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Subduced Selection Rules for Vibronic Transitions in d^3 Octahedral Complexes

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Forbidden electronic transitions are often weakly allowed through vibronic coupling to normal modes of the molecule. In transition metal complexes, the first order strong coupling appears in many cases to select specifically one of the available asymmetric modes. In this work the Intermediate Ligand Field model has been extended to vibronic coupling. The basis functions and tensor operators are described as species subduced from the vibronic generative group SU(3) which results from the diagonal restriction of the direct product of the electronic generative group SU(2) with the three dimensional harmonic oscillator group SU(3). This model implies that transitions between strongly coupled bases are permitted only through an overall octupole operator. All lower multipoles are forbidden and in particular the dipole is eliminated by the requirement for a translationally invariant centre of mass. The model permits any combination of multipole operators for separate electronic and vibrational transitions which result in the overall octupole. This theory is applied to two cases of d^3 complex spectra. It provides an unambiguous assignment of the $^4A_{2g}$–$^4T_{2g}$ transition in the absorption spectrum of solid $[MnF_6]^{4-}$ and of the MCD spectrum of the $^4A_{2g}$-($^2T_{1g}$, $^4T_{2g}$) region in $[Cr(H_2O)_6]^{3+}$. In the latter complex, the observed exclusive coupling of the $^2T_{1g}$ state to t_{1u} (stretch) and the $^4T_{2g}$ state to t_{1u} (twist) is predicted by the model.

Key words: Vibronic transitions – Metal complexes – Intermediate Ligand Field model.

1. Introduction

Most spectra of transition metal complexes provide evidence in some form of coupling of d–d transitions with vibrations in the first coordination sphere of

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atoms. In both absorption and emission spectra, resolved vibronic structures are often visible [1] but even in the case of unresolved bands, thermal studies reveal the presence of the same mechanism. Demonstrating the number and identity of the normal modes involved however is often quite difficult. The main criterion is usually comparison of observed separation energies with ground state normal modes but the differences in frequency are often so large as to make this comparison quite tenuous. In systems of low symmetry, static polarization and magnetic circular dichroism spectra [2, 3, 4, 5] can provide useful data concerning both degeneracy and orientation of the activating normal mode. In the highest symmetries including octahedral and tetrahedral complexes, the allowed modes are triply degenerate and of known orientation.

Several carefully analysed spectra [5, 6] suggest that not all the available modes participate in vibronic coupling and in some cases one mode may appear strongly in a progression to the exclusion of other modes of the same point group representation. This phenomenon is clearly evident in spectra of classical octahedral complexes in which progressions in one of the two available t_{1u} modes are observed on individual *d–d* transitions [7]. Selection rules employing only finite group representations cannot be used to predict these situations since the number of finite group labels for basis functions is too restricted to quantitatively describe the orthonormality conditions of the normal modes. The problem is often circumvented by adding some non group theoretic subscript or superscript to distinguish the basis functions but this does not facilitate the identification of selection rules nor aid in evaluation of matrix elements.

The strength of these selection rules suggests that the metal complex could be treated as a perturbed variant of a more symmetric system in which the normal modes bear unique group theoretic representations. Similar techniques are currently used to rationalize the observed electronic transitions in *d–d* systems [8, 9, 10]. In the purely electronic problem the finite group bases are regarded as projections of the bases of spherical ions. This permits the use of an augmented set of group theoretic labels from the infinite group SU(2) which in most cases of interest uniquely identify each basis function in the set. Unambiguous selection rules can then be used to calculate matrix elements of both the Hamiltonian and other multipole operators.

In this work a similar appeal to higher symmetry is made to provide a unique taxonomy of normal modes which may then be coupled to electronic transitions. The resulting model will be used to analyse two octahedral d^3 complexes which provide examples of strong selection of different t_{1u} modes for different *d–d* origins. These complexes of early transition metal ions provide particularly clear examples of vibronic coupling because the spin–orbit coupling is an order of magnitude smaller and the spinor manifold splittings do not interfere in first order with the vibronic progressions.

2. Experimental

A sample of 6.70 g of high purity chromium perchlorate $Cr(ClO_4) \cdot 36H_2O$ (M.W. = 899) was dissolved in 100 ml of distilled water. The absorption spectrum obtained on a Cary 14 spectrophotometer displayed band centres identical with previous values [5]. The optical densities of the two visible bands at 298 K were 0.97 and 1.16, reproducing very closely the previously observed ratio [5]. The magnetic circular dichroism spectra were obtained on a fully automated, custom built MCD spectrophotometer described earlier [11] using the driving routine MONITOR. This programme is designed to acquire data by a digital scan of the spectral region of interest. At a given spectral energy the scan halts and data are acquired over a predetermined period. The number of data readings is controlled directly by the standard deviation on the previous cycle. The difference between current and previous means is used to control the size of the next energy step. Scan energy, data mean and standard deviation are stored for subsequent plotting and processing. In operating this way the data are obtained at a constant level of quality throughout the scan range in the shortest possible time. For the present spectrum at a slit of 0.1 mm the scan rate was 5 cm^{-1}/sec with an average of 30 readings/sec. Baseline correction of these M.C.D. spectra was carried out with the routine MERGE.

The MCD spectrum of the red band was deconvoluted using a least squares fitting routine MCDFIT which is very similar to programmes used by several authors for treatment of absorption, emission and MCD data. The conditions of the fit are discussed below.

3. Results

Two sets of results will be considered as d^3 examples for analysis, a low temperature, highly resolved single crystal absorption spectrum of the $^4A_2 \rightarrow {}^4T_2$ transition in Cs_2MnF_6 [7] and the solution MCD spectrum of the same transition in $Cr(H_2O)_6{}^{3+}$ obtained in this work. The results of direct observation of absorption peaks are given in Table 1 and of deconvolution of the MCD spectrum are given in Table 2.

