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Adsorption dynamics of O₂ on Cu(100)

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Abstract

We have studied the adsorption of O₂ on the Cu(100) surface using both static potential energy surface (PES) calculations and ab initio molecular dynamics. The dynamical calculations complement the PES results, revealing steering effects which could not be predicted based on the static calculations only. We study the effect of oxidation and Ag doping on O₂ adsorption dynamics. The results are discussed in the light of recent molecular beam experiments.
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1. Introduction

The first step of the surface oxidation process is the arrival and subsequent atomic or molecular adsorption of the O₂ molecule on the surface. Understanding of the molecule–surface interaction is therefore an important prerequisite for a successful description of oxidation. The quantum mechanical treatment of such a dynamical process is, however, highly nontrivial even in the case of simple metal surfaces. When addressing real surfaces with defects such as vacancies, dopants and impurities, further complications arise, making the problem very hard to tackle with first principles methods. Experimentally, a powerful way of obtaining information on the adsorption dynamics and kinetics is the use of the molecular beam surface scattering (MBSS) technique which enables one to study the adsorption characteristics of molecules approaching the surface at different translational energies. In particular, with MBSS one can measure the sticking coefficient, which in turn is proportional to the dissociation probability of the mole-

cules on the surface in question. Recently, the effect of surface modifications on O₂ adsorption on Cu(100) was studied by Junell et al. using MBSS [1]. Pre-adsorbed oxygen was shown to alter the adsorption dynamics considerably whereas Ag doping only had a small effect. At small and intermediate translational energies, introducing Ag on Cu(100) yielded slightly smaller sticking coefficients than in the case of clean Cu(100), yet the overall shape of the sticking curve remained the same [1].

In the case of clean Cu(100), the experiments find that the sticking coefficient approaches zero at small translational energy of the O₂ molecule [1–3]. This would indicate the existence of an early barrier in the entrance channel, preventing the molecule from adsorbing on the surface either in a molecular or an atomic state. This kind of barrier, however, has not been observed in our earlier calculations [4], a situation similar to that for O₂ on Al(111), discussed by several authors [5–9]. A traditional way of addressing the O₂ adsorption from the theoretical point of view is to calculate elbow plots which can be considered as two-dimensional cuts of the true six-dimensional potential energy surface (PES). This approach has also been used in our work [4,10], but has been complemented by ab initio molecular dynamics (MD) calculations [11]. Our aim here is to discuss these results in the light of the recent

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experiments and provide further insight into the molecule–surface interactions on metal surfaces. Moreover, we discuss the computational strategies needed for a thorough interpretation of the experimental results. The rest of this paper is organized as follows: In Section 2 the relevant computational details are given together with a comparison of different computational methods. In Section 3 we present our results together with a brief review of the previous work, and discuss these results in the light of the experiments. Finally, some conclusions and future directions are provided in Section 4.

2. Computational details

In our calculations we used the Spanish Initiative for Electronic Structure with Thousands of Atoms (SIESTA) [12,13] package, which uses linear combinations of atomic orbitals as basis functions. Also, we used norm conserving [14,15] Troullier–Martins [16] type pseudopotentials within the generalized gradient approximation (GGA) scheme of Perdew, Burke, and Ernzerhof (PBE) [17]. To speed up the self-consistent field iterations we used smearing of 0.07 eV for the Methfessel–Paxton occupation function. We used an optimized basis set for copper and a standard double zeta basis with polarization orbitals and energy shift of 15 meV [18] for oxygen. In our molecular dynamics simulations we used surface temperature of 300 K controlled by a Nosè thermostat [22,23] and timestep of 3 fs and 1 fs per each ionic move for the lower and higher translational energies, respectively.

