

# The role of non adiabatic mechanisms in the dissociation dynamics of $O_2$ on silver surfaces

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## Abstract

The dissociation dynamics of oxygen on silver surfaces is studied theoretically. The method is based on a quantum-mechanical time-dependent non-adiabatic picture. A universal functional form for the potential energy surfaces is employed. The diabatic potentials describing the sequence of events leading to dissociation begin from the physisorption potential crossing over to a charged molecular chemisorption potential and crossing over again to the dissociated atomic-surface potential. Within such a potential surface topology, two different surfaces leading to dissociation are studied: the empirical potential of Spruit and the ab-initio potential of Nakatsuji. It is found that the system is captured by the molecular chemisorption well for a considerable length of time, long enough for thermalization. Thus the calculation is split into two parts: the calculation of “direct” dissociation probability and the calculation of nonadiabatic dissociative tunneling rate from the thermalized chemisorbed molecular state. For the direct probabilities, the Fourier method with the Chebychev polynomial expansion of the evolution operator is used to solve the time-dependent Schrödinger equation. For the tunneling rate calculation, a similar expansion of Green’s operator is used. The output of the direct-reaction calculation is the dissociation probability as a function of the initial energy content, while the tunneling calculation yields the dissociation rate. The dependence of the direct dissociation probability on the initial kinetic energy is found to be non-monotonic. A strong isotope effect has been found, favoring the dissociation of the light species.

**Keywords:** Ab initio quantum chemical methods and calculations; Catalysis; Molecular dynamics; Silver; Single crystal surfaces

## 1. Introduction

Silver is known as an effective heterogeneous catalyst for the partial oxidation of organic substrates, particularly, in the ethylene epoxidation process. Therefore the  $O_2/Ag$  system has been the subject of extensive study with the aim of revealing the detailed mechanism of the process [1–19]. The main line of research has been to identify the stable and meta-stable species of oxygen on the silver surface. The identification was carried out by surface-sensitive spectroscopic methods on different faces of a single crystal [1–3,5–9] or on polycrys-

talline silver films [10,11,20,21]. At least four oxygen species were identified [3,4]: (i) physisorbed oxygen, which is a slightly perturbed gas phase oxygen molecule [8], (ii) a superoxo-like molecular species ( $O_2^-$ ) characterized by a charge transfer from the metal to the oxygen molecule [2,11,22], (iii) peroxide ( $O_2^{2-}$ ), a molecular species with a larger charge transfer [8,11], and (iv) an atomic species of dissociated oxygen. The relative energetics of these species is still in dispute. Different crystal faces stabilize the different species differently. For example, on the Ag(111) face, the superoxo-like species is the only molecular species

identified, while on the Ag(110) and on polycrystalline films, both the peroxy and superoxy species have been identified [8].

The identified oxygen species on the silver surface are candidates for intermediates in a kinetic study. For the ethylene oxidation reaction, efforts have been made to identify the species responsible for the final stage of reaction. The possible candidates are the dissociated atomic oxygen or the molecular  $\text{O}_2^-$  species [23]. The kinetic approach tries to assign kinetic constants to the reactions which lead from the gas-phase oxygen to the candidate for oxidation. A central assumption of the kinetic theory is that for each individual species, internal degrees of freedom reach thermal equilibrium. This condition is fulfilled if the internal relaxation is faster than the rate of reaction. The nature of gas-surface reactions adds another complication arising from the possibility of island formation, which leads to a complicated dependence on surface coverage [24]. Other collective effects, such as surface reconstruction, can also blur the kinetic picture [4,25].

To clarify the picture of the dissociation mechanism, dynamical studies of the reaction of oxygen on silver have been performed. The goal was to study each elementary step individually. Dynamical experiments have been performed using molecular beams in ultra-high vacuum chambers [26,27]. It was found that dynamical factors such as the initial kinetic energy directly influence the dissociation probability. This means that there is a possibility of a dynamical route to dissociation without reaching equilibrium in the molecular chemisorbed species. This finding is in contrast to a kinetic picture, which assumes that equilibrium is reached in the intermediate steps to dissociation so that memory of the initial gas-phase dynamical factors is lost.

The possibility of a direct route to dissociation raises the question of the role of the intermediate species in the dynamics. The explanation followed in this work is that this dynamical event is quantum mechanical in nature, and that it involves a series of nonadiabatic transitions. The original idea can be traced to Lennard-Jones [28,29] and is strongly embedded in the field [30]. Support for a quantum picture is found in the large difference

in dissociation probability between the  $^{16}\text{O}$  and the  $^{18}\text{O}$  isotopes [31,32]. In the quantum dynamical view, the distinct chemical species are the labels of the diabatic surfaces. The diabatic picture involves a set of cross-potential manifolds. This is in contrast to the more common chemical picture of an adiabatic framework, where the reaction takes place on only one potential energy surface. The two pictures are equivalent if all surfaces involved are considered. The validity of the single surface adiabatic picture depends on the magnitude of the nonadiabatic coupling term  $V_{\text{gi}}$ , where a large value will make the adiabatic picture valid. In this work, it is argued that the value of the nonadiabatic coupling is small. The reason is that the electronic structure of the different chemical species is very different, so that the overlap between these electronic wavefunctions is small and will be reflected in the nonadiabatic coupling term. The result of this assumption is that the reaction is best described by a diabatic picture involving a manifold of many potential energy surfaces. Theoretical studies of nonadiabatic crossings [33–35] show that in the case of a small nonadiabatic coupling parameter, large deviations are found between the adiabatic approximation crossing probability and the full nonadiabatic calculation. The physical consequence is that the adiabatic dissociation probability saturates at a value of 1 for high incident energy, while the nonadiabatic dissociation probability reaches a maximum at a value less than 1.

The dissociation of oxygen on silver surfaces is not unique [4,36]. Similar molecular oxygen species have been identified on different faces of single crystals of copper, aluminum, palladium and platinum [37–41]. This means that the detailed understanding of the oxygen-silver system can be applied to other systems. The present study follows the non-adiabatic approach of previous work on the dissociation of  $\text{N}_2$  [42–49] and  $\text{H}_2$  [50] on metal surfaces. The numerical procedures used here have been developed for nitrogen studies. But, as will become apparent, the oxygen-metal and nitrogen-metal systems are actually quite distinct.

The present paper is based on a theoretical modeling of the dissociation process. Section 2 is a comprehensive analysis of the potential energy

surfaces. Section 3 summarizes the quantum time-dependent methods used for calculating the dissociation probability and the tunneling rate from the bound  $O_2^-$ . Section 4 describes the results of the calculation, in particular the dissociation probability as a function of initial kinetic energy, and tunneling rate as a function of temperature. Section 5 compares the results to the experiments and to other molecular metal systems. Section 6 contains the conclusions.

## 2. Potential energy surfaces

The potential energy surfaces used in this work are derived from two sources: ab initio calculations [8,51–58] and spectroscopic measurements [6,8,10]. Regrettably the reliability of the data is questionable. The ab initio calculations are hard to converge and their validity is only qualitative. One difficulty arises from the strong covalent bonds which oxygen can create with silver; the other problem is that the diabatic frame requires information on excited surfaces and on nonadiabatic coupling potentials. This fact rules out the naive use of density functional approaches [4]. On the other hand, spectroscopic data exists only for stable species. The determination of these species depends on the particular surface measured. The result is that large gaps exist in the knowledge of potential energy surfaces. The approach employed in this work is to define universal functional forms for the different potentials and to use a limited number of adjustable parameters to fit the potential to ab initio, spectroscopic and thermochemical data [2].

The functional form chosen describes the O–O bond by a Morse functional form, with parameters which depend on the distance from the surface. The interaction of the molecule with the surface is described by a combination of a short range exponential repulsion term and a long range electrostatic attraction. To eliminate the singularity of the electrostatic term at short distances, where the Pauli repulsion takes over [59], an interpolation function is introduced which turns off the electrostatic terms. This interpolation function is also used to interpolate the molecular parameters from

their gas-phase value to the value they attain on the surface.

Starting from the gas-phase oxygen molecule and approaching the surface, a free oxygen molecule is correlated to oxygen physisorbed on the surfaces. The forces operating on the molecule are dispersion forces. To a first approximation, these forces are universal and are the result of the attraction between the polarization of the molecule and its image charge distribution in the metal. The physical picture of the physisorbed state is of an oxygen molecule whose internal degrees of freedom are only slightly perturbed, i.e. an almost-freely rotating and vibrating molecule. This state can be characterized by a very low molecule–surface vibrational frequency.

