The Energetic and Electronic Properties of Atomic Hydrogen on MgO(001) Surface: Tight-Binding and Ab Initio Calculations

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Abstract−We report the computational results of hydrogen adsorption atop Mg and O atoms on the MgO(001) surface, followed by its absorption under the target atoms, using two approaches: tight-binding and ab initio methods. We present the energetic and electronic aspects of these interactions and discuss the qualities of the non-self-consistent field tight-binding results compared with the ab initio results. There is the qualitative reproduction of ab initio results in the hydrogen adsorption phase on both types of ions. The tight-binding results are found to be more accurate in the hydrogen absorption phase than in the adsorption phase. In the absorption calculations the introduction of the surface dipole term in the tight-binding total energy would be required to compensate for the absence of electronic relaxation in the MgO(001) surface.

Key words: Energetic and Electronic Properties, Hydrogen Atom, MgO(001) Surface, Tight Binding Method, Ab Initio Method

INTRODUCTION

The applications of MgO, clean or doped with alkaline metals, have made it a very studied material in the areas of science and industrial engineering [Maksimov et al., 1998; Kim and Kwon, 1999]. Its usage as catalyst (H_2-D_2 exchange, methanol hydrogenation, support for metallic catalyst, etc.) and its simplicity (large separation between anion and cation bands, and large band gap) have recommended it as an ideal candidate for molecular simulation studies. On the ionic surfaces, H_2 [Dercole and Pisani, 1999] and H_2O [Dai et al., 1995; Chacon-Taylor McCarthy, 1996] are physically adsorbed and can also be dissociated on surface defects as hydrogens [Kobayashi et al., 1994] or as H^+ and OH^- fragments [Ahlswede et al., 2000]. The free hydrogen tends to be bound onto the surface oxygen ions, forming new OH^- groups that cannot be easily distinguished from OH^- hydroxyl groups in water dissociation. This is the reason why, from the experimental point of view, we cannot directly interpret the hydrogen diffusion on or inside the ionic surface. In such cases we must choose the detailed description for the hydrogen-MgO interactions for the studies of hydrogen surface diffusion in the MgO(001) surface.

Computational approaches, such as equilibrium geometry searching methods, and molecular dynamics or Monte Carlo simulations employing ab initio calculations based on density functional or Hartree-Fock theories, have become an excellent tool in material science. However, in order to analyze phenomena on a large scale of time and space, we must be able to describe the potential energy surface in a great number of points for the nuclear configurational space. It is required to solve the electronic motion over 10^4-10^6 points or even more to obtain reliable statistics in a given system. As

these methods employ self-consistent or non-self-consistent field techniques, we are often limited in computational time and power for solving the electronic motion. For low degrees of freedom less than six, the potential energy surface from ab initio calculations can be analytically fitted for molecular-based computer simulations. When the number of degrees of freedom gets larger, it becomes very difficult to find the analytical form for the potentials.

The tight-binding (TB) method can be one of the good candidates in this area. In this work, we have tested the applicability of the TB computational method, namely, the extended Huckel method based on the atomic superposition and electron delocalization form [Anderson and Hoffman, 1974; Calzaferri et al., 1989; Calzafferi and Brandle, 1992], for the atomic hydrogen reactivity with the MgO (001) surface. To the best of our knowledge, such comparative studies using the TB method have not been reported yet for the hydrogen adsorption and diffusion phenomena on MgO surface. The resulting calculations are compared with the ab initio (AI) results. The capacity to reduce the effort of electronic structure calculations in hydrogen interaction with the MgO(001) surface allows us to characterize the hydrogen motion on and into the surface. We also discuss the energetic and electronic analysis obtained from both TB and AI calculations for the hydrogen adsorption and absorption atop Mg and O ions.

COMPUTATION METHOD

The extended Huckel method [Hoffman, 1963], which is known as a particular type of the tight-binding (TB) method, is one of the simplest approaches in quantum simulations. Their applications, based on the atomic superposition and electron delocalization form [Anderson and Hoffman, 1974; Calzaferri et al., 1989; Calzafferi and Brandle, 1992], have turned out to be useful even in the quantitative characterization of the equilibrium geometries [Calzafferi

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and Hoffman, 1991; Brandle and Calzafferi, 1994]. Such approaches have been used successfully to investigate the extended systems [Hoffmann, 1988] and adsorption systems [Schiott et al., 1990]. Another example is the simulation work of the metallic oxides with the electrostatic potential corrections [Halet and Hoffmann, 1989].

