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Dissociative dynamics of spin-triplet and spin-singlet O₂ on Ag(100)M. Alducin,^{1,2,a)} H. F. Busnengo,³ and R. Díez Muiño^{1,2}¹*Centro de Física de Materiales Centro Mixto CSIC-UPV/EHU, Edificio Korta, Avda. de Tolosa 72, 20018 San Sebastián, Spain*²*Donostia International Physics Center DIPC, P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain*³*Instituto de Física Rosario (CONICET-UNR) and Facultad de Ciencias Exactas, Ingeniería y Agrimensura, Universidad Nacional de Rosario, Avenida Pellegrini 250, 2000 Rosario, Argentina*

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We study the dissociative dynamics of O₂ molecules on the Ag(100) surface. Initially, the impinging molecules are either in the spin-triplet ground state or in the spin-singlet excited state. The molecule-surface interaction is obtained in each case by constructing the six-dimensional potential energy surface (PES) from the interpolation of the energies calculated with spin-polarized and non-spin-polarized density functional theories, respectively. Classical trajectory calculations performed in both PESs show that O₂ molecules initially in the spin-triplet ground state only dissociate for incidence energies above 1.05 eV. This result is consistent with molecular beam experiments performed in this system. Interestingly, our results also suggest that for the spin-singlet O₂ dissociation occurs even for incidence energies as low as 50 meV. We propose the use of spin-singlet excited O₂ molecules to improve the otherwise low dissociative reactivity of O₂ at clean Ag(100). © 2008 American Institute of Physics. [DOI: 10.1063/1.3012354]

I. INTRODUCTION

The interaction of oxygen with metal surfaces is a topic of enormous scientific and technological interest. Metal oxides are extensively used in industry because of their insulating properties and their ability to passivate corrosion in metals.¹ The active nature of oxygen atoms is behind many reactions happening in nature and it is commonly exploited in heterogeneous catalysis. A clear example is the epoxidation of ethylene ($C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$). The resulting ethylene oxide, apart from being a common sterilant in medical supplies, is mostly used as an intermediate in the production of ethylene glycol and other chemicals. The unique catalytic properties of silver powders for ethylene oxide production motivated a large number of experimental and theoretical studies in the 1980s in an attempt to understand the fundamentals behind this exceptional oxidation process.²⁻⁴

Since then, the reactivity of oxygen on different crystal Ag surfaces has been investigated combining a variety of techniques. Experimentally, the adsorbed oxygen species are rather well characterized.⁵ At crystal temperatures $T_s < 150$ K, oxygen adsorption on Ag(111), Ag(110), and Ag(100) is only molecular. Dissociation can be observed at higher surface temperatures. All these studies show that dissociation and molecular adsorption are sensitive not only to exposure conditions, such as surface temperature, oxygen coverage, temperature, and gas pressure, but also to surface structure. The closed-packed Ag(111) surface is extremely inert toward atom and molecular oxygen. The experimental dissociative and molecular sticking probabilities are among the lowest with values of the order of 10^{-7} – 10^{-6} .⁶⁻⁸ On the Ag(110) and Ag(100) surfaces, the probability for molecular

adsorption can exceed 0.5. Thermal desorption measurements show that dissociation is less effective than desorption for Ag(100) (the dissociation probability is $P_{diss} = 4 \times 10^{-3}$ at $T_s = 300$ K), whereas the two processes are comparable on Ag(110) ($P_{diss} = 0.63$ at $T_s = 300$ K).^{9,10}

The dynamics of molecular adsorption is studied combining molecular beam techniques with high resolution electron energy loss spectroscopy (HREELS). On Ag(100),^{9,11} the initial sticking probability increases monotonically with molecular incidence energy E_i up to a maximum value of 0.7 and then starts to decrease for $E_i > 0.8$ eV. A similar behavior was reported by Raukema *et al.*¹² for O₂/Ag(111), although in this system adsorption probabilities are orders of magnitude smaller, as mentioned above. Molecular adsorption also increases smoothly with E_i on the Ag(110) surface.¹³ In this case, however, the experimental energies (below 0.5 eV) are insufficient to determine whether the sticking probability reaches a stable value or instead decreases as observed on Ag(100) and Ag(111).

The dissociative dynamics on Ag(110) has also been investigated with molecular beam techniques.¹³⁻¹⁵ The sticking probability exhibits an E_i -dependence similar to the one observed for molecular adsorption on Ag(100). First, it increases from $\sim 10^{-4}$ up to 0.45 and then decreases rather smoothly for energies larger than 0.8 eV. The peculiarity of oxygen adsorption on the Ag(110) surface is the pronounced azimuthal dependence of both the dissociative and the molecular sticking probabilities,¹⁴ not observed in other systems.

All these experiments contributed to acquiring a detailed knowledge on O₂ interacting with flat silver surfaces. Nevertheless, none of these experiments has been able to reproduce the catalytic properties of Ag powders. At this respect, dissociation has been considered as a necessary step in the

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ethylene oxidation process.^{4,16,17} The low dissociation probabilities exhibited by the single-crystal Ag surfaces led to investigate more in detail possible mechanisms or experimental conditions to overcome this limitation. Defected surfaces have been proposed as a possible mechanism to enhance dissociation on Ag(100) crystals.¹⁸ Furthermore, atom impact collision is successfully used to induce dissociation of O₂ chemisorbed on Ag(110) (Ref. 19) and Ag(100).²⁰ Recent investigations show that dissociation is clearly enhanced on stepped surfaces.^{21,22} Here, we propose an alternative mechanism to increase the dissociative reactivity of clean crystal surfaces, the use of O₂ molecules initially excited to the metastable spin-singlet state (¹Δ_g), which is characterized by a long radiative lifetime.^{23,24}

We perform classical dynamics calculations to study the dissociative dynamics of O₂ on the Ag(100) surface. There are a few density functional theory (DFT) calculations aimed at characterizing the energetics and binding sites of the various oxygen species that adsorb on Ag(110),^{25,26} Ag(111),^{17,27–29} and Ag(100).^{30–32} Going beyond a purely static analysis, our main purpose here is to investigate the *dynamics* of the dissociative adsorption process using state-of-the-art interaction potentials. The six-dimensional (6D) adiabatic potential energy surface (PES) is constructed by interpolating a grid of DFT energies, which is previously obtained from spin-polarized (SP) DFT calculations. We also calculate a grid of non-spin-polarized (NSP) DFT energies and construct the corresponding NSP PES. The difference between the two calculations is that in the SP PES no restriction to the spin polarization of the system is imposed, whereas in the NSP PES the two spin states are always equally populated. Far from the surface, where the molecule-surface interaction is negligible, the SP PES and the NSP PES describe, respectively, the energetics of O₂ molecules in the spin-triplet ground state and in the spin-singlet excited state. Close to the surface, where hybridization of the O₂ and the Ag(100) states is significant, we will show that the SP and the NSP PESs converge to the same energy values.

