Rotation of hydrogen molecules during the dissociative adsorption on the Mg(0001) surface: a first-principles study*

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Using first-principles calculations, we systematically study the potential energy surfaces and dissociation processes of the hydrogen molecule on the Mg(0001) surface. It is found that during the dissociative adsorption process with the minimum energy barrier, the hydrogen molecule first orients perpendicularly, and then rotates tobecome parallel to the surface. It is also found that the orientation of the hydrogen molecule in the transition state is neither perpendicular nor parallel to the surface. Most importantly, we find that the rotation causes a reduction of the calculated dissociation energy barrier for the hydrogen molecule. The underlying electronic mechanism for the rotation of the hydrogen molecule is also discussed in the paper.

Keywords: first-principles, hydrogen, dissociation, rotation
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1. Introduction

It is of great scientific importance to study the dissociation of diatomic molecules on metal surfaces (dissociative sticking), to meet some intrinsic interest in the mechanisms for the bond breaking and bond formation, and the origins of activation energy barriers.[1,2] The dissociation of the hydrogen molecule (H_2) on metal surfaces is furthermore a key event for a lot of technological applications such as hydrogen storage for fuels,[3,4] hydrogen caused embrittlement,[5] and heterogeneous catalysis.[2,6] Among all the metals, the Mg(0001) surface is one of the prototypes studied extensively, both theoretically and experimentally.[4,7−11] However, some basic problems concerning the dissociation process and energy barrier still show discrepancies as yet. As early as 1981, Nørskov *et al.*[8] for the first time studied the dissociation of H_2 on the Mg(0001) surface, observing a molecularly adsorbed precursor state and an energy barrier of 0.5 eV for dissociation. Later, by using the more precise first-principles methods, Bird *et al.*[9] discovered that although the most energetically favourable site for dissociation is the bridge site as reported in Ref. [8], the dissociation energy barrier is 0.37 eV, rather than the reported 0.5 eV, and there is no precursor state. However, the discrepancy on the dissociation energy barrier remains ever since then. Vegge[10] reported a value of 1.15 eV for the dissociation, after systematically considered the zero point energy of H_2 within their first-principles calculations. Wu *et al.*[4] reported a value of 1.05 eV by employing first-principles calculations and transition state theory. Meanwhile, Johansson *et al.*[11] recently organized an experiment to study the dissociation energy barrier for H_2 at Mg(0001), and the barrier obtained is 0.6–0.9 eV, which disagrees with all the reported theoretical values. So it is still an open question as to the correct dissociation energy barrier for H_2 at Mg(0001) surface.

On the other hand, it has been recently suggested that steric effects might be important during the adsorption and dissociation of diatomic molecules on metal surfaces.[12] For the adsorption of D_2 on Cu(111), both experimental and theoretical investigations found that the dissociation of D_2 occurs preferentially when the molecule approaches with its bond parallel to the surface.[12] Similar dependence on po-

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lar angle has also been theoretically predicted for the dissociative sticking of O_2 on the Al(111) surface.[13] When considering the dissociative adsorption of H_2 on metal surfaces, steric effects might be more important because of the low inertia moment of H_2 and correspondingly high possibility to rotate. In fact, it has already been pointed out that during the dissociative adsorption of H_2 on the Pd(111) surface, the molecular axis orientation has a drastic effect on the molecular behaviours, and low activation barriers are only met over a small range of θ values from being parallel to the surface.[14] And for the adsorption on the NiAl(110) surface, H_2 molecules will rotate abruptly when they are getting close to the surface, which allows them to adopt the orientation that is more convenient for dissociation (i.e., nearly parallel to the surface).[15] For the adsorption of H_2 on the Mg(0001) surface, however, this important issue of steric effects has not been considered yet. Motivated by this observation, here using the first-principles calculations, we study the rotation of H_2 during the dissociative adsorption on the Mg(0001) surface and its influences on the dissociation energy barrier. We show that the most energetically favourable path for H_2 dissociation at Mg(0001) is fundamentally determined by the steric effect.

