differences between k_2 and k' in part to the greater sensitivity of the quantity $(h - c)$ of eq. 9 to experimental errors than the quantity h of eq. 5. On the other hand, the differences between $(h - c)$ and h are not great enough in the present experiments to produce the observed effects. Calculations of the types given in Table II showed that a given error in h_0, a_1, and a_2 produced about the same per cent errors in calculated k_2 and k'. If eq. 5 is the correct equation, under the experimental conditions, one could not expect the use of eq. 9 to produce very much greater scattering of k' values. The facts that calculated k' values did scatter more than k_2 values did and that such difference could not be produced by introducing errors from various possible sources into calculations support the choice of eq. 4 and 5 as being able to account for the data better than eq. 8 and 9. Consequently, mechanism (1b) may be more plausible than mechanism (2b).

If one considers certain trends in k_2 and k' as significant, one may use this as a clue to postulate a different mechanism which may account for the data better than either mechanisms (1b) and (2b). Mechanism (1b) assumes that the carbonato complex species is practically all $Co(en)_2CO_3^+$ while mechanism (2b) assumes that the species is practically all $Co(en)_2CO_3H^{2+}$. If one assumes that both $Co(en)_2CO_3^+$ and $Co(en)_2CO_3H^{2+}$ are present at significant concentrations, that they are in rapid equilibrium with one another according to eq. 10 and equilibrium constant K, and that the rate-determining reaction is (with rate constant k)

$$Co(en)_2CO_3^+ + H_3O^+ = Co(en)_2CO_3H^{2+} + H_2O \quad (10)$$

$$Co(en)_2CO_3H^{2+} \longrightarrow$$

or

$$Co(en)_2CO_3H^{2+} + H_2O \longrightarrow$$

one obtains the rate equation

$$-dc/dt = kK(H_3O^+)c/[K(H_3O^+) + 1] \quad (11)$$

The concentration (H_3O^+) is less than h but greater than $(h - c)$. If eq. 11 is the correct equation and eq. 5 and 9 are used to calculate the respective rate constants, the k_2 and k' calculated are approximately $kK/[K(H_3O^+) + 1]$. This will account for increasing k_2 and k' with decreasing h_0 at constant c_0 as well as for decreasing k_2 and k' with decreasing c_0 at constant h_0 in Table I (if one ignores experiments 1 and 2).

The present data are not useful in testing the last mechanism. The most direct approach is to determine the protonation constant independently.

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Semiempirical Molecular Orbital Theory. I. Permanganate and Related Anions[1]

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Received December 11, 1963

Although the Wolfsberg and Helmholz approach to molecular orbital theory for transition metal complexes is receiving increased attention, the results obtained in its prototype calculation on permanganate have been challenged by several authors. An alternative assignment of the energy levels, proposed by Ballhausen and Liehr, has gained acceptance through its use in the interpretation of e.s.r. measurements on manganate. Since the worth of a semiempirical method rests on its ability to correlate experimental results, this discrepancy casts some doubt on the usefulness of the method. This work consists of a systematic investigation of the modified Wolfsberg and Helmholz approach with particular attention to the effects of the parameters on the calculated energy levels. The method is applied to the series of complexes, MnO_4^-, MnO_4^{-2}, and MnO_4^{-3}. In addition to a study of the sensitivity of calculated energy levels to parameter choices, an attempt has been made to correlate the two alternative assignments with the absorption spectra of the complexes. The results indicate that the order of the energy levels is very dependent upon the amount of s and p character in the hybrid ligand orbitals. Use of the criterion proposed by Ballhausen and Gray to establish the degree of hybridization does not result in energy levels in accord with the e.s.r. results. By adjustment of the H_{ij} terms in the secular determinant, it is possible to obtain *either* set of energy levels and to rationalize the results with reasonable transition assignments for the three complexes. In fact, within the framework of the method employed, the Wolfsberg and Helmholz assignment would appear to yield better correlation with the experimental values. This is particularly true of the calculated transition intensities. In general, it appears that the results one obtains by the semiempirical method are strongly dependent upon the initial assumptions employed in the calculations.

Introduction

In an attempt to interpret the absorption spectra of the permanganate and chromate ions, Wolfsberg and Helmholz[2] proposed a semiempirical molecular orbital calculation of the energy levels of the complexes. However, the energy level assignment obtained by the approach was seriously questioned by Ballhausen and Liehr[3] on the basis of absorption intensity calculations and an alternative assignment was proposed by these authors. The Wolfsberg and Helmholz ordering

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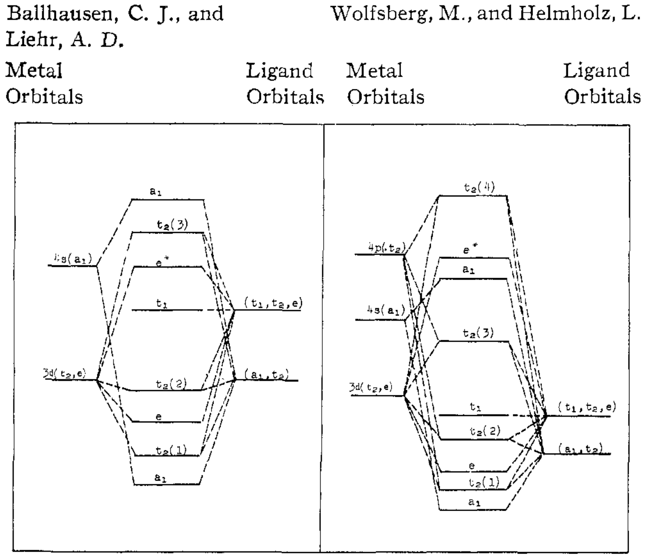
[1] Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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

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



J. Mol. Spectry., **2**, 342 (1958) *J. Chem. Phys.*, **20**, 837 (1952)

Fig. 1.—Proposed permanganate energy levels.

of the levels for permanganate was also challenged by Carrington and Schonland[4] on the basis of electron spin resonance measurements of the manganate ion. They found that the e.s.r. results could be readily interpreted in accord with the Ballhausen and Liehr (B and L) set of energy levels but not with those proposed by Wolfsberg and Helmholz (W and H).

