SYMMETRY ADAPTATION AND TWO-PHOTON SPECTROSCOPY
OF IONS IN MOLECULAR OR SOLID–STATE FINITE SYMMETRY*

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I. INTRODUCTION

Symmetry adaptation techniques, based on the use of chains of groups \( O(3) \supset G \), have been developed by many authors in the last twenty years. In particular, numerous studies have been achieved in connection with crystal- and ligand-field theories (see Refs. [1-3] and references therein).

The aim of this paper is to show how Wigner-Racah calculus for a chain of type \( O(3) \supset G \) (in terms of simple or double groups) can be applied to the determination of the intensity of two-photon transitions for an ion with configuration \( n\ell^N \) in a molecular or solid-state environment.
with symmetry $G$. (For classification and symmetry-breaking purposes, the group $G$ may be replaced by a chain of subgroups of $O(3)$, the relevant symmetry group being one of the groups of the chain.)

The rôle of symmetries in two-photon spectroscopy of partly-filled shell ions in finite symmetry, of interest in molecular and solid-state physics, is touched upon in Refs. [4-8]. In Ref. [7], the accent is put on the transition matrix elements between initial and final state vectors while emphasize is on the intensity strength in Ref. [8] and in the present paper.

Two distinct cases are studied in this work. The case of $(n\ell^N \rightarrow n\ell^N)$ intra-configurational two-photon transitions, which are parity allowed, is worked out in section II and the one of $(n\ell^N \rightarrow n\ell^{N-1}\ell')$ with $(-)^{\ell+\ell'} = -1$) inter-configurational two-photon transitions, which are parity forbidden, is examined in section III.

**II. INTRA-CONFIGURATIONAL TWO-PHOTON TRANSITIONS**

**Preliminaries**

We know that the electronic transition matrix element $M_{i\rightarrow f}$ between an initial state $i$ and a final state $f$ is, in the framework of the dipolar approximation, given by

$$M_{i\rightarrow f} = \sum_v \frac{1}{\Delta_1} \left( f|\vec{D}.\vec{E}_2|v \right) \left( v|\vec{D}.\vec{E}_1|i \right) + \sum_v \frac{1}{\Delta_2} \left( f|\vec{D}.\vec{E}_1|v \right) \left( v|\vec{D}.\vec{E}_2|i \right)$$

(1)

The two summations in (1) have to be extended over all the (virtual) intermediate states $v$ having a parity different from the one of the states $i$ and $f$. Furthermore, we have

$$\Delta_\lambda = \hbar\omega_\lambda - E_v \quad \text{for} \quad \lambda = 1, 2$$

(2)

where $E_v$ is the energy of the state $v$ with respect to that of the state $i$ and $\hbar\omega_\lambda$ the energy of the photon no. $\lambda$. (For Raman scattering, the sign of $\hbar\omega_2$ has to be changed.) In equation (1), the quantity $\vec{D}.\vec{E}_\lambda$ (with $\lambda = 1, 2$) stands for the scalar product of the electric dipolar moment operator

$$\vec{D} = -e \sum_{j=1}^N \vec{r}_j$$

(3)

for the $N$ electrons and the unit polarization vector $\vec{E}_\lambda$ for the photon no. $\lambda$. (We use single mode excitations, of polarization $\vec{E}_\lambda$ and energy $\hbar\omega_\lambda$, of the radiation field.) The two photon beams can be polarized either circularly with

$$(\vec{E}_\lambda)_q = -\delta(q,-1) \quad \text{if} \quad \vec{E}_\lambda = \vec{e}_{+1} \quad \text{while} \quad (\vec{E}_\lambda)_q = -\delta(q,+1) \quad \text{if} \quad \vec{E}_\lambda = \vec{e}_{-1} \quad \text{for} \quad \lambda = 1, 2$$

(4)
or linearly with

\[(\mathcal{E}_\lambda)_0 = \cos \theta_\lambda \quad \mathcal{E}_\lambda)_{\pm 1} = \mp \frac{1}{\sqrt{2}} \sin \theta_\lambda \exp(\pm i \varphi_\lambda) \quad \text{for} \quad \lambda = 1, 2 \quad (5)\]

In equations (4) and (5), we use the components

\[(\mathcal{E}_\lambda)_q = \vec{E}_\lambda \cdot \vec{e}_q \quad \text{for} \quad \lambda = 1, 2 \quad \text{and} \quad q = -1, 0, 1 \quad (6)\]

in the standard spherical basis \((\vec{e}_{-1}, \vec{e}_0, \vec{e}_{+1})\). In the case of a linear polarization, the angles \((\theta_\lambda, \varphi_\lambda)\) are the polar angles of the polarization vector \(\vec{E}_\lambda (\lambda = 1, 2)\) with respect to the crystallographic axis. For two-photon absorption, only one sum occurs in (1) when the two photons are identical.

Equation (1) can be derived from the time-dependent perturbation theory \([9,10]\) and goes back to the work of Göppert-Mayer. It is also possible to derive it, in an elegant way, from the method of the resolvent operator \([10,11]\).

