OPEN SHELL TETROXOANIONS: ELECTRONIC STRUCTURE AND SPECTRA*

G. DE MICHELIS, L. OLEARI, L. DI SIPIO AND E. TONDELLO

Istituto di Chimica Generale, University of Padova (Italy)

A. INTRODUCTION

This communication is concerned with the interpretation of the electronic spectra of those tetrahedral oxyanions of the first series transition metals which present a so called "open shell" electronic structure.

In Table 1 the known oxyanions of this group are listed according to their periodic classification and electronic structure; ions listed as d^0 can be depicted formally as X^{y+} central atom ions having rare gas configurations coordinated to four oxide O^{2-} ligands. Then d^1, d^2 and d^3 ions formally present one, two, and three "outer" electrons, respectively, having d-character on the metal. These ions have one or more unpaired electrons and are said to have an "open shell" electronic structure.

TABLE 1

KNOWN TETRAHEDRAL OXYIONS OF THE FIRST TRANSITION METAL SERIES
For ions listed in parentheses there is uncertainty in identification

d^0	VO_4^{3-}	CrO_4^{2-}	MnO_4^-		
d^1		CrO_4^{3-}	MnO_4^{2-}		
d^2			MnO_4^{3-}	FeO_4^{2-}	
d^3				(FeO_4^{3-})	(CoO_4^{2-})

As it is well established, these unpaired electrons are mainly localized on the central atom and, therefore, the electronic spectra of these ions will show, in addition to the charge transfer bands characteristic of chromate and permanganate, weak absorption bands corresponding to d–d one electron transitions ("crystal field" bands).

Moreover, all these open shell ions are much less stable than the corresponding "closed shell" ions and, therefore, the determination of their spectral properties is more difficult. As a consequence a theoretical study of the electronic structure of such ions would be extremely useful in order to interpret the experimental data. For this reason we have applied the same scheme of calculations, already used
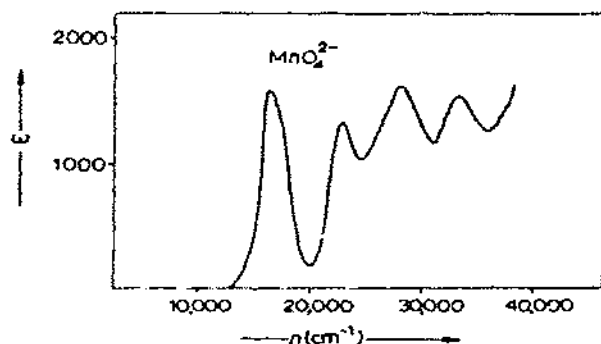
Fig. 1. Experimental spectrum for $[MnO_4]^{2-}$ (Taken from ref. 3.).

for chromate and permanganate[1], to the ions $[CrO_4]^{3-}$, $[MnO_4]^{2-}$, $[MnO_4]^{3-}$ and $[FeO_4]^{2-}$; *i.e.* to the four "open shell" tetroxoanions identified with certainty.

In Figs. 1 and 2 the experimental absorption spectra for the ions $[MnO_4]^{2-}$, $[MnO_4]^{3-}$ and $[FeO_4]^{2-}$ are reported, while in Table 2 the most important data concerning the same spectra and, moreover, the spectrum of the $[CrO_4]^{3-}$ ion are summarized. For this latter ion these data are the only ones reported in the literature and in the paper from which they are taken[2] the complete spectrum is not reproduced. It is only written that "both bands, devoid of any fine structure, are extremely broad and thus the values recorded for the molar extinction coefficients at the peaks are not a true measure of the transition probabilities".

For the other three ions, on the other hand, an examination of the spectra allows some useful and preliminary considerations:

(a) The experimental spectrum of the manganate[3] ion shows a quite intense absorption band followed by a complicated band structure which ranges from $20,000\ cm^{-1}$ to the end of the investigated spectrum. It is reasonable to imagine that more than three one-electron transitions correspond to this complicated band structure.

There is no evidence in the spectrum of Fig. 1, and neither in any other which we found in the literature, of the very weak band at $12,000\ cm^{1-}$ whose existence was asserted by Carrington[4] and recently postulated by Nyholm and co-workers[5] in their work on the temperature-independent paramagnetism of manganate.

