# Collision induced desorption and dissociation of $O_2$ chemisorbed on Ag(001)

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We have investigated desorption and dissociation of  $O_2$  chemisorbed on Ag(001) induced by collision with hyperthermal Xe and Ar atoms by high resolution electron energy loss spectroscopy and supersonic molecular beam technique. The cross section for both processes increases rapidly both as a function of angle of incidence and of total impact energy of the inert gas atom. While the increase with energy is expected, the increase with the angle is somewhat surprising and is sensibly larger than observed for previously investigated systems. The cross section for desorption decreases moreover with coverage. In the limit of high impact energy and high coverage its value is always larger than the one for dissociation. The branching ratio between the two processes depends thereby on energy and angle of incidence of the inert gas atom. Atomic oxygen is not removed under any impact condition, because of its larger binding energy. In order to explain the experimental results, molecular dynamics simulations have been performed using a simple model including multiple scattering. We find that the angular dependence of the cross section is determined by surface corrugation and by multiple scattering which suppresses desorption at normal incidence while the energetic threshold is determined by energy loss to the substrate. © *1998 American Institute of Physics*. [S0021-9606(98)00930-1]

### I. INTRODUCTION

Collision induced phenomena have been investigated<sup>1-5</sup> because of their possible role in explaining the pressure gap in catalysis and the effects connected with the presence of diluent gases.<sup>6</sup> In seminal papers Ceyer and co-workers demonstrated the occurrence of collision induced desorption<sup>7</sup> and dissociation<sup>8</sup> of methane physisorbed on Ni(111). Similar observations were later also reported for chemisorbed molecules (NH<sub>3</sub> on Pt(111),<sup>2</sup> H<sub>2</sub>O on Ru(001),<sup>3</sup> CO<sub>2</sub> on  $Re(0001)^4$ ). Recently production of CO<sub>2</sub> on O<sub>2</sub> and CO precovered Pt(111) was observed.<sup>5</sup> Although the existence of collision induced desorption, dissociation and reaction has been definitely demonstrated, the dependence of the corresponding cross sections on impact energy and geometry are not yet understood, except in the cases of physisorption, e.g.,  $CH_4$  on Ni(111),<sup>7,8</sup> and Xe on Pt(111).<sup>9</sup> In both cases a good agreement between model and experiment could be achieved by using in the former case a hard sphere model and in the latter a full classical dynamic simulation employing realistic potentials. The situation is more complex in the case of chemisorption. Thus, a larger set of data on different systems is needed. Moreover, such investigations are relevant for the general subject of gas-surface interaction, as chemisorption corresponds to a well-defined initial state, with known energy and adsorption geometry, including orientation with respect to the substrate. Since the noble gas atom cannot react chemically, it acts as a vehicle of energy for the molecule and the surface. The collision process samples directly the

molecule-surface adsorption well, since the response of the molecule to the inert gas depends on depth and curvature of the chemisorption well as well as on the energy transfer to the vibrational and electronic degrees of freedom of the surface.

Recently in our laboratory collision induced processes were studied for O2 chemisorbed on Ag(110) observing desorption and dissociation.<sup>10</sup> The angular dependence of the cross sections was, however, not investigated. In the present paper we shall present a complete study of the interaction of Xe and Ar with O<sub>2</sub> chemisorbed on Ag(001) at 100 K. The choice is motivated by the fact that O2-Ag has been thoroughly investigated in our  $lab^{11-18}$  and elsewhere<sup>19-24</sup> and the system is quite well known. The (111) surface is the least reactive and the sticking coefficient is extremely small<sup>18,20</sup> while on the (110) and (001) surfaces the molecular sticking probabilities are comparable. The main and most intriguing difference between the latter two surfaces is that on Ag(110)the thermally induced dissociation probability is quite large (its low coverage value reads  $p_{\text{diss}} = 0.63$  at 300 K<sup>12</sup>) while on Ag(001) desorption dominates ( $p_{\text{diss}} \approx 4 \times 10^{-3}$  at 300 K). Buatier et al. suggested dissociation to occur on Ag(001) only at special sites.<sup>13</sup> At 100 K oxygen chemisorbs molecularly in a peroxide state<sup>21</sup> characterized by two dipole active losses: the O-O stretching at about 80 meV and the surfacemolecule mode at 30 meV. Recent high resolution electron energy loss spectroscopy (HREELS) measurements<sup>25</sup> show that the loss at 80 meV actually consists of two losses close in energy (79 and 84 meV), corresponding to adsorption sites of similar binding energy as forecasted in a theoretical paper

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by Mehandru and Anderson.<sup>26</sup> The sticking probability increases with increasing  $O_2$  energy<sup>13</sup> and decreases rapidly with increasing oxygen coverage, as for the case of  $O_2$ -Ag(110). The binding energy of  $O_2$  has been estimated to be about 0.5 eV/molecule on Ag(110)<sup>19</sup> and about 0.4 eV on Ag(001).<sup>14</sup> Since at low coverage the oxygen thermal desorption spectroscopy (TDS) peak occurs at a similar temperature for Ag(001),<sup>13</sup> a comparable binding energy is expected.

We shall see that upon Xe and Ar bombardment, at high enough energy, both desorption and dissociation occur on Ag(001), as was the case also for Ag(110).<sup>10</sup> At high impact energy the ratio of dissociation to desorption is thereby much larger with respect to the thermal case. Most intriguing is that both cross sections increase if the Xe beam strikes the sample at grazing incidence. The implications of such an unusual and unexpected behavior will be discussed.

#### **II. EXPERIMENT**

The experimental layout has already been described elsewhere;<sup>27</sup> only a brief summary is given here. It consists of an ultrahigh vacuum (UHV) chamber, equipped with a commercial quadrupole mass spectrometer, an ion gun, a retarding field analyzer (RFA), a cylindrical mirror analyzer (CMA), a self-built high resolution electron energy loss spectrometer designed<sup>28</sup> following Ibach's (HREEL) prescriptions<sup>29</sup> and a supersonic molecular beam. The spectrometer is capable of a resolution of 3 meV with  $10^5$  cps in the reflected beam. The surface is cleaned in UHV by Ar ion sputtering and annealing cycles until no losses are present in the HREEL spectrum. Oxygen and Xe are dosed by the molecular beam. Impact energies as high as 0.8 eV for O<sub>2</sub> and 2.7 eV for Xe can be obtained by seeding in He and heating the nozzle up to  $\approx$ 730 K. The temperature of the nozzle is measured by a thermocouple and the energy is obtained by the standard equation:30

$$E_i = \frac{M_i}{\langle M \rangle} \left\langle \frac{\gamma}{\gamma - 1} \right\rangle k_B T, \tag{1}$$

where  $E_i$  and  $M_i$  are energy and mass of component *i* of the gas mixture,  $\langle M \rangle$  the average mass,  $\gamma$  is the ratio of constant pressure and constant volume specific heats,  $k_B$  is Boltzmann's constant and T the nozzle temperature. Equation (1)is strictly valid for a perfect adiabatic expansion. For O<sub>2</sub> seeded in He (3% concentration) the measured velocity of the  $O_2$  molecules was in reasonable agreement with Eq. (1) so that we assumed it to hold also for the same concentration of Xe in He. The flux is measured by a spinning rotor gauge, i.e., absolute values of the exposure are obtained. At the crystal position the beam has a diameter of 4 mm, while the diameter of the sample is 10 mm. This ensures that for an angle of incidence  $\theta_i \leq 60^\circ$ , measured with respect to the surface normal, all the atoms of the beam strike the surface. The experiment was performed at a crystal temperature  $T_s$ =100 K where thermally induced dissociation and desorption of  $O_2$  are negligible.<sup>13</sup>



FIG. 1. EEL spectra recorded in-specular with electron energy  $E_e = 3.3 \text{ eV}$ and  $\theta_e = 63^\circ$ . In the lower part we show the spectrum recorded after oxygen dosing, corresponding to a coverage of 0.19 ML; in the middle the spectrum recorded after an additional exposure of 21 ML of Xe; in the upper part the spectrum recorder after further 42 ML (for a total of 63 ML) of Xe. The Xe flux is 0.07 ML/s,  $E_{Xe} = 2.7 \text{ eV}$  and  $\theta_{Xe} = 0^\circ$ . 1 ML corresponds to 1.2  $10^{15}$  atoms/cm<sup>2</sup>, the surface density of Ag atoms on Ag(001). The sample was kept at  $T_s = 100 \text{ K}$ .

