Two-photon spectroscopy between states of opposite parities

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Magnetic and electric dipole two-photon absorption (MED-TPA), recently introduced as a spectroscopic technique for studying transitions between states of opposite parities, is investigated from a theoretical point of view. An approximation referred to as *weak quasiclosure approximation* is used together with symmetry adaptation techniques to calculate the transition amplitude between states having well-defined symmetry properties. Selection rules for MED-TPA are derived and compared to selection rules for parity-forbidden electric dipole two-photon absorption.

PRELIMINARIES

Two-photon spectroscopy is now an experimental technique widely used in various domains, as for instance transition ions in crystals and excitons in semiconductors and insulators. Two-photon spectroscopy experiments on excitons were first achieved by Hopfield and Worlock.[1] Recently, Fröhlich *et al.*[2] reported two-photon absorption measurements for the three alkali halides RbI, NaI, and NaBr. These authors considered nonlinear processes where two photons are simultaneously absorbed, one photon by magnetic dipole transition and the other by electric dipole transition. The resulting magnetic and electric dipole two-photon absorption (MED-TPA) has to be distinguished from the following.

(i) The *classical* electric dipole two-photon absorption (ED-TPA) where the two photons are simultaneously absorbed by electric-dipole transition between states of the same parity. The standard theory for parity-allowed ED-TPA was given by Axe[3] and the corresponding selection rules arising from the point symmetry group G of the absorbing site were derived by Inoue and Toyazawa[4] and by Bader and Gold.[5] Further investigations of parity-allowed ED-TPA were conducted in Refs. 6–11 on the basis of microscopic models and symmetry adaptation methods[12] for the chain of groups $SU(2)\supset G^*$ (where G^* is the double group of the group G).

(ii) The *forced* ED-TPA where the two photons are simultaneously absorbed by electric dipole transition between states of opposite parities. Several parity-violation mechanisms were introduced[13–16] for explaining parity-forbidden ED-TPA, especially for partly-filled shell ions in crystals. Selection rules based on the $SU(2)\supset G^*$ symmetry were obtained in Refs. 10, 11, and 17 for parity-forbidden ED-TPA.

Of course, MED-TPA and (parity-allowed and parity-forbidden) ED-TPA differ as far as simple considerations on spin are concerned. We may also *a priori* expect some differences regarding the selection rules coming from the point symmetry of the site. In this connection, the selection rules for MED-TPA used in Ref. 2 were obtained in the spirit of the pioneer work by Inoue and Toyazawa.[4] However, it is to be realized that the selection rules introduced in Ref. 4 and extended by Bader and Gold[5] were developed, on the basis of symmetry considerations only, for (parity-allowed) ED-TPA.

It is the aim of this paper to show that the $SU(2)\supset G^*$ selection rules for parity-forbidden ED-TPA hold for MED-TPA when the two absorbed photons in both processes are different. We shall show that when the two absorbed photons are identical (same energy, same polarization, and same wave vector), there exists some differences, besides the selection rules on spin, between the selection rules for MED-TPA and parity-forbidden ED-TPA. We shall illustrate these matters on the O_h symmetry considered in Ref. 2 for the paraexcitons in RbI, NaI, and NaBr. The approach followed in the present work is not restricted to qualitative arguments. It relies on the formalisms developed in Refs. 7–11 and 17 for intra- and interconfigurational two-photon transitions. The precise selection rules for MED-TPA shall be derived from a new approximation, which is less severe than the closure approximation used by Axe[3] for ED-TPA, and from a systematic use of symmetry adaptation techniques developed[12] in the framework of the Wigner-Racah algebra for a chain $SU(2)\supset G^*$. As a by-product, of great importance in two-photon spectroscopy of transition ions in crystalline environments, the weak quasiclosure approximation introduced in the present work is applied to parity-allowed ED-TPA.

MAGNETIC AND ELECTRIC DIPOLE TRANSITIONS

We begin with MED-TPA (parity-allowed) transitions between states of opposite parities. We first consider the case of two identical absorbed photons. From the second-order time-dependent perturbation theory, the transition matrix element between an initial state i and a final state f is

$$M_{i\to f}=\sum_{\ell}\frac{(f|\mathbf{b}\cdot\mathbf{M}|\ell)(\ell|\mathbf{e}\cdot\mathbf{D}|i)}{E_i-E_\ell+\hbar\omega}+\sum_{\ell}\frac{(f|\mathbf{e}\cdot\mathbf{D}|\ell)(\ell|\mathbf{b}\cdot\mathbf{M}|i)}{E_i-E_\ell+\hbar\omega}, \tag{1}$$

