\theta = 0°$	$\theta = 45°$	$\theta = 45°$
A[b,c]	Γ_{1g}	0.0154	0.0154	1.00
	$a\Gamma_{5g}$	0.00	26.1	1700
B[b]	Γ_{1g}	4.24	4.24	1.00
	$a\Gamma_{5g}$	0.00	25.2	5.94

[a] In units of $(10^{-16}\ \mathrm{cm}^2\langle 4f|r|5d\rangle^4/h^2c^2)$.
[b] The exact wavefunctions are used for the ground and final states of the $4f^6$ configuration in the calculations.
[c] The results are identical to those in table 2.

It can also be shown from the calculations of the free-ion energy levels of Eu^{3+} that $^7F_0$ and $^5D_2$ are almost pure Russell–Saunders multiplets. The electronic ground-state wavefunction consists of 93% of $^7F_0$ and some 7% of $^5D_0$. The terminal state for the transition comprises $^5D_2$ (92%), with small admixtures mainly of $^7F_2$ (3%) and $^5F_2$ (1%). These SL-admixtures are caused by the SO interactions within the ground $4f^6$ configuration. When they are neglected, the line strengths for the two transitions are remarkably reduced while the relative intensities and polarization dependence are almost the same, as shown by comparison between the data in row C and row A of table 3. The reduction of the line strengths can be explained as follows. These small SL-admixtures, $^5D_2$ and $^7F_2$, $^5F_2$, open subsidiary excitation channels of $^7F_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^5D_2$, $^5F_2$. These pathways, which are allowed by the direct second-order ($\Delta S = 0$) mechanism of Axe [3], produce much greater TPA intensities than mechanisms without the SL-mixing of $4f^6$ electron states. The invariance of the relative intensities and the polarization dependence may be accounted for by the fact that the final CF states of the two transitions originate from the same multiplet $^5D_2$ without the J-admixtures. This explanation is also

Table 5. Cross-term contributions to the transition moment M_D caused by $H_{S_1L_1}$, h_{sl}, H_{cf} and h_{cd} for $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ TPA transitions of Eu^{3+} doped into the Cs_2NaYF_6 host, with polarization $\theta = 45°$.

Final states	Direct calculation contributions to M_D^{a}				
	$H_{S_1L_1}$	h_{sl}	H_{cf}^{b}	h_{cd}	M_D
$^5D_2\Gamma_{5g}$	4.64	3.94	—	0.82	59.06
Γ_{3g}	1.12	1.86	—	0.46	34.32
$^5L_6^{c}\Gamma_{1g}$	1.86	−0.28	1.94	2.61	2.06
aΓ_{5g}	3.76	−0.42	−0.09	8.20	5.02

[a] All the values in the contribution columns are assumed to be real and in units of (10^{-8} cm $\langle 4f|r|5d\rangle^2/hc$).
[b] The CF interaction within the intermediate $4f^5$ configuration. This is only included in the calculations for the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a$\Gamma_{5g}$ transitions.
[c] The pure Russell–Saunders multiplets are used for $^7F_0$ and $^5L_6$.

apparent in previous studies [10, 11] in which the pure Russell–Saunders multiplets were used for the initial- and final-CF-state wavefunctions, whilst the calculated TPA relative intensities were in agreement with experimental results.

Table 5 shows that the important 'cross-term contributions' for the transitions $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} originate from $H_{S_1L_1}$ and h_{sl}, which is consistent with the earlier works [4, 8]. Because of the selection rule $\Delta S = 0$ for the subsidiary excitation channels of $^7F_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^5D_2, {}^5F_2$ (see above), the 'cross-term contributions' from $H_{S_1L_1}$ of $4f^5$, or h_{sl} of $5d^1$, are less than 10%, which is smaller than expected. The contributions from cross terms caused by h_{cd} are much smaller than those caused by $H_{S_1L_1}$ or h_{sl} and are not important, because of the selection rules $\Delta L = 1$ and $\Delta J = 2$.

4.2. $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, a Γ_{5g} *transitions*

Table 2 illustrates serious discrepancies between the theoretical and experimental results of transition relative intensities for the two $^7F_0 \rightarrow {}^5L_6$ TPA transitions. Since the exact wavefunctions were used for the ground and final states in the $4f^6$ ground configuration, we believe that the reason lies in the assumptions used in the direct calculation for the intermediate states of the $4f^55d$ configuration. Among these assumptions, the approximation of using free-ion wavefunctions $|4f^5[\bar{\alpha}\bar{S}\bar{L}]\overline{JJ_z}\rangle_A$ and energies in the intermediate $4f^55d$ configuration may be questioned. Because $\Delta L = 5$, $\Delta J = 6$ for the two transitions, the CF splitting effects of the free-ion $4f^5$ levels by the CF interactions $H_{cf} = \sum_{k,q} B_q^k C_q^k$ $(k = 4, 6)$ may be important to link $^7F_0$ and $^5L_6$, since the CF of the $5d^1$ electron has already been taken into account.

