Theor Chim Acta (1986) 69: 225-233

Theoretica Chimica Acta

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The calculation of electric dipole vibronic intensities in centrosymmetric coordination compounds using the crystal field-closure-ligand polarization model

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Equations are derived for the evaluation of the contribution to the electric dipole vibronic intensity of d-d and f-f transitions in octahedral complex ions. Expressions for the evaluation of the crystal-field and ligand polarization terms and the cross term between are presented in symmetry adapted form and tables of the required coupling constants are given.

Key words: Vibronic intensities—Crystal field—Ligand polarization—Complex ion

1. Introduction

A large body of experimental data on the intensities of individual vibronic origins in the electronic spectra of coordination compounds has accumulated in the past twenty years [1-4]. Whilst it is recognized that these vibronic intensities contain information on nuclear [5] and ligand electron density [6] motions in crystals as well as on the electronic processes themselves, there exists no unified theoretical model within which to interpret this data. Early approaches used a crystal field approach with some success ([7], and references therein) and the observation that, for certain model calculations, the relative intensities were independent of the model parameters was particularly encouraging. However Mason has argued convincingly that it is necessary to complement the crystal field with the so-called ligand polarization term ([8], and references therein). Evidence is accumulating that in systems as diverse as octahedral [9] and tetrahedral [10] transition metal compounds, octahedral and lower symmetry lanthanide complexes [11-13] and uranyl complex ions [14] the crystal field and ligand polarization contributions

are comparable. Under these circumstances the cross term (or interference term) between the two contributions which arises when the total transition moment is squared becomes significant.

Two difficulties then arise. Firstly the relative intensities of the vibronic origins become dependant on the model parameters such as radial integrals [9]. Secondly it is necessary to exercise extreme care in the evaluation of the various terms if the phase of the interference term is to be found correctly. Of course the crystal field and ligand polarization dipole strengths are necessarily positive for cubic systems and unpolarized light. All previous general discussions of vibronic coupling have failed to treat this problem although we have shown in one specific case that this leads to grossly incorrect vibronic intensities [9].

The purpose of this paper is to provide a symmetry adapted approach to the calculation of the total dipole strengths associated with individual vibronic origins in centrosymmetric complex ions of the transition metals, lanthanides and actinides. We use Griffith's choice of phases together with standard set of wavefunctions, operators and symmetry coordinates to evaluate symmetrized ligand polarization vibronic coupling constants and transition multipole moments. These have two advantages over the calculation via the geometrical factors with respect to the cartesian coordinates previously reported [20]. Firstly the resultant "master equations" are much easier to use and secondly all terms now have consistent phases and therefore may be added together. The vibronic coupling terms have been evaluated using symmetry coordinates that transform correctly according to Table A-16 of Griffith [15]. The symmetry coordinates of Liehr [16] do not transform in this way.

Whilst the master equations for the crystal field, ligand polarisation and interference terms are complex involving summations over many components this formal complexity enables all the contributions to be considered in a consistent way and their use is straightforward and quick.

2. Method of calculation

Let $\boldsymbol{\mu}^{\mathrm{CF}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}$ and $\boldsymbol{\mu}^{\mathrm{LP}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}$ be the contributions to the electric dipole transition moment of the electronic transition $|\Gamma_1\gamma_2\rangle\to|\Gamma_2\gamma_2\rangle$ from the crystal field-closure and ligand polarization mechanism, then the total transition dipole moment may be written as follows [8, 11]

$$\boldsymbol{\mu}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}=\boldsymbol{\mu}^{\mathrm{CF}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}+\boldsymbol{\mu}^{\mathrm{LP}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}. \tag{1}$$

