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

Yanfang Li¹,², Yu Yang²,³*, Bo Sun², Hong-Zhou Song², Yinghui Wei¹, Ping Zhang²†

¹College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, People’s Republic of China
²LCP, Institute of Applied Physics and Computational Mathematics, P.O. Box 8009, Beijing 100088, People’s Republic of China and
³Center for Advanced Study and Department of Physics, Tsinghua University, Beijing 100084, People’s Republic of China

(Dated: June 25, 2009)

Abstract

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 firstly orients perpendicular, and then rotates to be parallel to the surface. It is also found that the orientation of the hydrogen molecule at 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 reasons for the rotation of the hydrogen molecule is also discussed in our paper.

* Corresponding author. E-mail address: yang_yu@iapcm.ac.cn
† Corresponding author. E-mail address: zhang_ping@iapcm.ac.cn
I. INTRODUCTION

It is of great scientific importance to study the dissociation of diatomic molecules on metal surfaces (dissociative sticking), to meet some intrinsic interests on mechanisms for bond breaking and bond formation and origins of activation energy barriers\(^1,2\). The dissociation of the hydrogen molecule (H\(_2\)) on metal surfaces are furthermore key events for lots 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 most studied prototypes, both theoretically and experimentally\(^4,7,8,9,10,11\). However, some basic problems concerning the dissociation process and energy barrier still have discrepancies yet. As early as 1981, Nørskov \textit{et al.} 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\(^8\). Later, by using the more precise first-principles methods, Bird \textit{et al.} discovered that although the most energetically favorable site for dissociation is the bridge site as reported in Nørskov’s paper, the dissociation energy barrier is 0.37 eV, rather than the reported 0.5 eV, and there is no precursor state\(^9\). However, the discrepancy on the dissociation energy barrier remains ever since then. Vegge \textit{et al.} 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\(^10\). Wu \textit{et al.} reported a value of 1.05 eV by employing first-principles calculations and transition state theory\(^4\). Meanwhile, Johansson \textit{et al.} recently organized an experiment to study the dissociation energy barrier for H\(_2\) at Mg(0001), and the obtained barrier is 0.6 \(\sim\) 0.9 eV\(^11\), 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).

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 dissociation of D\(_2\) occurs preferentially when the molecule approaches with its bond parallel to the surface\(^12\). Similar dependence on polar 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 H₂ on the Pd(111) surface, the molecular axis orientation has a drastic effect and low activation barriers are only met over a small range of θ values from parallel the surface. And for the adsorption on the NiAl(110) surface, H₂ molecules rotate abruptly when they are close to the surface, which allows them to adopt the orientation that is more convenient for dissociation (i.e., nearly parallel to the surface). For the adsorption of H₂ on the Mg(0001) surface, however, this important issue of steric effects has not been considered yet. Motivated by this observation, here by using the first-principles calculations, we study the rotation of H₂ during the dissociative adsorption on the Mg(0001) surface and its corresponding influences on the dissociation energy barrier. We show that the most energetically favorable path for H₂ dissociation at Mg(0001) is fundamentally determined by the steric effect.

II. CALCULATION METHOD

Our calculations were performed within DFT using the Vienna ab-initio simulation package. The PW91 generalized gradient approximation and the projector-augmented wave potential 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. A 2 × 2 supercell was adopted in the study of the H₂ adsorption since our test calculations have showed 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 with 9 × 9 × 1 grid points. The calculated lattice constants of bulk Mg (a, c) and the bond length of isolated H₂ are 3.207 Å, 5.145 Å and 0.748 Å, respectively, in good agreement with the experimental values of 3.21 Å, 1.62 Å and 0.74 Å. The calculation of the potential energy surface was interpolated to 209 points with different bond length (d_H-H) and height (h_H₂) of H₂ at each surface site.

III. RESULTS AND DISCUSSION

After geometry optimization for the Mg(0001) surface, we build our model to study the potential energy surface (PES) of H₂ on the relaxed Mg surface. As shown in Fig. 1, there
are four different high-symmetry sites on the Mg(0001) surface, respectively 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 has been observed on the adsorption of oxygen molecules on the Pb(111) surface$^{22}$. And in the following, we will only give the results at the four high-symmetry sites. At each surface site, an adsorbed H$_2$ has three different principle orientations, respectively along the $x$ (i.e., [110]), $y$ (i.e., [110]), 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$_2$ at Mg(0001), according well with all previous reports, except for 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. I. 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 where $d_{H-H}=1.12$ 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 considering the rotational degree of freedom of H$_2$.

