Vibronic intensities for Er^{3+} in $Cs_2NaErCl_6$

R. Acevedo and G. Navarro

Departamento de Química Básica, Faculad de Ciencias Físicas y Matemáticas, Universidad de Chile
Beauchef 850, Casilla 2777, Santiago, Chile
e-mail: lindsey@cec.uchile.cl

T. Meruane

Departamento de Química, Universidad Metropolitana de Ciencias y Eduacación
Av. José Pedro Alesandri 774, Casilla 147-C Santiago, Chile
e-mail: mmeruana@hotmail.com

P.A. Tanner and Y.Y. Zhao

Department of Biology and Chemistry, City University of Hong Kong
Tat Chee Avenue, Kowlon, Hong Kong. S.A.R.
e-mail: bhtan@cityu.edu.hk

In this current study, we have undertaken vibronic intensity calculations for the absorptions $\left|(^4I_{15/2})\Gamma_k\right\rangle \rightarrow \left|(^4I_{13/2})\Gamma_l\right\rangle$ of the Er^{3+} in the $Cs_2NaErCl_6$ elpasolite type system. This system is extremely complicated to handle from both a theoretical and an experimental viewpoints. This theoretical work shows that over an energy range of about $400\ cm^{-1}$, a substantial amount of transitions are likely to take place (about 100 transitions; twenty five of them are magnetic dipole allowed and seventy five are vibronically allowed). It is then a formidable task to identify and assign all of these transitions in a non-ambiguous way. Also the experimental evidence available for these absorptions is related to a total of about twenty lines in the luminescence spectrum of this system. The spectrum itself is very challenging and the superposition of spectral features is most likely to occur. A careful analysis of the calculated vibronic intensities and overall oscillator strengths for the various transitions indicates that the current model used is both flexible and appropriate to deal with this kind of systems. In a forthcoming paper, we will examine the rather unusual high intensity associated with the $\left|(^4I_{15/2})\Gamma_k\right\rangle \rightarrow \left|(^4S_{3/2})\Gamma_l\right\rangle$ excitations.

Keywords: Vibronic intensities; the $Cs_2NaErCl_6$ system

En este trabajo, hemos realizado cálculos de intensidades vibrónicas para las absorciones $\left|(^4I_{15/2})\Gamma_k\right\rangle \rightarrow \left|(^4I_{13/2})\Gamma_l\right\rangle$ para Er^{3+} en el sistema del tipo elpasolita $Cs_2NaErCl_6$. Este sistema es extremadamente difícil de trabajar tanto desde un punto de vista teórico como experimental. En este trabajo se demuestra que en un rango de energías del orden de $400\ cm^{-1}$, es probable que una cantidad muy significativa de transiciones ocurra (alrededor de 100; siendo 25 de ellas del tipo dipolo magnético y las otras 75 de carácter vibrónico). Es en consecuencia, una tarea formidable, el identificar y asignar todas estas transiciones en forma inequívoca. Adicionalmente, la evidencia experimental para estas absorciones se refiere a un total de 25 líneas en el espectro de luminiscencia de este sistema. El espectro es en sí mismo muy desafiante y una importante superposición de líneas espectrales es altamente probable de ser observada. Un análisis cuidadoso de las intensidades vibrónicas calculadas y de las fuerzas del oscilador para esta variedad de excitaciones nos indica que el modelo de cálculo utilizado es flexible y apropiado para trabajar con este tipo de sistemas. En un próximo artículo, examinaremos la alta intensidad , bastante poco usual, asociada con las excitaciones $\left|(^4I_{15/2})\Gamma_k\right\rangle \rightarrow \left|(^4S_{3/2})\Gamma_l\right\rangle$

Descriptores: Intensidades vibrónicas; sistema $Cs_2NaErCl_6$

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1. Introduction

The electronic spectra of lanthanide ions imbedded in cubic elpasolite type crystals [1] show magnetic dipole and/or electric quadrupole allowed transitions, together with extensive vibronic sidebands. It is well known that the three odd parity vibrational modes of the $ErCl_6^{3-}$ complex ion (ν_3, ν_4, ν_6), which are coupled to electronic transitions, correspond to the most intense features of the vibronic spectra and the lattice mode structure appears to be rather weak. There are several vibronic intensity calculations reported in the literature [1–8]. The basic assumptions involved in these schemes of calculations are as follows:

a) A seven atom system model has been adopted, *i.e.*, it is assumed that the coupling among the internal and the external vibrations is either small or negligible.

b) The hyper surfaces of potential energy associated with the terminal electronic states have roughly the same shape and are only vertically displaced to one another along the totally symmetric normal mode of vibration for the seven atom system.

c) The energy gap between the terminal non degenerate electronic states is large enough so that the crude Born-Oppenheimer approximation is to a fair degree of approximation applicable.