Within the closure approximation the α-component of the crystal field contribution to the electric dipole vibronic transition dipole moment may be written in a symmetry adapted form, for simply reducible groups as [18, 19]

$$\boldsymbol{\mu}^{\mathrm{CF},\alpha}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}=\left(\frac{2}{\Delta\varepsilon}\right)\sum_{\bar\Gamma,\bar\gamma,k}\sum_{\Gamma,\gamma}V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma\\ \gamma_1 & \gamma_2 & \gamma\end{pmatrix}\lambda^{1/2}(\Gamma)$$
$$\times V\begin{pmatrix}\bar\Gamma & T_1 & \Gamma\\ \bar\gamma & \alpha & \gamma\end{pmatrix}\langle\Gamma_1\|0^{\Gamma}(k)\|\Gamma_2\rangle S^{\bar\Gamma}_{\bar\gamma}(k). \tag{2}$$

Here $\Delta\varepsilon$ stands for an effective energy, corresponding to the mean energy gap of the spin and parity allowed excitation, and $S_{\bar{\gamma}}^{\bar{\Gamma}}(k)$ corresponds to the $\bar{\gamma}$th component of a symmetry coordinate S which transforms under the $\bar{\Gamma}$th-irreducible representation. $\lambda(\Gamma)$ represents the dimension of Γ. k is used to label the various vibrational modes of motion of the molecular system. The reduced matrix elements $\langle\Gamma_1\|0^{\Gamma}(k)\|\Gamma_2\rangle$ have been worked out and tabulated for d-d and f-f type of electronic transitions [19].

The symmetry and normal coordinates are related to each other, by means of the transformation $S = LQ$ so that:

$$S_{\bar{\gamma}}^{\bar{\Gamma}}(k) = \sum_{\bar{\Gamma},\bar{\gamma}} L_{ki}\delta_{\bar{\Gamma}\bar{\Gamma}}\delta_{\bar{\gamma}\bar{\gamma}}Q_{\bar{\gamma}}^{\bar{\Gamma}}(i). \tag{3}$$

Thus, by combining Eqs. (2) and (3), we obtain the general identity.

$$\mu_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}^{\mathrm{CF},\alpha} = \left(\frac{2}{\Delta\varepsilon}\right)\sum_{\Gamma,\bar{\Gamma}}\sum_{\gamma,\bar{\gamma}}\sum_{i,k}\lambda^{1/2}(\Gamma)\,V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma\\ \gamma_1 & \gamma_2 & \gamma\end{pmatrix}$$
$$\times V\begin{pmatrix}\bar{\Gamma} & T_1 & \Gamma\\ \bar{\gamma} & \alpha & \gamma\end{pmatrix}L_{ki}\langle\Gamma_1\|0^{\Gamma}(k)\|\Gamma_2\rangle Q_{\bar{\gamma}}^{\bar{\Gamma}}(i). \tag{4}$$

The α-component of the ligand polarization contribution to the electric dipole vibronic transition dipole moment may be written for isotropic ligands as [20]

$$\mu_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}^{\mathrm{LP},\alpha} = \sum_{\Gamma,\bar{\Gamma}}\sum_{\gamma,\bar{\gamma}}\sum_{k,\tau} V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma\\ \gamma_1 & \gamma_2 & \gamma\end{pmatrix}B_{\bar{\Gamma}\bar{\gamma}}^{\Gamma\gamma,\alpha}(k,\tau)$$
$$\times\langle\Gamma_1\|M^{\Gamma}(\tau)\|\Gamma_2\rangle S_{\bar{\gamma}}^{\bar{\Gamma}}(k). \tag{5}$$

The symmetrized ligand polarization vibronic coupling constants, are defined by the relationship:

$$B_{\bar{\Gamma}\bar{\gamma}}^{\Gamma\gamma,\alpha}(k,\tau) = -\bar{\alpha}_L\sum_{L}\{\partial G_{\Gamma\gamma,\alpha}^{L,\tau}/\partial S_{\bar{\gamma}}^{\bar{\Gamma}}(k)\}_0 \tag{6}$$

where $\bar{\alpha}_L$ is the mean ligand polarizability, measured at the frequency of the electronic transition [8], and the $G_{\Gamma\gamma,\alpha}^{L,\tau}$ are the symmetry adapted geometrical factors [20]. Replacing the symmetry coordinates $S_{\bar{\gamma}}^{\bar{\Gamma}}(k)$ by the normal coordinates, we obtain the identity:

$$\mu_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}^{\mathrm{LP},\alpha} = \sum_{\Gamma,\bar{\Gamma}}\sum_{\gamma,\bar{\gamma}}\sum_{i,k,\tau} V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma\\ \gamma_1 & \gamma_2 & \gamma\end{pmatrix}L_{ki}B_{\bar{\Gamma}\bar{\gamma}}^{\Gamma\gamma,\alpha}(k,\tau)\langle\Gamma_1\|M^{\Gamma}(\tau)\|\Gamma_2\rangle Q_{\bar{\gamma}}^{\bar{\Gamma}}(i). \tag{7}$$

At this stage, it is convenient to assume that the potential energy surfaces of the terminal electronic states are described by identical harmonic functions. Whilst, this is only approximately true, the approximation is good for those cases where individual vibronic origins are well resolved.

The total dipole strength of the electronic transition is then:

$$D_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}^{\mathrm{Total}} = \sum_{\alpha=X,Y,Z}|\langle 0|\mu_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}^{\alpha(\mathrm{total})}|1\rangle|^2 \tag{8}$$

where:

$$D^{\text{Total}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2} = D^{\text{CF}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2} + D^{\text{LP}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2} + D^{(\text{CF,LP})}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}. \tag{9}$$

$D^{\text{CF}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}$, $D^{\text{LP}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}$ and $D^{(\text{CF,LP})}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}$ are the crystal field, the ligand polarization and the crystal field-ligand polarization cross components of the dipole strength. The third term is the so called interference term and represents the coupling of the crystal field and the ligand polarization transition dipole moments.

From Eqs. (4) and (7) we may obtain a general equation to account for the total dipole strength associated with the electronic transition $|\Gamma_1\gamma_1\to|\Gamma_2\gamma_2\rangle$, in cubic environments. A further simplification can be achieved by summing over all the components γ_1 and γ_2 of the overall electronic transition [18] giving the total dipole strength associated with the overall excitation $|\Gamma_1\rangle\to|\Gamma_2\rangle$ as:

$$D(\Gamma_1\to\Gamma_2) = \sum_{\nu_i}\sum_{\gamma_1,\gamma_2} D^{\text{Total}}_{\Gamma_1\gamma_1\to\Gamma_2\gamma_2}(\nu_i)$$

where the summations are over the components γ_1, γ_2; the vibronic origins (ν_i) and progressions in even parity modes based on them.

Thus the various contributions to the total dipole strength of the overall electronic transition are as given below:

(i) *The crystal field component (closure approximation)*

$$D^{\text{CF}}_{\Gamma_1\to\Gamma_2}(\nu_i) = \left(\frac{2}{\Delta\varepsilon}\right)^2 \sum_{\alpha}\sum_{\Gamma,\bar\Gamma}\sum_{\gamma,\bar\gamma} V\begin{pmatrix}\bar\Gamma & T_1 & \Gamma\\ \bar\gamma & \alpha & \gamma\end{pmatrix}^2 \sum_{k,m} L_{ki}L_{mi}$$
$$\times\langle\Gamma_1\|0^{\Gamma}(k)\|\Gamma_2\rangle\langle\Gamma_1\|0^{\Gamma}(m)\|\Gamma_2\rangle\,|\langle 0|Q^{\bar\Gamma}_{\bar\gamma}(i)|1\rangle|^2 \tag{10}$$