The absorption spectrum of the $[MnF_6]^{2-}$ chromophore (Fig. 1) shows a highly resolved series of peaks usually split further into three shoulders. The separation of the main series of seven peaks is consistently 490–510 cm^{-1} while the manifold splitting within each peak is approximately 200 cm^{-1}. The former series corresponds closely to the lower energy of two fundamental transitions observed in the infrared spectrum [7] of this species (Fig. 2) which occurs as a broad intense

Table 1. Observed band centres on $^4T_{2g}$ progression

Band symbol	Energy at band centre
1	—
2	20 850
3	21 350
4	21 850
5	22 360
6	22 860
7	23 365
8	23 900

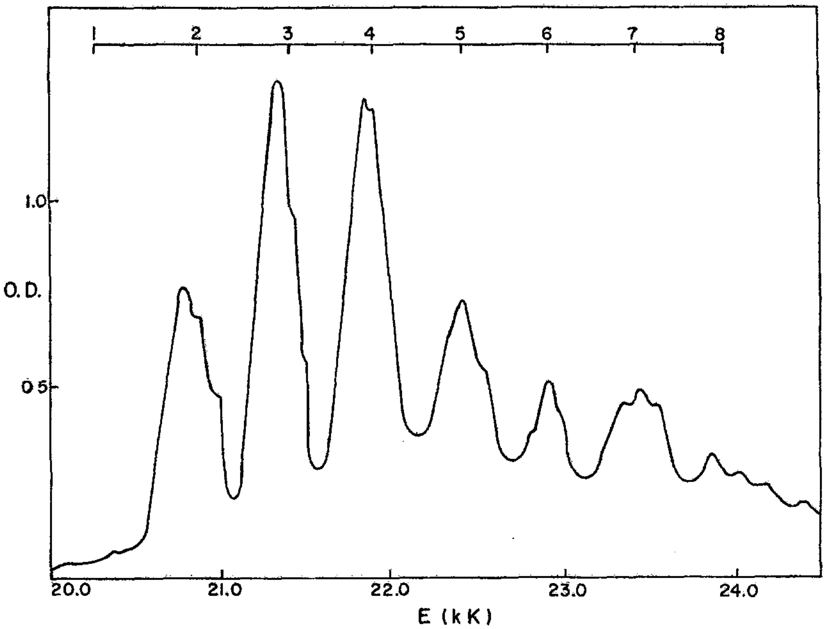

Fig. 1. Absorption spectrum of ${}^4A_{2g} \rightarrow {}^4T_{2g}$ band in $CsMnF_6$ at 80 K (adapted from Ref. 7)

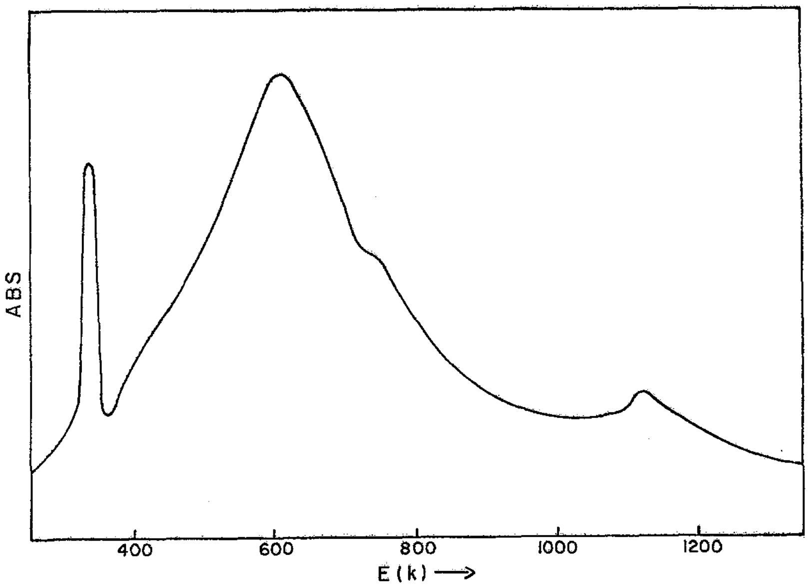

Fig. 2. Infrared spectrum of solid K_2MnF_6

shoulder at approximately 480 cm^{-1}. The higher energy fundamental mode occurs at about 620 cm^{-1}. These two bands can be assigned, by analogy with many octahedral species [5, 12, 13] as the lower energy t_{1u} (twist) and the higher energy t_{1u} (antisymmetric stretch). It thus appears that the $^4A_{2g} \rightarrow ^4T_{2g}$ transition is principally enhanced by the t_{1u} (twist) mode and the t_{1u} (stretch) is considerably less important. It is also useful to note that after Franck–Condon consideration there is an alternation of intensities in successive vibronic bands in the progression. The splitting of each vibronic band corresponds to the expected first order spinor splitting of the $^4T_{2g}$ state with a spin–orbit coupling constant near 80 cm^{-1} [7]. This splitting is small compared to the vibronic coupling and renders the spectrum relatively simple in first order.

The MCD spectrum of the corresponding band in $Cr(H_2O)_6^{3+}$ (Fig. 3) is less well resolved but provides greater structural detail than is visible in the absorption spectrum of this transition. It is more involved than the absorption spectrum of MnF_6^{2-} because a $^4A_{2g} \rightarrow ^2T_{1g}$ transition lies just below the transition of interest and could overlap some of its low energy features. The results which are given in Table 2 were obtained using a number of criteria designed to produce the simplest reasonable fit. Since these criteria are rigid and essential to understanding Table 2, they are considered in some detail here.

