come of the calculations. This is strikingly illustrated by the effects of the hybrid angle parameter, θ, on the ordering of the energy levels. It is further demonstrated by the sensitivity of the levels to the choices of F_σ and F_π.

For the ions considered, the hybridization criterion proposed by Ballhausen and Gray,[9] *viz.*, $\mathrm{VSIP}(\theta)/S(\theta)$ be a minimum, could not be applied successfully without adjustment of the F parameters. Even with this adjustment, if one were to make a choice between the W and H and B and L assignments strictly on the basis of correlation of transition energies and intensities with the observed spectra, the W and H ordering of the levels would be preferred. But the fact remains that the W and H assignment is incompatible with the e.s.r. results on manganate and hypomanganate.

Since a "reasonable" correlation of theoretical transition energies with experimental spectra could be obtained by either assignment, it is apparent that one must use caution in rationalizing any discrepancies that might appear. For example, the calculated results in accord with the B and L ordering tend to affirm the Carrington and Schonland[4] transition assignment. However, not only does this require one to ignore the $e^* \rightarrow t_2(3)$ transition in MnO_4^{-2} and MnO_4^{-3}, but the calculated transition intensities for such an assignment do not agree with the experimental values.

It seems that additional investigations, both theoretical and experimental, are required before approval of the method for general application is given.

Appendix

Valence State Ionization Potentials (VSIP).—The method used to evaluate the VSIP's in this work can be illustrated by considering the VSIP of a 4s electron from a neutral manganese atom. For simplicity, it was assumed that in the valence state, the seven electrons occupy σ-bonding orbitals.[25] Thus the valence state consisted of the configurations $(a_1^2t_2^5)$ and $(a_1^1t_2^6)$ weighted according to the statistical probability of their occurrence. In accord with the principles outlined by Moffitt,[26] those electrons in a configuration which shared a molecular orbital with a ligand electron were assigned arbitrary spins. For example, the a_1 electron in $(a_1^1t_2^6)$ could have either α or β spin.

The VSIP for the 4s electron is the energy necessary to remove an a_1 electron from this valence state. The valence state of the plus one ion consists of those configurations which arise as a result of the removal of the electron; in this case, the (t_2^6) and $(a_1^1t_2^5)$ configurations, properly weighted.

The promotional energy for the neutral atom, P^0, is the energy necessary to go from the ground state, $3d^54s^2 = {}^6S$, to the valence state. Similarly P^+ is the promotional energy for the ion from Mn^+ ($3d^54s^1 = {}^7S$) to its valence state. P^0 and P^+ are calculated by means of the electrostatic interaction integrals tabulated by Skinner and Sumner.[27] Additional electrostatic interaction terms have been obtained from the atomic energy levels.[28] Ionization potentials, I.P., have been obtained from the same source. The VSIP's can be calculated from the relationship

$$\mathrm{VSIP} = \mathrm{I.P.} + P^+ - P^0$$

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[25] While it possibly would have been more correct to assume occupancy of both σ- and π-orbitals, the differences in VSIP's are probably small since the valence state of the plus one ion would have been similarly adjusted and the two would tend to cancel one another.

[26] W. Moffitt, *Rept. Progr. Phys.*, **17**, 173 (1954).

[27] H. A. Skinner and F. H. Sumner, *J. Inorg. Nucl. Chem.*, **4**, 245 (1957).

[28] C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Vol. II.

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The Electronic Structure of Permanganate Ion

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The results of calculations of the molecular orbitals of MnO_4^- and other transition metal oxyanions are reported. The calculation of MnO_4^- indicates that the lowest unoccupied orbital is of e symmetry, as suggested by Ballhausen and Liehr. The bulk of the experimental evidence is shown to suggest the assignment of the first and second main bands in MnO_4^- to the one-electron transitions $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$, respectively. The value of Δ in MnO_4^- is estimated to be 26,000 cm.$^{-1}$.

Introduction

Twelve years ago Wolfsberg and Helmholz reported the results of semiempirical molecular orbital calculations on MnO_4^- and CrO_4^{2-}.[2] In their level scheme, the lowest unoccupied orbital is of t_2 symmetry and the next higher one is an e orbital. This result was somewhat surprising, since on the basis of simple crystal-field theory considerations, the lowest unoccupied level in a tetrahedral d^0 ion ought to be e, and the next higher one t_2—the reverse of Wolfsberg and Helmholz's results.

Subsequently, Ballhausen and Liehr proposed an MO scheme with t_2 higher than e and justified this

[1] National Science Foundation Postdoctoral Fellow, 1963–1964.

[2] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

Table I

Basis Functions

Irreducible representation	Row	Metal orbitals	Ligand orbitals
A_1	1	s	$^1/_2(s_1 + s_2 + s_3 + s_4)$, $^1/_2(p_{z_1} + p_{z_2} + p_{z_3} + p_{z_4})$
E	1	d_{z^2}	$^1/_2(p_{x_1} - p_{x_2} - p_{x_3} + p_{x_4})$
	2	$d_{x^2-y^2}$	$^1/_2(p_{y_1} - p_{y_2} - p_{y_3} + p_{y_4})$
T_2	1	p_x, d_{yz}	$^1/_2(p_{z_1} - p_{z_2} + p_{z_3} - p_{z_4})$, $^1/_2(s_1 - s_2 + s_3 - s_4)$, $^1/_4[p_{x_1} + p_{x_2} - p_{x_3} - p_{x_4} + \sqrt{3}(-p_{y_1} - p_{y_2} + p_{y_3} + p_{y_4})]$
	2	p_y, d_{xz}	$^1/_2(p_{z_1} + p_{z_2} - p_{z_3} - p_{z_4})$, $^1/_2(s_1 + s_2 - s_3 - s_4)$, $^1/_4[p_{x_1} - p_{x_2} +$
	2		$p_{x_3} - p_{x_4} + \sqrt{3}(p_{y_1} - p_{y_2} + p_{y_3} - p_{y_4})]$
	3	p_z, d_{xy}	$^1/_2(p_{z_1} - p_{z_2} - p_{z_3} + p_{z_4})$, $^1/_2(s_1 - s_2 - s_3 + s_4)$, $-^1/_2(p_{x_1} + p_{x_2} + p_{x_3} + p_{x_4})$
T_1	1	. . .	$^1/_4[\sqrt{3}(p_{x_1} + p_{x_2} - p_{x_3} - p_{x_4}) + p_{y_1} + p_{y_2} - p_{y_3} - p_{y_4}]$
	2	. . .	$^1/_4[\sqrt{3}(p_{x_1} - p_{x_2} + p_{x_3} - p_{x_4}) - p_{y_1} + p_{y_2} - p_{y_3} + p_{y_4}]$
	3	. . .	$^1/_2(p_{y_1} + p_{y_2} + p_{y_3} + p_{y_4})$

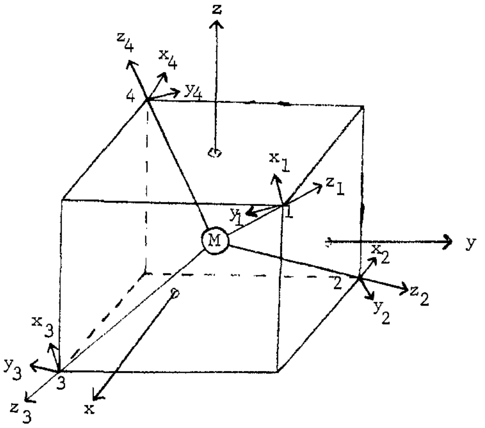

Fig. 1.—Coordinate system and numbering used in the molecular orbital calculation.

ordering by making appropriate intensity calculations.[3] Consistent with the Ballhausen–Liehr proposal of t_2 over e, Schonland, Carrington, *et al.*, concluded from e.s.r. measurements that the unpaired electron in the d^1 MnO_4^{2-} ion is in an e level.[4]

For a number of reasons, we have made a study of the electronic structure of MnO_4^-. First, the single-electron MO ordering is not settled to everyone's satisfaction. In fact, Fenske and Sweeney recently found that they could not obtain the Liehr–Ballhausen order of levels without substantially altering the so-called F factor used in estimating the H_{ij} elements in the secular equation and concluded that either the semiempirical MO method is not reliable with $F = 2.00$, or else the e.s.r. measurements were incorrectly interpreted.[5] Second, even conceding that the $t_2 > e$ issue is settled, the complete assignment of the MnO_4^- spectrum must be made. There are at least two quite different assignments possible with $t_2 > e$, depending on whether Δ is approximately 14,000[6] or approximately 26,000 cm.$^{-1}$. Finally, it is probable that the radial functions available now for Mn[7] and O,[8] and the methods of estimating the H_{ii} and H_{ij} integrals,[8] are somewhat better than the ones used in the original calculation.[2]

In this paper we present the results of extensive calculations of the one-electron MO energies in MnO_4^- and related oxyanions. It is our purpose to try to establish the most consistent assignment of the complete electronic spectrum of MnO_4^-, and, in the process, to obtain the most reasonable estimates of Δ for MnO_4^- and related oxyanions.

