Transient Trapping Desorption of Molecules at Surfaces

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Scattering studies of hyperthermal O_2 from Ag(111) for a backscattering geometry are reported. Three different scattering paths are observed: physisorption followed by desorption, direct-inelastic scattering, and transient trapping desorption. The latter process is attributed to transient adsorption of the molecule in an $O_2^{\delta-}$ state at the surface without equilibration of the vibrational degree of freedom. The molecule desorbs with hyperthermal energy.

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Chemical reactions at surfaces play a major role in fields like catalysis, semiconductor processing, and spacecraft interactions. Although such reactions have been studied for a long time, only one mechanism has been firmly established: the Langmuir-Hinshelwood reaction. In this mechanism the reactants adsorb, equilibrate, and possibly dissociate at the surface. Products are formed when the adsorbed reactants at the surface meet, react, and desorb. Recently another mechanism for surface reactions has been convincingly demonstrated: the Eley-Rideal reaction [1–4]. In this case the reaction product is formed in a collision between an adsorbed particle and a gas phase particle upon impact. An intermediate case between the Langmuir-Hinshelwood and Eley-Rideal mechanisms is a reaction in which the reactants only partially accommodate at the surface, for instance, by conserving their parallel momentum or rovibrational excitation [5]. The particle in this case can be considered to be in a metastable state, a transient intermediate to a chemical reaction. Particles in such states cannot be isolated in a static surface science experiment. In this study we will demonstrate that by a molecular beam intermediates at surfaces can be prepared that live only on a picosecond time scale. The topic of the present study is the interaction of O_2 molecules and the Ag(111) surface.

Four different states of oxygen on Ag(111) have been identified, as recently summarized by Besenbacher and Nørskov [6]. Most weakly bound is physisorbed O_2 that desorbs at a surface temperature $T_s < 50$ K. The corresponding trapping coefficient for thermal O_2 is of the order of unity [7]. Molecular chemisorbed O_2 desorbs at $T_s \approx 200$ K. Its vibrational frequency is considerably lower than that of gas phase O_2^-, which has been interpreted as due to significant electron transfer to the chemisorbed molecule [8]. Here we will refer to this state by $O_2^{\delta-}$. Dissociative chemisorption can take place at the surface leading to recombinative desorption at $T_s \approx 600$ K and in subsurface sites, desorbing at $T_s > 700$ K [6,9]. Both the molecular and dissociative sticking coefficient are on the order of 10^{-6} [10,11]. At the more open Ag(110) face the sticking probabilities are much higher [12,13].

The experiments reported here have been performed in a molecular beam surface scattering apparatus. A triply differentially pumped molecular beam line produces O_2 molecules with energies E_i from thermal to 1.8 eV using seeding of O_2 in (heated) He. The molecules impinge on the Ag(111) crystal mounted on a three axis goniometer in an ultrahigh vacuum vessel. The crystal has been prepared using standard methods and can be cooled to approximately $T_s = 120$ K. A differentially pumped rotatable quadrupole mass spectrometer detects angle resolved scattered O_2 density. The molecular beam is modulated by a mechanical chopper, which allows the measurement of time-of-flight (TOF) spectra. The spectra can be analyzed by fitting them to a (sum of) Maxwell-Boltzmann distribution(s), which can have a nonzero flow velocity. The experimental procedures and the data analysis are described elsewhere in detail [14,15].

The experiments presented here all have been carried out for backscattering geometries. TOF spectra for $\theta_i = 50°$ and $\theta_f = 10°$ are presented in Fig. 1; the initial and final polar angles θ_i and θ_f are measured with respect to the surface normal. The same relative density scale is used for all spectra, measured at different incident energies E_i. For this scattering geometry no direct-inelastic scattering is observed in experiments with N_2 or Ar [15]. The TOF spectrum for $E_i = 0.1$ eV is dominated by a single broad distribution, which can be fitted very well with a Maxwell-Boltzmann distribution, corresponding to a temperature slightly below the surface temperature as has been observed previously for this system [7]. Clearly physisorption and complete equilibration (accommodation) followed by desorption is the only important process at the given settings. When increasing E_i to 0.23 eV the signal intensity decreases, and the distribution is no longer a pure Maxwell-Boltzmann distribution corresponding to physisorption trapping desorption. The TOF distribution can be fitted by two distributions, one of which represents physisorption trapping desorption. From such experiments the relative intensity of the physisorption trapping-desorption signal can be measured as a function of E_i. The result is given in Fig. 2 as a function of

