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Two-photon spectroscopy of transition metal ions in cubical symmetry

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Abstract

Symmetry adaptation techniques are applied to the determination of the intensity of intraconfigurational two-photon transitions for transition metal ions in cubical symmetry. This leads to a simple model giving the polarization dependence of the intensity of two-photon (electric dipolar) transitions between Stark levels of the configuration $3d^N$ (N even or odd).

1. Introduction

With the availability of tunable dye lasers, two-photon spectroscopy of transition ions in molecular or solid state environments (generic symmetry G) has been the object of numerous developments from both an experimental and a theoretical viewpoint [1–23]. Indeed, two-photon spectroscopy turns out to be a useful complement to one-photon spectroscopy because it allows levels to be reached which cannot be seen in one-photon spectroscopy [1–13]. There are now many two-photon absorption spectra published for rare earth ions (generic configuration $4f^N$ for lanthanides or $5f^N$ for actinides) in various surroundings. In this respect, to name but a few recently published studies, let us mention Gd^{3+} ($N = 7$) in $Gd(OH)_3$ ($G = D_{3h}$) [14, 15], in $GdCl_3$ ($G = C_{3h}$) [14] and in the cubic elpasolite $Cs_2NaGdCl_6$ ($G = O_h$) [16], Sm^{2+} ($N = 6$) in BaClF ($G = C_{4v}$) [17, 18] and in SrClF ($G = C_{4v}$) [19], and, finally, Eu^{3+} ($N = 6$) in $LuPO_4$ ($G = D_{2d}$) [19]. Transition metal ions of the iron series (generic configuration $3d^N$) in crystals have also been the object of recent investigations. For example, the case of Ni^{2+} ($N = 8$) in MgO ($G = O$) has received a great deal of attention in the last three years [20–22]. Furthermore, there are also some data about Co^{2+} ($N = 7$) in $KZnF_3$ ($G = O$) [23].

It is the aim of the present paper to report on a simple model for describing $3d^N \longrightarrow 3d^N$ intraconfigurational two-photon transitions for a transition metal ion in an environment of cubical (octahedral) symmetry ($G = O$ or O_h). The main ingredients of the model (symmetry-adapted wavefunctions and second- plus third-order mechanisms) are given in Section 2 and the necessary formulae for applications are listed in Section 3.

2. Theory

Let us consider a (parity-allowed) two-photon transition between an initial state i, of symmetry Γ, and a final state f, of symmetry Γ', of the configuration $3d^N$; the labels Γ and Γ' stand for irreducible representations of the group O or its double group O^* according to whether the number N of 3d electrons is even or odd. The corresponding state vectors are denoted $|3d^N i\Gamma\gamma\rangle$ and $|3d^N f\Gamma'\gamma'\rangle$ where γ and γ' distinguish the various partners for Γ and Γ' respectively. These vectors can be expressed either in a strong field basis of type $|t_2^{N-M}(S_1\Gamma_1)e^M(S_2\Gamma_2)S_T\Gamma_T\beta\Gamma\gamma\rangle$ or in a weak field basis of type $|3d^N\alpha SLJa\Gamma\gamma\rangle$. We shall adopt here a weak field approach. (The weak and strong field approaches are equivalent in so far as we use in both approaches the same time-independent hamiltonian H_{i+e} for the ion in its environment [24].)

We have chosen to calculate the transition matrix element $M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')}$ within the following approximations.

(i) We use single-mode excitations (energy $\hbar\omega_\lambda$, wavevector $\boldsymbol{k}_\lambda$, polarization $\boldsymbol{\mathscr{E}}_\lambda$) of the radiation field and we suppose the two photons ($\lambda = 1, 2$) to be identical. (In fact, most of the experiments carried out until now use a single laser beam.)

(ii) We use a time-dependent hamiltonian of the type $H_{i+e} + H_{rf} + H_{int}$ for describing the system formed by the ion in its environment (H_{i+e}) and the radiation field (H_{rf}) which interact through H_{int} and we treat H_{int} in the framework of the electric dipole approximation.

