Unified picture of the molecular adsorption process: O_2/Pt(111)

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Tight-binding molecular dynamics simulations of the adsorption of O_2/Pt(111) have been performed based on an *ab initio* potential energy surface. We demonstrate that, contrary to common belief, in this system the whole adsorption probability as a function of the kinetic energy can be understood in terms of trapping into chemisorbed molecular precursor states. This provides a novel unified picture of the trapping process which is relevant for the general understanding of adsorption. Furthermore, by simple steric arguments we are able to explain why O_2 does not dissociate on cold Pt(111) surfaces even at kinetic energies that are much greater than the dissociation barrier.

Keywords: Computer simulations, density functional calculations, molecular dynamics, sticking, energy dissipation, oxygen, platinum, low index single crystal surface

I. INTRODUCTION

The interaction of molecular oxygen with Pt(111) represents one of the best studied systems in surface science [1–9]. Apart from the fundamental interest in this system these studies have also been motivated by the technological relevance of the adsorption of O_2 on Pt as a crucial microscopic reaction step occuring in the car-exhaust catalyst. On Pt(111), three molecular O_2 adsorption states have been identified. At surface temperatures below 30 K, a weakly bound physisorbed species exists [2, 3]. Up to 100 K, two different kinds of molecularly chemisorbed states are found [10, 11] which have been characterized as peroxo-like (O_2^{-2}) and superoxo-like (O_2^-), respectively. This assignment of the chemisorbed molecular states has been confirmed by total-energy calculations [12, 13] using density functional theory (DFT) within the generalized gradient approximation (GGA) [14].

The sticking probability of O_2/Pt(111) measured in molecular beam experiments first exhibits a strong decrease as a function of the kinetic energy [1], and then after passing a minimum at approximately 0.15 eV the sticking probability levels off at a value of about 0.3 [1, 8] (see Fig. 2 below). The initial decrease of the sticking probability has been reproduced in a low-dimensional treatment [4] using the hard-cube model [15]. According to this model, the sticking at low kinetic energies is due to a trapping into a shallow physisorption state with well depth of 0.12 eV [4]. The increase of the sticking probability at higher kinetic energies was attributed to a direct access of the chemisorbed molecular states [1, 4, 7, 8].

In order to study the microscopic details of the adsorption of O_2 on Pt(111), we have performed tight-binding molecular dynamics simulations based on an *ab initio* potential energy surface [12, 13]. Based on our simulations, we propose a novel interpretation of the molecular beam experiments. Our calculations suggest a unified picture of the molecular adsorption process of O_2/Pt(111): over the whole energy range the sticking probability is determined by the trapping into molecular chemisorption states. In addition, our simulations also provide a natural explanation in terms of steric arguments for the observation [4, 7, 8] that oxygen molecules do not dissociate at cold Pt surfaces, even at kinetic energies that are much greater than the dissociation barrier. These findings are also relevant for the interpretation of adsorption data in similar systems [16].

II. THEORETICAL METHODS

For the theoretical description of the adsorption process of O_2 on Pt(111), a realistic potential energy surface (PES) is needed that reliably describes both the molecular as well as the dissociative adsorption channels. In addition, the energy dissipation to the platinum substrate has to be properly taken into account in order to simulate trapping processes. This represents the great challenge in this system compared to, e.g., the dynamical description of hydrogen dissociation from first principles where the substrate degrees of freedom can usually safely be neglected [17–21]. In direct *ab initio* molecular dynamics simulations, a proper description of the interaction potential is taken into account, but *ab initio* electronic structure calculations are still computationally so demanding that not enough trajectories can be calculated in order to obtain sufficient statistics [20, 22]. Using empirical classical potentials, almost arbitrarily many trajectories can be computed, but these potentials are in general not flexible and accurate enough to describe the bond-making and breaking process on moving substrates.

