ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics Letters 373 (2003) 366–371

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

The role of nonadiabatic pathways and molecular rotations in the oxygen abstraction reaction on the Al(1 1 1) surface

Marcello Binetti [a], Olaf Weiße [a], Eckart Hasselbrink [a,*], Gil Katz [b], Ronnie Kosloff [b], Yehuda Zeiri [b]

[a] Fachbereich Chemie, Physikalische Chemie, Universität Essen, Essen D-45117, Germany
[b] Department of Chemistry and Fritz-Haber-Research Center, Jerusalem 91904, Israel

Received 10 February 2003

Abstract

The adsorption dynamics of O_2 on Al(1 1 1) has been studied experimentally using molecular beams and laser spectroscopy as well as theoretically using a multi-dimensional multi-electronic surfaces model. Experiments find that: (i) abstractive chemisorption is operative at all translational energies; (ii) it increases markedly with translational energy; and (iii) rotational excitation of the molecules suppresses the abstraction process. The model calculations semi-quantitatively reproduce the experimental findings and demonstrate that: (i) a nonadiabatic description is necessary to reproduce the experimental results and that (ii) the rotational hindrance is due to a restricted cone of acceptance in direction of the surface normal.

Dissociative adsorption of oxygen is a phenomenon of large relevance to catalysis and materials processing. Nevertheless, the microscopic steps of O_2 dissociative adsorption, surface migration and bulk penetration of adsorbed O, eventually leading to oxide formation are only rudimentary understood [1,2]. Recently, it has become evident that the interaction of O_2 with Al(1 1 1) cannot realistically be described by those methods which have successfully been applied to O_2 transition metal systems [3,4]. Combining results from scanning tunnelling microscopy (STM) studies and laser spectroscopic analysis of the scattered flux, it has been experimentally established that at low translational energies the abstraction channel is dominating [5]. In this process only one of the O atoms is adsorbed while the other remains in the gas phase. At higher energies ordinary dissociative chemisorption also takes place – in this case both of the atoms are adsorbed with only a small distance separating them. The total sticking probability at thermal energies is small ($s_0 \sim 10^{-2}$) and rises with increasing translational energy to reach 0.9 at about 900 meV [1].

These results are in sharp contrast to the predictions made by up-to-date density functional theory. Unanimously, these calculations predict

---

[*] Corresponding author. Fax: +49-201-183-3228.
E-mail address: eckart.hasselbrink@uni-essen.de (E. Hasselbrink).

0009-2614/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0009-2614(03)00586-4

nonactivated adsorption [6–8] resulting in a sticking coefficient close to unity even at low translational energies. This conflict has been interpreted to point to the significance of nonadiabatic effects in the adsorption of oxygen, which are beyond the scope of present DFT codes. It has been proposed that the abstraction channel results when molecules approach the surface in a nearly upright geometry, which is favorable for charge transfer. Rapid transfer of two electrons leads then to bond fission where one of the atoms may be expelled into gas phase as a neutral atom.

In this context a contribution from possible cannon ball like trajectories has also been discussed [9,10]. Here, one O atom adsorbs and the second oxygen atom is initially ejected to the gas phase but later is recaptured by the surface since it does not have enough energy to escape. Indisputable experimental evidence is not yet available for this channel. However, it cannot be ruled out that a fraction of the abstraction events leads to cannon ball like trajectories, because these events cannot be discriminated by STM from abstraction events if a distance exceeding approx. 50 Å finally separates the two oxygen atoms.

In this Letter we report the experimental observation of a marked suppression of the abstraction process by rotations of the incoming molecule. This experimental observation is corroborated by theoretical model calculations utilizing a multi-dimensional multi-electronic state model.

The molecular beam scattering experiments have been performed using an UHV apparatus [11]. A molecular beam is derived from a pulsed nozzle, skimmed, and chopped such that gas pulses of ~100 μs duration result. A ceramic tube of 4 cm length and 1 mm inner diameter has been attached by a Teflon adapter to the pulsed valve orifice (General Valve, type 9). The ceramic tube can be heated to a temperature of 500 K without hampering the functionality of the pulsed valve. Furthermore, the oxygen molecules are seeded in He. By these means, the translational energy of the molecules in the beam could be increased to 435 meV. By placing a quadrupole mass spectrometer in line with the beam, it has been carefully checked that heating the nozzle does not result in a decrease in beam flux. The translational energies have directly been measured by placing the mass spectrometer at two different distances along the molecular beam and recording the delay in arrival time of the molecular beam gas pulses.