State vectors

The initial state \(i\) with symmetry \(\Gamma\) is characterized by the state vectors \(|i\Gamma\gamma\rangle\) where \(\gamma (\gamma = 1, 2, \cdots, \text{dim } \Gamma)\) is a multiplicity label to be used if the dimension \(\text{dim } \Gamma\) of the irreducible representation class (IRC) \(\Gamma\) of the group \(G\) is greater than 1. The state vector \(|i\Gamma\gamma\rangle\) is taken in the form

\[|i\Gamma\gamma\rangle \equiv |n\ell^N i\Gamma\gamma\rangle = \sum_{J} |n\ell^N \alpha SLJa\Gamma\gamma\rangle c(\alpha SLJa\Gamma; i) \quad (7)\]

in terms of the \(O(3) \supset G\) symmetry adapted state vectors

\[|n\ell^N \alpha SLJa\Gamma\gamma\rangle = \sum_{M=-J}^{J} |n\ell^N \alpha SLJM\rangle (JM|Ja\Gamma\gamma\rangle \quad (8)\]

The coefficients \((JM|Ja\Gamma\gamma\rangle\) in (8) are reduction coefficients to pass from the chain \(O(3) \supset O(2)\) characterizing the \(\{JM\}\) scheme to the chain \(O(3) \supset G\) characterizing the \(\{Ja\Gamma\gamma\}\) scheme; they depend on the group \(G\) with a certain degree of freedom emphasized by the branching multiplicity label \(a\) to be used when \(\Gamma\) occurs several times in the IRC \((J)\) of \(O(3)\). In contradistinction, the coefficients \(c(\alpha SLJa\Gamma; i)\) in (7) depend on the Hamiltonian employed for obtaining the initial state \(i\). Similarly, for the final state \(f\) with symmetry \(\Gamma'\), we have the state vectors

\[|f\Gamma'\gamma'\rangle \equiv |n\ell^N f\Gamma'\gamma'\rangle = \sum_{a'\tilde{S}'L'J'a'} |n\ell^N \alpha'S'L'J'a'\Gamma'\gamma'\rangle c(\alpha'S'L'J'a'\Gamma'; f) \quad (9)\]

in terms of \(O(3) \supset G\) symmetry adapted state vectors.

The only good quantum numbers for the initial and final state vectors are \(\Gamma\gamma\) and \(\Gamma'\gamma'\), respectively. Although, the state vectors (7) and (9) are developed in a weak-field basis, it is to
be noted that the intensity calculation to be conducted in what follows is valid for any (weak-, intermediate- or strong-field) coupling scheme. The expansion coefficients c(αSLJaΓ; i) and c(α′S′L′J′a′Γ′; f) can be obtained by optimizing an Hamiltonian involving at least Coulomb, spin-orbit and crystal-field interactions; the introduction of more sophisticated interactions in the Hamiltonian may be useful to take covalency effects into account [3]. Alternatively, the expansion coefficients in (7) and (9) can be considered as free parameters entering in the phenomenological intensity parameters to be introduced below.

Transition matrix element

By using a quasi-closure approximation, it can be shown that the transition matrix element $M_{i \rightarrow f}$ between the state vectors $|i\Gamma \gamma \rangle$ and $|f\Gamma'\gamma' \rangle$ turns out to be given by

$$M_{i \rightarrow f} \equiv M_{i(\Gamma \gamma) \rightarrow f(\Gamma' \gamma')} = (f \Gamma' \gamma' | H_{\text{eff}} | i \Gamma \gamma)$$

(10)

where $H_{\text{eff}}$ is an effective operator [12-15]. This operator may be written as [7]

$$H_{\text{eff}} = \sum_{kS,kL,k} C[(kS)kL,k] \left\{ \{E_1 E_2\}^{(k)} \cdot W^{(kS,kL,k)} \right\}$$

(11)

In equation (11), $W^{(kS,kL,k)}$ is an electronic double tensor of spin rank $k_S$, orbital rank $k_L$ and total rank $k$. The information on the polarization of the two photons is contained in the tensor product $\{E_1 E_2\}^{(k)}$ of rank $k = 0, 1$ or 2. The right-hand side of (11) is a development in terms of scalar products (.) with expansion coefficients $C[(kS)kL,k]$. These coefficients depend on the ground configuration $n\ell N$ and on the configurations $n\ell N' - n'\ell'$ and/or $n'\ell'\ell'' + n\ell N + 1$, with $(-)^{\ell + \ell'} = 1$, from which the virtual states $\nu$ arise.

Only the contributions $(k_S = 0, k_L = 1, k = 1)$ and $(k_S = 0, k_L = 2, k = 2)$ correspond to the standard theory originally developed by Axe [12]. The other contributions $(k_S \neq 0, k_L, k)$, which may include $(k_S = 1, k_L = 1, k = 0)$ and $(k_S = 1, k_L = 1, k = 2)$, correspond either to mechanisms introduced by various authors [13-15] or to phenomenological contributions introduced in the spirit of Ref. [7]. The contributions $(k_S = 0, k_L = k, k)$ and $(k_S \neq 0, k_L, k)$ are often referred to as second-order and third-order mechanisms, respectively. It is in principle possible to find an expression for the parameters $C[(kS)kL,k]$. For example, for the contribution $(k_S = 0, k_L = k, k)$ we have

$$C[(0k)k] = -\sqrt{2} e^2 \sum_{n'\ell'} \left[ (-)^k (\Delta'_1)^{-1} + (\Delta'_2)^{-1} \right] (n\ell|r|n'\ell')^2 \left( \ell||C^{(1)}||\ell' \right)^2 \left\{ \frac{1}{\ell} \frac{1}{\ell'} \frac{k}{l} \right\}$$

(12)

where, according to the quasi-closure approximation, $\Delta'$ replaces $\Delta$ of equation (1) with

$$\Delta'_\lambda = \hbar \omega_\lambda - E(n'\ell') \quad \text{for} \quad \lambda = 1, 2$$

(13)
(Most of the other symbols in equation (12), and in the rest of this paper, have their usual significance.) Among the various contributions \( (k_S \neq 0, k_L, k) \), the contribution \((k_S = 1, k_L = 1, k = 0)\) arises from the spin-orbit interaction within the configuration \( n\ell N - n'\ell' \) as was shown for lanthanide ions [13,14].

