Revista Brasileira de Física, Vol. 11, Nº 2, 1981

Oscillating Quadrupole Moments and Hypersensitive $4f \leftrightarrow 4f$ Intensities

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Recebido ern 27 de março de 1981

The contribution to the pseudo-multipolar field, proposed by JBrgensen and Judd to account for hypersensitive, due to oscillating quadrupole moments is shown to be negligible. A discussion of the results is presented.

É demonstrado que a contribuição para o campo pseudo- multipolar, proposto por JBrgensen e Judd para explicar o fenômeno de hipersensitividade, devido a momentos quadripolares oscilante é negligível. Os resultados são discutidos.

1. INTRODUCTION

Considerable efforts have been made to understand the enormous variation of some lanthanide $4f \leftrightarrow 4f$ intensities which follows a change of chemical environment[1-8]. This hypersensitivity, as called by JBrgensen and Judd[1], is generally observed in transitions which obey electric quadrupole selection rules.

The dynamic coupling mechanism, proposed by Mason *et.al.*[3] to account for this phenomenon, has been shown recently by Judd[5] to be identical to the pseudo-multipolar field[7,8] originally proposed by JBrgensen and Judd[1]. The latter is based on the fact that oscillating dipoles induced on the ligands by the external radiation produce a field which is effective in inducing electronic transitions.

Recently, it has been argued[7,8] that this mechanism is able to explain the main features of hypersensitivity, and that not only the 2^2 8 -polar component of the field produced by those oscillating dipoles is important, infact the most one, but also its 2^4 and 2^6-polar components, specially for the case of the $4f \leftrightarrow 4f$ intensities of the Pr^{3+} ion.

The purposc of the present paper is to analyse the contribution to the pseudo-multipolar field, due to oscillating quadrupole moments induced on the ligands by the external radietion. It is then shown that this contribution is negligible, and it is in fact of the same order as the contribution due to the second term in the expansion of $e^{i\vec{k}\cdot\vec{R}}$ to the field produced hy the oscillating dipoles. This is rather a fortunate point since it shows the fast convergence of the multipolar series, a fact which seems to be not observed in the case of the contribution, due to multipole moments, to the static crystal potential in the ionic model[9].

2. OSCILLATING DIPOLE MOMENTS

The contribution to the pseudo-multipolar field due to oscillating dipoles índuced on the ligands by the external radiation, may be calculated[7,8] by considering the potential energy of the N equivalent electrons of a $n\ell^N$ configuration due to point dipoles localized at the ligands[10], i.e.

$$W = -e \sum_{\substack{kqq' \\ q''\mu j}} (-1)^{k+q+q''+1} \left[4\pi(k+1)(2k+1)\right]^{1/2} \frac{\langle r^k \rangle}{R_\mu^{k+2}} \times$$

$$\times P^{(1)}_{q''}(\mu)\, Y^{k+1\,*}_{q'}(\Omega_\mu)\; C^{(k)}_{q}(j) \qquad (1)$$

where j labels the $n\ell$ electronr and μ the ligands. The quantities $P^{(1)}_{\hat{q}''}(\mu)$ are the tensorial components of a dipole moment $\vec{P}(\mu)$ localized at $\vec{R}_\mu$ (the position of the p-th ligand), the $C_q^{(k)}$ are the usual Racah's tensor operators[*] and the $\langle r^k \rangle$ are the radial averages of r_j^k.

In the presence of the external radiation field, the dynamical part of the dipole moment $\vec{P}(\mu)$ is given by

$$\vec{P}(\mu) = \alpha_\mu \vec{E}(\mu) \tag{2}$$

where α_μ is the polarizability of the p-th ligand and $\vec{E}(\mu)$ the electric field of the external radiation at the ligand's position $\vec{R}_\mu$. By expressing the vector $\vec{E}(\mu)$, foi a given polarization, as

$$\vec{E}(\mu) = E_0 \, e^{i(\vec{K}.\vec{R}_\mu - \omega t)} \, \vec{e}_M \tag{3}$$

$\vec{e}_M$ $(M = 0, \pm 1)$ being a unit spherical vector, it is possible to find the following expression for the Einstein's coefficient of spontaneous emission related to the total transition probabiiity, between the manifolds ψJ and $\psi' J'$, due to the above mechanism[7,8]

$$S = \frac{4\,\omega^3\,\chi\,\alpha^2}{3\hbar c^3 g^2 e^2 (2J+1)} \sum_{kq'} (1-\sigma_k)^2 (k+1) \langle r^k \rangle^2 \langle \ell || C^{(k)} || \ell \rangle^2 \times$$

$$\times \; |\gamma_{q'}^{k+1}|^2 \langle (n\ell^N)\psi J || U^{(k)} || (n\ell^N)\psi' J' \rangle^2 \tag{4}$$

where it is assumed that

$$\alpha_\mu = \alpha_{\mu'} = \ldots = \alpha$$

and the coefficients $\gamma_{q'}^{k+1}$ are related to lattice sums by the expression

$$\gamma_{q'}^{k+1} = \left(\frac{4\pi}{2k+3}\right)^{1/2} \sum_\mu \frac{g e^2}{R_\mu^{k+2}} Y_{q'}^{k+1*} (\Omega_\mu) \tag{5}$$

In Eq. (4), the quantities χ and σ_k represent the Lorents local field correction and the shielding factors respectively[5].

