Ligand Field Distortion Parameters

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The factorization of ligand field parameters into angular and radial contributions is examined. The angular term breaks up into a product of geometric and chemical environment tensors each of which contributes to the magnitude of the distortion parameter. The purely geometric function may be expressed as axial projections which need not represent metal-ligand bond positions. This permits direct comparison of D_{nd} and D_{nh} group properties. This projection description involves no approximations and since the operators are Normalized Spherical Harmonic Hamiltonians the derived radial integrals are all scalars of the octahedron and comparable between groups in different subduction chains. The projection factorization aids the description of intermediate symmetries. The tetragonal antiprism, the trigonal prism and the trigonal bipyramid each are capable of intermediate symmetry derived from cubic figures. In each case the Hamiltonian contains only one independent parameter. Each of these special conditions can be used as the geometric origin in distortion space diagrams.

The radial function $\overline{r^4}$ is shown to be a function of n^8. Only a small increase in the principal number n of d orbitals is needed to account for observed values of DQ and these are justified using a United Atom model of transition metal complexes. The ratio of radial functions A^l in distortion parameters then represents slight variations in n induced by different ligands.

Key words: Ligand field theory – Distortion parameters, ligand field ~

1. Introduction

In the development of the theory of ligand fields, a single centre expansion of the perturbation of the central ion wave functions is often used. Such models require the definition of distortion parameters which, taken in multiples defined by the symmetry of the complex, are used to fit the observed separations of ligand field terms [1, 2]. If properly defined these parameters display the total symmetry of the point group of the complex. This does not imply that they behave as spherically symmetric objects. They may carry all the vector or tensor component properties allowed by the totally symmetric representation. It is always possible, however, to describe a vector or tensor component as a product of a scalar function and the unit vectors of the space. It is thus formally possible to factorize the distortion parameters into products of scalar energies and dimensionless functions of the geometry of the complex.

In ligand field theories, the ligand perturbation potential is usually described using Legendre polynomials. In polar coordinates this expansion does factorize into a product of a scalar energy depending only on radial functions and an angular description of the geometry. However, this geometric function depends

not only on the spatial arrangement of the ligands but also on their site strengths [3]. Thus the geometric description is properly defined only in a Hilbert space having chemical influence unit vectors. This space can be mapped onto three dimensional position space by factorizing these unit vectors into functions of ligand displacement and site strengths but such a factorization is arbitrary. One such factorization is developed in this work.

Whatever mapping into three dimensional position space is chosen however, the complete removal of angular terms from the radial energy functions can be achieved. After this separation, the Legendre expansion leaves a radial term in the form of a discontinuous sum of two integrals. This discontinuity arises because a mathematical singularity occurs in the expansion series at the metal-ligand distance. If the metal orbitals are compact the external integral is negligible. If the external integral cannot be neglected, the radial wave function itself can be regarded as an approximation to a more complete momentum space description [4]. As a first order correction in these circumstances, the use of radial wave functions with increasing, non-integer values of the principal quantum number n is proposed to account for the magnitude of ligand field parameters. This correction can be demonstrated semiquantitatively by construction of united atom diagrams of individual metal complexes.

2. General Theory

2.1. The Factorization of Angular and Radial Contributions

In a position space description, the complete Hamiltonian operator of a complexed ion can be expressed in single-centre form as [5],

$$H = \left[\sum_{i=1}^{N} -\frac{\hbar}{2m} V_i^2 + \frac{Z}{r_i} \right] + \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \sum_{\alpha=i}^{P} \frac{1}{r_{i\alpha}} \tag{1}$$

in which the operator acts on N electrons each of which is subjected to the perturbing potential H_p of off-centre atoms. This perturbation operator is expanded as a Legendre polynomial;

$$H_p = \sum_{\alpha=1}^{P} \frac{1}{r_{i\alpha}} = \sum_{\alpha=1}^{P} \sum_{k=0}^{\infty} \sum_{q=k}^{k} \frac{4\pi}{2k+1} Y_q^k(\theta\phi) \left[Z_\alpha \left(\frac{r_<^k}{r_>^{k+1}} \right) Y_q^{k*}(\theta_\alpha\phi_\alpha) \right]. \tag{2}$$

In ligand field theory one of the two distances $r_<$ or $r_>$ is taken as the metal ligand distance when performing the radial integration. It is clear from the last term of (2) however that perturbation is a function of both charge Z_α and distance r and is best represented as a field gradient vector. If the system has lower symmetry than cubic, then two or possibly three orthogonal field gradient vectors are required and the radial operator must be further factored to accomodate these requirements. As an example, for point groups having two orthogonal gradients,

$$\begin{aligned} H_p = \sum_{\alpha=1}^{P} \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \frac{4\pi}{2k+1} \ Y_q^k(\theta\phi) &\left[r_<^k \left(\frac{n_A}{a^{k+1}} + \frac{n_E}{b^{k+1}} \right) Y_q^{k*}(\theta_\alpha\phi_\alpha) \right. \\ &\left. + \frac{1}{r_>^{k+1}} (n_A a^k + n_E b^k) \ Y_q^{k*}(\theta_\alpha\phi_\alpha) \right] \end{aligned} \tag{3}$$

in which n_A and n_E are the number of occupied axial and equatorial ligand sites and a and b their respective field gradients. The presence of terms in the summations over k and q is governed by the requirement that the Hamiltonian has the total symmetry of the point group of the complex. The coefficients of each term are found by projection or symmetry adaptation techniques [2, 3] or may be found using the Subduction Criterion and tabulated values of Subduction Coefficients, $S(m)$ [6, 7].

Two types of subgroups of the generative group O_h will be considered [8]. The first type is those with a principal axis of order 4 or 3 which retains a degenerate representation and the second is the kind having only a C_2 quantization axis and no degenerate representations.

The first group (Type I) can be further subdivided. Those point groups D_n and C_{nv} in which $n \geq 3$ and all D_{nd} and D_{nh} groups retain a true E representation. The groups C_{nh} and C_n have formally non-degenerate representations but some pairs are conjugate, giving rise to identical physical observables and can be considered as degenerate. In both types of point group, by choosing the z axis of a Cartesian coordinate system to be colinear with the major axis, the x and y coordinate axes are degenerate. Thus for both types of group only two classes of tensor components of O_h can appear in the Hamiltonian of the subgroup. The combinations subduced from $|A_1\,0|_{O_h}^{C_n}$ are symmetric while those subduced from $|E\,0|_{O_h}^{C_4}$ or $|T_2\,0|_{O_h}^{C_3}$ and for C_3, $[T, 0]_{O_h}^{C_3}$ are antisymmetric [7].