(b) The experimental spectrum of hypomanganate[6] presents a weak band at $11,000\ cm^{1-}$ followed by a broad absorption band at $15,000\ cm^{-1}$. This fact was interpreted[7] by attributing the first band to the d–d transition $2e \rightarrow 3t_2$ ($^3A_2 \rightarrow {}^3T_2$) which is symmetry forbidden and the second one to the corresponding symmetry-allowed transition $2e \rightarrow 3t_2$ ($^3A_2 \leftarrow {}^3T_2$).

On the other hand Kingsley and co-workers[8] assign a very weak absorption peak, observed at $16,700\ cm^{-1}$ to the d–d symmetry-allowed transition.

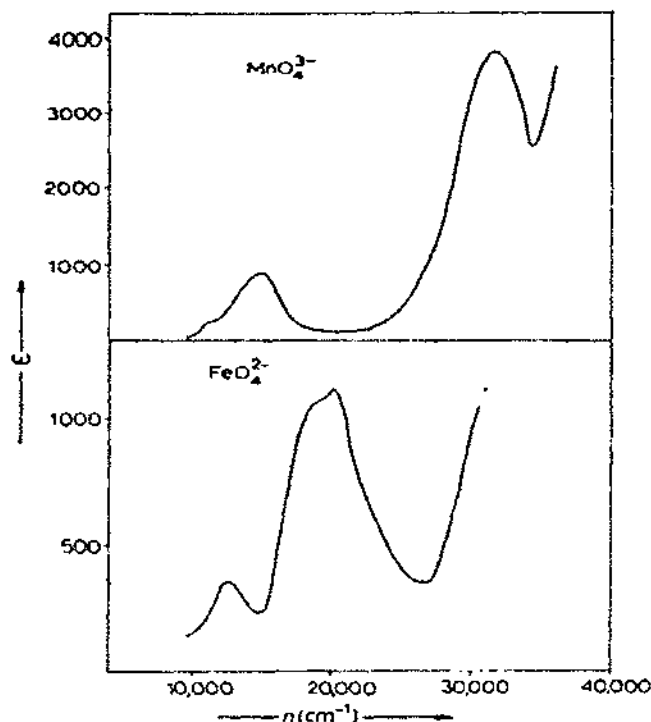With regard to the "charge-transfer" part of the spectrum it must be re-

Fig. 2. Experimental spectra for $[MnO_4]^{3-}$ (taken from ref. 6) and for $[FeO_4]^{2-}$ (taken from ref. 9).

called that the peak at 30,800 cm^{-1} has been examined in detail by Carrington and co-workers[9], who found that it is resolvable into two maxima of equal intensity at 30,500 cm^{-1} and 30,800 cm^{-1}; the same authors extended the spectral investigations further into the UV region, until the excess of hydroxide ion, necessary to prevent protonation of $[MnO_4]^{3-}$, began to absorb strongly (at 46,000 cm^{-1}). A maximum absorption was found at 46,300 cm^{-1} with a molar extinction coefficient (approximately 17,000) greatly in excess of any values previously observed for charge-transfer bands of transitior-metals oxyanions.

(c) The spectrum of the ferrate ion[9] is similar to that of hypomanganate, the second peak presenting a shoulder at about 17,300 cm^{-1}; so it could be supposed that the first observed band is a crystal field band. The spectral investigation was extended until 46,500 cm^{-1}, where the optical density continued to rise but the strong absorption of hydroxide ion prevented definition of the peak.

Summarizing, from an experimental point of view, we can state the following:

(i) For the d^1 ions there is no evidence on the identification of the crystal-field bands and the "charge-transfer" band system is quite complicated.

TABLE 2

THE VISIBLE AND ULTRAVIOLET SPECTRA OF OXYANIONS CONSIDERED

ion	band maxima (in cm^{-1})	ε
$[CrO_4]^{2-}$	16,000	250 ± 50
	28,200	500 ± 50
$[MnO_4]^{2-}$	(12,000)[a]	very weak
	16,580	1,598
	22,830	1,330
	28,170	1,635
	33,200	1,539
$[MnO_4]^{3-}$	11,000	very weak
	14,810	1,100
	(16,700)[b]	very weak
	30,800	3,800
$[FeO_4]^{2-}$	12,720	380
	17,800	shoulder
	19,600	1,120

[a] Reported by Carrington[4].
[b] Reported by Kingsley and coworkers[9].

