Vibronic intensities in centrosymmetric lanthanide complex ions. I.

A combined crystal field-ligand polarisation approach

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Summary. A theoretical model to calculate the vibronic intensities induced by the odd vibrational modes in centrosymmetric lanthanide complexes is developed and applied to octahedral complex ions, LnX_6^{3-}, such as occur in the hexachloroelpasolites $Cs_2NaLnCl_6$. Both the crystal field and the ligand polarisation contributions are evaluated using a standard set of symmetry coordinates. For the crystal field term a truncated expansion of the intermediates states is employed rather than the more conventional closure approximation. Special care is necessary to ensure that the phases of the contributions are correctly determined since the cross-term between the ligand polarisation and crystal field contributions is signed. General equations applicable to any f^n complex ion are derived and an example of their application to the $PrCl_6^{3-}$ ion is given The agreement with experiment is satisfactory.

1 Introduction

The intensities of $f \rightarrow f$ electronic transitions of the lanthanide ions are usually treated in terms of the Judd–Ofelt procedure [1, 2]. Hundreds of applications of this method have been published over the last thirty years. The procedure is general, although approximate, for cylindrically symmetric ligands within the independent systems model. Using this approach it is irrelevant, for the extraction of parameters from experimental intensity data, whether the intensity is derived from a static non-centrosymmetric ligand field or from odd parity vibrations of the environment of the metal ion. The parameterisation scheme employed was not intended to and cannot treat the intensities of individual vibronic origins associated with specific normal modes of the complex ion. In recent years a substantial

body of experimental data on the intensities of vibronic origins in the electronic spectra of octahedral complexes of the type LnX_6^{3-} which occur in the cubic hexahaloelpasolites, $Cs_2NaLnCl_6$, has been obtained, although most of it is at best semi-quantitative [3–7]. The relative intensities are observed to vary over several orders of magnitude from one electronic transition to another observed in the same crystal. It is therefore necessary to extend the Judd–Ofelt procedure to deal with this additional data and to attempt to understand and interpret the relative intensities of the vibronic origins.

It is now recognised that, in addition to the conventional crystal field intensity mechanism which mixes d or g atomic orbitals into the f orbitals under the non-centrosymmetric perturbation, it is necessary to include the dynamic coupling of the transition multipoles of the metal and the ligands [8–11]. To avoid confusion of this terminology with Herzberg–Teller vibronic coupling we refer to this contribution to the transition dipole as the "ligand polarisation" term. This concept has played a major rôle in the understanding of the Judd $T^{(2)}$ parameter and the mechanism of hypersensitivity [1, 9].

It is possible to parameterise the vibronic intensities [11–13] but the number of parameters is large and only rarely will their be sufficient experimental data for their values to be determined reliably. This will be especially difficult if the crystal field states are not derived from a preponderant Russell-Saunders term. The interpretation of the values of the derived parameters will then be uncertain.

In this series of papers we shall develop an alternative approach, the calculation of relative vibronic intensities for the vibronic origins of specific transitions between crystal field states based on simple, but well-defined, models and their testing against the experimental data. Our methods are similar to those developed by us to account for the relative vibronic intensities of the vibronic origins in the electronic spectra of transition metal compounds [14, 15 and references therein], but the extra complexity of the f^n configuration requires a more formal approach. In our treatment of the crystal field contribution for d^n systems we considered two ways of handling the sums over the intermediate states. The usual approach is to employ closure over a complete set of intermediate states to simplify the evaluation of the matrix elements, in this case the source of the intensity is unclear (indeed irrelevant for the relative intensity in the crystal field limit). An alternative treatment is to assume a single suitably chosen intermediate state (which we have termed the Liehr-Ballhausen approach after the pioneering work by those authors [16, 17]). An advantage of the latter method (apart from its conceptual explicitness) is that, for certain transitions, the relative intensity of the vibronic origins becomes independent of the metal ion radial functions (and other parameter values). Both methods are capable of accounting for the observed vibronic intensities for several electronic transitions but the model parameters are not identical in the two procedures. The Judd–Ofelt procedure relies on closure for the extraction of parameters but Judd uses both a single $f \rightarrow d$ transition and the sum of an $f \rightarrow d$ transition and an $f \rightarrow g$ transition as the intensity source to estimate parameter values.

Our experimental data is derived from the electronic spectra of the $Cs_2NaLnCl_6$ compounds where the $LnCl_6^{3-}$ ions occupy octahedral or nearly octahedral sites. These spectra consist (subject to selection rules) of relatively sharp magnetic dipole pure electronic origins and broader electric dipole vibronic origins corresponding to the three odd vibrational modes V_i ($i = 3, 4$ and 6) of the anions. The latter are coupled to lattice vibrations, particularly to the sodium ion motion, but this coupling is not included in our model at present.

The only previous detailed theoretical study on these vibronic intensities was by Richardson et al. [18]. Unfortunately the model was developed using an incorrect assignment of the vibrational modes and when this was corrected the agreement with experiment was not good [3, 7, 12, 13]. The method of calculation was also very different in that numerical differentiation of the potential field was used to calculate the vibronic interaction rather than the exact algebraic method that we adopt.