The SP PES is used to describe within the adiabatic approximation the dynamics followed by O₂ molecules that are initially (i.e., far from the surface) in the spin-triplet ground state. However, both the NSP and SP PESs are used to calculate the dynamics of O₂ molecules initially excited in the spin-singlet state. The molecule-surface interaction is described by the NSP PES during the whole trajectory calculation except for those few molecules that are reflected in the surface region where the SP and NSP PESs merge. When this happens, we assume that the evolution of molecules reaching this region and moving off the surface should continue through the SP PES. Close to the surface, molecules have lost the initial spin-singlet character and then the minimum energy configurations in the outgoing part of the trajectory are strictly given by the SP PES.³³ Performing classical trajectory calculations under such assumptions, we find that whereas dissociation of the spin-triplet O₂ is only possible for incidence energies above 1.05 eV, spin-singlet O₂ dissociate even for energies of about 50 meV. Interestingly, the use of spin-singlet O₂ to improve dissociation is indeed more

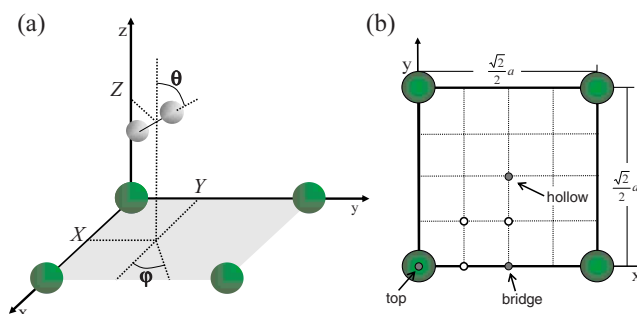


FIG. 1. (Color online) (a) Coordinate system used in our calculations: surface Ag atoms are in green and the O₂ nuclei in gray. (b) Geometry of the Ag(100) surface. DFT calculations for O/Ag(100) have been performed on all sites marked by circles. For O₂/Ag(100), DFT calculations are performed for configurations whose molecule center is over the sites marked by filled circles.

efficient than the use of spin-triplet O₂ with higher initial incidence energies under off-normal incidence angles.

The role of spin in the reactivity of O₂ with metal surfaces is an intriguing issue that has recently attracted much attention. The dissociative adsorption on Al(111) is probably the most representative example. The problem has been studied using state-of-the-art PESs calculated with SP DFT. The static analysis of the adiabatic SP DFT PESs made it difficult to understand the experimental low dissociative sticking probability^{34,35} and, among others, spin related effects were suggested.³⁵ More recently, classical trajectory calculations performed on various SP DFT PESs (Ref. 36) show that the low O₂ dissociation could be explained if a nonadiabatic spin-triplet PES, calculated with *constrained* DFT, is used instead. All these calculations focus on the reactivity of O₂ molecules in the ground state. The novelty of our work is to analyze also the reactivity of spin-singlet O₂.

The outline of this paper is as follows. The construction of the NSP and the SP PESs is described in detail in Sec. II. The static properties and a comparative analysis of both PESs are also discussed in that section. In Sec. III, we show and compare the results obtained for the dissociative dynamics of spin-triplet and spin-singlet O₂. Conclusions are given in Sec. IV.

II. CALCULATION OF THE PES

Within the rigid surface approximation, the interaction of O₂ with the Ag(100) surface is a 6D problem that depends on the position of the molecule center $\mathbf{R} \equiv (X, Y, Z)$, which is defined by the center of nuclear charge, the molecular interatomic distance r , and the molecular orientation relative to the surface, which is determined by the polar and azimuthal angles (θ, φ). The coordinate system is depicted in Fig. 1(a). The NSP and SP 6D PESs are constructed from the interpolation of 2280 and 1210 DFT energies, respectively. In both cases, the interpolation is performed using the corrugation reducing procedure (CRP).³⁷ The method consists of reducing first the corrugation of the O₂/Ag(100) PES by subtracting from it the potential energy between each of the two O atoms that form the molecule and the Ag(100) surface. The 6D energy surface, which remains after this operation, called “the 6D interpolation function” in Ref. 37, exhibits a

smoother dependence on the coordinates (X, Y, θ, φ) and can be interpolated within the required accuracy. To apply the CRP, we also have to calculate the O/Ag(100) PES.

All DFT data are obtained with the “Vienna *ab initio* simulation program” (VASP) (Ref. 38) that operates with a plane-wave basis set. The exchange-correlation (XC) energy is calculated with the generalized gradient approximation (GGA) and the Perdew–Wang energy functional (PW91).³⁹ The electron-core interaction is described by ultrasoft pseudopotentials.⁴⁰ We have verified that the PW91 functional reproduces relevant features of the O₂/Ag(100) system such as the depth of the chemisorption well better than the revised Perdew–Burke–Ernzerhof (RPBE) functional⁴¹ (see Sec. II E). Similar to what we found for the N₂/W(110) and N₂/W(100) systems,⁴² the RPBE energies are more repulsive than the PW91 ones. In particular, our tests indicate that due to the repulsive character of the RPBE PES, the “weak” adsorption well disappears in the O₂/Ag(100) RPBE PES. Therefore, we consider that the RPBE energies are less adequate than the PW91 ones in this system. Finally, we performed a series of preliminary calculations to determine the parameters that assure us an efficient computational calculation of all DFT energies to the required accuracy. Thus, the energy cutoff used in the pseudo-wave-function expansion is 515 eV. The fractional occupancies are calculated using the broadening approach of Methfessel and Paxton⁴³ with $N=1$ and $\sigma=0.3$.

