

Abstractive dissociation of oxygen over Al(111): A nonadiabatic quantum model

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The dissociation of oxygen on a clean aluminum surface is studied theoretically. A nonadiabatic quantum dynamical model is used, based on four electronically distinct potential energy surfaces characterized by the extent of charge transfer from the metal to the adsorbate. A flat surface approximation is used to reduce the computation complexity. The conservation of the helicopter angular momentum allows Boltzmann averaging of the outcome of the propagation of a three degrees of freedom wave function. The dissociation event is simulated by solving the time-dependent Schrödinger equation for a period of 30 femtoseconds. As a function of incident kinetic energy, the dissociation yield follows the experimental trend. An attempt at simulation employing only the lowest adiabatic surface failed, qualitatively disagreeing with both experiment and nonadiabatic calculations. The final products, adsorptive dissociation and abstractive dissociation, are obtained by carrying out a semiclassical molecular dynamics simulation with surface hopping which describes the back charge transfer from an oxygen atom negative ion to the surface. The final adsorbed oxygen pair distribution compares well with experiment. By running the dynamical events backward in time, a correlation is established between the products and the initial conditions which lead to their production. Qualitative agreement is thus obtained with recent experiments that show suppression of abstraction by rotational excitation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1635360]

I. INTRODUCTION

Oxidation of metal surfaces is a phenomenon of great importance in various fields from heterogeneous catalysis to corrosion.¹ The formation of oxides which lead to passivation and depassivation of surfaces² is a complex multistage reaction that is not completely understood on a molecular level. The initial step is dissociation of oxygen followed by the formation of an ordered monolayer. Additional dissociation, together with penetration of oxygen into the subsurface, leads to a reconstruction of the surface terminating in oxide layers. The present study is devoted to the first step of oxygen dissociation on a clean metal surface.

Oxygen dissociating over a clean aluminum surface is puzzling. Experimental measurement of the dissociation probability finds no threshold to the reaction.³ But, the reaction yield increases with incident kinetic energy until saturation at about 0.6 eV. Compared to the well-established system of hydrogen dissociation on copper, such an *S* curve would suggest a barrier of approximately ~ 0.3 eV.^{4,5} Density functional theory (DFT) calculations of the adiabatic potential energy surface, however, find no barrier to dissociation.^{6–8} Scanning tunneling microscope (STM) experiments of dissociated oxygen on a fresh Al(111) surface conducted by Ertl and Brune^{9,10} found, surprisingly, lone ad-

sorbed atoms with a mean separation of 80 Å between neighboring adsorbates. Wahnstrom *et al.*¹¹ performed extensive simulations of oxygen atoms moving along the surface and concluded that, at most, the dissociated pair can reach a separation of 12 Å. An alternative explanation of the experimental data is that ballistic trajectories of negatively charged oxygen atoms attracted to the surface by their image charge can lead to large distances between the atoms of the dissociated pair. Recently, Hasselbrink and Kummel,^{12,13} using a molecular beam source, found that the distance distribution among adsorbates is strongly dependent on the incident kinetic energy. High kinetic energy leads to appearance of adsorbed pairs of oxygen atoms on the surface, in contrast to low energies where large separations were observed. Using a REMPI laser technique, ejected neutral oxygen atoms were detected in the gas phase. Such events in which a lone oxygen atom remains on the surface and the second emerges to the gas phase were termed abstractive dissociation. Energetically this process can take place because of the strong oxygen–aluminum bond. The ratio between the yields of abstractive events to dissociative adsorption was found to decrease with increasing incident kinetic energy of incoming molecules. At the same time the total yield of neutral atoms emerging to the gas phase increased with incidence kinetic energy. However, no oxygen negative ions could be detected in the gas phase.

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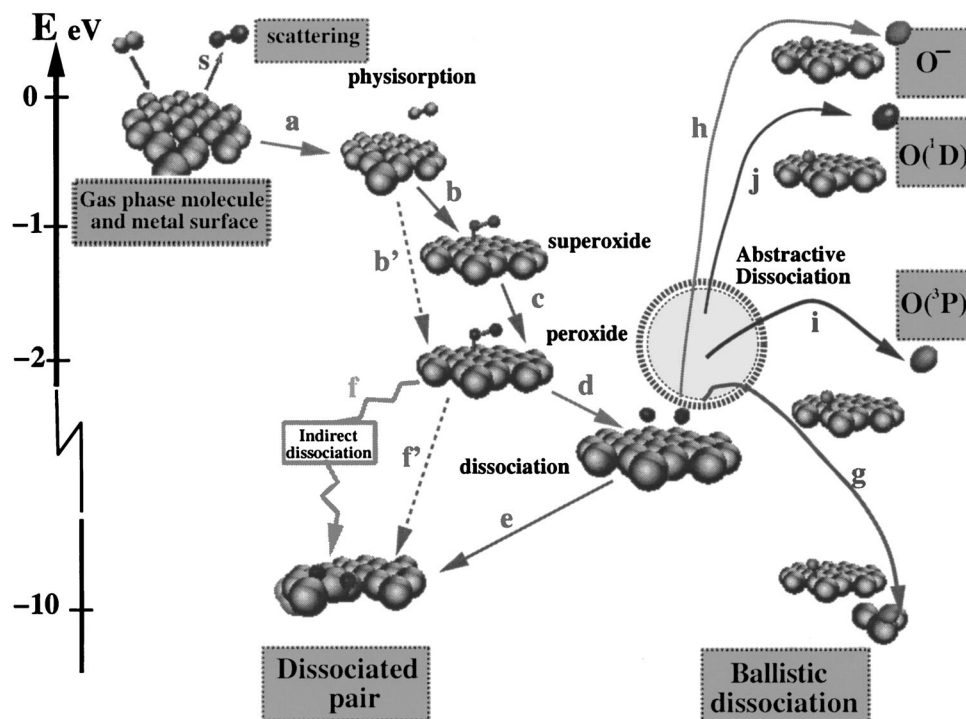


FIG. 1. Flowchart of the possible events leading to the dissociation of oxygen on aluminum. The asymptotic species are designated on the frame. The reactants are located in the upper left corner. The arrows represent charge transfer events. The dashed and broken arrows represent secondary reaction roots.

The present paper is devoted to a comprehensive theoretical and computational framework which describes all the above phenomena in a consistent way. The framework is based on a quantum dynamical nonadiabatic description emphasizing the charge transfer encounters from the metal to the oxygen species and vice versa. This approach has to abandon the more traditional description of a chemical reaction as taking place on a single adiabatic potential energy surface (PES). Regrettably, we have to partially abandon the powerful density functional methods (DFT) which have become popular in supplying structure and adiabatic potential energy surfaces for adsorbates on metal surfaces.¹⁴

The nonadiabatic framework has been employed previously for the dissociation of oxygen on various metals where the diabatic surfaces used represent charged oxygen species. The explored substrates included Ag,^{15,16} Cs, and Al.^{17–20} A similar nonadiabatic description was used to study dissociation of nitrogen on metal surfaces.^{19,21} Evidence of the important role of excited states in the dynamics of adsorbates has been obtained by photodesorption and photochemical reactions on metal surfaces.^{22–24} Recent 2PPE experiments using ultrashort pulses have provided direct evidence to the electronic character of the phenomena.²⁵ These experiments are in line with the Menzel, Gomer, Redhead (MGR) and Antoniewicz models^{26,27} that emphasize the dynamical role of the excited state. It is found that an excited state lifetime of 3–50 fs is in line with photodesorption experiments. These time scales are on the same order of magnitude as the time scale of direct dissociation, ~20 fs. The short time scale means that an effective width can be associated with each electronic surface due to the time-energy uncertainty. It is then more appropriate to consider each electronic surface to

represent a band of states with a finite energy spread. This approach is also behind the more rigorous *surrogate Hamiltonian* method.^{28,29}

A complete 6D solution of the nonadiabatic dynamics of oxygen is beyond current computational ability. However, by employing a flat surface approximation a cylindrical symmetry can be used to reduce the computational task. Within this description, the influence of translational, vibrational, and rotational degrees of freedom is accounted for. In a time-dependent approach the initial wave packet represents an approaching oxygen molecule. The time evolution of this wave function is thus followed from the gas phase to a wave function representing a dissociated pair of oxygen molecules close to the surface. The final fate of the dissociated oxygen atoms is determined by employing a semiclassical stochastic molecular dynamics (MD). The method is composed of an accurate quantum calculation of the surface hopping probability with a classical MD that includes energy transfer between the adsorbate and the substrate. The combination quantum and semiclassical MD methods allows a complete simulation of the process from its initial state to the final products. As a result, direct comparison to experimental results is possible.

The paper is constructed as follows: Section II describes the theoretical model starting with a description of the potential energy surfaces, the methods employed to solve the dynamics and the tools of analysis. Section III describes the main results of the computational model. Section IV is devoted to the discussion of the possible mechanisms that lead to specific products and to a comparison with an adiabatic description. The conclusions are given in Sec. V.

II. MODEL

When oxygen reacts with an aluminum surface, a complex dynamical process takes place involving many intermediate states accessed by nonadiabatic charge transfer events. Figure 1 displays a possible road map of the main processes which start from gas phase oxygen molecule, and lead to final products on an aluminum surface and in the gas phase.

- (i) The initial state of the encounter is a gas phase molecular oxygen approaching a clean aluminum surface. The initial wave function is described by Eq. (2.12).
- (ii) Process a represents the approach of the oxygen to the substrate and the formation of the physisorption state. The physisorption potential energy surface is described in Sec. II B 1.
- (iii) Process s represents the backscatter of nonreactive oxygen molecules.
- (iv) Process b represents a nonadiabatic charge transfer from the metal to the approaching molecule that results in the formation of a superoxide state. The corresponding PES is described in Sec. II B 2, while the nonadiabatic coupling potential between this state and channel a is described in Sec. II B 5. Process b' represents an additional charge transfer state that leads to the formation of a peroxide. The difference between process b and b' is in the amount of the charge transferred from the aluminum surface to the oxygen molecule.
- (v) Process c represents a transition between the superoxide and the peroxide states.
- (vi) Process d represents the breakup of the molecule leading to dissociation.
- (vii) Process e represent the formation of a dissociative state in which two oxygen atoms adsorbed to the surface. The corresponding potential are described in Sec. II B 4.
- (viii) Process f represents a slow indirect dissociation originating in the peroxide state. This event is caused by energy loss of the molecule to the surface. Process f' is a rare direct dissociation from the peroxide state which is due to tunneling.
- (ix) Process g represents the ballistic dissociation. Here, one oxygen atom is adsorbed in the vicinity of the initial impact point on the solid surface, whereas the other atom undergoes a ballistic-like motion and finally sticks to the surface far from the initial impact point.
- (x) Process h represents an abstractive dissociation channel. In this case, one atom adsorbs to the surface close to the point of impact, while the other atom escapes to the gas phase as a negative ion.
- (xi) Process i represents an additional abstractive dissociation channel with a different outcome in the gas phase. A back charge transfer from the outgoing ion to the surface results in a gas phase $O(^3P)$.
- (xii) Process j represents a back charge transfer from the outgoing ion to the surface that results in a gas phase $O(^1D)$.

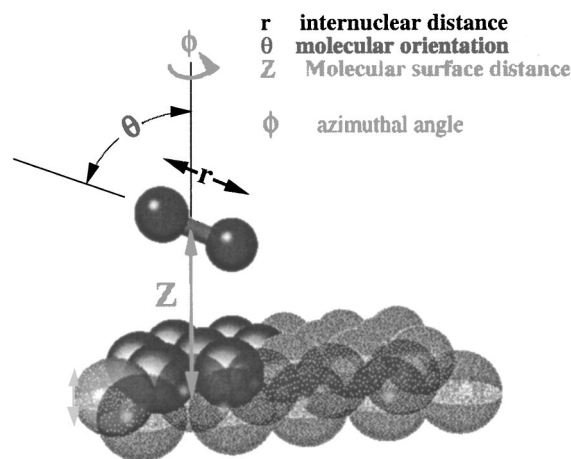


FIG. 2. Coordinate systems of the molecular surface encounter. r is the internuclear distance in the molecule. θ is the orientation angle of the molecule relative to the surface normal. Z is the distance of the molecular center of mass to the surface, and ϕ is the azimuthal angle. Other coordinates used are: z_1 and z_2 the distances of the oxygen atoms to the surface and $\rho = \frac{1}{2}r \sin \theta$ is the projection of r on the direction parallel to the surface.