# **III. RESULTS**

In a typical experimental run, see Fig. 1, the clean sample is dosed with oxygen by the supersonic molecular beam and then bombarded with rare gas atoms. Oxygen is seeded in helium so that its energy when the nozzle is at room temperature is 0.39 eV. The initial sticking probability in these conditions is 0.38.<sup>13</sup> After 18 s exposure at normal incidence a coverage of 0.19 ML of  $O_{2ad}$  is obtained as calibrated by the retarded reflection method<sup>31</sup> and by TDS. After recording an EEL spectrum, the sample is exposed to xenon (or argon) and another EELS spectrum is recorded and so on. With increasing exposure to Xe, the intensities of the O-O losses (at 78.5 and 84 meV) and of the Ag-O<sub>2</sub> loss (30) meV) decrease while the intensity of the loss of the Ag-O mode at about 35 meV shows up and grows. For oxygen coverages lower than  $\approx 0.22$  ML, the intensity of the losses at about 80 meV, normalized to the elastic reflectivity is linear in the coverage,  $\Theta_{O_2}$ :<sup>15,25</sup>

$$\Theta_{O_2} = c \frac{A_{80}}{A_0}.$$
 (2)

The calibration constant *c* is determined by the condition that at the end of the 18 s exposure to  $O_2$  the total coverage is 0.19 monolayers (ML). The coverage of atomic oxygen,  $\Theta_O$ , is obtained by the normalized intensity of the loss at 35 meV, assuming the same dipole moment as for O-Ag(110) (see Buatier de Mongeot *et al.*<sup>13</sup>). This assumption should affect our absolute calibration of  $\Theta_O$  by no more than 20%, thus leaving our conclusions unaffected. The uncertainty on coverage is estimated to be 0.01 ML. Moreover, we evaluated the contributions of the O<sub>2</sub> molecules vibrating at 78.5 and 84 meV by assuming the same numerical value of the dipole



FIG. 2. Enlargement of the upper spectrum of Fig. 1 at about 80 meV together with Gaussian fits of the peaks.

moment for the two species and fitting the peak around 80 meV with two Gaussians and a linear background, as shown in Fig. 2.

The molecular and atomic oxygen coverages are plotted as a function of Xe exposure, as shown in Fig. 3 for  $E_{Xe}$ = 2.2 eV,  $E_{Xe}$ = 1.1 eV, and normal incidence. As we show in the lower panel for  $E_{Xe}$ = 2.2 eV the O<sub>2</sub> coverage (+) decreases and the O coverage ( $\diamond$ ) increases with Xe exposure. As shown in the upper panel the decrease involves the coverage of both molecular oxygen species (× and  $\Box$ ) although at different rates as evidenced by the fact that the ratio of 84 and 78.5 meV peaks changes from 2.8 to 1.0. For  $E_{Xe}$ = 1.1 eV the behavior is different:  $\Theta_{O_2}$  remains almost unaffected by Xe bombardment, but a significant, although slow,



FIG. 3. Upper panels: coverage of the 84 meV O<sub>2</sub> moiety ( $\Box$ ) and of the 78.5 meV O<sub>2</sub> moiety (×) as a function of exposure to Xe. Lower panels: total  $O_{2ad}$  coverage (+) and the atomic oxygen coverage  $\Theta_{Oad}$  ( $\diamond$ ). The continuous and dashed lines report the best fit using the formulas given in the text. Two different measurement are reported for  $E_{Xe}$ =2.2 eV (left) and 1.1 eV (right).

increase in  $\Theta_0$  is observed. This indicates that under these conditions while desorption is negligible, dissociation is still important.

Once  $\Theta_{O_2}$  and  $\Theta_O$  as a function of Xe exposure are obtained, it is possible to fit the curves and to extract the cross sections for desorption  $\Sigma_{des}$  and for dissociation  $\Sigma_{diss}$ . We can start from the mass balance equations:

$$\frac{d\Theta_{O_2}}{dt} = -\Sigma_{des}\Phi\Theta_{O_2} - \Sigma_{diss}\Phi\Theta_{O_2}$$
(3)

and

$$\frac{d\Theta_{\rm O}}{dt} = 2\Sigma_{\rm diss} \Phi \Theta_{\rm O_2},\tag{4}$$

where  $\Phi$  is the Xe (or Ar) flux multiplied by the geometric factor  $\cos \theta_{Xe}$  to correct for the increase of the illuminated surface area. We first tried to fit the experimental data assuming that both  $\Sigma_{des}$  and  $\Sigma_{diss}$  do not depend on coverage, but this assumption did not lead to a reasonably good fit of the data for low Xe energy: the decrease in the oxygen coverage being initially faster than obtained by the exponential fit and later on slower, indicating that the total cross section increases with coverage. On the other hand the dependence of the atomic oxygen coverage with exposure is well fitted with the solution of Eqs. (1) and (2), with a coverage independent  $\Sigma_{diss}$ , at least within experimental accuracy.

We thus fitted the data assuming for

$$\Sigma_{\text{tot}}(\Theta_{O_2}) = \begin{cases} a + b \Theta_{O_2} & \text{for } \theta \ge \frac{\Sigma_{\text{diss}} - a}{b} \\ \Sigma_{\text{diss}} & \text{for } \theta < \frac{\Sigma_{\text{diss}} - a}{b} \end{cases}$$
(5)

with *b* positive.  $(\Sigma_{diss} - a)/b$  corresponds to the coverage at which  $\Sigma_{des}$  vanishes thus leaving open only the dissociation channel. Solving the differential equation for  $\Theta_{O_2}$  we obtain:

$$\Theta_{O_2}(t) = \frac{a \Theta_{O_2}(0) e^{-\Phi_{ta}}}{a + b \Theta_{O_2}(0)(1 - e^{-\Phi_{ta}})}.$$
(6)

Note that if *a* is positive removal of  $O_{2ad}$  goes on until all the molecular oxygen has desorbed or dissociated, while if *a* is negative  $\Sigma_{des}$  vanishes at the coverage  $\Theta_{O_2cr} = -(\Sigma_{diss} -a)/b$  and removal of  $O_2$  continues due to the dissociation channel *alone*. With these assumptions it was possible to fit all the data. Inclusion of second and higher order terms in the expansion of  $\Sigma_{tot}(\Theta_{O_2})$  is meaningless given the experimental accuracy. The result of our fit is reported by the lines in Fig. 3.

