

Oscillator Strength Calculations for Permanganate Ion^{1a}BY BRANDON H. WIERS^{1b} AND WARREN L. REYNOLDS

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Expressions are derived for the dipole length and dipole velocity transition moments of tetrahedral MO₄ species for the low-energy transition ¹A₁ → ¹T₂ (t₁ → 2e) and all charge-transfer, one- and two-center ligand integrals are evaluated. It is shown that the one-center ligand integral gives the largest contribution to the dipole length transition moment and that the e_g charge-transfer integral gives the most important contribution to the dipole velocity transition moment. The dominance of the dipole length transition moment by the one-center ligand integral renders it rather insensitive to change of AO parameters and gives the result that the antibonding e MO is largely metal AO regardless of the state of ionization of the metal. The dominance of the dipole velocity transition moment by the charge-transfer integral renders it more sensitive to changes of AO parameters and leads to the conclusion that the antibonding e MO is principally ligand AO. A comparative analysis of these results is given, and the conclusion is reached that the dipole velocity transition moment is the more correct first approximation to use in the calculation of oscillator strengths.

Introduction

The first theoretical analysis of the electronic structure of tetraoxy anions of transition metals by Wolfsberg and Helmholz² dealt with two distinct aspects of the visible spectra of permanganate. First the authors calculated an energy level scheme, on the basis of which an assignment of the absorption bands was made, and, second, they derived expressions for the calculation of the oscillator strengths, *i.e.*, the intensities, of the bands. The results of both analyses were disputed in the second paper to deal with the electronic structure of tetraoxy anions, by Ballhausen and Liehr.³ These authors argued from intuitive crystal field considerations that the first, *i.e.*, the long-wavelength, absorption band of permanganate and related ions should arise from the transition ¹A₁ → ¹T₂ (t₁ → 2e). As for the oscillator strength calculation, it was assumed that the approximation used by Wolfsberg and Helmholz, *viz.*, that all two-center integrals were negligible compared to integrals over the same atom, was incorrect. By neglecting all integrals except the two-center charge-transfer integral, Ballhausen and Liehr calculated new values for the oscillator strengths and found rather better agreement with experiment. Shortly thereafter, electron spin resonance studies of manganate ion,⁴ MnO₄²⁻, were found to support the Ballhausen and Liehr assignment of the first band, by showing that the highest filled MO of this ion is of e symmetry (doubly degenerate). However, the electron spin resonance study left the assignment of the other bands unresolved. This produced the circumstance that the more recent papers⁵⁻⁷ discussing the calculation of energy levels

of permanganate have been concerned primarily with the validation of the assignment of the first band and with making correct assignments of the other bands, but somewhat secondarily with the other of the two problems first discussed by Wolfsberg and Helmholz. In this paper we therefore wish to focus exclusively on the calculation of the oscillator strength of the first permanganate band, found experimentally to be *f* = 0.032, with the aim of understanding past difficulties as well as of discovering a more satisfactory approach.

The numerical result of Ballhausen and Liehr, the first to be obtained on the basis of the t₁ → 2e assignment, was *f* = 0.27.⁸ Their assumption concerning which integrals could be neglected was subsequently shown, in an essentially formal analysis performed by Carrington and Schonland,⁹ to be unsound. These authors derived an expression for the magnitude of the theoretical transition moment, *Q*_{theoret}, having two terms. In the terminology used here (see later), their expression is

$$Q_{\text{theoret}} = 2\sqrt{2}\langle t_1^y | y | e_a \rangle = 2\sqrt{2}\lambda I - \frac{\sqrt{2}\mu R}{\sqrt{3}} \quad (1)$$

