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Ab initio simulation of titanium dioxide clusters

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Abstract

Density functional calculations are performed on small neutral and negatively charged Ti_nO_{2n} clusters, with $n = 1–3$. The relative stability of the various isomers results from a subtle competition between ionic and covalent effects in the Ti–O bonding, and is affected by the overall charge state of the cluster. Electron affinities and optical excitation gaps, calculated through total-energy differences, are discussed and compared with recent anion photoelectron data. The excess electron of the negatively charged clusters is mostly localized on titanium with the weakest electrostatic potential, which permits a simple interpretation of the computed electron affinities based on the chemical shifts of the deep Ti levels. The trends obtained for both the electron affinities and the excitation gaps as a function of n help the identification of the most stable isomers consistent with the experimental conditions.

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1. Introduction

An increasing interest towards oxide clusters has appeared recently, due to the possible technological applications of these small systems in catalysis, and because they represent model systems for the oxidation processes taking place at surfaces. Especially interesting is the fact that, at small sizes, the local environment of the atoms strongly departs from the bulk, which induces specific site reactivity and selectivity.

Titanium oxide clusters have been considered in this context both theoretically and experimentally. Aside from the many works devoted to the TiO molecule [1], and from the experimental study of the TiO_2 trimer [2], positively charged titanium–oxygen clusters $Ti_nO_{2n-\delta}^+$ $(n = 1–7,\ \delta = 0–4)$ have been investigated with mass spectrometry and collision induced dissociation [3]. A simple pair-potential ionic model was used to calculate optimized geometric structures and showed that the lowest energy Ti_nO_{2n} isomers have pendant oxygen atoms. Recently, negatively charged TiO_y^- $(y = 1–3)$ and $(TiO_2)_n^-$ $(n = 1–4)$ clusters have been produced and studied using anion photoelectron spectroscopy [4]. The energy difference between the two peaks of lowest binding energy has been interpreted as the gap between the ground state and the lowest excited state of the neutral cluster (i.e., an electronic excitation at fixed electron number). It is important to note that this excitation gap is affected by excitonic effects and is therefore in principle different from the HOMO–

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LUMO gap usually defined as the difference between the ionization potential I and the electron affinity A. The authors stressed that the gaps obtained for the stoichiometric clusters $(TiO_2)_n$ ($n = 1, \ldots, 4$) are close to 2 eV, nearly independently of n.

From a theoretical point of view, TiO_y molecules ($y = 1$–2) have been studied with various methods [5,6]. Ab initio Hartree–Fock calculations have been performed on neutral and positively charged $Ti_nO_{2n-\delta}$ clusters ($n = 1$–3, $\delta = 0, 1$), in order to determine the equilibrium geometries, ionization potentials and vibrational spectra [5].

The aim of the present study is the analysis of the atomic and electronic properties of the series Ti_nO_{2n} ($n = 1, 2, 3$). Using an ab initio approach based on Density Functional Theory (DFT), we simulate low energy Ti_nO_{2n} isomers, both neutral and negatively charged. We discuss the size dependence of the electron affinity and the excitation gap. Through a careful comparison with the experimental results, we show that the electronic properties can be used to help in the identification of the most stable isomers. After a description of the numerical method in Section 2, we present our results in Section 3 and their discussion in Section 4.

2. Method

The electronic structure calculations are carried out within the DFT, using the Local Spin Density Approximation (LSDA) for the exchange and correlation energy [6]. The Kohn–Sham orbitals are expanded in a plane-wave basis set up to a kinetic energy cutoff E_{cut}, and soft, norm-conserving pseudopotentials are used to describe the interaction between the ionic cores ($1s$ Oxygen atomic states, $1s$, $2s$ and $2p$ titanium states), and the valence electrons. The inclusion of the titanium $3s$ and $3p$ states in the valence is found to be necessary to obtain a good agreement with experiment and accurate calculations available on TiO [7,8].

The interaction between core and valence electrons is described by norm-conserving pseudopotentials in the Kleinman–Bylander form [9] including s, p and d components for oxygen and titanium. A local reference potential is chosen (d component for oxygen, s for titanium). We follow the prescriptions given by Troullier and Martins [10] in the generation of pseudopotentials. The core radii chosen for O (Ti) are 1.38 (1.30) a.u., 1.60 (1.40) a.u. and 1.38 (1.80) a.u. for the s, p, and d components, respectively.