The so-determined values of the total cross section  $\Sigma_{\text{tot}}$  are summarized in Fig. 4 as a function of Xe (or Ar) energy  $E_{\text{Xe}}(E_{\text{Ar}})$  for normal  $(\theta_{\text{Xe}(\text{Ar})}=0^{\circ})$  and grazing incidence  $(\theta_{\text{Xe}(\text{Ar})}=60^{\circ})$  at the initial coverage  $\Theta_{O_2}=0.19$  ML.

Most points represent single measurements and the errors (*covariance error*) are obtained by a standard MINUIT routine, assuming for the data an error of 0.01 ML on  $\Theta_{O_2}$  and on  $\Theta_{O}$ , and disregarding the negligible error on the

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FIG. 4. Total cross section as a function of Xe (or Ar) energy at 0.19 ML coverage of O<sub>2</sub> for  $\theta = 60^{\circ}$ :  $\bigcirc$  (or  $\Box$  for Ar) and for  $\theta = 0^{\circ}$ :  $\times$  (or  $\diamond$  for Ar). The data reported in Ref. 10 for Xe/O<sub>2</sub>-Ag(110) (at normal incidence) are shown by  $\oplus$ .

exposure. Such an error (*covariance error*) is comparable to the difference in the cross sections obtained from different experimental runs (*statistical error*).

We focus for the moment the discussion on the larger set of data involving Xe projectiles ( $\bigcirc$  at  $\theta_{Xe}=60^{\circ}$  and  $\times$  at  $\theta_{Xe}=0^{\circ}$ ).

An angle dependent energetic threshold is present, which reads  $E_{\text{thr}} \approx 0.8 \text{ eV}$  at  $\theta_i = 60^\circ$  and  $E_{\text{thr}} \approx 1.8 \text{ eV}$  at  $\theta_{\text{Xe}} = 0^\circ$ .  $\Sigma_{\text{tot}}$  at  $\theta_{\text{Xe}} = 0^\circ$  could possibly match the value  $\Sigma_{\text{tot}}$  at  $\theta_{\text{Xe}} = 60^\circ$  with a smaller slope below 1.8 eV.

 $\Sigma_{\text{tot}}(E_i)$  increases by one order of magnitude over about 0.5 eV at large  $E_i$  and at  $\theta_{\text{Xe}} = 0^\circ$  while the increment is only a factor of 3 at  $\theta_{\text{Xe}} = 60^\circ$ . The different slopes are probably due to a saturation effect for the  $60^\circ$  data.

The critical value of the molecular oxygen coverage  $\Theta_{\rm cr}$ , for which  $\Sigma_{\rm des}$  vanishes, is shown in Fig. 5. Two possible situations occur: (i) at high Xe energy  $\Theta_{\rm cr}$  is negative, implying that desorption is active until complete removal of O<sub>2</sub> has taken place,  $\Sigma_{\rm des}$  being always non-negative; (ii) at low Xe energy  $\Theta_{\rm cr}$  is positive, i.e., desorption ends when there is still molecular oxygen on the surface, and further removal is due to dissociation alone.

The fitting procedure using Eq. (3) also was applied separately to the two oxygen moieties and yielded the results shown in Fig. 6. Obviously this analysis is physically meaningful only provided that site exchange is negligible. This assumption is neither proved nor disproved by our experiment. As one can see while the order of magnitude of the cross section is similar for both moieties  $\Sigma_{tot}$  is systematically larger for the species vibrating at 84 meV, indicating that preferential removal takes place. The difference between the cross sections for the two species is significant with respect to the experimental uncertainty as:

*all* the experimental point for the 84 meV moiety are higher than the corresponding value for the 78.5 meV moiety;



FIG. 5. Critical O<sub>2</sub> coverage, at which  $\Sigma_{des}$  vanishes, as a function of energy and angle of incidence for Xe bombardment. The symbols have the same meaning as in Fig. 4. The inset clarifies the definition of  $\Theta_{cr}$ .

(2) at large Xe exposures the coverages of the two species are comparable, while at the beginning the coverage of the 78.5 meV moiety is about one-third of the one of the 84 meV species, as evident from Fig. 1. The different values of  $\Sigma_{tot}$  for the two species indicate either a larger propension for desorption or for dissociation of the 84 meV moiety. However, since its relative concentration on the surface diminishes with Xe exposure while  $\Sigma_{diss}$ displays no marked dependence on  $\Theta_{O_2}$  we have to conclude that the relevant mechanism is enhanced desorption of the 84 meV moiety. This species should therefore sit in the short bridge site while the 79 meV moiety sits in the less exposed fourfold hollow site. This assignment is in accord with the smaller charge transfer to the O<sub>2</sub>



FIG. 6. Total cross section as a function of Xe (or Ar) energy at 0.19 ML coverage of  $O_2$  for the two  $O_2$  species corresponding to the losses at 78.5 meV (left) and 84 meV (right), as a function of angle and energy. Symbols have the same meaning as in Fig. 4.

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FIG. 7. Total cross section for removal of molecular oxygen, for the 78.5 meV moiety (×) and 84 meV moiety ( $\Box$ ) and the total value (+) as a function of  $\theta_{Xe}$ , at  $E_{Xe}$ =2.7 eV.

(and hence with the higher O-O vibrational frequency) expected for the site with lower coordination.

In Fig. 7 we show the angular dependence of the total cross section at high Xe energy for the two  $O_2$  moieties. The cross section increases *strongly* with  $\theta_{Xe}$ , contrary to expectation for normal energy scaling (decrease) or total energy scaling (constant).

The dependence of the atomic oxygen coverage on Xe exposure is obtained by solving Eqs. (3) and (4). It reads:

$$\Theta_{\rm O}(t) = 2 \frac{\Sigma_{\rm diss}}{b} \ln \frac{a + b \Theta_{\rm O_2}(0)(1 - e^{-\Phi_a t})}{a} \tag{7}$$

indicated by the dashed line in Fig. 3.  $\Sigma_{diss}$  is reported in Fig. 8, as a function of Xe (Ar) energy at normal and grazing



FIG. 9. Initial branching ratio  $(\Sigma_{diss}/\Sigma_{tot})$  as a function of Xe energy. The meaning of the symbols is the same as in Fig. 4.

incidence.

We observe also for  $\Sigma_{diss}$  a strong increase with  $E_{Xe}$  and  $\theta_{\rm Xe}$  (or  $E_{\rm Ar}$  and  $\theta_{\rm Ar}$ ) with similar thresholds as observed for  $\Sigma_{\text{tot}}$ .  $\Sigma_{\text{des}}$  is much larger than  $\Sigma_{\text{diss}}$  at large  $E_i$  while close to the threshold  $\Sigma_{diss}$  becomes dominant. This behavior is evidenced also when plotting the branching ratio  $(\Sigma_{\rm diss}/\Sigma_{\rm tot}(0.19 \text{ ML}))$  versus impact energy, as shown in Fig. 9. It decreases with  $E_{Xe}$  for  $\theta_{Xe} = 0^{\circ}$ , but it is independent of  $E_{\rm Xe}$  at  $\theta_{\rm Xe} = 60^{\circ}$ . While the error bars given by error theory are quite large the effect is clearly present. As shown in the right-hand panel of Fig. 3, the only effect of Xe bombardment at this low Xe energy is a slow increase of the dissociated oxygen coverage.

Alternatively, we also performed measurements of the cross section for desorption, recording the oxygen partial pressure by a residual gas quadrupole mass spectrometer (QMS). Two typical traces are shown in Fig. 10, with the Xe



FIG. 8. Cross section for dissociation. The meaning of the symbols is the same as in Fig. 4. The  $\oplus$  indicate the values reported for Xe/O<sub>2</sub>-Ag(110) (Ref. 10).