A. Preliminary steps: Ag(100) and O/Ag(100) PESs

The theoretical lattice constant, which minimizes the cohesive energy obtained from bulk calculations, is $a=4.165$ Å. The corresponding interlayer distance $d=2.0825$ Å agrees with the experimental value of 2.043 Å.⁴⁴ The Ag(100) surface is modeled by a periodic five-layer slab with a (2×2) surface structure and a supercell vector along the normal to the surface (Z -axis) of $14d$. The Brillouin-zone integration is performed using a $4\times 4\times 1$ Monkhorst–Pack grid of special k -points. Under these conditions we relax the slab to get the equilibrium geometry of the Ag(100) surface. Keeping the third layer fixed, the outermost layers are shifted inward by 0.069 Å, whereas the second and the fourth layers are shifted inward by 0.002 Å. The relaxation of the topmost layer is larger than the experimental value of 0.027 Å.⁴⁴ Despite this, we note that the theoretical forces on the surface atoms are negligible (~ 8.6 meV/Å). After relaxation, the periodic slabs are separated along the Z -axis by 20.89 Å of vacuum. DFT energies of O₂/Ag(100) and O/Ag(100) are calculated using this supercell and keeping the relaxed geometry of the slab fixed (frozen surface approximation).

The three-dimensional (3D) O/Ag(100) PES is constructed from the interpolation of 258 DFT energies using the 3D CRP.³⁷ Since it is only needed as an intermediate step to reduce the molecule-surface PES corrugation, the DFT energy values are obtained from NSP calculations, which require less computational effort. The sites used to construct the DFT energy grid are shown by white and black circles in Fig. 1. The accuracy of the O/Ag(100) PES is checked by

comparing a set of DFT energies, not included as input data in the interpolation procedure, with the values obtained from interpolation. Errors are below 10 meV for $Z\geq 1.5$ Å. At smaller distances, errors are still of the same order except for positions around the top site for which the potential energy becomes too repulsive. Additionally, we have verified that O adsorption takes place over hollow site, as reported in various DFT calculations.^{30–32} In particular, we obtain that O adsorbs at a distance from the surface $d_{O-Ag}=0.88$ Å and with an adsorption energy of $E_{O-Ag}\sim 3.86$ eV. The latter is calculated as $E_{O-Ag}=-(E_{O/Ag(100)}-E_{Ag(100)}-E_O)$, where the two first terms are the total NSP energies of the system with and without the O atom, respectively, and E_O is the SP energy of the isolated O atom. We remark that all these values are calculated with the frozen surface approximation. Despite this, they compare well with the values reported in Ref. 30 ($d_{O-Ag}=0.76$ Å and $E_{O-Ag}=4.1$ eV).

B. Spin-triplet and spin-singlet O₂ in vacuum

We check the accuracy of our DFT calculations in reproducing various features of O₂ in vacuum. In practice, the values are obtained for the molecule at a distance from the surface of 10.48 Å (i.e., midway between two slabs) using the same calculation parameters specified in Sec. II A. The properties of the O₂ molecule in the triplet $^3\Sigma_g^-$ ground state are derived from SP calculations of the molecular energy at various internuclear distances. The calculated bond length $r_{eq}=1.24$ Å and vibrational quanta $h\nu_0=0.190$ eV are in agreement with the experimental values of 1.21 Å (Ref. 45) and 0.195 eV,⁴⁶ respectively. In contrast, the theoretical binding energy of 6.4 eV notably differs from the experimental value of 5.2 eV.⁴⁵ The discrepancy, however, is not specific of our DFT calculations. The error arises from the unsatisfactory description of the exchange energy given by DFT calculations using approximate functional, which is particularly problematic in the O₂ molecule.^{47–49} The most accurate DFT and GGA calculations for O₂ isolated in vacuum predict binding energies between 5.7 and 6.1 eV. The particular value depends on the XC functional chosen in each case.^{36,41,48,49}

In principle, the use of DFT to describe the spin-singlet excited state $^1\Delta_g$ is not well justified. Present DFT describes it as a mixture of multiplet states.^{36,50} This limitation has been widely investigated in the context of atoms and molecules.^{47,51,52} However, our main concern in studying the molecule-surface dynamics is to have the energetics of the problem as accurate as possible even if the wave function of the system is not as well described. In this sense, a reasonable approximation to the energy difference between the $^3\Sigma_g^-$ spin-triplet ground state and the $^1\Delta_g$ spin-singlet state of the isolated O₂ molecule is given by NSP DFT calculations.³⁶ More recently, it has been shown that the excitation energy of the $^1\Delta_g$ spin-singlet state calculated with constrained SP DFT is half of the experimental value, whereas the error in the value calculated with NSP DFT is only of about 15%.⁵⁰ Here we also use NSP DFT to describe the interaction of spin-singlet O₂ with the Ag(100) surface. In our calculations, the bond length derived from the NSP energies midway be-

tween two slabs is also 1.24 Å, and the vibrational quanta are 0.184 eV [the experimental value is 0.1839 eV (Ref. 46)]. The difference between the NSP and SP energies of the O₂ molecule midway between the two slabs is 1.006 eV, including the small correction due to the different NSP and SP zero point energies. This value also compares well with the experimental excitation energy of the singlet state $E(^1\Delta_g)=0.977$ eV (Ref. 23) and 0.9817 eV.⁴⁶ In view of all these results, we think that the NSP PES can provide a good description of the energetics of the real spin-singlet state even though the use of NSP DFT cannot formally be justified. Our argument is that the calculated NSP PES is correct at least in two important regions for the dynamics: (i) in the entrance channel since the singlet-triplet energy difference far from the surface is in good agreement with experiments and (ii) close to the surface since the NSP and SP energy values coincide (see below) showing that any memory on the initial spin state is lost in contact with the surface if the molecule has time to relax. Having these two boundary regions reasonable well described, it may be expected that we are obtaining the right energetic displacement between the PES for the spin-singlet state and the adiabatic PES describing the ground state. After all, this is what really matters for the problem under investigation, namely, the dissociative dynamics of the spin-singlet O₂.

C. NSP O₂/Ag(100) PES

The NSP PES is used to represent the interaction energy of O₂ molecules that far from the surface are in the spin-singlet excited state and approach the surface following minimum energy configurations of zero spin polarization. The NSP DFT calculations are performed for 12 different configurations that are defined by the molecular orientation (θ, φ) and the position (X, Y) of the molecule center over the surface unit cell [black circles in Fig. 1(b)]. For each configuration, energies are calculated over the same (r, Z)-grid, in which Z varies from 0 to 4.5 Å in steps of 0.25 Å for ten values of r chosen between 0.9 and 2.5 Å. We select the following configurations in order to assure an adequate representation of the PES nonmonotonic dependence on the molecular orientation and on the surface symmetry.

