Differential Orbital Expansion in Tetragonal d^3 Systems

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Matrix elements for interelectronic repulsion, including differential orbital expansion, have been calculated for d^3 complexes with tetragonal symmetry. The expansion parameter ε influences the overall positions of the five components of the ^2E_g and $^2T_{1g}$ states and the separation between ^2E_g and $^2T_{1g}$, but is relatively unimportant with respect to the splittings within those states.

In a previous paper [1] we set forth the energy matrices for tetragonal d^3 complexes in a strong field basis set, including interelectronic repulsion, spin-orbit coupling, and an Angular Overlap Model parameterization of the ligand field potential. Use of the complete matrices is necessary in studying the splittings of the sharp-line doublets (of which there are eight in total), which can be attributed largely to configuration interaction with other states

Although Ferguson and Wood [2] have argued otherwise, it has been our experience [3] that obtaining a good fit to the doublet splittings, particularly in cases where these splittings are not greatly affected by the ligand field asymmetry, is impossible without some recourse to the concept which has been denoted "differential orbital expansion" [4]. Metal d orbitals which overlap substantially with ligand orbitals may be considered to have expanded relative to d orbitals with small ligand overlap, reducing the repulsion between electrons in expanded orbitals and any other d electrons [5].

Symmetry considerations lead to a large number of potentially independent electrostatic repulsion integrals, even for an octahedral complex [6], but clearly it is desirable to hold the number of parameters to a minimum in order to maintain the simplicity of the ligand field model, and even more importantly, to avoid overparameterization to the extent that little significance can be attributed to any of the parameters.

We have suggested one way to account for differential orbital expansion in six-coordinate complexes in terms of a single additional parameter, ε, defined so that [3]

$$\langle d_1 d_2 | \frac{e^2}{r_{ij}} | d_3 d_4 \rangle = \varepsilon^n \langle d_1 d_2 | \frac{e^2}{r_{ij}} | d_3 d_4 \rangle_0 . \quad (1)$$

The exponent n refers to the number of wave functions (denoted by d_1, d_2, d_3, and d_4) in the integral representing e_g orbitals, and the subscript 0 refers to the value the integral would have in the usual Racah-Slater-Condon formulation, in terms of B and C. Equation (1) is formally equivalent to the definitions of β_{33}, β_{35}, and β_{55} suggested by Koida and Price [7], and the parameter ε is equal to the ratio f_e/f_{t2} of the parameters used by Lohr [8]. With this definition, B and C refer now specifically to B_{55} and C_{55}, the repulsion within the t_{2g} orbital set of an octahedral complex. We continue to use this formulation for six-coordinate complexes of less than octahedral symmetry.

The interelectronic repulsion matrix elements appropriate to tetragonal symmetry are listed in the Appendix. Figure 1 illustrates the effects of the expansion parameter ε on the energies of the five components of the octahedral ^2E_g and $^2T_{1g}$ states for a typical tetragonal Cr(III) complex.

There are two features of Fig. 1 which should be pointed out. First, the variation in transition energies of these doublets with ε is counter to the variation among all the transition energies as a whole. As ε is decreased, diagonal elements in the Hamiltonian (relative to the ground state) decrease in value, and hence the sum of the eigenvalues (again relative to the ground state) is smaller. The five doublets are unaffected to first order: The diagonal energies are all $9B+3C$, with no off-diagonal elements among them, or between them and the ground state. Configuration interaction operates, however, to *increase* their transition energies with decreasing ε.