TABLE 3

SPECTRAL ASSIGNMENTS OF PREVIOUS AUTHORS

Ion	Band maxima (eV)	Carrington– Symons	Carrington– Jørgensen	Viste–Gray	Kingsley and coworkers	Orgel
$[MnO_4]^{2-}$	(1.49)	$2e \to 3t_2(^2T_2)$	—	—		
	2.05	$t_1 \to 2e(^2T_2)$	$2e \to 3t_1(?)$	$2e \to 3t_2$		
	2.84	$t_1 \to 2e(^2T_1)$	$t_1 \to 2e$	$t_1 \to 2e$		
	3.53	$t_1 \to 3t_2(^2T_2)$	$2t_1 \to 2e(?)$	$2t_2 \to 2e$		
	4.14	$t_1 \to 3t_2(^2T_1)$		$\leftarrow$		
$[MnO_4]^{3-}$	1.36	—	—	$2e \to 3t_2(^3T_2)$	$2e \to 3t_2(^3T_2)$	$2e \to 3t_2(^3T_2)$
	1.83	$t_1 \to 2e(^3T_1)$	$2e \to 3t_2$	$2e \to 3t_2(^3T_1)$	$t_1 \to 2e(^3T_1)$	$2e \to 3t_2(^3T_1)$
	(2.07)	—	—	—	$2e \to 3t_2(^3T_1)$	—
	3.82	$t_1 \to 3t_2(^3T_1)$	$t_1 \to 2e$	$t_1 \to 2e(^3T_1)$	$t_1 \to 3t_2(^3T_1)$	$t_1 \to 2e(^3T_1)$
$[FeO_4]^{2-}$	1.59	$t_1 \to 2e(^3T_1)$	$2e \to 3t_2$	$2e \to 3t_2(^3T_1)$		
	2.20 (sb)	—	—	—		
	2.43	$t_1 \to 3t_2(^3T_1)$	$t_1 \to 2e(?)$	$2e \to 3t_2(^3T_1)$		

(ii) For the d^2 ions the identification of the crystal-field bands is fairly certain and we observe only one charge transfer band.

This lack of experimental evidence makes it very difficult to advance a satisfactory and coherent interpretation and, in fact, none of the assignments of previous authors[7,8,10-13] are very convincing (Table 3).

For this reason, as we have stated above, only a rigorous calculation can give the necessary information, unobtainable from experimental data, and will permit a choice among the various alternative hypotheses.

B. RESULTS OF CALCULATIONS

The calculations were performed applying the semiempirical molecular orbital theory, employing linear combinations of atomic orbitals.

The calculation scheme is substantially that described in our paper on chromate and permanganate[1]. For further details and for the values of the integrals used in the calculations, we refer the readers to the individual papers already published or in the process of being published[14, 15].

The molecular orbitals have been calculated following the 'open shell' SCF Roothaan scheme[16] "zero differential overlap" approximation[17]. Subsequently, for each ion except hypochromate, we have carried out a configuration interaction calculation extended to all mono-excited configurations, corresponding to symmetry-allowed one-electron transitions.

