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Vibronic intensities in the electronic spectra of transition metal complex ions VIII: Vibrational coordinates for octahedral ions and their application to the $^4A_{2g} \leftrightarrow {}^2E_g$ transition of the MnF_6^{2-} ion

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Summary. A reexamination of the vibrational coordinates appropriate in vibronic intensity calculations in octahedral coordination compounds is presented. We derive a complete set of symmetry coordinates that is orthonormal and transforms correctly under the group generators. The vibronic hamiltonian for the crystal field and ligand polarization contributions to the intensity are calculated in the basis of these coordinates. The crystal field term is evaluated both using a truncated basis set for the intermediate electronic states and using the closure approximation. These methods have been applied to the calculation of the vibronic intensity distribution for the $^4A_{2g} \leftrightarrow {}^2E_g$ transition of the MnF_6^{2-} ion and close agreement wtih experiment achieved.

Key words: Vibronic intensities – Vibrational coordinates – Crystal field – Ligand polarization – Complex ion

1. Introduction

In previous papers in this series [1–7] we have attempted to calculate the relative contributions of the three odd parity vibrations of octahedral ML_6 transition metal coordination complexes to the total vibronic transition dipole of specific *d–d* electronic transitions. Three methods of calculation have been employed:

(a) The Liehr–Ballhausen approximation to the crystal field formulation where the vibronic intensity is assumed to be derived from a single $d \rightarrow p$ transition at high energy.

(b) The closure approximation to the crystal field formulation where the nature of the odd intermediate status is undefined.

(c) The ligand polarization procedure where the intensity is derived from a coupling of the metal ion transition multipoles with the radiation field induced transient ligand dipoles.

The conceptual and computational details of these metals have been developed and explained in this series. A common feature of each of the methods is the sensitivity of the vibronic intensity distribution to the details of the vibrational wavefunctions which in turn depend on the intermolecular potential. Indeed for the case of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of a d^3 complex ion, the vibronic intensity distribution is independent of all electronic factors in the case of methods (a) and (c). In the case of method (b) there is a relatively weak dependence on the dimensionless quantity $\alpha = \langle r^6 \rangle / R_0^2 \langle r^4 \rangle$ where R_0 is the metal ligand distance and radial functions are evaluated for the metal ion d-functions. A full calculation would require the inclusion of both crystal field [i.e. (a) or (b)] and ligand polarization [(c)] contributions as well as the cross term between them. In this case the assumed values of certain electronic quantities also influence the calculated vibronic intensity distribution.

Our initial calculations were based on an inadequate treatment of the vibrational coordinates. The need for great care in this area became apparent during attempts to compare the calculation of Kupka et al. [8, 9] on $ReCl_6^{2-}$ with our work on $ReBr_6^{2-}$ [7]. We now present a more formal treatment of the vibrational problem and the application of this method to the calculation of the vibronic intensity distribution for the $^4A_{2g} \leftrightarrow {}^4T_{2g}$ transition of MnF_6^{2-}. A significant conclusion is the necessity of using symmetry coordinates defined in a different way to those conventionally employed in normal coordinate analysis.

2. Normal modes of MnF_6^{2-}

The vibrational normal modes of an octahedral MnF_6^{2-} ion transform as $A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$ and are conventionally labelled ν_1 to ν_6. Of these, our particular concern is with the three odd vibrations which can act as vibronic origins for the $^4A_{2g} \rightarrow {}^4T_{2g}$ electronic transition. The vibrational symmetry coordinates in terms of an internal coordinate basis set were worked out by Pistorious [10]. Apart from (we assume) typographical errors, these symmetry coordinates transform correctly under the O_h group generators C_4z, C_4x, and C_3x,y,z according to the method of Griffith [11].

We require that the complete set of internal coordinates are orthonormal. We can then write the transformation between the symmetry coordinates $\boldsymbol{S}$ and the internal coordinates $\boldsymbol{s}$ as: $\boldsymbol{S} = \boldsymbol{U}\boldsymbol{s}$ where $\boldsymbol{U}$ is unitary.

The most general relationship between an internal coordinate s_k and the cartesian displacement coordinates R_i is:

$$s_k = \sum_i B_i^k R_i + \tfrac{1}{2} \sum_{ij} B_{ij}^k R_i R_j + \text{higher terms} \qquad (1)$$

It is usual to introduce the approximation that the vibrational amplitudes are infinitesimal and write $\boldsymbol{s} = \boldsymbol{B}\boldsymbol{R}$ where $\boldsymbol{B}$ is, in general, not square. To make $\boldsymbol{B}$ square so that it can be inverted it is usual to add to $\boldsymbol{s}$ the six external motions of the whole complex ion. Note however that $\boldsymbol{B}$ is not unitary so that if we write $\boldsymbol{S} = (\boldsymbol{U}\boldsymbol{B})\boldsymbol{R}$ then $\boldsymbol{U}\boldsymbol{B}$ is not unitary. The transformation $\boldsymbol{S} = (\boldsymbol{U}\boldsymbol{B})\boldsymbol{R}$ is given in Appendix 1. We emphasize that all previous vibronic intensity calculations employed vibrational symmetry coordinates with incorrect phases and/or normalization for this application. The correction of this error results in a significant change in both the calculated vibronic intensity distributions and their physical interpretation.