To test the pseudopotential we performed all electron calculations for a copper atom with a few excited states and found that the pseudopotential reproduces the all electron eigenvalues reasonably well. Also, we calculated 3.69 Å for the lattice parameter of bulk copper compared to the experimental value of 3.61 Å [19]. The lattice parameter differs by only 2.2% from the experimental one and thus is in the regime of the error rate of these calculations. This underbinding is also a typical feature of the GGA approximation used. For oxygen, we calculated the bond length of 1.237 Å vs. the experimental value of 1.207 Å [20], differing by only about 2.5%. In the slab calculation for clean Cu(100) we observed an inward relaxation of the first layer of 0.95% compared to the experimental result of 1.2% [21].

Also, for comparison we performed one of the PES calculations using Vienna ab initio Simulation Package (VASP) [24–27] with ultrasoft Vanderbilt type pseudopotentials [28] using the Perdew–Wang (PW-91) GGA correction [29]. The calculated PES figures (Figs. 1, VASP and 2(a), SIESTA) show a remarkable similarity when it comes to the shape of the PES. The difference between these two calculations is that the late barrier shown in both of the figures differs from 0.6 eV (VASP) to 0.5 eV (SIESTA) and the kinetic energy gain during the entrance as the molecule approaches the surface varies from 0.7 eV (VASP) to 0.9 eV (SIESTA). This discrepancy in the barrier heights
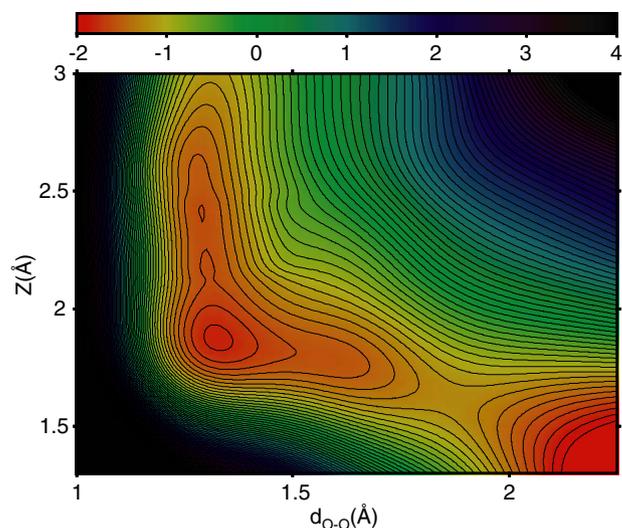

Fig. 1. Two-dimensional cut through the six-dimensional potential energy surface calculated for O_2 approaching the top site on clean Cu(100) calculated using VASP. The contour lines are drawn at 0.1 eV interval.

can, to some extent, be explained due to the different gradient corrections and basis functions used in the calculations. Despite the differences in the barriers, due to the fact that the kinetic energy gain is larger than the barrier in the late channel, similar interpretation emerges from the two figures: this trajectory is reactive and the molecule should dissociate through this trajectory spontaneously.

3. Results and discussion

In order to fully understand the behavior of a diatomic molecule approaching the surface, a first principles calculation for the six-dimensional potential energy surface should be performed. This is a formidable task even for the present-day supercomputers. For a frozen substrate, calculations for up to 1500 different configurations of the molecule have been performed in the case of O_2 on Al(111) [5]. A less demanding and therefore a more widely used approach is to calculate the two-dimensional cut of the PES, i.e. to plot the total energy of the molecule–substrate system as a function of the molecule bond length and its distance from the surface. Examples of such plots, called elbow plots due to their typical shape, relevant for the O_2 on Cu(100) case, are given in Fig. 2. It can be seen that depending on the way the surface has been modified, the adsorption characteristics indicated by the plots range from dissociative to strongly repulsive, as in the case of the oxygen precovered, reconstructed surface (Fig. 2(c)).

