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Electronic Structures of Tetrahedral CrO_4^{2-}, VO_4^{3-} and $TiCl_4$

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The electronic structures of the tetrahedral systems CrO_4^{2-}, VO_4^{3-} and $TiCl_4$ are discussed on the basis of semiquantitative LCAO MO calculations.

Die Elektronenstrukturen der Tetraedersysteme CrO_4^{2-}, VO_4^{3-} und $TiCl_4$ werden an Hand halbquantitativer LCAO-MO Rechnungen diskutiert.

Discussion des structures électroniques des systèmes tétraédriques CrO_4^{2-}, VO_4^{3-} et $TiCl_4$ sur la base de calculs semi-quantitatifs LCAO MO.

1. Introduction

The semiquantitative molecular orbital scheme described in the preceding paper [4] and applied there to the MnO_4^- ion, has been used to investigate the electronic structures of the systems CrO_4^{2-}, VO_4^{3-}, and $TiCl_4$. These compounds have, like MnO_4^-, tetrahedral symmetry in their ground states and contain the same number of valence electrons as this ion, i.e. they are d^0 systems in the language of crystal field theory.

The electronic structures of these tetrahedral systems are at the present time not well understood. So far as the ground states are concerned, our own calculations [3, 4] indicate that the metal 4*s* and 4*p* orbitals are heavily engaged in the bonding, but this result is in contrast to the findings of other authors [3]. With respect to the excited states, it has often been assumed that their nature could be understood on the basis of a MO level diagram, which is common to all tetrahedral systems of this type. Whereas this assumption is supported by the results from semiempirical calculations of the Wolfsberg-Helmholz type [1], it is not compatible with the results obtained by more extended methods. Thus Oleari *et al.* [7] found the order of the lowest unoccupied MO's to be different for MnO_4^- and CrO_4^{2-}, and it is also known that one cannot predict the order of excited states from the order of MO's alone [3, 7].

The present set of calculations leads to the conclusion that the order and nature of the excited states vary from one of the tetrahedral systems to the next. More theoretical and experimental studies are, however, needed in order to arrive at definite conclusions as to the exact nature of the excited states, and only very tentative assignments can be made at the present stage.

2. Geometry and Choice of Radial Functions

The systems studied were all treated as being strictly tetrahedral. The metal-ligand bond distances were taken as 1.600 Å [12], 1.568 Å [12] and 2.185 Å [10] for CrO_4^{2-}, VO_4^{3-}, and $TiCl_4$, respectively.

As in the MnO_4^- calculation [4], the radial functions were taken from Clementi and Raimondi's tables [2] for the ligands, and from the papers of Richardson *et al.* [8, 9] for the central ions. No attempt was made to vary the metal orbitals, but on the basis of the study in Ref. [4] the $4s$ and $4p$ orbitals were chosen as $4s(d^{n-2}s^2)$ and $4p(d^{n-2}p^2)$ respectively, and the $3d$ orbitals were taken as $3d(d^{n-1})$. n is the number of valence electrons supplied by the neutral metal atom, and the notation is that of Ref. [4].

3. Results and Discussion

In Tables 1–3 we present the MO coefficients and one-electron energies from our calculations, and MO energy level diagrams are shown in Fig. 1. The MnO_4^- results from [4], with radial functions chosen as above, are included for the sake of comparison. The filled orbitals are in all cases $1a_1$, $2a_1$, $1t_2$, $2t_2$, $3t_2$, $1e$ and t_1.

The characteristic feature mentioned in the introduction, that the $4s$ and $4p$ metal orbitals are heavily involved in the bonding, is evident from the tables. It is also seen, that the order of the highest occupied and the lowest empty orbitals changes in going from one system to another. It is especially noteworthy, that the $4t_2$ orbital has lower energy than the $2e$ orbital in VO_4^{3-} and $TiCl_4$. From the analysis of Ref. [4] it is known, that the position of the $2e$ orbital is very dependent on the form of the radial functions involved, so that the $4t_2 - 2e$ separation may have been overestimated for these two compounds. Especially for $TiCl_4$, however, the separation is so large, that very drastic changes would be required to reverse the order of the $4t_2$ and $2e$ orbitals, so that we believe the order to be correctly given here for this compound.

