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On the theory of radiative transitions in centrosymmetric complexes

A symmetry adapted crystal field approach

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The theory of radiative transitions, in centrosymmetric complexes, is examined in great detail, within the framework of the crystal field method.

In connection with radiative transitions, the current method of calculations, with and without invoking closure approximation, are considered from a purely theoretical point of view, by taking advantage of the irreducible tensor method put forward by Griffith.

Explicit equations are derived throughout the course of this work to account for the vibronic electric dipole moments, associated with $d-d$ and $f-f$ type of excitations.

Key words: Radiative transitions—Centrosymmetric complexes—A symmetry adapted crystal field approach.

1. Introduction

The general theory of radiative transitions, in molecular systems with spectroscopic interest, has been the subject of many research works during the last two decades.

Electric dipole transition moments for both centrosymmetric and non centrosymmetric complexes, have been evaluated by using:

I) A crystal field formulism [1–11], II) A dynamic coupling scheme [11–19], and also III) A combined crystal field and dynamic coupling mechanism [15, 16].

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Here we shall concentrate on the evaluation of transition dipole moments, in the case of centrosymmetric complexes, by employing a vibronic crystal field model. We shall introduce a symmetry adapted approach in order to deal with $d-d$ and $f-f$ type of excitations. We shall focus our attention on the explicit evaluation of both: total dipole strength and relative vibronic intensity distribution associated with each of the vibronic origins.

2. Method of calculation

The current methods of calculations, with and without invoking closure approximation for the wavefunctions, shall be formulated by taking advantage of the irreducible tensor method put forward by Griffith [20, 21].

In particular, and for the case of centrosymmetric inorganic complexes, there are several calculations in the literature dealing with the actual evaluation of the associated vibronic electric dipole transition moments [1–6, 9, 11, 14]. In all of these, the ligand systems have been regarded either as point charges or point dipoles.

This vibronic crystal field method, has also been extended to centrosymmetric inorganic complexes, having polyatomic ligands, such as amino groups [11]. There is, an alternative method of calculation, due to Mason [17–19] and Richardson [12, 13, 16], the so-called vibronic ligand polarization scheme, which assumes ligand dipoles induced by the radiation field, which then induce electric multipoles on the metal ion. It is worth mentioning at this point that the Faulkner–Richardson intensity model, in the case of lanthanide complexes, includes both the ligand point-charge and ligand polarization effects [12, 13, 16]. Both the vibronic crystal field and the vibronic ligand polarization methods are complementary to one another, and therefore the total dipole strength associated with a particular electronic excitation, should be computed by summing up: the crystal field, the ligand polarization and the interference terms, derived from this type of combined vibronic crystal field and dynamic coupling mechanisms.

The relative importance of these contributions has been pointed out by Richardson [16] in the case of lanthanide complexes. In the case of centrosymmetric inorganic complexes, we have also considered the dependence of the relative vibronic intensity distribution on the choice of the force field [15].

Within the framework of the vibronic crystal field method, two schemes of calculations have been proposed in the literature, namely the vibronic crystal field method of Liehr and Ballhausen [1, 9] and the vibronic crystal field method of Koide and Pryce [2, 3].

The vibronic approach of Liehr and Ballhausen [1, 9] starts from the assumption that, for a centrosymmetric inorganic compound, a $d-d$ type of excitation takes place by borrowing intensity from a $d-p$ parity allowed excitation through cooperation of the odd vibrational coordinates of the molecular system in question.

Following the same argument, one might argue that a parity forbidden $f-f$ type of excitation in a centrosymmetric complex could borrow intensity from a $d-f$ electronic excitation through cooperation of the ungerade vibrational motions of the complex.

In this scheme, the intermediate electronic states should have parity other than the terminal states of the electronic transition.

The method of Koide and Pryce, on the other hand, makes use of the closure properties of the wavefunctions. They assume, that all the intermediate electronic states which contribute to the transition dipole moment, occur at the same energy E and form a complete set of orthonormal functions. When this assumption is adopted, the nature of these states become totally irrelevant to the evaluation of the transition dipole moments, except on the choice of an effective energy gap.

Here we shall present a symmetry adapted formulism to evaluate the corresponding transition dipole moments, associated with parity forbidden electronic transitions in centrosymmetric complexes, by using the irreducible tensor method of Griffith [20, 21].

This approach offers several advantages, because the derivation of general formulae to express the total transition dipole moment associated with a vibronically allowed excitation, can be reduced to:

i) The evaluation of reduced matrix elements, involving the vibronic operators $(\partial V/\partial S_{\gamma}^{c})_0$, where V is the symmetry adapted form of the Coulombic interaction potential. S_{γ}^{c} stands for the γth component of a symmetry coordinates S which transforms under the cth irreducible representation of the molecular point group, and to

ii) The choice of the vibrational force field, in order to obtain a representative set of normal coordinates for the system.

Let us consider next in some detail, both the Liehr and Ballhausen and the Koide and Pryce's methods of calculation, to deal with radiative transitions.

3. The Koide and Pryce method

It can be shown that in most general terms, the α-vector component of the transition dipole moment associated with the $|\Gamma_1\gamma_1 j\rangle \rightarrow |\Gamma_2\gamma_2 l\rangle$ excitation may be written as follows [2, 3, 6, 11]

$$\mu^{\alpha}(\Gamma_1\gamma_1 j \rightarrow \Gamma_2\gamma_2 l) = \left(\frac{2}{\Delta E}\right) \sum_{\Gamma,\gamma,k} \langle\Gamma_1\gamma_1 j| W_{\gamma}^{\Gamma}(k)\mu_{\alpha}^{T_1}|\Gamma_2\gamma_2 l\rangle Q_{\gamma}^{\Gamma}(k) \tag{1}$$

where $W_{\gamma}^{\Gamma}(k) = (\partial V/\partial Q_{\gamma}^{\Gamma}(k))_0$ is the vibronic operator, and k, j and l are repeated representation labels. ΔE is some sort of effective energy, corresponding to the energy gap of a spin and parity allowed excitation. $Q_{\gamma}^{\Gamma}(k)$ stands for the γth-component of a normal coordinate Q which transforms under the Γth-irreducible representation of the point molecular group.

The tensorial product operator $W^{\Gamma}_{\gamma}(k)\mu^{T_1}_{\alpha}$ may be decomposed further on, by means of the relationship [21–23]

$$W^{\Gamma}_{\bar{\gamma}}(k)\mu^{T_1}_{\alpha}=\sum_{\Gamma,\gamma}\lambda^{1/2}(\Gamma)(-1)^{\Gamma+\gamma^{+}}V\begin{pmatrix}\bar{\Gamma} & T_1 & \Gamma\\ \bar{\gamma} & \alpha & \gamma^{+}\end{pmatrix}O^{\Gamma}_{\gamma}(k). \tag{2}$$

The above identity holds for all those cases in which the direct product $\bar{\Gamma}\times T_1$ is simple reducible. By combining Eqs. (1) and (2), we obtain the symmetry adapted form for the α-vector component of the transition dipole moment.

$$\begin{aligned}&\mu^{\alpha}(\Gamma_1\gamma_1 j\rightarrow\Gamma_2\gamma_2 l)\\ &\quad=\left(\frac{2}{\Delta E}\right)\sum_{\bar{\Gamma},\bar{\gamma},k}\ \sum_{\Gamma,\gamma,i}\lambda^{1/2}(\Gamma)(-1)^{\Gamma}+\gamma^{+}(-1)^{\Gamma_1}+\gamma_1^{+}\\ &\qquad V\begin{pmatrix}\bar{\Gamma} & T_1 & \Gamma\\ \bar{\gamma} & \alpha & \gamma^{+}\end{pmatrix}V_i\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma\\ \gamma_1^{+} & \gamma_2 & \gamma\end{pmatrix}\langle\Gamma_1 j||O^{\Gamma}(k)||\Gamma_2 l\rangle_i Q^{\bar{\Gamma}}_{\bar{\gamma}}(k).\end{aligned} \tag{3}$$

Note that the labels i, j and l may be dropped, when the direct product $\Gamma_1\times\Gamma_2$ is simply reducible.

Next, by assuming that the potential energy surfaces of the two terminal electronic states of the electronic transition have the same shape and are only vertically displaced to one another, we may evaluate the total dipole strength corresponding to the excitation as follows:

$$D_{01}(\Gamma_1\gamma_1 j, 0\rightarrow\Gamma_2\gamma_2 l, 1)=\sum_{\alpha}|\langle 0|\mu^{\alpha}(\Gamma_1\gamma_1 j\rightarrow\Gamma_2\gamma_2 l)|1\rangle|^2 \tag{4}$$

where the harmonic oscillator approximation for the vibrational wavefunctions has been employed [24–26].

It can be seen from Eq. (3) that the actual evaluation of the total transition dipole moment depends ultimately on the evaluation of both: The $\langle\Gamma_1 j||O^{\Gamma}(k)||\Gamma_2 l\rangle_i$ reduced matrix elements and on the choice of a representative vibrational force field for the molecule.

Consider next, the evaluation of these relevant reduced matrix elements. To do so, write the $O^{\Gamma}_{\gamma}(k)$ tensor operators as follows (21–23).

$$O^{\Gamma}_{\gamma}(k)=\lambda^{1/2}(\Gamma)(-1)^{\Gamma+\gamma^{+}}\sum_{\bar{\gamma},\alpha}V\begin{pmatrix}\bar{\Gamma} & T_1 & \Gamma\\ \bar{\gamma} & \alpha & \gamma^{+}\end{pmatrix}W^{\bar{\Gamma}}_{\bar{\gamma}}(k)\mu^{T_1}_{\alpha} \tag{5}$$

where the vector components of the first rank tensor operator $\mu^{T_1}_{\alpha}$ are defined by following Griffith's Table A-19 [20] as given below:

$$\mu^{T_1}_{+1}=D^1_{+1},\qquad \mu^{T_1}_{0}=D^1_{0},\qquad \mu^{T_1}_{-1}=D^1_{-1} \tag{6}$$

and the D^k_q tensor operators are given by: $D^k_q=-er^kC^k_q$, where the C^k_q are the standard Racah's tensor operators [11, 14, 15, 27]. Next, let us consider in some detail the actual evaluation of the vibronic operators $W^{\bar{\Gamma}}_{\bar{\gamma}}(k)$.

Here we may write the identity (11, 14, 15):

$$W^{\bar{\Gamma}}_{\bar{\gamma}}(k)\equiv[\partial V/\partial Q^{\bar{\Gamma}}_{\bar{\gamma}}(k)]_0=\sum_{\Gamma,\gamma,i}L_{ik}\delta_{\Gamma\bar{\Gamma}}\delta_{\gamma\bar{\gamma}}[\partial V/\partial S^{\Gamma}_{\gamma}(i)]_0 \tag{7}$$

where the L_{ij} are the matrix elements of the so called L-matrix, which relates the symetry and the normal coordinates of the molecular system, through the relationship: $S=LQ$[24, 25].

In our notation, $S^{\Gamma}_{\gamma}(i)$ stands for the γth-component of a symmetry coordinate S which transforms under the Γth-irreducible representation of the molecular group. Also, i is a repeated representation label.

Furthermore, these symmetry coordinates may be expressed in terms of Cartesian nuclear displacement coordinates of each nucleus, by means of the relationship $S=B\cdot R$ [24, 25] so that we may write the identity:

$$[\partial V/\partial S^{\Gamma}_{\gamma}(i)]_0=\sum_k\left[\frac{\partial V}{\partial X_k}\frac{\partial X_k}{\partial S^{\Gamma}_{\gamma}(i)}+\frac{\partial V}{\partial Y_k}\frac{\partial Y_k}{\partial S^{\Gamma}_{\gamma}(i)}+\frac{\partial V}{\partial Z_k}\frac{\partial Z_k}{\partial S^{\Gamma}_{\gamma}(i)}\right]_0 \tag{8}$$

where all the relevant derivatives, should be evaluated at the equilibrium nuclear configuration, $Q=Q_0$.

