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Crystal Field Theory with Covalency*

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The use of a covalency parameter in Crystal Field Theory calculations has been applied to sixteen octahedral complexes. The variables fitted to experiment have been correlated to theoretical parameters.

Kristallfeld-Berechnungen mit einem Kovalenz-Parameter werden an sechzehn oktaedrischen Komplexen durchgeführt. Die dem Experiment angepaßten Variablen wurden mit theoretischen Parametern in Beziehung gesetzt.

Introduction

The study of the effect on an electrostatic field originating from an environment of charged species around an atom having an incomplete shell of *d* electrons is the basis of Crystal Field Theory. Crystal Field Theory as developed by Bethe [1], Van Vleck [2], and others [3–5] has been reasonably successful and easy to apply. It predicts qualitatively the correct type of splittings that the *d*-orbitals experience; however, it fails to produce quantitative results. The consideration that the ligands are point charges is one basic shortcoming of Crystal Field Theory which has been overcome by Molecular Orbital Theory. However, complete molecular orbital calculations on transition metal complexes are so involved and time consuming, that in general, one can not afford to make such calculations for predictive or survey purposes.

Crystal field calculations on the other hand, even going through atomic Hartree-Fock self-consistent-field calculations first, take relatively little computer time, give nearly all of the correct symmetry properties, but ordinarily must have covalency effects added in *a posterori* and *ad hoc* fashions.

It seemed reasonable that the parameters from the free atom calculations that are used in crystal field calculations could be modified for covalency effects as a function of orbital overlaps. This approach was developed using atomic Hartree-Fock self-consistent-field wave functions.

Several reviews [6–8] have discussed the topics of Crystal Field Theory, covalency, and Molecular Orbital Theory. The recent review by Owen and Thornby [7] is particularly thorough.

Theory

In Crystal Field Theory [1–5], the radial parts of the several *nd* wave functions are equivalent in a cubic electrostatic field. However, if the ligands atoms interact through σ bonds, the radial parts of the e_g and t_{2g} wave functions may be

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different with the five-fold degenerate d orbits split into e_g and t_{2g} irreducible representations. The neglect of this electron delocalization or covalency of the e_g orbitals can be regarded as one reason that Crystal Field Theory fails to fit the observed spectra of the d electron systems in a quantitative manner. Koide and Pryce [9] introduced covalency in cubic fields within the Crystal Field Theory framework by the following method. The radial wave functions of the t_{2g} orbitals ($R_{t_{2g}}$) are taken as being equivalent to those of the free ion (R_{3d}), but the e_g orbitals (R_{e_g}) are expanded compared to the free ion radial functions through a covalency parameter, ε;

$$R_{t_{2g}} = R_{3d}$$

$$R_{e_g} = \frac{R_{3d}}{[1-\varepsilon]^{1/2}} = \frac{R_{3d}}{\eta}$$

where η is related to ε by

$$\eta = [1-\varepsilon]^{1/2}.$$

The extent to which η differs from unity is a measure of the covalency that the e_g orbitals experience. Pappalardo [10], Stout [11], and Stevenson [12] have used η or ε in a Crystal Field Theory framework to fit the spectra of manganous halides. This work is concerned with the determination of the various covalency parameters that are required to fit the observed spectra of a number of octahedral systems and the correlation of these values of η with the overlap integrals obtained from HF-SCF atomic wave functions for the various $3d$ metals and halide ligands.

Multiplet Matrices

The multiplet matrix elements for d electrons in an octahedral environment were developed by Tanabe and Sugano [13] in terms of the parameters B, C, and Δ. B and C are Racah's [14] electron interaction integrals. The parameter Δ is defined as the splitting of the five-fold degenerate d orbitals into the e_g doubly degenerate and t_{2g} triply degenerate orbitals in an octahedral field. These matrix elements were modified by R. Stevenson [15] in a manner suggested by Tanabe [16] so that the e_g orbitals were permitted to occupy a larger volume than the t_{2g} orbitals. This modification was accomplished by the following:

$$B_{e_g} = \eta^2 B_{t_{2g}}, \qquad C_{e_g} = \eta^2 C_{t_{2g}}.$$

The method suggested by Stevenson [15] for the crystal field calculation is as follows. First, the free ion spectrum is fitted by variations in B, C, α, and β, where α is the Trees' correction [17] and β is a seniority correction. The Trees' correction [17] allows for orbit-orbit interaction and the analytical form used by Stevenson is:

$$\alpha[L(L+1) - n\ell(\ell+1)]$$

where L refers to the angular momentum quantum number for a specific free ion state, ℓ is the orbital angular momentum quantum number for the electron system under consideration, and n is the number of d electrons for the ion studied. The seniority correction provides a means of treating differently, repeated multiplets of the same type. In this calculation, the strong crystal field matrices developed by Stevenson can be used with $\Delta = 0$ and $\eta = 1$.

