

# A theoretical study of the Na–TiO<sub>2</sub> (001) rutile interaction

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## Abstract

A theoretical study of the reduction of the TiO<sub>2</sub> (001) rutile surface by atomic Na is reported. The study is based on ab initio embedded cluster calculations carried out for two different sites of this surface. The first one (A) is represented by a TiO<sub>4</sub><sup>4-</sup> cluster and the second (B), an oxygen ending site, by a cluster of formula TiO<sub>6</sub><sup>8-</sup>. The calculations show that adsorption of Na is possible on both sites although site A is energetically favored. The electron transfer process has been examined from state averaged complete active self consistent field (CASSCF) calculations. The analysis of these wave functions shows that the Na 3s electron is transferred to a Ti 3d orbital of the surface only on site A. For site B such a transfer would involve an excited state of the cluster. The dissociation curves for several electronic states are reported.

*Keywords:* Sodium; Rutile; Adsorption; Reduction

## 1. Introduction

The ways in which a metal atom can interact with the surface of a metal oxide are potentially extremely varied and complex, and the questions here are only just beginning to be addressed. Experimentally, there is very little information available about the detailed geometric structures adopted by adsorbed metal atoms; information about the initial stages of metal deposition is confined largely to certain aspects of the electronic structure and the degree of charge transfer between the adsorbed metal and the surface. Aside from catalysis, one of the most important applications of metals on oxide surfaces is to lower the work function [1–7]. For this purpose, the most effective metals are

the alkalis, since the ionization potential for removing the single s electron is relatively small, and it is thus easy to transfer that electron to the oxide.

Because of both its catalytic properties and electronic structure simplicity, most of the experimental work on the interaction of non-transition metals with transition-metal-oxides surfaces has been done on TiO<sub>2</sub>. In one study [1], Na was deposited onto polished and annealed surfaces of both planar TiO<sub>2</sub> (110) and stepped TiO<sub>2</sub> (441). In both cases the large decrease in the work function (3.4 eV for the (110) surface; 2.3 eV for (441)) and the appearance of emission in the bulk bandgap in UPS spectra indicated that the Na adsorbed ionically, donating its 3s electron to the Ti<sup>4+</sup> ions in TiO<sub>2</sub> and creating surface Ti<sup>3+</sup> ions. The Na/TiO<sub>2</sub> interaction was found to be strong and the bonding

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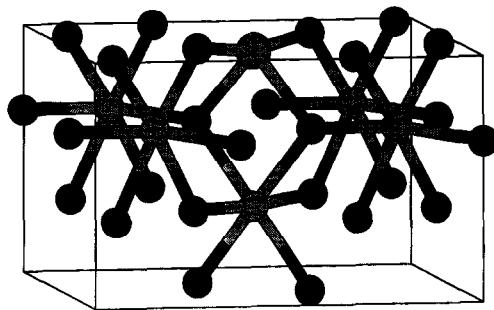
of Na to the surface was interpreted in terms of Na–O interactions and the creation of surface  $\text{Na}_2\text{O}$  units.

From a theoretical point of view, the electronic structure of rutile  $\text{TiO}_2$  has been the subject of considerable work using both periodical Hartree–Fock [8,9] and cluster model (see for instance Ref. [10]) calculations. However, despite its interest, no theoretical calculations on alkali/ $\text{TiO}_2$  systems have been reported. In the present work we report on a preliminary study of the Na/ $\text{TiO}_2$  system based on *ab initio* embedded cluster calculations. Our main goal is to understand how the electron transfer process takes place upon interaction between the alkali metal and the surface. For this we have considered two sites on the (001) rutile surface corresponding to four and six Ti coordination numbers on which a Na atom has been approached. In order to deal correctly with the problem associated to avoided crossings, state averaged multiconfigurational SCF wave functions have been employed.

