CROATICA CHEMICA ACTA CCACAA 62 (4) 783—797 (1989)

YU ISSN 0011-1643
CCA-1907 UDC 541
Original Scientific Paper

Energy Levels of Paramagnetic Ions: Algebra. VI. Transition Intensity Calculations

Maurice Kibler‡ and Jean-Claude Gâcon†

‡*Institut de Physique Nucléaire (et IN2P3) and* †*Physico-Chimie des Matériaux Luminescents (UA 442 du CNRS), Université Claude Bernard Lyon-1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

Received February 6, 1989

Symmetry adaptation techniques developed in the first papers of this series are applied to intensity calculations for one- and two-photon transitions between crystalline or molecular states arising from a configuration nl^N in a symmetry G. To illustrate the techniques, we begin with one-photon magnetic-dipole transitions. Then, we give a detailed treatment of the second-order mechanisms for two-photon electric-dipole transitions; the case of configuration $4f^6$ in symmetry C_{4v} serves as an illustration. We also give indications of the passage from second-order to higher-order mechanisms. Finally, some general symmetry considerations for one-photon electric-dipole transitions are briefly investigated.

I. INTRODUCTION AND PRELIMINARIES

In the previous papers (henceforth referred to as I, II, ..., V) of this series,[1] we have developed symmetry adaptation methods and crystal-field models for calculating the energy levels of a partly-filled shells ion situated in a crystalline or molecular environment. It is the aim of the present paper to apply the symmetry adaptation techniques described in I—V and in some related works (reviewed in Ref. 2) to intensity calculations for transitions between energy levels of an ion with configuration nl^N embedded in a crystal-field potential with arbitrary symmetry.

We shall deal with one- and two-photon radiative transitions.[3] The theoretical treatment of two-photon transitions goes back to Göppert-Mayer[4] and the origin of one-photon electric-dipole transition for (d^N or) f^N ions in crystalline fields has been elucidated by Van Vleck[5] and Broer, Gorter, and Hoogschagen[6] via the mechanisms of charge transfert (especially for covalent systems) and/or parity violation (especially for ionic systems). In particular, one-photon electric-dipole transitions are forbidden between (atomic) states of an nl^N configuration. However, admixture of the states of configurations nl^N and $nl^{N-1}\,n'l'$ with $(-)^{l+l'} = -1$ renders possible electric-dipole transitions to be induced between the (admixed) states of configuration nl^N. Such admixture may be caused by the non-centrosymmetric part of the crystal-field potential. (This odd part is dynamic or static depending on whether

the symmetry group G of the ion site contains or does not contain a center of inversion.) Following these ideas, intensity calculations for one-photon electric-dipole transitions have been conducted for d^N and f^N ions in various surroundings (see Refs. 7—11 and Refs. 12—18 for a non-exhaustive list of works concerning d^N and f^N ions, respectively). In the case of two-photon electric-dipole transitions, actual intensity calculations have been chiefly concerned with f^N ions.[18-25] The rofe of symmetry adaptation has been touched upon in Refs. 7—24.

The approach followed in this article is mainly, as in parts II—IV, of a phenomenological nature. In this respect, the intensity parameters to be introduced here ($B\,[\lambda\, k\alpha_0]$ for one-photon transitions and $C\,[(k_s k_i)\, k]$ for two-photon transitions) may be considered as phenomenological parameters like parameters $D\,[(k_1 k_2)\, k_S\, (k_3 k_4)\, k_L k a_0]$ introduced in IV and V for describing the combined action of electrostatic, spin-orbit, and crystal-field interactions. Emphasis is put here on global properties based on symmetry considerations rather than on (microscopic) models and on mechanisms from which the various parameters arise. Most of the formulas given in this paper are (modulo the closure approximations) valid for any configuration nl^N in any symmetry and for any strength of the crystal-field potential although they are developed in the weak-field coupling scheme $\{\alpha SLJa\Gamma\gamma\}$.

We shall deal with transitions between an initial state i and a final state f arising from a configuration nl^N in an arbitrary symmetry G. The state vectors corresponding to i and f will be in the form

$$|\,i) \equiv |\,nl^N i\Gamma\gamma) \qquad \text{and} \qquad |\,f) \equiv |\,nl^N f\Gamma'\gamma') \tag{1}$$

and will be (partly) characterized by irreducible representation classes (IRC's) Γ and Γ' of group G (if N is even) or its double group G^* (if N is odd). More precisely, we shall use state vectors of the type

$$|nl^N x\Gamma\gamma) = \sum_{\alpha SLJa} |\,nl^N \alpha SLJa\Gamma\gamma)\, c\,(\alpha SLJa\Gamma; x) \tag{2}$$

resulting from the diagonalization of the Hamiltonian H describing electrostatic, spin-orbit, and crystal-field interactions. Such state vectors are expressed in terms of the symmetry adapted state vectors $|\,nl^N\, \alpha SLJa\Gamma\gamma)$, defined in I—V, for configuration nl^N. The expansion coefficients $c\,(\alpha SLJa\Gamma; x)$ in the linear combination (2) depend on the strength of the different parts of H, the more general form of which is H_{wf} (cf., V) and the simpler form $H_1 + H_2 + H_3$ (cf., I—III).

In order to demonstrate how symmetry adaptation techniques enter into intensity calculations, we briefly examine in Sec. II the pedagogical example of one-photon magnetic-dipole transitions. Section III deals in a detailed way with two-photon electric-dipole transitions. Some points concerning one-photon electric-dipole transitions are considered in Sec. IV in the light of the formalism described for two-photon transitions. Finally, three appendices close this article.

II. ONE-PHOTON MAGNETIC-DIPOLE TRANSITIONS

Magnetic-dipole transitions provide a simple example for which symmetry adaptation techniques can be applied in a straightforward manner. These transitions are parity allowed between certain state vectors of configuration nl^N. More specifically, the transition matrix element $M_{i\to f}$ between the initial state i and a final state f under the action of operator $\beta\,(k\mathbf{L} + g_e\mathbf{S})$. β is simply given by

$$M_{i\to f} = \beta \sum_{J'a'} \sum_{aSL} \sum_{Ja} \sum_{a''\Gamma''\gamma''} c\,(aSLJ'a'\Gamma'; f)^*\, c\,(aSLJa\Gamma; i)$$

$$(-)^{J'-J}\,(nl^N aSLJ' \,\|\, kL + g_e S \,\|\, nl^N aSLJ)\, f \begin{pmatrix} J & J' & 1 \\ a\Gamma\gamma & a'\Gamma'\gamma' & a''\Gamma''\gamma'' \end{pmatrix}^* \beta_{a''\Gamma''\gamma''} \qquad (3)$$

Equation (3) exhibits the typical ingredients of the transition matrix elements to be discussed in the present paper. First, we have physical constants (like the electronic Bohr magneton β here). Second, we have terms which do not depend on the point symmetry group G (like the reduced matrix elements ($\|\ldots\|$), the values of which are listed in Appendix A). Third, the remaining quantities in Eq. (3) depend on group G or its double group G^*. On the one hand, we have the expansion coefficients $c\,(\ldots f)$ and $c\,(\ldots i)$ which depend on G or G^* through the strength of the crystal-field part of the total Hamiltonian H. On the other hand, coefficient $f\,(\ldots)$ is an $SU(2) \supset G^*$ symmetry adapted coupling coefficient that was introduced in I (see also II and III). The polarization dependence of transition $i \to f$ is indicated by the components $\beta_{a''\Gamma''\gamma''}$ of the unit vector of the magnetic field and the G^*-dependent selection rules for the matrix element $M_{i\to f}$ are the ones inherent to the existence of coefficient $f\,(\ldots)$. In particular, in order to have $M_{i\to f} \neq 0$, it is necessary that at least one of the G irreducible components of $\Gamma'^* \otimes \Gamma$ is contained in the decomposition of the IRC (1_g) of $O(3)$ into IRC's of G. The latter property also holds for the oscillator strength

$$S_{i\to f} = \sum_{\gamma'\gamma} |\, M_{i\to f}\,|^2 \qquad (4)$$

of transition $i \to f$. It is to be emphasized that the sum over γ' and γ in Eq. (4) can be effectuated by using the factorization property of the f coefficients for the chain of groups $SU(2) \supset G^*$ and an orthonormality property of the Clebsch-Gordan coefficients for group G^* (see Appendix B).

