Molecular-orbital Interpretation of the Electronic Spectra of Hexafluoro- and Hexa-aqua-complexes of the First Transition Series

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A theoretical model, based on integration of the molecular-orbital and ligand-field theories, is described. The utility of the method is demonstrated by its application to some hexafluoro- and hexa-aqua-complexes of the first transition-metal series. The computational procedure is straightforward and provides a satisfactory interpretation of excited-state properties.

THE calculation of the optical-absorption spectra of transition-metal complexes is an area in which molecular-orbital (m.o.) methods have, till now, had little success. *Ab initio* calculations, while theoretically rigorous, are computationally extremely demanding and, if a limited basis set is used, are of uncertain accuracy for excited-state calculations. On the other hand, semi-empirical m.o. methods, although less time-consuming, are generally unable to cope with the complexity of *d–d* transitions. Furthermore, ligand-field theory can accurately reproduce experimental spectra but lacks the predictive capabilities of a m.o. treatment. A computational framework having potential for both the predictive power of m.o. theory and the accuracy of ligand-field theory is described and applied to two series of transition-metal complexes. The advantages and disadvantages of the method are examined and improved calculation procedures are suggested.

CALCULATIONAL METHOD

First a slightly modified, CNDO, computational framework [1,2] is used to obtain an approximate ground-state wave function. For species containing unpaired electrons, a generalisation of Dewar's half-electron method [3] is employed to produce a single determinant approximation to the ground state. The consequent equivalence of the α-spin and β-spin secular equations is necessary if configuration-interaction studies are contemplated, the only alternative being a full SCF calculation for each excited state of the complex. In an octahedral environment, all the excited states arising from *d–d* transitions can be generated using only the t_{2g} and e_g molecular orbitals and hence extension of the half-electron method to d^n configurations allows rapid evaluation of excited-state properties.

It is found, however, that use of the CNDO approximations in the multielectron configuration interaction (MECI) calculation [4] yields results which are incompatible with experimental spectra in that the splittings of the free-ion terms are not well reproduced. This stems from the fact that, in the CNDO formalism, the only one-centre, two-electron, repulsion integrals considered are of the type (1)

$$\langle ii|jj\rangle = \langle ij|ij\rangle = \gamma_{\mathrm{MM}} \qquad (1)$$

where *i* and *j* are atomic orbitals centred on atom M. Inclusion of these integrals alone is clearly inadequate, and it is necessary to include additional electronic-interaction integrals in the excited-state calculation, namely those which explicitly include the metal *d* orbitals. A list of the independent non-zero two-electron integrals involving the metal *d* orbitals in terms of the traditional ligand-field parameters *A*, *B*, and *C* [5] is given in Table 1. It can be readily seen that, by using equation (1), only integrals involving the parameter *A* [types (A)—(E)] are included in the calculation and, moreover, these are not considered to be identical.

TABLE 1

Non-zero integrals between central metal *d* orbitals in terms of the Racah parameters

(A) $\langle d_{z^2}d_{z^2}|d_{z^2}d_{z^2}\rangle = \langle d_{xz}d_{xz}|d_{xz}d_{xz}\rangle = \langle d_{yz}d_{yz}|d_{yz}d_{yz}\rangle = \langle d_{x^2-y^2}d_{x^2-y^2}|d_{x^2-y^2}d_{x^2-y^2}\rangle = \langle d_{xy}d_{xy}|d_{xy}d_{xy}\rangle = A + 4B + 3C$

(B) $\langle d_{yz}d_{xz}|d_{yz}d_{xz}\rangle = \langle d_{xy}d_{xz}|d_{xy}d_{xz}\rangle = \langle d_{xy}d_{yz}|d_{xy}d_{yz}\rangle = \langle d_{x^2-y^2}d_{yz}|d_{x^2-y^2}d_{yz}\rangle = \langle d_{x^2-y^2}d_{xz}|d_{x^2-y^2}d_{xz}\rangle = A - 2B - C$

(C) $\langle d_{yz}d_{z^2}|d_{yz}d_{z^2}\rangle = \langle d_{xz}d_{z^2}|d_{xz}d_{z^2}\rangle = A + 2B - C$