The considerable evidence that the band is essentially vibronic in origin, and that the derivative shaped A terms are completely masked by the C terms has been fully presented [5]. Initially only one fundamental vibration interval was employed in the deconvolution. In this approximation the spectrum was resolved into a set of bands of equal width spaced at equal intervals which represent successive vibrational quanta. Within these criteria the choice of band separation, type and width was required. The band type depends largely on the physical state of the molecule and for room temperature spectra of dissolved complexes a Gaussian shape has been found most suitable [14]. This is confirmed in the present case by the very close fit of a single Gaussian band on the sharp, isolated C term of the adjacent doublet state. The choice of the band separation and width is less certain but the two cannot be chosen independently. It is probably easier to

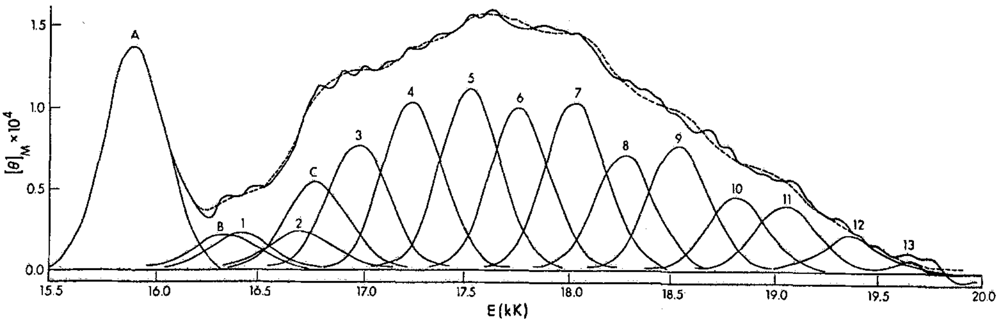

Fig. 3. MCD spectrum of $^4A_{2g} \rightarrow (^2T_{1g}, ^4T_{2g})$ band in aqueous $[Cr(H_2O)_6]^{3+}$ at 295 K (—) with final deconvolution assignments and comparison with fitted spectrum (– – –)

Table 2. Deconvoluted band characteristics[a] of $[Cr(H_2O)_6]^{3+}$

Band symbol	Energy $[cm^{-1}]$	Rotational strength $[\theta]_M \times 10^4$
Progression on $^2T_{1g}$ term		
A	15 900	1.368
B	16 345	0.201
C	16 775	0.510
Progression on $^4T_{2g}$ term		
1	16 410	0.203
2	16 700	0.223
3	16 980	0.725
4	17 240	0.955
5	17 510	1.003
6	17 760	0.900
7	18 020	0.915
8	18 280	0.625
9	18 545	0.662
10	18 820	0.375
11	19 080	0.326
12	19 350	0.176
13	19 630	0.028

[a] Band width is 350 cm^{-1} throughout both progressions

estimate an appropriate band width than band separation for two reasons. First, the chosen band width must yield a curve shape capable of following the most rapid change of intensity observed in the envelope. In fact, this requirement places severe restrictions on the range of available band widths. Second, the chosen band width should be consistent with known broadening perturbations. As seen in the previous case, the most important of these interactions is spin–orbit splitting of the spinor manifold of the $^4T_{2g}(F)$ term. In the present case the spin–orbit coupling constant is $\lambda \simeq 55\ cm^{-1}$ [15], yielding a total splitting of the four spinor states E', E'', $2U'$ of approximately 200 cm^{-1}. By using the first criterion to dictate the maximum width and the second the minimum, a band width of 350 cm^{-1} was chosen as the best approximation.

The chosen shape and band width was used together with the requirement of a regular spacing of bands to achieve the best fit of the observed MCD spectrum of the $^4T_{2g}$ term. The best quality of fit was achieved with a spacing of 270 cm^{-1} ± 10 cm^{-1}. The average deviation of the fit to any experimental point was less than 2.3% of the maximum observed rotational strength compared to an experimental precision of approximately 1.5%. This separation is close to the observed t_{1u} (twist) mode expected by analogy with $[Al(H_2O)_6]^{3+}$ for the ground state at approximately 280 cm^{-1}.

The major contributions to this fitting error occurred in two regions at 16 350 and 16 800 cm^{-1}. By broadening the fit region to include a fit of the sharp $^2T_{1g}$ transition at 15 900 and including two further C terms at the unfitted regions, an improvement in quality of fit to 1.9% was achieved. It seems clear that these three additional bands represent a progression on the $^2T_{1g}$ transition with a spacing of $440 \pm 10\ \mathrm{cm}^{-1}$. This spacing is close to the t_{1u} (stretch) mode observed in the ground state at $490\ \mathrm{cm}^{-1}$.

The final refinement of this fit is shown in Fig. 3. The average error is close to the experimental precision but more importantly all observable features are accounted for in the deconvolution. In addition to identification of band centres in both progressions, the fitting has again revealed an intensity alternation in the t_{1u} (twist) progression on the $^4T_{2g}$ term. This provides strong confirmation of the deconvolution. Odd numbered bands in the series shown in Fig. 3 appear to have distinctly greater rotational strength than the even numbered bands after taking into account the fact that band 5 probably represents the largest Franck–Condon factor in the series. While fewer bands were observable, the same alternation effect also appears in the t_{1u} (stretch) progression on the $^2T_{1g}$ term. The final data fit also suggests that the two vibronic progressions do not mix to first order. Using the assumption that the two independent progressions show no anharmonicity due to off-diagonal interactions, a fit is obtained close to the experimental error which could not be significantly improved by introduction of anharmonic behaviour.