Finally, we would like to mention that there is no further difficulty for one-photon electric-quadrupole transitions and the calculation of transition matrix elements and oscillator strengths for such transitions can be effected in exactly the same manner as for one-photon magnetic-dipole transitions.

III. TWO-PHOTON ELECTRIC-DIPOLE TRANSITIONS

1. *Second-order Mechanism*

We now examine in detail a second-order mechanism for two-photon electric-dipole transitions between the initial state i and a final state f. The matrix element $M_{i\to f}$ for such transitions is given by

$$M_{i\to f} = \sum_v \frac{1}{\Delta_1} (f \,|\, \vec{D}\cdot\vec{\varepsilon}_2 \,|\, v)\,(v \,|\, \vec{D}\cdot\vec{\varepsilon}_1 \,|\, i) + \sum_v \frac{1}{\Delta_2} (f \,|\, \vec{D}\cdot\vec{\varepsilon}_1 \,|\, v)\,(v \,|\, \vec{D}\cdot\vec{\varepsilon}_2 \,|\, i) \qquad (5)$$

where the sums over v extend on virtual intermediate states of parity opposite to the parity of states i and f. In Eq. (5), we have

$$\Delta_\lambda = E_\lambda - (E_v - E_i) \text{ for } \lambda = 1, 2 \tag{6}$$

which involves the energies E_v and E_i of states v and i as well as energies E_1 and E_2 of photons no. 1 and 2. Further, $\vec{\varepsilon}_1$ and $\vec{\varepsilon}_2$ are the polarization vectors of the two photons. Finally, the dipole moment $\vec{D} = -e\sum_j \vec{r}_j$ for the involved electrons may be developed as

$$\vec{D} = \sum_{q=-1}^{1} (-)^q D_{-q}^{(1)} \vec{e}_q \tag{7}$$

in the standard spherical basis $(\vec{e}_{-1}, \vec{e}_0, \vec{e}_{+1})$.

Equation (5) can be rewritten as

$$M_{i\to f} = \sum_{q=-1}^{1} \sum_{p=-1}^{1} (-)^{p+q} (\varepsilon_1)_{-p} (\varepsilon_2)_{-q} \sum_v \frac{1}{\Delta_1} (f \mid D_q^{(1)} \mid v)(v \mid D_p^{(1)} \mid i) + \sum_v \frac{1}{\Delta_2} (f \mid D_p^{(1)} \mid v)(v \mid D_q^{(1)} \mid i) \tag{8}$$

where

$$(\varepsilon_\lambda)_{-q} = \vec{\varepsilon}_\lambda \cdot \vec{e}_{-q} \text{ for } \lambda = 1, 2 \text{ and } q = -1, 0, 1 \tag{9}$$

Note that for linearly polarized photons, we have (in spherical polar coordinates)

$$(\varepsilon_\lambda)_0 = \cos\theta_\lambda, \quad (\varepsilon_\lambda)_{\pm 1} = \mp (1/\sqrt{2}) \sin\theta_\lambda \exp(\pm i\varphi_\lambda) \text{ for } \lambda = 1, 2 \tag{10}$$

while

$$(\varepsilon_\lambda)_{-q} = -\delta(q, \pm 1) \tag{11}$$

for circularly polarized photons with $\vec{\varepsilon}_\lambda = \vec{e}_{\pm 1}$.

The initial and final state vectors $\mid i)$ and $\mid f)$ are taken in the form given by Eqs. (1) and (2). The virtual state vectors $\mid v)$ are given by expressions similar to Eq. (2), except that the (ground) configuration nl^N is replaced by (excited) configurations $nl^{N-1}\, n'l'$ with $(-)^{l+l'} = -1$. (For the sake of simplicity, we do not consider here the case of core excitations involving configurations of type $n'l'^{(4l'+1)}\, nl^{N+1}$. Such configurations are taken into acount as far as parameters C_k to be defined below are considered as phenomenological parameters.) As a matter of fact, the quasi-closure procedure used in what follows makes it possible to take $\mid v)$ in the non-symmetry-adapted form $\mid nl^{N-1}\, n'l'\alpha''S''L''J''M'')$.

We now continue with the crude approximation that the energy E_v in Eq. (6) may be replaced by $E(n'l')$, so that Δ_λ is replaced by

$$\Delta_\lambda' = E_\lambda - [E(n'l') - E_i] \text{ for } \lambda = 1, 2 \tag{12}$$

independently of the particular state v arising from the configuration $nl^{N-1}\, n'l'$. In fact, such an approximation (cf., Refs. 5 and 7) has proven very successful

in the study of one-photon electric-dipole transitions for transition-metal[11] and rare-earth[13,14] ions in crystalline fields. (A relation similar to Eq. (12) is at the root of the derivation of Eq. (45) in Sec. IV for one-photon transitions.) By using Eq. (12), Eq. (8) becomes

$$M_{i\to f} = \sum_{p=-1}^{1} \sum_{q=-1}^{1} (-)^{p+q} (\varepsilon_1)_{-p} (\varepsilon_2)_{-q} \sum_{n'l'} \left(\frac{1}{\Delta_1'} S_{qp} + \frac{1}{\Delta_2'} S_{pq} \right) \tag{13}$$

where the (symmetry-adapted) quantity S_{pq} is defined as

$$S_{pq} = \sum_{\alpha' S' L' J' \alpha'} \sum_{\alpha S L J \alpha} \sum_{M'} \sum_{M} c\,(\alpha' S' L' J' \alpha' \Gamma'; f)^* \, c\,(\alpha S L J \alpha \Gamma; i)$$
$$(J' M' \mid J' \alpha' \Gamma' \gamma')^* \, (J M \mid J \alpha \Gamma \gamma) \, R_{pq} \tag{14}$$

in terms of the $SU(2) \supset U(1)$ corresponding quantity

$$R_{pq} = \sum_{\alpha'' S'' L'' J'' M''} (n l^N \alpha' S' L' J' M' \mid D_p^{(1)} \mid n l^{N-1} n' l' \alpha'' S'' L'' J'' M'')$$
$$(n l^{N-1} n' l' \alpha'' S'' L'' J'' M'' \mid D_q^{(1)} \mid n l^N \alpha S L J M) \tag{15}$$