A supercell geometry, with a face-centered cubic cell of lattice parameter equal to 35 a.u., is used, and integration in the Brillouin Zone is performed with a single $\vec{k} = \vec{0}$ point. A cutoff energy of 60 Ry is needed to get total energies converged within 0.1 eV/atom. Nevertheless, total energy differences between different clusters can be accounted for with a precision of about 0.2 eV/atom at lower $E_{cut} = 40$ Ry, as checked on some selected structures. For computational reasons, the calculations are performed by using $E_{cut} = 60$ Ry for TiO_2 and $(TiO_2)_2$, and $E_{cut} = 40$ Ry for $(TiO_2)_3$.

In order to find out the ground state configurations, we start from structures suggested in Ref. [3] by simple pair-potential simulations. Then, the geometries are optimized until the atomic forces do not exceed 0.03 eV/Å. The calculated electronic structures refer to the stable configurations optimized fully self-consistently.

3. Results

The computed bond length and bond angle of the TiO_2 molecule are equal to 3.076 a.u. and 109.50°, respectively. They are in agreement both with experiment [2] (3.061 ± 0.15 a.u. and $110° \pm 15°$), and previous calculations [5,6]. We find a dissociation energy into neutral atoms equal to 17.34 eV, which is overestimated with respect to the experimental value (13.18 eV) as usual in the LSDA. The adiabatic electron affinity $A = 1.58$ eV is calculated as the total-energy difference between the ground states of the TiO_2^- and TiO_2 molecule. The addition of an electron on TiO_2 weakens the titanium–oxygen bonds (3.134 a.u. vs. 3.076 a.u.) and increases the bond angle by 2°. The contribution of the atomic relaxations to A is 0.06 eV.

For $(TiO_2)_2$, we find two low energy isomers represented in Fig. 1, of C_{2h} and C_{3v} symmetry. The C_{2h} isomer is non-planar, as a result of the bent configuration of the TiO_2 trimer. As predicted by simple ionic arguments [3], the C_{2h} isomer is more stable. The calculated energy difference here is equal

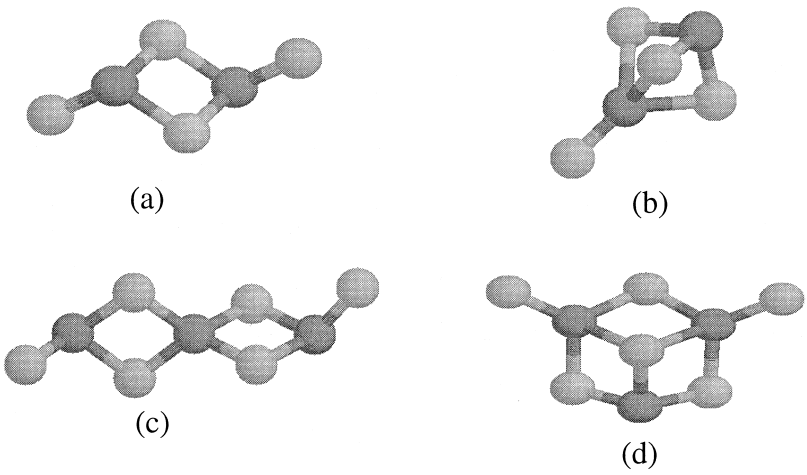

Fig. 1. Ball and Stick representation of the structure of $(TiO_2)_n$ clusters. (a) C_{2h}-$(TiO_2)_2$; (b) C_{3v}-$(TiO_2)_2$; (c) S_4-$(TiO_2)_3$; (d) C_s-$(TiO_2)_3$. O atoms are drawn in light grey, Ti atoms in dark grey.