4. Discussion

4.1. Transition Intensity Theory

(i) The Taxonomy of Basis and Operator Vectors. The appearance of band progressions with separations corresponding closely to t_{1u} fundamentals of the ground state suggest that a strong coupling vibronic model is appropriate for a study of transition intensities. There is no clear evidence in the two cases described here or in other analyses of similar systems that the weak coupling limit, resulting in progressions in the totally symmetric modes on one permitting odd quantum, is a useful approximation. In the strong coupling limit the vibronic bases can be constructed as adiabatic Born–Oppenheimer product functions [16];

$$|j\rangle = \Phi_m(q; Q)\Lambda_{mv}(Q) \tag{1}$$

in which q and Q are the electronic and nuclear normal mode coordinates respectively. Both these functions can be represented as basis vectors identified by finite group representation and component labels, $|\Gamma_m\gamma_m\rangle\,|\Gamma_v\gamma_v\rangle$ for the electronic and normal mode bases respectively.

In the strong coupling limit however, the angular momenta implied in these vectors are not conserved. As in all strongly coupled systems, only the total momentum can be used to label states of the system so that the product functions become

$$|\Gamma_m\gamma_m\rangle|\Gamma_v\gamma_v\rangle = \sum_{\Gamma_T\gamma_T} (-1)^{\Gamma_m+\Gamma_v+\gamma_T^*}\lambda[\Gamma_T]\begin{pmatrix}\Gamma_m & \Gamma_v & \Gamma_T\\ \gamma_m & \gamma_v & \gamma_T^*\end{pmatrix}|\Gamma_m\Gamma_v\Gamma_T\gamma_T\rangle\,. \tag{2}$$

Under these conditions, transition selection rules only apply directly to allowedness of changes in the total angular momentum implied in the coupled basis notation $|\Gamma_T\gamma_T\rangle$ and hence to all of the non-vanishing couplings of $|\Gamma_m\gamma_m\rangle$ with $|\Gamma_v\gamma_v\rangle$ which yield a particular $|\Gamma_T\gamma_T\rangle$. Thus for any transition between observable states of the strongly coupled vibronic system;

$$\begin{aligned}\langle\Gamma'_T\gamma'_T|\Gamma^0_T\gamma^0_T|\Gamma_T\gamma_T\rangle = \sum_{\substack{\Gamma'_m\gamma'_m\Gamma_m\gamma_m\\ \Gamma'_v\gamma'_v\Gamma_v\gamma_v}} & (-1)^{\Gamma'_m+\Gamma'_v+\gamma^{*\prime}_T+\Gamma^0_m+\Gamma^0_v+\gamma^{*0}_T+\Gamma_m+\Gamma_v+\gamma^*_T} \\ & \cdot\lambda[\Gamma'_T]\cdot\lambda[\Gamma^0_T]\cdot\lambda[\Gamma_T] \\ & \cdot\begin{pmatrix}\Gamma'_m & \Gamma'_v & \Gamma'_T\\ \gamma'_m & \gamma'_v & \gamma'^{*}_T\end{pmatrix}\begin{pmatrix}\Gamma^0_m & \Gamma^0_v & \Gamma^0_T\\ \gamma^0_m & \gamma^0_v & \gamma^{0*}_T\end{pmatrix}\begin{pmatrix}\Gamma_m & \Gamma_v & \Gamma_T\\ \gamma_m & \gamma_v & \gamma^*_T\end{pmatrix} \\ & \cdot\langle\Gamma'_m\gamma'_m|\Gamma^0_m\gamma^0_m|\Gamma_m\gamma_m\rangle\cdot\langle\Gamma'_v\gamma'_v|\Gamma^0_v\gamma^0_v|\Gamma_v\gamma_v\rangle. \qquad (3)\end{aligned}$$

This formulation of finite group selection rules does imply that only certain normal modes will couple with certain electronic states for any particular strongly coupled transition operator. It does not however provide a formalism for differentiation of orthonormal vibrational bases bearing identical representations.

The desired differentiation between such normal modes can be devised by appeal to a generative point group. This procedure is equivalent to one used to define the electronic bases in the Intermediate Ligand Field model [8, 9, 10]. Physically it corresponds to defining a body from which all normal modes in all symmetries of interest may be projected by standard hypergeometric algebra [17]. For the electronic functions, the basis vectors for molecules are projected out of the normal modes of the surface of a sphere which has the symmetry O(3) [9]. It is usually convenient to include half-integer spin and use the expanded group SU(2). The equivalent body for projection of molecular normal mode vibrations appears to be the solid sphere, using the point group for the isotropic three dimensional harmonic oscillator U(3) [18], which can be restricted without loss of generality to SU(3). The vibrational bases in three dimensional finite groups may then be projected from the four dimensional representations of SU(3) [19].

The formulation of vibronic basis functions as products of electronic and vibrational bases corresponds to the formation of the outer product of the two groups; $SU(2)\times SU(3)\in SU(6)$. In this six dimensional system the vectors all remain orthonormal. In order to define the coupling between the electronic and vibrational bases the representations of the SU(6) group must be restricted to subspaces in which only the total angular momentum vector may exist. By analogy with the restriction which yields the total momentum J from the outer product of L and S, the vibronic states will be defined in the diagonal subgroup of $SU(2)\times SU(3)$ [20]. In fact this cannot be done directly but since SU(2) is a normal subgroup of SU(3) then the diagonal subgroup of interest may be obtained by a restriction of the product $SU(3)\times SU(3)$. The diagonal group defining the total vibronic vector is then simply SU(3) [21].

