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Oscillator Strength Calculation of 1A_1 - 1T_2 (t_1 -2e) Transition of Chromate and Permanganate Ions

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OSCILLATOR STRENGTH CALCULATION OF $^1A_1 \rightarrow ^1T_2 (t_1 \rightarrow 2e)$

TRANSITION OF CHROMATE AND PERMANGANATE IONS

KEY WORDS: Oscillator strength, Linear Combination of Atomic Orbitals-Molecular Orbitals (LCAO-MO)

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The oscillator strength, f , of the $^1A_1 \rightarrow ^1T_2 (t_1 \rightarrow 2e)$ transition of both chromate and permanganate ions have been calculated by LCAO-MO method using Slater type orbitals¹ (STO's) and by crystal field approach². These computed values do not agree with the observed ones³. A detailed study of dipole moment of permanganate ion reveals⁴ that STO's do not represent true state of affairs and more exact atomic orbitals must be used. The double- ζ 3d AO's with radial functions of the form

$$R(3d) = \sum_{i=1}^2 C_i \chi_{3d}(\zeta_i)$$

where

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

derived by Richardson and his coworkers⁵ duplicate very nearly the SCF AO's determined by Watson⁶, which are quite exact. A LCAO-MO parametric calculation in terms of single parameter,

β , the ligand mixing coefficient using Richardson's orbitals and both dipole velocity and dipole length operators has been reported in the present paper.

Both chromate and permanganate ions are known to have the shape of a regular tetrahedron. Their one electron wave functions form bases for irreducible representations of the point symmetry group T_d . The nonbonding t_1^z and antibonding $2e^a$ orbitals are given by²

$$t_1^z = \frac{1}{2} (p_{y_1} + p_{y_2} + p_{y_3} + p_{y_4})$$

and

$$2e^a = \lambda d_{x^2-y^2} - \frac{1}{2} (p_{y_1} - p_{y_2} - p_{y_3} + p_{y_4})$$

where p_{y_i} 's are $2p_y$ AO's of the i^{th} oxygen atom and $d_{x^2-y^2}$ is the 3d metal AO. The coefficients λ and $1/2$ are related to the ligand mixing coefficient β as follows⁷

$$\lambda = \beta N_E, \text{ and } 1/2 = N_E(1 - \beta^2)^{1/2}$$

where the normalization factor

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

and the Group overlap integral

$$G_E(d, \pi) = \frac{2\sqrt{2}}{\sqrt{3}} \int (2p\pi, 3d\pi)$$

neglecting the ligand-ligand overlap integral⁸.

The oscillator strength f_{theoret} of the transition of energy ν a.u. is given by⁴

$$f_{\text{theoret}} = 4\nu | \langle t_1^z | \theta_z | e^a \rangle |^2$$

where the operator θ_z is given by z in the dipole length case and by $(\frac{1}{i\nu}) \frac{\partial}{\partial z}$ in the dipole velocity case leading to

the oscillator strength values f_{theoret}^L and f_{theoret}^V respectively.

The f_{theoret}^L and f_{theoret}^V values have been computed as functions of ligand mixing coefficient β on the bases of neutral atom 2p and 3d double- ζ Richardson's orbitals, (for chromate ion $C_1 = 0.506$, $C_2 = 0.675$, $\zeta_1 = 4.95$ and $\zeta_2 = 1.80$; for permanganate ion $C_1 = 0.547$, $C_2 = 0.605$, $\zeta_1 = 5.15$ and $\zeta_2 = 2.10$). The results are shown in Fig. 1. The observed³ f -values for chromate and permanganate ions are 0.09 and 0.04 respectively.

In LCAO-MO calculations it is assumed⁴ that the distribution of an electron around 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 uncombined AO. Since the dipole velocity operator as compared to dipole length operator stresses more the regions of space nearer an atom⁹ where the electron distribution presumably resembles the electron distribution in the uncombined AO, the dipole velocity operator is expected¹⁰ to yield better results than the dipole length operator. Our finding that for most of the range of β values the f_{theoret}^V values approximate f_{exp} values more than the f_{theoret}^L values do (Fig. 1), is in agreement with this. More precisely the f_{theoret}^L values approximate f_{exp} values for high β values (~ 0.95) whereas f_{theoret}^V values for low β values ($\sim 0.3-0.4$).

