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SCF-SW-Xα Studies of Octahedral Clusters in Molybdenum Oxides

I. Simple Octahedra[1]

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SCF-SW-Xα calculations for MoO_6^{6-}, MoO_6^{8-}, and MoO_6^{10-} clusters are reported. The dependency of the Mo 3d binding energy on the oxidation number of the metal atom was examined and compared with experimental ESCA results. An interpretation of the MoO_3 reduction process is suggested on the basis of this comparison, namely, that the molybdenum oxidation number is lowered from +6 to +4 without a change of crystal structure in the first stage while the structure changes from corner-linked zigzag strings of octahedra to clusters of edge-sharing octahedra in the second.

1. INTRODUCTION

The mechanism for the reduction of the oxides of group VIb transition metals and their oxysalts have in recent years been the subject of considerable interest, due in particular to the phenomenon of "crystallographic shear." It has been suggested that this process may be responsible for the very rapid transport of oxygen observed in the lattices of such oxides (*1*).

Recently X-ray photoelectron spectroscopy was employed to investigate the course of reduction of MoO_3, a system which is especially interesting because of its versatile catalytic properties in both selective oxidation and selective hydrogenation processes (*2*). In the last few years several investigations of the molybdenum oxides and molybdates by the ESCA method have been published (*3–8*), but the results were mostly interpreted in terms of formation of Mo^{5+} and Mo^{4+} ions, whereas in the recent paper of Haber *et al.* (*2*) a rather different interpretation involving formation of Mo^{4+} and Mo^{2+} ions was suggested.

For these reasons, it seemed to us of particular interest to utilize the virtues of the SCF-SW-Xα method (*9, 10*) to study MoO_6^{6-}, MoO_6^{8-}, and MoO_6^{10-} clusters and to compare with the binding energies obtained for several oxidation states of molybdenum by experiment. Such an approach was successfully used to study localized excitations in NiO (*11*) and in VO and TiO (*12*). In (*11*) and (*12*), spin-polarized calculations were carried out for octahedral clusters using the SCF-SW-Xα method, and good agreement was obtained with the experimental results based on photoelectron as well as optical spectra.

In the present paper spin-restricted SCF-SW-Xα calculations are reported for the electronic structure and 3d binding energies in molybdenum oxides for different oxida-

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tion numbers of the central metal atom. The results are compared with the experimental ESCA spectra for inner shells, and a tentative interpretation is given.

2. METHOD OF CALCULATION AND PARAMETERS

An idealized geometrical model for the MoO_6 cluster was assumed in which the central metal atom is surrounded by a regular octahedron of oxygen atoms. The metal–oxygen bond length can be easily found from the crystal lattice constants (*13*) as 2.431 Å. It is assumed to be the same for all simple molybdenum–oxygen octahedral clusters in the present study.

The calculations of MoO_6^{10-}, MoO_6^{8-}, and MoO_6^{6-} clusters have been carried out by the SCF-SW-Xα method in the muffin-tin approximation (*9*, *10*). Since the exchange polarization of the MOs in the case of VO_6^{10-} and TiO_6^{10-} was found to be very small (*12*), we decided to perform only spin-restricted calculations in the first stage of our investigation. The excess charges of 10, 8, and 6 electrons, respectively, are due to the formal valence of the elements and the occupation of the energy levels. In order to take into account the stabilizing effect of the electrostatic field of the crystal environment, the clusters were surrounded by a Watson sphere (*14*) carrying appropriate charges of +10, +8, and +6, respectively. Sphere radii in the muffin-tin approximation were chosen according to the "touching spheres" requirement. The ratio of radii for molybdenum and oxygen spheres was chosen according to the ratio of Slater's atomic radii, and these radii were assumed to be equal to 1.7195 and 0.7115 Å, respectively. The radius of the Watson sphere was taken to be equal to the outer sphere radius. The atomic values of the exchange parameter α were equal to 0.70341 for Mo and 0.74447 for O (*15*). The α values for the inter-sphere and outer-sphere regions were taken equal to the oxygen α value.

We used the frozen core approximation in the first step of the calculations, but later the molybdenum and oxygen core orbitals were permitted to relax and to adjust their orbital energies during the self-consistent procedure. The ionization potential for the molybdenum 3d level was next calculated according to Slater's transition state technique (*16*).