This completes the inductive step necessary to define the generative groups for both vibrational and vibronic bases. By including representation labels from both the infinite generative group and the finite subgroup in the specification of these bases it is possible to distinguish uniquely between the different normal modes in most symmetries of interest. This distinctive taxonomy applies equally to the coupled bases, their related Hamiltonians and transition operators so that it is now possible to state selection rules unambiguously.

(*ii*) *Selection Rules for Subduced Strongly Coupled Vibronic States.* Intermediate Ligand Field Theory [10] has provided a formalism for calculation of selection rules between electronic states in complexes. The technique can be adapted for either weakly or strongly coupled L and S vectors for the finite symmetries projected from the group SU(2). In this section an analogous formalism will be developed first for vibrational transitions (parallel to selection rules for L or S separately) and then extended to the case of strong coupling between electronic functions labelled by $|L\Gamma_L\gamma_L\rangle$ and vibrational functions $|V\Gamma_V\gamma_V\rangle$.

For electronic transitions the predominant term in the multipole expansion of the transition operator is the dipole which for projected O_h symmetry is

$$|L^0\Gamma_L^0\gamma_L^0| = |1T_{1u} \pm 1|. \tag{4}$$

This term is allowed because a separation of positive and negative charge within a molecule does not translate the centre of charge. Subsequent terms also fulfil this criterion but are much smaller in magnitude.

In contrast, although infrared transitions are usually attributed to a dipole [21] mechanism, internal modes of vibration are forbidden through the dipole operator since translation of mass in a dipole causes translation of the centre of mass or rotation of the molecule. Thus six degrees of freedom (five for linear systems), corresponding to these dipole allowed motions are removed from the analysis of internal modes. The same considerations lead to neglect of the dipole transition operator for transitions between fluctuating density states in γ-ray resonance spectroscopy of atomic nuclei [23].

The next term in the multipole expansion, the quadrupole, is equally unimportant since it does not provide an antisymmetric displacement of nuclear charge which can interact with photons. Thus, the first term which does provide the required antisymmetric charge displacement while not permitting motion of the centre of mass is the octupole. This essentially ungerade operator is in turn, orders of magnitude more effective than the gerade hexadecupole which has been postulated in the analysis of the circular dichroism of vibronic transitions [24]. Thus, to first order, the transition operator for vibrational modes of an O_h complex becomes;

$$|V^0\Gamma_V^0\gamma_V^0| = |3T_{1u} \pm 1|. \tag{5}$$

Since the generative point group of the strongly coupled vibronic bases is likewise SU(3) and since the same physical constraints which limit vibrational transitions must apply to those between vibronic states, the first important vibronic term is again the octupole and can be written as;

$$|D^0\Gamma_D^0\gamma_D^0| = |3T_{1u} \pm 1|. \tag{6}$$

Using vector coupling techniques the vibronic operator can be uncoupled to [25, 26] demonstrate the allowed combinations of electronic and vibrational transition operators which result in a strongly coupled octupole transition operator for vibronic systems

$$\begin{aligned} |D\Gamma_D\gamma_D| &= \sum_{J,V,\Gamma_J,\Gamma_V} (-1)^{J(\Gamma_D)+\gamma_D^*} \frac{(2D+1)^{1/2}}{\lambda[\Gamma_D]} \\ &\quad \cdot \begin{pmatrix} L & V & T \\ \Gamma_L & \Gamma_V & \Gamma_T \end{pmatrix} \begin{pmatrix} \Gamma_L & \Gamma_V & \Gamma_T \\ \gamma_L & \gamma_V & \gamma_T^* \end{pmatrix} |L\Gamma_L\gamma_L V\Gamma_V\gamma_V| \\ &= \sum (-1)^{J(T_{1u})+\gamma_T^*} \frac{(2(3)+1)^{1/2}}{\lambda[T_{1u}]} \\ &\quad \cdot \begin{pmatrix} L & V & 3 \\ \Gamma_L & \Gamma_V & T_{1u} \end{pmatrix} \begin{pmatrix} \Gamma_L & \Gamma_V & T_{1u} \\ \gamma_L & \gamma_V & \gamma_T^* \end{pmatrix} |L\Gamma_L\gamma_L V\Gamma_V\gamma_V| \end{aligned} \tag{7}$$

after substitution from Eq. (6). Any values of L and V and any representations subduced from them, Γ_L and Γ_V, which yield allowed couplings to 3 and T_{1u} respectively may appear in this sum. The allowed combinations of L and V respectively which yield and overall octupole moment of the strongly coupled system are;

(0, 3)	monopole–octupole
(1, 2)	dipole–quadrupole
(2, 1)	quadrupole–dipole
(3, 0)	octupole–monopole

i.e.

$$|\Delta L| + |\Delta V| = |\Delta D| = 3. \tag{8}$$

At least the first three of these combinations can be documented and two appear in the examples used in this work. The final combination, which would employ only the totally symmetric vibration, may appear as a perturbation of apparently weakly coupled systems.

The internal modes of an octahedral molecule include vibrations of A_{1g}, E_g and T_{2g} active in the Raman, $2T_{1u}$ active in the infrared and T_{2u} inactive [22]. Each of these modes can be identified with a representation V of the point group SU(3) by projection;

$$\begin{aligned} &V \to \Gamma_V \\ &0 \to A_{1g} \\ &1 \to T_{1u} \quad \text{(antisym stretch)} \\ &2 \to E_g + T_{2g} \\ &3 \to T_{1u} \quad \text{(twist)},\ T_{2u} \end{aligned} \tag{9}$$

and the basis functions of each mode can be manipulated using group theoretic techniques operating on unique sets of labels $|V\Gamma_V\gamma_V\rangle$.