The parameters associated with each l manifold of the antisymmetric combinations are known conventionally as distortion parameters because they measure the deviation of the electronic structure from that in cubic complexes. For d electrons, application of the Wigner-Eckart theorem yields non-vanishing parameters if $l = 2$ and 4. These integers will be used to identify the distortion parameters $D(k)$ whether they arise from $|E0+|$ or $|T_20+|$. These $D(k)$ are not the conventional parameters Ds and Dt since they are derived using Normalized Spherical Harmonic (N.S.H.) Hamiltonian operators. The set of $D(k)$ contain all angular contributions of the antisymmetric operator and all appropriate normalization coefficients. For clarity they will be labelled DS, DT [9].

With this approach to factorization the angular relationships of the central field can be evaluated irrespective of the form taken by the radial perturbation. For any order k of harmonics, the ratio of the two permitted combinations is;

$$\frac{D(k)_{\text{SYM}}}{D(k)_{\text{ANTI}}} = \frac{\displaystyle\sum_{n,k,q} S(m)_{\text{SYM}} \left[r_<^k \left(\frac{n_A}{a^{k+1}} + \frac{n_E}{b^{k+1}} \right) Y_q^k Y_q^{k*} \right.}{\displaystyle\sum_{n,k,q} S(m)_{\text{ANTI}} \left[r_<^k \left(\frac{n_A}{a^{k+1}} + \frac{n_E}{b^{k+1}} \right) Y_q^k Y_q^{k*} \right.}$$

$$\frac{\left. + \frac{1}{r_<^{k+1}} (n_A a^k + n_E b^k) Y_q^k Y_q^{k*} \right]}{\left. + \frac{1}{r_<^{k+1}} (n_A a^k + n_E b^k) Y_q^k Y_q^{k*} \right]}$$

$$= \frac{\displaystyle\sum_{nkq} S(m)_{\text{SYM}} Y_q^k Y_q^{k*}}{\displaystyle\sum_{nkq} S(m)_{\text{ANTI}} Y_q^k Y_q^{k*}} = \frac{(A0 \cdot A0^*)_{O_h}}{(\Gamma 0 \cdot \Gamma 0^*)_{O_h}}.$$

(4)

Thus the ratio of parameters is a function only of the angular relationship in the Hilbert space for the complex in which the orthogonal field gradients a and b are defined.

In cubic systems when $a = b$, the separation of the angular functions leaves a radial Hamiltonian. This operator is formulated from the Legendre expansion as a sum of two radial operators integrated over two separate spatial volumes with a discontinuity at the field gradient length a. For convenience the integrated radial quantity may be written;

$$
\begin{aligned}
\bar{r}^k &= \left[\frac{\langle R_{nlm} | r_<^k | R_{nlm} \rangle}{a^{k+1}} + a^k \langle R_{nlm} | \frac{1}{r_<^{k+1}} | R_{nlm} \rangle \right] \\
&= \left[\frac{\langle R_{nlm} | r_<^k | R_{nlm} \rangle}{a^{k+1}} \left(1 + a^{2k+1} \frac{\langle R_{nlm} | \frac{1}{r_<^{k+1}} | R_{nlm} \rangle}{\langle R_{nlm} | r_<^k | R_{nlm} \rangle} \right) \right].
\end{aligned}
\tag{5}
$$

In many traditional treatments of ligand field theory the second term in the expansion is neglected [10]. This is a valid approximation when the metal orbitals are compact and is especially applicable to ligand field treatments of lanthanide complexes. Its application to transition metal complexes is less valid [2, 10, 11], and a complete interpretation of parameter magnitudes requires estimation of the second integral. This may be done either in a central field model involving the matching of radial wave functions for continuity at the field gradient vector a [5] or by inclusion of ligand orbital character in the metal wave functions in an LCAO approach [11].

This discontinuous behaviour of the Legendre expansion can be transcended by a reformulation of ligand field theory in a momentum space realization of both the operator and the wave functions [4]. Momentum space is four dimensional and permits the use of the principal quantum number n as a well defined specification of the momentum wave functions. These are;

$$
\Psi(\Omega) = \frac{1}{p_0} \sum_{\nu\lambda\mu} \sum_j Z_j \sum_{nlm} \left\{ [S_{nlm}^{\nu^1\lambda^1\mu^1}(R_j)]^* \frac{1}{n} S_{nlm}^{\nu^1\lambda^1\mu^1}(R_j) \right\} C_{\nu^1\lambda^1\mu^1} Y_{\nu\lambda\mu}.
\tag{6}
$$

In these functions the orbitals of each atom centered at R_j and represented by the four dimensional spherical harmonics Y_{nlm} are projected by the $S_{nlm}^{\nu\lambda\mu}$ functions [12] onto the origin of the point group. Each of these orbitals has a root mean square energy $p_0 = \frac{Z}{n}$ and makes a contribution to the molecular eigenvalue according to the linear combination of central spherical harmonics $Y_{\nu\lambda\mu}$ making up the complete molecular orbital. The projection coefficients $S_{nlm}^{\nu\lambda\mu}$ when expressed in polar coordinates allow a separation of angular and radial functions. The mapping of l and m onto λ and μ is equivalent to conventional symmetry adaptation of both metal and ligand group orbitals except that the orthonomality conditions are uniquely defined by the structure of the momentum space group O (4).

The subduction of the radial functions from momentum space either into the chemical gradient Hilbert space or into three dimensional position space is less familiar and discussed in a later section.

2.2. Factorization of Angular Terms in Low Symmetries

The desired factorizations of the $D(k)$ are achieved by direct evaluation of the crystal field contributions of all ligands followed by rearrangement of terms. This is applicable to DQ as well as distortion parameters and is very instructive. Substituting point charges of an octahedral field quantized on C_4^z,

$$DQ\,|A_1 0+|_4 = \sqrt{\frac{1}{2\pi}}\,\sqrt{\frac{9}{128}}\,Ze^2\,\overline{r^4}\,\left|\sqrt{\frac{7}{12}}\left(\frac{8(2)}{a^5} + \frac{3(4)}{b^5}\right)Y_0^4\right.$$

$$\left. + \sqrt{\frac{35}{2}}\,\sqrt{\frac{5}{24}}\left(\frac{4}{b^5}\,Y_4^4 + \frac{4}{b^5}\,Y_{-4}^4\right)\right| \tag{7a}$$

in which a and b are the metal-ligand distances on the z axis and the x, y plane respectively. This of course collapses further at the perfect octahedron but left in this form the operator clearly demonstrates the "average environment rule" which has long been used to estimate Dq values in tetragonal complexes. A similar treatment of the antisymmetric combination yields DT;

$$DT\,|E0+|_4 = \sqrt{\frac{1}{2\pi}}\,\sqrt{\frac{9}{128}}\,ze^2\,\overline{r^4}\,\left|\sqrt{\frac{5}{12}}\left(\frac{8(2)}{a^5} + \frac{3(4)}{b^5}\right)Y_0^4\right.$$

$$\left. - \sqrt{\frac{35}{2}}\,\sqrt{\frac{7}{24}}\left(\frac{4}{b^5}\,Y_4^4 + \frac{4}{b^5}\,Y_{-4}^4\right)\right| \tag{7b}$$