The free ion values of B, C, α, and β are used in the crystal field calculations as fixed parameters, and Δ and η are varied to fit the crystal spectrum. However, an exact agreement of the observed and calculated free ion spectrum is not always possible. Thus, if Stevenson's [15] method is used, the crystal field calculations are dependent on the theoretical values for the free ion spectrum. In this work the errors in these values are eliminated by the direct use of the observed free ion multiplets in the calculation of the crystal spectrum. However, the coefficients of certain terms in η contain B and C; therefore numerical values of B and C obtained from the free ion spectrum are needed.

A program was written to determine the best least squares B, C, and α from the free ion spectrum. The least squares values obtained are given with the calculated spectral results in the next section. The parameter β was not needed.

Methods of Calculation

The matrices of Tanabe and Sugano [13] as modified by R. Stevenson [15] were used, and a computer program (Fortran IV) was written to determine the Δ and η that best fit the crystal field spectra. A subroutine was developed which determined one variable (either Δ or η) which fit exactly specific strongly allowed observed splittings. The other variable was adjusted to another observed band. The equations used for this calculation are given in the next section.

The free ion calculated multiplet baricenters were replaced by the observed free ion baricenters. (The free ion multiplets had been calculated by setting $\Delta = 0$ and $\eta = 1$).

It was necessary in each matrix to first determine the free ion multiplet from which each crystal term emerged. Each diagonal matrix element required a label to specify the crystal field term which it and the free ion term became as Δ approached 0 and η approached 1. By means of the Bethe notation for the labels of the diagonal matrix elements, a straightforward name matching subroutine was developed for correlation of observed and calculated bands. The same type of technique was used to determine the observed free ion band center that was to be added to a corresponding diagonal matrix element. The amount of information required to be read into the program has been kept at a minimum yet the program is general enough to handle any octahedrally treatable case from d^2 to d^8.

Results

This section contains the results of the calculations described in the preceding section. The system considered will be discussed and grouped according to the number of electrons in the $3d$ shell of the metal.

The results of the calculations to be found in Tables 1 through 5 are made with the Racah repulsion integrals determined in a least squares manner for the free ion baricenters. The 1st column contains the complex term multiplet and the next is the free ion multiplet from which it arose. The specific spectral data that is observed is described in the section considering that particular electronic configuration, the values are given in terms of $\mathrm{cm}^{-1} \times 1000$ frequently referred to as kilokaysers. The calculated column is made for the specific B and C given for the free ion and the values of Δ and η determined and are given at the bottom of the column with the results.

The free ion multiplet baricenters used in the calculations were determined from the spectral data given by Moore [19] (unless otherwise noted in the text) for each ion considered.

d^2 *Halides*

The ground state is $^3T_1$. The spectral values for the d^2 halides are given in Table 1 with the multiplets. The value of Δ was determined so that the calculated difference is given by the following.

$$\Delta = 2(^3T_2 \leftarrow {}^3T_1) + 20B(\eta^2 - 1) - (^3T_1' \leftarrow {}^3T_1) + FI(^3_2P) - FI(^3_2F)$$

where $FI(^3_2P)$ is the observed free ion baricenter for the ^3_2P multiplet. The spectra of VF_6^{-3}, VF_3, and VCl_3 were observed by reflectance [20] and of VCl_6^{-3} in absorption in $\mathrm{Cs_3ScCl_6}$ [21] all at ambient conditions. The values of η adjusted to the spectra of VX_6^{-3} and VX_3 indicate an increase in covalency when the halide (X) is shared with two metals.

d^3 *Halides*

The ground state is $^4A_2$. The spectral values for d^3 halides are given in Table 2 with the multiplets. The variable Δ is determined by the 1st observed allowed transition ($^4T_1 \leftarrow {}^4A_2$) to correspond to the observed value by the following.