The factors λ and μ are the coefficients of the 3d_{z²-y²} and the ligand symmetry orbitals, respectively, *R* is the Mn-O bond length, and *I* is the charge-transfer integral, so-called because it is a two-center integral involving metal 3d and ligand 2p orbitals. The second term in (1) results from integration over a ligand 2p orbital only and differs from the result obtained in the original calculation of Wolfsberg and Helmholz merely by virtue of the geometric factor and the symmetry orbital coefficient which arise from the revised band assignment of Ballhausen and Liehr. Carrington and Schonland allowed that fair agreement between the calculated and observed oscillator strength for the t₁ → 2e transition could be obtained with orbital exponents close to those given by Slater's rules, such as were used by Ballhausen and Liehr, if the charge-transfer

(1) (a) Abstracted in part from the Ph.D. thesis of Brandon H. Wiers, University of Minnesota, 1964; (b) The Procter & Gamble Co., Miami Valley Laboratories, Cincinnati, Ohio 45239.

(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); **4**, 190 (1960).

(4) A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland, and M. C. R. Symons, *Proc. Roy. Soc. (London)*, **A264**, 101 (1960); D. S. Schonland, *ibid.*, **A264**, 111 (1960).

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

(b) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).

(6) G. V. Ionova and M. E. Dyatkina, *Zh. Strukt. Khim.*, **6**, 128 (1965).

(7) L. Oleari, G. de Michelis, and L. di Sipio, *Mol. Phys.*, **10**, 111 (1966).

(8) This value is obtained by multiplication of the originally published value by the factor of 6 stated to be missing in the Erratum (9).³

(9) A. Carrington and D. S. Schonland, *Mol. Phys.*, **3**, 331 (1960).

integral only were used, *i.e.*, if it were assumed that $\lambda = 1$ and $\mu = 0$. It was also pointed out, however, that these same orbital exponents give a group overlap integral, $G_E(d, \pi)$, of approximately 0.4 and that this is inconsistent with the neglect of the second term on the right-hand side of (1) since such pronounced overlap implies considerable ligand orbital participation in the complete MO. More recently, Fenske and Sweeney^{5a} used symmetry orbital coefficients they determined on the basis of a new energy level calculation and obtained a value for the oscillator strength of $f = 0.62$. This result and the earlier result³ both leave a great deal to be desired and they suggest that an examination be made of the basic theory of such calculations.

It is to be noted that, in the references cited heretofore, each of the investigators who calculated oscillator strengths used the dipole length operator. However, there is no *a priori* reason for the matrix elements of this operator yielding better results than the matrix elements of the so-called dipole velocity operator.¹⁰ Indeed, if exact eigenfunctions were being used, both operators would give identical results for the transition moments.¹¹ The approximate wave functions usually employed are LCAO-MO's, the AO's in the linear combinations usually being Slater-type orbitals (STO's) or self-consistent field atomic orbitals (SCF AO's). In either case, it is assumed that the distribution of an electron around a given atom in a given MO, though somewhat modified by overlap with neighboring atoms contributing to the same MO, is proportional to the distribution that the electron would have in the same AO on the given atom in its uncombined state. Thus, it might be supposed that the dipole velocity operator would be better to use for LCAO-MO's because this operator, compared to the dipole length operator, stresses the regions of space nearer an atom¹¹ where the electron distribution presumably resembles the electron distribution in the uncombined AO most closely. While this may be true for some systems and not for others, there nevertheless are two comparative calculations which appear to give better results when using the dipole velocity operator. For example, Ellison and Shull,¹² using the SCF MO's they derived for water, calculated dipole length and dipole velocity oscillator strengths with both the theoretical and experimental values of the energy of the transition and found that both dipole velocity oscillator strengths agreed with the experimental value within a factor of 2 whereas the dipole length oscillator strength was too small by approximately four orders of magnitude. Moscovitz,¹³ in calculations for benzene, also found that the dipole velocity results agreed better with experimental results than did the dipole length results. While these may easily have been fortuitous, we submit that such a comparison may prove fruitful for permanganate.