- Three configurations over the top site ($X=0, Y=0$): $\theta=0^\circ, \theta=90^\circ$ with $\varphi=0^\circ$ and $\varphi=45^\circ$.
- Four configurations over hollow site [$X=a/(2\sqrt{2}), Y=a/(2\sqrt{2})$]. We add to the three previous orientations: $\theta=45^\circ$ and $\varphi=45^\circ$.
- Five configurations over bridge site [$X=a/(2\sqrt{2}), Y=0$]: $\theta=0^\circ, \theta=90^\circ$ with $\varphi=0^\circ$ and $\varphi=90^\circ$, and $\theta=45^\circ$ with $\varphi=0^\circ$ and $\varphi=90^\circ$.

The NSP PES is then constructed by interpolating the final grid of 2280 DFT energies with the 6D CRP.³⁷ The accuracy is checked by comparing the interpolated values with calculated DFT data not included in the interpolation procedure. Errors are below 100 meV for distances $Z \geq 1.5$ Å, which is the region of interest for the dynamics.

D. Adiabatic spin polarized O₂/Ag(100) PES

The SP PES provides at each point the minimum energy of the O₂/Ag(100) system without imposing any restriction to the spin polarization of the system. Far from the surface, the minimum energy corresponds to the molecule in the spin-triplet ground state. This property is correctly described by the SP PES. At closer distances, the interaction with the metal electrons is more important and the total system cannot be represented as two uncoupled subsystems, i.e., the Ag(100) surface and the O₂ molecule. On the contrary, there is a strong mixture of states and, in particular, the electron density nearby O₂ increases. As a consequence of electron exchange and correlation taking place between the molecule and the surface, the total spin around the molecule is reduced. The SP PES also describes this process. We note that the total spin of the system gradually changes from 1 to 0 in the SP PES, whereas no spin-orbit or other relativistic contributions are included in the calculation. The variation in the total spin is often necessary in SP DFT calculations to take into account that there is a change in the local spin density. This procedure is justified because the surface acts as a reservoir. The total energy of the Ag(100) surface will be the same if we calculate it for the pure paramagnetic case in which the number of spin-up and spin-down electrons are equal ($N^\uparrow=N/2$ and $N^\downarrow=N/2$) or for the case $N^\uparrow=N/2-1$ and $N^\downarrow=N/2+1$. In other words, we could phrase that phenomenon as a dilution of the initial spin polarization around the O₂ molecule as it approaches the surface due to electron exchange and correlation between the molecule and surface. We remark that the SP PES differs from the *constrained* spin-triplet PES (not calculated here) because in the latter O₂ is forced to stay in the spin-triplet configuration for all molecule-surface distances.³⁶ At distances where the molecule-surface interaction is still weak and therefore the system ground state corresponds to the O₂ molecule in the spin-triplet state, both PESs coincide.

The SP DFT energies are calculated for the same 12 configurations and internuclear distances described above, but for less values of Z 's. We observe that the difference between NSP and SP energies for each configuration and internuclear distance r varies smoothly with Z . The dependence is shown in Fig. 2 for a particular configuration, but similar curves are obtained for all configurations. Taking advantage of this feature, we only perform SP calculations at the distances marked by full symbols in Fig. 2. Next, the grid in Z 's is completed for each configuration and internuclear value in the r -grid using a cubic spline interpolation method. The new values are represented by open symbols in Fig. 2. At this stage, the set of points ($X, Y, Z, r, \theta, \varphi$), at which the SP energies are known, coincides with the one used in the interpolation of the NSP PES. The 6D SP PES is then constructed following the same steps as in the latter. This procedure allows us to overcome the convergency problems that appear in those regions where the SP and NSP energies differ in a few meV.⁵³

The accuracy of the constructed 6D PES is checked by

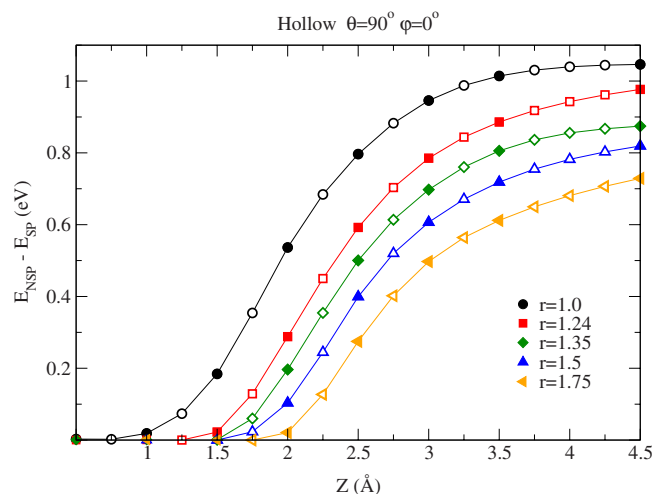


FIG. 2. (Color online) Dependence of the difference between NSP and SP energies on the distance from the surface Z . The molecule is over hollow with $\theta=90^\circ$ and $\varphi=0^\circ$. Different symbols correspond to different internuclear distances r . For each r , DFT and interpolated values are shown by filled and open symbols, respectively. Lines are plotted as a guide for the eyes.

comparing the interpolated values to the calculated DFT data not included in the interpolation procedure. Typical errors in the region of interest for the dynamics are below 100 meV.

E. Characteristics of the SP and NSP O₂/Ag(100) PESs

In order to analyze and compare the SP and NSP PESs, all potential energies are referred to the same zero energy, the energy of O₂ at the equilibrium bond length $r_{\text{eq}}=1.24$ Å in vacuum, obtained from a SP calculation. Zero point energy corrections are not included in the following analysis, unless otherwise stated. The dependence of the potential energy on Z is shown in Fig. 3 for various molecular configurations. The internuclear distance is set to r_{eq} in the left panel and to $r=1.35$ Å in the right panel. The former provides information on the entrance channel and the latter on the molecular potential well. Filled and open symbols represent SP and NSP energies, respectively. Concerning the difference between the NSP and SP energies in the entrance channel, practically all the configurations retain the singlet excitation energy of ~ 1 eV for distances $Z>3$ Å. At closer distances, the interaction with the surface becomes more important and the energy difference decreases. For certain configurations, the merging of the SP and NSP energies begins from $Z\sim 2$ Å. At distances of about 1 Å, the merging is completed for those configurations that play a relevant role in the dynamics.

