TETRAGONALLY DISTORTED TETRAHEDRAL ML_4-COMPLEXES. I

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

by

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Using the strong field approximation, the energies of the electronic states arising from the splittings in ligand field of D_{2d} symmetry, of configurations deduced from the d^2-system, have been presented in terms of the electrostatic and ligand field parameters and the angle of distortion.

For the time being, the ligand field theory is the most general, easiest and most effective method to be used [1] for the interpretation of the optical, magnetic and bonding properties of the first transition group complexes. Within the scope of this theory, the most frequently used of the two approximations and that suitable for most purposes is the strong field approach. Since the first theoretical study on the octahedral field by TANABE and SUGANO [2], the method has been extended to fields of lower symmetries; a great number of theoretical works [3] have dealt with the splittings of d^n-configurations, both qualitatively and quantitatively. By the strong field approximation, OTSUKA [4] presented the energy terms effective in tetragonal fields and KAMMER [5] those in trigonal fields. In ligand fields of tetrahedral and tetragonally distorted tetrahedral symmetries, GERLOCH [6] calculated the energy matrix elements for the d^8-configuration, using, however, the weak field approach.

The present paper can be regarded as a continuation of the series commenced with the study on distorted octahedral ligand fields [7] and its obvious aim is to investigate, in theory, the behaviour of d^2-configuration in strong ligand fields of D_{2d} (distorted tetrahedral) symmetry. This kind of study is all the more justified, because, though very much experimental work has been done on the topic, however, just a few theoretical steps have been made so far to explain the observations. The results naturally involve those for the single-electron energies, moreover, the equations derived can be easily adapted to the case of d^8-configuration.

Discussion

To start with, the case of four identical ligands L set around the central metal ion[1] M in a regular tetrahedral (T_d) arrangement is discussed. By convention, the tetrahedron is placed so that the origin is laid in the centre of a cube and the ligands in staggered position are located in the alternating apices of the cube (orientation 1). For convenience, the orientation of the cube is such that the Z-axis of the Cartesian coordinates passes through the centres of its parallel faces. Therefore, two of the ligands lie above the XY-plane, each forming an angle[2] β with the positive direction of the Z-axis. The other two ligands are below the XY-plane enclosing angles $\pi - \beta$ with the $+Z$-axis. For the sake of further discussions, it is worth establishing also a different arrangement (orientation 2) which can be obtained from the preceding one by a clockwise rotation of 45° around the Z-axis.

Using the expanded form[3], in polar coordinates, of the reciprocal distance of two particles

$$\frac{1}{r_{pq}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} r_l(r) Y_l^m(\vartheta_p, \varphi_p) \overline{Y}_l^m(\vartheta_q, \varphi_q), \tag{1}$$

the operator[4] representing the electron-ligand interactions, *i.e.* the ligand field potential, is

$$V(T_d) = -eq \left\{ \frac{4}{9} \left[\frac{7}{2} P_4^0(\cos\vartheta) + \frac{1}{96} P_4^4(\cos\vartheta)(e^{4i\varphi} + e^{-4i\varphi}) \right] r_4(r) \right\}, \tag{2}$$

in which e is the charge of the electron and q is that of the ligand.

If — in otherwise similar conditions — the tetragonal distortion of the regular tetrahedron is caused merely by a uniform change in the numerical value of the polar angle β, the problem is related with D_{2d} symmetry. In this general case, the ligand field potential[5] is

$$V(D_{2d}) = eq \left\{ 2(3\cos^2\beta - 1) P_2^0(\cos\vartheta) r_2(r) + \right.$$

$$+ \left[\frac{1}{2}(35\cos^4\beta - 30\cos^2\beta + 3) P_4^0(\cos\vartheta) \mp \right. \tag{3}$$

$$\left. \mp \frac{1}{96}(1 - \cos^2\beta)^2 P_4^4(\cos\vartheta)(e^{4i\varphi} + e^{-4i\varphi}) \right] r_4(r) \right\}.$$

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[1] All the ligands are equidistant (in distance R) from the central metal ion at the origin.
[2] $2\beta \cong 109°28'$ — angle of the regular tetrahedron.
[3] $r_l(r)$ stands for the quantity $\dfrac{r_<^l}{r_>^{l+1}}$ in which $r_<$ and $r_>$ indicate the lesser and the greater of r_p and r_q. The suffixes p and q are used to distinguish the coordinates of the two particles — the two pointlike charges interacting with each other (here the ligand and the electron).
[4] In orientation 1, the ligand coordinates $\{r_p\} = \{R, \vartheta_p, \varphi_p\}$ are: $\{r_1\} = \left\{R, \beta, \dfrac{\pi}{4}\right\}$, $\{r_2\} = \left\{R, \pi - \beta, \dfrac{3\pi}{4}\right\}$, $\{r_3\} = \left\{R, \beta, \dfrac{5\pi}{4}\right\}$ és $\{r_4\} = \left\{R, \pi - \beta, \dfrac{7\pi}{4}\right\}$ and the electron coordinate is $\{r_q\} = \{r, \vartheta, \varphi\}$.
[5] Of the $\mp$ signs occurring in the expression of the potential, the minus corresponds to orientation 1 and the plus to orientation 2.