(ii) *The ligand polarization component*

$$D^{\text{LP}}_{\Gamma_1\to\Gamma_2}(\nu_i) = \sum_{\alpha}\sum_{\Gamma,\bar\Gamma}\sum_{\gamma,\bar\gamma}\lambda^{-1}(\Gamma)\sum_{k,m}L_{ki}L_{mi}\sum_{\tau,\tau'}B^{\Gamma\gamma,\alpha}_{\bar\Gamma\bar\gamma}(k,\tau)$$
$$\times B^{\Gamma\gamma,\alpha}_{\bar\Gamma\bar\gamma}(m,\tau')\,\langle\Gamma_1\|M^{\Gamma}(\tau)\|\Gamma_2\rangle\langle\Gamma_1\|M^{\Gamma}(\tau')\|\Gamma_2\rangle\,|\langle 0|Q^{\bar\Gamma}_{\bar\gamma}(i)|1\rangle|^2 \tag{11}$$

(iii) *The interference term*

$$D^{(\text{CF,LP})}_{\Gamma_1\to\Gamma_2}(\nu_i) = 2\left(\frac{2}{\Delta\varepsilon}\right)\sum_{\alpha}\sum_{\Gamma,\bar\Gamma}\sum_{\gamma,\bar\gamma}\lambda^{-1/2}(\Gamma)\,V\begin{pmatrix}\bar\Gamma & T_1 & \Gamma\\ \bar\gamma & \alpha & \gamma\end{pmatrix}\sum_{k,m}L_{ki}L_{mi}$$
$$\times\langle\Gamma_1\|0^{\Gamma}(k)\|\Gamma_2\rangle\left\{\sum_{\tau}B^{\Gamma\gamma,\alpha}_{\bar\Gamma\bar\gamma}(m,\tau)\langle\Gamma_1\|M^{\Gamma}(\tau)\|\Gamma_2\rangle\right\}|0|Q^{\bar\Gamma}_{\bar\gamma}(i)|1\rangle|^2. \tag{12}$$

The above set of Eqs. (10), (11) and (12) should be scaled by a factor $\lambda^{-1}(\Gamma_1)$ being $\lambda(\Gamma_1)$ the orbital degeneracy of the initial electronic state. No correction for the refractive index of the medium has been included in our master equations.

The symmetrized ligand polarization vibronic coupling constants $B_{\bar{\Gamma}\bar{\gamma}}^{\Gamma\gamma,\alpha}(k, \tau)$ are tabulated in Appendix 1. For actual calculations, these vibronic coupling constants should be used in preference to the derivatives of the ligand polarization geometrical factors with respect to the Cartesian coordinates, reported in Ref. [17], since a few set of numerical errors and missprints may be found. We also list in Appendix 2, the transition multipole moments relevant to intensity calculations in octahedral centrosymmetric complexes. Observe that these vibronic coupling constants, listed in Appendix 1, have been derived using symmetry coordinates that transform correctly according to Table A-16 of Griffith [15]. The symmetry coordinates of Liehr [16] do not transform in this way.

3. The interference term

For illustrative purposes, we shall consider the evaluation of the interference term associated with the $|^4A_{2g} \leftrightarrow |^4T_{2g}\rangle$, electric hexadecapole, vibronically allowed transition, in a d^3-transition metal compound of the type ML_6, in O_h-symmetry.

For example, in the case of the ν_6-vibronic origin, a combined crystal field-closure-ligand polarization calculation leads us to the identity

$$D_{^4A_2 \leftrightarrow {}^4T_2}^{(\mathrm{CF,LP})}(\nu_6) = +12\sqrt{70}\,\frac{\bar{\alpha}_L R_0^{-7} L_{66}^2}{\Delta\varepsilon}\langle t_2\|0^{T_1}(6)\|e\rangle\,\langle t_2\|M^{T_1}(4)\|e\rangle|\langle 0|Q_6|1\rangle|^2. \quad (13)$$

Here L_{66} is defined by the relationship: $S_{6t} = L_{66}Q_{6t}$; $t = a, b, c$ and its numerical value depends upon the choice of the intermolecular force field. The vibrational integral, may be evaluated within the harmonic approximation to give [8, 21]

$$|\langle 0|Q_6|1\rangle|^2 = \frac{\hbar}{4\pi c\nu_6} \quad (14)$$

ν_6 is in wavenumbers and corresponds to the vibrational frequency of the τ_{2u}-bending vibration. R_0 is identified with the metal-ligand bond distance.