For the TB calculations employed in this work, we used the ICON&INPUTC package of Calzaferri and Brandle[Calzaferri and Brandle, 1992]. They have corrected the total energy by introducing the electrostatic core-core repulsion terms and electronic-core attraction terms. The Hamiltonian terms can be calculated through the formula

$$H_{\mu\nu} = K \frac{S_{\mu\nu}}{2} [(1+\Delta)H_{\mu\mu} + (1-\Delta)H_{\nu\nu}] \tag{1}$$

where

$$\Delta = \frac{H_{\mu\mu} - H_{\nu\nu}}{H_{\mu\mu} + H_{\nu\nu}} \tag{2}$$

$H_{\sigma\sigma}$ terms are estimated as the ionization potentials of atomic orbitals ($\sigma = \mu, \nu$) of free atoms, and $S_{\mu\nu}$ is the overlap matrix between μ and ν atomic orbitals. For the parameter K, we choose the standard value of 1.75 although the program allows its calculation as a function of the interatomic distance. We do not take the charge iterations into consideration for two reasons: the total CPU time proportionally increases with the number of SCF iterations, and, for nuclear configurations far from equilibrium geometries, the SCF convergence is scarce especially in ionic systems.

The parameters employed in this work are listed in Table 1. The values in parentheses indicate the implicit values in the ICON& INPUTC program. The parameters for oxygen and hydrogen atoms were taken from the ionic solid systems [Alemany et al., 1993]. In this case the charge of ions for the cluster structure has been improved from 1.2 electrons to 1.5 electrons, which is more reliable compared to the AI band structure calculations. The CRYSTAL 95 program [Dovesi et al., 1996] for ab initio (AI) calculations is based on the description for the linear combination of atomic orbitals using the Hartree-Fock and the density functional formalisms. In our AI calculations we have used only the Hartree-Fock formalism because it reproduces the excellent result for equilibrium geometry [Chihaia, 1999]. We have employed the tolerance parameters of integral calculations (TOLINTEG parameters, 6 6 6 7 14), and, for summations in the reciprocal space (IS, ISHF and ISP parameters, 8 6 8). For magnesium and oxygen, we have used the 8-61G basis set and 8-51G basis set [Causa et al., 1986], respectively, and, for hydrogen, a 3-1*G basis set [Ojamae et al., 1994].

Table 1. Parameters used in TB calculation for hydrogen adsorption and absorption in the MgO(001) surface. The values in parentheses are taken from the ICON&INPUTC package [Calzaferri and Brandle, 1992]

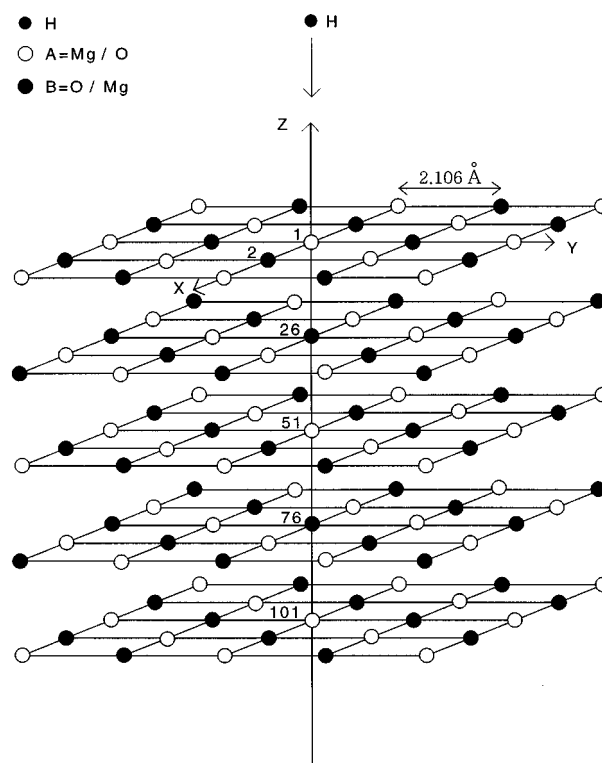| Atom	Atomic orbital	$H_{\sigma\sigma}$ [eV]	ζ-Slater exponent
O	2s	−32.024 (−28.200)	2.280 (2.575)
	2p	−14.800 (−12.400)	2.280 (2.575)
Mg	2s	−9.000 (−9.000)	1.100 (1.100)
	2p	−4.500 (−4.500)	1.100 (1.100)
H	1s	−15.540 (−13.600)	1.300 (1.300)