The transition matrix element (10) is easily calculated by means of Wigner-Racah calculus for the chain \( O(3) \supset G \). As a result, we have (see Ref. [7])

\[
M_{i(\Gamma\gamma)} \rightarrow f(\Gamma'\gamma') = \sum_{\alpha' \alpha''} \sum_{\alpha S \alpha L} \frac{c(\alpha S' L' J' a'^{T'} f^* c(\alpha S L J a; i))}{(-)^{k_S + k_L - k} C[(k_S k_L) k]} \left( n^N \alpha S L J \| W^{(k_S k_L) k} \| n^N \alpha S' L' J' \right)^* \sum_{a'' T'' \gamma''} f_{a'' T'' \gamma''} \left( J_{a T \gamma} J'_{a' T' \gamma'} k_{T T' \gamma''} \right)^* \{ \mathcal{E}_1 \mathcal{E}_2 \}_{a'' T'' \gamma''}^{(k)}
\]

where the \( f \) symbol denotes an \( O(3) \supset G \) symmetry adapted coupling coefficient defined by

\[
f\left( J_{a T \gamma} J'_{a' T' \gamma'} k_{T T' \gamma''} \right) = \sum_{M M' q} (-)^{J - M} \left( J_{a T \gamma} J'_{a' T' \gamma'} k_{T T' \gamma''} \right)^* (J M | J a T \gamma)^* (J' M' | J' a' T' \gamma') (k q | k a'' T'' \gamma'')
\]

Equation (14) immediately follows by developing (10) with the help of (7), (9) and (11).

### Intensity formula

The quantity of interest for a comparison between theory and experiment is the intensity \( S_{i(\Gamma) \rightarrow f(\Gamma')} \) of the two-photon transition between the initial state \( i \) and the final state \( f \). This intensity is given by

\[
S_{\Gamma \rightarrow \Gamma'} \equiv S_{i(\Gamma) \rightarrow f(\Gamma')} = \sum_{\gamma \gamma'} |M_{i(\Gamma\gamma) \rightarrow f(\Gamma'\gamma')}|^2
\]

By introducing (14) into (16), we get an expression involving

\[
X = \sum_{\gamma \gamma'} f\left( J_{a T \gamma} J'_{a' T' \gamma'} k_{T T' \gamma''} \right)^* f\left( \tilde{J}_{\tilde{a} T \tilde{\gamma}} \tilde{J}'_{\tilde{a}' T' \tilde{\gamma}'} k_{T T' \tilde{\gamma}''} \right) f\left( J_{a T \gamma} J'_{a' T' \gamma'} k_{T T' \gamma''} \right)^* f\left( \tilde{J}_{\tilde{a} T \tilde{\gamma}} \tilde{J}'_{\tilde{a}' T' \tilde{\gamma}'} k_{T T' \tilde{\gamma}''} \right)^*
\]

i.e., a sum over \( \gamma \) and \( \gamma' \) of the product of two particular \( f \) coefficients. This sum can be calculated to be

\[
X = ([J][\tilde{J}])^{-1/2} [\Gamma'']^{-1} [\Gamma] \delta(\tilde{\Gamma}'', \Gamma'') \delta(\tilde{\gamma}'', \gamma'') \sum_{\beta} (J a' T' + k r T'' | J a T \gamma) (J' a' T' + \ell s T'' | J' a T \gamma) ^*
\]
To derive the sum rule (18), it is sufficient to apply twice the factorization property \[16\]

\[
f \left( \frac{j_1}{a_1 \Gamma_1 \gamma_1} \frac{j_2}{a_2 \Gamma_2 \gamma_2} \frac{k}{a \Gamma} \right) = (-)^{2k} [j_1]^{-1/2} \sum_\beta (j_2 a_2 \Gamma_2 + k a \Gamma | j_1 a_1 \beta \Gamma_1)^* \left( \Gamma_2 \Gamma_2 \gamma_2 | \Gamma_2 \beta \Gamma_1 \gamma_1 \right)^* \tag{19}\]

for the \(f\) symbol and once the orthonormality-completeness property \[16\]

\[
\sum_{\gamma_1 \gamma} (\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \Gamma_1 \Gamma_2 \beta \Gamma \gamma)^* \left( \Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \Gamma_1 \Gamma_2 \beta \Gamma \gamma \right) = \\
\Delta(\Gamma | \Gamma_1 \otimes \Gamma_2) \delta(\Gamma_2, \Gamma_2) \delta(\gamma_2, \gamma_2) \delta(\beta, \beta) [\Gamma_2]^{-1} [\Gamma] \tag{20}\]

for the Clebsch-Gordan coefficients of \(G\). The \((+|\ )\) coefficients in equations (18) and (19) stand for isoscalar factors of the chain \(O(3) \supset G\). In (18) and (19), the labels of type \(\beta\) are internal multiplicity labels to be used for those Kronecker products which are not multiplicity-free. The introduction of (18) into (16) leads to the compact expression

\[
S_{\Gamma' \rightarrow \Gamma''} = \sum_{k \ell} \sum_{rs} \sum_{\Gamma'''} I[k \ell rs \Gamma'''; \Gamma \Gamma'] \sum_{\gamma''} \{\mathcal{E}_1 \mathcal{E}_2\}^{(k)}_{\gamma' \Gamma''} \left(\{\mathcal{E}_1 \mathcal{E}_2\}^{(\ell)}_{\gamma' \Gamma''}\right)^* \tag{21}\]