The Molecular Orbital Description of Permanganate Ion.—The coordinate system and numbering used are shown in Fig. 1. The atomic orbitals included in the calculation are manganese 3d, 4s, and 4p and oxygen 2s and 2p. Symmetry basis orbitals transforming according to definite rows of representations are given in Table I. The ligand–ligand overlap corrections to the normalizations are given in the Appendix. No initial hybridization of any of the atomic orbitals is assumed.

For manganese[7] and oxygen,[8] the radial functions were taken from recent publications. The analytical expressions for all of the group overlap integrals G_{ij} between properly normalized basis functions are given in Table II. The numerical values of the G_{ij} for MnO_4^- are given in Table III.

The diagonal elements H_{ii} of the secular equation are approximated as the negative of the VSIE's (valence state ionization energies) for the respective basis orbitals, corrected for ligand–ligand overlap. H_{ii} and H'_{ii} represent a diagonal element corrected and uncorrected, respectively, for ligand–ligand overlap. Details of this and other parts of the calculation are presented in the Appendix. The off-diagonal elements H_{ij} are approximated as $H_{ij} = -2.00G_{ij}(H'_{ii}H'_{jj})^{1/2}$. The factor 2.00 is used in this relationship *without change* throughout the calculation, just as in the vanadyl ion calculation. Ligand–ligand overlap is included, both in the normalization of the basis orbitals and in the calculation of G_{ij} and H_{ii}.

The secular equations were of order $3(a_1)$, $2(e)$, and $5(t_2)$. The t_1 basis orbital, a π combination, is nonbonding. The secular equations were solved for eigenvalues and eigenvectors using the IBM 7094 Fortran program written by P. T. Manoharan of this laboratory. A Mulliken population analysis[9] was carried out

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[3] C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry,*. **2**, 342 (1958); **4**, 190 (1960).

[4] (a) D. S. Schonland, *Proc. Roy. Soc.* (London), **A254**, 111 (1960); (b) A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland, and M. C. R. Symons, *ibid.*, **A254**, 101 (1960).

[5] R. F. Fenske and C. C. Sweeney, *Inorg. Chem.*, **3**, 1105 (1964).

[6] A. Carrington and C. K. Jørgensen, *Mol. Phys.*, **4**, 395 (1961).

[7] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); *ibid.*, **38**, 796 (1963).

[8] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

[9] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

TABLE II

GROUP OVERLAP INTEGRALS

A_1	$G_{A_1}(s,\sigma_s)$	=	$\dfrac{2S(s_M,s_L)}{[1 + 3S(s_L,s_L)]^{1/2}}$
	$G_{A_1}(s,\sigma_p)$	=	$\dfrac{-2S(s_M,p_{\sigma L})}{[1 + 2S(p_{\sigma L},p_{\sigma L}) + S(p_{\pi L},p_{\pi L})]^{1/2}}$
	$G_{A_1}(\sigma_s,\sigma_p)$	=	$\dfrac{-\sqrt{6}S(s_L,p_{\sigma L})}{[1 + 3S(s_L,s_L)]^{1/2}[1 + 2S(p_{\sigma L},p_{\sigma L}) + S(p_{\pi L},p_{\pi L})]^{1/2}}$
E	$G_E(d,\pi)$	=	$\dfrac{2\sqrt{6}S(d_{\pi M},p_{\pi L})}{3[1 + {}^1/_2S(p_{\sigma L},p_{\sigma L}) - {}^1/_2S(p_{\pi L},p_{\pi L})]^{1/2}}$
T_2	$G_{T_2}(p,\sigma_p)$	=	$\dfrac{-2\sqrt{3}S(p_{\sigma M},p_{\sigma L})}{3[1 - {}^2/_3S(p_{\sigma L},p_{\sigma L}) - {}^1/_3S(p_{\pi L},p_{\pi L})]^{1/2}}$
	$G_{T_2}(p,d)$	=	0
	$G_{T_2}(p,\sigma_s)$	=	$\dfrac{2\sqrt{3}S(p_{\sigma M},s_L)}{3[1 - S(s_L,s_L)]^{1/2}}$
	$G_{T_2}(p,\pi)$	=	$\dfrac{-2\sqrt{6}S(p_{\pi M},p_{\pi L})}{3[1 + {}^1/_6S(p_{\sigma L},p_{\sigma L}) + {}^{11}/_6S(p_{\pi L},p_{\pi L})]^{1/2}}$
	$G_{T_2}(d,\sigma_p)$	=	$\dfrac{-2\sqrt{3}S(d_{\sigma M},p_{\sigma L})}{3[1 - {}^2/_3S(p_{\sigma L},p_{\sigma L}) - {}^1/_3S(p_{\pi L},p_{\pi L})]^{1/2}}$
	$G_{T_2}(\sigma_p,\sigma_s)$	=	$\dfrac{\sqrt{6}S(p_{\sigma L},s_L)}{3[1 - {}^2/_3S(p_{\sigma L},p_{\sigma L}) - {}^1/_3S(p_{\pi L},p_{\pi L})]^{1/2}[1 - S(s_L,s_L)]^{1/2}}$
	$G_{T_2}(\sigma_p,\pi)$	=	$\dfrac{2\sqrt{2}[S(p_{\sigma L},p_{\sigma L}) - S(p_{\pi L},p_{\pi L})]}{3[1 - {}^2/_3S(p_{\sigma L},p_{\sigma L}) - {}^1/_3S(p_{\pi L},p_{\pi L})]^{1/2}[1 + {}^1/_6S(p_{\sigma L},p_{\sigma L}) + {}^{11}/_6S(p_{\pi L},p_{\pi L})]^{1/2}}$
	$G_{T_2}(d,\sigma_s)$	=	$\dfrac{2\sqrt{3}S(d_{\sigma M},s_L)}{3[1 - S(s_L,s_L)]^{1/2}}$
	$G_{T_2}(d,\pi)$	=	$\dfrac{2\sqrt{2}S(d_{\pi M},p_{\pi L})}{3[1 + {}^1/_6S(p_{\sigma L},p_{\sigma L}) + {}^{11}/_6S(p_{\pi L},p_{\pi L})]^{1/2}}$
	$G_{T_2}(\sigma_s,\pi)$	=	$\dfrac{-2\sqrt{3}S(s_L,p_{\sigma L})}{3[1 - S(s_L,s_L)]^{1/2}[1 + {}^1/_6S(p_{\sigma L},p_{\sigma L}) + {}^{11}/_6S(p_{\pi L},p_{\pi L})]^{1/2}}$

TABLE III

GROUP OVERLAP INTEGRALS

E	$G_E(d,\pi)$ =	0.262	T_2	$G_{T_2}(p,\sigma_p)$ =	0.108
A_1	$G_{A_1}(s,\sigma_s)$ =	0.677		$G_{T_2}(p,d)$ =	0.000
	$G_{A_1}(s,\sigma_p)$ =	−0.229		$G_{T_2}(p,\sigma_s)$ =	0.353
	$G_{A_1}(\sigma_s,\sigma_p)$ =	−0.091		$G_{T_2}(p,\pi)$ =	−0.258
				$G_{T_2}(\sigma_p,d)$ =	−0.167
				$G_{T_2}(\sigma_p,\sigma_s)$ =	0.035
				$G_{T_2}(\sigma_p,\pi)$ =	0.052
				$G_{T_2}(d,\sigma_s)$ =	0.246
				$G_{T_2}(d,\pi)$ =	0.151
				$G_{T_2}(\sigma_s,\pi)$ =	−0.047

for each of the eigenvectors. Successive cycles were carried out until the computed configuration and charge (output) agreed with the assumed charge and configuration (input) within reasonable limits. At this point, the solution was considered self-consistent.

Two calculations were carried out for MnO_4^-, differing in their treatment of the oxygen VSIE's.

(1) **Isolated Atom Method.**—In this calculation, the VSIE's for oxygen 2s and 2p are evaluated as a function of charge and configuration on the basis of Moore's data[10] for the isolated oxygen atom or ion, very similar to the treatment of the manganese VSIE's. Self-consistency is then required for both manganese and oxygen in the final solution.

(2) **Hydride Ionization Potential (I.P.) Method.**—In this calculation, it is recognized that since the oxygen is adjacent to a positive center (manganese), the oxygen VSIE's will decrease much less rapidly with increasing negative charge on the oxygen than would be the case in an isolated oxygen atom. The effect is clearly shown in a simple analogous case involving iodine. The ionization potentials of I and I^- are 10.4 and 3.3 e.v., respectively. The ionization potential of KI (giving KI^+) is 8.3 ± 0.2 e.v.,[11] even though KI is believed to be almost completely ionic (K^+I^-) and even though the electron is presumably removed from an essentially nonbonding p orbital on the iodine. Since the oxygen VSIE's are thus expected to vary much less rapidly with the oxygen charge than the free atom data would indicate, the 2p VSIE is, for simplicity, assigned an appropriate fixed value: the ionization potential of H_2O, 12.61 e.v.[12]; the 2s VSIE is also assigned a fixed value, as described in the Appendix.