Fig. 1. The 5×5×5 cluster used in the simulation of atomic hydrogen atom interacted with the MgO(001) surface. The hydrogen atom moves along the normal z-direction to the target atoms, magnesium (A=Mg, B=O) or oxygen (A=O, B=Mg) in the MgO(001) surface.

We have simulated the MgO(001) surface in two ways since each program is based on a different formalism (i.e., the molecular orbital formalism in the ICON&INPUTC program, and the crystal orbital formalism in the CRYSTAL 95 program). In our TB calculations, the MgO(001) surface was modeled as a 5×5×5 cluster. As shown in Fig. 1, the cluster structure is constructed by five atomic layers and each layer contains 25 atoms of A type or B type (A= Mg or O and B=O or Mg) in the 5×5 rectangular lattice. We have built two such structures depending on the type of adsorption site, which is the central Mg or O ion in the first layer in this structure (numbered as 1 in Fig. 1). Such a model cluster cannot reproduce the detailed electrostatic field of the crystal, but, near the adsorption site, it has a reliable description for the electrostatic field. In our AI calculations the MgO(001) surface was modeled through a slab-supercell structure: the slab contains five layers and the surface supercell is $(2\sqrt{2} \times 2\sqrt{2})45°$. The unit of the supercell structure for AI computations is the same as in the 5×5×5 cluster employed in the TB method. The supercell in our computations is large enough so that we can eliminate the direct interactions (less than 10^{-6} hartree) and the indirect interactions mediated by the surface (less than 10^{-5} hartree) between two hydrogen atoms from two neighboring supercells. In the cluster and supercell structure, the distance between two neighboring ions was fixed as the experimental value of 2.106 Å [Wyckoff, 1931].

The two preferred adsorption/absorption states are located atop and under Mg and O ions. In both TB and AI methods, we treated the adsorption/absorption processes for hydrogen atom on Mg and

O ions as follows: the hydrogen atom approaches to the target ion (A_1) normal to the MgO(001) plane from z=2.5 Å to z=0.5 Å above the first MgO(001) layer, and, in the same direction, from z=−0.5 Å to z=−2Å under the first surface layer. The section above the first surface layer (z>0) corresponds to hydrogen adsorption, and the section under the surface (z<0) to the hydrogen absorption. When the hydrogen atom approaches the surface from a larger distance, an energetic potential dip is located between 4.5 Å and 3 Å as the pre-adsorption state. This pre-adsorption state is not considered in this work because we are interested in hydrogen atoms near the surface layer.

The adsorption (E_{ad}) and the absorption (E_{ab}) energies were computed from the difference between the energy in the whole hydrogen-substrate system and that in the isolated hydrogen and substrate. It is noted that 'substrate' means the cluster in TB calculations and the supercell in AI calculations, respectively. The negative value represents the stable adsorption/absorption of the hydrogen atom. The values for E listed in Tables 2 and 3 correspond to the bonding energies for each system, i.e., the total energy of the system minus the sum of energies of isolated atoms.

Table 2. The hydrogen equilibrium positions (z_e), the net charges of the hydrogen atom (Q_H), the target cation (Q_{Mg1}) and the anion (Q_{O26}) at z=z_e, the total energies at z=z_e [E(z_e)] and z=∞ [E(z_e)], and the adsorption (E_{ad}) and the absorption energies (E_{ab}) atop the Mg cation determined from the tight-binding and the ab initio calculations