In equation (21), the parameter \(I[\cdots]\) reads

\[
I[k \ell rs \Gamma'''; \Gamma \Gamma'] = [\Gamma''']^{-1} [\Gamma] \sum_{J' a'} \sum_{J a} \sum_{J' a} \sum_{J a} Y_{k}(J' a' \Gamma', J a \Gamma) Y_{\ell}(J' a' \Gamma', J a \Gamma)^* \\
\sum_{\beta} (J' a' \Gamma' + k r \Gamma''; J a \beta \Gamma') (J' a' \Gamma' + \ell s \Gamma''; J a \beta \Gamma)^* \tag{22}\]

where \(Y_{k}\) is defined by

\[
Y_{k}(J' a' \Gamma', J a \Gamma) = [J]^{-1/2} \sum_{\alpha' S' L'} \sum_{\alpha S L} \sum_{k s k L} c(\alpha' S' L' J' a' \Gamma; f)^* c(\alpha S L J a \Gamma; i) C[(k s k L) k] \\
(-)^{k S + k L - k} (n \ell N \alpha S L J [W((k s k L) k)] | n \ell N \alpha' S' L' J')^* \tag{23}\]

and \(Y_{\ell}\) by a relation similar to (23).

Properties and rules

The \(I\) parameters in (21) can be calculated in an \textit{ab initio} way or can be considered as phenomenological parameters. In both approaches, the following properties and rules are of central importance.

\textbf{Property 1.} In the general case, we have the (hermitean) property

\[
I[k \ell rs \Gamma'''; \Gamma \Gamma']^* = I[k \ell rs \Gamma'''; \Gamma \Gamma'] \tag{24}\]
which ensures that $S_{\Gamma \rightarrow \Gamma'}$ is a real quantity.

**Property 2.** In the case where the group $G$ is multiplicity-free, we have the factorization formula

$$I[k\ell rs\Gamma''; \Gamma\Gamma'] = \chi[kr\Gamma''; \Gamma\Gamma'] \chi[\ell s\Gamma''; \Gamma\Gamma']^* \tag{25}$$

where the function $\chi$ is defined through

$$\chi[kr\Gamma''; \Gamma\Gamma'] = [\Gamma'']^{-1/2} [\Gamma]^{1/2} \sum_{J'a'} \sum_{Ja} Y_k(J'a'\Gamma', Ja\Gamma) (J'a'\Gamma' + kr\Gamma''|Ja\Gamma) \tag{26}$$

(In a less restrictive sense, equation (25) is valid when the Kronecker product $\Gamma'^* \otimes \Gamma$, of the complex conjugate IRC of $\Gamma'$ by the IRC $\Gamma$, is multiplicity-free.)

The number of independent parameters $I[\cdots]$ in the expansion (21) can be *a priori* determined from the two following selection rules used in conjunction with Properties 1 and 2.

**Rule 1.** In order to have $S_{\Gamma \rightarrow \Gamma'} \neq 0$, it is necessary that

$$\Gamma'' \subset \Gamma'^* \otimes \Gamma \tag{27}$$

and

$$\Gamma'' \subset (k_g) \quad \Gamma'' \subset (\ell_g) \tag{28}$$

where $(k_g)$ and $(\ell_g)$ are *gerade* IRC’s of the group $O(3)$ associated to the integers $k$ and $\ell$, respectively.

**Rule 2.** The sum over $k$ and $\ell$ in the intensity formula (21) is partially controlled by the selection rule

$$\mathcal{E}_1 \neq \mathcal{E}_2 \quad k, \ell = 1, 2 \quad \text{for} \quad k_S = 0$$

$$k, \ell = 0, 1, 2 \quad \text{for} \quad k_S = 0 \quad \text{and} \quad k_S \neq 0 \tag{29}$$

or

$$\mathcal{E}_1 = \mathcal{E}_2 \quad k, \ell = 2 \quad \text{for} \quad k_S = 0$$

$$k, \ell = 0, 2 \quad \text{for} \quad k_S = 0 \quad \text{and} \quad k_S \neq 0 \tag{30}$$

according to as the two photons have different or the same polarization. (Note that the situation $\mathcal{E}_1 = \mathcal{E}_2$ surely occurs for identical photons but may also occur for non-identical photons.)