3. GROUND STATE ENERGY DIAGRAMS

The calculated MO energies for MoO_6^{n-} (n = 6, 8, and 10) clusters are summarized in Table 1, columns 1, 2, and 3. In the case of MoO_6^{6-}, the $2t_{2g}$ level containing mostly the metal 4d orbital is empty; in the case of MoO_6^{8-} the same level contains two

TABLE 1

MO Energies (Ry)[a]

Mo^{6+}		Mo^{4+}		Mo^{2+}	
Symmetry	$-E_i$	Symmetry[b]	$-E_i$	Symmetry[b]	$-E_i$
$4a_{1g}$	0.117	$3e_g$	0.087	$3e_g$	0.038
$3e_g$	0.181	$4a_{1g}$	0.134	$2t_{2g}$	0.138
$2t_{2g}$	0.308		0.204	$4a_{1g}$	0.165
$1t_{1g}$	0.374		0.336		0.344
$4t_{1u}$	0.381		0.342		0.349
$1t_{2u}$	0.396		0.360		0.369
$3t_{1u}$	0.432		0.402	$2e_g$	0.408
$3a_{1g}$	0.475	$2e_g$	0.424	$3t_{1u}$	0.410
$1t_{2g}$	0.488	$3a_{1g}$	0.429	$1t_{2g}$	0.428
$2e_g$	0.495	$1t_{2g}$	0.437		0.438
$2t_{1u}$	1.469	$1e_g$	1.424		1.429
$1e_g$	1.471	$2t_{1u}$	1.425		1.430
$2a_{1g}$	1.480		1.436		1.440
$1t_{1u}$	2.943		2.799		2.702
$1a_{1g}$	4.653		4.505		4.405
Mo 3d	16.848		16.677		16.569
Mo 3p	27.768		27.598		27.490
Mo 3s	33.701		33.531		33.424
O 1s	37.275		37.200		37.184
Mo 2p	182.217		182.032		181.928
Mo 2s	197.609		197.425		197.320
Mo 1s	1420.007		1419.825		1419.724

[a] 1 Ry = 13.605 eV = 2.1796×10^{-18} *J*.

[b] Those levels for which the symmetry designation is not given have the same as given in column 1 for Mo^{6+}.

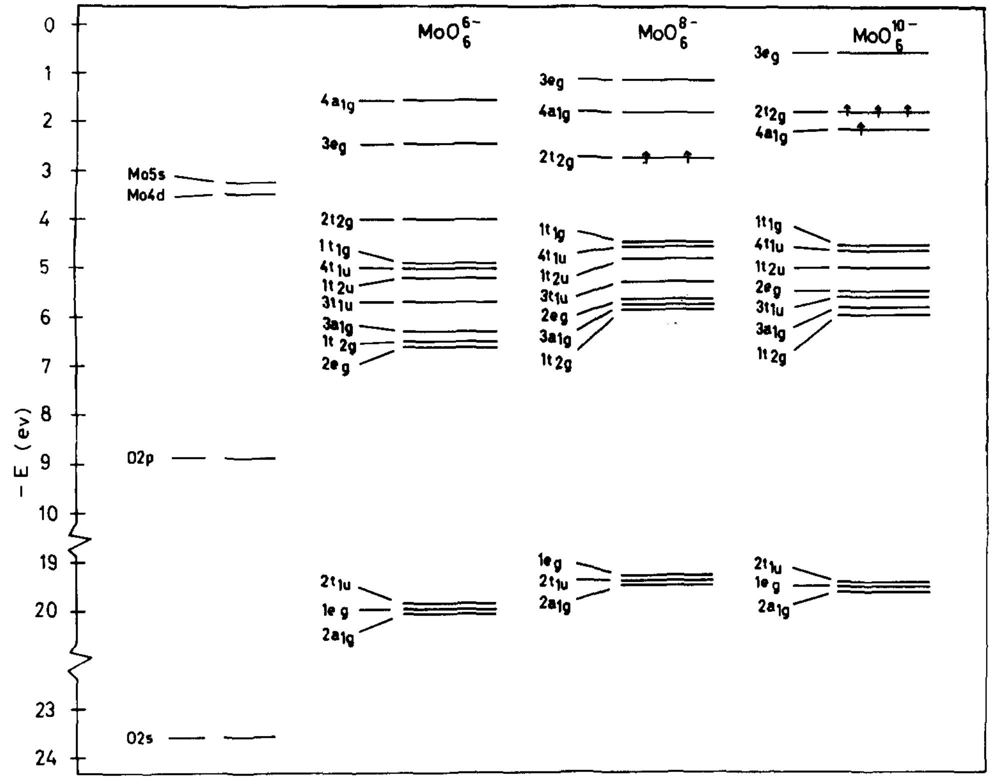

FIG. 1. MO eigenvalue spectra of MoO$_6^{6-}$, MoO$_6^{8-}$, and MoO$_6^{10-}$ clusters.