In this communication, we use the results of such configuration interaction calculations to give a proper interpretation of the experimental spectra.
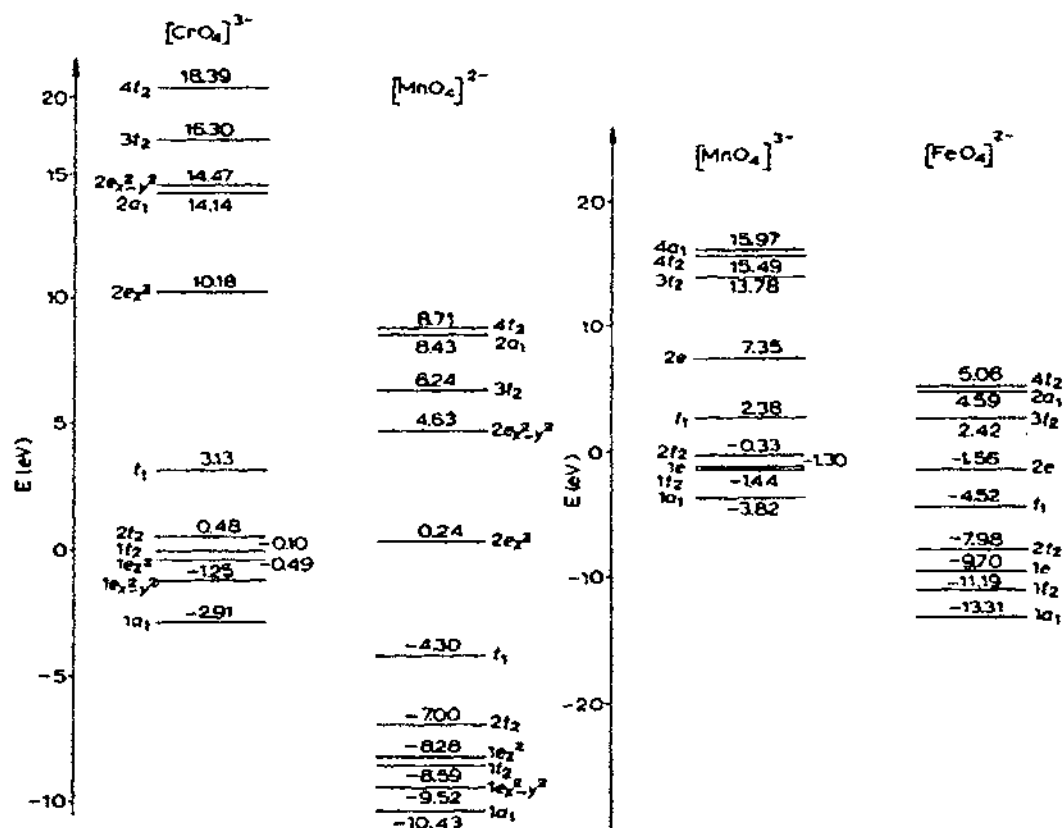
Fig. 3. Molecular orbital energy levels for [CrO₄]³⁻ and [MnO₄]²⁻.

Fig. 4. Molecular orbital energy levels for [MnO₄]³⁻ and [FeO₄]²⁻.

Such values of the transition energies will be attributed, for the sake of simplicity, to transitions from a filled molecular orbital to an empty one. Actually they are eigenvalues of the energy matrix of the configuration interaction and, therefore, do not correspond to a single one-electron transition, but to a linear combination of mono-excited configurations.

However, there is always a configuration which participates in a preponderant manner in the linear combination and, thus, as a first approximation, it is possible to consider the mono-electronic excitation as a transition from one molecular orbital to another.

In Figs. 3 and 4 the molecular level orders for the d^1 and d^2 ions, as given by SCF calculations on the basis of the eigenvalues*, are shown. As it is well known, the MO's from $1a_1$ to t_1 are doubly filled, while the unpaired electrons occupy the $2e$ MO's. The molecular orbitals show the following features:

(i) The filled MO's are characterized by two strongly bonding MO's ($1e$ and $1t_2$) and two slightly bonding MO's mainly localized on the ligands ($1a_1$ and $2t_2$).

(ii) The t_1 MO's, for symmetry purposes, are localized only on the ligands.

(iii) The empty MO's are almost completely localized on the central atom. The $2e$ MO's present a strong d-character, while the $3t_2$ MO's show an increasing 4p–3d mixing, from d^1 to d^2 ions.

C. DISCUSSION OF THE ELECTRONIC SPECTRA

The assignment which follows from the present calculations for manganate ion is presented in Table 4; note the satisfactory quantitative agreement between calculated and experimental values.

