

DFT description of structure and bonding in transition metal oxides

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Abstract

The electronic structure of vanadium and molybdenum monoxides have been studied by means of the DFT method, with special attention being paid to bonding characteristics in the oxides. Various physical properties of neutral and ionized molecules are discussed in order to understand their reactivity and catalytic properties.

1. Introduction

Transition metal oxides (TMO) are systems of great importance from both a theoretical and an experimental point of view. For experimentalists, properties of the metal–oxygen bonds are crucial for understanding the bonding pattern and the reactivity of various oxides as one proceeds along the periodic table. Thus, theoretical characterization of the electronic structure and molecular bonding in TMO diatomic molecules, neutral and ionic, may bring an interesting insight into the properties of surface groups and catalytic centers on oxide surfaces. As vanadium and molybdenum oxides are materials of special importance in catalysis, this paper deals with the electronic structure of VO and MoO molecules and their positive ions. Attention will be paid in particular to a proper description of the bonding features in the studied systems. Various physical properties such as spectroscopic constants, ionization potentials and photoelectron spectra will be derived from quantum chemical calculations and will be compared with those from experiments to give an overall impres-

sion of the successes and failures of the theory.

On the theoretical side, transition metal systems are extremely difficult to handle by quantum chemical methods because of many unpaired electrons. Only when the application of density functional (DFT)-based methodologies [1] became available could these highly open-shell structures be properly described. In the following study, LCGTO implementation of the spin-polarized density functional method [2] has been employed to theoretically describe the electronic structure of vanadium and molybdenum oxide diatomics. The detailed description of the method and the computer program deMon have already been given in previous papers and will not be repeated here. Also numerical details of the calculations have already been described elsewhere [3–6].

2. Ground state properties of vanadium and molybdenum oxides

The ground state of VO has been definitely identified by both experiment and theory as the

Table 1

Ground state properties of neutral and ionized VO and MoO with non-local corrections^a; CPF [7]^b; from ref. [8]^c; from ref. [9]^d

		VO $^4\Sigma^-$	VO ⁺ $^3\Sigma^-$	MoO $^5\Pi$	MoO ⁺ $^4\Sigma^-$
R_e (Å)	Exp.	1.59 ^c	1.54 ^c	1.70 ^d	–
	DFT	1.58	1.54	1.73	1.65
ω_e (cm ⁻¹)	Exp.	1002 ^c	1060 ^c	893 ^d	–
	DFT	993	1146	879	1035
D_e (eV)	Exp.	6.44 ^c	5.98 ^c	5.00 ^d	–
	DFT ^a	7.04	6.82	5.45	4.88
μ (D)	DFT	3.328	2.885	3.048	2.028
	ab initio ^b	2.499	–	2.287	–
Q_{Me}	DFT	0.34	1.15	0.42	1.16
	ab initio ^b	0.34	–	0.43	–

$X^4\Sigma^-$, coming from $\sigma\delta^2$ configuration. A molybdenum oxide molecule has one electron more placed in antibonding d_π -type orbitals which leads to the $\delta^2\sigma^1\pi^1$ configuration and a $^5\Pi_r$ ground state term. In the valence (chemical) region of both molecules six electrons occupy strongly bonding, oxygen-centered σ_b and π_b orbitals. The next three levels, σ and δ , coming from metal s and d_δ orbitals, are essentially non-bonding and they comprise three unpaired electrons in both cases. The major difference between the two oxides comes from antibonding d_π levels occupied in MoO by one electron. This electronic pattern would lead to a formal bond order close to 3 in VO and to 2.5 in MoO. Experiments show, indeed, an increase in the bond length of 0.11 Å and a decrease in the dissociation energy of 1.44 eV while passing from VO to MoO (DFT calculations predict the shift of 0.15 Å and 1.60 eV, respectively).

A full list of calculated ground state properties of the oxides under consideration is given in Table 1. It comprises equilibrium bond distances, dissociation energies, vibrational frequencies, dipole moments and metal charges for both molecules, both neutral as well as ionized. The density functional estimates when compared with experimental results, where available, show the excellent performance of density functional methodology for transition metal systems. All but one theoretical value was obtained within the simplest LDA approximation. The non-local exchange–correlation functional was only used for bond energy

where the electronic correlation was known to be the most crucial factor. The atomic total energies computed with BSSE correction and non-spherical density were taken as the reference level.

The electronic properties of the cations are also important factors in discussing bonding and the reactivity of the oxides. The ground state of VO⁺ is predicted to be $^3\Sigma^-$, with a bond length of 1.54 Å and a harmonic frequency of 1146 cm⁻¹, which is in excellent agreement with experimental results. The data for molybdenum oxide cation cannot be compared with experimental results. However, in view of the good agreement between predicted and experimental results in the former case, we are led to believe that the same will also be the case for molybdenum oxide. Shortening of the metal–oxygen bond on ionization is twice as large as for vanadium oxide, also the decrease in the dissociation energy is twice as large for MoO as for VO. Comparison with experimental results shows that DFT bond energies are overestimated for neutral molecules by 10% and even more for cations. Thus the bond energy for MoO⁺ should not exceed 100 kcal/mol.

There exist no experimental data regarding dipole moments and atomic charges and thus only a comparison of these quantities with other ab initio calculations can be given for neutral molecules [7]. The metal charge agrees very well with other calculations which gives a valuable argument in the discussion on the prevailing covalent contribution to bonding in the studied oxides. Theoretical DFT dipole moments should be fairly

close to experimental in view of the well known tendency of ab initio methods to underestimate their value. As a consequence of shorter bond distances, dipole moments decrease on ionization even if the metal charge increases. Again the effect is much more pronounced for molybdenum oxide. The presented data will form the basis for the discussion of the character of metal–oxo bonds below.

