A SIMPLE OVERLAP MODEL FOR LIGAND-FIELD EFFECT IN CHLOROCUPRATES (II)[1]

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Abstract. Ligand-field effects in the tetragonally distorted $CuCl_6^{-4}$ chromophore are discussed in terms of a simple overlap model recently introduced in Lanthanide ligand-field theory. Three d-d bands are predicted at 12.7 kK, 10.7 kK and 6.5 kK in general agreement with what is expected from experimental observations in chlorocuprates (II). Emphasis is given to the fact that the model may be regarded as a starting point to perform practical ligand-field "ab-initio" calculations.

In a recent work[1,2] we have proposed an overlap model in an attempt to give a comparatively simple representation of lanthanide ligand field effects. The model, based on the potential produced by an effective charge distribution, proportional to overlap integrals, and situated between the central ion and the ligands, was found to reproduce satisfactorily the experimental crystal-field parameters for the $LaCl_3:Nd^{3+}$ and $YOCl:Eu^{3+}$ systems.

In the present article we wish to briefly discuss the theoretical aspects of the simple overlap model as applied to transition metal compounds. For practical purposes we will concentrate on copper (II) chromophores. A more complete analysis is in progress.

It is a common feature in spectroscopic studies of d and f elements to express their interaction energy with a chemical environment through the expansion

$$V = \sum_{kqi} B_q^k C_q^{(k)}(i) \qquad (1)$$

where the $C^{(k)}$'s are Racah tensor operators[3] and i labels an outside closed shell electron of the centran ion. Equation (1) is a very convenient one to those who are accustomed with the use of tensor operator techniques[4].

From the phenomenological point of view equation (1) has succeeded in the interpretation of d-d and f-f spectra. Kibler[5,6] has discussed how the B_q^k parameters of this equation may be related to the e_λ parameters of the AOM.

In the point charge electrostatic model (PCEM) the B_q^k parameters are given by

$$B_q^k(\text{PCEM}) = \langle r^k\rangle\left(\frac{4}{2k+1}\right)^{1/2} \sum_\mu \frac{g_\mu e^2}{R_\mu^{k+1}} Y_q^{k*}(\Omega_\mu) \qquad (2)$$

where $\langle r^k\rangle$ is the radial expectation value of r_i^k and the sum runs over all neighboring atoms considered to be point charges of magnitude g_e.

In the simple overlap model[1,2] we assume the following:

i) The potential energy of equation (1) is produced by charges uniformely distributed over small regions centered around the mid-point of the distance metal-ligand.

ii) The total charge in each region is equal to $-ge\rho$, where ρ is the magnitude of the total overlap between the pair metal-ligand.

We may show[2] that the radial matrix element of V is then given by

$$\langle n\ell|V|n\ell\rangle = e^2 \sum_{kq\mu i} g_\mu \rho_\mu \left(\frac{4\pi}{2k+1}\right)^{1/2} \frac{Y_q^{k*}(\Omega_\mu)}{r_\mu^{k+1}} R_{k\mu} C_q^{(k)}(i) \qquad (3)$$

where

$$R_{k\mu} = \langle r^k\rangle + r_\mu^{k+1} \int_{r_\mu}^{\infty} \left(\frac{r_\mu^k}{r^{k+1}} - \frac{r^k}{r_\mu^{k+1}}\right)\phi_{n\ell}^2 r^2 dr \qquad (4)$$

$\phi_{n\ell}$ being the appropriate radial wavefunction of the d (or f) electrons. In equations (3) and (4) r_μ is defined by

$$r_\mu = \frac{R_\mu}{2\beta} \qquad (5)$$

where R_μ is the distance from the metal to the μ-th ligand and the dimensionless quantity β should account for the fact that the centroid of the overlap region may be displaced from the mid-point distance. If Δ is defined as this displacement, it is easy to show that[4]

$$\beta = \frac{1}{1 - \frac{2\Delta}{R_\mu}} \qquad (6)$$

Further, if we let R_μ define the x axis it can be shown that[7]

$$\Delta = \langle\phi_{n\ell}|x|\phi_L\rangle \qquad (7)$$

where $|\phi_L\rangle$ is the approximate linear combination of s and p orbitals of the μ-th ligand. Now, following a suggestion of Barnett et al[8] we have used the approximation

$$|\Delta| = \frac{1}{2}\rho_\mu R_\mu \qquad (8)$$

to obtain

$$\beta = \frac{1}{1 \pm \rho_\mu} \qquad (9)$$

We somewhat arbitralily assume that the minus sign should be used in the case of sizable ligands like chlorine while the plus sign should apply to the case of oxygen and fluorine ligands.