In this paper we present a method for the calculation of the vibronic intensity distribution for specific electronic transitions in $LnCl_6^{3-}$ complex ions and provide an explicit example in Sect. 4. However, the method may be readily extended to other lanthanide complexes.

2 Vibronic model

To the first order in the nuclear Cartesian displacement, the Hamiltonian for the $LnCl_6^{3-}$ ion may be written as

$$\mathscr{H} = \sum_i h_i^{\text{eff}} + \sum_{i>j} \left\{ \frac{e^2}{r_{ij}} \right\} + \sum_i \xi_{so}(l_i \cdot s_i) + V(O_h) + \sum_{kt} \left\{ \frac{\delta V(O_h)}{\delta S_{kt}} \right\}_0 S_{kt} \cdots \quad (1)$$

The first three terms represent the free ion Hamiltonian, $V(O_h)$ is the coulombic potential due to the ligands at the static reference geometry, octahedral in our discussion. The symmetry coordinates S_{kt} are linear combinations of the internal coordinates which transform according to the irreducible representations of the O_h point group and can be derived from the internal coordinates s_a by the transformation $S = Us$ where U is unitary. The internal coordinates are related to the complete set of Cartesian nuclear displacement coordinates as $s = BR$. B is, in general, not square, and this causes some technical difficulties [14]. Thus $R = (UB)^{-1}S$ where UB is not unitary [14]. Later we shall need to distribute the vibronic intensity amongst the true vibrational coordinates, the normal modes Q_{st} using the matrix transformation $S = LQ$. The required L matrix is found by solving the nuclear equations of motion $GFL = LA$ [14]. F is the force constant matrix which may be taken as defining the force field of the molecular system, A is the diagonal matrix containing the vibrational frequencies and G contains the atomic masses and geometric information. For our purposes Eq. (1) may be written as

$$\mathscr{H} = \mathscr{H}^{(0)} + \sum_{kt} \left\{ \frac{\delta V(O_h)}{\delta S_{kt}} \right\}_0 S_{kt}. \quad (2)$$

Here the zeroth-order Hamiltonian appropriate for calculations within the f^n configuration may be parameterised by fitting a sufficient set of experimental energy levels to a full free-ion/crystal field calculation. This will give the required interelectron repulsion, crystal field and spin-orbit parameters. Since, in many cases, the position of a rather large number of energy levels may be studied with a degree of accuracy (typically 0.01%) incompatible with both the use of a pure metal ion configuration and with the independent systems model, it has become common to introduce other parameters to "improve the fit". The physical interpretation of these parameters is not always transparent.

Within the independent systems model, the interaction between the metal (M) and ligand sybsystems (L) may be described by a coulombic potential. Following

Carlson and Rushbrook [19] this may be written as

$$V(O_h) = \sum_L \sum_{k_1 q_1} \sum_{k_2 q_2} \mathcal{T}_{-(q_1+q_2)}^{(k_1+k_2)}(R_L, \Theta_L, \Phi_L) D_{q_1}^{k_1}(M) D_{q_2}^{k_2}(L), \tag{3}$$

where $\mathcal{T}_{-(q_1+q_2)}^{(k_1+k_2)}(R_L, \Theta_L, \Phi_L)$ is a tensor describing the spatial arrangement of the charge distributions due to the metal and ligands. It has become usual to refer to the $k_2 = 0$ contribution as the crystal field component and the $k_2 = 1$ contribution as the ligand polarisation component and to truncate the expansion at this point. The physical bases of these labels and procedures have been described previously [14].

The perturbation in [2] may be then written as the sum of two contributions [14, 20]:

$$\mathcal{H}_{CF}^{(1)} = -\sum_L Z_L e(\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} D_{q_1}^{k_1}(M) \{ V_L \mathcal{G}_{k_1 q_1}^{CF}(L) \}_0, \tag{4}$$

$$\mathcal{H}_{LP}^{(1)} = \sum_L (\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} D_{q_1}^{k_1}(M) \sum_{\alpha=X,Y,Z} \{ V_L \mathcal{G}_{k_1 q_1, \alpha}^{LP}(L) \}_0 \mu_L^{\alpha}, \tag{5}$$

where the $(\vec{s}_L - \vec{s}_M)$ are the nuclear cartesian displacement coordinates of the L-th ligand with respect to the metal ion. The crystal field $\mathcal{G}_{k_1 q_1}^{CF}(L)$ and ligand polarisation $\mathcal{G}_{k_1 q_1, \alpha}^{LP}(L)$ geometric factors have been tabulated previously in [8] and references therein. Thus the total electric dipole transition moment will be the sum of two contributions which are independent in the first order.