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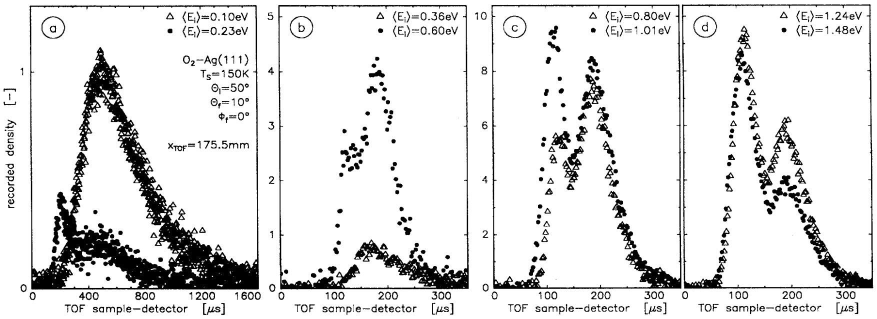

FIG. 1. TOF spectra of O_2 scattered from Ag(111) for $E_i = 0.10$ to 1.48 eV, $\theta_i = 50°$, and $T_s = 150$ K. The scattered molecules are detected in the incident plane ($\phi_f = 0°$) at $\theta_f = 10°$. The intensity axis is displayed in the same relative units in all panels. The time axis is the measured flight time corrected for a trigger delay, the flight time from the chopper to the sample according to the flow velocity of the incident molecules, and the ion flight time through the detector.

the "normal energy" $E_n = E_i \cos^2\theta_i$. Scaling of results with E_n indicates that parallel momentum is conserved in the interactions. The characteristic monotonic decreasing intensity distributions familiar for physisorption trapping desorption are seen. Returning to Fig. 1(b) we observe that a new process arises at increasing E_i. Physisorption trapping desorption only gives a small contribution to the signal at 0.36 eV. Increasing E_i to 0.6 eV yields a much larger intensity. Remarkably, the TOF spectrum shows a double peak, a slow one and a fast one. At 0.6 eV the slow one dominates, but with increasing E_i the fast one is observed to take over.

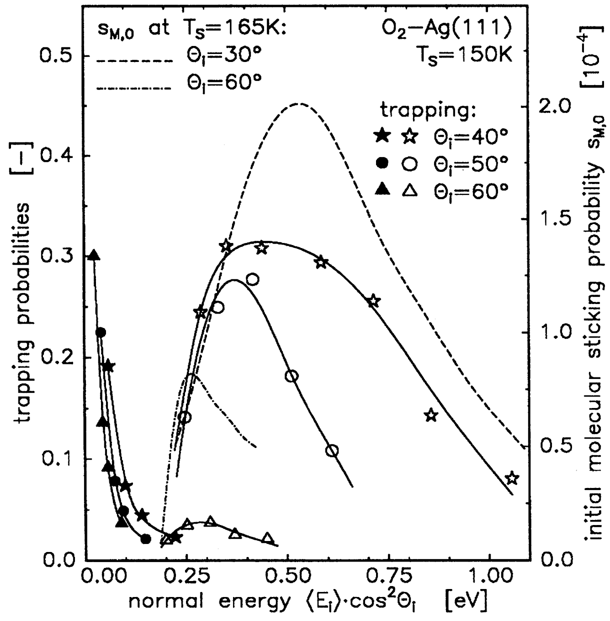

FIG. 2. Physisorption trapping (closed symbols) and transient trapping (open symbols) probability as a function of E_i for three different θ_i. The full lines through the data points are to guide the eye only. The values for the trapping probabilities are an estimate only and are based on hard cube calculations. Also shown is the initial molecular sticking probability $s_{M,0}$ by the dashed and dash-dotted line. These are also lines to guide the eye. The corresponding data points are not reproduced here.

