

**D<sub>2</sub> reactions on Si(100) surfaces: Adsorption and desorption dynamics**

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We have measured polar angle ( $\theta$ )-resolved time-of-flight spectra of D<sub>2</sub> molecules desorbing from the Si(100) surface. The desorbing D<sub>2</sub> molecules exhibit a considerable translational heating in the entire angle region tested for  $0^\circ \leq \theta \leq 40^\circ$ . The extent of the translational heating tends to weakly decrease with increasing  $\theta$ . Taking a simple energy scaling into account the  $\theta$  dependences of desorption dynamics is related to the reported adsorption dynamics. Detailed balance is fulfilled in the adsorption/desorption of deuterium on the Si(100) surface.

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The dynamics of dissociation and association of molecules at a surface is related by the principle of detailed balance.<sup>1</sup> This has been successfully applied to the hydrogen reactions on metal surfaces,<sup>2</sup> but not to the case on the Si surfaces. In the latter case, it was considered that the desorbing hydrogen molecules do not carry a main fraction of  $\sim 1$  eV energy barrier for adsorption, since almost no translational heating was observed in the pulsed-laser-desorption (PLD) (heating rate  $\sim 10^{10}$  K/s) experiments.<sup>3</sup> In the last decade this so called barrier puzzle has been a subject of theoretical controversy.<sup>4-7</sup>

However, results in the recent dynamics experiments on adsorption<sup>8,9</sup> and desorption<sup>10</sup> of hydrogen on the Si(100) surface contradict the previous results,<sup>3</sup> but seem to validate detailed balance: According to Dürr and his collaborators,<sup>8</sup> sticking coefficients of hydrogen on the Si(100) surface can be expressed with a sigmoidal curve as a function of translational energy  $E$ , polar angle  $\theta$ , and surface temperature  $T_s$ ,

$$s(E, \theta, T_s) = \frac{A_0}{2} \left\{ 1 + \tanh \left( \frac{E \cos^n \theta - E_0}{W(T_s)} \right) \right\}, \quad (1)$$

where  $A_0$  is the saturated sticking probability at large  $E$ ,  $E_0$  the threshold energy at which  $s$  becomes a half of  $A_0$ , and  $W(T_s)$  the width of the curve. Here, the simple energy scaling for the effective energy available for adsorption  $E_{\text{eff}}(\theta) = E \cos^n \theta$  for the scaling parameter  $n$  has been applied for a later discussion. From curve fitting analysis of the measured  $s$  data for  $\theta=0$ ,  $E_0=0.82 \pm 0.2$  eV, and  $W(680 \text{ K})=0.193$  eV which decreases slightly super linearly to  $W(440 \text{ K})=0.113$  eV with decreasing  $T_s$ , were determined for  $A_0=10^{-2 \pm 1}$ . Recently, Sagara *et al.*<sup>10</sup> measured time-of-flight (TOF) distributions of deuterium molecules desorbed by means of the temperature-programmed-desorption (TPD) (heating rate 6 K/s) for  $\theta=0$ . Contrary to the previous PLD results,<sup>3</sup> considerable translational heating was observed, i.e., the mean translational energy was evaluated to be  $\langle E_{\text{trans}} \rangle \approx 0.35$  eV. This translational heating suggests that the molecules have overcome the adsorption barrier even in desorption. In the context of detailed balance, desorption dynamics is, in principle, related to adsorption dynamics or  $s$  by the energy flux function

$$F(E, \theta, T_s) dE = E e^{-E/kT_s} s(E, \theta, T_s) \cos \theta dE. \quad (2)$$

Indeed, Sagara *et al.*<sup>10</sup> confirmed that  $\langle E_{\text{trans}} \rangle \approx 0.35$  eV is reproduced with  $F$  for the same  $E_0$  as denoted above and for  $W(780 \text{ K})=0.195$  eV. Dürr and Höfer<sup>9</sup> further measured both the azimuthal and polar angle dependences of  $s$  at a single domain surface and found that the surface is geometrically corrugated: The sticking coefficient measured along Si dimer rows is characterized with a quite sharp cosine function, but for the direction perpendicular to the dimer rows it is characterized with a broader distribution. They also measured the  $\theta$  dependence of  $s$  at the double domain surface and found that  $s \propto \cos^{6-7} \theta$ . This is not at variance with the TPD angular distributions<sup>11</sup> within a framework of detailed balance.

In this report we intend to quantitatively rationalize the validity of detailed balance in adsorption/desorption of deuterium on the Si(100) surface. We measure polar angle-resolved time-of-flight spectra and relate results to the Dürr's sticking data<sup>8,9</sup> via the principle of detailed balance or Eq. (2).

