

## On the Evaluation of the Geometrical Factors Utilized in Ligand Polarization Calculations

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The utility of the Ligand polarization model in solving many physical problems in quantum mechanics has been appreciated among scientists during the last years. Problems such as electric dipole strength, vibronic electric dipole strength, optical activity calculations have been carried out within the framework of a dynamic coupling mechanism.

Taking advantage of the irreducible tensor method put forward by Griffith in the case of molecular symmetry groups, both the molecular states and relevant operators can be classified in terms of irreducible representations of the molecular group in question, and therefore it is most convenient to express the relevant operators involved in any specific calculation in a symmetry adapted form. As a starting point, we may classify our molecular states and operators in the 0-rotation group and lower symmetry groups may also be studied by using simple correlation properties.

Here we aim to deal with  $d-d$  and  $f-f$  type of transitions, and hence the  $2^2$  (electric quadrupole),  $2^4$  (electric hexadecapole) and the  $2^6$ -multipoles are considered in some detail. We have adopted, the octahedral set of functions as given by Griffith to define the  $2^l$  ( $l=2, 4, 6$ ) multipoles and obtain the corresponding geometrical factors for the various irreducible representations.

**Key words:** Geometric factors - Ligand polarization model.

### 1. Introduction

The Ligand polarization set of equations has been derived and applied by several authors [1-5] to various physical systems.

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It has been shown that the  $\alpha$ -vector component of the transition dipole moment associated with the  $0 \rightarrow a$  excitation may be written the case of centrosymmetric complexes as follows [4, 6]

$$\begin{aligned} \mu_{0a}^\alpha = & - \sum_{\lambda, K} S_K^{(\lambda)} \sum_{l \neq 0} \frac{2E_l}{E_l^2 - E_a^2} \\ & \times \sum_L \sum_{\beta\gamma\dots\delta} M_{0a}^{\beta\gamma\dots} \left( \frac{\partial G_{\beta\gamma\dots\delta}^L}{S_K^{(\lambda)}} \right)_0 \mu_{l0}^\delta \mu_{0l}^\alpha \end{aligned} \quad (1)$$

where:  $\alpha, \delta = X, Y, Z$ . The notation is as follows:  $S_K^{(\lambda)}$  stands for the  $K$ th symmetry co-ordinates which transforms under a given ungerade irreducible representation of the point molecular group and  $\lambda$  is a repeated representation label.  $G_{\beta\gamma\dots\delta}^L$  are the corresponding geometrical factors and finally  $M_{0a}^{\beta\gamma\dots}$  stands for the transition multipole moment associated with the  $\beta\gamma\dots$  component of the  $2^l$ -multipole.

It is seen that the above expression corresponds to a symmetry adapted form for the  $\alpha$ -vector component of the transition dipole moment. It can also be seen that the  $\alpha$ -vector component of the transition dipole moment is made up of two components, namely the isotropic part and the anisotropic contribution to the transition dipole moment. The isotropic part is afforded by setting  $\alpha = \delta$  in Eq. (1) and the anisotropic bit is obtained by setting  $\alpha \neq \delta$ , in the above equation. For isotropic ligands, such as halide ions, the nonvanishing part of the transition dipole moment becomes:

$$\begin{aligned} \mu_{0a}^\alpha = & - \sum_{\lambda, K} S_K^{(\lambda)} \sum_{l \neq 0} \frac{2E_l}{E_l^2 - E_a^2} \sum_L \sum_{\beta\gamma\dots\alpha} M_{0a}^{\beta\gamma\dots} \\ & \times \left( \frac{\partial G_{\beta\gamma\dots\alpha}^L}{S_K^{(\lambda)}} \right)_0 |\mu_{0l}^\alpha|^2 \end{aligned} \quad (2)$$

and the polarizability tensor of the ligands adopts a diagonal form, and all the non-diagonal tensorial components vanish [7]. We then write:

$$\alpha_{XX} = \alpha_{YY} = \alpha_{ZZ} = \bar{\alpha}_L = \sum_{l \neq 0} \frac{2E_l}{E_l^2 - E_a^2} |\mu_{0l}^\alpha|^2 \quad (3)$$

and by combining Eqs. (2) and (3), the symmetry adapted  $\alpha$ -vector component of the transition dipole moment adopts the form:

$$\begin{aligned} \mu_{0a}^\alpha = & - \sum_{\lambda, K} S_K^{(\lambda)} \sum_{\beta\gamma\dots\alpha} \sum_L M_{0a}^{\beta\gamma\dots} \\ & \times \left( \frac{\partial G_{\beta\gamma\dots\alpha}^L}{\partial S_K^{(l)}} \right)_0 \bar{\alpha}_L(\nu_{0a}) \end{aligned} \quad (4)$$

where  $\bar{\alpha}_L(\nu_{0a})$  is the mean ligand polarizability measured at the frequency of the electronic transition  $0 \rightarrow a$ , that is  $\nu_{0a}$ . [8].

## 2. Transition Multipole Moments

Let us consider in some detail the evaluation of the transition multipole moment  $M_{0a}^{\beta\gamma\dots}$ . Let  $M$  be an ITO which transforms under the  $\Gamma$  irreducible representation of the relevant molecular group, and assume that the wavefunctions  $|0\rangle$  and  $|a\rangle$  transform under the  $\Gamma_1$  and  $\Gamma_2$  irreducible representations respectively. Then, we write:

$$\begin{aligned} M_{0a} &= \langle \Gamma_1 \gamma_1 | M_{\bar{\gamma}}^{\Gamma} | \Gamma_2 \gamma_2 \rangle \\ &= V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1 & \gamma_2 & \bar{\gamma} \end{pmatrix} \langle \Gamma_1 || M^{\Gamma} || \Gamma_2 \rangle \end{aligned} \quad (5)$$

where the Wigner-Eckart theorem has been employed [9]. The labels  $\gamma_1$ ,  $\gamma_2$ , and  $\bar{\gamma}$  indicate the components of the  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma$  irreducible representations respectively.