The final energies corresponding to the different TOF contributions can be obtained from fits to the TOF distributions. For E_i below 0.5 eV the spectra are fitted by a single shifted Maxwell-Boltzmann distribution plus a Maxwell-Boltzmann distribution for physisorption trapping desorption. Above 0.5 eV the two peaks in the TOF spectra can be fitted by two different shifted Maxwell-Boltzmann distributions. The resulting final energies E_f are shown in Fig. 3. The E_f of the fast peak observed above $E_i = 0.5$ eV scales roughly with E_i. This E_f is somewhat lower than would correspond to a single collision of a spherical mass 32 colliding with a Ag atom leading to a total deflection angle $\theta_t = 180° - (\theta_i + \theta_f) =$

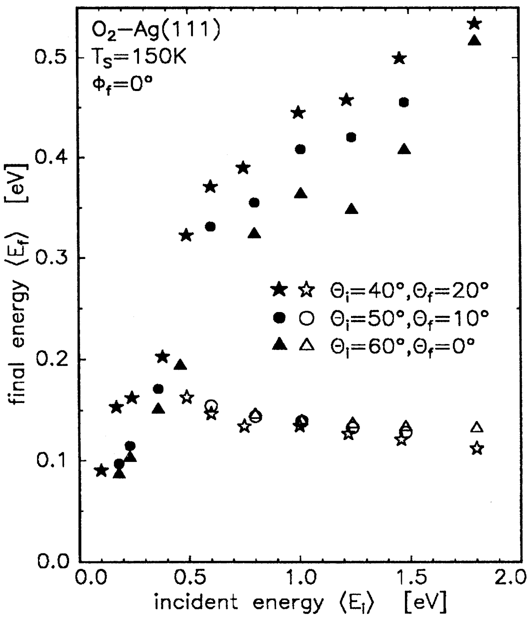

FIG. 3. E_f of the different contributions to the TOF spectra of scattered O_2 as a function of E_i for different scattering geometries. TOF spectra for one of these geometries are shown in Fig. 1. The open symbols hold for the transient desorption. Results for physisorption trapping desorption, as observed below $E_f = 0.5$ eV, are not shown.

120°. The data for different scattering geometries but the same $\theta_t = 120°$ give roughly the same E_f. This suggests that the fast peak corresponds to direct-inelastic scattering of an O_2 molecule with essentially a single Ag atom, and that in the collision considerable rotational excitation occurs [16,17]. From measurements of the full angular distributions we conclude that the fast peak corresponds to direct-inelastic scattering from the chemisorption potential, which, in contrast to the physisorption potential, shows a very corrugated repulsive wall [15].

The slow TOF peak observed above $E_i = 0.5$ eV exhibits a roughly E_i independent E_f of approximately 0.14 eV. In the determination of E_f no surface residence time has been assumed. Fits using a surface residence time did not result in consistent and meaningful results, especially when varying T_s. The constant E_f as a function of E_i suggests that these molecules result from (activated) desorption.

Activated desorption is known to result in strongly peaked angular distributions and excess translational energy [18,19]. Therefore, we measured this angular distribution which is shown in Fig. 4. As expected for activated desorption, the angular distribution is strongly peaked around the surface normal, and can be fitted by a $\cos^{15}\theta_f$ distribution. Desorption also implies that the desorbed intensity is independent of the final azimuthal angle ϕ_f, measured with respect to the incident plane; the signal is symmetric around the surface normal. We carried out experiments where we detect out of the incident plane and vary ϕ_f while keeping the final polar angle θ_f constant.

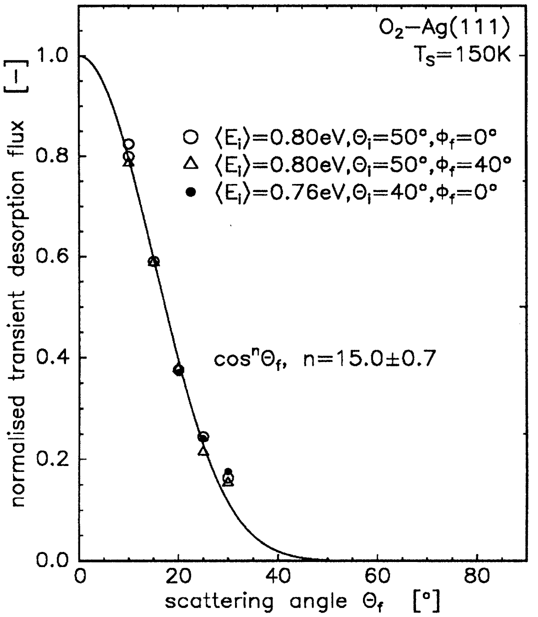

FIG. 4. Normalized angular resolved desorbed flux from the transient O_2 state as a function of θ_f for three different scattering geometries. The results are normalized to the value found for $\theta_f = 0°$.