In passing, let us say that the Cs_2NaMX_6 type lattices belong to the space group $Fm3m(O_h^5)$ [5–7, 9–12] in which the M^{3+} ions occupy sites of perfect octahedral symmetry. The vibrational symmetry species for these crystals are as follows: $Na^{1+}(\tau_{1u})$, $Cs^{1+}(\tau_{2g}+\tau_{1u})$, $MX_6^{3-}(\alpha_{1g}+\varepsilon_g+2\tau_{1u}+\tau_{2g}+\tau_{2u})$. As we observe, in addition to the fifteen degrees of freedom of the MX_6^{3-} complex ion, classified according to the octahedral irreducible representations there exists four lattice modes according to the following symmetry species: $2\tau_{1u}$ (I.R., active), τ_{2g} (Raman active) and τ_{1g} (inactive). Lenz [9], in an outstanding paper, discussed the lattice vibrations for both the $A_3B'X_6$ and $A_2BB'X_6$ systems, in the space group $Fm3m$ and using a modified version of a valence type force field, concluded that ten force constants are needed in order to estimate all the fundamental vibrations in the $\vec{k}=\vec{0}$ approximation. In the notation put forward by Lenz, the symmetry coordinates corresponding to the unit cell are labelled as follows:

$$S_1 = S_1\left(X^{1-}\right) : \alpha_{1g},$$

$$S_2 = S_2\left(X^{1-}\right) : \epsilon_g,$$

$$S_3 = S_3\left(X^{1-}\right) : \tau_{1g},$$

$$S_4 = S_4\left(X^{1-}\right) : \tau_{2g},$$

$$S_5 = S_5\left(Cs^{1+}\right) : \tau_{2g},$$

$$S_6 = S_6\left(M^{3+}, X^{1-}, Na^{1+}\right) : \tau_{1u},$$

$$S_7 = S_7\left(M^{3+}, X^{1-}, Cs^{1+}, Na^{1+}\right) : \tau_{1u},$$

$$S_8 = S_8\left(M^{3+}, Na^{1+}\right) : \tau_{1u},$$

$$S_9 = S_9\left(M^{3+}, X^{1-}, Na^{1+}, Cs^{1+}\right) : \tau_{1u},$$

$$S_{10} = S_{10}\left(X^{1-}\right) : \tau_{2u}.$$

When this notation is adopted, it is clear that the symmetry blocks are as follows: $\alpha_{1g}(1\times 1)$, $\epsilon_g(1\times 1)$, $\tau_{1g}(1\times 1)$, $\tau_{1u}(4\times 4)$, $\tau_{2g}(2\times 2)$ and $\tau_{2u}(1\times 1)$. Thus, the odd parity symmetry coordinates (S) are related to the normal coordinates (Q), by means of the transformation: $S = LQ$, where the L matrix depends on the details of the interacting force field. Then in a matrix notation, we may write

a) the τ_{1u} symmetry block

$$\begin{pmatrix} S_{6t} \\ S_{7t} \\ S_{8t} \\ S_{9t} \end{pmatrix} = \begin{pmatrix} L_{66} & L_{67} & L_{68} & L_{69} \\ L_{76} & L_{77} & L_{78} & L_{79} \\ L_{86} & L_{87} & L_{88} & L_{89} \\ L_{96} & L_{97} & L_{98} & L_{99} \end{pmatrix} \begin{pmatrix} Q_{6t} \\ Q_{7t} \\ Q_{8t} \\ Q_{9t} \end{pmatrix},$$

b) the τ_{2u} symmetry block

$$(S_{10t}) = (L_{10,10})\,(Q_{10t}), \quad \text{for} \quad t = a, b, c.$$

It is interesting to make a few comments with regards to the transformation given above: for the τ_{1u} symmetry block, there is an obvious coupling between the internal and the external vibrations, being the extent of this mixing determined

by the details of the interacting vibrational force field. It is also to be noticed that we have not included, in this preliminary analysis of the vibronic intensities, the long range Coulombic interactions. A proper treatment of the problem is to actually solve the dynamical equation of motion [9, 12–14]; $D(\vec{k})E(\vec{k}) = E(\vec{k})\Omega^2(\vec{k})$. In this notation $\Omega^2(\vec{k})$ is a diagonal matrix whose eigenvalues are $w_{p\vec{k}}^2$ and $E(\vec{k})$, represents the matrix of the eigenvectors $e_\alpha(\mu i \mid p\vec{k})$. To build up the dynamic matrix is, by no means a trivial task, and we also need to include the long range interaction contributions to the total potential energy (Coulombic terms). The lattice sums over the direct and the reciprocal lattices are carried out, by employing the Ewald's method [15, 16]. A full discussion of the lattice dynamics as applied for the M_2XY_6 systems, for the Fm3m-space group may be found in references [13, 17, 18], where the advantages and disadvantages of the model calculations putforward are discussed in detail.

