The Spectra and Electronic Structure of the Tetrahedral Ions MnO4 −, CrO4 −−, and ClO4 −

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The Spectra and Electronic Structure of the Tetrahedral Ions MnO4-, CrO4--, and ClO4-*†

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We have made use of a semiempirical treatment to calculate the energies of the molecular orbitals for the ground state and the first few excited states of permanganate, chromate, and perchlorate ions. The calculation of the excitation energies is in agreement with the qualitative features of the observed spectra, i.e., absorption in the far ultraviolet for ClO4-, two strong maxima in the visible or near ultraviolet for MnO4- and CrO4- with the chromate spectrum displaced toward higher energies. An approximate calculation of the relative f-values for the first transitions in CrO4- and MnO4- is also in agreement with experiment.

The data on the absorption spectra of permanganate ion in different crystalline fields is interpreted in terms of the symmetries of the excited states predicted by our calculations.

INTRODUCTION

IN the past twenty years the electronic structures of many organic molecules, particularly benzene and related compounds, have been discussed in terms of the molecular orbital and valence bond methods.[1] During the same period the structures of inorganic ions have been inferred from the bond distances;[2] a bond distance shorter than the sum of the conventional radii has been attributed to the resonance of double bonded structures with the single bonded or Lewis structure.
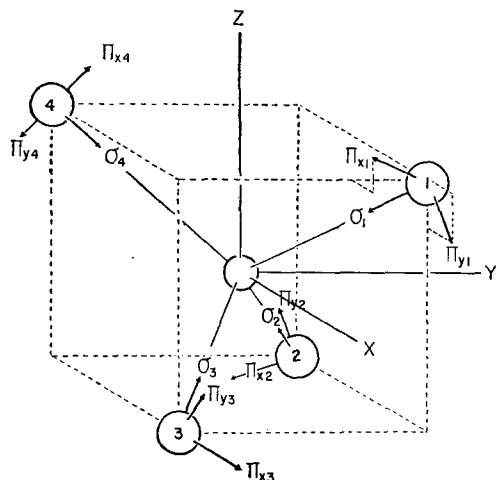

FIG. 1. Orientation of the orbitals. The orientation of the oxygen orbitals relative to the axes on the central atom is shown in this figure. The direction cosines of the O_1 orbitals are σ_1: $-1/3^{\frac{1}{2}}$, $-1/3^{\frac{1}{2}}$, $-1/3^{\frac{1}{2}}$; πx_1: $1/6^{\frac{1}{2}}$, $-2^{\frac{1}{2}}/3^{\frac{1}{2}}$, $1/6^{\frac{1}{2}}$; πy_1: $1/2^{\frac{1}{2}}$, 0, $-1/2^{\frac{1}{2}}$. The direction cosines of the other oxygen orbitals may be obtained from these by the action of the twofold axes of T_d, which coincide with the x, y, and z axes shown. The central atom orbitals are defined with respect to the axes on the central atom.

[1] For reference on both methods see R. S. Mulliken, J. chim. phys. 46, 497 (1949).

[2] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).

It has been shown[3], however, that this shortening need not necessarily be attributed to double bond formation. We hope to come to some conclusion concerning the bonding in inorganic molecules from molecular orbital calculations which can be checked against the observed spectra.

We have applied to inorganic complex ions a semiempirical method similar to that which has yielded significant results in the case of organic molecules and have chosen to treat permanganate, chromate, and perchlorate ions because the existing data[4] seem to afford the greatest number of tests of the correctness of the calculations.

The tetrahedral ions, $PO_4^{\equiv} SO_4^=$ and ClO_4^- show no near ultraviolet absorption whereas the ions, XO_4^-, of the fourth-row transition elements, which have the same number of valence electrons, show characteristic visible and near ultraviolet absorption, two strong maxima with the corresponding peaks displaced toward shorter wavelengths with decreasing atomic number of the central atom. This trend is also observed for the fifth- and sixth-row transition element compounds. A satisfactory theory must account for these differences and regularities.

The relative intensities of absorption calculated may be compared with those observed as an additional check of the method.

Data on the absorption of permanganate ion in different crystalline fields[4] indicate the existence of several excited states to which dipole transitions are forbidden in the absence of perturbing effects. The correlation of these data with the results of our calculations gives important evidence as to their correctness.

PROCEDURE

The molecular orbital method in its LCAO form is employed. We assume that the nonvalence shell electrons of X and O are unaffected by the bonding and that the X and O nuclei plus these inner shell electrons form an effective core into the field of which the mo-

[3] K. S. Pitzer, J. Am. Chem. Soc. 90, 2140 (1948).

[4] J. Teltow, Z. Phys. Chem. B43, 198 (1939); Z. Phys. Chem. B40, 397 (1938).

TABLE I. Molecular orbital combinations—XO₄, symmetry T_d.