(D) $\langle d_{xy}d_{z^2}|d_{xy}d_{z^2}\rangle = \langle d_{x^2-y^2}d_{z^2}|d_{x^2-y^2}d_{z^2}\rangle = A - 4B - C$

(E) $\langle d_{xy}d_{x^2-y^2}|d_{xy}d_{x^2-y^2}\rangle = A + 4B - C$

(F) $\langle d_{yz}d_{yz}|d_{xz}d_{xz}\rangle = \langle d_{xz}d_{xz}|d_{xy}d_{xy}\rangle = \langle d_{xy}d_{xy}|d_{yz}d_{yz}\rangle = \langle d_{yz}d_{yz}|d_{x^2-y^2}d_{x^2-y^2}\rangle = \langle d_{xz}d_{xz}|d_{x^2-y^2}d_{x^2-y^2}\rangle = 3B + C$

(G) $\langle d_{z^2}d_{z^2}|d_{x^2-y^2}d_{x^2-y^2}\rangle = \langle d_{xy}d_{xy}|d_{z^2}d_{z^2}\rangle = 4B + C$

(H) $\langle d_{yz}d_{yz}|d_{z^2}d_{z^2}\rangle = \langle d_{xz}d_{xz}|d_{z^2}d_{z^2}\rangle = B + C$

(I) $\langle d_{xy}d_{xy}|d_{x^2-y^2}d_{x^2-y^2}\rangle = C$

(J) $\langle d_{yz}d_{xz}|d_{xy}d_{z^2}\rangle = \langle d_{xz}d_{yz}|d_{xy}d_{z^2}\rangle = \langle d_{xz}d_{yz}|d_{z^2}d_{x^2-y^2}\rangle = (3B)^{\frac{1}{2}}$

(K) $\langle d_{xz}d_{xy}|d_{yz}d_{z^2}\rangle = \langle d_{xz}d_{z^2}|d_{xz}d_{x^2-y^2}\rangle = -2(3B)^{\frac{1}{2}}$

(L) $\langle d_{yz}d_{xz}|d_{xy}d_{x^2-y^2}\rangle = 3B$

(M) $\langle d_{xz}d_{yz}|d_{xy}d_{x^2-y^2}\rangle = -3B$

(N) $\langle d_{yz}d_{yz}|d_{z^2}d_{x^2-y^2}\rangle = -(3B)^{\frac{1}{2}}$

(O) $\langle d_{yz}d_{z^2}|d_{xy}d_{x^2-y^2}\rangle = 2(3B)^{\frac{1}{2}}$

In carrying out a MECI calculation, two-electron integrals over molecular orbitals must be evaluated. This is accomplished by expanding the molecular orbitals in LCAO and summing the atomic integrals in the usual way. We now propose the following modification to the MECI method: when these atomic integrals involve four transition-metal *d* orbitals the expressions given in Table 1 should be used, otherwise the CNDO approximation is employed. This change can be regarded as using ligand-field quantities as a perturbation to the MECI calculation. The parameters *A*, *B*, and *C* are related to γ_{MM} by expression (2)

$$A + 4B + 3C = \gamma_{\mathrm{MM}} \qquad (2)$$

The Racah parameters *B* and *C* controlling the magnitude of the two-electron repulsion integrals are, theoretically, dependent on the orbital exponents assigned to the metal *d* orbitals *in* the *ground-state* calculation. Since the exponents used are those relevant to the neutral atom,[6] it is

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[1] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S129.

[2] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc.* (*A*), 1971, 3674.

[3] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 1968, **90**, 1953.

[4] D. R. Armstrong, R. Fortune, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Faraday II*, 1972, 1893.

[5] H. Watanabe, ' Operator Methods in Ligand Field Theory,' Prentice–Hall, Englewood Cliffs, New Jersey, 1966.

[6] G. Burns, *J. Chem. Phys.*, 1964, **31**, 1521.

consistent to use the values of B and C for the metal in its zeroth oxidation state (although in ligand-field theory these would be treated as variable parameters). Alternative methods of choosing B and C are, of course, possible. For example, B and C pertaining to the metal in its formal oxidation state or related to the calculated charge on the central metal atom could be used. In the latter case, B and C would be obtained by interpolation between values for different oxidation states of the metal in question. Both of these parametrisation schemes will be discussed, but it should be emphasised here that, since B and C are never variable parameters subject to no constraints, the method is genuinely predictive.