The computational model for the reaction is described in Fig. 1. The first step is to acquire a PES that describes all the electronic states participating in the reaction (Sec. II B). This is followed by a quantum dynamical description that traces the evolution of the multichannel wave function from the initial state through the nonadiabatic transitions to dissociation. The quantum wave packet in the dissociation state is used to initiate stochastic molecular dynamics (MD) trajectory simulations. The calculation includes energy dissipation due to interaction with the surface degrees of freedom. The fate of each oxygen atom is followed by using surface hopping semiclassical simulation. The possibility of back charge transfer to form gas phase oxygen atoms is examined by quantum-mechanical calculations at the crossing points.

The output of the calculations are yields of different products (branching ratios) and the distance distribution among adsorbed atoms. In addition, the energy and angular distributions of the gas phase products are obtained, i.e., molecular oxygen, singlet, triplet, and ionic oxygen atoms. In the following we shall describe in more detail the various aspects of the model used.

A. Coordinate system

The coordinates describing the encounter of an oxygen molecule with the aluminum surface consists of six degrees of freedom of the oxygen atoms and an additional three degrees of freedom for each Al atom included in the description (see Fig. 2). Quantum computational effort scales exponentially with the number of degrees of freedom. Therefore, to simulate the encounter with its full dimensionality is not realistic. As a consequence, a reduced dimensional approach is adopted where only the most significant coordinates are included explicitly. For the charge transfer events at the initial stages of the encounter, the surface nuclear motion can be neglected due to large time scale differences. Far from the surface only a very small band of electronic excitations close to the top of the Fermi level is coupled to the charge transfer

event. This band is represented by a finite number of electronic degrees of freedom. Next, it is assumed that the surface is flat, which means that surface corrugation is neglected. This assumption allows an elimination of the translational coordinates parallel to the surface. By the use of cylindrical symmetry, the number of effective degrees of freedom is further reduced to four (cf. Fig. 2). The azimuthal angle, ϕ , that describes the helicopter motion of the molecule is only coupled to the remaining degrees of freedom by the centrifugal potential, and therefore can be included implicitly. The choice of the coordinates to describe the remaining three degrees of freedom is subject to convenience. For the description of the potential energy surface, the coordinates (z_1, z_2, r) were chosen. For the kinetic energy operator (Sec. II C 1) the coordinates chosen are $\rho = \frac{1}{2}r \sin \theta$, $c = \sin \theta$, and Z , where z_i corresponds to the separation of O_i from the surface, r is the molecular coordinate, θ the polar angle, and z the separation of the molecular center of mass from the substrate (cf. Fig. 2).

This reduced set of coordinates is sufficient to describe the short-time nonadiabatic events leading to dissociation. Once the molecule has dissociated, additional degrees of freedom are included which allow energy loss to the surface and the tracing of individual atomic trajectories.

B. Potential energy surfaces

In the nonadiabatic approach for modeling chemical reactions over solid surfaces, all species that participate in the encounter are assigned an exclusive electronic state. The first step is to develop a potential energy surface that describes each participating chemical species together with its nonadiabatic coupling terms. In the asymptotic region these species are well defined in a particular electronic state. Their asymptotic energy can be estimated from the knowledge of the surface work function, and the electronic state of the gas phase particle. The oxygen molecule has many low-lying electronic states; in the present study only a minimal set is considered. At decreasing particle surface separation the intermolecular bond weakens and new chemical bonds are formed with the metal surface. When the event involves charge transfer, there is an electrostatic stabilization due to the interaction with the image charge. (Despite the large electronic changes a diabatic assignment is kept for each species starting from the isolated asymptote to close range with the surface.)

Ab initio calculations supply adiabatic potential energy surfaces. For studies in gas surface encounters, the most common electronic structure method is the density functional theory (DFT). The drawback of this method is that it is designed to calculate only the ground electronic potential energy surface. This means that the traditional DFT approach cannot supply direct input for the task of constructing diabatic potential energy surfaces. For the $O_2/\text{Al}(111)$ system, extensive first principle DFT calculations have been performed by Yourdshahyan *et al.*^{6–8} By analysis of the charge distribution or local density of states and by searching for kinks in the PES, charge transfer states were identified where a negative charge from the surface is stabilized on the incoming molecule.

The approach chosen in the present study, on the other hand, is to construct diabatic semiempirical PESs for each species as previously described in detail.³⁰ The DFT calculations could be used in the construction, provided a reliable assignment of potential wells could be found. To facilitate a comparison between the two approaches, the ground-state adiabatic potential energy surface is calculated by diagonalizing the diabatic semiempirical potentials. A possible complication in the comparison arises since the DFT calculations were fully relaxed, meaning that the aluminum atoms are at their minimum energy position. The present study models an ultrafast dissociation event during which the metal atoms do not have time to relax. Following is a short review of the semiempirical PESs used to examine the dissociative adsorption of O_2 onto $\text{Al}(111)$. A MATLAB program reconstruction of the potential is available.³¹

1. Physisorption

Far from the surface, a neutral molecule is attracted to the surface by van der Waals forces. At short molecule surface separation, Pauli repulsion takes over. This phenomenon can be cast into a Born–Mayer potential form to describe the interaction between each of the oxygen atoms and the surface (z_1, z_2) . A Morse potential is used to describe the intermolecular potential along the molecular coordinate (r)

$$\begin{aligned} \hat{V}_{\text{phys}}(z_1, z_2, r) = & A e^{-b z_1} - \frac{C_3}{z_1^3} (1 - \Gamma_2(z_1, 0, 2b)) \\ & + A e^{-b z_2} - \frac{C_3}{z_2^3} (1 - \Gamma_2(z_2, 0, 2b)) \\ & + D_{O_2} (1 - e^{-\alpha_{O_2}(r - r_{eq})})^2. \end{aligned} \quad (2.1)$$

The incomplete gamma function, $\Gamma_{n=2}$, is used as an interpolation function from the gas phase to the adsorbed state. This interpolation eliminates the singularities of the long range part of the potential close to the surface.³²

$$\Gamma_m(z, z_0, a) = \sum_{k=0}^{k=m} \frac{(a(z - z_0))^k}{k!} e^{-a(z - z_0)}. \quad (2.2)$$

The potential energy surface is shown in Fig. 3, while the parameters used are summarized in Table I.

2. Superoxide

The gas phase O_2^- molecular ion is the asymptotic origin of the superoxide species. Compared to neutral O_2 the molecular bond weakens and the equilibrium bond length increases. Upon approaching the surface this state is stabilized by its image charges induced in the metal. Close to the surface, exponential repulsive interactions take over. A Morse potential is used to describe the molecular bond in r_{12} .

The O_2^-/Al PES has the form

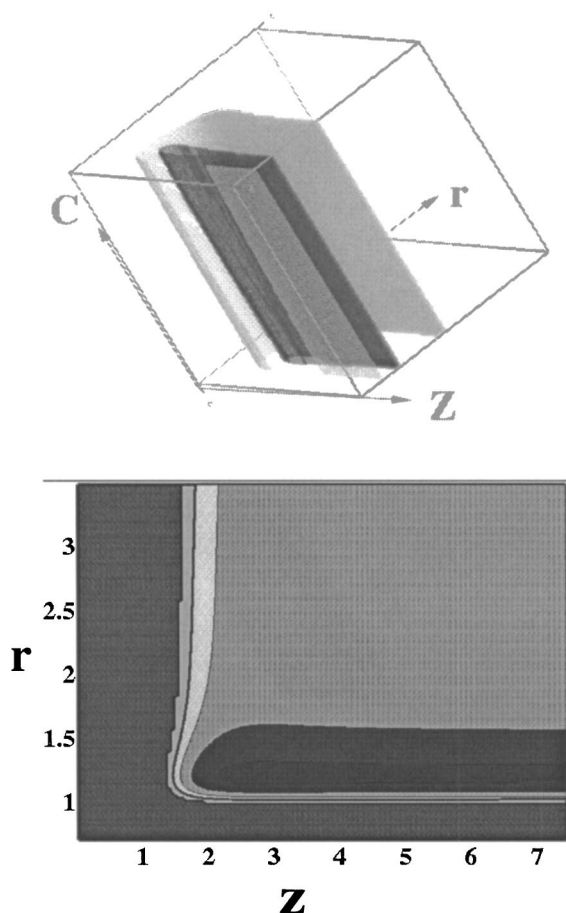


FIG. 3. A contour plot and a stereoscopic projection of the physisorption PES. Top: isoenergetic potential values. $c = \sin(\theta)$, where θ is the angular orientation of the molecule with respect to the surface normal ($c = 1$ for the horizontal orientation and $c = 0$ for the perpendicular orientation). Bottom: contour plot of a cut in the PES at the perpendicular orientation. Distance is in Å.

$$\begin{aligned} \hat{V}_{O_2}^-(z_1, z_2, r) &= A'e^{-b'z_1} + A'e^{-b'z_2} - \frac{(Z_{efc}^{rcm}(z_1) + \delta)^2}{2z_1} \\ &- \frac{(Z_{efc}^{rcm}(z_2) - \delta)^2}{2z_2} - \frac{(Z_{efc}^{rcm}(z_1) + \delta)^2}{\sqrt{(r^2 - (z_1 - z_2)^2) + (z_2 + z_1)^2}} \\ &- \frac{(Z_{efc}^{rcm}(z_2) - \delta)^2}{\sqrt{(r^2 - (z_1 - z_2)^2) + (z_2 + z_1)^2}} + \alpha(r\delta)^2 \\ &+ D_{O_2} - (1 - e^{-\alpha_{O_2} - (r - r_{eq})})^2 + Wf + Ea(O_2). \quad (2.3) \end{aligned}$$

The charge distribution in the molecule can vary by an

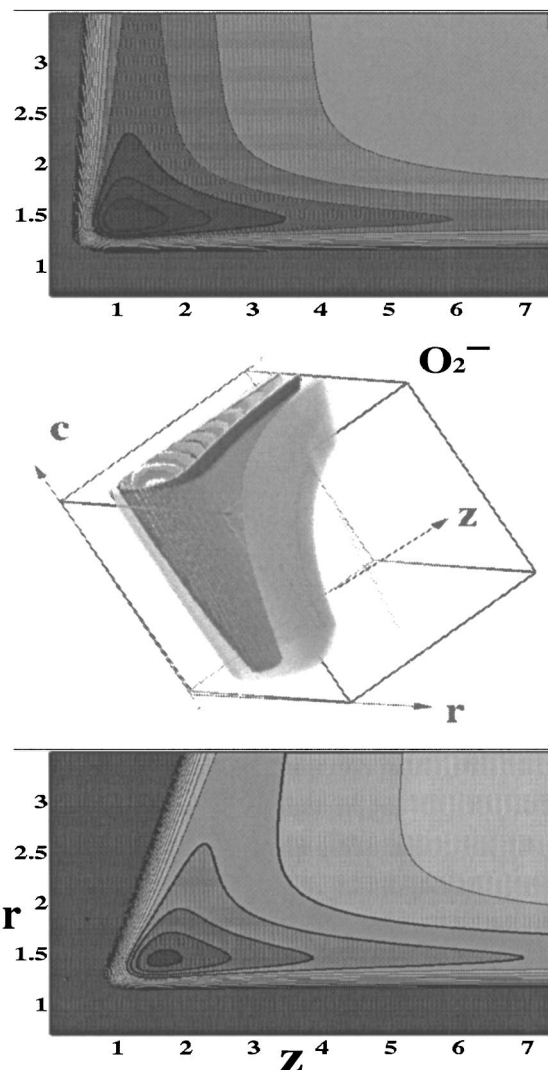


FIG. 4. The superoxide potential. Middle: PES isoenergetic potential values. Top: contour 2D plot of the horizontal orientation. Bottom: contour 2D plot of the perpendicular orientation. The potential well of the perpendicular orientation is about .5 eV higher in energy than the one in the horizontal orientation. There is also a location difference between the orientations of 0.3 Å in the coordinate z . Distance is in Å.

amount δ that changes as a function of the molecular orientations. The magnitude of δ is determined by an optimization of the electrostatic contribution leading to

$$\delta = \frac{Z_{efc} \left(\frac{1}{z_2} - \frac{1}{z_1} \right)}{(4r^2\alpha)}, \quad (2.4)$$

where α is the polarization of the molecule. The potential is

TABLE I. Parameters of the physisorption PES.