Despite this supposed failure in its prototype calculation,[5] renewed interest in the method has developed. Recently it has been applied, with certain modifications, to the evaluation of the energy levels of several transition metal complexes[6,8,9] as well as to the noble gas fluorides.[10,11] Its success in these applications suggested that use of SCF wave functions,[12,13] together with the modifications in the method, might result in an ordering of the levels of permanganate in agreement with the experimental results.

Therefore, it was decided that a systematic investigation of the W and H method with the particular view of examining the influence of various inherent parameters on the calculated energy levels be carried out. The system chosen for study was the series of transition metal complexes, permanganate, manganate, and hypomanganate.

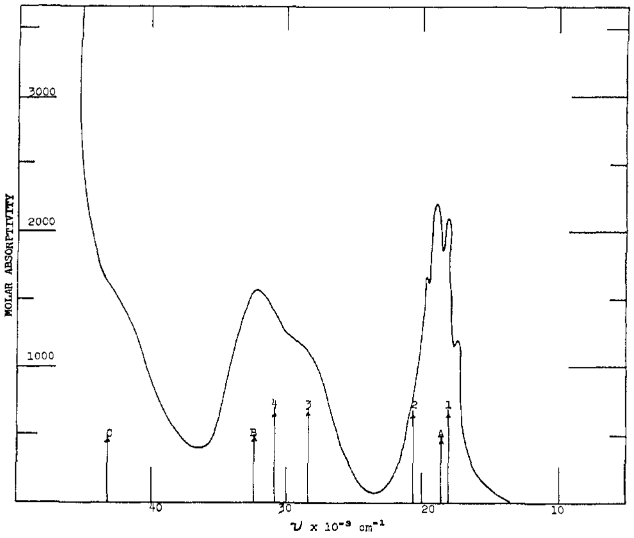


Fig. 2.—Permanganate absorption spectrum. Theoretical absorption maxima predicted by the Ballhausen and Liehr ordering of the energy levels are indicated numerically to correspond to the theoretical transition energies given in Fig. 6. Analogous predictions according to the Wolfsberg and Helmholz ordering are indicated alphabetically to correspond to the theoretical transition energies given in Fig. 7.

In addition to the fact that the MnO_4^- levels are in question, these three ions offer distinct advantages for an investigation of this sort. The visible and ultraviolet absorption spectra of all three display at least two maxima whose intensities indicate they arise from charge-transfer transitions. Furthermore, if the reasonable assumption of tetrahedral symmetry is accepted for all three, the ordering of the energy levels should remain unchanged and the differences in the absorption spectra should simply reflect the effects of electron differences in the three species. In terms of the calculations, this means that certain parameters chosen for the MnO_4^- study should be applicable to the MnO_4^{-2} and MnO_4^{-3} calculations.

The Alternative Assignments.—The W and H and B and L proposals for the energy levels are given in Fig. 1. Since there are 24 electrons in permanganate which are to occupy the orbitals, the ground state according to either set would be the same, namely, $(a_1)^2(1t_2)^6(e)^4(2t_2)^6(t_1)^6 = {}^1A_1$. The distinction between the two arises in the assignment of the next energy level. Thus, in manganate the W and H order indicates the electron would occupy the $t_2(3)$ orbitals and the ground state would be ${}^2T_2$; B and L would predict the electron to be in the antibonding e orbital which results in a ${}^2E$ ground state. Similarly, hypomanganate would have a ${}^3T_1$ or ${}^3A_2$ ground state according to W and H and B and L, respectively.

It is of interest that the B and L ordering of the e* and $t_2(3)$ levels is what one would expect according to crystal field theory while the W and H assignment has the two levels inverted.

Previous Spectral Interpretations.—The visible and ultraviolet absorption spectra of MnO_4^-, MnO_4^{-2}, and MnO_4^{-3} are given in Fig. 2, 3, and 4, respectively.

(4) A. Carrington and D. S. Schonland, *J. Mol. Phys.*, **3**, 331 (1960). See also: A. Carrington, D. J. E. Ingram, D. S. Schonland, and M. C. R. Symons, *J. Chem. Soc.*, 4710 (1956); A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland, and M. C. R. Symons, *Proc. Roy. Soc.* (London), **A254**, 101 (1960).

(5) It might be noted in passing that Lohr and Lipscomb[6] ascribe the W and H "incorrect" ordering of the levels as due to an error of $\sqrt{3}$ in the group overlap, $G_E(d,\pi)$. Our calculations indicate that this is not the case. Indeed, Cruickshank[7] has independently reported that the error was in the printed tabulation of the *general* form of the group overlaps, not in the *calculated* values.

(6) L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963).

(7) D. W. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(8) H. Yamatera, *J. Inst. Polytech., Osaka City Univ.*, **5**, 163 (1956).

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

(10) L. L. Lohr and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 240 (1963).

(11) L. L. Lohr and W. N. Lipscomb, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 347.

(12) R. E. Watson, Tech. Rept. No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology.