In order to test the potential of the method outlined above, calculations have been carried out on a number of hexafluoro- and hexa-aqua-complexes of the first transition series. These species were selected because they have already been extensively studied, both experimentally and theoretically.[7-11] First the electronic structure of each complex was computed using two different values for the Wolfsberg–Helmholtz proportionality constant k.[12] This defines the magnitude of the off-diagonal terms in the core Hamiltonian matrix and is normally the only parameter of the modified CNDO method. In these preliminary calculations, the Racah parameters B and C were chosen for the metal in its zeroth oxidation state.[13] Further trials were then carried through in an attempt to provide an accurate parametrisation scheme. These two sets of calculations will be discussed after the ground-state electronic properties have been summarised.

RESULTS AND DISCUSSION

Charge Distribution.—The ground-state electron distributions of the complexes studied are summarised in Table 2. The labels (A) and (B) refer to the two values of k used, 1.0 and 1.5 respectively. The atom charges and bond indices quoted are those evaluated by the SCF procedure and do not correspond rigorously to the ground state resulting from a superimposed MECI calculation. This is because, by intermixing two-electron excitations with the ground state, the MECI process will result in a modified electron distribution (although the changes are expected to be minimal). The ground-state electronic properties of these complexes exhibit the expected trends.[10] First, it should be noted that the calculated charge on the central metal ion is always significantly less than its formal charge. This is a natural consequence of using m.o. theory and thereby introducing some covalency. The reduction of charge on the central metal ion is associated with d-orbital populations in excess of those normally assumed for a d^n configuration. Significant electron density in the higher-energy $4s$ and $4p$ metal orbitals is also evident. On crossing the Periodic Table from vanadium to nickel (for a given ligand and k value) the nett charge on the central metal ion is reduced and the metal–ligand bond index[14] increases. Also, as k is increased for a given ligand the nett charge on the metal ion decreases and a concomitant increase in bond index occurs. Therefore, by increasing k we are enhancing the degree of covalent bonding in a complex. In turn this widens the t_{2g}–e_g orbital gap and effectively simulates a higher ligand-field strength. This is reflected in the calculated excited-state energies and increasing k may be considered analogous to increasing the electrostatic field strength in ligand-field theory.[13]

TABLE 2

Valence-electron populations of the central metal ion in selected hexafluoro- and hexa-aqua-complexes of the first transition series

Complex		Nett charge on central metal ion	Atomic-orbital populations of central metal ion			Metal–ligand bond index
			s	*p*	*d*	
$[VF_6]^{2-}$	(A)	+2.34	0.34	0.52	1.82	0.48
	(B)	+1.57	0.47	0.84	2.12	0.66
$[VF_6]^{3-}$	(A)	+1.37	0.37	0.55	2.71	0.46
	(B)	+0.74	0.48	0.86	2.92	0.61
$[V(OH_2)_6]^{3+}$	(A)	+1.72	0.29	0.52	2.46	0.31
	(B)	+1.16	0.38	0.68	2.78	0.43
$[V(OH_2)_6]^{2+}$	(A)	+0.97	0.29	0.51	3.23	0.25
	(B)	+0.49	0.39	0.69	3.42	0.36
$[CrF_6]^{2-}$	(A)	+1.95	0.35	0.50	3.19	0.54
	(B)	+1.16	0.48	0.82	3.54	0.71
$[CrF_6]^{3-}$	(A)	+1.04	0.39	0.55	4.02	0.52
	(B)	+0.45	0.50	0.88	4.17	0.65
$[Cr(OH_2)_6]^{3+}$	(A)	+1.54	0.32	0.55	3.58	0.35
	(B)	+0.98	0.41	0.71	3.89	0.46
$[MnF_6]^{2-}$	(A)	+1.85	0.41	0.66	4.07	0.57
	(B)	+1.19	0.52	1.02	4.26	0.70
$[Mn(OH_2)_6]^{2+}$	(A)	+0.91	0.35	0.61	5.14	0.28
	(B)	+0.48	0.45	0.84	5.23	0.37
$[FeF_6]^{3-}$	(A)	+0.93	0.46	0.75	5.86	0.56
	(B)	+0.45	0.54	1.11	5.89	0.66
$[Fe(OH_2)_6]^{3+}$	(A)	+1.44	0.42	0.74	5.41	0.39
	(B)	+0.97	0.50	0.95	5.58	0.49
$[CoF_6]^{3-}$	(A)	+0.82	0.49	0.51	6.88	0.59
	(B)	+0.47	0.56	1.18	6.79	0.66
$[Co(OH_2)_6]^{3+}$	(A)	+1.32	0.45	0.79	6.44	0.43
	(B)	+0.88	0.52	1.02	6.58	0.52
$[Co(OH_2)_6]^{2+}$	(A)	+0.79	0.39	0.70	7.12	0.31
	(B)	+0.39	0.48	0.95	7.18	0.38
$[NiF_6]^{2-}$	(A)	+1.14	0.51	0.85	7.49	0.68
	(B)	+0.87	0.57	1.24	7.31	0.76
$[Ni(OH_2)_6]^{2+}$	(A)	+0.75	0.40	0.73	8.13	0.31
	(B)	+0.38	0.49	0.98	8.15	0.38