For calculations on highly symmetric ions it is convenient to write Eqs. (4) and (5) in symmetry-adapted from [14, 20].

$$\mathcal{H}_{CF}^{(1)} = -\sum_L Z_L e \sum_{kt} \sum_{\Gamma \gamma i} \sum_{\tau} \left\{ \frac{\delta \mathcal{G}_{\Gamma \gamma}^{CF,L}(i,\tau)}{\delta S_{kt}} \right\}_0 M_{\gamma}^{\Gamma}(i,\tau) S_{kt}, \tag{6}$$

$$\mathcal{H}_{LP}^{(1)} = \sum_L \sum_{\alpha} \sum_{kt} \sum_{\Gamma \gamma i} \sum_{\tau} \left\{ \frac{\delta \mathcal{G}_{\Gamma \gamma, \alpha}^{LP,L}(i,\tau)}{\delta S_{kt}} \right\}_0 M_{\gamma}^{\Gamma}(i,\tau) \mu^{\alpha}(L) S_{kt}, \tag{7}$$

where i is the rank of the central metal ion multipoles and τ is a repeated representation label. $M_{\gamma}^{\Gamma}(i, \tau)$ is the central ion multipole transforming as the γ-th component of the Γ-th irreducible representation and $\mu^{\alpha}(L)$ is the α-th component of the induced transient dipole on the L-th ligand subsystem.

2.1 Crystal field term

We now use the perturbation of Eq. (6) to mix opposite parity states $\Gamma_i \gamma_i n$ into the initial and final states involved in the transition $\Gamma_1 \gamma_1 l \to \Gamma_2 \gamma_2 m$. The crystal field contribution to transition dipole moment is then

$$\mu_{\Gamma_1 \gamma_1 l \to \Gamma_2 \gamma_2 m}^{CF, \beta} = \sum_{\Gamma_i \gamma_i n} (\Delta E_{i1})^{-1} \langle \Gamma_1 \gamma_1 l | \mathcal{H}_{CF}^{(1)} | \Gamma_i \gamma_i n \rangle \langle \Gamma_i \gamma_i n | \mu^{\beta} | \Gamma_2 \gamma_2 m \rangle$$

$$+ \sum_{\Gamma_i \gamma_i n} (\Delta E_{i2})^{-1} \langle \Gamma_1 \gamma_1 l | \mu^{\beta} | \Gamma_i \gamma_i n \rangle \langle \Gamma_i \gamma_i n | \mathcal{H}_{CF}^{(1)} | \Gamma_2 \gamma_2 m \rangle. \tag{8}$$

The usual way to proceed is to employ he closure approximation to write

$$\mu_{\Gamma_1 \gamma_1 l \to \Gamma_2 \gamma_2 m}^{CF, \beta} = 2(\Delta E)^{-1} \langle \Gamma_1 \gamma_1 l | \mathcal{H}_{CF}^{(1)} \mu^{\beta} | \Gamma_2 \gamma_2 m | \rangle \tag{9}$$

and we shall investigate this approach in a later paper in this series. Here we adopt a different strategy and write

$$\mu^{CF,\beta}_{\alpha_1(L_1S_1J_1)\Gamma_1\gamma_1 l \to \alpha_2(L_2S_2J_2)\Gamma_2\gamma_2 m} = \mu^{\beta}_{\alpha_1 \to \alpha_2} = -(Z_L e/\Delta E)$$

$$\times \sum_{kt} S_{kt} \sum_{\Gamma\gamma} \sum_{i\tau} A^{\Gamma\gamma}_{kt}(i,\tau)$$

$$\times \sum_{\alpha'} \{ \langle \alpha_1 | M^{\Gamma}_{\gamma}(i,\tau) | \alpha' \rangle \langle \alpha' | \mu^{\beta} | \alpha_2 \rangle$$

$$+ \langle \alpha_1 | \mu^{\beta} | \alpha' \rangle \langle \alpha' | M^{\Gamma}_{\gamma}(i,\tau) | \alpha_2 \rangle \}. \qquad (10)$$

Where for simplicity of notation we have abbreviated the initial and final states as α_1 and α_2, denoted the intermediate state $\alpha'(L'S'J')\Gamma'\gamma'n$ as α', assumed that $\Delta E_{i1} = \Delta E_{i2} = \Delta E$, and defined the crystal field quantity:

$$A^{\Gamma\gamma}_{kt}(i,\tau) = \sum_{L} \left\{ \frac{\delta \mathscr{G}^{CF,L}_{\Gamma\gamma}(i,\tau)}{\delta S_{kt}} \right\}_0.$$

These quantities have been evaluated for all components that occur for f electrons, a table is available on request from RA. Note that the spin quantum numbers S_1, etc. are all equal. We expand the operator $M^{\Gamma}_{\gamma}(i,\tau)$ in terms of the standard Garstang operators $D^i_q = -er^iC^i_q$ as $M^{\Gamma}_{\gamma}(i,\tau) = \sum_q R^{\Gamma\gamma}_{iq}(\tau)D^i_q$. The expansion coefficients are available [21, 22].