Though, it is worth mentioning that the experimental data available to undertake full lattice dynamic calculations is either limited or scarce. Only very rarely we do have a large and accurate enough database to fully test the theoretical models against the experimental data for these systems. We have, however initiated a program to undertake these kind of calculations for the elpasolite type systems and work on the pure $Cs_2NaErCl_6$, $Cs_2NaEuCl_6$ and $Cs_2NaMoCl_6$ and on the doped $Cs_2NaScCl_6{:}MoCl_6^{3-}$ are in progress in our laboratory [19]. It is well known that the set of symmetry coordinates does not represent the normal modes of vibrations for the crystal, then it is necessary to solve the dynamical equation of motion so as to have a semiquantitative idea about the actual mixing of the various symmetry coordinates belonging to the same symmetry species, and in this way to support the assignments of the various peaks in the spectra of these crystals. At first glance, the pure symmetry coordinates representing internal motion of the cluster $ErCl_6^{3-}$ are as follows: $S_1(\alpha_{1g}, \nu_1)$, $S_2(\epsilon_g, \nu_2)$, $S_4(\tau_{2g}, \nu_5)$ and $S_{10}(\tau_{2u}, \nu_6)$. The standard ν_3(stretching, τ_{1u}) and ν_4(bending, ν_6) are mixed up with the counter ion motions of the Cs^{1+} and Na^{1+} ions and therefore at this stage it does not seem convenient to adopt the usual convention $S_6(\tau_{1u}, \nu_3)$ and $S_7(\tau_{1u}, \nu_4)$, unless we have solid evidence of either small or negligible coupling between the internal $ErCl_6^{3-}$ vibrations and those of the counter ions [12, 15–19]. As we mentioned earlier, in this research work we will introduce a molecular model for the $ErCl_6^{3-}$ complex ion, and therefore will assume a negligible coupling among both the internal and the external vibrations. We can anticipate that the results to be obtained will depend critically on the assumptions adopted in the model calculation, though they will be useful for more comprehensive and sophisticated approaches regarding these complex phenomena in the solid state spectroscopy. Having discussed and pointed out the approximations upon which the seven atom model is applicable, we can mention that Richardson and co-workers [1, 4, 20–22] have applied transition vibronic coupling models to the parameterization of the relative

vibronic intensities in cubic elpasolite within the set of approximation outlined earlier on (a)–(c) in the text. In all of these calculations, the strategy followed by these authors relies upon a full parametrization model either when a vibronic crystal field-closure-ligand polarization or an extension of the superposition [15] models have been applied. It is interesting to compare results from a full parameterization scheme as done by Richardson *et al.* and some calculations put forward by Acevedo *et al.* [23] On the basis, of an extension of the superposition model due to Newman [24–27], Richardson *et al.* [4] employed a rather complex parameterization model to fit the ν_3 (stretching mode) against the experimental data for the UCl$_6^{2-}$ complex ion in the octahedral point molecular group and within the seven atom model approximation. It is observed that, in spite of the efforts of these authors, the experimental data for this system is either scarce or incomplete so that there is no sensible formalism to fit all the necessary parameters involved in such a general calculation.

Instead, in a latter attempt, Acevedo *et al.* [23], decided to carry out a generalized vibronic crystal field-with and without invoking closure approximation-ligand polarization based upon a fairly accurate database for systems such as PrCl$_6^{3-}$ and UBr$_6^{2-}$ complex ions in cubic hosts.

For these latter systems, the success of the calculated vibronic intensity distributions due to the three odd parity moiety modes was as good as expected and many interesting conclusions were obtained regarding mechanistic aspects and most likely sources for improvement.

Based upon, the accumulated experience and the need for understanding, we have chosen in this research work, the Er^{3+} ion in the Cs$_2$NaErCl$_6$ elpasolite type system for which the experiment tells us that these central metal ions occupy sites of octahedral symmetry, even at liquid helium temperature [28] and are bonded to six Cl^{1-} anions. This system is quite appropriate to perform vibronic intensity calculations, mainly because of the wealth of well-resolved transitions that it exhibits.

For this system, the energy levels have been studied extensively [22, 29–33] and the model hamiltonian for the system has been partitioned into two contributions [31]; namely H_A and H_{CF}, where the first contribution includes the isotropic atomic contributions and the second term, represents the non spherically symmetric components of the even parity crystal field (CF). Much of this work was advanced and put forward by Richardson and Reid in many outstanding research papers [3, 4, 20–22, 34–36] where they established a methodology to deal with full parameterization of energy levels for the elpasolite and other related systems.

The complexity of the optimization procedure to minimize the mean error deviation and also to attach some physical meaning to these many parameters is still open for discussion and deserves the attention of future research in this field. It is indeed interesting to examine the optimized parameter values for a series of lanthanide type systems [31]. It can be concluded that the derived values for the crystal field parameters are rather sensitive to the number of energy levels employed

in the fitting procedure. It is then clear, that since the database is either scarce or incomplete then in most cases this prevents us to make a reliable analysis and the inclusion of new additional parameters such as the spin-correlated crystal field (SCCF) or other configuration interaction may become necessary. Also, for a number of crystals it is seen that the standard deviations range from 0 cm^{-1} up to 43 cm^{-1}, also depending upon the number of energy levels available.

The expected ordering of the energy levels is reproduced fairly well, except for the spectroscopic terms like $\left[v^{2S+1}L_J\right]$ with higher J-values. There are also other conclusions which may be drawn from this type of analysis, however it does seem to us that the answer does not sit on the inclusion of more fitting parameters in the electronic hamiltonian for these systems. We, have instead chosen an alternative approach which consists in including a minimum set of parameters to be fitted from experiment and to focus our attention upon those factors which are most likely to play a major role upon the mechanistic aspects regarding the observed spectral intensities and the main sources from which the intensity is derived from. We feel that there is a long way to go and full lattice dynamic calculations should be prompted to analyze the various electronic and vibrational factors, which influence most greatly the intensities. We also need to create new physical models to undertake full lattice dynamic calculations for these and related systems, bearing in mind that we will always lack enough experimental data. It is essential to elaborate some new models to include both the short and the long range interaction terms in the dynamic matrix $D(\vec{k})$. Our models should be more transparent and include some additional constraints with specific physical meaning so as to be able to advance the state of the art in this complex area of the solid state physics. With regards to the Er^{3+} ion in the Cs$_2$NaErCl$_6$ system, the full parameterization approach of Richardson, Reid *et al.* [3, 4, 20–22, 33–35] give rise to a set of energy levels accurately determined up to about 26 500 cm^{-1}, and the use of this set of wavefunctions has given sensible answers for the magnetic dipole intensities in the spectrum of this system. There is an interesting issue that could make this study attractive. It is known that this compound exhibits unusual optical properties, being the first stoichionmetric upconverter to be reported [32, 37–39]. Additional experimental data is also available from spin-lattice relaxation rates measurements [40].