In connection with the crystal field potential V, this may be written in a symmetry adapted form, by considering the Coulombic interaction potential between two non overlapping charge distributions, (M) and (L) and separated at a distance R_L, where R_L is identified here with the metal–ligand bond distance [27, 28].

In a symmetry adapted form, we write the crystal field potential, as follows:

$$V=\sum_L V_L=\sum_L q_L e \sum_{\Gamma,\gamma,k} G^L_{\Gamma\gamma}(k)M^{\Gamma}_{\gamma}(k). \tag{9}$$

The above identity represents the interaction potential between a 2^l central metal ion multipole and the ligand point charges. Here q_L stands for the nuclear effective charge on the Lth ligand position.

Also, $G^L_{\Gamma\gamma}(k)$ stands for the crystal field geometrical factors, and $M^{\Gamma}_{\gamma}(k)$ represents the symmetry adapted form of the central metal ion multipoles. k is a repeated representation label. The Coulombic interaction potential between a 2^k central metal ion multipoles and ligand dipoles has been reported recently [27].

Here we shall follow Griffith's convention, see Table A-19 [20], and will define the central metal ion's multipoles according to behavior of the kets $|JM\rangle$ under the symmetry operations of the O-rotation group. Thus for $k=2$, we define the symmetry adapted form of the central metal ion, electric quadrupole:

$$\begin{aligned}
M^E_{\theta}&=D^2_0\\
M^E_{\varepsilon}&=\frac{1}{\sqrt{2}}(D^2_{+2}+D^2_{-2})\\
M^{T_2}_{+1}&=D^2_{-1}\\
M^{T_2}_{0}&=\frac{1}{\sqrt{2'}}(D^2_{+2}-D^2_{-2})\\
M^{T_2}_{-1}&=-D^2_{+1}.
\end{aligned} \tag{10}$$

To obtain the real components of the central metal ion, electric quadrupole, we use the transformations given by Griffith in Table A-16 [20]. Griffith listed octahedral sets of wavefunctions for $J \leq 6$, and an extension of Griffith's work was considered by Golding [29] for $J > 6$. Observe than in Eqs. (10), the ket $|JM\rangle$ of Griffith's have been replaced by the tensor operators $D_q^k = -er^k C_q^k$.

For the sake of completeness, in Appendix I we list the octahedral set of wavefunctions for $J = 7$, a case which is relevant to account for the vibronic intensity associated with $f-f$ type of excitations, within the framework of the Koide and Pryce's method.

Having adopted this convention to define the central metal ion's multipoles, it is a straightforward process to obtain the symmetry adapted form of the Coulombic interaction potential corresponding to the electric quadrupole-point charge interaction. The associated geometrical factors are given in Appendix II. Higher order interaction terms are also included in this appendix. (The cases we have considered correspond to the Coulombic interaction, between a 2^k central metal ion's electric multipole and ligand point charges, for $k = 1$ up to 7).

Having defined, this symmetry adapted form of the crystal field potential V, we may proceed further on and obtain the explicit form of the vibronic operators, defined by Eq. (7). Assuming that the transformation $S = L \cdot Q$ is known, the problem is then reduced to obtain the derivatives of the symmetry adapted form of the crystal field potential with respect to the symmetry coordinates of the molecular system. Observe that these derivatives are to be evaluated at the nuclear equilibrium configuration of the molecular system. This may be achieved by Combining Eqs. (7) and (8).

Next, consider a specific application of this symmetry adapted, crystal field method, to account for the vibronic intensity associated with $d-d$ and $f-f$ type of excitations in a centrosymmetric ML_6 compound.

It is well known, that a molecular system of this type has three odd parity vibrational motions, namely: A $t_{1u}(\nu_3)$ stretching, a $t_{1u}(\nu_4)$ bending and a $t_{2u}(\nu_6)$ bending vibrations. The corresponding odd parity symmetry coordinates are reported in Refs. [9] and [11], and are given in terms of Cartesian nuclear displacement coordinates of each nucleus of the molecular system.

We shall denote the set of odd parity symmetry coordinates, as S_{kt} where $k = 3$, 4, 6 and $t = a$, b, c. Thus the vibronic operators, say $V_{kt} = (\partial V/\partial S_{kt})_0$ can be obtained by direct differentiation of the Coulombic interaction potential with respect to the relevant odd parity symmetry coordinates of the molecular system, in question.

Thus, assuming that all the ligand systems are equivalent and carry a nuclear effective charge of q, we may write, in the most general sense, the V_{kt} operators as follows:

$$V_{kt} = qe \sum_{\Gamma,\gamma,i} A_{kt}^{\Gamma\gamma}(i) M_\gamma^\Gamma(i) \tag{11}$$

where the $A_{kt}^{\Gamma\gamma}(i)$ are the vibronic crystal field coefficients, defined by means of the relationship:

$$A_{kt}^{\Gamma\gamma}(i) = \sum_{L} \left[\frac{\partial G_{\Gamma\gamma}^{L}(i)}{\partial X_L} \frac{\partial X_L}{\partial S_{kt}} + \frac{\partial G_{\Gamma\gamma}^{L}(i)}{\partial Y_L} \frac{\partial Y_L}{\partial S_{kt}} + \frac{\partial G_{\Gamma\gamma}^{L}(i)}{\partial Z_L} \frac{\partial Z_L}{\partial S_{kt}} \right]_0 . \tag{12}$$

The vibronic crystal field coefficients, are listed in Appendix III, for $\Gamma = T_{1u}$, T_{2u}. The crystal field geometrical factors, $G_{\Gamma\gamma}^{L}(i)$ are listed in Appendix II, and the central metal ion's multipoles, $M_{\gamma}^{\Gamma}(i)$ are given by Griffith [20] in Table A-19. The relevant cases for this kind of calculation correspond to the following values of J: $J = 1, 3, 5, 7$.

For the irreducible representations $\Gamma = T_1, T_2$, Griffith [20] writes the transformations:

$$|\Gamma X\rangle = +\frac{i}{\sqrt{2}}(|\Gamma+1\rangle - |\Gamma-1\rangle)$$

$$|\Gamma Y\rangle = +\frac{1}{\sqrt{2}}(|\Gamma+1\rangle + |\Gamma-1\rangle) \tag{13}$$

$$|\Gamma Z\rangle = -i|\Gamma O\rangle$$

which relate, the real and complex vector components of these irreducible representations in the O-rotation group, for J even.

When $\Gamma = T_1$ and T_2, and J is odd, the transformations defined by Eq. (13), give purely imaginary $|\Gamma X\rangle$, $|\Gamma Y\rangle$ and $|\Gamma Z\rangle$ vector components.

For the sake of completeness, we list in Appendix IV, the symmetry adapted complex vector components of the central metal ion, electric multipoles, for $J = 1, 3, 5, 7$ and $\Gamma = T_1$ and T_2.

These symmetry adapted complex vector components of the central metal–ion multipoles are *consistent*, with the crystal field geometrical factors $G_{\Gamma\gamma}^{L}(i)$ informed in Appendix II, as well as with the definition of the crystal field potential given by Eq. (9).

To illustrate the utility of both Appendixes III and IV, let us find next the vibronic operators V_{kt} for $k = 3, 4, 6$ and $t = a$.

It is a straightforward process to write, from Appendix III and Eq. (11), these vibronic operators as follows:

$$V_{3a} = qe\{(i2\sqrt{2})R_0^{-3}M_Z^{T_1}(J=1) + (i4\sqrt{2})R_0^{-5}M_Z^{T_1}(J=3)$$
$$+ (i6\sqrt{2})R_0^{-7}M_Z^{aT_1}(J=5) + (i8\sqrt{2})R_0^{-9}M_Z^{bT_1}(J=7) + \cdots\} \tag{14.1}$$

$$V_{4a}=qe\left\{(-2i)R_0^{-3}M_Z^{T_1}(J=1)+(3i)R_0^{-5}M_Z^{T_1}(J=3)\right.$$
$$+\left(-i\frac{15}{4}\right)R_0^{-7}M_Z^{a_{T_1}}(J=5)\left(-i\frac{3\sqrt{35}}{4}\right)R_0^{-7}M_Z^{b_{T_1}}(J=5)$$
$$\left.+\left(i\frac{3\sqrt{231}}{8}\right)R_0^{-9}M_Z^{a_{T_1}}(J=7)+\left(i\frac{35}{8}\right)R_0^{-9}M_Z^{b_{T_1}}(J=7)+\ldots\right\} \qquad (14.2)$$

$$V_{6a}=qe\left\{(-i\sqrt{15})R_0^{-5}M_Z^{T_2}(J=3)+\left(i\frac{\sqrt{105}}{2}\right)R_0^{-7}M_Z^{T_2}(J=5)\right.$$
$$+\left(-i\frac{\sqrt{6006}}{16}\right)R_0^{-9}M_Z^{a_{T_2}}(J=7)$$
$$\left.+\left(-i\frac{15\sqrt{42}}{16}\right)R_0^{-9}M_Z^{b_{T_2}}(J=7)+\cdots\right\}. \qquad (14.3)$$

Next, we replace the explicit forms of the symmetry adapted central metal ion's multipoles, given in Appendix IV, and obtain the final form of the vibronic operators V_{ka} for $k=3$, 4, 6 as given below:

$$V_{3a}=\frac{1}{\sqrt{2}}qe\{4Z_{10}+8Z_{30}+12Z_{50}+16Z_{70}+\cdots\} \qquad (15.1)$$

$$V_{4a}=\frac{1}{2}qe\left\{-4Z_{10}+6Z_{30}-\frac{15}{2}Z_{50}-\frac{3\sqrt{35}}{2}Z'_{54}+\frac{3\sqrt{231}}{4}Z'_{74}+\frac{35}{4}Z_{70}+\cdots\right\}$$
$$(15.2)$$

$$V_{6a}=\frac{1}{2}qe\left\{-2\sqrt{15}Z'_{32}+\sqrt{105}Z'_{52}-\frac{\sqrt{6006}}{8}Z'_{76}-\frac{15\sqrt{42}}{8}Z'_{72}+\cdots\right\} \qquad (15.3)$$

where:

$$Z_{lm}=R_0^{-(l+2)}\frac{1}{\sqrt{2}}(-D^l_m+D^l_{-m})=R_0^{-(l+2)}B^l_{+m}$$

$$Z'_{lm}=R_0^{-(l+2)}\frac{1}{\sqrt{2}}(D^l_m+D^l_{-m})=R_0^{-(l+2)}B^l_{-m} \qquad (16)$$

$$Z_{10}=R_0^{-(l+2)}D^l_0=R_0^{(l+2)}B^l_0$$

where the $D^l_m=-er^lc^l_m$ are the standard Garstang' tensor operators, and the tensor operators B^l_{+m} and B^l_0 are defined by Eq. (16).

To obtain the vibronic operators V_{kt} for $k=3$, 4, 6 and $t=b$, c, we can either follow the same method as described earlier on, or perform three fold rotations $C_3^-(X\rightarrow Z\rightarrow Y\rightarrow X)$ and/or $C_3^+(X\rightarrow Y\rightarrow Z\rightarrow X)$ on the vibronic operators V_{3a}, V_{4a} and V_{6a}, respectively (11).