The transition dipole for the $\Gamma_1\gamma_1 l \to \Gamma_2\gamma_2 m$ transition may then be expressed in terms of the transition dipoles associated with transitions between individual Russell–Saunders terms. Writing

$$|\alpha(LSJ)\Gamma\gamma l\rangle = \sum_{M} C(\alpha JM|\Gamma\gamma l)|\alpha(LS)JM, \quad \text{etc.}$$

the matrix elements in Eq. (10) become

$$\langle \alpha_1 | M^{\Gamma}_{\gamma}(i,\tau) | \alpha' \rangle = \delta(S_1, S') \sum_{M_1 M'} \sum_q R^{\Gamma\gamma}_{iq}(\tau) C^*(\alpha_1 J_1 M_1 | \Gamma_1 \gamma_1 l)$$

$$\times C(\alpha' J' M' | \Gamma'\gamma'n) \langle \alpha_1(L_1 S_1)J_1 M_1 | D^i_q | \alpha'(L'S')J'M' \rangle, \qquad (11)$$

Applying the Wigner–Eckart theorem to both sides gives

$$\langle \alpha_1 \| M^{\Gamma}_{\gamma}(i,\tau) \| \alpha' \rangle_r = \delta(S_1, S') \mathscr{L}^{\Gamma}_{(i,\tau);r}(\Gamma_1 J_1 | \Gamma' J')$$

$$\times \langle \alpha_1(L_1 S_1)J_1 \| D^i \| \alpha'(L'S')J' \rangle,$$

where it is convenient to introduce the component independent symmetry determined coefficients:

$$\mathscr{L}^{\Gamma}_{(i,\tau);r}(\Gamma_1 J_1 | \Gamma' J') = \sum_{\gamma_1\gamma'\gamma} (-1)^{\Gamma_1 + \gamma_1^{\dagger}} V_r \begin{bmatrix} \Gamma_1 & \Gamma' & \Gamma \\ \gamma_1^+ & \gamma' & \gamma \end{bmatrix}$$

$$\times \sum_{M_1 M'} \sum_q R^{\Gamma\gamma}_{iq}(\tau) C^*(\alpha_1 J_1 M_1 | \Gamma_1 \gamma_1 l)$$

$$\times C(\alpha' J' M' | \Gamma'\gamma'n)(-1)^{J_1 - M_1} \begin{pmatrix} J_1 & i & J' \\ -M_1 & q & M' \end{pmatrix}, \qquad (12)$$

where $r = 1, 2 \ldots$. These coefficients are readily evaluated for the various $f \to f$ electronic transitions using the tables of Griffith [21] and Rotenberg et al. [24]. Clearly $\Gamma \subset \Gamma_1 \otimes \Gamma'$; $i = 1, 3, 5, 7$, etc. and $\tau = a, b$ where applicable. A Table is

available from RA. Similarly:

$$\langle \alpha_1 \| \mu^{T_1} \| \alpha' \rangle_r = \delta(S_1, S') \mathscr{L}_{(1);r}^{T_1}(\Gamma_1 J_1 | \Gamma' J') \langle \alpha_1 (L_1 S_1) J_1 \| D^i \| \alpha'(L'S')J' \rangle.$$

(13)

Inserting these in Eq. (10) results in an expression involving the product of two reduced matrix elements, this product may be further simplified as

$$\langle \alpha_1 (L_1 S) J_1 \| D^{k_1} \| \alpha'(L'S)J' \rangle \langle \alpha'(L'S)J' \| D^{k_2} \| \alpha_2 (L_2 S) J_2 \rangle$$

$$= (-1)^{k_1 + k_2 + L_1 + L' + J' + J_2}(2J' + 1)\sqrt{(2J_1 + 1)(2J_2 + 1)}$$

$$\times \begin{Bmatrix} L_1 & J_1 & S \\ J' & L' & k_1 \end{Bmatrix} \begin{Bmatrix} L' & J' & S \\ J_2 & L_2 & k_2 \end{Bmatrix}$$

$$\times \langle \alpha_1 (L_1 S) \| D^{k_1} \| \alpha' L' S \rangle \langle \alpha' L' S \| D^{k_2} \| \alpha_2 (L_2 S) \rangle$$

(14)

in the approximation we adopt, the intermediate states are derived from $4f^{n-1}5d$ configuration so we have

$$\langle L_1 S(f^n) \| D^{k_1} \| L'S(f^{n-1}d) \rangle \langle L'S(f^{n-1}d) \| D^{k_2} \| L_2 S)(f^n) \rangle$$

$$= n(-1)^{k_1 + k_2 + L_2 + L'}(2L' + 1)\sqrt{(2L_1 + 1)(2L_2 + 1)}$$

$$\times \sum_{L_3 S_3} \langle L_1 S(f^n) | \{ f^{n-1}(L_3 S_3)d(L_1 S) \rangle$$

(15)

$$\times \langle f^{n-1}(L_3 S_3)d(L_2 S) | L_2 S(f^n) \rangle$$

$$\times \begin{Bmatrix} 3 & L_1 & L_3 \\ L' & 2 & k_1 \end{Bmatrix} \begin{Bmatrix} 2 & L' & L_3 \\ L_2 & 3 & k_2 \end{Bmatrix} \langle f \| D^{k_1} \| d \rangle \langle d \| D^{k_2} \| f \rangle.$$

The coefficients of fractional parentage are available from Nielson and Koster [23].