The dependence of the physisorption potential of most collision energies, on the orientation angles  $\theta$  and  $\phi$  can be omitted. Only at very low temperatures does the anisotropic part of the polarization become important, causing a preferable perpendicular orientation. The following functional form has been chosen to describe the physisorption potential:

$$V_g(r, z, \theta) = A_g e^{-b_g z} - \frac{C_g(\theta)}{z^3} (1 - \Gamma_4(z, 0, 2b_g)) + D_g (1 - e^{-\alpha_{O-O}(z)(r - r_e(z))})^2, \quad (1)$$

where  $z$  is the distance of the center of mass of the molecule from the top atom of the metal,  $r$  is the inter-nuclear distance in the molecule,  $\theta$  is the orientation angle, and  $\theta = 0$  represents a molecule perpendicular to the surface. The dependence of  $C_g(\theta)$  can be described as  $C_g(\theta) = C_g^0 + C_g^2 P_2(\cos(\theta))$ .  $\phi$  is the azimuthal angle and since silver is very flat, the physisorption potential is independent of  $\phi$ . The incomplete gamma function  $\Gamma$  [60] is used as an interpolation function from the gas phase values to the adsorbed values

$$\Gamma_m(z, z_0, a) = \sum_{k=0}^{k=m} \frac{a(z - z_0)^k}{k!} e^{-a(z - z_0)}. \quad (2)$$

The molecular parameters become:

$$\begin{aligned} \alpha_{O-O}(z) &= \alpha_{O-O}^{ad} \quad \text{for } z < z_e, \\ \alpha_{O-O}(z) &= \alpha_{O-O}^g - (\alpha_{O-O}^g - \alpha_{O-O}^{ad}) \Gamma_4(z, z_e, b_g) \\ &\quad \text{for } z > z_e, \end{aligned} \quad (3)$$

and:

$$r_e(z) = r_e^g - (r_e^g - r_e^{ad}) \Gamma_4(z, z_c, b_g). \quad (4)$$

This potential form has to be adjusted to the gas phase, to adsorbate vibrational frequencies, and to the gas phase dissociation  $D_g$ . Also, the potential should fit to the  $O_2$  surface vibrational frequency and to the adsorption energy. In this potential form, the plane where  $z = 0$  is somewhat arbitrary. Physically it represents the plane where the gradient in electron density is maximized when going from the bulk of the metal into the gas phase. Since the source of the physisorption potential is the dispersion forces, it has a universal character depending only on the polarization properties of the molecule [61]. As a result, scaling relations exist between the gas-phase polarization and the surface potential parameters. These scaling relations are used to check the consistency of the potential parameters used in the calculation.

The species on the other side of the reaction is the dissociated oxygen. This species is characterized by a strong oxygen–surface bond resulting in a high vibrational frequency and a net negative charge on the oxygen. For each oxygen atom  $i$  this part of the potential can be characterized as

$$2V_a^i(z_i) = A_a e^{-b_a z_i} - \frac{C_a}{z_i} (1 - \Gamma_4(z_i, 0, 2b_a)). \quad (5)$$

The net negative charge on the oxygen atoms results in a long range dipole–dipole repulsion between them which can be characterized by

$$V_r(r, z_1, z_2) = \frac{F(z_1)F(z_2)}{r^2} + S(r), \quad (6)$$

where  $S(r)$  is a short range repulsion  $S(r) \approx S_0(1 + e^{-\beta_s(r-r_{sp})^2}) - S_0$ . The function  $F(z)$  is proportional to the atom surface dipole. Combining the contributions the atom–surface potential becomes:

$$V_a(r, z_1, z_2) = V_r(r, z_1, z_2) + V_a^1(z_1) + V_a^2(z_2) + E_a, \quad (7)$$

where  $\frac{1}{2}E_a$  is the difference between work function of the metal and the electron-affinity of atomic oxygen.

Two candidates have been suggested for the

intermediate molecular species. The first is the superoxide  $O_2^-$ . Due to the partial charge transfer from the metal, the O–O bond is weakened resulting in a reduced frequency of the O–O vibration [22,58]. Also, an increase in the oxygen–silver vibrational frequency is expected in comparison to the physisorbed species. They typical vibrational O–O frequency of the superoxide species is 950–1100  $cm^{-1}$ . The second candidate is the peroxide species  $O_2^{2-}$ . This species has a larger amount of charge transfer from the metal and a further weakening of the O–O bond in comparison with the superoxide. The typical frequency is from 600 to 700  $cm^{-1}$ . The potential has a strong orientation dependence where a flat orientation  $|\theta| = \pi/2$  is preferable, representing directional chemical bonds. The potential describing these species has the form

$$V_m(r, z, \theta, \phi) = A_m(\theta, \phi) e^{-b_m z} - \frac{C_m(\theta, \phi)}{z} (1 - \Gamma_2(z, 0, 2b_m)) + D_m(1 - e^{-\alpha_{O-O}(z)(r-r_e(z))})^2 + E_m, \quad (8)$$

where  $E_m$  is the difference between the work function of the metal and the electron-affinity of the molecule. The functional dependence of the molecular parameters on the molecule surface distance is as in Eqs. (3) and (4). The relative energetics of these species is important in determining their accessibility in different experiments.

Finally, a common functional form is used for the nonadiabatic coupling terms, which vanishes asymptotically

$$V_{ij}(r, z) = G e^{-\alpha_z z} e^{-\alpha_r r}. \quad (9)$$

Other functional forms [46] may be more appropriate. The use of a diabatic representation requires special attention to the electronic basis function and its variation with the nuclear configuration [62]. To calculate the nonadiabatic coupling term  $V_{ij}$ , extensive CI calculations have to be performed. The dipped adcluster model of Nakatsuji et al. [56] moves in the right direction, but does not calculate this parameter. The calculations do show that distinct ground and excited electronic states can be defined on the metal surface. The coupling

potentials  $V_{ij}$  can have a strong angular dependence, since from symmetry considerations, the coupling can vanish when  $\theta = \pi/2$ . To adjust for this fact in a reduced dimensional study, an empirical coupling has to be estimated averaged on the angular degree of freedom. Extended Hückel calculations estimate the coupling as 1 eV for the perpendicular orientation, and less than 0.1 eV for the parallel orientation. The small coupling in the parallel orientation is due to a small mixing of excited d-orbitals. A complication to be considered is the influence of scattering metal electrons on the molecular energy levels. Gadzuk has included the phenomena by introducing an effective coupling constant in the range 0.1–0.5 eV [63]. In this calculation the coupling constant at the region of the crossing seam is approximately 0.1 eV, which should be considered as a reasonable guess similar to the value used by Gates et al. [50] for hydrogen on metals.

With the functional forms of the potential set, calculations can be done with various sets of parameters. Although the orientation of the molecule is important, due to limited computational resources the calculations presented here are restricted to molecules parallel to the surface. The first set of potential parameters, summarized in Table 1, corresponds to a small modification of the potential suggested by Spruit for Ag(111) crystal faces [26]. The sequence of events leading to the dissociation described is



Fig. 1 shows a stereoscopic projection of the three superimposed potentials of this sequence.

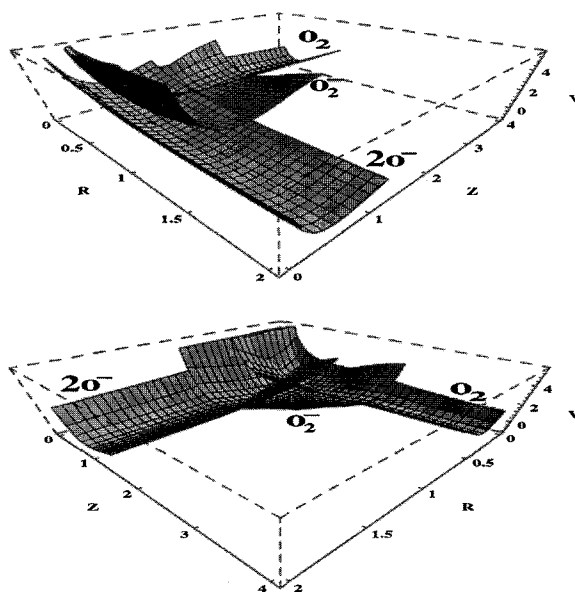


Fig. 1. A stereoscopic projection of the superposition of the three diabatic potential surfaces corresponding to the sequence of Spruit et al. The topmost potential surface is the physisorption ( $\text{O}_2$ ) and the lowest one is the dissociated state ( $2\text{O}^-$ ). Energy units are in eV and distances in Å.

