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I. THEORETICAL; SPECTROSCOPIC

MOLECULAR ORBITAL THEORY FOR TETRAHEDRAL METAL COMPLEXES

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I would like to express my sincere appreciation to the members of the staff of the Universita di Padova, particularly to Professor Aldo Turco, for inviting me to this conference. For an inorganic chemistry meeting, I cannot imagine a better place than Bressanone.

This paper presents an interpretation of the electronic spectra of certain important metal oxyanions and tetroxides, including MnO_4^- and CrO_4^{2-}. Several calculations and interpretations of the MnO_4^- spectrum have been presented[1-7]. The calculations of MnO_4^-, MnO_4^{2-}, MnO_4^{3-}, and CrO_4^{2-} which are set out in Table I are by the so-called SCCC–MO method which is outlined in detail elsewhere[8,9]. These calculations are probably better than our previous efforts[7], due to slightly improved estimates of the coulomb integrals for Mn and Cr.

The important levels in order of increasing energy are labelled $3t_2$ (slightly bonding), t_1 (nonbonding oxygen level), $2e$ (antibonding), and $4t_2$ (antibonding). The ground state electronic structure of MnO_4^- is $(3t_2)^6(t_1)^6 = {}^1A_1$. The electronic spectrum[7] of MnO_4^- shows two major band systems, with maxima at 18,300 ($f = 0.032$) and 32,200 cm^{-1} ($f = 0.070$), and, in addition, a shoulder indicating a fairly intense maximum at 44,000 cm^{-1} ($\varepsilon \approx 1500$). At first glance, there are at least two reasonable assignments for this spectrum. The first scheme assumes that the separation of $4t_2$ and $2e$, which is defined as Δ_t, is approximately 15,000 cm^{-1}, and further that $3t_2$ and t_1 are either very close together or very widely separated. This scheme leads to the following assignments[2]:

18,300 cm^{-1}	$t_1 \rightarrow 2e$
32,200 cm^{-1}	$t_1 \rightarrow 4t_2$

That is, the spacing of the first two bands is closely related to the Δ_t value in MnO_4^-.

The second assignment scheme is suggested by the results in Table I. Here the Δ_t in MnO_4^- is considerably larger than 15,000 cm^{-1}, and the spacing of the first (18,300 cm^{-1}) and third (44,000 cm^{-1}) bands is related to Δ_t. In this pattern the second band (32,200 cm^{-1}) is due to the $3t_2 \rightarrow 2e$ transition. Summarizing, we have:

18,300 cm^{-1}	$t_1 \rightarrow 2e$
32,200 cm^{-1}	$3t_2 \rightarrow 2e$
44,000 cm^{-1}	$t_1 \rightarrow 4t_2$

We believe the interpretation of the MnO_4^- spectrum that suggests the larger value of Δ_t is much closer to the truth than the assignment that gives a Δ_t less than 15,000 cm^{-1}, for the following reasons:

1. The Δ_t values of MnO_4^{2-} and MnO_4^{3-}; the lowest electronic band[7] in MnO_4^{2-} is at 16,500 cm^{-1}. The only reasonable assignment for this band is $2e \rightarrow 4t_2$, since ligand-to-metal charge transfer should be higher energy in MnO_4^{2-} (electron to Mn^{VI}) than in MnO_4^- (electron to Mn^{VII}). This means that Δ_t cannot be smaller than 16,500 cm^{-1} in MnO_4^{2-}, and, allowing for 2,500 cm^{-1} configuration interaction, $\Delta_t(MnO_4^{2-})$ is probably about 19,000 cm^{-1}. Furthermore, the measured Δ_t for MnO_4^{3-} is 11,000 cm^{-1}, from the position of the ${}^3A_2 \rightarrow {}^3T_2$ band[10]. The assignment scheme that fits this pattern is definitely the one that gives a $\Delta_t(MnO_4^-)$ of *ca.* 26,000 cm^{-1}. Thus we have:

$\Delta_t(MnO_4^{3-}) = 11,000\ cm^{-1}$
$\Delta_t(MnO_4^{2-}) \approx 19,000\ cm^{-1}$
$\Delta_t(MnO_4^{-}) \approx 26,000\ cm^{-1}$