The monoelectronic reduced matrix elements have the following values:

$$\langle d \| D^1 \| f \rangle = + \sqrt{3} e \langle r \rangle_{df} \quad \text{and} \quad \langle d \| D^3 \| f \rangle = -2/\sqrt{3} e \langle r^3 \rangle_{df}.$$

3 Ligand polarization contribution

For isotropic ligand subsystems the ligand subsystems we have from Eq. (5) the ligand polarisation contribution to the total transition dipole moment [14, 15]:

$$\mu_{\alpha_1 (L_1 S_1 J_1)\Gamma_1 \gamma_1 l \to \alpha_2 (L_2 S_2 J_2)\Gamma_2 \gamma_2 m}^{LP, \alpha} =$$

$$\mu_{\alpha_1 \to \alpha_2}^{LP, \alpha} = \sum_{st} S_{st} \sum_{\Gamma \gamma} \sum_{i\tau} B_{st}^{\Gamma \gamma}(i, \tau) \langle \alpha_1 | M_\gamma^\Gamma(i, \tau) | \alpha_2 \rangle,$$

(16)

where the ligand polarisation vibronic coupling constants

$$B_{st}^{\Gamma \gamma}(i, \tau) = -\alpha_L \sum_L \left\{ \frac{\delta \mathscr{G}_{\Gamma \gamma, \alpha}^{LP, L}(i, \tau)}{\delta S_{st}} \right\}_0$$

are readily evaluated. A table is available from RA. The matrix element may be successively simplified as in the previous section to give firstly

$$\mu_{\alpha_1 \to \alpha_2}^{LP,\alpha} = \sum_{kt} S_{kt} \sum_{\Gamma\gamma,\alpha} \sum_{i\tau} B_{kt}^{\Gamma\gamma}(i,\tau) \sum_r V_r \begin{bmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1^+ & \gamma_2 & \gamma \end{bmatrix} \langle \alpha_1 | M^\Gamma(i,\tau) | \alpha_2 \rangle_r. \quad (17)$$

The matrix element can then be expressed in terms of reduced matrix elements using the $\mathscr{L}_{(i,\tau);r}^\Gamma(\Gamma_1 J_1) | \Gamma' J')$ coefficients. The reduced matrix element can then be further reduced to

$$\langle f^n \alpha_1(L_1 S) J_1 \| D^i \| f^n \alpha_2(L_2 S) J_2 \rangle = (-1)^{S+i+L_1+J_2} \sqrt{(2J_1+1)(2J_2+1)}$$

$$\times \begin{Bmatrix} J_1 & J_2 & i \\ L_2 & L_1 & S \end{Bmatrix} \langle \alpha_1(L_1 S) \| D^i \| \alpha_2(L_2 S) \rangle, \quad (18)$$

$$\langle \alpha_1(L_1 S) \| D^i \| \alpha_2(L_2 S) \rangle = n \sqrt{(2L_1+1)(2L_2+1)} \langle 3 \| D^i \| 3 \rangle$$

$$\times \sum_{(\alpha L S)} (-1)^{L+i+L_1+3} \begin{Bmatrix} L_1 & L_2 & i \\ 3 & 3 & L \end{Bmatrix} \langle f^n(\alpha_1 L_1 S)$$

$$\times \{| f^{n-1}(\alpha L S), f \rangle \langle f^{n-1}(\alpha L S), f |\} f^n(\alpha_2 L_2 s) \rangle \quad (19)$$

and finally,

$$\langle 3 \| D^i \| 3 \rangle = 7e \langle r^i \rangle_{ff} \begin{pmatrix} 3 & i & 3 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{for } i = 2, 4, 6.$$

4 Application to the $|{}^3P_0, A_{1g}\rangle \to |{}^3H_4, \Gamma\rangle$, transition of the $PrCl_6^{3-}$

To provide a simple application of this method for illustrative purposes, we have evaluated the relative intensities of the vibronic origins associated with the $|{}^3P_0, A_{1g}\rangle \to |{}^3H_4, \Gamma\rangle$, $\Gamma = A_{1g}, E_g, T_{1g}, T_{2g}$ transitions. For this system Tanner has provided semiquantitative data on the relative intensities of the vibronic origins associated with the four electronic transitions [5]. It is important to recognise that our model of the vibronic intensities contains no adjustable parameters. No doubt it would be possible to fit the experimental data more precisely by varying the model parameters, we believe that this process tends to obscure the physics of the processes involved.