One common feature in both PESs is the absence of energy barriers in the entrance channel (left panel). In principle, this result is surprising in view of the sticking probability curve measured in molecular beam experiments for the O₂/Ag(100) system.¹¹ Chemisorption, which at the experimental surface temperature of 110 K is totally molecular, starts for an incidence energy of ~ 0.1 eV. Above this energy, the sticking probability increases quite abruptly, reaching a maximum value of about 0.7 for E_i between 0.6 and

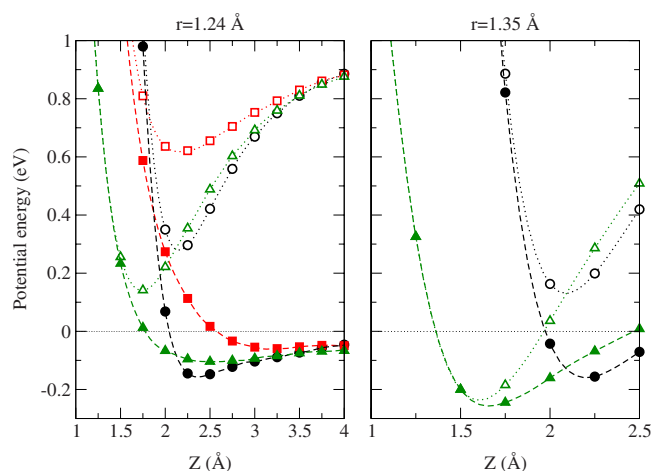


FIG. 3. (Color online) Dependence of the potential energy of O₂/Ag(100) on the molecule center of charge distance from the surface Z . The internuclear distance is the equilibrium bond length $r=1.24$ Å on the left panel and $r=1.35$ Å on the right panel. Filled (open) symbols show the SP (NSP) DFT values for various configurations: Bridge, $\theta=90^\circ$, $\varphi=0^\circ$ by black circles; bridge, $\theta=90^\circ$, $\varphi=90^\circ$ by red squares; and hollow, $\theta=90^\circ$, $\varphi=0^\circ$ by green triangles. Lines show the corresponding interpolated energies.

0.8 eV, and then rapidly decreases to 0.5 for $E_i\sim 1$ eV, the highest experimental energy. The authors suggest the existence of potential energy barriers in order to understand the initial activated behavior of the molecular sticking probability. However, we have carefully looked for possible energy barriers in the entrance channel without success. Interestingly, the same apparent discrepancy between theory and experiments is found in the chemisorption of O₂ on Ag(110). Molecular beam studies carried by different groups show that molecular chemisorption on this surface is also an activated process;^{13–15} whereas DFT calculations performed by Gravil *et al.*²⁵ show no barriers into the chemisorbed state from the gas phase. Although recent dynamics calculations of N₂ dissociation on W(110) demonstrate that an activatedlike sticking curve is compatible in the absence of barriers,^{54,55} we will show in Sec. III that other arguments should be invoked to explain the inconsistency in the O₂/Ag(100) case.

Recent analysis of HREELS measurements done for O₂/Ag(100) allows one to identify two distinct chemisorbed states.⁵⁶ A first inspection of the SP PES also suggests the existence of two possible molecular adsorption sites: one over hollow (Fig. 3, right panel) and one over bridge (Fig. 3, left panel). In both cases the molecular axis is oriented parallel to the surface along the X -axis ($\varphi=0^\circ$). We have checked whether these local minima correspond to the real minima in the 6D PES following the procedure of Ref. 57, which is based on dynamical calculations. Our results show that O₂ adsorption occurs on the potential well over hollow with an adsorption energy of about 0.295 eV. In the potential well, the molecule is ~ 1.58 Å above the surface and stretched to a bond length of ~ 1.4 Å. Experimentally, the chemisorption energy is 0.4 eV,⁵⁸ i.e., larger than the value we obtain. This difference is reasonable within the frozen surface approximation. We have verified that the adsorption energy is 0.380 eV when surface relaxation is allowed. The analysis of the bridge minimum shows that only molecules with initial energies below 70 meV (referred to the bottom of

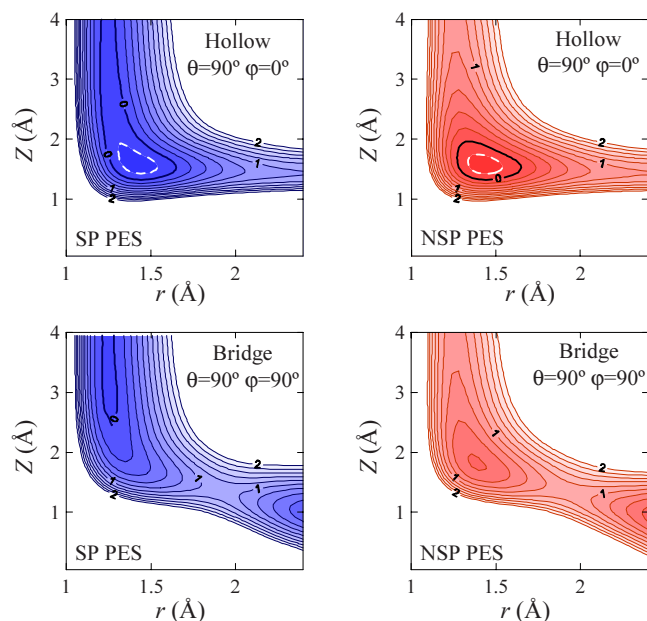


FIG. 4. (Color online) (r, Z) cuts of the $O_2/Ag(100)$ PES obtained from SP (left panels) and NSP (right panels) calculations. The zero potential energy (thick solid lines) is in all cases the SP energy of O_2 in vacuum. Contour lines separate intervals of 0.2 eV. Solid (dashed) contour lines correspond to positive (negative) potential energy values.

this well) stay on this minimum. Molecules with energies above 200 meV start to escape into vacuum. For energies between 70 and 200 meV, most of the molecules end up on the well over hollow. Diffusion from bridge to hollow sites may explain the existence of the two experimental chemisorption states with same desorption energies. Note, however, that the analysis of the bridge well is limited by the interpolation error that can be tens of meV. Theoretical DFT calculations performed in Ref. 32 to characterize the chemisorption properties of O and O_2 on Ag(100) identify as candidates to the experimental chemisorbed species the same configurations over hollow and bridge that we observe. Comparison between theoretical and experimental scanning tunneling images shows that O_2 adsorbs parallel to the surface with its molecular axis oriented toward the bridge positions.⁵⁹

The calculated SP and NSP (r, Z) cuts of the chemisorption configuration are depicted in Fig. 4 (upper panels). For $Z \leq 1.5$ Å both calculations merge to the same energy values, and the chemisorption properties are then identical. The spin state of the adsorbed molecule is zero. We also show two-dimensional cuts of the molecule over bridge with the axis parallel to the surface and perpendicular to the X -axis ($\theta=90^\circ$, $\varphi=90^\circ$). From the 12 configurations calculated with DFT, this is the only one that might lead to dissociation. Within this configuration, the activation energy for dissociation is about 1.1 eV if the molecule is initially in the spin-triplet ground state. However, a small activation energy of 0.1 eV is required if the O_2 molecule is initially in the spin-singlet excited state. This feature suggests that O_2 dissociation on Ag(100) can be enhanced by first exciting the molecules to the singlet state. The idea will be confirmed by the 6D dynamical study performed in Sec. III.