Excited-state Calculations.—The results from the MECI calculations are presented in Table 3, where (A) and (B) again refer to $k = 1.0$ and 1.5 respectively. Although the hexa-aqua-complexes belong to the point group T_h, the band assignments are given in terms of perfect octahedral symmetry in order to facilitate comparison with previous theoretical and experimental work on these complexes. This causes no serious problems, since state degeneracy is maintained in the descent in symmetry from O_h to T_h.

In general, the calculated spectra are in reasonable agreement with experiment. When judging these re-

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[13] J. S. Griffith, 'Theory of Transition Metal Ions,' Cambridge University Press, 1961.

[14] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1973, 838.

sults, it must be borne in mind that the Racah parameters B and C, normally adjusted to fit spectra in ligand-field theory, have not been varied. Nevertheless, the results are erroneous in specific cases and these will be discussed separately after the overall trends have been examined.

TABLE 3

Results of excited-state calculations on selected hexafluoro- and hexa-aqua-complexes

Complex	Transition energy/10^3 cm^{-1} Calc. (A)	Calc. (B)	Expt.	Band assignments
$[\mathrm{VF}_6]^{2-}$ d^1	11.00	20.59	20.25 [a]	$^2T_{2g}(D) \rightarrow {}^2E_g(D)$
$[\mathrm{VF}_6]^{3-}$ d^2	7.86	7.59	10.20 [b]	$^3T_{1g}(F) \rightarrow {}^1T_{2g}(D)$
	8.08	7.73	10.20	$^1E_g(D)$
	8.90	15.68	14.80	$^3T_{2g}(F)$
	15.38	22.54	23.25	$^3T_{1g}(P)$
	18.32	32.96		$^3A_{2g}(F)$
$[\mathrm{V(OH_2)_6}]^{3+}$ d^2	8.02	7.78		$^3T_{1g}(F) \rightarrow {}^1T_{2g}(D)$
	8.24	7.89		$^1E_g(D)$
	8.68	18.37	17.80 [c]	$^3T_{2g}(F)$
	15.54	24.44	25.60	$^3T_{1g}(P)$
	18.14	27.40		$^3A_{2g}(F)$
$[\mathrm{V(OH_2)_6}]^{2+}$ d^3	5.35	11.21	12.00 [d]	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
	8.77	16.08	18.00	$^4T_{1g}(F)$
	10.42	10.67		$^2E_g(G)$
	10.93	11.28		$^2T_{1g}(G)$
	13.93	15.85		$^2T_{2g}(G)$
	14.18	19.86		$^2A_{1g}(G)$
	15.46	25.27	26.50	$^4T_{1g}(P)$
$[\mathrm{CrF}_6]^{2-}$ d^2	8.74	8.04	11.40 [a]	$^3T_{1g}(F) \rightarrow {}^1T_{2g}(D)$
	8.99	8.31	11.40	$^1E_g(D)$
	18.07	32.00	20.20	$^3T_{2g}(F)$
	25.81	39.12	27.50	$^3T_{1g}(P)$
	36.52	64.06		$^3A_{2g}(F)$
$[\mathrm{CrF}_6]^{3-}$ d^3	15.87	19.30	14.9 [e]	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