2. Calculation method

Our calculations were performed within density functional theory (DFT) using the Vienna *ab-initio* simulation package.[16] The PW91[17] generalized gradient approximation (GGA) and the projector-augmented wave potential[18] were employed to describe the exchange–correlation energy and the electron–ion interaction, respectively. The cutoff energy for the plane wave expansion was set to 250 eV. The Mg(0001) surface was modeled by a five-atomic-layer slab plus a vacuum region of 20 Å(1 Å=0.1 nm). A 2×2 supercell was adopted in the study of the H_2 adsorption since our test calculations have shown that it is large enough to avoid the interaction between adjacent hydrogen molecules. Integration over the Brillouin zone was done using the Monkhorst–Pack scheme[19] with $9 \times 9 \times 1$ grid points. The calculated lattice constants of bulk Mg (a, c) and the bond length of isolated H_2 are 3.207, 5.145, and 0.748 Å, respectively, in good agreement with the experimental values of 3.21, 1.62,[20] and 0.74 Å.[21] The calculation of the potential energy surface was interpolated to 209 points with different bond length (d_{H-H}) and height (h_{H_2}) of H_2 at each surface site.

3. Results and discussion

After geometric optimisation for the Mg(0001) surface, we build our model to study the potential energy surface (PES) of H_2 on the relaxed Mg surface. As shown in Fig. 1, there are four different high-symmetry sites on the Mg(0001) surface: the top, bridge (bri), hcp and fcc hollow sites. After PES calculations, we find that the dissociation barrier of H_2 at low-symmetry sites is always larger than at high-symmetry sites, proving that high-symmetry sites play crucial roles in the adsorption of diatomic molecules, similar to that observed on the adsorption of oxygen molecules on the Pb(111) surface.[22] And in the following, we will only give the results for the four high-symmetry sites. At each surface site, an adsorbed H_2 has three different principal orientations: along the x (i.e., $[11\bar{2}0]$), y (i.e., $[\bar{1}100]$), and z (i.e., [0001]) directions. Herein, we use top-x, y, z, bri-x, y, z, hcp-x, y, z and fcc-x, y, z respectively to represent the total twelve high-symmetry channels for the adsorption of H_2 on the Mg surface.

Throughout our PES calculations, we find no molecular adsorption precursor states for H_2 on Mg(0001), well consistent with all previous reports, except the one by Nørskov *et al.* using jellium model.[8] Our calculated result for the lowest dissociation energy barrier, as well as that in other theoretical and experimental reports, is given in Table 1. The minimum energy path (MEP) for the dissociation of H_2 on the Mg(0001) surface is found to be along the bri-y channel, which is consistent with all previous first-principles studies. The transition state obtained from our PES calculations along the bri-y channel is at the point with $d_{H-H} = 1.12$ Å and $h_{H_2} = 1.16$ Å, which accords with previous results.[4,23] However, as we will see later, this transition state needs to be modified after taking into consideration the rotational degree of freedom of H_2.

