A Complementation of the Crystal Field for Tetrahedral Intensities

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Summary The perturbation of the ligands by the metal ion, in contrast to the converse procedure of traditional crystal field theory, accounts satisfactorily for the relatively strong *d*-electron absorption bands of the tetrahedral transition-metal tetrahalides.

EARLY in the development of crystal field theory an apparent shortcoming was encountered, in that the theory failed to rationalise the relatively strong *d*-electron absorption bands of simple tetrahedral transition metal complexes, $[MX_4]^{2-}$, where X is a halide or analogous anion. Ballhausen and Liehr showed, on the assumption that the static Coulombic field of the ligands mixed the 3*d* with the 4*p* orbitals of the metal ion, that the calculated oscillator strengths of the *d*-electron bands of such complexes as $[CoCl_4]^{2-}$ were as much as two orders of magnitude smaller than the corresponding experimental values.[1] In contrast the relatively weak absorption intensities of analogous octahedral complexes were satisfactorily reproduced on the same assumption, employing the Herzberg–Teller vibronic mechanism.[2] From the beginning crystal-field theory directed attention to the perturbation of the electronic states of the central metal ion by the encompassing field of the ligands,[3,4] although the metal–ligand perturbations are reciprocal. Through a consideration of the perturbation of the ligands by the charge distribution of a pure *d*-electron transition of the metal ion in a tetrahedral complex, we find that the corresponding oscillator strengths are reproduced in fair approximation (Table).

In a two-system no-overlap model the Coulombic perturbations between the metal ion A and the ligand B in a complex are mutual, but only the perturbation of the ground $|A_0)$ and excited state $|A_a)$ of the metal ion by the ground state $|B_0)$ field of the ligands is considered in traditional crystal field theory. The complementary perturbation of the ligands by the metal ion is represented to first order within a basis of simple product functions by

$$|A_0B_0> = |A_0B_0) - \sum_b (E_a + E_b)^{-1}(A_aB_b|V|A_0B_0)|A_aB_b) \qquad (1)$$

equation (1) for the ground state of the complex and by equation (2) for the excited state $|A_a)$ of the metal ion in

$$|A_aB_0> = |A_aB_0) - \sum_b (E_b - E_a)^{-1}(A_0B_b|V|A_aB_0)|A_0B_b) \qquad (2)$$

the complex. Although the metal *d*-electron transition is forbidden in the zero order, it has a first order electric dipole moment in the tetrahedral complex given by equation (3). The electric dipole moments μ_{0b} located in the ligands are correlated coulombically by the potential from the

$$<A_0B_0|\hat{\mu}|A_aB_0> = -\sum_{B=1}^{4} \sum_b 2E_b(E_b^2 - E_a^2)^{-1}(A_0A_a|V|B_0B_b)\vec{\mu}_{0b} \qquad (3)$$

d-electron transitional charge distribution of the metal ion (Figure). The correlation is dependent upon the matrix element $(A_0A_a|V|B_0B_b)$, where V is the operator for the potential between the charge distributions of the metal ion A and the ligand B. The element is evaluated by expanding each of the transitional charge distributions (A_0A_a) and (B_0B_b) as a multipole series centred on the respective co-ordinate origin. Only the leading term of each expansion is retained, namely an electric dipole, μ_{0b}, for the ligand and an electric quadrupole, θ_{0a}, or hexadecapole, H_{0a}, for the d-electron transition of the metal ion.