In this research paper, we will study the absorptions $\left|^4I_{15/2}\Gamma_k\right\rangle \rightarrow \left|^4I_{13/2}\Gamma_l\right\rangle$, which in cubic environments are parity forbidden but vibronically allowed. There is also detailed experimental data on the $\left|^4I_{15/2}\Gamma_n\right\rangle \rightarrow \left|^4S_{3/2}\Gamma_m\right\rangle$ in both Cs$_2$NaErCl$_6$ and Cs$_2$LiErCl$_6$ at temperatures down 10 K. A detailed theoretical study is in due course in our laboratory, so as to gain understanding in the mechanistic aspects which rules the physics behind radiative transitions.

We will discuss on the basis of our model calculation, the various possible sources of disagreement between previous experimental studies and our current theoretical predictions.

At a first glance, we may argue that several assigned peaks of the spectrum might correspond to a superposition of several transitions allowed via both a magnetic dipole and a vibronic mechanisms. A careful and detail analysis will be carried out in order to test our models against the latest experimental data and the proposed experimental assignments for the various lines.

2. Method of calculations

The theory of the vibronic coupling is undeergoing a careful review, since a substantial amount of very accurate database , with different pure and doped crystals, and measurements from infrared, luminiscence and Raman spectroscopies has become available at different temperatures. The inherent complexity of these systems is indeed recognized and many research groups are engaged in different projects with reference to these materials, which exhibit both academic and applied interest. In this section, we will put forward the model calculation so as to focus the reader attention upon those points, which need more hard work to improve the many approximations involved. Judd [41] and Olfet [42] developed a systematic calculation method to rationalize on a semi quantitative basis the obseved spectral intensities essentially in non centrosymmetric coordination compounds of the rare earths. Their approach was mainly devoted to the static (crystal field) contribution to the transition dipole moment. The mechanistic aspects are such that $f \to f$ electronic transitions acquire intensity from either $f \to d$ or $f \to g$, or both excitations through the odd parity components of the crystal field potential. This assumption is generalized with reference to centro-symmetric coordination compounds, where the $f \to f$ transitions acquire spectral intensity by borrowing it from $f \to d$ or $f \to g$, or both transitions with the explicit cooperation of the odd parity normal modes of vibration of the system. As for centrosymmetric sytems, it is observed that it is essential to obtain the best possible description for the normal modes of vibrations of the system. As for the $Cs_2NaErCl_6$ crystal in the Fm3m-space group, the nuclei ions vibrate according to the following irreducible representations in the factor group O_h:$Na^{1+}(\tau_{1u})$, $Cs^{1+}(\tau_{2g} + \tau_{1u})$ and $ErCl_6^{3-}(\alpha_{1g} + \varepsilon_g + 2\tau_{1u} + \tau_{2g} + \tau_{2u})$. Thus, at first glance there is a coupling among the $\tau_{1u}(4 \times 4)$ and the $\tau_{2g}(2 \times 2)$, vibrational modes for the lattice.

A proper description of the vibrational behavior for this system requires the inclusion of the short and long range interactions to build up the dynamical matrix $D(\vec{k})$ and to attempt to solve the set of dynamic equations

$$D(\vec{k})E(\vec{k}) = E(\vec{k})\Omega^2(\vec{k}) \qquad (1)$$

where $\Omega^2(\vec{k})$ is the diagonal matrix of the eigenvalues w_{pk}^2

and $E(\vec{k})$ is the matrix of the eigenvectors $e_\alpha(\mu i \mid p\vec{k})$. The Fourier transformed matrix $D(\vec{k})$, with elements $D_{\alpha\beta}\begin{pmatrix} \mu & i \\ \nu & j \end{pmatrix}\vec{k}$ is of dimension $3ZN \times 3ZN$ and it is called the dynamic matrix. This matrix has the following properties: (a) $D(\vec{k})^* = D(-\vec{k})$ and (b) $D(\vec{k})^+ = D(\vec{k})$. A complete discussion of the dynamic matrix and its properties is found in Ref. 17 and 43.

As for the symmetry coordinates are concerned, a pictorial representation of them is given in the magnificent paper by Lenz [10]. Much effort has been placed upon the normal modes of vibrations of the free octahedral anionic groups $LnCl_6^{3-}$. It is indeed a major task to deal, in detail with remaining lattice vibrations of the cations Cs^{1+} and Na^{1+} and their coupling to the internal vibrations of the $LnCl_6^{3-}$ complex ion. There is great interest for the specific influences of these counter ions with regard to all the force constants between all atoms in the unit cell with respect to symmetry and coordination. In this research work, we will assume a seven atom system to model the observed overall and vibronic intensity distributions associated with a manifold of absorptions with reference to the $ErCl_6^{3-}$ in the $Cs_2NaErCl_6$ elpasolite type system. Although the model adopted throughout this calculation is approximate, we will show that it has some utility and flexibility and could be improved, adding the long and the short range interactions to the dynamical matrix, as well as some major improvements in the description of the interacting vibrational force field.