A (eV)	b (Å ⁻¹)	C ₃ (eV Å ³)	D _{O₂} (eV)	α_{O_2} (Å ⁻¹)	r_{eq} (Å)
Repulsive strength	Repulsive range	VDW attraction	Morse dissociation	Morse range	Equilibrium distance
2350	3.13	1.79	5.1	0.3825	1.208

TABLE II. Parameters of the superoxide PES.

A (eV)	b ($\text{\AA}^{-1}$)	z_{eq} ($\text{\AA}$)	$D_{O_2^-}$ (eV)	$\alpha_{O_2^-}$ ($\text{\AA}^{-1}$)	r_{eq} ($\text{\AA}$)	Wf (eV)	$Ea(O_2)$ (eV)
900	3.73	1.6	3.1	0.243	1.4	4.2	0.46

shown in Fig. 4, while the parameters used are summarized in Table II. Here, α stands for the polarizability of O_2^- .

In Eq. (2.3) Wf represents the work function of the Al surface and Ea stands for the molecular electron affinity. The effective charge assigned to the atoms in the adsorbed molecule is interpolated from the gas phase value to its lower value on the metal surface^{30,33,34} using the form

$$Z_{efc}(z) = Z_{efc}^{ad} \text{ for } z < z_e, \quad (2.5)$$

$$Z_{efc}(z) = Z_{efc}^g - (Z_{efc}^g - Z_{efc}^{ad})(1 - e^{-\gamma/z}) \text{ for } z > z_e.$$

For the superoxide state, the effective atomic charge varies

from 0.5 units per atom in the gas phase to 0.4 for an adsorbed molecule, and γ was chosen to be 0.6.

3. Peroxide

The gas phase O_2^{-2} molecular ion is the asymptotic origin of the peroxide species. However, in the gas phase this ion is unstable and dissociates. However, on the surface it is stabilized by the image charge. The peroxide potential function is identical to that of the superoxide. The difference is in the parameters describing bond length, bond strength, effective charge, and charge distribution.

The O_2^{-2} potential is described as

$$\begin{aligned} \hat{V}_{O_2^{-2}}(z_1, z_2, r) = & A''e^{-b''z_1} + A''e^{-b''z_2} - \frac{(Z_{efc}'^{rcm}(z_1) + \delta')^2}{2z_1} - \frac{(Z_{efc}'^{rcm}(z_1) - \delta')^2}{2z_2} - \frac{(Z_{efc}^{rcm}(z_1) + \delta)^2}{\sqrt{(r^2 - (z_1 - z_2)^2) + (z_2 + z_1)^2}} \\ & - \frac{(Z_{efc}^{rcm}(z_2)^2 - \delta)}{\sqrt{(r^2 - (z_1 - z_2)^2) + (z_2 + z_1)^2}} + \frac{Z_{efc}'^{rcm}(z_1)Z_{efc}'^{rcm}(z_2)}{r} \\ & + D_{O-O}(1 - e^{-\alpha_{O_2^{-2}}(r - r_{eq})})^2 + \alpha(r\delta)^2 + Wf - Ea(O_2) + Wf - Ea(O_2^-). \end{aligned} \quad (2.6)$$

The potential is shown in Fig. 5 and the parameters used are summarized in Table III.

The charge distribution in the molecule is calculated in analogy with Eq. (2.5). The effective charge per atom varies from -1 in the gas phase to -0.8 at small molecular-surface distance.

4. Dissociation

Dissociation products are atomic oxygen fragments, either in the gas phase or bound to the surface. The PES is a combination of Coulomb repulsion between the ions and a Coulomb attraction to their image in the surface. In addition, chemical bonding between the oxygen atomic fragments and the surface is described by a Morse potential. An anti-Morse is added as an additional repulsion between the two ions. The dissociation potential has the form

$$\begin{aligned} \hat{V}_{diss}(z_1, z_2, r) = & D_{O-Al}(1 - e^{-\alpha_{O-Al}(z_1 - z_1^{eq})})^2 + D_{O-Al}(1 - e^{-\alpha_{O-Al}(z_2 - z_2^{eq})})^2 - \frac{(Z_{efc}^{atom}(z_1))^2}{2z_1} \\ & \times (1 - \Gamma_2(z_1, 0, 2b_m)) - \frac{(Z_{efc}^{atom}(z_2))^2}{2z_2} - (1 - \Gamma_2(z_2, 0, 2b_m)) + \frac{Z_{efc}^{atom}(z_1) \cdot Z_{efc}^{atom}(z_2)}{\sqrt{(r^2 - (z_1 - z_2)^2) + (z_2 + z_1)^2}} \\ & + D_{O-O}(1 + e^{-\alpha_{O-O}(r - r_{eq})})^2 + \frac{Z_{efc}^{atom}(z_1) \cdot Z_{efc}^{atom}(z_2)}{r} + 2Wf - 2E_a^{atom}. \end{aligned} \quad (2.7)$$

TABLE III. Parameters of the peroxide PES.

A (eV)	b ($\text{\AA}^{-1}$)	z_{eq} ($\text{\AA}$)	$D_{O_2^{-2}}$ (eV)	$\alpha_{O_2^{-2}}$ ($\text{\AA}^{-1}$)	r_{eq} ($\text{\AA}$)	$Ea(O_2^-)$ (eV)
433	2.7	1.2	2.9	0.27	2.	1.46

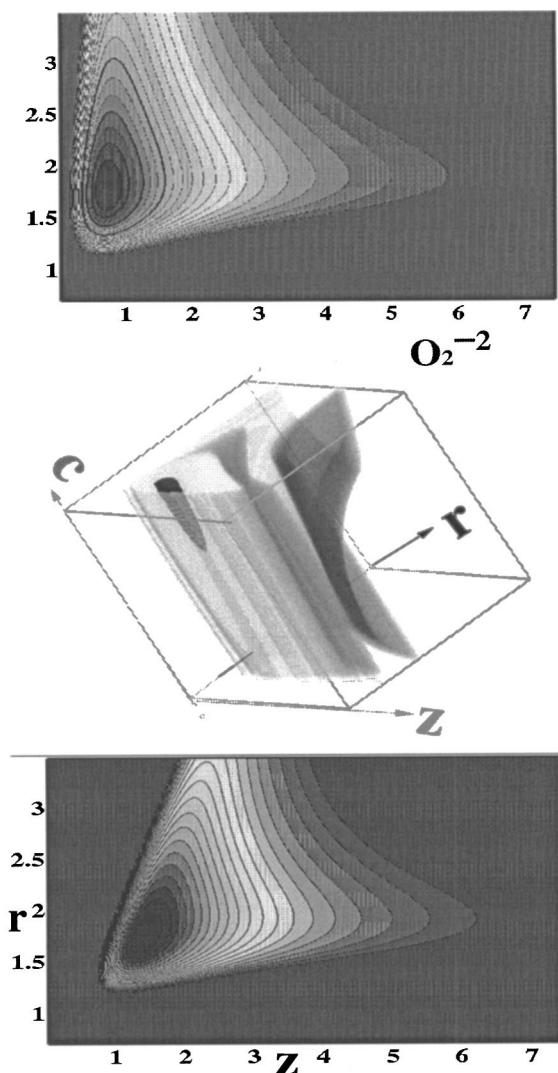


FIG. 5. The peroxide potential. Middle: the PES shown as isoenergetic potential values. Top: contour plot of the potential in the horizontal orientation. Bottom: contour plot of the potential in the perpendicular orientation. Distance is in Å.

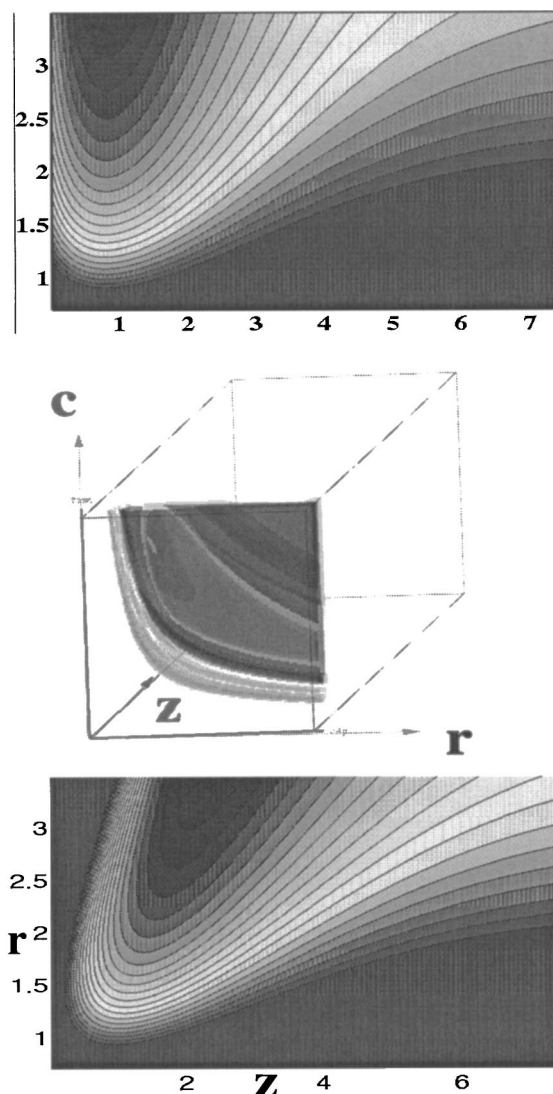


FIG. 6. The dissociation potential. Center: PES shown as isoenergetic potential values. Top: contour plot of the potential in the horizontal orientation. Bottom: contour plot of the potential in the perpendicular orientation. Distance is in Å.

The potential is shown in Fig. 6 and the parameters used are summarized in Table IV.

5. Nonadiabatic coupling interaction

The nonadiabatic coupling between each pair of states determines the amplitude of transition from one state to the other. The coupling term is chosen to be proportional to the electron density of the metal. The electron density decays exponentially into the vacuum in the classically forbidden region outside the metal.³⁰ The exponential selection means that only a narrow band of electronic surface states close to

the Fermi level has significant nonadiabatic coupling terms. The decay parameter is estimated using the metal work function and the effective charge difference

$$V_{\text{int}}(z) = A_{ab} e^{-\alpha_{\text{int}}(z/\hbar)}, \quad (2.8)$$

where the decay parameter is given by $\alpha_{\text{int}} = \sqrt{-2(Wf)|Z_{\text{efc}}^a - Z_{\text{efc}}^b|/m_e \cdot e}$, Z_{efc}^i is the effective charge in state i . A_{ab} is the interaction matrix element whose magnitude is estimated below and is in the same range of recent nonadiabatic calculations by Lara-Castells *et al.* for the O_2/TiO system.³⁵

TABLE IV. Parameters of the dissociation PES.