Both methods gave the same order of MO levels. The energy levels computed by the two methods are presented in Table IV.

For purposes of comparison, very rough calculations were done for MnO_4^{2-} and CrO_4^{2-}, using the following simplifying assumptions: group overlap integrals were taken to be numerically equal to those for MnO_4^-, and for CrO_4^{2-} the VSIE for a Cr orbital for a given charge, s, and p character was taken to be numerically equal to the corresponding VSIE for Mn, for the same charge, s,

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[10] C. E. Moore, "Atomic Energy Levels," NBS Circular 467, 1949 and 1952.

[11] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p. 295.

[12] Reference 11, p. 280.

Table IV

Calculated Orbital Energies for MnO_4^-

MO	Isolated atom method energy, 10^3 cm.$^{-1}$	Hydride I.P. method energy, 10^3 cm.$^{-1}$
$3a_1$	+122	+136
$5t_2$	−13	−15
$4t_2$	−41	−47.2
2e	−62	−72.7
t_1	−81	−95.3
$3t_2$	−90	−105.9
$2a_1$	−96	−113
$2t_2$	−109	−126
1e	−118	−136
$1t_2$	−223	−238
$1a_1$	−236	−252
Mn input charge	+0.41	+0.53
input configuration	$d^{6.03}s^{0.20}p^{0.36}$	$d^{5.87}s^{0.23}p^{0.37}$
output charge	+0.40	+0.60
output configuration	$d^{6.06}s^{0.18}p^{0.36}$	$d^{5.81}s^{0.22}p^{0.37}$
Oxygen assumed charge	−0.35	. . .
assumed configuration	$s^{1.90}p^{4.45}$	. . .
output charge	−0.35	−0.40
output configuration	$s^{1.90}p^{4.45}$	$s^{1.87}p^{4.53}$

Table V

Calculated Orbital Energies for Pseudo-MnO_4^{2-} and Pseudo-CrO_4^{2-}

	Pseudo-MnO_4^{2-}		Pseudo-CrO_4^{2-}	
MO	Isolated atom method energy, 10^3 cm.$^{-1}$	Hydride I.P. method energy, 10^3 cm.$^{-1}$	Isolated atom method energy, 10^3 cm.$^{-1}$	Hydride I.P. method energy, 10^3 cm.$^{-1}$
$3a_1$	+99	+130	+94	+127
$5t_2$	−10	−15	−10	−14
$4t_2$	−30	−45.9	−30	−45.1
2e	−46	−70.9	−46	−69.8
t_1	−59	−95.3	−60	−95.3
$3t_2$	−66	−105.7	−67	−105.5
$2a_1$	−70	−113	−72	−113
$2t_2$	−81	−122	−79	−120
1e	−88	−131	−85	−128
$1t_2$	−198	−237	−198	−236
$1a_1$	−209	−251	−210	−250
Metal input charge	+0.20	+0.50	+0.18	+0.47
input configuration	$d^{6.35}s^{1.15}p^{0.30}$	$d^{6.00}s^{0.20}p^{0.30}$	$d^{5.47}s^{0.10}p^{0.25}$	$d^{5.04}s^{0.20}p^{0.29}$
output charge	+0.07	+0.76	+0.21	+0.51
output configuration	$d^{6.50}s^{1.01}p^{0.32}$	$d^{5.76}s^{0.18}p^{0.31}$	$d^{5.46}s^{0.07}p^{0.25}$	$d^{5.06}s^{0.16}p^{0.27}$
Oxygen input charge	−0.55	. . .	−0.54	. . .
input configuration	$s^{1.96}p^{4.59}$	. . .	$s^{1.97}p^{4.57}$	. . .
output charge	−0.52	−0.69	−0.55	−0.63
output configuration	$s^{1.96}p^{4.56}$	$s^{1.89}p^{4.80}$	$s^{1.98}p^{4.57}$	$s^{1.90}p^{4.72}$

and p character. Because of the simplifying assumptions, we refer to the species calculated as pseudo-CrO_4^{2-} and pseudo-MnO_4^{2-}. The resulting energy levels are given in Table V. In each case the order of levels is the same as in MnO_4^-.

The MnO_4^- and CrO_4^{2-} complexes have 32 valence electrons, and hence the levels are filled through t_1. The MnO_4^{2-} complex has 33, and the odd electron is thus put in 2e. The ground state of MnO_4^- and CrO_4^{2-} is $^1A_1$; the ground state of MnO_4^{2-} is ^2E.

The results of the isolated atom method have been presented mainly for purposes of comparison. We consider the results of the hydride I.P. method more reliable for the following reasons.

(1) The VSIE's of oxygen are not expected to fall off as rapidly with increasing negative charge as the isolated atom method assumes, since the oxygen in an oxyanion is adjacent to a positive metal center. In the analogous case of KI, the effect of the positive center K^+ is very marked, as shown previously.

(2) The hydride I.P. method worked satisfactorily for Bedon, Horner, and Tyree in the case of TiF_6^{3-}.[13] Also in the case of vanadyl ion, fixed values for the VSIE's of the vanadyl oxygen were used with satisfactory results (the appropriate VSIE's of a neutral oxygen atom were taken).[8]

(3) The first two observed charge-transfer bands in CrO_4^{2-} occur at 26,800 and 36,600 cm.$^{-1}$.[14] The first two allowed bands are predicted at 15,000 and 22,000 cm.$^{-1}$ by the isolated atom method, at much lower energy than experiment. The results of the hydride ionization potential method, on the other hand, predict the first two charge-transfer bands at 26,000 and 36,000 cm.$^{-1}$. Even though the pseudo-CrO_4^{2-} calculation is admittedly quite simplified, the inadequacy of the isolated atom method for CrO_4^{2-} seems rather clear-cut.

For these reasons, only the results of the hydride I.P. method will be considered in detail.

The MO level diagram for MnO_4^- is shown graphically in Fig. 2, using the results of the hydride I.P. method. The eigenvectors and population analysis for MnO_4^- (hydride I.P. method) are presented in Tables VI and VII.

Discussion

Order of Levels.—By including the 2s valence orbital of oxygen and using $H_{ij} = -2.00G_{ij}(H_{ii}H_{jj})^{1/2}$ for all H_{ij}, it has been possible to obtain the Ballhausen–Liehr order of t_2 over e ($4t_2$ above 2e)[3] for MnO_4^-, in

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[13] H. Bedon, S. Horner, and S. Y. Tyree, *Inorg. Chem.*, **3**, 647 (1964).

[14] For example, see A. Carrington and M. C. R. Symons, *Chem. Rev.*, **63**, 443 (1963).

TABLE VI

EIGENVECTORS FOR MnO_4^- (HYDRIDE I. P. METHOD)

MO	d	s	p	σ_s	σ_p	π
$3a_1$		1.39		−1.02	0.25	
$5t_2$	0.22		1.10	−0.44	−0.09	0.29
$4t_2$	0.80		−0.12	−0.34	0.67	−0.58
2e	−0.73					0.90
t_1						1.00
$3t_2$	0.16		0.01	−0.08	−0.71	−0.64
$2a_1$		−0.01		0.14	1.00	
$2t_2$	0.62		−0.17	−0.18	−0.32	0.52
1e	0.73					0.52
$1t_2$	−0.20		0.02	−0.94	−0.02	0.03
$1a_1$		0.14		0.90	−0.02	

TABLE VII

POPULATION ANALYSIS FOR MnO_4^- (HYDRIDE I.P. METHOD)

MO	d	s	p	σ_s	σ_p	π
$3a_1$		0.89		0.10	0.01	
$5t_2$	0.04		0.94	0.01	0.00	0.02
$4t_2$	0.42		0.00	0.04	0.32	0.22
2e	0.37					0.63
t_1						1.00
$3t_2$	0.03		0.00	0.00	0.55	0.42
$2a_1$		0.00		0.01	0.99	
$2t_2$	0.44		0.07	0.02	0.13	0.34
1e	0.63					0.37
$1t_2$	0.08		−0.00	0.92	0.00	0.00
$1a_1$		0.11		0.89	0.00	

agreement with the e.s.r. measurements[4] on MnO_4^{2-}.[15] It is essential to include the oxygen 2s orbital because the t_2 σ_s symmetry orbital has substantial overlap with the metal d and p t_2 orbitals. Thus the oxygen 2s is an important valence orbital in a tetrahedral oxyanion, and any calculation based mainly on the 2p valence orbitals of oxygen must be considered as incomplete. From Table III, we see that the σ_s overlaps are *larger* than the σ_p overlaps with the metal orbitals. The oxygen 2s orbital has not been included as a distinct level in previously published calculations.[2,5]

To show the importance of including the 2s valence orbital, we carried out a calculation by the hydride I.P. method using only the oxygen 2p orbitals. Not unexpectedly, this calculation gives the Wolfsberg–Helmholz e > t_2 ordering, with e and t_2 calculated at −69,900 and −76,600 cm.$^{-1}$, respectively.[16]

It is apparent that in applying the semiempirical MO method to a metal complex, a complete set of valence orbitals for the ligand must be included. The valence orbitals for second-row, one-atom ligands are 2s and 2p; for more complicated molecular ligands, appropriate molecular orbitals must be utilized.