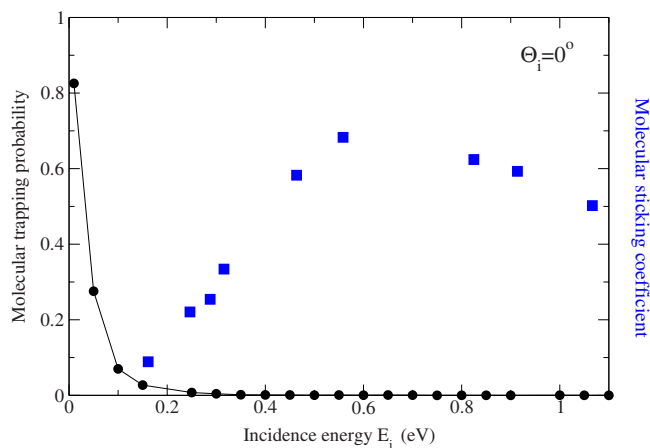


FIG. 5. (Color online) Molecular trapping probability as a function of the incidence energy. Closed black circles show the results obtained with the SP PES. For comparison, we also show the molecular sticking probability obtained in the experiments in Ref. 11. Although related, a direct comparison between molecular adsorption and molecular trapping is incorrect (see text for details).

III. DYNAMICS OF THE O_2 MOLECULES ON THE Ag(100) SURFACE

The dynamics is analyzed with classical trajectory calculations using a conventional Monte Carlo procedure to sample the initial (X, Y) values over the unit cell and the molecular orientation. All results discussed along this section are derived from the evaluation of 5000 trajectories. Each trajectory starts at $Z=9$ Å from the surface. At this distance, the SP PES value for O_2 at its equilibrium bond length r_{eq} is zero. Under these conditions we perform a quasiclassical calculation that includes the initial zero point energy of the molecule. We use a classical microcanonical distribution of r and its conjugate momentum p_r for O_2 in its ground rovibrational state. The initial zero point energies obtained, respectively, from SP and NSP calculations are $E_0=97.5$ meV for the molecule in the triplet ground state and $E_0=93.3$ meV for the molecule in the excited singlet state.

Along the trajectory calculations we distinguish the following reaction events: (i) dissociation, when the molecule internuclear distance reaches the value $r=2.4$ Å ($\sim 2r_{eq}$) with a positive radial velocity; (ii) reflection, when the molecule center reaches the initial starting distance of 9 Å with a positive Z -velocity; and (iii) molecular trapping, when the molecule is neither dissociated nor reflected after 15 ps.

Calculations performed with the adiabatic SP PES show that molecular trapping is the dominant event for very low incident energies, with probability close to 1 for $E_i < 10$ meV. The absence of energy barriers in the entrance channel for most of the configurations is what causes the trapping of practically all the incident low-energy molecules in the potential well. As the incidence energy increases, molecular trapping is abruptly suppressed in favor of molecular reflection. For $E_i > 0.1$ eV, the probability is already less than 0.1. The results are shown in Fig. 5 together with the molecular sticking probability measured by Vattuone *et al.*¹¹ The existence of molecular trapping in our theoretical calculations might be linked to molecular adsorption processes. Experimentally, molecular adsorption occurs for incidence

energies above 0.1 eV with a maximum sticking probability of about 0.7 for $E_i \sim 0.6\text{--}0.8$ eV. These measurements are clearly at variance with our calculations, but there are reasons to understand partially the differences. Note, for example, that the present theoretical model neglects energy dissipation through the surface. Friction effects due to electron-hole excitations are not expected to play a significant role.⁶⁰ However, phonons and any possible rearrangement of the surface atoms, not included in our calculations, could affect the adsorption process. For instance, the DFT adsorption energy of O₂ in the potential well over hollow changes to about 0.1 eV when surface relaxation is allowed. To some extent, the observed discrepancies between the theoretical molecular trapping and the experimental molecular sticking probabilities may be due to the limitations of the model: the inclusion of dissipation channels and surface relaxation will probably favor molecular trapping in a larger energy range. Nevertheless, we find it difficult to understand how these two factors could change our results at low energies in a qualitative manner.

Discrepancies between adiabatic calculations and experiments are by no means new when dealing with the reactivity of O₂ on metal surfaces. The role of transitions between potential energy surfaces that model different charge states of O₂ interacting with Ag surfaces has been discussed by various authors.^{61–63} Interestingly, the experimental low dissociative adsorption of O₂ on Al(111) has been explained using four semiempirical PESs of reduced dimensionality (3D) that characterize distinct extents of charge transfer from the metal to the molecule.⁶⁴ More recently and using a unique 6D PES, the same experimental data are explained if the spin state of the incident O₂ is constrained to a triplet state.³⁶ We are working along this direction to determine whether these kinds of effects are responsible for the activated behavior of the molecular adsorption probability.

In the following, we focus on the dissociation process for which the two main approximations, i.e., frozen surface and nonenergy dissipation mechanisms, have widely shown to be valid.^{65–70} As already mentioned, there is no experimental evidence of dissociative adsorption in the O₂/Ag(100) system at least for the initial kinetic energies used in the experiments (up to ~ 1 eV). This observation agrees with the dissociation probabilities we obtain from classical dynamics calculations for the O₂ molecules initially in the spin-triplet ground state (adiabatic SP PES). The results are shown in Fig. 6 (left panel) for different incidence angles Θ_i . The minimum energy required to observe dissociation is about 1.05 eV at normal incidence and slightly higher as Θ_i increases. The dissociative sticking coefficient shows an increasing behavior with E_i for all Θ_i except for $\Theta_i=60^\circ$ for which there is no dissociation. Despite the large incidence energies considered, the probability of dissociation is, in all cases, extremely small ($<0.05\%$). Regarding the Θ_i -dependence, neither the total energy nor the normal energy scaling is obtained.