These familiar forms of DQ and DT may be parameterized in an alternative way. By addition of Eqs. (7a) and (7b), two new equations in the coefficients of Y_0^4 and $(Y_4^4 + Y_{-4}^4)$ can be generated. Solving these equations and retaining the expanded evaluation of Y_q^{4*}, the alternative form of DQ becomes;

$$DQ = \sqrt{\frac{1}{2\pi}}\,\sqrt{\frac{9}{128}}\,Ze^2\,\overline{r^4}\,\sqrt{\frac{7}{12}}\,\left|16\left(\frac{1}{a^5} + \frac{2}{b^5}\right)\right| \tag{8a}$$

An equivalent set of substitutions yields:

$$DT = \sqrt{\frac{1}{2\pi}}\,\sqrt{\frac{9}{128}}\,ze^2\,\overline{r^4}\,\sqrt{\frac{5}{12}}\,\left|28\left(\frac{1}{a^5} - \frac{1}{b^5}\right)\right|. \tag{8b}$$

As required, DT like the un-normalized Dt vanishes at the perfect figure and as written obtains magnitude only if a geometric distortion occurs. A similar factorization of the second order parameter $D(2)$ yields;

$$DS\,|E0+|_4 = \sqrt{\frac{1}{2\pi}}\,\sqrt{\frac{5}{8}}\,ze^2\,\overline{r^2}\,\left|\left(\frac{2(2)}{a^3} - \frac{(4)}{b^3}\right)Y_0^2\right|^4$$

$$\therefore DS = \sqrt{\frac{1}{2\pi}}\,\sqrt{\frac{5}{8}}\,ze^2\,\overline{r^2}\,\left|4\left(\frac{1}{a^3} - \frac{1}{b^3}\right)\right|. \tag{9}$$

In both $D(4)$ and $D(2)$ parameters a further modification is necessary if axial and equatorial ligands are chemically different. Each ligand produces a different second and fourth order effect on the d electrons and thus the $(ze^2 \, \overline{r^k})$ must be different on the axis and the plane. This has been previously recognized [3] by writing the $D(k)$ as

$$D(k) = C^k Z_E e^2 \, \overline{r_E^k} \left| \left(\frac{1}{a^{k+1}} - \frac{A^l}{b^{k+1}} \right) \right| \tag{10}$$

in which $A^k = \dfrac{Z_A \, \overline{r_A^k}}{Z_E \, \overline{r_E^k}}$.

Here A^k is defined as the ratio of the chemical effects on the axis and plane for the k manifold. It must be emphasized that as defined, the chemical ratio is a necessary factor but its origin remains unspecified. Its use is discussed in a later section.

The factorizations (7)–(9) are useful if a and b are identified as metal-ligand distances only in a restricted number of point groups. Fully generalized factored forms would be much more useful in distorted prisms and antiprisms and are necessary if the D_{3h} physical chain is to be examined. Such general forms can be derived most conveniently from the symmetric and antisymmetric combinations written in polar coordinates. For the second order effect (9) becomes;

$$DS\,|E0+|_4 = \sqrt{\frac{1}{2\pi}} \, \sqrt{\frac{5}{8}} \, \frac{Ze^2 \, \overline{r^2}}{a^3} \, |(3\cos^2\theta - 1)\, Y_0^2|$$

$$= \sqrt{\frac{1}{2\pi}} \, \sqrt{\frac{5}{8}} \, \frac{Ze^2 \, \overline{r^2}}{a^3} \, |(2\cos^2\theta - \sin^2\theta)\, Y_0^2| \tag{11}$$

$$= \sqrt{\frac{1}{2\pi}} \, \sqrt{\frac{5}{8}} \, \frac{Ze^2 \, \overline{r^2}}{a} \, \left| \left(\frac{2}{(a\sec\theta)^2} - \frac{1}{(a\csc\theta)^2} \right) Y_0^2 \right| .$$

By defining

$$R = a\sec\theta$$
$$S = a\csc\theta . \tag{12}$$

Substitution into (10) defines DS as

$$DS = \sqrt{\frac{1}{2\pi}} \, \sqrt{\frac{5}{8}} \, \frac{Ze^2 \, \overline{r^2}}{a} \left(\frac{2(n_A)}{R^2} - \frac{1(n_E)}{S^2} \right) . \tag{13}$$

Here n_A and n_E are the number of general identical symmetry points on the z and x (or y) axes respectively. These two positions in each case may or may not be occupied, that is, the Hamiltonian may refer either to sets of identical ligands or identical symmetry holes. Developments similar to those giving (11) yield the redefined fourth order parameters. The general form for the totally symmetric Hamiltonian is:

$$DQ\,|A_1 0+|_n = \left|\left| \sqrt{\frac{1}{2\pi}} \, \sqrt{\frac{9}{128}} \, \frac{Ze^2 \, \overline{r^4}}{a^5} \, [C_{4A_1}^0 (35\cos^4\theta - 30\cos^2\theta + 3)\, Y_0^4 \right.\right.$$

$$\left.\left. + C_{4A_1}^k (Y_4^{k*} Y_4^k \pm Y_{-4}^{k*} Y_{-4}^k)] \right|\right| . \tag{14}$$

Quantized on a four-fold axis the parameter becomes;

$$(DQ)_4 \quad \sqrt{\frac{1}{2\pi}} \sqrt{\frac{9}{128}} \frac{Ze^2 \overline{r^4}}{a} \left[\sqrt{\frac{7}{12}} \left(\frac{8(n_A)(z)}{(a\sec\theta)^4} - \frac{24(n_E)(x)(\cotan\theta)^2}{(a\cosec\theta)^4} \right. \right.$$

$$\left. \left. + \frac{3(n_E)(x)}{(a\cosec\theta)^4} \right) - \sqrt{\frac{5}{24}} \sqrt{\frac{35}{2}} \left(\frac{2(n_E)(x)}{(a\cosec\theta)^4} \right) \right] \quad (15)$$

$$= \sqrt{\frac{1}{2\pi}} \sqrt{\frac{9}{128}} \frac{Ze^2 \overline{r^4}}{a} \sqrt{\frac{7}{12}} \left[\frac{4(z)}{(a\sec\theta)^4} - \frac{7(x)}{(a\cosec\theta)^4} \right].$$