The second point is that the ^2E_g components are affected approximately twice as strongly as the $^2T_{1g}$ components by changes in ε, but the splittings within each state are relatively uninfluenced. Thus

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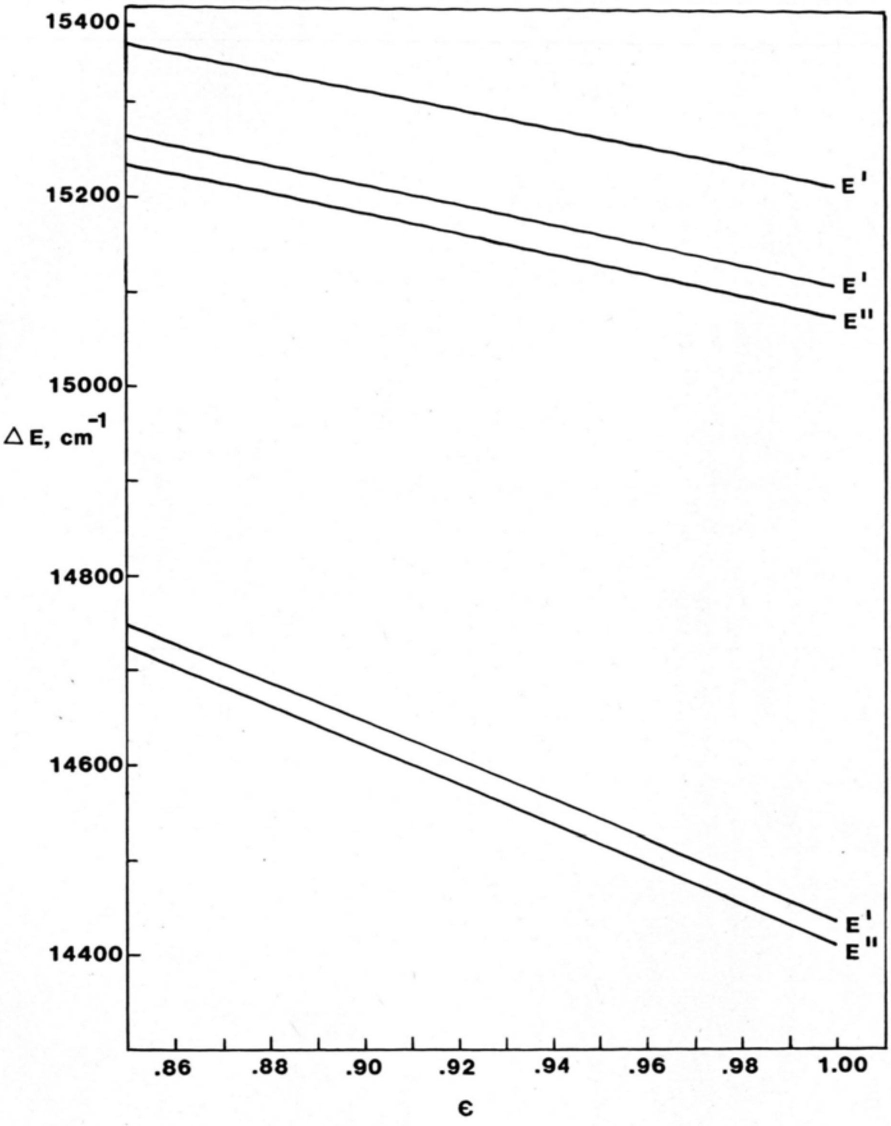

Fig. 1. Variation of the transition energies of the components of the ^2E_g and $^2T_{1g}$ states as a function of the expansion parameter, ε, for a tetragonal Cr (III) complex described by the following parameters (in cm^{-1}): $e_{\sigma X} = e_{\sigma Z} = 7000$, $e_{\pi Z} = 750$, $B = 800$, $C = 2850$, $\zeta = 230$.

the value of ε affects both the overall position of the 5-level doublet manifold and the separation between the ^2E_g and $^2T_{1g}$ states. With a larger tetragonal distortion, the same effects occur, but because the ^2E_g and $^2T_{1g}$ components are less readily identified, the apparent effects of variation of ε are more complex.

Acknowledgement

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Appendix

Table 1. Nonzero interelectronic repulsion matrix elements for d^3 complexes in tetragonal symmetry. Wavefunctions are labelled as in [1].