Expressions of the R_{pq} type are familiar in intensity calculations (cf., Refs. 13, 14, and 19). The summation over $\alpha'' S'' L'' J'' M''$ in Eq. (15) can be evaluated by (quasi-closure) procedures based on the use of the Racah methods and of the Wigner-Racah calculus for the chain $SU(2) \supset U(1)$. This leads to

$$R_{pq} = \sum_{k=0,1,2} R_{kpq} \tag{16}$$

with

$$R_{kpq} = e^2 (n l \mid r \mid n' l')^2 \, (l \,\|\, C^{(1)} \,\|\, l')^2$$
$$(-)^{k+p+q+1} [k] \begin{pmatrix} 1 & k & 1 \\ -p & p+q & -q \end{pmatrix} \begin{Bmatrix} 1 & k & 1 \\ l & l' & l \end{Bmatrix}$$
$$(n l^N \alpha' S' L' J' M' \mid U_{p+q}^{(k)} \mid n l^N \alpha S L J M) \tag{17}$$

where $U_{p+q}^{(k)}$ stands for the $(p+q)$-th spherical component of a many-electron Racah unit tensor $\mathbf{U}^{(k)}$ of orbital rank k. The various quantities in Eq. (17) bear their usual meaning.

The next step is to express the products $(\varepsilon_1)_{-p} (\varepsilon_2)_{-q}$ occurring in Eq. (13) in a symmetry adapted form. This may be done as follows. First, we use the product

$$(\varepsilon_1)_p (\varepsilon_2)_q = \sum_{KQ} (-)^{K-Q} [K]^{1/2} \begin{pmatrix} 1 & K & 1 \\ p & -Q & q \end{pmatrix} \{\varepsilon_1 \varepsilon_2\}_Q^{(K)} \tag{18}$$

where $K = 0$, 1 and 2 corresponds to a scalar form, an axial-vector form, and a (second-rank) tensor form, respectively. Second, we introduce in Eq. (18) the $O(3) \supset G$ symmetry adapted tensor product

$$\{\varepsilon_1 \varepsilon_2\}_{\alpha\Gamma\gamma}^{(K)} = \sum_{Q} \{\varepsilon_1 \varepsilon_2\}_Q^{(K)} \, (KQ \mid K \alpha \Gamma \gamma) \tag{19}$$

where $(KQ \mid K\alpha\Gamma\gamma)$ is a reduction coefficient for the chain $O(3) \supset G$ to pass from the $\{JM\}$ scheme to the $\{J\alpha\Gamma\gamma\}$ scheme. (Formulas for the various components of $\{\varepsilon_1\varepsilon_2\}^{(K)}$ are given in Appendix C for the chain $O(3) \supset C_{4v}$.)

We are now able to find an interesting expression for the right-hand side of Eq. (13). By combining Eqs. (14)—(19) with Eq. (13), we obtain after some straightforward calculations

$$M_{i\to f} = \sum_{\alpha'S'L'J'a'} \sum_{\alpha SLJa} \sum_{k=0,1,2} \sum_{\alpha''\Gamma''\gamma''} c\,(\alpha'S'L'J'a'\Gamma'; f)^* \, c\,(\alpha SLJa\Gamma; i)$$

$$C_k \{\varepsilon_1\varepsilon_2\}^{(k)}_{\alpha''\Gamma''\gamma''} \,(nl^N\alpha'S'L'J'a'\Gamma'\gamma' \,|\, [U^{(k)}_{\alpha''\Gamma''\gamma''}]^\dagger \,|\, nl^N\alpha SLJa\Gamma\gamma) \tag{20}$$

where the three coefficients C_k ($k = 0, 1, 2$) are defined by

$$C_k = -\sum_{n'l'} [k]^{1/2} (l \,\|\, C^{(1)} \,\|\, l')^2 \begin{Bmatrix} 1 & k & 1 \\ l & l' & l \end{Bmatrix}$$

$$e^2 (nl \,|\, r \,|\, n'l')^2 [(-)^k (\Delta_1')^{-1} + (\Delta_2')^{-1}] \tag{21}$$

Except for Rayleigh scattering, the scalar term (corresponding to $k = 0$) does not contribute to Eq. (20) owing to the orthogonality of the initial and final state vectors $|\, i)$ and $|\, f)$. Therefore, as a general result, we have the closed-form expression

$$M_{i\to f} = \sum_{\alpha'S'L'J'a'} \sum_{\alpha SLJa} c\,(\alpha'S'L'J'a'\Gamma'; f)^* \, c\,(\alpha SLJa\Gamma; i)$$

$$\sum_{k=1,2} C_k \,(nl^N\alpha SLJ \,\|\, U^{(k)} \,\|\, nl^N\alpha'S'L'J')^*$$

$$\sum_{\alpha''\Gamma''\gamma''} f\begin{pmatrix} J & J' & k \\ a\Gamma\gamma & a'\Gamma'\gamma' & a''\Gamma''\gamma'' \end{pmatrix}^* \{\varepsilon_1\varepsilon_2\}^{(k)}_{\alpha''\Gamma''\gamma''} \tag{22}$$

and the strength $S_{i\to f}$ of transition $i \to f$ is obtained by inserting Eq. (22) into Eq. (4) and by evaluating the summations over γ' and γ with the help of a decomposition of the f coefficient in terms of the Clebsch-Gordan coefficients for group G^* (cf., Appendix B).

Some comments on the master formula (22) are called for. The sum over $\alpha''\Gamma''\gamma''$ in Eq. (22) concerns symmetry dependent quantities: coefficient $f(\ldots)$ is an $SU(2) \supset G^*$ coupling coefficient,[1,2] similar to the one occurring in Eq. (3), and factor $\{\ldots\}$ depends on the polarization of the two photons. The factor ($\|\, U^{(k)} \,\|$) and coefficient C_k (for $k = 1$ or 2) do not depend on the point symmetry group G: ($\|\, U^{(k)} \,\|$) is an (atomic) reduced matrix element for the ground configuration nl^N and C_k depends solely on configuration nl^N and the excited configurations $nl^{N-1}\, n'l'$. It is to be pointed out that the axial-vector terms (corresponding to $k = 1$) vanish both in Eq. (22) and in Eq. (20) if the two involved photons have either the same energy (since $C_1 = 0$ in that case in view of Eq. (21)) or the same polarization (since the vector product $\{\varepsilon_1\varepsilon_2\}^{(1)}$ is zero for $\vec{\varepsilon}_1 = \vec{\varepsilon}_2$). In other words, a non-zero contribution of the $k = 1$ terms requires two photons of different energies and different polarizations. In a general case, it should be noted that coefficients C_1 and C_2 may be considered as phenomenological parameters. In most cases, the parameter C_1 is certainly negligible but it may be important for Raman and Rayleigh scattering. Finally, products $c(\ldots f)^* \, c(\ldots i)$ depend on the strength of the different components of the total Hamiltonian H under consideration; as a consequence, they generally depend on group G^*. (The sole good quantum numbers in Eq (22) are Γ and γ for the initial state and Γ' and γ' for the final state.)