	21.79	23.82	22.7	$^4T_{1g}(F)$
	12.25	12.11	15.7	$^2E_g(G)$
	12.90	12.69	16.4	$^2T_{1g}(G)$
	18.71	19.30	22.0	$^2T_{2g}(G)$
	25.18	32.72		$^2A_{1g}(G)$
	34.22	30.14	34.4	$^4T_{1g}(P)$
$[\mathrm{Cr(OH_2)_6}]^{3+}$ d^3	12.10	20.12	17.4 [f]	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
	17.98	23.76	24.4	$^4T_{1g}(F)$
	12.56	12.76	14.9	$^2E_g(G)$
	13.28	13.37	15.1	$^2T_{1g}(G)$
	18.25	20.13	21.0	$^2T_{2g}(G)$
	22.03	32.53		$^2A_{1g}(G)$
	28.37	48.21	37.0	$^4T_{1g}(P)$
$[\mathrm{MnF}_6]^{2-}$ d^3	18.46	20.98	21.80 [e]	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
	24.17	34.85	28.65	$^4T_{1g}(F)$
	13.28	13.02	16.26	$^2E_g(G)$
	31.81	13.49	17.30	$^2T_{1g}(G)$
	20.53	28.96	25.71	$^2T_{2g}(G)$
	28.74	30.71		$^4A_{1g}(P)$
	38.35	58.37		$^4T_{1g}(P)$
$[\mathrm{Mn(OH_2)_6}]^{2+}$ d^5	20.29	17.07	18.9 [g]	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
	21.69	20.06	23.0	$^4T_{2g}(G)$
	21.79	21.22	25.0	$^4A_{2g}(G)$
	21.89	21.37	25.0	$^4E_g(G)$
	26.42	25.19	28.0	$^4T_{2g}(D)$
	26.68	27.09	29.75	$^4E_g(D)$
$[\mathrm{FeF}_6]^{3-}$ d^5	7.46	$^2T_{2g}(I)$ [h]	14.2 [e]	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
	14.80		19.7	$^4T_{2g}(G)$
	19.52		25.4	$^4A_{2g}(G)$
	20.14		25.4	$^4E_g(G)$
	24.44		28.8	$^4T_{2g}(D)$
	25.33		30.2	$^4E_g(D)$
$[\mathrm{Fe(OH_2)_6}]^{3+}$ d^5	16.89		12.3 [i]	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
			(14.2) [j]	
	20.66		17.5	$^4T_{2g}(G)$
			(20.0) [j]	
	22.68		23.0	$^4A_{2g}(G)$
	22.91		23.0	$^4E_g(G)$
	27.11		26.5	$^4T_{2g}(D)$
	30.73			$^4E_g(D)$
$[\mathrm{CoF}_6]^{3-}$ d^6	$^1A_{1g}$	$^1A_{1g}$	11.8, 14.4 [k]	$^5T_{2g}(D) \rightarrow {}^5E_g(D)$
$[\mathrm{Co(OH_2)_6}]^{3+}$ d^6	$^5T_{2g}$	6.31	8.0 [l]	$^1A_{1g} \rightarrow {}^3T_{1g}$
		10.18		$^3T_{2g}$
		13.89	16.5	$^1T_{1g}$
		19.78	24.7	$^1T_{2g}$
$[\mathrm{Co(OH_2)_6}]^{2+}$ d^7	3.19	5.80	8.1 [l]	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	12.86	9.58	11.3	$^2E_g(G)$
	6.98	12.49	16.0	$^4A_{2g}(F)$
	14.04	16.17	19.4— 21.5	$^4T_{1g}(P)$
$[\mathrm{NiF}_6]^{2-}$ d^6	t_{1u}/t_{2g} [m]	26.09	12.9 [n]	$^1A_{1g} \rightarrow {}^3T_{1g}$
		31.11	16.0	$^3T_{2g}$
		31.74	16.0	$^1T_{1g}$
		41.12	25.3	$^1T_{2g}$
$[\mathrm{Ni(OH_2)_6}]^{2+}$ d^8	5.84	8.42	8.5 [l]	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	9.96	13.87	13.5	$^3T_{1g}(F)$
	13.96	13.93	15.4	$^1E_g(D)$
	19.98	22.73	22.0	$^1T_{2g}(D)$
	21.94	25.64	25.3	$^3T_{1g}(P)$

