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# Modeling Alkali Atoms Deposition on TiO<sub>2</sub> (110) Surface

M. A. San Miguel,\* C. J. Calzado,<sup>†</sup> and J. F. Sanz

Departamento de Química Física, Universidad de Sevilla, E-41012, Sevilla, Spain

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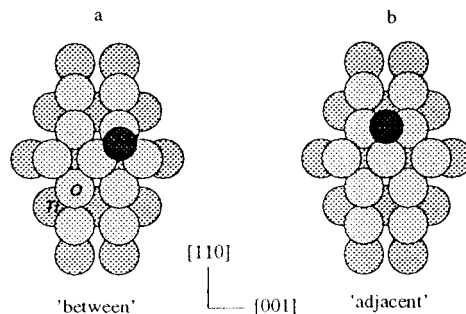
A few studies of alkali atoms deposition on the (110)-rutile surface have been reported in the last years. The process involves a selective electron transfer from the alkali atoms to the surface penta-fold Ti atoms, and it has been well characterized by both experimental and theoretical techniques. However, the adsorption site of the alkali atoms on the surface is still unclear and different models have been proposed. In our previous works we omitted some aspects which have been considered in this study. In particular, we have examined the role of the relaxation of bridging oxygen atoms and those factors responsible for adsorption structure from *ab initio* calculations and molecular dynamics simulations. The results indicate that there exist two characteristic adsorption sites described as “between” and “adjacent” sites. At very low coverages, in agreement with our previous work, alkali metal atoms do only occupy “between” sites binding to two bridging oxygen atoms. However, the number of alkali atoms in “adjacent” sites, at which the adsorbate binds to one bridging oxygen atom, increases as coverage does and as ionic radius decreases, but even at high coverages a nonnegligible percentage of alkali atoms in “between” sites is still present.

## I. Introduction

The deposition of alkali metal (AM) on TiO<sub>2</sub> (110) surface has been extensively studied in recent years, because of their ability to promote the quite inert stoichiometric TiO<sub>2</sub> (110) surface.<sup>1–8</sup> The adsorption of AM on this surface produces the reduction of Ti atoms, manifested as the appearance of an occupied gap state at around 1 eV below the conduction band edge.<sup>1–8</sup> This gap state has a strong Ti 3d character. *Ab initio* embedded cluster calculations have shown that this reduction is selective, involving only the 5-fold Ti atoms on the surface.<sup>9–12</sup>

The geometrical disposition of the adsorbed AM on the surface has been analyzed by different techniques. The adsorption of Na on the TiO<sub>2</sub> rutile (110)–(1 × 1) surface has been investigated by Onishi et al.<sup>13</sup> using X-ray photoemission spectroscopy (XPS), X-ray Auger electron spectroscopy (XAES), electron energy lost spectroscopy (EELS), and low-energy electron diffraction (LEED) and by Nerlov et al.<sup>14</sup> using synchrotron-radiation-induced photoemission. Both of them suggested a model of adsorption where Na is bound to two bridging protruded oxygen atoms and one basal oxygen atom in a symmetric arrangement, called hereafter in “between” (Scheme 1a). The same model results from our *ab initio* embedded cluster calculations and molecular dynamics (MD) simulations.<sup>9,10</sup> Moreover, when this model was used in periodic Hartree–Fock calculations, both the changes induced on the photoelectron spectrum and the work function drop observed after Na deposition were satisfactorily accounted for.<sup>12</sup> On the other hand, the experimental results concerning K adsorption are not conclusive.<sup>15–19</sup> No LEED pattern of the K/TiO<sub>2</sub> (110) system has been observed to date. The absence of a model based on experiments for K/TiO<sub>2</sub> enhances the importance of theoretical studies.<sup>11,20–22</sup> Our calculations at low coverage predicted

SCHEME 1



the same adsorption site to that found for Na, although distances between adsorbate and surface atoms increased lightly because of the larger K ionic radius.<sup>11</sup> These results are in agreement with those reported by Bredow et al.<sup>21,22</sup> for the K/TiO<sub>2</sub> system, by using cluster and slab calculations. However, MD simulations at high coverage showed the appearance of a new adsorption site, not predominant, where AM (Na, K) are bound to two basal oxygen atoms and one protruded oxygen atom (“adjacent” coordination, Scheme 1b).<sup>9–11</sup> Also, the metastable impact electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS) spectra for Cs/TiO<sub>2</sub> (110) reported by Brause et al.<sup>23</sup> suggest two different chemical environments for adsorbed Cs ions at high coverages. Recently Hird and Armstrong,<sup>24</sup> on the basis of ion shadowing/blocking measurements, have proposed that Na atoms on TiO<sub>2</sub> (110)–(1 × 1) surface occupy “adjacent” sites, and they are not placed “between” two protruded oxygen atoms. Since this result is in direct contradiction with our *ab initio* calculations and classical MD simulations, an objective inspection of our methods is mandatory, and this is the aim of this article.