3. The vibronic hamiltonian

The independent systems model vibronic hamiltonian in a relative nuclear Cartesian displacement coordinate basis may be written to the first order as:

$$H^{(1)} = \sum_{L} (\vec{s}_L - \vec{s}_M)\nabla_L(V_{CF} + V_{LP}) = H^{(1)}_{CF} + H^{(1)}_{LP} \tag{2}$$

where $\vec{s}_L$ and $\vec{s}_M$ are the ligand and metal nuclear Cartesian displacement vectors, V_{CF} and V_{LP} are the crystal field and ligand polarization potential operators and the summation is over the ligand subsystem.

The two potential operators can be calculated in tensorial form following the method of Carlson and Rushbrooke and their symmetry adapted forms are given in [12] and references therein;

$$V_{CF} = -\sum_{L} Z_L e \sum_{k_1 q_1} G^{CF}_{k_1 q_1}(L) D^{k_1}_{q_1}(M) \tag{3}$$

where the crystal field geometrical factors are:

$$G^{CF}_{k_1 q_1}(L) = (-1)^{q_1+1} R_L^{-(k_1+1)} C^{k_1}_{-q_1}(\theta_L \Phi_L) \tag{4}$$

and Garstang's operators are defined as $D^k_q = -er^k C^k_q(\theta, \Phi)$ where the $C^k_q(\theta, \Phi)$ are the standard Racah tensorial operators. Similarly, the ligand polarization potential is:

$$V_{LP} = \sum_{L} \sum_{k_1, q_1} D^{k_1}_{q_1}(M) \sum_{X, Y, Z} G^{LP}_{k_1, q_1, \alpha}(L) \mu^{\alpha}_L \tag{5}$$

Here the ligand polarization geometrical factors are:

$$\begin{aligned}
G^{LP}_{k_1 q_1, X}(L) &= \tfrac{1}{2}(-1)^{(q_1+1)} R_L^{-(k_1+2)} \{ \sqrt{(k_1+q_1+2)(k_1+q_1+1)}\, C^{(k_1+1)}_{-(q_1+1)} \\
&\qquad - \sqrt{(k_1+q_1+2)(k_1+q_1+1)}\, C^{(k_1+1)}_{-(q_1-1)} \}_L \\
G^{LP}_{k_1 q_1, Y}(L) &= \tfrac{1}{2} i (-1)^{(q_1+1)} R_L^{-(k_1+2)} \{ \sqrt{(k_1+q_1+2)(k_1+q_1+1)}\, C^{(k_1+1)}_{-(q_1+1)} \\
&\qquad + \sqrt{(k_1-q_1+2)(k_1-q_1+1)}\, C^{(k_1+1)}_{-(q_1-1)} \}_L \\
G^{LP}_{k_1 q_1, Z}(L) &= (-1)^{(q_1+1)} R_L^{-(k_1+2)} \{ \sqrt{(k_1+q_1+1)(k_1-q_1+1)}\, C^{(k_1+1)}_{-q_1} \}_L
\end{aligned} \tag{6}$$

From Eqs. (1), (2) and (4), the vibronic crystal field and the vibronic ligand polarization operators are to the first order:

$$H^{(1)}_{CF} = -\sum_{L} Z_L e(\vec{s}_L - \vec{s}_M) \sum_{k_q q_1} D^{k_1}_{q_1}(M) \{\nabla_L G^{CF}_{k_1 q_1}(L)\}_0 \tag{7}$$

$$H^{(1)}_{LP} = \sum_{L} (\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} D^{k_1}_{q_1}(M) \sum_{X, Y, Z} \{\nabla_L G^{LP}_{k_1 q_1, \alpha}\}_0 \mu^{\alpha}_L \tag{8}$$

the vibronic crystal field operator, Eq. (7), there are two alternative, but ivalent, methods to evaluate the vibronic perturbation in terms of the central al tensorial operators. Firstly, the vibronic perturbation may be expressed in a basis set of the standard symmetry coordinates S_{kt}, (Appendix 1) using:

$$H^{(1)} = \sum_{kt} (\delta V_{CF}/\delta S_{kt})_0 S_{kt} + \sum_{kt} (\delta V_{LP}/\delta S_{kt})_0 S_{kt} = H^{(1)}_{CF} + H^{(1)}_{LP} \tag{9}$$

Both the vibronic crystal field and the vibronic ligand polarization operators to the first order may be found from Eqs. (7), (8) and (9). This is equivalent to the method used by Liehr and Ballhausen [13–15] although they employed a non-standard set of symmetry coordinates. An alternative method to work out the explicit forms for these two vibronic operators makes use of the following procedure.

