

Ab initio molecular dynamics simulations of the O₂/Pt(111) interaction

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The interaction of molecular oxygen with Pt(111) has been studied using ab initio molecular dynamics simulations based on periodic density functional theory (DFT) calculations. The adsorption probability has been determined as a function of the initial kinetic energy and the surface temperature. In addition, the effect of coupling the substrate to a thermostat has been studied. In agreement with experiment, no direct dissociation event has been observed in the molecular dynamics simulations. Characteristic discrepancies between theory and experiment are identified which are related to the choice of the functional used in the DFT calculations. At low kinetic energy and low surface temperature trapping into a weakly bound molecular state was observed that has not been identified before.

Keywords: density functional calculations, oxygen, platinum, adsorption, dissociation, energy transfer

INTRODUCTION

The adsorption and dissociation of oxygen on platinum are of significant technological importance. These processes do not only represent crucial reaction steps in the car exhaust catalyst [1], but they are also relevant in the oxygen reduction reaction in fuel cells whose small efficiency still constitutes one of the major obstacles in improving the efficiency of fuel cells [2]. This important role of the O₂-platinum interaction has motivated numerous experimental [3–14] and theoretical [15–30] studies addressing the adsorption of O₂ on Pt(111). It is well-known that oxygen can adsorb in three different molecular adsorption states on Pt(111) [14]. A weakly bound physisorbed species is stable at surface temperatures below 30 K [5, 6]. Up to surface temperatures of about 100 K, chemisorbed peroxo-like (O₂⁻²) and superoxo-like (O₂⁻) molecular states are observed [3, 31]. The assignment of the chemisorbed molecular states has been confirmed by total-energy calculations [16, 17] using density functional theory (DFT) within the generalized gradient approximation (GGA) [32] for the exchange-correlation effects. Above 100 K, chemisorbed O₂ on Pt(111) dissociates. After dissociation, the oxygen atoms occupy two fcc sites on the Pt(111) surface separated by a mean difference of two Pt lattice constants [10]. As kinetic Monte Carlo simulations indicate [24], this is a direct ballistic *hot atom* process rather than a diffusive event.

In spite of this detailed information, the reaction steps occurring in the O₂-Pt interaction are still debated [30], in particular as far as the oxygen reduction reaction is concerned [33]. Tight-binding molecular dynamics (TBMD) simulations have shown [22, 23] that O₂ does not directly dissociate on Pt(111), but due to steric hindrance of the underlying potential energy surface first adsorbs molecularly, and only in a second step dissociates caused by thermal fluctuations, in agreement with experimental observations [7, 10, 34]. However, these simulations were performed using a tight-binding parameterization of the O₂/Pt(111) potential energy surface (PES) derived

from periodic DFT calculations using the so-called PW91 functional [32]. Furthermore, molecular dynamics simulations of the O₂/Pt(111) interaction dynamics using an ab initio based reactive force field were carried out [29]. Parametrizations and interpolations of potential energy surfaces always introduce errors which leads to uncertainties in the calculated reaction probabilities. These can be particularly substantial in the case of adsorption on a PES with non-activated paths to adsorption as the interaction dynamics is then rather sensitive to fine details of the PES [35].

As the PES of the O₂/Pt(111) PES exhibits such paths, I have performed ab initio molecular dynamics (AIMD) simulations of the sticking of O₂ on Pt(111) as a function of the kinetic energy and the surface temperature. In AIMD simulations, the forces necessary to integrate the classical equations of motion are determined “on the fly” so that uncertainties caused by any interpolation scheme are avoided. In this work, the sticking probability of O₂/Pt(111) as a function of the kinetic energy is determined, the reaction dynamics and the energy redistribution upon adsorption and scattering are analyzed, and the issue of energy dissipation is addressed.