The  $V$ -coefficients can be found in Griffith's work [9], and hence the actual evaluation of the transition multipole moment may be achieved by computing the reduced matrix element on the right hand side of the above equation.

Let us now introduce the Garstang's tensorial operators  $T_q^K$  [10].

$$T_q^K = -er^K C_q^K \quad (6)$$

where  $-e$  is the electron charge, and the  $C_q^K$  are the standard Racah's tensor operators [11]. For those cases, such as  $d-d$  and/or  $f-f$  type of transitions, the central metal ion multipoles involved have  $k$  lying in the range:  $K = 2l, \dots, 0$ , where  $l$  is the azimuthal quantum number of a  $d$  and/or  $f$  type of atomic orbital, therefore we only need to consider  $2^2, 2^4, 2^6, \dots$  multipoles.

The behaviour of general kets  $|KM\rangle$  under the octahedral group  $O$  has been considered in detail by Griffith [12] and this is the convention we shall adopt in this work. For example, when  $K = 2$ , Griffith finds:

$$\begin{aligned} |E\theta\rangle &= T_0^2 \\ |E\varepsilon\rangle &= 2^{-1/2}(T_{+2}^2 + T_{-2}^2) \\ |T_2+1\rangle &= T_{-1}^2 \\ |T_20\rangle &= 2^{-1/2}(T_{+2}^2 - T_{-2}^2) \\ |T_2-1\rangle &= -T_{+1}^2 \end{aligned} \quad (7)$$

and in the same way, we may define the symmetry adapted form of the central metal ion higher order multipoles. (Table A-19). Note that in the above set of equations, the kets  $|JM\rangle$  have been replaced by the Garstang operators [10]. Having defined these symmetry adapted tensorial operators, it is straightforward to evaluate the transition multipole moment given by Eq. (5) for a given electronic transition.

### 3 Geometrical Factors

Let us now consider the derivation of the geometrical factors involved in the calculation of the transition dipolar moment, see Eq. (4).

This can be afforded by considering the electrostatic form of the Coulombic interaction potential between two non-overlapping charge distributions, say ( $M$ ) and ( $L$ ). In fact, Carlson and Rushbrooke [13] give a general relation for the potential between the multipole components of two non-overlapping charge distributions with an arbitrary relative orientation of co-ordinate frames and centres separated by a distance  $R_L$ , which is identified here with the metal–ligand bond length [5].

The perturbation, say  $V$  representing this interaction may be written as follows:

$$V = \sum_i \sum_{j(L)} \frac{e_i(M)e_j(L)}{r_{ij}} \quad (8)$$

where  $r_{ij}$  is the distance between the charge  $e_i$  of the metal ion ( $M$ ) and the charge  $e_j$  of the ligand ( $L$ ).

Following Carlson and Rushbrooke [13], the electrostatic potential may be represented in tensorial form, as follows:

$$V = \sum_{K_1, q_1} \sum_{K_2, q_2} T_{-(q_1+q_2)}^{(K_1+K_2)} |R_L, \theta_L, \Phi_L| D_{q_1}^{K_1}(M) D_{q_2}^{K_2}(L) \quad (9)$$

where  $D_{q_1}^{K_1}(M) = T_{q_1}^{K_1}(M)$  and  $D_{q_2}^{K_2}(L) = T_{q_2}^{K_2}(L)$  are the corresponding Garstang's tensor operators associated with the central metal and the ligand multipoles, respectively.

The tensorial quantities  $T_{-(q_1+q_2)}^{(K_1+K_2)}$  represent the geometrical dependence of the interaction and are expressed as follows:

$$T_{-(q_1+q_2)}^{(K_1+K_2)} |R_L, \theta_L, \Phi_L| = (-1)^{q+1} R_L^{-(K+1)} (B_{K_1, K_2}^{q_1, q_2})^{1/2} C_{-q}^K(\theta_L, \Phi_L) \quad (10)$$

with  $K = K_1 + K_2$  and  $q = q_1 + q_2$ . Furthermore, the scalars  $B_{K_1, K_2}^{q_1, q_2}$  are obtained by means of the relation:

$$B_{K_1, K_2}^{q_1, q_2} = \frac{(K+q)!(K-q)!}{(K_1+q_1)!(K_1-q_1)!(K_2+q_2)!(K_2-q_2)!} \quad (11)$$