In order to apply the model described in the previous section we have chosen the $CuCl_6^{-4}$ chromophore, with a tetragonal elongation, which is contained in a number of chlorocuprates (II). It has been argued[9] that the d-d bands in these systems lie in the range 10-14 kK (1kK=1000 cm^{-1}).

In the tetragonally distorted $CuC\ell_6^{-4}$ chromophore the symmetry of the site occupied by the Cu(II) ion is lowered from O_h to D_{4h}. The ligand field interaction of equation (1) is in this case given by[10]

$$V_{D_{4h}} = \sum_i [B_o^2 C_o^{(2)}(i) + B_o^4 C_o^{(4)}(i) + B_4^4 (C_4^{(4)}(i) + C_{-4}^{(4)}(i))] \quad (10)$$

In order to evaluated the B^k parameters, in the above equation, from the simple overlap model all we need are the values of the radial integrals $\langle r^k \rangle_{free}$ ion and an estimate for the overlap integrals ρ_μ. The formers may be found in ref.11 from which $\langle r^2 \rangle = 1.07$ $(a.u.)^2$ and $\langle r^4 \rangle = 2.76$ $(a.u.)^4$.

Overlap integrals are larger for transition metal than for lanthanide compounds where typical values are of the order of 0.05[11]. If we consider that the 3d orbitals are more susceptible to expand, due to penetrating ligands orbitals, than the very localized 4f orbitals and that 3d-4s mixing may be of considerable importance we are not being unrealistic in assuming values between 0.1 and 0.2 for the quantities ρ_μ in equation (3).

Typical distances R_μ in the tetragonally distorted octahedron are 2.3 Å for the ligands in the equatorial plane and 2.7 Å for the axial ligands[11].

With these values in equation (3) we find $B_o^2 = -14129$ cm^{-1}, $B_o^4 = 13227$ cm^{-1}, $B_4^4 = 15907$ cm^{-1} where for the equatorial ligands we have assumed $\rho_\mu = 0.2$ while for the axial ligands $\rho_\mu = 0.1$. The matrix elements for the d^9 configuration of copper (II) are simply related to those of d^1 through the relation[12]

$$\langle d^9\psi | \sum_i C_q^{(k)}(i) | d^9\psi' \rangle = -\langle d^1\psi | C_q^{(k)} | d^1\psi' \rangle \quad (11)$$

They may be evaluated by simple angular momentum algebra.

Thus, diagonalizing $V_{D_{4h}}$ in equation (10) we readily obtain the following eigenvalues $E(d_{xy}) = 1671$ cm^{-1}, $E(d_{z^2}) = -258$ cm^{-1}, $E(d_{xz,yz}) = -4538$ cm^{-1} and $E(d_{x^2-y^2}) = -11004$ cm^{-1}. Where the notation in terms of d orbitals should be understood as representing states of d^9 or one-hole states.

Three bands, at 12.7 kK, 10.7 kK and 6.5 kK, are threfore predicted. This is in general agreement with what has been observed in tetragonally distorted chlorocuprates (II)[9]. The predicted band at 6.5 kK does not seem to correspond to any experimental observation. On the other hand only at most two bands, in the range 10-14 kK, have been in general observed in these systems and the possibility that the 6.5 kK band is of very low intensity should not be discardrd.

With the B_q^k parameters as given by equation (2), the point charge electrostatic model would predict three bands in the region 0.5-1.3 kK in large disagreement with observations. In the PCEM it is usual to define the radial parameters

$$a_k = g \frac{\langle r^k \rangle}{R^{k+1}} \quad (12)$$

Thus, it has been argued[9] that good agreement with experiment may be obtained if the ratio a_2/a_4 is close to unity. With a typical value of R=2.4 Å and the Hartree-Fock values $\langle r^2 \rangle = 1.07$ $(a.u.)^2$ and $\langle r^4 \rangle = 2.76$ $(a.u.)^4$, as we have used previously, we obtain $a_2/a_4 = 8$. On the other hand the present simple overlap model predicts

$$\frac{a_2}{a_4} = \frac{\langle r^2 \rangle}{\langle r^4 \rangle} \frac{R^2}{(2\beta)^2} \quad (13)$$

from where for $\beta = 1.25$ ($\rho = 0.2$) we obtain $a_2/a_4 = 1.3$. This is an interesting feature of the model in the sence that apparentely there is no need to assume different values for $\langle r^2 \rangle / \langle r^4 \rangle$ with respect to the value given by a free-ion Hartree-Fock calculation.

The present model has the purpose of providing a simple way of performing "ab-initio" calculation of ligand-field effects in transition metal and lanthanide compounds. While it obviously contains contributions of the type given by equation (2) the model is more concerned with aspects of molecular orbital theory since it depends explicitely on the overlap between the central ion and ligand orbitals.

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