The reduced matrix elements which occur in Eq. (13) $\langle t_2\|O^{T_1}(6)\|e\rangle$ and $\langle t_2\|M^{T_1}(4)\|e\rangle$ are given by the identities; see [15] and Appendix II of the present work.

$$\langle t_2\|O^{T_1}(6)\|e\rangle = -\sqrt{6}\,\{\tfrac{5}{14}\langle\gamma_4\rangle + \tfrac{5}{11}\langle\gamma_6\rangle\}$$

$$\langle t_2\|M^{T_1}(4)\|e\rangle = +\frac{\sqrt{105}}{21}[-e\langle r^4\rangle]$$

Here $\langle\gamma_k\rangle = qe^2\langle r^k\rangle/R_0^{k+1}$, being $\langle r^k\rangle$ the expectation value of r^k between two d-radial functions, see Ref. [6, 12, 14, 15].

Following the method described in the present work, it is straightforward to evaluate the total dipole strength associated with a vibronically allowed excitation in the case of centrosymmetric ML_6 complex ions, in octahedral symmetry.

Acknowledgments. This work was supported by grant No. 1708-8533 from the DIB of the University of Chile. It was started during the tenure of a British Council travel award to R.A. at Birkbeck College and completed during a visit by C.D.F. to the University of Chile under the Royal Society-CONICYT exchange agreement.

Appendix 1. The ligand polarization vibronic coupling constants for a centrosymmetric ML_6 complex ion in the isotropic case

Here, we define: $B_{\Gamma\bar{\gamma}}^{\Gamma\gamma,\alpha}(k,\tau) = -\alpha_L \sum_L [\partial G_{\Gamma\gamma,\alpha}^{L,\tau}/\partial S_{\bar{\gamma}}^{\bar{\Gamma}}(k)]_0$

Note for $k=6$, $\bar{\Gamma} = T_2$.

Table A.1. The quadrupole-dipole coupling (the $B_{\Gamma\bar{\gamma}}^{\Gamma\gamma,\alpha}(k)$ coefficients are given in units of $-\bar{\alpha}_L R_0^{-5}$)

	$k=3$ $\tau=2$	$k=4$ $\tau=2$	$k=6$ $\tau=2$
$B_{T_1X}^{E\theta,X}$	$-6\sqrt{6}$	$-\frac{9}{2}$	$\frac{15}{2}$
$B_{T_1X}^{E\varepsilon,X}$	$6\sqrt{6}$	$9\sqrt{3}/2$	$5\sqrt{3}/2$
$B_{T_1Z}^{T_2Y,X}$	$-4\sqrt{6}$	$-3\sqrt{3}$	$-5\sqrt{3}$
$B_{T_1Y}^{T_2Z,X}$	$-4\sqrt{6}$	$-3\sqrt{3}$	$5\sqrt{3}$
$B_{T_1Y}^{E\theta,Y}$	$-6\sqrt{2}$	$-\frac{9}{2}$	$-\frac{15}{2}$
$B_{T_1Y}^{E\varepsilon,Y}$	$-6\sqrt{6}$	$-9\sqrt{3}/2$	$5\sqrt{3}/2$
$B_{T_1Z}^{T_2X,Y}$	$4\sqrt{6}$	$3\sqrt{3}$	$-5\sqrt{3}$
$B_{T_1X}^{T_2Z,Y}$	$-4\sqrt{6}$	$-3\sqrt{3}$	$-5\sqrt{3}$
$B_{T_1Z}^{E\theta,Z}$	$12\sqrt{2}$	9	0
$B_{T_1Z}^{E\varepsilon,Z}$	0	0	$-5\sqrt{3}$
$B_{T_1Y}^{T_2X,Z}$	$-4\sqrt{6}$	$-3\sqrt{3}$	$-5\sqrt{3}$
$B_{T_1X}^{T_2Y,Z}$	$-4\sqrt{6}$	$-3\sqrt{3}$	$5\sqrt{3}$