Let us now introduce the ligand dipole vector components, defined as given below:

$$\begin{aligned} \mu_{+1} &= -(2)^{-1/2} (\mu_L^X + i\mu_L^Y) = D_{+1}^1(L) \\ \mu_0 &= \mu_L^Z = D_0^1(L) \\ \mu_{-1} &= +(2)^{-1/2} (\mu_L^X - i\mu_L^Y) = D_{-1}^1(L) \end{aligned} \quad (12)$$

and the quantities  $\beta_{0,\pm 1}^{q_1}$  ( $q_1 = 0, \pm 1$ ) in the following way:

$$\begin{aligned} \beta_{+1}^{q_1} &= T_{-(q_1+1)}^{(K_1+1)} \\ \beta_0^{q_1} &= T_{-(q_1+0)}^{(K_1+1)} \\ \beta_{-1}^{q_1} &= T_{-(q_1-1)}^{(K_1+1)} \end{aligned} \tag{13}$$

and then, setting  $K_2 = 1$ , and combining Eqs. (9), (12) and (13) we obtain:

$$\begin{aligned} V = \sum_{q_1=-K_1}^{+K_1} D_{q_1}^{K_1}(M) \{ &-(2)^{-1/2}(\beta_{+1}^{q_1} - \beta_{-1}^{q_1})\mu_L^X \\ &+ \beta_0^{q_1}\mu_L^Z - i(2)^{-1/2}(\beta_{+1}^{q_1} + \beta_{-1}^{q_1})\mu_L^Y \} = A_1 + B_1 + C_1, \quad \text{say.} \end{aligned} \tag{14}$$

The above expression describes the tensorial form of the interaction potential between two  $2^{K_1}$ -central metal ion multipoles and the  $2^l$ -ligand dipoles. It is customary in the ligand polarization model to choose the ligand dipoles as the leading multipole (1, 2, 3, 4, 5, 6) and depending upon the electronic transition in question, the central metal ion multipole with the smallest  $K$ -value is chosen as the leading term.

For  $d-d$  type of transitions, we only need to consider the situations corresponding to  $K_1 = 2$ , and 4 to have transition multipole moment other than zero, whereas for  $f-f$  type of transitions  $K_1$  can afford the following values:  $K_1 = 2, 4$  and 6.

The simplest situation arises when  $K_1 = 2$  and  $K_2 = 1$ , that is the quadrupole-dipole interaction potential. Once the symmetry adapted form of the central metal ion multipoles has been defined, for example by adopting Griffith's convention (12), we only need to evaluate the terms  $A_1, B_1$  and  $C_1$  given by Eq. (14) for all possible choices of  $q_1$ , and generate as a result the relevant symmetry adapted geometrical factors, for any specific application.

In most general terms, choosing the leading term of the ligands to be a dipole, the interaction potential energy  $V$ , see Eq. (14) may be expressed as follows.

$$V = \sum_L \sum_{\alpha\beta\dots\gamma} G_{\alpha\beta\dots\gamma}^L M^{\alpha\beta\dots} \mu^{\gamma}(L) \tag{15}$$

where the geometrical factors are represented by  $G_{\alpha\beta\dots\gamma}^L$ , the  $\alpha\beta\dots$ th component of the central metal ion multipole is denoted by  $M^{\alpha\beta\dots}$  and  $\mu^{\gamma}(L)$  stands for the  $\gamma$ th-component of the ligand dipoles.

We have considered three cases, which are relevant to  $d-d$  and  $f-f$  type of electronic transitions. The  $2^l$ -multipole-dipole interaction potential is worked out for  $l = 2, 4$  and 6.

We also presented the derivatives of the symmetry adapted geometrical factors with respect to the cartesian nuclear displacements ligand coordinates.

These derivatives are relevant in ligand polarization vibronic intensity calculations [6].

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## Appendix

**Table 1a.** geometrical factors associated with the corresponding symmetry components of the electric quadrupole-dipole interaction potential in a perfect octahedral symmetry. ( $A_{\pm q}^3$  are the coefficients of  $(C_q^3 \pm C_{-q}^3)R^{-4}$ , where the  $C_{\pm q}^3$  are the standard Racah's tensor operators)

$G_{\Gamma_i(X,Y,Z)}^L$	$A_0^3$	$A_{+1}^3$	$A_{-1}^3$	$A_{+2}^3$	$A_{-2}^3$	$A_{+3}^3$	$A_{-3}^3$
$G_{E\theta(X)}^L$	0	0	$\sqrt{3}$	0	0	0	0
$G_{Ee(X)}^L$	0	0	$-1/2$	0	0	0	$\sqrt{15}/2$
$G_{T_{2(e)(X)}}^L$	0	0	0	0	$i\sqrt{10}/2$	0	0
$G_{T_{2(n)(X)}}^L$	$-\sqrt{3}$	0	0	$\sqrt{10}/2$	0	0	0
$G_{T_{2(t)(X)}}^L$	0	$i/2$	0	0	0	$-i\sqrt{15}/2$	0
$G_{E\theta(Y)}^L$	0	$-i\sqrt{3}$	0	0	0	0	0
$G_{Ee(Y)}^L$	0	$-i/2$	0	0	0	$-i\sqrt{15}/2$	0
$G_{T_{2(e)(Y)}}^L$	$\sqrt{3}$	0	0	$\sqrt{10}/2$	0	0	0
$G_{T_{2(n)(Y)}}^L$	0	0	0	0	$-i\sqrt{10}/2$	0	0
$G_{T_{2(t)(Y)}}^L$	0	0	$-1/2$	0	0	0	$-\sqrt{15}/2$
$G_{E\theta(Z)}^L$	$-3$	0	0	0	0	0	0
$G_{Ee(Z)}^L$	0	0	0	$-\sqrt{10}/2$	0	0	0
$G_{T_{2(e)(Z)}}^L$	0	$-2i$	0	0	0	0	0
$G_{T_{2(n)(Z)}}^L$	0	0	$-2$	0	0	0	0
$G_{T_{2(t)(Z)}}^L$	0	0	0	0	$i\sqrt{10}/2$	0	0

