Molecular trapping of oxygen at metal surfaces

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The dynamics of the oxygen adsorption on Pt(111) have been studied by tight-binding molecular dynamics simulations based on an *ab initio* potential energy surface. The calculations lead to a novel unified picture of the molecular adsorption process of O_2/Pt(111). Oxygen adsorption always proceeds through molecular chemisorption states. The trapping dynamics are dominated by the steering effect at low kinetic energies whereas a dynamical precursor is involved at higher kinetic energies. Direct dissociative adsorption turns out to be very unlikely even for kinetic energies much larger than the dissociation barrier because of the particular topology of the potential energy surface. These results are also relevant for related adsorption systems.

1 Introduction

The interaction of molecules with surfaces is of tremendous technological importance. All materials under atmospheric conditions are exposed to a permanent flux of impinging molecules, either from the gas phase or the liquid phase. Reactions of these molecules with the surface atoms can lead to corrosion and rust. However, not only harmful processes but also very advantageous reactions can occur on surfaces. This is used in heterogeneous catalysis where the presence of a catalyst leads to strongly enhanced reaction rates. In fact, most reactions employed in the chemical industry utilize catalysts[1].

Catalysts are not only used to increase the output of a chemical reaction but also to convert hazardous waste into less harmful products. One particular example that everybody is aware of is the car exhaust catalyst in which the exhaust gas is purified from poisonous molecules such as CO and NO by catalytic oxidation processes[2]. One of the fundamental microscopic reaction steps occuring in the car exhaust catalyst is the dissociative adsorption of molecular oxygen, O_2, on platinum. The atomic oxygen reacts for example with adsorbed CO molecules to form CO_2 which then desorbs. Because of its importance, the interaction of molecular oxygen with Pt(111) represents one of the best studied systems in surface science, both experimentally [3–9] as well as theoretically[10–12].

In recent years, the theoretical description of surface structures and processes on surfaces has made tremendous progress[13]. This is partially caused by the ever-improving computer power, but the development of efficient and accurate first-principles methods for total energy calculations has been at least equally important. In particular, electronic structure calculations based on density-functional theory (DFT)[14,15] have contributed significantly to this success. *First-principles* or, equivalently, *ab initio* means that no empirical parameters enter the computations. The only input is given by the positions and the chemical nature of the atoms. Although there are some exceptions[16,17], DFT calculations are rather accurate so that theory and experiment contribute on an equal footing and often in very fruitful collaborations to the progress and microscopic understanding in surface science. Dynamical simulations offer the additional advantage that they allow a microscopic analysis of the relevant dynamics at any step along the reaction paths while in experiments usually only the initial and final states can be determined.

In this contribution I will present the results of a microscopic simulation of the molecular trapping of oxygen on Pt(111) based on first-principles input[12]. It turns out that even a seemingly simple process such as the molecular trapping had not been fully understood before[3,5,9]. The dynamical simulations provide a novel and unified picture of the trapping process. The microscopic analysis of the interaction dynamics leads to the identification of fundamental dynamical concepts. The results of the study of the trapping of O_2/Pt(111) are therefore not only relevant for this particular system but also for the interpretation of adsorption data in similar systems[18].

This article is structured as follows. In the next section the theoretical concepts and algorithms underlying the calculations are addressed. Then the results of the dynamical simulations are presented and discussed. The article ends with some concluding remarks.

2   Theoretical methods

The basic theoretical quantity describing the interaction of atoms or molecules with surfaces is the potential energy surface (PES). Within the Born-Oppenheimer approximation one assumes that the light electrons follow the motion of the much heavier nuclei instantaneously. Under this assumption, the PES is given by the total electronic energy as a function of the coordinates of all atoms of the system. Thus, it corresponds to a multi-dimensional hyperplane. This makes it impossible to present it graphically as a whole. Usually two-dimensional cuts through the PES are plotted in order to illustrate the most relevant reaction pathways. Figure 1 shows two examples, so-called elbow plots of the PES as a function of the molecular center of mass distance from the surface and the intramolecular distance while all other degrees of freedom have been kept fixed. The PES can be obtained by total-energy electronic structure calculations. In theoretical surface science, the most commonly used electronic structure methods are based on density functional theory due to its computational efficiency and reliability[19,20].