X orbitals	O orbitals		Irreducible representations
s	$(\frac{1}{2})[\sigma_1+\sigma_2+\sigma_3+\sigma_4]$		A_1
d_{z^2}ᵃ		$(\frac{1}{4})[\pi_{x1}+\pi_{x2}+\pi_{x3}+\pi_{x4}-3^{\frac{1}{2}}(\pi_{y1}+\pi_{y2}+\pi_{y3}+\pi_{y4})]$	E
d_{x2-y2}		$(\frac{1}{4})[\pi_{y1}+\pi_{y2}+\pi_{y3}+\pi_{y4}+3^{\frac{1}{2}}(\pi_{x1}+\pi_{x2}+\pi_{x3}+\pi_{x4})]$	
p_x, d_{yz}	$(\frac{1}{2})[\sigma_1+\sigma_3-\sigma_2-\sigma_4]$	$(\frac{1}{4})[\pi_{x4}+\pi_{x2}-\pi_{x1}-\pi_{x3}+3^{\frac{1}{2}}(\pi_{y4}+\pi_{y2}-\pi_{y1}-\pi_{y3})]$	T_2
p_y, d_{xz}	$(\frac{1}{2})[\sigma_1+\sigma_2-\sigma_3-\sigma_4]$	$(\frac{1}{2})[\pi_{x1}+\pi_{x2}-\pi_{x3}-\pi_{x4}]$	
p_z, d_{xy}	$(\frac{1}{2})[\sigma_1+\sigma_4-\sigma_2-\sigma_3]$	$(\frac{1}{4})[\pi_{x3}+\pi_{x2}-\pi_{x1}-\pi_{x4}+3^{\frac{1}{2}}(\pi_{y4}+\pi_{y1}-\pi_{y2}-\pi_{y3})]$	
		$(\frac{1}{4})[\pi_{y2}+\pi_{y4}-\pi_{y3}-\pi_{y1}+3^{\frac{1}{2}}(\pi_{x1}+\pi_{x3}-\pi_{x2}-\pi_{x4})]$	T_1
		$\frac{1}{2}[\pi_{y1}+\pi_{y2}-\pi_{y3}-\pi_{y4}]$	
		$(\frac{1}{4})[\pi_{y2}+\pi_{y3}-\pi_{y1}-\pi_{y4}+3^{\frac{1}{2}}(\pi_{x2}+\pi_{x3}-\pi_{x1}-\pi_{x4})]$	

ᵃ The designation of the d-orbitals is that given by Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944). We have also used throughout the group theoretical symbolism which is essentially that of these same authors.

lecular electrons are to be placed. Thus we consider only the $3d$, $4s$, and $4p$ atomic orbitals of the central atoms ($3s$ and $3p$ in the case of Cl) and only the $2p$ atomic orbitals of the oxygen atoms in constructing the molecular orbitals. In the case of the molecule ions here discussed twenty-four electrons are to be placed in the molecular orbitals, the ground state being constructed by placing twenty-four electrons in the lowest-lying molecular orbitals.

In setting up molecular orbitals for a system possessing equivalent atomic orbitals on equivalent atoms one finds that the requirement that the individual molecular orbitals belong to irreducible representations of the point symmetry group of the system determines immediately the relative coefficients with which these equivalent orbitals enter into the final molecular orbitals. With the oxygen orbitals and X orbitals oriented as in Fig. 1, one finds by standard group theoretical methods[5] the irreducible representations to which the central atom orbitals belong and determines the appropriate linear combinations of oxygen orbitals transforming according to the same rows of the same irreducible representations as the central atom orbitals. The final results are shown in Table I. The sets of combinations of oxygen orbitals are considered normalized, the overlap of oxygen wave functions being neglected for the time being in view of the qualitative nature of our calculations.

The calculations of the molecular orbital energies ϵ (which we employ in the same manner as is usual in the semiempirical methods for organic molecules) and the evaluation of the coefficients of the atomic orbitals and sets of atomic orbitals in Table I in the final molecular orbital requires the solution of secular determinants (one for each irreducible representation) of the form $|H_{ij}-G_{ij}\epsilon|=0$, where H_{ij} has its usual meaning and G_{ij} is the group overlap integral to be further defined later. It is seen from Table I that this involves the solution of a quartic for the orbitals with symmetry T_2 and quadratics for the orbitals of symmetries E and A_1. The orbital of symmetry T_1 will be nonbonding and is fully determined by symmetry considerations.

The values of H_{ii} (the energy of an electron in the ith orbital in the field of the nuclear skeleton and the remaining valence electrons) have been used essentially as parameters in the solution of the equations for the case of chromate ion. The values were chosen not greatly different from the valence state ionization potentials[6] for Cr⁰ and estimated for oxygen from the ionization energies of some inorganic compounds in which the formal charge on oxygen has been estimated to be in the neighborhood of minus one-half. The values thus obtained were altered by trial and error to satisfy the following requirements: (1) the first and second excitation energies should be at least qualitatively correct and (2) the resulting charge distribution should lead to formal charges approximately those assumed in setting up the atomic orbital wave functions. The values of H_{ii} for permanganate were then obtained from the chromate values by varying them in accord with what seems reasonable chemically; the oxygen and central atom should be somewhat less negative and the values of H_{ii} should correspondingly decrease. The values assumed are shown in Fig. 2. For oxygen we have assigned $H_{\sigma\sigma}$ smaller values than $H_{\pi\pi}$ to take into account the fact that the σ-orbitals penetrate farther into the region of positive charge on the central atom. That this is not unreasonable is indicated by the results of a more exact calculation for the CO_2 molecule[7] in which the calculated $H_{\sigma\sigma}$ for the oxygen atoms was found to be considerably lower than for the $H_{\pi\pi}$.