	Tight-binding		Ab initio	
	Adsorption	Absorption	Adsorption	Absorption
z_e [_]	1.513	−1.211	1.172	−1.184
$Q_H(z_e)$ [|e|]	−0.497	0.113	0.003	−0.105
$Q_{Mg1}(z_e)$ [|e|]	1.277	1.570	1.948	1.882
$Q_{O26}(z_e)$ [|e|]	−1.482	−0.773	−1.436	−1.578
E(z_e) [eV]	−97.232	−84.301	−564.823	−565.549
E(z=∞) [eV]	−88.811		−574.872	
E_{ad} [eV]	−8.421		10.049	
E_{ab} [eV]		4.511		9.323

Table 3. The hydrogen equilibrium positions (z_e), the net charges of the hydrogen atom (Q_H), the target anion (Q_{O1}) and the cation (Q_{Mg26}) at z=z_e, the adsorbate-surface energies at z=z_e [E(z_e)] and z=∞ [E(z)], and the adsorption (E_{ad}) and the absorption energies (E_{ab}) atop the O anion determined from the tight-binding and the ab initio calculations

	Tight-binding		Ab initio	
	Adsorption	Absorption	Adsorption	Absorption
z_e [Å]	0.812	−0.862	0.905	−0.901
$Q_H(z_e)$ [|e|]	0.114	−0.031	−0.119	−0.116
$Q_{O1}(z_e)$ [|e|]	−0.803	−0.596	−1.692	−1.962
$Q_{Mg26}(z_e)$ [|e|]	1.486	1.514	1.909	1.982
E(z_e) [eV]	−95.563	−89.613	−565.003	−565.176
E(z=∞) [eV]	−91.050	−574.872		
E_{ad} [eV]	−4.513		9.869	
E_{ab} [eV]		1.437		9.696

RESULTS AND DISCUSSION

1. Adsorption and Absorption Atop/Under Mg Cation

TB calculations indicate that the hydrogen atom tends to be captured near the target cation (Mg_1) at the height of 1.513 Å, whereas, in the AI results, the Mg-H equilibrium distance becomes shorter (1.172 Å, see in Table 2). For a free molecule, the Mg-H distance was measured to be 1.664 Å in the experimental observation [Suchard, 1975]. This value can be compared with 1.735 Å and 1.657 Å obtained from our additional computations using the restricted Hartree-Fock ab initio method in the 6-311G basis set (RHF-AI/6-311G) for neutral and for MgH$^+$ ionized molecule, respectively. The TB result was close to the equilibrium distance between Mg and H in MgH$^+$ ionized molecule. The adsorption energies were determined as −8.421 eV in TB calculations and 10.049 eV in AI calculations. In AI calculations the adsorption appears energetically unfavorable in relation to the infinite H-surface distance: the hydrogen atom should have the supplementary energy to be adsorbed atop Mg on the MgO (001) surface. This energetic discrepancy can be expected in the hydrogen adsorption phase because our TB method is non-SCF, and, in this way, the electrons cannot be relaxed. In the adsorption phase the error can be reduced by adding the contribution to the total energy due to the surface dipole moment [Neugebauer and Schefler, 1992].

Under the first layer, the hydrogen undergoes an energetic potential dip and would be bound to O_{26} in the second layer located under Mg_1 ion. The OH distance (0.895 Å in TB and 0.922 Å in AI calculations) is smaller than the experimental measurement of the hydroxyl group (0.967 Å) [Suchard, 1975] or the distance determined through RHF-AI/6-311G (0.967 Å for OH, and 0.970 Å for OH$^-$, respectively). The Mulliken population analysis, as shown in Fig. 2, indicates that the hydrogen gains the electronic charge along its trajectory in TB calculations (0.497 electrons in equilibrium adsorption geometry) or remains almost neutral in AI calculations. In the absorption phase, it loses small parts of its electrons in TB calculations (0.113 electrons for hydrogen net charges in the equilibrium site) and gains small quantities in AI calculations (−0.105 electrons). Even though the hydrogen charge dependence on the normal z-axis is different from its absolute value, we may observe a similar dependence, as displayed in Fig. 2(a) where it indicates more 0.3 electrons in AI calculations than in TB calculations. In both calculations the positive net charge of the target cation Mg_1 is modified in the hydrogen adsorption. As the electrons are accumulated, the net charge decreases, and, in the absorption phase, the net charge on the target cation decreases rapidly in TB calculations rather than AI calculations. Similar behavior is registered in the case of Mg_{51} cation in the third layer, and the difference between TB and AI calculations was found to be approximately 0.5 electrons.