As a compromise, we have performed tight-binding molecular dynamics (TBMD) simulations [23] of the adsorption of O_2/Pt(111) using the NRL tight binding (TB) method [24–26] with all TB parameters derived from ab initio electronic structure calculations. The Pt-Pt interactions were fitted to bulk calculations which have been shown to give a good representation of the pure Pt surface as well [24] . The Pt-O and the O-O TB parameters

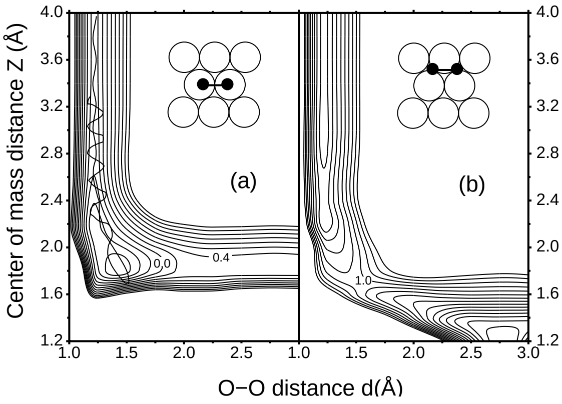

FIG. 1: Potential energy surface of the dissociation of O_2/Pt(111) determined by the *ab initio* derived tight-binding Hamiltonian. The coordinates in the figure are the O_2 center-of-mass distance from the surface Z and the O-O interatomic distance d. The configurations of the remaining O_2 degrees of freedom are illustrated in the insets. The contour spacing is 0.2 eV per O_2 molecule. In (a) a trajectory of an O_2 molecule with an initial kinetic energy of 0.6 eV scattered at Pt(111) is also plotted.

have been adjusted to reproduce the DFT calculations of the O_2/Pt(111) potential energy surface [12, 13] using the so-called PW91-GGA functional [14]. The evaluation of the tight-binding Hamiltonian still requires the diagonalization of a matrix. Nevertheless, the tight-binding calculations are about three orders of magnitude faster than the DFT calculations making the evaluation of hundreds of trajectories possible. Furthermore, since tight-binding takes the quantum nature of bonding into account, it allows a reliable fit of the *ab initio* data with a root mean square error of below 0.1 eV [25] which is in the range of the error of the GGA-DFT calculations.

Within the TB approach, the surface has been modelled in the supercell approach by a slab of five layer thickness. For the fit the same $c(4 \times 2)$ surface unit cell as used in the DFT calculations has been employed. The PES of O_2/Pt(111) calculated from the tight-binding Hamiltonian is illustrated in Fig. 1. Two two-dimensional cuts, so-called elbow plots, are plotted which show the PES as a function of the distance Z of the O_2 center of mass from the surface and the O-O distance d while the lateral center of mass degrees of freedom and the molecular orientation are kept fixed. These plots might be compared with the corresponding original DFT contour graphs shown in Ref. [13].

Panel (a) corresponds to the superoxo molecular precursor state located above the bridge site which can be accessed along a non-activated path from the gas phase. The same is true for the peroxo state above the three-fold hollow sites which is energetically almost degenerate with the superoxo state [12]. Figure 1(b) demonstrates the large corrugation of the O_2/Pt(111) PES. Although the molecule is only shifted by about 1 Å in lateral direction compared to Fig. 1(a), the nature of the interaction is changed from attraction towards the molecular precursor to strong repulsion with a barrier towards dissociation of almost 1 eV. Furthermore, the PES is also highly anisotropic. For molecules approaching the surface in an upright fashion, the PES is repulsive, i.e., O_2 can only adsorb and dissociate on Pt(111) with its axis being close to parallel to the surface. In fact, the majority of adsorption channels are hindered by barriers; direct non-activated access of the molecular precursor states is possible for only a small fraction of initial conditions. As Fig. 1 shows, there is no indication of a physisorption well. This is caused by the inability of DFT calculations using present functionals to reproduce the long-range van der Waals attraction. We have made no attempt to deliberately add a physisorbed molecular state.