**Table 1b.** Non-zero derivatives of the quadrupole-dipole geometrical factors, evaluated at the equilibrium internuclear distance  $R_0$ , for each ligand position (in units of  $R_0^{-5}$ )

Derivative	Ligand position		
	0, 2	1, 3	4, 5
$\frac{\partial E_\theta(X)}{\partial X}$	-6	$\frac{3}{2}$	-6
$\frac{\partial E_\epsilon(X)}{\partial X}$	$6\sqrt{3}$	$\frac{7\sqrt{3}}{2}$	$\sqrt{3}$
$\frac{\partial T_{2(\eta)(X)}}{\partial Z}$	$-4\sqrt{3}$	$\sqrt{3}$	$-4\sqrt{3}$
$\frac{\partial T_{2(\xi)(X)}}{\partial Y}$	$-4\sqrt{3}$	$-4\sqrt{3}$	$\sqrt{3}$
$\frac{\partial E_\theta(Y)}{\partial Y}$	$\frac{3}{2}$	-6	-6
$\frac{\partial E_\epsilon(Y)}{\partial Y}$	$-\frac{7\sqrt{3}}{2}$	$-6\sqrt{3}$	$-\sqrt{3}$
$\frac{\partial T_{2(\xi)(Y)}}{\partial Z}$	$\sqrt{3}$	$-4\sqrt{3}$	$-4\sqrt{3}$
$\frac{\partial T_{2(\xi)(Y)}}{\partial X}$	$-4\sqrt{3}$	$-4\sqrt{3}$	$\sqrt{3}$
$\frac{\partial E_\theta(Z)}{\partial Z}$	$\frac{9}{2}$	$\frac{9}{2}$	12
$\frac{\partial E_\epsilon(Z)}{\partial Z}$	$-\frac{10\sqrt{3}}{4}$	$\frac{10\sqrt{3}}{4}$	0
$\frac{\partial T_{2(\xi)(Z)}}{\partial Y}$	$\sqrt{3}$	$-4\sqrt{3}$	$-4\sqrt{3}$
$\frac{\partial T_{2(\eta)(Z)}}{\partial X}$	$-4\sqrt{3}$	$\sqrt{3}$	$-4\sqrt{3}$

**Table 2a.** Geometrical factors associated with the symmetry components of the electric hexadecapole-dipole interaction potential in a perfect octahedral symmetry. ( $A_{\pm q}^5$  are the coefficients of  $(C_q^5 \pm C_{-q}^5)R^{-6}$ )

$G_{T_1(X,Y,Z)}^L$	$A_0^5$	$A_{\pm 1}^5$	$A_{\pm 2}^5$	$A_{\pm 3}^5$	$A_{\pm 4}^5$	$A_{\pm 5}^5$	
$G_{A_1(X)}^L$	0	0	$\sqrt{70}/4$	0	0	0	$5\sqrt{3}/4$
$G_{Eg(X)}^L$	0	0	$-5\sqrt{2}/4$	0	0	0	$-\sqrt{105}/4$
$G_{Eg(X)}^L$	0	0	$-\sqrt{6}/2$	0	0	0	0
$G_{T_1(X)(X)}^L$	0	0	0	0	$-i\sqrt{6}$	0	0
$G_{T_1(Y)(X)}^L$	$-\sqrt{35}/2$	0	0	$\sqrt{6}$	0	0	0
$G_{T_1(Z)(X)}^L$	0	0	0	0	0	0	0
$G_{T_2(X)(X)}^L$	0	0	0	$-i\sqrt{42}/4$	0	0	$3\sqrt{5}/2$
$G_{T_2(Y)(X)}^L$	0	0	0	0	0	0	0
$G_{T_2(Z)(X)}^L$	0	0	$-i\sqrt{6}/2$	0	0	0	0
$G_{A_1(Y)}^L$	0	$-i\sqrt{70}/4$	0	0	0	0	$-i5\sqrt{3}/4$
$G_{Eg(Y)}^L$	0	$i5\sqrt{2}/4$	0	0	0	0	$-i\sqrt{105}/4$
$G_{Eg(Y)}^L$	0	$-i\sqrt{6}/2$	0	0	0	0	0



$G_{T_1(e)XY}^L$	$-\sqrt{35}/2$	0	0	$-\sqrt{6}$	0	0	0	0	$-3\sqrt{2}/4$	0	0	0
$G_{T_1(p)XY}^L$	0	0	0	0	$-13\sqrt{6}/4$	0	0	0	0	$i3\sqrt{2}/4$	0	0
$G_{T_1(e)Y}^L$	0	0	0	0	0	0	1/2	0	0	0	0	$3\sqrt{5}/2$
$G_{T_2(e)XY}^L$	$-\sqrt{5}/2$	0	0	0	0	0	0	0	$3\sqrt{14}/4$	0	0	0
$G_{T_2(p)XY}^L$	0	0	0	0	$i\sqrt{42}/4$	0	0	0	0	$\frac{3\sqrt{14}}{i^2-4}$	0	0
$G_{T_2(e)Y}^L$	0	0	$-\sqrt{6}/2$	0	0	0	$\sqrt{7}$	0	0	0	0	0
$G_{A_{1 Z}}^L$	$-5\sqrt{21}/6$	0	0	0	0	0	0	0	$-\sqrt{30}/4$	0	0	0
$G_{E_0(Z)}^L$	$5\sqrt{15}/6$	0	0	0	0	0	0	0	$-\sqrt{42}/4$	0	0	0
$G_{E_1(Z)}^L$	0	0	0	0	$-\sqrt{42}/2$	0	0	0	0	0	0	0
$G_{T_1(e)Z}^L$	0	0	$i\sqrt{42}/2$	0	0	0	$i$	0	0	0	0	0
$G_{T_1(p)Z}^L$	0	0	0	$-\sqrt{42}/2$	0	0	1	0	0	0	0	0
$G_{T_1(e)Z}^L$	0	0	0	0	0	0	0	0	0	$-13\sqrt{2}/2$	0	0
$G_{T_2(e)Z}^L$	0	$i\sqrt{6}/2$	0	0	0	0	$-i\sqrt{7}$	0	0	0	0	0
$G_{T_2(p)Z}^L$	0	0	$\sqrt{6}/2$	0	0	0	0	$\sqrt{7}$	0	0	0	0
$G_{T_2(e)Z}^L$	0	0	0	0	$-i\sqrt{42}/2$	0	0	0	0	0	0	0