Within the $4f^n$ complex ions (and especially within the $5f^n$ series) there are many cases of spectroscopic states not being derived from a pure Russell–Saunders term. In the present case the $|{}^3P_0, A_{1g}\rangle$ state is well separated from the other $J = 0$ state whereas the $|{}^3H_4, \Gamma\rangle$ is well separated from the other $J = 4$ states. Since the crystal field and therefore "J-mixing" is relatively small, the states under consideration here are nearly pure Russell–Saunders terms, nevertheless we include the small correction to illustrate the technique. Fitting the observed energy levels of Tanner with a simple "complete" electron–electron repulsion ($B = 274$ cm^{-1}, $C = 27$ cm^{-1}, $D = 2400$ cm^{-1}); crystal field ($\langle B_4 \rangle = 272$ cm^{-1}, $\langle B_6 \rangle = 71$ cm^{-1})

and spin–orbit coupling ($\zeta_{so} = 750$ cm^{-1}) model gives the following wavefunctions:

$$|^3P_0, A_1\rangle = 0.996|^3P_0, A\rangle - 0.011|^3F_4, A_1\rangle + \cdots$$

$$|^3H_4, A_1\rangle = 0.986|^3H_4, A_1\rangle - 0.036|^3F_4, A_1\rangle + 0.014|^3H_6, A_1\rangle +$$

$$|^3H_4, E\rangle = 0.987|^3H_4, E\rangle - 0.036|^3F_2, E\rangle - 0.029|^3F_4, E\rangle + \cdots$$

$$|^3H_4, T_1\rangle = 0.986|^3H_4, T_1\rangle - 0.0033|^3F_4, T_1\rangle + \cdots$$

$$|^3H_4, T_2\rangle = 0.988|^3H_4, T_2\rangle - 0.018|^3F_2, T_2\rangle - 0.024|^3F_4, T_2\rangle + \cdots$$

The transition dipoles of the spectroscopic transitions are then readily expressed in terms of the transition dipoles between pure Russell–Saunders terms.

4.1 Crystal field component

The crystal field component for each of these can then be evaluated using Eq. (10). The electronic part of Eq. (10) associated with a particular symmetry coordinate s_t for $|^3P_0, A_1\rangle \rightarrow |^3H_4\Gamma\gamma\rangle$ transition then becomes

$$\mathscr{U}_{st}^z(^3P_0A_1 \rightarrow {}^4H_4\Gamma_2\gamma_2) = \frac{1}{\sqrt{3}}\sum_k C_k^{CF} A_{st}^{\Gamma\gamma}(k)\left[\mathscr{L}_{(k)}^\Gamma(A_1 0/\Gamma k)\mathscr{L}_{(1)}^{T_1}(\Gamma k/\Gamma_2 4)\right.$$

$$\times V\begin{bmatrix} \Gamma & \Gamma_2 & T_1 \\ \gamma & \gamma_2 & z \end{bmatrix}\langle ^3P_0 \| C^k \| ^3G_3\rangle\langle ^3G_3 \| C^1 \| ^3H_4\rangle$$

$$+ \mathscr{L}_{(1)}^{T_1}(A_1 0/T_1 1)\mathscr{L}_{(k)}^\Gamma(T_1 1/\Gamma 4)$$

$$\left.\times V\begin{bmatrix} T_1 & \Gamma_2 & \Gamma \\ z & \gamma_2 & \gamma \end{bmatrix}\langle ^3P_0 \| C^1 \| ^3D_1\rangle\langle ^3D_1 \| C^k \| ^3H_4\rangle\right]$$

where the $\mathscr{L}$ coefficients are defined by Eq. (12). Note how the symmetry of the initial and terminal states of the transition restricts the Russell–Saunders designation of the intermediate states. The crystal field factor $c_k^{CF} = Z_L e^3 \Delta E^{-1}\langle r\rangle_{fd}\langle r^3\rangle_{fd} R^{-k-2}$ is readily evaluated using $Z_L = 1$, $\langle r^3\rangle_{fd} = 0.810$ Å^3, $\langle r\rangle_{fd} = 0.475$ Å, $\Delta E = 55\,000$ cm^{-1} and $R_0 = 2.82$ Å [25]. Using the following two identities:

$$\mathscr{L}_{(1)}^{T_1}(A_1 0|T_1 1) = -1 \quad \text{and} \quad \mathscr{L}_{(1)}^{T_1}(\Gamma k|\Gamma_2 4) = (-1)^{T_2+\Gamma+\Gamma_2+k+5}\mathscr{L}_{(k)}^\Gamma(T_1 1|\Gamma 4),$$

the electronic factor becomes

$$\mathscr{U}_{st}^z(^3P_0A_1 \rightarrow {}^3H_4\Gamma_2\gamma_2) = 0.002435\, A_{st}^{\Gamma\gamma}(3)\, V\begin{bmatrix} \Gamma & \Gamma_2 & T_1 \\ \gamma & \gamma_2 & z \end{bmatrix}\mathscr{L}_{(1)}^{T_1}(\Gamma 3 | \Gamma_2 4)$$

in units of the electron charge.