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In almost all of the complexes studied, the MECI procedure predicts the correct ground state. The spin-allowed transitions are, in most cases, well reproduced and the relative energies of intra- and inter-shell transitions, characterised by $\delta M_S \neq 0$ and $\delta M_S \geqslant 0$, respectively (where M_S is the state vector having boundaries $M_S = \pm S$ in the Russell–Saunders coupling scheme) illustrate a characteristic feature of the MECI process. This is best exemplified by consideration of an individual complex, *e.g.* the d^2 complex, $[\mathrm{VF}_6]^{3-}$.

The total number of configurations (N) resulting from n occupied and m unoccupied orbitals is $N = (n + m)!/n!m!$. Thus, for two electrons permuted amongst the t_{2g} and e_g, and generating spin orbitals, the dimension of the CI matrix to be diagonalised is $N \times N$, where $N = 10!/2!8! = 45$, *i.e.* there is a total of 45 possible states for a d^2 complex in an octahedral environment. However, configurations of different multiplicity do not interact (spin orthogonality) and the calculation is simplified by considering each M_S value separately and defining the spin space *via* shift operators.

M_S	α	β	$N_\alpha \cdot N_\beta$
1	$\dfrac{5!}{2!3!}$	$\dfrac{5!}{0!5!}$	10
0	$\dfrac{5!}{1!4!}$	$\dfrac{5!}{4!1!}$	25
−1	$\dfrac{5!}{0!5!}$	$\dfrac{5!}{2!3!}$	10

The size of the CI calculations clearly depends on the M_S value of the component configurations. Thus, for $[VF_6]^{3-}$ the larger CI for $M_S = 0$ means that the resulting states will be better represented than those for $M_S = \pm 1$. Consequently the singlet states are found to have lower energies with respect to the triplets than would otherwise be expected. A similar explanation also accounts for the appearance of incorrect ground states when the complexes are close to their high spin–low spin crossover points. For example, in the d^6 species $[CoF_6]^{3-}$, analysis shows that the number of singlet, triplet, and quintuplet configurations included in the CI calculation are 100, 50, and 5, respectively. There is, therefore, more freedom in the CI to improve the energies of the singlet and triplet states relative to the quintuplet.

Discrepancies may also arise through the semiempirical nature of the SCF procedure. For an octahedral d^n complex the d electrons should be distributed between the largely metal-localised t_{2g} and e_g molecular orbitals. This condition is not fulfilled for $[NiF_6]^{2-}$ with $k = 1.0$, an obvious failure of the CNDO method. Furthermore, since the value of k used in the SCF calculation effectively defines the ligand-field strength, the accuracy of the method is expected to be sensitive to this parameter. Significant changes may be induced by increasing k from 1.0 to 1.5. Thus, for the d^6 complex $[NiF_6]^{2-}$ a high-spin ground state is predicted when $k = 1.0$. When k is increased to 1.5, however, a low-spin ground state is obtained, in agreement with experiment and corresponding to a higher ligand-field strength. Clearly, the correct ligand-field strength may be readily acquired by varying k for each individual complex, and we have indeed obtained such a set of k values (see below). However, we do not conceive this to be the main purpose of the work, which should be the development of a more predictive method of calculating excited-state properties. The results quoted above encourage the belief that this is feasible. For example, using $k = 1.5$, the electronic spectra of a wide range of hexa-aqua-complexes are found to be adequately reproduced despite the severe limitations imposed on the choice of B and C. Conversely, the electronic spectra of many of the hexafluoro-complexes are less well represented, the sensitivity to k being higher. However, this may be due to the cluster approximation itself,[15] and not to any serious deficiency in the method. The choice of k value is currently being investigated for a wide range of ligand types.