The values of H_{ij} we have approximated by setting them proportional to the corresponding overlap integrals according to the following relation:

$$H_{ij}=F_xG(i,j)(H_{ii}+H_{jj})/2.$$

[5] E. Wigner, *Gruppen Theorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Friedr. Vieweg und Sohn, Braunschweig, 1931).

[6] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).
[7] J. F. Mulligan, J. Chem. Phys. **19**, 347 (1951).

The $G(i, j)$ are the "group overlap" integrals, for example:

$$\int 4s(X)\cdot\tfrac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)d\tau=GA_1(s, \sigma).$$

These may be obtained in terms of the simple σ and π diatomic overlaps[8] (S_{ij}) by expressing the central atom orbitals in terms of a linear combination of equivalent orbitals oriented relative to the axes on the oxygen atoms.

The relationship between the G_{ij} and S_{ij} is given in Table II and the values of G_{ij} for the three cases under discussion are given in Table III. The group overlap integrals calculated using wave functions derived by

FIG. 2. The calculated molecular orbital energies for $MnO_4{}^-$, $CrO_4{}^-$, and $ClO_4{}^-$.

the Slater formulas[9] were found to give results which could not be reconciled with experiment. In particular, the $GA_1(s, \sigma)$'s were so small that the first excited orbital was one of symmetry A_1. As will be seen later, this is in disagreement with the spectra. The Slater $2p$ and $3d$ atomic wave functions differ radically from the self-consistent field functions. We have therefore derived a general set of analytic atomic wave functions[10] which more closely approximates the existing self-consistent field functions and, with the exception of the

[8] For the system of coordinates used and general method see Mulliken, Rieke, Orloff, and Orloff, J. Chem. Phys. 17, 1248 (1949).

[9] J. C. Slater, Phys. Rev. 36, 57 (1930).

[10] The general form of these functions and a discussion of the method of obtaining them will be submitted for publication in the near future.

TABLE II.

$$GT_2(d, \sigma) = (2/\sqrt{3})S(d\sigma, p\sigma)$$
$$GT_2(d, \pi) = (2\sqrt{2}/\sqrt{3})S(d\pi, p\pi)$$
$$GT_2(p, \sigma) = (2/\sqrt{3})S(p\sigma, p\sigma)$$
$$GT_2(p, \pi) = -(2\sqrt{2}/\sqrt{3})S(p\pi, p\pi)$$
$$GE(d, \pi) = (2\sqrt{2}/\sqrt{3})S(d\pi, p\pi)$$
$$GA_1(s, \sigma) = 2S(s, p\sigma)$$

$(4p, x)$ overlaps, these functions have been used to calculate the values in Table III. The values of $GT_2(4p, \sigma)$ and $GT_2(4p, \pi)$ we have estimated from the calculations using Slater orbitals by varying the values in accordance with the trends observed in the $GT_2(3d, x)$ from $CrO_4{}^-$ to $MnO_4{}^-$. This is certainly a doubtful procedure but, since the omission of the $4p$ orbitals from the calculation entirely produces no qualitative change in the energy levels§ or the relative intensities, we do not feel that this approximation is serious for our present purposes. The values of F_x employed were $F_\sigma=1.67$ for σ overlaps and $F_\pi=2.00$ for π-overlaps. These values are in moderately good agreement with those found by us to give satisfactory results in making calculations of the energy levels of homonuclear diatomic molecules of first and second row elements. These values are $F_\sigma=1.6$, $F_\pi=1.87$.

With the simplifications outlined above the solution of the secular equations is straightforward and leads to the energies of the molecular orbitals illustrated in Fig. 2. The twenty-four valence electrons are to be placed in the orbitals of lowest energy. It is seen that there exist four t_2 orbitals (threefold degenerate) each capable of holding six electrons. The orbital $1t_2$‖ is strongly bonding and $2t_2$ slightly bonding while $3t_2$ and $4t_2$ are antibonding. In addition there are two e orbitals (twofold degenerate), $1e$ strongly bonding and $2e$ antibonding. The strong bonding of the $1e$ electrons is π-oxygen bonding with the central atom and may be considered as similar to the effect of double bonding in the simple valence bond treatment. It is to be remarked, however, that the stability of the $1e$ orbital as given by our calculations is much greater than is ordinarily attributed to the π-electrons in a double

TABLE III.

G	$MnO_4{}^-$	$CrO_4{}^-$	$ClO_4{}^-$
GT_2 (p, σ)	0.10	0.00	0.33
GT_2 (p, π)	-0.25	-0.20	-0.26
GT_2 (d, σ)	0.12	0.11	$\cdots$
GT_2 (d, π)	0.15	0.18	$\cdots$
GE (d, π)	0.26·	0.32	$\cdots$
GA_1 (s, σ)	0.28	0.27	0.56

§ The fact that the neglect of the $4p$ orbitals in the $CrO_4{}^-$ and $MnO_4{}^-$ cases lead to no qualitative change in the calculated orbital energies has led us to neglect also the $3d$ orbital in the $ClO_4{}^-$ calculation. For this case the $3p-3d$ separation is certainly greater than the $3d-4p$ separation in $MnO_4{}^-$ and $CrO_4{}^-$.