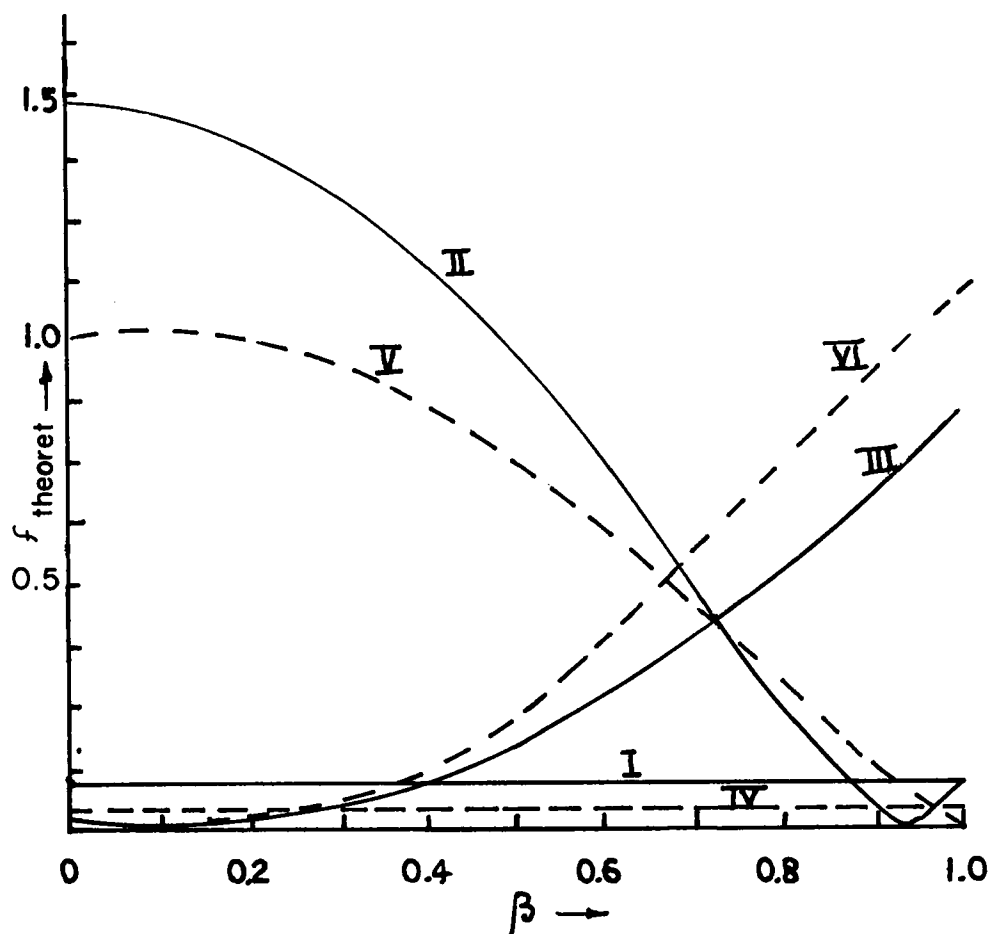


Fig. 1

Oscillator strengths for ${}^1A_1 - {}^1T_2$ ($t_1 \rightarrow 2e$) transitions as functions of ligand mixing coefficient, β , for chromate and permanganate ions.

- | | |
|--|---|
| I. f_{exp} for chromate. | VI. f_{exp} for permanganate. |
| II. $f_{\text{theoret}}^{\text{I}}$ for chromate. | V. $f_{\text{theoret}}^{\text{I}}$ for permanganate. |
| III. $f_{\text{theoret}}^{\text{V}}$ for chromate. | VI. $f_{\text{theoret}}^{\text{V}}$ for permanganate. |

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