electrons. In the case of MoO$_6^{10-}$ the ordering of the highest valence levels is changed; the electronic configuration $4a_{1g}^1\ 2t_{2g}^3$ has been forced by the self-consistency requirements. This configuration is consistent with $4d^5\ 5s^1$ configuration of the neutral molybdenum atom. It may seem somewhat strange that the $3e_g$ orbital remains empty but such an arrangement of occupation numbers still satisfies Hund's rules and gives the maximal spin value for the compound. However, this is in full agreement with the high-spin behavior of molybdenum–oxygen complexes predicted by ligand-field theory (*17*).

The valence MOs of the clusters under consideration are shown in Fig. 1. For comparison the corresponding energy levels of the free atoms are presented in the same figure. The Fermi levels of the three clusters are not aligned in this figure because molybdenum ions are in three different oxidation states and there is no reason to have the same Fermi levels in different oxides. On the other hand, the experimental circumstances do not indicate the necessity of shifting the levels because the binding energies of the three forms of molybdenum oxides were established in three separate measurements during the course of reduction.

We shall discuss now in more detail the arrangement of the levels of column 3. The MO system of the cluster consists of three bands. One of them, in the energy range −19.4 to −19.6 eV, contains those orbitals with a large contribution of the oxygen 2s states and is located close to the 2s level of free oxygen. The group of levels in the range −4.7 to −6 eV is mainly the 2p oxygen band with covalent contributions of 4d, 5s, and 5p metal states to the t_{2g}, e_g, and t_{1u} orbitals. The energy distance between the 2s and 2p bands is about 14 eV. This value agrees reasonably well with the difference of the 2s and 2p energy levels of oxygen. The characteristic feature of the diagram in Fig. 1 is the small splitting of the energy levels of the 2s band, the width of which is much less than for the 2p band. Indeed the orbitals in the former group of MOs are almost pure atomic O 2s orbitals, whereas O 2p orbitals mix significantly with molybdenum valence orbitals. The location of the 4d band is very sensitive to the number of electrons in the cluster under consideration. The width of the empty 4d band is very large, and there is almost no splitting between the 2p and 4d bands. The addition of 4d electrons shifts the band to higher energy values, but the splitting between the $2t_{2g}$ and $3e_g$ levels still remains equal to about 1.4 eV.

All these conclusions regarding energy levels are in very good agreement with MO diagrams obtained for octahedral clusters in titanium and vanadium monoxides (*12*).

4. IONIZATION POTENTIALS AND THEIR INTERPRETATION

The main purpose of this work was to calculate ionization potentials for the molybdenum 3d level in the series of molybdenum oxides with different oxidation numbers of the central metal atom. We calculated the corresponding binding energies according to Slater's transition state method by performing the self-consistent procedure after removal of 0.5 electron from the level under consideration (*16*). Since the calculations were performed in a spin-restricted manner we did not obtain the splitting between the $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ doublet. The results are shown in Table 2. The experimental binding energies were taken from the work of Haber *et al.* (*2*). These results have been obtained in solid state measurements by means of ESCA spectroscopy, so the discrepancies between them and the values obtained in small cluster calculations are easy to explain. Our aim was not to compare absolute values of the binding energies but to establish the trends.