The complicated structure of the crossing diabatic surfaces is apparent. Fig. 2 shows a contour map of the lowest part of the three potentials. The seams where the potential energy surfaces cross are clearly marked.

Recalculating the spectroscopic quantities from the potentials leads to the following values: the physisorption O–O vibration changes from  $1580\text{ cm}^{-1}$  in the gas phase to  $1545\text{ cm}^{-1}$  in the adsorbed state. The molecular surface vibration

Table 1  
Parameters of the Spruit potential (energy in eV, distance in Å)

|                       |                                                |                                                                                      |                                                               |                                       |
|-----------------------|------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------|
| Physisorption         | $A_g = 829$<br>$b_g = 3.73$<br>$r_g^e = 1.208$ | $C_g = 3.79$<br>$\alpha_{\text{O-O}}^{\text{ad}} = 2.63$<br>$r_e^{\text{ad}} = 1.24$ | $D_g = 5.1$<br>$\alpha_{\text{O-O}}^e = 2.69$<br>$z_e = 2.47$ |                                       |
| Dissociated oxygen    | $A_a = 207$<br>$b_a = 3.01$                    | $C_a = 14.6$<br>$S_0 = 20$                                                           | $F^2 = 2.1$<br>$\beta_a = 3.5$                                | $E_a = 5.68$<br>$r_{\text{ep}} = 0.5$ |
| Molecular species     | $A_m = 1400$<br>$b_m = 3.76$<br>$r_m^e = 1.35$ | $C_m = 10.1$<br>$\alpha_{\text{O-O}}^{\text{ad}} = 1.21$<br>$r_e^{\text{ad}} = 1.47$ | $D_m = 4.1$<br>$\alpha_{\text{O-O}}^e = 2.07$<br>$z_e = 2.04$ | $E_m = 3.84$                          |
| Interaction potential | $G = 2.2$                                      | $\alpha_z = 1.0$                                                                     | $\alpha_r = 1.0$                                              |                                       |

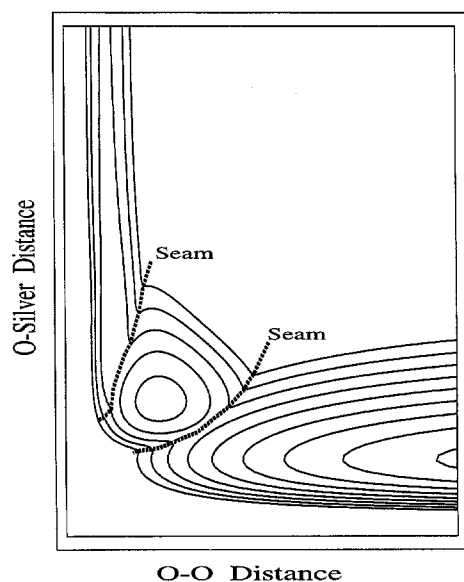


Fig. 2. A contour map of the lowest parts of the three diabatic potential surfaces corresponding to the sequence of Spruit et al. The dashed lines represent the seams where the potential energy surfaces cross. The lowest contour is  $-1$  eV and intervals are of  $0.2$  eV. The total distance in the  $z$  direction is  $4$  Å and in the  $x$  direction is  $2$  Å.

then becomes  $74\text{ cm}^{-1}$  with a well depth of  $0.17$  eV. For the molecular chemisorption species, the O–O vibration becomes  $640\text{ cm}^{-1}$  and the molecular surface vibration becomes  $240\text{ cm}^{-1}$  with a well depth of  $0.5$  eV compared to the free oxygen molecule. The molecular chemisorption frequencies were re-checked by calculating the vibrational eigenfunctions and eigenvalues by the relaxation method [64]. They led to  $634\text{ cm}^{-1}$  for the O–O vibrational transition frequency and  $239\text{ cm}^{-1}$  for

the molecular surface vibration transition frequency. The dissociated species has a frequency of  $300\text{ cm}^{-1}$ . Its well depth is  $1.8$  eV compared to the free oxygen molecule.

The second set of parameters, summarized in Table 2, corresponds to a potential fitted to the ab initio calculation of Nakatsuji et al. [53–56] for the Ag(110) face with the sequence:



Fig. 3 shows a contour map of the three superimposed potentials of this sequence. The spectro-

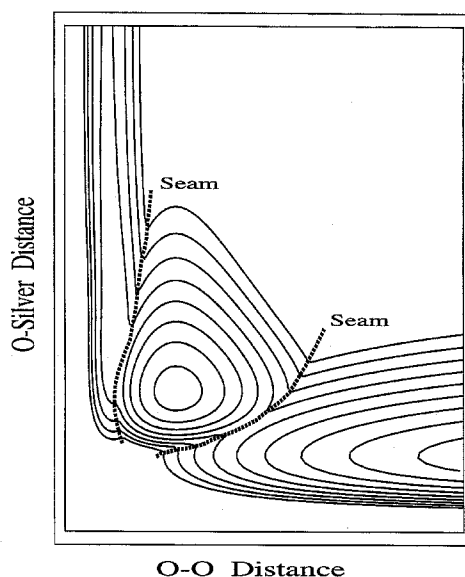


Fig. 3. Contour map of the lower part of the diabatic part of the three potential surfaces corresponding to the potential of Nakatsuji et al. The setup is as in Fig. 2.

Table 2  
Parameters of the Nakatsuji potential (energy in eV, distance in Å)

|                       |                                                |                                                                                      |                                                               |              |
|-----------------------|------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------|--------------|
| Physisorption         | $A_g = 829$<br>$b_g = 3.73$<br>$r_g^e = 1.208$ | $C_g = 3.79$<br>$\alpha_{\text{O-O}}^{\text{ad}} = 2.63$<br>$r_e^{\text{ad}} = 1.24$ | $D_g = 5.1$<br>$\alpha_{\text{O-O}}^g = 2.69$<br>$z_e = 2.47$ |              |
| Dissociated oxygen    | $A_a = 207$<br>$b_a = 3.01$                    | $C_a = 14.6$<br>$S_0 = 0$                                                            | $F^2 = 5.0$<br>$\beta_s = 2.0$                                | $E_a = 5.68$ |
| Molecular species     | $A_m = 1300$<br>$b_m = 3.56$<br>$r_e^g = 1.55$ | $C_m = 11.5$<br>$\alpha_{\text{O-O}}^{\text{ad}} = 1.31$<br>$r_e^{\text{ad}} = 1.55$ | $D_m = 4.1$<br>$\alpha_{\text{O-O}}^g = 1.31$<br>$z_e = 2.1$  | $E_m = 3.84$ |
| Interaction potential | $G = 2.2$                                      | $\alpha_z = 1.0$                                                                     | $\alpha_r = 1.0$                                              |              |

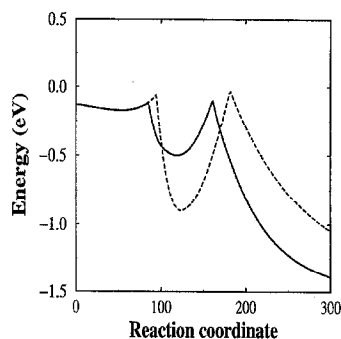


Fig. 4. The minimum energy profile leading from  $O_2$  to  $2O^-$  for the Spruit potential (solid line) and the Nakatsuji potential (dashed line). The zero of energy is set at the gas-phase molecular state. The reaction coordinate is in arbitrary units.

scopic quantities obtained are the same as the Spruit potential except for the molecular chemisorption O–O vibration which is  $690\text{ cm}^{-1}$ .

Despite the fact that the vibrational frequencies of the two potentials are quite similar the topology of the two surfaces is different. Fig. 4 shows the minimum energy path of the two surfaces leading from the gas phase to dissociation. For both potentials there is no apparent barrier for dissociation. The Nakatsuji potential has a deeper molecular chemisorption well. Another important difference is the direction of the seams where the nonadiabatic transition take place. The first crossing seam, leading from the physisorption to the intermediate well, is quite similar. A significant difference is found in the direction of the second seam, which is more parallel to the  $r$  axis in the Nakatsuji potential.