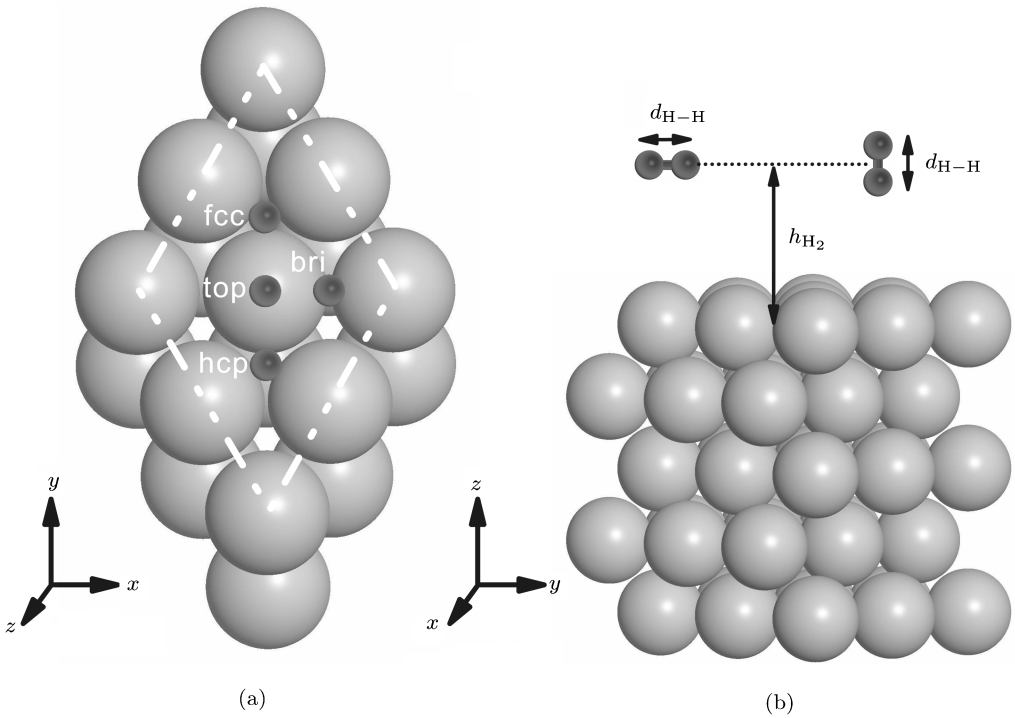


Fig. 1. (a) The $p(2 \times 2)$ surface cell of Mg(0001) and four on-surface adsorption sites. Here only the outmost two layers of the surface are shown. (b) The sketch map showing that the molecule (with vertical or parallel orientation) is initially away from the surface at a hight h_{H_2}.

Table 1. Our calculated minimum energy barrier for the dissociation of H_2 molecules on the Mg(0001) surface, and other reported results.

references	methods	dissociation barrier/eV
[8]	Jellium model (LDA)	0.50
[9]	DFT (LDA)	0.37
[3]	DFT (RPBE)	0.50
[10]	DFT (GGA)	1.15
[23]	DFT (LDA)	0.35
[23]	DFT (PBE-GGA)	1.05
[4]	DFT (GGA)	1.05
[11]	Experiment	0.59–0.90
this work	DFT (GGA)	0.85

At the bridge site, however, we find that the total energy of the H_2/Mg system is not always smaller along the bri-y channel than along other channels. This is a key point in this paper. In fact, for large values of H_2 height from Mg(0001) surface, we find that the total energy is smaller along the bri-z channel than along the bri-y channel. To show this, we plot in Figs. 2(a)–2(c) the two-dimensional cuts of the PES along the bri-x, y, z channels. Correspondingly, the minimum energy paths in Figs. 2(a)–2(c) are collected and plotted in Fig. 2(d). It can be clearly seen that there is a prominent crossing point in the minimum energy paths along bri-y and bri-z channels, at which the distance of the H_2 molecule from the surface takes a value of $h_{H_2} = 1.26$ Å. Before this crossing, the total energy of the adsorption system along the bri-z channel is always lower than along the bri-y channel. This finding indicates that H_2 prefers to orient perpendicular to the Mg(0001) surface until it reaches the height lower than 1.26 Å. After the crossing point, however, the system along the bri-y channel has a smaller total energy than along the bri-z channel, and H_2 tends to rotate from the bri-z to the bri-y channel.