(13) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

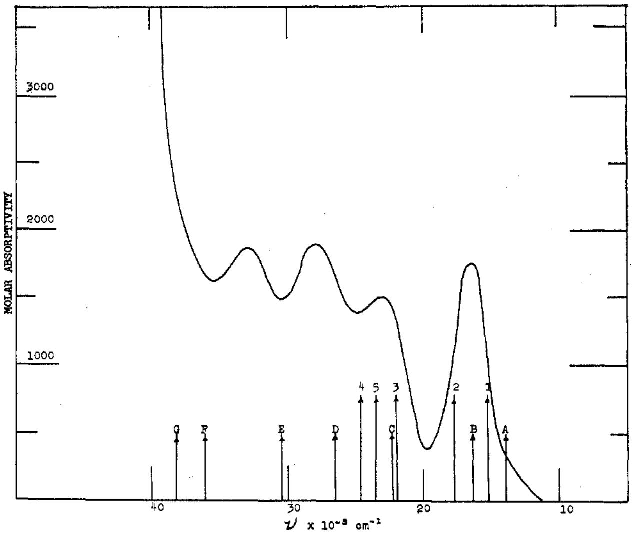


Fig. 3.—Manganate absorption spectrum. See comments in caption to Fig. 2 for explanation of the indicated theoretical absorption maxima.

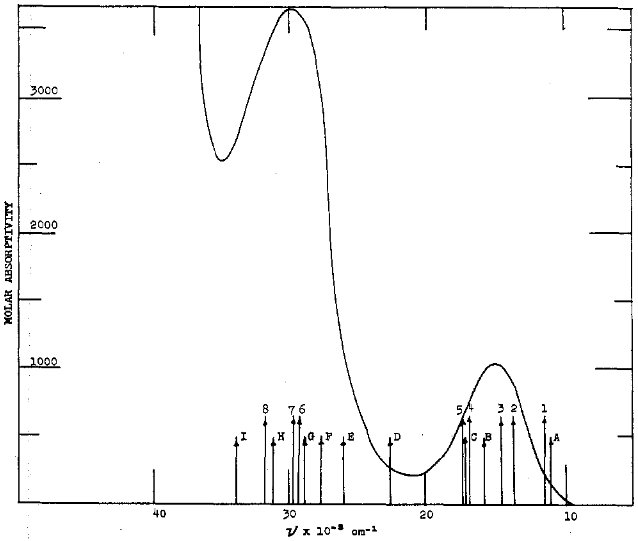


Fig. 4.—Hypomanganate absorption spectrum. See comments in caption to Fig. 2 for explanation of the indicated theoretical absorption maxima.

The large molar absorptivities of the maxima readily identify the transitions as due to charge transfer.

Of the three ions, W and H and B and L attempted an interpretation of permanganate only. Carrington and Schonland[4] presented an analysis of all three complexes in the framework of the B and L assignment of the energy levels. Later, Carrington, in cooperation with Jørgensen,[14] reassigned some of the transitions.

In the MnO_4^- spectrum two peaks are apparent, plus a shoulder on a very intense band just prior to the limit of the spectrophotometer. In the W and H assignment the two peaks are due to the $t_1 \rightarrow t_2(3)$ and $t_2(2) \rightarrow t_2(3)$ transitions. Alternatively, B and L and Carrington and Schonland[4] ascribe the two maxima to the $t_1 \rightarrow e^*$ and $t_1 \rightarrow t_2(3)$ transitions. The shape of the second maximum gives some indication of being composed of two overlapping bands. Carrington and Jørgensen[14] suggest that the $t_1 \rightarrow t_2(3)$ and $t_2 \rightarrow e^*$ transitions are similar enough in energy to explain this appearance.

In the sequence MnO_4^-, MnO_4^{-2}, and MnO_4^{-3}, the first absorption maximum is seen to shift to lower frequencies. Carrington and Schonland[4] assumed that the same transition, $t_1 \rightarrow e^*$, is involved in each case. Such an assumption requires that: (1) the two levels come closer together as one proceeds through the series; (2) the transition, $e^* \rightarrow t_2(3)$, which is possible in MnO_4^{-2} and MnO_4^{-3}, is not seen because of its low energy and low intensity. Since one is dealing with tetrahedral symmetry, this transition is dipole allowed and the authors argued that it was not observed because its theoretical dipole strength was much smaller than those for the other transitions.

Later, Carrington and Jørgensen[14] reassigned the first peak in MnO_4^{-2} as due to the $t_1 \rightarrow e^*$ and/or the $e^* \rightarrow t_2(3)$ transition. This latter transition was also reassigned as the cause of the first maximum in MnO_4^{-3}.

In the Carrington and Schonland[4] assignment, the three peaks in MnO_4^{-2} at 22,940, 28,940, 28,940, and 33,440 cm.$^{-1}$ are all due to the $t_1 \rightarrow t_2(3)$ transition. The separations are believed to arise from differences in the electrostatic interactions of the possible excited states of the $(t_1)^5(t_2)^1$ configuration. No reassignment was given these maxima by Carrington and Jørgensen.

In addition to these analyses of the solution spectra, W and H interpreted the absorption spectrum of MnO_4^- imbedded in various lattices in accord with their energy level assignment. Recently, Ballhausen[15] has re-examined the results in accord with the B and L ordering of the levels. Both papers assert reasonable agreement can be obtained.

The bases for the various interpretations are worthy of comment. The W and H assignment was derived from energy level calculations. Both the B and L ordering and the Carrington and Schonland assignments were based on intensity considerations, a topic which is covered later in this report. The Carrington and Jørgensen assignments were rationalized by comparison with other oxyanions.

The Modified Wolfsberg and Helmholz Method.—The secular determinant, $|H_{ij} - EG_{ij}| = 0$, which arises from the adoption of the linear combination of atomic orbitals (LCAO) approach to molecular orbital theory, is conveniently factored by application of group theory The wave functions of the central metal and ligand orbitals associated with the irreducible representations of the group have been tabulated by W and H and need not be reproduced here.

In the secular determinant G_{ij} are the group overlap integrals. These can be expressed in terms of two center overlap integrals multiplied by suitable coefficients. Because of the confusion[5] which has resulted from the error in the W and H tabulation, the general expressions of the group overlaps in tetrahedral symmetry are given in Table I.