Having obtained these vibronic operators V_{kt}, we can now proceed further on and evaluate, within the framework of the Koide and Pryce's method, all the non zero reduced matrix elements, relevant to the $d-d$ and $f-f$ type of excitations, see Eq. (3). To do so, we need to form the irreducible tensor operators $O^{\Gamma}_{\gamma}(k)$ given by Eq. (5).

Thus, by employing the V-coefficients of Griffith [21], we can easily find the symmetry adapted ITO given by Eq. (5).

For example, the Z^{th} component of the T_1 irreducible representation give rises to three operators, each of them associated with a particular ungerade symmetry coordinate, of the ML_6-octahedral complex.

Thus, we find;

$$\begin{aligned}
O^{T_1}_{Z}(3) &= \frac{1}{\sqrt{2}}(V_{3b}\mu^{X} - V_{3c}\mu^{Y}) \\
O^{T_1}_{Z}(4) &= \frac{1}{\sqrt{2}}(V_{4b}\mu^{X} - V_{4c}\mu^{Y}) \qquad (17) \\
O^{T_1}_{Z}(6) &= \frac{-1}{\sqrt{2}}(V_{6c}\mu^{Y} + V_{6b}\mu^{X})
\end{aligned}$$

and, in the same way, we may find the other relevant irreducible tensor operators.

The vector components μ^X, μ^Y and μ^Z of the electric dipole moment are chosen as given below (11, 27).

$$\begin{aligned}
\mu^{X} &= B^{1}_{+1} = \frac{1}{\sqrt{2}}(-D^{1}_{+1} + D^{1}_{-1}) \\
\mu^{Y} &= iB^{1}_{-1} = \frac{i}{\sqrt{2}}(D^{1}_{+1} + D^{1}_{-1}) \qquad (18) \\
\mu^{Z} &= B^{1}_{0} = D^{1}_{0}.
\end{aligned}$$

At this stage, it is important to observe that the symmetry adapted tensor operators $O^{\Gamma}_{\gamma}(k)$, defined by Eq. (5) can ultimately be expressed as linear combinations of product operators of the form: $B^{l}_{+m}B_{q}$, $B^{l}_{-m}B^{1}_{q}$ and $B^{l}_{0}B^{1}_{q}$, for $l = 1, 3, 5, 7$ and $q = 0, \pm 1$.

These product of operators can be simplified further on, and expressed as linear combinations of operators of the form $e^2 r^{k+1} C^k_q$, where the C^k_q have been defined in the text and correspond to the standard Racah's tensor operators.

Having worked out all these products, we can construct the vibronic crystal field operators, defined by Eq. (5) for $\Gamma = A_1, A_2, E, T_1, T_2$ and $k = 3, 4, 6$. In the case of a ML_6 cluster in O_h symmetry, we list the explicit form of these operators in Appendix V. Observe that a ligand-point charge model has been adopted throughout the course of this work.

Finally, we have evaluated all those non vanishing reduced matrix elements relevant to the evaluation of transition dipole moments, associated with $d-d$

and $f-f$ type of excitations in the case of a octahedral ML_6 complex ion. We list them in Appendix VI. We have used real set of central metal ion's wavefunctions to evaluate these reduced matrix elements [32] and the V-coefficients informed by Griffith [21].

4. The Lieher and Ballhausen method

This method starts from the assumption that a parity forbidden electronic transition in a centrosymmetric complex borrows its intensity from a parity allowed excitation through cooperation of the odd vibrational motions of the complex ion [1, 5, 9, 11, 13, 14, 15].

In this approach, the α-vector component of the transition dipole moment associated with the $|\Gamma_1\gamma_1\rangle \rightarrow |\Gamma_2\gamma_2\rangle$ excitation may be written as given below (11, 14)

$$\begin{aligned}\mu^{\alpha}(\Gamma_1\gamma_1 \rightarrow \Gamma_2\gamma_2) \\ = \sum_{k,t} S_{kt} \sum_{\Gamma_i\gamma_i} \{ |E(\Gamma_1)-E(\Gamma_i)|^{-1} \langle \Gamma_1\gamma_1|V_{kt}|\Gamma_i\gamma_i\rangle\langle\Gamma_i\gamma_i|\mu^{\alpha}|\Gamma_2\gamma_2\rangle \\ + |E(\Gamma_2)-E(\Gamma_i)|^{-1}\langle\Gamma_1\gamma_1|\mu^{\alpha}|\Gamma_i\gamma_i\rangle\langle\Gamma_i\gamma_i|V_{kt}|\Gamma_2\gamma_2\rangle\}. \qquad (19)\end{aligned}$$

Here the V_{kt} are the so-called vibronic crystal field operators, as defined by Eq. (11) and the S_{kt} are the odd parity symmetry coordinates of the system. The intermediate electronic states $|\Gamma_i\gamma_i\rangle$ are supposed to have parity other than the terminal electronic states $|\Gamma_1\gamma_1\rangle$ and $|\Gamma_2\gamma_2\rangle$, respectively.

It is customary to assume that $E(\Gamma_1)-E(\Gamma_i) \simeq E(\Gamma_2)-E(\Gamma_i)$, and therefore to replace the energy denominators in Eq. (19) by an effective energy gap, say ΔE which would correspond to the energy difference associated with the parity allowed excitation.

Thus Eq. (19) becomes:

$$\begin{aligned}\mu^{\alpha}(\Gamma_1\gamma_1 \rightarrow \Gamma_2\gamma_2) \\ = \frac{1}{\Delta E} \sum_{k,t} S_{kt} \sum_{\Gamma_i\gamma_i} \{ \langle \Gamma_1\gamma_1|V_{kt}|\Gamma_i\gamma_i\rangle\langle\Gamma_i\gamma_i|\mu^{\alpha}|\Gamma_2\gamma_2\rangle \\ + \langle\Gamma_1\gamma_1|\mu^{\alpha}|\Gamma_i\gamma_i\rangle\langle\Gamma_i\gamma_i|V_{kt}|\Gamma_2\gamma_2\rangle\}. \qquad (20)\end{aligned}$$

Next consider a typical matrix element of Eq. (20) involving the vibronic operators V_{kt}, one of the terminal electronic states and the intermediate states $|\Gamma_i\gamma_i\rangle$.

Let us, then write a general matrix elements as follows:

$$\begin{aligned}\langle \alpha\Gamma_1\gamma_1|V_{kt}|\alpha'\Gamma_i\gamma_i\rangle \\ = qe \sum_{\Gamma,\gamma,j} (-1)^{\Gamma_1+\gamma_1^{+}} V\begin{pmatrix}\Gamma_1 & \Gamma_i & \Gamma \\ \gamma_1^{+} & \gamma_i & \gamma\end{pmatrix} A_{kt}^{\Gamma\gamma}(j)\langle\alpha\Gamma_1||M^{\Gamma}(j)||\alpha'\Gamma_i\rangle \qquad (21)\end{aligned}$$

where Eq. (11) and the Wigner–Eckart theorem have been employed. The labels α and α' denote the nature of the electrons involved in the integral to be evaluated.

For a perfect octahedral ML_6 cluster, the vibronic crystal field coefficients $A_{kt}^{\Gamma\gamma}(j)$ are tabulated in Appendix III, the V-coefficients have been listed in Refs. [21–23], so that, the explicit evaluation of the integrals given by Eq. (21) may ultimately be reduced to the evaluation of the reduced matrix elements $\langle \alpha\Gamma_1 || M^{\Gamma}(j) || \alpha'\Gamma_i \rangle$. We have evaluated all the relevant reduced matrix elements in Appendix VII, involving integrals of the form: $\langle d\Gamma_1 || M^{\Gamma}(j) || p\Gamma_2 \rangle$, for $j = 1$, 3 and $\langle f\Gamma_1 || M^{\Gamma}(j) || d\Gamma_2 \rangle$, for $j = 1$, 3, 5. In both cases $\Gamma = T_1$ and T_2.

The simplest case arises, for a $d-d$ type of electronic transition in centrosymmetric environments. Here, we assume that the $d-d$ excitation borrows its intensity from a parity allowed $d-p$ excitation through cooperation of the odd parity normal coordinates of the system. Thus for this particular situation, the vibronic coupling matrix elements defined by means of Eq. (20) become:

$$\begin{aligned}&\langle d\Gamma_1\gamma_1 || V_{kt} || pT_1\gamma_i \rangle \\ &\quad = qe \sum_{\Gamma,\gamma,j} (-1)^{\Gamma_1+\gamma_1^+} V\begin{pmatrix} \Gamma_1 & T_1 & \Gamma \\ \gamma_1^+ & \gamma_i & \gamma \end{pmatrix} A_{kt}^{\Gamma\gamma}(j) \langle d\Gamma_1 || M^{\Gamma}(j) || pT_1 \rangle \end{aligned} \tag{22}$$

where $\Gamma_1 = E,\ T_2$.

For a $3d-3d$ electronic transition in a centro symmetric complex ion (O_h symmetry) we follow, Liehr and Ballhausen [1, 9] and truncate the above summation, so as to include only the $4p$-central metal ion's wavefunctions as the so called intermediate electronic states.

For this particular case, the vibronic matrix elements defined by Eq. (22) correspond to the vibronic coupling constant of Liehr and Ballhausen [9, 11, 14].

To illustrate the utility of Appendices III, IV and VII, we shall evaluate in particular $d-p$ and $f-d$ interaction vibronic matrix elements.

i) The vibronic matrix element $\langle dE\theta | V_{3a} | pT_1 z \rangle = \gamma_{T_1 z,3a}^{dE\theta}$.

Direct application of Eq. (22) and the appendices, mentioned above leads us to the identity;

$$\begin{aligned}\gamma_{T_1 z,3a}^{dE\theta} &= qeV\begin{pmatrix} E & T_1 & T_1 \\ \theta & z & z \end{pmatrix} \{(i2\sqrt{2}) R_0^{-3} \langle dE || M^{T_1}(j=1) || pT_1 \rangle \\ &\quad + (i4\sqrt{2}) R_0^{-5} \langle dE || M^{T_1}(j=3) || pT_1 \rangle \\ &= -\frac{4\sqrt{30}}{15} qe^2 \left\{ \frac{\langle r \rangle}{R_0^3} + \frac{9}{7} \frac{\langle r^3 \rangle}{R_0^5} \right\} \end{aligned} \tag{23}$$

where: $\langle r^k \rangle_{3d,4p} = \langle R(3d) | r^k | R(4p) \rangle$. R_0 is identified with the metal–ligand bond distance.

ii) The vibronic matrix element $\langle fT_1 x | V_{6a} | dT_2 y \rangle = \gamma_{dT_2 y,6a}^{fT_1 x}$.

Once again, the direct application of our Appendices and Eq. (21) allows us to write the identity:

$$\gamma^{fT_1x}_{dT_2y,6a} = qeV\begin{pmatrix} T_1 & T_2 & T_2 \\ x & y & z \end{pmatrix}\{(-i\sqrt{15})R_0^{-5}\langle fT_1||M^{T_2}(j=3)||dT_2\rangle$$

$$+\left(i\frac{\sqrt{105}}{2}\right)R_0^{-7}\langle fT_1||M^{T_2}(j=5)||dT_2\rangle\}$$

$$=\frac{\sqrt{105}}{42}qe^2\left\{\frac{\langle r^3\rangle}{R_0^5}+\frac{35}{11}\frac{\langle r^5\rangle}{R_0^7}\right\} \tag{24}$$

where $\langle r^k\rangle_{nf,(n+1)d}=\langle R\,|\,nf||r^k\,|\,R(|n+1|d)\rangle$, and R_0 is identified with the metal–ligand bond distance.

In the case of a $nd \rightarrow nd$ vibronically allowed electronic transition, explicit evaluation of both the total oscillator strength and relative vibronic intensity distribution have been carried out [1, 5, 9, 11, 14] and a fair agreement with experiment has been achieved.

