TETRAGONALLY DISTORTED TETRAHEDRAL ML_4-COMPLEXES. III*

Splitting of the d^4-Configuration in Strong Ligand Field of D_{2d} Symmetry

By

M. I. BÁN

Institute of General and Physical Chemistry, Attila József University, Szeged

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The energies of spectroscopic terms arising from the splittings, in ligand field of D_{2d} symmetry, of d^4 strong field configurations have been given in expressions of the electronic repulsion parameters B and C, the three ligand field parameters K, L and M and the distortion angle β.

By using the assumptions made and the procedure described in the previous papers [1] of the series, the matrix elements of electron-electron and electron-ligand field interactions[1] have been calculated.

In the matrices, B and C are the usual electronic repulsion (Racah's) parameters and

$$K = \frac{5}{42} D_4 (35 \cos^4 \beta - 30 \cos^2 \beta + 3),$$

$$L = \pm \frac{5}{6} D_4 (1 - \cos^2 \beta)^2,$$

$$M = D_2 (3 \cos^2 \beta - 1),$$

where D_2 and D_4 denote — apart from numerical factors — the integrals related to second-order and fourth-order spherical harmonics, and the plus and minus signs occurring in the expression of L correspond[2] to orientation 1 and orientation 2, resp., described in [1a].

The complete energy matrices are:

$$^5A_1 [b_1 b_2 e^2]: \; -6K - 2M \tag{1}$$

$$^5B_1 [a_1 b_2 e^2]: \; 6L + 2M \tag{2}$$

$$^5B_2 [a_1 b_1 e^2]: \; -6L + 2M \tag{3}$$

$$^5E [a_1 b_1 b_2 e]: \; 6K - M \tag{4}$$

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[1] The corresponding integrals are composed of determinantal functions [2] and the operators (3) and (8) of [1a].

[2] Through the series, all the calculations are based on orientation 1.

$^3A_1$	$a_1b_1e^2$	$a_1b_2e^2$	$a_1b_2e^2$	$b_1b_2e^2$
$a_1b_1e^2$	$10B+4C-6L+2M$	$3B$	$\sqrt{3}\,B$	$-\sqrt{6}\,B$
$a_1b_2e^2$		$10B+4C+6L+2M$	$-\sqrt{3}\,B$	$-\sqrt{6}\,B$
$b_1b_2e^2$			$6B+4C-6K-2M$	0
$b_1b_2e^2$				$12B+4C-6K-2M$

(5)

$^3A_2$	$a_1^2e^2$	$b_1^2e^2$	$b_2^2e^2$	$a_1^2b_1b_2$	$a_1b_1e^2$	$a_1b_2e^2$	$b_1b_2e^2$
$a_1^2e^2$	$26B+5C+6K+6M$	$4B+C$	$4B+C$	$6B$	$-\sqrt{6}\,B$	$\sqrt{6}\,B$	0
$b_1^2e^2$		$6B+5C-6K-12L-2M$	C	0	$\sqrt{6}\,B$	0	$-\sqrt{18}\,B$
$b_2^2e^2$			$6B+5C-6K+12L-2M$	0	0	$-\sqrt{6}\,B$	$-\sqrt{18}\,B$
$a_1^2b_1b_2$				$5B+5C+18K$	$-\sqrt{6}\,B$	$\sqrt{6}\,B$	$\sqrt{2}\,(B+C)$
$a_1b_1e^2$					$10B+4C-6L+2M$	$-3B$	$-\sqrt{75}\,B$
$a_1b_2e^2$						$10B+4C+6L+2M$	$\sqrt{75}\,B$
$b_1b_2e^2$							$18B+6C-6K-2M$

(6)

$^3B_1$	$a_1b_1b_2^2$	$a_1b_1e^2$	$a_1b_2e^2$	$a_1b_2e^2$	$b_1b_2e^2$
$a_1b_1b_2^2$	$13B+5C+12K+6L-4M$	$\sqrt{2}\,(3B+C)$	$-\sqrt{18}\,B$	$6B$	$-\sqrt{6}\,B$
$a_1b_1e^2$		$16B+6C-6L+2M$	$-3B$	$\sqrt{18}\,B$	$-\sqrt{75}\,B$
$a_1b_2e^2$			$12B+4C+6L+2M$	$-\sqrt{8}\,B$	$-\sqrt{3}\,B$
$a_1b_2e^2$				$8B+4C+6L+2M$	$-\sqrt{6}\,B$
$b_1b_2e^2$					$12B+4C-6K-2M$