For the adsorption phase, the charge modification is reduced on the first neighboring anions (O_2) for the target cation (Mg_1) in the first layer, and this is characterized by the accumulation of electrons. Those modifications are similar in these two types of calculations. Even though, at the infinite hydrogen-surface separation, the net charge on the O_{26} anion is different in two methods, both calculations resulted in comparable values for the adsorption phase. In AI calculations, O_{26} is dispossessed of electrons, but it is not reproduced in TB computations. In the absorption phase, the net charge
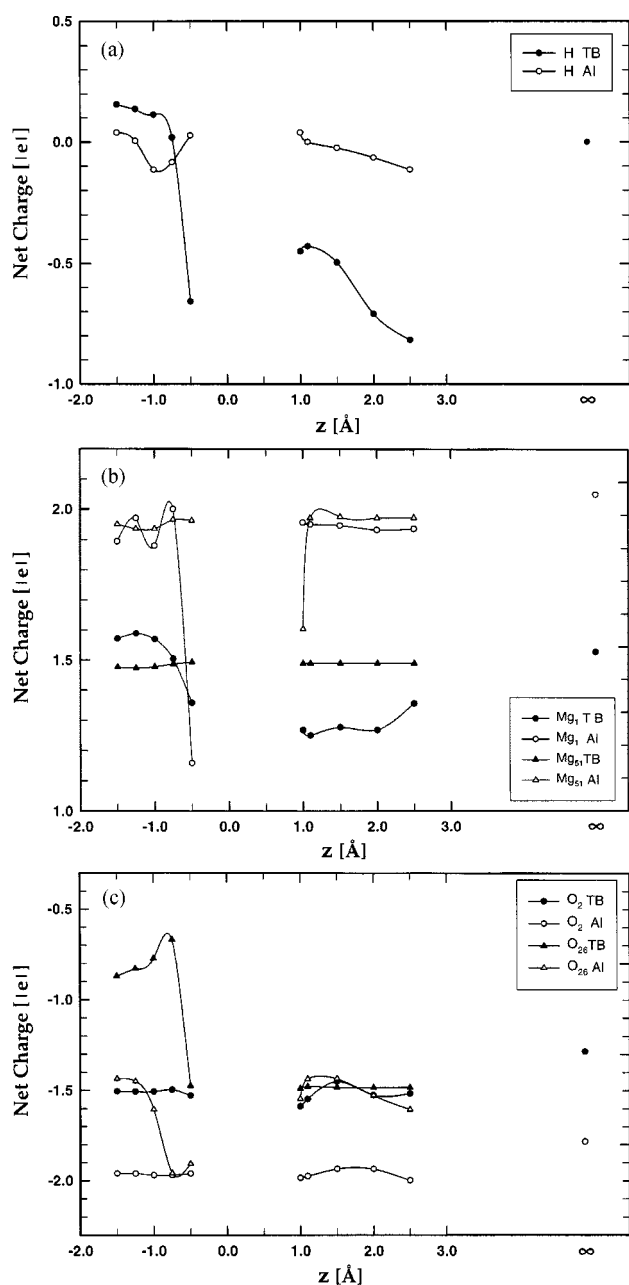
Fig. 2. The net charges as a function of z-positions for the adsorption atop/under the magnesium cation.
(a) Hydrogen; (b) Cation; (c) Anion. The open and the solid symbols correspond to the tight-binding (TB) and the ab initio (AI) calculations, respectively.

trons from Mg to H. In the absorption phase, it is formed the $O^{-a}H^{+b}$ quasi-molecule (a=0.773, b=0.113 in TB calculations and a=1.882, b=−0.105 in AI calculations). For the OH⁻ molecule, RHF-AI/6-311 calculations show 0.167 electrons transfer from hydrogen to oxygen, and, in this case, the oxygen has a surplus of 1.167 electrons.