With regards to $nf - nf$ electronic transitions, several calculations can be found in the literature [7, 8, 12, 13, 16–19]. In all of these, the crystal component has been evaluated by using a closure procedure for the central metal–ion's wavefunctions. As it has been pointed out, earlier on in the text, when this approach is adopted the nature of the intermediate electronic states becomes totally irrelevant to the evaluation of the transition dipole moment, except on the choice of the so-called effective energy gap, ΔE, although, in the Faulker–Richardson model intensity for the lanthanide complexes, the closure procedure is employed in the static coupling calculations, but special attention is paid to the nature of the intermediate states ($5d$ versus ng). This follows from Judd's treatment of $4f-4f$ electric dipoles intensities [7, 12, 13]. On the other hand in the Liehr and Ballhausen's approach the intermediate electronic states $|\Gamma_i\gamma_i\rangle$, see Eq. (20) are considered explicitly in the calculation of the transition dipole moment,

In principle, the summation in Eq. (20) should be carried out over all those states with parity other than the terminal electronic states involved in the transition. In this work, we have truncated the above mentioned summation so as to include only $(n+1)d$ electronic states of the central ion. Some $f-d$ energy gaps have been measured and reported in literature [33–35].

Once the vibronic matrix elements, defined by Eq. (21) are known, the next step in the calculation is to replace the symmetry coordinates S_{kt} by the normal coordinates Q_{kt} of the molecular system, in question. This procedure has already been discussed in the text in connection with the Koide and Pryce's method of calculation. Finally, it can easily be shown that the total oscillator strength, shall also depend on the explicit value of the oscillator strength associated with the parity allowed $nf \rightarrow (n+1)d$ electronic transition [1, 5, 11, 14].

5. Appendix I

Symmetry adapted octahedral wavefunctions ($J=7$)

$$|A_2a_2\rangle=\frac{\sqrt{33}}{12}(|76\rangle-|7-6\rangle)+\frac{\sqrt{39}}{12}(|72\rangle-|7-2\rangle)$$

$$|E\theta\rangle=\frac{1}{\sqrt{2}}(|74\rangle-|7-4\rangle)$$

$$|E\varepsilon\rangle=\frac{\sqrt{39}}{12}(-|76\rangle+|7-6\rangle)+\frac{\sqrt{33}}{12}(|72\rangle-|7-2\rangle)$$

$$|{}^aT_11\rangle=-\frac{\sqrt{91}}{32}|7-7\rangle+\frac{\sqrt{11}}{32}|7-3\rangle-\frac{3\sqrt{33}}{32}|71\rangle+\frac{25}{32}|75\rangle$$

$$|{}^aT_10\rangle=\frac{1}{\sqrt{2}}(|74\rangle+|7-4\rangle)$$

$$|{}^aT_1-1\rangle=-\frac{\sqrt{91}}{32}|77\rangle+\frac{\sqrt{11}}{32}|73\rangle-\frac{3\sqrt{33}}{32}|7-1\rangle+\frac{25}{32}|7-5\rangle$$

$$|{}^bT_11\rangle=-\frac{\sqrt{429}}{32}|7-7\rangle-\frac{3\sqrt{21}}{32}|7-3\rangle-\frac{5\sqrt{7}}{32}|71\rangle-\frac{\sqrt{231}}{32}|75\rangle$$

$$|{}^bT_10\rangle=|70\rangle$$

$$|{}^bT_1-1\rangle=-\frac{\sqrt{429}}{32}|77\rangle-\frac{3\sqrt{21}}{32}|73\rangle-\frac{5\sqrt{7}}{32}|7-1\rangle-\frac{\sqrt{231}}{32}|7-5\rangle$$

$$|{}^aT_21\rangle=-\frac{\sqrt{7}}{32\sqrt{2}}|73\rangle+\frac{3\sqrt{143}}{32\sqrt{2}}|73\rangle+\frac{\sqrt{429}}{32\sqrt{2}}|7-1\rangle+\frac{5\sqrt{13}}{32\sqrt{2}}|7-5\rangle$$

$$|{}^aT_20\rangle=\frac{1}{\sqrt{2}}(|76\rangle+|7-6\rangle)$$

$$|{}^aT_2-1\rangle=-\frac{\sqrt{7}}{32\sqrt{2}}|7-7\rangle-\frac{3\sqrt{143}}{32\sqrt{2}}|7-3\rangle+\frac{\sqrt{429}}{32\sqrt{2}}|71\rangle+\frac{5\sqrt{13}}{32\sqrt{2}}|75\rangle$$

$$|{}^bT_21\rangle=-\frac{\sqrt{1001}}{32\sqrt{2}}|77\rangle+\frac{19}{32\sqrt{2}}|73\rangle+\frac{15\sqrt{3}}{32\sqrt{2}}|7-1\rangle+\frac{\sqrt{11}}{32\sqrt{2}}|7-5\rangle$$

$$|{}^bT_20\rangle=\frac{1}{\sqrt{2}}(|72\rangle+|7-2\rangle)$$

$$|{}^bT_2-1\rangle=-\frac{\sqrt{1001}}{32\sqrt{2}}|7-7\rangle+\frac{19}{32\sqrt{2}}|7-3\rangle+\frac{15\sqrt{3}}{32\sqrt{2}}|71\rangle+\frac{\sqrt{11}}{32\sqrt{2}}|75\rangle$$

6. Appendix II

Crystal field geometrical factors (point charge approximation)

To utilize the tables, observe that $A^k_{\pm q} = (C^k_q \pm C^k_{-q}) R_L^{-(k+1)}$ and $A^k_0 = C^k_0 R_L^{-(k-1)}$, where the C^k_q stands for the standard Racah's tensor operators.

Table 1. Dipole–point charge interaction

$G^L_{\Gamma\gamma}$	A^1_{+1}	A^1_0	A^1_{-1}
T_1X	0	0	$\frac{i}{\sqrt{2}}$
T_1Y	$\frac{1}{\sqrt{2}}$	0	0
T_1Z	0	$-i$	0

Table 2. Electron quadrupole–point charge interaction

$G^L_{\Gamma\gamma}$	A^2_{+2}	A^2_{+1}	A^2_0	A^2_{-1}	A^2_{-2}
$E\varepsilon$	$-\frac{1}{\sqrt{2}}$	0	0	0	0
$E\theta$	0	0	-1	0	0
T_2X	0	$-\frac{i}{\sqrt{2}}$	0	0	0
T_2Y	0	0	0	$\frac{1}{\sqrt{2}}$	0
T_2Z	0	0	0	0	$\frac{i}{\sqrt{2}}$

Table 3. Electric octapole–point charge interaction

$G^L_{\Gamma\gamma}$	A^3_{+3}	A^3_{+2}	A^3_{+1}	A^3_0	A^3_{-1}	A^3_{-2}	A^3_{-3}
A_2a_2	0	0	0	0	0	$+\frac{1}{\sqrt{2}}$	0
T_1X	0	0	0	0	$-\frac{i\sqrt{3}}{4}$	0	$+\frac{i\sqrt{5}}{4}$
T_1Y	$-\frac{\sqrt{5}}{4}$	0	$-\frac{\sqrt{3}}{4}$	0	0	0	0
T_1Z	0	0	0	$-i$	0	0	0
T_2X	0	0	0	0	$-\frac{i\sqrt{5}}{4}$	0	$-\frac{i\sqrt{3}}{4}$
T_2Y	$-\frac{\sqrt{3}}{4}$	0	$+\frac{\sqrt{5}}{4}$	0	0	0	0
T_2Z	0	$-\frac{i}{\sqrt{2}}$	0	0	0	0	0

Table 4. Electric hexadecapole–point charge interaction

$G^L_{\Gamma\gamma}$	A^4_{+4}	A^4_{+3}	A^4_{+2}	A^4_{+1}	A^4_0	A^4_{-1}	A^4_{-2}	A^4_{-3}	A^4_{-4}
A_1a_1	$-\frac{\sqrt{5}}{2\sqrt{6}}$	0	0	0	$-\frac{\sqrt{7}}{2\sqrt{3}}$	0	0	0	0
$E\theta$	$-\frac{\sqrt{7}}{2\sqrt{6}}$	0	0	0	$+\frac{\sqrt{5}}{2\sqrt{3}}$	0	0	0	0
$E\varepsilon$	0	0	$-\frac{1}{\sqrt{2}}$	0	0	0	0	0	0
T_1X	0	$+\frac{i}{4}$	0	$+\frac{i\sqrt{7}}{4}$	0	0	0	0	0
T_1Y	0	0	0	0	0	$+\frac{\sqrt{7}}{4}$	0	$-\frac{1}{4}$	0
T_1Z	0	0	0	0	0	0	0	0	$+\frac{i}{\sqrt{2}}$
T_2X	0	$-\frac{i\sqrt{7}}{4}$	0	$+\frac{i}{4}$	0	0	0	0	0
T_2Y	0	0	0	0	0	$-\frac{1}{4}$	0	$-\frac{\sqrt{7}}{4}$	0
T_2Z	0	0	0	0	0	0	$+\frac{i}{\sqrt{2}}$	0	0

Table 5. 2^5 multipole–point charge interaction

$G^L_{\Gamma\gamma}$	A^5_{+5}	A^5_{+4}	A^5_{+3}	A^5_{+2}	A^5_{+1}	A^5_0	A^5_{-1}	A^5_{-2}	A^5_{-3}	A^5_{-4}	A^5_{-5}
$E\theta$	0	0	0	0	0	0	0	0	0	$+\frac{1}{\sqrt{2}}$	0
$E\varepsilon$	0	0	0	0	0	0	0	$-\frac{1}{\sqrt{2}}$	0	0	0
aT_1X	0	0	0	0	0	0	$+\frac{i\sqrt{30}}{16}$	0	$-\frac{i\sqrt{35}}{16}$	0	$+\frac{i3\sqrt{7}}{16}$
${}^aT_1Y$	$+\frac{3\sqrt{7}}{16}$	0	$+\frac{\sqrt{35}}{16}$	0	$+\frac{\sqrt{30}}{16}$	0	0	0	0	0	0
${}^aT_1Z$	0	0	0	0	0	$-i$	0	0	0	0	0
${}^bT_1X$	0	0	0	0	0	0	$+\frac{i\sqrt{42}}{16}$	0	$+\frac{9i}{16}$	0	$+\frac{i\sqrt{5}}{16}$
${}^bT_1Y$	$+\frac{\sqrt{5}}{16}$	0	$-\frac{9}{16}$	0	$+\frac{\sqrt{42}}{16}$	0	0	0	0	0	0
${}^bT_1Z$	0	$-\frac{i}{\sqrt{2}}$	0	0	0	0	0	0	0	0	0
T_2X	0	0	0	0	0	0	$+\frac{i\sqrt{14}}{8}$	0	$-\frac{i\sqrt{3}}{8}$	0	$-\frac{i\sqrt{15}}{8}$
T_2Y	$+\frac{\sqrt{15}}{8}$	0	$-\frac{\sqrt{3}}{8}$	0	$-\frac{\sqrt{14}}{8}$	0	0	0	0	0	0
T_2Z	0	0	0	$-\frac{i}{\sqrt{2}}$	0	0	0	0	0	0	0

Table 6. 2^6 multipole-point charge interaction.