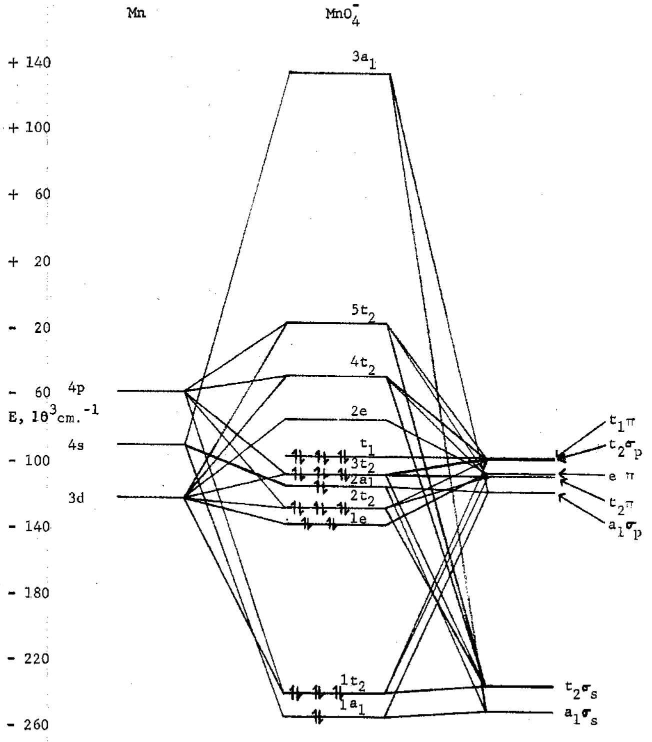

Fig. 2.—Molecular orbital energy levels for MnO_4^-.

Electronic Spectrum of MnO_4^-.—The electronic spectrum of MnO_4^- has been reported by several investigators.[14,17] There are three main absorption bands below 50,000 cm.$^{-1}$, at 18,300, 32,200, and a shoulder indicating a maximum at 44,000 cm.$^{-1}$. In addition, there are weaker absorptions at approximately 14,000 and 28,000 cm.$^{-1}$. The three main absorptions are probably due to allowed transitions, and the weak absorptions are probably either spin-forbidden or orbitally-forbidden.

With the ordering of levels shown in Fig. 2, the first allowed band must be assigned as $^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 2e$), in agreement with Ballhausen and Liehr.[3] The calculated one-electron energy of this transition is 22,600 cm.$^{-1}$. Since the transition is from a filled level to an empty level, the total interelectronic-repulsion energy in the excited state is probably less than in the ground state. Thus the calculation is in good agreement with the $t_1 \rightarrow 2e$ assignment for the 18,300 cm.$^{-1}$ band.

Returning to Fig. 2, the second band can be assigned as either $^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 2e$) or $^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 4t_2$). The calculation presented above definitely indicates the $^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 2e$) assignment, since 33,200 cm.$^{-1}$ is the predicted difference in energy of the 2e and $3t_2$ molecular orbitals. This leaves the third band, observed at 44,000 cm.$^{-1}$, to be assigned as the $^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 4t_2$) transition. The calculated one-electron energy of this transition is 48,100 cm.$^{-1}$, in good agreement with experiment.

The weak absorptions at 14,000 and 28,000 cm.$^{-1}$ are

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[15] In addition, the ground state of MnO_4^{3-} is almost certainly $^3A_2[(2e)^2]$. We have been informed by Dr. J. S. Prener that the spin-forbidden transition $^3A_2 \rightarrow {}^1E$ within the $(2e)^2$ configuration has been identified in the near-infrared.

[16] L. L. Lohr and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963), recently claimed that the numerical value of the group overlap integral $G_E(d,\pi)$ given by Wolfsberg and Helmholz[2] was in error by a factor of $\sqrt{3}$, and that if this error was corrected, the Wolfsberg–Helmholz calculation would give the Ballhausen–Liehr level order, with t_2 0.5 e.v. above e. As Fenske and Sweeney have pointed out,[5] this claim was apparently based on a misunderstanding. (1) It is $G_{T_2}(d,\pi)$, and not $G_E(d,\pi)$, for which Wolfsberg and Helmholz gave an analytical expression which is too large by a factor of $\sqrt{3}$. (2) This error is merely a misprint in the analytical form given for $G_{T_2}(d,\pi)$. The numerical values given for $G_{T_2}(d,\pi)$ and $G_E(d,\pi)$ are apparently not in error, since they are correctly related to each other [D. W. Cruickshank, *J. Chem. Soc.*, 5486 (1961)]: $G_E(d,\pi)/G_{T_2}(d,\pi) = \sqrt{3}$ (neglecting ligand–ligand overlap). (3) The Wolfsberg–Helmholz calculation thus yields e over t_2 as reported originally,[2] and not the t_2 over e order claimed by Lohr and Lipscomb.

[17] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Company, Reading, Mass., 1962.

probably forbidden states arising from the transitions $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$, respectively. Ballhausen has recently published a complete vibrational analysis of the first allowed band in MnO_4^-.[18] In this paper, the weak absorption at about 14,500 cm.$^{-1}$ is assigned $^1A_1 \rightarrow {}^1T_1$ ($t_1 \rightarrow 2e$), an orbitally-forbidden transition. Also, there appears to be a very weak spin-forbidden system at approximately 13,200 cm.$^{-1}$. It is reasonable to assign the weak absorption at 28,000 cm.$^{-1}$ to the orbitally forbidden $^1A_1 \rightarrow {}^1T_1$ ($3t_2 \rightarrow 2e$) transition. The complete assignment of the MnO_4^- spectrum indicated by the present molecular orbital calculation is given in Table VIII.

TABLE VIII

CALCULATED AND OBSERVED TRANSITION ENERGIES IN MnO_4^-

Band maxima,[14,17,18] cm.$^{-1}$	*f*	Assignments	Calcd. one-electron energies, cm.$^{-1}$
(14,500)	Weak	$^1A_1 \rightarrow {}^1T_1$ ($t_1 \rightarrow 2e$)	22,600
18,300	0.032	$^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 2e$)	22,600
(28,000)[a]	*a*	$^1A_1 \rightarrow {}^1T_1$ ($3t_2 \rightarrow 2e$)	33,200
32,200	0.070	$^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 2e$)	33,200
(44,000)[b]	*b*	$^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 4t_2$)	48,100

[a] Weak shoulder. [b] Shoulder indicating a band with $\epsilon \approx 1500$.

The Value of Δ in MnO_4^-.—The spectral assignments suggest a Δ value of approximately 26,000 cm.$^{-1}$ for MnO_4^-. There are several reasons why this large value is more reasonable than the value of approximately 14,000 cm.$^{-1}$ that would be obtained by assigning the first two bands to the one-electron transitions $t_1 \rightarrow 2e$ and $t_1 \rightarrow 4t_2$, respectively.[19] First, the first two allowed bands in the isoelectronic CrO_4^{2-} ion are at 26,800 and 36,600 cm.$^{-1}$, which with the $t_1 \rightarrow 2e$ and $t_1 \rightarrow 4t_2$ assignments would give a Δ value of only 10,000 cm.$^{-1}$. It is known tnat the Δ value of VCl_4 is 9000 cm.$^{-1}$.[20] Comparing VCl_4 (V^{4+}, Cl^-) with CrO_4^{2-} (Cr^{6+}, O^{2-}), one would expect a substantially larger Δ value for CrO_4^{2-}. Thus the assignment of the second band in CrO_4^{2-} (and in MnO_4^-) is more likely $3t_2 \rightarrow 2e$.

Second, the first band in the d^1 MnO_4^{2-} ion is located at 16,500 cm.$^{-1}$.[14,21] This band must be assigned as $^2E \rightarrow {}^2T_2$ ($2e \rightarrow 4t_2$), an allowed transition. Since the transition $t_1 \rightarrow 2e$ gives two $^2T_2$ states at about the same energy, configuration interaction among the three $^2T_2$ states may well have a significant effect on the final energies. Thus, 16,500 cm.$^{-1}$ is a *lower limit* for the value of Δ in MnO_4^{2-}, and the assignment which gives the smaller Δ value in MnO_4^- must be rejected.

