Angular and energy distributions of D_2 molecules desorbing from sulfur and oxygen modified V(111) surfaces

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The energy and angular distribution of deuterium molecules desorbing from a vanadium (111) surface modified either by oxygen or by sulfur has been studied, using time-of-flight spectroscopy. It has been shown that the desorption flux contains two contributions, a thermal and a hyperthermal contribution. The mean translational energy of the hyperthermal part can be described by $\langle E \rangle = 8.3 \cdot kT_s$ and $5.8 \cdot kT_s$ for the sulfur and oxygen covered V(111) surface, respectively. Interestingly, the mean translational energy of the hyperthermal contribution is independent of the desorption angle. The angular distribution of the hyperthermal desorption flux is forward focused and can be described by $\cos^{3.3} \theta$ and $\cos^{4.3} \theta$ functions for the sulfur and oxygen modified surface, respectively. From the angular flux distribution and the angle independent mean translational energy of the hyperthermal contribution does not exist for this adsorption/desorption channel. This is mainly due to the strong geometric corrugation of the modified V(111) surfaces. (© 2002 American Institute of Physics. [DOI: 10.1063/1.1483849]

I. INTRODUCTION

The investigation of energy and angle resolved adsorption and desorption parameters has led to a quite good understanding of the adsorption/desorption process in the recent past. From the experimental point of view well defined molecular beams^{1,2} can be prepared to study differential sticking coefficients. Time-of-flight (TOF) spectroscopy^{3,4} and resonance enhanced multiphoton ionization (REMPI) spectroscopy^{5,6} can be applied to investigate all degrees of freedom of desorbing molecules. From the theoretical point of view a number of computational methods exist which allow the modeling of the adsorption and desorption process in detail. These methods reach from classical trajectory calculations⁷ via quantum-classical calculations⁸ to pure quantum treatments in several dimensions.^{9,10} Although great progress has been made in this context in the recent years, experimentally obtained adsorption and desorption parameters are still the essential ingredients for the proper modeling of the adsorption/desorption dynamics. The most thoroughly investigated systems concerning the adsorption and desorption dynamics involve hydrogen and deuterium on well defined single crystal metal surfaces. The reason for this is that hydrogen plays an important role in a number of modern technologies, like heterogeneous catalysis, nuclear fusion or energy storage. From the theoretical point of view the interaction of hydrogen with surfaces can be treated with the highest accuracy possible so far.

In this article we will present experimental results on the desorption of deuterium from a vanadium (111) single crystal surface covered with either sulfur or oxygen. These adsorption systems are of technological importance for energy stor-

age because vanadium is able to store huge amounts of hydrogen/deuterium in the bulk. On the other hand vanadium has also a great affinity to other elements like carbon, oxygen or sulfur, which segregate to the surface. This means that technologically relevant vanadium surfaces are always covered with additives to some degree. The detailed understanding of the interaction of hydrogen/deuterium with such modified vanadium surfaces is therefore of great interest, both from the experimental as well as from the theoretical point of view.

II. EXPERIMENTAL DETAILS

The experiments were performed in an ultrahigh vacuum chamber with a base pressure of $<3 \times 10^{-11}$ mbar, which was equipped with Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) for surface analysis and a sputter gun and gas dosers for surface preparation. A recently constructed TOF spectrometer was attached to the main chamber, which will be described in some detail below. The vanadium (111) single crystal (Matek company, 10 mm diam, 2 mm thickness) was polished with diamond paste down to 0.25 μ m grain size. The crystal was fixed to the sample holder via thin molybdenum wires (0.25 mm diam) which were inserted into grooves at the rim of the sample. A Chromel-Alumel thermocouple was spot-welded to the rear of the crystal. The single crystal could be cooled to 100 K via a LN₂ cooling system and heated to 1300 K via resistive heating. The sample could be tilted within $\pm 60^{\circ}$ around a horizontal axis for angle resolved measurements.