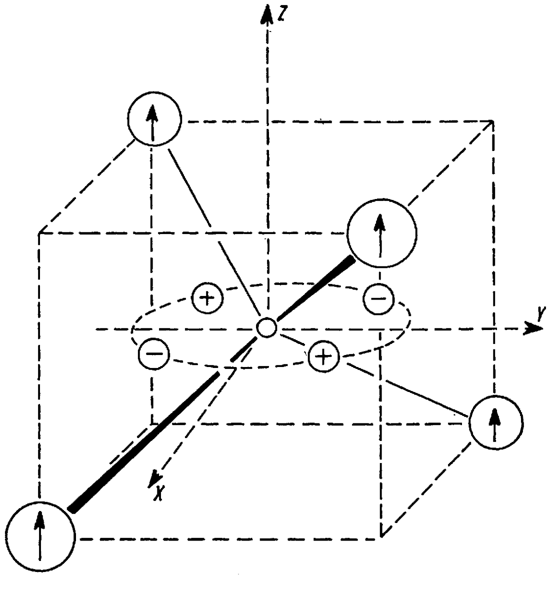

FIGURE. The coulombic correlation of the z-component of the transient dipoles induced in the ligands by the xy-component of the quadrupole moment of a metal-ion d-electron transition in a tetrahedral complex.

In the tetrahedral group, T_d, the xy, yz, and xz component of a quadrupole transform under the same row of the T_2 representation as the z, x, and y component of a dipole, respectively, and only these particular quadrupole–dipole correlations (Figure) give a non-zero value for the perturbation matrix element by the criterion requiring the element to transform totally-symmetrically. The matrix element thus reduces to equation (4) where the tensor $G^{B}_{\alpha\beta,\gamma}$ is the

$$(A_0A_a|V|B_0B_b) = \sum_{\alpha\beta,\gamma} \theta^{\alpha\beta}_{oa}\, \mu^{\gamma}_{bo}\, G^{B}_{\alpha\beta,\gamma} \tag{4}$$

angular and radial geometric factor for the potential between the $\alpha\beta$ component of the transition quadrupole, θ_{0a}, and the γ component of the transition dipole μ_{0b}, with α, β_1 and γ representing x, y, and z and their permutations. The γ component of the first-order electric dipole moment (equation 3) of a d-electron transition in a tetrahedral complex accordingly will be given by equation (5). On the

$$\mu^{\gamma}_{oa} = -\sum_{B=1}^{4}\sum_{\alpha\gamma}\sum_{b} 2E_b(E_b^2 - E_a^2)^{-1} \mu^{\gamma}_{ob}\mu^{\delta}_{bo}\theta^{\alpha\beta}_{oa}G^{B}_{\alpha\beta,\delta} \tag{5}$$

assumption that the ligands B are isotropic, the principal component $\alpha_{\gamma\gamma}$ of the ligand polarisability tensor, extracted from equation (5), is equated to the corresponding mean value, $\bar{\alpha}(B)$ at the transition wave number $\bar{\nu}_{0a}$, so that equation (6) is obtained. The ligand polarisability $\bar{\alpha}(B)$

$$\mu^{\gamma}_{oa} = -\sum_{B=1}^{4}\sum_{\alpha\beta}\bar{\alpha}(B)\theta^{\alpha\beta}_{oa}G^{B}_{\alpha\beta,\gamma} \tag{6}$$

is afforded by ion-refractivity data,[5] and the non-zero geometric terms of the tensor $G^{B}_{\alpha\beta,\gamma}$ for the quadrupole–dipole potential,[6] $(-15XYZ/R^7)$ for each ligand, are dependent solely on the bond length R and the tetrahedral geometry. Thus the only term in equation (6) to be obtained theoretically is the quadrupole transition moment, $\theta^{\alpha\beta}_{oa}$. Griffith,[7] whose definition we follow, has evaluated the quadrupole moment of the transition connecting a d_{xy} with a d_{z^2} orbital in units of the expectation value of r^2 for a d-electron, $<3d|r^2|3d>$ in the present cases (Table), and the corresponding moments of other d-electron transitions are thence derivable through his coupling coefficients.[8] Double-exponent $3d$ wavefunctions[9] were employed to determine the units $<3d|r^2|3d>$ (Table).

TABLE

Observed and calculated oscillator strengths, f, of the second and third d-electron transitions in the tetrahedral metal complexes $[MX_4]^{2-}$.