**Table 2b.** Non-zero derivatives of the hexadecapole-dipole geometrical factors, evaluated at the equilibrium internuclear distance  $R_0$ , for each ligand position (in units of  $R_0^{-9}$ )

Derivative	Ligand position		
	0, 2	1, 3	4, 5
$\frac{\partial A_1(X)}{\partial X}$	$5\sqrt{21}$	$-\frac{5\sqrt{21}}{2}$	$-\frac{5\sqrt{21}}{2}$
$\frac{\partial E_\theta(X)}{\partial X}$	$\frac{5\sqrt{15}}{2}$	$-\frac{33\sqrt{15}}{12}$	$\frac{5\sqrt{15}}{2}$
$\frac{\partial E_e(X)}{\partial X}$	$-\frac{15\sqrt{5}}{2}$	$-\frac{9\sqrt{5}}{4}$	$3\sqrt{5}$
$\frac{\partial T_{1(y)(X)}}{\partial Z}$	$-3\sqrt{35}$	0	$3\sqrt{35}$
$\frac{\partial T_{1(z)(X)}}{\partial Y}$	$3\sqrt{35}$	$-3\sqrt{35}$	0
$\frac{\partial T_{2(n)(X)}}{\partial Z}$	$-3\sqrt{5}$	$-3\sqrt{5}$	$-3\sqrt{5}$
$\frac{\partial T_{2(\ell)(X)}}{\partial Y}$	$-3\sqrt{5}$	$-3\sqrt{5}$	$-3\sqrt{5}$
$\frac{\partial A_1(Y)}{\partial Y}$	$-\frac{5\sqrt{21}}{2}$	$5\sqrt{21}$	$-\frac{5\sqrt{21}}{2}$
$\frac{\partial E_\theta(Y)}{\partial Y}$	$-\frac{33\sqrt{15}}{12}$	$\frac{5\sqrt{15}}{2}$	$\frac{5\sqrt{15}}{2}$
$\frac{\partial E_e(Y)}{\partial Y}$	$\frac{9\sqrt{5}}{4}$	$\frac{15\sqrt{5}}{2}$	$-3\sqrt{5}$
$\frac{\partial E_{1(x)(Y)}}{\partial Z}$	0	$-3\sqrt{35}$	$3\sqrt{35}$
$\frac{\partial T_{1(z)(Y)}}{\partial X}$	$3\sqrt{35}$	$-3\sqrt{35}$	0
$\frac{\partial T_{2(\ell)(Y)}}{\partial Z}$	$3\sqrt{5}$	$3\sqrt{5}$	$3\sqrt{5}$
$\frac{\partial T_{2(\ell)(Y)}}{\partial X}$	$-3\sqrt{5}$	$-3\sqrt{5}$	$-3\sqrt{5}$
$\frac{\partial A_1(Z)}{\partial Z}$	$\frac{5\sqrt{21}}{2}$	$\frac{5\sqrt{21}}{2}$	$5\sqrt{21}$
$\frac{\partial E_\theta(Z)}{\partial Z}$	$\frac{\sqrt{15}}{4}$	$\frac{\sqrt{15}}{4}$	$-5\sqrt{15}$
$\frac{\partial E_e(Z)}{\partial Z}$	$\frac{21\sqrt{5}}{4}$	$-\frac{21\sqrt{5}}{4}$	0
$\frac{\partial T_{1(x)(Z)}}{\partial Y}$	0	$-3\sqrt{35}$	$3\sqrt{35}$
$\frac{\partial T_{1(y)(Z)}}{\partial X}$	$-3\sqrt{35}$	0	$3\sqrt{35}$

**Table 2b**—*contd.*

	Ligand position		
$\frac{\partial T_{2(\xi)(Z)}}{\partial Y}$	$3\sqrt{5}$	$3\sqrt{5}$	$3\sqrt{5}$
$\frac{\partial T_{2(\eta)(Z)}}{\partial X}$	$-3\sqrt{5}$	$-3\sqrt{5}$	$-3\sqrt{5}$

**Table 3a.** Geometrical factors associated with the octahedral symmetry components of the electric  $2^6$ -dipole interaction potential ( $A_{\pm q}^7$  are the coefficients of  $(C_q^7 \pm C_{-q}^7)R^{-8}$ )