2. The spectrum of CrO_4^{2-}; the first two bands in CrO_4^{2-} are located[7] at 26,810 and 36,630 cm^{-1}. The estimate of $\Delta_t(CrO_4^{2-}) \approx 10,000\ cm^{-1}$ that would be obtained from the $t_1 \rightarrow 2e$, $t_1 \rightarrow 4t_2$ scheme is too small, because $\Delta_t(CrO_4^{3-})$ is known[7] to be not lower than 16,000 cm^{-1}; surely then, $\Delta_t(CrO_4^{2-})$ must be larger than 16,000 cm^{-1}; also, considering the fact[11] that $\Delta_t(VCl_4)$ is *ca.* 9,000 cm^{-1}, a reasonable extrapolation from V^{IV} to Cr^{VI} and from Cl^- to O^{2-} gives $\Delta_t(CrO_4^{2-})$ of *at least* 20,000 cm^{-1}, thus the only reasonable assignment for the two bands in CrO_4^{2-} is $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$. The splitting is related to the interaction of the oxygen levels, not the ligand field splitting of $4t_2$ and $2e$.

3. The spectrum of TcO_4^-; the first two bands in TcO_4^- are located at 34,900 and 40,700 cm^{-1}, a separation[7] of 5,700 cm^{-1}. We expect $\Delta_t(TcO_4^-)$ to be considerably larger than $\Delta_t(MnO_4^-)$. Therefore the consistent assignment of the first two bands in MnO_4^- and TcO_4^- is $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$.

In summary, the experimental evidence is definitely consistent with the assignment scheme suggested for MnO_4^- by the results of the molecular orbital calculation presented in Table I.

For discussion here, the energy of the first charge transfer band and the separation of the first two bands in d^0 complexes are given in Table II. Notice that the separation of the bands assigned $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$ does indeed correlate with the expected oxygen–oxygen distance, since the splitting is much larger in the first-row complexes than in the second- and third-row complexes. It is important to note that there are no inconsistencies in the results in Table II. For

TABLE I

RESULTS OF SCCC CALCULATIONS OF VARIOUS TETRAHEDRAL COMPLEXES
(all energies in 1000 cm^{-1})

SCCC results[a]	*Complexes*			
	MnO_4^-	*MnO_4^{2-}*	*MnO_4^{3-}*	*CrO_4^{2-}*
bond distance, Å	1.59[b]	1.63[c]	1.67[c]	1.60[d]
VOIP (ligand p_σ)	−260.8	−260.8	−260.8	−260.8
VOIP (ligand p_π)	−101.7	−101.7	−101.7	−101.7
3d VOIP	−121.3	−115.4	−109.3	−110.0
4s VOIP	−93.4	−90.1	−86.7	−88.2
4p VOIP	−58.4	−56.0	−53.4	−56.0
metal charge	+0.66	+0.63	+0.60	+0.66
3d population	5.82	5.91	6.00	4.885
4s population	0.18	0.17	0.16	0.13
4p population	0.34	0.29	0.24	0.32
$3t_2$ eigenvalue	−105.7	−105.5	−105.3	−105.0
t_1 eigenvalue	−96.4	−97.1	−97.6	−96.6
2e eigenvalue	−73.0	−74.5	−75.4	−64.5
$4t_2$ eigenvalue	−49.3	−52.9	−55.8	−40.3
2e occupation	0	1	2	0
$4t_2$ occupation	0	0	0	0
calculated Δ	23.7	21.6	19.6	24.1
observed Δ	26.0[e]	19.0[e]	11.0[e]	—
first allowed L → M charge transfer:				
calculated orbital energy	23.4	22.6	22.2	32.1
observed band	18.3[e]	22.9[e]	30.8[e]	26.8[e]

[a] SCCC means self-consistent charge and configuration; see ref. 8 and ref. 9.
[b] From ref. 12. [c] Estimated value. [d] From ref. 13. [e] From ref. 7.

TABLE II

COMPARISON OF THE CHARGE-TRANSFER BANDS IN TETRAHEDRAL OXYANIONS AND TETROXIDES*

Complex	*Metal oxidation number*	*First charge transfer (cm^{-1})*
First-row metal ions		
VO_4^{3-}	V	36,900
MnO_4^{3-}	V	30,800
CrO_4^{3-}	V	28,200
CrO_4^{2-}	VI	26,810 (9,820)**
MnO_4^{2-}	VI	22,940
MnO_4^-	VII	18,320 (13,890)
Second-row metal ions		
MoO_4^{2-}	VI	44,500
TcO_4^-	VII	34,900 (5,800)
RuO_4^-	VII	31,700
RuO_4	VIII	26,000 (6,200)
Third-row metal ions		
WO_4^{2-}	VI	50,300
ReO_4^-	VII	44,000 (5,000)
OsO_4	VIII	33,500 (8,000)