The preparation of individually modified V(111) surfaces was accomplished by proper sputtering and annealing cycles. A freshly installed V(111) sample usually exhibits sulfur, carbon and oxygen on the surface. After short sputtering (10 min) and annealing to 1300 K (5 min) only sulfur contami-

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nation can be detected with the Auger spectrometer. The corresponding LEED pattern shows a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure which can be attributed to a sulfur coverage of 0.33 monolayers (Auger ratio S152/V473=0.90). Extended annealing (some hours) of the vanadium sample finally increases the sulfur coverage to a saturation coverage of about 0.4 monolayers of sulfur (Auger ratio of 1.05). In this case the LEED pattern changes to a very complex structure, with strong evidence for a microfaceted surface. For all the experiments described below we have used the sulfur saturated surface for the reasons of reproducibility. In order to obtain a purposely oxygen covered vanadium surface we have sputtered the vanadium sample for about 100 h at a temperature of 1000 K. After this procedure and additional heating/ sputtering cycles the sulfur concentration in the bulk has been reduced to such an extent that no significant surface segregation could be observed. However, in this case oxygen is the dominant species on the surface due to surface segregation, which again shows a highly reproducible saturation coverage after annealing to 1300 K. Recently we have calibrated the Auger spectrometer in our lab for carbon and oxygen on vanadium,¹¹ which allows us to determine the oxygen saturation coverage to 1.0 monolayers in the present case. However, 0.3 monolayers of carbon were co-adsorbed after this preparation procedure, due to co-segregation. The corresponding LEED pattern exhibited again strong evidence for a faceted surface. Varga et al.¹¹ have investigated the microscopic structure of the oxygen covered V(111) surface with the help of scanning tunneling microscopy (STM). They have observed a strong faceting of the V(111) surface resulting in pyramids made up of (433) planes, which are inclined about 8° with respect to the (111) plane.

A totally clean V(111) surface which remains clean even after long annealing at 1300 K is difficult to obtain.¹² This would require extremely long cleaning procedures and/or annealing temperatures above 2000 K. Since the purpose of this work was to investigate the influence of an activation barrier on the desorption characteristics, which only exists on the technologically relevant modified vanadium surfaces, we did not attempt to get a totally clean surface.

Adsorption and in particular absorption of rather large amounts of deuterium in the V(111) sample has been performed with the help of a doser for atomic hydrogen (deuterium). In this case the gas flows through an electron beam heated tungsten tube which yields nearly 100% of deuterium (hydrogen) in atomic form if the tube temperature is above 1900 K (Bertel-type doser¹³). We have recently characterized this doser with respect to the degree of dissociation and the angular variation of the effusing flux, which allows us to determine the impingement rate of atomic hydrogen (deuterium) quantitatively.¹⁴

A. Experimental setup of the time-of-flight spectrometer

A schematic drawing of the homebuilt TOF spectrometer can be seen in Fig. 1. In this drawing the actual main chamber is replaced by a simple 8 in. six way cross chamber containing the sample (S) and the Knudsen source (K) for calibration. The TOF apparatus consists of two 8 in. six way



FIG. 1. Schematic drawing (top view) of the time-of-flight (TOF) spectrometer. S: sample, K: Knudsen source, A1–A5: apertures, CP1, CP2: cryopanels, M: chopper motor, CB: crossbeam ion source of the mass spectrometer (QMS) with 90° off-axis SEV.

cross chambers differentially pumped by turbopumps (pumping speed 500 l/s each). In addition, in both chambers specifically designed LN₂ cryopanels are installed to get optimum pumping speed for hydrogen and deuterium. The base pressure in both chambers is in the 10^{-11} mbar region. The first chamber, containing the chopper motor, is attached to the main chamber via a tube extension terminated by an aperture of 8 mm diam (A1). The distance between this entrance aperture and the sample is 30 mm. Within the tube extension the first cryopanel (CP1) is located. It consists of a LN₂ cooled copper tube with several apertures (A2, A3, diameter 10 mm) and two titanium filaments (not shown) to produce a getter film on the inner surface of the tube. The chopper motor (M) is attached to a linear motion system which allows either to chop the molecular beam or to withdraw the chopper. The aluminum chopper blade with a diameter of 80 mm contains two opposite sector slits (11 mm long, 6° radial opening). The chopper motor [Minimotor SA (Ref. 15) is a brushless three-phase motor with a specific vacuum compatible lubricant for the ball bearings. This rather cheap conventional motor turned out to be very suitable for this purpose. At a motor frequency of 400 Hz and during water cooling (15 °C) the pressure in the motor chamber remains in the low 10^{-10} mbar region. An optical gate consisting of a photodiode and a photodetector served as a trigger device. The second six way cross chamber (detection chamber) is separated from the motor chamber via a 6 mm diam aperture (A4). It contains again a specifically designed LN₂ cooled cryopanel (CP2) and titanium getter filaments. The exit aperture (A5) of this device is directly in front of the quadrupole mass spectrometer [QMS, Balzers QMA 140 with cross beam (CB) ion source, entrance aperture 5 mm in diameter, and 90° off-axis SEV]. The distance between the sample (or the Knudsen source) and the mass spectrometer entrance aperture is 870 mm, the distance *l* between the chopper blade and the QMS is 476.5 mm.