Since this expression involves — in the special case of $\beta = \text{arc cos} \, \dfrac{1}{\sqrt{3}}$ — the regular tetrahedron, therefore the further description will be restricted to the general case[1] only. Employing the potential (3), the single-electron matrix elements $\langle d_m | V(D_{2d}) | d_m \rangle$ are defined as

$$\langle d_0 | V(D_{2d}) | d_0 \rangle = \frac{36}{5} K + 2M, \tag{4.1}$$

$$\langle d_{\pm 1} | V(D_{2d}) | d_{\pm 1} \rangle = -\frac{24}{5} K + M, \tag{4.2}$$

$$\langle d_{\pm 2} | V(D_{2d}) | d_{\pm 2} \rangle = \frac{6}{5} K - 2M, \tag{4.3}$$

$$\langle d_{\pm 2} | V(D_{2d}) | d_{\mp 2} \rangle = -6L, \tag{4.4}$$

and the energies of the real d-orbitals[2] are

$a_1:$ $\langle d_{z^2} | V(D_{2d}) | d_{z^2} \rangle = \dfrac{36}{5} K + 2M, \tag{5.1}$

$b_1:$ $\langle d_{x^2-y^2} | V(D_{2d}) | d_{x^2-y^2} \rangle = \dfrac{6}{5} K - 6L - 2M, \tag{5.2}$

$b_2:$ $\langle d_{xy} | V(D_{2d}) | d_{xy} \rangle = \dfrac{6}{5} K + 6L - 2M, \tag{5.3}$

$e:$ $\langle d_{yz} | V(D_{2d}) | d_{yz} \rangle = \langle d_{zx} | V(D_{2d}) | d_{zx} \rangle = -\dfrac{24}{5} K + M, \tag{5.4}$

where[3]

$$K = \frac{5}{42} D_4 (35 \cos^4 \beta - 30 \cos^2 \beta + 3), \tag{6.1}$$

$$L = \frac{5}{6} D_4 (1 - \cos^2 \beta)^2, \tag{6.2}$$

$$M = D_2 (3 \cos^2 \beta - 1). \tag{6.3}$$

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[1] This form is equally holds for any angles from 0° to 90°, thus for the cases of linear and square planar conformations, too.

[2] In the field of D_{2d} symmetry, the fivefold d-orbital is split into four sub-levels differing in energies:

$$d(D_{2d}) = a_1 + b_1 + b_2 + e.$$

[3] D_4 denotes here the radial integral expressed in fourth-order spherical harmonics [7]:

$$D_4 = \frac{1}{6} R_4(r),$$

and D_2 that related with the corresponding second-order term:

$$D_2 = \frac{2}{7} R_2(r).$$

For other d^n-configurations, the part of the many-electron states, originating from the ligand-electron interactions, can in any case be deduced from these single-electron energies. The many-electron ("molecular"-) orbitals must be, however, corrected with regard to the interelectronic repulsion energies. A brief survey of the procedure is as follows. First, all the possible two-electron strong field configurations [8] are made, then, starting with the antisymmetrized functions belonging to a given configuration, the symmetry-adapted wave-functions ψ in the subspaces arising from the splitting of the configuration in question are set up. The integrals written down with these functions and the potential (3) determine the actual "molecular-orbital" energies. If — in the second step — the interelectronic repulsions between the two electrons are taken into account, the evaluation of the integrals of the type

$$\langle \psi | V(\text{el.}) | \psi \rangle, \tag{7}$$

composed from the same functions and the two-electron operator

$$V(\text{el.}) = \sum_{j>i} \frac{e^2}{r_{ij}}, \tag{8}$$

give the corrections required.

The energy equations[1] (9.1—9.9) have been obtained in the manner described.

$$^1A_2: \quad 12B + 2C - 12L - E = 0, \tag{9.1}$$

$$^1B_1: \quad \begin{vmatrix} 9B + 2C - 12K - 12L + 6M - E & -2\sqrt{3}B \\ -2\sqrt{3}B & 8B + 2C + 6K - 18L + 4M - E \end{vmatrix} = 0, \tag{9.2}$$

$$^1B_2: \quad \begin{vmatrix} 9B + 2C - 12K - 12L + 6M - E & 2\sqrt{3}B \\ 2\sqrt{3}B & 8B + 2C + 6K - 6L + 4M - E \end{vmatrix} = 0, \tag{9.3}$$