The numbers (z) and (x) will be called the site strengths because (15) may refer either to an octahedron or a cube. Conventional ligand field substitution [10] gives the ratio of octahedral to cubic splittings as $-8/9$. Moreover, examining the ratio of effectiveness of each of the eight ligands in a cube compared to each of the six in an octahedron reveals that the site strength of a ligand on a three-fold axis is $-2/3$ that of a ligand on a four-fold axis. Thus, in order to adapt (15) to include cubic or tetrahedral as well as octahedral geometry, a factor selecting either three-fold or four-fold sites, the number of ligands and a normalizing constant must be introduced. The final general form for $(DQ)_4$ becomes

$$(DQ)_4 = \left(\frac{9}{8}\right)\left(\frac{-2n_3}{18} + \frac{n_4}{6}\right) \frac{3\sqrt{7}}{8\sqrt{3\pi}} \frac{Ze^2 \overline{r^4}}{a} \left[\frac{4(z)}{(a\sec\theta)^4} - \frac{7(x)}{(a\cosec\theta)^4} \right]. \quad (16)$$

In this form n_3 and n_4 are respectively the number of ligands lying on three-fold or four-fold axes. In perfect cubic figures $z = x = 1$ but these relative site strengths may change with ligand replacement.

The same set of parameters also force both DS and DT to vanish at cubic limits as expected. For the fourth order;

$$(DT)_4 = \left(\frac{9}{8}\right)\left(\frac{-2n_3}{18} + \frac{n_4}{6}\right) \sqrt{\frac{1}{2\pi}} \sqrt{\frac{9}{128}} \frac{Ze^2 r^4}{a} \left[\sqrt{\frac{5}{12}} \left(\frac{8n_A(z)}{(a\sec\theta)^4} \right. \right.$$

$$\left. \left. - \frac{24(n_E)(x)(\cotan\theta)^2}{(a\cosec\theta)^4} + \frac{3(n_E)(x)}{(a\cosec\theta)^4} \right) + \sqrt{\frac{7}{24}} \sqrt{\frac{35}{2}} \left(\frac{2(n_E)(x)}{(a\cosec\theta)^4} \right) \right]$$

$$= \left(\frac{9}{8}\right)\left(\frac{-2n_3}{18} + \frac{n_4}{6}\right) \frac{3\sqrt{5}}{8\sqrt{3\pi}} \frac{Ze^2 r^4}{a} \left[\frac{4(z)}{(a\sec\theta)^4} - \frac{(x)}{(a\cosec\theta)^4} \right]. \quad (17)$$

With this formalism, one no longer identifies the axial and equatorial tensor components with bond lengths. Their ratio is a measure of the effective geometric distortion of a cubic scalar potential. The factorization has the important advantage that this distortion is described in terms of square and fourth power projections of a single scalar radius a. Thus, all parameters DQ, DS, and DT are essentially functions only of a and the projection angle θ. This places the "radial"

distortions of D_{nh} groups and the "angular" distortions of D_{nd} groups in the same model, permitting direct comparisons of all parameters between these groups.

The second important advantage of this treatment is that it clarifies the meaning of the chemical ratio A^k. This quantity (10) is clearly the ratio of the relative site strengths and most appear as a factor in *all three* parameters, not just the distortion parameters as indicated in earlier models [3]. The site strength ratio clearly appears in (16) as part of the average environment rule.

The analysis of Type II symmetry groups can be derived as a natural extention of the Type I. There are now two classes of distortion parameters in each k manifold. The subduction rules leading to the desired components of O_h in the Hamiltonian have been given elsewhere [9].

The first type of parameter describes the difference between the axial environment and the average of that in the plane perpendicular to the quantizing axis. They may be defined as;

$$D_A(k) = C_A^k Z e^2 \, \overline{r^k} \left[\frac{1}{a^{k+1}} - \frac{1}{2} \left(\frac{A_x^k}{b_x^{k+1}} + \frac{A_y^k}{b_y^{k+1}} \right) \right] \tag{18}$$

in which the A_x and A_y ratios are used to recognize the different chemical environment on each Cartesian axis.

The second type of parameter reflects the two in-plane projections. These parameters always arise from combinations of spherical harmonics of the type $Y_l^{\pm 2}$ in these digonal quantizations. The parameters are;

$$D_E(k) = C_E^k Z e^2 \, \overline{r^k} \left(\frac{A_x^k}{b_x^{k+1}} - \frac{A_y^k}{b_y^{k+1}} \right). \tag{19}$$

Both types of parameter $D_A(k)$ and $D_E(k)$ can be recast into the component projection form by introducing a secondary projection angle ϕ subtended with either the x or y axis in the xy plane. Clearly when $\phi = 45°$ $D_E(k)$ vanishes and $D_A(k)$ becomes simply $D(k)$ of Type I point groups [9].

3. Applications to Intermediate Symmetries

The forms of $D(k)$ just discussed make the occurance of special solutions very obvious. Often in point groups of low formal symmetry one or more of the expected distortion parameters may vanish because of special angular relationships of the ligands. Many of these systems have been studied in isolation but may now be placed in the general subduction framework. Two types of intermediate symmetry which have not been systematically explored are the tetragonal antiprisms and trigonal prisms related directly to the octahedron.

3.1. Tetragonal Antiprisms

Physically the tetragonal antiprism with D_{4d} symmetry can be obtained by rotation of one face of a cube by 45°. Unlike any other D_{4d} figure, this specific antiprism requires only one independent parameter to completely specify the Hamiltonian.

The second order effect remains zero during the facial rotation. This is proven either by direct substitution of ligand positions into the conventional form of Eq. (11) or by retaining the angle $\theta = 54°44'$ in the projection form. This latter procedure is possible because Y_0^2 does not depend on the equatorial angle ϕ.