Equations (20) and (22) can be given a simpler form in the special case where the J-mixing is negligible, a situation frequently encountered for lanthanide ions, at least as a first approximation. We thus take J (for the initial state) and J' (for final state) as good quantum numbers and further assume that Γ, Γ' and Γ'' occur only once in the decomposition of the IRC's (J), (J'), and (k) of $SU(2)$, respectively. (The latter assumption is quite reasonable for low values of J and J' and high symmetry groups G.) Thus, for a linear polarization of the two photons, Eq. (20) specializes to

$$M_{i\to f} = \sum_{k=1,2} (-)^k C_k (nl^N [\alpha' S' L'] J' \| U^{(k)} \| nl^N [\alpha SL] J) \sum_{\Gamma''\gamma''} f\begin{pmatrix} J' & J & k \\ \Gamma'\gamma' & \Gamma\gamma & \Gamma''\gamma'' \end{pmatrix} (\{\varepsilon_1\varepsilon_2\}^{(k)}_{\Gamma''\gamma''})^* \tag{23}$$

where the notation $[\alpha SL]J$ refers (in the intermediate coupling scheme) to the state vector whose principal component corresponds to the α-th multiplet $^{2S+1}L_J$. Here, in order to have a non-zero contribution to $M_{i\to f}$ of the $k = 1$ terms, it is necessary for the selection rule $\Delta J = 0, \pm 1$ (with $0 \leftrightarrow 0$ excluded) to be satisfied in addition to the fact that the two photons must have different energies and different polarizations. Similarly, the tensor terms (corresponding to $k = 2$) do not contribute to $M_{i\to f}$ if the selection rule $\Delta J = 0, \pm 1, \pm 2$ (with $0 \leftrightarrow 0$, $1/2 \leftrightarrow 1/2$, and $0 \leftrightarrow 1$ excluded) is not satisfied. Equation (23) can be further specialized if the photons have either the same energy or the same polarization. In both cases, and for $\Delta J = 0, \pm 1, \pm 2$ (with $0 \leftrightarrow 0$, $1/2$, 1 excluded), Eq. (23) contains only one working parameter, viz., the parameter C_2. Then, by introducing Eq. (23) into Eq. (4) and by applying Racah's lemma[26] to the involved f coefficients, we end up with

$$S_{i\to f} = [J']^{-1} [\Gamma'] \left| C_2 (nl^N [\alpha' S' L'] J' \| U^{(2)} \| nl^N [\alpha SL] J) \right|^2 \sum_{\beta\Gamma''} [\Gamma'']^{-1} \left| (J\Gamma + 2\Gamma'' \mid J'\beta\Gamma') \right|^2 \sum_{\gamma''} \left| \{\varepsilon_1\varepsilon_2\}^{(2)}_{\Gamma''\gamma''} \right|^2 \tag{24}$$

where the $(+|)$ coefficient is an isoscalar factor for the chain $SU(2) \supset G^*$ (see Appendix B).

2. *Higher-order Mechanisms*

Equation (22) suggests defining the operator

$$H_{eff} = \sum_{k=1,2} \sum_{a''\Gamma''\gamma''} C_k \{\varepsilon_1\varepsilon_2\}^{(k)}_{a''\Gamma''\gamma''} [U^{(k)}_{a''\Gamma''\gamma''}]^\dagger \tag{25}$$

which can be cast in the form

$$H_{eff} = \sum_{k=1,2} (-)^k C_k \sum_{a_1\Gamma_1\gamma_1 a_2\Gamma_2\gamma_2} \begin{pmatrix} & k & \\ a_1\Gamma_1\gamma_1 & & a_2\Gamma_2\gamma_2 \end{pmatrix} \{\varepsilon_1\varepsilon_2\}^{(k)}_{a_1\Gamma_1\gamma_1} U^{(k)}_{a_2\Gamma_2\gamma_2} \tag{26}$$

where the metric tensor $(\mu_1{}^k\mu_2)$ is defined in I and II (see also Ref. 2). Operator H_{eff} is independent of the particular chain $SU(2) \supset G^*$ chosen since

$$H_{eff} = \sum_{k=1,2} C_k (\{\varepsilon_1\varepsilon_2\}^{(k)} \cdot \mathbf{U}^{(k)}) \tag{27}$$

where (.) indicates a scalar product (cf., II). Clearly, the operator H_{eff} is an effective operator because Eq. (22) can be written in the compact form

$$M_{i\to f} = (nl^N f\Gamma'\gamma' \,|\, H_{eff} \,|\, nl^N i\Gamma\gamma) \tag{28}$$

Hence, to obtain the transition matrix element $M_{i\to f}$ resulting from second-order mechanisms, it is sufficient to calculate the matrix element of H_{eff} between the initial and final state vectors. This result is in agreement with the corresponding result, originally obtained by Axe,[19] for two-photon processes in complex atoms. In the particular case of two identical photons issued from a single beam, H_{eff} reduces to the operator (involving only one parameter) derived by Judd and Pooler[22] in the framework of the second quantization formalism and further discussed by Downer and Bivas.[23]

Equation (26) shows that H_{eff} is a linear combination of components of irreducible tensor operators $\mathbf{T}^{(\Gamma_2)}$ for group G. Then, by introducing Eq. (28) into Eq. (4) and applying the Wigner-Eckart theorem for the chain $SU(2) \supset G^*$, we obtain the following selection rule for the two-photon transition $i \to f$ induced by second-order mechanisms: to have $S_{i\to f} \neq 0$, it is necessary that at least one of the G irreducible components of $\Gamma'^* \otimes \Gamma$ is contained in the decomposition of the IRC (k_g), with $k = 1$ or 2, of $O(3)$ into IRC's of G.

We now give a form to H_{eff} which turns out to be appropriate for an extension to other mechanisms than the second-order mechanisms described by expressions of type $\Delta^{-1}(f \,|\, \ldots \,|\, v)(v \,|\, \ldots \,|\, i)$. By introducing

$$\mathbf{U}^{(k)} = \left(\frac{2}{2k+1}\right)^{1/2} \mathbf{W}^{(0\,k)k} \tag{29}$$

where $\mathbf{W}^{(k_s k_l)k}$ denotes a double tensor of spin rank k_s, orbital rank k_l, and total rank k, Eq. (27) can be rewritten as

$$H_{eff} = \sum_{k=1,2} C\,[(0k)k]\,(\{\varepsilon_1\varepsilon_2\}^{(k)} \cdot \mathbf{W}^{(0\,k)k}) \tag{30}$$

with coefficient $C\,[(0k)\,k]$ replacing C_k. An immediate generalization of Eq. (30) reads

$$H_{eff} = \sum_{k_s k_l k} C\,[(k_s k_l)k]\,(\{\varepsilon_1\varepsilon_2\}^{(k)} \cdot \mathbf{W}^{(k_s k_l)k}) \tag{31}$$

Thus, Eq. (28) is amenable to the very general form

$$M_{i\to f} = \sum_{\alpha' S' L' J' \alpha'} \sum_{\alpha S L J \alpha} c\,(\alpha' S' L' J' \alpha' \Gamma'; f)^*\, c\,(\alpha S L J \alpha \Gamma; i)$$

$$\sum_{k_s k_l k} (-)^{k_s + k_l - k}\,([J]\,[J']\,[k])^{1/2} \begin{Bmatrix} S & S' & k_s \\ L & L' & k_l \\ J & J' & k \end{Bmatrix} (nl^N \alpha S L \,\|\, W^{(k_s k_l)} \,\|\, nl^N \alpha' S' L')^*$$

$$C\,[(k_s k_l)\,k] \sum_{\alpha''\Gamma''\gamma''} f \begin{pmatrix} J & J' & k \\ \alpha\Gamma\gamma & \alpha'\Gamma'\gamma' & \alpha''\Gamma''\gamma'' \end{pmatrix}^* \{\varepsilon_1\varepsilon_2\}^{(k)}_{\alpha''\Gamma''\gamma''} \tag{32}$$

which is an extension of Eq. (22). Therefore, the aforementioned selection rule for second-order mechanisms can be applied to higher-order mechanisms by extending the range of values of k.