COMPUTATIONAL DETAILS

Periodic DFT calculations have been performed using the Vienna *ab initio* simulation package (VASP) [36]. The exchange-correlation effects have been described within the generalized gradient approximation (GGA) using the functional of Perdew, Burke and Ernzerhof (PBE) [37] and the revised PBE functional (RPBE) [38]. Note that the PBE functional usually yields interaction energies very close to those obtained with the PW91 functional [32]. The one-electron valence states were expanded in plane waves with kinetic energies up to the cut-off energy of 400 eV, and the ionic cores were represented by projector augmented wave (PAW) potentials [39] as constructed by Kresse and Joubert [40]. The Pt(111) surface was modeled by a slab of five layers within a

3×3 geometry with the uppermost two layer free to move while the three bottom layers were kept fixed at the bulk geometry.

The AIMD simulations were performed using the Verlet algorithm with a time step of 1 fs within the microcanonical ensemble. The trajectories were started 5 Å above the surface, only normal incidence was considered in this study. The trajectories were started with random lateral position and orientation of the O_2 molecules. RPBE sticking probabilities were derived by averaging over $N = 200 - 350$ trajectories. The statistical error of the sticking probabilities is given by $\sigma = \sqrt{S(1-S)}/\sqrt{N}$ where S is the sticking probability [41]. For $N \geq 200$, the statistical error is $\sigma \leq 0.05$.

Vibrational zero-point effects in the initial conditions were not considered which is motivated by the fact that the sum of all zero-point energies typically stays approximately constant along the reaction path for dissociative adsorption [42]. Quantum effects in the nuclear dynamics such as tunneling and zero-point effects [43] or diffraction [44] are not taken into because of the relatively large mass of oxygen. For the adsorption dynamics of hydrogen, these effects matter, but for non-activated systems their inclusion changes reaction probabilities usually only quantitatively, not qualitatively [45].

In order to assess the influence of the surface temperature on the interaction dynamics, AIMD simulations have been carried out with Pt(111) at a surface temperature of $T_s = 200$ K. From a thermalization run of the Pt(111) substrate alone, several substrate configurations were used as initial conditions for the runs at non-zero temperatures.

Most of the AIMD simulations presented in this study have been performed in the microcanonical ensemble, i.e. the total energy was conserved in these runs. Thus the energy transfer from the molecule to the substrate leads to a heating of the two surface layers, as the energy can not be dissipated further into the bulk since the other substrate atoms are fixed at the bulk positions. Recently, an embedding scheme has been proposed [46] that allows for energy transfer out of the AIMD simulation box. In order to check whether the artificial heating of the substrate in the simulations within the microcanonical ensemble introduces artifacts, we have coupled the atoms of the second Pt layer to an Anderson thermostat [47, 48] with collision rates of 0.04 and 0.02 fs^{-1} . This avoids that the thermostat directly couples to the O_2 motion and thus influences the adsorption dynamics, but it allows for energy dissipation out of the simulation box.

The simulations have been performed in the Born-Oppenheimer approximation which means that electronically non-adiabatic effects [49] are not taken into account. In the adsorption dynamics of $O_2/\text{Al}(111)$, electronic non-adiabatic simulations indicate that spin selection rules might be important [50, 51]. For $O_2/\text{Pt}(111)$, non-adiabatic spin transitions are expected to be less im-

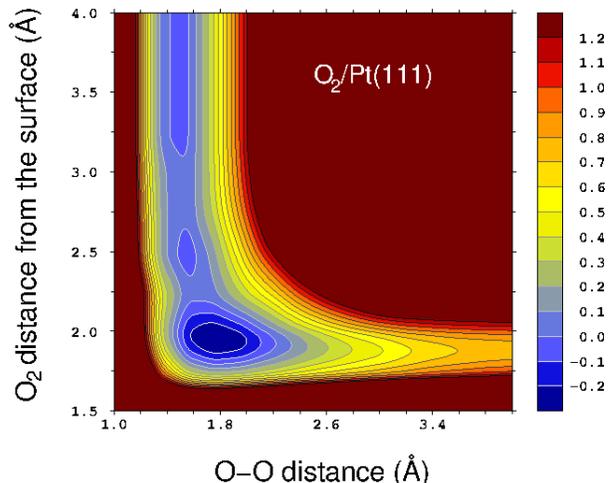


FIG. 1. Two-dimensional cut through the six-dimensional $O_2/\text{Pt}(111)$ potential energy surface as a function of the O-O distance and the O_2 center of mass distance from Pt(111) in a t-b-t geometry (see text). The contour spacing in 0.1 eV.