(7)

$^3B_2$	$a_1b_1^2b_2$	$a_1b_1e^2$	$a_1b_1e^2$	$a_1b_2e^2$	$b_1b_2e^2$
$a_1b_1^2b_2$	$13B+5C+12K-6L-4M$	$-\sqrt{18}\,B$	$-6B$	$\sqrt{2}\,(3B+C)$	$\sqrt{6}\,B$
$a_1b_1e^2$		$12B+4C-6L+2M$	$\sqrt{8}\,B$	$-3B$	$\sqrt{3}\,B$
$a_1b_1e^2$			$8B+4C-6L+2M$	$-\sqrt{18}\,B$	$-\sqrt{6}\,B$
$a_1b_2e^2$				$16B+6C+6L+2M$	$\sqrt{75}\,B$
$b_1b_2e^2$					$12B+4C-6K-2M$

(8)

^3E	a_1e^3	b_1e^3	b_2e^3	$a_1^2b_1e$	$a_1^2b_2e$	$a_1b_1^2e$	$b_1^2b_2e$	$a_1b_2^2e$	$b_1b_2^2e$	$a_1b_1b_2e$	$a_1\bar{b}_1b_2e$	$a_1b_1b_2\bar{e}$
a_1e^3	$22B+5C-6K+5M$	$-\sqrt{12}\,B$	$\sqrt{12}\,B$	$-\sqrt{3}\,B$	$\sqrt{3}\,B$	$3B+C$	0	$3B+C$	0	$3B$	$\sqrt{\frac{9}{2}}\,B$	$\sqrt{\frac{81}{2}}\,B$
b_1e^3		$6B+5C-12K-6L+M$	0	$B+C$	0	$-\sqrt{3}\,B$	$3B$	0	$3B+C$	$-\sqrt{3}\,B$	$\sqrt{\frac{3}{2}}\,B$	$\sqrt{\frac{3}{2}}\,B$
b_2e^3			$6B+5C-12K+6L+M$	0	$B+C$	0	$3B+C$	$\sqrt{3}\,B$	$3B$	0	$-\sqrt{6}\,B$	0
$a_1^2b_1e$				$11B+5C+12K-6L+3M$	$-3B$	$-\sqrt{12}\,B$	0	0	$4B+C$	$-\sqrt{27}\,B$	$\sqrt{\frac{27}{2}}\,B$	$\sqrt{\frac{3}{2}}\,B$
$a_1^2b_2e$					$11B+5C+12K+6L+3M$	0	$4B+C$	$\sqrt{12}\,B$	0	$\sqrt{3}\,B$	$-\sqrt{\frac{75}{2}}\,B$	$\sqrt{\frac{3}{2}}\,B$
$a_1b_1^2e$						$7B+5C+6K-12L-M$	$-\sqrt{27}\,B$	C	0	$3B$	$\sqrt{\frac{9}{2}}\,B$	$\sqrt{\frac{9}{2}}\,B$
$b_1^2b_2e$							$21B+5C-6L-5M$	0	0	$-\sqrt{3}\,B$	$-\sqrt{\frac{75}{2}}\,B$	$-\sqrt{\frac{3}{2}}\,B$
$a_1b_2^2e$								$7B+5C+6K+12L-M$	$\sqrt{27}\,B$	0	0	$\sqrt{18}\,B$
$b_1b_2^2e$									$21B+5C+6L-5M$	$-\sqrt{12}\,B$	$\sqrt{6}\,B$	$\sqrt{24}\,B$
$a_1b_1b_2e$										$8B+4C+6K-M$	$-\sqrt{2}\,B$	0
$a_1b_1b_2e$											$12B+4C+6K-M$	$3B$
$a_1\underline{b}_1\underline{b}_2e$												$10B+4C+6K-M$

(9)