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

(15) C. J. Ballhausen, *Theoret. Chim. Acta* (Berlin) **1**, 285 (1963)

TABLE I

GROUP OVERLAP INTEGRALS

General form	MnO_4^-	MnO_4^{-2}	MnO_4^{-3}
$G_{T_2}(d,\sigma) = (2/\sqrt{3})S(d,\sigma)$	0.254[a]	0.258	0.264
$G_{T_2}(d,\pi) = (2\sqrt{2}/3)S(d_\pi,\pi)$	0.175	0.182	0.193
$G_{T_2}(p,\sigma) = (2/\sqrt{3})S(p,\sigma)$	0.140	0.090	0.025
$G_{T_2}(p,\pi) = -(2\sqrt{2}/\sqrt{3})S(p,\pi)$	−0.317	−0.290	−0.250
$G_E(d,\pi) = (2\sqrt{2}/\sqrt{3})S(d_\pi,\pi)$	0.303	0.315	0.334
$G_{A_1}(s,\sigma) = 2S(s,\sigma)$	0.491	0.491	0.491

[a] The numerical values are those obtained for the B and L assignment, $\theta = 22°$; $F_\sigma = 1.90$; $F_\pi = 1.475$; $R = 1.60$ Å.

The diagonal terms, H_{ii}, are estimated by the negative value of the valence state ionization potential (VSIP) of the atoms or ions. From the literature[2,6,9] it is apparent that various methods for evaluating the VSIP's are used. The degree of agreement or disagreement in the approaches and their influence on the results are difficult to assess from the limited data available. In all the approaches, the VSIP's are functions of the assumed charge on the ion and are extremely sensitive to the value of the charge. VSIP's for nonintegral charge values are obtained by interpolation.

The off-diagonal elements, H_{ij}, are approximated either by[2,8]

$$H_{ij} = F_x G_{ij}(H_{ii} + H_{jj})/2$$

or by the relation[6,9]

$$H_{ij} = F_x G_{ij}\sqrt{H_{ii}H_{jj}}$$

The F_x values depend on whether the overlaps involve σ- or π-bonding. W and H set $F_\sigma = 1.67$ and $F_\pi = 2.00$, and these values have been adopted by certain authors.[8] Others[6,9] have used $F_\sigma = F_\pi = 2.00$.

In the W and H method as modified by Ballhausen and Gray[9] it is assumed that the σ-bonding orbitals of the ligands consist of hybridized atomic orbitals. For example, the σ-bonding orbitals of oxygen would be a hybrid of the 2s and 2p functions. The normalized wave function can be conveniently written as: $\psi(\text{hybrid}) = (\sin\theta) \times \Phi(2s) + (\cos\theta) \times \Phi(2p)$. The degree of hybridization, determined by the value chosen for θ, will affect the overlap integrals and the VSIP's for the σ-bonding orbitals.

Thus the results of a calculation are dependent upon the choices for the four parameters, θ, F_σ, F_π, and the charge on the central metal ion. The ligand ion charge is specified by the charge on the central metal since the sum of the charges must equal the total charge of the complex.

Two restrictions on the values of the parameters have been suggested. The most important is the requirement that the assumed charge on the central metal be the same as that obtained when the electrons in the molecular orbitals are distributed over the atomic centers according to Mulliken's electron population analysis.[16,17] The second restriction[9] is that the value of σ be such that the ratio $\text{VSIP}(\sigma)/S(\sigma)$ be a minimum, where $S(\sigma)$ is the overlap integral between the hybrid orbital and the appropriate orbital on the neighboring atom. For fixed values of F_σ and F_π, the results are completely determined when the two restrictions are employed.

The Present Investigation.—If one accepts the B and L ordering of the energy levels as correct, then it follows that the W and H semiempirical calculation is wrong either in its basic assumptions or in its application to the permanganate ion. At the outset, the second alternative seemed to be a distinct possibility. At the time the original work was carried out, W and H had to make approximations of the H_{ii} terms for the manganese by analogy to their estimates for chromium. Hence the H_{ii} were treated as individual parameters and not VSIP's associated with a particular charge on the ion. This meant that the charge distribution *via* the population analysis was correlated to the wave functions only. In the paper the inference is given that the H_{ii} correspond roughly to the VSIP's of the neutral atom. However, a charge distribution calculated from the W and H values of the terms in the secular determinant indicated the manganese would have a charge of +2.54.

W and H did not have the advantage of the SCF wave functions which are presently available.[12,13] There existed the possibility that the overlap integrals based on these functions might be sufficiently different from those originally used as to appreciably alter the results.

While the above uncertainties held out the promise that the modified approach might yield the B and L ordering of the energy levels and resolve the dilemma, other data tended to indicate the problem might be more fundamental.

In their study of the hexaaquochromium(III) complex, Tanabe and Sugano[18] compared the off-diagonal terms, H_{ij}, as estimated by the W and H method with those determined by their more rigorous approach and found appreciable differences. To obtain identical results between the two methods, one would have to change the F_π parameter in the W and H calculation from 2.00 to 1.36, while the F_σ term would remain essentially unchanged. As has been noted, the empirical choices of F_σ and F_π have been quite arbitrary. The Tanabe and Sugano results raised the question as to the proper values for these parameters. Thus the effects of variations in F_σ and F_π on the energy levels became of particular interest in the investigation.

Some preliminary calculations on the suggested criterion for choosing the amount of s and p orbital character in the ligand hybrid orbitals yielded some disconcerting results. When the overlaps of the hybrid orbitals with the 3d orbitals of the manganese were studied, the ratio $\text{VSIP}(\theta)/S(\theta)$ was a minimum when θ

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(16) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).

(17) Ballhausen and Gray[9] also require that the electron distribution obtained by the population analysis correspond to that assumed in deriving the VSIP values (H. B. Gray, private communication).