$G_{T(X,Y,Z)}^L$	$A_0^7$	$A_{+1}^7$	$A_{-1}^7$	$A_{+2}^7$	$A_{-2}^7$	$A_{+3}^7$
$G_{A_1(X)}^L$	0	0	$-\frac{2\sqrt{7}}{4}$	0	0	0
$G_{A_2(X)}^L$	0	0	$-\frac{\sqrt{165}}{8}$	0	0	0
$G_{E\theta(X)}^L$	0	0	$-\frac{7}{2}$	0	0	0
$G_{Ee(X)}^L$	0	0	$\frac{5\sqrt{3}}{8}$	0	0	0
$G_{T_{1(x)}(X)}^L$	0	0	0	0	$i\frac{11\sqrt{3}}{8}$	0
$G_{T_{1(y)}(X)}^L$	$\frac{3\sqrt{7}}{4}$	0	0	$-\frac{\sqrt{3}}{8}$	0	0
$G_{T_{1(z)}(X)}^L$	0	0	0	0	0	$-i\frac{\sqrt{6}}{2}$
$G_{T_{2(\epsilon)}(X)}^L$	0	0	0	0	$i\frac{15\sqrt{10}}{32}$	0
$G_{T_{2(n)}(X)}^L$	$-\frac{\sqrt{210}}{16}$	0	0	$-\frac{3\sqrt{10}}{32}$	0	0
$G_{T_{2(z)}(X)}^L$	0	$-i\frac{\sqrt{15}}{2}$	0	0	0	$i\frac{3\sqrt{10}}{2}$
$G_{T_{2(\epsilon)}(X)}^L$	0	0	0	0	$i\frac{13\sqrt{22}}{32}$	0
$G_{T_{2(n)}(X)}^L$	$-\frac{3\sqrt{462}}{16}$	0	0	$\frac{23\sqrt{11}}{32}$	0	0
$G_{T_{2(t)}(X)}^L$	0	0	0	0	0	0
$G_{A_1(Y)}^L$	0	$-i\frac{2\sqrt{7}}{4}$	0	0	0	$i\frac{\sqrt{21}}{4}$
$G_{A_2(Y)}^L$	0	$-i\frac{\sqrt{165}}{8}$	0	0	0	$-i\frac{3\sqrt{55}}{8}$
$G_{E\theta(Y)}^L$	0	$-i\frac{7}{2}$	0	0	0	$-i\frac{\sqrt{3}}{4}$
$G_{Ee(Y)}^L$	0	$-i\frac{5\sqrt{3}}{8}$	0	0	0	$i\frac{15}{8}$
$G_{T_{1(x)}(Y)}^L$	$\frac{3\sqrt{7}}{4}$	0	0	$\frac{\sqrt{3}}{8}$	0	0
$G_{T_{1(y)}(Y)}^L$	0	0	0	0	$i\frac{11\sqrt{3}}{8}$	0
$G_{T_{1(z)}(Y)}^L$	0	0	0	0	0	0

$A_{-3}^7$	$A_{+4}^7$	$A_{-4}^7$	$A_{+5}^7$	$A_{-5}^7$	$A_{+6}^7$	$A_{-6}^7$	$A_{+7}^7$	$A_{-7}^7$
$\frac{\sqrt{21}}{4}$	0	0	0	$\frac{\sqrt{231}}{4}$	0	0	0	0
$-\frac{3\sqrt{55}}{8}$	0	0	0	$\frac{\sqrt{5}}{8}$	0	0	0	$\frac{\sqrt{455}}{8}$
$\frac{\sqrt{3}}{4}$	0	0	0	$-\frac{\sqrt{33}}{4}$	0	0	0	0
$-\frac{15}{8}$	0	0	0	$\frac{\sqrt{11}}{8}$	0	0	0	$-\frac{\sqrt{1001}}{8}$
0	0	$-i\frac{\sqrt{66}}{4}$	0	0	0	$-i\frac{\sqrt{429}}{8}$	0	0
0	$\frac{-3\sqrt{66}}{4}$	0	0	0	$\frac{\sqrt{429}}{8}$	0	0	0
0	0	0	$i\frac{\sqrt{66}}{2}$	0	0	0	0	0
0	0	0	$-i\frac{3\sqrt{55}}{8}$	0	0	0	$i\frac{3\sqrt{1430}}{32}$	0
0	$\frac{3\sqrt{55}}{16}$	0	0	0	$\frac{3\sqrt{1430}}{32}$	0	0	0
0	0	0	0	0	0	0	0	0
0	0	$i\frac{13}{8}$	0	0	0	$i\frac{\sqrt{234}}{32}$	0	0
0	$-\frac{29}{16}$	0	0	0	$\frac{\sqrt{234}}{32}$	0	0	0
0	0	0	$-\frac{i}{2}$	0	0	0	$i\frac{\sqrt{91}}{2}$	0
0	0	0	$i\frac{\sqrt{231}}{4}$	0	0	0	0	0
0	0	0	$i\frac{\sqrt{5}}{8}$	0	0	0	$i\frac{\sqrt{455}}{8}$	0
0	0	0	$i\frac{\sqrt{33}}{4}$	0	0	0	0	0
0	0	0	$-i\frac{\sqrt{11}}{8}$	0	0	0	$i\frac{\sqrt{1001}}{8}$	0
0	$-\frac{3\sqrt{66}}{8}$	0	0	0	$-\frac{\sqrt{429}}{8}$	0	0	0
0	0	$i\frac{\sqrt{66}}{4}$	0	0	0	$-i\frac{\sqrt{429}}{8}$	0	0
$\frac{\sqrt{6}}{2}$	0	0	0	$\frac{\sqrt{66}}{2}$	0	0	0	0

Table 3a—contd.