### 3. Dynamical calculations

#### 3.1. Time-dependent propagation

The dynamics of the system are simulated by solving the time-dependent Schrödinger equation on three coupled potential energy surfaces. As has been discussed in Section 2, a fourth species may contribute to the dynamics. Nevertheless it will be omitted from the calculation, the reason being that its participation in the process is questionable. The system is treated as an initial-value problem, start-

ing with amplitude in the gas-phase species. The state of the system is treated as a three-component wavefunction corresponding to the labeling of the three chemical species. With these characteristics the wavefunction has the form

$$\psi = \begin{pmatrix} \psi_g(z,r) \\ \psi_m(z,r) \\ \psi_a(z,r) \end{pmatrix}. \quad (12)$$

The state of the system evolves by the Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad (13)$$

where

$$\hat{H} = \begin{pmatrix} H_g & V_{gm} & V_{ga} \\ V_{mg} & H_m & V_{ma} \\ V_{ag} & V_{am} & H_a \end{pmatrix}, \quad (14)$$

and  $H_l = P^2/2\mu + V_l$  where  $l$  is the index of the species:  $g$  for the gas phase species,  $m$  for the molecular surface species and  $a$  for the atomic dissociated species. Since the  $z$ - and  $r$ -coordinate systems contain kinetic energy coupling, the propagation is carried out in mass scaled coordinates [46]. In this model there is no coupling between the physisorbed oxygen and the atomic species, i.e.  $V_{ga} = V_{ag} = 0$ . The reduced mass  $\mu$  can be estimated by the hard cube model [65]. For this system, it is very close to the mass of two oxygen atoms.

The framework of chemical species defines the stage on which the dynamical events are to take place. A set of three spatial grids is constructed in the  $z$  and  $r$  coordinates, which cover the range of coordinates on which each species acquires a significant amplitude. Table 3 describes the grid parameters used in the calculation. On these grid points the values of the species potential  $V_l$  are calculated. The crucial step in solving the dynamics is to calculate the operation of the Hamiltonian equation (Eq. (14)) on the wavefunction  $\psi$ . The operation is divided into a kinetic part and a potential energy part. The potential operation is local in coordinate space, and thus becomes a

Table 3  
Parameters of propagation (a.u.)

|                    |                      |                     |              |              |
|--------------------|----------------------|---------------------|--------------|--------------|
| Grid               | $\Delta z = 0.01$    | $\Delta r = 0.0125$ | $z_0 = 1.00$ | $r_0 = 1.00$ |
| Physisorption grid | $N_z = 400$          | $N_r = 50$          |              |              |
| Dissociated oxygen | $N_z = 400$          | $N_r = 200$         |              |              |
| Molecular species  | $N_z = 400$          | $N_r = 200$         |              |              |
| Time propagation   | $\Delta t = 0.01$ ps | $N_t = 400$         |              |              |

multiplication of the potential matrix at a specific grid point for each chemical species by the wavefunction at that grid point. The coupling between species is by the potential non-diagonal terms at each grid point. The kinetic energy operator is implemented by transforming the wavefunction to momentum space where the operation is local via the fast Fourier transform (FFT) algorithm [66,67]. Once in momentum space, the wavefunction is multiplied by  $\hat{p}^2/2m$  and transformed back to coordinate space.

The evolution in time is then carried out by a polynomial expansion of the evolution operator [66,68]:

$$\begin{aligned}\psi(t) &= e^{-(i/\hbar)Ht}\psi(0) \\ &= \sum_{n=0}^N a_n(\Delta Et/2\hbar) T_n(H_N)\psi(0) \\ &= \sum_{n=0}^N a_n(\Delta Et/2\hbar) \phi_n,\end{aligned}\quad (15)$$

where  $a_n$  are the expansion functions  $a_n(x) = 2i^{-n} J_n(x)\Phi$ ,  $a_0(x) = J_0(x)\Phi$ ,  $J_n(x)$  are the Bessel functions, and  $\Phi = e^{i/h(\Delta E/2 + E_{\min})t}$ .  $T_n$  are the Chebychev polynomials where the functions  $\phi_n$  are calculated by the recursion

$$\phi_{n+1} = 2H_N\phi_n - \phi_{n-1}, \quad (16)$$

where the recursion is initiated by  $\phi_0 = \psi$ ,  $\phi_1 = H_N\psi$ .  $H_N$  is the normalized Hamiltonian operator:

$$H_N = \frac{H - IE_{\text{avg}}}{\Delta E/2} \quad (17)$$

where  $\Delta E$  is the spectral range of the Hamiltonian and  $E_{\text{avg}}$  is the center of the spectral range. The calculation scheme is similar to the one used for the simulation of nitrogen dissociation on rhenium and iron surfaces [44,46].

In order to eliminate the effects arising from the

finite size of the grids, the wavepacks  $\psi_g$  and  $\psi_a$  are absorbed by an optical potential of the form  $V_{\text{NIP}} = -iU_0/\cosh^2(\alpha x)$  as they approach the edges [64]. The dissociation probability is calculated by integrating the flux of  $\psi_a$  passing through a dividing plane just before the absorbing potential starts. The flux is calculated by the expression:

$$\begin{aligned}F_r(z,t) &= \frac{i\hbar}{2m} \left[ \psi(z,r,t) \frac{\partial \psi^*(z,r,t)}{\partial r} \right. \\ &\quad \left. - \psi^*(z,r,t) \frac{\partial \psi(z,r,t)}{\partial r} \right]\end{aligned}\quad (18)$$

The derivatives are calculated by using the Fourier method. The flux is integrated to give the accumulated dissociation probability:

$$P_n(t) = \int_0^t \int_{z_{\min}}^{z_{\max}} F_r(z,t') dz dt' \quad (19)$$

To check the convergence of the calculation, a flux integration is also performed on the  $\psi_g$  wavefunction by calculating the non-reactive accumulated probability. The sum of the integrated fluxes and the wavepackets remaining on the grids are calculated after every time-step to check for normalization conservation.

### 3.2. Non-adiabatic tunneling rates

Non-adiabatic dissociative tunneling from the chemisorbed molecular state is relevant to this work for two reasons. First, it complements the direct reaction probability calculation, where part of the wavepacket coming from the gas phase is trapped in the chemisorbed molecular state for a considerable length of time. As a result of its protracted residence in the molecular well, the wavepacket eventually thermalizes to surface tem-



perature. In the model presented here, any subsequent dissociation is then due to tunneling. The tunneling rate can also be measured directly, by starting from the molecular desorbed species. These measurements, followed by tunneling rate calculations, can shed light on the potential energy surfaces and the non-adiabatic coupling strengths.

The non-adiabatic tunneling calculation consists of two main phases. In the first phase, the lowest eigenstates of the molecular chemisorption well are calculated, approximately 20 or 30 states. The relaxation method [64] is used, where the relaxation function is  $D(H, t) = \exp(-H\tau)$ . Starting from an energetic wavepacket  $\Psi$  in the molecular chemisorption well, a small orthogonal basis is constructed which spans a low energy subspace of the molecular chemisorption Hilbert space. This is done by operating on  $\Psi$  with  $D(H_n, \tau)$ , i.e.

$$H_n = H \left( 1 - \sum_{k=1}^{n-1} |\psi_k\rangle\langle\psi_k| \right), \quad (20)$$

where  $\psi_k$  are the previously found eigenstates, and

$$\Psi_n = D(H_n, \tau)\Psi. \quad (21)$$

The relaxation function  $D(\tau)$  is very efficient in damping of highly energetic components of  $\Psi$ . Operating with a very large  $\tau$  can in principle completely resolve the eigenstates, but this is inefficient and suffers from instability due to the projection operators in Eq. (20). For the final resolution, one should use a diagonalization of the Hamiltonian restricted to the small dimensional relaxed subspace [69]. The relaxation stage is therefore only done for relatively small  $\tau$  values. After diagonalization, the basis is extended by adding basis functions (more relaxations) and then re-diagonalization. The low eigenstates converge extremely rapidly. Thus, in order to obtain 20 converged eigenstates, one needs to relax (with small  $\tau$  values) about 30 or 40 eigenstates.