Angle-resolved TOF spectra were measured using a cross-correlation method as described previously.<sup>10</sup> We changed  $\theta$  by means of sample rotation in the range  $0^\circ \leq \theta \leq 40^\circ$ . For each TOF spectrum 100 cycles of  $\beta_1$  channel TPD scan with a 6 K/s heating rate were repeated to collect data. The clean Si(100) surface was exposed to D atoms to prepare 1.05 ML D coverage ( $\theta_D$ ) prior to each TPD scan. The main fraction of the  $\beta_1$  channel TPD for  $0.1 \text{ ML} \leq \theta_D \leq 0.8 \text{ ML}$  was selectively collected. Thus the average desorption temperature is 780 K at which the  $\beta_1$  TPD rate becomes maximal. Since the angular distribution of the desorption yield is strongly forward peaked  $Y(\theta) \sim \cos^5 \theta$ ,<sup>10,11</sup> the desorption intensity at  $\theta = 40^\circ$  is very small, causing a somewhat poor  $S/N$  ratio.

Figure 1 shows the angle-resolved D<sub>2</sub> TOF density spectra measured for  $\theta=20$  and  $40^\circ$  on the Si(100) surface. The flux correction of the density data to evaluate mean translational energies turns out to apparently increase the  $S/N$  ratio for the tailing region beyond the maximum of the TOF curve, however, with an opposite effect for the earlier time region. The latter effect inevitably leads to an overestimation of  $\langle E_{\text{trans}} \rangle$ . In practice of evaluating  $\langle E_{\text{trans}} \rangle$ , two methods were cross checked. In the first, as shown in Fig. 1 we fitted the TOF data with two non-shifted Maxwellian density functions characterized with two fitting parameters, intensity and tem-

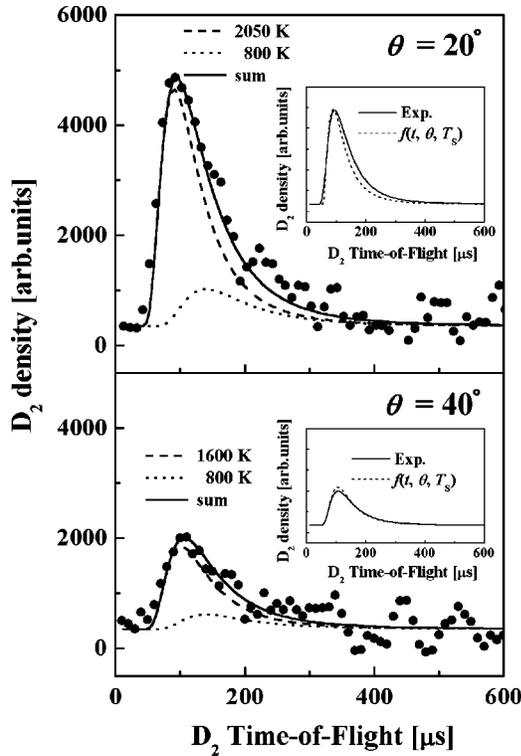


FIG. 1. TOF density spectra of  $D_2$  molecules desorbing from the  $D(0.1\text{--}0.8\text{ ML})/\text{Si}(100)$  surface for the desorption angles  $\theta = 20$  and  $40^\circ$ . The TOF curves are fitted with two Maxwellian functions characterized with a high (dashed curve) and a low (dotted curve) translational temperatures. The solid lines are the sum of the two components. Inset: Comparison of the theoretical and experiment TOF density curves. The solid lines are the experimental one obtained in the main figure by means of curve fitting. The dotted lines are the theoretical TOF density function  $f(t, \theta, T_s) dt \propto (t^{-4} \exp[-mL^2/2t^2kT_s])s(mL^2/2t^2, \theta, T_s) \cos \theta dt$  where  $L$  is the flight distance (33.2 cm) and  $m$  is the mass of a  $D_2$  molecule.

perature, and thereby evaluate  $\langle E_{\text{trans}} \rangle$  from the fitted parameters. In the second, we evaluated  $\langle E_{\text{trans}} \rangle$  directly from the flux corrected raw TOF data after ignoring data for the first three channels. The energies so evaluated by the two methods were in agreement with each other within  $\sim 10\%$  accuracy. The error evaluated after three times measurements of  $\langle E_{\text{trans}} \rangle$  was within  $\pm 0.03$  eV for  $\theta = 0$ , but it increased to  $\pm 0.04$  eV at  $\theta = 40^\circ$  due to the poor  $S/N$  ratio in the TOF curve.