## 2. The model

Among the low-index rutile surfaces the (001) one exhibits a high symmetry which makes it easy to model. Although this surface has been

Site A



Site B

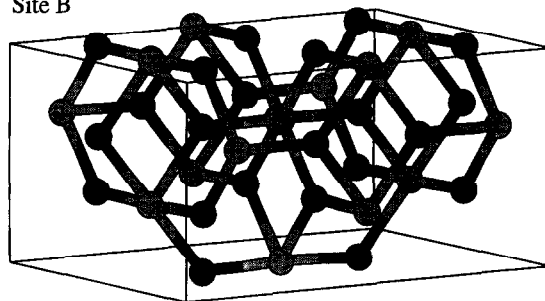


Fig. 2. Detailed structure of sites A and B showing the clusters and the set of TIPs. The clusters consist of the highlighted Ti centers plus the nearest oxide anions (four for site A and six for site B).

found to be less stable [11] we expect that the conclusions drawn in this work will be of general application. From experimental work, two kinds of surface reconstruction have been proposed for this plane [12]. In order to obtain

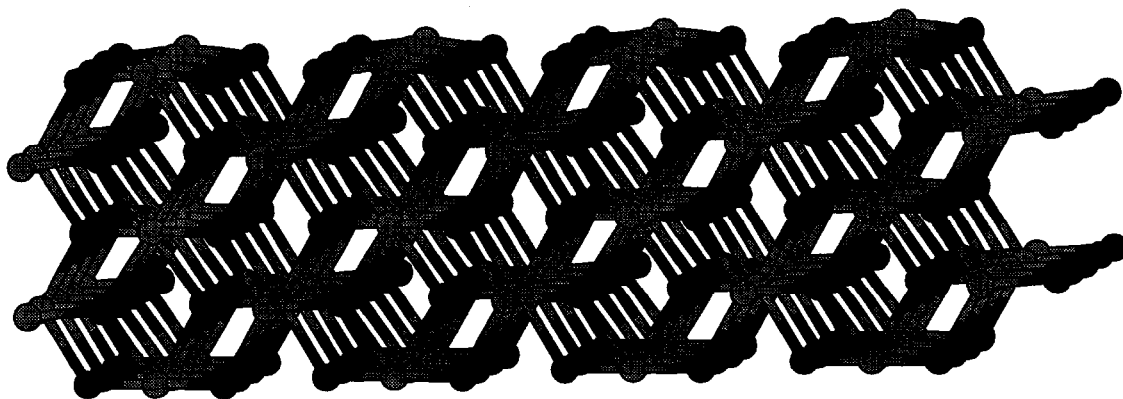


Fig. 1. General view of the  $\text{TiO}_2$  (001) rutile surface as obtained from molecular dynamics simulations.

reliable models for this face, we firstly carried out molecular dynamics simulations of the surface and the details will be given elsewhere [13]. The results show that a slight contraction of the two first layers takes place. As shown in Fig. 1, two different Ti sites are present in this surface. The first, site A, consists in a low coordinated Ti center surrounded by four oxide anions. The second, site B corresponds to a near octahedral  $\text{TiO}_6$  unit slightly elongated.

To model these sites two clusters were employed:  $\text{TiO}_4^{4-}$  for site A and  $\text{TiO}_6^{8-}$  for site B. These clusters were surrounded by a set of total ion potentials (TIPs, see Fig. 2) and embedded in an array of point charges (PCs) at the lattice positions corresponding to a fully ionic description (27 TIPs and 760 PCs for site A, and 29 TIPs and 758 PCs for site B).

### 3. Computational details

Ab initio cluster embedded calculations were undertaken using the effective core potentials of Stevens et al. [14,15] to describe the  $1s^2$ ,  $2s^2$  and  $2p^6$  electrons of Ti and Na atoms. The basis sets were (8s8p6d/4s4p3d) for Ti and (4s4p/2s2p) for Na. For oxygen atoms the (9s5p/4s3p) basis set proposed by Broughton and Bagus [16] for oxide anions was used. In order to avoid instabilities in the wave function during the electron transfer reaction, state averaged CASSCF calculations [17] within each symmetry were carried out. Details concerning the active space will be given later. The geometry of the surface was always kept fixed at the symmetrized positions issue from the MD simulations. For site A, the Ti–O distances were 1.87 Å (surface oxygens) and 1.88 Å (bulk oxygens), while for site B the distances were 1.98, 1.94 and 2.0 Å for surface, central and bulk oxygens, respectively. All the calculations were performed under  $C_{2v}$  constraint using a locally modified version of HONDO8.4 program [18] running on HP-735 and IBM-RS6000/590 work stations.