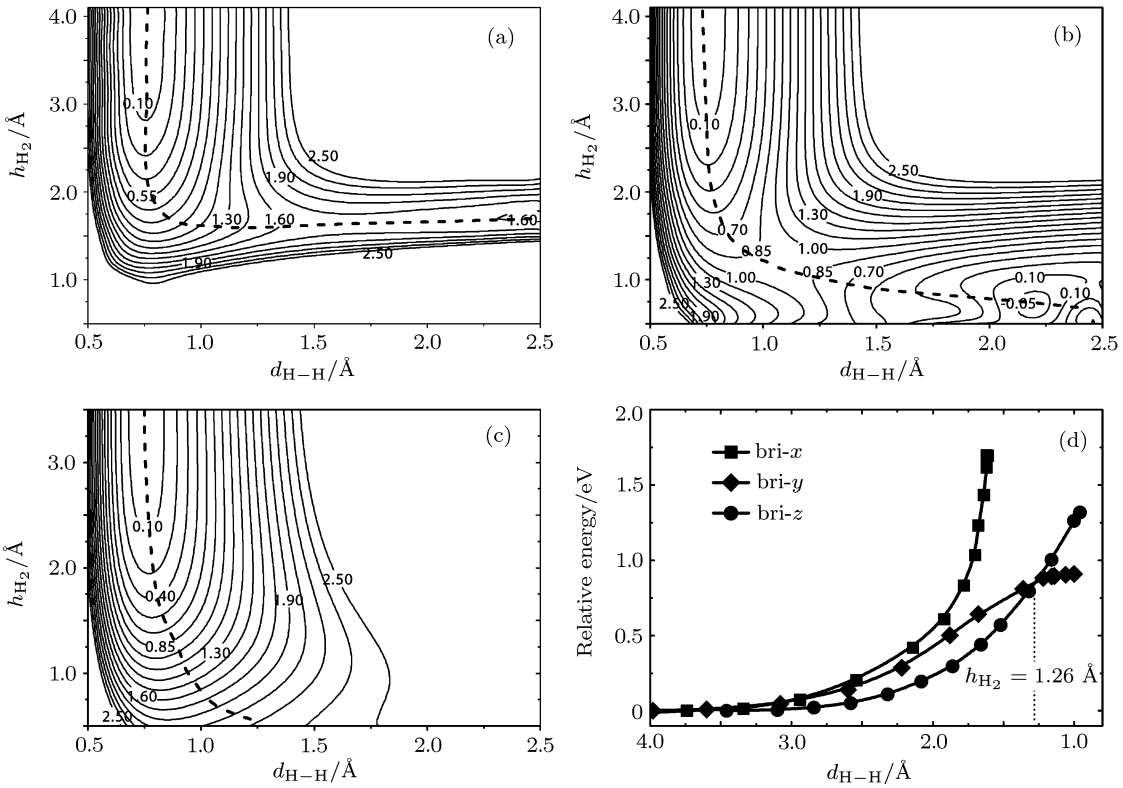


Fig. 2. Contour plots of the two-dimensional cuts of the potential energy surfaces (PESs) for the H_2/Mg(0001) system versus the bond length (d_{H-H}) and the height (h_{H_2}), with H_2 at the bridge site orienting along x (a), y (b) and z (c) directions. (d) Minimum energy paths obtained along the three different channels with different heights of H_2 (h_{H_2}) from the Mg surface.

We then further study the influence of the molecular rotation on the dissociation energy barrier of H_2. For this we have calculated the total energy by fixing the mass centre of H_2 at the bridge site with the height of 1.16 Å and the molecular bond length of 1.12 Å, while allowing H_2 to rotate around its mass centre in the $y-z$ plane (see the inset in Fig. 3). The calculated angle dependence of the total energy is shown in Fig. 3. Clearly, it can be seen that the transition state (namely, the saddle point in the PES for H_2 dissociation) should be the structure where the orientation of H_2 is 21° from the $x-z$ plane. This rotation of H_2 results in an 86 meV modification on the dissociation energy barrier. This finding suggests that steric factors, which were not considered in previous theoretical calculations, might be (at least partially) responsible for their discrepancies with experimental measurement.