We have included four important considerations that were omitted previously. (i) The first concerns the geometry of the adsorption site. In our previous work the position of the AM was optimized, while the surface atoms were kept frozen at

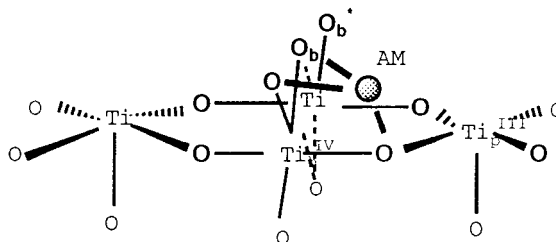
\* Corresponding author. E-mail: smiguel@cica.es.

<sup>†</sup> Current address. Laboratoire de Physique Quantique, IRSAMC, Université Paul Sabatier, 118, route de Narbonne, F-31062, Toulouse, France.

**TABLE 1: Optimized AM–Surface Distances (in Å) from Quantum Cluster Calculations for Different Alkali Metal Ions and Including Surface Relaxation<sup>a</sup>**

AM	AM–Ti <sub>h</sub> <sup>IV</sup>	AM–Ti <sub>p</sub> <sup>III</sup>	AM–O <sub>bridge</sub>	AM–O <sub>bridge</sub> <sup>b</sup>	AM–O <sub>bridge</sub> height
Li	2.20	4.39	1.91	4.30	+1.32
Na	3.02 (3.05)	4.54 (4.54)	2.32 (2.36)	4.44	+1.84
K	3.19 (3.25)	4.56 (4.61)	2.47 (2.52)	4.48	+2.00

<sup>a</sup> Distances previously calculated with surface constraint are indicated in parentheses. <sup>b</sup> O<sub>bridge</sub> is represented by O<sub>b</sub> in the graphic below Table 1.



positions obtained from MD simulations of a (110)-rutile slab. However, both Hird<sup>24</sup> and Nerlov<sup>14</sup> have noticed that Na atoms produce a de-relaxation of the bridging oxygen atoms. This fact has been taken into account in our present work through ab initio geometry optimizations carried out on embedded clusters. These relaxations and its effect on the AM adsorption site will be investigated in Section II.

(ii) The pair potential functions used in the MD simulations have been revised. As we have pointed out, the structure of the adsorbed AM atoms at high coverages results from a compromise between the AM–AM and AM–surface interactions. In our previous study, the pair potentials associated with AM species were of the Pauling type, including as a unique parameter the ionic radii. To obtain a more realistic description of the system, classical MD simulations have been carried out in the present work using AM<sup>+</sup>–AM<sup>+</sup> pair-potential functions fitted from ab initio embedded cluster calculations.

(iii) Also, as a third aspect, we have examined the dependence on the AM ionic radius of the Pauling-type pair potential, used to model the surface–AM interactions.

(iv) Finally, with the purpose of a better understanding of this adsorption process, we have extended the study to the Li case, which due to its smaller ionic radius may exhibit new features.

## II. Derelaxation of Protruded Oxygen Atoms

The adsorption geometry of the alkali atom on the TiO<sub>2</sub> (110) surface has been analyzed, as previously, by means of ab initio embedded cluster calculations. In contrast with the preceding studies, the positions of both AM and bridging oxygen atoms have been optimized as the rest of the atoms in the cluster were frozen at positions obtained from MD simulations.<sup>10</sup> These simulations were undertaken for the isolated TiO<sub>2</sub> (110) surface and the results were in good agreement with experimental data reported by Charlton et al.,<sup>25</sup> with periodic HF<sup>21,26</sup> and LDA<sup>27</sup> calculations and also with other classical simulations of molecular mechanics.<sup>28</sup> The aim of this analysis is to check whether the effect of the relaxation of the protruded oxygen atoms modifies the adsorption geometry with respect to that found in our previous HF calculations. Certainly, the size of the cluster is adequate to this purpose although is too limited to simulate the whole relaxation process of the surface.