The molecular beam strikes the Al(1 1 1) sample at an angle of incidence of 45° with a cross-section of 4 mm. The Al(1 1 1) sample (±0.5°, $\varnothing = 10$ mm, purity = 99.999%) was cleaned following standard procedures. Immediately after sputtering, the surface cleanliness was checked by Auger electron spectroscopy (AES) and the order of the surface by low-energy electron diffraction (LEED).

In the scattered flux of O_2 molecules, O-atoms are detected by 2 + 1-photon resonant multi-photon ionization (REMPI) at 226 nm utilizing the resonant transition from the (2p) $^3P_2$ ground state to the (3p) $^3P_{0,1,2}$ state as intermediate [12]. For this purpose, a frequency-doubled, tunable dye laser producing 2.5 mJ/pulse is focused by a 250 mm lens with the focus located 10 mm away from the sample. Due to this geometrical arrangement, the experiment is largely insensitive to the angular distribution of the O-atoms released from the surface reaction. The surface was exposed to a limited number of gas pulses in order to stay within the low coverage limit ($\Theta < 0.05$ ML). The scattering experiments were performed with the sample held at room temperature.

The particular design of the heatable pulsed nozzle has peculiar implications on the beam properties. First of all, the expansion is not as good as it would be without the attached tube, resulting in a loss in beam flux of about one order of magnitude. Secondly, the rotational cooling is not as effective as in a conventional expansion. Hence, when heating the nozzle we expect to increase not only the translational energy of the molecules, but also their rotational temperature. Direct determination of the rotational state distribution in the O_2 molecular beam is not feasible. Hence, we resorted to measuring the rotational temperature using (1 + 1)-REMPI for a beam of NO produced under the same experimental conditions. Indeed a marked increase of the rotational temperature from 36 to 154 K is observed when the nozzle is heated and the beam seeded. We expect the rotational temperatures to be somewhat higher for O_2 since the energy gap for rotational state changing collisions is larger due to the $\Delta J = \pm 2$ selection rule [13].

Theoretical modeling of the complicated sequence of charge transfer events prior and during the dissociation demands the construction of several diabatic potential energy surfaces (PESs). Hence, we constructed a set of semi-empirical PES that will allow an adequate description of the O_2/Al(1 1 1) dissociation dynamics. The parameters required for the evaluation of the PES were obtained using available experimental data as well as results of related first principle calculations.

Four molecular states were considered: the first PES is the physisorption state in which the neutral oxygen molecule approaches the Al surface. The two ionic states labeled superoxide and peroxide represent adsorbed molecular ions resulting from charge transfer from the substrate to the molecule. The two states differ in the amount of charge transferred to the molecule. The last diabatic PES describes the dissociated state leading to oxygen ions bound to the Al surface. The potentials included the long range attraction of the ions to their image polarization or charge depending on the state, and short range repulsive terms. In the ionic states the molecular bond was weakened according to the excess of negative charge transferred to the molecule. In addition, nonadiabatic coupling potentials were introduced coupling the physisorption to both superoxide and peroxide states. The two ionic states were in turn coupled to the dissociative state. The functional form of these potentials is described in detail elsewhere [14]. By diagonalizing the diabatic PESs the adiabatic ground electronic PES could be compared to the results of DFT calculations. The main discrepancies were found in the long range part of the PES but the general topology was very similar to the DFT counterpart [14].

This set of coupled diabatic PES was employed for a time dependent nonadiabatic simulation of the dynamics. The cylindrical symmetry induced by the a flat surface approximation allows a description of the O_2/Al(1 1 1) system using only three degrees of freedom, r being the internuclear distance, z the distance of the molecular center of mass from the surface and θ the orientation angle of the molecular axis relative to the surface normal. The angular momentum along the azimuthal angle is conserved in this setup and was added as a centrifugal term to the potentials.

The initial state of the system was a compact wavefunction on the physisorption PES varying in the incident kinetic, vibrational and rotational energy. The experimental molecular beam was simulated by averaging the results from many initial states using Boltzmann weights.

The coupled time dependent wavefunction was represented on four Fourier grids of $N_z \times N_r \times N_\theta = 200 \times 400 \times 64$ representing a box of 5.4×3.0 Å^2 with all orientations. Propagation for 30 fs, measured from the first crossing event, was sufficient for the initial wavefunction to approach the surface and reflect back on the physisorption surface. At this time the norm on each diabatic surface was calculated. We assume that the dissociation probability can be calculated from the norm on the direct dissociation channel and the norms on the superoxide and peroxide surfaces. Due to the long lifetime of the wavefunction on these surfaces it is strongly influenced by dissipative surface interactions which will eventually lead to loss of energy and dissociation.