The two fourth order parameters DQ and DT are linearly dependent at the D_{4d} limit. This can be demonstrated by solving the natural Hamiltonian operator in terms of the cubic parameters. The D_{4d} fourth order Hamiltonian is simply;

$$H_{D_{4d}} = [D(4)]_4 \, Y_0^4 . \tag{20}$$

This operator eigenstate is derived from those of the cube by the linear combination;

$$\sqrt{\frac{7}{12}} \, (DQ)_4 |A_1 0 +| + \sqrt{\frac{5}{12}} \, (DT)_4 |E0 +| = [D(4)]_4 \, Y_0^4 . \tag{21a}$$

The antisymmetric combination vanishes;

$$\sqrt{\frac{5}{24}} \, (DQ)_4 |A_1 0 +| - \sqrt{\frac{7}{24}} \, (DT)_4 |E0 +| = 0 . \tag{21b}$$

This may be seen physically since the four ligand contributions of the top face exactly cancel those of the bottom face at $45°$. By the addition of (21 a) and (21 b) to eliminate $(DT)_4$, the form of $(DQ)_4$ in D_{4d} becomes;

$$(DQ)_4 \, Y_0^4 = \sqrt{\frac{7}{12}} \, [D(4)]_4 \, Y_0^4$$

$$\therefore (DQ)_4 = \sqrt{\frac{7}{12}} \, D_4^4 \left[\frac{8(z)}{(a \sec \theta)^4} - \frac{9(x)}{(a \csc \theta)^4} \right] . \tag{22a}$$

By subtraction to eliminate $(DQ)_4$, $(DT)_4$ becomes;

$$(DT)_4 \, Y_0^4 = \sqrt{\frac{5}{12}} \, [D(4)]_4 \, Y_0^4$$

$$\therefore (DT)_4 = \sqrt{\frac{5}{12}} \, D_4^4 \left[\frac{8(z)}{(a \sec \theta)^4} - \frac{9(x)}{(a \csc \theta)^4} \right] \tag{22b}$$

in which D_4^4 are the constants of (15) and (17).

Clearly $(DQ)_4$ and $(DT)_4$ display exactly the same projection dependence [13]. They are simply two contributions to a single parameter in the ratio

$$\frac{(DQ)_4}{(DT)_4} = \sqrt{\frac{7}{5}} . \tag{23}$$

Moreover this ratio is independent of the axial and equatorial projection lengths and thus gives no information concerning the geometry of a tetragonal antiprism.

Generalized forms of these parameters for D_4 complexes in terms of the relative facial twist angle α can be derived. From (15) and (21 a);

$$(DQ)_4 = \sqrt{\frac{7}{12}}\,\frac{D_4^4}{a}\left[\frac{16(z)}{(a\sec\theta)^4} - \frac{23(x)}{(a\operatorname{cosec}\theta)^4} - \frac{5(x)\cos 4\alpha}{(a\operatorname{cosec}\theta)^4}\right] \quad (24\,\text{a})$$

and (17) and (21 b) yielding;

$$(DT)_4 = \sqrt{\frac{5}{12}}\,\frac{D_4^4}{a}\left[\frac{16(z)}{(a\sec\theta)^4} - \frac{11(x)}{(a\operatorname{cosec}\theta)^4} + \frac{7(x)\cos 4\alpha}{(a\operatorname{cosec}\theta)^4}\right] \quad (24\,\text{b})$$

which collapse to the cubic or antiprismatic solutions at $\alpha = 0°$ and $45°$ respectively. The projection contribution containing α arises solely from the ϕ dependence of the $Y_{\pm 4}^4$ harmonics.

From this analysis two statements can be made. The second order effect $(DS)_4$ measures only the distortion of the axial and equatorial projections away from their cubic ratio, that is compression or elongation of the antiprism. The fourth order effect $(DT)_4$ measures the facial twist angle which has two high symmetry positions, the cubic and D_{4d} geometries. At both these limits there is only one independent fourth order parameter, $[D(4)]_4$.

3.2. Trigonal Prisms

In the same spirit by which the tetragonal antiprism was formed by the facial twist of a cube, a trigonal prism may be formed by a $60°$ facial twist of an octahedron. The trigonal prism so formed displays exactly the same kind of intermediate symmetry as the D_{4d} body. Again the second order effect remains zero and at the D_{3h} limit the fourth order parameters become linearly dependent. It is useful however to demonstrate their fully expanded forms.

The trigonal quantization of the octahedron or cube requires the use of a projector which like that in the tetragonal case, passes through points containing the other set of defining axes, and must again subtend an angle of $54°44'$ with the three fold quantizing axis (Fig. 2). The general forms of the parameters may be developed again in polar coordinates. Like the tetragonal quantization (13), (16), and (17), the trigonal Hamiltonian has two obvious symmetry sites on the axis. If the x axis is coincident with a C_2' symmetry axis it also clearly contains two identical symmetry sites. Thus the projected form of parameters under three-fold quantization is very similar in appearance to that developed above. The second order parameter $(DM)_3$ is identical to $(DS)_4$ and the fourth order parameters differ only in the substitution of $Y_{\pm 3}^4$ for $Y_{\pm 4}^4$ with a new normalization. The form of $Y_{\pm 3}^4$ demands projection and this is taken by convention onto the plane.

$$(DQ)_3 = \left(\frac{9}{8}\right)\left(\frac{2n_3}{18} - \frac{n_4}{6}\right)\frac{3}{\sqrt{2\pi}\sqrt{128}}\,\frac{ze^2\,\overline{r^4}}{a}\left[\frac{\sqrt{7}}{\sqrt{27}}\left(\frac{8(n_A)(z)}{(a\sec\theta)^4}\right.\right.$$

$$\left.- \frac{24(n_E)(x)(\cotan\theta)^2}{(a\operatorname{cosec}\theta)^4} + \frac{3(n_E)(x)}{(a\operatorname{cosec}\theta)^4}\right) - 2\sqrt{\frac{20}{54}}\sqrt{35}\left.\left(\frac{(n_E)(x)\cotan\theta}{(a\operatorname{cosec}\theta)^4}\right)\right]$$