The dissociative dynamics in this system is rather simple. The analysis of the trajectories, followed by the dissociating molecules, shows that it is basically ruled by high energy barriers (around 1.05 eV) existing between 1 and 2 Å

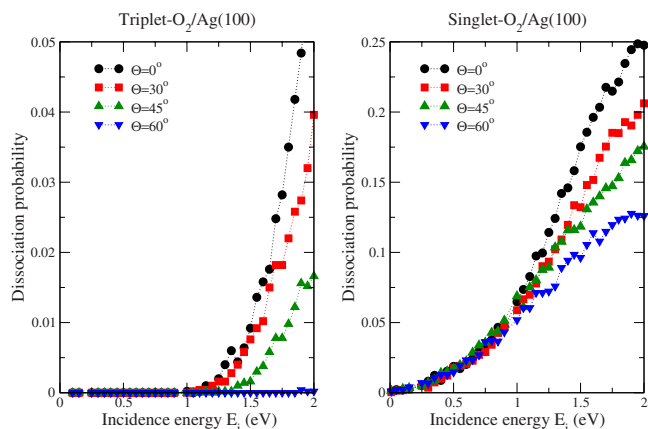


FIG. 6. (Color online) Dissociative sticking probability of O₂ on the Ag(100) surface as a function of the initial kinetic incidence energy E_i . Left panel: O₂ is initially (far from the surface) in the spin-triplet ground state. Right panel: O₂ is initially in the spin-singlet excited state. Different symbols correspond to different incidence angles.

from the surface in positions midway between the bridge and the hollow sites. Most of the molecules that approach over these positions with an incidence energy large enough to overcome the energy barriers dissociate. Otherwise they are reflected. The dissociating trajectories are quite direct in the sense that neither trapping around the molecular well over hollow nor rebounds in the surface vicinity are observed. In view of the dissociation mechanism we obtain, nonadiabatic spin effects as those discussed for molecular adsorption are not expected to play a significant role. The energy barriers of the constrained spin-triplet PES in the entrance channel have to be lower than 1 eV, the difference between the SP and NSP PES in vacuum. Therefore, dissociation will be still ruled by the barriers existing close to the surface, which are larger.

The low efficiency of O₂ to dissociate on the Ag(100) surface is clearly improved if the molecules are initially excited into the singlet state. In such a case, O₂ molecules do dissociate even for incidence energies of about 50 meV. The calculation of the dynamics followed by singlet O₂ is more involved. The NSP PES provides the behavior of singlet O₂ for the incoming part of the trajectory, which describes the approach to the surface. Close to the surface, the NSP PES merges with the SP PES. Thus, the molecules lose their memory on the initial spin-singlet state. From this point, we assume that those molecules moving away from the surface follow the SP PES, i.e., the minimum energy configurations. Our results for spin-singlet O₂ are represented in the right panel of Fig. 6. The dissociating probability exhibits a clear dependence on the total incidence energy up to energies of about 1 eV. For higher energies, it deviates from total energy scaling but neither following normal energy scaling. The reason is that singlet O₂ with incidence energies below 1 eV dissociates after suffering a small number of rebounds. In this energy range, the mean number of rebounds is rather similar for all Θ_i ; it is larger than 10 for $E_i < 0.25$ eV and about 5 otherwise. For incidence energies above 1 eV, direct dissociation is the dominant mechanism, particularly at low incidence angles. Still there is a rather constant fraction of molecules that dissociates after bouncing near the surface.

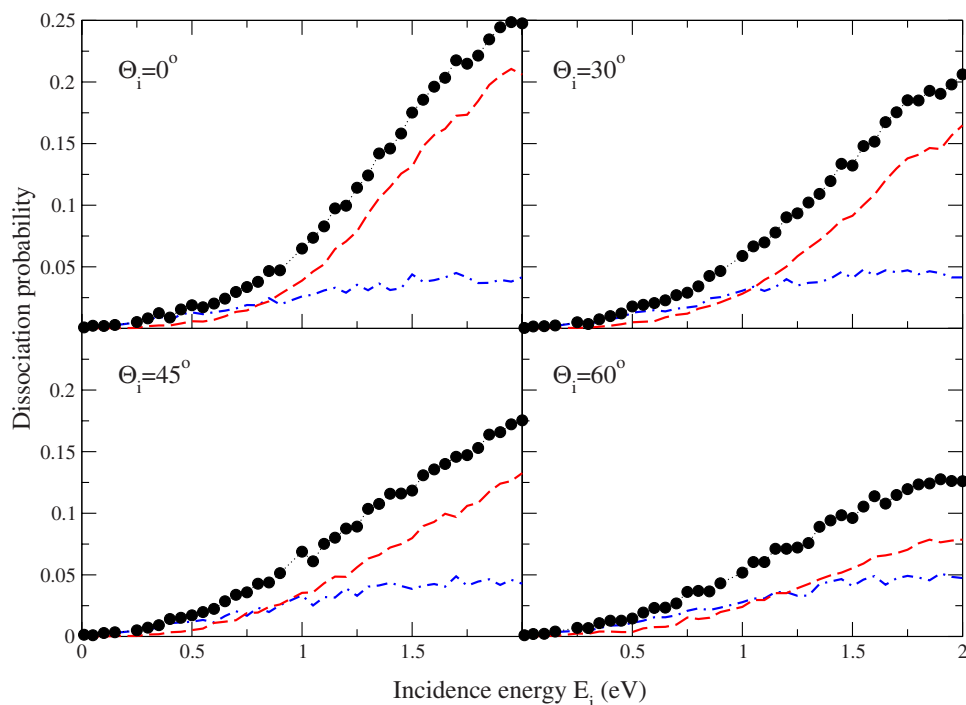


FIG. 7. (Color online) Dissociative sticking probability of spin-singlet O_2 as a function of the initial kinetic incidence energy E_i (small black circles). Different panels correspond to different incidence angles. Red dashed and blue dashed-dotted lines show the contribution to the dissociation probability coming from the direct and the indirect channels, respectively.

All these features are shown in Fig. 7. The dissociation probability S_0 is separated into two contributions: the direct mechanism, defined by those molecules that dissociate after two rebounds at most (red dashed curves), and the indirect mechanism, defined by molecules dissociating after more than two rebounds (blue dashed-dotted curves).