An eigenstate with energy  $E$  of the chemisorption well are good initial approximations for the tunneling energy and eigenstate of the complete non-adiabatic Hamiltonian  $H$ . The final synthesis of a tunneling eigenstate then proceeds by operating on the chemisorption eigenstate with the Green's operator  $G(E) = (E - H)^{-1}$ , where  $E$  is the energy

of the chemisorption eigenstate. It is immediately apparent that the operation of  $G(E)$  on a wavepacket results in amplification of the components of energy close to  $E$ . This procedure is not sufficient to ensure a correct calculation of the tunneling state since the tunneling resonance boundary conditions are not enforced. The relevant boundary conditions have an outgoing-only solution in the asymptotic channels. In order to impose this boundary condition a negative imaginary potential [64,70,71–74]  $V_{\text{NIP}}$  is employed in each asymptotic channel. In the  $\text{O}_2/\text{Ag}$  system there are two such channels – the dissociation and the physisorption channels. Thus, the effective Hamiltonian is  $H' = H + V_{\text{NIP}}$  and the filtering function for the tunneling state is  $G(E) = (E - H')^{-1}$ . One operates with the Greenian a few times (usually once is enough) on the molecular chemisorption eigenstate and obtain the full-Hamiltonian tunneling state.

The eigenvalues of tunneling states are discrete and complex, valued  $\Lambda_n = E_n - i\Gamma/2$ , where  $E_n$  is the tunneling energy and the total tunneling rate is  $\Gamma_n$ . The tunneling eigenstates are also “complex” in the sense that they have non-zero flux in asymptotic channels. Strictly speaking, they are the right eigenstates of  $H'$ . The tunneling rate into a certain asymptotic channel can be determined from the total tunneling eigenstate by calculating the flux through a dividing surface defining this channel. The resulting product vibrational content can also be determined by using vibrational projection operators while calculating the flux [75].

The numerical implementation of this algorithm is based on the principles discussed in Section 3.1. The Hamiltonian takes the form of Eq. (14) and the three wavepackets are represented on a uniform grid, using FFT to perform the kinetic energy operation as described above. The numerical implementation of the Green's operator is also based on that of the evolution operator described above. In fact, since the polynomial expansion of the evolution operator in Eq. (16) effectively separates time and space, and since the Green's operator is a half Fourier-transform of the evolution operator, it too can be represented by a Chebychev-polynomial expansion  $G(E)\Psi = -i \sum_{n=0}^N b_n(E) T_n(H_N) \Psi$ , where the coefficients  $b_n$  are just the half Fourier-transforms of the Bessel func-

tions [66,76], and can be written as

$$b_n(E) = (2 - \delta_{n0})(\Delta E/2)^{-1} \frac{\exp(-inz)}{\sin z}, \quad (22)$$

where  $\cos z = E_N = (E - A_{\text{avg}})/(\Delta E/2)$  is the normalized complex energy, whose parameters we discuss now. The normalization of the Hamiltonian as given by Eq. (17) is rigorously correct only for completely hermitian Hamiltonians. For non-hermitian operators, modifications of this procedure have been developed [76–78], as well as methods based on Newtonian polynomials [68,79]. In practice the Chebychev scheme is stable in the presence of imaginary potentials, provided  $tV_{\text{NIP}} \ll 1$ . But, since the Green's operator is an integration of the evolution operator up to infinite times, the Hamiltonian must be normalized, enabling arbitrary long time-steps. The procedure of Huang et al. [77,80] was used to perform the normalization. This procedure is based on the theory of Faber polynomial interpolation, and involves the location of an ellipse contained in the lower part of the complex energy plane, which encircles all the eigenvalues of the complex Hamiltonian operator  $H'$ . Designating the center of the ellipse (a complex number)  $A_{\text{avg}}$  and the major axis length (a real number) by  $\Delta E$ , the normalization of the Hamiltonian is then given by:

$$H_N = \frac{H' - A_{\text{avg}}}{\Delta E/2} \quad (23)$$

In practice there is no need to actually locate the ellipse parameters, and  $\Delta E$  is given by the real part of Hamiltonians' spectral range multiplied by a factor greater than 1 (usually about 2–3).

The convergence of the expansion representing the Green's operator is determined by the size of the imaginary part of  $z$  in Eq. (22): the series will be converged once  $n \gg \text{Im}(z)$ . In the calculations presented below, approximately 1500–3000 terms are needed.

The procedure of calculating the tunneling states using an absorbing potential is similar to the complex coordinate scaling method (CCSM) [81] method for calculating resonances, where the NIP parameters are analogous to the complex rotation parameters. In CCSM one searches for optimal

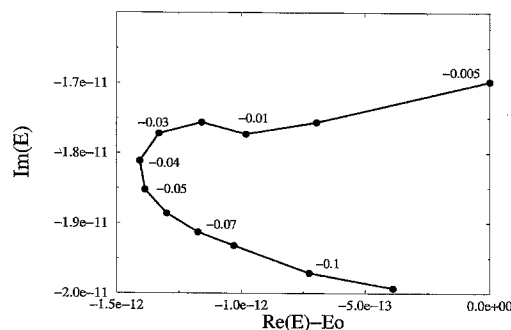


Fig. 5. The trajectory of eigenvalues for different negative imaginary potential (NIP) heights in Hartree. The NIP height is varied by a factor of 10 throughout the trajectory. The eigenstate at the cusp is the optimal eigenstate.

scaling parameters by looking for cusps in the complex energy plane of a scaling-parameter trajectory [82]. The analogous trajectory here is the sensitivity to the NIP parameters.

In Fig. 5 the sensitivity to the NIP height is shown. It is seen that the energy of the tunneling state changes in the ninth or tenth digit when the NIP strength is varied by a factor of 10. The tunneling rate changes by less than a factor of 2. The figure has the structure of a cusp and, strictly speaking, one should take the eigenstate at the cusp. It should be emphasized that if the total tunneling rate at a certain temperature is needed, the calculation is much more sensitive to the eigenstate energy than to the eigenstate tunneling rate (due to the Boltzmann factor).

Tunneling calculations were also carried out on an adiabatic single potential by a very similar procedure. A comparison of the adiabatic and diabatic resonance lifetimes are shown in Section 4.3

## 4. Results

### 4.1. Direct reaction

A series of calculations was performed starting from a wavepacket in the asymptotic gas phase state. Using the potential of Spruit, the incident kinetic energy and incident vibration were altered. Fig. 6 shows the wavepacket at its turning point

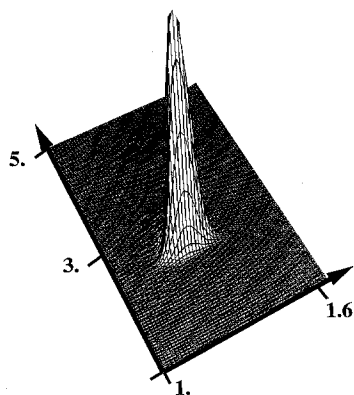


Fig. 6. The absolute value of  $|\psi_g|^2$  at the classical turning point of the physisorption potential ( $t = 0.1$  ps). The distances are in Å and amplitude is multiplied by a factor of 50.

position on the physisorption molecular surface. The wavepacket is only slightly modified from its initial state. After the collision with the repulsive wall most of the amplitude is reflected back to the gas phase, while a small fraction is transferred to the molecular chemisorption potential. This means that the event of creating the molecular chemisorption species is very fast. Fig. 7 shows the nascent wavepacket on the molecular chemisorption surface. Fig. 8 shows  $\psi_m$  at a later time. Due to the shape of the molecular chemisorption potential,  $\psi_m$  becomes scrambled, filling all the energetically allowed configuration space. Once the wavepacket fills the molecular chemisorption potential, it leaks very slowly into the dissociation channel and back

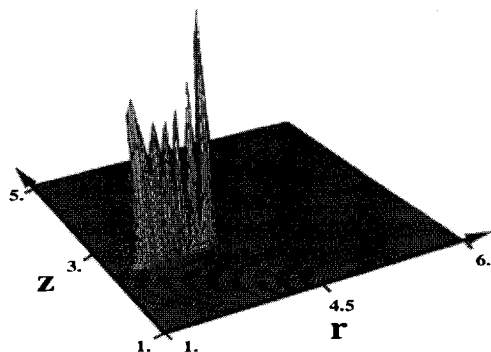


Fig. 7. The absolute value of  $|\psi_m|^2$  just after it was created by crossing from the physisorption potential ( $t = 0.1$  ps). The amplitude of the wavefunction is amplified by  $\sim \times 10^3$ .