It is important to note that in the development of Eq. (4), the long-wavelength approximation $(e^{i\vec{K}.\vec{R}_\mu} \simeq 1)$ has been assumed.

Thus, this equation has been used to prediet, for example, the intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions of the Eu^{3+} ion doped in the Y_2O_3 host[7]. For $\alpha = 3$ Å^3, the calculated intensities were equal to 643 and 63 s^{-1} respectively whereas the experimental values of Krupke[12] were 732 and 75 s^{-1} respectively.

The qualitative aspects of Eq. (4), and how it may account for hypersensitivity, has been discussed by Judd[5] and Peacock[6].

3. OSCILLATING QUADRUPOLE MOMENTS

In order to see how oscillating quadrupoles, induced on the ligands by the external radiation, can contribute to the pseudo- multipolar field, we have developped, by the procedure described in ref.10, the following expression for the potential energy of the $n\ell$ electrons due to point quadrupole moments localized at the ligands:

$$W = e\left(\frac{5}{6}\right)^{1/2} \sum_{\substack{kqq'p \\ \mu j}} (-1)^{k+q+p} \left[4\pi(k+1)(k+2)(2k+1)\right]^{1/2} (2k+3) \times$$

$$\frac{\langle r^k \rangle}{R_\mu^{k+3}} Y_{q'}^{k+2*}(\Omega_\mu) \begin{Bmatrix} 1 & k+2 & k+1 \\ k & 1 & 2 \end{Bmatrix} \begin{pmatrix} k & k+2 & 2 \\ q & -q' & p \end{pmatrix} M_p^{(2)}(\mu)\, C_q^{(k)}(j) \tag{6}$$

where $M_p^{(2)}(\mu)$ is a tensorial component of the point quadrupole localized at the μ-th ligand. This expression has been checked with that given by Hutchings and Ray[9].

The oscillating moments $M_p^{(2)}(\mu)$ are given by

$$M_p^{(2)}(\mu) = \alpha_R(\mu)(30)^{1/2} \sum_{mn} (-1)^p \begin{pmatrix} 1 & 1 & 2 \\ m & n & -p \end{pmatrix} \left[\nabla_m^{(1)} E_n^{(1)}\right](\mu) \tag{7}$$

where $\alpha_R(\mu)$ is the quadrupolar polarizability of the μ-th ligand and $[\nabla_m^{(1)} E_n^{(1)}](\mu)$ expresses the gradient, of the electric field, at $\vec{R}_\mu$.

Following the same procedure as for the oscillating dipoles, if we express the electric field of the external radiation for a given component of a given polarization as in Eq. (3) we find

$$E_n^{(1)} = (-1)^M E_0 e^{i(\vec{K}.\vec{R}-\omega t)} \delta_{n,-M} \tag{8}$$

and therefore

$$M_p^{(2)}(\mu)=(-1)^{M+p} (30)^{1/2} \alpha_R(\mu) E_0 e^{-i\omega t} \begin{pmatrix} 1 & 1 & 2 \\ M+p & -M & -p \end{pmatrix} \left[\nabla_{M+p}^{(1)} e^{i\vec{K}.\vec{R}}\right](\mu) \tag{9}$$

Now, using the expansion[13]

$$e^{i\vec{K}.\vec{R}} = \sum_{k'q''} 4\pi i^{k'} J_{k'}(KR) Y_{q''}^{k'*}(\Omega_K) Y_{q''}^{k'}(\Omega_R) \tag{10}$$

and approximating the spherical Bessel's functions by

$$J_{k'}(KR) \simeq \frac{(KR)^{k'}}{(2k'+1)!!} \tag{11}$$

we may use the equation[13]

$$\{\nabla_{M+p}^{(1)} |R^{k'} Y_{q''}^{k'}(\Omega_R)|\}(\mu) = (-1)^{k'+q''+M+p+1} \left[k'(2k+1)(2k'+2)\right]^{1/2} \times$$

$$\times \begin{vmatrix} k'-1 & k' & 1 \\ q''+M+p & -q'' & -M-p \end{vmatrix} R_\mu^{k'-1} Y_{q''+M+p}^{k'-1}(\Omega_\mu) \tag{12}$$

to obtain

$$|\nabla_{M+p}^{(1)} e^{i\vec{K}.\vec{R}}|(\mu) = \sum_{k'q''} (-1)^{k'+q''+M+p+1} \frac{4\pi i^{k'}\left[k'(2k'+1)(2k'+2)\right]^{1/2}}{(2k'+1)!!} \times$$

$$\times K^{k'} Y_{q''}^{k'}(\Omega_K) \begin{pmatrix} k'-1 & k' & 1 \\ q''+M+p & -q' & -M-p \end{pmatrix} R^{k'-1} Y_{q''+M+p}^{k'-1}(\Omega_\mu) \tag{13}$$