Next and within the independent system model (ISM), the total transition dipole moment may be written as a sum of two contributions, as given below

$$\vec{\mu}_{1\to2}^{Total,\alpha} = \vec{\mu}_{1\to2}^{CF,\alpha} + \vec{\mu}_{1\to2}^{LP,\alpha} ; \qquad (2)$$

where $\alpha = X, Y, Z$. Both the zero-th order eigenvalues and eigenvectors are obtained by solving the general equation, in the group-subgroup chain $SO_3 \supset O_h$

$$\hat{H}^{(0)} = \hat{H}_{eff} + \hat{H}_{e-e} + \hat{H}_{s-o} + V(O_h). \qquad (3)$$

The next step is to assume that the system is stable along all polarization directions for each and all the nuclei ions for the overall system $(\vec{Q} = \vec{Q}^{(0)})$, and therefore to a first order approximation, we write the model hamiltonian for the system as follows [7, 8, 23, 44, 45]:

$$\hat{H}' = \hat{H}^{(0)} + \hat{H}^{(1)}, \quad \hat{H}^{(1)} = \sum_{\Gamma,\gamma,i} \left[\frac{\delta V}{\delta S_\gamma^\Gamma(i)}\right]_{Q=Q_0} S_\gamma^\Gamma(i); \quad (4)$$

where $V = V_{CF} + V_{LP}$. It is straightforward to write the following two identities in order to take into account the first order correction due to both the crystal field and the ligand polarization schemes [10, 13, 23]

$$V_{CF}^{(1)} = \sum_L Z_L e \sum_{\nu_t} \sum_{\Gamma,\gamma} \sum_{i,\tau} \left\{\frac{\delta G_{\Gamma,\gamma}^{CF,L}(i,\tau)}{\delta Q_{\nu_t}}\right\} M_\gamma^\Gamma(i,\tau)Q_{\nu_t}, \qquad (5)$$

and also

$$V_{LP}^{(1)} = \sum_L \sum_{\nu_t} \sum_{\Gamma,\gamma} \sum_{i,\tau} \sum_\alpha \left\{ \frac{\delta G_{\Gamma,\gamma}^{LP,L}(i,\tau)}{\delta Q_{\nu_t}} \right\} M_\gamma^\Gamma(i,\tau) \mu^\alpha(L) Q_{\nu_t}, \tag{6}$$

where Q_{ν_t} represents the normal mode of vibration, transforming according to the irreducible representation Γ_t in the octahedral point molecular group. In the above notation, the index "i" stands for the rank of the central metal ion's multipoles, τ is a repeated representation label, M_γ^Γ stands for the symmetry adapted multipoles, transforming according to the γ-th component of the irreducible representation Γ and $\mu^\alpha(L)$ represents the α-th vector component of the ligand transient induced dipoles by the radiation field. The symmetry adapted geometric factor and the normal coordinates are represented by $G_{\Gamma,\gamma}^{K,L}$ (K=CF or LP) and Q_{ν_t}, respectively [10, 13, 23]. Next, we will introduce the crystal field (closure) and the ligand polarization contributions to the total transition dipole moments.

2.1. Vibronic crystal field contribution to the total transition dipole moment

The crystal field contribution to the overall transition dipole moment associated with the excitation $|1\rangle \rightarrow |2\rangle$, will be introduced within the well known closure approximation, widely employed in both atomic and molecular spectroscopy. This approximation lies on the assumption that all and each of the intermediate central metal's electronic states form a biorthonormal and complete set of wavefunctions at the same energy. This is indeed a rather crude approximation, which should be handled with care [8]. There are several drawbacks to this approximation:

$$\langle 1| U_{\nu_m}^{CF,\alpha} |2\rangle = \sum_\Gamma \sum_k C_k^{CF} (-1)^{\Gamma_1 + \gamma_1^+} V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1^+ & \gamma_2 & \gamma \end{pmatrix} \langle (LSJ)\Gamma_1| O_{\nu_t}^\Gamma(k,\tau) |(L'SJ')\Gamma_2\rangle A_{\nu_t}^{\Gamma\gamma}(k-1,\tau) \tag{8}$$

Also

$$A_{\nu_t}^{\Gamma\gamma}(i,\tau) = \sum_L \left\{ \frac{\delta G_{\Gamma\gamma}^{CF,L}(i,\tau)}{\delta S_{\nu_t}} \right\}_0, \quad C_k^{CF} = \frac{2e}{\Delta E} \langle \gamma_k \rangle, \tag{9}$$

where $\langle \gamma_k \rangle = e^2 \langle r^k \rangle / R_0^{k+1}$. Full tabulation of the above quantities (7)–(9), may be obtained upon request to R.A.