$G^L_{\Gamma\gamma}$	A^6_{+6}	A^6_{+5}	A^6_{+4}	A^6_{+3}	A^6_{+2}	A^6_{+1}	A^6_0	A^6_{-1}	A^6_{-2}	A^6_{-3}	A^6_{-4}	A^6_{-5}	A^6_{-6}
A_1a_1	0	0	$+\frac{\sqrt{7}}{4}$	0	0	0	$-\frac{1}{2\sqrt{2}}$	0	0	0	0	0	0
A_2a_2	$+\frac{\sqrt{5}}{4\sqrt{2}}$	0	0	0	$-\frac{\sqrt{11}}{4\sqrt{2}}$	0	0	0	0	0	0	0	0
$E\theta$	0	0	$-\frac{1}{4}$	0	0	0	$-\frac{\sqrt{7}}{2\sqrt{2}}$	0	0	0	0	0	0
$E\varepsilon$	$-\frac{\sqrt{11}}{4\sqrt{2}}$	0	0	0	$-\frac{\sqrt{5}}{4\sqrt{2}}$	0	0	0	0	0	0	0	0
T_1X	0	$+\frac{i\sqrt{22}}{8\sqrt{2}}$	0	$+\frac{i\sqrt{30}}{8\sqrt{2}}$	0	$-\frac{i\sqrt{3}}{4\sqrt{2}}$	0	0	0	0	0	0	0
T_1Y	0	0	0	0	0	0	0	$-\frac{\sqrt{3}}{4\sqrt{2}}$	0	$-\frac{\sqrt{30}}{8\sqrt{2}}$	0	$+\frac{\sqrt{22}}{8\sqrt{2}}$	0

T_1Z	0	0	0	0	0	0	0	0	0	0	$+\frac{i}{\sqrt{2}}$	0	0
^aT_2X	0	$-\frac{i\sqrt{165}}{16\sqrt{2}}$	0	$+\frac{i9}{16\sqrt{2}}$	0	$-\frac{i\sqrt{10}}{16\sqrt{2}}$	0	0	0	0	0	0	0
^aT_2Y	0	0	0	0	0	0	0	$+\frac{\sqrt{10}}{16\sqrt{2}}$	0	$+\frac{9}{16\sqrt{2}}$	0	$+\frac{\sqrt{165}}{16\sqrt{2}}$	0
^aT_2Z	0	0	0	0	0	0	0	0	$+\frac{i}{\sqrt{2}}$	0	0	0	0
^bT_2X	0	$-\frac{i\sqrt{3}}{16\sqrt{2}}$	0	$-\frac{i\sqrt{55}}{16\sqrt{2}}$	0	$-\frac{i3\sqrt{22}}{16\sqrt{2}}$	0	0	0	0	0	0	0
^bT_2Y	0	0	0	0	0	0	0	$+\frac{3\sqrt{22}}{16\sqrt{2}}$	0	$-\frac{\sqrt{55}}{16\sqrt{2}}$	0	$+\frac{\sqrt{3}}{16\sqrt{2}}$	0
^bT_2Z	0	0	0	0	0	0	0	0	0	0	0	0	$+\frac{i}{\sqrt{2}}$

Table 7. 2^7 multipole–point charge interaction

$G^L_{\Gamma\gamma}$	A^7_{+7}	A^7_{+6}	A^7_{+5}	A^7_{+4}	A^7_{+3}	A^7_{+2}	A^7_{+1}	A^7_0	A^7_{-1}	A^7_{-2}	A^7_{-3}	A^7_{-4}	A^7_{-5}	A^7_{-6}	A^7_{-7}
A_2a_2	0	0	0	0	0	0	0	0	0	$+\frac{\sqrt{39}}{12}$	0	0	0	$+\frac{\sqrt{33}}{12}$	0
$E\theta$	0	0	0	0	0	0	0	0	0	0	0	$+\frac{1}{\sqrt{2}}$	0	0	0
$E\varepsilon$	0	0	0	0	0	0	0	0	0	$+\frac{\sqrt{33}}{12}$	0	0	0	$-\frac{\sqrt{39}}{12}$	0
${}^aT_1X$	0	0	0	0	0	0	0	0	$-\frac{i3\sqrt{33}}{32\sqrt{2}}$	0	$-\frac{i\sqrt{11}}{32\sqrt{2}}$	0	$+\frac{i25}{32\sqrt{2}}$	0	$+\frac{i\sqrt{91}}{32\sqrt{2}}$
${}^aT_1Y$	$-\frac{\sqrt{91}}{32\sqrt{2}}$	0	$+\frac{25}{32\sqrt{2}}$	0	$+\frac{\sqrt{11}}{32\sqrt{2}}$	0	$-\frac{3\sqrt{33}}{32\sqrt{2}}$	0	0	0	0	0	0	0	0
${}^aT_1Z$	0	0	0	$-\frac{i}{\sqrt{2}}$	0	0	0	0	0	0	0	0	0	0	0
${}^bT_1X$	0	0	0	0	0	0	0	0	$-\frac{i5\sqrt{7}}{32\sqrt{2}}$	0	$+\frac{i3\sqrt{21}}{32\sqrt{2}}$	0	$-\frac{i\sqrt{231}}{32\sqrt{2}}$	0	$+\frac{i\sqrt{429}}{32\sqrt{2}}$

${}^bT_1Y$	$-\frac{\sqrt{429}}{32\sqrt{2}}$	0	$-\frac{\sqrt{231}}{32\sqrt{2}}$	0	$-\frac{3\sqrt{21}}{32\sqrt{2}}$	0	$-\frac{5\sqrt{7}}{32\sqrt{2}}$	0	0	0	0	0	0	0	0
${}^bT_1Z$	0	0	0	0	0	0	0	$-i$	0	0	0	0	0	0	0
${}^aT_2X$	0	0	0	0	0	0	0	0	$-\frac{i\sqrt{429}}{64}$	0	$-\frac{i3\sqrt{143}}{64}$	0	$-\frac{i5\sqrt{13}}{64}$	0	$-\frac{i\sqrt{7}}{64}$
${}^aT_2Y$	$-\frac{\sqrt{7}}{64}$	0	$+\frac{5\sqrt{13}}{64}$	0	$-\frac{3\sqrt{143}}{64}$	0	$+\frac{\sqrt{429}}{64}$	0	0	0	0	0	0	0	0
${}^aT_2Z$	0	$-\frac{i}{\sqrt{2}}$	0	0	0	0	0	0	0	0	0	0	0	0	0
${}^bT_2X$	0	0	0	0	0	0	0	0	$-\frac{i15\sqrt{3}}{64}$	0	$+\frac{i19}{64}$	0	$-\frac{i\sqrt{11}}{64}$	0	$-\frac{i\sqrt{1001}}{64}$
${}^bT_2Y$	$-\frac{\sqrt{1001}}{64}$	0	$+\frac{\sqrt{11}}{64}$	0	$+\frac{19}{64}$	0	$+\frac{15\sqrt{3}}{64}$	0	0	0	0	0	0	0	0
${}^bT_2Z$	0	0	0	0	0	$-\frac{i}{\sqrt{2}}$	0	0	0	0	0	0	0	0	0

7. Appendix III

Vibronic crystal field coefficients for $\Gamma = T_{1u}$, T_{2u} and $J = 1, 3, 5, 7$, in units of $R_0^{-(J+2)}$. Here, R_0 is identified with the metal–ligand, bond distance.

J	$\tau_{1u}(\nu_3)$	$\tau_{1u}(\nu_4)$	$\tau_{2u}(\nu_6)$
1	T_1, X $A_{3c} = i2\sqrt{2}$	T_1, X $A_{4c} = -i2$	0
	T_1, Y $A_{3b} = i2\sqrt{2}$	T_1, Y $A_{4b} = -i2$	0
	T_1, Z $A_{3a} = i2\sqrt{2}$	T_1, Z $A_{4a} = -i2$	0
3	T_1, X $A_{3c} = i4\sqrt{2}$	T_1, X $A_{4c} = i3$	T_2, X $A_{6c} = -i\sqrt{15}$
	T_1, Y $A_{3b} = i4\sqrt{2}$	T_1, Y $A_{4b} = i3$	T_2, Y $A_{6b} = -i\sqrt{15}$
	T_1, Z $A_{3a} = i4\sqrt{2}$	T_1, Z $A_{4a} = i3$	T_2, Z $A_{6a} = -i\sqrt{15}$
5	$^aT_1, X$ $A_{3c} = i6\sqrt{2}$	$^aT_1, X$ $A_{4c} = -i\frac{15}{4}$	T_2, X $A_{6c} = i\frac{\sqrt{105}}{2}$
	$^aT_1, Y$ $A_{3b} = i6\sqrt{2}$	$^aT_1, Y$ $A_{4b} = -i\frac{15}{4}$	T_2, Y $A_{6b} = i\frac{\sqrt{105}}{2}$
	$^aT_1, Z$ $A_{3a} = i6\sqrt{2}$	$^aT_1, Z$ $A_{4a} = -i\frac{15}{4}$	T_2, Z $A_{6a} = i\frac{\sqrt{105}}{2}$
		$^bT_1, X$ $A_{4c} = -i\frac{3\sqrt{35}}{4}$	
		$^bT_1, Y$ $A_{4b} = -i\frac{3\sqrt{35}}{4}$	
		$^bT_1, Z$ $A_{4a} = -i\frac{3\sqrt{35}}{4}$	
7	$^bT_1, X$ $A_{3c} = i8\sqrt{2}$	$^aT_1, X$ $A_{4c} = i\frac{3\sqrt{231}}{8}$	$^aT_2, X$ $A_{6c} = -i\frac{\sqrt{6006}}{16}$
	$^bT_1, Y$ $A_{3b} = i8\sqrt{2}$	$^aT_1, Y$ $A_{4b} = i\frac{3\sqrt{231}}{8}$	$^aT_2, Y$ $A_{6b} = -i\frac{\sqrt{6006}}{16}$
	$^bT_1, Z$ $A_{3a} = i8\sqrt{2}$	$^aT_1, Z$ $A_{4a} = i\frac{3\sqrt{231}}{8}$	$^aT_2, Z$ $A_{6a} = -i\frac{\sqrt{6006}}{16}$

J	$\tau_{1u}(\nu_3)$	$\tau_{1u}(\nu_4)$	$\tau_{2u}(\nu_6)$
		${}^bT_1, X$	${}^bT_2, X$
		$A_{4c} = i\frac{35}{8}$	$A_{6c} = -i\frac{15\sqrt{42}}{16}$
		${}^bT_1, Y$	${}^bT_2, Y$
		$A_{4b} = i\frac{35}{8}$	$A_{6b} = -i\frac{15\sqrt{42}}{16}$
		${}^bT_1, Z$	${}^bT_2, Z$
		$A_{4a} = i\frac{35}{8}$	$A_{6a} = -i\frac{15\sqrt{42}}{16}$

8. Appendix IV

Symmetry adapted complex components of the central metal–ion, electric multipoles, for $J = 1, 3, 5, 7$ and $\Gamma = T_1, T_2$.