In the case J and J' are good quantum numbers, we can calculate the oscillator strength for the transition between the J manifold and the J' manifold. We get

$$S_{[\alpha SL]J\to[\alpha'S'L']J'} = \sum_{k_s'k_l'k_sk_lk} \sum_q \left|\{\varepsilon_1\varepsilon_2\}_q^{(k)}\right|^2 [k]^{-1}\, C[(k_s'k_l')k]\; C[(k_sk_l)k]$$

$$(nl^N\,[\alpha'S'L']\,J' \,\|\, W^{(k_s'k_l')k} \,\|nl^N\,[\alpha SL]\,J)^*\,(nl^N\,[\alpha'S'L']\,J' \,\|\, W^{(k_sk_l)k} \,\|\, nl^N\,[\alpha SL]\,J) \qquad (33)$$

The latter sum rule generalizes the one derived by Axe[19] for two-photon processes in complex atoms and is valid for circular and linear polarizations. (Note that for two identical photons ($\vec{\varepsilon}_1 = \vec{\varepsilon}_2 = \vec{\varepsilon}$), the sum $\Sigma_q \left|\{\varepsilon\varepsilon\}_q^{(k)}\right|^2$ in Eq. (33) is equal to $[1 - \delta(k, 1)]\,\delta(k, 2)$ or $[1 - \delta(k, 1)]\,[1 + \delta(k, 2)]/3$ depending on whether the polarization is circular or linear.)

Parameters $C[(k_sk_l)k]$ in Eqs. (32) and (33) can be considered as phenomenological parameters. Alternatively, they can be interpreted as originating from higher-order mechanisms, for instance the third-order mechanisms described by expressions of the type $(\Delta\Delta')^{-1}\,(f\,|\ldots|\,v')\,(v'\,|\ldots|\,v)\,(v\,|\ldots|\,i)$. In this connection, mechanisms of the third- and fourth-order have been used in Refs. 22 and 23 for interpreting the anomalous strength of the two-photon transitions of Gd^{3+} in LaF_3.

3. The Case of $4f^6$ in C_{4v}

As a typical example, let us consider the ${}^7F_{J=0} \to {}^5D_{J'}$ two-photon transitions for an ion of configuration $4f^6$ embedded in an environment of symmetry C_{4v}. We shall assume that the J-mixing is negligible. Then, we have $\Gamma = A_1$ and $J = 0$ for the initial state. For the first three final states ${}^5D_{J'}$, we have $\Gamma' = A_1$ for $J' = 0$, $\Gamma' = A_2$ or E for $J' = 1$, and $\Gamma' = A_1, B_1, B_2$, or E for $J' = 2$. By using the general relation[27]

$$f\begin{pmatrix} 0 & J' & k \\ A_1 & \alpha'\Gamma'\gamma' & \alpha''\Gamma''\gamma'' \end{pmatrix} = \delta(k, J')\,[J']^{-1/2} \begin{pmatrix} k \\ \alpha'\Gamma'\gamma' \quad \alpha''\Gamma''\gamma'' \end{pmatrix}^* \qquad (34)$$

we get, from Eq. (22), the transition matrix element

$$M_{i\to f} = [J']^{1/2} \sum_{k=1,2} \delta(k, J')\, C_k\, (4f^6\,[^7F_0] \,\|\, U^{(k)} \,\|\, 4f^6\,[^5D_k])^*$$

$$\sum_{\Gamma''\gamma''} \begin{pmatrix} k \\ \Gamma'\gamma' \quad \Gamma''\gamma'' \end{pmatrix} \{\varepsilon_1\varepsilon_2\}^{(k)}_{\Gamma''\gamma''} \qquad (35)$$

where we employ the notation $[^{2S+1}L_J]$ for $[\alpha SL]\,J$.

Some conclusions immediately emerge from Eq. (35). In the case where the J-mixing can be neglected, the sole ${}^7F_0 \to {}^5D_{J'}$ two-photon transitions allowed by second-order mechanisms correspond to $J' = 1$ and $J' = 2$. In other words, the observation of the other ${}^7F_0 \to {}^5D_{J'}$ two-photon transitions should give information on the importance of the J-mixing and/or of higher-order mechanism contributions. In particular, the observation of the ${}^7F_0 \to {}^5D_0$ two-photon transition would result from the contribution of tensors $\mathbf{W}^{(0k)k}$ arising from the second-order mechanism (which turns out to be operative here only if the J-mixing is taken into consideration) and/or of the scalar term $\mathbf{W}^{(11)0}$ arising from the third-order correction involving matrix elements

of the spin-orbit interaction within the intermediate states of the $4f^5\, n'l'$ configurations.

We continue with the cases $J' = 1$ and $J' = 2$ separately in the situation where the two photons are linearly polarized. For $J' = 1$, the introduction of Eq. (35) into Eq. (4) yields the line strengths

$$S_{A_1 \to A_2} = \frac{3}{4} S_{0\to 1} [\sin\theta_1 \sin\theta_2 \sin(\varphi_1 - \varphi_2)]^2$$

$$S_{A_1 \to E} = \frac{3}{8} S_{0\to 1} [2(\cos\theta_1 \sin\theta_2)^2 + 2(\sin\theta_1 \cos\theta_2)^2 - \sin 2\theta_1 \sin 2\theta_2 \cos(\varphi_1 - \varphi_2)] \tag{36}$$

with

$$S_{0\to 1} = \frac{2}{9} | C_1 (4f^6 [^5D_1] \| U^{(1)} \| 4f^6 [^7F_0]) |^2 \tag{37}$$

Similarly for $J' = 2$, we obtain

$$S_{A_1 \to A_2} = \frac{1}{4} S_{0\to 2} [2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2)]^2$$

$$S_{A_1 \to B_1} = \frac{3}{4} S_{0\to 2} [\sin\theta_1 \sin\theta_2 \cos(\varphi_1 + \varphi_2)]^2$$

$$S_{A_1 \to B_2} = \frac{3}{4} S_{0\to 2} [\sin\theta_1 \sin\theta_2 \sin(\varphi_1 + \varphi_2)]^2$$

$$S_{A_1 \to E} = \frac{3}{8} S_{0\to 2} [2(\cos\theta_1 \sin\theta_2)^2 + 2(\sin\theta_1 \cos\theta_2)^2 + \sin 2\theta_1 \sin 2\theta_2 \cos(\varphi_1 - \varphi_2)] \tag{38}$$

with

$$S_{0\to 2} = \frac{2}{15} | C_2 (4f^6 [^5D_2] \| U^{(2)} \| 4f^6 [^7F_0]) |^2 \tag{39}$$

The line strengths (36) and (38) are expressed in terms of the directions $(\theta_\lambda, \varphi_\lambda)$ of the polarization vectors $\vec{\varepsilon}_\lambda$ $(\lambda = 1, 2)$. They all depend on a single multiplicative parameter ($S_{0\to 1}$ for $J' = 1$ and $S_{0\to 2}$ for $J' = 2$). It should be observed that for identical photons (the same energy, the same wave vector, and the same polarization), we have $S_{0\to 1} = 0$ and

$$S_{0\to 2} = \sum_{\Gamma' = A_1, B_1, B_2, E} S_{A_1 \to \Gamma'} \tag{40}$$

so that the latter sum is independent of the common polarization, a property that does not hold if the two photons have different polarizations.