As you can see, the observed charge-transfer spectrum is originated by eight one-electron transitions, instead of by four as in the case of permanganate. Man-

TABLE 4

$[MnO_4]^{2-}$ OBSERVED AND CALCULATED TRANSITION ENERGIES

Observed band maxima (eV)	Calculated transition energies (eV)	Assignments
1.49	0.98	$^2T_2(2e \rightarrow 3t_2)$
2.05	1.99	$^2T_1 (t_1 \rightarrow 2e)$
2.84	3.24	$^2T_1(t_1 \rightarrow 2e)$
	3.43	$^2T_1(2t_2 \rightarrow 2e)$
3.53	3.55	$^2T_2(t_1 \rightarrow 3t_2)$
	4.14	$^2T_2(2t_2 \rightarrow 2e)$
	4.21	$^2T_1(2t_2 \rightarrow 3t_2)$
4.14	4.30	$^2T_2(2t_2 \rightarrow 3t_2)$
	4.38	$^2T_1(t_1 \rightarrow 3t_2)$

* Actually, for open shell systems, the eigenvalues are only Lagrange multipliers; however, as a first approximation, they can be considered MO energies.

ganate, indeed, has a ^2E ground state and, therefore, both $^2E \rightarrow {}^2T_2$ and $^2E \rightarrow {}^2T_1$ transitions are symmetry-allowed.

Moreover, the presence of the unpaired electron in the $2e$ MO's removes the accidental degeneracy of the energies of both pairs of transitions:

$$
\begin{array}{cc}
t_1 \rightarrow 2e & 2t_2 \rightarrow 2e \\
t_1 \rightarrow 3t_2 & \text{and} \quad 2t_2 \rightarrow 3t_2
\end{array}
$$

a degeneracy, which we found for the permanganate ion[1].

Finally, it must be pointed out that the clear energetic separation between the two excited states $^2T_2$ ($t_1 \rightarrow 2e$) and $^2T_1$ ($t_1 \rightarrow 2e$) is derived from the fact, that, for symmetry reasons, in the first case the excited electron jumps into an empty $2e$ MO and in the second, into a singly-occupied one.

In this way we explain the energetic difference between the first experimental charge-transfer band and the subsequent complicated band system.

With regard to the d–d transition, our results confirm the hypotheses that it must correspond, in the experimental spectrum, to a very weak absorption band with an energy lower than that of the first charge-transfer band; i.e., the band at 2.05 eV. In this way we are led to accept the existence of the 1.49 eV band observed by Carrington[4].

The experimental data are inadequate for a proper interpretation of the spectral properties of hypochromate: only a few considerations are possible on the basis of the analogy of electronic structure with manganate. Very likely, the first of the two observed maxima corresponds to a d–d transition, while the second one represents the first band of the system, originated by the eight symmetry-allowed charge-transfer bands. In this way we correctly conclude that the charge-transfer bands have a higher energy for hypochromate, than for manganate.

Our interpretation of the experimental spectrum of the $[MnO_4]^{3-}$ ion is reported in Table 5 and again the quantitative agreement is good. We confirm the assignment of most other authors of the band at 1.83 eV to a d–d transition and, moreover, on the basis of our calculations, we can afford an explanation for

TABLE 5

$[MnO_4]^{3-}$: OBSERVED AND CALCULATED TRANSITION ENERGIES

Observed band maxima (eV)	Calculated transition energies (eV)	Assignments
(1.36)	a	$^2T_2(2e \rightarrow 3t_2)$
1.83	1.64	$^2T_1(2e \rightarrow 3t_2)$
	3.78	$^2T_1(t_1 \rightarrow 2e)$
3.82	4.14	$^2T_1(t_1 \rightarrow 3t_2)$
	4.56	$^2T_1(2t_2 \rightarrow 2e)$
>4.5	4.92	$^2T_1(2t_2 \rightarrow 3t_2)$

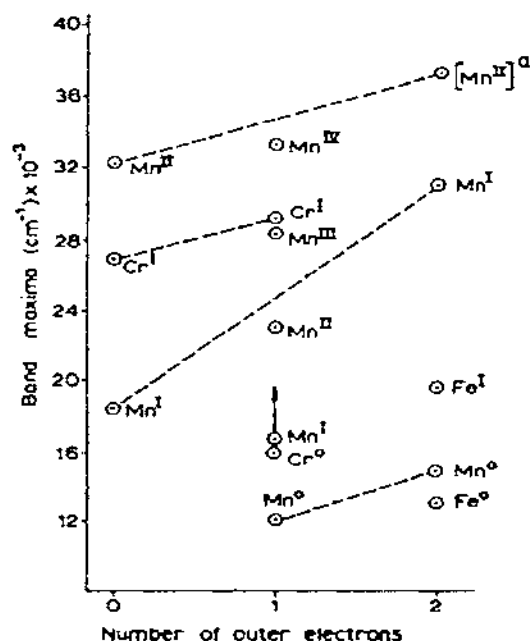a We evaluated only the values of the symmetry allowed transitions.