$E'_{1/2}$ Matrix

$\langle 1 | 1 \rangle = -15\,B$
$\langle 2 | 2 \rangle = (-5 - 10\,\varepsilon^2)\,B$
$\langle 3 | 3 \rangle = (-5 + 2\,\varepsilon^2)\,B$
$\langle 3 | 4 \rangle = 6\,\varepsilon\,B$
$\langle 4 | 4 \rangle = (-4\,\varepsilon^2 - 8\,\varepsilon^4)\,B$
$\langle 5 | 5 \rangle = (-5 - 10\,\varepsilon^2)\,B$
$\langle 6 | 6 \rangle = (-5 - 10\,\varepsilon^2)\,B$
$\langle 7 | 7 \rangle = (-5 + 2\,\varepsilon^2)\,B$
$\langle 7 | 9 \rangle = 6\,\varepsilon\,B$
$\langle 8 | 8 \rangle = (-5 + 2\,\varepsilon^2)\,B$
$\langle 8 | 10 \rangle = 6\,\varepsilon\,B$
$\langle 9 | 9 \rangle = (-4\,\varepsilon^2 - 8\,\varepsilon^4)\,B$
$\langle 10 | 10 \rangle = (-4\,\varepsilon^2 - 8\,\varepsilon^4)\,B$
$\langle 11 | 11 \rangle = (1 - 12\,\varepsilon^2)\,B + (2 + \varepsilon^2)\,C$
$\langle 12 | 12 \rangle = -6\,B + 3\,C$

Table 1 contin.

$\langle 12 | 13\rangle = -6\sqrt{2}\,\varepsilon B$

$\langle 12 | 14\rangle = -3\sqrt{2}\,\varepsilon B$

$\langle 13 | 13\rangle = (10 - 2\varepsilon^2) B + (5 + \varepsilon^2) C$

$\langle 13 | 14\rangle = 10\,\varepsilon^2 B$

$\langle 13 | 15\rangle = \sqrt{3}\,\varepsilon^2 (2B + C)$

$\langle 14 | 14\rangle = (1 - 2\varepsilon^2) B + (2 + \varepsilon^2) C$

$\langle 14 | 15\rangle = 2\sqrt{3}\,\varepsilon^2 B$

$\langle 15 | 15\rangle = -8\varepsilon^4 B + 4\varepsilon^4 C$

$\langle 16 | 16\rangle = -6B + 3C$

$\langle 16 | 17\rangle = 3\varepsilon B$

$\langle 16 | 18\rangle = -3\varepsilon B$

$\langle 16 | 20\rangle = -2\sqrt{3}\,\varepsilon^2 B$

$\langle 17 | 17\rangle = (-5 + 5\varepsilon^2) B + 3\varepsilon^2 C$

$\langle 17 | 18\rangle = -3\varepsilon^2 B$

$\langle 17 | 19\rangle = -3\varepsilon B$

$\langle 17 | 20\rangle = -3\sqrt{3}\,\varepsilon B$

$\langle 18 | 18\rangle = (1 - 7\varepsilon^2) B + (2 + \varepsilon^2) C$

$\langle 18 | 19\rangle = 3\varepsilon B$

$\langle 18 | 20\rangle = \sqrt{3}\,\varepsilon B$

$\langle 19 | 19\rangle = (2\varepsilon^2 - 8\varepsilon^4) B + 3\varepsilon^2 C$

$\langle 19 | 20\rangle = 2\sqrt{3}\,\varepsilon^2 B$

$\langle 20 | 20\rangle = -2\varepsilon^2 B + (\varepsilon^2 + 2\varepsilon^4) C$