		$10^4f(\nu_2)$		$10^3f(\nu_3)$			
Complex		exp.[a]	.[b]	exp.[a]	calc.[b]	R_{MX}/ Å	$\bar{\alpha}(X^-)$[c]/ Å^3
$[CoCl_4]^{2-}$	..	7·21	5·15	5·09	2·93	2·252[d]	3·5
$[CoBr_4]^{2-}$	..	7·10	4·90	5·89	3·05	2·42[e]	4·85
$[CoI_4]^{2-}$	..	11·1	7·9	8·12	5·15	2·53[e]	7·7
$[NiCl_4]^{2-}$	..	1·42	0·75	2·24	0·63	2·245[f]	3·5
$[NiBr_4]^{2-}$	..	2·61	0·85	3·15	0·66	2·40[e]	4·85

[a] From ref. 10. [b] Calculated with $<3d|r^2|3d>$ values of 0·3663 and 0·3283 Å^2 for cobalt(II) and nickel(II), respectively, using the $3d$ wavefunctions of ref. 9. [c] From ref. 5, p. 42. [d] From B. N. Figgis, M. Gerloch, and R. Mason, *Acta Cryst.*, 1964, **17**, 506. [e] Estimates based on bond-length changes observed in other metal halide series. [f] From G. D. Stucky, J. B. Folkers, and T. J. Kistenmacher, *Acta. Cryst.*, 1967, **23**, 1064.

From the first-order electric dipole transition moments (equation 6) the corresponding oscillator strengths, f_{0a}, were evaluated (Table) through equation (7), where g_0

$$f_{0a} = (8\pi^2mc/3h)(\bar{\nu}_{0a}/g_0)\sum_{o\to a}|\mu_{0a}|^2 \tag{7}$$

represents the ground-state degeneracy and the sum is taken over all components of the transition $|A_0) \to |A_a)$ at the wavenumber $\bar{\nu}_{0a}$. The oscillator strengths of the second and third d-electron transitions, to higher frequencies of the tetrahedral $[MX_4]^{2-}$ complexes, $f(\nu_2)$ and $f(\nu_3)$ in the nomenclature of Cotton and his co-workers,[10] calculated from equation (7) are minimum values (Table), since the $<3d|r^2|3d>$ unit adopted refers to the gaseous dipositively charged metal ion. If the $3d$ charge-cloud expansion due to the ligand field is included, the f-values are increased, the multiplying factor being 4·3 if the metal ions become effectively neutral.

Without any allowance for the nephelauxetic effect, the degree of agreement between the calculated and experimental f-values (Table) suggests that the mechanism postulated makes a major contribution to the tetrahedral absorption intensities. Where the d-electron transition is quadrupole-forbidden, as in the case of the lowest-energy transition of $[CoX_4]^{2-}$, ${}^4A_2 \to {}^4T_2$, the f-value is an order of magnitude smaller than that of the higher-energy transitions. The hexadecapole moments of this transition transform as T_1 in T_d and cannot constructively correlate the transient induced dipoles in the ligands. From single-crystal measurements with Cs_3CoCl_5 and the corresponding bromide we estimate $f(\nu_1)$ from the absorption near 3000 cm^{-1} to be 4×10^{-5}. In contrast the lowest-energy transition of $[NiBr_4]^{2-}$, $^3T_1\ (F) \rightarrow {}^3T_2$, is quadrupole allowed, and $f(\nu_1)$ has a magnitude[11] (3×10^{-4}) comparable to that of $f(\nu_2)$ (Table).

Independent of the nephelauxetic effect, the $f(\nu_3)/f(\nu_2)$ ratios calculated to first order are smaller than the corresponding observed ratios (Table). On proceeding to second order it is found that the transient induced dipoles in the ligands, which are constructively correlated by the *d*-electron quadrupole transition moment of the metal ion (Figure, equation 6), themselves correlate in turn collinear electric dipole moments of higher-energy transitions, notably the high-intensity metal-ligand charge-transfer excitations in the near u.v. region. The subsidiary second-order intensity-borrowing favours $f(\nu_3)$ over $f(\nu_2)$, by a factor of 2·3 in the case of $[CoCl_4]^{2-}$, and raises both theoretical *f*-values nearer to the corresponding values observed.

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