Figure 2 shows plots of  $\langle E_{\text{trans}} \rangle$  so determined from the curve fitting method as a function of  $\theta$ . It is found that  $\langle E_{\text{trans}} \rangle$  is larger than  $2kT_s$  ( $= 0.13$  eV for  $T_s = 780$  K) for any  $\theta$  tested, suggesting that barriers for adsorption are present in desorption for the entire direction. Notice that  $\langle E_{\text{trans}} \rangle$  tends to weakly decrease with  $\theta$ , similarly to the case on Cu surfaces.<sup>12</sup> Such a decreasing trend of  $\langle E_{\text{trans}} \rangle$  with  $\theta$  is never explained with a crude, one dimensional barrier model since it predicts an increase of  $\langle E_{\text{trans}} \rangle$  with  $\theta$ .<sup>13</sup> Using the same values for  $W(780\text{ K})$  and  $E_0$  as determined previously, the mean translational energies were calculated as a function of  $\theta$  for various  $n$  and plotted in Fig. 2 for  $n = 2.0$  (dashed line), 1.4 (solid line), and 1.0 (dot-dashed line). Ne-

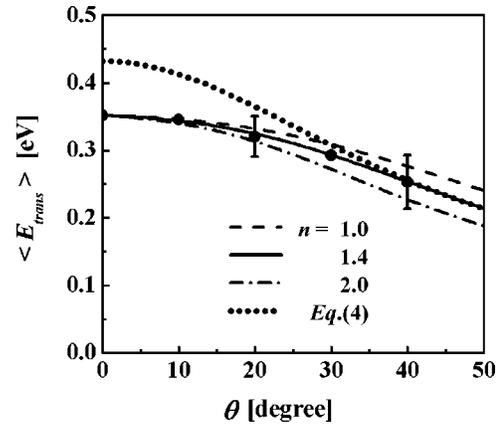


FIG. 2. Plots of mean translational energies  $\langle E_{\text{trans}} \rangle$  as a function of  $\theta$ . The dot-dashed, solid, and dashed curves, are the theoretical ones calculated from Eq. (2) in the text for the scaling parameters denoted in the figure. The dotted line is the curve of  $2kT_s(T_s, \theta)$  calculated from the approximated method of Eq. (4) in the text.

glecting the somewhat large error bars given in the data plots, the curve for  $n = 1.4$  yields the best fit result. In order to further test detailed balance, we derive a TOF density (not flux) function  $f(t, \theta, T_s)$  inserting  $E = (m/2)(L/t)^2$  in the energy flux function  $F$  (see the caption of Fig. 1). Here,  $m$  and  $L$  are the mass of a  $D_2$  molecule and the flight distance (33.2 cm), respectively. We then calculated  $f(t, \theta, T_s)$  for the same parameters as employed above, i.e.,  $W(780\text{ K}) = 0.195$  eV,  $E_0 = 0.82$  eV, and  $n = 1.4$ . Results were plotted in the inset of Fig. 1, (dotted lines) and compared with the experimental results (solid line). Notice that the fit to the experimental TOF data is comfortable in line shape as well as in intensity. Strictly speaking, however, the calculated curves are found to be slightly sharper than the experimental curves particularly at small  $\theta$ . This may require a second component presumably attributable to the vibrationally excited molecules at  $v = 1$ , since some fraction ( $\sim 8\%$ ) of the desorbing  $D_2$  molecules was reported to be vibrationally excited.<sup>14</sup> However, since we have not known values of the parameters in a sigmoidal curve of  $s$  relevant to the  $v = 1$  molecules we treat the TOF data as vibrationally averaged one.

The reasonable fit of  $f(t, \theta, T_s)$  to the TOF data in Fig. 1 suggests that the angular distribution of the desorption yields can be also fit to Eq. (2) after integrating with  $E$ . This is confirmed in Fig. 3 where the experimental and calculated yields  $Y(\theta)$  normalized at  $\theta = 0$  are plotted as a function of  $\theta$ . Here, the experimental data points were obtained from the TOF data in Fig. 1, and the dot-dashed curve,  $\cos^{5.2}\theta$ , was obtained from the independent measurement of angle-resolved TPD spectra for  $\theta_D = 1$  ML.<sup>10</sup> The curve  $\cos \theta$  was plotted for comparison. One can notice that the calculated  $Y(\theta)$  from Eq. (2) can well fit the both experimental data.