$$B^k_{\pm q} = \frac{1}{\sqrt{2}}(\mp D^k_q + D^k_{-q})$$

$$B^k_0 = D^k_0$$

J	Central metal–ion, multipoles complex components
1	$M^{T_1}_X = -iB^1_{+1}$ $M^{T_1}_Y = +B^1_{-1}$ $M^{T_1}_Z = -iB^1_0$
3	$M^{T_1}_X = -i\frac{\sqrt{10}}{4}B^3_{+3} + i\frac{\sqrt{6}}{4}B^3_{+1}$ $M^{T_1}_Y = -\frac{\sqrt{10}}{4}B^3_{-3} - \frac{\sqrt{6}}{4}B^3_{-1}$ $M^{T_1}_Z = -iB^3_0$ $M^{T_2}_X = +i\frac{\sqrt{6}}{4}B^3_{+3} + i\frac{\sqrt{10}}{4}B^3_{+1}$ $M^{T_2}_Y = -\frac{\sqrt{6}}{4}B^3_{-3} + \frac{\sqrt{10}}{4}B^3_{-1}$ $M^{T_2}_Z = -iB^3_{-2}$
5	$M^{aT_1}_X = -i\frac{3\sqrt{14}}{16}B^5_{+5} + i\frac{\sqrt{70}}{16}B^5_{+3} - i\frac{2\sqrt{15}}{16}B^5_{+1}$ $M^{aT_1}_Y = +\frac{3\sqrt{14}}{16}B^5_{-5} + \frac{\sqrt{70}}{16}B^5_{-3} + \frac{2\sqrt{15}}{16}B^5_{-1}$ $M^{aT_1}_Z = -iB^5_0$ $M^{bT_1}_X = -i\frac{\sqrt{10}}{16}B^5_{+5} - i\frac{9\sqrt{2}}{16}B^5_{+3} - i\frac{2\sqrt{21}}{16}B^5_{+1}$

J	Central metal–ion, multipoles complex components
	$M_{Y}^{{}^{b}T_{1}} = +\frac{\sqrt{10}}{16}B^{5}_{-5} - \frac{9\sqrt{2}}{16}B^{5}_{-3} + \frac{2\sqrt{21}}{16}B^{5}_{-1}$
	$M_{Z}^{{}^{b}T_{1}} = -iB^{5}_{-4}$
	$M_{X}^{T_{2}} = +i\frac{\sqrt{30}}{8}B^{5}_{+5} + i\frac{\sqrt{6}}{8}B^{5}_{+3} - i\frac{2\sqrt{7}}{8}B^{5}_{+1}$
	$M_{Y}^{T_{2}} = +\frac{\sqrt{30}}{8}B^{5}_{-5} - \frac{\sqrt{6}}{8}B^{5}_{-3} - \frac{2\sqrt{7}}{8}B^{5}_{-1}$
	$M_{Z}^{T_{2}} = -iB^{5}_{-2}$
7	$M_{X}^{{}^{a}T_{1}} = -i\frac{\sqrt{91}}{32}B^{7}_{+7} - i\frac{25}{32}B^{7}_{+5} + i\frac{\sqrt{11}}{32}B^{7}_{+3} + i\frac{3\sqrt{33}}{32}B^{7}_{+1}$
	$M_{Y}^{{}^{a}T_{1}} = -\frac{\sqrt{91}}{32}B^{7}_{-7} + \frac{25}{32}B^{7}_{-5} + \frac{\sqrt{11}}{32}B^{7}_{-3} - \frac{3\sqrt{33}}{32}B^{7}_{-1}$
	$M_{Z}^{{}^{a}T_{1}} = -iB^{7}_{-4}$
	$M_{X}^{{}^{b}T_{1}} = -i\frac{\sqrt{429}}{32}B^{7}_{+7} + i\frac{\sqrt{231}}{32}B^{7}_{+5} - i\frac{3\sqrt{21}}{32}B^{7}_{+3} + i\frac{5\sqrt{7}}{32}B^{7}_{+1}$
	$M_{Y}^{{}^{b}T_{1}} = -\frac{\sqrt{429}}{32}B^{7}_{-7} - \frac{\sqrt{231}}{32}B^{7}_{-5} - \frac{3\sqrt{21}}{32}B^{7}_{-3} - \frac{5\sqrt{7}}{32}B^{7}_{-1}$
	$M_{Z}^{{}^{b}T_{1}} = -iB^{7}_{0}$
	$M_{X}^{{}^{a}T_{2}} = +i\frac{\sqrt{14}}{64}B^{7}_{+7} + i\frac{5\sqrt{26}}{64}B^{7}_{+5} + i\frac{3\sqrt{286}}{64}B^{7}_{+3} + i\frac{\sqrt{858}}{64}B^{7}_{+1}$
	$M_{Y}^{{}^{a}T_{2}} = -\frac{\sqrt{14}}{64}B^{7}_{-7} + \frac{5\sqrt{26}}{64}B^{7}_{-5} - \frac{3\sqrt{286}}{64}B^{7}_{-3} + \frac{\sqrt{858}}{64}B^{7}_{-1}$
	$M_{Z}^{{}^{a}T_{2}} = -iB^{7}_{-6}$
	$M_{X}^{{}^{b}T_{2}} = +i\frac{\sqrt{2002}}{64}B^{7}_{+7} + i\frac{\sqrt{22}}{64}B^{7}_{+5} - i\frac{19\sqrt{2}}{64}B^{7}_{+3} + i\frac{15\sqrt{6}}{64}B^{7}_{+1}$
	$M_{Y}^{{}^{b}T_{2}} = -\frac{\sqrt{2002}}{64}B^{7}_{-7} + \frac{\sqrt{22}}{64}B^{7}_{-5} + \frac{19\sqrt{2}}{64}B^{7}_{-3} + \frac{15\sqrt{6}}{64}B^{7}_{-1}$
	$M_{Z}^{{}^{b}T_{2}} = -iB^{7}_{-2}$

9. Appendix V

Symmetry adapted vibronic operators[1]

The Koide and Pryce Method. A point charge approximation. A ML$_6$ octahedral cluster (In units of e)

$$\gamma_k = \frac{qe^2 r^k}{R_0^{k+1}}$$

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[1] The Kets $|\Gamma\gamma\rangle_{J=2,4,6}$ are given by Griffith [20], in Table A-19, as linear combinations of the kets $|JM\rangle$. To utilize, Appendix V, we write the identity: $|JM\rangle = C^J_M$, where the C^J_M are the standard Racah's tensor operators

i) A_1-symmetry

$$O_{a_1}^{A_1}(3)=\frac{2\sqrt{6}}{3}\gamma_2+\frac{8\sqrt{14}}{7}\gamma_4|A_1a_1\rangle_{J=4}+\left\{\frac{15\sqrt{14}}{11}|A_1a_1\rangle_{J=4}\right.$$

$$\left.+\frac{18\sqrt{3}}{11}|A_1a_1\rangle_{J=6}\right\}\gamma_6+\frac{28\sqrt{3}}{15}\gamma_8|A_1a_1\rangle_{J=6}+\cdots$$

$$O_{a_1}^{A_1}(4)=-\frac{2\sqrt{3}}{3}\gamma_2+\frac{6\sqrt{7}}{7}\gamma_4|A_1a_1\rangle_{J=4}+\left\{-\frac{15\sqrt{7}}{11}|A_1a_1\rangle_{J=4}\right.$$

$$\left.+\frac{15\sqrt{6}}{22}|A_1a_1\rangle_{J=6}\right\}\gamma_6-\frac{14\sqrt{6}}{15}\gamma_8|A_1a_1\rangle_{J=6}+\cdots$$

$$O_{a_1}^{A_1}(6)=0.$$

ii) A_2-symmetry

$$O_{a_2}^{A_2}(3)=0$$

$$A_{a_2}^{A_2}(4)=0$$

$$O_{a_2}^{A_2}(6)=\frac{3\sqrt{770}}{22}\gamma_6|A_2a_2\rangle_{J=6}-\frac{\sqrt{770}}{10}\gamma_8|A_2a_2\rangle_{J=6}+\cdots.$$

iii) E-symmetry:

$$O_{\varepsilon}^{E}(3)=-\frac{4\sqrt{3}}{3}\gamma_2|E\varepsilon\rangle_{J=2}+\left\{-\frac{12\sqrt{3}}{7}|E\varepsilon\rangle_{J=2}+\frac{8\sqrt{5}}{7}|E\varepsilon\rangle_{J=4}\right\}\gamma_4$$

$$+\left\{\frac{15\sqrt{5}}{11}|E\varepsilon\rangle_{J=4}-\frac{9\sqrt{42}}{11}|E\varepsilon\rangle_{J=6}\right\}\gamma_6-\frac{14\sqrt{42}}{15}\gamma_8|E\varepsilon\rangle_{J=6}+\cdots$$

$$O_{\varepsilon}^{E}(4)=\frac{2\sqrt{6}}{3}\gamma_2|E\varepsilon\rangle_{J=+2}\left\{-\frac{9\sqrt{6}}{14}|E\varepsilon\rangle_{J=2}+\frac{3\sqrt{10}}{7}|E\varepsilon\rangle_{J=4}\right\}\gamma_4$$

$$+\left\{-\frac{3\sqrt{10}}{44}|E\varepsilon\rangle_{J=4}+\frac{15\sqrt{21}}{22}|E\varepsilon\rangle_{J=6}\right\}\gamma_6-\frac{43\sqrt{21}}{60}\gamma_8|E\varepsilon\rangle_{J=6}+\cdots$$

$$O_{\varepsilon}^{E}(6)=\left\{\frac{15\sqrt{2}}{14}|E\varepsilon\rangle_{J=2}+\frac{3\sqrt{30}}{7}|E\varepsilon\rangle_{J=4}\right\}\gamma_4-\left\{\frac{21\sqrt{30}}{44}|E\varepsilon\rangle_{J=4}\right.$$

$$\left.+\frac{15\sqrt{7}}{22}|E\varepsilon\rangle_{J=6}\right\}\gamma_6+\frac{23\sqrt{7}}{20}\gamma_8|E\varepsilon\rangle_{J=6}+\cdots.$$

iv) T_1-symmetry:

$$O_{Z}^{T_1}(3)=-\frac{4\sqrt{35}}{7}\gamma_4|T_1Z\rangle_{J=4}+\left\{\frac{6\sqrt{35}}{11}|T_1Z\rangle_{J=4}+\frac{9\sqrt{7}}{11}|T_1Z\rangle_{J=6}\right\}\gamma_6$$

$$-\frac{4\sqrt{7}}{5}\gamma_8|T_1Z\rangle_{J=6}+\cdots$$

$$O_Z^{T_1}(4) = -\frac{3\sqrt{70}}{14}\gamma_4|T_1Z\rangle_{J=4} + \left\{-\frac{3\sqrt{70}}{11}|T_1Z\rangle_{J=4} + \frac{15\sqrt{14}}{44}|T_1Z\rangle_{J=6}\right\}\gamma_6$$

$$+\left\{\frac{2\sqrt{14}}{5}\gamma_8|T_1Z\rangle_{J=6} + \cdots\right.$$

$$O_Z^{T_1}(6) = O_Z^{T_1}(4).$$

v) T_2-symmetry:

$$O_Z^{T_2}(3) = -\frac{4\sqrt{3}}{3}\gamma_2|T_2Z\rangle_{J=2} + \left\{\frac{8\sqrt{3}}{7}|T_2Z\rangle_{J=2} + \frac{4\sqrt{5}}{7}|T_2Z\rangle_{J=4}\right\}\gamma_4$$

$$-\left\{\frac{6\sqrt{5}}{11}|T_2Z\rangle_{J=4} + \frac{3\sqrt{210}}{44}|{}^aT_2Z\rangle_{J=6} + \frac{9\sqrt{462}}{44}|{}^bT_2Z\rangle_{J=6}\right\}\gamma_6$$

$$+\left\{\frac{\sqrt{210}}{15}|{}^aT_2Z\rangle_{J=6} + \frac{\sqrt{462}}{5}|{}^bT_2Z\rangle_{J=6}\right\}\gamma_8 + \cdots$$

$$O_Z^{T_2}(4) = \frac{2\sqrt{6}}{3}\gamma_2|T_2Z\rangle_{J=2} + \left\{\frac{3\sqrt{6}}{7}|T_2Z\rangle_{J=2} + \frac{3\sqrt{10}}{14}|T_2Z\rangle_{J=4}\right\}\gamma_4$$

$$+\left\{-\frac{6\sqrt{10}}{11}|T_2Z\rangle_{J=4} + \frac{21\sqrt{105}}{88}|{}^aT_2Z\rangle_{J=6} + \frac{15\sqrt{231}}{88}|{}^bT_2Z\rangle_{J=6}\right\}\gamma_6$$

$$+\left(-\frac{\sqrt{105}}{15}|{}^aT_2Z\rangle_{J=6} + \frac{\sqrt{231}}{5}|{}^bT_2Z\rangle_{J=6}\right\}\gamma_8 + \cdots$$

$$O_Z^{T_2}(6) = \left\{\frac{5\sqrt{6}}{7}|T_2Z\rangle_{J=2} - \frac{9\sqrt{10}}{14}|T_2Z\rangle_{J=4}\right\}\gamma_4$$

$$+\left\{-\frac{\sqrt{105}}{8}|{}^aT_2Z\rangle_{J=6} + \frac{15\sqrt{231}}{88}|{}^bT_2Z\rangle_{J=6}\right\}\gamma_6$$

$$+\left\{\frac{\sqrt{105}}{5}|{}^aT_2Z\rangle_{J=6} + \frac{\sqrt{231}}{5}|{}^bT_2Z\rangle_{J=6}\right\}\gamma_8 + \cdots.$$