* Taken from ref. 7.
** The separation of the first two bands in the d^0 complexes is given in parentheses.

example, for first-row complexes, the energy of the $t_1 \rightarrow 2e$ transition increases in the order metal(VII) < metal(VI) < metal(V). It is also a general result that the $t_1 \rightarrow 2e$ transition increases in energy proceeding from first-row to third-row in an analogous series of complexes, *e.g.*:

$$ReO_4^- > TcO_4^- > MnO_4^-$$

Since the antibonding character of 2e gets *larger* in the order $MnO_4^- < TcO_4^- < ReO_4^-$, we have evidence that the covalent bonding between oxygen valence orbitals and the metal *d* valence orbitals increases in the order $3d < 4d < 5d$.

TABLE III

THE VALUE OF THE ORBITAL PARAMETER Δ_t IN TETRAHEDRAL METAL OXYANIONS*

Complex	$\Delta_t (cm^{-1})$
CrO_4^{3-}	16,000
CrO_4^{2-}	(24,000)
MnO_4^{3-}	11,000
MnO_4^{2-}	(19,000)**
MnO_4^-	26,000
FeO_4^{2-}	12,700
RuO_4^{2-}	21,600
RuO_4^-	(28,500)[b]

* Taken from ref. 7.

** Corrected for an estimated configuration interaction of 2500 cm^{-1}.

We present in Table III for discussion the Δ_t values of various MO_4^- complexes. There are some very obvious trends in the Δ_t values. For example, comparing complexes of metals in the same oxidation state, the Δ_t's decrease in the order Cr > Mn > Fe. Extrapolating from CrO_4^{3-}, $\Delta_t(CrO_4^{2-})$ is probably about 24,000 cm^{-1}, $\Delta_t(MnO_4^{2-})$ is about 19,000 cm^{-1} and $\Delta_t(FeO_4^{2-})$ is only 12,700 cm^{-1}; also, $\Delta_t(CrO_4^{3-})$ is larger than $\Delta_t(MnO_4^{3-})$. This decrease in the splitting of the antibonding MO's derived from the *d* valence orbitals as one proceeds to *higher Z* in first-row complexes is also found in octahedral halide complexes[8].

In the one case where splittings in *3d* and *4d* levels *are known* in an analogous series of MO_4^{n-} complexes, we obtain the expected result $\Delta_t(4d) > \Delta_t(3d)$. The two complexes are FeO_4^{2-} and RuO_4^{2-}, having Δ_t values of 12,700 and 21,600 cm^{-1}, respectively.

The established experimental Δ_t's for MnO_4^-, MnO_4^{2-}, and MnO_4^{3-} are very important, because they allow a more complete evaluation of the approximation of the H_{ij} elements in the secular equation. It is clear from Table I that the large observed variation of Δ_t with metal oxidation number (VII = 26,000, VI = 19,000, V = 11,000) is not obtained in the calculation, which uses a constant *F* factor of 2.00. Indeed, it appears that the *F* factor must be decreased as the metal oxidation number decreases in order to obtain splittings in close agreement with experiment.

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REFERENCES

1 M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 20 (1952) 837.
2 C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, 2 (1958) 342; 4 (1960) 190.
3 (a) D. S. Schonland, *Proc. Roy. Soc. (London)*, A254 (1960) 111; (b) A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Shonland and M. C. R. Symons, *ibid.*, A254 (1960) 101.
4 R. F. Fenske and C. C. Sweeney, *Inorg. Chem.*, 3 (1964) 1105.
5 A. Carrington and C. K. Jørgensen, *Mol. Phys.*, 4 (1961) 395.
6 C. J. Ballhausen, *Theoret. Chim. Acta (Berlin)*, 1 (1963) 285.
7 A. Viste and H. B. Gray, *Inorg. Chem.* 3 (1964) 1113.
8 H. Basch, A. Viste and H. B. Gray, *J. Chem. Phys.*, 44 (1966) 9.
9 C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, Benjamin, New York, 1964, Appendix 8-II.
10 L. E. Orgel, *Mol. Phys.*, 7 (1964) 397.
11 L. E. Orgel, *J. Chem. Phys.*, 23 (1955) 1004.
12 *Chem. Soc. (London), Spec. Publ. No. 11* (1958), Tables of interatomic Distances and configurations in Molecules and Ions.
13 H. W. Smith and M. Y. Colby, *Z. Krist.*, 103 (1940) 90.