‖ We are using here a notation similar to that used in atomic structures, designating molecular orbitals of a given symmetry by numbers 1, 2, 3, etc., in order of increasing energy.

TABLE IV. Calculated and observed excitation energies.

| | MnO_4^- | | $CrO_4^=$ | | ClO_4^- | |
	Obs	Calc	Obs	Calc	Obs	Calc
1st transition	2.29 ev	1.68 ev	3.25 ev	2.42 ev	6 ev	5.23 ev
2nd transition	3.96	2.78	4.59	3.15	⋯	⋯

bond in the valence bond treatment.¶ There exist further two a_1 orbitals, one bonding ($1a_1$), and one antibonding ($2a_1$). Finally there is one nonbonding oxygen orbital, t_1 (threefold degenerate). Placing the twenty-four electrons in the lowest lying orbitals gives the ground state:

$$(1e)^4(1t_2)^6(1a_1)^2(2t_2)^6(t_1)^6 \text{ with symmetry } A_1.$$

RELATIVE EXCITATION ENERGIES

The first excited orbital has the symmetry T_2, and it is assumed that the first absorption maximum corresponds to the excitation of a nonbonding t_1 electron to the lowest-lying unfilled orbitals $3t_2$. Such an excitation

$$(1e)^4(1t_2)^6(1a_1)^2(2t_2)^6(t_1)^6 \rightarrow$$
$$(1e)^4(1t_2)^6(1a_1)^2(2t_2)^6(t_1)^5(3t_2)^1$$

gives rise to four states of symmetries A_2, E, T_1, and T_2 (both singlet and triplet states, of which only the singlet states are considered here since no spectral evidence of the triplet states has been found). For the symmetry T_d only the transitions $A_1 \rightarrow T_2$ are allowed for dipole radiation. Transitions to the other levels are forbidden in the absence of perturbing effects but are observable in the spectra of solid solutions of MnO_4^- in $KClO_4$, $NaClO_4$, etc., and will be discussed later in connection with these spectra.

The second excitation according to Fig. 2 should involve the excitation of an electron from the $2t_2$ orbital to the $3t_2$ orbital which is at least partially bonding. The resulting configuration,

$$(1e)^4(1t_2)^6(1a_1)^2(2t_2)^5(t_1)^6(3t_2)^1,$$

gives rise again to four states of symmetries A_1, E, T_1, and T_2. The second maximum characteristic of the MnO_4^- and $CrO_4^=$ spectra is accordingly attributed to the transition from the $^1A_1$ ground state to the $^1T_2$ state of this configuration. The existence of the states to which transitions are forbidden is not so clearly given in this case by the crystal absorption data because of the diffuseness of the spectra. The presence of a T_1 state, however, seems reasonably certain.

If the assumption is made that the energy absorbed in the transition $^1A_1 \rightarrow {}^1T_2$ is equal to the difference in energy of the final and initial molecular orbitals for the first transition, $\epsilon_{t_2} - \epsilon_{t_1}$, then the calculations show

¶ We have also computed molecular orbital combinations and group overlap integrals for symmetries D_{3h}, O_h, and D_{4h}. It again would appear that bonding between R atom orbitals and π-orbitals on X in compound-RX_n is of no small importance. Thus in predicting configurations of complex molecules one probably has to consider such bonding in addition to the usual single bonding.

qualitative agreement with the experimental data. This assumption is incorrect, and in more exact calculations terms of the type neglected here have been shown to be far from negligible. The correct expressions for the energies of the transitions involving the excitation of a t_1 electron to the $3t_2$ orbital are given in the appendix.

Table IV shows the calculated and observed energies of transition in the three ions considered here, and it is seen that the first absorption by ClO_4^- lies well into the ultraviolet and MnO_4^- and $CrO_4^=$ show two maxima in the visible and near ultraviolet. The rather surprising quantitative agreement probably arises from the empirical nature of our calculations. This agreement can be improved by changes in the values of the H_{ii}'s and the F_x's, but these changes are limited severely by the requirement that the intensities of absorption be given correctly.

INTENSITIES OF ABSORPTION

Evaluation of the transition moments has been carried out for the allowed transitions neglecting all integrals except those over the same atom. The results can be given in terms of the coefficients of the various atomic orbitals making up the molecular orbitals involved. The f-value (oscillator strength) for the first transition is found (with the above assumptions) to depend on the coefficients of the π-combination in the $3t_2$ orbitals and is