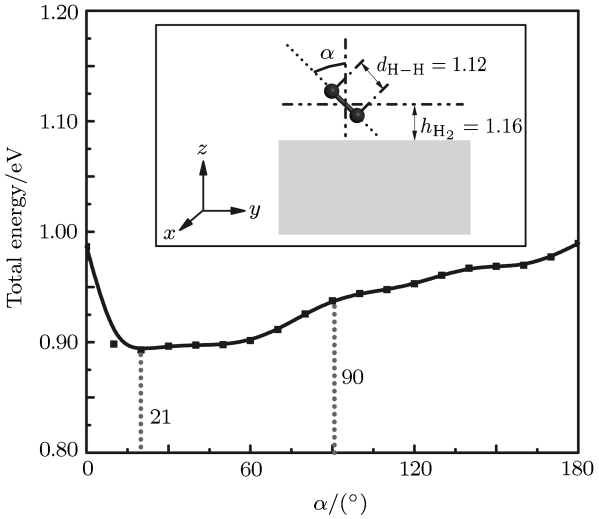


Fig. 3. The total energy of the adsorption system versus orientation of H_2 at the transition state point along the bri-y channel with d_{H-H} = 1.12 Å at h_{H_2} = 1.16 Å. The inset depicts the definition of the angle α, in which the grey area and black balls represent the Mg surface and the two H atoms respectively.

Although steric effect on the dissociative adsorption of diatomic molecules on metal surfaces has long been explored, the specific reasoning has seldom been discussed yet. Herein we will try to find the underlying mechanisms for the rotation of H_2 during the dissociative adsorption on the Mg(0001) surface, by analysing carefully the charge distributions and electronic interactions in the adsorption process of H_2. Figures 4(a)

and 4(b) show the difference of electron density for the adsorption system with h_{H_2} being 2.00 and 1.16 Å along the bri-y channel, namely,

$$\Delta\rho = \rho(H_2 + Mg(0001)) - \rho(H_2) - \rho(Mg(0001)), \quad (1)$$

where $\rho(H_2 + Mg(0001))$, $\rho(H_2)$ and $\rho(Mg(0001))$ are respectively the electron densities of the adsorption system, the H_2 molecule and the clean Mg(0001) surface. To calculate $\Delta\rho$, the atomic positions in the last two terms in Eq. (1) have been kept at those of the first term. Through careful wavefunction analysis, we find that at the beginning of the adsorption process, the molecular orbitals of H_2 orthogonalize with electronic states of Mg and thus are broadened. As shown in Fig. 4(a), the surface electrons of Mg are repelled from the region occupied by the H_2 bonding electrons due to these orthogonalizations. This interaction has also been observed during the interacations of H_2 with other metals such as the Al(111)[24] and transition metal surfaces.[25] When the H_2 molecule is close enough to the Mg(0001) surface and comes to the transition state for its dissociation, electrons are transferred from electronic states of Mg to the antibonding orbital of H_2, which can be clearly seen from Fig. 4(b). We can also see from Fig. 4(b) that the orthogonalizations between electronic states of Mg and the bonding orbital of H_2 still exist in the transition state.