(18) Y. Tanabe, and S. Sugano, *J. Phys. Soc. Japan*, **11**, 864 (1956).

$= 22°$. When the overlaps with the manganese 4s orbital were considered, the minimum was achieved when $\theta = 30°$.

It became evident that a systematic investigation of the influences of all four parameter choices on the calculated energy levels was desirable. The following approach was used.

The VSIP's of the oxygen 2s and 2p electrons for different degrees of ionization were obtained from data compiled by Hinze and Jaffé.[19] An analogous approach was used to estimate the VSIP's for the manganese ions. Details of the method are outlined in the Appendix. VSIP's for nonintegral charges were obtained by interpolation.

The radial functions for the manganese 3d, 4s, and 4p orbitals were taken from Richardson's analytic expressions[13,20] of Watson's SCF functions.[12] The SCF functions for the oxygen 2s and 2p orbitals were the same as those employed by Ballhausen and Gray.[9] Overlaps were computer calculated by means of the expressions given by Loftus.[21]

Both the overlap integrals and the VSIP's used to estimate the H_{ii} terms were sensitive to the assumed charges on the ions. As previously mentioned, it was required that the assumed charge and the final charge calculated from electron population analysis be the same.

A feature of the B and L energy level scheme offered a unique opportunity to study the effects of F_σ and F_π. According to their assignment, the first absorption maximum in permanganate should be due to an electron transition from the t_1 nonbonding π-orbitals on the ligands to the e* antibonding π-orbitals. The energies of these two orbitals depend only on the assumed charge and the value of F_π and are independent of F_σ and θ. Thus, for a given charge, F_π was fixed by the transition energy, 18,500 cm.$^{-1}$.

For chosen values of F_σ and θ, one then obtained the relation between the assumed charges on the manganese to that calculated by electron population analysis of the resultant energy levels. This quickly established the self-consistent charge. Calculations were made for values of θ equal to 0, 2.5, 5.0, 10.0, 20.0, 22.0, 30.0, and 45.0°. F_σ was varied between 1.00 and 3.00.

Similar calculations were made in which the W and H order was presumed to be valid. The data for the two sets were analyzed and in each case the best fit to the permanganate spectrum was chosen. It was then presumed that the values of θ, F_σ, and F_π would be unchanged in the sequence MnO_4^-, MnO_4^{-2}, and MnO_4^{-3}. Of course, the additional electrons in the manganate and hypomanganate affected the VSIP relations between the manganese and oxygens as well as the electron distribution. The resultant energy levels were then used to predict transition energies and these were compared with experimental values.

Oscillator strengths for the various electric dipole transitions were calculated by standard techniques.[22] These were compared to the tabulated values.[4]

In addition to the methods previously described, a set of computations was made which employed the exact technique given by Ballhausen and Gray.[9] F_σ and F_π were fixed at 2.00; θ was set at 22, 30, 33, and 45°; the VSIP's were made to vary as a function of the electron configuration as well as the charge on the central ion; and self-consistency between the charge distribution of the starting configuration and that calculated from electron population analysis was required.

Results and Discussion

Transition Energies.—In terms of the method suggested by Ballhausen and Gray,[9] the energy levels should be completely specified by $F_\sigma = F_\pi = 2.00$, $\theta = 22°$, and the self-consistent charge. Had such a calculation given reasonable results, further studies would have been superfluous. As seen from column 2 of Table II, the desired results were not achieved. Not only are the possible transition energies too high, but the order of the levels is not in accord with the B and L assignment. This is indicated by the fact that the calculated $t_1 \rightarrow e^*$ transition is greater than the $t_1 \rightarrow t_2(3)$ transition.

TABLE II

CALCULATED TRANSITION ENERGIES FOR PERMANGANATE, WITH $F_\sigma = F_\pi = 2.00$, AND SELF-CONSISTENCY BETWEEN THE INITIAL AND FINAL CHARGES

	Transition energies, 10^3 cm.$^{-1}$			
	B and G method[a]	Present work		
Transition	$\theta = 22°$	$\theta = 22°$	$\theta = 33°$	$\theta = 45°$
$t_1 \rightarrow e^*$	42.5	44.0	42.2	40.6
$t_1 \rightarrow t_2(3)$	38.5	40.2	44.2	44.7
$t_2(2) \rightarrow e^*$	50.9	52.9	54.5	55.6
$t_2(2) \rightarrow t_2(3)$	46.9	49.1	56.5	59.7
Self-consistent charge	+0.40	+0.40	+0.43	+0.47

Experimental transition energies = 18,300, (28,000), 32,200

[a] Results by the method employed by Ballhausen and Gray.[9]

Table II also illustrates the general result that the method for VSIP determination used by Ballhausen and Gray[9] and that employed for the major portion of this study yield very similar results. Inclusion of higher configurations, such as d^5sp, in the Ballhausen and Gray method tends to increase the VSIP values. A similar effect is obtained in this work by the consideration that in the molecular orbital the spin state of the electrons associated with a given atom will not be that of highest multiplicity but rather will be that linear combination of free atom states which corresponds to the valence state configuration.

A detailed analysis of the many computations has brought to light several interesting features. For example, the value of the self-consistent charge is dependent upon θ, the hybridization parameter, but is essentially independent of the values of F_σ and F_π.

The relative insensitivity of the charge as calculated

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[19] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[20] J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, **38**, 796 (1963).

[21] A. Loftus, *J. Mol. Phys.*, **5**, 105 (1962).

[22] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 170.