$$f_{t_1 \rightarrow 3t_2} = (8\pi^2 mc\nu/3h)3S^2h^2,$$

where S is the projection of the $X-O$ bond on the x or y or z axis (see Fig. 1) and h is the coefficient of the π-combination in the excited state, ν is the average frequency (observed wave number) in the absorption band. The observed f-values for this first transition are $f(MnO_4^-) = 0.032$ and $f(CrO_4^=) = 0.089$; those calculated are 0.076 and 0.22, respectively. Of more significance for our qualitative calculations, perhaps, is the ratio of $f(MnO_4^-)/f(CrO_4^=)$, which is calculated to be 2.62 and observed 2.9. The ratio of the f-values of the
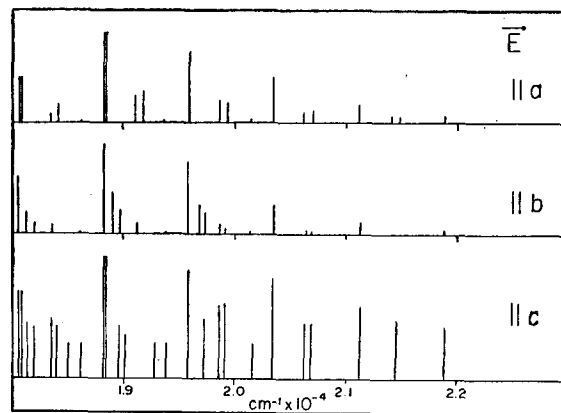

FIG. 3. The portion of the spectrum of permanganate ion dissolved in $KClO_4$ corresponding to the first allowed transition. The position and relative intensities only are indicated.

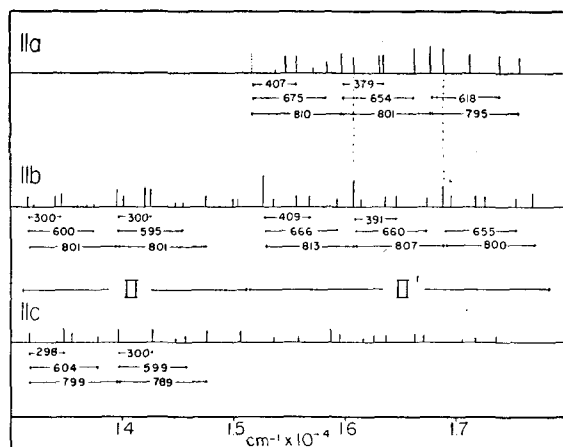FIG. 4. The spectrum of permanganate ion dissolved in NaClO₄ in the region corresponding to forbidden transitions. The dotted line in the spectrum parallel to a is the assumed position of the vibrationless transition A_1-A_1 (of E). The indicated separations were obtained by measuring a similar diagram given by Teltow and are consequently subject to considerable error.

first and second transitions can also readily be calculated with the same assumptions as above and the neglect of the central atom integrals. The ratio is calculated 1.17 for permanganate and observed 1.99. The results for chromate are qualitatively in error giving 0.71 calculated and 1.20 observed.

SPECTRA OF MnO₄⁻ IN DIFFERENT SOLID SOLUTIONS

Potassium permanganate and potassium perchlorate are isomorphous with very nearly the same unit cell dimensions. It should be possible therefore to dissolve appreciable amounts of MnO_4^- in the perchlorate lattice without great distortion. The site symmetry of the perchlorate (permanganate) ions in this lattice is C_s, that is, of all the symmetry elements of the free MnO_4^- ion the only one remaining in the solid solution is a plane of symmetry which lies perpendicular to the b axis of the crystal. In this environment the T_2 state should be completely split into two A' states and one A'' state of symmetry C_s. The transition $A'\rightarrow A'$ is allowed with the electric vector parallel to the $a-c$ plane and the transition $A'\rightarrow A''$ with the electric vector perpendicular to this plane, that is, parallel to the b axis. The portion of the spectrum of permanganate involving the first allowed transition is shown in Fig. 3. With E parallel to a and c axes one observes doublets with a splitting of about 30 cm⁻¹ which one would expect from a slightly perturbed T_2 state in symmetry C_s. With the electric vector parallel to b one finds, again in agreement with prediction, single lines. The relatively large f-value for this absorption indicates that it is probably an allowed transition $^1A_1\rightarrow^1T_2$. The splitting of the level in the field of symmetry C_s renders this conclusion almost certain.

Of greater interest for our purposes is a discussion of the portion of the spectrum corresponding to the lower

energy forbidden transitions of MnO_4^-. A calculation of the relative energies of the states arising from the configuration $(e)^4(1t_1)^6(2t_2)^6(1a_1)^2(t_1)^5(3t_2)^1$ has been carried out (see Appendix), again, as in the calculation of f-values, with the neglect of all integrals except those over the same atom. This calculation gives the energies of the states in the order of increasing energy A_2, E, T_1, and T_2. One should accordingly expect to find evidence of transitions to the A_2, E, and T_1 states on the long wavelength side of the first strong absorption maximum.

