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Calculated Spectra of Hydrated Ions of the First Transition-Metal Series

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In extending the intermediate neglect of differential overlap model to include the atoms of the second and third transition-metal series, we have reexamined the nature of the d-orbital basis set, using the spectroscopy of hexaaquo complexes for calibration. Renormalized basis sets from Clementi and Roetti of the valence "double-ζ" type are very successful for this purpose, not only reproducing the known spectra of these systems but also suggesting new assignments and reassignments. We report and discuss here the results we obtain for the hydrated ions of the first transition series, as well as the modifications in the INDO/S model required to obtain them.

Introduction

The optical spectra of hydrated transition-metal ions provides one of the earliest confirmations of crystal field theory.[1-4] The d atomic orbitals of the metal show very little mixing with the chelating oxygen atom orbitals, leading to very little forward- or back-bonding in these complexes. In addition, the charge-transfer bands from metal to water, or vice versa, and the ligand spectra are at much higher energies than the d–d spectra: thus the $t_{2g} \rightarrow e_g$ excitations in O_h, either Laporte (symmetry) forbidden or Laporte and spin forbidden, are not masked by the presence of these more intense transitions.

The intermediate neglect of differential overlap model[5] adopted for spectroscopy,[6,8] INDO/S, and extended to include the first transition-metal series[9,10] has been in use for some time for studying the spectroscopy of large complexes.[11,12] In most of these studies, inductive shifts in the ligand spectra, or charge-transfer excitations, were of principal interest. In extending this model to include the second and third transition-metal series we have found that certain changes in the model concerning the basis set representation of the d orbitals were desirable, even for the first transition-metal series, which was well treated by the original theory. We present these changes here and use for test cases the optical spectra of the hydrated ions of the transition metals. Although these spectra are often easy to deduce within the crystal field theory from relatively few empirical parameters, molecular-orbital-based theories are not usually as successful. The theory presented below, based on a self-consistent field molecular orbital calculation, followed by a modest configuration interaction (CI), does appear to accurately reproduce the known spectra of these complexes. In addition, predictions of bands as yet not observed can be made, and even some reassignments of these well-studied complexes are suggested on the basis of these calculations.

When the spectroscopy of more complicated systems is considered, for example, the spectroscopy of transition-metal porphyrins,[13-18] in which the more intense ligand and charge-transfer bands are of prime interest, it is rather essential to know the ground "state" of the central transition element. In such large complexes a simple model such as the INDO/S method described here can play a major role in understanding the nature of the excitations, but only if the transition metal itself is well enough described to sort out the lowest of many low-lying states that differ only by spin multiplicities and d–d excitations.

The INDO/S Model

We seek first the solutions of the Hartree–Fock equations of the form

$$\mathbf{F}^k\mathbf{C}^k = \Delta\mathbf{C}^k\epsilon^k \qquad (1a)$$

$$F_{\mu\nu}{}^k = T_{\mu\nu} - \sum_{\mathrm{B}} Z_{\mathrm{B}}(\chi_\mu|R_{\mathrm{B}}{}^{-1}|\chi_\nu) + \sum_{\sigma,\lambda}[P_{\sigma\lambda}(\chi_\mu\chi_\nu|\chi_\sigma\chi_\lambda) - P_{\sigma\lambda}{}^k(\chi_\mu\chi_\sigma|\chi_\nu\chi_\lambda)] \qquad (1b)$$

$$T_{\mu\nu} = (\chi_\mu|-{}^1\!/_2\nabla^2|\chi_\nu) \qquad (1c)$$

where the superscript k either designates α or β spin for the closed-shell spin-restricted case or the spin-unrestricted case[9,19] or most often designates a shell structure for an open-shell spin-restricted calculation.[20,22] $\mathbf{F}$ is the Fock or energy matrix, $\Delta_{\mu\nu} = (\chi_\mu|\chi_\nu)$, elements of the overlap matrix, and $\mathbf{P}$ is the first-order Fock–Dirac density matrix defined over the molecular orbital (MO) coefficients $\mathbf{C}^k$ as

$$P_{\mu\nu}{}^k = \sum_a^{\mathrm{MO}} N_a{}^k C_{\mu a} C_{\nu a} \qquad (1d)$$

$$P_{\mu\nu} = \sum_k^{\mathrm{shells}} P_{\mu\nu}{}^k \qquad (1e)$$

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Table I. INDO/S–CI Atomic Parameters (×1000 cm^{-1})^a