A final important comparison is between MnO_4^- and TcO_4^-. The first two allowed bands in TcO_4^- are at 34,400 and 40,700 cm.$^{-1}$. If anything, Δ should increase in going from MnO_4^- to TcO_4^-. However, if the second band were $t_1 \rightarrow 4t_2$, Δ would decrease from 14,000 to 6000 cm.$^{-1}$ from Mn(VII) to Tc(VII), a very improbable circumstance. It is much more satisfactory to assign the second band of TcO_4^- as $3t_2 \rightarrow 2e$.[6]

Electronic Spectra of Transition Metal Oxyanions and Tetroxides.—Using the assignment of the MnO_4^- spectrum as a guide, we shall now attempt to assign consistently the spectra of the other important tetrahedral d^0, d^1, and d^2 metal oxyanions and tetroxides.

(1) **d^0 Systems: VO_4^{3-}, CrO_4^{2-}, MoO_4^{2-}, TcO_4^-, WO_4^{2-}, ReO_4^-, RuO_4, OsO_4.**—The ground state of the d^0 complexes is . . . $(3t_2)^6(t_1)^6 = {}^1A_1$. Assuming in all cases a Δ value of 15,000 cm.$^{-1}$ or larger, we expect the lowest energy allowed transitions to be $^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 2e$) and $^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 2e$). The spectral assignments for the d^0 complexes are given in Table IX. In most cases the two allowed bands are present, separated by 5000 to 10,000 cm.$^{-1}$.

TABLE IX

ELECTRONIC SPECTRA OF TETRAHEDRAL METAL OXYANIONS AND TETROXIDES[14,17]

	Band maxima in cm.$^{-1}$		
d^0 complexes	$^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 2e$)	$^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 2e$)	
VO_4^{3-}	36,900 (0.150)[a]	*b*	
CrO_4^{2-}	26,810 (0.089)	36,630 (0.110)	
MnO_4^-	18,320 (0.032)	32,210 (0.070)	
MoO_4^{2-}	44,500 (0.106)	*b*	
TcO_4^-	34,900 (0.04)	40,700 (0.095)	
WO_4^{2-}	50,300	*b*	
ReO_4^-	44,000	49,000	
RuO_4	26,000 (0.020)	32,200 (0.044)	
OsO_4	33,500	41,500	
	Band maxima in cm.$^{-1}$		
d^1 complexes	$^2E \rightarrow {}^2T_2$ ($2e \rightarrow 4t_2$)	$t_1 \rightarrow 2e$ bands	
CrO_4^{3-}	16,000	28,200	
MnO_4^{2-}	16,530 (0.025)	22,940; 28,490 (0.12)	
RuO_4^-	26,000 (0.027)	31,700 (0.037)	
	Band maxima in cm.$^{-1}$		
d^2 complexes	$^3A_2 \rightarrow {}^3T_2$ ($2e \rightarrow 4t_2$)	$^3A_2 \rightarrow {}^3T_1$ ($2e \rightarrow 4t_2$)	$t_1 \rightarrow 2e$ bands
MnO_4^{3-}[c]	11,000	15,000 (0.017)	30,800 (0.112)
FeO_4^{2-}	12,720 (0.009)	19,600 (0.035)	*b*
RuO_4^{2-}	21,600 (0.031)	*b*	*b*

[a] *f* value in parentheses. [b] Not reported. [c] L. E. Orgel, *Mol. Phys.*, **7**, 397 (1964).

(2) **d^1 Systems: CrO_4^{3-}, MnO_4^{2-}, RuO_4^-.**—The ground state of the d^1 ions is $(3t_2)^6(t_1)^6(2e) = {}^2E$. We expect one so-called d–d transition, $^2E \rightarrow {}^2T_2$ ($2e \rightarrow 4t_2$). The lowest energy charge-transfer bands arise from the one-electron transitions $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$. The spectral assignments are given in Table IX.

(3) **d^2 Systems: MnO_4^{3-}, FeO_4^{2-}, RuO_4^{2-}.**—The ground state of the d^2 ions is $(3t_2)^6(t_1)^6(2e)^2 = {}^3A_2$. With a large Δ value, we anticipate two spin-allowed d–d bands, corresponding to the one-electron transition $(2e)^2 \rightarrow (2e)(4t_2)$. The $^3A_2 \rightarrow {}^3T_2$ transition has energy Δ, while the $^3A_2 \rightarrow {}^3t_1$ transition has energy $\Delta + 12B$. Both bands are reported for FeO_4^{2-} and MnO_4^{3-}. The assignment of these bands as $^3A_2 \rightarrow {}^3T_2$ and $^3A_2 \rightarrow$

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(18) C. J. Ballhausen, *Theoret. chim. Acta* (Berlin), **1**, 285 (1963).

(19) The assignment of MnO_4^- suggested by Carrington and Jørgensen[6] is as follows: 18,320 cm.$^{-1}$ ($t_1 \rightarrow 2e$); 28,000 cm.$^{-1}$ ($3t_2 \rightarrow 2e$); 32,210 cm.$^{-1}$ ($t_1 \rightarrow 4t_2$). According to the Carrington–Jørgensen assignment, an intense band due to the strongly-allowed $3t_2 \rightarrow 4t_2$ transition should appear at approximately 42,000 cm.$^{-1}$. This assignment must be rejected, since there is no intense band in MnO_4^- between 32,000 and 44,000 cm.$^{-1}$. According to our assignments, the $^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 4t_2$) band in MnO_4^- should appear at approximately 58,000 cm.$^{-1}$. We believe that the steeply-rising absorption in MnO_4^-, which does not peak at 52,000 cm.$^{-1}$, is the tail of the strongly-allowed $^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 4t_2$) band.

(20) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(21) G. den Boef, H. J. van der Beek, and Th. Braaf, *Rec. trav. chim.*, **77**, 1064 (1958).

${}^3T_1$ gives the values $B \cong 575$ cm.$^{-1}$ for FeO_4^{2-} and $B \cong 335$ cm.$^{-1}$ for MnO_4^{3-}. The ${}^3A_2 \rightarrow {}^3T_2$ band is observed in RuO_4^{2-}, but the ${}^3A_2 \rightarrow {}^3T_1$ band has not been reported—it may be obscured by the first charge-transfer band. In all the d^2 oxyanions, the first charge-transfer band is assigned as the one-electron transition $t_1 \rightarrow 2e$.

The spectral assignments for the d^2 complexes are given in Table IX.

Δ Values for the Metal Oxyanions.—From the assignments given in Tables VIII and IX the Δ values for a number of metal oxyanions can be estimated. These Δ values are set out in Table X. It is important to note that the Δ values are internally consistent, *i.e.*

$$\Delta[\mathrm{Mn(VII)}] > \Delta[\mathrm{Mn(VI)}] > \Delta[\mathrm{Mn(V)}]$$

$$\Delta[\mathrm{Ru(VII)}] > \Delta[\mathrm{Ru(VI)}] > \Delta[\mathrm{Fe(VI)}]$$

It is of interest that the Δ values appear to decrease proceeding from the Cr to the Mn complexes. For example, we have the order $CrO_4^{3-} > MnO_4^{3-}$.

TABLE X

THE VALUE OF THE ORBITAL PARAMETER Δ IN TETRAHEDRAL METAL OXYANIONS

Complex	Δ, cm.$^{-1}$
CrO_4^{3-}	16,000
MnO_4^{3-}	11,000
MnO_4^{2-}	(19,000)[a]
MnO_4^-	26,000
FeO_4^{2-}	12,720
RuO_4^{2-}	21,600
RuO_4^-	(28,500)[a]

[a] Corrected for an estimated configuration interaction of 2500 cm.$^{-1}$—see text.

Charge-Transfer Bands.—It is convenient for the purpose of discussion to present the energy of the first charge-transfer band, and, in the d^0 complexes, to present the energy separation of the first two allowed bands. This information is given in Table XI, following the assignments of Table IX.

TABLE XI

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)[a]
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)

[a] The separation of the first two bands in the d^0 complexes is given in parentheses.

We believe the correlation in the charge-transfer energies provides considerable support for our assignments of the spectra of the MO_4^{n-} complexes. Comparing complexes containing central metals of the same row, the first charge-transfer band moves to lower energy on increasing the oxidation number of the central metal ion. This is an *expected* correlation for a ligand-to-metal charge-transfer process. The assignment schemes[5,14] which ignore the $2e \rightarrow 4t_2$ transition predict that the oxygen-to-metal charge transfer occurs at lower energy in MnO_4^{2-} than in MnO_4^-, which is very unlikely. There are several such discrepancies if the $2e \rightarrow 4t_2$ transition is not considered.

Finally, it is clear from the separations of the first two allowed bands in the d^0 MO_4^{n-} complexes that the assignments $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$ are much preferred over $t_1 \rightarrow 2e$ and $t_1 \rightarrow 4t_2$. The Δ values one would estimate from the latter assignments would be contrary to all expectations.

In summary, the spectral assignments presented here for MnO_4^- and related ions are consistent with the best one-electron calculation we are able to perform, and, in addition, they lead to a self-consistent set of Δ values and oxygen–metal charge-transfer energies.