Fig. 1 shows the calculated dissociation probability as a function of translational energy (E_{trans}) in comparison to an adiabatic calculation performed on the ground adiabatic PES and to the

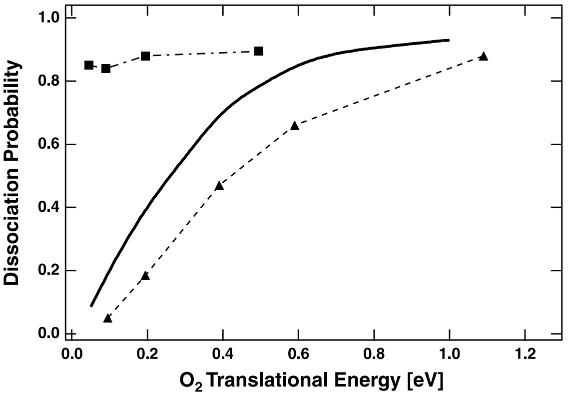

Fig. 1. Calculated total dissociation probability as a function of incident energy. – , Experiments of [1]; ▲, diabatic calculation for $v = 0$ and rotational temperature of 100 K; ■, dissociation probability calculated from the adiabatic ground state surface only.

experimental data of [1]. The nonadiabatic calculation reproduces the experimental trend, i.e., an increase in the dissociation probability as a function of the incident energy reaching saturation with 60% dissociation at 0.5 eV, compared to 80% in the experiment. The adiabatic calculation fails drastically predicting >80% dissociation at every energy consistent with the barrierless topology of the adiabatic PES. The existence of nonadiabatic coupling is the prerequisite for the low dissociation probability at low incident energy. The dominant crossing region is associated with slowing down of the projectile. The magnitude of the nonadiabatic coupling increases as the molecule approaches the surface. Thus, an increase in the incident translational energy is expected to lead to a closer approach to the solid with an increased probability of charge transfer. Similarly, stretching the internuclear distance, by vibrational or rotation excitations, is also expected to result in configurations that are more favorable for curve crossing [15].

To predict the eventual result of the scattering event a surface hopping molecular dynamics (MD) calculation was performed. The MD simulation was invoked to properly describe the many body system and to include the energy transfer processes realistically. It also allowed to follow the event for a time period that was sufficient to completely determine the products. The wavefunction on the dissociative PES, at the end of the quantum simulation, was used to generate the initial conditions for the MD. The forces were calculated using the same PES used for the quantum calculation with the addition of a friction force [10]. The friction coefficient used was adapted from [10] where it was demonstrated that the main contribution is due to interaction with the phonones rather than with the electrons of the substrate. When a trajectory reached the crossing seam its surface hopping probability was calculated based on its normal energy and a nonadiabatic constant estimated from electronic wavefunction overlap: $V_{12} = 124$ meV and $V_{12} = 46$ meV to the triplet and singlet states, respectively. These values are similar to that used to describe the coupling between the physisorption and the superoxide PES. Each dissociative wavepacket was sampled by 10^4 trajectories leading to the calculated product state probabilities.

Fig. 2 shows the experimental data obtained for the oxygen atom yield when the sample is exposed to an O_2 beam at various translational energies. The original data have been corrected for the varying flux of the O_2 beam due to dilution in the seeding gas. Furthermore, it has been assumed that the final velocity of the O atoms resulting from the abstraction process does not significantly vary with the translational energy of the incoming molecule. This assumption is supported by the theory. Under these assumptions the corrected numbers are directly proportional to the partial sticking coefficient for the abstraction process, i.e., the probability for an incoming molecule to undergo that particular process. Where available, we have labeled the data points with the approximate rotational temperature of a NO beam under the same experimental conditions.

The data show a marked increase of the abstraction sticking coefficient with translational energy. Moreover, it is immediately apparent that an increase in rotational temperature of the beam results in a strong reduction in abstraction. At the highest points apparently a reduction of a factor 3 results when the rotational temperature increases from ca. 50 to 150 K. This effect is remarkable as it indicates that an increase in available energy is counterproductive for the reaction studied.