FIG. 10. QMS signal of  $O_2$  recorded during exposure to Xe for two different angles of incidence. The Ag(001) surface is precovered with  $O_2$  and at time t=0 the Xe beam hits on the surface.

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beam impinging on the sample at normal and grazing incidence ( $\theta_i = 60^\circ$ ). The beam initially enters the chamber without striking the sample. Then, at t=0, the flag in front of the Ag crystal is turned down and the Xe beam hits the surface. Oxygen desorption is monitored by the QMS signal at mass 32,  $I_{O_2} = I - I_{\text{background}}$ , which is proportional to the flux of oxygen desorbing from the Ag(001) surface  $[I_{O_2}(t) = -k_{\text{QMS}}d\Theta_{O_2}/dt, k_{\text{QMS}}$  being a calibration constant]. The signal at mass 32,  $I_{O_2}$ , is calibrated with the signal recorded when an oxygen beam of known flux enters the chamber under the same pumping conditions as in the collision experiment. It is evident from Fig. 10 that the oxygen yield at normal incidence (the upper panel) is much smaller than under grazing impact conditions (the lower panel). This independently confirms the EELS result.

From measurements such as the one reported in Fig. 10, we can derive the time dependence of the oxygen coverage, given by

$$\Theta_{O_2}(t) = \Theta_{O_2}(0) - \frac{1}{k_{QMS}} \int_0^t I_{O_2}(\tau) d\tau - \frac{1}{2} \Theta_O(t)$$
(8)

and from the definition of the cross section for desorption:

$$\frac{d\Theta_{O_2}}{dt} = -\Sigma_{des}(\Theta_{O_2})\Theta_{O_2}\Phi t, \qquad (9)$$

we obtain:

$$\Sigma(\Theta_{O_2}) = \frac{I_{O_2}(t)}{k_{\text{QMS}} \Phi \Theta_{O_2}(t)}.$$
(10)

In determining  $\Theta_{O_2}(t)$  we neglected the last term in Eq. (8) as for grazing incidence data, the only one for which the QMS signal is high enough to be suitable for the present direct analysis, the branching ratio is very small, as apparent from Fig. 9. The QMS signal,  $I_{O_2}(t)$ , the corresponding residual coverage of oxygen,  $\Theta(t)$ , and the result of Eq. (10), i.e.,  $\Sigma(\Theta_{O_2})$ , are shown in Fig. 11. In the upper panel the QMS data (dashed line) are compared with the EELS result for  $\Theta_{O_2}$  ( $\Box$ ) and  $\Theta_O$  ( $\bigcirc$ ).  $\Theta_O$  is negligible except for large exposure time, thus justifying our assumption of neglecting it.

As apparent from the bottom panel of Fig. 11,  $\Sigma_{des}$  increases linearly with  $\Theta_{O_2}$  above  $\Theta_{O_2}=0.05$  ML, thus supporting the linear dependence of the cross section on  $\Theta_{O_2}$  used to fit the EELS data. The spread in the data points at low coverage is caused by the divergence of the error, as Eq. (10) corresponds then to the ratio of small quantities. This method is in this case simpler and faster than the EELS method, but for a correct analysis it needs independent information (obtained in our case by EELS) about  $\Theta_0$ . It is moreover limited to relatively large values of the cross section and it can therefore be applied only for a very limited range of energies and angles of incidence. As shown in the upper panel of Fig. 11, the QMS data analysis is in good agreement with the EELS result.

We finally performed a similar experiment dosing oxygen on the sample at room temperature, when  $O_2$  chemisorbs



FIG. 11. Upper panel: residual O<sub>2</sub> coverage (as evaluated by integrating the QMS signal reported in the lower panel of Fig. 10) as a function of time, and lower panel: cross section for O<sub>2</sub> desorption as a function of coverage ( $\diamond$ ). In the upper panel we also report the molecular oxygen coverage ( $\Box$ ) and the atomic oxygen coverage ( $\bigcirc$ ) obtained by EELS under the same conditions.  $E_{\rm Xe}$ =2.7 eV and  $\theta_{\rm Xe}$ =60°.

dissociatively, and then exposing the surface to an energetic Xe beam at normal and grazing incidence. No desorption could be detected by our residual gas analyzer and no decrease in the intensity of the Ag-O loss was observed even after an exposure to Xe as large as 263 ML. Assuming a coverage independent cross section as reasonable since the coverage of atomic oxygen is lower than 0.06 ML, and a relative reproducibility of the EELS intensities of 10%, we obtain an upper limit of the cross section for desorption of atomic oxygen of  $5 \times 10^{-3}$  Å<sup>2</sup>. This result is in accord with the large binding energy ( $\approx 1.8 \text{ eV}^{19}$ ) of dissociated oxygen.

In order to investigate the dependence of the cross section on the mass of the incident particle, we investigated desorption and dissociation of O<sub>2</sub> on Ag(001) also for Ar bombardment. Because of the smaller mass ratio with the He carrier gas, the impact energy is in this case limited to  $E_{Ar} \leq 1.3$  eV. The data are reported by  $\Box$  ( $\theta_i = 60^\circ$ ) and  $\diamond$  ( $\theta_i = 0^\circ$ ) in Figs. 4 and 8 for the total and the dissociation cross section, respectively. In the energy range accessible both by Ar and by Xe the energy and angle dependence of  $\Sigma_{tot}$  and  $\Sigma_{diss}$  are quite similar. This indicates that processes other than collisions are of marginal importance, e.g., if the processes would have been mediated by the formation of a negative ion resonance induced by the creation of hot electrons during the collision a larger cross section would have been expected for Xe than for Ar.<sup>32</sup>

A closer inspection of Figs. 4 and 8 reveals that Ar is slightly more efficient than Xe for both desorption and dissociation. This effect is due to the mass mismatch between the noble gas atom and oxygen so that the energy transfer in the  $Ar-O_2$  collision is more efficient: 99% of the initial Ar energy is transferred to dioxygen in a head-on collision, compared to 63% when the projectile is a xenon atom.

# IV. DISCUSSION OF THE DATA

The maximum value of  $\Sigma_{tot}$  is observed at  $\theta_{Xe} = 60^{\circ}$  and reads (28±8) Å<sup>2</sup>. Such a value is quite large, but not unreasonable as the maximum value expected for a hard sphere model would be 46 Å<sup>2</sup>. This value compares moreover with  $\Sigma_{des} \approx 20$  Å<sup>2</sup> found by Ceyer *et al.* for Ar collision with CH<sub>4</sub>-Ni(111).<sup>7</sup> For Ag(110) Åkerlund *et al.*<sup>10</sup> found at normal incidence  $\Sigma_{tot} = 0.08$  Å<sup>2</sup> at  $E_{Xe} = 1.6$  eV and 0.22 Å<sup>2</sup> at  $E_{Xe} = 2.6$  eV which should be compared with  $\Sigma_{tot} = 0.016$  $\pm 0.005$  Å<sup>2</sup> and  $0.3 \pm 0.1$  Å<sup>2</sup> for Ag(001) under the same conditions. The discrepancy is in our opinion not significant in view of the limited set of data for Ag(110). Also the branching ratios between desorption and dissociation for the two surfaces are similar in agreement with the local nature of the collision process.

In the following we shall limit the discussion to the Xe case for which the data basis is larger. We shall analyze separately the different observed effects.