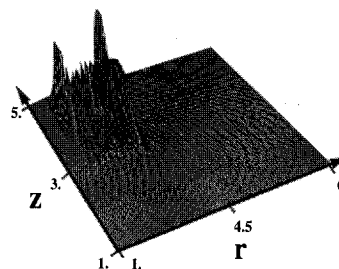


Fig. 8. The absolute value of  $|\psi_m|^2$  100 fs later than in Fig. 7. Most of the wavepacket motion is a recoil from the surface.

into the gas phase. The fast buildup of the norm in  $\psi_m$ , and its slow decay, can be observed in Fig. 9.

The wavefunction on the dissociative chemisorption potential is the source of the wavefunction in the dissociative channel. The peak at small  $r$  values is in the region of the source. On the dissociative atomic surface a highly excited wavepacket is created, as can be seen in Fig. 10.

The excitation of the translational motion means that the dissociated oxygen can find itself far from the point at which it was created. Considering the balance of energy, the initial incident kinetic energy is transformed to vibration and molecule/surface vibrational energy of the intermediate  $O_2^-$ . This excess energy adds to the exoergidity of the reaction and is channeled to translational motion parallel to the surface and atom/surface vibration. Only at incident energies above 2 eV does the

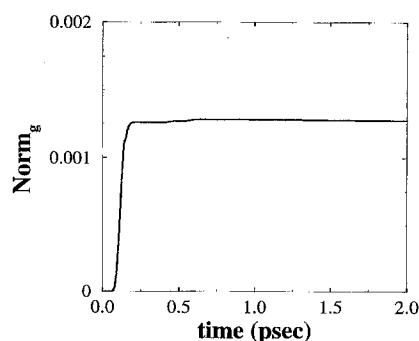


Fig. 9. The norm of the molecular chemisorption potential energy surface as a function of time. Notice the fast rise describing the initial collision of the molecule from the gas phase with the repulsive part of the physisorption potential where amplitude crosses to the molecular chemisorption potential.

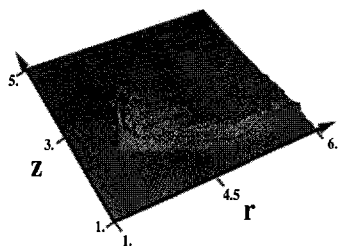


Fig. 10. The absolute value of  $|\psi_a|^2$  1 ps after the collision ( $t = 0.6$ ). The amplitude of the wavefunction is amplified  $\sim \times 10^6$ .

desorption channel of  $O_2^-$  open, leading to the production of negative ions in the gas phase.

The accumulation of the dissociated product is very slow, and will continue as long as there is amplitude in the molecular chemisorption well. The slow accumulation leads to considerable numerical difficulties since very long integration times are needed. Therefore, careful attention has been devoted to the numerical convergence of the results by changing the integration time and the grid parameters.

In Fig. 11 the dissociation probability and the accumulated intermediate species are shown for different incident kinetic energies. Fig. 11 shows an initial decline in the dissociation probability as a function of initial kinetic energy. For higher energies the trend is reversed, and an increase in dissociation probability is observed. This result is in accordance with the work of Spruit et al. [27]. Since the dissociation probability follows the

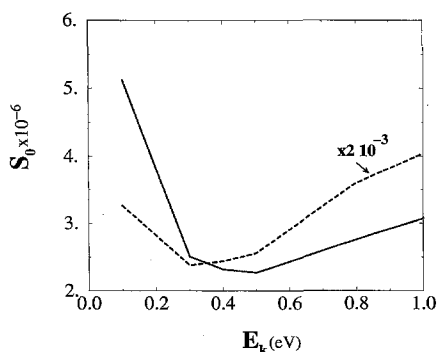


Fig. 11. Dissociation probability as a function of energy for the Spruit potential (solid line) accumulated in 10 ps. The dashed line represents the probability of  $O_2^-$  molecular chemisorption potential at 1 ps.

amplitude accumulated as  $O_2^-$ , it seems that the physisorption well is responsible for the initial decline. These results are in conflict with the more recent study of Raukema [83] where only an increase in dissociation probability was observed. This observation would suggest a direct route from the physisorption potential to the dissociative chemisorption potential. In this study, since the relevant non-adiabatic coupling potential  $V_{ag}$  is zero, this channel is blocked.

Note, however, that in accordance with the experiment, the total dissociation probability is very small despite the fact that the total energy in all runs is above the lowest point in the non-adiabatic crossing seams. This is a manifestation of the non-adiabatic nature of the reaction. The shape of the dissociation probability follows the magnitude of the amplitude trapped on the molecular chemisorption surface (the dashed line in Fig. 11). Once temporarily trapped, the molecule can either dissociate or desorb back into the gas phase. The ratio of these processes decreases with the incident energy. By changing the non-adiabatic coupling constant, it was found that the functional dependence on kinetic energy does not change, and the whole graph shifts monotonically. Exciting the initial vibrational energy leads to a flat kinetic energy dependence.

Non-adiabatic reaction mechanisms are very sensitive to isotopic substitution. Fig. 12 compares the dissociation probability obtained for  $^{16}O$  with that of  $^{18}O$ . For almost all energies, the lighter isotope has a larger dissociation probability. This

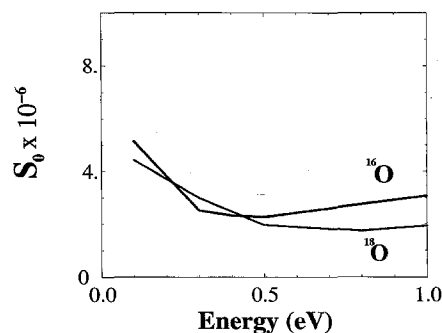


Fig. 12. Dissociation probability as a function of incident kinetic energy accumulated in 10 ps for the  $^{16}O$  and  $^{18}O$  isotopes on the Spruit potential.

finding is in accord with the thermal experiment [31] where the lighter isotope was found to dissociate faster.

A similar series of calculations was also run for the Nakatsuji potential. A comparison of the results with the Spruit potential is shown in Fig. 13. The initial decline in dissociation probability is less apparent in the Nakatsuji potential calculations. At higher energies both potentials show an increase in dissociation probability.

Fig. 14 compares the population  $P_m$ , in the molecular chemisorption potential after 1 ps. The Nakatsuji potential shows a monotonic decline in the population in the intermediate state as a

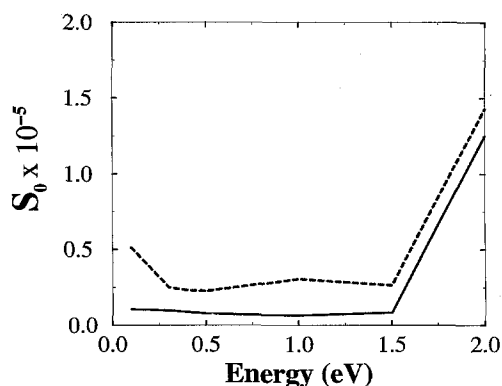


Fig. 13. Dissociation probability as a function of incident kinetic energy for the Nakatsuji potential (solid) compared with the Spruit potential (dashed line) accumulated in 10 ps.

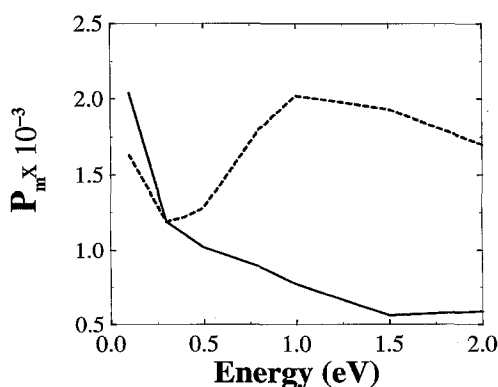


Fig. 14. Probability amplitude on the molecular chemisorption potential as a function of incident kinetic energy for the Nakatsuji potential (solid line) compared with the Spruit potential (dashed line) after 1 ps.

function of incident kinetic energy, as would be expected from a Landau–Zener case above the crossing point. This decline in the intermediate population does not seem to affect the dissociation probability.

Qualitatively, the two potentials show similar behavior. The dissociation probability stays low and is not very sensitive to the incident kinetic energy. Amplitude accumulates for very long times in the molecular chemisorption surface, which means that there is ample time for thermalization. For this reason tunneling from a thermalized state is considered.