2.2. Vibronic ligand polarization contributions to the total transition dipole moments

The α-th component of the ligand polarization electric dipole moment associated with the $|1\rangle \rightarrow |2\rangle$, electronic transition

a) When the crystal field contribution to the total transition dipole moment is evaluated for some selected excitations in perfect tetrahedral environments [46, 47], it vanish identically. This failure of the closure approximation is lifted when the explicit nature of some selected central metal's wavefunctions is included. Nevertheless, if one needs to use closure anyway we will be able to explain how some of the observed spectral intensity involve higher order approximation (second order).

b) In the two photon spectroscopy, has also shown to be inadequate. A direct calcualtion carried out by Tanner and Chua [48], regarding the $|(^7F_0)A_{1g}\rangle \rightarrow |(^5D_0)A_{1g}\rangle$ two photon transition of Sm^{3+} in SrF_2, also showed that the use of closure was inappropriate [49].

Bearing in mind that closure is likely to introduce several sources of errors which should be lifted, by including at least a truncated set of intermediate electronic states for the central metal's ion, we have worked out a fairly general expression to evaluate the crystal field contribution to the overall electronic transition dipole moment. Thus, we may write the identity [8, 10, 11, 23, 44–47].

$$\mu_{1\rightarrow2}^{CF,\alpha}(\nu_t) = \sum_m \langle 1| U_{\nu_m}^{CF,\alpha} |2\rangle L_{mt} \langle 0| Q_{\nu_t} |1\rangle, \tag{7}$$

where

is written as given by Eq. (7), where CF must be replaced by LP for the sake of completeness. Do observe that the transition dipole moment is referred to the excitation $\Gamma_1 \rightarrow \Gamma_2 + \nu_t$. Next, we define the ligand polarization vibronic coupling constants as follows

$$B_{\overline{\Gamma}\overline{\gamma}}^{\Gamma\gamma,\alpha}(k,t) = \sum_L \left\{ \frac{\delta G_{\Gamma\gamma,\alpha}^{LP,L}(k)}{\delta S_{\overline{\gamma}}^{\overline{\Gamma}}(t)} \right\}_0, \tag{10}$$

and it is straightforward to show that the ligand polarization electronic factors, associated with the $\Gamma_1 \rightarrow \Gamma_2 + \nu_t$ transition may be written as follows

$$U_{\nu_t}^{LP,\alpha} = \sum_L \sum_k C_k^{LP} (-1)^{\Gamma_1 + \gamma_1^+} V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1^+ & \gamma_2 & \gamma \end{pmatrix} \langle (LSJ)\Gamma_1 \| M_{\nu_t}^\Gamma(k) \| (L'SJ')\Gamma_2\rangle B_{\nu_t}^{\Gamma\gamma,\alpha}(k,t) \tag{11}$$

where: $C_k^{LP} = (\alpha_L \langle r^k \rangle / R_0^{k+3})e$. Full tabulations of the above quantities (10) and (11), may be obtained upon request to R.A.

TABLE I. Eigenvectors and eigenvalues for the Er^{3+} free ion (in cm^{-1}).

eigenvector		eigenvalue
$|^4I_{15/2}\rangle$	$0.958|^4I\rangle + 0.173|^2K\rangle + 0.019|^2L\rangle + \ldots$	0
$|^4I_{13/2}\rangle$	$0.994|^4I\rangle + 0.097|^2K\rangle - 0.045|^2I\rangle + \ldots$	6 474
$|^4I_{11/2}\rangle$	$0.910|^4I\rangle + 0.110|^4G\rangle + 0.120|^2H^{(1)}\rangle - 0.383|^2H^{(2)}\rangle + \ldots$	10 000
$|^4I_{9/2}\rangle$	$0.676|^4I\rangle + 0.076|^4G\rangle + 0.456|^4F\rangle - 0.272|^2G^{(1)}\rangle + 0.235|^2G^{(2)}\rangle + 0.188|^2H^{(1)}\rangle - 0.407|^2H^{(2)}\rangle + \ldots$	12 264
$|^4F_{9/2}\rangle$	$-0.581|^4I\rangle + 0.002|^4G\rangle + 0.742|^4F\rangle - 0.0232|^2G^{(1)}\rangle + 0.204|^2G^{(2)}\rangle - 0.032|^2H^{(1)}\rangle + 0.125|^2H^{(2)}\rangle + \ldots$	15 015
$|^4S_{3/2}\rangle$	$0.913|^4S\rangle + 0.041|^4D\rangle + 0.123|^4F\rangle + 0.366|^2P\rangle - 0.119|^2D^{(1)}\rangle + 0.041|^2D^{(2)}\rangle + \ldots$	18 208

TABLE II. Wavefunctions and eigenvectors [in units of (γ_4)].