Similarly the other required electronic factors may be calculated:

$$\mathscr{U}_{st}^z(^3P_0A_1 \rightarrow {}^3F_4\Gamma_2\gamma_2) = 0.002692\, A_{st}^{\Gamma\gamma}(3)\, V\begin{bmatrix} T_1 & \Gamma_2 & \Gamma \\ z & \gamma_2 & \gamma \end{bmatrix}\mathscr{L}_{(3)}^{T_1}(T_1 1 | \Gamma 4),$$

$$\mathscr{U}_{st}^z(^3P_0A_1 \to {}^3H_6\Gamma_2\gamma_2) = -0.000431\,A_{st}^{\Gamma\gamma}(5)\,V\begin{bmatrix} T_1 & \Gamma_2 & \Gamma \\ z & \gamma_2 & \gamma \end{bmatrix}\mathscr{L}_{(5)}^{\Gamma}(T_1 1\,|\,\Gamma_2 6),$$

$$\mathscr{U}_{st}^z(^3P_0A_1 \to {}^3F_2\Gamma_2\gamma_2) = 0.01658\,A_{st}^{\Gamma\gamma}(1)\,V\begin{bmatrix} T_1 & \Gamma_2 & \Gamma \\ z & \gamma_2 & \gamma \end{bmatrix}\mathscr{L}_{(1)}^{\Gamma}(T_1 3\,|\,\Gamma 2),$$

$$+\,0.00160\,A_{st}^{\Gamma\gamma}(3)\,V\begin{bmatrix} T_1 & \Gamma_2 & \Gamma \\ z & \gamma_2 & \gamma \end{bmatrix}\mathscr{L}_{(3)}^{\Gamma}(T_1 3\,|\,\Gamma 2).$$

These electronic factors are given in Table 1.

4.2 Ligand polarization component

The ligand polarisation contribution to the transition dipole is given by Eq. (17). The electronic factors for the $^3P_0A_1 \to {}^3H_4\Gamma_2\gamma_2$ transition may be written:

$$\mathscr{U}_{st}^z(^3P_0A_1 \to {}^3H_4\Gamma_2\gamma_2) = \sum \alpha_L B_{st}^{\Gamma\gamma}(i,\tau)\langle\alpha_1|M_\gamma^\Gamma(i,\tau)|\alpha_2\rangle.$$

The ligand polarization vibronic coupling constants are available from RA, the matrix element is evaluated as in Sect. 4.1. Using $\langle r^2\rangle_{ff} = 0.410$ Å^2 and $\langle r^4\rangle_{ff} = 0.418$ Å^4 [25], and evaluating the matrix elements as in Eqs. (18) and (19). The ligand polarisation electronic factors are then given in Table 2.

4.3 Vibrational analysis

We use the experimental ground state vibrational wavenumbers of $v_3 = 263$ cm^{-1}, $v_4 = 95$ cm^{-1} and $v_6 = 76$ cm^{-1} [5]. The required vibrational integrals

Table 1. Calculated crystal field electronic factors for the $^3P_0 \to {}^3H_4$ transition of PrCl$_6^{3-}$

Symmetry coord/ electronic state	A_1	E	T_1	T_2
			$\mathscr{U}/10^{-4}e$	
S_3	−26.24	16.81	15.51	16.81
S_4	9.84	−11.79	−6.04	−0.05
S_6	–	−14.01	8.96	−10.33

Table 2. Calculated ligand polarisation electronic factors for the $^3P_0 \to {}^3H_4$ transition of PrCl$_6^{3-}$

Symmetry coord/ electronic state	A_1	E	T_1	T_2
			$\mathscr{U}/10^{-4}e$	
S_3	42.29	−30.43	55.04	4.27
S_4	21.15	−4.97	−27.52	−14.95
S_6	–	−23.35	−27.52	−10.68

$|\langle 0| Q_S |1\rangle|^2$ may then be evaluated. Using a seven atom model of the $PrCl_6^{3-}$ ion [14], the L-matrix elements are found to be $L_{33} = 0.205$, $L_{34} = 0.013$, $L_{43} = -0.158$, $L_{44} = 0.297$ and $L_{66} = 0.237$.

4.4 Intensity calculations

The remaining steps in the calculation are to collect the contributions due to the various components of the electronic eigenfunctions, evaluate the ligand polarisation and crystal field components, and the cross-term between team and then distribute the intensity amongst the normal models. The resulting oscillator strengths are for each transition:

$$f(v_3) = 6.94 \times 10^{-7} \, \Delta\varepsilon (\mathscr{U}_3 L_{33} + \mathscr{U}_4 L_{43})^2,$$

$$f(v_4) = 1.95 \times 10^{-6} \, \Delta\varepsilon (\mathscr{U}_3 L_{34} + \mathscr{U}_4 L_{44})^2,$$

$$f(v_6) = 2.39 \times 10^{-6} \, \Delta\varepsilon (\mathscr{U}_6 L_{66})^2.$$

Inserting the experimental transition energies $\Delta\varepsilon$ from Eq. (5) gives the calculated oscillator strengths in Table 3, for ease of comparison with the experimental relative intensities in emission we also give the individual contributions (Table 4) and the relative intensity ratios of the vibronic origins within each electronic transition (Table 5).