The translation of an ML_6 molecule along the z-axis is represented by the coordinate T_z

$$T_z = (6m + M_0)^{-1/2} \left[M_0 Z_M + m \sum_L z_L \right]$$

where m is the ligand mass and M_0 the central metal mass. Since $\boldsymbol{R} = (\boldsymbol{UB})^{-1}\boldsymbol{S}$:

$$V(T_z) = (\delta V/\delta T_z) = (6m + M_0)^{-1/2} \left\{ \delta/\delta z_M + \sum_L \delta/\delta z_L \right\} V \tag{10}$$

Here the total interaction potential expressed as $V = \sum_L V_{LM}$, V_{LM} being the interaction among the central metal (M) and the ligand subsystem (L) charge distributions. Thus, as for the vibronic operators appropriate to the v_{3a}, v_{4a} and v_{6a} coordinates, we find from the $\boldsymbol{R} = (\boldsymbol{UB})^{-1}\boldsymbol{S}$ transformation:

$$\begin{aligned}
V_{3a} &= -\sqrt{2} \left[\{m/(6m + M_0)\} \left\{ \delta/\delta z_M + \sum_L \delta/\delta z_L \right\} - (\delta/\delta z_6 + \delta/\delta z_7) \right] V \\
V_{4a} &= \sqrt{2} \left[\{m/(6m + M_0)\} \left\{ \delta/\delta z_M + \sum_L \delta/\delta z_L \right\} \right. \\
&\quad \left. - \tfrac{1}{4}(\delta/\delta z_2 + \delta/\delta z_3 + \delta/\delta_4 + \delta/\delta z_5) \right] V \\
V_{6a} &= = + \sqrt{2}/4(-\delta/\delta z_2 - \delta/\delta z_3 + \delta/\delta z_4 + \delta/\delta z_5) V
\end{aligned} \tag{11}$$

Since the interaction potential must be translationally invariant:

$$\left\{ \delta/\delta z_M + \sum_L \delta/\delta z_L \right\} V \equiv 0$$

and similar equations apply for translations along the X and Y axes, then the vibronic operators are:

$$\begin{aligned}
V'_{3a} &= +(1/\sqrt{2})\{\delta/\delta z_6 + \delta/\delta z_7\} V \\
V'_{4a} &= -(1/2\sqrt{2})\{+\delta/\delta z_2 + \delta/\delta z_3 + \delta/\delta z_4 + \delta/\delta z_5\} V \\
V'_{6a} &= +(1/2\sqrt{2})\{-\delta/\delta z_2 - \delta/\delta z_3 + \delta/\delta z_4 + \delta/\delta z_5\} V
\end{aligned} \tag{12}$$

and similar expressions can readily be found for V'_{kt} for $k = 3, 4, 6$ *and* $t = b$ and c, respectively. These vibronic crystal field operators, from $k_1 = 1$ to $k = 5$ (to deal with d–d excitations) are given in Appendix 2. These correct our previous tabulation [1]. We also list the terms for $k_1 = 7$, which have not been previously reported to include all the relevant terms to deal with f–f excitations. It is important to observe from the above set of equations and from Appendix 1, that the transformation $\dot{\boldsymbol{S}} = (\boldsymbol{UB})\boldsymbol{R}$ is not unitary. Of course both methods give identical results which demonstrates that these two different approaches are equivalent.

For the crystal field contribution to the total transition dipole moment $\vec{\mu}^{CF}_{0\to a}$, it is necessary to consider both methods (a) and (b) of Sect. 1. Within the Liehr–Ballhausen method in which the intermediate state is truncated to a single p function we have for the transition dipole moment associated with the $|\Gamma_1\gamma_1\rangle \to |\Gamma_2\gamma_2\rangle$ excitation may be written:

$$\begin{aligned}\mu^{CF,\alpha}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2} = -\Delta E^{-1} \sum_{\Gamma\gamma}\sum_{L} z_L e(\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} \{&\langle\Gamma_1\gamma_1|D^{k_1}_{q_1}(M)|\Gamma\gamma\rangle\langle\Gamma\gamma|\mu^{\alpha}|\Gamma_2\gamma_2\rangle \\ &+ \langle\Gamma_1\gamma_1|\mu^{\alpha}|\Gamma\gamma\rangle\langle\Gamma\gamma|D^{k_1}_{q_1}(M)|\Gamma_2\gamma_2\rangle\}\{\vec{\nabla}_L G^{CF}_{k_1 q_1}\}_0 \end{aligned} \tag{13}$$

where the intermediate central metal's wavefunctions are represented by the set $|\Gamma\gamma\rangle$ and ΔE is taken as an effective energy gap corresponding to a parity and spin allowed electronic transition.

When the closure procedure is adopted to evaluate the crystal field transition dipole moment associated with the $|\Gamma_1\gamma_1\rangle \to |\Gamma_2\gamma_2\rangle$ excitation, the αth-component of the transition dipole moment becomes:

$$\mu^{CF,\alpha}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2} = 2\Delta E^{-1}\langle|\Gamma_1\gamma_1|\mu^{\alpha}H^{(1)}|\Gamma_2\gamma_2\rangle \tag{14}$$

where:

$$\begin{aligned}\mu^{x}H^{(1)} = e^3 \sum_{L} z_L(\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} (-1)^{q_1}\{r^{k_1+1}/\sqrt{6(2k_1+1)}\} \sum_{k} (2k+1) \\ \times \{c^k(11|k_1\ -q_1)C^k_{(q_1+1)} - c^k(1\ -1|k_1\ -q_1)C^k_{q_1-1}\}[\vec{\nabla}_L G^{CF}_{k_1 q_1}(L)]_0\end{aligned}$$