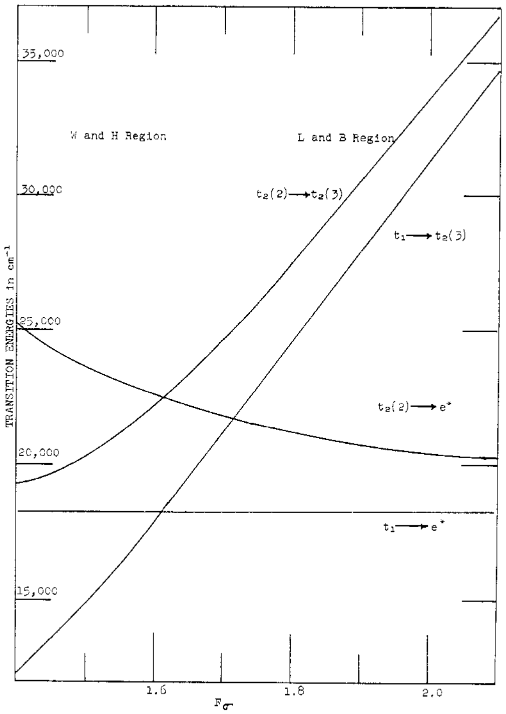

Fig. 5.—Permanganate transition energies: $\theta = 22°$, $F_\pi = 1.48$, charge = self-consistent.

by Mulliken's population analysis to the F parameters is to be expected in those instances where the values of H_{ii} and H_{jj} are nearly equal. In fact, for a determinant of order two, it can be readily shown that under the assumptions of the method, the fractional charge is independent of F when $H_{ii} = H_{jj}$. As the actual values come close to this identity, the influence of F on the fractional charge diminishes. This is precisely the situation with regard to the permanganate levels. Furthermore, since the hybridization parameter affects the position of H_{ii} relative to H_{jj}, its value should influence the calculated fractional charge.

The self-consistent charge on the manganese in permanganate ranged from $+0.37$ for $\theta = 0°$, to $+0.48$ for $\theta = 45°$. Such results are in keeping with Pauling's electroneutrality principle.[23]

A significant result of this study is that the ordering of the levels is extremely sensitive to the values of the H_{ij} terms in the secular determinant. Whether one obtains the W and H order or that given by B and L depends on the chosen values of F_σ, F_π, and θ.

For $F_\sigma = F_\pi = 2.00$, the W and H order is always obtained with $\theta < 27°$ while the B and L order results for all values of $\theta > 27°$. As θ is increased, the values of the σ-bonding overlap integral, $G_{T_2}(d,\sigma)$, increase since the d–σ_s overlap is greater than the d–σ_p overlap. But of equal significance is the increase in the value of H_{ij} as more s character is introduced in the hybrid orbital. Since $H_{ij} = FG_{ij}\sqrt{H_{ii}H_{jj}}$, the two increases reinforce one another and consequently have a strong effect on the $t_2(3)$ level. The value of the e* level is indirectly affected by the change in θ by virtue of its effect on the self-consistent charge, which in turn dictates the H_{ii} and H_{jj} values used in the calculation.

The combined effects of these factors can be seen by comparison of columns 3, 4, and 5 in Table II. The $t_1 \rightarrow e^*$ transition energies decrease from 22 to 45°, while the $t_1 \rightarrow t_2(3)$ transition energies increase. It should also be noted that in all cases the transition energies are much greater than the experimental values.

Further illustration of the sensitivity of the antibonding levels to the values of the H_{ij} terms can be obtained by examination of the trends in the energy levels as a function of an F parameter. In Fig. 5, the energies of allowed transitions in permanganate are plotted as a function of F_σ. For these calculations θ was set at 22° and F_π was adjusted such that the $t_1 \rightarrow e^*$ transition energy would correspond to the first absorption maximum in permanganate.

The results indicate that for $\theta = 22°$ the W and H ordering will always be obtained when $F_\sigma = F_\pi$. Furthermore, it is apparent that any desired ordering of the levels, together with transition energies that will correspond to experimental values, can be achieved by adjustment of the F_σ and F_π values.

Obviously, freedom to vary F_σ and F_π is undesirable as a standard technique. But in view of the arbitrary choice of these parameters and the previously mentioned results by Tanabe and Sugano,[18] calculations at several values of θ were carried out and adjustments of F_σ and F_π were made to achieve the best possible spectral correlation with MnO_4^- for both the B and L and W and H energy level assignments. The same values of θ, F_σ, and F_π were then used to evaluate the energy levels in MnO_4^{-2} and MnO_4^{-3}.

Reasonable correlation with the three spectra within the framework of the B and L ordering has been obtained for various combinations of θ, F_σ, and F_π. Since all the results displayed similar advantages and limitations, only those obtained for $\theta = 22°$, $F_\sigma = 1.90$, and $F_\pi = 1.48$ are reported here. The resultant energy levels, labeled with those allowed transitions whose energies fall within the observable range of the spectrophotometer, are given in Fig. 6. The agreement with the experimental absorptions is shown in Fig. 2, 3, and 4, in which the transitions in accord with the B and L assignment are labeled numerically. When one considers the approximations involved in the calculations, the agreement appears to be quite good.

Several aspects of the results are noteworthy. The decrease in energy of the $t_1 \rightarrow e^*$ transition as one proceeds through the series correlates well with the observed positions of the first absorption maximum and tends to support the Carrington and Schonland[4] assignment. The values of the $t_1 \rightarrow t_2(3)$ transition decrease even more sharply and suggest that the second absorption maximum in hypomanganate has its origin in transitions to the $t_2(4)$ energy level. This level roughly corresponds to the 4p orbital on the manganese. Such a possibility was overlooked in the previous transition assignment.[4]

Gratifying as the results are, they have some serious

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(23) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 172.