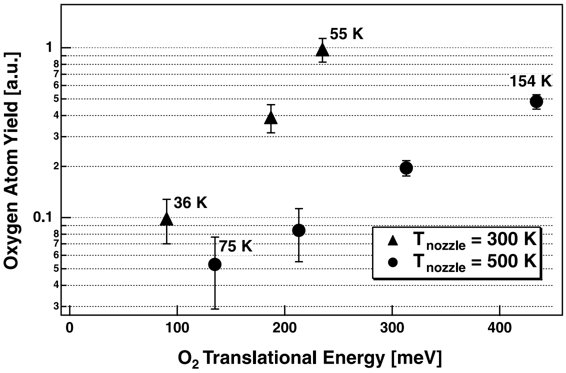

Fig. 2. Partial sticking coefficient for the abstraction reaction, i.e., probability of undergoing the abstraction process per incoming molecule as a function of translational energy. The data is in relative units, since REMPI does not allow for an accurate absolute calibration. The labels at the data points give the rotational temperature of an NO beam at the same experimental conditions.

It should not be ignored that also the extent to which the first vibrationally excited state is populated varies when the nozzle is heated. If we assume for the moment that no vibrational relaxation in the beam occurs then the population in $v = 1$ increases from 7×10^{-4} to 1×10^{-2} when the gas temperature is increased from 300 to 500 K. In fact, we expect some vibrational cooling to occur such that the populations are even smaller. The population in even higher vibrational states is negligible ($<10^{-4}$). Hence, regardless of the nozzle temperature 99% of the molecules are in the vibrational ground state.

Therefore, the observed effect has to be explained on the basis of the rotational state distribution in the beam. It has also been observed for H_2/Cu and H_2/Pd(1 1 1) [16–19] that rotational excitation hinders dissociative adsorption, but the effect has been rather subtle. E.g., Gostein and Sitz [19] find that the dissociative sticking coefficient for H_2/Pd(1 1 1) at $E_{\mathrm{trans}} = 73$ meV is 0.76 and 0.54 for $J = 0$ and $J = 3$, respectively. The measurements reported here indicate that the reaction probability decreases by roughly a factor 3 when the mean rotational quantum number in the beam increases from 5 to 9. Using the rotational constant of O_2 in the ground state ($B_{\mathrm{rot}} = 1.4456$ cm^{-1}) we calculate the fractional population in $J = 0$ to $J_{\max}$ at a given temperature and obtain $F(J_{\max} = 1, T_{\mathrm{rot}} = 35\ \mathrm{K}) = 0.25$ and $F(J_{\max} = 1, T_{\mathrm{rot}} = 155\ \mathrm{K}) = 0.062$. This reduction is comparitible to the experimental observation. Hence, we conclude that the reaction probability is an order of magnitude smaller for $J \geqslant 3$ than for low J.

This interpretation of the experiment can be further rationalized by looking at the correlation between the intermediate state of the dissociating molecule and the fate of the atomic products as calculated. Fig. 3 exhibits a clear correlation between the polar angle right after crossing onto the dissociation PES, θ, and the final outcome of the dissociation process. Three distinct orientation cones are clearly seen: (i) flat orientations lead to a pair of adsorbates; (ii) intermediate polar angles result in ballistic motion and large separation among adsorbates; (iii) nearly normal orientations result in the escape of one oxygen atom to the gas phase. An increase in rotational temperature results in a reduced probability for abstraction by approx. a factor 5 and an increase in yield of pairs.

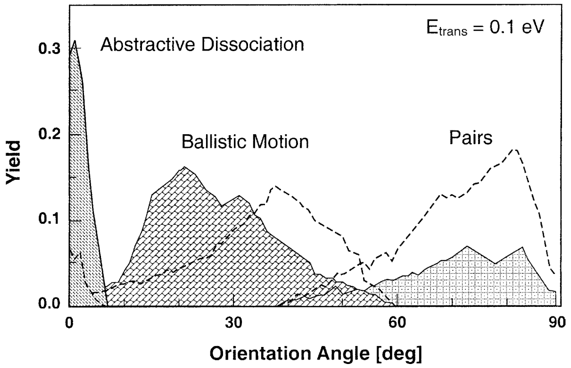

Fig. 3. Differential yield of the various final products as a function of the orientation of the O_2 molecular axis with respect to the surface normal when the system enters the dissociative state for $E_{\mathrm{trans}} = 0.1$ eV. Pairs of adatoms separated by more than 12 Å are regarded as consequence of ballistic motion. The solid lines and shaded areas represent the results for $T_{\mathrm{rot}} = 50$ K, the dashed lines those for $T_{\mathrm{rot}} = 150$ K. Note, the area under the various curves is the absolute yield of the corresponding process. The yield of the scattered molecules is not included in the figure.