B. Data acquisition and data analysis

The QMS is operated in the counting mode. The TTL pulses are fed to a multichannel analyzer (EG&G Ortec with Turbo MCS T914) in which they are recorded either as function of mass (mass spectrometer) or as function of time at constant mass (TOF spectrometer). In the TOF mode the MCA is triggered by the signal from the optical gate. Unfortunately, the obtained TOF spectrum is not only a function of

the velocity distribution f(v) = f(l/t) which has to be evaluated but depends also on some experimental parameters like the sensitivity of the detector, the chopper gate function, the dwell time of the MCS, the finite extension of the ionization region and the phase jitter of the motor. Whereas it can be shown that the last three factors are of negligible importance the influence of the gate function and the detector sensitivity on the measured TOF spectrum have to be considered. A mass spectrometer with a cross beam ion source is in the ideal case a detector which is sensitive to the gas density (not to the gas flux). However, deviations from this ideal case can appear if the potentials of the ion source are not properly adjusted (trapping effect). Therefore we have carefully optimized the individual potentials of the ion source to obtain the lowest sojourn time of the generated ions in the ionization region. The validity of the sensitivity to gas density of the QMS for hydrogen and deuterium has been checked with the help of a Knudsen source. For this purpose the (unchopped) QMS signal at constant effusion flux *j* has been measured for different Knudsen cell temperatures. In the case of a perfect density detector the obtained signal should be proportional to the density $n = j/\langle v \rangle \propto j/\sqrt{T}$. Indeed, a plot of the measured signal (after subtraction of the background signal) versus $T^{-1/2}$ resulted in a perfect straight line. Then the correlation between the measured time-of-flight spectrum z(t) and the original velocity distribution f(v) = f(l/t) of the molecular beam is given by the convolution integral,

$$z(t) = \int_0^t P(t-t') \cdot \frac{l}{t'} \cdot f\left(\frac{l}{t'}\right) dt', \qquad (1)$$

with P(t) being the chopper gate function and l the distance between the chopper blade and the quadrupole ion source. The actual gate function is determined by the slit width of the chopper, the cross section of the molecular beam at the chopper location and the chopper frequency. This function will in general be of trapezoid form, but it can be shown that a rectangular gate function with proper effective gate opening time is sufficient for proper deconvolution.¹⁶ A second experimental factor which determines the position of the TOF spectrum is the trigger delay time. We have determined both the effective gate opening time as well as the trigger delay with the help of well defined Maxwellian beams at different temperature. The experimentally obtained TOF spectra as shown in Fig. 2 have been fitted by using Eq. (1). Correlating the fit temperatures with the actual Knudsen source temperatures led in all cases to the same effective gate opening time and the same delay time.

For the evaluation of TOF spectra from real desorption experiments we have applied different methods. Although in principle the deconvolution of the TOF spectra according to Eq. (1) would yield the velocity or energy distribution directly, in general the data statistics is not good enough for this method. It is therefore common to assume that the unknown velocity distribution of a desorption flux can still be fitted by one or by the sum of several well known velocity distributions, but usually of Maxwellian-type. The mean kinetic energies of these distributions are described by $\langle E \rangle$ = $2 \cdot kT_{\text{eff}}$, or by $\langle E \rangle = nkT_s$, with n > 2 for hyperthermal and n = 2 for thermal beams. Finally we have also applied



FIG. 2. Time-of-flight spectra obtained for deuterium effusing from a Knudsen source at different temperatures T_1-T_5 . The curves are best fits of Maxwellians convoluted with a rectangular gate function. Fit parameters are the gate opening time and the trigger delay time.

the moment method to evaluate the TOF spectra,^{17,18} which does not require any assumptions. The first moment of the velocity distribution yields the mean velocity and the second moment the mean energy of the desorption flux. However, for this method one needs again a very good signal to noise ratio and we have applied it only for test and control purposes.