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
F^0(ss)	3.89	4.50	5.07	5.60	6.09	6.54	6.96	7.34	7.68
F^0(sd)	4.71	5.38	6.01	6.60	7.16	7.68	8.16	8.61	9.01
F^0(dd)	7.02	7.98	8.91	9.81	10.68	11.52	12.32	13.10	13.84
F^2(pp)	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0
F^2(pd)	11.0	13.7	11.2	11.4	8.0	5.0	6.3	6.0	10.7
F^2(dd)	29.5	44.9	50.8	63.5	66.0	61.0	64.5	79.8	86.0
F^4(dd)	14.6	29.7	35.4	36.8	37.9	38.4	48.1	53.3	58.0
G^1(sp)	12.1	13.1	15.1	14.4	18.9	16.3	22.7	19.4	20.7
G^2(sd)	5.87	6.20	6.24	5.22	6.11	6.64	6.34	6.70	4.46
G^3(pd)	2.21	10.30	1.71	0.30	4.97	3.52	2.26	3.25	6.93
G^1(pd)	5.65	7.32	5.18	5.58	1.24	2.45	3.17	3.01	5.62

^{a}From ref 9 and 10.

With $N_a^k = 0$ or 1, the occupancy of the ath MO in the kth shell, ϕ_a^k, is given by

$$\phi_a^k = \chi C_a^k \qquad (2)$$

Within the INDO approximation, basis orbitals χ are envisioned to be strongly orthogonal

$$\chi^+\chi = \Delta = 1 \quad \text{(integration implied)} \qquad (3a)$$

and

$$\begin{aligned}(\chi_\mu{}^A\chi_\nu{}^B|\chi_\sigma{}^C\chi_\lambda{}^D) &\equiv \delta_{AB}\delta_{CD}\int d\tau(1)\, d\tau(2)\, \chi_\mu{}^A(1) \times \\ &\qquad \chi_\nu{}^B(1)\, r_{12}{}^{-1}\, \chi_\sigma{}^C(2)\, \chi_\lambda{}^D(2) \\ &= (\chi_\alpha{}^A\chi_\beta{}^A|\chi_\sigma{}^A\chi_\lambda{}^A) \quad A = C \\ &= (\bar\chi_\alpha{}^A\bar\chi_\alpha{}^A|\bar\chi_\sigma{}^C\bar\chi_\sigma{}^C) = \gamma_{\alpha\sigma} \quad A \neq C \qquad (3b)\end{aligned}$$

where $\chi_\mu{}^A$ is the atomic orbital χ_μ centered on atom "A", and δ_{AB} is the Kronicker delta. In order to maintain rotational invariance, two-center integrals (A ≠ C) are evaluated over atomic orbitals $\bar\chi_\mu{}^A$ that are s symmetric but have the same exponents and expansion coefficients as $\chi_\mu{}^A$. Equation 3b also suggests that all one-center integrals are maintained in this theory. Although not essential for the SCF, we have found that the subsequent accuracy of calculated spectra from the CI computation requires these terms.[10]

Under the INDO model

$$\begin{aligned}F_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A} Z_B(\chi_\mu|R_B{}^{-1}|\chi_\mu) + \\ \sum_\sigma P_{\sigma\sigma}\gamma_{\mu\sigma} - P_{\mu\mu}{}^k\gamma_{\mu\mu} + \Delta G_{\mu\mu}{}^{AA} \quad \mu\epsilon A \qquad (4a)\end{aligned}$$

$$F_{\mu\nu}{}^k = \beta_{\mu\nu} - P_{\mu\nu}{}^k\gamma_{\mu\nu} + \Delta G_{\mu\nu}{}^{AB} \qquad \mu \neq \nu \qquad (4b)$$

$$U_{\mu\mu} = (\chi_\mu|-\tfrac{1}{2}\nabla^2 - Z_A/R_A|\chi_\mu) + V_{\mu\mu} \qquad (4c)$$

$$\beta_{\mu\nu}{}^{AB} = \bar S_{\mu\nu}(\beta_\mu{}^A + \beta_\mu{}^B)/2 \qquad (4d)$$