Acknowledgments.—We thank the National Science Foundation and the Public Health Service (Research Grant No. CA-07016-01 from the National Cancer Institute) for support of this research. Grateful acknowledgment is made to Professor R. F. Fenske for a useful discussion and for communicating to us the results of his calculations prior to publication.

Appendix

Basis Functions.—The atomic orbitals used in this calculation are $2s_L(4)$, $2p_L(12)$, $3d_M(5)$, $4s_M(1)$, and $4p_M(3)$, a total of 25 orbitals. From these atomic orbitals, symmetry basis functions transforming according to definite rows of irreducible matrix representations have been generated by standard methods[22] and are given in Table I. The basis functions Ψ_i in Table I have been normalized neglecting ligand–ligand overlap. In order that $N_i\Psi_i$ shall be correctly normalized including ligand–ligand overlap, the normalization correction factors N_i given in Table XII are required.

Radial Functions Used. Manganese.[7]—3d: Mn^+ (MnII), d^6

$$R(3d) = 0.532\Phi_3(5.15) + 0.649\Phi_3(1.90)$$

4s

$$R(4s) = -0.02110\Phi_1(24.385) + 0.07200\Phi_2(9.325) - 0.1794\Phi_3(4.27) + 1.0133\Phi_4(1.35)$$

4p: Mn^0 (MnI), d^6p

$$R(4p) = 0.01245\Phi_2(10.15) - 0.04345\Phi_3(3.955) + 1.00086\Phi_4(0.79)$$

$$\Phi_n(\mu) = N_\mu r^{n-1} e^{-\mu r}$$

Oxygen.—The same radial functions were used as in the vanadyl ion calculation.[8]

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[22] E. P. Wigner, "Group Theory," Academic Press, New York, N. Y., 1959, p. 114.

TABLE XII[a]

Irreducible representation	Basis function, Ψ_i	Correction factor, N_i
A_1 (Γ_1)	σ_s	$[1 + 3S(s_L,s_L)]^{-1/2}$
	σ_p	$[1 + 2S(p_{\sigma L},p_{\sigma L}) + S(p_{\pi L},p_{\pi L})]^{-1/2}$
E (Γ_3)	π	$[1 + {}^1/_2S(p_{\sigma L},p_{\sigma L}) - {}^1/_2S(p_{\pi L},p_{\pi L})]^{-1/2}$
T_2 (Γ_4)	σ_p	$[1 - {}^2/_3S(p_{\sigma L},p_{\sigma L}) - {}^1/_3S(p_{\pi L},p_{\pi L})]^{-1/2}$
	σ_s	$[1 - S(s_L,s_L)]^{-1/2}$
	π	$[1 + {}^1/_6S(p_{\sigma L},p_{\sigma L}) + {}^{11}/_6S(p_{\pi L},p_{\pi L})]^{-1/2}$
T_1 (Γ_5)	π	$[1 - {}^1/_2S(p_{\sigma L},p_{\sigma L}) - {}^3/_2S(p_{\pi L},p_{\pi L})]^{-1/2}$

[a] The subscripts σ and π denote the type of overlap involved; L means ligand orbital.

Bond Distances.[23,24]—Mn–O = 1.59 Å. = $3.01a_0$; O–O = $4.91a_0$.

Overlap Integrals.—The diatomic overlap integrals were evaluated as linear combinations of overlap integrals for Slater-type orbitals using the appropriate values of p and t.[25] Most of the Slater overlaps were taken from tables prepared by Harold Basch of these laboratories, who used an IBM 7090 computer. The diatomic overlap integrals are given in Table XIII. With these diatomic overlap integrals, the group overlap integrals are as given in Table III.

TABLE XIII

DIATOMIC OVERLAPS

$S(4s_M,2s_L) = 0.347$

$S(4s_M,2p_{\sigma L}) = 0.123$

$S(4p_{\sigma M},2s_L) = 0.303$

$S(4p_{\sigma M},2p_{\sigma L}) = -0.091$

$S(4p_{\pi M},2p_{\pi L}) = 0.161$

$S(3d_{\sigma M},2s_L) = 0.211$

$S(3d_{\sigma M},2p_{\sigma L}) = 0.141$

$S(3d_{\pi M},2p_{\pi L}) = 0.163$

$S(2s_L,2s_L) = 0.017$

$S(2s_L,2p_{\sigma L}) = 0.041$

$S(2p_{\sigma L},2p_{\sigma L}) = 0.071$

$S(2p_{\pi L},2p_{\pi L}) = 0.016$

Coulomb Integrals.—The coulomb integrals H_{ii} which appear in the secular equation are approximated as valence state ionization energies (VSIE's) corrected for ligand–ligand overlap, if any. In general, each VSIE is a function of both the charge and the configuration of the atom in question. The procedures used for evaluating these VSIE's are discussed separately for metal and for ligand.

Metal.—For a given charge and atomic configuration, the VSIE for a particular kind of electron (s, p, d) is evaluated as follows. The VSIE is taken as the energy required to remove the electron in such a way that the L quantum number of the initial term is the same as that of the final term, and the S quantum number is reduced by $^1/_2$.

$$\Delta L = 0$$
$$\Delta S = -{}^1/_2$$

The VSIE is thus evaluated from experimental data of Moore.[10] When there is more than one starting term which could give an ionization satisfying the rules $\Delta L = 0$ and $\Delta S = -{}^1/_2$, the starting term chosen is usually the one with the lowest energy relative to the ground state.

Since essentially one-electron MO energies are to be calculated, it is hoped that this procedure for evaluating $H'_{ii} = -$VSIE largely excludes the part of the electron repulsions which separate the terms arising from a given configuration.

As a concrete example, the VSIE for an s electron in Mn^0, d^6s, was evaluated as follows.

$$Mn^0\ d^6s(^6D_{5/2}) \longrightarrow d^6(^5D_2)$$
$$\text{VSIE} = 59{,}960 + 14{,}781 - 17{,}452 = 57{,}289\ \text{cm.}^{-1}$$

Here 59,960 cm.$^{-1}$ is the I.P. of Mn^0, 14,781 is the energy of $d^6(^5D_2)$ relative to the ground state of Mn^+, and 17,452 is the energy of $d^6s(^6D_{5/2})$ relative to the ground state of Mn^0.

Similar procedures were used to evaluate the other VSIE's for various combinations of charge and configuration. In a few cases, the position of a needed term was roughly estimated.

The p VSIE's for Mn were estimated by interpolating VSIE data for p electrons along the first transition series, for particular charge and configuration types.

VSIE's are tabulated in Table XIV for s, p, and d electrons of manganese, as a function of initial charge and configuration. Thus, in the table of Mn s VSIE's, configuration d^ns, charge 0 refers to the ionization $d^6s \rightarrow d^6$. The data are shown graphically as VSIE curves in Fig. 3–5.

TABLE XIV

	Charge			
Configuration	0	+1	+2	+3
	Mn d VSIE's (10^3 cm.$^{-1}$)			
d^n	46.6	143.8	270.6	431
$d^{n-1}s$	75.4	185.5 (estd.)	325.5 (estd.)	493
$d^{n-1}p$	83.0	199.5	333.5	501
	Mn s VSIE's (10^3 cm.$^{-1}$)			
d^ns	57.3	126.1	209.3	316
$d^{n-1}s^2$	69.4	142.6		
$d^{n-1}sp$	80.0	154.7		
	Mn p VSIE's (10^3 cm.$^{-1}$)			
d^np	32.7	88	157.8	
$d^{n-1}sp$	41	96		
$d^{n-1}p^2$	41.3			

To evaluate H'_{ii} for an arbitrary charge and configuration, the configuration is represented as a linear combination of the three configurations for which VSIE curves have been set up. $-H'_{ii}$ is then taken as the same linear combination of the respective VSIE's. As an example, H_{ss} will be evaluated for $Mn^{+0.53}$, $d^{5.87}s^{0.23}p^{0.37}$. Using the configurations at charge +0.53 on the curves for d^ns, $d^{n-1}s^2$, and $d^{n-1}sp$

$$d^{5.87}s^{0.23}p^{0.37} = ad^{5.47}s + bd^{4.47}s^2 + cd^{4.47}sp$$
$$a = 1.40,\ b = -0.77,\ c = 0.37$$

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(23) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p. M89.

(24) R. C. L. Mooney, *Phys. Rev.*, **37**, 1306 (1931).