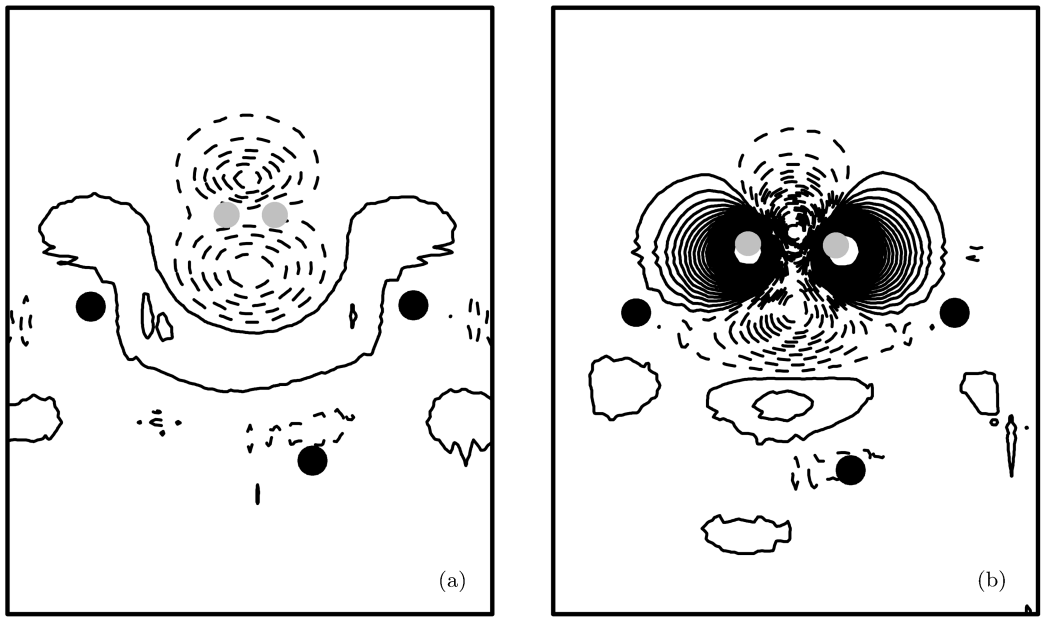


Fig. 4. The difference of electron densities for the H_2/Mg(0001) system with the height of H_2 being 2.00 Å (a) and 1.16 Å (b). Grey and black balls represent respectively hydrogen and Mg atoms. Solid and dashed lines represent respectively the positive and negative values, i.e., electron accumulation and depletion.

In a word, the orthogonalizations between molecular orbitals of H_2 and electronic states of Mg can cause repulsive interactions between electrons of H and Mg, and thus will enlarge the total energy of the adsorption system, while the transfer of electrons from Mg to H_2 causes attractive interactions between H and Mg atoms and lowers the total energy. So during the adsorption process of H_2, the total energy of the system firstly goes up, then lowers down. This analysis explains why an energy barrier is needed for the dissociation of H_2 on the Mg(0001) surface. Moreover, both the orthogonalizations and electrons transfer are always weaker along the bri-z channel than along the bri-y channel. Therefore, at the beginning of the adsorption process, when no electrons transfer happens, the total energy of the system is smaller along the bri-z channel than along the bri-y channel. And in the vicinity of the transition, when the H_2 molecule is very close to the Mg(0001) surface, electrons transfer begins to dominate the molecule–metal interaction. So the total energy along the bri-y channel is smaller for the transition state. The rotation of H_2 can be re-

garded as the result of the different interactions that favour the bri-y and bri-z channels. As a result, the minimum energy path for the dissociation of H_2 is neither along the bri-y nor along the bri-z channels. And the corresponding transition state is the one when H_2 makes an angle 21° with the $x-z$ plane, as shown in Fig. 3.

4. Conclusion

In conclusion, we have systematically studied the PESs for the dissociative adsorption of the hydrogen molecule on the Mg(0001) surface. Our results accord well with previous reports on the direct dissociative adsorption process. More importantly, we have found that the hydrogen molecule does not always orient parallel to the surface along the dissociation channel with the lowest energy barrier. At large heights of the H_2 molecule, it orients perpendicular to the surface. When getting closer to the surface, the molecule begins to rotate such that in the transition state, it makes an angle 21° with the $x-z$ plane, inducing a 86 meV modification on the dissociation energy barrier. We have revealed that this molecular rotation is due to the two different interactions between H_2 and Mg: the orthogonalizations between molecular orbitals of H_2 and electronic states of Mg, and the electrons transfer from the Mg(0001) surface to the anti-bonding orbital of H_2. As a final concluding remark, here based on the present results, we would like to point out that steric effects are important for understanding the adsorption behaviours of H_2 on metal surfaces.

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