#### 4.2. Tunneling rates and thermal averages

To check this hypothesis, the tunneling states and rates from the diabatic molecular chemisorption well were calculated, by the method described in Section 3.2. The 16 lowest dissociative tunneling energies and rates for three values of the non-adiabatic coupling parameter ( $G$  in Eq. (9)) are shown in Fig. 15. It is seen that the energy spectrum is simply shifted towards high tunneling rates when the  $G$  parameter increases. This phenomenon is a result of the small  $V_{ma}$  coupling. Another important

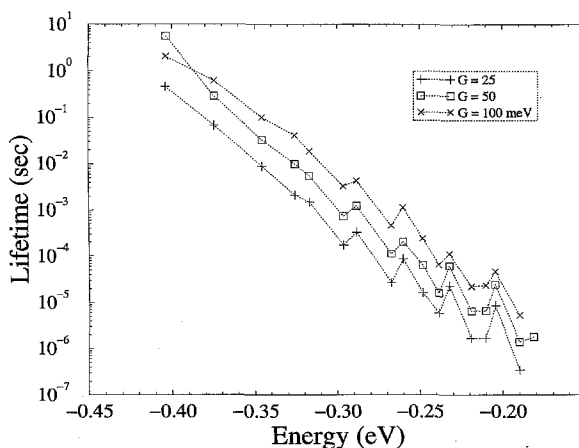


Fig. 15. The energies and lifetimes of the low-lying tunneling states of  $^{16}\text{O}_2$  from the molecular chemisorption well. The lifetimes depend on the diabatic coupling strength  $V_{ma}$ . Since this coupling is weak, the pattern of a weaker coupling simply shifts the spectrum to longer lifetimes. The zero of energy is approximately at the diabatic intersection of the molecular chemisorption and atomic chemisorption diabatic potentials.

result is that the tunneling is mode-selective. Increasing the vibrational energy inside the chemisorption well does not always result in increased tunneling rates. Thus the O–O mode is more effective in inducing tunneling than the O–O/surface mode. The isotopic effect of tunneling was also studied and it was found, as was expected, that the heavier mass tunnels at a slower rate, as shown in Fig. 16.

The energy-dependent tunneling rates are Boltzmann-averaged to yield the total tunneling rate as a function of temperature, as shown in Fig. 17. The bending of the Arrhenius plot is caused by the fact that at higher temperatures the tunneling flux shifts to higher energies. In any case, the “activation” energy is below the non-adiabatic crossing point.

An interesting experimental probe of the non-adiabatic coupling can be achieved by monitoring the molecular-chemisorption coverage of the surface as a function of temperature starting, at a low temperature and increasing it at a constant rate. This is similar to a TPD (thermal programmed desorption) experiment, but the molecules dissociate on the surface instead of desorbing after recombination. Usual TPD experiments on Ag(111) show that recombination is achieved at a surface temperature of 600 K [2] and recombinative

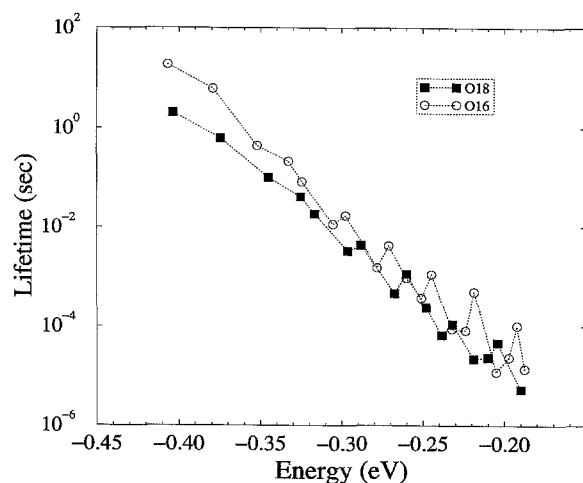


Fig. 16. Isotope effect for the tunneling from the chemisorption well. Energy versus lifetime is shown for  $^{16}\text{O}$  and  $^{18}\text{O}$ . The heavier mass has more states and longer lifetimes inside the well.

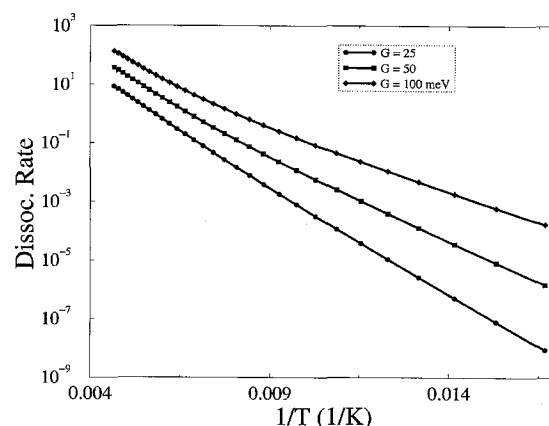


Fig. 17. The total tunneling rate as a function of temperature for  $^{16}\text{O}$ . The three lines represent the different values of the diabatic coupling potential  $V_{\text{am}}$ . The lowest curve, corresponding to a small diabatic coupling, can be fitted to an Arrhenius activation energy of  $E_a = 0.15$  eV, and the highest curve to  $E_a = 0.087$  eV at low temperature and  $E_a = 0.15$  eV at high temperature.

desorption from the molecular well occurs at about 190–200 K [2,83]. So far, non-adiabatic tunneling rates from molecular into dissociated states have not been measured. Anticipating a measurement of this kind, the dynamical results are employed to obtain a kinetic picture of the non-adiabatic tunneling dissociation as a function of temperature. If the surface temperature is raised at a constant rate of  $\alpha$  degrees per second then the total tunneling rate of temperature  $T$  is proportional to  $k(T)N(T)/N(T_0)$ , where  $N(T)$  is the number of chemisorbed molecules on the surface at temperature  $T$ , i.e.

$$N(T) = N(T_0) \exp\left(-\frac{1}{\alpha} \int_{T_0}^T k(T) dT\right), \quad (24)$$

and  $k(T)$  is the thermally averaged tunneling rate

$$k(T) = \sum_v k_v e^{-(E_v/k_B T)}, \quad (25)$$

where  $k_v$  and  $E_v$  are, the nonadiabatic tunneling rate and energy of the  $v$ th vibrational state,  $k_B$  is Boltzmann's constant. Using the dynamical results, the tunneling rate as a function of surface temperature in such a TPD experiment is shown in Fig. 18. It should be noted that at this energy range, there is essentially no escape of wavefunction

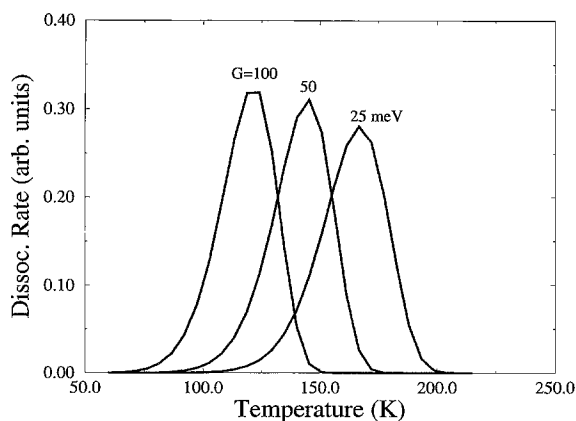


Fig. 18. Tunneling rate from the molecular well to the dissociative state as a function of surface temperature for a heating rate of  $10 \text{ K s}^{-1}$ . The different lines correspond to different diabatic  $V_{\text{am}}$  coupling coefficients  $G$ . It is seen that the strength of the diabatic coupling determines the peak temperature.

amplitude into the physisorption channel, due to its high asymptotic potential energy. The sensitivity of the TPD experiment to the nonadiabatic coupling parameters should also be noted.

Tunneling rates are extremely sensitive to mass. This is shown in Fig. 19, where the different tunneling rates for the different isotopes are reflected in the TPD signal. The calculations predict isotope sensitivity of the position of TPD peaks.

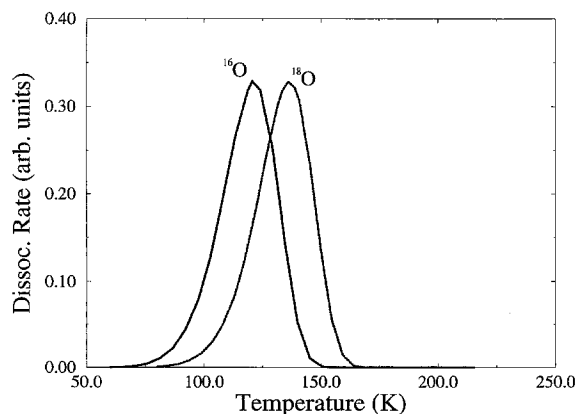


Fig. 19. Comparison of the tunneling rate of  $^{16}\text{O}$  and  $^{18}\text{O}$  from the molecular well to the dissociative state as a function of surface temperature for a heating rate of  $10 \text{ K s}^{-1}$ . The diabatic  $V_{\text{am}}$  coupling coefficient is  $G = 100 \text{ meV}$ .