#### A. Branching ratio

At grazing incidence the initial branching ratio for Xe bombardment is independent of energy within experimental error (see Fig. 9); at normal incidence, on the other hand, it increases with decreasing Xe energy. At large  $E_i$  the branching ratio is independent of  $\theta_i$ . The measured branching ratio reads in the latter conditions  $\approx 4 \times 10^{-2}$  and is  $\approx 10$  times larger than the thermal value ( $\approx 4 \times 10^{-3}$ ) appropriate for O<sub>2</sub>-Ag(001).<sup>13</sup> At normal incidence and low  $E_i$  it goes up to more than 0.5 thus becoming  $\approx 100$  times larger than thermally. This situation corresponds to the right-hand panels in Fig. 3: under such conditions only  $\Sigma_{diss}$  contributes significantly to  $\Sigma_{tot}$ , giving accordingly a positive  $\Theta_{cr}$ , as shown in Fig. 5.

The low energy limit at normal incidence is comparable to the thermal value for O<sub>2</sub>-Ag(110) at room temperature ( $\approx 0.5$  at large O<sub>2</sub> coverage<sup>12</sup>) and to the collision induced ratio for the same surface under similar conditions ( $\approx 0.20^{10}$ ).

This effect can be rationalized remembering that the barrier for desorption is slightly larger than the barrier for dissociation as demonstrated by TDS.<sup>19</sup> When  $E_{Xe}$  is comparable to  $E_{thr}$  (as is indeed the case at normal incidence) the difference in the energy thresholds for the two phenomena cannot be neglected any more and dissociation becomes more important. The fact that the branching ratio measured under these conditions compares well with the one found for Ag(110) indicates that the barrier height difference is similar. At grazing incidence, when  $E_{\rm Xe}$  is by far larger than  $E_{\rm thr}$ , the branching ratio is no longer affected by the energetics and it reflects the available phase space at disposition for dissociation and desorption. The much smaller thermal value for Ag(001) with respect to Ag(110) indicates therefore that the available phase space for dissociation and not the difference in the barrier heights is responsible for the different thermal branching ratio of the two surfaces and that in the collision process only part of the phase space is sampled.

#### B. Coverage dependence

The increase of the cross section with O<sub>2</sub> coverage is explained by the decrease in the heat of adsorption due to lateral repulsive interactions between the admolecules. The desorption yield is consequently not exponential with time. This result is at variance with the data obtained by Åkerlund *et al.* for Pt(111)<sup>10</sup> where a very good fit was obtained with a coverage-independent cross section. The difference is in accord with the different thermal desorption spectra which show for the case of O<sub>2</sub>-Ag(001) an intense shoulder on the low temperature side at high coverage,<sup>14</sup> while such a feature is absent for Pt(111). However, a similar dependence of  $\Sigma_{tot}$ on  $\Theta_{O_2}$  was observed also for O<sub>2</sub>-Ag(110)<sup>10</sup> although no high coverage shoulder is present in the thermal desorption spectra.<sup>24</sup>

#### C. Energy and angle dependence

In literature the energy dependence of  $\Sigma_{diss}$  was described by the function:

$$\Sigma_{\rm diss}(E_i) = k \frac{(E_i - E_{\rm thr})^N}{E_i},\tag{11}$$

where  $E_{thr}$  is the threshold energy. The formula was developed for bimolecular collision leading to dissociation in gas phase scattering, a situation which is different from our case, but it was also used as an interpolation formula by Lewis *et al.*<sup>2</sup> to describe collision induced cross sections for desorption on surfaces. Analyzing the data of Fig. 4 according to Eq. (11) we obtain  $E_{thr}=1.56$  eV and N=3.7 at normal incidence and  $E_{thr}=0.92$  eV and N=2.8 at grazing incidence. Ignoring for the moment the angular dependence of  $E_{thr}$  we note that both values are much larger than the binding energy of molecular oxygen ( $U_{O_2}=0.4$  eV/molecule<sup>14</sup>). The discrepancy can be explained by the following argument suggested by Szulcewski and Lewis:<sup>2</sup> The kinetic energy of the O<sub>2</sub> molecule after head on collision with a Xe atom impinging normally onto the surface with energy  $E_{Xe}$  is:

$$E_{O_2}^{i} = E_{Xe} \frac{4m_{Xe}m_{O_2}}{(m_{Xe} + m_{O_2})^2}.$$
 (12)

In the collision with the surface the  $O_2$  molecule undergoes an energy loss to the Ag atoms and is reflected with energy

$$E_{O_2}^f = E_{O_2}^i \left( 1 - \frac{4m_{\text{eff}}m_{O_2}}{(m_{\text{eff}} + m_{O_2})^2} \right), \tag{13}$$

where  $m_{\text{eff}}$  is the effective mass of Ag. Desorption occurs if  $E_{O_2}^f$  is larger than the binding energy of chemisorbed O<sub>2</sub>, so that  $U_{O_2}$  can be estimated from the energy threshold  $E_{\text{thr}}$ :

$$U_{\rm O_2} = E_{\rm thr} \left( 1 - \frac{4m_{\rm eff}m_{\rm O_2}}{(m_{\rm eff} + m_{\rm O_2})^2} \right) \left( \frac{4m_{\rm Xe}m_{\rm O_2}}{(m_{\rm Xe} + m_{\rm O_2})^2} \right).$$
(14)

This approach leads for our normal incidence value ( $E_{\text{thr}} = 1.56 \text{ eV}$ ) and with  $m_{\text{eff}} = 2m_{\text{Ag}} = 216$  amu to a reasonable estimate of  $U_{\text{O}_2} = 0.5 \text{ eV}$ .

This result is, however, not rigorous for the following reasons.

- (1) The effective mass is not known *a priori* and has to be obtained by scattering experiments or complicated calculations.
- (2) The formula works exactly only for head on collisions (zero impact parameter).
- (3) For a chemisorbed molecule the assumption of a twobody collision between Xe and  $O_2$  and then between  $O_2$ and Ag may not be correct, as when the Xe atom collides with the  $O_2$  molecule, the latter immediately experiences the repulsive potential energy surface, so that the motion of  $O_2$  is influenced by the positions of Ag atoms. In other words, the  $O_2$  molecule is squashed in between the Xe atom and the surface and the collision involves many bodies.

Moreover, Eqs. (11) and (14) do not contain an angle dependence of  $E_{thr}$ , contrary to the experimental results. A more complicated angular dependent relation (see, i.e., Ref. 9), but still true only for single collisions, gives a higher energy threshold at grazing incidence, contrary to experiment. The disagreement has to be ascribed to multiple scattering effects, not included in the theoretical relation of Ref. 9, which suppress the cross section at normal incidence, thus obscuring the simpler single-scattering behavior. We shall come back to this point later. In trying to explain the angular enhancement we observe experimentally, one might consider the possibility of an enhancement of  $\Sigma_{tot}$  by a cascade effect, i.e., taking into account the possibility that the energetic Xe atom hits an oxygen molecule which then, having acquired a large parallel momentum, hits another O<sub>2</sub> molecule leading to multiple desorption events. This hypothesis has to be rejected because the increase of  $\Sigma_{tot}$  with  $\theta_{Xe}$  is observed also in the low coverage limit, where the O<sub>2</sub> molecules are too far apart to make multiple desorption significant. Moreover, such a process would contribute only in the high energy limit and has thus to be excluded near threshold.