$$\Delta = (^4T_2 \leftarrow {}^4A_2) - 10B(1 - \eta^2)\,.$$

The value of η is determined by fitting to the 1st observed $^4T_1$ transition. The crystal spectra of $(\mathrm{CrF}_6)^{-3}$ and CrCl_3 were observed in absorption [22] at liquid nitrogen temperature; the crystal spectra of CrBr_3 in absorption [22] at liquid helium temperature. Wood, Ferguson, Knox and Dillon [22] have assigned several weak bands for each compound. The CrF_6^{-3} weak band assignments are at approximately 15,000 cm^{-1} for $^2T_1$ and 23,000 cm^{-1} for $^2T_2$. The CrCl_3 and CrBr_3 weak band assignments are at approximately 14,000 cm^{-1} for ^2E; 14,500 cm^{-1} for $^2T_1$. One additional weak band assignment [22] in CrBr_3 is $^2T_2$ at approximately 19,000 cm^{-1}.

d^5 *Halides*

The ground state is $^6A_1$. The observed and calculated spectra are given in Table 3 with the multiplets. The transition ($^4T_{1g} \leftarrow {}^6A_1$) is independent of Δ and the value of η is determined directly from the observed transition by the following.

$$\eta^2 = \frac{(^4T_1 \leftarrow {}^6A_1) - FI(^4_5G) + 10B + 5C}{10B + 5C}\,.$$

The variable Δ was fitted to the 1st $^4T_2$ transition in all three spectra. This transition was selected because it was the most sensitive to the change in Δ, and was observed in all three spectra. The spectrum of single crystals of MnF_2 was observed

Table 1. d^2 *cases* ($B = 912$ and $C = 3216$ for V^{+3})

		$(VF_6)^{-3}$		VF_3		$(VCl_6)^{-3}$		VCl_3	
		obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
$^1T_2$	$(^1D_2)$		11.8		11.8		11.7		11.6
^1E	$(^1D_2)$		12.2	12.3	12.2		12.2		12.1
$^3T_2$	$(^3F_2)$	14.8	14.8	14.7	14.7	11.0	11.0	12.5	12.5
$^3T_1$	$(^3P_2)$	23.2	23.2	22.5	22.5	18.0	18.0	19.6	19.6
$^1T_2$	$(^1G_2)$		26.3		25.4		20.9		21.7
$^1T_1$	$(^1G_2)$		28.5		27.4		22.3		23.1
$^1A_1$	$(^1G_2)$		27.0		27.0		24.8		26.2
$^3A_2$	$(^3F_2)$	31.0	30.9	31.0	30.5		22.6		25.6
^1E	$(^1G_2)$		39.5		38.0		28.6		30.7
^1S	$(^1S_0)$		59.7		57.1		48.5		47.9
		$\Delta = 14747$		$\Delta = 14286$		$\Delta = 9881$		$\Delta = 11557$	
		$\eta = 0.867$		$\eta = 0.834$		$\eta = 0.783$		$\eta = 0.793$	

Table 2. d^3 *cases* ($B = 1070$ and $C = 3237$ for Cr^{+3})

		$(CrF_6)^{-3}$		$CrCl_3$		$CrBr_3$	
		obs.	calc.	obs.	calc.	obs.	calc.
$^4T_2$	$(^4F_3)$	16.1	16.1	13.7	13.7	13.4	13.4
^2E	$(^2G_3)$		18.1		18.3		18.5
$^2T_1$	$(^2G_3)$		19.0		19.0		19.0
$^4T_1$	$(^4F_3)$	23.6	23.6	19.0	19.0	17.5	17.5
$^2T_2$	$(^2G_3)$		25.8		23.2		21.0
$^2T_1$	$(^2P_3)$		26.9		21.3		18.3
$^2A_1$	$(^2G_3)$		30.6		28.0		27.5
$^2T_2$	$(^2H_3)$		31.5		27.7		27.4
$^4T_1$	$(^4P_3)$	36.5	35.7		29.4		27.2
^2E	$(^2H_3)$		36.6		33.2		32.1
$^2T_1$	$(^2H_3)$		37.7		31.8		30.2
$^2T_2$	$(^2D_3)$		42.2		32.5		28.7
		$\Delta = 14069$		$\Delta = 9433$		$\Delta = 7711$	
		$\eta = 0.900$		$\eta = 0.775$		$\eta = 0.684$	