### 4. Results and discussion

Let us first consider the splitting of the Ti d levels for sites A and B. Preliminary RHF calculations for these sites show that the energy ordering is  $d_{z^2} < d_{xz} \approx d_{x^2-y^2} \approx d_{yz} < d_{xy}$  for site A and  $d_{z^2} < d_{yz} \approx d_{xy} < d_{xz} < d_{x^2-y^2}$  for site B. Let us now assume that one Na atom approaches vertically to a Ti surface ion (formally  $d^0$ ) in such a way that the local  $C_{2v}$  symmetry is preserved. Since for both sites the lowest d orbital is of  $a_1$  symmetry it is expected that the electron transferred from Na will occupy this orbital and therefore, in terms of cluster localized states, the ground state will be the  ${}^2A_1$ . Our calculations support this analysis as reported in Table 1, where the relative energies obtained at the CASSCF level for states of  ${}^2A_1$ ,  ${}^2B_1$ , and  ${}^2B_2$  symmetry are summarized. In these calculations the active spaces involve the relevant orbitals of each symmetry which basically are:  $d_{z^2} + s(\text{Na})$  for  $A_1$ ;  $d_{xz} + p_x(\text{Na})$  for  $B_1$ ; and  $d_{yz} + p_y(\text{Na})$  for  $B_2$ .<sup>1</sup>

Starting the analysis with site A, we see in Table 1 that the  ${}^2B_1$  and  ${}^2B_2$  states are found to be quasidegenerated and lying 37.8 kcal/mol above the ground state. The Na–Ti distance appears to be almost the same for the three states (about 2.8 Å) although the adsorption energies are larger for the  ${}^2B_1$  and  ${}^2B_2$  states than for the  ${}^2A_1$  one. These adsorption energies are corrected for the basis set superposition error using the counterpoise method, and are computed taking into account that the dissociation limit for the states is not the same. Thus, the  ${}^2A_1$  state dissociates towards  $\text{Na}({}^2S)$  while  ${}^2B_1$  and  ${}^2B_2$  states dissociate towards  $\text{Na}({}^2P)$ .

<sup>1</sup> The ordering of the states obtained from preliminary UHF calculations is just the same than that reported in Table 1. However, since for the dissociation curves reported in Fig. 3 and Fig. 4 state averaged CASSCF calculations have been performed, we have preferred to limit this discussion to the CASSCF results. Notice that both the relative and adsorption energies reported in Table 1 as well as the wave function analysis have been performed on the *pure* states.

Table 1  
Relative energies and adsorption energies corrected for BSSE (kcal/mol)

State	Site A		Site B	
	$E_{\text{rel}}$	$E_{\text{ads}}$	$E_{\text{rel}}$	$E_{\text{ads}}$
${}^2\text{B}_2$	37.8	31.2	30.2	28.8
${}^2\text{B}_1$	37.8	31.2	35.8	23.0
${}^2\text{A}_1$	0	24.2	0	13.6

The largest adsorption energies obtained for the  ${}^2\text{B}_1$  and  ${}^2\text{B}_2$  states suggest that the stabilization of the Na electron is favored when the electron is transferred to the  $d_{xz}$  or  $d_{yz}$  orbitals even though the ground state is obtained when the  $d_{z^2}$  orbital is occupied. (This differential stabilization may be due, of course, to an unsuitable description of the  ${}^2\text{P}$  states of the Na atom, since the p orbitals are just polarization functions. To clarify this point would involve to use an adequate all electron basis set which is beyond the scope of this work.)

In order to get a deeper insight into the electron transfer process the potential energy curves for the dissociation of the three states have been computed. Since in these dissociations an avoided crossing is involved, and with the aim to obtain smooth curves, these energies have been computed from state averaged CASSCF wave functions. As shown in the top of Fig. 3, the interaction between the ground states of the cluster and the Na atom (labelled as  $\text{Ti } d^0 + \text{Na } s^1$ ) gives rise through an avoided crossing to the ground state of the Na-surface system ( $\text{Ti } d^1 + \text{Na } s^0$ ). The region of the avoided crossing (about 4.5–5.5 Å) corresponds to a MC state in which the two configurations  $\text{Ti } d^0 + \text{Na } s^1$  and  $\text{Ti } d^1 + \text{Na } s^0$  are strongly mixed. Similar behavior is observed for the  ${}^2\text{B}_1$  and  ${}^2\text{B}_2$  states (middle and bottom of Fig. 3) which, in turn, dissociate towards the excited configuration  $\text{Ti } d^0 + \text{Na } p^1$ . Notice that for these states the avoided crossing appears at Na-surface distances shorter than for the  ${}^2\text{A}_1$  state. This is because for this state there is a mix between the s and  $p_z$  Na orbitals which im-

proves the overlap with the  $\text{Ti } d_{z^2}$  orbital and, consequently, an earlier interaction occurs.