$$\begin{aligned}\Delta G_{\mu\nu}{}^{AB} = \{\sum_{\sigma,\lambda}^{A}[P_{\sigma\lambda}(\mu\nu|\sigma\lambda) - P_{\sigma\lambda}{}^k(\mu\sigma|\nu\lambda)] + \\ P_{\mu\nu}{}^k\gamma_{\mu\nu} - \sum_\sigma^A P_{\sigma\sigma}\gamma_{\mu\sigma}\delta_{\mu\nu}\}\delta_{AB} \qquad (4e)\end{aligned}$$

The details of the implementation of these equations are given in ref 9 and 10. The only pure empirical parameter introduced to correct for the neglect of integrals are the resonance integrals $\beta_\mu{}^A$ of eq 4d. For this, each atom has at most two parameters, $\beta_s{}^A = \beta_p{}^A \neq \beta_d{}^A$, and these values are set to reproduce experimental spectra. $\bar S_{\mu\nu}$ is related to the overlap matrix $\Delta_{\mu\nu}$[6,7]

$$\bar S_{\mu\nu} = \sum f_{l,m} g_{l,m} \Delta_{\mu(m)\nu(m)} \qquad (4f)$$

in which $f_{l,m}$ are the Eulerian transformation matrices required to rotate the orbitals from the localized coordinate system to the molecular system, $g_{l,m}$ are empirical factors to better order the σ and π type orbitals,[6,7] and $\Delta_{\mu(m)\nu(m)}$ are the σ or π or δ components of the overlap integrals in the local system, where appropriate. This degree of freedom is only used at present for p-type orbitals; $g_{1,\sigma} = 1.267$ and $g_{1,\pi} = 0.585$, viz.

$$\bar S_{pp'} = 1.267 f_{1\sigma}\Delta_{\sigma\sigma'} + 0.585 f_{1\pi}\Delta_{\pi\pi'}$$

with all other $g_{l,m} = 1$. This modification is essential for the correct positioning of the π MO's relative to those of σ symmetry.

The SCF calculation is followed by a configuration interaction calculation. A Rumer diagram or valence bond technique is used to generate the CI matrix.[24-27] For most of these studies on hydrated transition-metal ions, an open-shell SCF[23] calculation is performed, followed by a CI that contains all single excitation from the SCF reference plus all possible excitations within the transition-metal d-orbital manifold. Without this CI the spectra of these complexes cannot be reliably predicted.

Specification of Parameters

The core integrals $U_{\mu\mu}$ are taken from experimental atomic spectroscopy[28,29] and thus incorporate the effects of the one-center core effective potential $V_{\mu\mu}$.[28-30] The two-center–two-electron integrals are taken from the modified Mataga–Nishimoto formula[31,32]

$$\gamma_{\bar\mu\bar\nu} = 1.2(R_{AB} + 2.4/(F^0(\mu\mu) + F^0(\nu\nu)))^{-1} \qquad (5a)$$

in which $F^0(\mu\mu)$ are the Slater–Condon one-center–two-electron integrals[33] chosen from the Pariser approximation[28]

$$F^0(\mu\mu) = I_\mu - A_\mu \qquad (5b)$$

These values for the first transition series were given in ref 10 and the values of all the other Slater–Condon factors needed for this theory given in ref 9. They are presented in Table I for completeness and are unchanged.

In the spectroscopic version of the INDO theory discussed here, specification of the basis set only affects the evaluation of the resonance integral β. In the nonspectroscopic version[5,9] the basis set is also used to calculate the two-electron integrals $F^0(\mu\mu)$ and $\gamma_{\bar\mu\bar\nu}{}^{AB}$ that are here estimated from experiment. Slater-type orbitals have been traditionally used for this purpose, and we, as well as others, have found that a minimum basis set is satisfactory for the INDO description of hydrogen and atoms of the first and second row of the periodic table. For the first transition series, Sc–Cu, a single STO ("single ζ") also proved successful for the 4s and 4p orbitals, but not for the 3d. For this a multiple expansion ("double ζ" or better) is required to better describe the true shape of the atomic 3d function.[35] A trick, however, was discovered