The intensity of the slow peak in the TOF turned out to be independent of ϕ_f, while, as expected, the intensity of direct-inelastic scattering in the fast peak decreases out of the incident plane. These results are also shown in Fig. 4.

Additional information concerning the activated desorption process can be obtained from the E_i dependence of the process. This is also shown in Fig. 2. A threshold of $E_n = 0.2$ eV is observed for all θ_i. This strongly supports the inference that the slow peak is due to an activated adsorption-desorption process. The threshold of 0.2 eV is not inconsistent with the observed final energy of 0.14 eV, assuming that large recoil and tunneling effects are important in the adsorption step [9,20]. Since the interaction for direct-inelastic scattering seems to be dominated by only a single Ag surface atom, such a recoil effect is to be expected, as has been observed for the O_2^- Cu adsorption [21]. The activated adsorption-desorption process seems to be governed by a rather shallow potential well behind the activation barrier, because the transient trapping decreases sharply with increasing E_i. In Fig. 2 it can also be seen that there is a strong θ_i dependence on the magnitude of the adsorption process. Parallel momentum decreases the adsorption probability.

There is a very large T_s effect on the E_f of the activated desorption process, which will be discussed in detail elsewhere. E_f increases with T_s ($E_f = 0.06 + 6k_BT_s/e$ [eV]) making the two peaks observed above $E_i = 0.5$ eV in Figs. 1(b)–1(d) indistinguishable for $T_s > 350$ K. Our results in that regime are in agreement with our earlier measurements [14]. The transient trapping probability does not change with T_s.

Summarizing, we directly observe for the first time trapping of molecules at the surface without complete equilibration of the molecules, followed by desorption. We refer to this process by transient trapping desorption.

The E_i dependence of the sticking coefficient for molecular chemisorption in the $O_2^{\delta-}$ state was studied to obtain further information about which (metastable) state is responsible. It is reproduced in Fig. 2 as well and shows a strong similarity to the transient trapping curve, suggesting that transient trapping and molecular chemisorption are mediated by the same state.

Assuming that the $O_2^{\delta-}$ well is responsible for both transient trapping and molecular chemisorption we can think of two possible transient trapping mechanisms. The first is that the $O_2^{\delta-}$ well is extremely shallow for most sites and that adsorption in it will lead to rapid desorption. This implies that different $O_2^{\delta-}$-like states can be populated, only one of which is stable on Ag(111). Several loosely bound $O_2^{\delta-}$ states have been seen on Pd(111), see, e.g., [22]. Most of these states on Ag(111) would then only be metastable at $T_s = 120$ K, allowing only a small saturation coverage. Against this interpretation is that the stable $O_2^{\delta-}$ species can build up a large coverage (0.25 monolayer) [10].

A second explanation of the transient trapping-desorption effect is that molecules are quasitrapped in the $O_2^{\delta-}$ well, without equilibration leading to molecular chemisorption. This effect has been predicted to occur by Holloway and Gadzuk [23,24]. They have shown for model systems using classical trajectory and wave packet calculations that A_2 molecules that overcome the barrier between the physisorbed A_2 and $A_2^{\delta-}$ states become strongly vibrationally excited because the $A_2^{\delta-}$ has a higher binding energy and a much larger internuclear distance. The molecules were shown to exhibit a complicated motion in the $A_2^{\delta-}$ well. Some molecules can perform several intramolecular vibrations. The lifetimes of vibrationally excited CO molecules are known to be around a few picoseconds [25,26]. The $O_2^{\delta-}$ molecule can execute more than 20 vibrations in that time. While the intramolecular vibration does not quench, the molecule surface vibration will be quenched more rapidly. Ar atoms colliding with Pt(111) equilibrate their normal momentum in about one Ar-surface vibration [27]. Since the $O_2^{\delta-}$-Ag potential is very corrugated, the accommodation of parallel momentum of the O_2 molecule is also expected to be fast with respect to the lifetime of the intramolecular vibration. Therefore we expect that in transient trapping rapid accommodation of the translational energy occurs. The presence of vibrational excitation of $O_2^{\delta-}$ will allow the molecule to revisit the barrier, desorb, and regain the activation energy. This will occur on a subpicosecond time scale, and the data tell us that the process is more efficient than equilibration into the $O_2^{\delta-}$ well. Recent calculations for dissociative adsorption of O_2 on Ag(111) by Kosloff and Citri have demonstrated that the molecules spend up to a picosecond in the $O_2^{\delta-}$ well before dissociation occurs [28,29]. The dissociation probability is very low, which is due to the fact that leaving the $O_2^{\delta-}$ well back into the vacuum, as observed in the present study, is much more likely than dissociative adsorption.