Focussing now on the site B results, it is found that the ordering of the states also agree with the ordering of the d levels found for the isolated surface with the exception of the  $d_{xy}$  orbital ( $a_2$  symmetry). This is because upon adsorption there is a strong destabilization of the  $d_{xy}$  level that pushes the  ${}^2\text{A}_2$  state up. ( ${}^2\text{A}_2$  states are not explicitly considered in this work since their dissociation limit would involve the much more energetic  ${}^2\text{D}$  states of Na.)

Adsorption energies computed as above are found to be lower than those obtained for site A, mainly for the ground state, suggesting thus that adsorption on site A is preferred. The analysis of the wave function for site B states shows that at the equilibrium Na-surface distance the leading configuration does not involve occupation of the Ti d orbitals. Effectively, as shown in Fig. 4, the lowest state of each symmetry is represented by a configuration corresponding to a Ti formally  $d^0$  with the lone electron borne by the Na atom. In these cases, the avoided crossing does not take place and dissociation occurs directly towards the lowest states of each fragment (for each symmetry). These results show that although upon adsorption there is a stabilization of the system, no electron transfer from the Na atom to the surface site B occurs. Though this conclusion could appear in principle somewhat amazing, it is perfectly coherent with the structure of the Na-surface system. With the aim to illustrate this point, let us consider for instance the  ${}^2\text{A}_1$  state. Thus, to get the ( $\text{Ti } d^0 + \text{Na } s^1$ ) and ( $\text{Ti } d^1 + \text{Na } s^0$ ) configurations mixed a good overlap between the Ti d orbitals and the Na s one is needed. However, because of the surface oxygens present at site B, the Ti and Na atoms are not allowed to be close enough to interact efficiently. Actually, the minimum of the interaction curve is found now to be at about 3.8 Å (see Fig. 4), and the potential energy rapidly increases for shorter Ti–Na distances because of the repulsion between Na atom and surface oxygens. In fact, the  $\text{Ti } d^1 +$