**Discussion**

For most of the cases of interest, there is no summation on $r$ and $s$, two branching multiplicity labels of type $a$, in the intensity formula (21). (In other words, the frequency of $\Gamma''$ in $(k_g)$ and $(\ell_g)$ is rarely greater than 1.) The group-theoretical selection rules (27) and (28) impose strong limitations on the summation over $\Gamma''$ in (21) once $\Gamma$ and $\Gamma'$ are fixed and the range of values of $k$ and $\ell$ is chosen.
The number of independent intensity parameters $I \cdot \cdot \cdot$ in the formula (21) is determined by: (i) the nature of the photons, cf. Rule 2; (ii) the group $G$, cf. Rule 1; (iii) the symmetry property (24), cf. Property 1; (iv) the use of $k_S = 0$ (second-order mechanism) or $k_S = 0$ and $k_S \neq 0$ (second- plus third-order mechanisms), cf. Rule 2; (v) the kind of the (weak-, intermediate- or strong-field) coupling used for the state vectors, cf. equations (22) and (23).

Points (i)-(iii) depend on external physical conditions. On the other hand, points (iv) and (v) are model-dependent. In particular, in the case where the $J$-mixing, cf. point (v), can be neglected, a situation of interest for lanthanide ions, the summations on $k$ and $\ell$ in (21) are further reduced by the triangular rule $|J - J'| \leq k, \ell \leq J + J'$, where $J$ and $J'$ are the total angular quantum numbers for the initial and final states, respectively. Similar restrictions apply to $k_S$ and $k_L$ in (23) if the $S$- and $L$-mixing are neglected.

The computation, via equations (22) and (23), of the $I$ parameters generally is a difficult task. Therefore, they may be considered, at least in a first step, as phenomenological parameters. In this respect, equations (22) and (23) should serve as a guide for reducing the number of $I$ parameters.

Once the number of independent parameters $I \cdot \cdot \cdot$ in the intensity formula (21) has been determined, we can obtain the polarization dependence of the intensity strength $S_{\Gamma \rightarrow \Gamma'}$ by calculating the tensor products $\{E_1 E_2\}_a^{(K)}_{\Gamma'' \gamma''}$ (with $K = k, \ell$ and $a'' = r, s$) occurring in equation (21). For this purpose, we use the development

$$\{E_1 E_2\}_a^{(K)}_{\Gamma'' \gamma''} = \sum_{Q = -K}^{K} \{E_1 E_2\}_Q^{(K)} (KQ|Ka''\Gamma''\gamma'')$$  

in terms of the spherical components $\{E_1 E_2\}_Q^{(K)}$, the coefficients in the development (31) being reduction coefficients for the chain $O(3) \supset G$. Then, we use in turn the development

$$\{E_1 E_2\}_Q^{(K)} = (-)^{K-Q} [K]^{1/2} \sum_{x=-1}^{1} \sum_{y=-1}^{1} \begin{pmatrix} 1 & K & 1 \\ x & -Q & y \end{pmatrix} (E_1)_x (E_2)_y$$

in terms of the spherical components $(E_\lambda)_q$ defined by (4) or (5) for circular or linear polarization, respectively.

**Illustration**

As an illustrative example, we consider the case of the configuration $nd^8$ in cubical symmetry with $G \equiv O$. Let us examine the intra-configurational two-photon absorption transitions from the initial state $i = ^3A_2(T_2)$ to the final states taken as the first excited states $f = ^3T_2(E, T_1, T_2, A_2)$. Therefore, we have $\Gamma = T_2$ for the initial state and $\Gamma' = A_2, E, T_1, T_2$.
for the various final states. Furthermore, there is no sum on the multiplicity labels \( r \) and \( s \) in the intensity formula (21). Let us begin with non-identical photons. Then, the possible values of \( k \) and \( \ell \) in (21) are 0, 1, 2. Since the restriction \( SO(3) \to O \) yields

\[
(0) = A_1 \quad (1) = T_1 \quad (2) = E \oplus T_2
\]

we have \( k = \ell \) in (21). Consequently, the intensity parameters \( I[ \cdots ] \) assume the form

\[
I[kk''\Gamma'; \Gamma''] = |\chi[kk''\Gamma'; \Gamma'']|^2 \quad \text{with} \quad \Gamma'' = A_1, T_1, E, T_2
\]

since the group \( O \) is multiplicity-free. More precisely, we are left with 10 independent parameters for non-identical photons; we shall take the following normalization:

\[
\begin{align*}
    a_{T_2T_2}(0A_1) &= \frac{1}{3} I[00A_1; T_2T_2] &
    a_{T_2T_2}(2E) &= \frac{1}{6} I[22E; T_2T_2] \\
    a_{T_2T_2}(2T_2) &= \frac{1}{4} I[22T_2; T_2T_2] &
    a_{T_2T_2}(1T_1) &= \frac{1}{4} I[11T_1; T_2T_2] \\
    a_{T_2T_2}(2E) &= \frac{1}{6} I[22E; T_2T_1] &
    a_{T_2T_2}(2T_2) &= \frac{1}{4} I[22T_2; T_2T_1] \\
    a_{T_2T_1}(1T_1) &= \frac{1}{4} I[11T_1; T_2T_1] &
    a_{T_2E}(2T_2) &= \frac{1}{4} I[22T_2; T_2E] \\
    a_{T_2E}(1T_1) &= \frac{1}{4} I[11T_1; T_2E] &
    a_{T_2A_2}(1T_1) &= \frac{1}{4} I[11T_1; T_2A_2]
\end{align*}
\]