Parameter $S_{0\to k}$ is proportional to the square of parameter C_k given by Eq. (21). Since configuration $4f^5\, 5d$ is the first (opposite parity) excited configuration above the ground configuration $4f^6$, the sum on $n'l'$ in Eq. (21) can be restricted to $n'l' = 5d$. Such an approximation gives

$$S_{0\to k} = 6e^4\,(4f \mid r \mid 5d)^4\,[(-)^k\,(\Delta_1')^{-1} + (\Delta_2')^{-1}]^2$$

$$\begin{Bmatrix} 1 & k & 1 \\ 3 & 2 & 3 \end{Bmatrix}^2 \mid (4f^6\,[^5D_k] \,\|\, U^{(k)} \,\|\, 4f^6\,[^7F_0]) \mid^2 \qquad (41)$$

and parameters $S_{0\to k}$ ($k = 1, 2$) can be calculated from the first principles. Alternatively, they can be taken as phenomenological parameters. This line of thought has been recently followed in Ref. 25 for the analysis of the intensities and the polarization dependence of the Stark components arising from the $^7F_0 \to {}^5D_2$ two-photon transitions observed, in the case of two identical photons (single-beam arrangement), for the ion Sm^{2+} in a $BaClF$ single-crystal.

IV. ONE-PHOTON ELECTRIC-DIPOLE TRANSITIONS

The basic formula giving the transition matrix element $M_{i\to f}$ for a one-photon electric-dipole transition between the initial state i and a final state f can be, in the last analysis, formally deduced from the one corresponding to a two-photon electric-dipole transition. It is enough in Eq. (5) to replace $\vec{D}\cdot\vec{\varepsilon}_1$ by $\vec{D}\cdot\vec{\varepsilon}$ and $\vec{D}\cdot\vec{\varepsilon}_2$ by the Hamiltonian H_{wf} defined in V or, in a more realistic way, by a part of H_{wf} and to make the necessary modifications in the denominators (see also Refs. 18, 19, and 23). We are thus left with

$$M_{i\to f} = \sum_v \frac{1}{\Delta_{fv}} (f \mid H_{wf} \mid v)\,(v \mid \vec{D}\cdot\vec{\varepsilon} \mid i) + \sum_v \frac{1}{\Delta_{iv}} (f \mid \vec{D}\cdot\vec{\varepsilon} \mid v)\,(v \mid H_{wf} \mid i) \qquad (42)$$

where, in evident notation, $\Delta_{xv} = E_x - E_v$ for $x = i$ or f. Here, the state vectors $\mid i)$, $\mid f)$, and $\mid v)$ are the same as is Sec. III and the sums over v can be achieved by means of the quasi-closure procedure based on the approximation that Δ_{xv} can be replaced by the difference $\Delta(n'l')$ between the barycenters of the ground configuration nl^N and the excited configuration $nl^{N-1}n'l'$ with $(-)^{l+l'} = -1$.

Equation (42) describes various second-order mechanisms and, as in Refs. 11 and 13—15 (see also II), we may restrict H_{wf} to the non-centrosymmetric part of the crystal-field Hamiltonian H_3 defined by

$$H_3 = \sum_{ka_0} D\,[ka_0]\,U^{(k)}_{a_0\Gamma_0\gamma_0} \qquad (43)$$

where Γ_0 ($= A_1$ in Mulliken's notation) stands for the identity IRC of G. In Eq. (43), the crystal-field parameters $D\,[k\alpha_0]$ with k even do not contribute to $M_{i\to f}$ and we shall denote $O\,[k\alpha_0]$ the parameters $D\,[k\alpha_0]$ with k odd. Parameters $O\,[k\alpha_0]$ (and their $O(3) \supset O(2)$ counterparts $O\,[kq]$) are connected to the commoner (Rajnak-Wybourne) parameters B_q^k by the relationship

$$O\,[ka_0] = \sum_q O[kq]\,(kq \mid ka_0\Gamma_0\gamma_0)^* = (l' \,\|\, C^{(k)} \,\|\, l) \sum_q B_q^k\,(kq \mid ka_0\Gamma_0\gamma_0)^* \qquad (44)$$

(Equation (44) gives back the relation derived in III for $l' = l$ and k even.) Then, the calculation of $M_{i\to f}$ amounts to a simple symmetry-adapted version of the one in Refs. 13—15. As a net result, we obtain

$$M_{i\to f} = \sum_{\alpha' S' L' J' \alpha'} \sum_{\alpha S L J \alpha} c\,(\alpha' S' L' J' \alpha' \Gamma'; f)^{*} c\,(\alpha S L J \alpha \Gamma; i)$$

$$\sum_{\lambda k a_0} \sum_{\alpha'' \Gamma'' \gamma''} \sum_{\alpha \overline{\Gamma \gamma}} (\mathrm{n}l^N \alpha' S' L' J' \,\|\, U^{(\lambda)} \,\|\, nl^N \alpha S L J)$$

$$B\,[\lambda k a_0]\; \varepsilon_{\alpha \overline{\Gamma \gamma}}\; f \begin{pmatrix} J' & J & \lambda \\ \alpha' \Gamma' \gamma' & \alpha \Gamma \gamma & \alpha'' \Gamma'' \gamma'' \end{pmatrix} f \begin{pmatrix} \alpha_0 \Gamma_0 \gamma_0 & \alpha \overline{\Gamma \gamma} & \alpha'' \Gamma'' \gamma'' \\ k & 1 & \lambda \end{pmatrix}^{*} \tag{45}$$

Under the hypothesis of the simple parity violation mechanism considered here, the intensity parameters $B\,[\lambda k a_0]$ in Eq. (45) are given by

$$B\,[\lambda k a_0] = 2\,e\,O\,[k a_0]\,[\lambda]$$

$$\sum_{n' l'} (-)^{l}\,([l]\,[l'])^{1/2} \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & \lambda & k \\ l & l' & l \end{Bmatrix} (nl \,|\, r \,|\, n' l') \,/\, \Delta\,(n' l') \tag{46}$$

Parameters $O\,[k a_0]$ can be calculated in the framework of the electrostatic model involving point-charge, dipolar, and quadrupolar contributions. Therefore, parameters $B\,[\lambda k a_0]$ are calculable from the first principles. However, the fact of treating these parameters as adjustable parameters to be determined from experimental data may account for other mechanisms, such as, for example, core excitations, pseudo-multipolar field or ligand polarizations, and vibronic interactions.

Equation (45) shows that to have $M_{i\to f} \neq 0$, it is necessary for at least one of the G irreducible components of $\Gamma'^{*} \otimes \Gamma$ to be contained simultaneously in the IRC (1_u) and in one of the IRC's (λ_g), with $\lambda = 2(2)2l$, of $O(3)$.