Table 3. d^5 *cases* ($B = 920$ and $C = 3227$ for Mn^{+2})

		MnF_2		$MnCl_2$		$MnBr_2$	
		obs.	calc.	obs.	calc.	obs.	calc.
$^4T_1$	$(^4G_5)$	19.44	19.32	18.50	17.80		17.52
$^4T_2$	$(^4G_5)$	23.50	23.50	22.00	22.00	21.65	21.65
$^4T_1$	$(^4G_2)$	25.20	25.20	23.59	23.59	23.08	23.08
^4E	$(^4G_5)$	25.42	25.34	23.83	23.61	23.35	23.02
$^4T_2$	$(^4D_5)$	28.16	29.36	26.75	28.40	26.52	28.15
^4E	$(^4D_5)$	30.42	30.50	28.07	29.03	27.51	28.64
$^2T_1$	$(^2I_5)$		31.84		29.61		29.09
$^2A_2$	$(^2I_5)$		32.20		30.64		30.33
$^4T_1$	$(^4P_3)$	33.07	33.07		31.93		31.44
$^2A_1$	$(^2I_5)$		36.68		34.55		33.89
		$\Delta = 8508$		$\Delta = 8962$		$\Delta = 8914$	
		$\eta = 0.967$		$\eta = 0.934$		$\eta = 0.923$	

Table 4. *d^7 cases* ($B = 1014$ and $C = 3978$ for Co^{+2})

	$KCoF_3$		$CoCl_2$		$CoBr_2$	
	obs.	calc.	obs.	calc.	obs.	calc.
$^4T_2$ ($^4F_3$)	7.2	6.8	6.6	5.8	6.2	5.0
^2E ($^2G_3$)		8.9		7.0		7.1
$^4A_2$ ($^4F_3$)	15.1	14.7	13.3	12.5	12.0	10.8
$^2T_2$ ($^2G_3$)	17.5	15.7		13.3		12.7
$^2T_1$ ($^2G_3$)		16.3	15.1	14.6		14.1
$^4T_1$ ($^4P_3$)	19.3	19.3	17.3	17.3	16.4	16.4
$^2T_1$ ($^2P_3$)	21.6	18.7		16.4		15.8
$^2A_1$ ($^2G_3$)	22.8	23.2	19.9	22.0		21.2
$^2T_2$ ($^2H_3$)		24.8		21.8		20.7
$^2T_1$ ($^2H_3$)		27.3		25.6		24.6
^2E ($^2H_3$)		29.4		27.9		26.9
	$\Delta = 7389$		$\Delta = 5728$		$\Delta = 4722$	
	$\eta = 0.962$		$\eta = 0.918$		$\eta = 0.906$	

in absorption [11, 12] at ambient conditions, and the absorption spectra of $MnCl_2$ and $MnBr_2$ [10] at liquid nitrogen temperature. Because of the sharpness of the bands in Mn^{+2} halides, the observed and calculated values are given to one additional digit. The Mn^{+2} doublets used in the calculations were determined from the parameters given by Stevenson [12] as no doublets have been observed in the free ion spectrum for this ion.

d^7 Halides

The ground state is $^4T_1$. The observed and calculated spectral transitions are given in Table 4 with the multiplets. The value of Δ was determined so that the calculated difference between $^4A_2$ and $^4T_2$ is the same as the observed difference by the following:

$$\Delta = (^4T_2 \leftarrow {}^4T_1) - (^4A_2 \leftarrow {}^4T_1) - B(20 - 12\eta^2 - 8\eta^4) + C(5 - \eta^2 - 4\eta^4)\,.$$

The variable η is fitted to the $^4T_1' \leftarrow {}^4T_1$ transition. The assignments of the observed absorption spectra of crystals of $KCoF_3$, $CoCl_2$, and $CoBr_2$ are reported by Ferguson, Wood, and Knox [23]. The spectra of $CoCl_2$ and $CoBr_2$ were observed at 20° K while $KCoF_3$ was observed at about 150° K. The calculated weak bands are in reasonable agreement with the observed weak bands in these d^7 electron systems. The ^2P for Co^{+2} was taken from Ferguson, Wood, and Knox [23].