$^1A_1$	e^4	$a_1^2b_1^2$	$a_1^2b_2^2$	$b_1^2b_2^2$	$a_1^2e^2$	$b_1^2e^2$	$b_2^2e^2$	$a_1b_1e^2$	$a_1b_2e^2$	$b_1b_2e^2$
e^4	$15B+8C-$ $-18K+4M$	0	0	0	$\sqrt{2}(B+C)$	$\sqrt{2}(3B+C)$	$\sqrt{2}(3B+C)$	$\sqrt{12}\,B$	$-\sqrt{12}\,B$	$-\sqrt{108}\,B$
$a_1^2b_1^2$		$5B+8C+18K-$ $-12L$	C	$4B+C$	$\sqrt{2}(3B+C)$	$\sqrt{2}(B+C)$	0	$\sqrt{12}\,B$	0	0
$a_1^2b_2^2$			$5B+8C+18K+$ $+12L$	$4B+C$	$\sqrt{2}(3B+C)$	0	$\sqrt{2}(B+C)$	0	$-\sqrt{12}\,B$	0
$b_1^2b_2^2$				$45B+8C+$ $+6K-8M$	0	$\sqrt{2}(3B+C)$	$\sqrt{2}(3B+C)$	0	0	$-\sqrt{108}\,B$
$a_1^2e^2$					$38B+9C+$ $+6K+6M$	$4B+C$	$4B+C$	$\sqrt{150}\,B$	$-\sqrt{150}\,B$	0
$b_1^2e^2$						$18B+9C-6K-$ $-12L-2M$	C	$\sqrt{150}\,B$	0	$-\sqrt{54}\,B$
$b_2^2e^2$							$18B+9C-6K+$ $+12L-2M$	0	$-\sqrt{150}\,B$	$-\sqrt{54}\,B$
$a_1b_1e^2$								$18B+6C-$ $-6L+2M$	$-3B$	$-3B$
$a_1b_2e^2$									$18B+6C+$ $+6L+2M$	$3B$
$b_1b_2e^2$										$18B+6C-$ $-6K-2M$

(10)

$^1B_1$	$a_1^2e^2$	$b_1^2e^2$	$b_2^2e^2$	$a_1b_1b_2^2$	$a_1b_1e^2$	$a_1b_2e^2$	$b_1b_2e^2$
$a_1^2e^2$	$32B+7C+6K+$ $+6M$	$4B+C$	$4B+C$	0	$\sqrt{150}\,B$	$-\sqrt{18}\,B$	0
$b_1^2e^2$		$12B+7C-6K$ $-12L-2M$	C	0	$\sqrt{150}\,B$	0	$-\sqrt{18}\,B$
$b_2^2e^2$			$12B+7C-6K+$ $+12L-2M$	$-\sqrt{12}\,B$	0	$\sqrt{18}\,B$	$\sqrt{18}\,B$
$a_1b_1b_2^2$				$21B+7C+12K+$ $+6L-4M$	$\sqrt{2}\,(3B+C)$	$-\sqrt{54}\,B$	$-\sqrt{6}\,B$
$a_1b_1e^2$					$24B+8C-6L+$ $+2M$	$-\sqrt{27}\,B$	$-\sqrt{75}\,B$
$a_1b_2e^2$						$12B+6C+6L+$ $+2M$	$3B$
$b_1b_2e^2$							$12B+6C-6K-$ $-2M$

(11)

$^1B_2$	$a_1^2e^2$	$b_1^2e^2$	$b_2^2e^2$	$a_1b_1^2b_2$	$a_1b_1e^2$	$a_1b_2e^2$	$b_1b_2e^2$
$a_1^2e^2$	$32B+7C+6K+6M$	$4B+C$	$4B+C$	0	$\sqrt{18}\,B$	$-\sqrt{150}\,B$	0
$b_1^2e^2$		$12B+7C-6K-12L-2M$	C	$\sqrt{12}\,B$	$-\sqrt{18}\,B$	0	$\sqrt{18}\,B$
$b_2^2e^2$			$12B+7C-6K+12L-2M$	0	0	$-\sqrt{150}\,B$	$-\sqrt{18}\,B$
$a_1b_1^2b_2$				$21B+7C+12K-6L-4M$	$-\sqrt{54}\,B$	$\sqrt{2}\,(3B+C)$	$\sqrt{6}\,B$
$a_1b_1e^2$					$12B+6C-6L+2M$	$-\sqrt{27}\,B$	$-3B$
$a_1b_2e^2$						$24B+8C+6L+2M$	$\sqrt{75}\,B$
$b_1b_2e^2$							$12B+6C-6K-2M$

(12)