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Table II. Basis Set Exponents and Coefficients

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
				Single ζ				
2.02000	2.49700	2.73800	2.96600	3.19500	3.38290	3.58030	3.77650	3.97210
1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
				Double ζ				
4.22244	4.67000	5.05186	5.13843	5.76739	6.06828	6.38612	6.70551	6.79466
0.35922	0.36461	0.37378	0.40714	0.38984	0.40379	0.41333	0.42120	0.44729
1.74647	1.98614	2.17279	2.07723	2.50969	2.61836	2.74495	2.87381	2.76527
0.76601	0.75561	0.74564	0.73242	0.72965	0.71984	0.71262	0.70658	0.69683

Table III. Resonance Integrals for the First Transition-Metal Series (eV)

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$\beta_p = \beta_s$	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0
β_d	-18.0	-18.0	-18.0	-18.0	-18.0	-23.0	-39.0	-45.0	-62.0

to keep these calculations simple. A single ζ was chosen as a function of internuclear separation between the 3d orbital of interest and the other orbital of the integral, in this case only the overlap. It was found that such a single ζ reproduced all the integrals of this theory when compared with those obtained by using the accurate Watson–near-Hartree–Fock multiple-ζ functions[36] from $R = 0$ to $R = 5$ Å, beyond which all integrals are either small (the overlap) or are dominated by R^{-1} (two-electron Coulomb integrals in the nonspectroscopic versions of INDO). In our recent studies of elements of the second and third transition-metal series, a simplification with equal accuracy was not found. The Coulomb integrals (essentially R^{-1}) were easily matched, but the $(s^A|d_\sigma{}^B)$ $(p_\sigma{}^A|d_\sigma{}^B)$ and $(p_\pi{}^A|s_\pi{}^B)$ overlap could not be reproduced with the same single Slater exponent ζ. As a result we have adopted a contracted double-ζ basis for all d orbitals, including those of the first transition-metal series. These are presented in Table II and are those of Clementi and Roetti.[37] Since the overlap $\bar{S}_{\mu\nu}$ of eq 4d has changed, new β values are required, and they have been chosen from these studies and from a study on ferrocene. These new β values are given in Table III.

For completeness Table II also contains the "single-ζ" exponents used in the nonspectroscopic version of this program to calculate $F^0(\mu\mu)$ and $\gamma_{\mu\nu}$. These single-ζ_d values are chosen to reproduce exactly the value obtained for F^0(dd) with use of the Watson basis. Two-center Coulomb integrals at normal bonding lengths are not very sensitive to this choice. The 3d orbitals are compact, and $\gamma_{\mu\nu}{}^{AB} \approx R_{AB}{}^{-1}$ for $R_{AB} \geqslant 1.5$ Å.

With this choice of parameters, the spectroscopy of the states generated within the 3d4s4p manifold of transition-metal atoms and their monopositive ions are well reproduced, a task very difficult to achieve by ab initio methods.[38-40]

Results

The hexaaquo and hexahydrated ions of the transition series represent the nearly classical crystal field. The covalent mixing between ligand and metal is very small. Electrostatic considerations should dominate the ligand field splittings and transitions. Unlike the hexahalides or -cyanides, these complexes are all positive, facilitating the calculation and interpretation. In keeping with the assumption of the crystal field approach, we find that the calculated spectra of these complexes are very insensitive to a wide choice of $\beta_\mu{}^A$ parameters (eq 4d). Only the distance between the metal and the chelating oxygen atom has a marked effect on the calculated spectra.

A. $V^{II}(H_2O)_6{}^{2+}[d^3]$. The ground state is $^4A_{1g}$, corresponding to one electron in each of the three t_{2g} orbitals. The calculated spectrum appears in Table IV, where it is compared with the observed spectrum compiled by Jørgensen[2] and that of Holmes and McClure.[4] The vanadium(II) ion is a strong reducing agent, and there seems to be some question of the existence of the band observed at 13000 cm^{-1}. The assignments of the observed bands, including the uncertain observation at 13100 cm^{-1}, are in agreement with those of the calculations. If these experimental assignments are correct, then our model is able to reproduce the spectrum of both multiplicities from a single configuration interaction calculation with use of the $^4A_{1g}$ state as the reference.