3. Ionization of vanadium and molybdenum oxides

The study of a transition metal oxide in the gas phase by photoelectron spectroscopy (PES) offers a unique opportunity to probe the electronic structure of the isolated molecule. A good quality PES investigation of vanadium monoxide has already been reported [8], providing interesting material on which the theoretical electronic structure of the molecule could be tested more extensively. Unfortunately, the MoO molecule has only recently become the subject of spectroscopic studies [9] and no PES data could be found. Nevertheless, the results of the DFT study on the photoelectron spectroscopy of both molecules are given here to complement data for an electronic structure investigation.

Table 2 shows the calculated adiabatic ionization potentials obtained as the difference of the optimum ground state total energy of the neutral molecule and the minimum energy point of the appropriate state of the cation. As the total energy differences are considered here, they have been estimated again with non-local exchange–correlation potential to include correlation in the most efficient way. For each ionization one-electron description is given in order that the physical process can be better visualized. However, the actual basis for calculations is the transition between the appropriate multi-electronic states of the neutral and ionized molecule. The initial and final state of the process are given in the second column. PES measured ionization energies of VO are given in parentheses. For each final state of the cation the DFT equilibrium bond distance, the vibrational frequency and the dissociation energy are listed, although a comparison with experimental results is available only for the ground state of VO^+ . Ionizations from both, α - and β -manifolds have been considered, however in the case of MoO only the lowest β -ionization could be reached due to the state-symmetry requirements in DFT.

One can see from Table 2 that the agreement between theoretical and experimental results for vanadium monoxide is strikingly good. This allows one to assume a high level of confidence

Table 2

Ionisation potentials and properties of ionized states of VO and MoO: ^aa broad band observed in the range of 10.0–13.0 eV; experimental values given in parentheses taken from ref. [8]

Ionized electron	<i>I</i> and <i>F</i> states	<i>I</i> _p (eV)	<i>R</i> _e (Å)	ω_e (cm ⁻¹)	<i>D</i> _e (eV)
<i>VO</i>					
$(\sigma_{4s})^{-1}$	$^4\Sigma^- \rightarrow ^3\Sigma^-$	7.18 (7.25)	1.54 (1.54)	1146 (1060)	6.815 (5.98)
$(\delta_{3d})^{-1}$	$^4\Sigma^- \rightarrow ^3\Delta$	8.50 (8.42)	1.56	1065	5.46
$(\pi_b\beta)^{-1}$	$^4\Sigma^- \rightarrow ^5\Pi$	10.50 ^a	1.79	696	3.46
$(\sigma_b\beta)^{-1}$	$^4\Sigma^- \rightarrow ^5\Sigma^-$	11.04 ^a	1.73	750	2.90
<i>MoO</i>					
$(\pi_{4d})^{-1}$	$^5\Pi \rightarrow ^4\Sigma^-$	8.05	1.65	1035	4.88
$(\sigma_{5s})^{-1}$	$^5\Pi \rightarrow ^4\Pi$	8.26	1.69	1007	4.67
$(\sigma_b\beta)^{-1}$	$^5\Pi \rightarrow ^6\Sigma, ^6\Delta$	11.41	–	–	–

also for the molybdenum results. A comparison of the VO DFT results with experimental results confirms the previous assumption that the first ionization process can be described approximately as a metal $(4s)^{-1}$ ionization whereas the second VO band can be attributed essentially to a metal $(3d)^{-1}$ ionization. Detailed experimental resolution of the β -ionization region (10.0–13.0 eV) is not possible but it is thought that this band may be attributed to components arising from the $(\sigma_b^*)^{-1}$ and $(\pi_b^*)^{-1}$ ionizations of VO, which is in very good agreement with the present results. Thus the electronic structure of vanadium monoxide seems to be revealed and interpreted precisely enough. Other data listed in Table 2 should stimulate further PES studies on vanadium oxides and should promote such investigations on molybdenum oxides.

4. Discussion

The strength of the metal–oxygen bond in neutral and cationic MoO places this molecule in the intermediate position between early and late transition metal oxides (compare e.g. the values of 118 kcal/mol and 100 kcal/mol for MoO vs. MoO⁺ with experimental values of 146 kcal/mol vs. 131 kcal/mol for vanadium and 87 kcal/mol vs. 64 kcal/mol for cobalt). Early oxo complexes (e.g. VO⁺) exhibit high stability, are relatively inert and are characterized by very strong M–O bonds while late TMO's tend to be highly reactive oxidizing agents with much weaker M–O bonds. According to this, molybdenum oxides can be expected to reveal moderate activity, being mild oxidants for hydrocarbons and alcohols. Indeed, almost triply-bonded oxygen in VO⁺ is relatively

inert, as observed towards a variety of hydrocarbon substrates, whereas iron and ruthenium oxides are exceedingly powerful oxidising agents. The reactivity of metal–oxo systems can be understood by considering the type of metal–oxygen bond formed [10], with early metals forming strong, unreactive triple bonds and late metals forming weak, reactive biradical double bonds. The present calculations have given a bond order for vanadium close to 2.5 (neutral) and 3.0 (cationic). For MoO the numbers were close to 2.1 and 2.5, respectively, which confirms its intermediate character and the moderate, selective oxidative properties of the oxygen involved in the bonding with molybdenum.

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