2. Adsorption and Absorption Atop/Under O Anion

The hydrogen is captured near O_1 in the energy potential dip at z=0.812 Å in TB calculations and z=0.905 Å in AI calculations. The hydrogen adsorption energy was measured to be −4.513 eV in TB calculations and 9.869 eV in AI calculations. Although a small
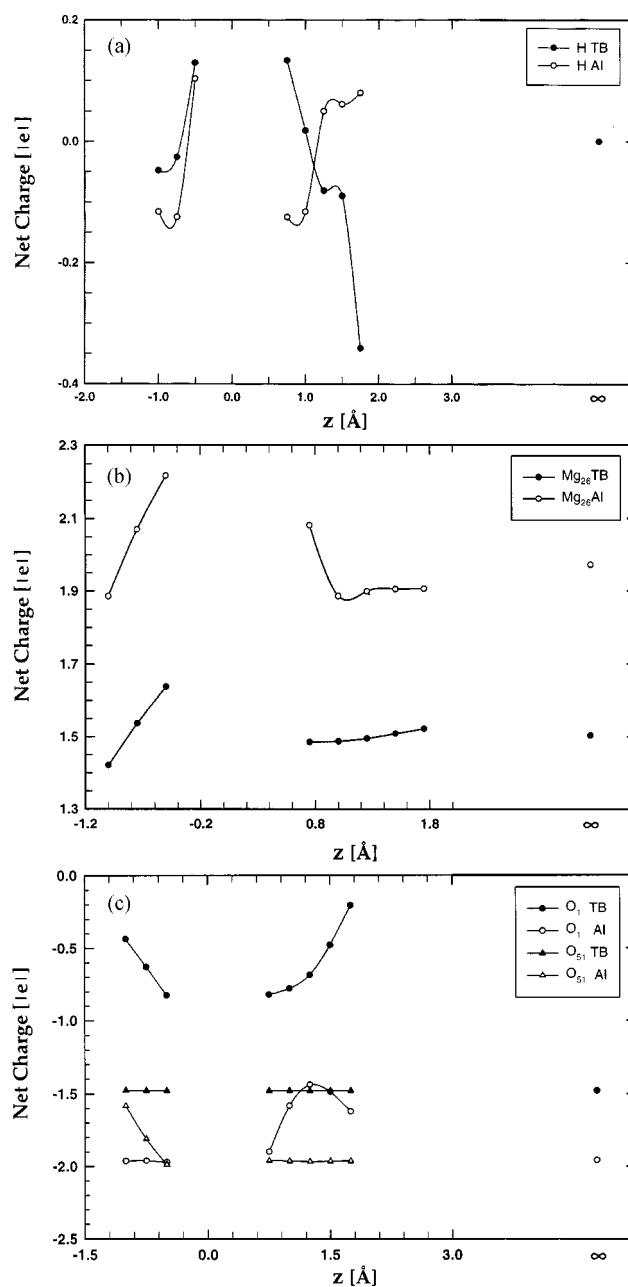

Fig. 3. The net charges as a function of z-positions for the adsorption and absorption a top/under the oxygen anion.
(a) Hydrogen; (b) Cation; (c) Anion. The open and the solid symbols correspond to the tight-binding (TB) and the ab initio (AI) calculations, respectively.

effect on O_{26} is very different from each other. In this case the net charge increases monotonically with decreasing the H-O_{26} distance in TB calculations, while it is exhibited as an S-shaped curve in AI calculations. For other ions, both methods give similar characteristics for the net charge in which it is unperturbed in the adsorption phase and weakly perturbed in the absorption phase.

In the adsorption phase, the $Mg^{+a}H^{-b}$ quasi-molecule is formed (a=1.277, b=0.497 in TB calculations and a=1.948, b=0.003 in AI calculations) in comparison with RHF-AI/6-311G calculations for the $(MgH)^{+1}$ molecule, which indicates the transfer of 0.145 elec-

difference was observed between the two methods for the adsorption atop O atom, the energetic discrepancy is similar with the hydrogen adsorption atop Mg atom.