d^8 Halides

The ground state is $^3A_2$. The observed and calculated spectral values are given in Table 5 with the multiplets. The value of Δ was determined by the 1st observed allowed transition ($^3T_2 \leftarrow {}^3A_2$) to correspond to the observed value by the following.

$$\Delta = -(^3T_2 \leftarrow {}^3A_2) - B(10 + 6\eta^2 - 16\eta^4) + C(5 - \eta^2 - 4\eta^4)\,.$$

Table 5. d^8 *cases* ($B = 1116$ and $C = 4000$ for Ni^{+2})

	KNiF$_3$		NiCl$_2$		NiBr$_2$	
	obs.	calc.	obs.	calc.	obs.	calc.
^1E ($^1D_2$)		9.5		8.5		6.0
$^3T_2$ ($^3F_2$)	7.6	7.6	7.5	7.5	7.3	7.3
$^3T_1$ ($^3F_2$)	11.4	12.2	12.6	11.9	12.0	10.9
$^1A_1$ ($^1G_2$)		17.9		16.2		12.1
$^1T_2$ ($^1D_2$)		19.5		18.8		16.8
$^3T_1$ ($^3P_2$)	23.2	23.2	22.6	22.6	20.7	20.7
$^1T_1$ ($^1G_2$)		25.2		24.2		21.6
^1E ($^1G_2$)		34.0		33.6		32.4
	$\Delta = 6027$ $\eta = 0.887$		$\Delta = 5645$ $\eta = 0.863$		$\Delta = 4481$ $\eta = 0.797$	

The variable η is adjusted to make the observed and calculated transition $^3T_1 \leftarrow {}^3A_2$ be the same. The ^1D and ^1G for Ni^{+2} were taken from Ferguson [8]. The crystal spectra of $KNiF_3$ was observed in absorption [24] at liquid nitrogen temperature. The powder spectra of $NiCl_2$ and $NiBr_2$ were observed in absorption [25] at ambient conditions. However, the transition $^3T_1 \leftarrow {}^3A_2$ was not reported for $NiBr_2$. This transition ($^3T_1 \leftarrow {}^3A_2$) was observed at 20,700 cm^{-1} in the reflection spectrum [26] of $NiBr_2$, and the other allowed transition $3T_1 \leftarrow {}^3A_2$ was in agreement by the two different techniques.

Therefore, this value was used in the calculation. The variable η could not be fitted to the transition $^3T_1 \leftarrow {}^3A_2$ with values of $\eta < 1$.

No d^4 or d^6 halides were considered because the general occurrence of tetragonal distortion in d^4 halides, and a paucity of spectral data for both halides.

Correlation

The experimentally calculated values of Δ and η obtained in the previous section will be used in this section to determine what correlation exists between certain theoretical values and the experimental values. The theoretical Δ for an octahedral system is calculated by the following:

$$\Delta = A_0^4 \langle r^4 \rangle$$

where A_0^4 depends on the geometry and can be calculated by the equation given by Moorjani and McAvoy [27] and $\langle r^4 \rangle$ is the expectation value of the 4th power of r for the $3d$ wave function. The overlap integral values used in this section will be the sum of the σ overlap integral values for sd and pd atomic wave functions.

The ratio of $\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}}$ is a nearly linear function of the sum of σ overlaps when the values are plotted for a particular metal ion bonded to the halide ligands.

A graph indicating the observed trends is given in Fig. 1. The values plotted in Fig. 1 are collected on Table 6.

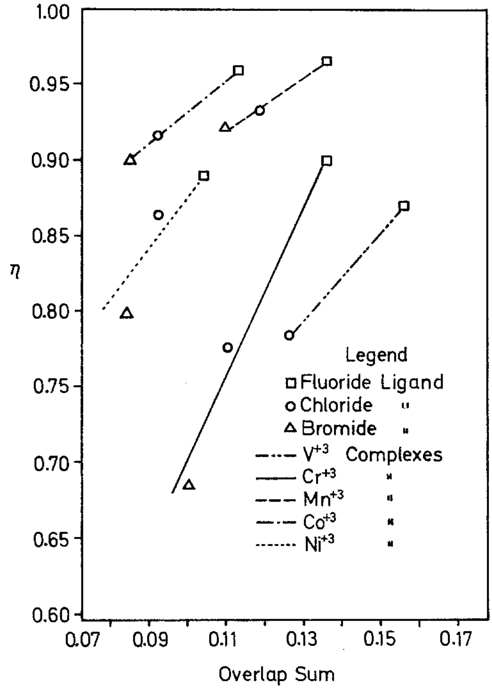

Fig. 1. Variation of $\left[\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}}\right]$ with overlap sum