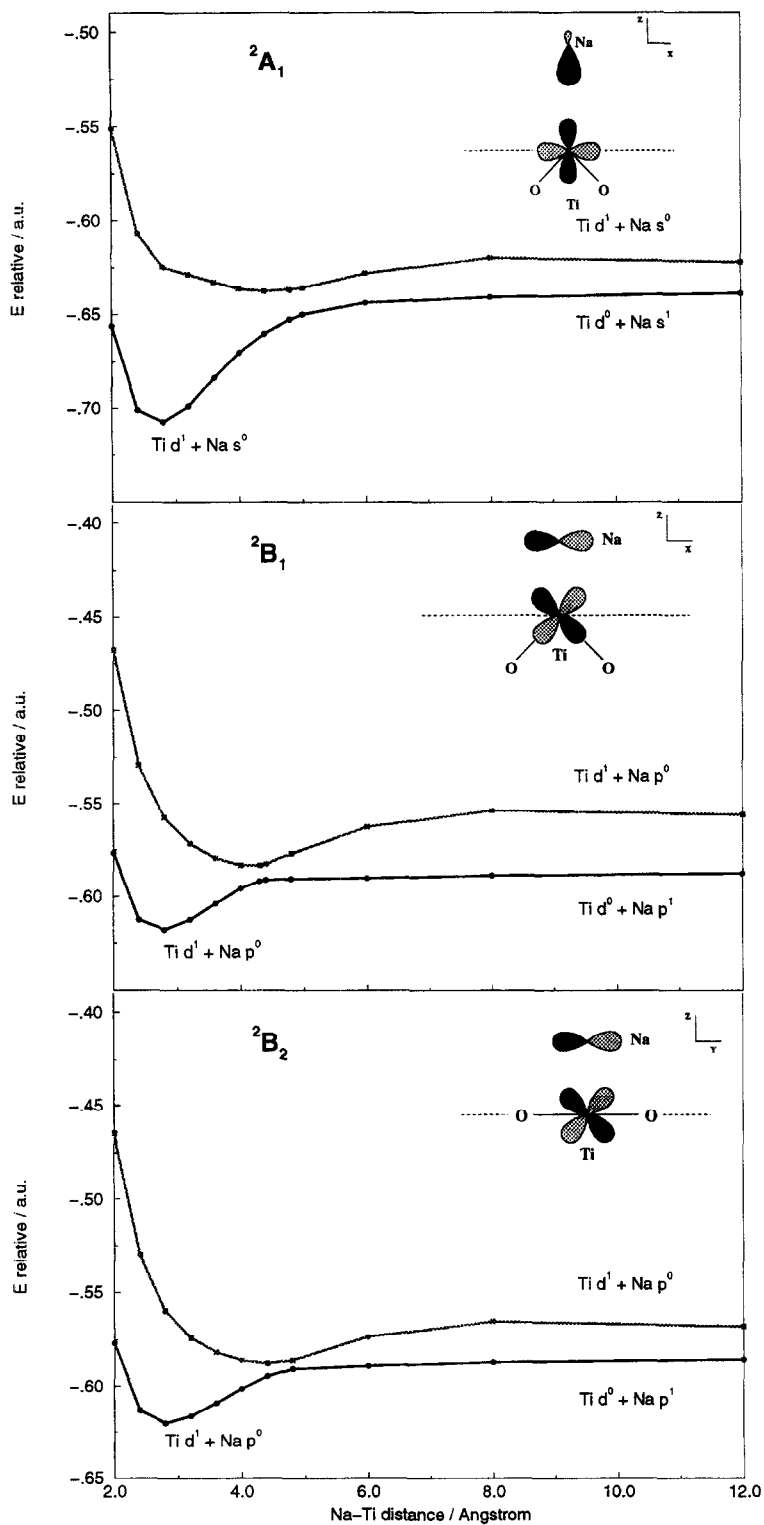


Fig. 3. Dissociation curves obtained from averaged CASSCF calculations and pictorial description of the orbital interactions for site A.