Oxygen can adsorb both molecularly, i.e. as an intact molecule, as well as dissociatively on Pt(111)[4,6,8,9]. Since the molecular trapping process requires the transfer of the molecular energy to the surface mainly through substrate vibrations or *phonons*, the molecular dynamics simulations have to include a sufficient number of surface atoms. Most modern DFT algorithm allow the evaluation of the potential gradients which is necessary for the integration of the equations of motion. Hence, direct *ab initio* molecular dynamics simulations can be performed. However, in spite of the progress in the computational efficiency *ab initio* electronic structure calculations are still computationally so demanding that not enough trajectories can be calculated in order to obtain sufficient statistics for the determination of reaction probabilities[21,22].

In order to be able to run enough trajectories but still keep the accuracy and reliability of *ab initio* caculations, the results of DFT calculations of the O_2/Pt(111) potential energy surface[10,11] employing the so-called PW91-GGA functional[23] have been used to adjust a tight-binding (TB) Hamiltonian[24–26]. Tight-binding calculations are about three orders of magnitude faster than the DFT calculations making the evaluation of hundreds of trajectories possible. The tight-binding method is based on an implicit expansion of the eigenstates of the effective one-particle Hamiltonian in an atomic-like basis set. The atomic-like basis functions are usually not considered explicitly but the exact many-body Hamiltonian is replaced by parametrized Hamiltonian matrix elements[27].
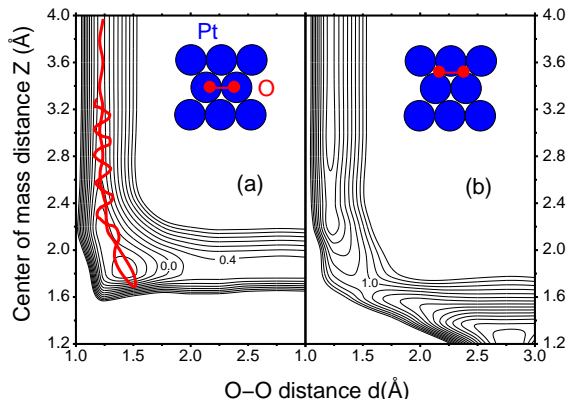
Figure 1. Potential energy surface of the dissociation of O_2/Pt(111) determined by the *ab initio* derived tight-binding Hamiltonian. The coordinates in the figure are the O_2 center-of-mass distance from the surface Z and the O-O interatomic distance d. The configurations of the remaining O_2 degrees 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.

Since tight-binding takes the quantum nature of bonding into account, it allows a reliable fit of the *ab initio* O_2/Pt(111) PES with a root mean square error of below 0.1 eV (which is in the range of the error of the GGA-DFT calculations) using relatively few fitting points[25]. However, the DFT calculations have only be performed for fixed positions of the Pt substrate atom. Thus the coupling of the O_2 molecule to the Pt lattice vibration which determines the energy transfer to the substrate is only modeled on a tight-binding level, not on an *ab initio* level.

All dynamical TB simulations have been performed on the Cray T3E of the John-von-Neumann center for scientific computing (NIC) using the TBMD code[28]. The evaluation of the tight-binding Hamiltonian still requires the diagonalization of a matrix that scales as N^3 where N corresponds to the number of electronic states considered in the calculations. N is typically of the order 200-400 which is not too large. Still the diagonalization represents the main computational challenge since it has to be done for any molecular dynamics step. The parallel version of the TBMD code has been written using a message-passing programming model relying on the MPI library to deal with communications[29].

3   Results and discussion

On Pt(111), three molecular O_2 adsorption states have been identified[30,4], one weakly bound physisorption state and two more strongly bound chemisorption states. The minimum shown in Fig. 1a corresponds to the so-called superoxo molecular precursor state above the bridge site with a binding energy of 0.72 eV[10,11] (for the molecular configuration, see the insets of Fig. 1). The other chemisorption state, a peroxo state, is located above the threefold hollow sites with its axis slightly tilted from the parallel orientation; it is energetically almost degenerate with the superoxo state[10]. The access of the molecular chemisorption states is non-activated, i.e. it is not hindered by any energetic barrier.