In the work reported here we have therefore calculated both dipole length and dipole velocity transition mo-

ments for various ionization states of manganese (1) using STO's for all atoms and (2) using STO's for the oxygen atoms but analytical wave functions for manganese given by Richardson, *et al.*,¹⁴ which closely approximate the SCF AO's¹⁵ of manganese. We also report the values of the mixing coefficient for the ligand orbital combination in the e bonding MO which give agreement between dipole length and experimental oscillator strengths and between dipole velocity and experimental oscillator strengths for various states of ionization of manganese. All one- and two-center integrals were evaluated including those between different oxygen atoms.

Results and Discussion

A coordinate system and numbering convention identical with that of Ballhausen and Liehr was used.³ Thus, the nonbonding orbitals which span the T_1 irreducible representation of the T_d point group are

$$t_1^x = \frac{1}{4}[\sqrt{3}(px_1 + px_2 - px_3 - px_4) + (py_1 + py_2 - py_3 - py_4)]$$

$$t_1^y = \frac{1}{4}[\sqrt{3}(px_1 - px_2 + px_3 - px_4) - (py_1 - py_2 + py_3 - py_4)]$$

$$t_1^z = \frac{1}{2}(py_1 + py_2 + py_3 + py_4)$$

and the 2e antibonding orbitals are

$$2e^a = \lambda d_{x^2-y^2} - \frac{\mu}{2}(py_1 - py_2 - py_3 + py_4)$$

$$2e^b = \lambda d_{z^2} - \frac{\mu}{2}(px_1 - px_2 - px_3 + px_4)$$

where px_i and py_i are the 2px and 2py AO's of the *i*th oxygen atom and $d_{x^2-y^2}$ and d_{z^2} are the 3d AO's of manganese. The coefficients λ and μ are related to the ligand mixing coefficients β as follows: $\lambda = \beta N_E$ and $\mu = N_E \sqrt{1 - \beta^2}$ where the normalization factor, N_E , is given by

$$N_E = [1 - 2\beta(1 - \beta^2)^{1/2}G_E(d, \pi)]^{-1/2}$$

and where $G_E(d, \pi)$ is the group overlap integral given by Wolfsberg and Helmholz as equal to $2\sqrt{2}S(2p\pi, 3d\pi)/\sqrt{3}$. In this expression for N_E we neglect the ligand-ligand overlap integrals which appear in the exact expression.^{5b} The sign preceding the ligand AO combination and the sign of the second term in N_E are reversed in the 1e bonding MO, and the factors β and $\sqrt{1 - \beta^2}$ are interchanged.

In atomic units (1 au = 27.21 eV) the expression for the oscillator strength to be evaluated is

$$f_{\text{theoret}} = \frac{2}{3} \nu D_{\text{theoret}} \quad (2)$$

(10) S. R. LaPaglia and O. Sinanoglu, *J. Chem. Phys.*, **44**, 1888 (1966).

(11) S. Ehrenson and P. E. Phillipson, *ibid.*, **34**, 1224 (1961).

(12) F. O. Ellison and H. Shull, *ibid.*, **23**, 2348 (1955).

(13) A. Moscovitz, Ph.D. Thesis, Harvard University, 1957.

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

(15) R. E. Watson, *Phys. Rev.*, **118**, 1036 (1960); **119**, 1934 (1960); Technical Report No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, June 15, 1959.

TABLE I
 TRANSITION MOMENT CONTRIBUTIONS^a

Charge-transfer integral	One-center ligand integral	Two-center ligand integral
$Q_{\text{theoret}}^L = 2\sqrt{2}\lambda\langle py_1 z d_{x^2-y^2} \rangle$	$-\sqrt{2}\mu\langle py_1 z py_1 \rangle$	$-\sqrt{2}\mu\langle py_1 z py_4 \rangle$
$= \lambda I_1$	$-\frac{\sqrt{2}}{\sqrt{3}}\mu R$	$+\mu I_2$
$Q_{\text{theoret}}^V = \frac{2\sqrt{2}}{\nu}\lambda\langle py_1 \frac{\partial}{\partial z} d_{x^2-y^2} \rangle$	$-\frac{\sqrt{2}}{\nu}\mu\langle py_1 \frac{\partial}{\partial z} py_1 \rangle$	$+\frac{2\sqrt{2}}{\nu}\mu\langle py_1 \frac{\partial}{\partial z} py_4 \rangle$
$= -\frac{\lambda}{\nu} I_3$	$+0$	$+\frac{\mu}{\nu} I_4$