III. EXPERIMENTAL RESULTS

The TOF-desorption experiments for deuterium from the sulfur and oxygen covered V(111) surfaces have been performed as follows. Atomic deuterium has been used for sample dosing. This is necessary, because the sticking coefficient for molecular deuterium on the modified vanadium surfaces is very small^{11,19} ($s_0 \approx 2 \times 10^{-4}$). However, for atomic deuterium^{20,21} the sticking coefficient is in the range of 0.1–0.2. Similarly as in the case of the V(100) surface²² adsorbed deuterium can easily diffuse into the bulk. The absorption coefficient depends on the sample temperature and reaches a maximum of 0.36 at about 500 K. Typically the V(111) sample has been dosed at 520 K with atomic deuterium using the Bertel-type doser¹³ for about 60 min at a deuterium partial pressure increase of about 2×10^{-7} mbar. This results in absorbed deuterium of several hundred monolayer equivalents. Previous investigations¹¹ have shown that adsorbed deuterium desorbs in the temperature range of 100-500 K, but the huge amount of dissolved deuterium desorbs only above 800 K, with a desorption peak maximum at about 1200 K (heating rate, 3 K/s). For the measurement of the time-of-flight spectra we have heated the pre-dosed sample to 950 K and then almost all of the absorbed deuterium has been desorbed at this temperature (isothermal desorption).

Before we present the experimental data concerning the desorption flux we have to mention that also some scattered particles contribute to the total flux originating from the surface. To take into account this contribution in the TOF spectra we have first investigated the accommodation behavior of deuterium molecules at room temperature as a function of



FIG. 3. Time-of-flight spectrum of deuterium molecules scattered on a sulfur covered V(111) surface into normal direction after isotropic impingement. Gas temperature T_{in} =300 K, surface temperature T_s =1173 K. The sum of two Maxwellians with T_1 =330 K and T_2 =950 K gives the best fit and yields a mean kinetic energy of the scattered molecules in terms of a Maxwellian temperature T_{out} = $\langle E \rangle/2k$ =627 K.

sample temperature. In Fig. 3 we present a TOF spectrum for deuterium at 300 K scattered in normal direction from a sulfur covered V(111) surface at 1173 K. Evaluation of this spectrum with the moment method yields a mean kinetic energy of 0.11 eV. It is more common to express the mean energy in terms of an effective temperature of a Maxwelliantype distribution for a molecular beam, $T = \langle E \rangle / 2k$. In our particular case this yields a temperature of 627 K for the scattered particles. In addition, we have calculated the mean translational energy by fitting two Maxwellian distributions with temperatures T_1 and T_2 to the data points and the sum of the corresponding energies led to the same result as obtained with the moment method. Similar experiments have been performed on a V(111) surface covered with oxygen. In Fig. 4 all data for the scattering of deuterium at room temperature T_{in} from the sulfur and oxygen covered V(111) surface at various surface temperatures T_s are compiled. Interestingly, all data points lay on a straight line with the slope α ,



FIG. 4. Mean translational energy of deuterium molecules scattered from the oxygen (circular data points) and sulfur (squared data points) covered V(111) surface, respectively, as a function of surface temperature T_s . Isotropic impingement of deuterium at room temperature $T_{\rm in}$. The translational energy was calculated from TOF spectra using the moment method.



FIG. 5. TOF spectra of deuterium molecules after desorption from the sulfur (a) and oxygen (b) covered V(111) surface at T_s =950 K. The data points were fitted by the sum of two contributions in the desorption flux (thermal and hyperthermal) and a scattered contribution. For details see text.

which correlates the temperature T_{out} of the scattered particles to the surface temperature T_s as described by the simple equation

$$T_{\text{out}} = \alpha \cdot T_s + (1 - \alpha) \cdot T_{\text{in}} \tag{2}$$

with $\alpha = 0.37$. The value of α is equivalent with the energy accommodation coefficient according to

$$\alpha = \frac{T_{\rm in} - T_{\rm out}}{T_{\rm in} - T_{\rm s}}.$$
(3)

For the isothermal desorption experiments which were performed at a surface temperature of 950 K one has therefore to consider a contribution of scattered deuterium molecules in the total molecular beam which can be approximated, according to Fig. 4, by a Maxwell–Boltzmann distribution of 540 K.