3

It is important to note that the PES of O_2/Pt(111) is strongly corrugated and anisotropic, i.e., the interaction depends sensitively on the lateral position and orientation of the O_2 molecule. This is demonstrated in Fig. 1b which shows the elbow plot of the PES for the molecule situated between the three-fold hollow and the on-top site. Although the molecule is only shifted by about 1 Å from the position of Fig. 1a, there is no longer any chemisorption well present but rather a large barrier of about 1 eV towards dissociative adsorption which becomes even larger for the molecule directly at the on-top site. In fact, the majority of adsorption pathways are hindered by barriers; direct non-activated access to the adsorption states is possible for only a small fraction of initial conditions. The weakly bound physisorption state does not show up in the DFT calculations since present DFT functionals are not able to reproduce the long-range van der Waals attraction[13]. For the present study this does not matter since physisorption is unimportant in the considered energy range.

Sticking in molecular beam experiments corresponds to a process in which molecules hit the surface at arbitrary positions. To simulate this process, trajectories of O_2 molecules impinging on the Pt(111) surface are started with initial conditions picked at random. The trajectories are computed by solving the classical equations of motion numerically within the microcanonical ensemble using the Verlet algorithm[31] with a time step of 1 fs. The sticking probability is then obtained by averaging over the outcomes of the trajectories. In total, 150 trajectories have been determined for each kinetic energy leading to a statistical error of $1/\sqrt{150} \approx 0.07$ associated with the calculated probabilities. Using periodic boundary conditions, the Pt(111) substrate was modeled by a slab of five layers with $c(4 \times 2)$ and $c(4 \times 4)$ surface unit cells depending on the kinetic energy. The bottom layer of the Pt slab was kept fixed while all other Pt atoms were treated dynamically in order to allow energy transfer from the impinging molecule to the substrate. A trajectory was considered to correspond to a trapping event when the molecule remained for more than 2 ps at the surface or if it had transfered more than its initial energy to the surface at $T_s = 0$ K.

According to molecular beam experiments O_2 molecules impinging on Pt(111) at surface temperatures below 100 K do not dissociate, even at kinetic energies up to 1.3 eV[5,32,9]. This is very surprising since this energy is much larger than the dissociation barrier. In our simulations we did not obtain any direct dissociation event either. There is a simple explanation for this result in terms of the topology of the elbow plots (Fig. 1). Dissociation corresponds to an event in which the molecules enter the exit channel towards the lower right corner of the figures. To enter this channel directly from the gas phase through the molecular adsorption state requires a sharp turn of the trajectories. Although this is not impossible, it is very unlikely. In Fig. 1a, a trajectory of an O_2 molecule directly aimed at the molecular precursor state is included. Its kinetic energy of 0.6 eV is much higher than the dissociation barrier (~ 0.2 eV[11]); still it does not dissociate. It becomes accelerated by the attractive potential, hits the repulsive wall of the potential and is scattered back.

We thus conclude that because of this steric hindrance, dissociation of O_2 on Pt(111) is a two-step process. First the molecule becomes trapped and accommodated in the molecular chemisorption state, and only subsequently it dissociates at sufficiently high surface temperatures due to thermal fluctuations which will make the O_2 molecules enter the dissociation channel.