In Fig. 3, the net atomic charge is presented for the adsorption and absorption atop/under the O anions, which illustrates the significance of electronic charge changes. In the adsorption phase, a dissimilar trend is clearly observed for the net charges of hydrogen in Fig. 3(a) and O_1 target anion in Fig. 3(c) between the two methods. In TB calculations, with decreasing the z-axis in the adsorption phase, the hydrogen atom tends to lose the electronic charge and this causes the accumulation of the electronic charge for the target oxygen. In the equilibrium position (z=0.812 Å in TB calculations), the hydrogen atom has 0.114 electrons deficit and O_1 recovers parts of the lost charge, −0.803 electron net charge, which is 0.676 electrons less than the free surface case before reaching this equilibrium position. The formal charge of the OH group molecule was −0.690 electrons. In AI calculations, however, the hydrogen loses small amounts of electrons to the surface, and gains electronic charge near the adsorption equilibrium position, where the net charge of O_1 was −1.692 electrons. Beyond this regime, it is shown to be changed drastically. The formal charge of the OH quasi-molecule was −1.811 electrons, and, in AI calculation, there was no indication of the existence of $(OH)^-$ quasi-molecule.

As shown in Fig. 3(b), the net charge for the central cation Mg_{26} located in the second layer becomes near the constant values in both calculations. For the case of z<1.0 Å in AI calculations, the rapid change in the net charge can be explained by the fact that the cation can transfer its two electrons completely from the 3sp shell of the cation to the 2sp shell of the target oxygen. This electronic transfer effect is propagated into the net charges changes of O and H atoms. The electron transfer from the surface indicates the hybridization of the 1s hydrogen orbital with the 2s and the 2p orbitals of the O_1 target oxygen. The large value for the electronic transfer is associated with the strong bond formation between hydrogen and oxygen. Based on the dependence of the electronic level as a function of z, we have observed that the energy level of the 2p electronic shell for the target oxygen was displaced around the hydrogen energy level, and, in this way, a very strong OH bonding can appear.

According to the Lewis classification, the surface oxygen, which is the electron donor, can be considered as the Lewis base. The transferred electronic charge does not remain localized on the O-H bond and it perturbs the nearest neighbor ions. In this regard, it can be assumed to be a two-step process for the electronic transfer between the surface and the hydrogen atoms as follows:

(i) The hybridization orbital induces the electronic transfer on the hydrogen atom and this results in the decreasing of the electronic charge on the target oxygen,

(ii) The electrons from ions in the neighboring layer are displaced to the target oxygen, namely, the charge perturbation screening.

After the penetration of the hydrogen atom through the first layer, the hydrogen is captured in the potential energy dip. The hydrogen is bounded with O_1 (z=−0.862 Å in TB calculations and z=−0.901 Å in AI calculations). For the penetrating hydrogen atom, the distance to the oxygen ion in the first layer is shorter than that to the oxygen in the second layer. The resulting O-H distance becomes

shorter than that in the case of Mg ions described in the previous section. The absorption energies are computed as 1.437 eV and 9.869 eV in the TB and the AI methods, respectively. The net charge behaviors of the hydrogen atom and the surface ions are similar to each other in both calculations. In the absorption equilibrium position, the net charge of hydrogen and the formal charge of the OH quasi-molecule are, respectively −0.031 and −0.627 electrons in TB calculations, and −0.116 and −2.078 electrons in AI calculations. The discrepancy for the formal charges maybe partly be due to the inadequate description for the long-ranged Coulombic field, in the cluster model used in TB calculations.

CONCLUSIONS

In the present work both tight-binding (TB) and ab initio (AI) calculations have been carried out to investigate the electronic and energetic properties of the hydrogen atom atop/under the MgO(001) surface. The qualitative reproductions of ab initio results on both types of ions are obtained. In the hydrogen absorption phase, the TB results are found to be more accurate than in the adsorption phase. The marginal discrepancies in two methods can be mainly due to their different approaches: TB and AI computations are based on the basis sets of molecular systems and for ionic systems, respectively, and the electronic net charges obtained from the TB method become underestimated using the Mulliken population analysis. For both adsorption and absorption phases, the perturbation of the charge distribution is found to be significant only for the hydrogen atom and its nearest-neighbor ions. The formations of MgH^+ and OH^- quasi-molecules are indicated in both methods. The equilibrium H-O distances determined by the two methods are comparable, while the equilibrium H-Mg distances determined by the TB method are larger than those obtained by the AI method. In this case the detailed parameters for the magnesium ion are required for the better qualities of TB calculations. Furthermore, the proper descriptions for the Coloumbic field are also required to improve TB results. This could be achieved by considering the periodic boundary structure, e.g., the band structure in the central point of the first Brillouin zone.

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