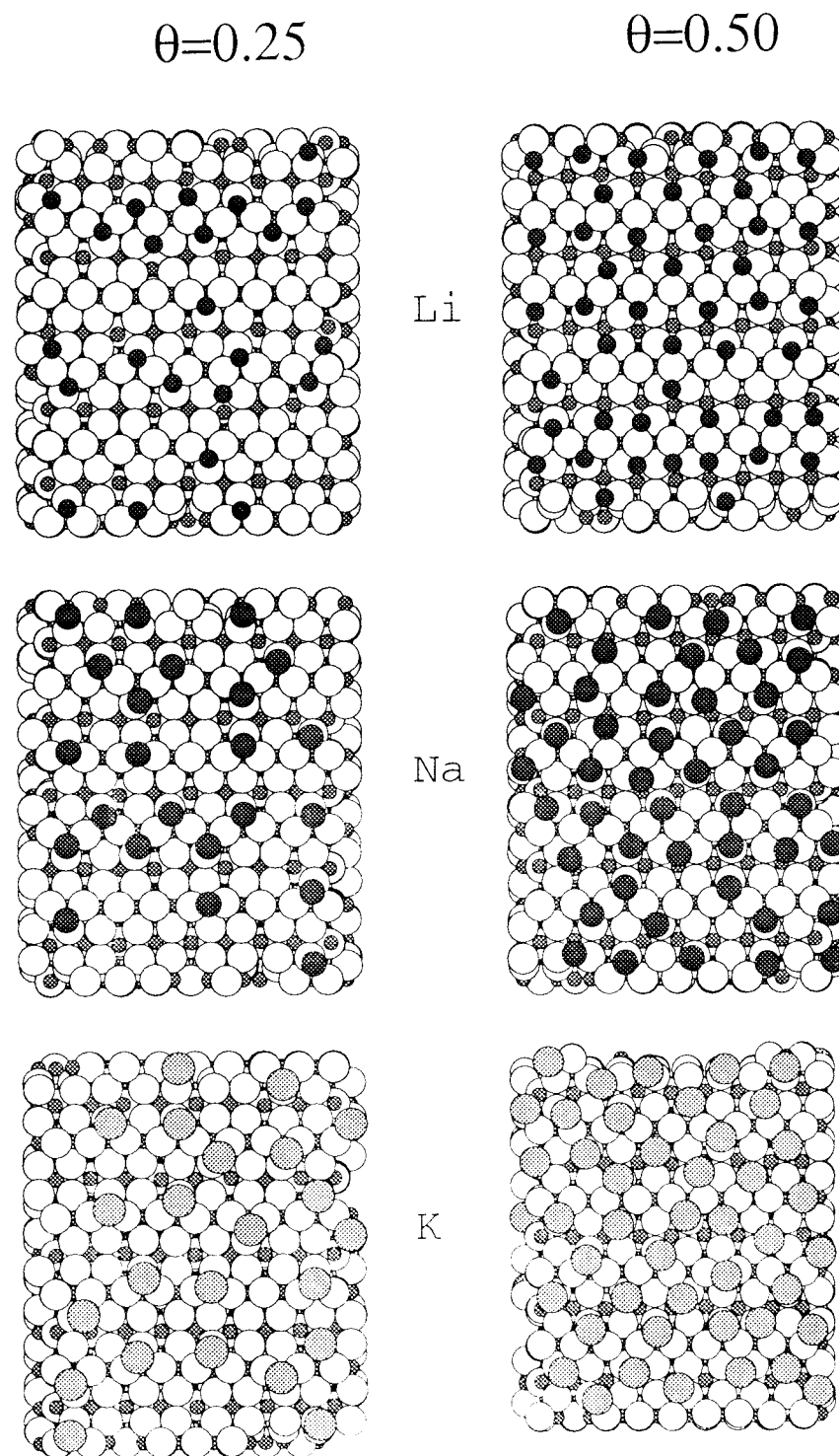
We have considered a cluster of formula Ti<sub>4</sub>O<sub>16</sub>, which contains two 5-fold Ti atoms and two 6-fold Ti atoms.<sup>9–11</sup> An array of 1404 formal point charges surrounding the cluster was used to model the Madelung potential of an infinite lattice. As