Closer inspection of the computational results shows that for all reaction pathways the key step is the charge transfer event to form O_2^-. At low translational energies the favorable geometry for the curve crossing is the upright orientation. The time scale of the reaction, 30 fs, is not sufficient for a large orientation change. Hence, the initial orientation is preserved and an abstraction event is expected. With increasing rotational energy this argument loses weight. Hence, the number of abstraction events is expected to decrease. At the same time the channel to dissociation opens because of the increased rotations.

At elevated translational energies the molecules reach higher repulsive parts of the potential leading to a torque that reorients the molecule. This opens up a larger cone of acceptance for dissociative events. At the same time, the number of abstraction events continues to increase since a larger fraction of the incident flux crosses to the dissociation PES. However, the increase in dissociative events is much stronger.

Combining the results from theory and experiment a clearer picture of the abstraction reaction dynamics evolves. Abstraction is confined to a narrow cone in which the molecules that pass the crossing seam to the dissociation PES are in an upright geometry. Rotational excitation of the molecules suppresses abstraction, since the molecule rotates out of the cone of acceptance. The results presented here clearly demonstrate that a nonadiabatic description is necessary in order to reproduce the apparently activated behaviour of the sticking coefficient and the suppression by rotations. Hence, we are convinced that our experimental and theoretical results represent a significant progress in our understanding of the reaction of O_2 with Al(1 1 1), nonwithstanding the quantitative discrepancy with respect to the relative weight of abstraction vs. pairwise adsorption and ballistic events. The latter must be attributed to the still present limitations in the model PESs.

Acknowledgements

We are pleased to acknowledge stimulating discussions with B. Lundqvist, A.C. Kummel, A.C. Luntz, G. Darling, S. Holloway and D. Bird. We thank Claudia Wesenberg and Kristian Laß for their help during the final stages of the experiment. We acknowledge support by the EU through the TMR-program (ERB FMRX-CT98-0249) and by GIF and IAEC-ICHE.

References

[1] L. Österlund, I. Zoric, B. Kasemo, Phys. Rev. B 55 (1997) 15452.
[2] V. Zhukov, I. Popova, J.T. Yates Jr., Surf. Sci. 441 (1999) 251.
[3] A. Eichler, J. Hafner, Phys. Rev. Lett. 79 (1998) 4481.
[4] F. Mittendorfer, A. Eichler, J. Hafner, Surf. Sci. 435 (1999) 756.
[5] A.J. Komrowski, J.Z. Sexton, A.C. Kummel, M. Binetti, O. Weiße, E. Hasselbrink, Phys. Rev. Lett. 87 (2001) 246103.
[6] Y. Yourshahyan, B. Razaznejad, B.I. Lundqvist, Solid State Commun. 117 (2001) 531.
[7] K. Honkala, K. Laasonen, Phys. Rev. Lett. 84 (2000) 705.
[8] T. Sasaki, T. Ohno, Phys. Rev. B 60 (1999) 7824.
[9] C. Engdahl, G. Wahnström, Surf. Sci. 312 (1994) 429.
[10] G. Wahnström, A.B. Lee, J. Strömquist, J. Chem. Phys. 105 (1996) 326.
[11] E. Hasselbrink, S. Jakubith, S. Nettesheim, M. Wolf, A. Cassuto, G. Ertl, J. Chem. Phys. 92 (1990) 3154.
[12] D.J. Bamford, L.E. Jusinski, W.K. Bishel, Phys. Rev. A 34 (1986) 185.
[13] J. Mettes, B. Heijmen, J. Reuss, D.C. Lainé, Chem. Phys. 87 (1984) 1.
[14] G. Katz, Y. Zeiri, R. Kosloff, 2002 (to be published).
[15] G. Katz, Y. Zeiri, R. Kosloff, Surf. Sci. 425 (1999) 1.
[16] H.A. Michelsen, C.T. Rettner, D.J. Auerbach, Phys. Rev. Lett. 6 (1992) 2678.
[17] H.A. Michelsen, C.T. Rettner, D.J. Auerbach, R.N. Zare, J. Chem. Phys. 98 (1993) 8294.
[18] M. Beutl, M. Riedler, K.D. Rendulic, Chem. Phys. Lett. 247 (1995) 249.
[19] M. Gostein, G. Sitz, J. Chem. Phys. 106 (1997) 7378.