$D_{\text{O-Al}}$ (eV)	$\alpha_{\text{O-Al}}$ ($\text{\AA}^{-1}$)	$r_{\text{eq}}^{\text{O-Al}}$ ($\text{\AA}$)	$D_{\text{O-O}}$ (eV)	$\alpha_{\text{O-O}}$ ($\text{\AA}^{-1}$)	$r_{\text{eq}}^{\text{O-O}}$ ($\text{\AA}$)
7.1	0.66	1.1	3.4	.06	2.2

C. Simulation of the dynamics

The description of the dissociative adsorption dynamics is divided into two consecutive parts: a quantum-mechanical part describing the impinging gas phase molecule and its interaction with the solid. This process includes a sequence of charge transfer events. The quantum description ends once the molecular wave function enters the dissociation PES. The molecular wave packet in the dissociative state is used to determine the energy and angular distributions at the initiation of the dissociation event. These distributions are used in the second part to sample initial conditions in a classical simulation. The molecular dynamics is used to follow the motion of the dissociating O atoms until the process is complete. Hence, the description of the full dissociation process is obtained by using a combination of a quantum-mechanical calculation together with a molecular dynamical simulation. This picture is based on the assumption that once the molecular system has crossed onto the dissociative PES, it will not recross back into a molecular PES. This assumption is justified by the rapid energy release of the highly exothermic dissociative adsorption of O₂ onto the Al(111) surface. The reader should consider that this study is devoted to the understanding of direct ultrafast events which is faster than the time scale of dissipative molecular surface interactions. Encounters where a long-lived molecular ion is formed prior to dissociation or prior to molecular adsorption are excluded from the present investigation. The following is a more detailed description of the simulations used.

1. Quantum-mechanical model

The system is described by four coupled potential energy surfaces describing the O₂-Al, O₂⁻-Al, O₂²⁻-Al, and 2 O⁻-Al interactions.^{30,36} The nonadiabatic dynamics of the molecular dissociation is followed by solving the multichannel time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{\mathbf{H}}\psi. \quad (2.9)$$

The Hamiltonian is described as

$$\hat{\mathbf{H}} = \begin{pmatrix} \hat{\mathbf{H}}_{\text{phys}} & \mathbf{V}_{\text{phys-super}} & \mathbf{V}_{\text{phys-per}} & \mathbf{V}_{\text{phys-diss}} \\ \mathbf{V}_{\text{super-phys}} & \hat{\mathbf{H}}_{\text{superoxide}} & \mathbf{V}_{\text{super-per}} & \mathbf{V}_{\text{super-diss}} \\ \mathbf{V}_{\text{per-phys}} & \mathbf{V}_{\text{per-super}} & \hat{\mathbf{H}}_{\text{peroxide}} & \mathbf{V}_{\text{per-diss}} \\ \mathbf{V}_{\text{diss-phys}} & \mathbf{V}_{\text{diss-super}} & \mathbf{V}_{\text{diss-per}} & \hat{\mathbf{H}}_{\text{diss}} \end{pmatrix}. \quad (2.10)$$

The single channel Hamiltonian of surface i is

$$\hat{\mathbf{H}}_i = \mathbf{T}_i + \mathbf{V}_i. \quad (2.11)$$

Using the reduced coordinate system defined in Fig. 2, and assuming cylindrical symmetry, the kinetic energy operator $\hat{\mathbf{T}}_i$ is

$$\hat{\mathbf{T}}_i(z, \rho, c) = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho^2} \frac{\partial}{\partial \rho} + \frac{m}{\rho^2} \right. \\ \left. + \left(\frac{1}{z^2} + \frac{1}{\rho^2} \right) \left((1-c^2) \frac{\partial^2}{\partial c^2} + 2c \frac{\partial}{\partial c} \right) \right),$$

where $\rho = \frac{1}{2}r \cos \theta$. Replacing the internal coordinate θ with the variable $c = \cos \theta$ avoids the singularity in θ . This provides a simple grid suitable for the Fourier method.³⁷ In cylindrical symmetry, m is a conserved quantum number characterizing the helicopter motion.

The off-diagonal terms $\hat{\mathbf{V}}_{ij}$ are defined in Sec. II B. In this representation the wave function has the form

$$\psi = \begin{pmatrix} \psi_{\text{phys}}(z, \rho, c) \\ \psi_{\text{super}}(z, \rho, c) \\ \psi_{\text{per}}(z, \rho, c) \\ \psi_{\text{diss}}(z, \rho, c) \end{pmatrix}. \quad (2.12)$$

The initial wave packet for the calculation represents a free impinging oxygen molecule in the gas phase and is therefore located on the physisorption potential. It is composed of a product of a Gaussian wave function in the translational z coordinate, a vibrational eigenstate in the r direction, and a rotational wave packet in θ

$$\psi_{\text{phys}}(z, \rho, c, t=0) = e^{-[(z-z_0)^2]/2\sigma_z^2} \chi_v(r) \phi(c), \quad (2.13)$$

where $\chi_v(r)$ is the vibrational eigenstate of molecular oxygen and $\phi(c)$ is the cartwheel wave function. For zero total angular momentum $\phi(c) = 1/\sqrt{2\pi}$ and $m=0$.

The procedure chosen to simulate a thermal initial rotational distribution begins with the thermal density operator

$$\hat{\rho}(\theta, \phi, T) = \frac{1}{Z} \sum_{l,m} e^{-[E_l/k_b T]} |Y_{lm}(\theta, \phi)\rangle \langle Y_{lm}(\theta, \phi)|, \quad (2.14)$$

where T is the temperature, Z is the rotational partition function, and $Y_{lm}(\theta, \phi)$ are the eigenfunctions of angular energy $E_l = \hbar^2 l(l+1)/\frac{1}{2}\mu r^2$. For high temperatures, Eq. (2.14) can be approximated by the classical equal partition law and by the fact that m is a constant of motion

$$\hat{\rho}(\theta, \phi, T) \approx \sum_m \frac{e^{-[(\hbar^2 m^2)/(1/2\mu \rho^2 k_b T)]}}{Z'} \hat{\rho}_m(\theta, T). \quad (2.15)$$

The dependence of the density operator $\hat{\rho}_m(\theta, T)$ on m is through the centrifugal term in the kinetic energy operator used for propagation. The partial density operator for the cartwheel motion $\hat{\rho}_m(\theta, T)$ is described as

$$\hat{\rho}_m(\theta, T) = \sum_j \frac{e^{-(E_j/k_b T)}}{Z_j} |\zeta_j(\theta)\rangle \langle \zeta_j(\theta)| \\ = \lim_{N \rightarrow \infty} \sum_{n=1}^N |\Phi_n(\theta)\rangle \langle \Phi_n(\theta)|, \quad (2.16)$$

where $\zeta_j(\theta)$ is the eigenvalue of the θ -dependent part of the kinetic energy operator. The right-hand side of Eq. (2.16) describes a sum of random phase wave functions

$$\Phi_n(\theta) = \sum_j \frac{e^{i\phi_{nl} - (E_j/2k_b T)}}{\sqrt{Z_j}} \zeta_l(\theta), \quad (2.17)$$

where ϕ_{nl} is a random phase. For a rotational temperature of 150 K the results were averaged with ten m values. The convergence of the sum in Eq. (2.16) was checked for disso-

TABLE V. Typical grid and initial wave function parameters.

$N_z = 600$	$dz = 0.009 \text{ \AA}$	$N_\rho = 800$	$\Delta\rho = 0.003 \text{ 25 \AA}$	$N_c = 64$	$dc = 0.015$
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ciation. It was found that the sum converged for $n=1$, to 3% accuracy. This means that the dissociation process is not phase sensitive.

The time-dependent Schrödinger equation Eq. (2.9) is solved using a Fourier grid representation and a Chebyshev polynomial propagator^{38,39} (see Table V).

Propagation of the wave packet was carried out for a typical time of 30 fs for several initial incident kinetic energies, rotational temperatures, and initial O₂ vibrational states. To synchronize the different calculations the time is measured from the instant the wave function reaches the first crossing seam. This time period is sufficient to include all direct nonadiabatic transitions. It is assumed that the trapped part of the wave function will lose energy to the surface and eventually will dissociate. The outcome of such dissociative adsorption will be two adjacent oxygen atoms adsorbed on the surface in close proximity.

The final outcome of the direct dissociated state still has to be determined. In order to include dissipative effects involving more degrees of freedom, the dynamics is followed using classical molecular dynamics. To carry out this transformation the quantum state ψ_{diss} has to be represented as a distribution in phase space serving as the initial distribution for the classical molecular dynamics calculation.^{40–42} The first step is to define the density operator: $\hat{\rho} = |\psi(c, r, z)\rangle\langle\psi(c', r', z')|$, from which the six-dimensional phase space distribution is obtained by the Wigner transform

$$W(c, p_c, r, p_r, z, p_z) = \int \int \int \rho(c, r, z, c', r', z') \times e^{i(1/2)(c-c')p_c} e^{i(1/2)(r-r')p_r} \times e^{i(1/2)(z-z')p_z} d(c-c') \times d(r-r') d(z-z'). \quad (2.18)$$

Practically evaluating Eq. (2.18) is beyond numerical capability. More insight can be obtained from partial phase space distributions. For example, the angular phase space distribution can be calculated from the reduced density operator in the angular coordinate $c = \cos \theta$

$$\hat{\rho}(c, c') = \int \int \psi(c, r, z) \psi(c', r, z) dr dz. \quad (2.19)$$

The joint probability density of noncommuting observables is obtained from the Wigner transform of $\rho(c, c')$

$$W(C, P_c) = \int e^{ip_c Q} dQ \rho(c+Q, c-Q), \quad (2.20)$$

where $C = (c+c')/2$ and $Q = (c-c')/2$.

Joint distributions of commuting variables can also be calculated. For example

$$P(c, p_r) = \int |\psi(c, p_r, z)|^2 dz. \quad (2.21)$$

2. Atomic fragmentation dynamics

The phase space distributions generated by the dissociation state in Eq. (2.18) contain all the information required to initiate the classical trajectories.⁴³ However, as stated before, the calculation of the Wigner function of a 6D distribution is beyond present computational ability. For this reason an alternative procedure was developed to define appropriate initial conditions for the classical trajectories.⁴³ The following steps were performed to generate the required initial conditions:

- A reduced density operator is constructed for each reaction coordinate: $\hat{\rho}(q_i, q'_i) = \int dq_j dq_k \psi^*(q_i, q_j, q_k) \psi(q'_i, q_j, q_k)$. This density operator is transformed to a phase space distribution $W(q_i, p_i)$ of that coordinate.
- A point in phase space is randomly selected. Using a Monte Carlo scheme, this point is accepted if it resides within the probability distribution of each of the coordinates.
- A classical energy shell restricting an inner volume of phase space is defined by the energy range of the quantum calculations.⁴³ The energy associated with the chosen phase space point is then calculated by using the classical Hamiltonian

$$\hat{H}_{\text{point}}(z, p_z, \rho, p_\rho, c, p_c) = -\frac{1}{2\mu} \left(p_z^2 + p_\rho^2 + \frac{1}{\rho^2} p_\rho + \frac{m}{\rho^2} + \left(\frac{1}{z^2} + \frac{1}{\rho^2} \right) \times ((1-c^2)p_c^2 + 2cp_c) \right) + \hat{V}(z, \rho, c). \quad (2.22)$$

If this point is outside the classical energy shell, the selected point is rejected and a new point is chosen.

- If all the above conditions are met, the selected point in phase space is used to define initial conditions for semiclassical trajectories simulating dissociation.