usual, a set of total ion potentials have been included in the interface cluster-point charges, to avoid the excessive polarization of oxygen ions. As known, there exists certain controversy concerning the appropriate way to model the Madelung potential of a *partially* ionic lattice as TiO<sub>2</sub>. Rigorous studies by Ritter et al.<sup>29</sup> on the adsorption of N<sub>2</sub> on TiO<sub>2</sub> (110) surface and the work by Bredow<sup>22</sup> involving embedded cluster calculations on K/TiO<sub>2</sub> system have demonstrated that once the size and composition of the cluster correctly reproduce the electric field above the TiO<sub>2</sub> surface and the electronic structure of the adsorption site, the ionicity of the Madelung field has only a small (or negligible) effect on the adsorption energy. Following these conclusions and according to the study of the CO adsorption on TiO<sub>2</sub> (110) by Reinhardt et al.,<sup>30</sup> where they have shown that the molecular orbital energies of the cluster surrounded by formal charges (+4/–2) fit better with the energies of the slab calculations, than those obtained by using partial charges, we have decided to use the formal charges (+4, –2) to model the environment.

The basis sets for Ti and O atoms were described in refs 10 and 11. For Li atom, an all electron basis set has been used, namely (11s5p1d)/4s3p1d.<sup>31</sup> For Na and K, the core electrons have been represented by effective core potentials proposed by Hay and Wadt<sup>32</sup> and the valence electrons have been described by a (3s1p)/2s1p basis set.<sup>32</sup>

In the geometry optimization process two different starting configurations have been investigated. One corresponds to that previously reported, in which Na and K atoms occupy “between” sites (for Li, the same starting point as for Na has been used). The second geometry corresponds to an “adjacent” coordination, where the distances proposed by Hird and Armstrong<sup>24</sup> have been used. In both cases, the final structure found is the same and therefore, it does not depend on the starting point. The UHF geometry optimizations lead to a stationary point at which the AM binds to two bridging oxygen atoms and a basal one. The AM is located near the normal surface across the hexa-fold Ti, lying toward the reduced 5-fold Ti atom and as closer as ionic radius increases. The analysis of the electronic structure shows that the *ns* electron of the AM is transferred selectively to a 5-fold Ti atom.

Table 1 shows the optimized distances found for Li, Na, and K adsorbed on the TiO<sub>2</sub> (110) surface. For comparison purposes, those distances reported in the previous constrained optimization are indicated in parentheses. In general, the relaxation of the bridging oxygen atoms produces a shortening of the M–Ti and M–O distances. All the distances increase as the ionic radius



**Figure 1.** Snapshots of final configurations after relaxation at 300 K for every AM at coverages of 0.25 and 0.5 ML.

**TABLE 2: Pair-Potential Parameters for AM–AM (Lennard-Jones) and AM–Surface (Pauling) Interactions**

AM	$E(\text{kcal mol}^{-1})$	Lennard-Jones	Pauling
		$R(\text{\AA})$	$R(\text{\AA})$
Li	0.6918	1.48	0.60
Na	0.6918	2.08	0.95
K	2.0754	2.78	1.33

does, but this increase is not linear. The results for Na and K are quite similar and they do not respond to the increase of their ionic radii. The height of AM with respect to the basal oxygen plane also manifests this nonlinear behavior. These

observations seem to indicate the presence of a threshold radius which marks two different ranges of behavior, and it will be examined in the next section.

### III. AM–AM Interactions

We have reported previously classical molecular dynamics simulations to model the process associated with the deposition of Na and K on  $\text{TiO}_2$  (110) surface at different coverages.<sup>10,11</sup> The interactions between particles were described by potential functions consisting of Coulombic and short-range terms which were explained in detail in ref 11. The interaction between AM and the surface proceeds through an electron-transfer process,