Table 6. *Values used in Fig. 1, Fig. 2, and regression equations*

	Δ Theo.	$\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}}$	η	Sum of overlaps	$R = [R_{ML} - (\langle r_M \rangle + \langle r_L \rangle)]$
VF_6^{-3}	3156	4.67	0.867	0.157	1.2470
VCl_6^{-3}	1112	8.89	0.783	0.127	1.3236
CrF_6^{-3}	2572	5.45	0.900	0.137	1.3000
$CrCl_3$	902	10.23	0.775	0.111	1.3770
$CrBr_3$	664	11.55	0.684	0.101	1.3950
MnF_2	2103	4.04	0.967	0.137	1.6290
$MnCl_2$	904	9.91	0.934	0.119	1.5920
$MnBr_2$	689	12.93	0.923	0.110	1.5820
$KCoF_3$	1623	4.55	0.962	0.114	1.3190
$CoCl_2$	602	9.52	0.918	0.093	1.6980
$CoBr_2$	458	10.31	0.902	0.086	1.6880
$NiCl_2$	622	9.08	0.863	0.093	1.5413
$NiBr_2$	468	9.58	0.797	0.085	1.5310

The covalency parameter η is plotted versus the sum of the σ overlap integral values in Fig. 2. The trend found for the fitted values of η to the experimentally observed spectrum is in the same sequence as that observed chemically; the fluoride ligand is less covalent than chloride, which is less covalent than bromide.

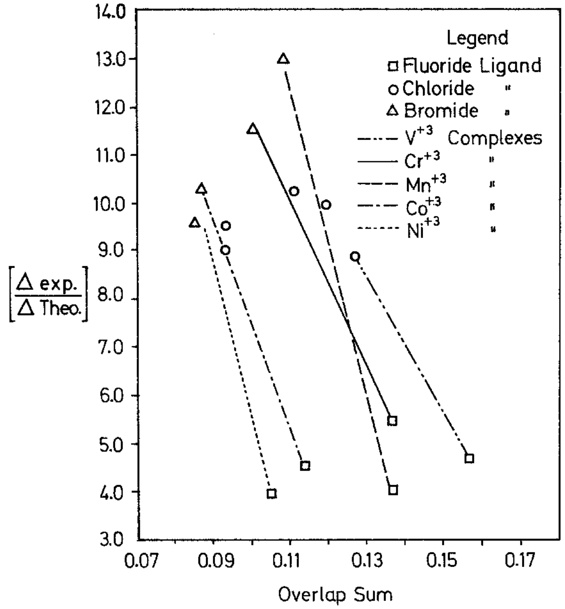

Fig. 2. Variation of η with overlap sum

Conclusions

Calculations have been made for 16 octahedral 3*d* transition metal halide complexes by varying only *two* parameters, the crystal field splitting parameter Δ and the covalency parameter η, to fit the specific observed splittings. This technique has advantages over molecular orbital calculations due to its simplicity and is of more general application than similar calculations made on d^5 systems such as that of Low and Rosengarten [28] in that the total number of variables for *all* calculations is two.

Some very detailed studies have been made of d^5 systems as this is one of the only systems which has enough observed splittings to allow the three or four variables frequently used to be determined. It is felt that there is a need for a theoretical model which can be applised to systems other than d^5 and also improve the chemist's feeling for the amount of covalency present with a limited number of variables. The values of the Racah repulsion integrals are determined by a least squares technique to represent the splittings observed for the free ions and are not varied to improve the calculated complex spectra. Calculations were made with three different sets of the free ion values to determine the importance of the specific Racah Repulsion integrals used. The degree of fitting of the complex spectra was for the most part only slightly changed. The other calculations were made with the values of B and C given in Griffith [18] and one set which included the Trees [17] correction. The authors will be glad to furnish upon request the results of the other calculations.