$\langle 21 | 21\rangle = -6B + 3C$

$\langle 21 | 22\rangle = 3\varepsilon B$

$\langle 21 | 23\rangle = -3\varepsilon B$

$\langle 21 | 25\rangle = -2\sqrt{3}\,\varepsilon^2 B$

$\langle 22 | 22\rangle = (-5 + 5\varepsilon^2) B + 3\varepsilon^2 C$

$\langle 22 | 23\rangle = -3\varepsilon^2 B$

$\langle 22 | 24\rangle = -3\varepsilon B$

$\langle 22 | 25\rangle = -3\sqrt{3}\,\varepsilon B$

$\langle 23 | 23\rangle = (1 - 7\varepsilon^2) B + (2 + \varepsilon^2) C$

$\langle 23 | 24\rangle = 3\varepsilon B$

$\langle 23 | 25\rangle = \sqrt{3}\,\varepsilon B$

$\langle 24 | 24\rangle = (2\varepsilon^2 - 8\varepsilon^4) B + 3\varepsilon^2 C$

$\langle 24 | 25\rangle = 2\sqrt{3}\,\varepsilon^2 B$

$\langle 25 | 25\rangle = -2\varepsilon^2 B + (\varepsilon^2 + 2\varepsilon^4) C$

$\langle 26 | 26\rangle = 5C$

$\langle 26 | 27\rangle = 3\sqrt{3}\,\varepsilon B$

$\langle 26 | 28\rangle = -5\sqrt{3}\,\varepsilon B$

$\langle 26 | 29\rangle = 4\varepsilon^2 B + 2\varepsilon^2 C$

$\langle 26 | 30\rangle = -2\varepsilon^2 B$

$\langle 27 | 27\rangle = (-5 - \varepsilon^2) B + 3\varepsilon^2 C$

$\langle 27 | 28\rangle = -3\varepsilon^2 B$

$\langle 27 | 29\rangle = 3\sqrt{3}\,\varepsilon B$

$\langle 27 | 30\rangle = -3\sqrt{3}\,\varepsilon B$

$\langle 28 | 28\rangle = (1 + 3\varepsilon^2) B + (2 + \varepsilon^2) C$

$\langle 28 | 29\rangle = -\sqrt{3}\,\varepsilon B$

$\langle 28 | 30\rangle = -\sqrt{3}\,\varepsilon B$

$\langle 29 | 29\rangle = (-2\varepsilon^2 + 8\varepsilon^4) B + (\varepsilon^2 + 4\varepsilon^4) C$

$\langle 29 | 30\rangle = -10\,\varepsilon^2 B$

$\langle 30 | 30\rangle = -2\varepsilon^2 B + (\varepsilon^2 + 2\varepsilon^4) C$

$\mathbf{E''_{3/2}}$ Matrix

The interelectronic repulsion elements of the $E''_{3/2}$ matrix are the same as those of the $E'_{1/2}$ matrix except for the following:

$\langle 11 | 11\rangle = (1 + 8\varepsilon^2) B + (2 + \varepsilon^2) C$

$\langle 12 | 14\rangle = 3\sqrt{2}\,\varepsilon B$

$\langle 13 | 14\rangle = -10\,\varepsilon^2 B$

$\langle 14 | 15\rangle = -2\sqrt{3}\,\varepsilon^2 B$

$\langle 16 | 16\rangle = 5C$

$\langle 16 | 17\rangle = 3\sqrt{3}\,\varepsilon B$

$\langle 16 | 18\rangle = -5\sqrt{3}\,\varepsilon B$

$\langle 16 | 19\rangle = 4\varepsilon^2 B + 2\varepsilon^2 C$

$\langle 16 | 20\rangle = -2\varepsilon^2 B^2$

$\langle 17 | 17\rangle = (-5 - \varepsilon^2) B + 3\varepsilon^2 C$

$\langle 17 | 19\rangle = 3\sqrt{3}\,\varepsilon B$

$\langle 18 | 18\rangle = (1 + 3\varepsilon^2) B + (2 + \varepsilon^2) C$

$\langle 18 | 19\rangle = -\sqrt{3}\,\varepsilon B$

$\langle 18 | 20\rangle = -\sqrt{3}\,\varepsilon B$

$\langle 19 | 19\rangle = (-2\varepsilon^2 + 8\varepsilon^4) B + (\varepsilon^2 + 4\varepsilon^4) C$

$\langle 19 | 20\rangle = -10\,\varepsilon^2 B$

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