As a result, the intensity strengths are given by

\[
\begin{align*}
    S_{T_2\to T_2} &= 3 a_{T_2T_2}(2E) + 2 a_{T_2T_2}(2T_2) \\
    S_{T_2\to T_1} &= 3 a_{T_2T_1}(2E) + 2 a_{T_2T_1}(2T_2) \\
    S_{T_2\to E} &= 2 a_{T_2E}(2T_2) \\
    S_{T_2\to A_2} &= 0
\end{align*}
\]

for circular polarization (the two photons having the same circular polarization) and by

\[
\begin{align*}
    S_{T_2\to T_2} &= a_{T_2T_2}(0A_1) \varpi_1 + a_{T_2T_2}(2E) \varpi_2 + a_{T_2T_2}(2T_2) \varpi_3 + a_{T_2T_2}(1T_1) \varpi_4 \\
    S_{T_2\to T_1} &= a_{T_2T_1}(2E) \varpi_2 + a_{T_2T_1}(2T_2) \varpi_3 + a_{T_2T_1}(1T_1) \varpi_4 \\
    S_{T_2\to E} &= a_{T_2E}(2T_2) \varpi_3 + a_{T_2E}(1T_1) \varpi_4 \\
    S_{T_2\to A_2} &= a_{T_2A_2}(1T_1) \varpi_4
\end{align*}
\]

for linear polarization. The angular functions \( \varpi_i \) \( (i = 1, 2, 3, 4) \) in equation (37) read

\[
\begin{align*}
    \varpi_1 &= [\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2)]^2 \\
    \varpi_2 &= [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2)]^2 \\
    &\quad + 3 \sin^2 \theta_1 \sin^2 \theta_2 \cos^2(\varphi_1 + \varphi_2) \\
    \varpi_3 &= 2 \sin^2 \theta_1 \cos^2 \theta_2 + 2 \cos^2 \theta_1 \sin^2 \theta_2 \\
    &\quad + \sin 2\theta_1 \sin 2\theta_2 \cos(\varphi_1 - \varphi_2) + 2 \sin^2 \theta_1 \sin^2 \theta_2 \sin^2(\varphi_1 + \varphi_2) \\
    \varpi_4 &= 2 \sin^2 \theta_1 \cos^2 \theta_2 + 2 \cos^2 \theta_1 \sin^2 \theta_2 \\
    &\quad + \sin 2\theta_1 \sin 2\theta_2 \cos(\varphi_1 - \varphi_2) + 2 \sin^2 \theta_1 \sin^2 \theta_2 \sin^2(\varphi_1 - \varphi_2)
\end{align*}
\]
We now continue with the particular case where the two photons are identical. In this case, we get \( \varpi_4 \equiv 0 \) so that the number of independent parameters in equations (36) and (37) is reduced from 10 to 6: the parameter \( a_{T_2 T_2}(0A_1) \) describes third-order mechanisms while the parameters \( a_{T_2 T_2}(2E), a_{T_2 T_2}(2T_2), a_{T_2 T_1}(2E), a_{T_2 T_1}(2T_2) \) and \( a_{T_2 E}(2T_2) \) may be thought to mainly describe second-order mechanisms.

Similar results hold for the other intra-configurational two-photon transitions of \( nd^8 \) in \( O \). For example, let us consider the transition between the initial state \( i = 3A_2(T_2) \) with \( \Gamma = T_2 \) and the final state \( f = 3T_1(A_1) \) with \( \Gamma' = A_1 \). By putting

\[
a_{T_2 A_1}(2T_2) = \frac{1}{4} I[22T_2; T_2 A_1]
\]

we obtain (for identical or non-identical photons)

\[
S_{T_2 \rightarrow A_1} = a_{T_2 A_1}(2T_2) \varpi_3 \quad \text{or} \quad 2 a_{T_2 A_1}(2T_2)
\]

according to as the polarization is linear or circular.

Indeed, all the two-photon transitions arising from an initial state of symmetry \( T_2 \) are given by formulas of the type (36), (37) and (39). The formulas (36) and (37) generalize to the case of non-identical photons the formulas for identical photons derived in Ref. [18] in order to explain the experimental results of Ref. [17] concerning \( \text{Ni}^{2+} \) in \( \text{MgO} \).

**III. INTER-CONFIGURATIONAL TWO-PHOTON TRANSITIONS**

**Sketch of the theory**

We now consider two-photon transitions between Stark levels arising from the configurations \( n\ell^N \) and \( n\ell^{N-1}n'\ell' \) of opposite parities \((-\ell + \ell' = -1)\). For the sake of simplicity, we deal here with identical photons. The initial and final state vectors are (respectively) taken in the form

\[
|\ell \Gamma \gamma \rangle \equiv |n\ell^N \ell \Gamma \gamma \rangle = \sum_{\alpha S L J a} |n\ell^N \alpha S L J a \ell \Gamma \gamma \rangle c(n\ell^N; \alpha S L J a \ell; i)
\]

and

\[
|\ell' \Gamma' \gamma' \rangle \equiv |n\ell^{N-1}n'\ell' \ell' \Gamma' \gamma' \rangle = \sum_{\alpha' S' L' J' a'} |n\ell^{N-1}n'\ell' \alpha' S' L' J' a' \ell' \Gamma' \gamma' \rangle c(n\ell^{N-1}n'\ell'; \alpha' S' L' J' a'; f)
\]

to be compared with equations (7) and (9).