This region of the spectrum for MnO_4^- dissolved in anhydrous $NaClO_4$ is shown in Fig. 4. The site symmetry of the tetrahedral ions in this lattice is C_{2v}. The degenerate levels should be completely split in this symmetry, the symmetries of the resulting states (in C_{2v}) and the polarization of the transitions rendered allowed by the perturbation are given in Table V. As indicated in this table a T_1 state in a field of symmetry C_{2v} should show absorption with electric vector parallel to the b and c axes, for an E state absorption with electric vector parallel to the a axis, the direction of the twofold axis at position of the ion. The spectrum in the region II (Teltow's designation) corresponds precisely to what one would expect from a T_1 state.**

There is no way of regarding the region designated by II' as a continuation of the bands II. The strong absorption with E parallel to a would (Table V) then correspond to a transition A_1 of $C_{2v}\rightarrow A_1(C_{2v})$ arising from an E state of T_d. In order to classify the spectra it is necessary to assume that the vibrationless transition $A_1\rightarrow A_1$ (of E) does not appear. This is a phe-

TABLE V. Only the transitions of importance to our calculations are listed in the table. Transitions from the A_1 ground state. The polarizations are given relative to the crystal axes of the indicated structures.

T_d	C_s (KClO₄)	Allowed transitions	polarization
A_1	A'		
A_2	A''		
E	$A'+A''$	$A'-A'$	$\| a, \| c$
T_1	$A''+A''+A'$	$A'-A''$	$\| b$
T_2	$A''+A'+A'$		
	C_{2v} (NaClO₄)		
A_1	A_1	A_1-A_1	$\| a$
A_2	A_2		
E	A_1+A_2	A_1-A_2	forbidden
T_1	$A_2+B_1+B_2$	A_1-B_1	$\| b$
T_2	$A_1+B_1+B_2$	A_1-B_2	$\| c$
	C_{3v} (LiClO₄)		
A_1	A_1		
A_2	A_2		
E	E	A_1-A_1	$\| c$
T_1	A_2+E	A_1-A_2	forbidden
T_2	A_1+E		
		A_1-E	$\| c$

** The a and b axes given in Fig. 4 are the b and a axes given by Teltow. He expressed doubt as to the correct assignment of axes and gave the axes in terms of the optical axes of the crystal. Because of the suggestion contained in our calculations we have correlated x-ray pictures with the optical constants and have found that, indeed, Teltow's a and b axes should be interchanged. For assistance with this work we are indebted to Professor A. F. Fredrickson of the geology department of Washington University.

TABLE VI.

(cm^{-1})	I	Obs		Calc		Transition
		E	Tr	E	T$_1$	
∥ b 14,446	0.5	0		0		$A'-A''(E)$
14,526	0.3	80		80ᵃ		$-A''(E) +v_0^1$
14,592	0.2	146		151ᵃ		$-A''(E) +v_0^2$
14,681	0.05		0		0	$-A''(T_1)$
14,844	0.2	398		...		$-A''(E) +v_2(E)$ᵇ
15,172	0.3		491		...	$-A''(T_1) +v_4(T_2)$
15,246	0.9	800		...		$-A''(E) +v_1(A_1)$
15,324	1.0	878		880		$-A''(E) +v_1(A_1) +v_0^1$
15,472	0.2		791		...	$-A''(T_1) +v_1(A_1)$
15,620	0.2	1174		1198		$-A''(E) +v_1(A_1) +v_2(E)$
15,958	0.2		1277		1282	$-A''(T_1) +v_1(A_1) +v_4(T_2)$
16,049	1.0	1603		1600		$-A''(E) +2v_1(A_1)$
16,117	1.0	1671		1680		$-A''(E) +2v_1(A_1) +v_0^1$
16,256	0.2		1575		1582	$-A''(T_1) +2v_1(A_1)$
16,860	0.5	2414		2440		$\begin{cases} A''(E) +3v_1(A_1) \\ A''(E) +3v_1(A_1) +v_0^1 \end{cases}$
∥ a 14,460	0.0	0		0		$-A'(E)$
14,567	0.1	107		80		$-A'(E) +v_0^1$
14,632	0.2	172		151		$-A'(E) +v_0^2$
14,670	0.0		0		0	$-A'(T_1)$
14,793	0.15		123		151	$-A'(T_1) +v_0^2$
15,002	0.15	542		491		$-A'(E) +v_4(T_2)$
15,538	0.6		868		867	$\begin{cases} A'(T_1) +v_1(A_1) \\ A'(T_1) +v_1(A_1) +v_0^2 \end{cases}$
15,793	0.1	1333		1291		$-A'(E) +v_1(A_1) +v_4(T_2)$
16,320	0.6		1650		1658	$-\begin{cases} A'(T_1) +2v_1(A_1) \\ A'(T_1) +2v_1(A_1) +v_0^2 \end{cases}$
17,078	0.4		2408		2449	$-\begin{cases} A'(T_1) +3v_1(A_1) \\ A'(T_1) +3v_1(A_1) +v_0^2 \end{cases}$
∥ c 14,460	0.0	0		0		$A'-A'(E)$
14,605	0.1	145		151		$-A'(E) +v_0^2$
14,670	0.0		0		0	$-A'(T_1)$
14,705	0.1		35		80	$-A'(T_1) +v_0^1$
14,962	0.06	502		491		$-A'(E) +v_4(T_2)$
15,260	0.3	800		800		$-A'(E) +v_1(A_1)$
15,342	0.2	882		880		$-A'(E) +v_1(A_1) +v_0^1$
15,460	0.4		790		791	$-A'(T_1) +v_1(A_1)$
15,640	0.2	1180		1198		$-A'(E) +v_1(A_1) +v_2(E)$
16,051	0.5	1591		1600		$-A'(E) +2v_1(A_1)$
16,138	0.3	1678		1680		$-A'(E) +2v_1(A_1) +v_0^1$
16,252	0.6		1582		1582	$-A'(T_1) +2v_1(A_1)$
16,402	0.2	1942		1998		$-A'(E) +2v_1(A_1) +v_2(E)$
16,900	0.5	2440		2440		$-\begin{cases} A'(E) +3v_1(A_1) \\ A'(E) +3v_1(A_1) +v_0^1 \end{cases}$