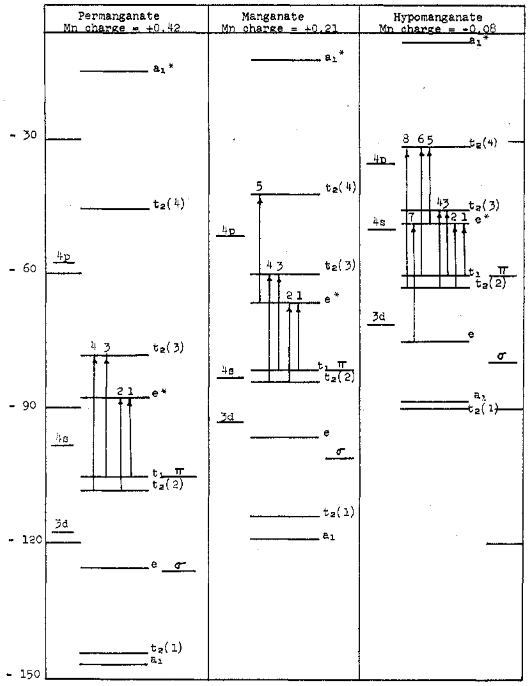

Fig. 6.—Theoretical energy levels, Ballhausen and Liehr ordering: $\theta = 22°$, $F_\sigma = 1.90$, $F_\pi = 1.48$.

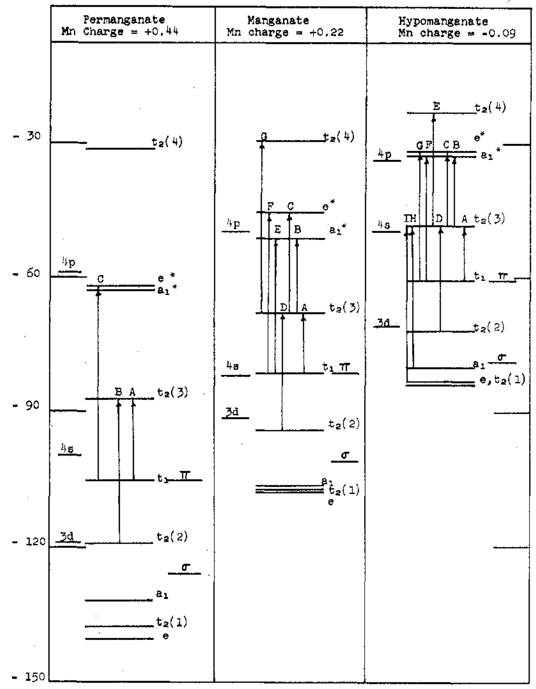

Fig. 7.—Theoretical energy levels, Wolfsberg and Helmholz ordering: $\theta = 22°$, $F_\sigma = 1.44$, $F_\pi = 2.20$.

limitations. In permanganate, it is impossible to account for the shoulder on the very intense band just prior to the limit of the spectrophotometer. In manganate, the absorption maxima at 28,490 and 33,440 cm.$^{-1}$ can be explained only in terms of the same transition, $t_1 \rightarrow t_2(3)$, used for the maximum at 22,940 cm.$^{-1}$. That is, one must then accept the Carrington and Schonland hypothesis that the transition gives rise to eight allowed excited states some of which differ sufficiently in their electrostatic interaction terms to result in three separate peaks. Furthermore, the $e^* \rightarrow t_2(3)$ transition which is possible in MnO_4^{-2} and MnO_4^{-3} cannot be found experimentally at the low transition energies predicted by the energy level diagram in Fig. 6. Finally, major discrepancies arise in the calculation of theoretical intensities of the absorption bands. The discussion of these latter results is deferred to a later section of this report in order to compare them with those obtained in connection with the W and H assignment.

It is possible to duplicate the W and H ordering of the energy levels for $\theta = 22°$ by adjustment of the F values. When F_σ and F_π are given values of 1.43 and 2.02, respectively, the resultant energy levels for the complexes are as indicated in Fig. 7. The correspondence between the allowed transitions and the experimental absorption maxima is indicated in Fig. 2, 3, and 4 by lines labeled alphabetically.

As indicated in Fig. 7, the self-consistent charges on the manganese in the three complexes are very close to those obtained for the B and L ordering. This further illustrates the relative independence of the charge from the F_σ and F_π values.

In terms of spectral correlation, the W and H assignment offers several improvements over that given by the B and L ordering. In permanganate, the shoulder which could not be assigned from the B and L set is ascribed to the $t_1 \rightarrow e^*$ transition. This same transition in manganate makes it unnecessary to resort to electrostatic interaction differences to interpret the absorption maximum at 33,400 cm.$^{-1}$. Similarly the maximum at 28,490 cm.$^{-1}$ can be assigned to the $t_2(2) \rightarrow t_2(3)$ and/or $t_1 \rightarrow a_1^*$ transitions.

Several of the transitions in the W and H assignment which do not appear to correlate well with the experimental results can be easily rationalized to give improved agreement. Specifically, the $t_1 \rightarrow t_2(3)$ transitions in manganate and hypomanganate, labeled "A" in both cases, have predicted energies below the observed maxima. But if one considers that the $t_2(3)$ orbital is occupied by one or two electrons in these complexes whereas in permanganate the orbital is empty, energy in addition to that indicated by the level separations would be required and the experimental energy should be somewhat higher. The same argument could be applied to the "D" transition in hypomanganate, $t_2(2) \rightarrow t_2(3)$, and its location in the valley between the peaks could be rationalized away.

The significance of this is that on the basis of the energetics of the absorption spectra *either assignment could be justified.* In fact, were it not for the e.s.r. substantiation of the B and L ordering, one would be prone to accept the W and H assignment as giving better agreement. This choice is enhanced by calculations of the theoretical intensities of the transitions.

Intensity Calculations.—To simplify the discussion of intensities, only the permanganate spectrum will be considered. Analogous considerations apply to manganate and hypomanganate with similar results.