^a See Appendix for definition of I_1, \dots, I_4 .

where ν is the energy of the $t_1 \rightarrow 2e$ absorption band maximum (0.0835 au) and D_{theoret} is the dipole strength ($D_{\text{exptl}} = 0.576$ au). For a transition from a non-degenerate A_1 state to a triply degenerate T_2 state, D_{theoret} is equal to $3Q_{\text{theoret}}^2$ where the theoretical transition moment is given by

$$\bar{Q}_{\text{theoret}} = \langle \Psi(^1A_1) | \bar{\Sigma}^-_i | \Psi_q(^1T_2) \rangle \quad (3)$$

$\Psi(^1A_1)$ and $\Psi_q(^1T_2)$ are the antisymmetrized wave functions of the initial and final states. The subscript on the latter differentiates between members of the 1T_2 set according to whether they transform as the Cartesian coordinate x , y , or z . The operator $\bar{\Sigma}^-_i$ is given by \bar{r}_i in the dipole length case and by $(1/\nu)\bar{\nabla}_i$ in the dipole velocity case.

In the coordinate system employed it is expedient to evaluate (3) in terms of the member of the 1T_2 set of functions which transforms as z . Hence, as determinantal wave functions we use

$$\Psi(^1A_1) = \frac{1}{\sqrt{6!}} | t_1^x t_1^{\bar{x}} t_1^y t_1^{\bar{y}} t_1^z t_1^{\bar{z}} |$$

and

$$\Psi_z(^1T_2) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{6!}} (| t_1^x t_1^{\bar{x}} t_1^y t_1^{\bar{y}} t_1^z e^{\bar{a}} | + | t_1^x t_1^{\bar{x}} t_1^y t_1^{\bar{y}} e^{\bar{a}} t_1^z |)$$

Inserting these expressions in (3) leads to the expression for the magnitude of \bar{Q}_{theoret}

$$Q_{\text{theoret}} = \sqrt{2} \langle t_1^z | Q_z | e^{\bar{a}} \rangle \quad (4)$$

From this expression by the application of group theoretical techniques it is found that the dipole length and dipole velocity transition moments, henceforward distinguished by superscripts L and V, respectively, can each be expressed as a sum of three contributions, namely, a charge-transfer integral, a one-center ligand integral, and a two-center ligand integral, as shown in Table I. For the convenience of the discussion to follow we shall refer to the three contributions of Q_{theoret}^L as Q^L_1 , Q^L_2 , and Q^L_3 , respectively, and similarly for Q_{theoret}^V . Note, for example, that Q^L_2 is independent of orbital shapes, except for the dependence of the normalization constant on the group overlap integral, and that Q^V_2 is identically zero.

By substituting for λ and μ the definitions given earlier, it is possible to evaluate Q_{theoret}^L and Q_{theoret}^V as functions of β , the ligand-mixing coefficient, for