portant due to the larger mass of Pt compared to Al which makes the spin-orbit coupling larger. Still, the calculations have to be performed in a spin-polarized fashion. This increases the computational effort substantially, not only because of the fact that the calculations have been done for both spin up and spin down components of the electron density but also because convergence in the self-consistent field (SCF) cycles is usually slower for spin-polarized calculations [52]. In fact, the AIMD simulations have to be monitored carefully as one not-truly converged DFT calculation renders a whole trajectory useless. The convergence in the calculations has been improved by using optimized parameters in the Broyden mixing scheme.

RESULTS AND DISCUSSION

Figure 1 shows a two-dimensional cut through the six-dimensional $O_2/\text{Pt}(111)$ potential energy surface (PES) as a function of the O-O distance and the O_2 center of mass distance from Pt(111) using the RPBE functional. The lateral center of mass coordinates and the molecular orientation correspond to a top-bridge-top geometry, i.e., the O_2 center of mass is located above a bridge position between two Pt atoms, and the two oxygen atoms are oriented towards the adjacent top sites. The features of this cut are rather similar to those derived from the PW91 calculations [17, 23], but the molecular chemisorption well is shallower. The molecular chemisorption energy of -0.25 eV is similar to a previously calculated RPBE value [53]. The PES determined with the PBE functional looks rather similar, however, the molecular adsorption

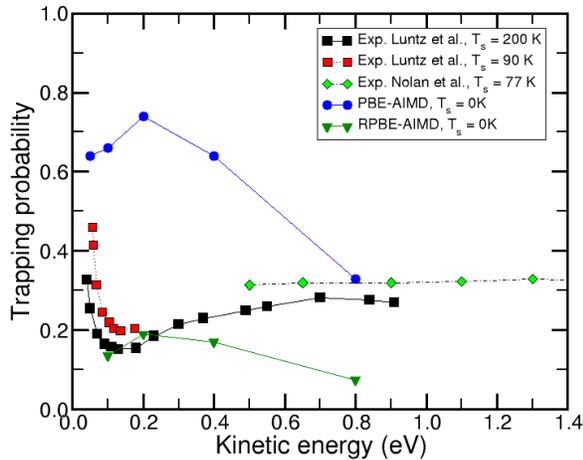


FIG. 2. Trapping probability of $O_2/Pt(111)$ as a function of the kinetic energy for normal incidence. Computational results derived from AIMD simulations for the surface initially at rest ($T_s = 0$ K) are compared to molecular beam experiments for surface temperatures of 90 K and 200 K (Luntz *et al.* [4]) and 77 K (Nolan *et al.* [12]).

well is energetically significantly deeper with a well-depth of -0.7 eV.

The sticking probabilities of O_2 impinging on Pt(111) as a function of the initial kinetic energy with the substrate atoms initially at rest ($T_s = 0$ K) are plotted in Fig. 2. The PBE-PES exhibits non-activated paths to adsorption leading to a high sticking probabilities at low kinetic energies consistent with the experiment, but in general the PES seems to be too attractive resulting in trapping probabilities that are much larger than the experimental values [4, 12, 34], in particular at medium kinetic energies. The trapping probabilities derived from RPBE-AIMD simulations are significantly smaller than the PBE-AIMD results due to the fact that the RPBE functional usually produces weaker interactions than the PBE functional [38].