Tanabe–Sugano-type Diagrams.—Since a convenient way of using ligand-field theory is through the media of Tanabe–Sugano diagrams,[16] the construction of a m.o. analogue of these is of interest. The ion $[Mn(OH_2)_6]^{2+}$ was chosen for this purpose and a series of calculations, varying k from 1.0 to 2.0, was carried out. In this way the excited-state energies, depicted in Figure 1, were obtained for a range of ligand-field strengths.

It is pertinent to note here that Tanabe–Sugano diagrams evaluated *via* a m.o. approach have been obtained previously by Clack.[17,18] The procedure entails the construction of potential-energy curves for ground and excited states and the Tanabe–Sugano diagrams are formulated from the vertical transition energies at different internuclear separations. Conversely, vertical transition energies imply fixed nuclear co-ordinates and, for the purpose of spectral analysis, attention may therefore be confined to the established ground-state geometry. By adopting a fixed geometry, the time-consuming process of calculating total energies for excited states of individual complexes at sets of internuclear distances may be by-passed. This consideration, in conjunction with the unpredictable convergence difficulties often encountered in the manipulation of excited electronic configurations, has prompted the present authors to adhere to the less laborious, albeit spectrally orientated, method described herein.

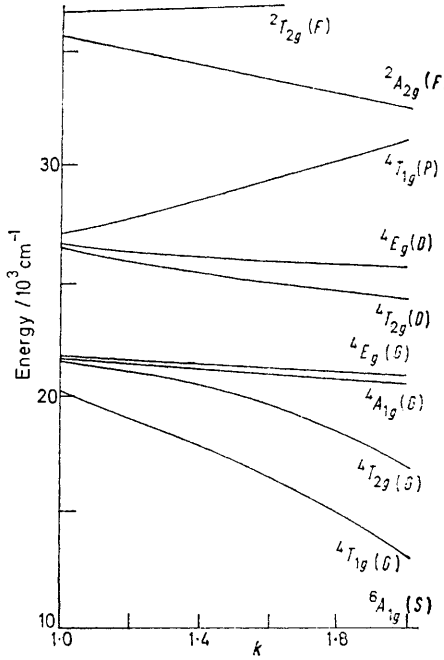

FIGURE 1 Tanabe–Sugano-type diagram for $[Mn(OH_2)_6]^{2+}$

Inspection of Figure 1, in which only the low-energy excited states directly applicable to the interpretation of the electronic spectrum are given, establishes the essential compatibility of the method with the ligand-field approach. The results agree with the experimental observation that, as the two lowest-energy transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^4T_{2g}(G)$ are most sensitive to change in ligand-field strength, their band width will be broadened to the greatest extent by a vibronic mechanism. Therefore, although the calculation of absolute intensities *via* the coupling of the multitude of electronic and vibrational wave functions remains a formidable quantum-mechanical problem, it is comparatively easy to determine which absorption bands will be most influenced by a vibronic mechanism. This may be done

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by calculating directly the effect of a vibrational perturbation on the excited states of the complex. Figure 2 shows the variation in the calculated spectrum of $[Mn(OH_2)_6]^{2+}$ as the complex is subjected to a simulated totally symmetric vibration. The transitions most affected by alteration of the Mn–O bond lengths are expected to be most broadened by a vibrational mechanism, since they are the most sensitive to small changes in the electronic environment. These calculations again show that the transitions to the two lowest-energy states are most susceptible to broadening, in agreement with experimental data.[19]

Improvements to the Method.—Although the calculations outlined above demonstrate the applicability of the method, alternative parametrisation schemes have also been investigated in an attempt to improve the overall agreement with experiment. The initial choice of *k* is clearly of paramount importance and a method of evaluating a more exact value has been applied to selected complexes of vanadium. The calculated electronic spectrum of the d^1 complex $[VF_6]^{2-}$ is independent of the Racah parameters, as the energy of the single transition ${}^2T_{2g}(D) \rightarrow {}^2E_g(D)$ is uniquely determined by the ligand-field strength. If this transition energy is reproduced by varying *k* in the SCF calculation, then the metal–ligand interactions should be correctly specified and a good approximation to the ground-state wave function should be obtained. It is then possible to transfer this *k* value to other vanadium complexes and improved transition energies may then be expected. It was found that $k = 1.483$ reproduced the experimental ${}^2T_{2g} \rightarrow {}^2E_g(D)$ transition energy exactly. This value was then used in a study of the complexes $[V(OH_2)_6]^{2+}$, $[VF_6]^{3-}$, and $[V(OH_2)_6]^{3+}$.