Table A.2. The hexadecapole-dipole coupling (the $B_{\Gamma\bar{\gamma}}^{\Gamma\gamma,\alpha}(k)$ coefficients are given in units of $-\bar{\alpha}_L R_0^{-7}$)

	$k=3$ $\tau=4$	$k=4$ $\tau=4$	$k=6$ $\tau=4$
$B_{T_1X}^{A_1\nu,X}$	$5\sqrt{42}$	$-5\sqrt{21}$	0
$B_{T_1X}^{E\theta,X}$	$5\sqrt{30}/2$	$-\sqrt{15}/4$	$-21\sqrt{15}/4$
$B_{T_1X}^{E\varepsilon,X}$	$-15\sqrt{10}/2$	$-39\sqrt{5}/4$	$-21\sqrt{5}/4$
$B_{T_1Z}^{T_1Y,X}$	$-3\sqrt{70}$	$3\sqrt{35}$	$3\sqrt{35}$
$B_{T_1Y}^{T_1Z,X}$	$3\sqrt{70}$	$-3\sqrt{35}$	$3\sqrt{35}$
$B_{T_1Z}^{T_2Y,X}$	$3\sqrt{10}$	$6\sqrt{5}$	0
$B_{T_1Y}^{T_2Z,X}$	$3\sqrt{10}$	$6\sqrt{5}$	0

Table A.2—continued

	$k=3$ $\tau=4$	$k=4$ $\tau=4$	$k=6$ $\tau=4$
$B_{T_1Z}^{T_1X,Y}$	$3\sqrt{70}$	$-3\sqrt{35}$	$3\sqrt{35}$
$B_{T_1X}^{T_1Z,Y}$	$-3\sqrt{70}$	$3\sqrt{35}$	$3\sqrt{35}$
$B_{T_1Z}^{T_2X,Y}$	$3\sqrt{10}$	$6\sqrt{5}$	0
$B_{T_1X}^{T_2Z,Y}$	$3\sqrt{10}$	$6\sqrt{5}$	0
$B_{T_1Y}^{T_1X,Z}$	$-3\sqrt{70}$	$3\sqrt{35}$	$3\sqrt{35}$
$B_{T_1X}^{T_1Y,Z}$	$3\sqrt{70}$	$-3\sqrt{35}$	$3\sqrt{35}$
$B_{T_1Y}^{T_2X,Z}$	$3\sqrt{10}$	$6\sqrt{5}$	0
$B_{T_1X}^{T_2Y,Z}$	$3\sqrt{10}$	$6\sqrt{5}$	0

Table A.3. The 2^6-pole-dipole coupling (the $B_{\Gamma\tilde{\gamma}}^{\Gamma\gamma,\alpha}(k)$ coefficients are given in units of $-\tilde{\alpha}_L R_0^{-9}$)