It is clear that the transition matrix element

\[
M_{\ell \Gamma \gamma \rightarrow \ell' \Gamma' \gamma'} = \sum_{\nu} \frac{1}{\Delta} \left( f \Gamma' \gamma' | \vec{D} \cdot \vec{E} | \nu \Gamma \gamma \nu \right) \left( \nu \Gamma \gamma \nu | \vec{D} \cdot \vec{E} | \ell \Gamma \gamma \right)
\]
is identically zero. In order to obtain \( M_{i(\Gamma_\gamma) \rightarrow f(\Gamma'\gamma')} \neq 0 \), it is necessary to pollute the state vectors (41) and (42) with state vectors of the type \( |n\ell^{N-1} n'\ell' x' \Gamma'\gamma' \rangle \) and \( |n\ell^N x\Gamma_\gamma \rangle \), respectively. This may be achieved by using first-order perturbation theory where the polluting agent is the crystal-field potential \( H_3 \) of odd order, which is static or dynamic according to as the group \( G \) does not or does have a center of inversion. We thus produce state vectors noted \( |n\ell^N i\Gamma_\gamma \rangle \) and \( |n\ell^{N-1} n'\ell' f\Gamma'\gamma' \rangle \) from which we can calculate a non-vanishing transition matrix element

\[
M_{i(\Gamma_\gamma) \rightarrow f(\Gamma'\gamma')} = \sum_{\nu_1, \nu_2} \frac{1}{\Delta(v_1)} \frac{1}{\Delta(v_2)} < f\Gamma'\gamma'| \vec{D}.\vec{E}|v_\Gamma_\gamma v_\nu >\nu_\Gamma_\gamma \nu_v |\vec{D}.\vec{E}|i\Gamma_\gamma >
\]

(44)

Then, we apply a quasi-closure approximation both for the initial, intermediate (virtual), and final state vectors and the transition matrix element. This approximation can be summarized by

\[
E(n'\ell') - E(n\ell) = 2\hbar \omega
\]

(45)

We thus obtain a closed form formula for \( M_{i(\Gamma_\gamma) \rightarrow f(\Gamma'\gamma')} \).

At this stage, it should be mentioned that the so-obtained formula is equivalent to that we would obtain, within the same approximation (45), by using third order mechanisms described by

\[
M_{i(\Gamma_\gamma) \rightarrow f(\Gamma'\gamma')} = \sum_{\nu_1, \nu_2} \frac{1}{\Delta(v_1)} \frac{1}{\Delta(v_2)} (f\Gamma'\gamma'| \vec{D}.\vec{E}|v_1\Gamma_1\gamma_1)(v_1\Gamma_1\gamma_1|\vec{D}.\vec{E}|v_2\Gamma_2\gamma_2)(v_2\Gamma_2\gamma_2|H_3|i\Gamma_\gamma) \\
+ \sum_{\nu_1, \nu_2} \frac{1}{\Delta(v_1)} \frac{1}{\Delta(v_2)} (f\Gamma'\gamma'|H_3|v_1\Gamma_1\gamma_1)(v_1\Gamma_1\gamma_1|\vec{D}.\vec{E}|v_2\Gamma_2\gamma_2)(v_2\Gamma_2\gamma_2|i\Gamma_\gamma)
\]

(46)

where the initial, intermediate (virtual) and final state vectors are non-polluted state vectors.

By following the same line of reasoning as in the case of intra-configurational transitions, we are left with the intensity formula

\[
S_{\Gamma \rightarrow \Gamma'} = \text{Re} \left[ \sum_{k, \ell = 0, 2} \sum_{rs} \sum_{\Gamma''} \sum_{\gamma''} I_1[k\ell rs\Gamma''; \Gamma\Gamma'] \sum_{\gamma''} \{ \mathcal{E}\mathcal{E} \}^{(k)}_{s\Gamma''\gamma''} \left( \{ \mathcal{E}\mathcal{E} \}^{(l)}_{s\Gamma''\gamma''} \right)^* \right] + \sum_{k=0} \sum_{rs} \sum_{\Gamma''} \sum_{\gamma''} I_2[k2rs\Gamma''; \Gamma\Gamma'] \sum_{\gamma''} \{ \mathcal{E}\mathcal{E} \}^{(k)}_{s\Gamma''\gamma''} \{ \mathcal{E}\mathcal{E} \}^{(2)}_{s\Gamma''\gamma''} \right]
\]

(47)

which parallels the formula (21).

**Illustration**

Let us consider the case of the configuration 4\( f \) in tetragonal symmetry with \( G \equiv C_{4v} \) and examine the two-photon transitions between the Stark levels of the shells 4\( f \) and 5\( d \) (i.e.,
\( n\ell \equiv 4f, \, N \equiv 1, \, n'\ell' \equiv 5d \). There are four possible transitions since the initial and final states may have the symmetries \( \Gamma_6 \) and \( \Gamma_7 \). For a linear polarization, the application of the intensity formula (47) leads to

\[
\begin{align*}
S_{\Gamma_6 \rightarrow \Gamma_6} &= a + b \pi_1 + c \pi_1^2 + d \pi_2 + e \pi_3 \\
S_{\Gamma_7 \rightarrow \Gamma_7} &= a' + b' \pi_1 + c' \pi_1^2 + d' \pi_2 + e' \pi_3 \\
S_{\Gamma_6 \rightarrow \Gamma_7} &= f \pi_2 + g \pi_3 + h \pi_4 + i \pi_5 \\
S_{\Gamma_7 \rightarrow \Gamma_6} &= f' \pi_2 + g' \pi_3 + h' \pi_4 + i' \pi_5
\end{align*}
\]

where the angular functions \( \pi_i \) (\( i = 1, 2, 3, 4, 5 \)) are defined by

\[
\begin{align*}
\pi_1 &= 3 \cos^2 \theta - 1 \\
\pi_2 &= \sin^2 2\theta \\
\pi_3 &= \sin^2 2\theta \cos 2\varphi \\
\pi_4 &= \sin^4 \theta \cos^2 2\varphi \\
\pi_5 &= \sin^4 \theta \sin^2 2\varphi
\end{align*}
\]

The various parameters \( a, \cdots, i \) and \( a', \cdots, i' \) are simple functions of the intensity parameters \( I_1[\cdots] \) and \( I_2[\cdots] \) occurring in (47).