to 0.44 eV. It is interesting to note that the same isomer ordering was found in $(Li_2O)_2$ clusters [11,12], a system with a reversed stoichiometry, but not in $(Cs_2O)_2$ clusters [13]. This stresses the delicate competition existing between attractive cation–oxygen interactions and repulsive forces between alike ions. This fine balance is also revealed when considering the two negatively charged $(TiO_2)_2^-$ isomers, whose energy difference is equal to a few meV. The adiabatic electron affinities are equal to 1.28 and 1.73 eV for the C_{2h} and C_{3v} isomers, respectively. The experimental value is 2.1 eV [4]. The two $(TiO_2)_2$ isomers present structural features which fulfill the general trends found in undercoordinated systems, i.e., an increase of the bond lengths when the coordination numbers of one or the other of the two partner atoms increases. When one excess electron is present, a bond length expansion occurs as in TiO_2. It is symmetric with respect to the center of the cluster for C_{2h}-$(TiO_2)_2^-$. In the C_{3v} isomer, the largest expansion (0.08 a.u.) takes place around the three-fold coordinated titanium, which suggests that the excess electron is not equally distributed around the two Ti sites.

For $(TiO_2)_3$, we obtain two low energy isomers represented in Fig. 1, of S_4 and C_s symmetry. At variance with the results of pair-potential calculations [3] which predict a small energy difference of 0.04 eV in favor of S_4-$(TiO_2)_3$, we find the C_s isomer lower in energy by 0.45 eV. The stability of this isomer, which was not recognized previously [7], is an indication that covalent effects are important in the physics of TiO_2 clusters, a well-known fact as far as bulk TiO_2 is concerned. The adiabatic electron affinities of the C_s and S_4 isomers are 2.33 eV and 1.74 eV, respectively.

As in $(TiO_2)_2$, a correlation exists between the bond lengths in the neutral clusters and the atomic coordination numbers. For instance, in C_s-$(TiO_2)_3$, the mean bond lengths $\bar{d}(Ti^{(Z)})$ and $\bar{d}(O^{(Z)})$ around titanium or oxygen Z-fold coordinated are: $\bar{d}(Ti^{(3)}) = 3.28$ a.u., $\bar{d}(Ti^{(4)}) = 3.53$ a.u., $\bar{d}(O^{(1)}) = 3.11$ a.u., $\bar{d}(O^{(2)}) = 3.45$ a.u., $\bar{d}(O^{(3)}) = 3.73$ a.u.

When an electron is added in the C_s isomer, relaxation effects mainly involve a bond expansion around the three-fold coordinated titanium accompanied by a contraction further away. In the S_4 isomer, the bond lengths around the central Ti remain unchanged, while a bond expansion takes place around the outer titanium. The analysis of bond lengths in $(TiO_2)_2^-$ and $(TiO_2)_3^-$ isomers shows that bond weakening predominantly occurs around the most undercoordinated titanium. Indeed, by visualizing the HOMOs, we find that the excess electron is mostly localized on the titanium with the lowest coordination number, i.e., three, in C_{3v}-$(TiO_2)_2$, C_s-$(TiO_2)_3$ and S_4-$(TiO_2)_3$ (see Fig. 1).

In order to compare our theoretical results to the experiments and get insight into the connection between the structure and the electronic properties of

these clusters, we calculate the total energy of the first excited state of the neutral cluster by forcing both the LUMO and the HOMO to be filled by a single electron (instead of 0 and 2, respectively), either with antiparallel or parallel spins. Full electronic self consistency and geometry optimization of the excited $(TiO_2)_n^*$ clusters are then performed under this constraint. The difference G between the computed total energies of the excited and the ground state is equal to 2.35, 3.48, 2.71, 2.44 and 3.20 eV for TiO_2, C_{2h}-$(TiO_2)_2$, C_{3v}-$(TiO_2)_2$, C_s-$(TiO_2)_3$ and S_4-$(TiO_2)_3$, respectively. We check that exchange effects coming from the electron-hole interaction in the case of parallel or antiparallel spin are small: the two gaps are equal within 0.03 eV for C_{3v}-$(TiO_2)_2$ and C_s-$(TiO_2)_3$. DFT calculations on other clusters showed that reliable energy gaps (either including excitonic effects [14] or not [15]) can be obtained in that way, although DFT is known to give a poor description of electronic excitations when considering the Kohn–Sham eigenvalues obtained at fixed number of electrons [16]. We thus expect that our computed Gs give a good estimate of the optical charge transfer excitations in these closed shell systems.