To our knowledge, none of the previously investigated systems exhibits a similar enhancement of  $\Sigma$  with the angle of impact of the projectile.

Beckerle *et al.*<sup>7</sup> found a limited increase (of about a factor of 2) in the cross section for desorption of CH<sub>4</sub> on Ni(111) at high Ar energy (51.8 kcal/mol $\approx$ 2.2 eV/atom) as  $\theta_{Ar}$  changes from 0° to 70°. This increase was quantitatively accounted for by the contribution of mirror collisions. The inert gas atom may directly hit the methane molecule (direct collision) or hit first the surface and, after reflection, hit the physisorbed gas molecule (mirror collision). The latter contribution is substantial at high energy and at grazing incidence, since the Ar atom retains a significant part of its energy after being reflected from the surface and it is still capable of transferring to methane a sufficient amount of energy to make it desorb.

The steric factors, i.e., the radius of the rare gas atom, the dimensions of the molecule and, above all, its equilibrium distance from the surface, play a key role in determining the importance of the mirror collision contribution to the cross section. At low energy the effect is small because the noble gas atom may not be energetic enough to cause methane desorption after being reflected by the surface. Beckerle *et al.* were able to explain the complex energetic and angular dependence of  $\Sigma_{des}$  by a hard sphere model,<sup>7</sup> allowing energy transfer to the surface by introducing an effective mass, used as a fitting parameter. With similar arguments and using a reasonable interpolation function for the dissociation probability they could also explain the energetic and angular dependence of  $\Sigma_{diss}$ .<sup>8</sup>

A complex angular dependence of  $\Sigma_{des}$  on the angle of incidence of Ar was found for NH<sub>3</sub> chemisorbed on Pt(111):  $\Sigma_{des}$  initially increases with  $\theta_{Ar}$  and then decreases again.<sup>2</sup> Szulczewski and Lewis<sup>2</sup> explained the value of the energy threshold in a straightforward way and attributed the complex angular dependence of  $\Sigma_{des}$  to surface corrugation. Ammonia was also reported to dissociate by collision with Ar with an energy independent  $\Sigma_{diss}$ , which increases monotonically by about a factor of 3 when moving from normal to grazing incidence. The role of the surface corrugation was invoked to explain the complete breakdown of normal energy scaling but no quantitative model was suggested.

A small increase of  $\Sigma_{diss}$  was observed also for CO on Ni(111)<sup>1</sup> but, even in this case, no explanation was given. For H<sub>2</sub>O on Ru(001)<sup>3</sup> and CO<sub>2</sub> on Re(0001)<sup>4</sup> the angular dependence of the cross section was not reported.

To the best of our knowledge, for *no system* the increase in  $\Sigma_{des}$  and  $\Sigma_{diss}$  with the angle of incidence of the inert gas atom is as large as we find for O<sub>2</sub>-Ag(001). Mirror collision cannot account for such an increase, as the chemisorption distance of the O<sub>2</sub> molecule is too small (1.75 Å<sup>26</sup>).

## V. MOLECULAR DYNAMICS SIMULATION

#### A. Description of the model

In order to account for the unexpected and anomalous results, we performed classical molecular dynamics (MD) simulations. We modeled the surface as a grid of  $10 \times 10$ silver atoms of radius  $r_{Ag}$ =1.44 Å of mass  $m_{eff}$ , with (001) geometry and lattice parameter l=2.88 Å. The oxygen atom is represented by a sphere of radius 1.125 Å, intermediate between the O-O distance (1.5 Å) and the O radius (0.75 Å). First, we put the oxygen molecule in the fourfold-hollow site, at a height h above the surface plane given by

$$h = \sqrt{(r_{\rm Ag} + d + r_{\rm O_2})^2 - (l/2)^2} - r_{\rm Ag}, \qquad (15)$$

where *d* is the separation between the surfaces of the hard spheres used to model the Ag atoms and the oxygen molecule. It is the maximum distance the  $O_2$  molecule may travel freely from its initial equilibrium position before colliding with the Ag surface. The separation *d* is arbitrarily set to 0.1 Å, for a chemisorbed molecule, a substantially larger value being more appropriate for a physisorbed system, where the adsorbate sits well above the surface plane.

The description of the surface as a square array of rigid spheres in fixed position is very similar to the model used by Beckerle *et al.*, with the additional inclusion of corrugation. In conclusion, our model describes the  $O_2$  and Xe (or Ar)surface interaction as a collision between hard spheres (Xe, Ar or  $O_2$ ) with a rigid surface, whose corrugation is determined by  $r_{Ag}$ . When  $r_{Ag} = 1.44$  Å, the surface is strongly corrugated, while when  $r_{Ag}$  is large, the limit of a flat surface is approached. From simple geometrical considerations we can define a corrugation parameter across the Ag atoms along the  $\langle 1\bar{1}0 \rangle$  direction,  $c_{Ag}$ :

$$c_{\rm Ag} = r_{\rm Ag} \left[ 1 - \sqrt{1 - \left(\frac{l}{2r_{\rm Ag}}\right)^2} \right],$$
 (16)

which can be varied between 1.44 Å and  $\approx 0$ . A hard wall is assumed for the Xe-O<sub>2</sub> interaction as well as for the Xesurface and O<sub>2</sub>-surface interaction. In the time between collisions both Xe and O<sub>2</sub> do not experience any force. Within this simple model, the trajectories can be determined analytically as follows: (i) for Xe-O<sub>2</sub> collisions the velocities of both particles after the interaction are determined by energy and momentum conservation and by the requirement that the central force approximation holds; (ii) for Xe-surface and O<sub>2</sub>-surface collisions, conservation of momentum in the direction orthogonal to the *local* surface normal is imposed, while along that direction we impose that O<sub>2</sub> (or Xe or Ar) transfers the fraction of its kinetic energy given by:

$$\frac{\Delta E}{E_n} = \frac{4mm_{\rm eff}}{\left(m + m_{\rm eff}\right)^2},\tag{17}$$

where *m* is the mass of  $O_2$  (or Xe or Ar) and  $m_{eff}$  is the effective mass of Ag. The local surface normal is defined as the direction connecting the centers of the Ag surface atom involved in the collision to the impact point of the projectile atom (Xe) or molecule (oxygen).

The simulation is started with the Xe (or Ar) atom at 100 Å away from the surface, with velocity along a direction forming an angle  $\theta_i$  with the surface normal. O<sub>2</sub> is at rest in the fourfold hollow site.

The first collision to take place is uniquely determined by the initial positions and velocities of Xe. The subsequent evolution of the system is determined analytically imposing the rules (i) and (ii). In between two collisions both Xe (or Ar) and  $O_2$  move with *constant* velocity.

When no further collisions occur,  $O_2$  is considered to be desorbed if: (a) its final normal kinetic energy is larger than the binding energy,  $U_{O_2}=0.4$  eV/molecule, and (b) its velocity is directed away from the surface.

The cross section for each Xe (or Ar) energy and angle is evaluated by running a large number  $N_{\text{tot}}$  of trajectories, with Xe (or Ar) initial positions randomly chosen over a 20 Å×20 Å square. If  $N_{\text{des}}$  trajectories end with desorption, the cross section is given by

$$\Sigma_{\rm des} = \frac{N_{\rm des}}{N_{\rm tot}} \, 400 \, \text{\AA}^2. \tag{18}$$

The relative *statistical* error of  $\Sigma_{des}$  is estimated to be  $1/\sqrt{N_{des}}$ . A set of 10 000 trajectories was found to give converged results, for cross sections larger than about 0.02 Å<sup>2</sup>.