$$\begin{aligned}\mu^{y}H^{(1)} = -ie^3 \sum_{L} z_L(\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} (-1)^{q_1}\{r^{k_1+1}/\sqrt{6(2k_1+1)}\} \sum_{k} (2k+1) \\ \times \{c^k(11|k_1\ -q_1)C^k_{(q_1+1)} + c^k(1\ -1|k_1\ -q_1)C^k_{q_1-1}\}[\vec{\nabla}_L G^{CF}_{k_1 q_1}(L)]_0\end{aligned}$$

$$\begin{aligned}\mu^{z}H^{(1)} = -e^3 \sum_{L} z_L(\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} (-1)^{q_1}\{r^{k_1+1}/\sqrt{3(2k_1+1)}\} \sum_{k} (2k+1) \\ \times c^k(10|k_1\ -q_1)C^k_{q_1}[\vec{\nabla}_L G^{CF}_{k_1 q_1}(L)]_0\end{aligned} \tag{15}$$

The $c^k(lml'm')$ coefficients are tabulated in Ref. [16] and the Racah operators in terms of the Cartesian coordinates are in [17].

The ligand polarization contribution to the total transition dipole moment associated with the $|\Gamma_1\gamma_1\rangle \to |\Gamma_2\gamma_2\rangle$ transition for isotropic ligands becomes:

$$\mu^{LP,\alpha}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2} = -\sum_{L} \bar{\alpha}_L(\vec{s}_L - \vec{s}_M) \sum_{k_1 q_1} \langle\Gamma_1\gamma_1|D^{k_1}_{q_1}(M)|\Gamma_2\gamma_2\rangle[\vec{\nabla}_L G^{LP}_{k_1 q_1,\alpha}]_0 \tag{16}$$

where $\bar{\alpha}_L$ is the mean ligand polarizability measured at the frequency of the electronic transition. Equations (14), (15) and (16) are generally applicable to the evaluation transition dipole moments for vibronically allowed transitions for complexes of monoatomic ligands. For polyatomic ligands it is necessary to include the anisotropy of the ligand polarizability.

3. Application to the $^2E_g \leftrightarrow {}^4A_{2g}$ transition of the MnF_6^{2-} ion

To investigate the effect of these corrections to the vibrational coordinates on the vibronic intensity, we have recalculated the vibronic intensity associated with the $\nu_6(\tau_{2u})$, $\nu_4(\tau_{1u})$ and $\nu_3(\tau_{1u})$ vibronic origins of the $^2E_g \leftrightarrow {}^4A_{2g}$ transition of the MnF_6^{2-} ion. The reasons behind this choice and the details of the intensity mechanism have been discussed in detail in [1]. In brief, the intensity is derived principally from the $^4A_{2g} \leftrightarrow {}^4T_{2g}$ transition due to the spin-orbit mixing of the ^2E_g and $^4T_{2g}$ states which are separated by about 5600 cm^{-1}; all six vibrational modes of the perfectly octahedral complex ion diluted into Cs_2SiF_6 are known [1]; and the internal modes of the complex ion are not strongly coupled to the vibrational modes of the lattice. In addition the vibronic spectrum is exceptionally well resolved and their relative intensities are easily measured.

Using the standard ***GF*** matrix formulism and notation for the normal coordinate analysis there will be seven independent symmetrized force constants F_{ii} $(i = 1 \rightarrow 6)$ and $F_{34} = F_{43}$. Since there are only six observable vibrational frequencies an additional criterion is necessary to define the normal modes. The criterion we have adopted is to minimize the off-diagonal term in the potential energy distribution

$$\sum_{k \neq l} L_{ki} L_{li} F_{kl} \quad \text{where } \boldsymbol{GFL} = \boldsymbol{L\Lambda} \tag{17}$$

This criterion has been implemented by writing the relationship between the trans-bond stretching and the cis-stretching interaction $f'_{dd} = kf_{dd}$ where k is generally a positive constant less than unity. k may then be varied to minimize the potential energy cross term subject to exactly fitting the observed vibrational

Table 1. The L-matrices[a] and potential energy distributions for different force fields applied to the MnF_6^{2-} ion[b]

Force field	L_{33} PED_{33}	L_{34} PED_{34}	L_{43} PED_{43}	L_{44} PED_{44}
Ref. [19]	0.296 (92.5%)	−0.034 (7.4%)	−0.292 (7.4%)	−0.408 (92.5%)
Ref. [20]	0.298 (99.9%)	0.0 (0.0%)	−0.245 (0.0%)	0.437 (99.9%)
MGVFF with $k = 1.67$	0.298 (81.0%)	−0.073 (18.9%)	−0.343 (18.9%)	−0.366 (81.0%)
MGVFF with $k = 1.59$	0.294 (88.7%)	−0.048 (11.2%)	−0.311 (11.2%)	−0.394 (88.7%)
MGVFF with $k = 1.50$	0.297 (94.0%)	0.027 (5.9%)	−0.284 (5.9%)	0.412 (94.0%)
MGVFF with $k = 1.40$	0.298 (97.6%)	0.011 (2.3%)	−0.261 (2.3%)	−0.427 (97.6%)
MGVFF with $k = 1.33$	0.298 (99.4%)	0.003 (0.5%)	−0.249 (0.5%)	0.434 (99.4%)

[a] In each case $L_{66} = 0.3243$

[b] Vibrational data as in Ref. [1]

wavenumbers. We have used a modified general valence force field for k values between 1.67 and 1.33 as well as the force fields used by Pandey [19] and by Mohan [20], the corresponding $\boldsymbol{L}$ matrices and the potential energy distributions (using the vibrational wavenumbers from [1]) are given in Table 1.