$G_{\Gamma(X,Y,Z)}^L$	$A_0^7$	$A_{+1}^7$	$A_{-1}^7$	$A_{+2}^7$	$A_{-2}^7$	$A_{+3}^7$
$G_{T_{2(\epsilon)}(Y)}^L$	$\frac{\sqrt{210}}{16}$	0	0	$-\frac{3\sqrt{10}}{32}$	0	0
$G_{T_{2(n)}(Y)}^L$	0	0	0	0	$-i\frac{15\sqrt{10}}{32}$	0
$G_{T_{2(c)}(Y)}^L$	0	0	$\frac{\sqrt{15}}{2}$	0	0	0
$G_{T_{2(\epsilon)}(Y)}^L$	$\frac{3\sqrt{462}}{16}$	0	0	$\frac{23\sqrt{11}}{32}$	0	0
$G_{T_{2(n)}(Y)}^L$	0	0	0	0	$i\frac{23\sqrt{11}}{32}$	0
$G_{T_{2(c)}(Y)}^L$	0	0	0	0	0	0
$G_{A_1(Z)}^L$	$-\frac{7\sqrt{2}}{4}$	0	0	0	0	0
$G_{A_2(Z)}^L$	0	0	0	$-\frac{3\sqrt{110}}{8}$	0	0
$G_{E\theta(Z)}^L$	$-\frac{7\sqrt{14}}{4}$	0	0	0	0	0
$G_{E\epsilon(Z)}^L$	0	0	0	$-\frac{15\sqrt{2}}{8}$	0	0
$G_{T_{1(\omega)}(Z)}^L$	0	$-i\frac{3\sqrt{2}}{2}$	0	0	0	$i\frac{5\sqrt{6}}{4}$
$G_{T_{1(\nu)}(Z)}^L$	0	0	$\frac{3\sqrt{2}}{2}$	0	0	0
$G_{T_{1(\sigma)}(Z)}^L$	0	0	0	0	0	0
$G_{T_{2(\epsilon)}(Z)}^L$	0	$-i\frac{\sqrt{15}}{4}$	0	0	0	$i\frac{9\sqrt{5}}{4}$
$G_{T_{2(n)}(Z)}^L$	0	0	$-\frac{\sqrt{15}}{4}$	0	0	0
$G_{T_{2(c)}(Z)}^L$	0	0	0	0	$-i\frac{3\sqrt{5}}{2}$	0
$G_{T_{2(\epsilon)}(Z)}^L$	0	$-i\frac{3\sqrt{33}}{4}$	0	0	0	$-i\frac{5\sqrt{11}}{8}$
$G_{T_{2(n)}(Z)}^L$	0	0	$-\frac{3\sqrt{33}}{4}$	0	0	0
$G_{T_{2(c)}(Z)}^L$	0	0	0	0	0	0

$A_{-3}^7$	$A_{+4}^7$	$A_{-4}^7$	$A_{+5}^7$	$A_{-5}^7$	$A_{+6}^7$	$A_{-6}^7$	$A_{+7}^7$	$A_{-7}^7$
0	$-\frac{3\sqrt{55}}{8}$	0	0	0	$\frac{3\sqrt{1430}}{32}$	0	0	0
0	0	$-i\frac{3\sqrt{55}}{8}$	0	0	0	$i\frac{3\sqrt{1430}}{32}$	0	0
$\frac{3\sqrt{5}}{2}$	0	0	0	0	0	0	0	0
0	$\frac{29}{16}$	0	0	0	$\frac{\sqrt{234}}{32}$	0	0	0
0	0	$-i\frac{29}{16}$	0	0	0	$i\frac{\sqrt{234}}{32}$	0	0
0	0	0	0	$\frac{1}{2}$	0	0	0	$\frac{\sqrt{91}}{2}$
0	$\frac{\sqrt{231}}{4}$	0	0	0	0	0	0	0
0	0	0	0	0	$\frac{\sqrt{130}}{8}$	0	0	0
0	$-\frac{\sqrt{33}}{4}$	0	0	0	0	0	0	0
0	0	0	0	0	$-\frac{\sqrt{286}}{8}$	0	0	0
0	0	0	$i\frac{\sqrt{66}}{4}$	0	0	0	0	0
$\frac{5\sqrt{6}}{4}$	0	0	0	$-\frac{\sqrt{66}}{4}$	0	0	0	0
0	0	$-i\frac{\sqrt{66}}{2}$	0	0	0	0	0	0
0	0	0	$-i\frac{\sqrt{495}}{8}$	0	0	0	0	0
$-\frac{9\sqrt{5}}{4}$	0	0	0	$-\frac{\sqrt{495}}{8}$	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	$-i\frac{3}{8}$	0	0	0	0	0
$\frac{5\sqrt{11}}{8}$	0	0	0	$-\frac{3}{8}$	0	0	0	0
0	0	0	0	0	0	$-i\frac{\sqrt{26}}{2}$	0	0

**Table 3b.** Non-zero derivatives of the  $2^6$ -dipole geometrical factors in octahedral symmetry, evaluated at the equilibrium internuclear distance  $R_0$ , for each ligand position (in units of  $R_0^{-13}$ )