The problem with the static PES calculations is, however, that they do not take into account the dynamics of the surface and the dynamical molecule–surface interactions. The MBSS experiments are typically performed at room temperature, which means that the thermal movement of both the molecule and the surface cannot be neglected. Even more importantly, the static calculation does not take into account the translational energy of the
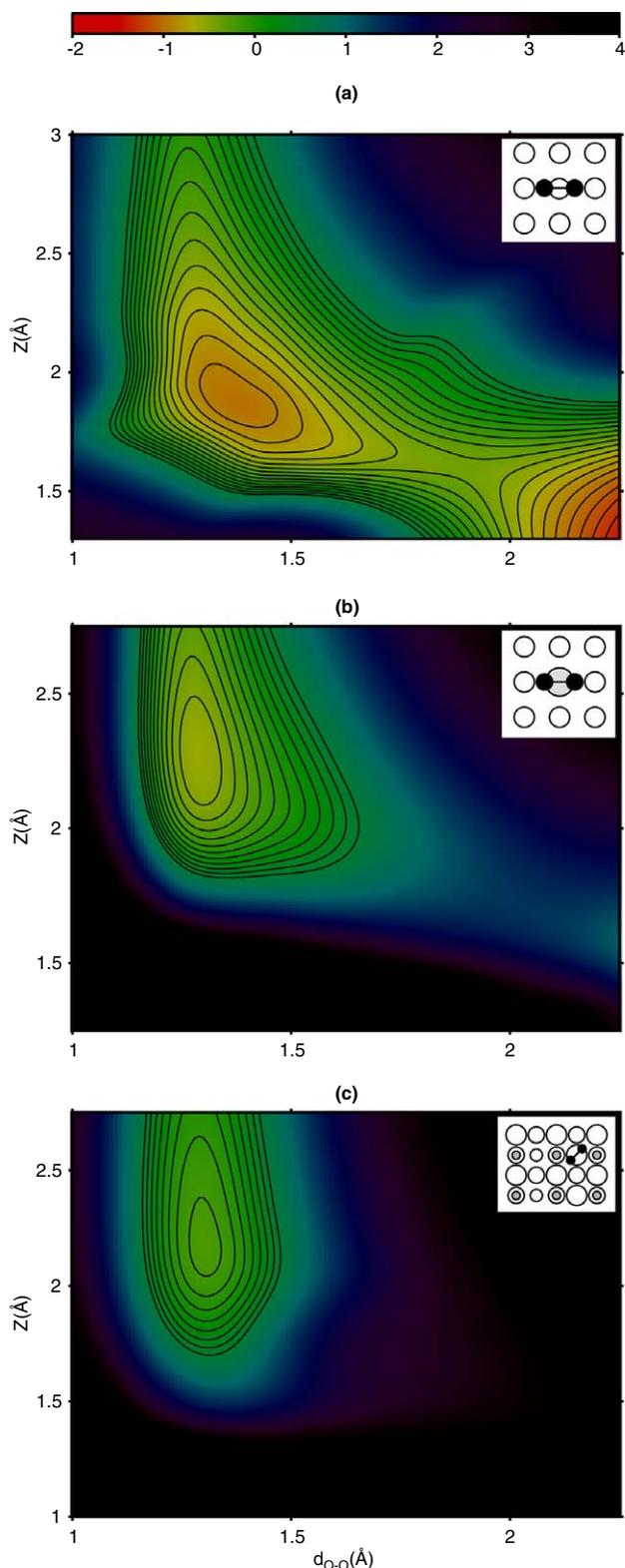
Fig. 2. Two-dimensional cuts through the six-dimensional potential energy surfaces calculated for O_2 approaching (a) the top site on clean Cu(100), (b) top site of an Ag adatom on Cu(100) and (c) oxygen precovered, $(2\sqrt{2} \times \sqrt{2})R45°$ reconstructed Cu(100). The contour lines are drawn at intervals of 0.1 eV. The configurations of the O_2 and the surface are given as insets. The white circles denote Cu atoms, the small grey circles the surface oxygen atoms, and the large grey circle the Ag adatom.

molecule which may introduce large deformations on the surface. Therefore, we have performed ab initio molecular dynamics calculations for O_2 on both clean, oxidized and doped Cu(100) in order to obtain further information on the adsorption dynamics. Fig. 2(a)–(c) represents the two-dimensional PES for O_2 approaching the top site on the clean, Ag doped, and O precovered Cu(100). Snapshots of the corresponding molecular dynamics trajectories at low and high translational energies are shown in Fig. 3(a)–(f). In Fig. 2(a) the barrier between the two minima seen in the figure is approximately 0.5 eV. However, the kinetic energy gain of the molecule approaching the first minimum is the order of 1 eV, which indicates direct dissociation. In Fig. 2(b) the barrier between the two minima is of the order of 2 eV whereas the kinetic energy gain is only 0.3 eV indicating a rather repulsive behavior. Finally, in Fig. 2(c) the kinetic energy gain is very small and the barrier is of the order of several eV showing extremely repulsive dissociation characteristics.