Table IV. Calculated and Observed Spectra of $V^{II}(H_2O)_6{}^{2+}[d^3]$ (R(V–O) = 2.15 Å; ×1000 cm^{-1})

	calcd	obsd *b*	obsd *c*
$^4A_{1g}(t_xt_yt_z)^a$	0.0	0.0	0.0
$^4T_{2g}(t_xt_ye)$	12.4	12.4	11.8
$^4T_{1g}(t_xt_ye)$	17.5	18.5	17.5
$^4T_{1g}(te_xe_y)$	28.3	27.9	
$^2E_g(t_xt_yt_z)$	13.6	13.1	
$^2T_{1g}(t_xt_y{}^2)$	13.2	13.1?	
$^2T_{2g}(t_xt_y{}^2)$	18.6	...	
$^2T_{2g}(t_xt_ye)$	23.2	...	
$^2T_{1g}(t_xt_ye)$	24.4	...	

[a] t_x, t_y, and t_z are simply convenient labels for the three different t_{2g} molecular orbitals. [b] Reference 2. [c] Reference 4.

Table V. Calculated and Observed Spectra of $Cr^{III}(H_2O)_6{}^{3+}[d^3]$ (R = 2.15 Å; ×1000 cm^{-1})

	calcd	obsd *a*	obsd *b*
$^4A_{1g}(t_xt_yt_z)$	0.0	0.0	0.0
$^4T_{2g}(t_xt_ye)$	18.1	17.4	17.6
$^4T_{1g}(t_xt_ye)$	24.7	24.6	24.7
$^4T_{1g}(te_xe_y)$	40.7	37.8	
$^2E_g(t_xt_yt_z)$	15.8	15.0	
$^2T_{1g}(t_xt_y{}^2)$	15.5	15.0	
$^2T_{2g}(t_xt_y{}^2)$	21.8	21.0	
$^2T_{2g}(t_xt_ye)$	29.8	...	
$^2T_{1g}(t_xt_ye)$	31.6	...	

[a] Reference 2. [b] Reference 4.

B. $Cr^{III}(H_2O)_6{}^{3+}[d^3]$. This system is isoelectronic with $V^{II}(H_2O)_6{}^{2+}$. Both the quartet and doublet spectra are in remarkably good accord with experiment (Table V). The $^4T_{1g}(te_xe_y)$ band has been experimentally observed as high as 39100 cm^{-1}.[2] The ^2E_g and $^2T_{1g}$ states are reported with uncertainty at 15000 cm^{-1}. On the basis of the more intense lines observed in $Cr(urea)_6{}^{3+}$ a maximum splitting of 650 cm^{-1} might be expected for these two transitions, to be compared with our calculated difference of 300 cm^{-1}. The $^2T_{2g}$ and $^2T_{1g}$ states have not been observed, but these transitions are both g → g and spin forbidden.

C. $Mn^{II}(H_2O)_6{}^{2+}[d^5]$. The ground state is $^6A_{1g}$. All d–d excitations are spin as well as g → g forbidden. The calculated quartet spectrum is in very good accord with that observed (Table VI). The largest deviation of 2700 cm^{-1} is found for the nearly

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Table VI. Calculated and Observed Spectra of $Mn(H_2O)_6^{2+}[d^5]$ (R(Mn–O) = 2.15 Å; ×1000 cm^{-1})

	calcd	obsd	
		a	*b*
$^{6}A_{1g}(t_xt_yt_ze_xe_y)$	0.0	0.0	0.0
$^{4}T_{1g}(t_xt_yt_z{}^2e)$	18.6	18.9	18.9
$^{4}T_{2g}(t_xt_yt_z{}^2e)$	21.9	23.1	23.0
$^{4}A_{1g}(t_xt_yt_ze_xe_y)$	22.4	24.95	25.0
$^{4}E_{g}(t_xt_yt_ze_xe_y)$	22.6	25.3	
$^{4}T_{2g}(t_x{}^2t_ye_xe_y)$	27.9	28.0	28.0
$^{4}E_{g}(t_xt_yt_ze_xe_y)$	28.5	29.75	29.75
$^{4}T_{1g}(t_x{}^2t_ye_xe_y)$	31.3	32.95	32.4
$^{2}T_{1g}(t_xt_yt_z{}^2e)$	29.1	...	
$^{2}T_{1g}(t_xt_yt_z{}^2e)$	31.0	...	
$^{2}A_{1g}(t_xt_yt_ze_xe_y)$	32.3	...	