The low energy of the $3a_1$ orbital is also of great interest. In crystal field treatments this orbital is assumed to be situated above the $2e$ and $4t_2$ orbitals, and this is also where it is found in calculations of the extended Wolfsberg-

Table 1. *Molecular orbitals for* CrO_4^{2}

	Eigenvalues (eV)	Eigenvectors				
		s	σ_s	σ_p		
a_1	10.136	−0.2814	−0.1104	0.9532		
	−10.613	0.6809	0.6769	0.2794		
	−31.465	−0.6761	0.7277	−0.1153		
		d	π			
e	8.692	0.8530	−0.5219			
	− 8.107	0.5219	0.8530			
		p	d	σ_p	σ_s	π
t_2	19.373	−0.1954	−0.6117	0.7367	0.1521	0.1477
	8.493	−0.6263	0.4090	0.1586	−0.4103	0.4969
	− 5.549	−0.0630	0.3661	0.4895	−0.2541	−0.7468
	−17.015	0.6719	0.4272	0.4353	0.0703	0.4143
	−29.568	−0.3379	0.3768	0.0545	0.8597	−0.0436
		π				
t_1	− 5.032	1.0000				

Helmholz type [3]. A low position of the $3a_1$ orbital was, however, also found by Oleari *et al.* [7] for the CrO_4^{2-} ion.

By means of the approximate expression (22) of Ref. [4] we have calculated the one-electron transition energies in Table 4. Each transition listed gives rise to just one orbitally allowed transition ${}^1A_1 \rightarrow {}^1T_2$ (besides orbitally non-allowed transitions). For comparison we have again included the results from the relevant MnO_4^- calculation of Ref. [4].

The experimentally observed absorption maxima for the systems under study are listed in Table 5. It is seen that the experimentally observed trend,

Table 2. *Molecular orbitals for* VO_4^{3-}

	Eigenvalues (eV)	Eigenvectors				
		s	σ_s	σ_p		
a_1	16.305	−0.2363	−0.1343	0.9624		
	− 3.289	0.6604	0.7043	0.2604		
	−25.528	−0.7128	0.6971	−0.0777		
		d	π			
e	18.887	0.8676	−0.4972			
	− 2.447	0.4972	0.8676			
		p	d	σ_p	σ_s	π
t_2	29.172	−0.0911	−0.7202	0.6251	0.2477	0.1449
	15.687	0.6139	−0.3415	−0.3757	0.4296	−0.4252
	2.222	0.0808	0.2554	0.5560	−0.1834	−0.7651
	−10.216	0.7201	0.3474	0.3831	0.0385	0.4611
	−23.931	−0.2997	0.4229	0.1107	0.8479	−0.0134
		π				
t_1	1.438	1.0000				

Table 3. *Molecular orbitals for* $TiCl_4$

	Eigenvalues (eV)	Eigenvectors				
		s	σ_s	σ_p		
a_1	− 5.335	−0.3373	−0.0145	0.9413		
	−18.109	0.9186	0.2135	0.3325		
	−27.267	−0.2058	0.9768	−0.0587		
		d	π			
e	4.101	0.9471	−0.3208			
	−14.896	0.3208	0.9471			
		p	d	σ_p	σ_s	π
t_2	8.460	0.1062	0.8178	−0.5104	−0.2026	−0.1357
	− 4.279	−0.6842	0.2855	0.2391	−0.2056	0.5924
	−13.993	−0.1214	0.3011	0.6907	−0.1704	−0.6233
	−20.998	0.7036	0.2517	0.4428	−0.0602	0.4918
	−29.634	−0.1037	0.3094	0.0958	0.9402	0.0187
		π				
t_1	−13.354	1.0000				

that the absorption edge is shifted towards higher energies in passing from MnO$_4^-$ through CrO$_4^{2-}$ to VO$_4^{3-}$, is well represented by our calculations. An assignment of the electronic spectrum was made in Ref. [4] for MnO$_4^-$; it is tempting to suggest that the maxima observed for CrO$_4^{2-}$ are associated with the transitions $3t_2 \rightarrow 2e$ and $t_1 \rightarrow 2e$, and that the transition observed in VO$_4^{3-}$ is $3t_2 \rightarrow 3a_1$. In spite of the good numerical agreement such assignments must, however, be considered with great caution.