In the medium energy range between 0.1 and 0.4 eV, the RPBE-AIMD simulations yield trapping probabilities in agreement with the experiment, but at higher kinetic energies the trapping probability is significantly lower than in the experiment. Note furthermore that there is a small barrier in the entrance channel of the $O_2/Pt(111)$ RPBE-PES which is true for all considered cuts. Hence non-activated adsorption is not possible on the RPBE-PES, in contrast to the experimental observation [4]. Therefore the RPBE-AIMD simulations cannot reproduce high sticking probabilities at low kinetic found in the experiment. The erroneous absence of non-activated paths for adsorption can most likely be corrected by taking the long-range attractive van der Waals interaction into account which is not included in semi-local GGA functionals [54]. It has in fact already been shown that

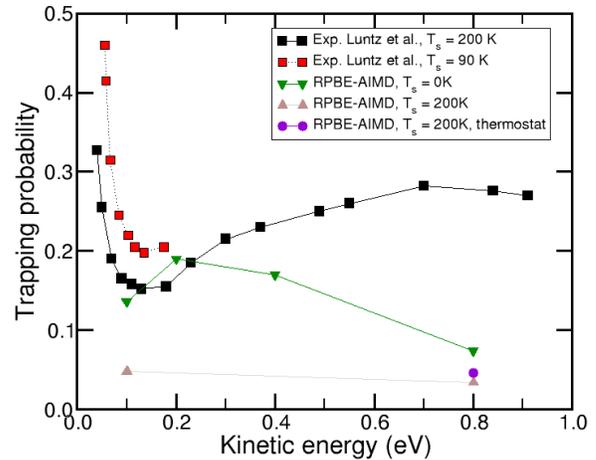


FIG. 3. Calculated surface temperature effects on the trapping probability of $O_2/Pt(111)$ as a function of the kinetic energy for normal incidence. In addition to the results shown in Fig. 2, RPBE-AIMD results at a surface temperature of $T_s = 200$ K obtained within a microcanonical ensemble and invoking an Anderson thermostat are plotted.

RPBE calculations including dispersion corrections [55] yield reliable molecule-surface interaction energies, for example for the adsorption of water on Pt(111) [56, 57]. The effect of dispersion corrections on the $O_2/Pt(111)$ interaction dynamics is the subject of an ongoing study.

As the sticking probability determined on a PES with the coexistence of activated and non-activated paths sensitively depends on details of the PES already at larger distance of the molecule from the surface [45, 58], it is hard to predict how the inclusion of dispersion effects modifies the sticking probability. In the present study we will focus on properties that only weakly depend on the consideration of dispersion corrections such as energy transfer upon adsorption and scattering or surface temperature effects.

The molecular beam results by Luntz *et al.* shown in Fig. 2 demonstrate that increasing the surface temperature from $T_s = 90$ K to $T_s = 200$ K leads to a reduction in the sticking probability [4]. This can be explained by the fact that at higher surface temperatures more energy can be transferred from the substrate to the impinging molecules which reduces the trapping probability.

In order to address surface temperature effects, RPBE-AIMD simulations with the substrate initially at a temperature of $T_s = 200$ K have been performed for two initial kinetic energies, $E_i = 0.1$ and 0.8 eV. In fact we find a substantial reduction in the trapping probability upon increasing the surface temperature from $T_s = 0$ K to $T_s = 200$ K, in qualitative agreement with the experiment (see Fig. 3). The size of the reduction at $E_i = 0.1$ eV is in fact consistent with the experiment regarding the fact that the temperature change is almost twice as large in