In this way, we understand that the measured angle-resolved desorption dynamics is well related to the adsorption dynamics via Eqs. (1) and (2). Therefore, we conclude that detailed balance is fulfilled in the adsorption/desorption dynamics of deuterium on the Si(100) surface. Since Eq. (2) is not a function of  $\theta_D$ , adsorption/desorption of deuterium

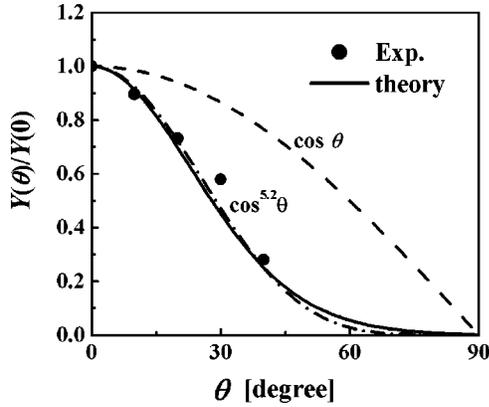


FIG. 3. Angular distribution of  $D_2$  desorption yield  $Y(\theta)$  and fit with the theory predicted by detailed balance Eq. (2) in the text. Dots are the experimental data evaluated from the TOF data in Fig. 1. The dot-dashed line,  $\cos^{5.2}\theta$ , represents the experimental data obtained from the independent measurement of angle-resolved TPD spectra (Ref. 10). The dashed line,  $\cos \theta$ , is plotted for comparison.

at  $T_s \sim 780$  K is suggested to obey a unique mechanism independent of  $\theta_D$  for a quite wide D coverage region from 0.1 to 0.8 ML.

The evaluated scaling parameter  $n=1.4$  infers that the deuterium-surface interaction potential  $V(x,y,z)$  is corrugated on the surface. Here  $x$  and  $y$  denote the position of a molecule in the surface plane and  $z$  is the height from the surface. The  $x$  axis is taken along a Si dimer row, and thus the  $y$  axis perpendicular to it. Corrugation is the variation of  $z=z_c$  at which  $V(x,y,z)$  is kept constant as  $x$  and  $y$  are varied;<sup>15</sup> here we consider such a case as  $V(=E=\langle E_{\text{trans}} \rangle) \approx 0.35$  eV. On the Si(100) ( $2 \times 1$ ) surface, since Pauli repulsion contributes to the repulsive potential energy,  $z_c$  becomes maximum above Si dimers and becomes minimum above troughs between two Si dimer rows. This is because the surface is more densely packed along the dimer rows than along the direction perpendicular to it. Thus corrugation is less serious along the  $x$  axis than along the  $y$  axis. In other words, for the  $\sim 0.35$  eV molecules approaching the surface along the  $(x,z)$  plane the scaling parameter,  $n_x$  tends to be closer to 2, i.e., normal energy scaling, as was found in the beam experiment.<sup>9</sup> On the other hand, when they approach the surface along the  $(y,z)$  plane, the scaling parameter  $n_y$  tends to be small towards, e.g., zero, i.e., total energy scaling. Qualitatively applying this to Eq. (1), the spectrum of  $s$  as a function of  $\theta$  will become broader for the incidence along the  $(y,z)$  plane than for the case along the  $(x,z)$  plane. This expected feature is indeed recognized in the experimental data obtained by Dürr and Höfer,<sup>9</sup> although they explained the observed broad  $s$  spectrum along the  $(y,z)$  plane in a different way; they decomposed it into two components with a sharp maximum, respectively, at  $\theta \sim \pm 20^\circ$  which are the directions of the Si-H bonds at both sides of Si dimers. Going back to our surface which is the two-domain surface reconstructed into  $2 \times 1$  and  $1 \times 2$  structures, the surface was set in a desorption chamber so that the detection of desorbing  $D_2$  molecules was in line with the  $(y,z)$  plane in either of  $2 \times 1$  or  $1 \times 2$  terraces. Hence the evaluated scaling param-

eter  $n=1.4$  is understood as an average of  $n_x$  and  $n_y$  over the two-domain terraces, and the observed corrugation may be attributed to the plane perpendicular to the dimer rows.