Dissociation is not included in our model, as we believe that a much more realistic and complex potential is required to describe energy transfer to the internal degrees of freedom of the oxygen molecule. In particular it is known that as  $O_2$ approaches the Ag surface, the O-O distance increases, the



FIG. 12. Map of the initial position of Xe leading to desorption of  $O_2(\bigcirc)$  at  $E_{Xe}=3.5$  eV and  $\theta_{Xe}=60^{\circ}$  (140 events out of 10 000). The  $O_2$  molecule sits in the center of the frame and has a radius of 1.125 Å. The isolated events leading to desorption correspond to indirect collision where the Xe atom first hits the surface and then the oxygen molecule.

potential being dependent both on molecule-surface distance and intermolecular elongation.<sup>33</sup> This extension is, however, well beyond the scope of the present paper, as even the most sophisticated available simulations of the relatively simpler process of O<sub>2</sub> interaction with  $Ag(110)^{34}$  do not fully explain the experimental data and a realistic simulation of collision induced dissociation would be an even more difficult task.

However, as dissociation is negligible compared to desorption except for a very limited energy range at normal incidence, our assumption is not unreasonable. We shall see *a posteriori* that with our simple and rough model the qualitative behavior of the experimental cross sections is well described and we shall demonstrate that the present model is moreover able to give a qualitative description of a large variety of systems.

We have also checked our program by computing the cross sections for the Ar-CH<sub>4</sub>-Ni system of Beckerle *et al.* at different energies and angles, obtaining the same results.

#### B. Results of MD simulations

A typical outcome of the simulation is shown in Fig. 12, where the initial positions of the trajectories leading to desorption are reported. We note that the contribution of mirror collisions is negligible. This holds also for other impact energies and angles. This behavior is at variance with what was found for physisorbed systems and is due to the fact that the chemisorbed  $O_2$  molecule sits close to the surface. For the physisorbed CH<sub>4</sub>-Ni system mirror collisions gave a factor of 2 increase in the cross section at high energy and grazing incidence.

We have calculated  $\Sigma_{\text{des}}$  as a function of  $E_{\text{Xe}}$  for different  $\theta_{\text{Xe}}$  and for three different values of  $m_{\text{eff}}=150$ , 300, and 1500 amu, as well as for three different values of the surface corrugation  $c_{\text{Ag}}=1.44$ , 0.44, and 0.04 Å. The results are shown in Fig. 13.



FIG. 13. Cross section as a function of  $E_{Xe}$  at different  $\theta_{Xe}$  for different values of  $m_{eff}$  and  $c_{Ag}$ .  $\times$ :  $\theta_{Xe}=0^{\circ}$ ;  $\diamond: \theta_{Xe}=30^{\circ}$ ;  $\Box: \theta_{Xe}=60^{\circ}$ .

We note the following.

(a) when  $m_{\rm eff}$  is small (bottom row of panels), i.e., when energy loss to the substrate is important, the energy threshold is higher and the value of the cross section smaller than for large  $m_{\rm eff}$  (top row of panels). In the latter case a negligible amount of energy is indeed transferred to the sample.

(b) The angular dependence of  $\Sigma_{des}$  is *energy dependent*: For fixed values of  $c_{Ag}$  and  $m_{eff}$  the cross section tends to become angle independent in the high Xe energy limit, where it approaches saturation.

(c) If the surface is *corrugated* enough (see the panel in the left and central column in Fig. 13), at intermediate and low energy the cross section at grazing incidence is much larger than at normal incidence. Such behavior is due to two effects.

(i) the ability of the corrugation to convert parallel into normal momentum, thus favoring desorption at grazing incidence and (ii) suppression of desorption for normal incidence caused by multiple collisions. For  $m_{\rm eff}$  about 1.5 times the Ag mass and  $c_{\rm Ag}$  larger than 0.44 Å (see the bottom left and bottom central panels) this effect occurs at comparable energy as observed for our system.

(d) On the contrary for a flat surface at low energy we observe for large  $m_{\rm eff}$  a decrease of  $\Sigma$  with  $\theta$  due to the lower normal energy available for desorption. Normal energy scaling is approached as observed for a physisorbed system such as CH<sub>4</sub>-Ni at low energy, as long as mirror collisions are negligible.

(e) At intermediate corrugations and small  $m_{\rm eff}$  the effects (c) and (d) overlap and the angular dependence of  $\Sigma_{\rm des}$  can be *nonmonotonic*. This effect was indeed observed for desorption of NH<sub>3</sub> on Pt(111).<sup>2</sup>

The model is, however, too crude to give full quantitative results. Since the absolute value of the cross section depends on the assumptions about the radius of Xe and above all on the approximation of  $O_2$  as a hard sphere, no attempt is made to *fit* the experimental data, but we limit the discussion to a semiquantitative description of the dynamics.



FIG. 14. Cross section as a function of  $E_{Ar}$  at different  $\theta_{Ar}$  for  $c_{Ag} = 1.44$  Å and  $m_{eff} = 150$  amu. Symbols indicate:  $\times$ :  $\theta_{Ar} = 0^{\circ}$ ;  $\diamond$ :  $\theta_{Ar} = 30^{\circ}$ ;  $\Box$ :  $\theta_{Ar} = 60^{\circ}$ .

In particular the model has the following limits.

(a) It completely neglects the effect of the presence of an adsorption well for oxygen and for Xe, implying a *refraction* effect, i.e., a change of direction when the Xe approaches the surface or when the  $O_2$  desorbs. Such effect is negligible at energies much larger than the well depth (about 0.1 eV for Xe and 0.4 eV for oxygen) and affects the angular distribution of scattering.

(b) The collision is treated as *impulsive*, an approximation whose validity has to be checked by self-consistency of the result. In our case it is reasonable except for the lowest energies.

(c) The effective mass and the surface corrugation are assumed to be *energy independent*, for sake of simplicity and to avoid further arbitrary assumptions. While this cannot affect the qualitative conclusions attained, it may change the values of the parameters while attempting a fit to the experimental data.

The results of the calculations for  $c_{Ag}=1.44$  Å and  $m_{eff}=150$  amu for Ar in the energy range 0.5–1.5 eV are shown in Fig. 14. It is apparent that  $\Sigma_{des}(E_i, \theta_i)$  is similar to the one obtained for Xe projectiles. The larger efficiency of Ar in the momentum transfer process, its mass being closer to the oxygen mass than that of Xe, is partly balanced by the smaller size of the Ar atom, so that the resulting cross sections are comparable to those obtained with Xe at similar energies.

We finally investigated the cross section for a corrugated surface with  $c_{Ag} = 1.44$  Å with  $m_{eff} = 150$  amu, with the oxygen molecule placed in the short bridge site with its axis connecting two Ag atoms. Two equivalent sites are possible by symmetry. As shown in the inset of Fig. 15 the symmetry is broken by the direction of the impinging Xe atom. The cross section is different, being larger when Xe impinges along the molecular axis. Note that as oxygen is treated as a sphere, the difference is *not* due to the different geometrical area of the O<sub>2</sub> molecule viewed by Xe. When impinging parallel to the molecular axis (the left-hand panel), Xe forces the molecule to immediately collide with Ag while when



FIG. 15. Cross section as a function of  $E_{Xe}$  at different  $\theta_{Xe}$  for  $c_{Ag} = 1.44$  Å and  $m_{eff} = 150$  amu. Oxygen is now in the short bridge site, Xe atoms impinge along the O-O axis (left) and normally to it (right). Symbols have the same meaning as in Fig. 13. The initial conditions are generated by the Monte Carlo method. The statistical uncertainty is shown by the error bars. The data for  $\theta_{Xe} = 0^{\circ}$  were obtained with twice as many trajectories as for  $\theta_{Xe} = 30^{\circ}$  and  $\theta_{Xe} = 60^{\circ}$ .

impinging normally to it the  $O_2$  moves toward a valley in the local surface corrugation before colliding with Ag. The different collision geometry is, therefore, essential in determining the magnitude of the angular enhancement of the cross section for desorption. In the former case our simulations yield a larger cross section than for a molecule sitting in the fourfold hollow site (see the bottom left-hand panel of Fig. 13), in the latter case a slightly smaller value. On the average the  $O_2$  in the bridge site is removed more efficiently in accord with experiment.