The calculated sticking probabilities of O_2/Pt(111) as a function of the kinetic energy for normal incidence are plotted in Fig. 2. In the simulations, the surface was initially at rest

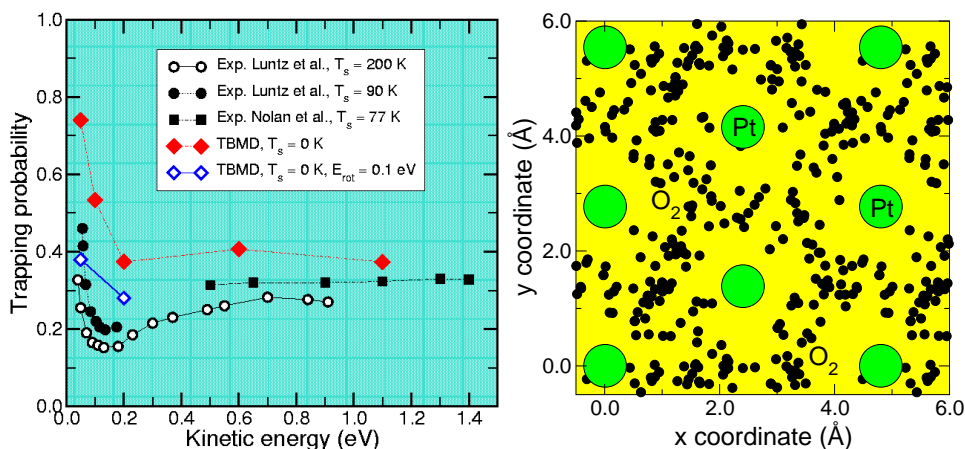Figure 2. Molecular trapping of O_2 on Pt(111). Left panel: trapping probability of O_2/Pt(111) as a function of the kinetic energy for normal incidence. Results of molecular beam experiments for surface temperatures of 90 K and 200 K (Luntz *et al.*[3]) and 77 K (Nolan *et al.*[9]) are compared to tight-binding molecular dynamics simulations for the surface initially at rest (T_s = 0 K); right panel: lateral positions of the O_2 center of mass upon adsorption for kinetic energies $\leq$ 0.2 eV.

(T_s = 0 K). The results of molecular beam experiments are also included in the figure. The agreement between theory and experiment is satisfactory although the theoretical results are systematically larger than the measured ones. This can be attributed to the fact that the PW91-GGA functional[23] used in the DFT calculations overestimates the binding energies of the molecular adsorption state by 0.2–0.3 eV[10,11,33] compared to the experiment[34,35]. Hence the PES is too attractive which causes the larger sticking probabilities.

Still, the qualitative trend of the experiment is well-reproduced. In Fig. 2, also results of molecular dynamics simulations for initially rotating molecules are included. This additional rotational motion leads to a suppression of the sticking probability compared to non-rotating molecules. Since in the molecular beam experiment the incoming molecules are rotating[36], taking into account the rotational motion of the incoming molecules reduces the discrepancy between theory and experiment.

In the right panel of Fig. 2, we have recorded the lateral positions of the O_2 center of mass upon adsorption for kinetic energies $\leq$ 0.2 eV. Note that the O_2 molecules are still not fully equilibrated, therefore the molecules are not exactly at their local equilibrium positions. It is obvious that the top position is unfavorable for adsorption since there is a depletion zone around the Pt atoms. The molecular chemisorption states at the bridge, the fcc hollow and the hcp hollow sites are approximately equally populated. This means that there is no preferential adsorption at neither the peroxo nor the superoxo state.

