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Journal of Alloys and Compounds 323–324 (2001) 726–730

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Parametrization of f^N–f^N electric dipole transitions in point-group bases

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Abstract

Two parametrizations of $f^N - f^N$ electric dipole transitions for both the zero-phonon case and the vibronic case are defined using a point-group basis. The relationship between the two parameterizations and between the parameters for a point-group basis and the *JM* basis are given. By factorizing the coupling and summing over the partners of the transition states and vibration modes, the calculation of dipole transition strength is simplified. This method is implemented in the RACAH computer program. Ambiguities in the parametrizations and the issue of the number of independent polarization measurements required in low symmetry cases are also discussed.

Keywords: Crystal and ligand fields; Electronic states (localized); Optical properties

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1. Introduction

The first theoretical treatments of f^N–f^N transitions were provided by Judd [1] and Ofelt [2]. Later Newman and Balasubramanian [3] gave two different parameterizations for general transitions between crystal-field levels. One was adapted by Reid and Richardson [4–6] and has been widely applied, with parameters denoted as A^{λ}_{tp}. Recently Burdick et al. [7] used the other crystal-field level parameterization in which the parameters are denoted as B^{λ}_{lq} for spherical polarization q ($q = 0, \pm 1$). They discussed the ambiguities in the parameterization and showed that several different parameter sets can give the same calculated intensities.

Most calculations of transition intensities have been done in the *JM* basis. Reid and Richardson [4–6] and Kibler et al. [8] have discussed the use of point-group couplings to clarify the number of independent parameters and selection rules but few calculations have used point-group bases.

In this paper we define the two parameterizations discussed by Newman and Balasubramanian [3] for a point-group basis using the notation of Butler [9] and give the relations between the parameters of the different parameterizations. The calculation of transition intensities is simplified by factorizing the vector coupling coefficients and summing over partners of degenerate states. This is implemented in RACAH computer program [10]. The complex conjugation property and ambiguities of parameters and number of independent polarization measurements required to characterize a transition are also discussed.

2. Definition of point-group parametrizations

Electric–dipole transitions within the $4f^N$ configuration are parity forbidden in a free ion and only become allowed when opposite-parity configurations on the ion or its ligands are mixed with the $4f^N$ states. This admixture of states with opposite parity is not included in the standard crystal-field eigen functions calculated with a $4f^N$ effective Hamiltonian. To take this admixture into account an even-parity effective electric–dipole vector operator is required, as discussed in Refs. [1–4,11,12]. The generalization of Reid and Richardson's definition of a vector unit tensor operator **U** to the point-group case is

$$\mathbf{U}^{\lambda^+\cdot 1^- t^- cvj} = \sum_{b\mu l}\sum_{aqi} U^{\lambda^+ b\mu l}\,\mathbf{e}^{1^- aqi} \times \langle \lambda^+ b\mu l, 1^- aqi | \lambda^+ \cdot 1^- t^- cvj \rangle, \quad (1)$$

where $U^{\lambda^+ b\mu l}$ is a scalar unit tensor and $\mathbf{e}^{1^- aqi}$ is a unit vector, $\lambda^+ b\mu l$, $1^- aqi$ and $t^- cvj$ are partners (basis states) of the group chain $O_3 \supset G \supset C_1$ (μ, q, ν are irreps of G, and a, b, c, i, l, j are branching multiplicities), $\lambda^+ \cdot 1^-$ is

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01060-X

an irrep label of the group $O_3 \times O_3$ and $\langle \lambda^+ b\mu l, 1^- aqi | \lambda^+ \cdot 1^- t^- cvj \rangle$ is a vector coupling coefficient.

This equation emphasizes that the electric dipole transition becomes allowed due to the coupling of the odd-parity electric dipole operator, transforming as 1^- of O_3, with an odd-parity potential, transforming as t^-, to give an even-parity effective operator, transforming as λ^+.