$$= \left(\frac{9}{8}\right)\left(\frac{2n_3}{18} - \frac{n_4}{6}\right)\frac{3\sqrt{7}}{24\sqrt{3\pi}}\,\frac{ze^2\,\overline{r^4}}{a}\left[\frac{8(z)}{(a\sec\theta)^4} - \frac{19(x)}{(a\operatorname{cosec}\theta)^4}\right]. \quad (25)$$
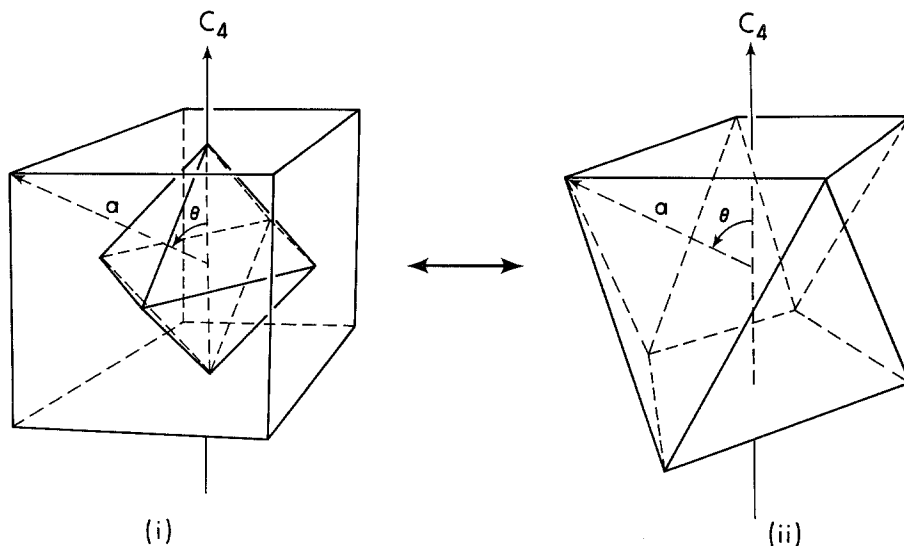
Fig. 1. The three tetragonal prismatic bodies. (i) The cube and inscribed octahedron. (ii) The tetragonal antiprism derived by 45° facial rotation
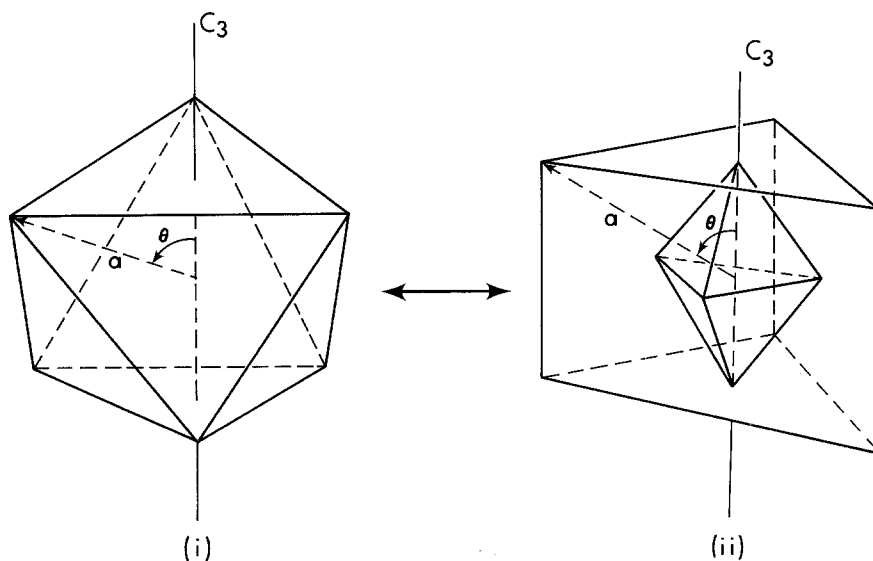

Fig. 2. The three trigonal prismatic bodies. (i) The octahedron. (ii) The trigonal prism derived by 60° facial rotation and the inscribed trigonal bipyramid

This version of $(DQ)_3$ has exactly the same value as $(DQ)_4$ of Eq. (16) since the operator eigenstate functions are fully normalized in both developments. The conventional introduction [1] of the ratio of normalizing constants between $(DQ)_4$ and $(DQ)_3$ into the trigonal wave functions is not necessary. The corresponding fourth order distortion parameter becomes;

$$(DN)_3 = \left(\frac{9}{8}\right)\left(\frac{2n_3}{18} - \frac{n_4}{6}\right)\frac{3\sqrt{5}}{24\sqrt{3}} \frac{ze^2\,\overline{r^4}}{a}\left[\frac{8(z)}{(a\sec\theta)^4} - \frac{2(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right]. \qquad (26)$$

Note that the normalizing factor is now $-\left(\dfrac{9}{8}\right)$ compared to $\left(\dfrac{9}{8}\right)$ in (16) reflecting again difference between a four-fold ligand site used to project the octahedron and the three-fold site used to project the cube in (15).

The octahedron quantized on the three fold axis displays all the symmetry features of the D_{3d} point group and rotation of one face creating a trigonal prism achieves the D_{3h} point group limit. This is exactly opposite to the kinds of starting and finishing limits of facial rotation described above in a cube. The D_{3h} figure obtained again has intermediate symmetry, the second order parameter $(DM)_3$ remains zero and for fourth order;

$$H_{D_{3h}} = [D(4)]_3 Y_0^4 . \tag{27}$$

Using operator eigenstates derived [7] from the $|A_1 0+\rangle$ and $|T_2 0+\rangle$ sets quantized under C_3^z, steps analogous to Eqs. (21) and (22) yield at the D_{3h} limit;

$$(DQ)_3 = \left|\sqrt{\frac{7}{27}}\right. \frac{D_4^3}{a} \left[\frac{8(z)}{(a \sec \theta)^4} - \frac{9(x)}{(a \operatorname{cosec} \theta)^4} \right], \tag{28a}$$

$$(DN)_3 = \left|\sqrt{\frac{20}{27}}\right. \frac{D_4^3}{a} \left[\frac{8(z)}{(a \sec \theta)^4} - \frac{9(x)}{(a \operatorname{cosec} \theta)^4} \right], \tag{28b}$$

in which D_4^3 are the constants of (23) and (24). The parameter ratio in this case is;

$$\frac{(DQ)_3}{(DN)_3} = \left|\sqrt{\frac{7}{20}}\right. \tag{29}$$

and the fully generalized forms of (26) displaying the dependence on facial twist angle are;

$$(DQ)_3 = \left|\sqrt{\frac{7}{27}}\right. \frac{D_4^3}{a} \left[\frac{8(z)}{(a \sec \theta)^4} - \frac{9(x)}{(a \operatorname{cosec} \theta)^4} - \frac{10(x) \cos 3\alpha}{(a \operatorname{cosec} \theta)^4} \right], \tag{30a}$$

$$(DN)_3 = \left|\sqrt{\frac{20}{27}}\right. \frac{D_4^3}{a} \left[\frac{16(z)}{(a \sec \theta)^4} - \frac{11(x)}{(a \operatorname{cosec} \theta)^4} + \frac{7(x) \cos 3\alpha}{(a \operatorname{cosec} \theta)^4} \right]. \tag{30b}$$

As under D_4^z, these parameters collapse to those of (28) at the prism limit and (25) and (26) at the antiprism.