Finally, it should be mentioned that periodic DFT calculations using state-of-the-art GGA functionals are still problematic if the studied system contains oxygen. The O_2 binding energy is significantly overestimated [27] which limits the reliability of any DFT calculations addressing O_2 dissociative adsorption. For the adsorption of CO, NO and O_2, the so-called RPBE functional [27] is usually more accurate than the PW91 functional which is the basis of the PES [12] used in this study. However, for the molecular adsorption states of O_2/Pt(111) the PW91 functional seems to be more appropriate than the RPBE functional which yields an unrealistically low binding energy of the molecular chemisorption states of 0.1 eV [28, 29]. On the other hand, the PW91 functional still overestimates the molecular chemisorption energies by 0.2–0.3 eV [12, 13] compared to the experiment [10, 30]. The tight-binding parametrization represents a reliable interpolation of the PW91 PES. However, in the DFT calculations the PES has only been calculated for fixed positions of the Pt substrate atom. Note that it is the coupling of the O_2 molecule to the Pt lattice vibrations which determines the energy transfer to the substrate. The strength of this coupling in our simulations is thus only modeled on a tight-binding level, not on an *ab initio* level.

III. RESULTS AND DISCUSSION

The sticking probabilities have been determined by averaging over 150 trajectories for each energy so that there is a statistical error of $1/\sqrt{150} \approx 0.07$ associated with the calculated probabilities. A trajectory was considered to correspond to a trapping event when the molecule stayed for more than 2 ps at the surface or if it had transferred more than its initial energy to the surface at $T_\mathrm{s} = 0$ K. The bottom layer of the Pt slab was kept frozen while all other Pt atoms were treated dynamically in order to allow energy transfer from the impinging molecule to the substrate. The trajectories with a time step of 1 fs have been started with random initial conditions, however, for each kinetic energy we have used the same sequence of

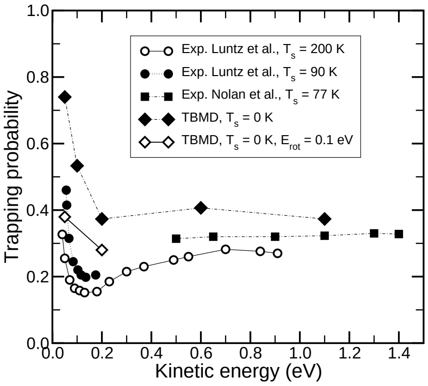

FIG. 2: Trapping probability of O_2/Pt(111) as a function of the kinetic energy for normal incidence. Results of molecular beam experiments for surface temperatures of 90 K and 200 K (Luntz *et al.* [1]) and 77 K (Nolan *et al.* [8]) are compared to tight-binding molecular dynamics simulations for the surface initially at rest ($T_\mathrm{s} = 0$ K).

random initial conditions.

No zero-point energies were taken into account in the initial conditions. This has been shown to be appropriate for the classical simulation of non-activated adsorption processes when the decrease in the molecular vibrational zero-point energy is compensated for by the building up of zero-point energies in the other molecular degrees of freedom [31, 32].

For lower kinetic energies, a $c(4 \times 2)$ surface unit cell has been used while for kinetic energies of 0.6 eV and 1.1 eV a $c(4 \times 4)$ surface unit cell has been employed to minimize the interaction between the cells. The simulations were performed within the microcanonical ensemble. We also coupled the bottom layer of the slab to a heat bath via the generalized Langevin equation which, however, did not change the outcome of molecular trajectories. The spin state of the oxygen molecule has not been explicitly considered in the TB simulations. This corresponds to the assumption that the electron spins follow the motion of the nuclei adiabatically and remain in their ground state.

The calculated sticking probabilities of O_2/Pt(111) as a function of the kinetic energy for normal incidence are compared to molecular beam experiments in Fig. 2. In the simulations, the surface was initially at rest ($T_\mathrm{s} =$ 0 K). The decrease of the sticking probability at lower kinetic energies and the subsequent leveling off are well-reproduced by the TBMD calculations in spite of the fact that no molecular physisorption well is present in the calculations. Still, the calculated sticking probabilities are systematically larger than the measured ones. We attribute this mainly to the fact that the PW91-GGA functional [14] used in the DFT calculations overestimates the binding energies of the molecular adsorption state by 0.2–0.3 eV [12, 13, 28] compared to the experiment [10, 30] so that the PES is too attractive. In addition, a proper consideration of the population of internal O_2 degrees of freedom in the simulations leads to a reduction of the calculated sticking probabilities, as will be discussed below.