	$|^4I_{15/2}\Gamma_6\rangle =$	$|^4I_{15/2}\Gamma_6\rangle$	$E = +0.348$
	$|^4I_{15/2}\Gamma_7\rangle =$	$|^4I_{15/2}\Gamma_7\rangle$	$E = +0.014$
$J = \dfrac{15}{2}$	$|^4I_{15/2},^a\Gamma_8\rangle =$	$0.982|^a\Gamma_8\rangle + 0.175|^c\Gamma_8\rangle$	$E = +0.304$
	$|^4I_{15/2},^b\Gamma_8\rangle =$	$0.868|^b\Gamma_8\rangle - 0.496|^c\Gamma_8\rangle$	$E = -0.145$
	$|^4I_{15/2},^c\Gamma_8\rangle =$	$-0.190|^a\Gamma_8\rangle + 0.491|^b\Gamma_8\rangle + 0.852|^c\Gamma_8\rangle$	$E = -0.442$
	$|^4I_{13/2}\Gamma_6\rangle =$	$|^4I_{13/2}\Gamma_6\rangle$	$E = -0.239$
	$|^4I_{13/2},^a\Gamma_7\rangle =$	$0.856|^a\Gamma_7\rangle + 0.516|^b\Gamma_7\rangle$	$E = +0.124$
$J = \dfrac{13}{2}$	$|^4I_{13/2},^b\Gamma_7\rangle =$	$-0.516|^a\Gamma_7\rangle + 0.856|^b\Gamma_7\rangle$	$E = -0.042$
	$|^4I_{13/2},^a\Gamma_8\rangle =$	$0.930|^a\Gamma_8\rangle + 0.367|^b\Gamma_8\rangle$	$E = +0.216$
	$|^4I_{13/2},^b\Gamma_8\rangle =$	$-0.367|^a\Gamma_8\rangle + 0.930|^b\Gamma_8\rangle$	$E = -0.133$
	$|^4I_{11/2}\Gamma_6\rangle =$	$0.910|^4I_{11/2}\Gamma_6\rangle - 0.380|^2H^{(2)}_{11/2},\Gamma_6\rangle$	$E = -0.211$
	$|^4I_{11/2}\Gamma_7\rangle =$	$0.910|^4I_{11/2}\Gamma_7\rangle - 0.380|^2H^{(2)}_{11/2},\Gamma_7\rangle$	$E = -0.110$
$J = \dfrac{11}{2}$	$|^4I_{11/2},^a\Gamma_8\rangle =$	$0.905|^4I_{11/2},^a\Gamma_8\rangle - 0.377|^2H^{(2)}_{11/2},^a\Gamma_8\rangle$	$E = -0.150$
	$|^4I_{11/2},^b\Gamma_8\rangle =$	$0.905|^4I_{11/2},^b\Gamma_8\rangle + 0.377|^2H^{(2)}_{11/2},^b\Gamma_8\rangle$	$E = +0.205$

3. Results and applications

A trial set of wavefunctions has been obtained for the free ion, using the parameter values reported by Richardson et al. [30]. These are as follows:

$$F^2 = 97\,295, \quad F^4 = 69\,361, \quad F^6 = 48\,588, \quad \text{and} \quad \xi_{so} = 2\,362,$$

where all the values are given in cm^{-1}. According to the above given values, the lowest lying energy levels are shown in Table I.

As for the vibronic intensity calculation the following database has been utilized with $R_0 = 2.70 \times 10^{-8}$ cm^{-1}, and the radial expectation values $(r^2)_{ff} = 0.233 \times 10^{-16}$ cm^2, $(r^4)_{ff} = 0.1527 \times 10^{-32}$ cm^4, $(r^6)_{ff} = 0.2301 \times 10^{-48}$ cm^6.

For the quantity $(\gamma_4) = e^2(r^2)_{ff}/R_0^{k+1}$, and it follows $[(\gamma_4)/(\gamma_6)] = (r^4)_{ff}/(r^6)_{ff}(R_0^2) = 4.84$ (calculated ratio, using free ion wavefunctions).

The crystal field energy levels are evaluated using the manifold $|(vLJ)J\rangle$. It is seen that the interactions among wavefunctions having different J-values, when the $V(O_h)$ is the connecting operator are very small indeed. Calculated wavefunctions and energies in units of (γ_4) are displayed in Table II.

4. Discussion

The results displayed in Tables I, II, III, and IV are as good as could be expected for such a complex system. It is seen

TABLE III. Overall and vibronic intensity distributions for the $|^4I_{15/2}\Gamma_i\rangle \rightarrow |^4I_{13/2}\Gamma_j\rangle$ absorptions. Database for the General Valence Force Field (GVFF): $L_{33} = -0.197765$, $L_{34} = 0.032448$, $L_{43} = 0.166329$, $L_{44} = 0.276727$ and $L_{66} = 0.23751$.

odd parity vibrational frequencies (in cm^{-1})	Oscillator strenghts for each vibronic origin; where $U_k = U_k^{CF} + U_k^{LP}$, $\Delta E_{i,j}^{\nu t} = [E(\Gamma_i) - E(\Gamma_j)] + E(\nu_t)$ and $t = 3, 4, 6$
$\nu_3 = 268$	$f(\nu_3) = 6.812.10^{-7}(\Delta E_{i,j}^{\nu_3})(U_3L_{33} + U_4L_{43})^2$
$\nu_4 = 116$	$f(\nu_4) = 1.578.10^{-6}(\Delta E_{i,j}^{\nu_4})(U_3L_{34} + U_4L_{44})^2$
$\nu_6 = 86$	$f(\nu_6) = 2.122.10^{-6}(\Delta E_{i,j}^{\nu_6})(U_6L_{66})^2$

TABLE IV. Relative vibronic intensity distributions and overall oscillator strengths for some selected vibronic transitions.