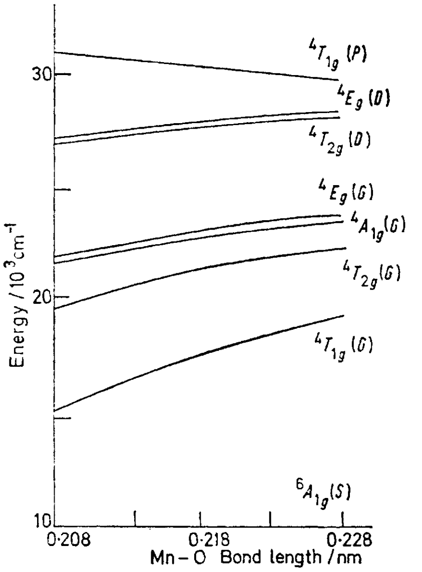

FIGURE 2 Effect of a totally symmetric vibration on the excited states of $[Mn(OH_2)_6]^{2+}$

Implementation of this procedure is only justifiable when high accuracy is required within a series of complexes and the technique has been applied in relation to the spectral properties of transition-metal-ion impurities embedded in crystals.[20] The optimum *k* values derived for complexes of the first-row transition-metal ions are given in Table 4. In addition to a more judicious choice of *k*, the different methods of determining *B* and *C*, discussed earlier, have been investigated. The values adopted were: (1), *B* and *C* for the metal in its zeroth oxidation state; (2), *B* and *C* evaluated by interpolation taking into account the calculated charge on the metal; and (3), *B* and *C* for the metal ion in its formal oxidation state. The results of these calculations are given in Table 5. These results, with $k = 1.483$, are in good agreement with experiment and the application of related methods to other series of complexes is currently being examined. However, the marginal improvement obtained by using the alternative values of *B* and *C* does not seem to us to outweigh the inherent theoretical consistency of retaining the values relevant to the metal ion in its zeroth oxidation state.

TABLE 4

Optimum Wolfsberg–Helmholtz *k* values for complexes containing first-row transition-metal ions

	k		*k*
V^{III}	1.48	Fe^{III}	1.26
V^{II}	1.56	Fe^{II}	2.25
Cr^{III}	1.27	Co^{III}	1.67
Cr^{II}	1.57	Co^{II}	1.83
Mn^{III}	1.85	Ni^{II}	1.50
Mn^{II}	1.23		

TABLE 5

Transition energies for vanadium complexes calculated using $k = 1.483$

	Method			
	(1)	(2)	(3)	Assignment
$[VF_6]^{3-}$ d^2	7.61	8.31	12.82	${}^3T_{1g}(F) \rightarrow {}^1T_{2g}(D)$
	7.75	8.48	13.09	${}^1E_g(D)$
	15.55	15.62	16.44	${}^3T_{2g}(F)$
	21.55	22.49	25.45	${}^3T_{1g}(P)$
	31.55	31.77	33.54	${}^3A_{2g}(F)$
$[V(OH_2)_6]^{3+}$ d^2	7.79	8.79	13.13	${}^3T_{1g}(F) \rightarrow {}^1T_{2g}(D)$
	7.91	8.94	13.37	${}^1E_g(D)$
	18.02	18.10	18.82	${}^3T_{2g}(F)$
	24.11	25.29	28.02	${}^3T_{1g}(P)$
	36.71	37.00	38.56	${}^3A_{2g}(F)$
$[V(OH_2)_6]^{2+}$ d^3	10.99	11.09	11.57	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
	15.85	16.15	17.43	${}^4T_{1g}(F)$
	24.89	25.35	27.57	${}^4T_{1g}(P)$

It may be concluded that the model, being physically realistic, can be successfully further parameterised, and can be applied to a variety of other types and symmetries of complexes.

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