[a] Reference 2. [b] Reference 4.

Table VII. Calculated and Observed Spectra of $Fe^{III}(H_2O)_6^{3+}[d^5]$ (*R* = 2.15 Å; ×1000 cm^{-1})

	calcd	obsd[a]
$^{6}A_{1g}(t_xt_yt_ze_xe_y)$	0.0	0.0
$^{4}T_{1g}(t_xt_yt_z{}^2e)$	13.2	12.6
$^{4}T_{2g}(t_xt_yt_z{}^2e)$	17.2	18.5
$^{4}A_{1g}(t_xt_yt_ze_xe_y)$	19.6	24.3
$^{4}E_{g}(t_xt_yt_ze_xe_y)$	19.8	24.6
$^{4}T_{2g}(t_x{}^2t_ye_xe_y)$	24.3	
$^{4}E_{g}(t_xt_yt_ze_xe_y)$	25.0	
$^{4}T_{1g}(t_x{}^2t_ye_xe_y)$	30.1	
$^{4}A_{1g}(t_xt_yt_ze_x{}^2)$	30.7	
$^{2}T_{1g}(t_xt_yt_z{}^2e)$	20.8	
$^{2}T_{1g}(t_xt_yt_z{}^2e)$	23.8	
$^{2}A_{1g}(t_xt_yt_ze_xe_y)$	28.3	
$^{2}T_{2g}(t_xt_yt_z{}^2e)$	28.4	

[a] Reference 2.

Table VIII. Calculated and Observed Spectra of $Co^{III}(H_2O)_6^{3+}[d^6]$ (*R*(Co–O) = 1.95 Å; ×1000 cm^{-1})

	calcd	obsd[a]	calcd[b]
$^{1}A_{1g}(t^6)$	0.0	0.0	0.0
$^{1}T_{1g}(t^5e)$	16.7	16.6	18.9
$^{1}T_{2g}(t^5e)$	24.9	24.9	28.1
$^{1}T_{1g}(t^4e^2)$	52.9		
$^{1}A_{1g}(t^4e^2)$	53.8		
$^{1}E_{g}(t^4e^2)$	53.9		
$^{1}T_{2g}(t^4e^2)$	54.6		
$^{3}T_{1g}(t^5e)$	10.7		
$^{3}T_{2g}(t^5e)$	15.0		

[a] Reference 2. [b] Reference 41.

Table IX. Calculated and Observed Spectra of $Ni^{II}(H_2O)_6^{2+}[d^8]$ (*R* = 2.05 Å; ×1000 cm^{-1})

	calcd	obsd	
		z	*b*
$^{3}A_{1g}(t^6e_xe_y)$	0.0	0.0	0.0
$^{3}T_{2g}(t^5e^3)$	8.5	8.5	8.6
$^{3}T_{1g}(t^5e^3–t^4e^4)$	14.1	13.5	14.7
$^{3}T_{1g}(t^5e^3–t^4e^4)$	25.3	25.3	25.5
$^{1}E_{g}(t^6e_xe_y)$	12.8	(15.4)	...
$^{1}T_{2g}(t^5e^3)$	13.3	(22.0)	...
$^{1}A_{1g}(t^6e^2)$	21.3		
$^{1}T_{1g}(t^5e^3)$	26.5		

[a] Reference 2. [b] Reference 4.

degenerate $^4A_{1g}$ and ^4E_g states calculated at 22 400 and 22 600 cm^{-1}, respectively. None of the doublet lines are reported for comparison.

D. $Fe^{III}(H_2O)_6^{3+}[d^5]$. The first two transitions in this complex are well reproduced. Those observed at 24 300 and 25 000 cm^{-1} have been previously assigned to $^4A_{1g}$ and ^4E_g, respectively, as indicated in Table VII. On the basis of the calculated values it is tempting to assign these transitions to states of $^4T_{2g}$ and ^4E_g symmetry as indicated in the table. However, it must be recalled that in the better resolved isoelectronic $Mn^{II}(H_2O)_6^{2+}$ spectra transitions to $^4A_{1g}$ and ^4E_g were calculated 2700 cm^{-1} too low. The error in this case, however, for this $^4A_{1g}$ and ^4E_g assignment to hold would be nearly 5000 cm^{-1}, much larger than our typical error.