3.3. Trigonal Bipyramid

This study of the Hamiltonian operators makes it obvious that one further figure, the regular trigonal bipyramid should be considered. Indeed it completes the set of regular figures available in this group. On the four fold axis there are two fully cubic regular solids, the cube and the octahedron. These may be regarded as the regular tetragonal prism and bipyramid respectively. The regular tetragonal antiprism discussed above completes this group. We should expect therefore that the operators quantized on the three-fold axis would also refer to three trigonal bodies. Two such have already been identified, the trigonal antiprism

(octahedron) and the trigonal prism discussed immediately above. There remains the definition of the *regular* trigonal bipyramid obtained by a holes for points inversion from the regular trigonal prism, in the same sense that the octahedron is obtained from the cube (Fig. 2).

This body is a further example of intermediate symmetry. Unique among D_{3h} bipyramids it has nine edges of equal length implying six equilateral faces. We propose the special name "trigonal hexahedron" (or simply "hexahedron", understanding that the name does not apply to a cube) to distinguish it from distorted forms in which there must be a lower edge permutation symmetry.

The hexahedron preserves many features of cubic symmetry. The orthogonal set of Cartesian axes which pass through the cusps of an octahedron are retained. They now pass through the middles of the triangular faces at one end and the corresponding edge at the other. This retention of a set of orthogonal, equivalent Cartesian axes is in general a defining feature of tetragonal or trigonal intermediate symmetries. This definition does *not* require either that both ends of each axis be identical, nor that these axes correspond to symmetry axes of the body. It does require that all three axes have identical environments.

A second important feature is that the highest D_{3h} symmetry is defined when all ligand-ligand distances are equal, *not* when all metal-ligand distances are the same. Again it is a general feature of intermediate symmetries that the maximum number of possible equal edge lengths is achieved. This condition is masked in cubic figures but is clear in less symmetric systems.

The Hamiltonian for the hexahedron is given by Eq. (28) with a change in sign of the site strengths (z) and (x). This isomorphism is equivalent to that expressed on the four fold axis between the cube and the octahedron in Eq. (16). Since the projections in (28) now coincide with the actual metal-ligand bond lengths their ratio is;

$$\frac{R}{S} \quad \frac{(a \sec \theta)}{(a \operatorname{cosec} \theta)}$$

$$= \frac{1}{\sqrt{2}}.$$

This ratio is easily confirmed by geometry (Fig. 2), and identifies the hexahedron as the body with five vertices lying on the surface of a $\pi/4$ prolate spheroid. It is thus related to cubic bodies by reducing the angle of the projection circle in the xy plane from $\pi/2$ for cubic bodies to $\pi/4$.

The isomorphism between the trigonal prism and the hexahedron shows that there is one identifiable one-parameter, trigonal pyramid solution. This figure can be used in the same sense as the octahedron was used for tetragonal complexes, as an undistorted parent figure [3] in the preparation of ground state energy diagrams [13] in five coordinate systems. It makes available a geometric origin at which $(DM)_3$ vanishes and $(DN)_3$ depends on $(DQ)_3$. This makes spectroscopic analysis of distorted D_{3h} systems possible in terms of completely defined parameters which are independent of the symmetry and coordination number. It also means that spectrochemical data from five and six coordinate systems can be directly compared and the information used in predicting properties of D_{3h} new complexes.

3.4. The Central Field Formulation of D(l)

In Eq. (6) the momentum space wave functions are expanded as infinite sums of four dimensional spherical harmonics. These functions can be further expanded as products of radial and angular spherical harmonics [4, 12];

$$Y_{nlm}(\alpha\theta\phi) = \pi_l(n\alpha) \, Y_{lm}(\theta\phi) \tag{31}$$

in which the $Y_{lm}(\theta\phi)$ are conventional three dimensional position space spherical harmonics. The functions $\pi_l(n\alpha)$ can be subduced into position space in different forms, the most familiar of which is as a Lagueure polynomial [14]. These are normally used as the hydrogenic radial wave functions and define one-electron atomic energies. The eigenvalues in momentum space are derived from overlap integrals [12] of the eigenvectors (6) and from the form of (6) molecular energies are clearly factored as infinite sums of functions depending on different values of n. On subduction into three dimensional position space these molecular overlap integrals become radial integrals in which the single value of n, which characterizes the wave function, appears to be non-integer. Indeed, Bishop [5] and others remark that in single centre treatments of molecules in three dimensional space, non-integer values of n are usually observed to improve the fit of calculated eigenvalues.

Such non integral values of n also occur as a natural phenomenon in United Atom correlation diagrams [15] of complex molecules. They reflect the changing number of radial nodes present in molecular orbitals as the interatomic distance is decreased. Indeed for compounds of the type AB_n where B is heavier than hydrogen, the principal quantum number of the HOMO is almost invariably greater than that of the highest occupied orbital of A in its ground state [16]. As an example, the molecular orbitals of $[Ti(H_2O)_6]^{3+}$ in the United Atom model are shown in Fig. 3. The diagram was constructed using observed orbital electronegativities of the metal ion and ligand [17] at the separated atom limit and the observed energies [18] of the free trivalent lead ion at the united atom limit. Correlation of orbitals in octahedral symmetry requires that the $3dt_{2g}$ level of titanium become $4dt_{2g}$ of lead and that $3de_g$ become the $6de_g$ of lead. In the complex at its equilibrium internuclear distance (R_{eq}) the principal quantum number of both levels is probably between 3 and 4 but clearly must be greater than 3.

Accepting this condition the magnitude of the average power radium integral may be re-examined. This integral may be evaluated in terms of n l and Z and for fourth order [14],

$$\overline{r^4} = \frac{n^4}{8Z^4} [63n^4 - 35n^2(2l^2 + 2l - 3) + 5l(l+1)(3l^2 + 3l - 10) + 12]$$

$$= \frac{1}{8Z^4} [63n^8 - 315n^6 + 252] \tag{32}$$

for d electrons.