These selection rules apply only to the coupling of the electronic states with the first vibrational quantum. Since the vibronic transition octupole is ungerade in character, an allowed transition occurs only when one vector changes $(g \rightarrow u)$ or $(u \rightarrow g)$ while the other remains constant $(g \rightarrow g)$ or $(u \rightarrow u)$. This results in two distinct types of vibronic progression. For Laporte allowed electronic transitions the vibrational quanta remain $(g \rightarrow g)$ assuming that no hot bands appear. Thus the successive vibronic intensities in this situation would reflect only the magnitudes of successive Franck–Condon factors.

In contrast, Laporte forbidden electronic origins require coupling of generade electronic excited states to ungerade normal modes in the absence of hot bands. However the even overtones of ungerade modes are gerade [27] and hence the even transitions in the vibronic progression are forbidden under the octupole operator. This forbiddeness can be broken in second order by any molecular motions which destroy centres of symmetry but the successive intensities in the vibronic progression will be characterized by an alternation superimposed upon the envelope of Franck–Condon factors. The observation of an alternation on a Laporte forbidden transition is therefore an indication of strong coupling to an ungerade normal mode.

4.2. *Applications to Complex Spectra*

(*i*) *The Absorption Spectrum of the* $^4A_{2g} \rightarrow {}^4T_{2g}$ *Band in* $[\mathrm{MnF_6}]^{2-}$. The order of importance of potential terms in the Hamiltonian of this complex can be assigned from the spectrum as

$$\text{L.F.} > \text{I.E.R.} > \text{Vib} > \text{L.S.}\,. \tag{10}$$

Ignoring spin–orbit coupling, convenient bases for the resulting states can be identified as basis vectors [28]

$$|(L\Gamma_L,\, V\Gamma_V)D\Gamma_D S\Gamma_S T\Gamma_T\rangle\,.$$

In the present case $\Delta S = 0$ and the coupling of the vibronic vector $D\Gamma_D$ with spin $S\Gamma_S$ to give the total vector $T\Gamma_T$ can be ignored. The selection rule is

$$\begin{aligned}
&\langle L'\Gamma'_L V'\Gamma'_V D'\Gamma'_D\gamma'_D | L^0\Gamma^0_L V^0\Gamma^0_V D^0\Gamma^0_D\gamma^0_D | L\Gamma_L V\Gamma_V D\Gamma_D\gamma_D\rangle \\
&\quad = (-1)^{J(\Gamma'_L)+J(\Gamma'_V)+\gamma'^*_D+J(\Gamma^0_L)+J(\Gamma^0_V)+\gamma^{0*}_D+J(\Gamma_L)+J(\Gamma_V)+\gamma^*_D} \\
&\qquad \cdot \frac{(2D'+1)^{1/2}}{\lambda[\Gamma'_D]} \cdot \frac{(2D^0+1)^{1/2}}{\lambda[\Gamma^0_D]} \cdot \frac{(2D+1)^{1/2}}{\lambda[\Gamma_D]} \\
&\qquad \cdot \begin{pmatrix} L' & V' & D' \\ \Gamma'_L & \Gamma'_V & \Gamma'_D \end{pmatrix} \begin{pmatrix} \Gamma'_L & \Gamma'_V & \Gamma'_D \\ \gamma'_L & \gamma'_V & \gamma'^*_D \end{pmatrix} \begin{pmatrix} L^0 & V^0 & D^0 \\ \Gamma^0_L & \Gamma^0_V & \Gamma^0_D \end{pmatrix} \\
&\qquad \cdot \begin{pmatrix} L^0_L & \Gamma^0_V & \Gamma^0_D \\ \gamma^0_L & \gamma^0_V & \gamma^{0*}_D \end{pmatrix} \begin{pmatrix} L & V & D \\ \Gamma_L & \Gamma_V & \Gamma_D \end{pmatrix} \begin{pmatrix} \Gamma_L & \Gamma_V & \Gamma_D \\ \gamma_L & \gamma_V & \gamma^*_D \end{pmatrix} \\
&\qquad \cdot \langle L'\Gamma'_L\gamma'_L | L^0\Gamma^0_L\gamma^0_L | L\Gamma_L\gamma_L\rangle \cdot \langle V'\Gamma'_V\gamma'_V | V^0\Gamma^0_V\gamma^0_V | V\Gamma_V\gamma_V\rangle
\end{aligned} \tag{11}$$

in which the fully specified selection rule on the total vectors $|D\Gamma_D\gamma_D\rangle$ is written in terms of products of selection rules on the individual vectors $|L\Gamma_L\gamma_L\rangle$ and $|V\Gamma_V\gamma_V\rangle$. The observed vibronic sequence can now be assigned by substitution of Eqs. (8) and (9) into (11). In brief, the absorption spectrum depends on the square of elements;

$$\langle 3A_{2g}0A_{1g}3A_{2g}0|4T_{1g}3T_{1u}3T_{1u}\gamma_T^0|3T_{2g}3T_{1u}D\Gamma_{T_u}\gamma_T\rangle$$

which depends in turn on the magnitude of products of matrix elements

$$\langle 3A_{2g}0|4T_{1u}\pm 1|3T_{2g}\mp 1\rangle \cdot \langle 0A_{1g}0|3T_{1u}\pm 1|3T_{1u}\mp 1\rangle.$$

By these rules a vibronic coupling involving

$$\langle 3A_{2g}0|4T_{1g}\pm 1|3T_{2g}\mp 1\rangle \cdot \langle 0A_{1g}0|1T_{1u}\pm 1|1T_{1u}\mp 1\rangle$$

should be equally allowed. However the hexadecupole acts as a scalar for octahedral symmetry since the four fold axis is the highest order [25].

$$\left.\begin{array}{l}\text{Therefore an assignment } L^0=4\\ \text{is effectively equivalent to } L^0=0\end{array}\right\} \tag{12}$$