Following Reid and Richardson's definition, the zero-phonon effective electric dipole vector field for a point group basis is:

$$\begin{aligned}\mathbf{V} &= \sum_{\lambda tc} A_{\lambda^+ \cdot 1^- t^- c0} \mathbf{U}^{\lambda^+ \cdot 1^- t^- c00} \\ &= \sum_{\lambda tc} A_{\lambda^+ \cdot 1^- t^- c0} \sum_{b\mu laqi} \langle \lambda^+ b\mu l, 1^- aqi | \lambda^+ \cdot 1^- t^- c00 \rangle \\ &\quad \times U^{\lambda^+ b\mu l} \mathbf{e}^{1^- aqi},\end{aligned} \tag{2}$$

where $A_{\lambda^+ \cdot 1^- t^- c0}$ is a parameter.

The $1^- aqi$ component of $\mathbf{V}$ is defined by

$$\begin{aligned}V_{1^- aqi} &= \mathbf{e}^{1^- aqi} \cdot \mathbf{V} \\ &= \sum_{\lambda tc} A_{\lambda^+ \cdot 1^- t^- c0} \sum_{\lambda b\mu l} U^{\lambda^+ b\mu l} (-1) \begin{pmatrix} 1^- \\ a \\ q \\ i \end{pmatrix} \\ &\quad \times \langle \lambda^+ b\mu l, 1^- a^* q^* i^* | \lambda^+ \cdot 1^- t^- c00 \rangle\end{aligned} \tag{3}$$

where the second last bracket is a *2jm* [9].

A different (*JM*-basis) parametrization was used by Burdick et al. [7]. The point-group basis version of that parametrization is:

$$V_{1^- aqi} = \sum_{\lambda b\mu l} B_{\lambda^+ b\mu l, 1^- aqi} U^{\lambda^+ b\mu l}, \tag{4}$$

where $B_{\lambda^+ b\mu l, 1^- aqi}$ is a parameter. As in the case of the B^{λ}_{lq} of Burdick et al. [7] the $B_{\lambda^+ b\mu l, 1^- aqi}$ are not necessarily independent. In order to have a set of independent parameters, we define the general reduced tensor at the group G level for both vibronic and zero-phonon ($\nu = 0$ in the following formula) transitions:

$$V_{1^- aq}(d\nu)_{\mu} = \sum_{\lambda b} B_{\lambda^+ b\mu, 1^- aq;\nu}(d) U^{\lambda^+ b\mu} \tag{5}$$

$$\begin{aligned}&= \sum_{\lambda tc, b} (-1) A_{\lambda^+ \cdot 1^- t^- c\nu}(d) \begin{pmatrix} 1^- \\ a \\ q \end{pmatrix} U^{\lambda^+ b\mu} \\ &\quad \times \langle \lambda^+ b\mu 1^- a^* q^*, \nu | \lambda^+ \cdot 1^- t^- c\nu \rangle,\end{aligned} \tag{6}$$

where d is a multiplicity number needed in some cases to distinguish different reduced tensors. The relationship between the A parameters and the B parameters is

$$\begin{aligned}A_{\lambda^+ \cdot 1^- t^- c\nu} &= \sum_{\lambda b\mu aq} \langle \lambda^+ b\mu, 1^- a^* q^*; \nu | \lambda^+ \cdot 1^- t^- c\nu \rangle^* (-1) \\ &\quad \times \begin{pmatrix} 1^- \\ a \\ q \end{pmatrix} B_{\lambda^+ b\mu, 1^- aq;\nu}\end{aligned} \tag{7}$$

and

$$\begin{aligned}B_{\lambda^+ b\mu, 1^- aq;\nu} &= \sum_{tc} (-1) \begin{pmatrix} 1^- \\ a \\ q \end{pmatrix} A_{\lambda^+ \cdot 1^- t^- c\nu} \\ &\quad \times \langle \lambda^+ b\mu, 1^- a^* q^*; \nu | \lambda^+ \cdot 1^- t^- c\nu \rangle.\end{aligned} \tag{8}$$

We can rewrite the component of $\mathbf{V}$ with this reduced tensor as:

$$\begin{aligned}V_{1^- aqi} &= V_{1^- aq}(0)_{qi} \begin{pmatrix} q \\ i \end{pmatrix} \langle qiq^* i^* | 00 \rangle \\ &= V_{1^- aq}(0)_{qi} \frac{1}{[q]^{1/2}},\end{aligned} \tag{9}$$

where $V_{1^- aq}(0)_{qi}$ means the *qi* partner of reduced tensor $V_{1^- aq}(0)_q$. Therefore the zero-phonon transition intensities are parametrized by either $A_{\lambda^+ \cdot 1^- t^- c0}$ or $B_{\lambda^+ bq, 1^- aq,0}$. $B_{\lambda^+ bq, 1^- aq;0}$ corresponding to the parameters used by Burdick et al. [7], where they are denoted as $B^{\lambda^+}_{lq}$ or linear combinations. The symmetry properties are clearer in our case since we explicitly use the point-group irreps.