Fig. 5. Experimental band energies for tetroxo-anions as a function of the number of "outer" electrons. (X^0 denotes maxima for the d–d bands; X^I, X^{II}, etc. denote maxima for the first, second, etc. charge-transfer bands).
* Hypothetical value.

the high intensity of this band. Actually, hypomanganate is the ion, among those which we have investigated in which the $3t_2$ MO's has the highest character.

With regard to the charge-transfer band at 3.82 eV we postulate, as for the permanganate ion, an energetic degeneracy of two charge-transfer one-electron transitions. This could find experimental support in the resolution into two maxima of the experimental peak obtained by Carrington and co-workers[9].

TABLE 6

[FeO$_4$]$^{3-}$: OBSERVED AND CALCULATED TRANSITION ENERGIES

Observed band maxima (eV)	Calculated transition energies (eV)	Assignments
1.59	0.32	$^3T_1(2e \rightarrow 3t_2)$
2.20 (sh)	0.61	$^3T_1(t_1 \rightarrow 2e)$
2.43	1.53	$^3T_1(t_1 \rightarrow 3t_2)$
>5.5	3.54	$^3T_1(2t_2 \rightarrow 2e)$
	4.17	$^3T_1(2t_2 \rightarrow 3t_2)$

Finally, let us consider the [FeO$_4$]$^{2-}$ ion (Table 6). As can be seen, the assignments are analogous to those of the hypomanganate ion, as expected, con-

sidering the similar electronic structure of the two ions. In this case, however, the experimental evidence (a shoulder at 2.20 eV) of the overlapping of two charge-transfer transitions is much clearer. On the other hand, the agreement between experimental and calculated values is unsatisfactory: in fact the calculation has been carried out only using one-centre atomic integrals corresponding to the oxidation state +1 of Fe. Therefore, in order to approach the actual situation of the molecule, it would be necessary to carry out a second calculation with the integrals corresponding to an oxidation state 0 and to interpolate the results of both calculations.

Conclusions

Summarizing, we point out two considerations in support of our interpretations:

(a) The same calculation procedure and the use of identical one-centre atomic integrals for identical central atoms have given an interpreation of the spectral properties of six different tetroxoions (including chromate and permanganate), a rather satisfactory situation both from a quantitative and a qualitative point of view.

(b) On the basis of our interpretations it is possible to find regular trends in the one-electron transition energies with regard both to the atomic number of the central atom and to the charge of the ions. This fact was not possible on the basis of previous interpretations.

The latter consideration is brought up in Fig. 5 where the energies of the experimental band maxima are reported as a function of the number of "outer" electrons. As you can see, the following conclusions are evident:

(i) The energy of the d–d and charge-transfer bands decreases with the atomic number, if we consider isoelectronic sequences of ions.

(ii) The energy of the d–d and charge-transfer bands increases regularly, for a given central atom, with the negative charge of the ion; *i.e.*, with decreasing formal positive charge of the central atom.

In such a way the objections, advanced by Carrington and Symons[18] while discussing a similar diagram on the basis of their interpretations, are avoided.

These trends confirm the conclusions of other authors[19] with regard to the charge-transfer bands, while they are completely different from the trends, up until now accepted, of the d–d transitions.

Till now, the d–d bands have been interpreted on the basis of the "crystal-field" theory and, therefore, they have been discussed with the aid of the CF parameter, known as Δ.

Now in the complexes (mostly octahedral) successfully investigated with the aid of the CF theory, we can see that the values of Δ increase with the formal positive charge of the central atom[20].

On this basis, Basch, Viste and Gray[19] have reached the general conclusion that "for metal complexes, which do not have appreciable π acceptor ability, Δ is known to increase as the formal positive charge on the ion increases", and, consequently, Viste and Gray[13] have based their interpretation of the spectra of tetroxo-anions, and in particular the assignment of the $2e \to 3t_2$ transition, on the assumption that the Δ value should increase from $[MnO_4]^{3-}$ to $]MnO_4]^{-}$.