While considering the elbow plot shown in Fig. 2(a) in the light of the MBSS measurements, we observe that the adsorption characteristics on the clean surface is in contrast to the results observed in the experiments, because
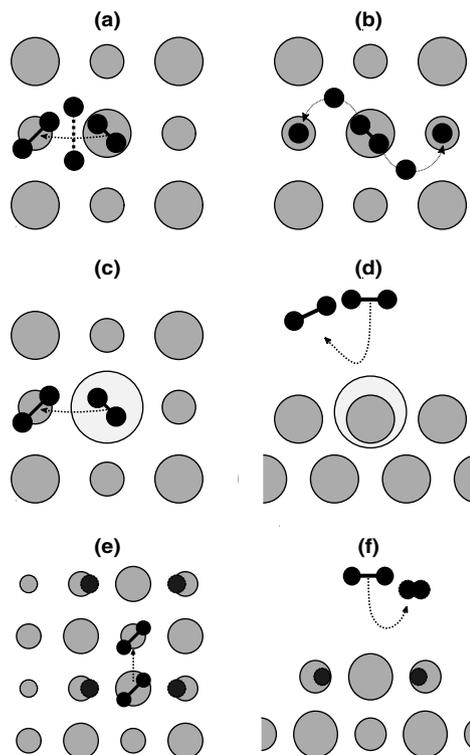

Fig. 3. Schematic presentations of the calculated molecular dynamics trajectories for O_2 on (a) clean Cu(100) with 25 meV, (b) clean Cu(100) with 600 meV, (c) Ag/Cu(100) with 50 meV, (d) Ag/Cu(100) with 600 meV, (e) $(2\sqrt{2} \times \sqrt{2})R45°$ O/Cu(100) with 50 meV, and (f) $(2\sqrt{2} \times \sqrt{2})R45°$ O/Cu(100) with 600 meV. In the figures the black circles denote oxygen atoms, the grey circles Cu atoms, and the large light grey the Ag adatom. The size of the Cu atoms indicates the layer: largest, first layer, etc. (a)–(c), and (e) top view; (d), and (f), side view.
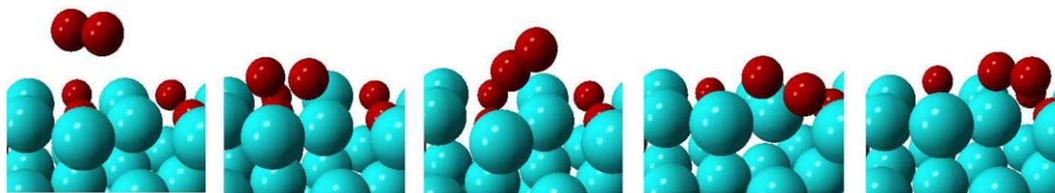
Fig. 4. Molecular dynamics trajectory of O_2 over the reconstructed Cu(100) starting from similar orientation as the PES calculation in Fig 2(c). The initial translational energy in this case was 50 meV. As can be observed from the final snapshot, the molecule ends up in a molecular adsorption state over the nearest hollow site.