We have shown [1, 2] that within both the Liehr–Ballhausen crystal field model and the ligand polarization of the vibronic intensity, the *relative* intensity of the vibronic origins are independent for all electronic factors and depends only on the vibrational wavefunctions. This is not the case for the crystal field model when closure is employed [1] or when the crystal field and ligand polarization contributions to the transition dipole are added to produce the total transition dipole. It is necessary therefore in these estimates to adopt a value for the effective ligand charge z_L. One method [1] is to use the electrostatic model for the crystal field in which $Dq = z_L e^2 \langle r^4 \rangle / 6R_0$. Using the metal ligand bond length $R_0 = 174 \times 10^{-12}$ m [1] the experimental value for Dq and near SCF quality radial functions appropriate for an isolated Mn^{4+} ion [18] invariably leads to unrealistically high (i.e. much greater than unity) values for z_L and corresponding large values for the crystal field component of the total dipole strength, the reasons for this have been extensively discussed throughout the history of crystal field theory. For the purposes of calculating vibronic perturbations it seems more reasonable to apply the electroneutrality principle to the region of the central metal ion which leads to $z_L = 1/3$.

The ${}^4A_{2g} \leftrightarrow {}^4T_{2g}$ transition is composed of three one-electron transitions $|xy\rangle \rightarrow |x^2 - y^2\rangle$ and its cyclic permutations. For the Liehr–Ballhausen model we find from Eq. (12) for the three components of the transition dipole moment of the $|xy\rangle \rightarrow |x^2 - y^2\rangle$ transition.

$$\begin{aligned}
\mu^{CF,x} &= +\Omega[\beta_3^{CF} Q_{3b} + \beta_4^{CF} Q_{4b} + \beta_6^{CF} Q_{6b}] \\
\mu^{CF,y} &= -\Omega[\beta_3^{CF} Q_{3c} + \beta_4^{CF} Q_{4c} - \beta_6^{CF} Q_{6c}] \\
\mu^{CF,z} &= 0
\end{aligned} \tag{18}$$

where $\Omega = +(3\sqrt{10}/28)[z_L e^2 \mu^x(xy \rightarrow y)\langle r^3 \rangle_{dp} / R_0^5 \Delta E]$, $\mu^x(xy \rightarrow y)$ is the xth component of the transition dipole associated with the $3d_{xy} \rightarrow 4p_y$ parity allowed transition at energy ΔE, and

$$\beta_3^{CF} = -8L_{33} + 3L_{43}, \qquad \beta_4^{CF} = -8L_{34} + 3L_{44}, \qquad \beta_6^{CF} = -3L_{66}$$

For the closure approximation we find from Eq. (14) that the relative vibronic intensities of the vibronic origins depends on the value of the dimensionless parameter $\alpha = \langle r^6 \rangle / R_0^2 \langle r^4 \rangle$:

$$\begin{aligned}
\mu^{CF',x} &= -\Omega'[\beta_3^{CF'} Q_{3b} + \beta_4^{CF'} Q_{4b} - \beta_6^{CF'} Q_{6b}] \\
\mu^{CF',y} &= -\Omega'[\beta_3^{CF'} Q_{3c} + \beta_4^{CF'} Q_{4c} - \beta_6^{CF'} Q_{6c}] \\
\mu^{CF',z} &= 0
\end{aligned} \tag{19}$$

where

$$\beta_3^{CF'} = (2\kappa - \tfrac{1}{3})L_{33} + \kappa L_{43}, \qquad \beta_4^{CF'} = (2\kappa - \tfrac{1}{3})L_{34} + \kappa L_{44}, \qquad \beta_6^{CF'} = \kappa L_{66},$$

$$\kappa = \frac{1}{14} + \frac{\alpha}{11} \quad \text{and} \quad \Omega' = 30\sqrt{2}\, eDq / \Delta E$$

Finally, for the ligand polarization term we find from Ref. (16)

$$\begin{aligned} \mu^{LP,x} &= -\Omega''[\beta_3^{LP}Q_{3b} + \beta_4^{LP}Q_{4b} - \beta_6^{LP}Q_{6b}] \\ \mu^{LP,y} &= +\Omega''[\beta_3^{LP}Q_{3c} + \beta_4^{LP}Q_{4c} + \beta_6^{LP}Q_{6c}] \\ \mu^{LP,z} &= 0 \end{aligned} \tag{20}$$

where $\Omega'' = (-5/\sqrt{2})[e\bar{\alpha}_L\langle r^4\rangle_{dd}/R_0^7]$ and

$$\beta_3^{LP} = 2L_{33} + L_{43}, \qquad \beta_4^{LP} = 2L_{34} + L_{44}, \qquad \beta_6^{LP} = L_{66}$$