The efficiency of the singlet- O_2 molecules to dissociation is remarkable. At normal incidence, it can be understood in terms of the extra energy of about 1 eV necessary to excite the molecule from the triplet to the singlet state. This excitation energy plays the role of extra kinetic incidence energy. Interestingly, as the incidence angle increases, the use of spin-excited molecules is more efficient than the use of molecules in the triplet state but with higher kinetic energies. The left and right panels of Fig. 8 show the dissociative sticking probability of singlet (filled red circles) and triplet (filled blue triangles) O_2 at normal and $\Theta_i=45^\circ$ incidence, respectively. The open triangles represent the sticking probability of the triplet molecules shifted to the left by -1 eV, i.e., the energy difference between the triplet and the singlet states. At normal incidence, the shifted data practically lie on the curve representing the sticking probability of the singlet O_2 . At $\Theta_i=45^\circ$, the sticking probabilities of singlet O_2 are a factor of 2 larger than the shifted data. All these results support the high efficiency of the singlet O_2 to improve reactivity under any incidence condition.

We have analyzed the reasons for the dissociation enhancement reached with the singlet O_2 . The surface-molecule interaction is different depending on whether the molecule is initially in the triplet ground state or in the singlet excited state. The NSP PES cannot be reproduced from the SP PES by a simple energy shift. Analyzing the trajectories in both cases, we observe that for the singlet O_2 , there

are paths to dissociation not allowed for triplet O_2 . In particular, this effect is more important for off-normal incidence conditions. At any incidence angle, most of the singlet O_2 reach a distance of 1.5 \AA from the surface. This distance is only reached by triplet O_2 under normal incidence. The insets in each panel of Fig. 8 show the molecule center position over the surface unit cell of the dissociating molecules as first reaching the distances $Z=3.5 \text{ \AA}$ and $Z=1.5 \text{ \AA}$. Upper (lower) panels show the evolution of triplet O_2 with incidence

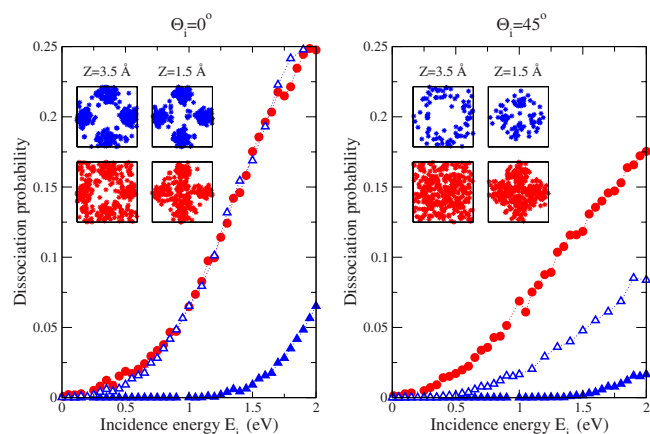


FIG. 8. (Color online) Dissociative sticking probability as a function of the incidence energy E_i for normal (left panel) and 45° (right panel) incidence angles. Probabilities calculated for the spin-singlet and spin-triplet O_2 are represented by filled red circles and filled blue triangles, respectively. Open blue triangles are the spin-triplet results shifted by -1.0 eV (the initial potential energy difference between both calculations). The insets show the position of the molecule center over the unit cell, when the dissociating molecules are at $Z=3.5 \text{ \AA}$ (left panels) and $Z=1.5 \text{ \AA}$ (right panels). Upper (lower) panels display the evolution of initially spin-triplet (spin-singlet) O_2 for an incidence energy of 2.0 eV (1.0 eV).

energy of 2 eV. Lower panels display the same information for singlet O₂ with incidence energy of 1 eV, which corresponds to the same total energy of 2 eV. At normal incidence, the dissociation paths of the singlet and triplet molecules are rather similar. At $\Theta_i=45^\circ$, we observe that there are more available paths for the singlet O₂ despite the lower kinetic energy.

IV. CONCLUSIONS

Dissociation of spin-triplet O₂ is an activated process, characterized by minimum energy barriers of about 1.05 eV that exist between bridge and hollow sites in the region of 1–2 Å from the surface. Only molecules coming over these sites with a kinetic energy large enough to surmount such barriers dissociate. Our findings explain the observed absence of dissociation in molecular beam experiments that were performed up to incidence energies of ~ 1 eV.

We propose a possible alternative to favor O₂ dissociation on this surface: the use of molecular beams with O₂ excited to the spin-singlet state. Our dynamics calculations suggest then that dissociation also occurs for thermal molecules ($E_i < 0.1$ eV). Furthermore, for incidence energies in the range where spin-triplet O₂ starts to dissociate (around 1.05 eV), the probability might increase by almost one order of magnitude. The efficiency to dissociation reached with the excited spin-singlet molecules is remarkable. In particular, under off-normal incidence conditions, the reactivity enhancement induced by singlet O₂ exceeds the one that would be obtained with an initial kinetic extra energy of 1 eV, i.e., the excitation energy of the spin-singlet state. The reason for such efficiency is that spin-triplet and spin-singlet O₂ interact differently with the surface. As a result, the number of available paths to dissociation is significantly larger for the latter. We hope that our findings, which may possibly be generalized to other Ag surfaces, will stimulate further molecular beam studies to check whether our predictions on the *spin* efficiency to dissociation can be supported experimentally.⁷¹

Molecular adsorption still remains an open question that requires further analysis. Experimentally, O₂ adsorption on Ag(100) is an activated process that occurs for incidence energies above 0.1 eV. Such a behavior was attributed to the existence of energy barriers from gas phase to chemisorption. Our DFT calculations of the SP PES, in which the system evolves along the minimum energy configurations without any restriction to the O₂ spin state, show a total absence of energy barriers in the entrance channel for most of the configurations. According to our classical trajectory calculations, this large-distance property of the adiabatic PES is indeed what causes the dynamic trapping around the hollow site of practically all molecules with incident energies below 0.05 eV. Despite the limitations of the present calculations to describe molecular adsorption since surface relaxation, as well as energy dissipation to the surface, is neglected, the discrepancy between theory and experiments at these low energies is surprising. None of the two neglected factors are expected to modify the dynamics in the entrance channel. The disagreement might be related to nonadiabatic spin effects. Further calculations in which the spin state of the in-

cident molecule is constrained to the spin-triplet state³⁶ would help to disentangle the ultimate reasons for the discrepancy between DFT results and experiments. In this respect, more experimental measurements aimed to identify the spin state of the reflected or desorbing molecules will provide invaluable information to support or not the relevance of spin effects in the reactivity of O₂ on different metal surfaces.

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