The sampling procedure was checked by comparing to Eq. (2.21)

The trajectories of the oxygen atoms were obtained by integrating the equations of motion. To describe the energy exchange of the oxygen with the substrate, a Langevin approach was used.^{44–46} The Al atoms were kept fixed at their lattice points, while the O atoms moved according to the following equation of motion:

$$m\ddot{\mathbf{R}} = -\frac{dV}{d\mathbf{R}} - \beta\dot{\mathbf{R}} + \mathbf{f}_r, \quad (2.23)$$

where R represents the position vector of the O atoms, β is the friction coefficient, and $\mathbf{f}_r$ represent a random force. The forces between the oxygen atoms and between the oxygen

and the slab were calculated from the dissociative potential¹¹ energy surface (cf. Sec. II B 4). The distribution of the random force is related to the friction coefficient by the second fluctuation–dissipation theorem.⁴⁷ A similar procedure was used to describe the motion of hot oxygen atoms along an Al(111) surface.¹¹ The friction constant used here is identical to that of Wahnstrom. This coefficient includes contributions from both phonons and electronic excitations. When the oxygen atom is far from the surface, both β and f_r are therefore expected to vanish

$$\beta(z) = \begin{cases} \beta_0 & z < 2.5 \text{ Å} \\ \beta_0 \cdot (1 - \Gamma_2) & z \geq 2.5 \text{ Å} \end{cases}, \quad (2.24)$$

where $\beta_0 = 3 \cdot \text{ps}^{-1}$ is the value calculated and used by Wahnstrom.¹¹

The motion of the dissociated ion relative to the fixed adsorbed oxygen ion was followed in time. One of the oxygen atoms was found to always stick close to the dissociation point. Depending on initial conditions, the other atom was either ejected to the gas phase, or performed a ballistic motion and returned to the surface further away. The discrimination between these processes depends on the incident kinetic energy, and on the possibility of a back charge transfer from the oxygen ion to the surface.

3. Back charge transfer from the outgoing atom

Once the oxygen atom has started its ballistic motion, its fate is determined by its translational energy normal to the surface, and by its initial direction of motion. An oxygen ion ejecting to the gas phase may transfer its charge back to the solid and emerge as a neutral atom in the ground state $O(^3P)$ or in the excited state $O(^1D)$. These back charge transfer processes are possible due to curve crossing between the oxygen–metal PES of these two neutral states and the ionic state (cf. Fig. 7).

The curve-crossing probability among the various potential surfaces can be estimated using the Landau–Zener formula.^{48,49} A more accurate alternative used in this work was to calculate the dissociation probability for each channel from a series of one-dimensional wave packet propagations. In these propagations, initial wave packets were positioned at the minimum of the ionic surface and each wave packet was assigned a different kinetic energy. The dissociation probability for each channel as a function of incident energy was obtained and tabulated. The table of probabilities served as the surface hopping probability for each trajectory when reaching a crossing point.

The curve-crossing probability is proportional to the nonadiabatic coupling terms between the electronic states. A rough estimation of this coupling can be obtained by relating it to the overlap between the molecular orbitals of oxygen and Al at the curve-crossing points. This overlap was estimated by employing the extended Hückel theory,^{50–55} where $\beta = \langle \phi(\text{Al})_S | H_{ij} - e_0 S_{ij} | \phi(\text{O})_{pz} \rangle$ and S_{ij} is the orbital overlap. The nonadiabatic coupling function constructed shows an exponential decay from the surface. The calculated values at the crossing points are: $v_{12} = 0.084 \text{ eV}$ for the ion– $O(^3P)$ and $v_{12} = 0.46 \text{ eV}$ for the ion– $O(^1D)$ coupling.

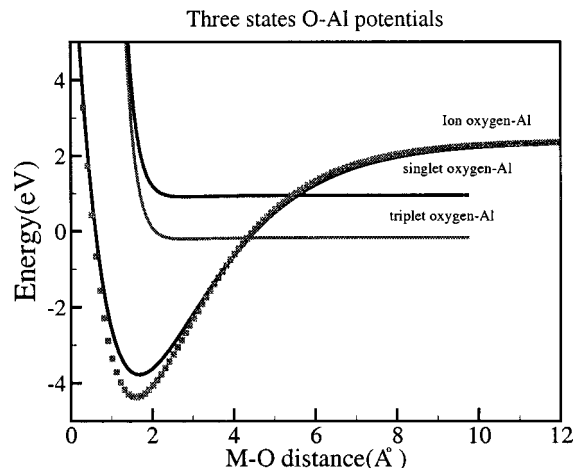


FIG. 7. Back charge transfer channels represented in a 1D potential energy of both neutral states and ion in the normal to the surface coordinate. The neutral species potentials were described by a Born–Mayer form similar to the physisorption PES. The ionic potential is the dissociation PES in the relevant coordinate. The asymptotic shift between these states is determined by the energy difference between the $O(^1D)$ and $O(^3P)$ states. The asymptotic energy difference between the ionic state is related to the difference between the metal work function and the electron affinity of $O(^3P)$. A deeper oxygen–aluminum well is also shown, indicating the uncertainty in the oxygen–aluminum bond strength.

Using the above procedures, each trajectory could be followed either to yield a gas phase O^- , $O(^3P)$, $O(^1D)$, or an adsorbed O^- . Once a projectile reached a separation of 10 Å from the Al(111), it was assumed that it completed the escape to the gas phase and the trajectory was terminated. A termination was also induced if the atom became stationary on the surface. From the output of the classical simulation, translational energy and angular distributions of the ejected species were calculated as well as the distance distribution between adsorbed pairs.

III. RESULTS

The main products of the encounter between oxygen molecules and an aluminum surface are: dissociative adsorption, abstractive dissociation, and reflected oxygen molecules. The dissociative adsorption products are either pairs of adsorbed oxygen atoms or isolated atoms resulting from ballistic-like trajectories. The abstractive dissociation can result in O^- , $O(^3P)$, $O(^1D)$ in the gas phase and an isolated oxygen atom on the surface. The yields of each species depends on the incident kinetic energy and on the excitation of vibrational and rotational degrees of freedom (cf. Fig. 1).

A. The dissociation yield

Quantum wave packet calculations describe the initial nonadiabatic steps of the oxygen/aluminum interaction. The propagation is terminated after a period of 30 fs. This time is sufficient for the wave function to hit the surface and recoil back to the gas phase. At the final time of the propagation the norm of the wave function on each diabatic surface is calculated. The fraction of the wave packet reflected back to the physisorption channel defines the nonreactive fraction. All the remaining fractions, i.e., of the wave function found on the peroxide, superoxide, and dissociation states are ac-

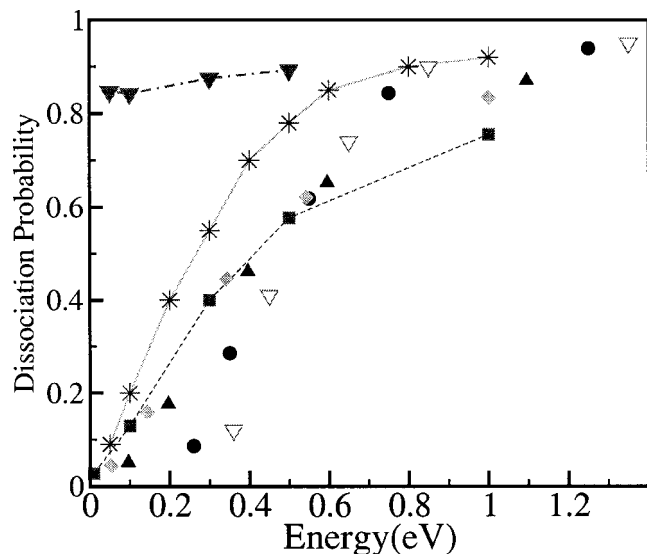


FIG. 8. The dissociation probability as a function of incident total energy: quantum calculations and experimental results. The labels are as follows: Squares: $v=0$, $T_R=0$ K. Circles: $v=1$, $T_R=0$ K. Diamonds: $v=0$, $T_R=50$ K. Empty triangles pointing down: $v=1$, $T_R=50$ K. Empty triangles: $v=0$, $T_R=100$ K. Stars: the experimental results from Ref. 3 plotted vs incident translational energy. Full (blue) triangles pointing down: adiabatic calculation, $v=0$, $T_R=0$ K. Notice: To reconstruct the experiment one has to know the internal energy for each translational energy value. This will add to the $v=0$, $T_R=0$ K line.

counted as reactive. It is assumed that the trapped amplitude on both peroxide and superoxide states will eventually dissociate, constituting the indirect dissociation channel. Proper description of the indirect dissociation requires the inclusion of energy and phase dissipation terms in the model. The present study, which does not contain such terms, therefore deals only with direct dissociation. This approach is justified by the fact that the yield of the indirect dissociation channel is small, a few percent in the energy range considered. The dissociation probability as a function of incident total energy is shown in Fig. 8.

The figure shows an increase in the dissociation probability as a function of both initial kinetic and internal energy. The calculations of $v=0$, $T_R=0$ are slightly lower in value than the experiment, which is plotted with respect to the incident kinetic energy. If the internal energy of the experiment would be known, the dissociation probabilities with excited internal energy could be included in an averaging procedure and values closer to the experiment would be obtained. For total energies below 0.5 eV, it is found that translation is more effective than internal energy in producing dissociation. For total energies above 0.5 eV this trend is reversed, and internal energy in particular vibrational energy becomes more effective.

The amplitude trapped on the superoxide and peroxide states is expected to lose energy slowly due to interaction with phonons and electron-hole pairs, finally leading exclusively to dissociative absorption. This indirect dissociation channel is expected to produce oxygen atoms settling at nearby adsorption sites on the lattice.

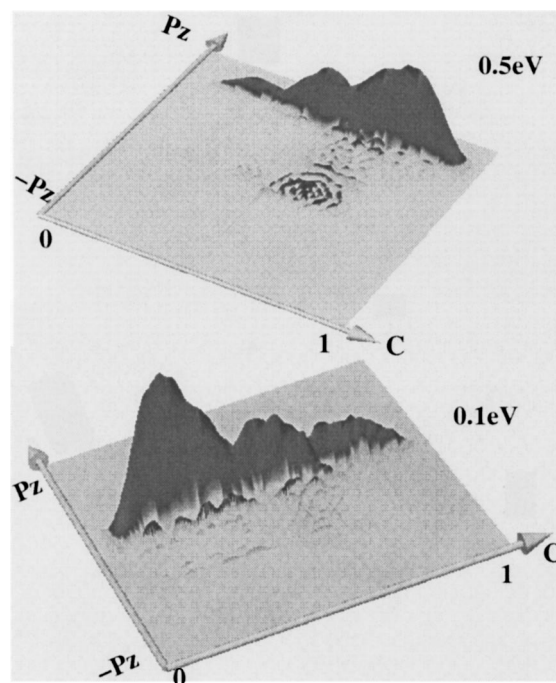


FIG. 9. Marginal probability $p(c, p_z)$ as a function of the angle $c = \sin(\theta)$ and the momentum p_z in the normal direction of the dissociation wave packet for two different incident kinetic energies. $c=0$ is the perpendicular orientation. Higher incident kinetic energy forces a more parallel orientation.

B. Dissociative adsorption versus abstractive dissociation

The fate of the amplitude on the dissociative channel still has to be decided. The two main variables which determine the branching ratio between dissociative adsorption and abstractive dissociation are the angle between the molecular axis and the surface normal together with the kinetic energy of the outgoing atom in the normal direction. Figure 9 shows the probability distribution for these variables for two incident kinetic energies. It is clear from the figure that at low incident kinetic energy there is a tendency for a perpendicular orientation which flattens out when the incident kinetic energy increases.

The fate of the oxygen molecule that has emerged into the dissociation channel is determined by a molecular dynamics simulation. The initial conditions for the MD calculation are drawn from the phase space distribution of the quantum wave packet on the dissociation surface at the termination time. The MD simulations employed 10 000 trajectories with typical propagation time of 1 ps. In all trajectories the oxygen atom close to the surface almost immediately found rest on the aluminum surface at a position adjacent to where it started. The fate of the other oxygen is more complex. If it has sufficient perpendicular energy it may emerge into the gas phase either as an O^- ion, or as a neutral atom $O(^3P)$, or $O(^1D)$. If the ejected atom does not pose enough energy to escape into the gas phase, it will perform a ballistic motion and find rest at a large distance from the first oxygen atom. The distribution of the separation distance between adsorbed pairs for different initial kinetic energies are shown in Fig. 10.