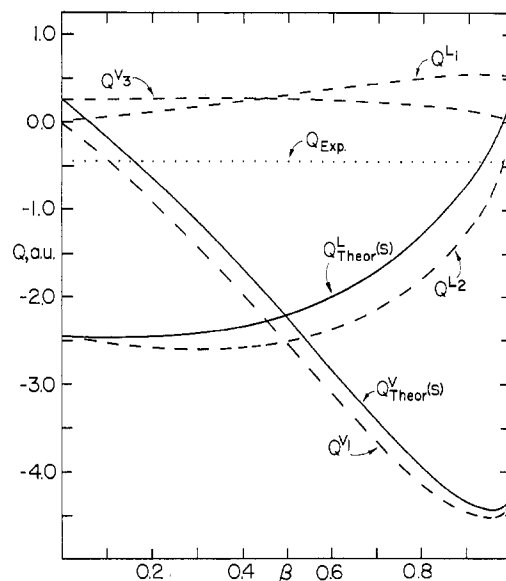


Figure 1.—Components of the dipole length and dipole velocity $t_1 \rightarrow 2e$ transition moments as functions of ligand mixing coefficient. (Orbital parameters are those for neutral atom Slater AO's.)

given sets of orbital parameters. The results of one such calculation are exhibited in Figure 1. In this plot Q^L_1 , Q^L_2 , Q^V_1 , Q^V_3 , and the sums Q_{theoret}^L and Q_{theoret}^V are evaluated as functions of β on the basis of neutral atom 2p and 3d single- ζ STO's ($\zeta_{2p} = 2.275$, $\zeta_{3p} = 1.867$). Q^L_3 is never greater than 0.006 and hence is omitted from the figure. It is to be noted that Q_{theoret}^L is dominated throughout by Q^L_2 . This behavior essentially confirms the assumption made by Wolfsberg and Helmholtz in the original oscillator strength calculations and is contrary to the assumption of Ballhausen and Liehr. Note also that Q^L_1 is positive and approximately equal to $|Q_{\text{exptl}}|$ for all values of $\beta \gtrsim 0.7$. Thus calculation of Q^L_1 alone on the basis of Slater orbitals for neutral manganese and oxygen implies that the LCAO approximation is quite satisfactory for the calculation of intensities. That this is not true is shown by the behavior of Q_{theoret}^V . The quantity Q_{theoret}^V is dominated by Q^V_1 , the charge-transfer term, since Q^V_3 , the two-center ligand term, is never greater than ~ 0.3 (for $\beta = 0$) nor less than zero (for $\beta = 1$). We remark in passing that the choice of sign for Q_{exptl} ($= -0.44$) as shown in Figure 1 is made on the basis of the fact that $Q_{\text{theoret}}^V = Q_{\text{theoret}}^L$ only in the negative domain.

Ultimately, this sign is determined by the choice of phase that is made in the wave function used to describe the system.

Figure 2 provides a comparison of the behavior of Q^L_{theoret} and Q^V_{theoret} as functions of β when calculated on the basis of STO's (as in Figure 1) and a combination of 2p STO's with double- ζ 3d AO's, *i.e.*, AO's with radial functions of the form derived by Richardson, *et al.*,¹⁴ *viz.*

$$R(3d) = \sum_i c_i \chi_{3d}(\zeta_i)$$

where

$$\chi_{3d}(\zeta_i) = \left[\frac{(2\zeta_i)^7}{(6!)} \right]^{1/2} r^2 e^{-\zeta_i r}$$

For the manganese ion, Mn^{2+} , $c_1 = 0.547$, $c_2 = 0.605$, $\zeta_1 = 5.15$, and $\zeta_2 = 2.10$. The principal observations to be made concerning Figure 2 are as follows. (1) Q^V_{theoret} is rather more sensitive to change of 3d radial function than Q^L_{theoret} . (2) Q^L_{theoret} and Q^V_{theoret} have quite different values over most of the range of β , and where they are equal, at approximately -2.4 and -1.8 for STO's and double- ζ functions, respectively, the value of Q_{theoret} is approximately 4-5.5 times larger than the experimental value. (3) At $Q^L_{\text{theoret}} = Q_{\text{exptl}}$ the 2e MO is predominantly metal AO (β large) whereas at $Q^V_{\text{theoret}} = Q_{\text{exptl}}$ the 2e MO is predominantly ligand in character (β small). (4) The β value obtained by the latter criterion is in better agreement with the β value obtained in the Viste and Gray^{5b} energy level calculation than is the β value obtained from the criterion $Q^L_{\text{theoret}} = Q_{\text{exptl}}$. Viste and Gray used a 3d radial function with $c_1 = 0.532$, $c_2 = 0.649$, $\zeta_1 = 5.15$, $\zeta_2 = 1.90$, and a 2p SCF function for oxygen (both of which differ from the functions used by us in this calculation, but which do not produce significantly different results) and found that the magnitude of the coefficient of the 3d AO in the bonding 1e MO was larger than that for the ligand symmetry orbital (0.73 and 0.52, respectively) and that the magnitude of the coefficient of the 3d AO in the antibonding 2e MO was smaller than that for the ligand symmetry orbital (0.73 and 0.90, respectively).