(iii) We use a quasi-closure approximation to deal with the Göppert–Mayer formula for two-photon processes.

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As a result, the transition matrix element can be calculated to be [1, 5, 6]

$$M_{i(\Gamma\gamma)\longrightarrow f(\Gamma'\gamma')} = \langle 3d^N f\Gamma'\gamma'|H_{\text{eff}}|3d^N i\Gamma\gamma\rangle$$

where the effective operator H_{eff} is written [10]

$$H_{\text{eff}} = \sum_{k=0,2}\sum_{k_S k_L} C[(k_S k_L)k](\{\mathscr{E}\mathscr{E}\}^{(k)}\cdot \boldsymbol{W}^{(k_S k_L)k})$$

The term $\{\mathscr{E}\mathscr{E}\}^{(k)}$ is the tensor product of rank k of the polarization unit vectors $\mathscr{E}$ for the two photons. The dependence on the ion appears in the electronic double tensor $\boldsymbol{W}^{(k_S k_L)k}$ of spin rank k_S, orbital rank k_L and total rank k. Furthermore, the $C[(k_S k_L)k]$ parameters are expansion coefficients which may be calculated from first principles. The contributions ($k_S = 0, k_L = 2, k = 2$) and ($k_S \neq 0, k_L, k$) correspond to the standard second-order mechanisms [1–4] and to the so-called third-order mechanisms (which may take into account ligand, crystal field and spin–orbit effects) [5–9] respectively.

The intensity of the $i(\Gamma) \longrightarrow f(\Gamma')$ two-photon transition, *i.e.*

$$S_{\Gamma\longrightarrow\Gamma'} = \sum_{\gamma\gamma'} |M_{i(\Gamma\gamma)\longrightarrow f(\Gamma'\gamma')}|^2$$

can be calculated by using the symmetry adaptation techniques developed in refs. 24 and 25. We thus obtain

$$S_{\Gamma\longrightarrow\Gamma'} = \sum_{k=0,2}\sum_{l=0,2}\sum_{\Gamma''} I[kl\Gamma'';\Gamma\Gamma'] \sum_{\gamma''}\{\mathscr{E}\mathscr{E}\}_{\Gamma''\gamma''}^{(k)} \times (\{\mathscr{E}\mathscr{E}\}_{\Gamma''\gamma''}^{(l)})^*$$

where the I parameters, which depend on the ion in its environment, have been derived in the weak field coupling scheme [11–13, 22]. These intensity parameters depend on the wavefunctions used for the initial and final states, on the atomic parameters $C[(k_S k_L)k]$, on atomic reduced matrix elements and on isoscalar factors for the chains of groups $SO(3) \supset O$ (for N even) or $SU(2) \supset O^*$ (for N odd). The number of independent parameters I is controlled by a set of properties and rules [11–13]. For the purpose of this paper, it is sufficient to note that the sum over Γ'' is limited by the following selection rule: Γ'' is of the type A_1, E or T_2 and must be contained in the representation $\Gamma'^* \otimes \Gamma$ of the octahedral group O. In addition, the polarization dependence is completely contained in the factors of type $\{\mathscr{E}\mathscr{E}\}$.

3. Application

By applying the above-mentioned selection rule, we can rewrite $S_{\Gamma\longrightarrow\Gamma'}$ as

$$S_{\Gamma\longrightarrow\Gamma'} = \tfrac{1}{3}I[00A_1;\Gamma\Gamma']\varpi_1 + \tfrac{1}{6}I[22E;\Gamma\Gamma']\varpi_2 + \tfrac{1}{4}I[22T_2;\Gamma\Gamma']\varpi_3$$

where the functions ϖ_i ($i = 1, 2, 3$) can be readily derived by means of Wigner–Racah calculus for the chain of groups $SO(3) \supset O$ [24, 25]. As a matter of fact, we obtain

$$\varpi_1 = 3|\{\mathscr{E}\mathscr{E}\}_{A_1}^{(0)}|^2 = 1 \quad \text{or} \quad 0$$