As far as the qualititative trend of the trapping probability as a function of the initial kinetic energy is concerned, there is first a strong decrease of the trapping probability before the sticking probability slightly rises again and levels off at higher energies. Note that in molecular trapping the sticking probability usually decreases as a function of the kinetic energy[13]. Trapping requires the transfer of the kinetic energy of the impinging molecule to the substrate; otherwise the molecule would be scattered back. This transfer
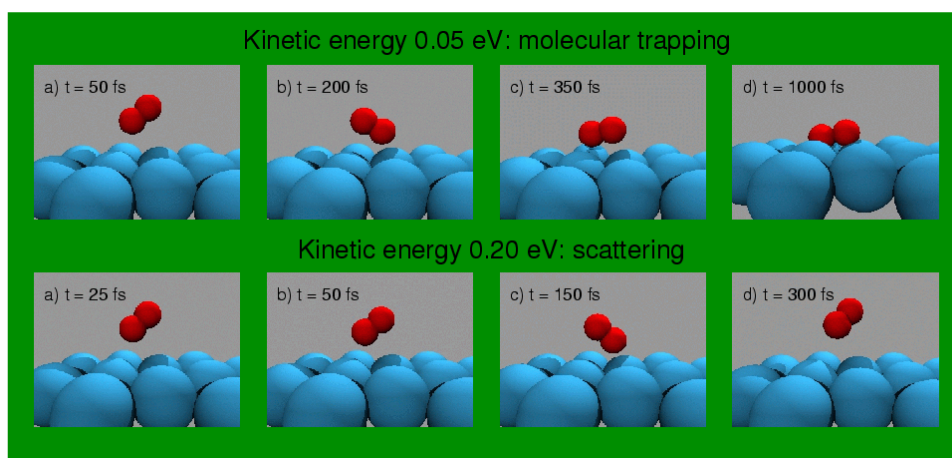
Figure 3. Snapshots of TBMD trajectories of an O_2 molecule impinging on a Pt(111) surface with the same initial conditions except for the kinetic energy of 0.05 eV and 0.20 eV, respectively.

becomes less efficient at higher energies thus leading to decreasing sticking probabilities.

Because of the non-monotonous behavior of the trapping probability as a function of the kinetic energy, two different mechanisms had been invoked in the low-energy and high-energy in order to explain the observations. At low kinetic energies, the strong decrease had been associated with the trapping into a shallow physisorption state with a binding energy of 0.12 eV[5]. The increase of the sticking probability at higher kinetic energies was attributed to a direct activated access of the chemisorbed molecular states[3,5,32,9]. The TBMD simulations, on the other hand, clearly show that the trapping over the whole energy range considered occurs into the chemisorption state. The question still remains why this process exhibits such a different energy dependence at low and high kinetic energies. Since the molecular dynamics simulations allow the analysis of the entire adsorption dynamics, they make an identification of the underlying mechanisms possible. At low kinetic energy, the so-called steering effect[37] dominates the trapping process while at higher kinetic energies, dynamical precursors play a dominant role. Both mechanisms that are intimately related to the multidimensionality of the PES will be illustrated in the following.

At low kinetic energies, incoming molecules can be very efficiently redirected by the forces acting on the molecule. Even if the molecules approach the surface in an unfavorable configuration for adsorption, most of them are *steered* to a favorable configuration for adsorption. This steering effect is illustrated in the upper panel of Fig. 3 where snapshots of the atomic configuration along typical trajectories are plotted. The incoming O_2 molecule with a kinetic energy of 0.05 eV is oriented in a canted configuration in which it cannot bind to the surface. However, the molecule is slow enough that it can be reoriented. In fact, it even overshoots a little bit (200 fs) but after 350 fs its molecular axis is approximately parallel to the surface. After 1000 fs = 1 ps, the molecule is located in the chemisorption well above the three-fold hollow site with its axis slightly tilted away from the parallel orientation. According to the simulations, at kinetic energies below 0.2 eV all molecules reaching the molecular precursor get trapped. This means that it is in fact *not* the energy
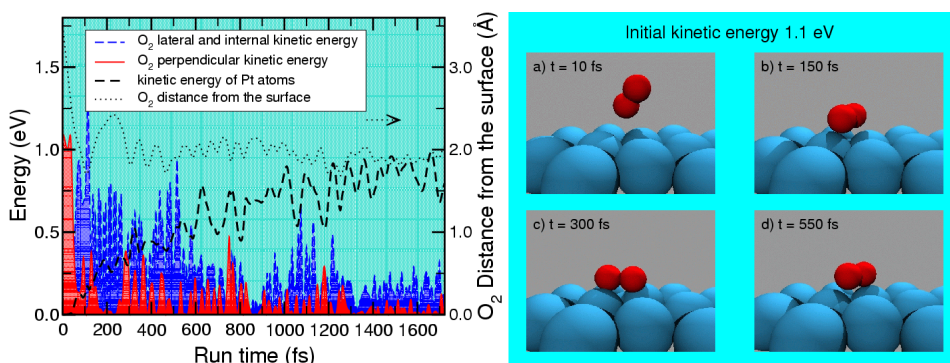
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Figure 4. Illustration of a O_2 molecule impinging on the Pt(111) surface with an intial kinetic energy of 1.1 eV. Left panel: distance from the surface and energy redistribution as a function of time. The lateral and internal kinetic energy and the perpendicular kinetic energy curves are indicated by the blue and red-shaded areas, respectively; right panel: four snapshots of the molecular trajectory.