Now if equation of Q^V_{theoret} or Q^L_{theoret} to Q_{exptl} is viewed as a means of obtaining an "experimental" value of β , denoted β_{exptl} , then the variation of β_{exptl} with variation of the ionization states of manganese and oxygen can be examined. Thus a series of calculations like those forming the basis of Figures 1 and 2 was performed using STO's for the manganese electron configurations d^0 through d^7 ($2.450 \geq \zeta_{3d} \geq 1.283$) and double- ζ AO's for the configurations d^0 through d^7 . Each set of manganese AO's was combined with two different 2p STO's, one with $\zeta_{2p} = 2.275$ (neutral oxygen) and one with $\zeta_{2p} = 2.000$ (oxidation state between -1 and -2). The results for $\zeta_{2p} = 2.000$ are shown in Figure 3. This value of ζ_{2p} gives a slightly greater separation between the curves for $\beta^L(\text{R})$ and $\beta^L(\text{S})$ than $\zeta_{2p} = 2.275$ (there is no qualitative difference

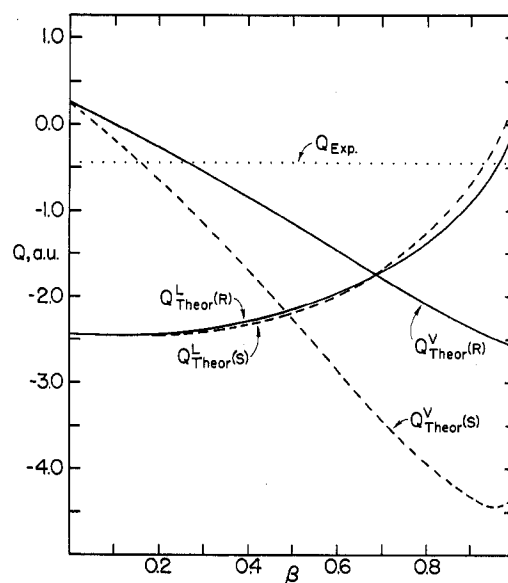


Figure 2.—Dipole length and dipole velocity $t_1 \rightarrow 2e$ transition moments as functions of ligand mixing coefficient for two kinds of 3d AO. (S denotes Slater orbital; R denotes an orbital of the form derived by Richardson, *et al.*)¹⁴

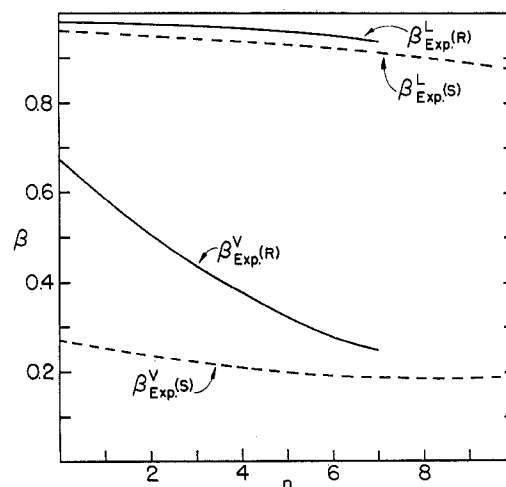


Figure 3.—Experimental ligand mixing coefficients of the e symmetry MO's of MnO_4^- as functions of free-atom orbital occupancy (n is the number of electrons in 3d AO's).