$$\varpi_2 = 6\sum_{\gamma''}|\{\mathscr{E}\mathscr{E}\}_{E\gamma''}^{(2)}|^2 = (3\cos^2\theta - 1)^2 + 3\sin^4\theta\cos^2 2\varphi \quad \text{or} \quad 3$$

$$\varpi_3 = 4\sum_{\gamma''}|\{\mathscr{E}\mathscr{E}\}_{T_2\gamma''}^{(2)}|^2 = 2(\sin^4\theta\sin^2 2\varphi + \sin^2 2\theta) \quad \text{or} \quad 2$$

according to whether the polarization is linear or circular. For linear polarization, (θ, φ) are the polar angles of the polarization vector $\mathscr{E}$ with respect to the crystallographic axis and, for circular polarization, the wave vector $\boldsymbol{k}$ is parallel to the crystallographic axis. (Of course, the angular functions ϖ_i ($i = 1, 2, 3$) do not depend on the labels γ'', *i.e.* on the chain $SO(3) \supset G = O \supset G' \supset G''$ used in practical computations.)

We give below the intensities $S_{\Gamma\longrightarrow\Gamma'}$ for N even (Γ and Γ' belong to O) and for N odd (Γ and Γ' belong to O^*). To pass from $S_{\Gamma\longrightarrow\Gamma'}$ to $S_{\Gamma'\longrightarrow\Gamma}$, it is sufficient to change $\Gamma\Gamma'$ into $\Gamma'\Gamma$ in the intensity parameters I. For N even, the results are the following:

$$S_{A_1\longrightarrow A_1} = \tfrac{1}{3}I[00A_1;A_1A_1]\varpi_1$$
$$S_{A_1\longrightarrow A_2} = 0$$
$$S_{A_1\longrightarrow E} = \tfrac{1}{6}I[22E;A_1E]\varpi_2$$
$$S_{A_1\longrightarrow T_1} = 0$$
$$S_{A_1\longrightarrow T_2} = \tfrac{1}{4}I[22T_2;A_1T_2]\varpi_3$$
$$S_{A_2\longrightarrow A_2} = \tfrac{1}{3}I[00A_1;A_2A_2]\varpi_1$$
$$S_{A_2\longrightarrow E} = \tfrac{1}{6}I[22E;A_2E]\varpi_2$$
$$S_{A_2\longrightarrow T_1} = \tfrac{1}{4}I[22T_2;A_2T_1]\varpi_3$$
$$S_{A_2\longrightarrow T_2} = 0$$
$$S_{E\longrightarrow E} = \tfrac{1}{3}I[00A_1;EE]\varpi_1 + \tfrac{1}{6}I[22E;EE]\varpi_2$$
$$S_{E\longrightarrow T_1} = \tfrac{1}{4}I[22T_2;ET_1]\varpi_3$$
$$S_{E\longrightarrow T_2} = \tfrac{1}{4}I[22T_2;ET_2]\varpi_3$$
$$S_{T_1\longrightarrow T_1} = \tfrac{1}{3}I[00A_1;T_1T_1]\varpi_1 + \tfrac{1}{6}I[22E;T_1T_1]\varpi_2 + \tfrac{1}{4}I[22T_2;T_1T_1]\varpi_3$$
$$S_{T_1\longrightarrow T_2} = \tfrac{1}{6}I[22E;T_1T_2]\varpi_2 + \tfrac{1}{4}I[22T_2;T_1T_2]\varpi_3$$
$$S_{T_2\longrightarrow T_2} = \tfrac{1}{3}I[00A_1;T_2T_2]\varpi_1 + \tfrac{1}{6}I[22E;T_2T_2]\varpi_2 + \tfrac{1}{4}I[22T_2;T_2T_2]\varpi_3$$