For vibronic transitions, if the mode of the vibration is $(d\nu^* j^*)$, where ν^* is the irrep, j^* is the partner and d is the multiplicity number, then the electronic part of perturbation transforms as partner νj. Therefore the vector effective electric dipole transition operator is:

$$\begin{aligned}\mathbf{V}(d\nu j) &= \sum_{\lambda tc} A_{\lambda^+ \cdot 1^- t^- c\nu j} \mathbf{U}^{\lambda^+ \cdot 1^- t^- c\nu j} \\ &= \sum_{\lambda tc} A_{\lambda^+ \cdot 1^- t^- c\nu} \mathbf{U}^{\lambda^+ \cdot 1^- t^- c\nu j}.\end{aligned} \tag{10}$$

The last equation is obtained by using the fact that $A_{\lambda^+ \cdot 1^- t^- c\nu j}(d)$ does not depend on j [5]. The $1^- aqi$ component of $\mathbf{V}$ can be parametrized with another set of parameters similar to Eq. (4):

$$V_{1^- aqi}(d\nu j) = \sum_{\lambda b\mu l} B_{\lambda^+ b\mu l, 1^- aqi}(d\nu j) U^{\lambda^+ b\mu l} \tag{11}$$

However as $A_{\lambda^+ \cdot 1^- t^- c\nu j}(d)$ does not depend on j, the $B_{\lambda^+ b\mu l, 1^- aqi}(d\nu j)$ are not independent. In fact, by a similar derivation to Eq. (9), we have

$$V_{1^- aqi}(d\nu j) = \sum_{\mu l} V_{1^- aq}(d\nu)_{\mu l} \begin{pmatrix} q \\ i \end{pmatrix} \langle \mu l q^* i^* | \nu j \rangle, \tag{12}$$

which shows that only the $B_{\lambda^+ b\mu, 1^- aq;\nu}(d)$ in Eq. (5) are independent and the $B_{\lambda^+ b\mu l, 1^- aqi}(d\nu j)$ are related to them by coupling coefficients. Later we will show that the intensity only depends on the reduced tensor defined by Eq. (5).

The vector unit tensor transforms as partners of irrep t^- of the group O_3. From the transformation properties between partners of two different group chains, we obtain the relationship between A parameters for a point group basis and for the *JM* basis:

$$A^{\lambda^+}_{t^-p}(d\nu j)=\sum_c \langle t^-p|t^-c\nu j\rangle A_{\lambda^+\cdot 1^-t^-c\nu}(d), \tag{13}$$

where t^-p is the *JM* label and the parameters depend on the vibration mode $(d\nu^*j^*)$. Similarly, we have the relationship between *B* parameters

$$\begin{aligned} B^{\lambda^+}_{m_\lambda m}(d\nu j) &= \sum_{b\mu l,aqi} \langle \lambda^+ m_\lambda|\lambda^+ b\mu l\rangle \\ &\quad \times \langle 1^-aqi|1^-m\rangle B_{\lambda b\mu l,1^-aqi}(dvj) \\ &= \sum_{b\mu l,aqi} \langle \lambda^+ m_\lambda|\lambda^+ b\mu l\rangle \langle 1^-aqi|1^-m\rangle \\ &\quad \times B_{\lambda b\mu,1^-aq;\nu}(d)\begin{pmatrix} q \\ i\end{pmatrix}\langle \mu l q^* i^*|\nu j\rangle, \end{aligned} \tag{14}$$

where λm_λ is the *JM* label of the unit tensor and m is the label of the spherical polarization.