	$k=3$ $\tau=6$	$k=4$ $\tau=6$	$k=6$ $\tau=6$
$B_{T_1Z}^{T_1,X}$	$6\sqrt{14}$	$-6\sqrt{7}$	$-6\sqrt{7}$
$B_{T_1Y}^{T_1Z,X}$	$-6\sqrt{14}$	$6\sqrt{7}$	$-6\sqrt{7}$
$B_{T_1Z}^{aT_2Y,X}$	$-\sqrt{105}$	$\sqrt{210}/2$	$-3\sqrt{210}/2$
$B_{T_1Y}^{aT_2Z,X}$	$-\sqrt{105}$	$\sqrt{210}/2$	$3\sqrt{210}/2$
$B_{T_1Z}^{bT_2Y,X}$	$-3\sqrt{231}$	$-3\sqrt{462}/2$	$-3\sqrt{462}/2$
$B_{T_1Y}^{bT_2Z,X}$	$-3\sqrt{231}$	$-3\sqrt{462}/2$	$3\sqrt{462}/2$
$B_{T_1Z}^{T_1X,Y}$	$-6\sqrt{14}$	$6\sqrt{7}$	$-6\sqrt{7}$
$B_{T_1X}^{T_1Z,Y}$	$6\sqrt{14}$	$-6\sqrt{7}$	$-6\sqrt{7}$
$B_{T_1Z}^{aT_2X,Y}$	$-\sqrt{105}$	$\sqrt{210}/2$	$3\sqrt{210}/2$
$B_{T_1X}^{aT_2Z,X}$	$-\sqrt{105}$	$\sqrt{210}/2$	$-3\sqrt{210}/2$
$B_{T_1Z}^{bT_2X,Y}$	$-3\sqrt{231}$	$-3\sqrt{462}/2$	$3\sqrt{462}/2$
$B_{T_1X}^{bT_2Z,Y}$	$-3\sqrt{231}$	$-3\sqrt{462}/2$	$3\sqrt{462}/2$
$B_{T_1Y}^{T_1X,Z}$	$6\sqrt{14}$	$-6\sqrt{7}$	$-6\sqrt{7}$
$B_{T_1X}^{T_1Y,Z}$	$-6\sqrt{14}$	$6\sqrt{7}$	$-6\sqrt{7}$
$B_{T_1Y}^{aT_2X,Z}$	$-\sqrt{105}$	$\sqrt{210}/2$	$-3\sqrt{210}/2$
$B_{T_1X}^{aT_2Y,Z}$	$\sqrt{105}$	$-\sqrt{210}/2$	$-3\sqrt{210}/2$
$B_{T_1Y}^{bT_2X,Z}$	$-3\sqrt{231}$	$-3\sqrt{462}/2$	$-3\sqrt{462}/2$
$B_{T_1X}^{bT_2Y,Z}$	$-3\sqrt{231}$	$-3\sqrt{462}/2$	$3\sqrt{462}/2$

Appendix 2. Transition multipole moments non zero reduced matrix elements (in units of $-e\langle r^{\tau}\rangle$)

I. *d–d reduced matrix elements*

(i) A_1-symmetry:

$$\langle e\|M^{A_1}(4)\|e\rangle = \frac{\sqrt{42}}{21}$$

$$\langle t_2\|M^{A_1}(4)\|t_2\rangle = -\frac{2\sqrt{7}}{21}$$

(ii) E-symmetry

$$\langle e\|M^{E}(2)\|e\rangle = -\frac{4}{7}$$

$$\langle t_2\|M^{E}(2)\|t_2\rangle = \frac{2\sqrt{3}}{7}$$

$$\langle e\|M^{E}(4)\|e\rangle = \frac{2\sqrt{15}}{21}$$

$$\langle t_2\|M^{E}(4)\|t_2\rangle = \frac{4\sqrt{5}}{21}$$

(iii) T_1-symmetry

$$\langle e\|M^{T_1}(4)\|t_2\rangle = -\frac{\sqrt{105}}{21}$$

(iv) T_2-symmetry

$$\langle t_2\|M^{T_2}(2)\|t_2\rangle = -\frac{3\sqrt{2}}{7}$$

$$\langle e\|M^{T_2}(2)\|t_2\rangle = \frac{2\sqrt{3}}{7}$$

$$\langle e\|M^{T_2}(4)\|t_2\rangle = -\frac{\sqrt{5}}{7}$$

$$\langle t_2\|M^{T_2}(4)\|t_2\rangle = -\frac{2\sqrt{30}}{21}$$

II. *f–f reduced matrix elements*

(i) A_1-symmetry

$$\langle a_2\|M^{A_1}(4)\|a_2\rangle = -\frac{2\sqrt{21}}{33}$$

$$\langle a_2\|M^{A_1}(6)\|a_2\rangle = \frac{20\sqrt{2}}{143}$$

$$\langle t_1\|M^{A_1}(4)\|t_1\rangle = \frac{\sqrt{7}}{11}$$

$$\langle t_1\|M^{A_1}(6)\|t_1\rangle = \frac{25\sqrt{6}}{429}$$

$$\langle t_2\|M^{A_1}(4)\|t_2\rangle = -\frac{\sqrt{7}}{33}$$

$$\langle t_2\|M^{A_1}(6)\|t_2\rangle = -\frac{15\sqrt{6}}{143}$$

(ii) A_2-symmetry

$$\langle t_1\|M^{A_2}(6)\|t_2\rangle = \frac{5\sqrt{462}}{429}$$

(iii) E-symmetry

$$\langle t_1\|M^{E}(2)\|t_1\rangle = -\frac{4\sqrt{3}}{15}$$

$$\langle t_1\|M^{E}(4)\|t_1\rangle = \frac{\sqrt{5}}{11}$$

$$\langle t_1\|M^{E}(6)\|t_1\rangle = -\frac{25\sqrt{42}}{429}$$

$$\langle t_1\|M^{E}(2)\|t_2\rangle = -\frac{2\sqrt{15}}{15}$$

$$\langle t_1\|M^{E}(4)\|t_2\rangle = -\frac{1}{11}$$

$$\langle t_1\|M^{E}(6)\|t_2\rangle = \frac{5\sqrt{210}}{429}$$

$$\langle t_2\|M^{E}(4)\|t_2\rangle = -\frac{7\sqrt{5}}{33}$$

$$\langle t_2\|M^{E}(6)\|t_2\rangle = -\frac{5\sqrt{42}}{143}$$

(iv) T_1-symmetry

$$\langle a_2 \| M^{T_1}(4) \| t_2 \rangle = \frac{\sqrt{105}}{33}$$

$$\langle a_2 \| M^{T_1}(6) \| t_2 \rangle = \frac{10\sqrt{21}}{143}$$

$$\langle t_1 \| M^{T_1}(4) \| t_2 \rangle = \frac{\sqrt{14}}{11}$$

$$\langle t_1 \| M^{T_1}(6) \| t_2 \rangle = -\frac{5\sqrt{70}}{143}$$

(v) T_2-symmetry

$$\langle a_2 \| M^{T_2}(2) \| t_1 \rangle = -\frac{2\sqrt{15}}{15}$$

$$\langle a_2 \| M^{T_2}(4) \| t_1 \rangle = -\frac{1}{11}$$

$$\langle a_2 \| M^{aT_2}(6) \| t_1 \rangle = \frac{20\sqrt{42}}{429}$$

$$\langle a_2 \| M^{bT_2}(6) \| t_1 \rangle = 0$$

$$\langle t_1 \| M^{T_2}(2) \| t_1 \rangle = \frac{\sqrt{2}}{10}$$

$$\langle t_1 \| M^{T_2}(4) \| t_1 \rangle = -\frac{\sqrt{30}}{11}$$

$$\langle t_1 \| M^{aT_2}(6) \| t_1 \rangle = -\frac{5\sqrt{35}}{572}$$

$$\langle t_1 \| M^{bT_2}(6) \| t_1 \rangle = \frac{25\sqrt{77}}{572}$$

$$\langle t_1 \| M^{T_2}(2) \| t_2 \rangle = \frac{\sqrt{30}}{30}$$

$$\langle t_1 \| M^{T_2}(4) \| t_2 \rangle = \frac{2\sqrt{2}}{11}$$

$$\langle t_1 \| M^{aT_2}(6) \| t_2 \rangle = \frac{5\sqrt{21}}{132}$$

$$\langle t_1 \| M^{bT_2}(6) \| t_2 \rangle = \frac{5\sqrt{1155}}{572}$$

$$\langle t_2 \| M^{T_2}(2) \| t_2 \rangle = \frac{1}{\sqrt{2}}$$

$$\langle t_2 \| M^{T_2}(4) \| t_2 \rangle = -\frac{\sqrt{30}}{33}$$

$$\langle t_2 \| M^{aT_2}(6) \| t_2 \rangle = \frac{35\sqrt{35}}{572}$$

$$\langle t_2 \| M^{bT_2}(6) \| t_2 \rangle = -\frac{15\sqrt{77}}{572}$$

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