Table 3. Calculated oscillator strengths of vibronic origins for the $^3P_0 \rightarrow {}^3H_4$ transition of $PrCl_6^{3-}$

Vibronic origin/ electronic state	$f(v_i)/10^{-9}$			
	A_1	E	T_1	T_2
v_3	0.38	0.003	54.0	6.0
v_4	35.6	10.0	35.0	6.0
v_6	–	37.0	9.0	11.0

Table 4. Calculated contributions to the dipole strengths of vibronic origins for the $^3P_0 \rightarrow {}^3H_4$ transition

Vibronic origin/ electronic state	$D(v_i)/10^{-7}$ Debyes^2			
	A_1	E	T_1	T_2
$D^{CF}(v_3)$	7.08	4.14	2.51	1.75
$D^{LP}(v_3)$	4.18	4.38	36.02	1.54
$D^{CF,LP}(v_3)$	−10.87	−8.50	18.53	3.31
$D^{CF}(v_4)$	2.76	4.47	1.05	0.01
$D^{LP}(v_4)$	19.35	1.45	23.06	7.97
$D^{CF,LP}(v_4)$	14.73	5.09	9.85	−0.74
$D^{CF}(v_6)$	–	5.59	2.28	3.03
$D^{LP}(v_6)$	–	15.57	21.56	3.24
$D^{CF,LP}(v_6)$	–	18.63	−14.04	6.29

Table 5. Calculated relative intensities of vibronic origins for the $^3P_0 \to {}^3H_4$ transition (Experimental values in parentheses)

Vibronic origin/ electronic state	A_1	E	T_1	T_2
v_3	0.01 [0.25]	0.00 [0.04]	1.00 [1.00]	0.55 [0.04]
v_4	1.00 [1.00]	0.27 [0.00]	0.60 [0.04]	0.55 [0.60]
v_6	–	1.00 [1.00]	0.17 [0.07]	1.00 [1.00]

5 Comparison with experiment

Semi-quantitative relative intensity data for the above transitions are available for the $PrCl_6^{3-}$ ion in the cubic elpasolite $Cs_2NaPrCl_6$ from [5]. No measurements of the oscillator strengths are available. The lifetime of the $^3P_0$ state in very dilute crystals is about 500 μs, but transitions to states other than $^3H_4$ contribute to the relaxation process. Since the intensity mechanism involves a vibronic perturbation rather than a static distortion, it would be reasonable to expect the oscillator strengths would be at the lower end of the range observed in lanthanide complexes. The range of the calculated intensities is consistent with or a little higher than these expectations. In our previous work on the MnF_6^{2-}-ion [14, 16] we have emphasised that this type of calculation cannot be expected to give good agreement with observed absolute intensities. For example the crystal field contributions is strongly dependent on the assumed ligand charge, for simplicity and in the spirit of having no adjustable parameters we have assumed unit negative charge resides effectively at the nuclear position. A somewhat lower value, consistent with the electroneutrality principle [14], would appreciably reduce the calculated dipole strength from the crystal field contribution and also improve the agreement between the calculated and observed vibronic intensity distribution. In cases where the crystal field and ligand polarisation contributions to the transition dipole have opposite signs the cross term between them will make a negative contribution to the dipole strength. This occurs for 4 out of the 11 non-zero contributions. The value of the dipole strength, and hence the calculated relative intensities, will then be particulary sensitive to the assumed parameter values.

An interesting property of the experimental results is the enormous variation in the intensity ratios of the v_6, v_4 and v_3 vibronic origins. For each of the $^3P_0 A_1 \to {}^3H_4\Gamma_2$ transitions, $\Gamma_2 = A_1$, E and T_1, a different vibronic origin dominates the intensity of the electronic transition whilst for $\Gamma_2 = T_2$ transition all three have comparable intensity. The calculation nicely reproduces this exacting test.

The major disagreement in the intensity ratios is in the ratio of the v_4 and v_3 vibronic origins. There are at least two difficulties with the calculation of this ratio. Firstly, the negative contribution from the cross-term occurs for three out of the four transitions for either v_4 or v_3. For the $A_1 \to A_1$, and $A_1 \to E$ transitions the oscillator strength of the v_3 vibronic origin is calculated to be particularly low due to the almost exact "accidental" cancellation of the contributions from $D^{CF}(v_3)$, $D^{LP}(v_3)$, and $D^{CF,LP}(v_3)$. A small change in any of the parameters or wavefunctions makes a large change in the calculated intensities, indeed a reduction in the charge on the ligands reduces the crystal field contribution but thereby increases the total intensity improving the fit with experiment. Secondly, this calculated ratio of oscillators strengths is strongly dependant on the vibrational wavefunctions. There is no doubt that our vibrational potential function is inadequate for the $Cs_2NaPrCl_6$,

since the sodium motion which has a wavenumber intermediate between the v_4 and v_3 modes acquires significant intensity by mixing with these modes.

It is clear that the agreement between calculation and experiment is dependent on the inclusion of crystal field, ligand polarisation terms and the signed cross term between them.

6 Conclusions

The agreement between the calculation and experiment is as good as could be expected for such a simple physical model. It appears therefore that the main features of intensity mechanism have been understood and accurately modelled. Further improvement will require better description of the charge distribution in the molecule and a more accurate description of the vibrational potential via using a full lattice dynamical model. Work in this direction is in progress, together with the application of this isolated ion model to other complex ions.

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