In fact, the sticking probability for the whole energy range can be understood in terms of trapping into the chemisorption states. At kinetic energies below 0.2 eV we have observed that all molecules reaching the molecular precursor well get trapped. Thus it is *not* the energy transfer to the substrate *per se* that determines the sticking probability at low kinetic energies but rather the probability to enter the attractive adsorption channels. Although the majority of pathways towards adsorption are blocked by barriers, at low kinetic energies most of the incoming molecules with unfavorable initial conditions are redirected towards attractive adsorption paths. This dynamical steering effect [18, 33] leads to the high sticking probability. The steering mechanism becomes rapidly suppressed at higher kinetic energies which causes the strong decrease of the sticking probability.

The steering mechanism is not only suppressed at higher kinetic energy but also by additional rotational motion [34]. Indeed, we obtain a significant rotational hindering [35], i.e., a strong reduction in the sticking probability, at $E_i = 0.05$ eV for molecules initially rotating with a rotational energy of $E_\mathrm{rot} = 0.1$ eV, as Fig. 2 shows. This confirms that it is the steering mechanism that dominates the trapping dynamics at low energies. Furthermore, it shows that a physisorption state is not needed in order to reproduce the strong initial decrease of the trapping probability at low energies.

A rotational energy of $E_\mathrm{rot} = 0.1$ eV also causes rotational hindering at $E_i = 0.2$ eV. The assumption of such an initial rotational population of the O_2 molecules in the molecular beam experiments at this kinetic energy is reasonable [36]; thus the discrepancy between theory and experiment can partially be accounted for.

Experimentally, it is well established that at surface temperatures below 45 K the O_2 physisorption state on Pt(111) can be populated [2, 3]. However, the normal incident energies used to populate the physisorbed state were below 25 meV while the lowest kinetic energy considered in this calculations is 50 meV. Our results thus suggest that not only very low surface temperatures but also incident kinetic energies below $\sim$25 meV are needed in order to populate the physisorption state.

At higher energies, the simulations yield a slight increase in the sticking probabilities, which is, however, not statistically significant with respect to the uncertainty of the results. The lack of a sizable increase in the calculations is most probably also caused by the overestimation of the molecular chemisorption energies. Still, the leveling off of the measured sticking probability at higher energy is reproduced by the calculations. To the best of our knowledge, such a behavior has not been obtained before in molecular dynamics simulation which usually yield a monotonously decreasing sticking probability for molecular trapping processes. The underlying mechanism which is intimately related to the corrugation and anisotropy of the PES is illustrated in Fig. 3 where we have plotted the

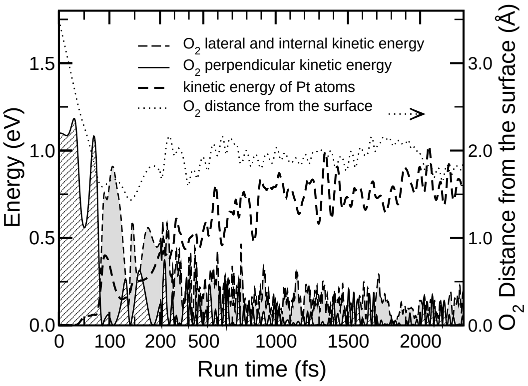

FIG. 3: Distance from the surface and energy redistribution as a function of time for an O_2 molecule impinging on the Pt(111) surface with an initial kinetic energy of 1.1 eV. The lateral and internal kinetic energy and the perpendicular kinetic energy curves are indicated by the grey-shaded and hatched areas, respectively. Note the different scale of the time axis for the first 200 fs.

energy redistribution along a typical trajectory of an O_2 molecule impinging on the surface with a kinetic energy of 1.1 eV.

At such a high energy, a large fraction of the impinging molecules enters the molecular adsorption wells via pathways hindered by barriers. Along the trajectory depicted in Fig. 3, e.g., a barrier of about 0.5 eV is crossed at $t = 50$ fs. Still, there is only a small probability that in the first collision the high energy particles will transfer enough energy to the surface to remain trapped. In the case of Fig. 3, only about 0.4 eV are taken up by the substrate phonons. However, it is important to note that the impinging molecules also transfer energy into internal molecular degrees of freedom such as rotation and vibration and into lateral motion along the surface. This energy is then not available for a direct escape from the adsorption well. If enough of the initial perpendicular kinetic energy is transferred in the first collision into these other degrees of freedom, the molecule becomes dynamically trapped for a while [31, 37]. While being trapped, the molecule hits the surface several times and transfers successively more and more energy to the substrate until it equilibrates. As Fig. 3 shows, at about 1 ps after the first collision the O_2 molecule has become accommodated at the Pt(111) surface for this particular trajectory.