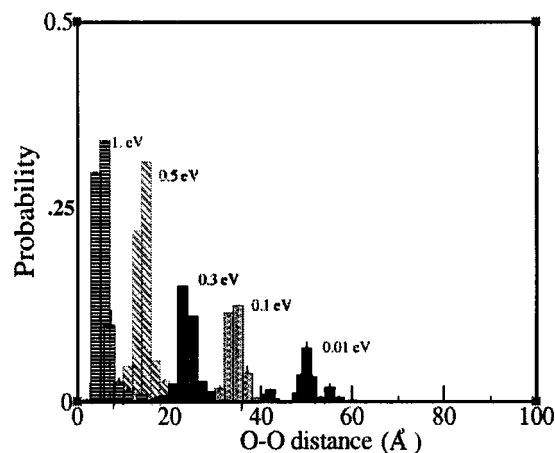


FIG. 10. Distribution of distances between dissociated adsorbed pairs for different incident kinetic energies, for $v=0$ and $T_R=0$.

We define a pair of adsorbed oxygen atoms if their separation is less than 12 Å, otherwise the adsorbates are defined as singles (isolated atoms). The variation of the ratio between singles and pairs as a function of initial kinetic energy is shown in Fig. 11. The computation data are shown together with the experimental results. The three sets of calculated points differ in the value of the friction coefficient used in the MD simulation. The value of β in Eq. (2.24) used in Ref. 11 is 3.0 ps^{-1} , a slight variation to $\beta=3.5 \text{ ps}^{-1}$ and $\beta=2.5 \text{ ps}^{-1}$ is also shown in Fig. 11.

A small reduction of the friction value β of Wahnstrom¹¹ results in an excellent agreement with the experimental data.

The relation between the distribution of neighboring adsorbate separation and the incident kinetic energy and rotational energy is shown in Fig. 12.

The results shown in Fig. 12 clearly demonstrate that increase in both kinetic and rotational energies results in a shift of the distribution to shorter distances. The discretization of the separation between adsorbates in a given distribution is related to the tendency of adsorbed oxygen atoms to be localized at well-defined adsorption sites separated by multiples of the lattice constant.

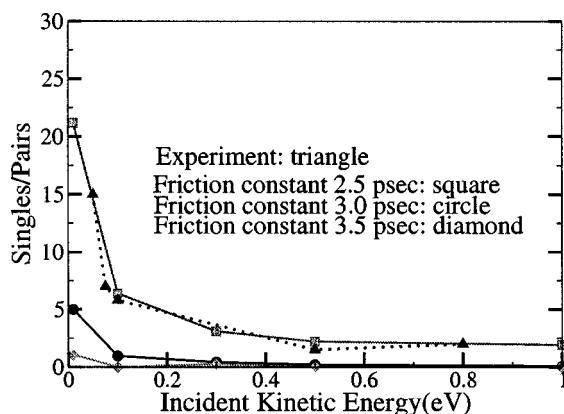


FIG. 11. The ratio between lone atoms and pairs adsorbed on the surface as a function of incident kinetic energy for three values of the friction parameter. The experimental values of Ref. 13 are also indicated. (A pair is defined by a distance smaller than 12 Å.) The yield of the indirect dissociation fraction was added to the pair count.

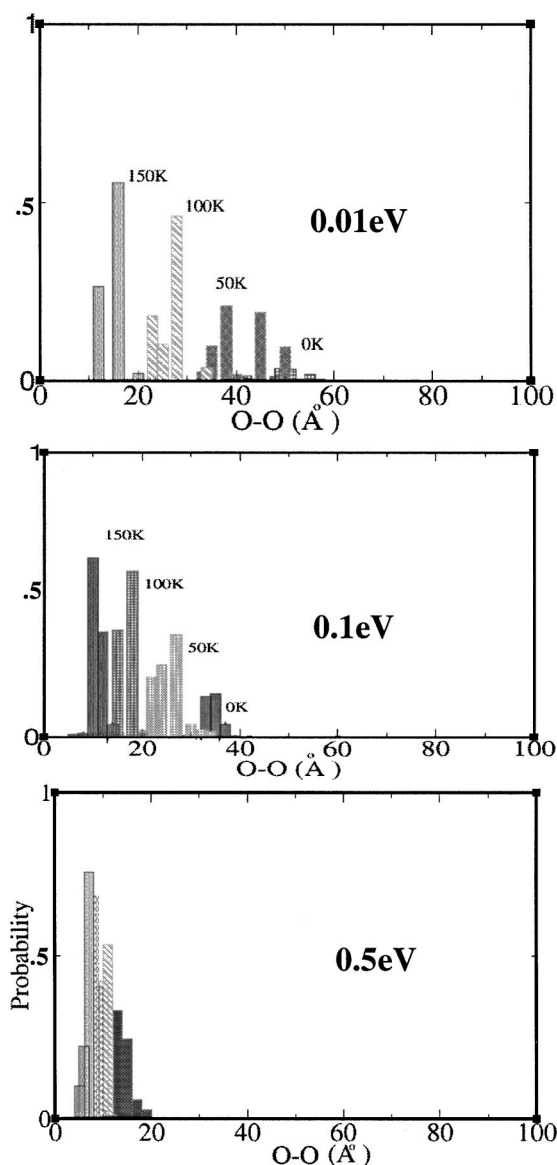


FIG. 12. The distance distribution between adsorbed pairs for different rotational temperatures, for three incident kinetic energy values.

The branching ratio of the oxygen atomic species appearing in the gas phase was derived from the crossing probability of each trajectory (cf. Sec. II C 3). Each curve-crossing event is terminated and is then accounted as an outgoing $\text{O}(^3P)$ or $\text{O}(^1D)$. Noncrossing events were accounted as ions if they reached a distance of 10 Å from the surface.

The abstraction yield as a function of incident kinetic energy is shown for three initial vibrational states in Fig. 13. It is clear that vibrational excitation enhances abstraction. The magnitude of this enhancement goes down as incident kinetic energy goes up.

The product yields as a function of the orientation axis of the oxygen molecule on the dissociation channel at the time of termination of the quantum propagation are shown in Fig. 14 for four different initial conditions. These results were obtained by correlating the final product identity of each trajectory to the value of the intermediate angle when the trajectory was initiated.

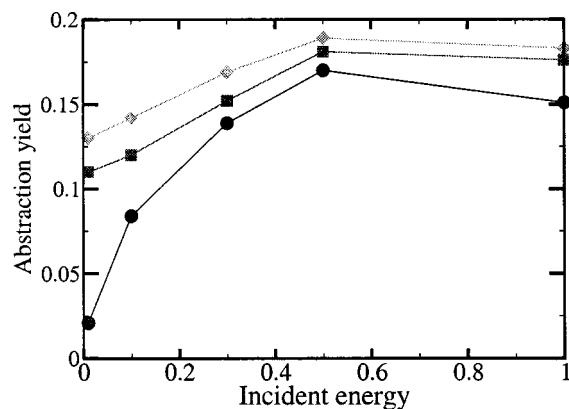


FIG. 13. Abstraction yield dependence on the initial vibrational state and incident kinetic energy. From bottom up $v=0$, $v=1$, and $v=2$.

It is clear from Fig. 14 that each final product is strongly correlated to a small range of molecular orientations. A perpendicular orientation is necessary to produce $O(^1D)$; a slightly larger tilt leads to $O(^3P)$. Flat orientations lead to neighboring pairs, while intermediate angles lead to ballistic trajectories producing two lone adsorbed oxygen atoms. Different initial conditions change the branching ratio between products, but have only a minor influence on the angular distribution of each product.

IV. DISCUSSION

The purpose of the computational model is to supply insight into the detailed mechanism of oxygen dissociation over aluminum. To carry out this task the results of the simulations and calculations have to be integrated into a consistent picture. The discussion is led by the following mechanistic questions:

- (i) Can the dissociation mechanism be interpreted by an adiabatic framework?

- (ii) What is the connection between the adiabatic DFT-PES and the nonadiabatic potentials used in the current calculations?
- (iii) What is the mechanism that leads to abstractive dissociation?
- (iv) How is the oxygen distribution on the Al surface^{9,10,12,13} influenced by the experimental parameters?

A. The dissociation mechanism

The experimental dissociation probability of oxygen over aluminum shows no threshold to reaction with respect to incident kinetic energy.³ This is in accordance with DFT calculations which show no barrier to reaction.^{6–8} However, in the experiment the dissociation probability increases with incident kinetic energy reaching a saturation at ~ 0.6 eV. This observation seems to be in conflict with an adiabatic framework based on the Born–Oppenheimer approximation, where a single PES describes the topology of reaction. The nonadiabatic framework employed in this study is consistent with the experimental observations as shown in Fig. 8. In this case the dissociation probability is dominated by the first nonadiabatic crossing. The probability of this transition depends on the location of the nonadiabatic crossing seam between the physisorption PES and the superoxide PES. The topology of this seam and the increase in the strength of the nonadiabatic coupling when the oxygen molecule is closer to the surface results in an enhancement of the dissociation probability when the incident kinetic energy increases. In order to verify the dominant role of the nonadiabatic framework, the reaction was simulated using only the lowest adiabatic surface. This PES was obtained by diagonalizing the four diabatic PESs together with their nonadiabatic coupling terms [cf. Eq. (2.10)]. The results of these calculations can be compared to the nonadiabatic calculations and the experi-

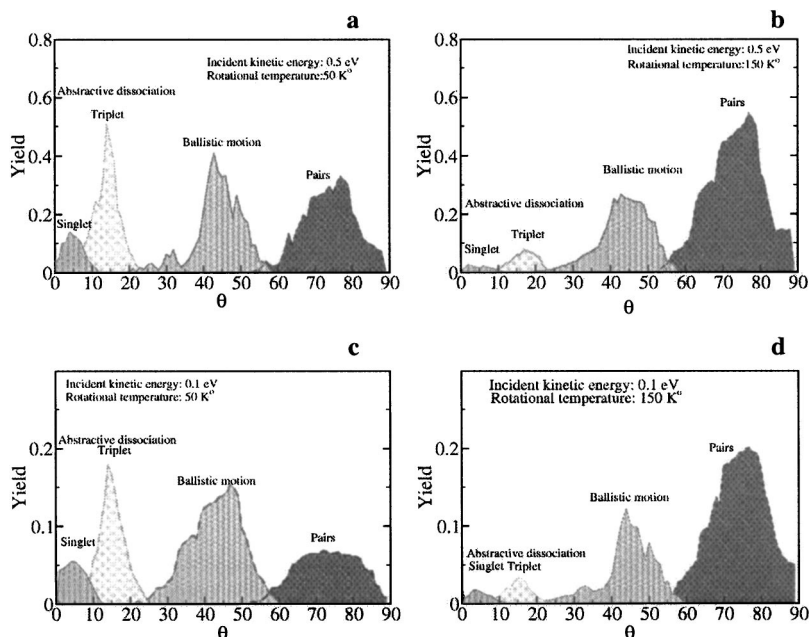


FIG. 14. The product yield as a function of the molecular axis orientation at the dissociation channel.

ment in Fig. 8. As expected, the dissociation probability has no threshold and reaches saturation of 80% yield already at an incident energy of 0.01 eV.

At extremely low incident energy adiabatic dynamics should take over, resulting in an increase in dissociation probability when the incident energy is decreased. Such an effect was found in the oxygen silver system,⁵⁶ where the dissociation probability values are much lower. For the present system this effect was identified only in 1D models. The increase in dissociation configurations with dimensionality seems to overcome this effect in 3D.

