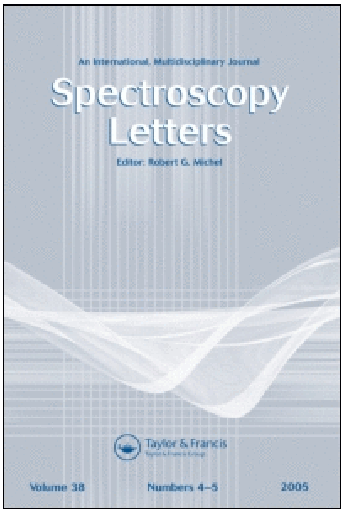

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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

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To cite this Article Tandon, S. P. , Surana, S. S. L. and Tandon, K.(1969) 'Oscillator Strength Calculation of $^1A_1$-$^1T_2$ (t_1-2e) Transition of Chromate and Permanganate Ions', Spectroscopy Letters, 2: 10, 295 — 299
To link to this Article: DOI: 10.1080/00387016908050212
URL: http://dx.doi.org/10.1080/00387016908050212

SPECTROSCOPY LETTERS, 2(10), 295-299 (1969)

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 orbitals[1] (STO's) and by crystal field approach[2]. These computed values do not agree with the observed ones[3]. A detailed study of dipole moment of permanganate ion reveals[4] 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 coworkers[5] duplicate very nearly the SCF AO's determined by Watson[6], 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 by[2]

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

and

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

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 μ are related to the ligand mixing coefficient β as follows[7]

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

where the normalization factor

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

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 integral[8].

The oscillator strength $f_{theoret}$ of the transition of energy ν a.u. is given by[4]

$$f_{theoret} = 4\nu \left| \langle\, t_1^z \mid \theta_z \mid e^a \,\rangle \right|^2$$

where the operator θ_z is given by z in the dipole length case and by $(\frac{1}{\nu})\,\frac{\partial}{\partial z}$ in the dipole velocity case leading to the oscillator strength values f^L_{theoret} and f^V_{theoret} respectively.

The f^L_{theoret} and f^V_{theoret} 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 observed[3] f-values for chromate and permanganate ions are 0.09 and 0.04 respectively.

In LCAO-MO calculations it is assumed[4] 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 atom[9] where the electron distribution presumably resembles the electron distribution in the uncombined AO, the dipole velocity operator is excepted[10] to yield better results than the dipole length operator. Our finding that for most of the range of β values the f^V_{theoret} values approximate f_{exp} values more than the f^L_{theoret} values do (Fig. 1), is in agreement with this. More precisely the f^L_{theoret} values approximate f_{exp} values for high β values (~ 0.95) whereas f^V_{theoret} values for low β values (~ 0.3-0.4).

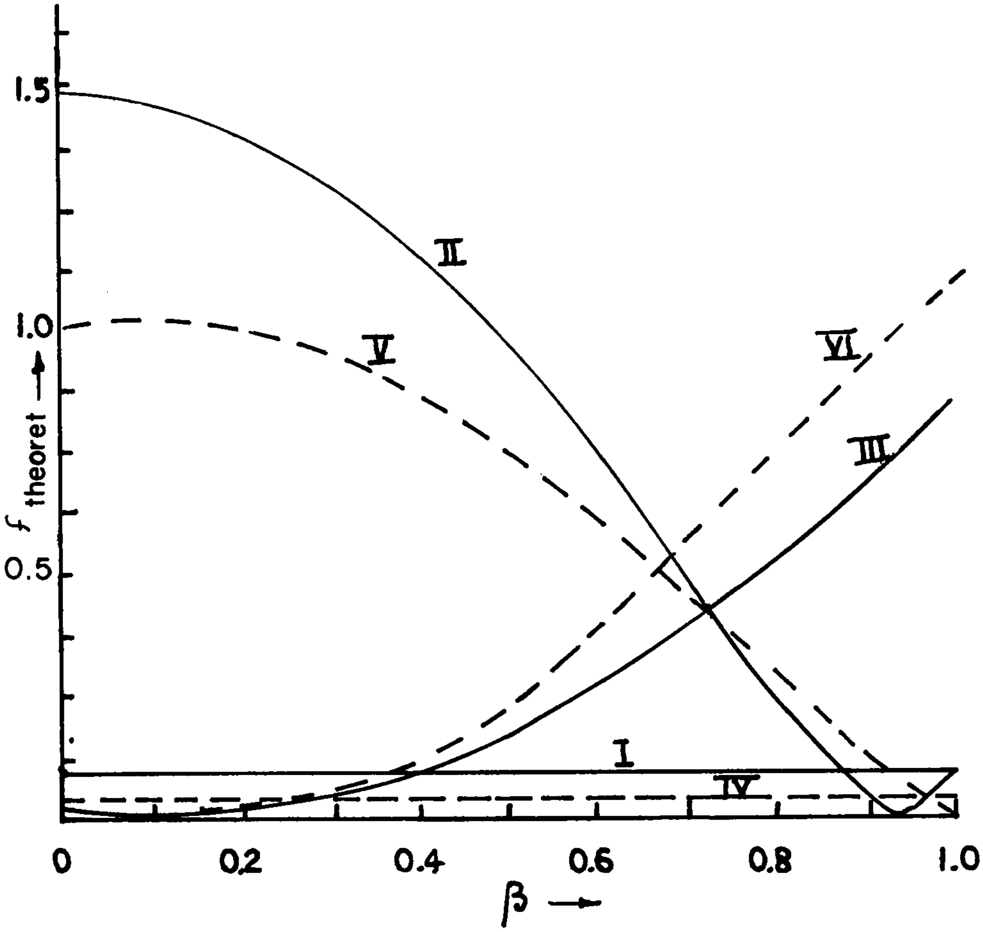

Fig. 1

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

I. f_{exp} for chromate.
II. $f^{L}_{theoret}$ for chromate.
III. $f^{V}_{theoret}$ for chromate.
VI. f_{exp} for permanganate.
V. $f^{L}_{theoret}$ for permanganate.
VI. $f^{V}_{theoret}$ for permanganate.

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