10. Appendix VI

Non-zero vibronic crystal field, reduced matrix elements. Closure procedure. Point charge model. A ML_6 octahedral cluster.

$$\langle\gamma_k\rangle = \frac{qe^2\langle r^k\rangle}{R_0^{k+1}} \quad \text{(In units of } e\text{).}$$

10.1 *d−d Excitations*

i) A_1-symmetry

$$\langle dE||O^{A_1}(3)||dE\rangle = \sqrt{3}\left(\tfrac{4}{3}\langle\gamma_2\rangle + \tfrac{16}{21}\langle\gamma_4\rangle + \tfrac{10}{11}\langle\gamma_6\rangle\right)$$

$$\langle dE||O^{A_1}(4)||dE\rangle=\sqrt{6}(-\tfrac{2}{3}\langle\gamma_2\rangle+\tfrac{2}{7}\langle\gamma_4\rangle-\tfrac{5}{11}\langle\gamma_6\rangle)$$

$$\langle dT_2||O^{A_1}(3)||dT_2\rangle=\sqrt{2}(2\langle\gamma_2\rangle-\tfrac{16}{21}\langle\gamma_4\rangle-\tfrac{10}{11}\langle\gamma_6\rangle)$$

$$\langle dT_2||O^{A_1}(4)||dT_2\rangle=(-2\langle\gamma_2\rangle-\tfrac{4}{7}\langle\gamma_4\rangle+\tfrac{10}{11}\langle\gamma_6\rangle).$$

ii) A_2-symmetry: They all vanish.

iii) E-symmetry:

$$\langle dE||O^{E}(3)||dE\rangle=\sqrt{3}(\tfrac{16}{21}\langle\gamma_2\rangle+\tfrac{32}{21}\langle\gamma_4\rangle+\tfrac{50}{77}\langle\gamma_6\rangle)$$

$$\langle dE||O^{E}(4)||dE\rangle=\sqrt{6}(-\tfrac{8}{21}\langle\gamma_2\rangle+\tfrac{4}{7}\langle\gamma_4\rangle-\tfrac{5}{154}\langle\gamma_6\rangle)$$

$$\langle dE||O^{E}(6)||dE\rangle=-\frac{15\sqrt{2}}{22}\langle\gamma_6\rangle$$

$$\langle dT_2||O^{E}(3)||dT_2\rangle=(-\tfrac{8}{7}\langle\gamma_2\rangle-\tfrac{8}{21}\langle\gamma_4\rangle+\tfrac{100}{77}\langle\gamma_6\rangle)$$

$$\langle dT_2||O^{E}(4)||dT_2\rangle=\sqrt{2}(\tfrac{4}{7}\langle\gamma_2\rangle-\tfrac{1}{7}\langle\gamma_4\rangle-\tfrac{5}{77}\langle\gamma_6\rangle)$$

$$\langle dT_2||O^{E}(6)||dT_2\rangle=\left(\frac{5\sqrt{6}}{7}\langle\gamma_4\rangle-\frac{5\sqrt{6}}{11}\langle\gamma_6\rangle\right).$$

iv) T_1-symmetry:

$$\langle dE||O^{T_1}(3)||dT_2\rangle=\sqrt{3}(\tfrac{20}{21}\langle\gamma_4\rangle-\tfrac{10}{11}\langle\gamma_6\rangle)$$

$$\langle dE||O^{T_1}(4)||dT_2\rangle=\sqrt{6}(\tfrac{5}{14}\langle\gamma_4\rangle+\tfrac{5}{11}\langle\gamma_6\rangle)$$

$$\langle dE||O^{T_1}(6)||dT_2\rangle=\langle dE||O^{T_1}(4)||dT_2\rangle$$

$$\langle dT_2||O^{T_1}(3)||dE\rangle=-\langle dE||O^{t_1}(3)||dT_2\rangle$$

$$\langle dT_2||O^{T_1}(4)||dE\rangle=-\langle dE||O^{T_1}(4)||dT_2\rangle$$

$$\langle dT_2||O^{T_1}(6)||dE\rangle=-\langle dE||O^{T_1}(6)||dT_2\rangle.$$

v) T_2-symmetry:

$$\langle dE||O^{T_2}(3)||dT_2\rangle=(-\tfrac{8}{7}\langle\gamma_2\rangle+\tfrac{4}{7}\langle\gamma_4\rangle+\tfrac{30}{77}\langle\gamma_6\rangle)$$

$$\langle dE||O^{T_2}(4)||dT_2\rangle=\sqrt{2}(\tfrac{4}{7}\langle\gamma_2\rangle+\tfrac{3}{14}\langle\gamma_4\rangle+\tfrac{30}{77}\langle\gamma_6\rangle)$$

$$\langle dE||O^{T_2}(6)||dT_2\rangle=+\frac{15\sqrt{2}}{14}\langle\gamma_4\rangle$$

$$\langle dT_2||O^{T_2}(3)||dE\rangle=\langle dE||O^{T_2}(3)||dT_2\rangle$$

$$\langle dT_2||O^{T_2}(4)||dE\rangle=\langle dE||O^{T_2}(4)||dT_2\rangle$$

$$\langle dT_2||O^{T_2}(6)||dE\rangle=\langle dE||O^{T_2}(6)||dT_2\rangle$$

$$\langle dT_2||O^{T_2}(3)||dT_2\rangle=\sqrt{6}(\tfrac{4}{7}\langle\gamma_2\rangle-\tfrac{16}{21}\langle\gamma_4\rangle+\tfrac{20}{77}\langle\gamma_6\rangle)$$

$$\langle dT_2||O^{T_2}(4)||dT_2\rangle=\sqrt{3}(-\tfrac{4}{7}\langle\gamma_2\rangle-\tfrac{4}{7}\langle\gamma_4\rangle+\tfrac{40}{77}\langle\gamma_6\rangle)$$

10.2. f−f excitations

i) A_1-symmetry

$$\langle fA_2||O^{A_1}(3)||fA_2\rangle=\sqrt{6}(\tfrac{2}{3}\langle\gamma_2\rangle-\tfrac{16}{33}\langle\gamma_4\rangle-\tfrac{50}{143}\langle\gamma_6\rangle+\tfrac{112}{429}\langle\gamma_8\rangle)$$

$$\langle fA_2||O^{A_1}(4)||fA_2\rangle=\sqrt{3}(-\tfrac{2}{3}\langle\gamma_2\rangle-\tfrac{4}{11}\langle\gamma_4\rangle+\tfrac{10}{13}\langle\gamma_6\rangle-\tfrac{112}{429}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{A_1}(3)||fT_1\rangle=\sqrt{2}(2\langle\gamma_2\rangle+\tfrac{8}{11}\langle\gamma_4\rangle+\tfrac{15}{13}\langle\gamma_6\rangle+\tfrac{140}{429}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{A_1}(4)||fT_1\rangle=(-2\langle\gamma_2\rangle+\tfrac{6}{11}\langle\gamma_4\rangle-\tfrac{90}{143}\langle\gamma_6\rangle-\tfrac{140}{429}\langle\gamma_8\rangle)$$

$$\langle fT_2||O^{A_1}(3)||fT_2\rangle=\sqrt{2}(2\langle\gamma_2\rangle-\tfrac{8}{33}\langle\gamma_4\rangle-\tfrac{115}{143}\langle\gamma_6\rangle-\tfrac{84}{143}\langle\gamma_8\rangle)$$

$$\langle fT_2||O^{A_1}(4)||fT_2\rangle=(-2\langle\gamma_2\rangle-\tfrac{2}{11}\langle\gamma_4\rangle-\tfrac{20}{143}\langle\gamma_6\rangle+\tfrac{84}{143}\langle\gamma_8\rangle).$$

ii) A_2-symmetry

$$\langle fT_1||O^{A_2}(6)||fT_2\rangle=\sqrt{15}(\tfrac{35}{143}\langle\gamma_6\rangle-\tfrac{7}{39}\langle\gamma_8\rangle)$$

$$\langle fT_2||O^{A_2}(6)||fT_1\rangle=\langle fT_1||O^{A_2}(6)||fT_2\rangle$$

iii) E-symmetry

$$\langle fT_1||O^{E}(3)||fT_1\rangle=(\tfrac{16}{15}\langle\gamma_2\rangle+\tfrac{104}{55}\langle\gamma_4\rangle+\tfrac{375}{143}\langle\gamma_6\rangle+\tfrac{980}{429}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{E}(4)||fT_1\rangle=\sqrt{2}(-\tfrac{8}{15}\langle\gamma_2\rangle+\tfrac{39}{55}\langle\gamma_4\rangle-\tfrac{45}{52}\langle\gamma_6\rangle+\tfrac{1505}{1716}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{E}(6)||fT_1\rangle=\sqrt{6}(-\tfrac{1}{11}\langle\gamma_4\rangle+\tfrac{35}{572}\langle\gamma_6\rangle-\tfrac{805}{1716}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{E}(3)||fT_2\rangle=\sqrt{5}(\tfrac{8}{15}\langle\gamma_2\rangle+\tfrac{22}{55}\langle\gamma_4\rangle-\tfrac{75}{143}\langle\gamma_6\rangle-\tfrac{196}{429}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{E}(4)||fT_2\rangle=\sqrt{10}(-\tfrac{4}{15}\langle\gamma_2\rangle+\tfrac{12}{55}\langle\gamma_4\rangle+\tfrac{9}{52}\langle\gamma_6\rangle-\tfrac{301}{1716}\langle\gamma_8\rangle)$$

$$\langle fT_1||O^{E}(6)||fT_2\rangle=\sqrt{30}(-\tfrac{2}{11}\langle\gamma_4\rangle-\tfrac{7}{572}\langle\gamma_6\rangle+\tfrac{161}{1716}\langle\gamma_8\rangle)$$

$$\langle fT_2||O^{E}(3)||fT_1\rangle=-\langle fT_1||O^{E}(3)||fT_2\rangle$$

$$\langle fT_2||O^{E}(4)||fT_1\rangle=-\langle fT_1||O^{E}(4)||fT_2\rangle$$

$$\langle fT_2||O^{E}(6)||fT_1\rangle=-\langle fT_1||O^{E}(6)||fT_2\rangle$$

$$\langle fT_2||O^{E}(3)||fT_2\rangle=(-\tfrac{40}{33}\langle\gamma_4\rangle-\tfrac{35}{143}\langle\gamma_6\rangle+\tfrac{196}{143}\langle\gamma_8\rangle)$$