in the results obtained with the two values). The figure shows that there is little variation in β_{exptl} with change of manganese formal oxidation states over the range studied except in the case of β^V_{exptl} , based on the double- ζ 3d radial function. Thus, insofar as the results are less divergent when double- ζ orbitals are used, these are the preferred orbital expressions. This conclusion is corroborated by means of a calculation designed to find the value of ζ_{3d} for an STO on manganese and the value of β at which $Q^V_{\text{theoret}} = Q^L_{\text{theoret}} = Q_{\text{exptl}}$. Using $\zeta_{2p} = 2.000$, it was found that the equation was satisfied by $\zeta_{3d} = 4.0$ and $\beta = 0.97$. The value of ζ_{3d} thus obtained is considerably above the values given by Slater's rules for the ionization states of manganese. If a similar calculation had been performed by allowing double- ζ orbital parameters to vary without limit, it would again have been found that the 3d AO would be more contracted than the

most contracted free-atom 3d AO, but the difference would be less than with the STO's.

Finally, a separate analysis was made of the quantities most dependent on orbital parameters, I_1 and I_3 . Figure 4 shows contour maps of these integrals in ρ, τ coordinate space. The variables ρ and τ are restricted to the ranges $\rho \geq 0$ and $+1 \geq \tau \geq -1$. The maximum value of I_3 , 0.45, occurs at $(\rho, \tau) = (2.5, 0.15)$ and the maximum value of I_1 , 0.45, occurs at $(\rho, \tau) = (4.5, 0.0)$. Except when $\beta \cong 1$, I_1 can never be large enough so that Q_1^L will outweigh the Q_2^L contribution; hence, Q_{theoret}^L must have essentially the values shown in Figure 2 for any set of orbitals for the two atoms bonded together and must depend on the nature of these two atoms only through the group overlap integral in the denominator of the normalization factor N_B and the bond length R . Now for the chromate ion, CrO_4^{2-} , the metal-oxygen bond length differs from that in MnO_4^- by less than 1%, and $G_B(d, \pi)$ would therefore not be expected to be a great deal different either. However, the value of the experimental transition moment for the $t_1 \rightarrow 2e$ transition of chromate is $Q_{\text{exptl}} = -0.606$. Referring to Figure 2, the consequence is that the calculation of β_{exptl} for chromate from the equation $Q_{\text{theoret}}^L = Q_{\text{exptl}}$ leads to a smaller value than for permanganate. This is contrary to the intuitive expectation that the metal-oxygen bond in chromate should be the more nearly ionic because the chromium atom has the smaller formal charge. To be sure, the metal-oxygen bond distance in vanadate, VO_4^{3-} , is rather larger than that in either chromate or permanganate, but, since $Q_{\text{exptl}} = -0.671$, the increase in bond length is partially offset. At best, β for vanadate would be only slightly larger than the value for permanganate when calculated from Q_{theoret}^L . In short, the dipole length transition moment implies that the extent of mixing of the metal and ligand e orbitals is small and approximately equal in all three ions. Similar remarks apply to the isoelectronic species RuO_4 , TcO_4^- , and MoO_4^{2-} whose experimental transition moments are -0.292 , -0.356 , and -0.515 , respectively, and whose metal-oxygen bond lengths are the same to within 10%.