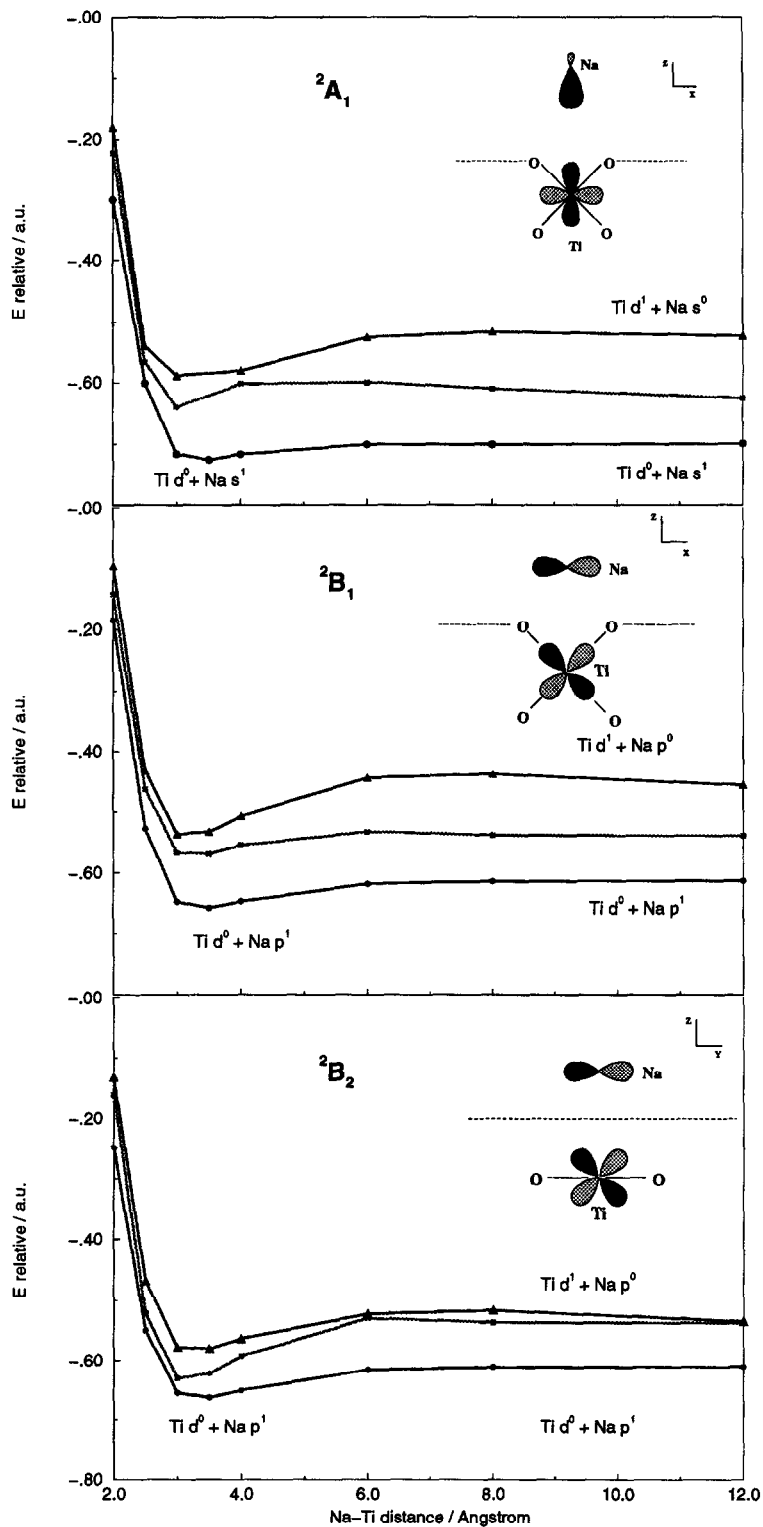


Fig. 4. Dissociation curves obtained from averaged CASSCF calculations and pictorial description of the orbital interactions for site B. The middle curves at short Ti-Na distances correspond to the equilibrium  $Ti d^1 + Na s^0$  (or  $p^0$ ) states.

Na  $s^0$  state is found to be as the first excited state in the region of the minimum, and although at shorter Ti–Na distances this state does cross the ground state, the energetic situation would be so bad that the system would relax to Ti  $d^0 + Na s^1$  state or even better, a long range electron transfer towards a site A Ti ion would take place.

An additional aspect to be explained here is the third curve drawn in Fig. 4. As explained in the preceding paragraph, the second curve in the region of the minima corresponds to the Ti  $d^1 + Na s^0$  (or  $p^0$ ) state. However, at larger Ti–Na distances, this state loses this nature and mixes with a configuration involving a  $p$  correlation orbital. Therefore, in order to obtain correct dissociation curves this orbital has to be added to the active space and in fact, all the curves of Fig. 4 have been obtained by averaging the three states. It should be noticed however that we have checked that the presence of this configuration does not affect the conclusions drawn for the ground state of each symmetry <sup>1</sup>.

Finally, before closing this section, a comment about the possible surface relaxation induced by the adsorbate. As stated in the computational methods section, all calculations have been carried out with a fixed surface geometry. It is expected, however, that after the electron transfer process, a lengthening of the Ti–O interatomic bond distances will occur since now the cation has a formal charge of +3. For site A such a relaxation will not change the description; but, for site B the ground and the first excited states could appear to be interchanged, thus modifying the interaction description. We think, however, that such a reordering of the states is rather unlikely since there is a considerable electronic gap between them (25 kcal/mol).

## 5. Concluding remarks

The  $TiO_2$  (001) rutile surface exhibits two different sites which basically can be described

as a four coordinated Ti center (site A) and an oxygen ending quasi octahedral  $TiO_6$  unit (site B). Ab initio calculations for the adsorption of one Na atom at these sites using a cluster embedded approach show that there is a noticeable interaction between the surface and the Na atom at both sites however, the origin of such an interaction is essentially different. At site A, the preferred one, the stabilization of the Na-surface system arises from an electron transfer from the 3s Na orbital towards a Ti  $d$  level. For site B such an electron transfer involves excited states of the system that appears to be unfavored with respect to a situation in which the hopping electron remains on the Na atom, and, of course with respect to reduction of site A Ti centers. For site B ground state, the Na-surface interaction would be therefore of electrostatic nature. The models used here to represent the adsorption process are of course limited, at least as far as basis sets, symmetry restrictions and embedding techniques are concerned, however we feel that the essence of the problem has been addressed and to improve the models would not change our main conclusions.

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