$$\langle fT_2||O^{E}(4)||fT_2\rangle=\sqrt{2}(-\tfrac{5}{11}\langle\gamma_4\rangle-\tfrac{245}{572}\langle\gamma_6\rangle+\tfrac{301}{572}\langle\gamma_8\rangle$$

$$\langle fT_2||O^{E}(6)||fT_2\rangle=\sqrt{6}(-\tfrac{5}{11}\langle\gamma_4\rangle+\tfrac{35}{52}\langle\gamma_6\rangle-\tfrac{161}{572}\langle\gamma_8\rangle.$$

iv) T_1-symmetry

$$\langle fA_2||O^{T_1}(3)||fT_2\rangle=\sqrt{3}(-\tfrac{20}{33}\langle\gamma_4\rangle+\tfrac{140}{143}\langle\gamma_6\rangle-\tfrac{56}{143}\langle\gamma_8\rangle)$$

$$\langle fA_2||O^{T_1}(4)||fT_2\rangle=\sqrt{6}(-\tfrac{5}{22}\langle\gamma_4\rangle-\tfrac{35}{286}\langle\gamma_6\rangle+\tfrac{28}{143}\langle\gamma_8\rangle)$$

$$\langle fA_2||O^{T_1}(6)||fT_2\rangle=\langle fA_2||O^{T_1}(4)||fT_2\rangle$$

$$\langle fT_1||O^{T_1}(3)||fT_2\rangle=\sqrt{10}(-\tfrac{4}{11}\langle\gamma_4\rangle+\tfrac{21}{143}\langle\gamma_6\rangle+\tfrac{28}{143}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_1}(4)||fT_2\rangle=\sqrt{5}(-\tfrac{3}{11}\langle\gamma_4\rangle-\tfrac{147}{286}\langle\gamma_6\rangle-\tfrac{28}{143}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_1}(6)||fT_2\rangle=\langle fT_1||O^{T_1}(4)||fT_2\rangle$$
$$\langle fT_2||O^{T_1}(3)||fA_2\rangle=\langle fA_2||O^{T_1}(3)||fT_2\rangle$$
$$\langle fT_2||O^{T_1}(4)||fA_2\rangle=\langle fA_2||O^{T_1}(4)||fT_2\rangle$$
$$\langle fT_2||O^{T_1}(6)||fA_2\rangle=\langle fA_2||O^{T_1}(6)||fT_2\rangle$$
$$\langle fT_2||O^{T_1}(3)||fT_1\rangle=\langle fT_1||O^{T_1}(3)||fT_2\rangle$$
$$\langle fT_2||O^{T_1}(4)||fT_1\rangle=\langle fT_1||O^{T_1}(4)||fT_2\rangle$$
$$\langle fT_2||O^{T_1}(6)||fT_1\rangle=\langle fT_1||O^{T_1}(6)||fT_2\rangle.$$

v) T_2-symmetry

$$\langle fA_2||O^{T_2}(3)||fT_1\rangle=\sqrt{5}(\tfrac{8}{15}\langle\gamma_2\rangle-\tfrac{28}{55}\langle\gamma_4\rangle-\tfrac{12}{143}\langle\gamma_6\rangle+\tfrac{56}{429}\langle\gamma_8\rangle)$$
$$\langle fA_2||O^{T_2}(4)||fT_1\rangle=\sqrt{10}(-\tfrac{4}{15}\langle\gamma_2\rangle-\tfrac{21}{110}\langle\gamma_4\rangle+\tfrac{81}{286}\langle\gamma_6\rangle-\tfrac{28}{429}\langle\gamma_8\rangle)$$
$$\langle fA_2||O^{T_2}(6)||fT_1\rangle=\sqrt{10}(-\tfrac{5}{22}\langle\gamma_4\rangle-\tfrac{35}{286}\langle\gamma_6\rangle+\tfrac{28}{143}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_2}(3)||fA_2\rangle=\langle fA_2||O^{T_2}(3)||fT_1\rangle$$
$$\langle fT_1||O^{T_2}(4)||fA_2\rangle=\langle fA_2||O^{T_2}(4)||fT_1\rangle$$
$$\langle fT_1||O^{T_2}(6)||fA_2\rangle=\langle fA_2||O^{T_2}(6)||fT_1\rangle$$
$$\langle fT_1||O^{T_2}(3)||fT_1\rangle=2\sqrt{6}(-\tfrac{1}{15}\langle\gamma_2\rangle-\tfrac{4}{55}\langle\gamma_4\rangle-\tfrac{30}{143}\langle\gamma_6\rangle+\tfrac{140}{429}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_2}(4)||fT_1\rangle=\sqrt{3}(\tfrac{2}{15}\langle\gamma_2\rangle-\tfrac{6}{55}\langle\gamma_4\rangle+\tfrac{285}{286}\langle\gamma_6\rangle+\tfrac{595}{858}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_2}(6)||fT_1\rangle=\frac{\sqrt{3}}{11}(8\langle\gamma_4\rangle+\tfrac{175}{26}\langle\gamma_6\rangle+\tfrac{175}{26}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_2}(3)||fT_2\rangle=\sqrt{10}(-\tfrac{2}{15}\langle\gamma_2\rangle+\tfrac{12}{55}\langle\gamma_4\rangle+\tfrac{579}{1573}\langle\gamma_6\rangle+\tfrac{196}{429}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_2}(4)||fT_2\rangle=\sqrt{5}(\tfrac{2}{15}\langle\gamma_2\rangle+\tfrac{9}{55}\langle\gamma_4\rangle+\tfrac{520}{1573}\langle\gamma_6\rangle+\tfrac{35}{429}\langle\gamma_8\rangle)$$
$$\langle fT_1||O^{T_2}(6)||fT_2\rangle=\frac{\sqrt{5}}{11}(-\langle\gamma_4\rangle+\tfrac{35}{208}\langle\gamma_6\rangle+\tfrac{42}{13}\langle\gamma_8\rangle)$$
$$\langle fT_2||O^{T_2}(3)||fT_1\rangle=-\langle fT_1||O^{T_2}(3)||fT_2\rangle$$
$$\langle fT_2||O^{T_2}(4)||fT_1\rangle=-\langle fT_1||O^{T_2}(4)||fT_2\rangle$$
$$\langle fT_2||O^{T_2}(6)||fT_1\rangle=-\langle fT_1||O^{T_2}(6)||fT_2\rangle$$
$$\langle fT_2||O^{T_2}(3)||fT_2\rangle=2\sqrt{6}(-\tfrac{1}{3}\langle\gamma_2\rangle+\tfrac{8}{33}\langle\gamma_4\rangle+\tfrac{135}{1573}\langle\gamma_6\rangle-\tfrac{56}{429}\langle\gamma_8\rangle)$$
$$\langle fT_2||O^{T_2}(4)||fT_2\rangle=\sqrt{3}(\tfrac{2}{3}\langle\gamma_2\rangle+\tfrac{23}{77}\langle\gamma_4\rangle+\tfrac{95}{286}\langle\gamma_6\rangle-\tfrac{469}{858}\langle\gamma_8\rangle)$$
$$\langle fT_2||O^{T_2}(6)||fT_2\rangle=\frac{\sqrt{3}}{11}(10\langle\gamma_4\rangle-\tfrac{175}{26}\langle\gamma_6\rangle+\tfrac{7}{26}\langle\gamma_8\rangle).$$

11. Appendix VII

Non zero reduced matrix elements (A Point charge model).
The Liehr and Ballhausen's Method.
($d-p$ and $f-d$, interaction matrix elements) In units of $-e\langle r^J \rangle$

11.1. *d − p interactions*

$J=1$

$$\langle dE||M^{T_1}||pT_1\rangle = +i\frac{2\sqrt{5}}{5}$$

$$\langle dT_2||M^{T_1}||pT_1\rangle = +i\frac{\sqrt{30}}{5}$$

$J=3$

$$\langle dE||M^{T_1}||pT_1\rangle = +i\frac{9\sqrt{5}}{35}$$

$$\langle dE||M^{T_2}||pT_1\rangle = -i\frac{3}{7}$$

$$\langle dT_2||M^{T_1}||pT_1\rangle = -i\frac{3\sqrt{30}}{35}.$$

$$\langle dT_2||M^{T_2}||pT_1\rangle = -i\frac{3\sqrt{2}}{7}.$$

Note: The $C^5(3m/2m')$ coefficients, tabulated by Tanabe, Sugano and Kamimura [30] are in error.
We have employed the $C^5(3m/2m')$ coefficients tabulated by Condon and Shortley [36].

11.2. *f − d interactions*

$J=1$

$$\langle fA_2||M^{T_1}||dT_2\rangle = -i\frac{\sqrt{21}}{14}$$

$$\langle fT_1||M^{T_1}||dE\rangle = +i\frac{3\sqrt{3}}{\sqrt{35}}$$

$$\langle fT_1||M^{T_1}||dT_2\rangle = +i\frac{3\sqrt{2}}{\sqrt{35}}$$

$$\langle fT_2||M^{T_1}||dE\rangle = -i\frac{\sqrt{21}}{7}$$

$$\langle fT_2||M^{T_1}||dT_2\rangle = -i\frac{\sqrt{42}}{7}.$$

$J = 3$

$$\langle fA_2||M^{T_1}||dT_2\rangle = +i\frac{2\sqrt{21}}{21}$$

$$\langle fT_1||M^{T_1}||dE\rangle = +i\frac{4\sqrt{3}}{3\sqrt{35}}$$

$$\langle fT_1||M^{T_2}||dE\rangle = -i\frac{2\sqrt{21}}{21}$$

$$\langle fT_1||M^{T_1}||dT_2\rangle = +i\frac{\sqrt{70}}{70}$$

$$\langle fT_1||M^{T_2}||dT_2\rangle = +i\frac{\sqrt{42}}{42}$$

$$\langle fT_2||M^{T_1}||dE\rangle = +i\frac{2\sqrt{21}}{21}$$

$$\langle fT_2||M^{T_1}||dT_2\rangle = -i\frac{\sqrt{42}}{42}$$

$$\langle fT_2||M^{T_2}||dT_2\rangle = -i\frac{\sqrt{70}}{14}.$$

$J = 5$

$$\langle fA_2||M^{aT_1}||dT_2\rangle = -i\frac{5\sqrt{21}}{231}$$

$$\langle fA_2||M^{bT_1}||dT_2\rangle = +i\frac{\sqrt{15}}{11}$$

$$\langle fT_1||M^{aT_1}||dE\rangle = +i\frac{10\sqrt{105}}{231}$$

$$\langle fT_1||M^{T_2}||dE\rangle = +i\frac{5\sqrt{3}}{33}$$

$$\langle fT_1||M^{aT_1}||dT_2\rangle = -i\frac{5\sqrt{70}}{154}$$

$$\langle fT_1||M^{bT_1}||dT_2\rangle = +i\frac{5\sqrt{2}}{22}$$

$$\langle fT_1||M^{T_2}||dT_2\rangle = -i\frac{5\sqrt{6}}{33}$$

$$\langle fT_2||M^{aT_1}||dE\rangle = -i\frac{5\sqrt{21}}{231}$$

$$\langle fT_2||M^{bT_1}||dE\rangle = -i\frac{\sqrt{15}}{11}$$

$$\langle fT_2||M^{T_2}||dE\rangle = +i\frac{\sqrt{15}}{11}$$

$$\langle fT_2||M^{aT_1}||dT_2\rangle = +i\frac{25\sqrt{42}}{462}$$

$$\langle fT_2||M^{bT_1}||dT_2\rangle = -i\frac{\sqrt{30}}{22}$$

$$\langle fT_2||M^{T_2}||dT_2\rangle = -i\frac{\sqrt{10}}{11}.$$

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