Owing to the leading term in the above expression ($k'=1$) we obtain

$$M_p^{(2)}(\mu) = (-1)^{M+p+1}\, i\left(\frac{160\pi}{3}\right)^{1/2} \alpha_Q(\mu)\, E_0\, e^{-i\omega t} \begin{pmatrix} 1 & 1 & 2 \\ M+p & -M & -p \end{pmatrix} K\, Y^1_{M+p}(\Omega_K) \quad (14)$$

Substituting (14) into (6), we may write the interaction energy

$$W(t) = \mathrm{Re}(W) \quad (15)$$

in the form

$$W(t) = W^+ e^{-i\omega t} + W^- e^{i\omega t} \quad (16)$$

and use Fermi's golden rule[14] to get the total transition probability between two manifolds ψJ and $\psi' J'$. To this end, we integrate over $d\,\Omega_K$ and sum over the assumed equally thermally populated M_J and $M_{J'}$ components. Then, after summation over free indices and the three values of M followed by multiplication by 2/3 [7], we obtain

$$S = \frac{64\pi e^2 \omega^5 \alpha_Q^2}{27\hbar c^5 (2k+1)} \sum_{kq\mu\mu'} \frac{(k+1)(k+2)(2k+3)}{(2k+5)} \langle r^k\rangle^2 \times$$

$$\times \langle \ell \| C^{(k)} \| \ell\rangle^2 \frac{Y_q^{k+2\,*}(\Omega_\mu)\, Y_q^{k+2}(\Omega_{\mu'})}{R_\mu^{k+3}\, R_{\mu'}^{k+3}} \langle (n\ell^N)\,\psi J \| U^{(k)} \| (n\ell^N)\,\psi' J'\rangle^2 \quad (17)$$

where we have used the fact that

$$\begin{Bmatrix} 1 & k+2 & k+1 \\ k & 1 & 2 \end{Bmatrix}^2 = \frac{1}{5(2k+3)}$$

The sums over μ and μ' in Eq. (17) may be related to lattice sums in the point charge electrostatic model of the crystal field, as for the case of oscillating dipoles, and we finally obtain

$$S = \frac{16\omega^5 \alpha_Q^2\, \chi}{27\hbar c^5 g^2 e^2 (2J+1)} \sum_{kq} (1-\sigma_k)^2 (k+1)(k+2)(2k+3) \langle r^k\rangle^2 \times$$

$$\times \langle \ell \| C^{(k)} \| \ell\rangle^2 |\gamma_q^{k+2}|^2 \langle (n\ell^N)\psi J \| U^{(k)} \| (n\ell^N)\psi' J'\rangle^2 \quad (18)$$

We are then in position to estimate the contribution of oscillating quadrupoles to the pseudo-multipolar field.

4. RESULTS AND DISCUSSION

For the case of $4f^n$ configurations $(n\ell \equiv 4f)$, the values of k in Eq.(18) are restricted to 2,4 and 6. If we consider the transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_2 \rightarrow {}^7F_0$ of the Eu^{3+} ion, and the equation

$$S = \frac{4\, e^2\, \omega^3\, \chi}{3\hbar c^3 (2J+1)} \sum_k \Omega_k \, <(4f^N)\, \psi J || U^{(k)} || \, (4f^N)\psi' J'>^2$$

$k = 2$, 4, 6, where the Ω_k are intensity parameters which contain contributions from the electric dipole mechanism[15,16] and from the pseudo- multipolar field, it seems that with the same Ω_2 parameter the intensity of both transitions above may be accounted for. Thus, we may already expect the contribution from oscillating quadrupoles to be indeed small since it predicts a R, which depends strongly on the transition frequency.

In fact, if we take a_Q for the O^{--} ion equal to 3.694 $Å^5$ [17] and the appropriate values for the quantities in Eq.(18)[5,18,19], we find for the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ intensities of the Eu^{+3} ion doped in Y_2O_3 contributions which are smaller than 10^{-2} s^{-1}. These values differ from those quoted by Krupke[12] (see section 2) by more than four orders of magnitude. These contributions are indeed of the same order of magnitude as those arising from the term $i\vec{K}.\vec{R}$ in the treatment of oscillating dipoles if the long wavelength approximation is not assumed.

It is interesting to note that Eq.(18) gives nonvanishing contributions (even though negligible) even in the case of site symmetries containing a center of inversion since it does not depend on lattice sums, γ_p^t, of odd rank.

The convergence of the multipolar series is clearly connected with the fact that the sensibility of a $n\ell$ electron to a pulsating ligand decreases as powers of KR.

The authors are deeply grateful to the Centre National de la Recherche Scientifique (C.N.R.S.) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support.

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