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Multi-Photon Laser Spectroscopy of Transition Ions in Crystals: Recent Progress in the Use of Symmetry Considerations*

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Abstract - The role of symmetry adaptation techniques in multi-photon spectroscopy of partly-filled shell ions in crystals is briefly reviewed. This leads to an intensity formula which is discussed from a qualitative point of view.

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1. INTRODUCTION

In recent years, electronic spectroscopy of transition ions (transition-metal ions and rare-earth ions) in crystalline environments has been the object of important developments. In particular, the advent of tunable dye lasers has made possible to perform two-photon spectroscopy experiments. (In p-photon spectroscopy, p photons *simultaneously* occur in the light-matter interaction. For example, p-photon absorption spectroscopy corresponds to the *simultaneous absorption* of p photons between an initial and a final level and has to be distinguished from the *sequential absorption* of p photons between the two levels.) Two-photon spectroscopy ($p = 2$) with laser beams is now a technique complementary of one-photon spectroscopy ($p = 1$). It gives many informations on the structural (and dynamical) properties of ions in crystals. More specifically, two-photon spectroscopy permits to reach excited levels which cannot be reached with one-photon spectroscopy. In addition, by playing with the polarization of the two involved photons, one may obtain interesting selection rules. Similar interests exist in principle for p-photon spectroscopy with $p > 2$ although experiments are hardly feasible (except for ions in vapors) when $p \geq 4$.

Since the pioneer works by Kaiser and Garrett [1] and Axe [2] in the sixties, there have been many progress, from an experimental and a theoretical viewpoint, in two-photon spectroscopy of d^N and f^N ions in crys-

tals. From the theoretical side, the progress have been achieved, for both parity-allowed and parity-forbidden transitions, in two directions: (i) the elaboration of more and more sophisticated models and (ii) the systematic use of symmetry considerations [3 - 20] based on symmetry adaptation techniques [21, 22]. In the present paper, we shall be concerned mainly with point (ii). More specifically, we shall give a brief review on the use of symmetry considerations, in conjunction with sophisticated models, for the description of electric-dipole two-photon transitions. A more detailed exposure may be found in [9, 10, 12, 13] for parity-forbidden transitions and in [11 - 13] for parity-allowed transitions (see also Ref. [23]).

For the sake of generality, we shall give the relevant intensity formulas for p-photon (electric-dipole) transitions. The case $p = 2$ shall follow as a particular case.

2. INTENSITY FORMULA

The electric-dipole moment is an odd operator. Therefore, for p arbitrary, parity-allowed transitions correspond to either $n\ell^N \rightarrow n\ell^N$ transitions for p even or $n\ell^N \rightarrow n\ell^{N-1}n'\ell'$ transitions with $\ell + \ell'$ odd for p odd while parity-forbidden transitions correspond to either $n\ell^N \rightarrow n\ell^N$ transitions for p odd or $n\ell^N \rightarrow n\ell^{N-1}n'\ell'$ transitions with $\ell + \ell'$ odd for p even.

Let us consider a p-photon (absorption) transition between an initial

level i of symmetry Γ and a final level f of symmetry Γ'. (Here, Γ and Γ' stand for two irreducible representations of the group G for N even or of its spinor group G^* for N odd. We note G the point symmetry group of the ℓ^N ion in its environment. Furthermore, we use γ and γ' to label the Stark components of the levels of symmetry Γ and Γ', respectively.) The transition matrix element $M_{i(\Gamma\gamma)\rightarrow f(\Gamma'\gamma')}$ can be calculated in the framework of the following approximations:

(i) we restrict ourselves to the electric-dipole (i.e., great wavelength) approximation,

(ii) single mode excitations (with given energy, wave number and polarization vector for each of the p photons) are used for describing the radiation field,

(iii) only p-th order mechanisms arising from time-dependent perturbation theory are considered,

(iv) a quasi-closure approximation (which amounts to ignore the internal structure of the intermediate configurations) is used,

(v) the only good quantum numbers are $\Gamma\gamma$ and $\Gamma'\gamma'$ (and the parity for parity-allowed transitions) for the initial and final state-vectors, respectively,

(vi) if necessary, as for parity-forbidden transitions, q-th order mechanisms ($q \geq 1$) arising from time-independent perturbation theory are

considered,

(vii) we use a weak-field basis adapted to the chain $SU(2) \supset G^*$ for describing the state-vectors and interactions.