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, at 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)-(c) the two-dimensional cuts of the PES along the bri-$x$, $y$, $z$ channels. Correspondingly, the minimum energy paths in Figs. 2(a)-(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, whereas, the system along the bri-$y$
channel has a smaller total energy than along the bri-z channel, and H\textsubscript{2} tends to rotate from the bri-z channel to the bri-y channel.

We then further study the influence of the molecular rotation on the dissociation energy barrier of H\textsubscript{2}. For this we have calculated the total energy by fixing the mass center of H\textsubscript{2} at the bridge site with the height of 1.16 Å and the molecular bond length of 1.12 Å, while allowing H\textsubscript{2} to rotate around its mass center 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\textsubscript{2} dissociation) should be the structure where the orientation of H\textsubscript{2} is 21° from the x-z plane. This rotation of H\textsubscript{2} results in a 86 meV modification on the dissociation energy barrier. This finding suggests that steric factors that has not been considered in previous theoretical calculations might be (at least partially) responsible for their discrepancies with experimental measurement.

Although it has long been explored for steric effects on the dissociative adsorption of diatomic molecules on metal surfaces, the specific reasoning has seldom been discussed yet. Herein we will try to find the underlying mechanisms on the rotation of H\textsubscript{2} during the dissociative adsorption on the Mg(0001) surface, by analyzing carefully the charge distributions and electronic interactions along the adsorption process of H\textsubscript{2}. Figures 4(a) and (b) show the difference electron density for the adsorption system with \(h_{H_2}\) to be 2.00 and 1.16 Å along the bri-y channel, namely,

\[
\Delta \rho = \rho(H_2 + Mg(0001)) - \rho(H_2) - \rho(Mg(0001)),
\]

where \(\rho(H_2 + Mg(0001)), \rho(H_2)\) and \(\rho(Mg(0001))\) are respectively the electron density of the adsorption system, the H\textsubscript{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\textsubscript{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\textsubscript{2} bonding electrons due to these orthogonalizations. This interaction has also been observed during the interactions of H\textsubscript{2} with other metals such as the Al(111)\textsuperscript{24} and transition metal surfaces\textsuperscript{25}. When the H\textsubscript{2} molecule is close enough to the Mg(0001) surface and come to the transition state for its dissociation, electrons transfer from electronic states of Mg to the antibonding orbital of H\textsubscript{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\textsubscript{2} still exist at the transition state.

In total, the orthogonalizations between molecular orbitals of H\textsubscript{2} and electronic states of Mg cause repulsive interactions between electrons of H and Mg, and thus will enlarge the total energy of the adsorption system, while the electrons transfer from Mg to H\textsubscript{2} causes attractive interactions between H and Mg atoms and lowers down the total energy. So during the adsorption process of H\textsubscript{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\textsubscript{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 at around the transition state, when the H\textsubscript{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 at the transition state. Herein, the rotation of H\textsubscript{2} can be seen as the result from the different interactions that respectively favors the bri-y and bri-z channels. As a result, the minimum energy path for the dissociation of H\textsubscript{2} is neither along the bri-y nor along the bri-z channels. And the corresponding transition state is the one where H\textsubscript{2} orients 21° away from the x-z plane, as shown in Fig. 3.

IV. 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 molecular heights, H\textsubscript{2} orients perpendicular to the surface. When getting closer to the surface, H\textsubscript{2} begins to rotate such that at the transition state, H\textsubscript{2} orients 21° away from the x-z plane, which causes a 86 meV modification on the dissociation energy barrier. We have revealed that this molecular rotation is because of the two different interactions between H and Mg, i.e., the orthogonalizations between molecular orbitals of H\textsubscript{2} and electronic states of Mg and electrons transfer from the Mg(0001)
surface to the antibonding orbital of $\text{H}_2$. As a final concluding remark, here based on the present results, we would like to point out that steric effects are important to understand the adsorption behaviors of $\text{H}_2$ on metal surfaces.

Acknowledgments

P.Z. was supported by the NSFC under Grants No. 10604010 and No. 60776063. Y.W. was supported by the NSFC under Grants No. 50471070 and No. 50644041.