In our opinion, however, it is not possible to attribute an observation based on the CF theory to complexes, such as tetroxo-anions, in which there is some covalent character in the bonding.

In fact in these cases we must use the MO description. Within such a scheme one can define a new parameter Δ as the difference between the energies of the $3t_2$ and $2e$ MO's in the field of the effective core and of the valence electrons which occupy the "closed shell" MO's.

It must be pointed out that for d^2 metal ion complexes such a Δ is different from the Δ which can be obtained from the experimental data on the basis of the CF theory.

Therefore, we must not expect the same trend observed in octahedral complexes.

According to the above MO Δ definition, we have obtained (Table 7) a

TABLE 7

THE CALCULATED VALUE OF THE MOLECULAR ORBITAL PARAMETER Δ (IN eV)

	Cr	Mn	Fe
d^1	1.4	1.2	—
d^2	—	2.2	0.9

set of values, very close to the energies of the d–d transitions. As you can see, these values present the same trends as the d–d band maxima, both with the atomic number and the formal oxidation number of the central atoms.

Considering the explicit expressions which can be derived for Δ, these trends can be understood by taking into account the variations, from the d^0 to the d^2 ions, in the field of ligands, due to the increasing negative charge on the oxygens, and in the interelectronic repulsion integrals, due to the different expansion of the $2e$ and $3t_2$ MO's.

In conclusion, in our opinion, it is evident, within the framework of the MO model that the values of Δ strongly depend upon the bonding situation.

REFERENCES

1   L. OLEARI, D. DE MICHELIS AND L. DI SIPIO, *Mol. Phys.*, 10 (1966) 111; *Coordin. Chem. Rev.*, 1 (1966) 18.
2   N. BAILEY AND M. C. R. SYMONS, *J. Chem. Soc.*, (1957) 203.

3   G. DEN BOEF, H. J. VAN DER BEEK AND T. BRAAF, *Rec. Trav. Chim.*, 77 (1958) 1064.
4   A. CARRINGTON, *Ph. D. Thesis, Univ. of Southampton*, 1959.
5   R. S. NYHOLM AND P. R. WOOLLIAMS, *Proc. 9th Intern. Conf. Coordin. Chem.*, (1966) 127.
6   P. D. JOHNSON, J. S. PRENER AND J. D. KINGSLEY, *Science*, 141 (1963) 1179.
7   L. E. ORGEL, *Mol. Phys.*, 7 (1963) 397.
8   J. D. KINGSLEY, J. S. PRENER AND B. SEGALL, *Phys. Rev.*, 137A (1965) 189.
9   A. CARRINGTON, D. SCHONLAND AND M. C. R. SYMONS, *J. Chem. Soc.*, (1957) 659.
10 A. CARRINGTON AND M. C. R. SYMONS, *J. Chem. Soc.*, (1960) 889.
11 A. CARRINGTON AND D. S. SCHONLAND, *Mol. Phys.*, 3 (1960) 331.
12 A. CARRINGTON AND C. K. JØRGENSEN, *Mol. Phys.*, 4 (1961) 395.
13 A. VISTE AND H. B. GRAY, *Inorg. Chem.*, 3 (1964) 1113.
14 L. DI SIPIO, G. DE MICHELIS, E. TONDELLO AND L. OLEARI, *Gazz. Chim. It.*, 96 (1966) 1775.
15 G. DE MICHELIS, L. OLEARI, L. DI SIPIO AND E. TONDELLO, unpublished results.
16 C. C. J. ROOTHAAN, *Rev. Mol. Phys.*, 32 (1960) 179.
17 J. A. POPLE, *Trans. Faraday Soc.*, 49 (1953) 1375.
18 A. CARRINGTON AND M. C. R. SYMONS, *Chem. Rev.*, 63 (1963) 443.
19 H. BASCH, A. VISTE AND H. B. GRAY, *J. Chem. Phys.*, 44 (1966) 10.
20 B. N. FIGGIS, *Introduction to ligand fields*, New York, 1966, p. 242.
21 L. OLEARI, G. DE MICHELIS AND L. DI SIPIO, *Atti Seminario Chim. Univ. Padova*, 1964-65.