(25) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

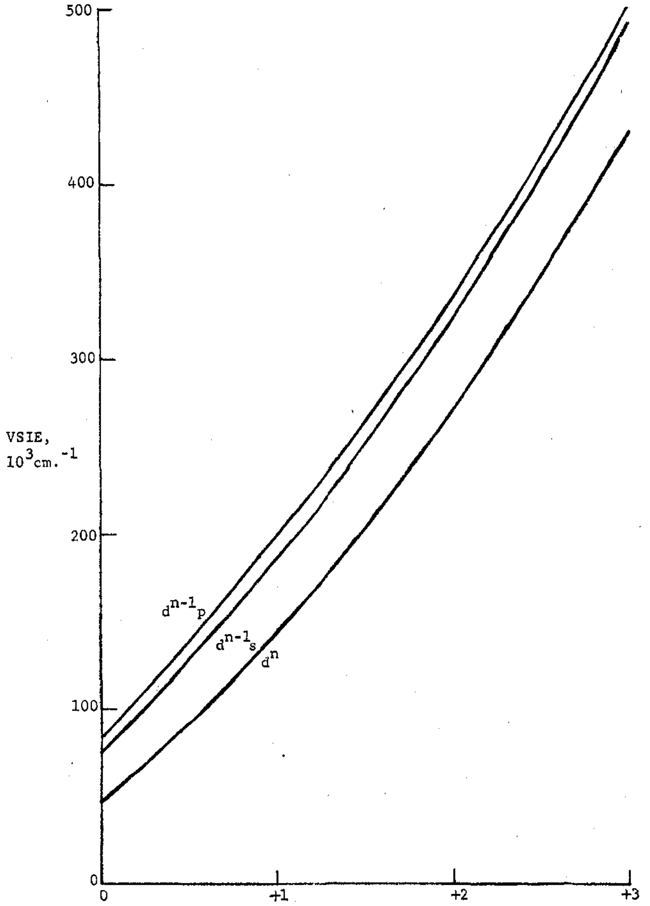

Fig. 3.—Ionization energy of a Mn 3d electron as a function of charge and orbital configuration.

At charge +0.53, the corresponding VSIE's can be read off the graph.

Configuration	VSIE (10^3 cm.$^{-1}$)
$d^{5.47}s$	90.5
$d^{4.47}s^2$	106.5
$d^{4.47}sp$	119.5

$$-H_{ss} = 1.40 \times 90.5 - 0.77 \times 106.5 + 0.37 \times 119.5$$

$$H_{ss} = -89\ (10^3\ \text{cm.}^{-1})$$

Oxygen.—Two methods were used for evaluating H_{ii} for oxygen.

(1) **Isolated Atom Method.**—The basic characteristic here is that the VSIE's of oxygen are treated as functions of charge and configuration, much the same as for the metal. The particular method we used to evaluate the VSIE's is as follows. To evaluate one VSIE, one ionization potential and two energies, one for each of the two configurations involved in the ionization, are needed. For oxygen, fairly complete term energy data are available for many of the configurations. Because of this, for each configuration there was calculated an average energy, E_{av}, the average being over all of the terms (or the J components of the terms) weighted according to the degeneracy of each term. A VSIE was then calculated by combining two such average-of-configuration energies and one ionization potential.

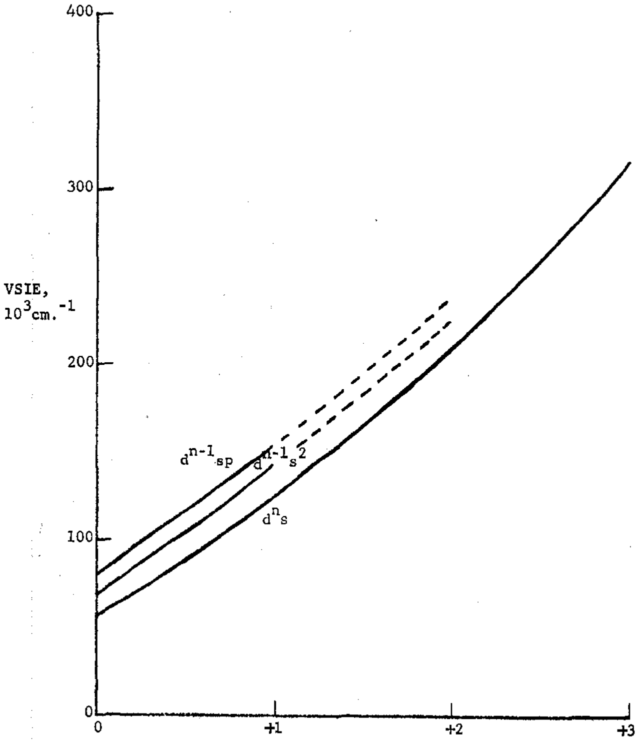

Fig. 4.—Ionization energy of a Mn 4s electron as a function of charge and orbital configuration.

For charge 0, sp^5

$$E_{av} = {}^1/_{12}[5E(^3P_2) + 3E(^3P_1) + 1E(^3P_0) + 3E(^1P_1)] = 142{,}187\ \text{cm.}^{-1}$$

For charge +1, sp^4, E_{av} = 158,881. The I.P. of O^0 is 109,837 cm.$^{-1}$. Hence, for charge +0, sp^5, the p VSIE = 109,837 + 158,881 − 142,187 = 126,531 cm.$^{-1}$.

Data for O^-, sp^5, were calculated using as the electron affinity of the oxygen atom EA = 1.465 ± 0.005 e.v. = 11,820 cm.$^{-1}$.[26]

VSIE's calculated for oxygen, using E_{av} values, are tabulated in Table XV.

TABLE XV

Configuration	Charge −1	Charge 0	Charge +1
E_{av} oxygen s VSIE's (10^3 cm.$^{-1}$)			
sp^n		285.6 (estd.)	417.3
s^2p^{n-1}	154.0	261.1	396.5
E_{av} oxygen p VSIE's (10^3 cm.$^{-1}$)			
sp^n		126.5	263.2
s^2p^{n-1}	19.4	127.8	267.8

Determination of H'_{ii} for nonintegral charge and configuration follows the same procedure as outlined for Mn. The prime is used in H'_{ii} because a correction factor must still be introduced to take into account ligand–ligand overlap. The form of this correction factor will be given after the exchange integrals H_{ij} have been discussed.

(2) **Hydride Ionization Potential Method.**—In this

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[26] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, *Phys. Rev.*, **111**, 504 (1958).

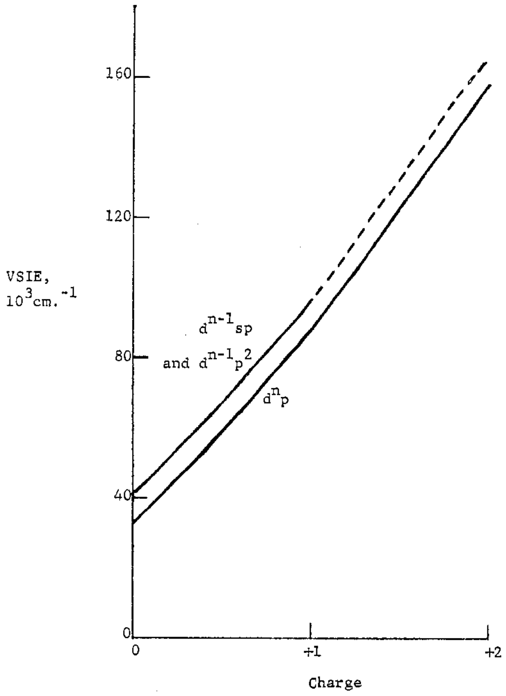

Fig. 5.—Ionization energy of a Mn 4p electron as a function of charge and orbital configuration.

procedure, the p VSIE of oxygen in the oxyanion is assigned a single fixed value, equal to the first ionization potential of H_2O. This is 12.61 e.v. = 101,700 cm.$^{-1}$.[12] The hydride I.P. is used to make rough allowance for the fact that in an oxyanion, the oxygen is not an isolated entity, but is adjacent to a positive center. Taking 101,700 cm.$^{-1}$ as the p VSIE for oxygen (s^2p^n), the equivalent effective charge on oxygen is about −0.21. Then assuming this charge, −0.21, the s VSIE for oxygen may be estimated (for $s^2p^{4.21}$) as about 236,500 cm.$^{-1}$.

So in the H_2O I.P. method, the fixed values used are

$$H'_{\sigma_s\sigma_s} = -236{,}500 \text{ cm.}^{-1}$$

$$H'_{\pi\pi} = H'_{\sigma_p\sigma_p} = -101{,}700 \text{ cm.}^{-1}$$

Exchange Integrals $(H_{ij})^8$

$$H_{ij} = -2G_{ij}[H'_{ii}H'_{jj}]^{1/2}$$

G_{ij} is the group overlap integral between the symmetry basis functions i and j.