Using this revised assignment, the term from (11)

$$\begin{pmatrix} L^0 & V^0 & D^0 \\ \Gamma_L^0 & \Gamma_V^0 & \Gamma_D^0 \end{pmatrix} = \begin{pmatrix} 0 & 3 & 3 \\ T_{1g} & T_{1u} & T_{1u} \end{pmatrix} \tag{13a}$$

is allowed but the term;

$$\begin{pmatrix} L^0 & V^0 & D^0 \\ \Gamma_L^0 & \Gamma_V^0 & \Gamma_D^0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 3 \\ T_{1g} & T_{1u} & T_{1u} \end{pmatrix} \tag{13b}$$

is forbidden [25]. Thus, there is a strong selection against the antisymmetric stretch in first order for the observed spectroscopic band and indeed no sequence is this stretch or any combination of the two t_{1u} modes is observed.

(ii) The MCD *Spectrum of the* $^4A_{2g}\rightarrow(^2T_{1g}, {}^4T_{2g})$ *Band of* $[\mathrm{Cr(H_2O)_6}]^{3+}$. The order of potential terms again follows Eq. (10) but both the vibrational separation and the spin-orbit coupling constant are smaller in this case since the nuclear charge has been reduced from Mn^{4+} to Cr^{3+}. The same basis functions may be used but since ΔS is not zero for the doublet state the complete coupling treatment will be needed.

$$\begin{aligned}&\langle (L'\Gamma_L', V'\Gamma_V')D'\Gamma_D'S'\Gamma_S'T'\Gamma_T'\gamma_T'|(L^0\Gamma_L^0, V^0\Gamma_V^0)D^0\Gamma_D^0S^0\Gamma_S^0T^0\Gamma_T^0\gamma_T^0|\\ &\quad(L\Gamma_L, V\gamma_V)D\Gamma_DS\Gamma_ST\Gamma_T\gamma_T\rangle\\ &=\langle L'\Gamma_L'V'\Gamma_V'D'\Gamma_D'\gamma_D'|L^0\Gamma_L^0V^0\Gamma_V^0D^0\Gamma_D^0\gamma_D^0|L\Gamma_LV\Gamma_VD\Gamma_D\gamma_D\rangle\\ &\quad\cdot(-1)^{J(\Gamma_D')+J(\Gamma_S')+\gamma_T'^*+J(\Gamma_D^0)+J(\Gamma_S^0)+\gamma_T^{0*}+J(\Gamma_D)+J(\Gamma_S)+\gamma_T^*}\\ &\quad\cdot\frac{(2T'+1)^{1/2}}{\lambda[\Gamma_T']}\cdot\frac{(2T^0+1)^{1/2}}{\lambda[\Gamma_T^0]}\cdot\frac{(2T+1)^{1/2}}{\lambda[\Gamma_T]}\end{aligned}$$

$$\cdot \begin{pmatrix} D' & S' & T' \\ \Gamma'_D & \Gamma'_S & \Gamma'_T \end{pmatrix} \begin{pmatrix} \Gamma'_D & \Gamma'_S & \Gamma'_T \\ \gamma'_D & \gamma'_S & \gamma'^{*}_T \end{pmatrix} \begin{pmatrix} D^0 & S^0 & T^0 \\ \Gamma^0_D & \Gamma^0_S & \Gamma^0_T \end{pmatrix}$$
$$\cdot \begin{pmatrix} \Gamma^0_D & \Gamma^0_S & \Gamma^0_T \\ \gamma^0_D & \gamma^0_S & \gamma^{0*}_T \end{pmatrix} \begin{pmatrix} D & S & T \\ \Gamma_D & \Gamma_S & \Gamma_T \end{pmatrix} \begin{pmatrix} \Gamma_D & \Gamma_S & \Gamma_T \\ \gamma_D & \gamma_S & \gamma^{*}_T \end{pmatrix}$$
$$\cdot < S'\Gamma'_S\gamma'_S | S^0\Gamma^0_S\gamma^0_S | S\Gamma_S\gamma_S\rangle. \tag{14}$$

in which the first matrix element in the expansion can be calculated from Eq. (11).

The inclusion of a final coupling to spin does not change the physical constraints on the selection rules. The generative groups for the definitions of both L and S are SU(2). The coupling in Eq. (14) represents the outer product SU(2) × SU(3) × SU(2) for which the restricted diagonal subgroup in which $|T\Gamma_T\gamma_T\rangle$ is defined is again SU(3). The introduction of this third vector however requires an expansion of Eq. (8). The augmented selection rule becomes;

$$|\Delta L| + |\Delta V| + |\Delta S| = |\Delta T| = 3. \tag{15}$$

The MCD spectrum of $[Cr(H_2O)_6]^{3+}$ has been analysed above in terms of predominant C terms [5] which depend on the product of the ground state magnetic moment with the square of the electronic moment [29]. For vibronic systems:

$$C(\Gamma_T \to \Gamma'_T) = \frac{3}{\lambda[\Gamma_T]} \sum_{\gamma_T\gamma'_T} \langle (L\Gamma_L V\Gamma_V) D\Gamma_D S\Gamma_S T\Gamma_T\gamma_T | (L^u\Gamma^u_L V^u\Gamma^u_V)$$
$$D^u\Gamma^u_D S^u\Gamma^u_S T^u\Gamma^u_T\gamma^u_T | (L\Gamma_L V\Gamma_V) D\Gamma_D S\Gamma_S T\Gamma_S T\Gamma_T\gamma_T\rangle$$
$$\cdot \langle (L\Gamma_L V\Gamma_V) D\Gamma_D S\Gamma_S T\Gamma_T\gamma_T | (L^m\Gamma^m_L V^m\Gamma^m_V) D^m\Gamma^m_D S^m\Gamma^m_S T^m\Gamma^m_T 1 |$$
$$(L'\Gamma'_L V'\Gamma'_V) D'\Gamma'_D S'\Gamma'_S T'\Gamma'_T\gamma'_T\rangle$$
$$\cdot \langle (L'\Gamma'_L V'\Gamma'_V) D'\Gamma'_D S'\Gamma'_S T'\Gamma'_T\gamma'_T |$$
$$\cdot (L^m\Gamma^m_L V^m\Gamma^m_V) D^m\Gamma^m_D S^m\Gamma^m_S T^m\Gamma^m_T - 1 |$$
$$(L\Gamma_L V\Gamma_V) D\Gamma_D S\Gamma_S T\Gamma_T\gamma_T\rangle. \tag{16}$$

Each term in this product can be expanded according to Eqs. (14) and (11) and on substitution back into (16) a product of three orbital with three vibrational and three spin matrix elements is obtained accompanied by the appropriate 3Γ symbols and partition coefficients.

This expanded form of the C term can be used to assign both progressions in the ${}^2T_{1g}$, ${}^4T_{2g}$ region. The magnetic dipole is allowed so the discussion can be limited to electronic moments. The latter progression involves the t_{1u} twist vibration and follows exactly the same analysis as the ${}^4A_{2g} \to {}^4T_{2g}$ assignment for $(MnF_6)^{2-}$ in the previous section. The assignment of the ${}^4A_{2g} \to {}^2T_{1g}$ requires a spin change in addition to orbital and vibrational changes so that the selection rules for any one matrix element in (16) depend on products of matrix elements;

$$\langle 3A_{2g}0|4T_{2g}\pm 1|4T_{1g}\mp 1\rangle$$
$$\langle 0A_{1g}0|1T_{1u}\pm 1|1T_{1u}\mp 1\rangle$$
$$\langle \tfrac{3}{2}U'\gamma_s|1T_{1u}\gamma_s^0|\tfrac{1}{2}E'\gamma_s'\rangle$$

in which $L^0=4$ again maps into $L^0=0$ according to Eq. (12). Since the t_{1u} (anti-symmetric stretch) mode is now involved, the selection rule for these products from Eq. (15) becomes;

$$|\Delta L|+|\Delta V|+|\Delta S|=1+1+1=3 \tag{17}$$

which again obeys the octupole rule for the overall transition moment. In this case the progression involving the t_{1u} (twist) mode is strongly forbidden since the partition coefficient;

$$\begin{pmatrix} D^0 & S^0 & T^0 \\ \Gamma_D^0 & \Gamma_S^0 & \Gamma_T^0 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 3 \\ \Gamma_D^0 & T_{1u} & T_{1u} \end{pmatrix} \tag{18}$$

in Eq. (14) vanishes [25].

5. Conclusions

(*i*) *The* RSBO *Basis Set.* In two favorable examples of transition metal complex spectra in which vibronic progressions are readily identified, an octupole selection rule on the total projected representations has been sufficient to assign the observed band structure. A simple explanation of this rule has been derived here from the requirement of a fixed centre of mass during the excitation of internal modes of vibration in a molecule. The requirement can be quantitatively expressed using a projected set of Russell–Saunders Born–Oppenheimer (RSBO) basis vectors and transition moment operators which uniquely identify all electronic and vibrational states. The coupled vectors, which are defined in restricted diagonal subgroups of the original generic point groups, can be factored to provide scalar products of matrix elements for the individual orbital, vibrational and spin bases. These factored expressions can be used to calculate the number of permissable ways in which the overall octupole rule can be observed in specific cases.

Neither the physical constraints nor the formalism used to express the intensities of transitions limit the analysis to special classes of transitions. The concepts have been applied here to Laporte forbidden and in one case spin forbidden bands but could equally have been used for Laporte allowed systems. The identification of vibronic transitions in singlet to singlet and singlet to triplet transitions in organic substances should provide further tests of the usefulness of the proposed model.

(*ii*) *Applications to Photochemistry.* These conclusions provide a basis for first-order predictions of photoreactions of the $[Cr(H_2O)_6]^{3+}$ ion. The reaction model developed by Bader [30], Pearson [31] and Salem [32] relates the most probable unimolecular dissociation coordinate of the ground state to the symmetry of both the normal mode motion and the nearest excited electronic states. These same concepts can be used in analysis of the reaction coordinates of vibrationally hot, excited electronic states [33]. The simplest relationship between reaction coordinates and normal modes is a diagonal anharmonic coupling model. At this level of approximation the symmetries of the molecular motion and the reaction coordinate are identical. In the present case this implies that excitation of the $[Cr(H_2O)_6]^{3+}$ complex into the T_{1g} and $^4T_{2g}$ terms respectively which appears to lead to two different molecular modes, the asymmetric stretch and the angular deformation, would lead in turn to two different photochemical reaction coordinates. The first of these, based on asymmetric stretching, would lead to bond breaking and a dissociative type of substitution reactions through a five coordinate square pyramidal intermediate. The twisting mode on the other hand tends to open the faces of the octahedron which could lead to more clearly associative mechanisms through trigonally distorted intermediates. The results could include substitution or real or pseudorotation of ligands.

This simple model applies only to those photochemical reactions which become pathological shortly after excitation. It could well form a useful model for reactions which occur within one or a few vibrations but becomes less valid as the vibrational excitation is lost to the surroundings. The model is also inadequate if two or more vibrational modes are strongly coupled or if the reaction coordinate differed from these normal coordinates due to anharmonic coupling.

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