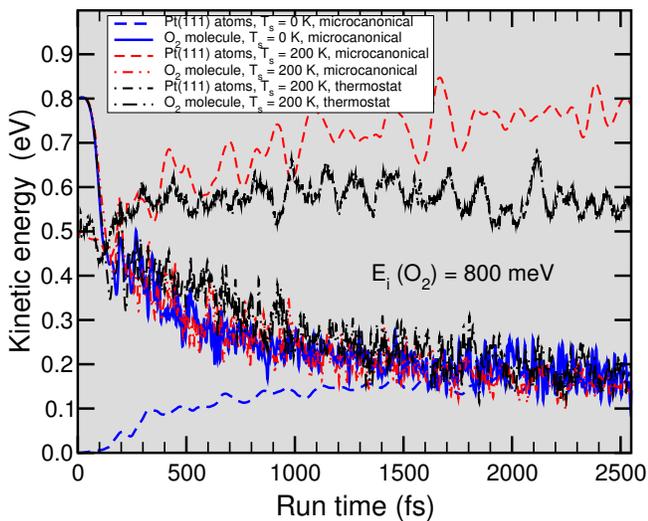


FIG. 4. Kinetic energy redistribution of the O_2 molecule and the Pt substrate atoms for an initial O_2 kinetic energy of 800 meV averaged over all adsorption events within the microcanonical ensemble for surface temperatures of $T_s = 0$ and 200 K and $T_s = 200$ K with the second layer Pt atoms coupled to an Andersen thermostat.

the simulations compared to the experiment.

At $E_i = 0.8$ eV, the calculated relative reduction is smaller than at $E_i = 0.1$ eV which is reasonable considering that at higher initial kinetic energies surface temperature effects matter less. However, at such a high initial kinetic energy a significant amount of energy has to be transferred to the substrate which leads to a heating of the substrate. This is illustrated in Fig. 4 where the kinetic energy redistribution of the O_2 molecule and the Pt substrate atoms is plotted for an initial kinetic energy of $E_i = 800$ meV averaged over all adsorption events. The simulations have been performed within a microcanonical ensemble for surface temperatures of $T_s = 0$ and 200 K. For $T_s = 200$ K, AIMD simulations have also been performed with the second layer Pt atoms coupled to an Andersen thermostat. Note that in non-dissociative molecular adsorption the molecules can only stay on the surface after entering the adsorption wells if they eventually transfer an energy amount larger than their initial kinetic energy to the substrate.

The molecules on the average first convert kinetic energy into potential energy upon approaching the surface because of the strong corrugation and anisotropy of the PES as in general they do not have the perfect minimum energy path configuration. It takes more than 1.5 ps to transfer the initial molecular energy to the substrate atoms. In spite of the inefficient energy transfer, still the molecules stick on the surface because temporarily their kinetic energy is transferred to molecular degrees of freedom such as inner-molecular vibration, rotation or lateral motion that are not directly coupled to scattering. This trapping into a dynamical precursor state [22, 23, 59, 60]

is essential for the sticking process. For $T_s = 0$ K, the Pt substrate atoms of the first two layers within the (3×3) surface unit cell take up about 200 meV in kinetic energy on the average upon the trapping of O_2 molecules. This corresponds to a temperature rise of about 75 K. A similar temperature rise also results within a microcanonical ensemble when the Pt surface was initially at a temperature of $T_s = 200$ K, as Fig. 4 shows. Note that the simulations for $T_s = 200$ K show a more pronounced oscillatory structure because of the smaller number of events considered in the average which leads to worse statistics.

The energy transferred to the surface atoms upon adsorption should eventually be dissipated into the bulk. However, using a slab model within the microcanonical ensemble does not allow for such a dissipation process. In order to model energy dissipation without directly influencing the interaction dynamics between impinging O_2 and the first Pt layer the Pt atoms of the second layer have been coupled to a Andersen thermostat [47]. Figure 4 demonstrates that this coupling indeed prevents the long-term heating of the substrate except for some fluctuations. Interestingly enough, the energy loss of the O_2 molecule is hardly influenced within the considered 2.5 ps run time by the presence of the thermostat. In Fig. 3, the sticking probability derived from the AIMD runs with the thermostat for an initial O_2 kinetic energy of $E_i = 800$ meV is also included. There is a slight increase compared to the results obtained within the microcanonical ensemble. It is tempting to assign this increase to the effectively lower surface temperature upon inclusion of the thermostat, as lower surface temperatures in general lead to higher sticking probabilities. Note, however, that this increase is not statistically significant within the uncertainties of the calculated sticking probabilities. Furthermore, hardly any differences were found when the collision rate in the simulations with the Andersen thermostat were reduced from 0.04 to 0.02 fs^{-1} .