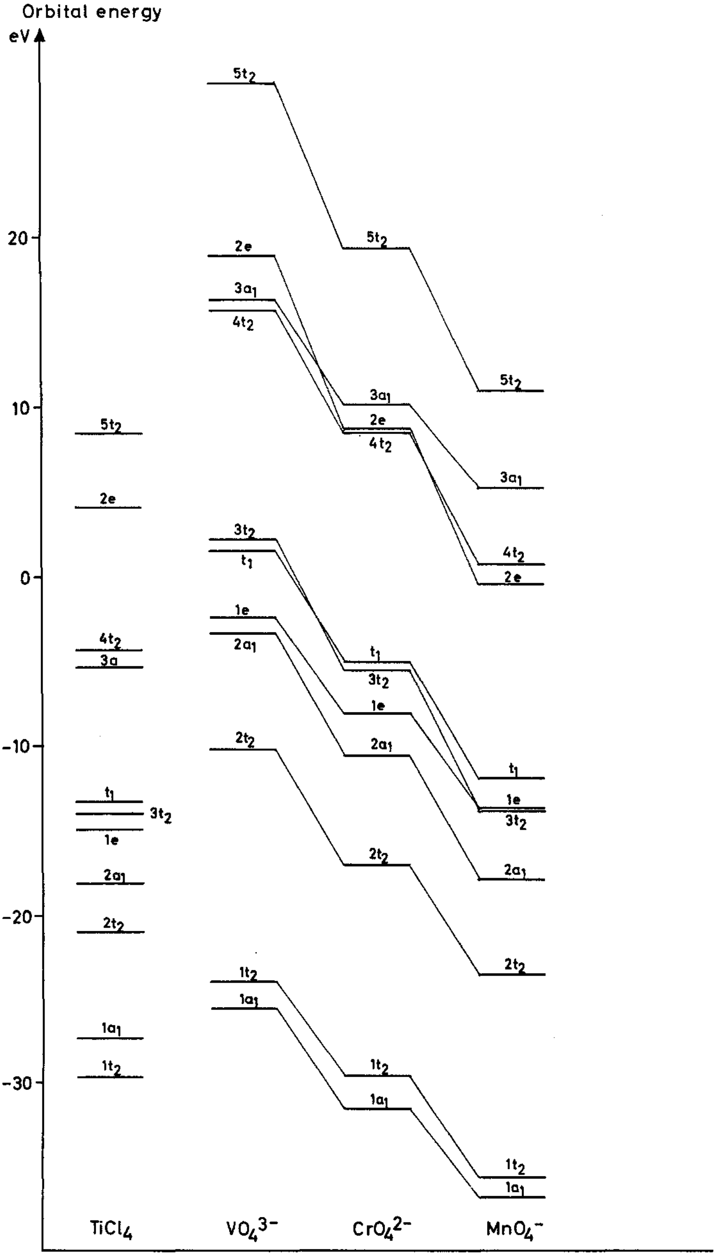

Fig. 1. MO energy level diagram

Table 4. *Calculated transition energies in eV*

$TiCl_4$	2.25	$(3t_2 \rightarrow 3a_1)$
	3.40	$(t_1 \rightarrow 4t_2)$
	3.91	$(3t_2 \rightarrow 4t_2)$
VO_4^{3-}	4.66	$(3t_2 \rightarrow 3a_1)$
	5.53	$(3t_2 \rightarrow 4t_2)$
	6.36	$(t_1 \rightarrow 4t_2)$
CrO_4^{2-}	4.23	$(3t_2 \rightarrow 2e)$
	4.64	$(t_1 \rightarrow 2e)$
	5.76	$(t_1 \rightarrow 4t_2)$
MnO_4^-	2.41	$(3t_2 \rightarrow 2e)$
	2.50	$(t_1 \rightarrow 2e)$
	4.75	$(t_1 \rightarrow 4t_2)$
	6.01	$(1e \rightarrow 4t_2)$
	6.16	$(3t_2 \rightarrow 4t_2)$

Table 5. *Observed transition energies in eV*

System	Band maximum	Reference
$TiCl_4$	4.32	[5]
	5.24	
VO_4^{3-}	4.57	[11]
CrO_4^{2-}	3.32	[11]
	4.54	
MnO_4^-	2.27	[6]
	3.47[a]	
	3.99	
	5.45	

[a] Shoulder.

The ligands in MnO_4^- and $TiCl_4$ are quite different, and it is probably for this reason that Table 4 predicts the erroneous result, that MnO_4^- and $TiCl_4$ should have absorption edges quite close together. It is possible that the conclusions arrived at for MnO_4^- regarding the choice of radial functions are invalid for $TiCl_4$. It is therefore dangerous to attempt an assignment for $TiCl_4$, although the observed separation between the first two transitions is quite reasonably represented by our calculation.

4. Conclusion

The semiquantitative method applied in this and the preceding article was originally suggested in Ref. [3], and its main advantage is, that it avoids the use of semiempirical parameters. The picture it presents for the isoelectronic series MnO_4^-, CrO_4^{2-}, VO_4^{3-} is quite satisfying, whereas it seems necessary to reconsider the choice of radial functions in the case of $TiCl_4$. A study of this molecule and the radical VCl_4 is under way.

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