**IV. CLOSING REMARKS**

We have shown how \( O(3) \supset G \) symmetry adaptation allows to derive intensity formulas for intra- and inter-configurational two-photon transitions for ions in molecular or solid-state environments. In particular, the number of independent parameters required for describing the polarization dependence of the transitions is determined by an ensemble of properties and rules which combine symmetry and physical considerations. The main results of this paper are equations (21) and (47) for intra- and inter-configurational transitions, respectively. The case of intra-configurational transitions has been treated in detail. The case of inter-configurational symmetry shall be developed again in forthcoming papers and in the thesis by one of us [11].

The reader should consult Refs. [18,19] where symmetry adaptation techniques, in the spirit of the present paper, have been applied to rare-earth and transition-metal ions in various symmetries.

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**REFERENCES**

[1] D.T. Sviridov and Yu.F. Smirnov, Theory of Optical Spectra of Transition-Metal Ions (Nauka, Moscow, 1977).

[2] Tang Au-chin, Sun Chia-chung, Kiang Yuan-sun, Deng Zung-hau, Liu Jo-chuang, Chang Chain-er, Yan Guo-sen, Goo Zien and Tai Shu-san, Theoretical Method of the Ligand Field Theory (Science Press, Beijing, 1979).
[3] M. Kibler and G. Grenet, Studies in Crystal-Field Theory (Report LYCEN/8656, IPNL, Lyon, 1986).

[4] M. Inoue and Y. Toyozawa, J. Phys. Soc. Japan 20 (1965) 363.

[5] T.R. Bader and A. Gold, Phys. Rev. 171 (1968) 997.

[6] P.A. Apanasevich, R.I. Gintoft, V.S. Korolkov, A.G. Makhanek and G.A. Skripko, Phys. Status Solidi (b) 58 (1973) 745 ; A.G. Makhanek and G.A. Skripko, Phys. Status Solidi (a) 53 (1979) 243 ; L.A. Yuguryan, Preprints N° 232 and 233, Inst. Fiz. Akad. Nauk BSSR, Minsk (1980).

[7] M. Kibler and J.C. Gáccon, Croat. Chem. Acta 62 (1989) 783.

[8] M. Kibler, in : Symmetry and Structural Properties of Condensed Matter, Eds. W. Florek, T. Lulek and M. Mucha (World, Singapore, 1991).

[9] R. Loudon, The Quantum Theory of Light (Clarendon, Oxford, 1973).

[10] C. Cohen-Tannoudji, J. Dupont-Roc et G. Grynberg, Processus d’interaction entre photons et atomes (InterEditions et Editions du CNRS, Paris, 1988).

[11] M. Daoud, thèse de Doctorat (Université Lyon-1, in preparation).

[12] J.D. Axe, Jr., Phys. Rev. 136 (1964) A42.

[13] B.R. Judd and D.R. Pooler, J. Phys. C : Solid State Phys. 15 (1982) 591.

[14] M.C. Downer and A. Bivas, Phys. Rev. B 28 (1983) 3677 ; M.C. Downer, G.W. Burdick and D.K. Sardar, J. Chem. Phys. 89 (1988) 1787 ; M.C. Downer, in : Laser Spectroscopy of Solids II, Ed. W.M. Yen (Springer, Heidelberg, 1989).

[15] J. Sztucki and W. Stręk, Phys. Rev. B 34 (1986) 3120 ; Chem. Phys. 143 (1990) 347.

[16] M. Kibler, C.R. Acad. Sc. (Paris) B 268 (1969) 1221 ; M.R. Kibler and P.A.M. Guichon, Int. J. Quantum Chem. 10 (1976) 87 ; M.R. Kibler, in : Recent Advances in Group Theory and Their Application to Spectroscopy, Ed. J.C. Donini (Plenum Press, N.Y., 1979) ; Int. J. Quantum Chem. 23 (1983) 115.

[17] C. Campochiaro, D.S. McClure, P. Rabinowitz and S. Dougal, Phys. Rev. B 43 (1991) 14.

[18] J. Sztucki, M. Daoud and M. Kibler, Phys. Rev. B (to be submitted for publication).

[19] J.C. Gáccon, J.F. Marcerou, M. Bouazaoui, B. Jacquier and M. Kibler, Phys. Rev. B 40 (1989) 2070 ; J.C. Gáccon, B. Jacquier, J.F. Marcerou, M. Bouazaoui and M. Kibler, J. Lumin. 45 (1990) 162 ; J.C. Gáccon, M. Bouazaoui, B. Jacquier, M. Kibler, L.A. Boatner and M.M. Abraham, Eur. J. Solid State Inorg. Chem. 28 (1991) 113.