In the following, therefore, we have introduced the CF wavefunctions $|4f^5[\bar{\alpha}\bar{S}\bar{L}\bar{J}]\Gamma\gamma\rangle_A$ for the $4f^5$ core states, instead of free-ion ones $|4f^5[\bar{\alpha}\bar{S}\bar{L}]\overline{JJ_z}\rangle_A$, into the calculation. These CF wavefunctions of the $4f^5$ core are produced from Reid's f-shell empirical programs and the input parameters of Sm^{3+} reported in [20]. Each of the 2002 derived microstates of the $4f^5$ core is combined with the ten microstates of $5d^1$ to form the intermediate states. The calculated results, which still neglect the Coulomb interaction between the $4f^5$ core and the $5d^1$ electron, are listed in row B of table 4. The calculated ratio of the TPA transition intensities of $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)a\Gamma_{5g}$ and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$ is estimated to be 5.94, which is much closer to the experimental result.

We can also see from table 4 that when the CF states of the $4f^5$ core are used instead of the free-ion ones the calculated line strength of the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$ transition

is greatly increased (row B) when compared with the corresponding value in row A. By contrast, the calculated line strength of $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)a\Gamma_{5g}$ is almost unchanged. This indicates that the use of CF wavefunctions for the $4f^5$ core states is especially necessary for the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$ transition.

To further clarify the above results, the 'cross-term contributions' to the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, $a\Gamma_{5g}$ transition moments M_D, caused by $H_{S_1L_1}$, h_{sl}, H_{cf} and h_{cd}, were also evaluated and these are shown in table 5. This table illustrates that two of the important 'cross-term contributions' for these two transitions originate from $H_{S_1L_1}$ of $4f^5$, and h_{cd} of $5d^1$, as has previously been noted [6,8]. It is observed that for $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$ the contribution from H_{cf} of $4f^5$ is almost as important as that from h_{cd}. This indicates that the mere inclusion of $H_{S_1L_1}$ and h_{cd}, as in other studies [6,8], is not sufficient to account for the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$ transition intensity, and that the CF splitting effects caused by H_{cf}, although small, need to be included. Finally, it is noted that the contributions from cross terms caused by h_{sl} are comparatively small.

5. Conclusions

A direct calculation of the $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} and $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, $a\Gamma_{5g}$ TPA transition line strengths of Eu^{3+} doped in Cs_2NaYF_6 has been presented. In such calculations, the wavefunctions and energies of the intermediate states are taken to be eigenfunctions and eigenvalues of the almost complete Hamiltonian of the whole $4f^55d$ configuration. The calculated relative intensities of $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} transitions are in reasonable agreement with experimental results, while those of the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, $a\Gamma_{5g}$ transitions disagree seriously with experimental ones. The J-mixing and SL-mixing effects involved in the ground and final states of $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}$, Γ_{3g} transitions have been explicitly evaluated. The results show that the J-mixing effects are negligibly small, and the SL-mixing effects can also be neglected without changing the relative intensities of these two transitions, although the absolute transition line strengths are greatly reduced. The agreement of theoretical relative intensities with experimental values for $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$, $a\Gamma_{5g}$ TPA transitions can be restored when using the CF wavefunctions for the $4f^5$ core states, instead of free-ion wavefunctions, in the uncoupled wavefunctions of the intermediate configuration $4f^55d^1$. The intermediate-state mixing effects upon the four transition matrix elements by different terms of the Hamiltonian have been evaluated. The results demonstrated that, for $(^7F_0)\Gamma_{1g} \rightarrow (^5D_2)\Gamma_{5g}, \Gamma_{3g}$, the important effects originate from $H_{S_1L_1}, h_{sl}$. For the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)a\Gamma_{5g}$ transition, intermediate-state mixing effects caused by $H_{S_1L_1}$ and h_{cd} are important, whereas for the $(^7F_0)\Gamma_{1g} \rightarrow (^5L_6)\Gamma_{1g}$ transition, these important effects originate from $H_{S_1L_1}$, h_{cd} and H_{cf}.

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