which reflects the fact that when one photon is absorbed by magnetic dipole transition the other is absorbed by electric dipole transition. In Eq. (1), $\mathbf{e}\cdot\mathbf{D}$ is the scalar product of the polarization vector $\mathbf{e}$ of the absorbed photons and of the electric dipolar operator $\mathbf{D}$ while $\mathbf{b}\cdot\mathbf{M}$ is the scalar product of the vector $\mathbf{b}=\mathbf{k}_0\times\mathbf{e}$ ($\mathbf{k}_0$ is the unit wave vector of the radiative field) and of the magnetic dipolar operator $\mathbf{M}$. We take the initial and final state vectors in the form $|i) = |\alpha J a \Gamma \gamma)$ and $|f) = |\alpha' J' a' \Gamma' \gamma')$, where Γ and Γ' are irreducible representation classes (IRC's) of the group G^*. (We follow the notations of Refs. 7–12 for the symmetry labels $a\Gamma\gamma$ and $a'\Gamma'\gamma'$ of the states i and f.) Similarly, the state vectors for the intermediate states ℓ are $|\ell) = |\alpha'' J'' a'' \Gamma'' \gamma'')$. For the three kinds of state vectors, we neglect the J mixing which may result, for example, from crystal-field effects. (The extension to the case where the J mixing is taken into consideration is trivial: It is sufficient to proceed as in Refs. 7–11 and 17.) The energy denominators in (1) have their usual meaning. In order to carry out the summations over ℓ in (1), we adopt the approximation that the energies E_ℓ are independent of the generalized magnetic quantum numbers $a''\Gamma''\gamma''$. Therefore, let us put

$$E_\ell = E(\alpha'' J''). \tag{2}$$

This yields a weak quasiclosure approximation that is less restrictive that the closure approximation used by Axe[3] for ED-TPA [the latter approximation amounts to replace $E_\ell = E(\alpha'' J'' a'' \Gamma'' \gamma'')$ by the barycenter of the intermediate states]. Then, by applying coupling and recoupling techniques for the chain $SU(2) \supset G^*$,[12] Eq. (1) is amenable to the form

$$M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')} = \sum_k \sum_{a''\Gamma''\gamma''} Y_k(\alpha J, \alpha' J') \{eb\}^k_{a''\Gamma''\gamma''} \times f\begin{pmatrix} J & J' & k \\ a\Gamma\gamma & a'\Gamma'\gamma' & a''\Gamma''\gamma'' \end{pmatrix}^*, \tag{3}$$

where the parameters Y_k are given by

$$\begin{aligned} Y_k(\alpha J, \alpha' J') = (-1)^{2J'} [k]^{\frac{1}{2}} \sum_{\alpha'' J''} \frac{1}{E_i - E(\alpha'' J'') + \hbar\omega} \\ \times [(-1)^k (\alpha' J' \| M^1 \| \alpha'' J'')(\alpha'' J'' \| D^1 \| \alpha J) \\ + (\alpha' J' \| D^1 \| \alpha'' J'')(\alpha'' J'' \| M^1 \| \alpha J)] \\ \times \begin{Bmatrix} J & k & J' \\ 1 & J'' & 1 \end{Bmatrix}. \end{aligned} \tag{4}$$

Equation (4) should be understood as comprising two sums over $\alpha'' J''$: The first (second) sum is to be expanded over states having the same parity as the final (initial) state. The f coefficients in (3) are essentially Clebsch-Gordan coefficients for $SU(2) \supset G^*$ since[12]

$$f\begin{pmatrix} j_1 & j_2 & k \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a\Gamma\gamma \end{pmatrix} = (-1)^{2k} [j_1]^{-1/2} (j_2 k a_2 \Gamma_2 \gamma_2 a \Gamma \gamma | j_1 a_1 \Gamma_1 \gamma_1)^*. \tag{5}$$

The selection rules for MED-TPA easily follow from Eqs. (3)–(5). The possible values of k in (3) are $k=1$ and 2. The value $k=0$ cannot contribute since $\mathbf{e}$ and $\mathbf{b}$ are perpendicular (remember that $\{eb\}^0 \sim \mathbf{e} \cdot \mathbf{b}$). Furthermore, the possible values of Γ'' in (3) are given by the existence conditions of the f coefficients. These conditions depend not only on the point symmetry group G but also on the rotation group O(3). To be more precise, in the case where the two photons are identical, the selection rules for the MED-TPA amplitude are the following: (i) $k=1$ and 2, (ii) the IRC Γ'' of G is contained in the direct product $\Gamma'^* \otimes \Gamma$ as well as in the IRC (k) of O(3), (iii) finally, parity selection rules [involving parity symbols u (or $-$) and g (or $+$)] have to be used together with (i) and (ii). The extension to the case where the two photons are not identical leads to the results (i) $k=0$, 1, and 2; (ii) remains true; (iii) remains true.