The total transition dipole moment associated with the $|0\rangle \rightarrow |a\rangle$ excitation, within the independent system model, is written:

$$\vec{\mu}_{0\rightarrow a}^{Total} = \vec{\mu}_{0\rightarrow a}^{CF} + \vec{\mu}_{0\rightarrow a}^{LP} \tag{21}$$

Assuming that the potential energy surfaces of the initial and terminal electronic states are described by identical harmonic oscillator functions we have:

$$D_{0\rightarrow a}^{Total} = \sum_{x,y,z} |\langle 0|\mu_{0\rightarrow a}^{Total,\alpha}|1\rangle|^2 \qquad \text{with } |\langle 0|Q_i|1\rangle|^2 = \frac{\hbar}{4\pi c\nu_i} \tag{22}$$

and hence the total dipole strength $D_{0\rightarrow a}^{Total}$ becomes:

$$D_{0\rightarrow a}^{Total} = D_{0\rightarrow a}^{CF} + D_{0\rightarrow a}^{LP} + D_{0\rightarrow a}^{(CF,LP)} \tag{23}$$

The calculated dipole strengths for the Liehr–Ballhausen crystal field, closure crystal field and ligand polarization models for seven different force fields using selected parameter values are given in Table 2. For the Liehr–Ballhausen crystal field model, the radial integral is taken for Mn^{4+} from [18], the transition dipole moments are proportional to the ligand charge, the oscillator strength of the $d \rightarrow p$ transition and the $\langle r^3\rangle_{dp}$ radial integral and inversely proportional to the energy of the $d \rightarrow p$ transition so that values for other parameter values are easily derived. Note the sensitivity of the relative intensities of the ν_3 and ν_4 vibronic origins to the magnitude of the force field parameter k. The calculated overall magnitude of the dipole strength is of the same order of magnitude as the experimental value [1] (although the calculated value relates to a hypothetical system in which the potential surfaces of the ground and excited states are identical), but the calculated intensity distribution is quite different from that observed for the ${}^4A_{2g} \rightarrow {}^2E_g$ transition with the ν_3 vibronic origin calculated to be much more intense than the vibronic origins due to the bending modes.

As discussed previously, the calculated vibronic intensity distribution using the crystal field model with closure depends on the radial functions. For expanded radial functions corresponding to an approximately neutral central metal ion, the bending modes have comparable vibronic intensity and are several times more intense than the stretching mode, in agreement with experiment. As the metal ion charge is increased, contracting the d-electron functions and reducing the magnitude of the parameter α, the calculated vibronic intensities of the bending modes decrease more rapidly than that of the stretching mode. For a radial function applicable for Mn^{4+} the intensity of these modes are reversed, Table 2. The total intensity is calculated to be of the correct order of magnitude.

Finally, for the ligand polarization term the calculated vibronic intensity distribution corresponds to the bending modes being several times more intense than the stretching mode in agreement with experiment and is again independent of the radial functions.

Table 2. Calculated dipole strengths [$D/10^{-4}$(Debyes)^2] for the vibronic origins of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of the MnF_6^{2-} ion. 1 Debye = 10^{-30} Cm

Dipole strength[a]	Force Field						
	Ref. [18]	Ref. [20]	$k = 1.67$	$k = 1.59$	$k = 1.50$	$k = 1.40$	$k = 1.33$
Liehr–Ballhausen crystal field[b]							
$D^{CF}(\nu_3)$	9.81	9.112	10.46	10.11	9.76	9.40	9.18
$D^{CF}(\nu_4)$	1.60	2.99	0.46	1.11	1.81	2.47	2.84
$D^{CF}(\nu_6)$	←			2.40			→
Closure crystal field[c]							
$D^{CF}(\nu_3)$	5.83	4.16	8.01	6.52	5.55	4.71	4.30
$D^{CF}(\nu_4)$	20.40	23.13	16.06	18.69	20.49	22.06	22.81
$D^{CF}(\nu_6)$	←			18.55			→
Closure crystal field[d]							
$D^{CF}(\nu_3)$	2.23	1.92	2.57	2.36	2.19	2.03	1.94
$D^{CF}(\nu_4)$	1.59	2.16	0.94	1.33	1.67	1.94	2.10
$D^{CF}(\nu_6)$	←			1.74			→
Ligand polarization[e]							
$D^{LP}(\nu_3)$	1.30	1.79	0.80	1.12	1.40	1.63	1.75
$D^{LP}(\nu_4)$	6.21	5.15	7.07	6.48	5.86	5.44	5.22
$D^{LP}(\nu_6)$	←			4.13			→

[a] Calculations using other parameter sets are available from the authors

[b] $\langle r^4 \rangle_{dp} = 0.565 \times 10^{-30}\,m^3$ (from Ref. [18] for Mn^{3+}), $\Delta E = 10^5\,cm^{-1}$, $f(3d_{xy} - 4p_y) = 0.2$

[c] $\langle r^4 \rangle_{dd} = 1.4736 \times 10^{-40}\,m^4$, $\langle r^6 \rangle_{dd} = 4.5718 + 10^{-60}\,m^6$ (from Ref. [22], for Mn^0), hence $\alpha = 1.0247$, $\Delta E = 10^5\,cm^{-1}$