TOF spectra for deuterium desorbing from a sulfur and oxygen covered V(111) surface in normal direction are depicted in Figs. 5(a) and 5(b). Comparing these spectra with Fig. 3 one can immediately see that the spectra are shifted to lower flight time, indicating a higher mean translational energy. In principle one can again calculate the mean energy of the molecular beam with the moment method, after proper subtraction of the scatter contribution. However, since this method overestimates the signal at very low flight times and due to the rather large scatter of the data points in this region the accuracy is not very high. We have therefore again tried to fit Maxwell–Boltzmann distributions to the data points. It

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FIG. 6. Angular distribution of the mean translational energy of desorbed deuterium from the sulfur (a) and oxygen (b) covered V(111) surface at 950 K. The data for the hyperthermal (activated) contribution are shown as squares, and the data for the total flux are shown as triangles.

turns out that a single MB distribution does not yield a good fit to the data points. However, we can obtain a good fit if we assume two contributions to the total desorption flux; a thermal contribution (equivalent to unactivated adsorption/ desorption) and a hyperthermal contribution (equivalent to activated adsorption/desorption). For the fit procedure the contribution of the scattered particles has been fixed at T_{scat} = 540 K, with a weight as calculated from the pressure-time integral during desorption. The thermal contribution is fixed at $T_s = 950$ K. The temperature of the hyperthermal contribution $T_{\rm hyper}$, as well as the weight of the thermal and hyperthermal contributions are open parameters for the fit. For the sulfur covered V(111) surface [Fig. 5(a)] we obtain a MB-temperature for the hyperthermal contribution of 3950 K, for the oxygen covered surface [Fig. 5(b)] we get T_{hyper} =2750 K.

We have performed similar TOF-desorption experiments for both, the sulfur and oxygen covered V(111) surface, at different desorption angles. Interestingly, the mean energy of the hyperthermal contribution did not change significantly with the increase of the desorption angle, as shown in Figs. 6(a) and 6(b) as squares. However, since the relative contributions of the thermal and hyperthermal flux change with desorption angle, the mean energy of the total desorption flux changes with angle as shown in Figs. 6(a) and 6(b) as triangles. The angle dependence of the normalized flux of the thermal and hyperthermal contributions are compiled in Figs. 7(a) and 7(b). For the distribution of the scattered flux we have assumed a cosine function (triangles). It turns out that the angular distribution of the thermal flux is also cosine



FIG. 7. Normalized angular flux distribution of the individual contributions during desorption of deuterium from the sulfur (a) and oxygen (b) covered V(111) surface at 950 K. Activated desorption contribution: squares, unactivated desorption contribution: circles, scatter contribution: triangles. The data are obtained from Maxwellian fits to the TOF spectra as shown in Fig. 5.

(circles), whereas the hyperthermal flux is somewhat forward focused (squares), with distributions of $\cos^{3.3} \theta$ and $\cos^{4.3} \theta$ for the sulfur and oxygen covered V(111) surface, respectively. This result supports in hindsight our assumption of an activated and unactivated contribution in the desorption process.

In order to check the reliability of the flux resolved angular distributions as obtained from TOF experiments we have also measured the total desorption flux (including the scatter contribution) as a function of angle directly by the QMS signal increase of the unchopped beam. The experimental data are plotted in Figs. 8(a) and 8(b) as circles for the sulfur and oxygen covered V(111) surface and yield angular distributions of $\cos^{1.3} \theta$ and $\cos^{2.3} \theta$, respectively. In addition, the values obtained by proper summing up the data points of Fig. 7 are plotted as triangles. The agreement of the two independent experiments is quite good and supports the applied evaluation procedures.

IV. DISCUSSION

The overall conclusions to be drawn from the experimental data set as described above for the desorption of deuterium from the sulfur and oxygen covered V(111) surfaces are straightforward: Apparently, for these adsorption systems an activation barrier for adsorption exists, which, on the one hand, results in a rather low integral sticking coefficient for



FIG. 8. Normalized angular flux distribution of deuterium desorbing from the sulfur (a) and oxygen (b) covered V(111) surface at 950 K. The circular data points are directly obtained from the QMS signal of the unchopped desorption flux. The triangular data points are calculated by summing the individual contributions of Fig. 7.

molecular deuterium, and on the other hand in a translational heating and forward focusing of the desorption flux. A closer and more quantitative inspection of the data yields more details concerning the potential energy surfaces which govern the adsorption and desorption process.