ᵃ v_0^1 and v_0^2 are assumed to be lattice frequencies and are taken from the $^1A_1 \rightarrow {}^1T_2$ spectrum.
ᵇ $v_2(X)$ indicates the frequency of the vibration of the tetrahedral ion of symmetry X. The designations are those given by Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand and Company, Inc., New York, 1945), p. 100.

nomenon which is met within all the forbidden transitions in different crystalline fields and one for which we have no explanation. The weakest point in the above argument is the strong absorption parallel to b in the region II'. With the assumption mentioned above the spectra can be ordered, and it is seen that the strong absorptions parallel to b coincide (as indicated by the dotted lines) with lines parallel to a which correspond to transitions $A_1 \rightarrow A_1$ (in C_{2v})+lattice vibrations. The lattice perturbations in NaClO$_4$ are certainly large compared to those in KClO$_4$ as may be seen from the splitting of the T_2 state (200 cm^{-1}) and it is perhaps not unreasonable to assume that this large perturbation is responsible for the large intensity of absorption parallel to b in the region II'. The intensity of absorption generally in this region is of the order of five times that in the region II. The difference between the characteristic vibrational intervals in the two regions offers additional evidence that they correspond to transitions to different states.

The ratio of the intensities of the forbidden transitions to those allowed is roughly five times as great in the case of NaClO$_4$ solid solutions as in the case of KClO$_4$ indicating again that the perturbation is greater in the former case causing a greater mixing of the T_2 wave functions with the E and T_1 functions allowed in C_{2v}.

In the KClO$_4$ lattice the site symmetry of the tetrahedral ions is C_s. The symmetries of the resulting states and the directions of polarization of the allowed transitions are shown in Table V. The spectrum shows one very sharp line (half-width 7 cm^{-1}) at the long wavelength extreme of the bands parallel to b. Close to this line there appear two lines, less sharp, which must be attributed to an electronic transition accompanied by the excitation of a lattice vibration since the intervals are too small to correspond to any frequencies of the ion even in an excited state. That this is so is also suggested by the fact that these same intervals occur in the allowed spectrum in which the vibrational frequencies are markedly different.

The sharp line at 14,446 cm^{-1} is attributed to a "vibrationless" transition from the A' ground state to the A'' (of C_s) state arising from E (of T_d) on the basis of the following argument: if this transition were $A' \rightarrow A''$ (of T_1 in T_d), one would expect to observe a doublet since T_1 splits into two A'' states in this symmetry; the splitting might well be small but should be observable because of the sharpness of the line. In the NaClO$_4$ lattice where the crystal perturbations are larger as indicated by the greater splitting of the T_2 level and the greater relative intensity of the forbidden spectrum relative to the allowed spectrum, the transitions to the states arising from E of T_d are five times as strong as those attributed to the A_1 to T_1 transition and in the absence of any evidence to the contrary it seems plausible to attribute a larger f-value to the $A_1 \rightarrow E$ transition.

No sharp lines appear when the electric vector is polarized parallel the $a-c$ plane. Internal consistency of all the crystal data demands that there exist at least one A' state in this solid solution; consequently, as mentioned above, it is assumed that the $A'-A'$ vibrationless transition is not observed. With this assumption one may classify the spectra in terms of the set of frequencies observed parallel to the b axis with the A' state arising from E occurring at 14460 cm^{-1}, 14 cm^{-1} from the A'' of E and an A' state arising from T_1 at 14,670 cm^{-1}, 11 cm^{-1} from the unresolved A'' states (from T_1 at 14,681 cm^{-1}). The results of such an analysis are given in Table VI. There is nothing unique about the assignment of frequencies given in Table VI. The table is given merely to indicate that the data may be accounted for in a relatively simple way and that the data which appeared to Teltow to be without regularity can be ordered in terms of the proposed scheme. Particularly is this true of the data in the sodium perchlorate solid solutions.

The spectra obtained in solid solutions LiCl(Mn)O₄ · 3H₂O are also compatible with the proposed assignment, showing sharp absorption perpendicular to the threefold axis of the crystal ($A_1 \rightarrow E$ transitions) and only weak and diffuse absorption parallel to the threefold axis which presumably arises from electronic transitions $A_1 \rightarrow E$ accompanied by vibrations.