As the groups around the transition metal ion are altered from fluoride to chloride to bromide, this method allows the spectral changes to be interpreted in terms of a different crystal field splitting and an altered radial distribution, as indicated by the covalency parameter η. Whereas, the three parameter fitted models may have different repulsion integral ratios C/B and the effect is spread over both e_g and t_{2g} orbitals.

The ratio of $\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}}$ is a nearly linear function of the sum of σ overlaps when the values are plotted for a particular metal ion bonded to the halide ligands. The values of this Δ ratio (Δr) are listed in Table 6 and plotted in Fig. 1. It may be noticed that for a given metal the trends with change of halide are $\Delta_{\text{theo}}(\text{F}) > \Delta_{\text{theo}}(\text{Cl}) > \Delta_{\text{theo}}(\text{Br})$; but for the Δ ratios (Δr); $\Delta r(\text{F}) < \Delta r(\text{Cl}) < \Delta r(\text{Br})$. The trend of the Δ_{theo} is simply that of CFT, where the metal to ligand distance increases as one goes from F^- to Cl^- to Br^- and thus the crystalline field potential at the metal due to the ligands as point charges decreases. The Δ ratio variation, on the other hand, shows that as the distances increase, the ratios increase rapidly, or that the effective $3d$ radial wavefunctions expands rapidly ($\Delta = A_0^4 \langle r^4 \rangle$).

The trends of the adjusted covalency parameter η with respect to the sum of the σ overlap integral values were noted. The experimentally fitted Δ was found to be related to the product of the theoretical and the sum of the σ overlap intergral values. Due to the trends observed for the experimentally fitted variables, Δ and η, with respect to the theoretically calculated parameters, it should be possible to predict transitions for systems as of yet not studied. It may be noted that the several quantities studied here may be described by multiple regression equations to very high significance levels.

$$\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}} = 0.10426\, Z_L - 1.20527\, Z_M - 124.58232\,(OS) + 51.01681$$

(Multiple correlation coefficient = 0.916; significance 99 %)

$$\eta = 0.03365 Z_M - 0.00021 Z_L + 4.20635(OS) + 0.10334 R^2 - 0.69152$$

$$\left(\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}} \text{ deleted; Mult. corr. coeff.} = 0.837\text{; significance } 95\,\%\right)$$

$$(OS) = -0.00753 Z_M - 0.0106 Z_L + 0.32546$$

$$\left(\frac{\Delta_{\text{exp}}}{\Delta_{\text{theo}}} \text{ and } \eta \text{ deleted; Mult. corr. coeff.} = 0.917\text{; significance } 99\,\%\right).$$

Where Z_M and Z_L are the atomic numbers of the metal and ligand, respectively; OS is the overlap sum; and R is the difference between the metal-ligand distance and the sum of the expectation values of r for the metal and ligand orbital wave functions.

Comparison

Since the method used to fit the spectra by Low and Rosengarten [28] (L & R) varying three parameters Δ (Dq), B, and C while this method has only two Δ (Dq) and covalency, η, it is to be expected that three parameters yield a better fit. The values of B and C used in this method are those which best fit the multiplets of the free ion and are not varied to fit the spectra of the complexes. If the interest is concerned with the spectral fitting of only one compound for each transition metal, the three parameter method of L & R will be expected to be more attractive. However, for several compounds having the same transition metal (MnF_2, $MnBr_2$, $MnCl_2$, etc.), this method has an attraction in that the same values of Racah repulsion integrals are used and only the crystal field splitting parameter Δ and covalency term are altered. In other words, we have used $2m$ adjustable parameters (Δ and η for each complex) to fit the spectra of the m complexes of a given transition metal. This method is applicable to most d^n systems.

A different approach has been applied by L & R to d^5 (half-filled d shell) systems by adjusting the splitting parameter Δ, and the Racah repulsion integrals, B and C. This method differs in that each molecule or complex must have three parameters to fit the observed spectra, which by necessity limits the method to systems which have at least three observed peaks. In addition, even for the d^5 systems, which do not have any spin allowed transitions, the parameters evaluated for one complex do not have "carry over" to another complex containing the same transition metal. The method described determines parameters (B and C) representative of the free ion and allows the covalency parameter to account for any differences between the free ion and the complexed ion. This method can be applied to complexes which have only two peaks.

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