In the case where J and J' remain good quantum numbers, we obtain from Eq. (45) the sum rule

$$S_{[\alpha S L] J \to [\alpha' S' L'] J'} = \sum_{\lambda = 2(2)2l} \Omega_{\lambda} \,|\, (nl^N\,[\alpha' S' L'] J' \,\|\, U^{(\lambda)} \,\|\, nl^N\,[\alpha S L] J) \,|^2 \tag{47}$$

where the intensity parameter Ω_{λ} reads in our notation

$$\Omega_{\lambda} = [\lambda]^{-1} \sum_{k a_0} [k]^{-1} \,|\, B\,[\lambda k a_0] \,|^2 \tag{48}$$

Relation (47) was first derived by Judd[13] (see also Ref. 15) for $4f^N$ configurations.

Following the approach in Ref. 18, we may introduce an effective operator H_{eff} which produces the transition matrix element $M_{i\to f}$ when sandwiched between the state vectors $(f\,|$ and $|\,i)$, cf., Eq. (28). Indeed, from Eq. (45), we find

$$H_{eff} = \sum_{k \text{ odd}} \sum_{\lambda = 2(2)2l} B\,[(1k)\,\lambda]\,(\{\varepsilon^{(1)}\,\mathbf{O}^{(k)}\}^{(\lambda)} \cdot \mathbf{U}^{(\lambda)}) \tag{49}$$

where the q-th spherical component of $\mathbf{O}^{(k)}$ is $(-)^{q}\,O\,[k, -q]$. Operator H_{eff} is responsible for the second-order mechanisms. Extensions of H_{eff}, involving for instance contributions of the type $(\{\varepsilon^{(1)}\,\mathbf{O}^{(k)}\}^{(\lambda)} \cdot \mathbf{W}^{(k_s k_l)\lambda})$, are useful for describing higher-order mechanisms and can be found in Ref. 18.

APPENDIX A

The reduced matrix elements

$$(nl^N\, \alpha' S'L'J' \,\|\, kL + g_e S \,\|\, nl^N\, \alpha SLJ) = \delta(\alpha',\alpha)\,\delta(S',S)\,\delta(L',L)$$

$$(nl^N\, \alpha SLJ' \,\|\, kL + g_e S \,\|\, nl^N\, \alpha SLJ)$$

which occur in Eq. (3) and in the treatment of the Zeeman term (see II and III) can be calculated very easily. By putting

$$a = g_e + k, \qquad b = g_e - k, \qquad g(J',J) = (nl^N\, \alpha SLJ' \,\|\, kL + g_e S \,\|\, nl^N\, \alpha SLJ)$$

we obtain

$$g(J,J) = (1/2)\,\{(2J+1)/[J(J+1)]\}^{1/2}\,[aJ(J+1) + bS(S+1) - bL(L+1)]$$

$$g(J,J-1) = -g(J-1,J) = (b/2)\,\{[(S+L+1)^2 - J^2]\,[J^2 - (L-S)^2]/J\}^{1/2}$$

which, in the limiting case $k = 1$ and $g_e = 2$, are in agreement with the formulas in Ref. 16 except for the sign of $g(J-1,J)$.

APPENDIX B

The coupling coefficient

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

defined in I (see also Refs. 27 and 28) for the chain $SU(2) \supset G^*$ can be developed as a sum of products involving the Clebsch-Gordan coefficients $(\Gamma_2\Gamma_2\gamma\gamma \mid \Gamma_2\Gamma\beta\Gamma_1\gamma_1)$ for group G^*. (Here β is a multiplicity label to be used if the IRC Γ_1 is contained several times in the Kronecker product $\Gamma_2 \otimes \Gamma$.) This may be achieved by applying the Racah factorization lemma[26] to the Clebsch-Gordan coefficients of $SU(2)$ in an $SU(2) \supset G^*$ basis. We thus obtain the factorization relation[27]

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

$$\sum_{\beta} (j_2 a_2\Gamma_2 + k a\Gamma \mid j_1 a_1\beta\Gamma_1)^*\,(\Gamma_2\Gamma_2\gamma\gamma \mid \Gamma_2\Gamma\beta\Gamma_1\gamma_1)^*$$

where the $(+\,|\,)$ coefficients are isoscalar factors for the chain $SU(2) \supset G^*$, the properties of which have been studied in Ref. 27.

Most of the transition matrix elements in this paper appear in the general form

$$M_{\Gamma\gamma\to\Gamma'\gamma'} = \sum R(\ldots J'a'\Gamma' J a\Gamma k a''\Gamma'' \ldots)\, f\begin{pmatrix} J' & J & k \\ a'\Gamma'\gamma' & a\Gamma\gamma & a''\Gamma''\gamma'' \end{pmatrix}$$

where the sum runs on all the involved quantum numbers except Γ, γ, Γ', and γ'. The calculation of the corresponding oscillator strength

$$S_{\Gamma\to\Gamma'} = \sum_{\gamma'\gamma} \left| M_{\Gamma\gamma\to\Gamma'\gamma'} \right|^2$$

can be done by using the just mentioned factorization relation of the f coefficients and the following (unusual) unitary-completeness relation[27] of the Clebsch-Gordan coefficients for G^*

$$\sum_{\gamma_1\gamma} (\Gamma_1\Gamma_2\gamma_1\gamma_2 \mid \beta\Gamma\gamma)^*\,(\Gamma_1\Gamma_2'\gamma_1\gamma_2' \mid \beta'\Gamma\gamma)$$

$$= \Delta(\Gamma \mid \Gamma_1 \otimes \Gamma_2)\,\delta(\Gamma_2',\Gamma_2)\,\delta(\gamma_2',\gamma_2)\,\delta(\beta',\beta)\,[\Gamma_2]^{-1}\,[\Gamma]$$

Thus, we obtain

$$S_{\Gamma\to\Gamma'} = \Sigma\,[\ldots]\,R\,(\ldots J'a'\Gamma' Ja\Gamma ka''\Gamma''\ldots)\,R\,(\ldots \overline{J'a'}\Gamma'\overline{Ja}\Gamma\overline{ka}''\Gamma''\ldots)^*$$
$$\Sigma_{\beta}\,(Ja\Gamma + ka''\Gamma'' \mid J'a'\beta\Gamma')^*(\overline{Ja}\Gamma + \overline{ka}''\Gamma'' \mid \overline{J'a'}\beta\Gamma')$$

where [...] stands for some dimensionality factors. The latter sum rule can be easily transcribed for the various transitions studied in this work.

APPENDIX C

A simple development of the inverse of Eq. (18) gives the expressions

$$\{\varepsilon_1\varepsilon_2\}^{(1)}_0 = (1/\sqrt{2})\,[(\varepsilon_1)_1\,(\varepsilon_2)_{-1} - (\varepsilon_1)_{-1}\,(\varepsilon_2)_1]$$

$$\{\varepsilon_1\varepsilon_2\}^{(1)}_{\pm1} = \pm\,(1/\sqrt{2})\,[(\varepsilon_1)_{\pm1}\,(\varepsilon_2)_0 - (\varepsilon_1)_0\,(\varepsilon_2)_{\pm1}]$$

$$\{\varepsilon_1\varepsilon_2\}^{(2)}_0 = (1/\sqrt{6})\,[2\,(\varepsilon_1)_0\,(\varepsilon_2)_0 + (\varepsilon_1)_1\,(\varepsilon_2)_{-1} + (\varepsilon_1)_{-1}\,(\varepsilon_2)_1]$$

$$\{\varepsilon_1\varepsilon_2\}^{(2)}_{\pm1} = (1/\sqrt{2})\,[(\varepsilon_1)_0\,(\varepsilon_2)_{\pm1} + (\varepsilon_1)_{\pm1}\,(\varepsilon_2)_0]$$

$$\{\varepsilon_1\varepsilon_2\}^{(2)}_{\pm2} = (\varepsilon_1)_{\pm1}\,(\varepsilon_2)_{\pm1}$$

valid for circular and linear polarizations.