### 4.3. Diabatic versus adiabatic tunneling calculations

It is interesting to compare the diabatic tunneling rates to the rates calculated using the adiabatic approximation. The calculation of adiabatic tunneling follows the same method as outlined above. There is a single potential surface which is the lowest eigenvalue of the diabatic potential matrix. Due to the small diabatic coupling, the adiabatic results grossly overestimate the tunneling rates, i.e. by more than four orders of magnitude. This is shown in Fig. 20. It can be concluded that adiabatic calculations for these systems can be orders of magnitude off-scale.

## 5. Discussion

It is appropriate to compare the results of the  $\text{O}_2$  dissociation on silver to other systems which have been studied quantum mechanically. The most extensively studied dissociative process is that of  $\text{H}_2$  on Cu. This system is unique in that extremely good state to state measurements of almost all dynamical variables have been performed [84,85]. The system has also been the subject of extensive theoretical study including high quality multi-dimensional quantum mechanical calculations [86,87], and mixed quantum-

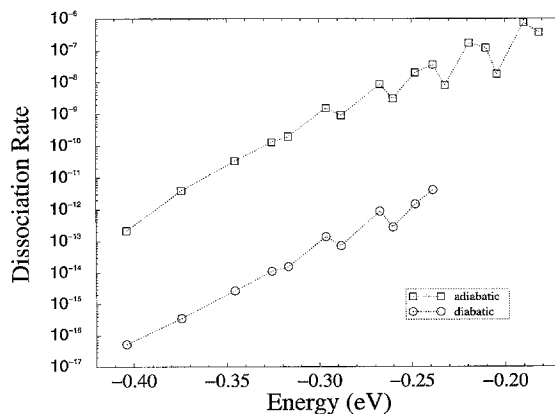


Fig. 20. Comparison between the tunneling rates of adiabatic and diabatic calculations on the Spruit potential. The adiabatic calculations overestimate the tunneling rates by 4 orders of magnitude.

classical calculations of all degrees of freedom of the molecule [47,88,89]. The quality of the investigations has brought about a detailed understanding of the ability of the different degrees of freedom to promote dissociation. For example, an “S” shaped monotonic increase in dissociation probability as a function of initial kinetic energy has been found for the  $\text{H}_2$ –Cu system.

The main difference between the  $\text{H}_2$ –metal studies and the  $\text{O}_2$ –on-silver study is that the hydrogen dissociation was modeled on one adiabatic potential energy surface. For the  $\text{H}_2$ –Cu system, such an assumption is probably justified due to the large non-adiabatic coupling term found for hydrogen. Oxygen is different and its ability to create directional bonds with the d bands of silver. Such an ability can significantly reduce the non-adiabatic coupling term due to the lack of an overlap between the different electronic wavefunctions. Considering theoretical treatments of charge transfer states of adsorbate on metal surfaces, there is a confusion between the lifetime of an excited state and the non-adiabatic coupling constant  $V_{ij}$ . The lifetime of excited states as measured by the spectral width is decreased due to scattering of metal electrons [63,90]. Typical timescales are in the range 10–100 fs. This phenomenon, due to loss of coherence of the total wavefunction, can alter the dynamics of the non-adiabatic crossing. Nevertheless, it can not be directly related to the non-adiabatic coupling constant. The dynamics of  $\text{O}_2$ –Ag would be significantly altered only if the adiabatic potential energy surface was considered. This becomes apparent since, for both potentials, the total energy is above the crossing seams, but nevertheless, the calculated dissociation probability is very low. An experimental confirmation of the existence of more than one potential energy surface has been obtained from scattering experiments, where a bimodal time of flight and angular distribution of the scattered oxygen molecules [83] might be interpreted as reflecting direct scattering from the physisorption potential and indirect scattering from the molecular chemisorption potential.

The calculations for the  $\text{O}_2$ –Ag system should be compared to the calculations for the  $\text{N}_2$ –Fe or  $\text{N}_2$ –Re systems [42–48,91]. The  $\text{O}_2$ –Ag system differs in that an intermediate molecular species is

incorporated enroute to dissociation. As a result, a very different dynamical picture emerges. It seems that the intermediate surface drastically reduces the direct effect of the initial kinetic energy on dissociation, causing a non-monotonic dependence. Qualitatively, the two potential energy surfaces studied are quite similar. The dissociation probability stays low even for energies above both crossing seams. These results are in conflict with the experimental results of [83], where a very strong increase in dissociation probability with kinetic energy was observed. To obtain this effect the direct dissociation channel has to be added to the model, i.e.  $V_{ag} \neq 0$ . The study in Ref. [83] also suggests an even smaller value for the molecular-atomic non-adiabatic coupling constant  $V_{ma}$ .

With the insight gained on details of the dissociation mechanism, the difference between a molecular beam and a thermal experiment can be considered. In the thermal experiment, oxygen spends a long period on the chemisorbed potential surface. This allows dissipative forces to equilibrate the chemisorbed oxygen molecule with the surface temperature. Once equilibrium has been reached, the energetics of the potentials are such that the route to dissociation can proceed only via a tunneling mechanism. An equilibrated oxygen species can be considered as a precursor to dissociation. Nevertheless it will not fit classical rate theory, since the transition to dissociation is governed by a quantum mechanical tunneling process. Both theoretical and experimental verification are required to establish such a mechanism. In the beam experiment, a competition between the direct reaction route and the dissipative forces takes place. Considering the very long residence times leading to dissociation in the intermediate energy range and the relaxation rates on surfaces, it is very probable that a significant number of molecules will equilibrate with the surface before they can dissociate. This will reduce the dissociation probability below the values calculated here, in accordance with the experimental results. An isotope substitution experiment can supply valuable confirmation of this picture. The picture presented here is also consistent with the experimental results of the dissociation of oxygen on Ag(110) [25,92–95]. The differences between the Ag(111)



and the Ag(110) surfaces within the non-adiabatic framework are mainly in the non-adiabatic coupling potentials. In such a description, the oxygen–silver bondings are very similar for the two surfaces. The large difference in reactivity can be traced to differences in non-adiabatic coupling between the different oxygen species on the surface.

The analysis presented here has to be considered with caution since it is based on a limited dimensionality study. The importance of surface degrees of freedom in causing relaxation has already been stressed. A possible technique is to include such degrees of freedom in a time-dependent mean-field approach or a time-dependent self-consistent field (TDSCF) [96]. Application of such a method to dissociation dynamics has been presented by Billing [47] and Jackson [88]. Their theory allows a mixing of classical and quantum degrees of freedom, which means that many degrees of freedom can be considered. The simple TDSCF theory fails in a non-adiabatic picture due to omission of correlations induced by the motion of multiple surfaces. In order to extend the theory to the framework presented here, a multi-configuration time-dependent self-consistent field should be used [97].

Another important degree of freedom is molecular orientation. There is some evidence that the molecular chemisorbed state can be tilted. Also, for O<sub>2</sub> on Ag(110), azimuthal dependence of the sticking probability has been observed [92]. Considering the model presented here, the non-adiabatic coupling terms which determine the sticking probability should be sensitive to the surface corrugation. Both these processes require a multi-dimensional calculation. Finally, the present model can address the phenomenon of the creation of negatively charged molecular ions from fast neutral molecular beams. The energy threshold for this process is above the one studied in this work.

## 6. Conclusions

A non-adiabatic picture of multi-crossing diabatic potential energy surfaces is essential in understanding the mechanism of dissociation of O<sub>2</sub> on

silver. This mechanism is also appropriate for other oxygen–metal dissociation processes.

The introduction of an intermediate chemical species in the O<sub>2</sub>–silver system drastically changes the dependence on the initial energy and leads to a non-monotonic dependence. Also, the total dissociation probability is reduced significantly.

The interplay between the direct reaction route and relaxation forces is an important factor in the O<sub>2</sub>–silver system.

The isotope effect as a function of dynamical variables such as the initial kinetic energy and surface temperature, makes a very sensitive probe for the detailed dynamics of the non-adiabatic process.

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