TABLE III

TRANSITION DIPOLE MATRIX ELEMENTS FOR MnO_4^-

Transitions	Dipole strength	Matrix elements[a]	Numerical form at 3.0 a.u.
$t_1 \rightarrow e^*$	$24A^2/N_e^2$	$A = 2\langle\pi_1\|y\|d_{x^2-y^2}\rangle + \gamma R/2\sqrt{3}$	$A = 0.160 + 0.866\gamma$
$t_1 \rightarrow t_2(3)$	$12B^2/N_{t_2}^2$	$B = 2\langle\pi_1\|y\|d_{xy}\rangle + \gamma R/2$	$B = 0.320 + 1.5\gamma$

$$\psi_{t_1} = \psi(\text{ligand})$$
$$\psi_e = 1/N_e[\psi(3d) + \gamma\psi(\text{ligand})]$$
$$\psi_{t_2} = 1/N_{t_2}[\psi(3d) + \alpha\psi(4p) + \beta\psi_\sigma(\text{ligand}) + \gamma\psi_\pi(\text{ligand})]$$

[a] In the matrix elements, π_1 is the $2P_y$ wave function on the oxygen ligand, y is the component of the dipole vector $\vec{r}$, the d functions are the appropriate orbitals on the central metal. See ref. 3.

The theoretical expression for the oscillator strength, f, of an electric dipole transition is given by

$$f = (1.085 \times 10^{11}\ \text{cm.}^{-1})(\nu)(D)$$

where ν is the frequency of the band in cm.$^{-1}$ and D, in cm.^{2}, is the "dipole strength" defined by

$$D = \text{av}_{\text{I}} \sum_{\text{II}} |\int \psi_{\text{I}} \vec{r} \psi_{\text{II}} d\tau|^2$$

ψ_{I} and ψ_{II} are the wave functions for the initial and final states, respectively; $\vec{r}$ is the "dipole vector." As indicated, the dipole matrix element is summed over the excited states and averaged over the initial states.[22]

From the energy diagrams in Fig. 6 and 7, it is seen that the pertinent transitions are from the t_1 and $t_2(2)$ orbitals to the e^* and $t_2(3)$ orbitals. The general expressions of dipole strengths for transitions from the t_1 orbital are given in Table III. These were chosen as illustrations because they are simpler in form than those which involve transitions from the $t_2(2)$ orbital.

It is important to recognize that the matrix elements, A and B in Table III, are composed of two terms. The first involves true charge transfer: *e.g.*, for A, π_1 is the expression for the ligand orbital; $d_{x^2-y^2}$ is the orbital on the central metal. The second term corresponds to the electron in the ligand t_1 orbital going to that portion of the molecular orbital e^* which is also on the ligand, that is, a ligand orbital–ligand orbital transition. When the wave functions are expressed as in Table III, this second term depends on γ, the coefficient of the ligand portion of the e^* orbital, and R, the metal–ligand internuclear distance. Upon evaluation of the terms with the appropriate wave functions at an internuclear distance of 3.0 atomic units (1.6 Å.), one obtains the numerical forms given in Table III. Since γ is a negative number in the antibonding e orbital, the two terms compete with one another for dominance. As is obvious from the numerical forms, relatively small amounts of ligand character in the e^* and $t_2(3)$ wave functions will make the second term the more significant of the two.

The importance of this ligand orbital–ligand orbital transfer was first indicated by Carrington and Schonland.[4] By assuming the B and L assignment to be correct and that the first term is much smaller than the second, they calculated what the ligand character of the e^* and $t_2(3)$ orbitals should be to obtain agreement with the experimental intensities. In the original B and L assignment based on intensities, just the reverse assumption was made, that is, B and L inadvertently[24] neglected the second term. Table III indicates that neither term should be ignored.

The coefficients for the contributions of the metal and ligand atomic orbitals to the molecular orbitals are readily calculated for the pertinent energy levels. The theoretical intensities, which are calculated by incorporation of these coefficients into the general expressions, are given in Table IV.

TABLE IV

PERMANGANATE TRANSITION DIPOLE STRENGTHS

Transition	Dipole strengths × 10^{17} (in cm.^{2})			
	B and L[a]	Exptl.[b]	W and H[c]	Exptl.[b]
$t_1 \rightarrow e^*$	30.97	1.62	. . .	. .
$t_2(2) \rightarrow e^*$	23.94			
$t_1 \rightarrow t_2(3)$	5.71	2.02	9.44	1.62
$t_2(2) \rightarrow t_2(3)$	8.12		29.68	2.02

[a] Theoretical dipole strengths for the transitions predicted by the results in accord with the Ballhausen and Liehr[3] ordering of the energy levels. [b] Experimental dipole strengths. [c] Theoretical dipole strengths for the transition in accord with the Wolfsberg and Helmholz[2] ordering of the energy levels.

While one should not expect perfect agreement in these cases, the results leave much to be desired. In the B and L assignment, not only do the combined transitions to the e^* level predict an intensity which is 34 times the experimental result, but the calculations indicate the first peak should be more intense than the second while the reverse is actually true. The large intensities predicted for the transitions reflect the appreciable ligand character in the calculated e^* molecular orbital. The ligand–ligand term in the dipole strength matrix element predominates.

The ligand character of the e^* orbital, like the self-consistent charge, is relatively insensitive to the F parameters. In fact, it is the self-consistent charge requirement that influences the degree of ligand participation. To obtain self-consistency in these complexes, it is necessary that the σ- and π-bonding orbitals have appreciable metal character. Hence the antibonding orbitals will automatically have a high degree of ligand character.

The W and H assignment also results in theoretical intensities which are too high. But in this case the second transition is predicted to be more intense than the first, in agreement with experiment.

Conclusions

Perhaps the most significant result of this work is the importance of the initial assumptions upon the final out-

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(24) A. D. Liehr, private communication.

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.*, $\text{VSIP}(\theta)/S(\theta)$ 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

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

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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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Received February 28, 1964

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

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

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