It is important to note that the experiments found a strong dependence of the O_2 sticking probability on the surface temperature at low kinetic energies [1, 38]. For example, at $E_i = 0.085$ eV the sticking probability is reduced from 0.23 to 0.09 if the surface temperature is increased from $T_s = 90$ K to $T_s = 300$ K [1]. At a kinetic energy of $E_i = 0.9$ eV there is a reduction from 0.29 to 0.26 in the same temperature range. The strong suppression of the sticking probability with increasing surface temperatures at low kinetic energies has usually been regarded as a signature of a precursor mechanism. The larger temperature-induced reduction at low kinetic energies does in fact lead to a stronger increase of the sticking probability with kinetic energies at $T_s = 350$ K [1] (not shown in Fig. 2).

We have also addressed surface temperature effects by determining the trapping probability for $E_i = 0.1$ eV and $E_i = 1.1$ eV at a Pt(111) slab thermalized at a temperature of $T_\mathrm{s} = 300$ K. At $E_i = 0.1$ eV, we found a reduction of the trapping probability by 40% compared to the result at $T_\mathrm{s} = 0$ K. This reduction is due to the fact that a heated substrate can also transfer energy to the impinging molecule. At $E_i = 1.1$ eV there is only a slight reduction by 2% since at such a high kinetic energy it hardly matters that the substrate atoms move with a mean kinetic energy of $\frac{3}{2}k_\mathrm{B}T \approx 0.04$ eV. With respect to the uncertainties in both theory and experiment, the agreement is satisfactory.

Molecular beam experiments have produced the surprising result that at surface temperatures below 100 K O_2 molecules impinging on Pt(111) do not dissociate, even at kinetic energies up to 1.3 eV which are much greater than the dissociation barrier [4, 7, 8]. We have found that this phenomenon can be explained by steric arguments. In terms of the elbow potentials plotted in Fig. 1, dissociation corresponds to an event in which the molecules enter the exit channel towards the lower right corner of the figures. However, as Fig. 1(a) demonstrates, there is a rather narrow curve connecting the entrance and exit channels through the molecular adsorption states. In Fig. 1, we have included a trajectory directly aimed at the molecular precursor state with an initial kinetic energy that is much higher than the dissociation barrier. Still the molecule does not dissociate. It becomes accelerated by the attractive potential so that it is much too fast “to make it around the corner”.

Direct dissociation is thus sterically hindered at the Pt(111) surface. In fact, we have not observed any single dissociation event in our molecular dynamics simulations, irrespective of the initial energy. We have also checked the influence of initial vibrational zero-point motion on the dissociation probability by running trajectories with an initial vibrational energy corresponding to the zero-point energy of O_2. Still, we did not obtain any dissociation event. Hence, dissociation of O_2 on Pt(111) is always a two-step process. First the molecule becomes trapped molecularly, and only in a second step will it dissociate at sufficiently high surface temperatures due to thermal fluctuations which will make the O_2 molecules enter the dissociation channel.

IV. CONCLUSIONS

In conclusion, based on *ab initio* derived tight-binding molecular dynamics simulations we propose a novel interpretation of the sticking probability observed in the system O_2/Pt(111): Over the whole considered energy range it can be understood by the trapping into non-activated molecular chemisorption states. The theoretical results are not all in quantitative agreement with the available experimental data. However, both experimental and theoretical results are associated with uncertainties. All qualitative aspects of the sticking probability in the system O_2/Pt(111) addressed by our study are reproduced by the calculations, giving credibility to our novel interpretation.

Furthermore, due to the topology of the underlying potential energy surface, oxygen molecules do not directly dissociate at Pt(111) but only after thermal accommodation in the molecular precursor states. Our results indicate that a derivation of the energetics of adsorption from simple one-dimensional models might be seriously in error; instead, the multidimensionality of the relevant potential energy surface has to be properly taken into account.

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