[d] $\langle r^4 \rangle_{dd} = 0.2268 \times 10^{-40}\,m^4$, $\langle r^6 \rangle_{dd} = 0.2838 + 10^{-60}\,m^6$ (from Ref. [22], for Mn^{4+}), hence $\alpha = 0.4133$, $\Delta E = 10^5\,cm^{-1}$

[e] $\langle r^4 \rangle_{dd} = 0.268 \times 10^{-40}\,m^4$, $\alpha_L = 1 \times 10^{-30}\,m^3$ [21]

Table 3. Calculated dipole strengths [$D/10^{-4}$(Debyes)^2] and relative intensity distributions for the vibronic origins of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of the MnF_6^{2-} ion in the Liehr–Ballhausen crystal field plus Ligand Polarization model[a,b]. 1 Debye = 10^{-30} Cm

Dipole strength[a]	Force field						
	Ref. [18]	Ref. [20]	$k = 1.67$	$k = 1.59$	$k = 1.50$	$k = 1.40$	$k = 1.33$
D^{CF}	13.81	14.50	13.31	13.61	13.96	14.26	14.42
D^{LP}	11.64	11.07	12.01	11.72	11.39	11.20	11.10
$D^{(CF,\,LP)}$	5.45	6.06	4.10	4.93	5.42	5.80	5.98
$f(\nu_3):f(\nu_4):f(\nu_6)$ $[f(\nu_3) = 1]$	3.56:3.23	5.66:4.54	2.04:2.35	2.87:2.84	3.76:3.40	4.77:4.01	5.41:4.40

[a] Calculations using other parameter sets are available from the authors

[b] $\langle r^3 \rangle_{dp} = 0.565 \times 10^{-30}\,m^3$ (from Ref. [18] for Mn^{3+}), $\Delta E = 10^5\,cm^{-1}$, $f(3d_{xy} - 4p_y) = 0.2$, $e\langle r^4 \rangle_{dd} = 0.269 \times 10^{-40}\,m^4$, $\alpha_L = 1 \times 10^{-30}\,m^3$

Table 3 shows the results of attempting to combine the crystal field and ligand polarization terms. As we have emphasized previously there is no logical way of doing this since both are scaled by imprecisely defined quantities. Nevertheless to illustrate the procedure the transition moments of the Liehr–Ballhausen crystal field and the ligand polarization methods have been combined according to Eqs. (21) and (23).

Overall we conclude that for this transition both the ligand polarization and crystal-field closure models are able to account for the observed intensity distribution either alone or in combination. The Liehr–Ballhausen procedure cannot on its own do this. The sensitivity of the calculated intensity distribution to the vibrational wavefunctions is confined using the corrected wavefunctions but detailed comparison of the results of this study with those of papers [1–3] illustrate the need to use correctly normalized functions of the appropriate phase.

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Appendix 1. The $S=(UB)R$ transformation for the MnF_6^{2-} ion

Symmetry species

α_{1g}-symmetry: $S_1=\{1/\sqrt{6}\}\{X_2-X_3+Y_4-Y_5+Z_6-Z_7\}$

metry: $S_2\theta=\{1/\sqrt{12}\}\{-X_2+X_3-Y_4+Y_5+2Z_6-2Z_7\}$

$S_2\varepsilon=\{1/2\}\{X_2-X_3-Y_4+Y_5\}$

τ_{1u}-symmetry: $S_{3c} = \{1/\sqrt{2}\}\{X_2 + X_3 - 2X_M\}$

$S_{3b} = \{1/\sqrt{2}\}\{Y_4 + Y_5 - 2Y_M\}$

$S_{3a} = \{1/\sqrt{2}\}\{Z_6 + Z_7 - 2Z_M\}$

$S_{4c} = \{1/\sqrt{2}\}\{-X_4 - X_5 - X_6 - X_7 + 4X_M\}$

$S_{4b} = \{1/\sqrt{2}\}\{-Y_2 - Y_3 - Y_6 - Y_7 + 4Y_M\}$

$S_{4a} = \{1/\sqrt{2}\}\{-Z_2 - Z_3 - Z_4 - Z_5 + 4Z_M\}$

τ_{2g}-symmetry: $S_{5c} = \{-Y_6 + Y_7 - Z_4 + Z_5\}$

$S_{5b} = \{-X_6 + X_7 - Z_2 + Z_3\}$

$S_{5a} = \{-X_4 + X_5 - Y_2 + Y_3\}$

τ_{2u}-symmetry: $S_{6c} = \{1/\sqrt{2}\}\{-X_4 - X_5 + X_6 + X_7\}$

$S_{6b} = \{1/\sqrt{2}\}\{Y_2 + Y_3 - Y_6 - Y_7\}$

$S_{6a} = \{1/\sqrt{2}\}\{-Z_2 - Z_3 + Z_4 + Z_5\}$

Appendix. Crystal field vibronic coupling operators

$$V_{3a} = 1/\sqrt{2}\{4Z_{10} + 8Z_{30} + 12Z_{50} + 16Z_{70} + \cdots\}$$

$$V_{4a} = 1/2\left\{4Z_{10} - 6Z_{30} + \frac{15}{2}Z_{50} + 3\sqrt{\frac{35}{8}}Z'_{54} - \frac{35}{4}Z_{70} - 3\sqrt{\frac{231}{32}}Z'_{74} + \cdots\right\}$$