The just obtained selection rules for parity-allowed MED-TPA transitions may be compared to the ones for parity-forbidden ED-TPA transitions allowed between states of different parities by a parity-violation mechanism. The transition moment $M_{i\to f}$ for such ED-TPA transitions is given[17] by a formula similar to Eq. (3) except that $\{eb\}^k$ is replaced by $\{ee\}^k$ and the parameters Y_k are generated by an expression other than Eq. (4). Then, the selection rules for ED-TPA transitions between states of opposite parities with identical (respectively, nonidentical) photons are (i) $k = 0$ and 2 (respectively, $k = 0$, 1, and 2); (ii) as for MED-TPA transitions; (iii) as for MED-TPA transitions. Therefore, the selection rules for ED- and MED-TPA transitions turn out to be the same (except for spin) when the two absorbed photons are not identical. However, a difference for the rule (i) occurs when the two photons are identical. This provides us with a further evidence that MED- and ED-TPA are two complementary spectroscopic techniques in the case of identical photons.

AN ILLUSTRATIVE EXAMPLE

As an illustration, we consider the $G = O_h$ symmetry. For identical photons, MED-TPA transitions $\Gamma = \Gamma_1^+ \to \Gamma' = \Gamma_1^-$ are forbidden (since the only possible IRC $\Gamma'' = \Gamma_1^-$ requires that $k = 0$), in agreement with Ref. 2. On the other hand, MED-TPA transitions $\Gamma = \Gamma_1^+ \to \Gamma' = \Gamma_4^-$ are allowed (since the only possible IRC $\Gamma'' = \Gamma_4^-$ requires $k=1$), in contradistinction to the assertion in Ref. 2. The opposite situation occurs for parity-forbidden ED-TPA transitions in the case of identical photons: The $\Gamma_1^+ \to \Gamma_1^-$ transitions are allowed and the $\Gamma_1^+ \to \Gamma_4^-$ transitions are forbidden.

Let us now illustrate, from a more quantitative point of view, the importance of the $k=1$ contribution (which is not taken into account in Ref. 2) for MED-TPA transitions with identical photons. By applying the formalism developed in Refs. 8–11, it is possible to get a closed-form expression for the intensity

$$S(\Gamma \to \Gamma') = \sum_{\gamma\gamma'} |M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')}|^2 \tag{6}$$

between the states of symmetry Γ and Γ' [the sum over γ and γ' in Eq. (6) is extended on all the Stark components of the initial and final states]. We have calculated $S(\Gamma \to \Gamma')$ for the following situation: The wave vector $\mathbf{k}_0$ is taken along the crystallographic axis (001) so that the polarization vector $\mathbf{e}$ has the components $e_0 = 0$ and $e_{\pm 1} = \mp (1/\sqrt{2}) e^{\pm i\varphi}$ in linear polarization. Then Eq. (6), used in conjunction with the selection rules (i)–(iii) for MED-TPA transitions, can be shown to yield

$$S(\Gamma_1^+ \to \Gamma_3^-) = a \sin^2 2\varphi,$$

$$S(\Gamma_1^+ \to \Gamma_5^-) = b \cos^2 2\varphi,$$

$$S(\Gamma_1^+ \to \Gamma_4^-) = c, \tag{7}$$

where a, b, and c are intensity parameters independent of the polarization. The experimental situations considered by Fröhlich *et al.*[2] correspond to $\mathbf{e}=(100)$, i.e., $\varphi=0$, and $\mathbf{e}=(1/\sqrt{2})(110)$, i.e., $\varphi=\pi/4$. From Eq. (7), it is uncorrect to assume that the transition observed in Ref. 2 for $\mathbf{e}=(100)$ is a transition to a Γ_5^- state because the transition to a Γ_4^- state has also a nonvanishing intensity. For the same reason (viz., $c\neq 0$), it cannot be assumed that the transition observed in Ref. 2 for $\mathbf{e}=(1/\sqrt{2})(110)$ is a transition to a Γ_3^- state. Consequently, a correct assignment of the symmetry of the excitons considered in Ref. 2 requires some further polarization dependence experiments. In this regard, it should be noted that in circular polarization Eq. (7) has to be substituted by

$$S(\Gamma_1^+ \to \Gamma_3^-) = a, \quad S(\Gamma_1^+ \to \Gamma_5^-) = b, \quad S(\Gamma_1^+ \to \Gamma_4^-) = 0. \tag{8}$$

Then, the intensity of the $\Gamma_1^+ \to \Gamma_4^-$ transition vanishes so that it might be possible to get the anisotropic exchange splitting ϵ_{ex} (discussed in Ref. 2) between the Γ_3^- and Γ_5^- states from measurements in circularly polarized light.