As outlined in the previous section the TOF spectra of the desorption flux could be best fitted by the sum of two Mawellian beams. Actually, this type of data fitting has been frequently applied in the literature. Already Comsa et al.²³ have proposed the so-called "activation barrier (AAH) model with holes" to describe their results of the H_2 -nickel system. More recently Allers et al. have applied fit procedures with two or more Maxwellians to a number of adsorption systems $[O_2/Pt(111),^{24} D_2/Ni(100),^{25} CO/Pt(111)]$ (Ref. 26)]. Matsushima et al. have investigated and analyzed TOF spectra of reaction products also by fitting several Maxwellians.^{27,28} The use of a Maxwellian to describe activated recombinative desorption is of course a compromise to approximate the flux distribution which is actually governed by the three-dimensional potential energy surface (activation barrier height distribution).

In the first step of the fit procedure we have used both, the temperature as well as the intensity of the two Maxwellians, as open parameters. Interestingly, we always obtained one hyperthermal contribution and one contribution which could be described by a temperature very close to the temperature of the sample during desorption (after proper subtraction of the scatter contribution). However, it is obvious from the experimental data points in Fig. 5 that this fit procedure cannot be unequivocal. In the following we have therefore always set one temperature to the sample temperature and have only used the second temperature and the intensities of both contributions as free fit parameters. The mean translational energy of the activated (hyperthermal) path can be described either by $2 \cdot kT_{hyper}$ or by nkT_s . In our particular case [Figs. 5(a) and 5(b)] we obtained for the sulfur covered V(111) surface $T_{hyper} = 3950 \text{ K}$ or $\langle E \rangle = 8.3$ $\cdot kT_s$ with $T_s = 950$ K (equivalent to $\langle E \rangle = 0.68$ eV), and for the oxygen covered surface $T_{\text{hyper}} = 2750 \text{ K}$ or $\langle E \rangle = 5.8$ kT_s (equivalent to $\langle E \rangle = 0.47$ eV). Interestingly, the mean translational energy does not change significantly with desorption angle [Figs. 6(a) and 6(b)]. The flux intensity of the hyperthermal contribution, however, changes with the desorption angle according to $\cos^{3.3} \theta$ for the sulfur covered and $\cos^{4.3} \theta$ for the oxygen covered V(111) surface, respectively [Figs. 7(a) and 7(b)].

The correlation between the angular distribution of the mean translational energy and the angular distribution of the flux should yield additional information on the particular potential energy surface, depending on the scaling behavior. For many systems, in particular with flat PES, normal-energy scaling usually holds.²⁹ This means that only the normal energy components of the impinging particles determine the sticking coefficient,

$$S(E,\theta) = S(E \cdot \cos^2 \theta, 0^\circ). \tag{4}$$

In addition, most of the experimental results concerning angular flux distributions can be described by a $\cos^{m} \theta$ distribution.³ If one separates the angle and energy dependence of the sticking coefficient in the form $S(E, \theta) = K_0$ $\cdot f(E) \cdot g(\theta)$, one can show that in the case of normal energy scaling the sticking coefficient is determined by the following relation:³⁰

$$S(E,\theta) = K_0 \cdot E^{(n-1)/2} \cdot \cos^{n-1} \theta, \qquad (5)$$

with K_0 being an appropriate factor. Via detailed balancing a similar expression holds for the desorption flux $D(E, \theta)$, having in mind that $D(\theta) = S(\theta) \cdot \cos \theta$,

$$D(E,\theta) = K_0 \cdot E^{(n-1)/2} \cdot \cos^n \theta.$$
(6)

Furthermore, one can show that for any scaling behavior which is described by

$$S(E,\theta) = S(E \cdot \cos^x \theta, 0^\circ), \tag{7}$$

similar expressions for $S(E, \theta)$ and $D(E, \theta)$ can be deduced,

$$S(E,\theta) = K_0 \cdot E^{(n-1)/x} \cdot \cos^{n-1}\theta, \tag{8}$$

$$D(E,\theta) = K_0 \cdot E^{(n-1)/x} \cdot \cos^n \theta.$$
(9)