$$^1E: \quad \begin{vmatrix} 9B + 2C - 6K - 6L + 3M - E & -\sqrt{3}B & 3B \\ -\sqrt{3}B & 11B + 2C - 12L + 7M - E & \sqrt{3}B \\ 3B & \sqrt{3}B & 9B + 2C - 6K - 18L + 3M - E \end{vmatrix} = 0, \tag{9.4}$$

$$^1A_1: \quad \begin{vmatrix} 15B + 4C - 12K - 12L + 6M - E & \sqrt{2}(3B+C) & \sqrt{2}(B+C) & \sqrt{2}(3B+C) \\ \sqrt{2}(3B+C) & 12B + 3C - E & 4B + C & C \\ \sqrt{2}(B+C) & 4B + C & 12B + 3C + 12K - 12L + 8M - E & 4B + C \\ \sqrt{2}(3B+C) & C & 4B + C & 12B + 3C - 24L - E \end{vmatrix} = 0, \tag{9.5}$$

$$^3B_2: \quad 6K - 6L + 4M - E = 0, \tag{9.6}$$

$$^3B_1: \quad 6K - 18L + 4M - E = 0, \tag{9.7}$$

$$^3A_2: \quad \begin{vmatrix} 3B - 12K - 12L + 6M - E & 6B \\ 6B & 12B - 12L - E \end{vmatrix} = 0, \tag{9.8}$$

$$^3E: \quad \begin{vmatrix} 3B - 6K - 6L + 3M - E & -3\sqrt{3}B & -3B \\ -3\sqrt{3}B & 9B - 12L + 7M - E & 3\sqrt{3}B \\ -3B & 3\sqrt{3}B & 3B - 6K - 18L + 3M - E \end{vmatrix} = 0. \tag{9.9}$$

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[1] B and C are Coulomb interaction (Racah's) parameters [9]. The electrostatic parameter A representing a constant energy contribution to all terms has been eliminated from the equations.

The energy equations can be easily transcribed for the case of configuration d^8. In this instance — apart from a constant energy term contributing to all diagonal elements — the Coulomb interaction matrix elements remain unchanged and the ligand field energies — apart from another additive constant — are found by reversing the signs of those for d^2-configuration.

Further details concerning the procedure followed and the results, including those for other d^n-configurations, numerical calculations (energy level diagrams) and applications of the theory will be reported elsewhere.

References

[1] *Griffith, J. S.:* The Theory of Transition Metal Ions. University Press, Cambridge, 1961; *Ballhausen, C. J.:* Introduction to Ligand Field Theory. McGraw-Hill Book Co., New York, 1962.
[2] *Tanabe, Y., S. Sugano:* J. Phys. Soc. Japan **9**, 753, 766 (1954).
[3] *Yamatera, H.:* Bull. Chem. Soc. Japan **31**, 95 (1958); *Gilde, F. J., M. I. Bán:* Acta Phys. et Chem. Szeged **5**, 3 (1959); *Piper, T. S., R. L. Carlin:* J. Chem. Phys. **33**, 1208 (1960); *Gilde, F. J., M. I. Bán:* Acta Phys. Hung. **12**, 13 (1960); *Figgis, B. N.:* J. Chem. Soc. **1965**, 4887; *Bán, M. I., F. J. Gilde:* Coordin. Chem. Rev. **2**, 137 (1967); *Reinen, D.:* Theoret. Chim. Acta (Berl.) **8**, 260 (1967); *Máthé, J.:* Revue Roumaine de Chimie **14**, 1003 (1969); *Perumareddi, J. R.:* Coordin. Chem. Rev. **4**, 73 (1969).
[4] *Otsuka, J.:* J. Phys. Soc. Japan **21**, 596 (1966).
[5] *Kammer, H.:* Acta Chim. Hung. **66**, 189, 203 (1970).
[6] *Gerloch, M., R. C. Slade:* J. Chem. Soc. (A) **1969**, 1012.
[7] *Bán, M. I.:* Acta Phys. Hung. **24**, 283 (1968).
[8] See *e.g. Bán, M. I., Gy. Dömötör, F. J. Gilde:* Acta Phys. Hung. **25**, 57 (1968); *Császár, J., M. I. Bán:* Optikai szinkép, ligandumtér elmélet, komplexszerkezet. Akad. Kiadó, Budapest, 1972.
[9] *Racah, G.:* Phys. Rev. **62**, 438 (1942); ibid **63**, 367 (1943).

ТЕТРАГОНАЛЬНО ДЕФОРМИРОВАННЫЕ ТЕТРАЭДРИЧЕСКИЕ КОМПЛЕКСЫ ML_4.

Расщепление d^2-конфигураций в сильных полях лигандов D_{2d} симетрий

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Используя приближение сильного поля, рассчитали энергетическое состояние электронов, происходящих из расщепления конфигураций создаваемых из d^2 электронных структур в лигандных полях D_{2d} (деформированные тетраэдрические) симетрии в зависимости от параметров B электростатического и лигандных полей, а также угла деформации.