the late barrier shown in Fig. 2 is smaller than the kinetic energy gain of the molecule. Despite this fact, the PES gives a qualitative understanding of the process, as we can explain the measured sticking coefficient at high translational energies by a direct dissociative trajectory on the surface, but according to the PES the dissociation should occur regardless of the initial translational energy of the molecules. Therefore, the sticking behavior at the low translational energies is in contrast to the PES. By performing molecular dynamics we could observe that the molecules in the low translational energy region will experience steering that rotates the molecule to another trajectory from which it gets steered towards the hollow site, which according to our earlier calculations is the most stable site for the molecular adsorption [4]. The low and high energy behavior has been shown in Fig. 3(a) and (b). Depending on the initial translational energy, the molecule will either dissociate or end up at a molecular state over the hollow site. This shows that the two-dimensional PES does not contain enough information for an accurate description of the adsorption dynamics of O_2 even in as simple case as the clean surface. When the molecule approaches the hollow site in lateral position the PES predicts again no barrier for the molecular sticking [4]. The molecular dynamics trajectory with 50 meV translational energy does not show any visible steering effect as the molecule approaches the surface. During the calculation the molecule ends up at a molecular adsorption state similar to the one observed after the steering from the top site to the hollow site in the previous runs.

If the Cu(100) surface is doped with Ag we observe that the PES shows even larger barrier in the dissociation pathway, see Fig. 2. If we consider the d-band density of states (DOS) of the Ag, we observe that this is consistent with the d-band theory [30], which suggests that the lowering of the d-band center causes the lowering of the reactivity of the surface by strengthening the molecular antibonding states of the incoming molecule. In this case, the d-band center at the site of the Ag adatom is about 2 eV lower in energy than that of the corresponding Cu. The molecular dynamics calculations, the results of which are shown in Fig. 3(c) and (d), give support for our interpretation of the PES. Applying a translational energy of 600 meV to the molecule makes it scatter back to the gas phase from the top site of the Ag adatom. With lower translational energies we find a strong steering from the top site towards

the closest hollow site. Again, this kind of behavior is very hard to extract from the PES calculations only.

When the oxygen coverage on Cu(100) rises above 0.5 ML, a $(2\sqrt{2} \times \sqrt{2})R45°$ reconstruction occurs. After the reconstruction the MBSS measurements show a completely different kind of dynamics for the O_2 dissociation. The sticking probability on this surface actually slightly decreases as the translational energy of the molecule increases. This gives a strong indication of a molecular precursor mediated process. In our calculations we find that the pre-adsorbed oxygen causes very large barriers in the PES plots. This indicates that direct dissociation can occur only at translational energies of well over 2 eV. Some of the recent experimental methods [31] are able to achieve such a high translational energy. These experiments have indeed shown that within this kinetic energy region the sticking of the O_2 molecule agrees with the first order kinetics, i.e. direct dissociation through collisional activation. The enhanced sticking at the lower translational energy regime, however, is not supported by the PES calculations. On the other hand, in the molecular dynamics calculations we find that at lower translational energy, the molecule steers towards certain sites over the missing row where it stays as a molecule. Due to the limitations of the timescale of the molecular dynamics runs we do not observe any dissociation on this surface. Fig. 4 represents a MD trajectory of O_2 calculated over the reconstructed Cu(100) surface. The calculated trajectory starts from the same initial position as the PES in Fig. 2(c) and the assigned initial translational energy is 50 meV. In this case, the final position of the molecule is at a rather weak molecular adsorption state over the nearest hollow site, for which the calculated adsorption energy is 0.67 eV [32]. In this surface there are also several other candidates [32] for the molecular precursor state, implying that the precursor mediated process on this surface is likely.

4. Conclusions

In this study we modelled the adsorption dynamics of O_2 on Cu(100) using ab initio molecular dynamics along with PES calculations. After the oxygen induced reconstruction, according to our calculations, the dissociation of O_2 is blocked by the on-surface oxygen, but the option of molecular precursors is supported by both the PES and the molecular dynamics calculations. We observed that

the behavior of the O_2 molecule on Cu(1 0 0) cannot directly be extracted from the elbow plots, but also molecular dynamics is needed for a true atomic level description of the adsorption dynamics. On the other hand, these kinds of calculations also fail to describe the experimental MBSS measurements because the molecular sticking over the hollow site is too strong. The sticking scenario that can be sketched according to these calculations indicates that the molecular states over the hollow sites dominate the sticking behavior at the lower translational energy and this should lead to the sticking probability of unity as the molecule can stick molecularly to the surface without any barrier. This description, however, does not take into account different kinds of rotational and vibrational excitations of the molecule, which have been shown to have a remarkable effect in the sticking behavior on other transition metals [33]. To study these excitations on a fully first principles basis remains a challenge for future work.