Electronic transition	$f(\nu_3) : f(\nu_4) : f(\nu_6)$	$f \times 10^9$
$\Gamma_6(15/2) \rightarrow \Gamma_6(13/2)$	0.50 : 0.80 : 1.00	0.03
$\Gamma_6(15/2) \rightarrow {}^b\Gamma_8(13/2)$	3.20 : 1.00 : 0.50	1.07
$\Gamma_6(15/2) \rightarrow {}^b\Gamma_7(13/2)$	5.40 : 1.00 : 0.01	0.08
$\Gamma_6(15/2) \rightarrow {}^a\Gamma_7(13/2)$	1.00 : 0.02 : 1.30	3.71
$\Gamma_6(15/2) \rightarrow {}^a\Gamma_8(13/2)$	4.44 : 1.00 : 0.00	0.30
${}^a\Gamma_8(15/2) \rightarrow \Gamma_6(13/2)$	1.00 : 8.10 : 0.20	1.26
${}^a\Gamma_8(15/2) \rightarrow {}^b\Gamma_8(13/2)$	9.80 : 1.00 : 0.20	1.11
${}^a\Gamma_8(15/2) \rightarrow {}^b\Gamma_7(13/2)$	1.00 : 0.04 : 1.30	2.88
${}^a\Gamma_8(15/2) \rightarrow {}^a\Gamma_7(13/2)$	1.00 : 0.06 : 0.30	1.31
${}^a\Gamma_8(15/2) \rightarrow {}^a\Gamma_8(13/2)$	1.00 : 0.08 : 0.00	6.25
$\Gamma_7(15/2) \rightarrow \Gamma_6(13/2)$	1.00 : 0.01 : 0.01	0.16
$\Gamma_7(15/2) \rightarrow {}^b\Gamma_8(13/2)$	1.00 : 1.00 : 0.80	2.07
$\Gamma_7(15/2) \rightarrow {}^b\Gamma_7(13/2)$	0.01 : 1.00 : 0.01	0.05
$\Gamma_7(15/2) \rightarrow {}^a\Gamma_7(13/2)$	1.00 : 2.40 : 1.50	0.01
$\Gamma_7(15/2) \rightarrow {}^a\Gamma_8(13/2)$	7.50 : 0.00 : 1.00	4.10
${}^b\Gamma_8(15/2) \rightarrow \Gamma_6(13/2)$	2.20 : 1.10 : 0.30	4.11
${}^b\Gamma_8(15/2) \rightarrow {}^b\Gamma_8(13/2)$	1.00 : 0.00 : 0.00	1.80
${}^b\Gamma_8(15/2) \rightarrow {}^b\Gamma_7(13/2)$	1.00 : 0.01 : 0.70	2.41
${}^b\Gamma_8(15/2) \rightarrow {}^a\Gamma_7(13/2)$	1.00 : 2.70 : 0.05	0.09
${}^b\Gamma_8(15/2) \rightarrow {}^a\Gamma_8(13/2)$	0.10 : 1.00 : 2.40	3.41
${}^c\Gamma_8(15/2) \rightarrow \Gamma_6(13/2)$	1.00 : 0.07 : 0.09	2.19
${}^c\Gamma_8(15/2) \rightarrow {}^b\Gamma_8(13/2)$	0.03 : 1.00 : 1.90	1.90
${}^c\Gamma_8(15/2) \rightarrow {}^b\Gamma_7(13/2)$	3.90 : 0.09 : 1.00	4.64
${}^c\Gamma_8(15/2) \rightarrow {}^a\Gamma_7(13/2)$	1.00 : 0.10 : 14.00	2.56
${}^c\Gamma_8(15/2) \rightarrow {}^a\Gamma_8(13/2)$	0.60 : 1.00 : 1.50	0.91

that both the overall oscillator strengths and relative vibronic intensity distributions follow the right pattern, and to a first degree of approximation reproduce nicely the experimental data on these systems. Thus, the model utilized has proved to be both flexible and useful to gain understanding in these complex radiative excitations involving $f \rightarrow f$ electronic transitions in highly relativistic systems. Both the relative vibronic intensity distribution and the overall values for the various oscillator strengths are fairly reproduced and modeled by this simple model calculation. There are, though several ways to improve the quality of our results and and work on the elpasolite type systems is in progress in our laboratory. It is essential to take into account, as we saw in the introduction of this paper, the coupling between the internal and the external vibrations. We also need to improve our knowledge of the line shapes for these vibronically allowed electronic transitions and to advance the state of the art, for the shape of the hyper surfaces of the potential energy functions corresponding to the terminal electronic states, involved in the excitations. A further test of the vibronic model employed in this article, may be carried out by evaluating the spectral intensities associated with the $|(^4S_{3/2})\Gamma_k\rangle \leftarrow |(^4I_{15/2})\Gamma_l\rangle$ in both, the Cs$_2$NaErCl$_6$ and Cs$_2$LiErCl$_6$ elpasolites at temperatures down to 10 K. This is indeed a formidable and challenging problem, since for this excitation $\Delta J = 6$, and the expected oscillator strength is about 10^{-11}–10^{-12}, however the experimental evidence tell us that these excitations are very strong indeed. For these excitations, we have explored a radiative cascades so as to account for the unexpected observed spectral intensities. The mechanistic aspects will be commu-

nicated in a forthcoming publication on the Cs$_2$NaErCl$_6$ system. A full discussion can be found in Ref. 23, regarding the advantages and disadvantages of our model calculation when compared with fully parametrized calculations, performed by Richardson et al. [2–4] and also when the superposition model is adopted [2–4, 23, 26, 27] with reference to these type of complex ions in pure and doped elpasolite systems.

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