For large  $\theta$  only a fraction of incident energy  $E$  is available for adsorption because of the partial conservation of the parallel momentum. Thus one might anticipate that the larger the desorption angle  $\theta$ , the higher incident energy is required in adsorption, and hence the higher energy is released to the molecule in desorption. However, the result shows up the opposite trend as demonstrated in Fig. 2. In the context of detailed balance this unexpected trend is reconciled with Eq. (2) (Ref. 16) as fitted in Fig. 2 (solid line). In order to more intuitively understand the underlying physics, we obtain an instructive expression for  $s$ . For  $E_0 - E \cos^n \theta > W(T_s)$ , Eq. (1) can be approximated as

$$s(E, \theta, T_s) \approx A'_0(T_s) \exp\left[\frac{2E \cos^n \theta}{W(T_s)}\right], \quad (3)$$

where  $A'_0(T_s) = A_0 \exp[-2E_0/W(T_s)]$ . Thence, we obtain the Maxwellian function  $F(E, \theta, T_s) \propto E \exp[-E/kT_t(T_s, \theta)] \cos \theta$  as a desorption energy flux, where  $T_t(T_s, \theta)$  stands for the heated translational temperature

$$\frac{1}{T_t(T_s, \theta)} = \frac{1}{T_s} - \frac{2k \cos^n \theta}{W(T_s)}. \quad (4)$$

For a large width regime  $W(T_s) > 3kT_s$ , we can derive  $\langle E_{\text{trans}} \rangle \approx 2kT_t(T_s, \theta)$ , which explains the observed decreasing trend of  $\langle E_{\text{trans}} \rangle$  with  $\theta$  since  $T_t(T_s, \theta) \rightarrow T_s$  as  $\theta \rightarrow 90^\circ$ . In order to check the implementation of the above argument, we calculate  $\langle E_{\text{trans}} \rangle = 2kT_t(T_s, \theta)$  for the same parameters as determined above and plot the result in Fig. 2 (dotted line). Although the approximated method overestimates  $\langle E_{\text{trans}} \rangle$  by about 20% for  $\theta \leq 15^\circ$ , we confirm that it well tends to the experimental data for  $\theta \geq 30^\circ$ , reproducing the decreasing trend of  $\langle E_{\text{trans}} \rangle$  with  $\theta$ . Admitting the overestimation in  $\langle E_{\text{trans}} \rangle$ , Eqs. (3) and (4) can thus intuitively explain the observed characteristic feature of the adsorption/desorption dynamics of deuterium on the Si(100) surface.

In order to provide favorable geometry for the transition state to adsorption, the substrate Si atoms have to be displaced from their equilibrium position. This will be done dynamically by the vibrational excitation of Si atoms relevant to the reaction site getting an activation energy  $E_{\text{Arr}}$  from the heat bath. The dynamics of the Si atoms after the reaction cannot be measured directly, but the energetics can be predictable owing to the principle of detailed balance. Equating Eq. (3) to the Arrhenius fashioned sticking coefficient  $s = A_0 \exp[-E_{\text{Arr}}/kT_s]$ , we obtain the approximated expression for the Arrhenius energy

$$E_{\text{Arr}} = \frac{2kT_s}{W(T_s)} (E_0 - E \cos^n \theta). \quad (5)$$

Supposing an adsorption occurring under a condition same as for the desorption, i.e.,  $E = 0.35$  eV and  $T_s = 780$  K, we obtain  $E_{\text{Arr}} = 0.31 \pm 0.10$  eV at  $\theta = 0$ .<sup>10</sup> This is the Si lattice vibrational energy required in adsorption for deuterium with

incident energy  $E=0.35$  eV. From the applicability of detailed balance confirmed here for the dynamics of the deuterium, we consider detailed balance is also fulfilled for the dynamics of the Si atoms relevant to the desorption site. In other words, upon desorption of a  $D_2$  molecule the relevant Si atoms are vibrationally excited, receiving the  $\sim 0.3$  eV energy release from the  $\sim 0.8$  eV adsorption barrier. The amount of vibrational energy release to the substrate depends on  $\theta$ . Namely, as  $\theta$  is increased, the energy released to the Si atoms increases as predicted from Eq. (5), compensating the decrease in the translational energy disposed to the desorbing molecules as plotted in Fig. 2.

The desorption dynamics of deuterium on the Si(100) surface is apparently determined by  $W(T_s)$  rather than  $E_0$ .  $W(T_s)$  implicitly includes the whole information concerning coupling between the vibrational motion of the substrate Si

atoms and the translational as well as vibrational motions of the molecules. The value  $W(780\text{ K})\sim 0.2$  eV evaluated on the Si(100) surface is compared to the value  $W(T_s)\sim 0.1$  eV around  $T_s=1000$  K on the Cu surfaces;<sup>16</sup>  $W(T_s)$  is much larger on the Si than on the Cu surfaces while the threshold energy  $E_0$  is nearly the same on both surfaces. Thus, we know that the Si atom-deuterium interaction is much stronger than the Cu atom-deuterium interaction. The strong Si atom-deuterium interaction is due to the covalent bond character of the Si atoms that accompanies a structural change caused by rehybridization/dehybridization of the Si dimer atoms relevant to the reaction sites.

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