It is certainly more realistic to mimic dissipation processes into the bulk through the coupling to a thermostat which can also be modeled using an embedding scheme [46]. Still, if the heating of the substrate upon energy transfer is not too pronounced which can for example be achieved by sufficiently large surface unit cells, apparently the correct inclusion of the energy dissipation into the bulk is not too crucial for the initial reaction dynamics. This is apparently even more true for scattering events. The average energy distribution of O_2 molecules scattered at Pt(111) with surface temperatures of $T_s = 0$ and 200 K for an initial kinetic energy of $E_i = 800$ meV is plotted in Fig. 5. The figure shows that the molecule loses half of its kinetic energy perpendicular to the surface upon scattering. The energy is transferred approximately in equal amounts to the center of mass lateral motion, O_2 vibrations and rotations and to the substrate atoms. For this energy distribution, the surface temper-

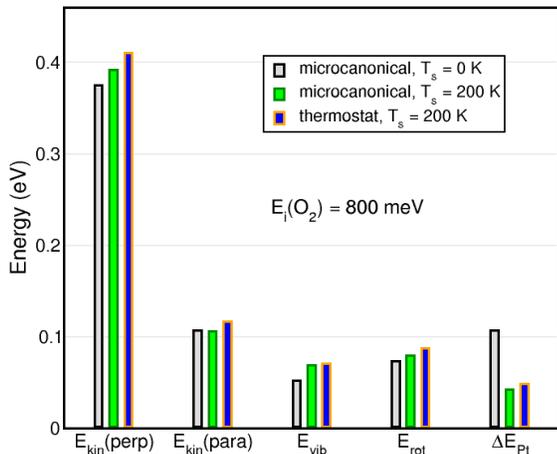


FIG. 5. Average energy distribution of O_2 molecules with an initial kinetic energy of $E_i = 800$ meV scattered at Pt(111) with surface temperatures of $T_s = 0$ and 200 K. For $T_s = 200$ K, additional simulations with the second layer coupled to a thermostat were performed.

ature and the coupling of the second-layer surface atoms to a thermostat hardly matter. This can be understood by the fact that scattering corresponds to an impulsive event with a rather short interaction time so that dissipation processes are not crucial.

Interestingly, at $T_s = 200$ K the heating of the substrate is smaller than at $T_s = 0$ K. This is due to the fact that at finite temperatures there can also be energy transfer processes from the substrate atoms to the impinging molecule which reduces the heating. Even more interestingly, the scattering events in the AIMD simulations with the thermostat also lead to a heating of the substrate. Note that the energy distribution plotted in Fig. 5 has been derived when the scattered molecules reached their initial height above the surface. The average time between the impact of O_2 on the Pt(111) surface and the return to a position 5 \AA above the surface is below 400 fs. This time is too short for an equilibration at the desired surface temperature of $T_s = 200$ K through the coupling to the thermostat. In fact it is more realistic that there is a temporary heating of the vicinity of the molecular impact point on the substrate.

Returning to the discussion of the O_2 trapping, note that during the equilibrium process, the O_2 center of mass also propagates laterally on the surface, but only about 3 \AA according to the AIMD simulations. Roughly this corresponds to one lattice unit of Pt and is much less than for example hydrogen atoms move after dissociative adsorption on Pd(100) [61]. This is probably caused by the smaller energy gain upon adsorption for $\text{O}_2/\text{Pt}(111)$ but also by the smaller mass ratio to the substrate atoms for oxygen which leads to a faster energy transfer.