Being essentially a function of n^8, $\overline{r^4}$ is very sensitive to small changes in the value of the principal quantum number.
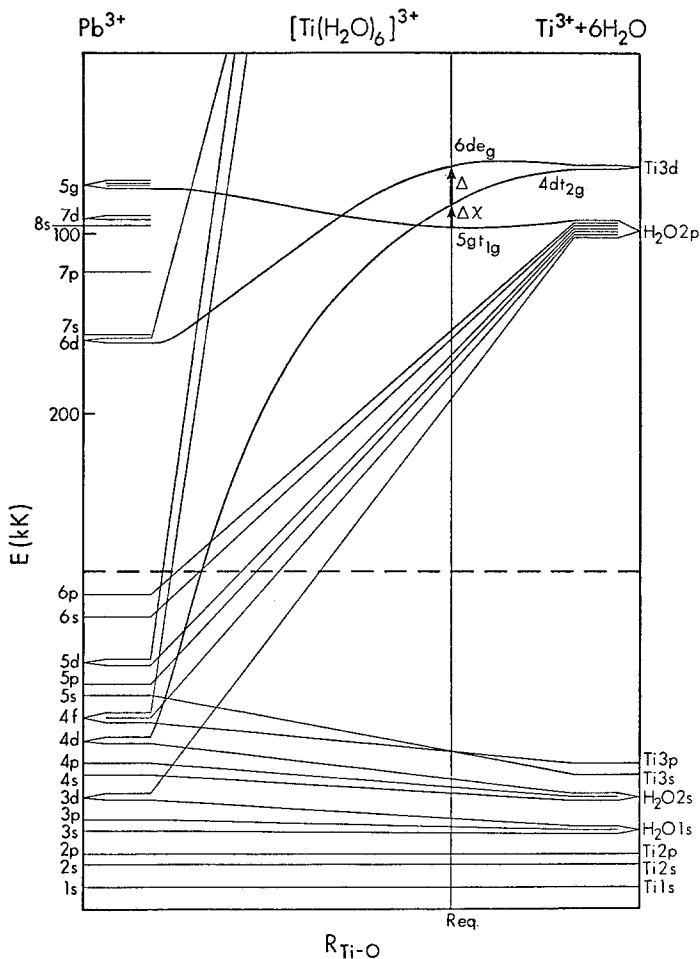
Fig. 3. The United Atom correlation diagram for $[Ti(H_2O)_6]^{3+}$. The vertical line represents the equilibrium ion. The HOMO is $4dt_{2g}$. The transition energy Δ is the crystal field separation and $\Delta\chi$ represents the first ligand to metal charge transfer energy

For example;

$$\frac{\overline{r^4}(n=3)}{\overline{r^4}(n=4)} \simeq \frac{1}{15}$$

and

$$\frac{\overline{r^4}(n=4)}{\overline{r^4}(n=5)} \simeq \frac{1}{7}.$$

(33)

It is well known [10] that conventional calculations of $\overline{r^4}$ for $3d$ octahedral complexes yield values which are a power of 10 too small. Clearly the point charge model is inaccurate simply because it fails to recognize the increased value of n appropriate to those d electrons as the metal ligand separation is reduced.

Calculations of central field models for complexes is rendered no easier by this insight. However one may reverse the procedure, using the observed value of $\overline{r^4}$ to assign an appropriate value of n in Eq. (32).

Similar use may be made of the $D(4)$ and $D(2)$ parameters in distorted complexes. These represent in this model a changing value of n for changing site strengths, that is (z) and (x) in Type I groups. Thus rather than reflecting significantly different radial distributions between axial and planar orbitals, DS and DT essentially reflect small changes in the effective principal quantum number induced by the ligands.

This conclusion provides a rational basis for Jorgensen's factorization [17] of DQ;
$$DQ = f_L \cdot g_M \tag{34}$$

because it essentially represents the factorization of n^8 into metal and ligand contributions. If the metal is assigned the n of the free ion d orbitals, it can be multiplied by a unique increasing factor assignable to each ligand.

The use of Eq. (32) in a United Atom model of metal complexes is being further explored. Similar equations for other observables such as B and λ are also being examined to ascertain whether there is quantative agreement between predicted and observed trends. Qualitatively, the predicted decreasing values of these parameters with increasing n does seem to correlate with the nephelauxetic series generated from both variables. Indeed, more subtle aspects of these trends are reproduced. The well documented [17] need to define three nephelauxetic ratios for B is accounted for in this model by different n values for the t_{2g} and e_g orbitals. In all octahedra;
$$n(e_g) > n(t_{2g}) \tag{35}$$
which implies;
$$\beta(e_g) < \beta(t_{2g})$$

as observed experimentally. The situation in tetrahedra is reversed.

Taken together these pieces of evidence indicate that the United Atom model can be a useful theory for the electronic structure of transition metal complexes. It is a simple extension of crystal field theory involving a more detailed analysis of the various radial parameters. Hopefully, one set of noninteger n (and occasionally l) values could be used to account for the magnitude of all parameters in any complex.

The chemical ratio defined in Eq. (10) can now be formulated, using the model subduced from momentum space, as the ratio of radial parameters defined by different values of Z and different non integer values of n for the axial and planar sets of ligands. Since the ligand field parameters appear in general to show a very high dependence on both n and Z, very small chemical differences between sets of ligands can result in substantial spectroscopic effects.

References

1. Ballhausen,C.J.: Introduction to ligand field theory. New York: McGraw Hill 1962
2. Gerlock,M., Slade,R.C.: Ligand field parameters. London: Cambridge University Press 1973
3. Donini,J.C., Hollebone,B.R., Lever,A.B.P.: J. Am. Chem. Soc. 93, 6455 (1971)
4. Wulfman,C.E.: In: Group theory and its application II, Loebl,E.M., Ed., p. 145. New York: Academic Press 1971

5. Bishop, D. M.: Advan. Quantum Chem. **3**, 25 (1967)
6. Hollebone, B. R., Lever, A. B. P., Donini, J. C.: Mol. Phys. **22**, 155 (1971)
7. Hollebone, B. R., Donini, J. C.: Theoret. Chim. Acta (Berl.) **37**, 233 (1975)
8. Lamont, J. S.: Applications of finite groups. New York: Academic Press 1959
9. Hemple, J. C., Donini, J. C., Hollebone, B. R., Lever, A. B. P.: J. Am. Chem. Soc. **96**, 1693 (1974)
10. Figgis, B. N.: Introduction to ligand fields, Sect. 2.c. New York: Interscience 1966
11. Shulman, R. G., Sugand, S.: J. Chem. Phys. **130**, 506 (1963)
12. Shibuya, T., Wulfman, C. E.: Proc. Roy. Soc. Ser A. **286**, 376 (1965)
13. Donini, J. C., Hollebone, B. R., London, G., Lever, A. B. P., Hemple, J. C.: Inorg. Chem. **14**, 455 (1975)
14. Condon, E. U., Shortley, G. H.: The theory of atomic spectra. London: Cambridge University Press 1970
15. Hollebone, B. R.: J. Chem. Soc. A., 3008 (1971), and Refs. therein
16. Herzberg, G.: Molecular spectra and molecular structure. III. Electronic spectra and electronic structure of polyatomic molecules. New Jersey: Van Nostrand 1966
17. Jorgensen, C. K.: Absorption spectra and chemical bonding in complexes. Oxford: Pergamon Press 1962
18. Moore, C. E.: Atomic energy levels. Natl. Bur. Stand. Circ. 467 (1958)

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