Overlap Correction for H_{ii}

$$\Psi_i = \sum_{\alpha} a_{i\alpha}\Phi_{i\alpha}$$

$$\int \Psi_i^2 \mathrm{d}\tau = \frac{1}{N_i^2} = \sum_{\alpha} a_{i\alpha}^2 + \sum_{\alpha \neq \beta}\sum a_{i\alpha}a_{i\beta}S(i\alpha,i\beta)$$

The basic assumption is that for two different atomic orbitals (two orbitals on different atoms, or different orbitals on the same atom), Φ_k and Φ_n

$$H_{kn} = -2.00(H_{kk}H_{nn})^{1/2}S(k,n)$$

Using this assumption

$$H_{ii} = \int (N_i\Psi_i)H(N_i\Psi_i)\mathrm{d}\tau$$

$$= N_i^2 H_{i\alpha i\alpha}\left[\sum_{\alpha} a_{i\alpha}^2 + 2\sum_{\alpha \neq \beta}\sum a_{i\alpha}a_{i\beta}S(i\alpha,i\beta)\right]$$

$H_{i\alpha i\alpha} = H'_{ii}$, the diagonal element uncorrected for ligand–ligand overlap. If ψ_i has already been normalized neglecting ligand–ligand overlap, then N_i is the correction factor for the normalization, which was tabulated previously. In this case, $\sum_{\alpha} a_{i\alpha}^2 = 1$. Let

$$X_i \equiv \sum_{\alpha \neq \beta}\sum a_{i\alpha}a_{i\beta}S(i\alpha,i\beta)$$

$$H_{ii} = H'_{ii}\left(\frac{1 + 2X_i}{1 + X_i}\right)$$

Using the diatomic overlaps and normalization correction factors previously tabulated, the ligand basis functions have the values of $(1 + 2X_i)/(1 + X_i)$ shown in Table XVI.

Table XVI

Representation	Basis function	$(1 + 2X_i)/(1 + X_i)$
E	π	1.027
A_1	σ_s	1.048
	σ_p	1.136
T_2	σ_p	0.945
	σ_s	0.983
	π	1.040
T_1	π	0.937

For the central metal atom orbitals of course, $H_{ii} = H'_{ii}$. That the off-diagonal elements H_{ij} are to be computed from the uncorrected H'_{ii} rather than the corrected H_{ii} can be shown as follows.

$$G_{ij} = \int (N_i\Psi_i)(N_j\Psi_j)\mathrm{d}\tau = N_iN_j \sum_{\alpha}\sum_{\mu} a_{i\alpha j\mu}\, S(i\alpha,j\mu)$$

$$H_{ij} = N_iN_j \sum_{\alpha}\sum_{\mu} a_{i\alpha}a_{j\mu}[-2.00(H_{i\alpha i\alpha}H_{j\mu j\mu})^{1/2}S(i\alpha,j\mu)]$$

(The assumption $\Phi_{i\alpha} \not\equiv \Phi_{j\mu}$ is a reasonable one, since Ψ_i and Ψ_j are symmetry basis functions belonging to the same row of the same irreducible representation.)

$$H_{ij} = -2.00(H'_{ii}H'_{jj})^{1/2}G_{ij}$$

Solution of Secular Equation.—The secular equation $|H_{ij} - EG_{ij}| = 0$ was solved using a Fortran program written by P. T. Manoharan of these laboratories. For a given cycle, an input electron configuration and charge are assumed for the metal, and the H_{ii} terms are computed. H_{ii} terms for ligand basis functions are computed by either of the two methods previously described. For each of the MO's calculated in the cycle, a Mulliken population analysis is performed, in which each overlap population is divided equally between the two basis functions involved.[9]

$$\Psi_n = \sum_{i} C_{ni}\Psi_i$$

$$POP_{ni} = \sum_{j} C_{ni}C_{nj}G_{ij} = C_{ni}^2 + \sum_{j \neq i} C_{ni}C_{nj}G_{ij}$$

If the nth MO is occupied by one electron, POP_{ni} represents the fraction of the time which the electron spends in basis function i, or the fraction of the electronic charge which resides in basis function i. By adding up the appropriate POP_{ni} terms, the output configuration can be computed for the metal and for oxygen.

In subsequent cycles the input configuration(s) are altered until a self-consistent result is obtained. The result is considered self-consistent if the input and output configuration(s) for the cycle are practically the same. For example, in the final cycle of the MnO_4^- calculation using H_2O I.P., Mn input charge was +0.53, $d^{5.87}s^{0.23}p^{0.37}$, and output charge +0.60, $d^{5.81}s^{0.22}p^{0.37}$.

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Infrared Spectra of $(CO)_5Mn–Re(CO)_5$ and the Carbonyls of Manganese, Technetium, and Rhenium; Assignment of C≡O and M=C Stretching Absorptions[1]

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The infrared spectrum of $(CO)_5Mn–Re(CO)_5$ in the region 3000 to 290 cm.$^{-1}$ is reported and compared to the spectra of the parent carbonyls, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. An assignment of the carbonyl and metal–carbon stretching bands for these compounds is proposed. The spectrum of $Tc_2(CO)_{10}$ in the region 800–290 cm.$^{-1}$ is reported for the first time.

Introduction

Recent determination under high resolution of the infrared spectra in the carbonyl stretching region of the carbonyls of Mn, Tc, and Re[2] has shown that their band patterns were similar but not superimposable. We were interested, therefore, to compare the absorptions in the new mixed metal carbonyl $(CO)_5Mn–Re(CO)_5$[3] to those in the parent carbonyls and if possible to assign these to the expected carbonyl stretching modes. Also, we have extended the comparisons between the mixed metal carbonyl and the parent carbonyls to the low energy region, 800–290 cm.$^{-1}$, and were able to scan this for $Tc_2(CO)_{10}$ for the first time.

Experimental

Preparation of Carbonyls.—$Mn_2(CO)_{10}$ was obtained from the Ethyl Corporation and resublimed before use. $Re_2(CO)_{10}$ was prepared as described earlier.[2] The new mixed metal carbonyl was prepared according to the Russian work,[3] from the treatment of $NaMn(CO)_5$ (from $Mn_2(CO)_{10}$ and Na–Hg)[4] in tetrahydrofuran with $Re(CO)_5Cl$ (from $Re_2(CO)_{10}$ and Cl_2).[2] After 24 hr. of stirring, the ether was removed under reduced pressure and cyclohexane brought in. The resulting solution gave a number of new bands in addition to a set of bands which were identically superimposable with those of $Mn_2(CO)_{10}$. Air oxidation of the solid product for about 4 days removed the $Mn_2(CO)_{10}$ (as observed through infrared spectra in cyclohexane solution). The product thus obtained was purified by sublimation at 0.5 mm. and 50°. The new derivative is resistant to air oxidation over short periods, in which it resembles $Re_2(CO)_{10}$. A purified sample was analyzed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Anal. Calcd. for $MnRe(CO)_{10}$: C, 23.04; Re, 35.73; Mn, 10.54; mol. wt., 521. Found: C, 23.26; Re, 35.00; Mn, 10.31; mol. wt., 538 (determined with a Mechrolab vapor pressure osmometer for a solution containing 59.3 mg. of compound in 6.42 g. of cyclohexane; molality interpolated from a log ΔR *vs.* log m plot using benzil as standard; we are indebted to Mr. J. M. Smith of this Department for assistance).

$Tc_2(CO)_{10}$ was prepared as described previously.[2]

Infrared Absorptions.—Using a combination of instruments, we were able to scan the region 3000–290 cm.$^{-1}$ in the infrared; the maxima observed are listed in Table I. The bands in the carbonyl stretching region, 2200–1900 cm.$^{-1}$, were much stronger than the other bands in the spectrum and also were greatly distorted by the pellet technique described below so they were observed separately in dilute cyclohexane solution. Samples of about 4×10^{-5} mole/ml. were taken to read the maxima of the weak carbonyl bands (and of about a tenfold dilution for the strong peaks) in cells of 0.081-mm. sample thickness. A Beckman I.R.-4 equipped with a LiF prism was used under the same instrumental conditions and calibration of spectra as described previously.[2] The absorptions for the mixed metal carbonyl in this region are shown in Fig. 1 along with those of the parent carbonyls for comparison at two concentrations. Spectra for the parent carbonyls have been reported before, but at lower resolution,[5] and for the parent carbonyls and technetium carbonyl at higher resolution but lower intensity[2] such that the weaker bands were not observed.

For all but the carbonyl stretching region, it was convenient to scan the samples in a KBr pellet; solubility problems were avoided for observations on the weaker bands, and KBr is essentially transparent in the entire region 3000–290 cm.$^{-1}$ for disks of approximately 0.2 to 0.3 mm. thickness. Most of the bands in this region other than the carbonyl stretching frequencies suffered little or no distortion with this sampling technique, and the few that looked suspicious could often be checked in cyclohexane solution. The suspicious features of the spectra are appropriately marked in Table I. The pellets contained carbonyl in about 1% concentration by weight to read the maxima of the strong bands, and 4% by weight for the weaker ones. The region 3000–580 cm.$^{-1}$ was scanned with a Perkin-Elmer 421, equipped with a ruled grating. The spectra in the region 900–290 cm.$^{-1}$ were scanned with a Beckman IR-5A, equipped with a CsBr prism, and are shown in Fig. 2. The natural broadness of the absorptions limited the reproducibility in reading the maxima to within 3 cm.$^{-1}$ in this region, which we have found to be the reproducibility of the instrument in this range without further calibration of each individual spectrum.

In the other parts of the region scanned here, *i.e.*, 3000–2200

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[1] This work has been supported in part by Grant No. GP 1696 from the National Science Foundation.

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