We can gain more insight into the mechanism underlying the angular enhancement of  $\Sigma_{des}$  by looking more closely at two effects: the average energy loss to the substrate  $\xi$  as a function of  $E_{Xe}$  and the contribution of multiple collisions during the desorption process. The former effect is shown in Fig. 16 for the corrugated and flat surface cases and for two values of the effective mass.

If  $m_{\rm eff}$  is high, the energy transfer to the Ag substrate plays a negligible role, so that a large fraction of the initial Xe energy is available to desorb or dissociate the O<sub>2</sub> molecule. When  $m_{\rm eff}$  is low, on the contrary, energy transfer to the substrate is substantial. This result is independent of surface corrugation. At normal incidence a large fraction of the initial energy is lost to the substrate, while at grazing incidence it is smaller, making more energy available for oxygen desorption or dissociation. The average energy available to the  $O_2$  molecules increases thereby by a factor of 1.5 (at 3.5 eV) when moving from normal to grazing incidence. Our simulations show that corrugation has little influence on the average energy loss but is essential in converting parallel momentum into normal momentum, thus enabling desorption of chemisorbed O<sub>2</sub>. Most probably, it also favors energy transfer into the internal degrees of freedom of the molecule, thereby determining the observed growth of  $\Sigma_{\text{diss}}$  with  $\theta_i$ .



FIG. 16. Energy transferred to the surface as a function of Xe initial energy for two values of  $m_{\rm eff}$  and two values of  $c_{\rm Ag}$ , for oxygen in the fourfold hollow site. Symbols have the same meaning as in Fig. 13.

Multiple collision effects are analyzed in Fig. 17, where we compare the results of the simulations when including multiple scattering (MS, bottom panels) and when allowing for a single one oxygen-Xe collision (SS, upper panels). In the last case the Xe atom is "switched off" immediately after the first collision with the O<sub>2</sub> molecule. The simulation was run for substantial energy transfer ( $m_{\rm eff}$ =300 amu, where the angular dependence is expected to be large in the expected energy range) for a corrugated (the left-hand pan-



FIG. 17.  $\Sigma_{\text{des}}$  vs  $E_{\text{Xe}}$  under conditions of significant energy loss to the substrate ( $m_{\text{eff}}$ =300 amu) for the corrugated ( $c_{\text{Ag}}$ =1.44 Å) and essentially flat Ag(100) surface ( $c_{aA}$ =0.04 Å) as calculated with inclusion of multiple oxygen-Xe collision (MS, as all the simulations presented in the previous figures, lower panels) and removing the Xe atom after the first Xe-oxygen collision (SS, upper panels). Symbols indicate:  $\times: \theta_{\text{Xe}}$ =0°;  $\Box: \theta_{\text{Xe}}$ =60°.

els) and flat (the right-hand panels) surface. The following is apparent.

- (1) In the single scattering approximation without corrugation the cross section at normal incidence is larger than (at low energy) or comparable with (at high energy) the cross section at grazing incidence. Inclusion of corrugation, always within the single scattering approximation, does not modify the qualitative features of the cross section curves.
- (2) The energy threshold under single scattering conditions is lower at normal incidence as theoretically expected.<sup>9</sup>
- (3) Both multiple scattering and corrugation are needed to explain the angular dependence of the cross section experimentally observed.
- (4) Inclusion of multiple scattering suppresses both normal and grazing incidence cross sections, but this action is stronger for normal incidence.

The calculated behavior is in agreement with the following mechanism: After collision with the  $O_2$  molecule the Xe atom continues its approach toward the surface because of momentum conservation, and thus it must collide again with the  $O_2$ . The oxygen molecule is then squashed between Xe and the surface, thus preventing it from desorbing. This effect is enhanced for adsorption in a highly coordinated site of a corrugated surface, where the substrate atoms surrounding the hollow delimit a volume where the molecule is trapped as is the case for  $O_2$  adsorbed in the fourfold hollow of Ag(001).

The collision induced desorption is thus a complex process, where at least three effects are fundamental in determining the real behavior, namely *energy loss to the substrate, surface corrugation and multiple scattering.* 

# **VI. CONCLUSIONS**

We have investigated the angular and energetic dependence of the cross section for desorption and dissociation of chemisorbed  $O_2$  on Ag(001) at 100 K by Xe bombardment. The main results can be summarized as follows.

(1) The cross section for dissociation is smaller than the one for desorption, except at low  $E_i$  and near normal incidence. The branching ratio for the two processes at high impact energy is thereby one order of magnitude larger than for the thermal case because of the larger energy available and of the different part of phase space which is sampled in the collision process. At low impact energy and normal incidence the branching ratio becomes even larger (100 times more than thermally) and comparable to the Xe/O<sub>2</sub>-Ag(110) case.

(2)  $\Sigma_{des}$  and  $\Sigma_{diss}$  increase strongly with increasing energy and angle of incidence of the impinging gas atom. While the former effect is expected, the angular dependence is much larger than observed in previous studies. The anomalous angular dependence of  $\Sigma_{des}$  and  $E_{thr}$  arises from the significant energy loss to the substrate and from the presence of substantial surface corrugation under realistic multiple scattering conditions, as demonstrated by MD calculations. The enhancement of  $\Sigma_{des}$  at grazing incidence is, thus, due to the larger energy available to the O<sub>2</sub> in the normal

direction after the collision process and to the efficient suppression of desorption at normal incidence because of multiple collisions and of the squeezing of the O<sub>2</sub> in the fourfold hollow. The effect on  $\Sigma_{diss}$  is less clear and is probably connected to the larger average energy transferred to O<sub>2</sub> at grazing incidence. This explanation is supported by the similar angular and energetic dependence of  $\Sigma_{des}$  and  $\Sigma_{diss}$ . Our simple hard sphere model including surface corrugation and multiple scattering explains why a large enhancement of  $\Sigma_{des}$ was not observed for the previous systems, dealing either with harder substrates with limited energy transfer to the surface, or with less corrugated systems. It is moreover able to describe a wide class of possible energy and angle dependences of the cross section for desorption, depending on the relative role of energy loss to the surface and corrugation.

(3)  $\Sigma_{des}$  increases with coverage, most probably because of the decrease of the heat of adsorption due to repulsive interactions between molecules.

(4) The behavior of  $\Sigma_{tot}$  is similar for molecules of oxygen vibrating at 78.5 and 84 meV, indicating a similar binding energy and, following the theory of Mehandru and Anderson,<sup>26</sup> supporting the assignment to fourfold hollow and short bridge sites, respectively.<sup>26</sup> The slightly higher value for the 84 meV species suggests that this moiety occupies the bridge site.

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