TABLE 2

Mo 3d Ionization Energies (eV)

Present calculations		Experiment	
MoO_6^{6-}	240.92	234.7	Mo^{6+} (MoO_3)
MoO_6^{7-}	240.00	—	—
MoO_6^{8-}	238.97	233.2	Form I
MoO_6^{10-}	237.85	231.4	Form II

There has been a great deal of discussion about the interpretation of the shifts of Mo 3d binding energies observed in the course of reduction of MoO_3. There are three forms of molybdenum ions in the sample during the reduction. Some authors (*8*) ascribe the three values of Mo 3d binding energy to Mo^{6+}, Mo^{5+}, and Mo^{4+} ions, respectively. But such an identification gives a nonlinear plot of binding energy versus oxidation number when the metallic core level is included (Fig. 2, curve c), whereas Siegbahn *et al.* (*18*) found such plots to be linear in the case of many other metallic species. This linearity of the binding energy plot was confirmed experimentally by Swartz and Hercules (*3*) for molybdenum. Based upon this, Haber *et al.* (*2*) proposed a quite different interpretation of the Mo 3d binding energies during the course of reduction. They assume that a linear relationship between E_B values, and the oxidation number should be obeyed in the case of molybdenum ions in oxidic systems.

Since the position of the Mo^{6+} ion and the position of metallic molybdenum are fixed, they fit the E_B values of the two other forms of molybdenum oxide. This is shown in Fig. 2 (curve a). It may be seen that the linear correlation is well obeyed if apparent oxidation numbers of +4 and +2 are assigned to forms I and II, respectively.

In order to check this interpretation we calculated Mo 3d ionization potentials for the formal valence of molybdenum equal to +6, +4, and +2 via the transition state SCF-SW-Xα procedure for MoO_6^{6-},

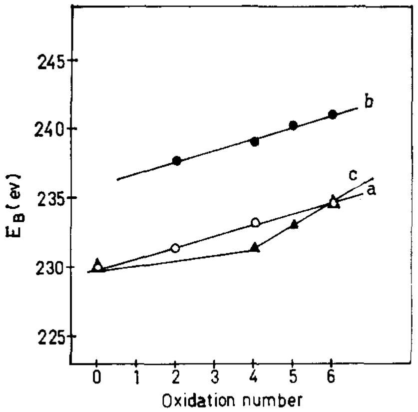

FIG. 2. Dependence of the ionization energies of Mo 3d on the apparent oxidation number. (a) Experimental values of Haber *et al.* (*2*) assigned to +6, +4, +2, and 0 (b) theoretical prediction (present calculation); (c) experimental values (*2*) assigned to +6, +5, +4, and 0 oxidation numbers.

MoO_6^{8-}, and MoO_6^{10-} clusters. In addition, we performed a similar calculation for a formal valence of +5, i.e., a MoO_6^{7-} cluster, in order to investigate the possible role of such a state in interpreting the experimental data. Our results are represented in Fig. 2 by curve b. It can be seen that linear correlation is well obeyed and that the slope of our line (b) is very similar to that of line (a). We include in this figure curve (c) which is based upon the assumption (*8*) that the experimental data reflects oxidation numbers of +6, +5, and +4. Comparison of (a), (b), and (c) shows clearly that the theoretical results support the interpretation of Haber *et al.* (*2*), namely line (a).

5. DISCUSSION

Our results presented in the last section enabled us to interpret the Mo 3d binding energy shifts in terms of formation of Mo^{6+}, Mo^{4+}, and Mo^{2+} ions. It is apparent that this interpretation is more reliable than the one of Cimino and de Angelis (*8*).

Our calculations were performed in all cases with the assumption of a simple geometrical model in which (a) the Mo–O bond distance was fixed and (b) the molybdenum ions were in an octahedral environment of oxygenions. Since there is no experimental evidence for the variation of the Mo–O bond distance as a function of the various oxidation states of the Mo ion, we employed a fixed Mo–O distance. The lack of the O 1s peak shift during the reduction leads us to conclude that the trend in the binding energies is due to the change in the oxidation number and not to a change in the chemical environment (such as a change in the coordination number or the Mo–O bond distance). However, in view of the well-known instability of divalent molybdenum ions in oxidic systems, the appearance of the apparent oxidation number of +2 for form II must have a different meaning. The existence of the Mo^{2+} ions can be explained by the change of MoO_3 crystal structure (*2*). The real structure of MoO_3 consists of strings of octahedra which are linked mostly by the corners, whereas in the case of MoO_2 there appear clusters of edge-sharing octahedra. In the latter arrangement the distance between two molybdenum ions decreases and it is possible to form a double bond between the two paired Mo^{4+} ions. In such a case the effective charge of each molybdenum ion may be regarded as corresponding to the apparent oxidation number of +2. In order to check this interpretation the model of the cluster composed of at least two octahedra should be examined. Calculations with this model are in progress.

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