3. Calculation of intensities in a point-group basis

The general polarization vector is:

$$\mathbf{E}=\sum_{aqi}\epsilon_{1^-aqi}\mathbf{e}^{1^-aqi}. \tag{15}$$

Denote the transition initial and final states as $|A\alpha\rangle$ and $|B\beta\rangle$,where the multiplicity and the irrep together is denoted as A or B, α and β are partners of the degenerate states. The transition dipole strength is then

$$\begin{aligned} I_{A\alpha\rightarrow B\beta}(d\nu j) &= |\langle B\beta|\mathbf{E}\cdot\mathbf{V}(d\nu j)|A\alpha\rangle|^2 \\ &= \sum_{a_1q_1i_1a_2q_2i_2} \epsilon_{1^-a_1q_1i_1}\epsilon^*_{1^-a_2q_2i_2}\langle B\beta|V_{a_1q_1i_1}(d\nu j)|A\alpha\rangle \\ &\quad \times \langle B\beta|V_{a_2q_2i_2}(d\nu j)|A\alpha\rangle^*, \end{aligned} \tag{16}$$

where we have summed over all the possible combinations of polarization vectors. We shall see below that not all combinations contribute.

The expectation value of the vibrational part of the transition has been absorbed into the parameters [4]. The intensities can be calculated from the dipole strength via standard formulae [11–13]. The experimental transition intensity is proportional to the line strength, which is a sum over the degenerate partners α, β of the initial and final states and the phonon partner j. By substituting V_{aqi} with Eq. (12), factorizing the coupling coefficients and using Wigner–Eckart theorem twice for group chain $\mathrm{G}\supset\mathrm{C}_1$ and making use of the orthogonality of the vector coupling coefficients [9], we obtain the line strength as:

$$\begin{aligned} I(d\nu) &= \sum_{\alpha\beta j} I_{A\alpha,B\beta}(d\nu j) \\ &= \sum_{a_1a_2q}\Big(\sum_i \epsilon_{1^-a_1qi}\epsilon^*_{1^-a_2qi}\Big) I_{a_1a_2,q} \\ &= \sum_{a_1\leq a_2,q} c_{a_1a_2,q}|I_{a_1a_2,q}|, \end{aligned} \tag{17}$$

where $c_{a_1a_2,q}$ is a real number that depends on the polarization. Note that orthogonality has required $i_1=i_2=i$, but not $a_1=a_2$. The partial strength is

$$\begin{aligned} I_{a_1a_2,q}(d\nu) &= \sum_\mu \langle A\|V_{a_1q}(d\nu)_\mu\|B\rangle\langle A\|V_{a_2q}(d\nu)_\mu\|B\rangle^*\frac{[\nu]}{[\mu][q]} \\ &= I^*_{a_2a_1,q}\ , \end{aligned} \tag{18}$$

where μ is limited to those irreps that form triad with irrep q and irrep ν, i.e. $\{q\nu\mu\}$. The zero-phonon case is recovered by setting $\nu=0$, in which case $\mu=q$.

Eq. (17) shows that when there is multiplicity in branching irrep 1^- of O_3 into irrep q of group G, there is an interference effect and we cannot characterize the transition by measuring only three independent polarizations. This will be discussed further in Section 5.

The Hamiltonian transforms as a scalar operator of the site symmetry G. The reduced matrices of the Hamiltonian and reduced transition tensors are calculated by applying the Wigner–Eckart theorem for group chain $\mathrm{O}_3\supset\mathrm{G}$ to every term of those tensors. By diagonalizing the reduced matrices of Hamiltonian we obtain the eigenvalues and eigenvectors. The reduced matrices of reduced transition tensor are transformed into eigenbasis and then the intensity is calculated with Eq. (18) directly. This is implemented in RACAH computer program [10].

4. Complex-conjugation symmetry of parameters and ambiguities in the parametrization

The effective vibronic transition operator can be written by coupling the electronic and vibrational operators to give a scalar as:

$$\begin{aligned} V_{ev} &= \sum_{d\nu}[\nu]^{1/2}[V(d\nu^*)Q_{d\nu}]^0 \\ &= \sum_{d\nu j}V(d\nu j)Q_{\nu j}\begin{pmatrix}\nu^* \\ j^*\end{pmatrix}, \end{aligned} \tag{19}$$

where $Q_{\nu j}$ is the vibration normal coordinate. The time reversal symmetry of the vibration shows that the vibration mode $d\nu$ and $d\nu^*$ are either the same or degenerate. It is possible to choose the phase of the normal coordinate so that