In the AIMD simulation I did not find any O_2 disso-

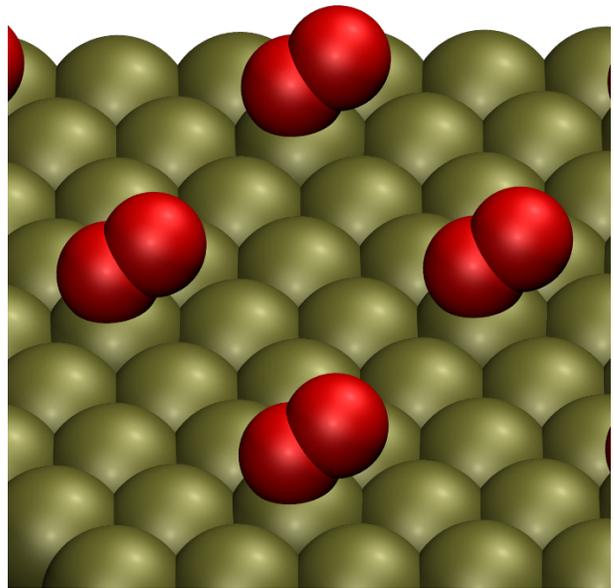


FIG. 6. Configuration of a metastable molecular adsorption state with an adsorption energy of $+50$ meV.

ciative events on Pt(111), thus confirming the findings of the previous TBMD study [22, 23] and experimental observations [7, 12, 34] that O_2 does not dissociate on cold Pt(111) surfaces even at kinetic energies that are much greater than the dissociation barrier. This is due to the topology of the PES as shown in Fig. 1. It is very unlikely that O_2 molecules entering the molecular adsorption well will subsequently directly propagate along the dissociation channel since the shape of the PES does not redirect the molecules towards this channel. Thus dissociation is a two-step process [22]: First the molecules become trapped in the molecular adsorption well, and dissociation is initiated by thermal fluctuations.

At the low kinetic energy of 100 meV, we found that about 5 per cent of the impinging molecules become trapped in a molecular adsorption state in a canted configuration above an ontop site for the surface atoms initially at rest. This molecular adsorption state is illustrated in Fig. 6. These molecules became trapped for at least 15 ps which was the maximum run time of the trajectories. The corresponding adsorption energy of this state is $+50$ meV which means that it is a metastable state that is energetically less favorable than the O_2 molecule in the gas phase. At a surface temperature of $T_s = 200$ K, still some molecules became temporarily trapped in this state, but not longer than 10 ps.

To the best of my knowledge, this state has not been identified before. This confirms that AIMD simulations can be used as an unbiased tool for the finding of unexpected binding sites. In spite of its low interaction energy, the magnetic moment of the O_2 molecule in this state is $1 \mu_B$, i.e. it corresponds to a superoxo state. This in-

dicates that there is a considerable rearrangement of the O₂ electronic structure upon entering this state so that it is not clear whether it can be associated with the physisorption state found in experiments [5, 6].

CONCLUSIONS

Ab initio molecular dynamics simulations of the interaction of O₂ with Pt(111) surfaces have been performed using periodic density functional theory calculations. Whereas simulations using the PBE functional yielded sticking probabilities in the intermediate energy range that are much higher than those obtained in the experiment, RPBE simulations resulted in probabilities that are smaller than the experimental values. It is probable that the inclusion of dispersion corrections might reduce the discrepancy between RPBE and experimental results. Higher surface temperatures lead to a sizable reduction in the trapping probability. Coupling the second layer atoms of the Pt(111) substrate to an Andersen thermostat had only little influence on the energy distribution upon adsorption and scattering.

In agreement with experiment, no direct dissociation event has been observed in the molecular dynamics simulations. It takes more than 1.5 ps before the O₂ molecules become accommodated on Pt(111) upon adsorption. Still, within this time, the O₂ molecules only move about 3.0 Å on the average laterally on the surface. A weakly bound molecular adsorption state in a canted configuration has been identified which becomes populated at low surface temperatures and small initial O₂ kinetic energies, but it is not clear whether this state can be associated with the experimentally observed physisorption state.

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