From recoupling techniques, it can be shown that (under the above-mentioned hypotheses) the transition matrix element $M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')}$ is given by

$$M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')} = (f\Gamma'\gamma'|H_{\text{eff}}|i\Gamma\gamma), \tag{1}$$

where H_{eff} is a model-dependent effective operator. The most general form of H_{eff} turns out to be

$$H_{\text{eff}} = \sum_{k_1 k_2 \cdots k_{p-1}} \sum_{t} \sum_{k_S k_L} \sum_{k} C[k_1 k_2 \cdots k_{p-1}; t; k_S k_L; k] \left(\{\mathbf{P}^{(k_{p-1})} \mathbf{X}^{(t)}\}^{(k)} . \mathbf{W}^{(k_S k_L)k} \right), \tag{2}$$

where (.) is a scalar product involving electronic ($\mathbf{W}^{(k_S k_L)k}$) and nonelectronic ($\mathbf{P}^{(k_{p-1})}$ and $\mathbf{X}^{(t)}$) tensors. In Eq. (2), $\mathbf{P}^{(k_{p-1})}$ is the polarization tensor

$$\mathbf{P}^{(k_{p-1})} = \{\cdots\{\{\mathbf{E}_1\mathbf{E}_2\}^{(k_1)}\mathbf{E}_3\}^{(k_2)}\cdots\mathbf{E}_p\}^{(k_{p-1})} \tag{3}$$

that describes the coupling of the unit polarization vectors $\mathbf{E}_i$ ($i = 1, 2, \cdots, p$). In addition, $\mathbf{W}^{(k_S k_L)k}$ and $\mathbf{X}^{(t)}$ are tensors relative to the ion and its environment: $\mathbf{W}^{(k_S k_L)k}$ is an electronic tensor (of spin degree k_S, orbital degree k_L and total degree k) whereas $\mathbf{X}^{(t)}$ is the ligand polarization tensor or the crystal-field tensor (of the degree t). Finally, the expansion coefficients C in (2) are calculable in an *ab initio* way.

The matrix element (1) can be easily calculated by using Wigner-Racah calculus (i.e., irreducible tensor methods) for a chain of groups $SU(2) \supset G^*$ as developed in Refs. [21, 22]. The quantity of importance for a comparison between theory and experiment is the intensity strength

$$S_{i(\Gamma)\to f(\Gamma')} = \sum_{\gamma\gamma'} \left|M_{i(\Gamma\gamma)\to f(\Gamma'\gamma')}\right|^2 \tag{4}$$

for the $i(\Gamma) \to f(\Gamma')$ transition. The sum over γ and γ' in Eq. (4) can be effectuated by means of the Racah lemma for the Clebsch-Gordan coefficients of the group $SU(2)$ in a $SU(2) \supset G^*$ basis. As a final result, we obtain the intensity formula [10 - 13]

$$\begin{aligned} S_{i(\Gamma)\to f(\Gamma')} = & \sum_{\{k_j\}}\sum_{\{\ell_j\}}\sum_{r}\sum_{s}\sum_{\Gamma''} \\ & I[\{k_j\}\{\ell_j\}rs\Gamma'';\Gamma\Gamma'] \sum_{\gamma''} P^{(k_{p-1})}_{r\Gamma''\gamma''} \left(P^{(\ell_{p-1})}_{s\Gamma''\gamma''}\right)^* \end{aligned} \tag{5}$$

with $1 \leq j \leq p-1$. The polarization dependence in (5) is contained in the two P factors. This dependence, which may involve linear and/or circular polarization types, is entirely under the control of the experimentalist. The intensity parameters I in (5) are given by expressions that depend on: (i) the nature (energy) of the p absorbed photons, (ii) the involved configurations via energy factors, wavefunctions and radial integrals, (iii) recoupling coefficients for the group $SU(2)$ and reduced matrix elements, (iv) the group G via coupling coefficients and isoscalar factors for the chain $SU(2) \supset G^*$, and (v) the order q of the (time-independent) mechanism used for treating some of the interactions (especially the spin-orbit interaction and the crystal-field interaction).