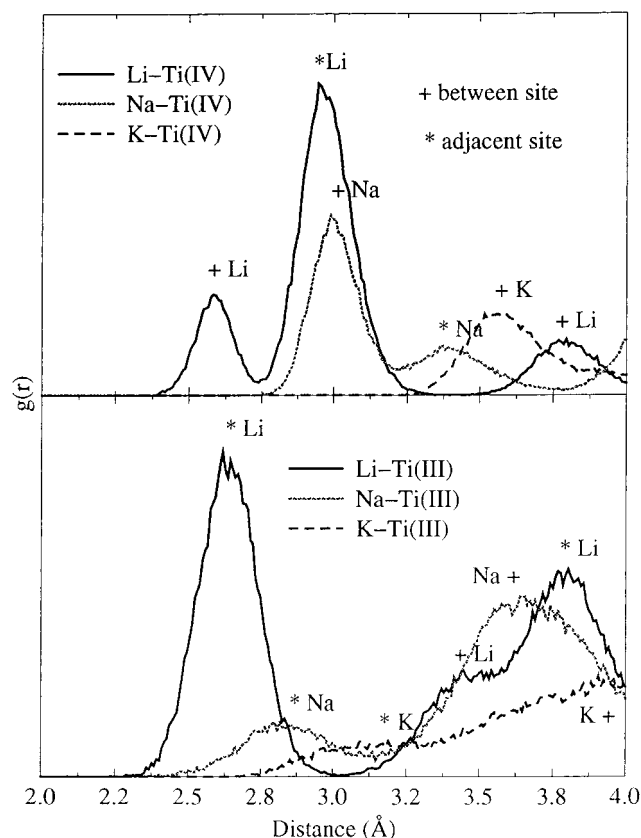
well documented from ab initio calculations<sup>9–12</sup> and also XPS, XAES, and LEED spectra,<sup>1–8,23</sup> where the unpaired  $ns^1$  electron of the AM atom is transferred to a 3d 5-fold-Ti orbital. Therefore, in the following text AM will actually mean AM<sup>+</sup>. This phenomenon has been modeled by using a charge of +1 e for every AM adsorbed and therefore by reducing to +1.196 e the charge of the same number of 5-fold Ti atoms.<sup>9–11</sup> As has already reported<sup>11</sup> this approximation is valid up to a critical coverage which is higher than all the ones considered in this work. Beyond this critical coverage, the experimentally observed clustering suggests some metallic character. The calculation of the corresponding electrostatic forces has been undertaken by means of the Ewald method. However, to obtain an adequate short-range potential for any system always constitutes a challenge and there is not a unique way to do it. In previous work, we used Pauling-type pair potentials to represent all these interactions, however we have found that these functions are slightly over-repulsive for AM–AM interactions. At high coverage these forces could be responsible of the geometry of the adsorbed layer. For that reason, in this work we have used new potential functions fitted from ab initio calculations. All electron restricted Hartree–Fock calculations on AM<sup>+</sup>–AM<sup>+</sup> dimers have been carried out for the series Li, Na, and K. The short-range energy was determined as the difference between the total and the Coulombic energies. The curves resulting were fitted to Lennard-Jones functions and the parameters obtained are reported in Table 2. In contrast to the potentials used previously, these functions present a well which may induce the AM to cluster.

Molecular dynamics simulations were undertaken using SIMULA.<sup>33</sup> Calculations were performed in the NVE ensemble with a time step of 1 fs. Periodic boundary conditions were used in the three directions to mimic the infinite system with a vacuum gap of 50 Å used to define the slab. The simulations consisted of a 3 ps trajectory at which the velocities of the particles were scaled every step to lead the system to a temperature of 300 K; a second 7 ps trajectory was carried out to verify the system had reached equilibrium, and finally a run of 10 ps for statistical analysis of the properties.

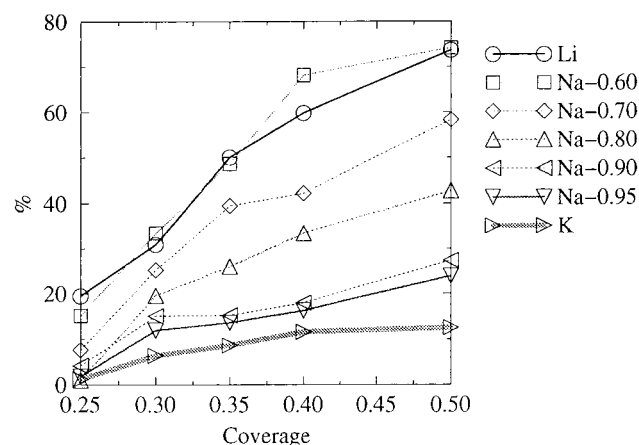
According to the definition of maximal coverage (i.e.,  $\theta = 1$  ML), at which there are as many adsorbed AM as surface Ti atoms (including 5- and 6-fold Ti atoms), we have considered coverages in the range of 0.25–0.50 ML. Figure 1 shows a snapshot of final configurations for every AM at the lowest and highest coverage. It can be seen that at  $\theta = 0.25$  ML, AM can occupy “adjacent” positions only for the Li case, although they are scarce. For a coverage of 0.50 ML, this adsorption site is exhibited by every AM, but it is predominant only for the smallest one, i.e., Li atoms.

Radial distribution functions for AM–Ti(IV) and AM–Ti(III) at a coverage of 0.5 ML are depicted in Figure 2. The two first peaks of every curve appear at typical distances of the two different adsorption sites. The first peak of AM–Ti(IV) is related to an AM in “between” sites, while the second one is due to AM in “adjacent” sites. The intensity of these peaks indicates that only for Li the “adjacent” site is more favorable. The same conclusion can be extracted from the AM–Ti(III) curve, in which the first peak corresponds to an “adjacent” site and the second one to a “between” site.