Then one obtains the mean translational energy of the adsorbing/desorbing molecules by proper integration,

$$\langle E \rangle = \left(\frac{n-1}{x} + 2\right) \cdot kT_s \,. \tag{10}$$

In the case of *normal energy scaling* (x=2), Eq. (10) reduces to^{30,31}

$$\langle E \rangle = \left(\frac{n+3}{2}\right) \cdot kT_s \,. \tag{11}$$

From the experimental results as shown in Fig. 6 (angle independent mean translational energy) and Fig. 7 (angular flux distributions) we can calculate the scaling factors according to Eq. (10) to x=0.37 and 0.87 for desorption of deuterium from the sulfur and oxygen covered V(111) surfaces, respectively. This clear deviation from the frequently observed normal energy scaling (x=2) might, according to Darling and Holloway,⁸ be due to a rather strong geometric corrugation of the potential energy surface, in addition to the electronic corrugation. This is plausible if one considers the intrinsic microscopically rough structure of a bcc(111) plane in general and the reconstructed and faceted surface of the oxygen or sulfur covered V(111) plane in particular, as observed by LEED and STM.¹¹

Finally a few words about the relationship between the sticking coefficient and the activation barrier on the surface. From the evaluation of all the experimental data as described above we can conclude that the potential energy surface for the system $D_2 - V(111) + O$, S is highly corrugated. That means that the incoming molecules experience different activation barrier heights as function of the impact position in the surface unit cell and of the internal degrees of freedom of the molecules. A simple approach to describe this situation is the above-mentioned "hole" model of Comsa et al.23 or the more refined model of Karikorpi et al.32 In this context the value of the sticking probability is not determined by a particular height of a single one-dimensional barrier but rather by the relative area of the surface unit cell with an activation barrier low enough to enable dissociative adsorption. From the desorption data we can conclude that there are areas in the surface unit cell with negligible activation barrier (thermal flux) as well as areas with an activation barrier in the order of 0.3–0.4 eV (hyperthermal flux). Through this part of the surface unit cell only adsorption can proceed. On the rest of the surface unit cell the incoming molecules are reflected on a high barrier. Only the small fraction of molecules (2 $\times 10^{-4}$) which are able to adsorb either activated or unactivated, is related by detailed balancing with the desorbing molecules. An integration of the angular flux distribution of Fig. 7 yields about 57% of hyperthermal and 43% of thermal molecules in the total desorption flux, for both the sulfur and oxygen covered V(111) surface.

Similarly, the impinging, but nonadsorbing molecules have to be connected by detailed balancing with the reflected molecules. This is manifested in Fig. 4: Deuterium molecules with room temperature when scattered from a room temperature surface possess a mean translational energy which is also equivalent to room temperature. The accommodation coefficient (α =0.37) as obtained from the scattering experiments is basically determined by the accommodation behavior of the huge amount of scattered (nonadsorbed) molecules. The tiny part of molecules which undergoes dissociative adsorption and recombinative desorption does not contribute significantly to the energy distribution of all molecules leaving the surface, and therefore does not influence the value of the accommodation coefficient.

V. SUMMARY

We have investigated the translational energy distribution of deuterium molecules desorbing from V(111) surfaces modified either by oxygen or by sulfur. In both cases the sticking coefficient for molecular deuterium is very small, indicating an activation barrier for adsorption. This is manifested in the desorption flux in form of a hyperthermal contribution. The mean translational energy of the hyperthermal part is $\langle E \rangle = 8.3 \cdot kT_s$ for the sulfur and $5.8 \cdot kT_s$ for the oxygen covered V(111) surface, respectively. In both cases the mean translational energy is nearly independent of the desorption angle. In addition to the hyperthermal contribution a thermal contribution with $\langle E \rangle = 2 \cdot kT_s$ exists, too. The angular flux distribution of the hyperthermal part is forward focused and can be approximated by $\cos^{3.3} \theta$ and $\cos^{4.3} \theta$ functions for the sulfur and oxygen modified surface, respectively. The thermal contribution can be described by a cosine distribution. From a comparison of the angular flux distribution and the angle independent mean translational energy of the hyperthermal contribution one can conclude that normal energy scaling does not exist for this adsorption/ desorption channel. This is most probably due to the strong geometric corrugation of the sulfur and oxygen covered V(111) surfaces.

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