On the other hand, values of β obtained for other isoelectronic ions by equating Q_{theoret}^V and Q_{exptl} depend on the value of ν and I_3 and hence on the values of ρ and τ chosen for each atom. Because the ν values for VO_4^{3-} , CrO_4^{2-} , and MnO_4^- are 0.166, 0.121, and 0.0835, respectively, the ν dependence suggests that the MnO_4^- curve will lie lowest, then the CrO_4^{2-} curve, with the VO_4^{3-} curve highest. From the $|Q_{\text{exptl}}|$ values given above it can be seen that in this case $\beta(\text{MnO}_4^-) < \beta(\text{CrO}_4^{2-}) < \beta(\text{VO}_4^{3-})$, *i.e.*, that MnO_4^- has the most metal 3d character in its bonding 1e orbital as expected from its higher oxidation state, CrO_4^{2-} is next, and VO_4^{3-} has the least metal character. Similarly from the ν values for the series MoO_4^{2-} , TcO_4^- , RuO_4 , the $Q_{\text{theoret}}^V = Q_{\text{exptl}}$ criterion would predict RuO_4 to have the most and MoO_4^{2-} the least metal character in the 1e bonding MO if values of I_3

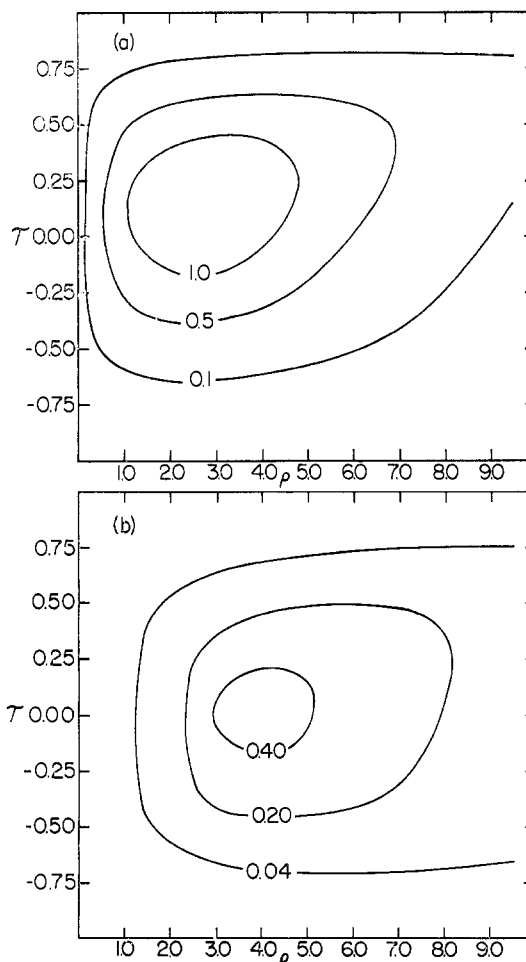


Figure 4.—Contour diagrams of charge-transfer integrals: (a) $I_1(\rho, \tau)$ and (b) $I_3(\rho, \tau)$, where $\rho = R(\xi_{2p} + \xi_{3d})/2$ and $\tau = (\xi_{2p} - \xi_{3d})/(\xi_{2p} + \xi_{3d})$.

did not qualitatively upset the order established by the ν values.

Conclusions

The comparison of transition moments presented above is concerned only with the degree of π covalency in tetraoxy anions, not with the degree of σ covalency. Information about the latter type of bonding must come from a transition, *e.g.*, $t_1 \rightarrow 2t_2$, which involves σ orbitals. To summarize the results concerning π bonding, it is found that, based on the customary LCAO-MO approximation, the dipole length transition moment leads to the conclusion that there is vanishingly small π covalency in all tetraoxy anions, whereas the dipole velocity transition moment leads to the conclusion that there is a high degree of π covalency in permanganate and smaller degrees in tetraoxy anions of metals with smaller formal charges. The dipole velocity transition moment calculation is therefore more reasonable qualitatively, in spite of the fact that the polarity of the metal-oxygen bond is calculated to be the reverse of that expected on intuitive grounds and also on the basis of the electron spin resonance studies of manganate.³ Finally, the observation that the polarity reversal and the resultant disparity between the two moments is not rectified by rather wide