E. $Co^{III}(H_2O)_6^{3+}[d^6]$. The ground state of this complex is $^1A_{1g}$, corresponding to double occupancy of the three t_{2g} orbitals. The observed spectrum is that of the singlets generated by $t_{2g} \rightarrow e_g$. the $t_{2g}{}^2 \rightarrow e_g{}^2$ transitions are predicted to lie much higher in energy. Two low-lying triplet states are predicted at 10 700 and 15 000 cm^{-1}, as summarized in Table VIII.

For comparison, results from an INDO-type calculation by Kai, Arakawa, and Nishimoto[41] are also presented in Table VIII. These calculations, also performed at a Co–O bond length of 1.95 Å, are in reasonable accord with our results for the two states that they report.

F. $Ni^{II}(H_2O)_6^{2+}[d^8]$. The ground state for this d^8 octahedral system is $^3A_{1g}$. The band in the infrared region has been assigned to a state of $^3T_{2g}$ symmetry, in accord with these calculations (Table IX). The two states of $^3T_{1g}$ symmetry calculated at 14 100 and 25 300 cm^{-1} are unusual in that they are heavy mixtures of t^5e^3 and t^4e^4 configurations. Even so, they are in excellent agreement with the observed values, lending credence to this description.

A band observed at 15 400 cm^{-1} has been assigned to a state of ^1E_g symmetry while that observed at 22 000 cm^{-1} has been assigned to $^1T_{2g}$. As suggested in Table IX, it may be that the ^1E_g and $^1T_{2g}$ states are both associated with the observed feature at 15 400 cm^{-1}, while that observed at 22 000 cm^{-1} is associated with the calculated $^1A_{1g}$ state at 21 000 cm^{-1}. We note, however, that the states of the Ni atom are especially difficult to calculate correctly.[39,40]

Solomon and Ballhausen have done a careful study of the spectroscopy of $Ni(H_2O)_6^{2+}$ structures.[42] From an examination of the spin–orbit effects they deduce the ^1E_g state to be nearly degenerate with the $^3T_{1g}$ state observed with a maximum at about 13 500 cm^{-1}. They present a concise argument that the ^1E_g state before this interaction should lie 1500–2000 cm^{-1} *above* the $^3T_{2g}$ state at the geometry of the $^3A_{1g}$ ground state. The relative positions of these states, however, are sensitive functions of the ground-state geometry as suggested in their work and from preliminary calculations on this question.

Conclusions

We have redesigned the d atomic orbital basis set within the INDO spectroscopic model in such a fashion that the second and third transition series may also be included in a systematic fashion. We have then checked this new basis for the results obtained against previous calculations that mostly focused on ligand to metal and metal to ligand charge-transfer excitations and found these new results equally successful in reproducing observed spectra. In this work we check this new basis for its ability to be used in calculations to predict and explain the classical d-d spectra of hexahydrated ions of the first transition series. The results that we obtain are sensitive to the d-orbital size, which are fixed in our case from model ab initio calculations, and the distance between central atom and chelating group. The calculated results are remarkably insensitive to the only pure parameter, the "resonance" parameter β, of the theory. This is mostly a consequence of the small overlap between metal d and ligand orbitals and the resulting small amount of covalency shown in the 3d orbital of this study.

The spectra that we report in the tables is at the geometry that gave the best fit with the observed spectrum of that complex. This geometry was searched with an oxygen to metal "mesh" of dis-

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(43) As an example, calculations on the $Fe^{III}(H_2O)_6^{3+}$ complex took 12 min on the VAX 11/780.

tances differing by 0.05 Å. No attempt at fine-tuning this distance was attempted. The resulting bond lengths are reasonable, but there is a paucity of accurate bond length information on these systems to compare. It may be that all of these "predicted" bond lengths are too long.