The polarization data discussed above seem to show definitely that more than one level exists lower lying than the T_2 level, that one of these is probably T_1 and the other E. There is no evidence for either an A_2 or A_1 state, the data in LiCl(Mn)O₄ tending to rule out the A_1 state more definitely than the A_2 state. We feel therefore that these data lend strong evidence in favor of the correctness of the calculations which predict that the first transition involves the excitation of a t_1 electron to a t_2 orbital since this is the only transition which gives rise to the states which are compatible with the observations. A transition $t_2 \rightarrow t_2$ would also give E, T_1, and T_2 states but would in addition give an A_1 state which might be expected to show up in the spectra, particularly in solid solution in which the site symmetry is C_{3v}(LiClO₄·3H₂O, or Ba(ClO₄)₂·3H₂O).

CONCLUSIONS

The qualitative aspects of the spectra are given correctly by our empirical calculations and we feel that the electronic structure of the ions discussed is essentially correct. The interpretation of the bond distance in terms of "double bonding" is seen to have some justification in view of the importance of π-bonding between the central atom and oxygen atoms. In the case of the transition element compounds all five d orbitals and the $4s$ orbital are apparently employed in bonding whereas in ClO₄⁻ the $3d$ atomic orbitals would have very small coefficients in the bonding molecular orbitals in an approximate calculation. This would correspond to a more important contribution of "double bonding" in MnO₄⁻ and CrO₄⁻ than in ClO₄⁻, but the term double bond loses much of its meaning in these cases since the structure can only with difficulty be considered as resulting from the resonance of localized double bonds.

The quantitative agreement gives some hope that a similar treatment applied to more ions might enable us to formulate rules for the empirical estimation of the H_{ii}'s and thus give a very simple method of making molecular orbital calculations for inorganic molecules. The method outlined above has been applied to the ion CrO₃F⁻ with very satisfactory results both as to relative excitation energies and intensities. Calculations on CrO₂Cl₂ and SO₂Cl₂ are under way at the present time.

APPENDIX

The energies of the excited singlet states arising from the configuration $\cdots (t_1)^5 (3t_2)^1$ relative to the ground state are given below where

$$(\phi_x{}^{t_1}\phi_y{}^{t_2})(\phi_z{}^{t_1}\phi_w{}^{t_2})$$

$$= \int \phi_x{}^{t_1}(1)\phi_y{}^{t_2}(1)e^2/r_{12}\phi_z{}^{t_1}(2)\phi_w{}^{t_2}(2)dr_1dr_2$$

and $\phi_x{}^{t_1}$ is the xth orbital function of the degenerate nonbonding set of symmetry T_1 and $\phi_y{}^{t_2}$ is the yth orbital function of the set $3t_2$.

$$E \text{ (singlet } T_2) - E \text{ (singlet } A_1) = \epsilon \, (3t_2) - \epsilon \, (t_1)$$
$$-K + 2C + J - 2D$$

$$E \text{ (singlet } E) - E \text{ (singlet } A_1) = \epsilon \, (3t_2) - \epsilon \, (t_1)$$
$$-H + 2A - 2B + J$$

$$E \text{ (singlet } T_1) - E \text{ (singlet } A_1) = \epsilon \, (3t_2) - \epsilon \, (t_1)$$
$$-K + 2C - J + 2D$$

$$E \text{ (singlet } A_2) - E \text{ (singlet } A_1) = \epsilon \, (3t_2) - \epsilon \, (t_1)$$
$$-H + 2A + 4B - 2J$$

$$A = (\phi_1{}^{t_2}\phi_1{}^{t_1})(\phi_1{}^{t_2}\phi_1{}^{t_1}) = (\phi_i{}^{t_2}\phi_i{}^{t_1})(\phi_i{}^{t_2}\phi_i{}^{t_1})$$
$$B = (\phi_1{}^{t_2}\phi_1{}^{t_1})(\phi_2{}^{t_2}\phi_2{}^{t_1}) = (\phi_i{}^{t_2}\phi_i{}^{t_1})(\phi_j{}^{t_2}\phi_j{}^{t_1})$$
$$C = (\phi_1{}^{t_2}\phi_2{}^{t_1})(\phi_1{}^{t_2}\phi_2{}^{t_1}) = (\phi_i{}^{t_2}\phi_j{}^{t_1})(\phi_i{}^{t_2}\phi_j{}^{t_1})$$
$$D = (\phi_1{}^{t_2}\phi_2{}^{t_1})(\phi_2{}^{t_2}\phi_1{}^{t_1}) = (\phi_i{}^{t_2}\phi_j{}^{t_1})(\phi_i{}^{t_2}\phi_j{}^{t_1})$$
$$H = (\phi_1{}^{t_2}\phi_1{}^{t_2})(\phi_1{}^{t_1}\phi_1{}^{t_1}) = (\phi_i{}^{t_2}\phi_i{}^{t_2})(\phi_i{}^{t_1}\phi_i{}^{t_1})$$
$$J = (\phi_1{}^{t_2}\phi_2{}^{t_2})(\phi_1{}^{t_1}\phi_2{}^{t_1}) = (\phi_i{}^{t_2}\phi_j{}^{t_2})(\phi_i{}^{t_1}\phi_j{}^{t_1})$$
$$K = (\phi_1{}^{t_2}\phi_1{}^{t_2})(\phi_2{}^{t_1}\phi_2{}^{t_1}) = (\phi_i{}^{t_2}\phi_i{}^{t_2})(\phi_j{}^{t_1}\phi_j{}^{t_1}).$$