It is remarkable that the structural form of (5) holds for both parity-allowed and parity-forbidden transitions. This forms (actually based on group theory) also holds when some of the absorbed photons are replaced by scattered photons (Raman or Rayleigh scattering). The general form of (5) is also valid for other multi-photon processes, as for example the simultaneous absorption of several photons, certain by electric-dipole absorption and others by magnetic-dipole and/or electric-quadrupole absorption. Note also that vibronic degrees of freedom may be incorporated in (5) (see Ref. [14]).

3. CLOSING REMARKS

The intensity parameters I may be calculated from first principles. This leads to a very much involved quantum chemistry problem. Alternatively, they may be considered, at least in a first approach, as phenomenological parameters to be adjusted on experimental data. It may be also interesting to combine the *ab initio* and *phenomenological* approaches. In all approaches the number of I parameters is limited by a set of properties and selection rules [10 - 13].

Once the number of independent parameters I in the intensity formula (5) has been determined, we can obtain the polarization dependence of the intensity strength $S_{i(\Gamma)\to f(\Gamma')}$ by calculating the tensor products $P^{(K)}_{a''\Gamma''\gamma''}$ (with $K = k_{p-1}, \ell_{p-1}$ and $a'' = r, s$) occurring in Eq. (5). For

this purpose, we use the development

$$P^{(K)}_{a''\Gamma''\gamma''} = \sum_{Q=-K}^{K} P^{(K)}_{Q} \, (KQ|Ka''\Gamma''\gamma'') \tag{6}$$

in terms of the spherical components $P^{(K)}_{Q}$, the coefficients in the development (6) being reduction coefficients for the chain $O(3) \supset G$. Then, in order to calculate $P^{(K)}_{Q}$, we use developments of the type

$$\{\mathbf{E}_1\mathbf{E}_2\}^{(k_1)}_{q_1} = (-1)^{k_1-q_1} \sqrt{2k_1+1} \sum_{x=-1}^{1} \sum_{y=-1}^{1} \begin{pmatrix} 1 & k_1 & 1 \\ x & -q_1 & y \end{pmatrix} (E_1)^{(1)}_{x} \, (E_2)^{(1)}_{y} \tag{7}$$

in terms of the spherical components $(E_i)^{(1)}_{q}$ characterizing the circular or linear polarization of the i-th photon ($i = 1, 2$). In general, we may have $k_1 = 0, 1, 2$. However, if the two involved photons are identical (one-color beam), k_1 assumes only the values 0 and 2. Equation (7) describes the polarization tensor for $p = 2$. If $p > 2$, repeated couplings of the type of the one entering Eq. (7) yield an expression for the polarization tensor.

In the case where $p = 2$, the symmetry adaptation techniques and models sketched through Eqs. (1 - 7) have been successfully applied to f^N ions [15 - 18] and d^N ions [19, 20] in crystals. As a brief résumé, we note the following tendencies. For intraconfigurational transitions within the configurations $3d^N$ ($N \neq 5$) and $4f^N$ ($N \neq 7$), second-order mechanisms ($p = 2, q = 0$) are generally sufficient for "nonhypersensitive" two-photon transitions. For "hypersensitive" two-photon transitions (like $^5D_0 \rightarrow {}^7F_0$

transitions within the $4f^6$ configuration in tetragonal symmetry), third-order mechanisms ($p = 2, q = 1$) are required for a satisfactory description of the polarization dependence. For interconfigurational two-photon transitions (like $4f^6 \rightarrow 4f^5 5d$ transitions in tetragonal symmetry), it is also necessary to consider at least third-order mechanisms ($p = 2, q = 1$) for a good agreement between theory and experiment.

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