Nevertheless, the results we have obtained using this model for the complexes of this study, and the results we have obtained on transition-metal halide and ethylenediamine complexes not reported here, are of very good accuracy. We feel these results are of sufficient accuracy to give the model disclosed here important utility for explaining and predicting the d–d spectra of transition-metal complexes in an efficient and inexpensive manner.[32]

As the bands of interest in this study are primarily d–d*, a configuration interaction including all single excitations generated from the SCF reference state plus all possible excitations within the d-orbital manifold as described seems most appropriate. A more economical CI limited to only single excitations reliably reproduces only the lower energy bands of these complexes, and the relative positions of the spin manifolds to each other are somewhat poorer. Single excited configuration interaction is required as the lowest level of acceptable theory in order to sort out properly the degeneracies of systems with high symmetry. For these particular complexes there is also a substantial mixing of configurations with different electron assignments, and this proves particularly important in the d^8 complexes, where there is t^5e^3–t^4e^4 mixing as noted for $Ni(H_2O)_6^{2+}$. A CI limited to only single excitations would be of great utility in examining larger systems, and especially systems in which charge-transfer and ligand spectra are of prime interest, for most of the computing time is spent in the configuration interaction calculation. Such a treatment will be of utility only if the ground spin state of the central transition-metal ion is known in advance or if the single excitations alone are able to reliably yield the lowest energy metal ion configuration. Unfortunately, the latter is not always the case,[13-15,17] and we cannot recommend this procedure as a blind procedure, even within this model Hamiltonian.

The procedure that we do describe here, though, seems dependable, and we have been able to successfully calculate the spectroscopy of larger complexes such as the porphyrins, where d–d*, charge transfer, and ligand–(ligand)* transitions are all of interest.

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Registry No. $V^{II}(H_2O)_6$, 15696-18-1; $Cr^{III}(H_2O)_6$, 14873-01-9; $Mn^{III}(H_2O)_6$, 15365-82-9; $Fe^{II}(H_2O)_6$, 15365-81-8; $Co^{III}(H_2O)_6$, 15275-05-5; $Ni^{II}(H_2O)_6$, 15365-79-4.

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Circular Dichroism of Chromium(III) Complexes. 11. Chiroptical Evidence for Solution Structure of a Sexidentate Chelate Coordination Mode in Chromium(III) Complexes with edta and Related Ligands

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The chiroptical spectra, specifically, circular dichroism, of the chiral edta (ethylenediaminetetraacetato)-like complexes of (*S*)-1,2-propylenediaminetetraacetate ((*S*)-pdta) and (*1S,2S*)-1,2-*trans*-cyclohexanediaminetetraacetate ((*S,S*)-cydta) with chromium(III) and magnetic circular dichroism of the corresponding racemates were measured in solutions of various acid concentrations and/or solid states as compared with those of the edtra (ethylenediaminetriacetato)-like complexes. It has been found that the chiroptical spectral variation in acid solution reflects a significant change of coordination mode in solution structures: a change from sexi- to quinquedentate edta coordination. This chiroptical behavior has substantiated the controversial solution structure of sexidentate edta coordination in the complexes more decisively than the recent ^2H NMR studies.

Introduction

Recently, there have been some significant developments in studies of the controversial sexi- or quinquedentate coordination of edta in $[Cr(edta)]^-$[1-5] (where edta refers to ethylenediaminetetraacetate): the X-ray crystal structure analyses for the hydrogen and sodium forms[6,7] and the ^2H NMR studies for deuterated edta and the closely related amino polycarboxylato complexes in solution.[8] Though these studies suggested possibilities of sexidentate edta coordination in solution, there has still remained some doubt of a pentagonal-bipyramidal structure with a sexidentate edta or a rapid exchange of the ligating atom (H_2O and acetate of the edta).[5b,8] There has been no direct spectroscopic information to prove the sexidentate octahedral coordination in solution so far.

Chiroptical spectroscopy in solution and/or the solid state will afford another kind of evidence for a sexi- or quinquedentate edta in a chromium(III) complex, since such spectra are expected to be more sensitive to the edta chelate coordination mode or to the change of the ligating atoms than are the ^2H NMR spectra.

This paper deals with the solution structure of edta-like complexes in comparison with solution and solid chiroptical spectra and in terms of spectral changes with acid concentration. As the chiroptical spectra, circular dichroism (CD) and magnetic circular dichroism (MCD) are utilized for chiral edta analogues such as

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