Acknowledgement

References

[1] P. Junell, M. Ahonen, M. Hirsimäki, M. Valden, Surf. Rev. Lett. 11 (2004) 457.
[2] M. Yata, H. Rouch, Appl. Phys. Lett. 75 (1999) 1021.
[3] J. Hall, O. Saksager, I. Chorkendorff, Chem. Phys. Lett. 216 (1993) 413.
[4] M. Alatalo, S. Jaatinen, P. Salo, K. Laasonen, Phys. Rev. B 70 (2004) 245417.
[5] J. Behler, B. Delley, S. Lorenz, K. Reuter, M. Scheffler, Phys. Rev. Lett. 94 (2005) 036104.
[6] K. Honkala, K. Laasonen, Phys. Rev. Lett. 84 (2000) 705.
[7] Y. Yourdshahyan, B. Razaznejad, B.I. Lundqvist, Phys. Rev. B 65 (2002) 75416.
[8] T. Sasaki, T. Ohno, Phys. Rev. B 60 (1999) 7824.
[9] A. Hellman, B. Razaznejad, B. Lundqvist, Phys. Rev. B 71 (2005) 205424.
[10] A. Puisto, H. Pitkänen, M. Alatalo, S. Jaatinen, P. Salo, A.S. Foster, T. Kangas, K. Laasonen, Catal. Today 100 (2005) 403.
[11] A. Puisto et al. unpublished.
[12] P. Ordejón, E. Artacho, J.M. Soler, Phys. Rev. B 53 (1996) R1044.
[13] J.M. Soler, E. Artacho, J.D. Gale, A. Garcia, J. Junquera, P. Ordejón, D. Sánchez-Portal, J. Phys.: Condens. Matter 14 (2002) 2745.
[14] D.R. Hamann, M. Schlüter, C. Chiang, Phys. Rev. Lett. 42 (1979) 1494.
[15] G.B. Bachelet, D.R. Hamann, M. Schlüter, Phys. Rev. B 26 (1982) 4199.
[16] N. Troullier, J.L. Martins, Phys. Rev. B 43 (1991) 1993.
[17] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[18] E. Artacho, D. Sánches-Portal, P. Ordejón, A. Garca, J.M. Soler, Phys. Status Sol. 215 (1999) 809.
[19] N.W. Ashcroft, D. Mermin, Solid State Physics, Thomson Publishing, New York, 1976.
[20] K.P. Huber, G. Hezberg, Molecular Structure and Molecular Spectra IV: Constants of Diatomic Molecules, Van Rostrand-Reinhold, New York, 1979.
[21] D.M. Lind, F.B. Dunning, G.K. Walters, Phys. Rev. B 35 (1987) 9037.
[22] S. Nosè, J. Chem. Phys. 81 (1984) 511.
[23] S. Nosè, Mol. Phys. 52 (1984) 255.
[24] G. Kresse, J. Hafner, J. Phys.: Condens. Matter 6 (1994) 8245.
[25] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[26] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
[27] G. Kresse, J. Joubert, Phys. Rev. B 59 (1999) 1758.
[28] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
[29] J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533.
[30] B. Hammer, J.K. Nørskov, Surf. Sci. 343 (1995) 211.
[31] M. Okada, K. Moritani, S. Goto, T. Kasai, A. Yoshigoe, Y. Teraoka, J. Chem. Phys. 119 (2003) 6994.
[32] A. Puisto, K. Laasonen, A.S. Foster, M. Alatalo, unpublished.
[33] A. Groß, A. Eichler, J. Hafner, M.J. Mehl, D.A. Papaconstantopoulos, Surf. Sci. Lett. 539 (2003) L542.