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Electronic Raman Effect in Lanthanide(III) Complexes. Ligand Polarization Contribution*

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Two-photon spectroscopy has recently become very popular as a source of spectroscopic data complementing the results of one-photon investigations. Due to different selection rules new transitions within the f shell of lanthanides can be observed [1]. The first theoretical description of two-photon absorption (TPA) was proposed by Axe [2] in 1964 on the basis of the standard Judd–Ofelt model. Its predictions appeared to be in disagreement with recent experiments. However, the corrections coming from the spin–orbit interaction and the metal–ligand interaction have given sufficient explanation of observed anomalies.

Electronic Raman scattering (ERS), formally equivalent to TPA, offers some new possibilities to experimentalists. Apart from the transition intensities, also the degree of asymmetry can be measured which, in turn, may inform us about the electronic structure of investigated ions. Recently, the ERS spectra for Er^{3+} and Tm^{3+} ions have been reported [3]. Like for TPA case the theory based on the Axe model turned out to be inadequate. Some attempts to improve it by means of contributions arising from the $4f^{N-1}5g$ excited states [4] seem to be unsatisfactory.

In this paper the influence of ligands surrounding the metal ion on the asymmetry of electronic Raman scattering will be discussed. Both crystal-field and ligand-polarization mechanisms can be described within the independent systems model where two independent chromophores (metal and ligand) interact via the Coulombic interaction

$$V_{\mathrm{ML}} = \sum_{k_1, k_2} \left(\frac{2k_1 + 2k_2}{2k_1}\right)^{1/2} T_{\mathrm{L}}^{(k_1+k_2)} \times (D_{\mathrm{M}}^{(k_1)} D_{\mathrm{L}}^{(k_2)})^{(k_1+k_2)} \qquad (1)$$

where $D^{(k)}$ are the multipole operators (M = metal, L = ligand) and the tensor $T_{\mathrm{L}}^{(k)}$ is defined by

$$T_{\mathrm{L}}^{(k)} = R_{\mathrm{L}}^{-k-1} C^{(k)}(\theta, \Phi)_{\mathrm{L}} \qquad (2)$$

In our approach the chromophore–light interaction is limited to the electric dipole part.

Using the second-order perturbation theory and the closure approximation [2] we get the simplest expression for ERS amplitude

$$\sum_{k=1,2} (\vec{\epsilon}_1^{(1)} \vec{\epsilon}_2^{(1)})^{(k)} \langle M_{\mathrm{g}} | (D_{\mathrm{M}}^{(1)} D_{\mathrm{M}}^{(1)})^{(k)} | M_{\mathrm{f}} \rangle \times [(-1)^k (E_{\mathrm{df}} - \hbar\omega_1)^{-1} + (E_{\mathrm{df}} + \hbar\omega_2)^{-1}] \qquad (3)$$

where E_{df} is an average energy of the intermediate configuration (in our case $4f^{N-1}5d$) above the ground state. $|M_{\mathrm{g}}\rangle$ and $|M_{\mathrm{f}}\rangle$ are the ground and final states of the metal ion and $\vec{\epsilon}_1$, $\vec{\epsilon}_2$ are the polarization vectors of incident and scattered light, respectively. Let us notice that the importance of the antisymmetric part of the transition tensor ($k = 1$) can be estimated by the ratio between the energy denominators of eqn. (3) for $k = 1$ and 2.

In the third order of perturbation theory we take into account the metal–ligand interaction. The two most significant terms of expansion (1) will be considered. For even k_1 and $k_2 = 0$ point charges on ligands give an effective crystal-field potential with parameters B_{dd}^{t} which mixes the $4f^{N-1}5d$ intermediate states

$$\sum_{k,t,\lambda,n} 15[k]([n][\lambda])^{1/2} \begin{pmatrix} 2 & t & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & k & t \\ 2 & 2 & 3 \end{Bmatrix} \begin{Bmatrix} k & \lambda & 1 \\ 3 & 2 & 3 \end{Bmatrix} \times \begin{Bmatrix} 1 & 1 & n \\ t & \lambda & k \end{Bmatrix} r_{\mathrm{df}}^2 \times (-1)^{\lambda} [(\vec{\epsilon}_1^{(1)} \vec{\epsilon}_2^{(1)})^{(n)} B_{\mathrm{dd}}^{(t)}]^{(\lambda)} \times \langle M_{\mathrm{g}} | U^{(\lambda)} | M_{\mathrm{f}} \rangle \times [(E_{\mathrm{df}} - \hbar\omega_1)^{-2} + (-1)^n (E_{\mathrm{df}} + \hbar\omega_2)^{-2}] \qquad (4)$$

The energy ratio for the crystal-field mechanism is two times smaller than for the second-order term but the expression (4) is too complicated to draw any final conclusions about its asymmetry based only on energy denominators. Particular site symmetries and light polarizations must be separately discussed.

The terms of (1) with odd k_1 and $k_2 = 1$ describe the situation where light induced electric dipoles on ligands interact with odd multipoles on the metal ion. It gives the ligand-polarization contribution:

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$$\sum_{\mathrm{L}} \sum_{\lambda, t, n} (-1)^{\lambda} \left(\frac{105(2t+3)[\lambda][n]}{3[t]} \right)^{1/2}$$

$$\times \begin{pmatrix} 2 & t & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & \lambda & t \\ 3 & 2 & 3 \end{Bmatrix} r_{\mathrm{fd}}^{t} r_{\mathrm{fd}}$$

$$\times [2E_{\mathrm{df}}/(E_{\mathrm{df}}^{2} - (\hbar\omega)^{2})] \langle M_{\mathrm{g}} | U^{(\lambda)} | M_{\mathrm{f}} \rangle$$

$$\times \{ [\vec{\epsilon}_{1}^{(1)} (T^{(t+1)} (\alpha_{2\mathrm{L}}^{(n)} \vec{\epsilon}_{2}^{(1)})^{(1)})^{(t)}]^{(\lambda)}$$

$$+ (-1)^{n} [\vec{\epsilon}_{2}^{(1)} (T^{(t+1)} (\alpha_{1\mathrm{L}}^{(n)} \vec{\epsilon}_{1}^{(1)})^{(1)})^{(t)}]^{(\lambda)} \} \qquad (5)$$

Linking the ligand-dependent tensors of eqn. (4) we form the field-polarization tensor:

$$F^{(k)} = \sum_{\mathrm{L}} (T_{\mathrm{L}}^{(t+1)} \alpha_{\mathrm{L}}^{(n)})^{(k)} \qquad (6)$$

Group theoretical considerations on the appearance of $F^{(k)}$ in particular site symmetries [5] lead us to the selection rules of two-photon ligand polarization mechanism. It is weak for point groups T, T_h, T_d, O, O_h. For other groups it works and in complexes with symmetries C_n, S_n, C_{nh} the ligand anisotropy introduces some additional terms while the remaining ones can well be described within the isotropic ligand approximation.

In conclusion the asymmetry of the ligand-polarization mechanism depends exclusively on the asymmetry of the polarizability tensor α_{L}. It suggests that for transparent ligands we obtain the contribution of symmetric character. Since in TPA case both mechanisms were shown to enhance the transition intensity up to 40% [6–8] we can expect the same contribution to ERS. Therefore the symmetry of the crystal-field and the ligand-polarization mechanisms can change considerably the asymmetry features of the electronic Raman scattering in lanthanide(III) complexes.

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