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, the steering effect leads to the high trapping probability at the low kinetic energies.

Steering becomes rapidly suppressed at higher kinetic energies. In the lower panel, snapshots of a molecule are plotted with the same initial conditions as in the upper panel except for higher kinetic energy of 0.2 eV. Now the molecule is too fast to be redirected in a parallel orientation. At $t = 50$ fs it hits the surface in the canted configuration. It then makes a rapid flip-flop motion, hits the surface with its other end (150 fs) and is scattered back into the gas phase. The strong suppression of the efficiency of the steering effects is thus the reason for the strong decrease of the trapping probability at low kinetic energies.

At higher energies, the measured sticking probability becomes roughly independent of the kinetic energy which is reproduced by the calculations. Recall that such a behavior is not typical for atomic and molecular trapping. In fact, an estimation of the sticking probability using the so-called hard cube model[38] yields a vanishing trapping probability into the molecular chemisorption state for a kinetic energy of more than 1 eV[39] because such a high energy cannot be transferred to the substrate in just one collision.

For an understanding of the trapping at high kinetic energies it is important to realize that the system O_2/Pt(111) does not correspond to a point-like object interacting with a flat surface but rather to a molecule with internal degrees of freedoms (vibrations and rotations) impinging on a strongly corrugated surface. Although a fast molecule will not transfer all its kinetic energy in one collision to the substrate, it can also transfer energy into lateral motion along the surface and into vibrations and rotations. This energy is then no longer available for a direct return into the gas-phase. The molecule becomes transiently trapped in a dynamical precursor[40,41]. In this state, it moves back and forth with respect to the surface thereby transfering more and more energy to the substrate vibrations.

This mechanism is illustrated in Fig. 4 where we have plotted the energy redistribution along a typical trajectory of an O_2 molecule impinging on the surface with a kinetic energy of 1.1 eV and some snapshots of this trajectory. As Fig. 4 shows, there is only very little

energy transfer to the substrate atoms when the O_2 molecule hits the surface at $t = 50$ fs. However, there is a significant energy transfer into the vibrational and rotational motion (see the snapshots at $t = 150$ fs and $t = 300$ fs indicating the rapid reorientation of the O_2 molecule). The sharp spikes in Fig. 4 correspond to the maxima in the vibrational kinetic energy. After approximately 1400 fs, the molecule has transfered most of its energy to the substrate and has become accomodated at the surface. The trapping probability into the dynamical precursors is approximately independent of the kinetic energy which is the reason for the leveling off of the sticking probability at high kinetic energies.

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 $T_s = 300$ K. At $E_i = 0.1$ eV, we found a reduction of the trapping probability by 40% compared to the result at $T_s = 0$ 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 $\frac{3}{2}k_B T \approx 0.04$ eV. With respect to the uncertainties in both theory and experiment, the agreement is satisfactory.

4 Conclusions

The adsorption of O_2 on Pt(111) has been studied by tight-binding molecular dynamics simulations based on an *ab initio* potential energy surface. The measured dependence of the sticking probability as a function of the kinetic energy has been semi-quantitatively reproduced. The microscopic analysis of the trajectories leads to a novel interpretation of the interaction dynamics. Oxygen molecules impinging on Pt(111) will first become trapped in the molecular chemisorption states. The multidimensionality of the relevant potential energy surface plays a crucial role for the understanding of the adsorption dynamics. At low energies, the high sticking probability is due to the steering effect which becomes strongly suppressed for larger energies. At high energies, trapping into a dynamical precursor makes an efficient energy transfer to the surface possible which leads to a sticking probability that is roughly independent of the kinetic energy.

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