$$Q^*_{\nu j}=\begin{pmatrix}\nu \\ j\end{pmatrix}Q_{\nu^*j^*}. \tag{20}$$

The Hermicity of V_{ev} together with Eq. (20) gives the complex conjugation of parameters as:

$$A^*{}_{\lambda^+\cdot 1^-t^-c\nu}=(-1)A_{\lambda^+\cdots 1^-t^-c^*\nu^*}\begin{pmatrix}t^- \\ c \\ \nu\end{pmatrix} \tag{21}$$

$$B_{\lambda b\mu 1^- aq,\nu} = (-1) B_{\lambda b\mu * 1^- aq*,\nu} \begin{pmatrix} 1^- \\ a \\ q \end{pmatrix} \begin{pmatrix} \lambda^+ \\ b \\ \mu \end{pmatrix}. \tag{22}$$

This restricts some parameters to be pure real or pure imaginary if the label is self-conjugate.

Experimentally we can only measure the intensities of different polarizations and resolve $I_{a_1 a_2 q}(d\nu)$, which is a bilinear form of those B parameters with a same q. Eq. (18) shows that for each μq pair there is a choice of overall phase of the subset of B parameters. Eq. (22) limits the phase to be ± 1 if $1^- aq = 1^- aq*$ and $\lambda^+ b\mu = \lambda^+ b\mu*$. It can be seen from Eq. (7) that the A parameters are linear combinations of the B parameters with various μq. If more than one μq pair appear in an A parameter, then different choices of the overall signs of subset of B parameters give A values different in both sign and magnitude, as shown by Burdick et al. [7].

5. Number of independent polarization measurements

Stedman [14] has discussed this issue of the number of polarization measurements needed to characterize a transition in a particular symmetry. From Eq. (17) we see that the number of independent polarization measurements depends on the number of independent $I_{a_1 a_2, q}$. In the case that the Hamiltonian has time reversal symmetry (i.e. there are no magnetic fields present) the energy levels A and $A*$ are degenerate (if they are different). The effective electric dipole transition operator is invariant under time reversal. Therefore after summing over those degenerate states we obtain

$$I_{a_1 a_1, q} = I_{a_1 a_1, q*}. \tag{23}$$

We denote the number of independent polarization measurements as N_p and the dimension of the irrep q that characterizes a particular polarization as $[q]$. From Eqs. (17) and (23) and the branching rules for irrep 1^- of O_3 for the point group of interest, we may obtain the number of independent polarization measurements necessary to fully characterize a transition. If we assume that the Hamiltonian has time reversal symmetry then the cases we need to consider are:

1. The irrep 1^- of O_3 branches into one irrep q with $[q]=3$. In this case $N_p = 1$.
2. 1^- branches to q_1 with $[q_1]=1$ and q_2 with $[q_2]=2$. In this case $N_p = 2$.
3. 1^- branches to three different q_i ($i=1,2,3$) but two of the irreps are complex conjugates. In this case $N_p = 2$, and the situation is not distinguishable from case (2).
4. 1^- branches to three different q_i ($i=1,2,3$) and there is no complex conjugate pair. In this case $N_p = 3$.
5. 1^- branches to q_1 with multiplicity 1 and to q_2 with multiplicity 2. In this case $N_p = 4$.
6. 1^- branches to q_1 with multiplicity 3. In this case $N_p = 6$.

These results are the same as those of Stedman [14]. In axial site symmetries we have case (2) or case (3) and only two polarization measurements (commonly referred to as σ and π) are required. However, it is important to realize that this is not the case in low symmetries.

6. Conclusion

A consistent treatment of f^N–f^N electric dipole transitions in point-group bases has been given. This treatment has been used to clarify the discussion of independent intensity parameters in the work of Burdick et al. [7]. In particular, the detailed relationship between the A and B parameters of Burdick et al. has been explained. The calculation of transition intensities may be simplified by summing over degenerate states and this method has been implemented in RACAH computer program [10]. Complex-conjugation symmetries have been derived and the question of the number of independent polarization measurements required to characterize transitions for ions in various site symmetries has been discussed.

Acknowledgements

The authors acknowledge support of this work by the Marsden Fund, Contract No. UOC704.

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