Derivative	Ligand position		
	0, 2	1, 3	4, 5
$\frac{\partial A_1(X)}{\partial X}$	$14\sqrt{2}$	$-7\sqrt{2}$	$-7\sqrt{2}$
$\frac{\partial A_2(X)}{\partial X}$	0	$-\frac{\sqrt{2310}}{4}$	$\frac{\sqrt{2310}}{4}$
$\frac{\partial E_\theta(X)}{\partial X}$	$-7\sqrt{14}$	$\frac{13\sqrt{14}}{8}$	$-7\sqrt{14}$
$\frac{\partial E_\epsilon(X)}{\partial X}$	$7\sqrt{42}$	$\frac{33\sqrt{42}}{8}$	$\frac{5\sqrt{42}}{4}$
$\frac{\partial T_{1(y)(X)}}{\partial Z}$	$6\sqrt{7}$	0	$-6\sqrt{7}$
$\frac{\partial T_{1(z)(X)}}{\partial Y}$	$6\sqrt{7}$	$-6\sqrt{7}$	0
$\frac{\partial T_{2(n)(X)}^a}{\partial Z}$	$\frac{\sqrt{210}}{2}$	$-\sqrt{210}$	$\frac{\sqrt{210}}{2}$
$\frac{\partial T_{2(t)(X)}^a}{\partial Y}$	$\frac{\sqrt{210}}{2}$	$\frac{\sqrt{210}}{2}$	$-\sqrt{210}$
$\frac{\partial T_{2(n)(X)}^b}{\partial Z}$	$\frac{3\sqrt{462}}{2}$	0	$\frac{3\sqrt{462}}{2}$
$\frac{\partial T_{2(t)(X)}^b}{\partial Y}$	$\frac{3\sqrt{462}}{2}$	$\frac{3\sqrt{462}}{2}$	0
$\frac{\partial A_1(Y)}{\partial Y}$	$-7\sqrt{2}$	$14\sqrt{2}$	$-7\sqrt{2}$
$\frac{\partial A_2(Y)}{\partial Y}$	$\frac{\sqrt{2310}}{4}$	0	$-\frac{\sqrt{2310}}{4}$
$\frac{\partial E_\theta(Y)}{\partial Y}$	$\frac{13\sqrt{14}}{8}$	$-7\sqrt{14}$	$-7\sqrt{14}$
$\frac{\partial E_\epsilon(Y)}{\partial Y}$	$-\frac{33\sqrt{42}}{8}$	$-7\sqrt{42}$	$-\frac{5\sqrt{42}}{4}$
$\frac{\partial T_{1(x)(Y)}}{\partial Z}$	$-\frac{135\sqrt{7}}{32}$	$\frac{327\sqrt{7}}{32}$	$-6\sqrt{7}$
$\frac{\partial T_{1(z)(Y)}}{\partial X}$	$6\sqrt{7}$	$-6\sqrt{7}$	0
$\frac{\partial T_{2(t)(Y)}^a}{\partial Z}$	$\frac{7\sqrt{210}}{8}$	$-\frac{5\sqrt{210}}{8}$	$-\frac{\sqrt{210}}{4}$
$\frac{\partial T_{2(t)(Y)}^a}{\partial X}$	$\frac{\sqrt{210}}{2}$	$\frac{\sqrt{210}}{2}$	$-\sqrt{210}$



Table 3b—contd.

Derivative	Ligand position		
	0, 2	1, 3	4, 5
$\frac{\partial T_{2(\epsilon)(Y)}^b}{\partial Z}$	0	$-\frac{3\sqrt{462}}{2}$	$-\frac{3\sqrt{462}}{2}$
$\frac{\partial T_{2(\epsilon)(Y)}^b}{\partial X}$	$\frac{3\sqrt{462}}{2}$	$\frac{3\sqrt{462}}{2}$	0
$\frac{\partial A_1(Z)}{\partial Z}$	$-7\sqrt{2}$	$-7\sqrt{2}$	$14\sqrt{2}$
$\frac{\partial A_2(Z)}{\partial Z}$	$-\frac{\sqrt{2310}}{4}$	$\frac{\sqrt{2310}}{4}$	0
$\frac{\partial E_g(Z)}{\partial Z}$	$\frac{43\sqrt{14}}{8}$	$\frac{43\sqrt{14}}{8}$	$14\sqrt{14}$
$\frac{\partial E_g(Z)}{\partial Z}$	$-\frac{47\sqrt{42}}{64}$	$\frac{47\sqrt{42}}{64}$	0
$\frac{\partial T_{1(x)(Z)}^b}{\partial Y}$	$\frac{15\sqrt{7}}{16}$	$-\frac{3\sqrt{7}}{2}$	$-18\sqrt{7}$
$\frac{\partial T_{1(y)(Z)}^b}{\partial X}$	$\frac{3\sqrt{7}}{2}$	$-\frac{15\sqrt{7}}{16}$	$18\sqrt{7}$
$\frac{\partial T_{2(\epsilon)(Z)}^a}{\partial Y}$	$\frac{337\sqrt{210}}{256}$	$\frac{11\sqrt{210}}{32}$	$-\frac{\sqrt{210}}{2}$
$\frac{\partial T_{2(n)(Z)}^a}{\partial X}$	$-\frac{11\sqrt{210}}{32}$	$-\frac{337\sqrt{210}}{256}$	$\frac{\sqrt{210}}{2}$
$\frac{\partial T_{2(\epsilon)(Z)}^b}{\partial Y}$	0	$-\frac{3\sqrt{462}}{2}$	$-\frac{3\sqrt{462}}{2}$
$\frac{\partial T_{2(n)(Z)}^b}{\partial X}$	$\frac{3\sqrt{462}}{2}$	0	$\frac{3\sqrt{462}}{2}$