If the molecule is a vibrationally excited $O_2^{\delta-}$ species, it is most presumably very reactive. This suggests that reactive intermediates can be produced for chemical reactions at surfaces that cannot be detected by any static surface analytical tool. The investigation of such transient or metastable intermediates might shed new light on the mechanisms of, for instance, oxidation reactions at surfaces.

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[1] P.J. Eenshuistra, J.H.M. Bonnie, J. Los, and H.J. Hopman, Phys. Rev. Lett. **60**, 341 (1988).
[2] E.W. Kuipers, A. Vardi, A. Danon, and A. Amirav, Phys. Rev. Lett. **66**, 116 (1991).
[3] C.T. Rettner, Phys. Rev. Lett. **69**, 383 (1992).
[4] C.T. Rettner and D.J. Auerbach, Science **263**, 365 (1994).
[5] J. Harris and B. Kasemo, Surf. Sci. **105**, L281 (1981).
[6] F. Besenbacher and J.K. Nørskov, Prog. Surf. Sci. **44**, 1 (1993).
[7] M.E.M. Spruit, E.W. Kuipers, F.H. Geuzebroek, and A.W. Kleyn, Surf. Sci. **215**, 421 (1989).
[8] C. Backx, C.P.M. de Groot, and P. Biloen, Surf. Sci. **104**, 300 (1981).
[9] P.H.F. Reijnen, A. Raukema, U. van Slooten, and A.W. Kleyn, Surf. Sci. **253**, 24 (1991).
[10] C.T. Campbell, Surf. Sci. **157**, 43 (1985).
[11] M.E.M. Spruit and A.W. Kleyn, Chem. Phys. Lett. **159**, 342 (1989).
[12] L. Vattuone, M. Rocca, C. Boragno, and U. Valbusa, J. Chem. Phys. **101**, 713 (1994).
[13] L. Vattuone *et al.*, Phys. Rev. Lett. **72**, 510 (1994).
[14] M.E.M. Spruit *et al.*, Surf. Sci. **214**, 591 (1989).
[15] A. Raukema, R.J. Dirksen, and A.W. Kleyn (to be published).
[16] G.O. Sitz, A.C. Kummel, and R.N. Zare, J. Chem. Phys. **89**, 2558 (1988).
[17] A.W. Kleyn, Surf. Rev. Lett. **1**, 157 (1994).
[18] W. van Willigen, Phys. Lett. **28A**, 80 (1968).
[19] G. Comsa and R. David, Surf. Sci. Rep. **5**, 145 (1985).
[20] J. Harris *et al.*, Phys. Rev. Lett. **67**, 652 (1991).
[21] J. Hall, O. Saksager, and I. Chorkendorff, Chem. Phys. Lett. **216**, 413 (1993).
[22] K.W. Kolasinski, F. Cemic, and E. Hasselbrink, Chem. Phys. Lett. **219**, 113 (1994).
[23] S. Holloway and J.W. Gadzuk, J. Chem. Phys. **82**, 5203 (1985).
[24] J.W. Gadzuk, J. Chem. Phys. **86**, 5196 (1987).
[25] R.R. Cavanagh, E.J. Heilweil, and J.C. Stephenson, Surf. Sci. **300**, 643 (1994).
[26] M. Morin, N.J. Levinos, and A.L. Harris, J. Chem. Phys. **96**, 3950 (1992).
[27] M. Head-Gordon *et al.*, J. Chem. Phys. **94**, 1516 (1991).
[28] R. Kosloff and O. Citri, Faraday Discuss. **96**, 175 (1993).
[29] O. Citri and R. Kosloff (to be published).