B. Comparison of the nonadiabatic description to DFT calculations

In the quest for a first principle understanding of molecular dynamics on surfaces, DFT *ab initio* calculations have been employed to provide PESs for a wide class of gas surface encounters. The advantage of the method is that it can address complex, multiple electron systems with reasonable accuracy, including the infinite reservoir of electrons in the metal substrate. The drawback is that, by definition, the functional is restricted to the ground-state adiabatic potential energy surface. Lundqvist *et al.*^{6–8,57} have performed an extensive study of the current system. At this stage it is appropriate to compare the results of DFT calculations to the lowest adiabatic PES used in the present study. This PES is shown in Fig. 15 for different molecular orientations.

A close examination of Fig. 15 shows a minima at the physisorption potential when the molecule reaches 3.3 Å. This minima is absent from the DFT calculations. For the DFT potential, the perpendicular molecular approach is slightly lower in energy. The difference arises from the C_3 coefficient. In the present study it was adopted from the work of Ihm *et al.*⁵⁸ based on the actual polarization of oxygen. This value is different from the C_3 which was directly calculated by DFT.⁷ As a result, the position of the minimum differs between the two orientations from 3.3 Å for the perpendicular orientation to 3.6 Å for the horizontal orientation. In the physisorbed state there is an energy gap of 0.03 eV favoring the horizontal orientation over the perpendicular orientation (cf. Fig. 16).

In an adiabatic picture, the energy differences are very small and will have minor influence on the dissociation probability. In the nonadiabatic approach these differences have a significant impact on the dissociation probability since the crossing seams between the physisorption and superoxide state change significantly, as seen in Fig. 16.

Another discrepancy between the DFT and semiempirical PES is a minima corresponding to the superoxide species. The DFT calculation is not able to identify a minima corresponding to the superoxide species. The semiempirical PES identifies a minima originating from the superoxide at a distance of 1.5 Å from the surface with an intermolecular distance of 1.4 Å, an energy of -0.9 eV at the perpendicular orientation, and -1.2 eV at the horizontal orientation.

The DFT calculation identifies a potential well associated with the peroxide species. This can be compared to the minima in the diabatic PES seen in Fig. 15. It has the value of -1.9 eV for the horizontal orientation and -1.2 eV for

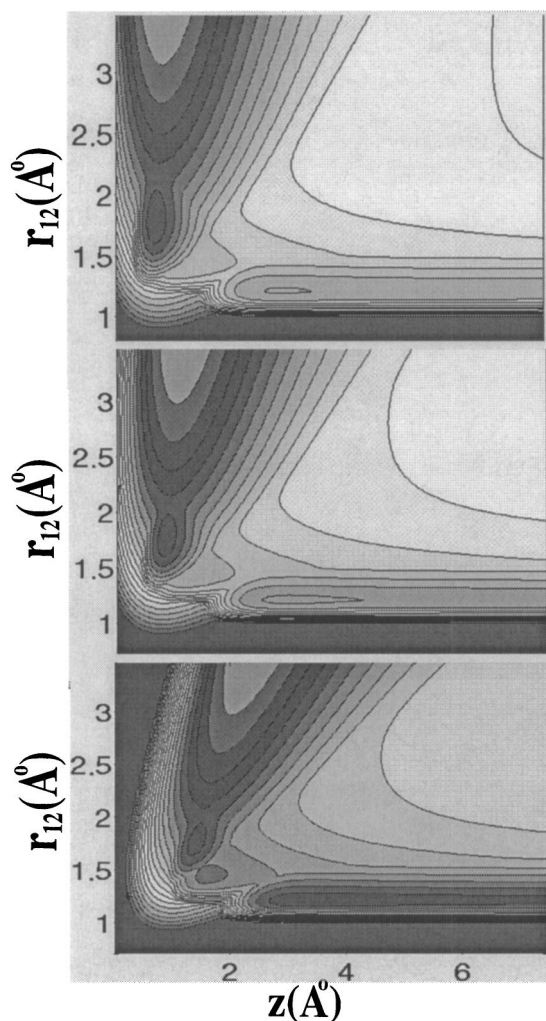


FIG. 15. A 2D cut of the adiabatic potential for three different molecular orientations. Top: horizontal $\theta=90^\circ$. Middle: $\theta=45^\circ$. Bottom: perpendicular $\theta=0$.

the perpendicular orientation. This value is 0.3 eV lower than the value of the DFT calculations. Also, the intermolecular distance is 0.1 Å smaller. Despite these differences, the general topology of the semiempirical adiabatic potential is quite similar to the DFT PES.

The dissociation yield depends on the nonadiabatic coupling terms. The nonadiabatic coupling to the first charge transfer event from the physisorbed state to the superoxide state was manipulated in order to supply a reasonable quantitative agreement with experimental results³ as shown in Fig. 17.

The fit to a parabola indicates that the nonadiabatic coupling is in the range of perturbation theory where the dissociation yield is quadratic in V_{12} . By changing the values of the nonadiabatic coupling interaction from 0.09 to 0.21 eV the diabatic PES topology becomes even closer to the DFT PES. This is shown by comparing Fig. 18 to Fig. 2 of Ref. 6.

The differences between the potentials are within the accuracy limits of both methods employed. This comparison enabled the use of the results of DFT calculations as input to define the strength of the nonadiabatic potential term.

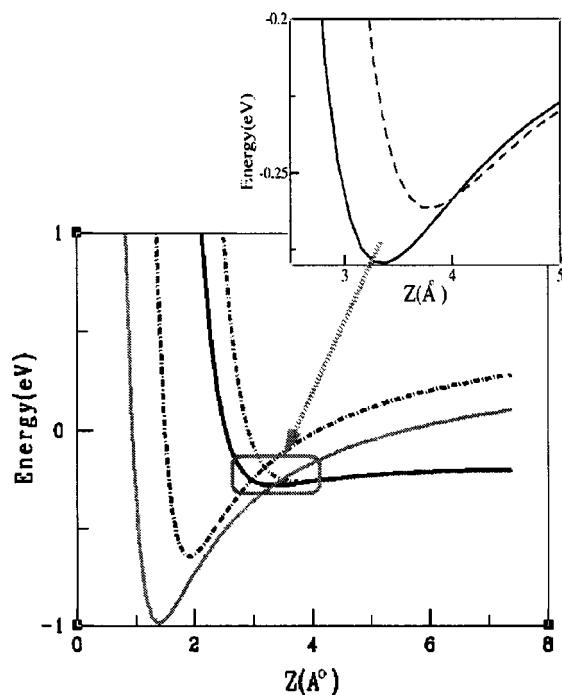


FIG. 16. A cut along the O_2 –Al distance of the physisorption PES and the superoxide PES at an internuclear distance 1.1 Å for two different molecular orientations. Perpendicular (dotted), horizontal (solid). For the horizontal orientation, no activation energy is required. For perpendicular orientation 0.1 eV is required to reach the maxima. A zoom on the physisorption well for the two orientations is also shown for the horizontal (solid) and perpendicular (dashed) molecular orientations.

C. The abstractive dissociation

Upon dissociation, the atoms pointing to the surface will almost immediately adsorb close to its impact position. The fate of the second atom will be determined by its momentum. The magnitude of the momentum is determined by the forces and kinetic energy along the interatomic distance. Initial internal energy, i.e., vibrational and rotational energy, contributes directly. The range of energy is 0.1 to 0.3 eV. The projection of the incident kinetic energy on the interatomic axis also contributes in the range of 0.1 to 1 eV at a perpendicular orientation. The main force along the axis is the Coulomb

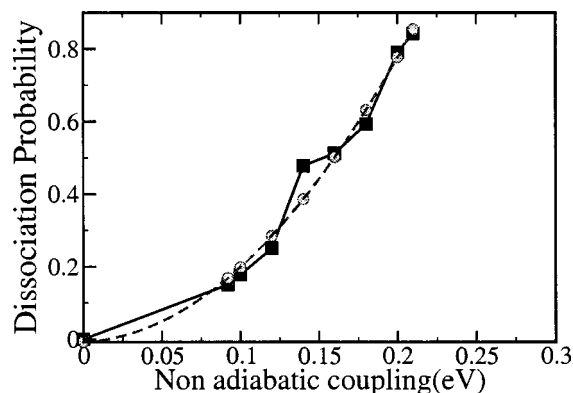


FIG. 17. The dependence of the dissociation probability of oxygen over Al on the nonadiabatic coupling term between the physisorption and the superoxide PES for 0.5 eV incident kinetic energy. (The dash line is a quadratic fit.)

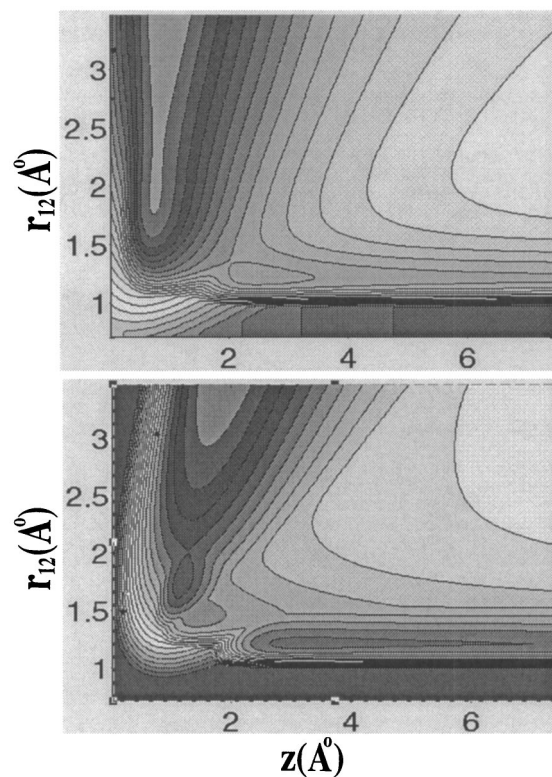


FIG. 18. A 2D contour plot of the adiabatic potential with the nonadiabatic parameter of $V_{12}=0.17$ eV, for two different molecular orientations. Top: horizontal. Bottom: perpendicular.

repulsion that contributes approximately 2 eV of energy. Upon dissociation of the bond this energy is equally divided between the two atoms. However, due to the repulsive forces of the surface, a momentum transfer between the two atoms takes place, meaning that the outgoing atom can acquire most of the available momentum.

The orientation of the molecule determines the energy distribution between normal and perpendicular directions. Only the vibrational energy and Coulomb repulsion can be distributed in the normal mode depending on the molecular orientation. The amount of energy in the normal mode selects between the reaction products. The abstraction of an atom to the gas phase requires an energy component perpendicular to the surface. The available energy in this direction can come from Coulomb repulsion and vibration, provided that the molecule is oriented accordingly (cf. Fig. 19). This orientation therefore determines the adsorbed pair distance distributions. Lone adsorbed atoms are also the result of the ballistic motion of the uppermost atom, not having sufficient normal energy to escape the surface. To verify this assumption, each final product is correlated with the intermediate phase space distribution of the dissociation wave packet (cf. Fig. 14). Comparing these results to the experimental findings shows that the experimental suppression of abstraction due to rotation is larger by a factor of 3 than in the calculation.⁵⁹ The experimental observation can be explained if the cone defining the abstraction is tighter 10° instead of 20° . Such a tighter cone is correlated to a loss of 0.5 eV of energy of the escaping oxygen atom. The probable reason for this discrepancy is the reduced description which limits the

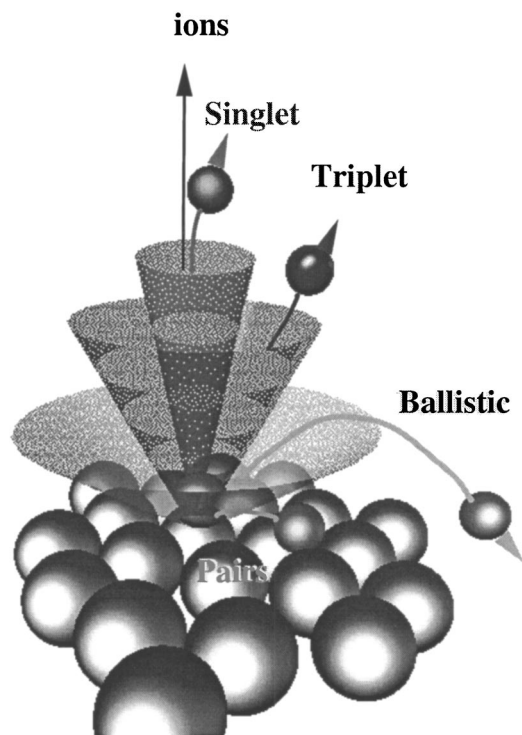


FIG. 19. The molecular axis orientation θ on the dissociation surface and its relation to the final possible products.

number of degrees of freedom. Inclusion of translational, electron-hole pairs and surface recoil degrees of freedom would account for this lost energy. A set of MD simulations with a reduced initial energy and a friction parameter $\beta = 2.5 \text{ ps}^{-1}$ is shown in Fig. 20.