ELECTRIC DIPOLE TRANSITIONS

An important facet that we would like to briefly address in this paper concerns the implication of the weak quasiclosure approximation, introduced above, on the Axe[3] standard model for ED-TPA transitions between states of the same parity. Indeed, the use of the approximation (2) leads, for identical photons, to the transition moment

$$M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')} = \sum_k \sum_{a''\Gamma''\gamma''} Z_k(\alpha J, \alpha' J') \{ee\}^k_{a''\Gamma''\gamma''} \times f\begin{pmatrix} J & J' & k \\ a\Gamma\gamma & a'\Gamma'\gamma' & a''\Gamma''\gamma'' \end{pmatrix}^*, \tag{9}$$

where

$$Z_k(\alpha J, \alpha' J') = (-1)^{2J'} [k]^{1/2} \sum_{\alpha'' J''} \frac{1}{E_i - E(\alpha'' J'') + \hbar\omega} \times (\alpha' J' || D^1 || \alpha'' J'')(\alpha'' J'' || D^1 || \alpha J) \times \begin{Bmatrix} J & k & J' \\ 1 & J'' & 1 \end{Bmatrix}. \tag{10}$$

From Eqs. (9) and (10), it is clear that the selection rules for (parity-allowed) ED-TPA transitions with identical photons are (i) $k=0$ and 2, (ii) as above, (iii) as above. In the case of nonidentical photons, we have (i) $k=0$, 1, and 2; (ii) as above; (iii) as above. The crucial difference with the selection rule in Ref. 3 is the occurrence of $k=0$ (for both identical or nonidentical photons). As a limiting case, when the energies $E(\alpha'' J'')$ in Eq. (10) are replaced by their barycenter, we recover the quasiclosure approximation employed by Axe.[3] In this case, Eq. (10) gives back the results that only $k=2$ contributes to Eq. (9).

As an example, a parity-allowed ED-TPA transition of type $\Gamma_1^\pm \to \Gamma_1^\pm$ (in any symmetry G) is not allowed in the Axe model (since $\Gamma' = \Gamma'' = \Gamma_1^+$ implies that the only possible value of k is $k=0$). On the contrary, such a transition becomes allowed if use is made of the weak quasiclosure approximation inherent to Eq. (2). It is to be emphasized that the observation[18,19] of parity-allowed ED-TPA transitions of type $J=0$ $(\Gamma_1^\pm) \to J'=0$ $(\Gamma_1^\pm)$ was always attributed to the occurrence of third- and higher-order mechanisms besides the second-order mechanisms taken into account in the Axe model. Our selection rules show that such transitions can be understood in the framework of second-order mechanisms only once the severe approximation $E_{\mathscr{E}} = E(\alpha'' J'' a'' \Gamma'' \gamma'') = \text{const}$ is relaxed. In this respect, the weak quasiclosure approximation based on Eq. (2) is phenomenologically equivalent to the introduction of third- and higher-order mechanisms.

CONCLUSIONS

In conclusion, we have derived a model for MED-TPA from the combination of (i) a weak quasiclosure approximation for handling the Göppert-Mayer series (1) and (ii) symmetry considerations based on the group chain SU(2) $\supset G^*$. When the two absorbed photons are identical, the obtained selection rules for MED-TPA exhibit some important differences (besides the selection rule on spin) with respect to those for ED-TPA between states of opposite parities. The use of the weak quasiclosure approximation in ED-TPA between states of the same parity leads to the important result that a scalar contribution ($k=0$) may contribute to the intensity in addition to the classical contributions ($k=2$ for identical photons and $k=1,2$ for nonidentical photons). It is to be observed that, for both ED- and MED-TPA, the structure of the intermediate states is taken into account through the weak quasiclosure approximation introduced in this paper. The selection rules for MED-TPA have been discussed in connection with the recent measurements on excitons by Fröhlich *et al.*;[2] it is hoped that the results in this work [particularly Eqs. (7) and (8)] would suggest some new MED-TPA experiments in order to understand the discrepancy between the values for ϵ_{ex} for RbI obtained from MED-TPA and three-photon absorption data.

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