^1E	a_1e^3	b_1e^3	b_2e^3	$a_1^2b_1e$	$a_1^2b_2e$	$a_1b_1^2e$	$b_1^2b_2e$	$a_1b_2^2e$	$b_1b_2^2e$	$a_1b_1b_2e$	$a_1b_1b_2e$
a_1e^3	$24B+7C-6K+5M$	$-\sqrt{48}\,B$	$\sqrt{48}\,B$	$-\sqrt{3}\,B$	$\sqrt{3}\,B$	$3B+C$	0	$3B+C$	0	$\sqrt{\frac{27}{2}}\,B$	$-\sqrt{\frac{81}{2}}\,B$
b_1e^3		$12B+7C-12K-6L+M$	$-6B$	$B+C$	0	$-\sqrt{3}\,B$	$-9B$	0	$3B+C$	$-\sqrt{\frac{9}{2}}\,B$	$\sqrt{\frac{3}{2}}\,B$
b_2e^3			$12B+7C-12K+6L+M$	0	$B+C$	0	$3B+C$	$\sqrt{3}\,B$	$-9B$	0	$-\sqrt{6}\,B$
$a_1^2b_1e$				$17B+7C+12K-6L+3M$	$3B$	$-\sqrt{48}\,B$	0	0	$4B+C$	$-\sqrt{\frac{81}{2}}\,B$	$\sqrt{\frac{3}{2}}\,B$
$a_1^2b_2e$					$17B+7C+12K+6L+3M$	0	$4B+C$	$\sqrt{48}\,B$	0	$-\sqrt{\frac{9}{2}}\,B$	$-\sqrt{\frac{75}{2}}\,B$
$a_1b_1^2e$						$9B+7C+6K-12L-M$	$-\sqrt{3}\,B$	C	0	$\sqrt{\frac{27}{2}}\,B$	$-\sqrt{\frac{9}{2}}\,B$
$b_1^2b_2e$							$27B+7C-6L-5M$	0	$-6B$	$\sqrt{\frac{9}{2}}\,B$	$-\sqrt{\frac{75}{2}}\,B$
$a_1b_2^2e$								$9B+7C+6K+12L-M$	$\sqrt{3}\,B$	0	$-\sqrt{18}\,B$
$b_1b_2^2e$									$27B+7C+6L-5M$	$-\sqrt{18}\,B$	$\sqrt{24}\,B$
$a_1b_1b_2e$										$12B+6C+6K-M$	$-\sqrt{27}\,B$
$a_1b_1b_2e$											$18B+6C+6K-M$

(13)

$^1A_2$	$a_1^2b_1b_2$	$a_1b_1e^2$	$a_1b_2e^2$	$b_1b_2e^2$	
$a_1^2b_1b_2$	$5B+7C+18K$	$-\sqrt{6}\,B$	$\sqrt{6}\,B$	$\sqrt{2}\,(B+C)$	
$a_1b_1e^2$		$18B+6C-6L+2M$	$3B$	$-\sqrt{75}\,B$	(14)
$a_1b_2e^2$			$18B+6C+6L+2M$	$\sqrt{75}\,B$	
$b_1b_2e^2$				$18B+8C-6K-2M$	

The energy expressions (1)—(14) can easily be transcribed for d^6-configuration. Then — apart from a constant energy contribution — the matrix elements related with interelectronic repulsions remain unchanged and the ligand field energies — apart from another additive constant — are found by reversing the signs of those for the d^4-configuration.

The energy matrices can be used — as was shown in [3] — for the interpretation of the electronic absorption spectra of d^n-complexes.

References

[1] *a) Bán, M. I.:* Acta Phys. et Chem. Szeged **18**, 45 (1972);
b) Bán, M. I.: ibid **18**, 185 (1972).
[2] *Gilde, F. J., M. I. Bán:* Acta Phys. et Chem. Szeged **5**, 3 (1959); Magy. Fiz. Folyóirat **8**, 95 (1960); and unpublished results.
[3] *Bán, M. I., J. Császár, M. Hegyháti:* J. Mol. Structure (in press).

ТЕТРАГОНАЛЬНО ДЕФОРМИРОВАННЫЕ ТЕТРАЭДРИЧЕСКИЕ КОМПЛЕКСЫ ML_4. III

РАСЩЕПЛЕНИЕ d^4-КОНФИГУРАЦИЙ В СИЛЬНЫХ ПОЛЯХ ЛИГАНДОВ D_{2d} СИММЕТРИЙ

М. И. Бан

Используя приближение сильного поля, рассчитали энергетическое состояние электронов, происходящих при расщеплении конфигурации создаваемых из d^4 электронных структур в лигандных полях D_{2d} (деформированные тетраэдрические) симметрии в зависимости от параметров электростатических и лигандных полей, а также угла деформации.