Figure 14 and Fig. 20 should be compared to Fig. 9, showing that flattening the intermediate distribution due to an increase in incident kinetic energy changes the ratio between the products.

D. Reverse propagation: Correlating the initial to the final product distribution

With the assumption that the molecular orientation and the perpendicular mode energy were responsible for the abstraction, tracking the abstractions dependence on the initial conditions was performed in the following procedure: Starting from the outcome to the source, the trajectories that ended in abstraction were backtracked to their initial conditions on the dissociation surface. From the Wigner distributions that led to abstraction on the MD, a projection operator was constructed which included the relevant modes θ , p_z , p_r . The projection operator was applied on the dissociation final wave packet ψ resolving a new wave packet χ , which represents only the part of ψ leading to abstraction. This wave packet was propagated backward in time, from the dissociation PES to the initial physisorbed states. Analysis of the wave packet on the physisorption state supplied the initial conditions leading to abstraction. The same procedure was repeated on a wave packet constructed from the remainder of the distributions which did not lead to abstraction. The initial states leading to the different products are shown in

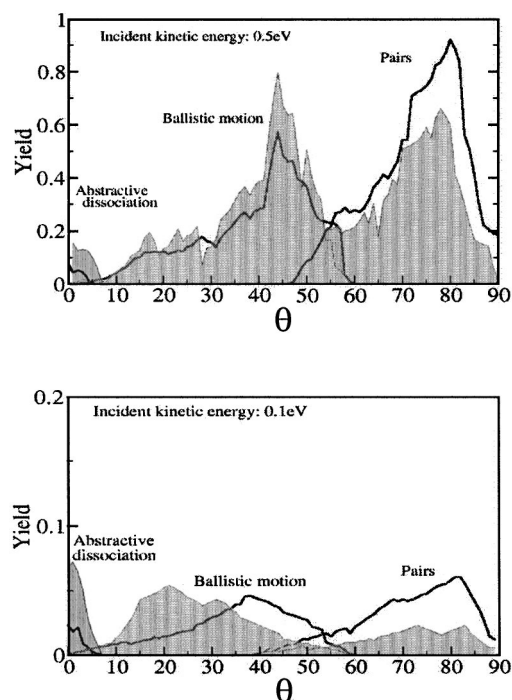


FIG. 20. Angular distributions leading to final products for two rotational temperatures filled graphs $T_R = 50 \text{ K}$, bold lines $T_R = 150 \text{ K}$: Top: $E_k = 0.5 \text{ eV}$. Bottom: $E_k = 0.1 \text{ eV}$. The plot was obtained by reversing the surface hopping molecular dynamics trajectories reducing the initial energy by 0.5 eV and $V_{12} = 0.124 \text{ eV}$.

Fig. 21. These are products of “backward in time” propagation from final states initiated from 0.5 eV incident energy, $v = 2$ and $T_R = 50 \text{ K}$ rotational temperatures.

The role of molecular orientation to abstraction is shown in Fig. 22. The “initial” Wigner distribution in $\sin(\theta)$ and p_c shows that perpendicular molecules are responsible for the abstraction.

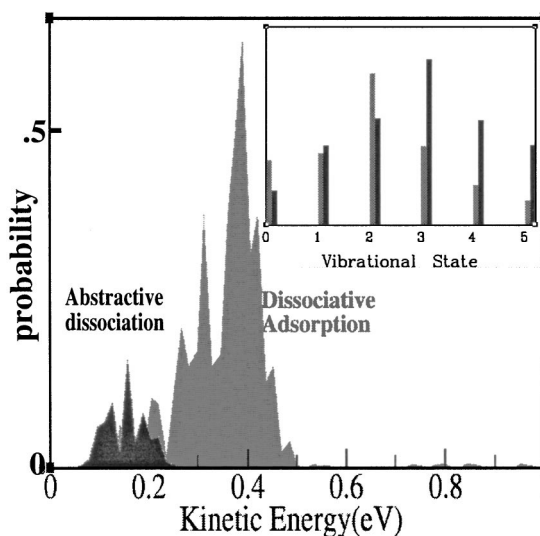


FIG. 21. The incident energy distributions leading to dissociative adsorption and abstractive dissociation. Inset: vibrational distributions leading to dissociative adsorption (right bar) and abstractive dissociation (left bar).

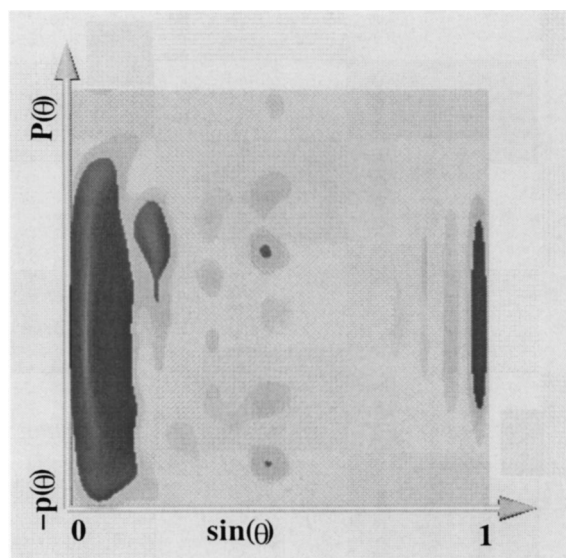


FIG. 22. The angular Wigner distributions of the initial wave function corresponding to abstraction. The wave function was obtained from reverse propagation of the projected dissociation wave function. The projection operator was obtained by correlating the abstraction products to the dissociation wave packet.

E. Product yield dependence on initial energy distribution

The previous analysis has shown that the final product is almost exclusively dependent on the molecular axis orientation and on the normal energy of the dissociation electronic state. Some control of the products can be obtained if the initial internal energy can be correlated with these variables. Each of the possible products has a different dependence on internal energy:

- (i) *Dissociation*: As has been shown in Fig. 8, internal energy, i.e., vibration and rotation, enhance dissociation. This is because both vibration and rotation extend the oxygen molecular bond. Since the superoxide bond is longer, the initial extension leads to more favorable configurations for the nonadiabatic crossing. At long range, the favorable crossing orientation is perpendicular. Internal energy excitation allows a less favorable orientation for crossing. High incident kinetic energy leads the molecule to the repulsive part of the potential, resulting in a reorientation of the molecule to a flat configuration leading predominantly to dissociative adsorption (cf. Fig. 19).
- (ii) *Abstractive dissociation*: Vibrational energy enhances abstraction (cf. Fig. 13). Since the energy is oriented along the molecular axis, vibrational energy will be a booster. As for the rotational energy, the cartwheel orientation will stretch the bond resulting in a similar effect to the vibrational enhancement. The helicopter motion, on the other hand, is oriented flat on the surface and therefore will suppress the abstraction. With an increase in rotational energy the total fraction of molecules with helicopter orientations will increase, and therefore rotation will suppress abstraction (cf. Fig. 12).

- (iii) *Ballistic pairs*: Intermediate orientations contribute to ballistic pairs. The total yield will be enhanced by vibration and by cartwheel rotation, but will be suppressed by high incident kinetic energy which will flatten the orientation and bring about helicopter rotation.

F. Critical evaluation of the model

The complexity of the model required to simulate the dissociation of oxygen over aluminum is apparent. It is therefore appropriate to assess the validity of the general assumptions and the sensitivity of the model to uncertainties in parameters. The quantum model is based on a small number of electronic states and the oxygen atom nuclear coordinates. The continuum of the surface electronic degrees of freedom as well as additional low-lying electronic levels of oxygen are ignored. Put differently, the diabatic energy surfaces have a finite width. The doorway to the encounter has been found to be the first charge transfer event with a characteristic time scale of a few femtoseconds. Being conservative, this means that an energy width of ~ 0.3 eV is within the time energy uncertainty. Moreover, due to the exponential decrease in electron density into the vacuum, only the highest metal electronic states close to the Fermi level have significant amplitude at the distance of the first crossing. As a result, at this charge transfer point the band of electronic states is well represented by two effective electronic states.⁶⁰ The position of this crossing is determined by the electron affinity of oxygen, its polarizability, and the work function of aluminum.

In principle, it is possible to go beyond the present model and to include the surface electronic degrees of freedom either implicitly or explicitly. An implicit treatment is based on an open quantum description replacing the wave function by a density operator and the Schrödinger equation by the Liouville–von Neumann equation.⁶¹ A simplified 1D model for oxygen dissociation was carried out⁶² including implicitly electronic quenching and coupling to the surface phonons. Only a small influence was found on the threshold behavior. An increase in the reaction yield, mostly due to electronic quenching, was found at incident energies above 0.5 eV. Extending the calculation to the current 3D case is beyond current computational abilities. The short time scale suggests the use of the “surrogate Hamiltonian” method^{28,29} to include the effect of the surface degrees of freedom explicitly. Again, the additional computational cost is beyond current capabilities.

Once the molecule approaches the surface the potential parameters of the model become more uncertain. The fit of the lowest adiabatic surface to the DFT calculations⁷ is somewhat reassuring. Methods to calculate excited electronic states embedded in the continuum are at their infancy⁶³ and are not yet able to deal with charge transfer. The main dynamical feature is the large acceleration toward the surface due to the formation of the oxygen–aluminum bond. The energetics is known only to within ~ 0.5 eV. In addition, the nonadiabatic effect become stronger, meaning extensive mixing of electronic states. The acceleration means that kinematic effects dominate until the atoms are stopped on the

repulsive short-range part of the potentials. The nonadiabatic dynamics can be loosely classified as diabatic at long range and more adiabatic at short range. These general trends are not affected by varying the potential parameters. Comparison to experiment suggest that at this stage up to ~ 1 eV of energy is lost to surface degrees of freedom. Relating to the work of Wahnstrom,¹¹ most of the energy is lost to surface vibrations.

V. CONCLUSION

- (i) Only a nonadiabatic framework can supply a consistent framework of the process of oxygen dissociation on a clean aluminum surface.
- (ii) The semiempirical potential parameters can be partially determined by comparing the lowest adiabatic surface to DFT calculations. Additional nonadiabatic parameters can be obtained by comparing the dynamical calculations to experiment.
- (iii) The total dissociation yield is determined by the bottleneck of the charge transfer crossing between the physisorption to the superoxide PES. This bottleneck widens with the increase of incident total energy.
- (iv) The branching ratio of the reaction channels is dominated by the molecular orientation and by normal energy. This branching can be influenced by the initial conditions. The abstraction channels are suppressed by an increase in rotational energy and by high incident kinetic energy, both leading to a flatter distribution of molecules on the dissociation surface.
- (v) A production of atomic oxygen negative ions is possible only from perpendicular orientations. It seems that the available energy at existing experimental conditions is not sufficient to produce ions. A highly vibrationally excited oxygen molecule with sufficient incident kinetic energy may lead to ion production.

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