For N odd, we have the following intensity formulae:

$$S_{\Gamma_6\longrightarrow\Gamma_6} = \tfrac{1}{3}I[00A_1;\Gamma_6\Gamma_6]\varpi_1$$
$$S_{\Gamma_6\longrightarrow\Gamma_7} = \tfrac{1}{4}I[22T_2;\Gamma_6\Gamma_7]\varpi_3$$
$$S_{\Gamma_6\longrightarrow\Gamma_8} = \tfrac{1}{6}I[22E;\Gamma_6\Gamma_8]\varpi_2 + \tfrac{1}{4}I[22T_2;\Gamma_6\Gamma_8]\varpi_3$$
$$S_{\Gamma_7\longrightarrow\Gamma_7} = \tfrac{1}{3}I[00A_1;\Gamma_7\Gamma_7]\varpi_1$$

$$S_{\Gamma_7 \to \Gamma_8} = \tfrac{1}{6} I[22E; \Gamma_7\Gamma_8]\varpi_2 + \tfrac{1}{4} I[22T_2; \Gamma_7\Gamma_8]\varpi_3$$

$$S_{\Gamma_8 \to \Gamma_8} = \tfrac{1}{3} I[00A_1; \Gamma_8\Gamma_8]\varpi_1 + \tfrac{1}{6} I[22E; \Gamma_8\Gamma_8]\varpi_2 + \tfrac{1}{4} I[22T_2; \Gamma_8\Gamma_8]\varpi_3$$

The intensity formulae given above cover all the possible ground states encountered for transition metal ions in cubical symmetry. We note that

$$S_{A_1 \to A_1} = S_{A_2 \to A_2} = S_{\Gamma_6 \to \Gamma_6} = S_{\Gamma_7 \to \Gamma_7} = 0$$

when the scalar contribution (characterized by $I[00A_1; \Gamma\Gamma]$) to the third-order mechanisms is not taken into consideration. Therefore, the observation, if any, of the latter transitions would prove the relevance of third-order mechanisms. In particular, it would be interesting to test the importance of the third-order mechanisms in the case of an ion with configuration $3d^5$ (such as Mn^{2+}).

The expression of the intensity parameters I has been described in Section 2 in the weak field coupling scheme. (They can be equally well expressed in the strong field coupling scheme.) There are three ways to deal with the I parameters. First, they may be considered as phenomenological parameters to be adjusted from experimental data. Second, they may be calculated from first principles. We then need to diagonalize–optimize the matrix of H_{i+e} (as done, for instance, in ref. 26 for Eu^{3+} in 15 compounds of interest in solid state chemistry) and to calculate isoscalar factors, reduced matrix elements and parameters characterizing second- and/or third-order mechanisms. Third, they may be handled in a mixed (semiphenomenological) way especially if we want to reduce the number of I parameters.

As an illustration, let us consider the case of Ni^{2+} in MgO. The two-photon transitions from the initial state $i = {}^3A_2(T_2)$ with $\Gamma = T_2$ to the final states $f = {}^3T_2(E)$ with $\Gamma' = E$ and $f = {}^3T_2(T_1)$ with $\Gamma' = T_1$ have been recently observed for various linear polarizations [20, 21]. The specialization to the configuration $3d^8$ of the model described here allows us to compute in an *ab initio* way the intensity ratios R_1 and R_2 defined in ref. 21. The theoretical values are $R_1 = 0.95$ and $R_2 = 1.04$, to be compared with the experimental values $R_1 = 1.5$–3 and $R_2 = 1.1$ [22].

4. Conclusion

In this paper we have concentrated on the intensities of two-photon transitions for $3d^N$ ions in octahedral symmetry. The model discussed in Section 2 is valid for any strength of the crystal field interaction. Therefore, the results of Sections 2 and 3 can be extended *mutatis mutandis* to any nd^N configuration ($n = 4$ for the palladium series and $n = 5$ for the platinum series). They can also be applied to tetrahedral symmetry in view of the isomorphism of O and T_d. Finally, the results given here concern one-colour transitions. The extension to two-colour transitions (using two different beams) is straightforward.

A particular version of the model presented in this paper has been successfully applied to Ni^{2+} in MgO; the main results have been discussed at REMCES V and will be published elsewhere in greater detail [22]. The model will be applied to some other experimental data (*e.g.* Co^{2+} in $KZnF_3$ [23]) in the thesis by one of us (M.D.) and in forthcoming papers.

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