By way of illustration, let us consider Eq. (19) in the special case where the point symmetry group is $G \equiv C_{4v}$. In this case, we may use the chain of groups $O(3) \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ for replacing the label $a\Gamma\gamma$ by $\Gamma\,(C_{\infty v})\,\Gamma\,(C_{4v})\,\Gamma\,(C_{2v})$, see Refs. 28 and 29. Then, we have

$$\{\varepsilon_1\varepsilon_2\}^{(1)}_{A_2A_2A_2} = \{\varepsilon_1\varepsilon_2\}^{(1)}_0$$

$$\{\varepsilon_1\varepsilon_2\}^{(1)}_{E_1EB_j} = (-)^j\,(1/\sqrt{2}\,[\{\varepsilon_1\varepsilon_2\}^{(1)}_1 - (-)^j\,\{\varepsilon_1\varepsilon_2\}^{(1)}_{-1}] \quad \text{for } j = 1,\ 2$$

$$\{\varepsilon_1\varepsilon_2\}^{(2)}_{A_1A_1A_1} = \{\varepsilon_1\varepsilon_2\}^{(2)}_0$$

$$\{\varepsilon_1\varepsilon_2\}^{(2)}_{E_1EB_j} = (-)^j\,(1/\sqrt{2})\,[\{\varepsilon_1\varepsilon_2\}^{(2)}_1 + (-)^j\,\{\varepsilon_1\varepsilon_2\}^{(2)}_{-1}] \quad \text{for } j = 1,\ 2$$

$$\{\varepsilon_1\varepsilon_2\}^{(2)}_{E_2B_jA_j} = (1/\sqrt{2})\,[\{\varepsilon_1\varepsilon_2\}^{(2)}_2 - (-)^j\,\{\varepsilon_1\varepsilon_2\}^{(2)}_{-2}] \quad \text{for } j = 1,\ 2$$

where the Mulliken notation is used for the IRC's of $C_{\infty v} \supset C_{4v} \supset C_{2v}$.

REFERENCES

1. M. Kibler, *J. Mol. Spectrosc.* **26** (1968) 111; *Int. J. Quantum Chem.* **3** (1969) 795; M. Kibler and G. Grenet, *Int. J. Quantum Chem.* **28** (1985) 213; **29** (1986) 11; **29** (1986) 485. (Cited as I—V.).
2. M. Kibler, *Croat. Chem. Acta* **57** (1984) 1075.
3. R. Loudon, *The Quantum Theory of Light*, Clarendon, Oxford, 1973.
4. M. Göppert-Mayer, *Ann. Physik* **9** (1931) 273.
5. J. H. Van Vleck, *J. Phys. Chem.* **41** (1937) 67.
6. L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, *Physica* **11** (1945) 231.
7. Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.* **9** (1954) 766; S. Sugano, *Prog. Theor. Phys. (Kyoto) Suppl.* **14** (1960) 66.
8. A. D. Liehr and C. J. Ballhausen, *Phys. Rev.* **106** (1957) 1161; C. J. Ballhausen and A. D. Liehr, *Mol. Phys.* **2** (1959) 123; *J. Mol. Spectrosc.* **2** (1958) 342; **4** (1960) 190.
9. S. Koide and M. H. L. Pryce, *Phil. Mag.* **3** (1958) 607; S. Koide, *Phil. Mag.* **4** (1959) 243.

10. J. S. Griffith, *Mol. Phys.* **3** (1960) 477.
11. S. Feneuille, *J. Physique* **27** (1966) C2—87.
12. R. A. Satten, *J. Chem. Phys.* **27** (1957) 286.
13. B. R. Judd, *Phys. Rev.* **127** (1962) 750.
14. G. S. Ofelt, *J. Chem. Phys.* **37** (1962) 511.
15. J. D. Axe, Jr., *J. Chem. Phys.* **39** (1963) 1154.
16. M. J. Weber, *Phys. Rev.* **157** (1967) 262.
17. O. L. Malta, A. A. S. da Gama, and S. Canuto, *Rev. Bras. Fis.* **12** (1982) 563.
18. M. C. Downer, G. W. Burdick, and D. K. Sardar, *J. Chem. Phys.* **89** (1988) 1787; see also M. C. Downer, in: *Laser Spectroscopy of Solids II*, W. M. Yen (Ed.), Springer, Heidelberg, 1989.
19. J. D. Axe, Jr., *Phys. Rev.* **136** (1964) A42.
20. T. R. Bader and A. Gold, *Phys. Rev.* **171** (1968) 997.
21. P. A. Apanasevich, R. I. Gintoft, V. S. Korolkov, A. G. Makhanek, and G. A. Skripko, *Phys. Status Solidi (b)* **58** (1973) 745.
22. B. R. Judd and D. R. Pooler, *J. Phys. C: Solid State Phys.* **15** (1982) 591.
23. M. C. Downer and A. Bivas, *Phys. Rev. B* **28** (1983) 3677.
24. J. Sztucki and W. Strek, *Phys. Rev. B* **34** (1986) 3120.
25. J. C. Gâcon, J. F. Marcerou, M. Bouazaoui, B. Jacquier, and M. Kibler, *Phys. Rev. B* submitted for publication, 1988.
26. G. Racah, *Phys. Rev.* **76** (1949) 1352.
27. 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*, J. C. Donini (Ed.), Plenum Press, N. Y., 1979; *Int. J. Quantum Chem.* **23** (1983) 115.
28. M. R. Kibler and G. Grenet, *Int. J. Quantum Chem.* **11** (1977) 359.
29. J. C. Gâcon, G. Grenet, J. C. Souillat, and M. Kibler, *J. Chem. Phys.* **69** (1978) 868; G. Grenet, M. Kibler, A. Gros, J. C. Souillat, and J. C. Gâcon, *Phys. Rev. B* **22** (1980) 5052; M. Kibler, G. Grenet, J. C. Gâcon, and B. Jacquier, *Phys. Status Solidi (b)* **124** (1984) 325; M. Kibler, J. C. Gâcon, G. Grenet, B. Jacquier, and L. C. Brunel, *Phys. Status Solidi (b)* **124** (1984) 731.

SAŽETAK

Energijske razine paramagnetnih iona: Algebra. VI. Račun intenziteta prijelaza

Maurice Kibler i Jean-Claude Gâcon

Primjenom teorije grupa razvijena je metoda računanja intenziteta jedno- i dvo-fotonskih prijelaza za konfiguraciju nl^N. Posebno se razmatraju jednofotonski prijelazi magnetskog dipola i dvofotonski prijelazi električnog dipola. Kao ilustracija dana je konfiguracija $4f^6$ u simetriji C_{4v}.