$$V_{6a} = 1/2\left\{\sqrt{30}Z'_{32} - 3\sqrt{\frac{35}{6}}Z'_{52} + 15\sqrt{\frac{21}{64}}Z'_{72} - \sqrt{\frac{3003}{64}}Z'_{76} + \cdots\right\}$$

$$\begin{aligned} V_{3b} = i/\sqrt{2}\Bigg\{&4Z'_{11} - 8\sqrt{\frac{3}{8}}Z'_{31} - 8\sqrt{\frac{5}{8}}Z'_{33} + 12\sqrt{\frac{15}{64}}Z'_{51} + 12\sqrt{\frac{35}{128}}Z'_{53} \\ &+ 12\sqrt{\frac{63}{128}}Z'_{55} - 20\sqrt{\frac{7}{64}}Z'_{71} - 12\sqrt{\frac{21}{64}}Z'_{73} - 4\sqrt{\frac{231}{64}}Z'_{75} - 4\sqrt{\frac{429}{64}}Z'_{77} + \cdots\Bigg\} \end{aligned}$$

$$\begin{aligned} V_{4b} = i/2\Bigg\{&2\sqrt{2}Z'_{11} + 3\sqrt{\frac{6}{8}}Z'_{31} + 3\sqrt{\frac{10}{8}}Z'_{33} + 9\sqrt{\frac{30}{64}}Z'_{51} - 3\sqrt{\frac{70}{128}}Z'_{53} \\ &+ 15\sqrt{\frac{14}{128}}Z'_{55} + 59\sqrt{\frac{7}{512}}Z'_{71} + 9\sqrt{\frac{21}{512}}Z'_{73} - 5\sqrt{\frac{231}{512}}Z'_{75} + 7\sqrt{\frac{429}{512}}Z'_{77} + \cdots\Bigg\} \end{aligned}$$

$$\begin{aligned} V_{6b} = i/2\Bigg\{&5\sqrt{\frac{6}{8}}Z'_{31} - 3\sqrt{\frac{10}{8}}Z'_{33} + 7\sqrt{\frac{30}{64}}Z'_{51} + 3\sqrt{\frac{70}{128}}Z'_{53} - 15\sqrt{\frac{14}{128}}Z'_{55} \\ &+ 69\sqrt{\frac{7}{512}}Z'_{71} - 9\sqrt{\frac{21}{512}}Z'_{73} + 5\sqrt{\frac{231}{512}}Z'_{75} - 7\sqrt{\frac{429}{512}}Z'_{77} + \cdots\Bigg\} \end{aligned}$$

$$\begin{aligned} V_{3c} = 1/\sqrt{2}\Bigg\{&4Z_{11} - 8\sqrt{\frac{3}{8}}Z_{31} + 8\sqrt{\frac{5}{8}}Z_{33} + 12\sqrt{\frac{15}{64}}Z_{51} - 12\sqrt{\frac{35}{128}}Z_{53} \\ &+ 12\sqrt{\frac{63}{128}}Z_{55} - 20\sqrt{\frac{7}{64}}Z_{71} + 12\sqrt{\frac{21}{64}}Z_{73} - 4\sqrt{\frac{231}{64}}Z_{75} + 4\sqrt{\frac{429}{64}}Z_{77} + \cdots\Bigg\} \end{aligned}$$

$$V_{4c} = 1/2\left\{2\sqrt{2}\,Z_{11} + 3\sqrt{\frac{6}{8}}\,Z_{31} - 3\sqrt{\frac{10}{8}}\,Z_{33} + 9\sqrt{\frac{30}{64}}\,Z_{51} + 3\sqrt{\frac{70}{128}}\,Z_{53}\right.$$
$$\left. + 15\sqrt{\frac{14}{128}}\,Z_{55} + 59\sqrt{\frac{7}{512}}\,Z_{71} - 9\sqrt{\frac{21}{512}}\,Z_{73} - 5\sqrt{\frac{231}{512}}\,Z_{75} - 7\sqrt{\frac{429}{512}}\,Z_{77} + \cdots\right\}$$

$$V_{6c} = 1/2\left\{-5\sqrt{\frac{6}{8}}\,Z_{31} - 3\sqrt{\frac{10}{8}}\,Z_{33} - 7\sqrt{\frac{30}{64}}\,Z_{51} + 3\sqrt{\frac{70}{128}}\,Z_{53}\right.$$
$$\left. + 15\sqrt{\frac{14}{128}}\,Z_{55} - 69\sqrt{\frac{7}{512}}\,Z_{71} - 9\sqrt{\frac{21}{512}}\,Z_{73} - 5\sqrt{\frac{231}{512}}\,Z_{75} - 7\sqrt{\frac{429}{512}}\,Z_{77} + \cdots\right\}$$

where, we define:

$$Z_{l0} = \frac{Ze^2r^l}{R_0^{l+2}}\,C_0^l$$

$$Z_{lm} = \frac{Ze^2r^l}{R_0^{l+2}}\left(\frac{-C_m^l + C_{-m}^l}{\sqrt{2}}\right)$$

$$Z'_{lm} = \frac{Ze^2r^l}{R_0^{l+2}}\left(\frac{C_m^l + C_{-m}^l}{\sqrt{2}}\right)$$