4. Isomer stability and electronic structure

The computed equilibrium geometries of $(TiO_2)_n$ clusters are very far from bulk derived structures. Even for the largest size, titanium are at most four-fold coordinated, while in bulk rutile they are at the center of an oxygen octahedra. Moreover, in these clusters there are terminal, one-fold coordinated oxygen, as also found in more complex titanium–oxygen derived systems [17]. These titanyl groups are believed to involve a rather covalent double bond between the two atoms, thus suggesting that the bond ionicity is much lower than in more compact structures with larger Ti–O coordination number. Even in bulk TiO_2, the Ti–O bond is far from being purely ionic, inasmuch as the mixing between titanium and oxygen states in the valence band has been revealed by resonant photoemission [18]. According to this scenario, we assign the origin of the discrepancy about the energy ordering of $(TiO_2)_n$ clusters, between the predictions of empirical potentials [3] and the results of our DFT simulations, to the delicate balance of ionocovalent effects in the Ti–O bonding.

The electron affinities A are intimately related to the localization of the excess electron in the negatively charged $(TiO_2)_n^-$ clusters. We find that in all the clusters that we study the excess electron is mostly localized on the $3d$ orbitals of the titanium(s) having the weakest electrostatic potential V_{es}. Consequently, we expect that the HOMO level of $(TiO_2)_n^-$ would experience approximatively the same chemical shift as the deeper Ti levels, e.g., the $3s$ ones ($\varepsilon_{Ti_{3s}}$), of the Ti on which the excess electron is localized. This simple model works pretty well, as proved by the fact that, among all the isomers of both $(TiO_2)_2$ and $(TiO_2)_3$, the sum $A + \varepsilon_{Ti_{3s}}(Ti_nO_{2n}^-)$ is constant within 0.2 eV, while A ranges from 1.28 eV for C_{2h}–Ti_2O_4 up to 2.33 eV for C_s-Ti_3O_6.

The comparison with the experimental values of both A and G [4] is complicated by the fact that, in anion photoelectron spectroscopy the measured values refer to the neutral Ti_nO_{2n} species, very likely in the topology of the most stable $Ti_nO_{2n}^-$ isomers. Therefore, comparison of our computed A and G for the various neutral clusters to experimental data may help the identification of the most stable negatively charged isomers in the experimental conditions. The values of the computed adiabatic electron affinities do not display a monotonic trend as a function of size. Rather, they are very sensitive to the specific isomer conformation. In $(TiO_2)_2$ and $(TiO_2)_3$, the smallest value is found for the linear isomers, which, because of their rather open geometries, have the weakest V_{es} acting on Ti ions. The best agreement with the experimental values A_{exp} is found for C_{3v}-$(TiO_2)_2$ at $n = 2$ ($A = 1.73$ eV vs. $A_{exp} = 2.1$ eV) and C_s-$(TiO_2)_3$ ($A = 2.33$ eV vs. $A_{exp} = 2.9$ eV) at $n = 3$. This supports our findings for the stability of $(TiO_2)_n^-$ species. It is also worth noting the excellent agreement with experiments obtained for the TiO_2 molecule ($A = 1.58$ eV vs. $A_{exp} = 1.59$ eV).

Likewise, the computed gaps G sensitively depend upon the atomic configurations, since G is strongly related to the localization of the electron-hole pair present in the excited state. A fair agreement with the measured gap [4] is found for TiO_2 ($G =$ 2.35 eV). As in the case of the adiabatic electron affinity A, for $n = 2$, 3 the best fit to the experimental values is found for C_{3v}-$(TiO_2)_2$ ($G = 2.71$ eV)

and for C_s-$(TiO_2)_3$ ($G = 2.44$ eV), respectively. This reinforces our prediction that the latter are the most stable charged isomers as seen in the experiments. As a function of n, these gaps display slight variations, as well as the experimental ones, although the latters are closer to 2 eV [4]. A better accordance with the experimental results might likely be obtained by considering the full dynamical behaviour of the clusters, since, as pointed out by the authors of Ref. [4], clusters of different size are not in the same thermal state.

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