We have also estimated the percentage of AM in “adjacent” sites for every coverage studied, and the plots can be seen in Figure 3. Solid lines correspond to the three AM, and the different behavior between Li and the other atoms is obvious. For Li, the increase of “adjacent” sites is quite significant,



**Figure 2.** Radial distribution functions for AM–Ti(IV) and AM–Ti(III) at coverage of 0.5 ML.



**Figure 3.** Percentage of AM in “adjacent” sites at different coverages.

becoming 75% at a coverage of 0.5 ML. However, for Na and K the increase is slow and less than 30% at all coverages, only a slightly larger percentage than those found when AM–AM Pauling-type pair potentials were used.<sup>10,11</sup>

These results indicate clearly that there is not a unique adsorption site as has been proposed to date both in theoretical and experimental work.<sup>10–12,14,15,21</sup> At very low coverage (i.e., 1 AM atom per 4 Ti atoms, that is,  $\theta = 0.25$  ML), ab initio optimizations and MD simulations demonstrate that the “between” adsorption site is the most favorable. However, at higher coverages as is expected in experimental conditions, both sites are present.

#### IV. AM–Surface Interactions

As was mentioned before, the interactions between AM species and the surface are modeled by means of a Pauling-

type potential. It is worth noticing that these functions depend on the ionic radii. Although the radii used for Ti and O ions have been fixed to reproduce some macroscopic properties of TiO<sub>2</sub> (rutile),<sup>34</sup> this is not the case with AM radii. Since these values can change as the coordination number does, and on the other hand, it is difficult to estimate them precisely, it would not be surprising that the values used here are not completely realistic. To overcome this problem, we have considered ghost Na atoms of ionic radius in the range of 0.60(Li)–0.95(Na) Å. In all cases, the Na–Na interaction has been represented by using the corresponding ab initio parameters for Na (Table 1). As shown in Figure 3, the number of Na atoms in “adjacent” sites increases when the radius decreases and for a radius of 0.60 Å the behavior is quite close to that featured by Li atoms. These findings reveal that the competition between AM–AM and AM–surface potentials are the origin of a threshold radius at which the adsorption geometry is modified. At high values of the ionic radius, the majority of the AM species are in “between” sites, while at low values the number of AM in “adjacent” sites increases rapidly as the coverage does, showing that AM–AM interactions are more intensive at higher coverage. The AM tends to occupy unsaturated 4-fold sites binding to three oxygen atoms. Although this can be achieved in both “between” and “adjacent” sites, the latter reduce more effectively the AM–AM repulsions because the AM is shielded by bridging oxygen atoms, while in “between” sites the height of the AM is above the plane defined by the protruded oxygen atoms and therefore, the AM–AM interactions become more significant. However, “adjacent” sites only can be occupied by atoms small enough, because otherwise the repulsive interactions with a neighbor 5-fold Ti would increase strongly.

## V. Conclusions

An objective inspection of the capability of some available first-principle based methods (ab initio and MD simulations) to study the AM deposition on TiO<sub>2</sub> (110) surface has been reported, and the following conclusions can be extracted:

1. The relaxation of bridging-oxygen atoms has been taken into account in geometry optimizations, and the most favorable adsorption site found for the three AM studied at low coverages is that called “between” site in agreement with our previous ab initio calculations for Na and K atoms.

2. A better description of the interactions between particles at high coverages has been obtained by using AM–AM potential functions extracted from ab initio calculations and examining the role of the ionic radius on the Pauling-type pair potentials. Simulations show that as coverage increases the “adjacent” site begins to be also present and to be more abundant as the ionic radius decreases; however, for all cases both “between” and “adjacent” sites coexist. These results disagree with the latest experimental work<sup>24</sup> which only suggested “adjacent” sites for Na adsorption. Although the coverage of these experiments was not reported, it is reasonable to think in a high coverage close to  $\theta = 0.50$  ML, and even in this case assuming a small ionic

radius for Na (i.e., 0.60–0.70 Å) our simulations would predict the “adjacent” site as the most abundant, but AM in “between” sites should be also observed.

The agreement with the majority of the reported experimental results and also with our previous calculations, gives us confidence in first principle methods as a useful tool to study and, sometimes, predict the features of metal deposition on metal oxides surfaces.

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