1 G.R. Darling and S. Holloway, Rep. Prog. Phys. 58 (1995) 1595.
2 D.A. King and D.P. Woodruff, The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Elsevier, Amsterdam, 1988.
3 N. Jacobson, B. Tegner, E. Schröder, P. Hyldgaard, and B.I. Lundqvist, Comput. Mat. Sci. 24 (2002) 273.
4 G.X. Wu, J.Y. Zhang, Y.Q. Wu, Q. Li, G.Z. Zhou, and X.H. Bao, Acta Phys. Chim. Sin. 24 (2008) 55.
5 G. Lu and E. Kaxiras, Phys. Rev. Lett. 94 (2005) 155501.
6 K. Gustafsson and S. Andersson, Phys. Rev. Lett. 97 (2006) 076101.
7 P.T. Sprunger and E.W. Plummer, Chem. Phys. Lett., 187 (1991) 559.
8 J.K. Nørskov, A. Houmøller, P.K. Johansson, and B.I. Lundqvist, Phys. Rev. Lett. 46 (1981) 257.
9 D.M. Bird, L.J. Clarke, M.C. Payne, and I. Stich, Chem. Phys. Lett. 212 (1993) 518.
10 T. Vegge, Phys. Rev. B 70 (2004) 035412.
11 M. Johansson, C.W. Ostenfeld, and I. Chorkendorff, Phys. Rev. B 74 (2006) 193408.
12 H. Hou, S.J. Gulding, C.T. Rettner, A.M. Wodtke, and D.J. Auerbach, Science 277 (1997) 80.
13 L. Österlund, I. Zorić, and B. Kasemo, Phys. Rev. B 55 (1997) 15452.
14 H.F. Busnengo, A. Salin, and W. Dong, J. Chem. Phys. 112 (2000) 7641.
15 P. Rivière, A. Salin, and F. Martína, J. Chem. Phys. 124 (2006) 084706.
16 G. Kresse and J. Furthmuller, Phys. Rev. B 54 (1996) 11169 and references therein.
17 J.P. Perdew and Y. Wang, Phys. Rev. B 45 (1992) 13244.
18 G. Kresse and D. Joubert, Phys. Rev. B 59 (1999) 1758.
19 H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13 (1976) 5188.
20 V. Amonenko, V.Y. Ivanov, G. Tikhinskij, and V. Finkel, Phys. Met. Metallogr. 14 (1962) 47.
21 K.P. Huber and G. Herzberg, Constants of Diatomic Molecules, Van Nostrand, New York, 1979.
22 Y. Yang, G. Zhou, J. Wu, W.H. Duan, Q.K. Xue, B.L. Gu, P. Jiang, X.C. Ma, and S.B. Zhang,
   J. Chem. Phys. 128 (2008) 164705.
23 A.J. Du, S.C. Smith, X.D. Yao, and G.Q. Lu, J. Phys. Chem. B 109 (2005) 18037.
24 B. Hammer, K.W. Jacobsen and J.K. Nørskov, Surf. Sci. 297 (1993) L68.
25 J. Harris and S. Anderson, Phys. Rev. Lett. 55 (1985) 1583.
TABLE I: Our calculated minimum energy barrier for the dissociation of H₂ 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                      |
List of captions

Fig.1  (Color online). (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 with a height $h_{H_2}$.

Fig.2  (Color online). Contour plots of the two dimensional cuts of the potential energy surfaces (PESs) for the H$_2$/Mg(0001) system as a function of the bond lengths ($d_{H-H}$) and the heights ($h_{H_2}$), 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.

Fig.3  (Color online). The total energy of the adsorption system with different orientations of H$_2$ at the transition state point along the bri-$y$ channel where $d_{H-H}$=1.12 Å and $h_{H_2}$=1.16 Å. The inset depicts the definition of the angle $\alpha$, in which the grey area and blue balls respectively represent the Mg surface and two H atoms.

Fig.4  (Color online). The difference electron density for the H$_2$/Mg(0001) system with the height of H$_2$ to be 2.00 (a) and 1.16 Å (b). Blue and grey balls respectively represent hydrogen and Mg atoms. Dark and dashed lines respectively represent plus and negative values, i.e., electrons accumulation and depletion.
FIG. 1: ...
FIG. 2:
Total energy (eV)

\[ \alpha (^\circ) \]

\[ d_{HH} = 1.12 \text{ Å} \]

\[ h_{H} = 1.16 \text{ Å} \]

FIG. 3:
