

Probability for the sticking of deuterium molecules on a W(110) surface at low temperatures (down to 5 K)

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The sticking probability S of deuterium is a complex, nonmonotonic function of the degree of coverage θ of a W(110) surface at a substrate temperature ~ 5 K. This functional dependence is evidence that different adsorption mechanisms are operating as the adsorbed layer forms: Langmuir adsorption and adsorption involving prestates. On the corresponding curve for hydrogen there is no characteristic maximum, and the sticking probability vanishes at a much lower degree of coverage. The differences between the $S(\theta)$ curves for D_2 and H_2 are interpreted as resulting from differences in the quantum-mechanical properties of these molecules. © 1994 American Institute of Physics.

Studies of adsorption kinetics are an important source of information on the mechanism for the adsorption of gases, in particular, on the nature of the molecule–surface interaction potential.^{1,2} Experiments at very low substrate temperatures make it possible to study weakly bound molecular-adsorption states and a possible role of these states as prestates in dissociative chemisorption^{3–7} We have previously studied^{4–7} the low-temperature adsorption of hydrogen (H_2) and deuterium (D_2) on the faces of a tungsten single crystal. However, the effect of the degree of surface coverage on the sticking probability of the molecules still requires further research. The nature of this effect can reveal whether prestates are involved in the chemisorption process.^{1,2,8}

In this letter we are reporting a study of the sticking probability of D_2 molecules at low temperatures, down to 5 K, on a W(110) surface as a function of the degree of surface coverage. For comparison we obtained data (on a considerably smaller scale) on the adsorption of hydrogen molecules. The experiments were carried out with the help of a thermal molecular beam in a “black chamber” apparatus as described in Refs. 3, 6, and 7. The sticking probability was determined from the time evolution of the flux density of the gas reflected by the surface of the test sample.¹

Figure 1 shows the time evolution of the sticking probability on the W(110) surface at a substrate temperature $T_s \approx 5$ K for various gas temperatures T_g in the source of the molecular beam. These curves are unusual. We first see a very rapid decrease in S with increasing surface coverage, which then gives way to an increase and a sharp maximum, whose height increases with decreasing T_g . Thereafter, S drops to zero, but in slightly different ways at different values of T_g . Although the maxima on the curves in Fig. 1 shift toward longer times with increasing T_g , along the scale of the degree of surface coverage θ (more on this below) they lie approximately on top of each other.

The T_g dependence of the initial sticking probability S_0 ($\theta \rightarrow 0$) is not monotonic (see the inset in Fig. 1). This behavior suggests that, in its decreasing region, the adsorp-

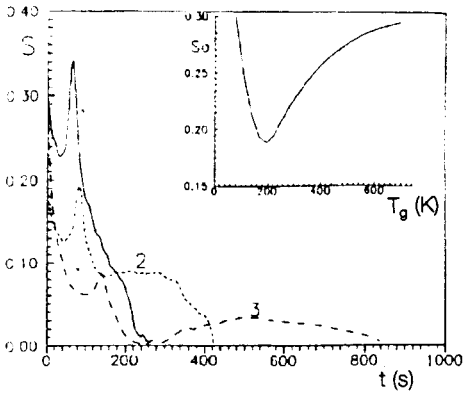


FIG. 1. The D_2 sticking probability versus the adsorption time at various values of T_g . 1— $T_g = 78$ K; 2—200 K; 3—700 K. The substrate temperature was $T_s = 5$ K. The inset shows the initial sticking probability versus T_g .

tion involves an intrinsic prestate, in which the trapping probability decreases with increasing kinetic energy of the incident particles. This behavior of S_0 as a function of the energy of the incident molecules was observed in Ref. 9 for the adsorption of hydrogen at $T_s = 300$ K on W(100) and W(111). It has also been observed in adsorption on W(110), but it is much less obvious in this case. As T_g is raised above 200 K, we observe an increase in S_0 , which we attribute to the onset of a new adsorption mechanism: one involving an activation barrier which exceeds the zero level of the energy. An activation-law adsorption of hydrogen on W(110) was also observed in Ref. 9. The adsorption of D_2 at $T_s \approx 5$ K on the clean W(110) surface thus occurs by two mechanisms: one involving an intrinsic prestate and another, at sufficiently high T_g , involving passage through an activation barrier.

Let us look at the dependence of the sticking probability on the degree of surface coverage, $S(\theta)$. The surface concentration of the adsorbate, n , or the degree of surface coverage, θ , can be extracted from the $S(t)$ curves in Fig. 1 with the help of the expression

$$n = \nu_0 \int_0^t S(t) dt. \quad (1)$$

Here ν_0 is the kinetic flux of molecules, whose exact value we did not determine, unfortunately. However, for a qualitative study of the effect of θ on S it is sufficient to construct a plot versus the area under the corresponding part of the $S(t)$ curve. This area is directly proportional to θ . Curve 1 in Fig. 2 shows $S(\theta)$ for D_2 adsorption at $T_s \approx 5$ K and $T_g = 200$ K. In accordance with the nature of the $S(\theta)$ curve, we break up the D_2 adsorption process into three stages (the stages are separated by the vertical dashed lines in Fig. 2).

Since in discussing the $S(\theta)$ dependence we will draw on a discussion of the participation of various adsorption states in the adsorption process, we show a spectrum of the thermal desorption of a deuterium film adsorbed at $T_s \approx 5$ K to the point of saturation (Fig. 3). This thermal-desorption spectrum for deuterium differs slightly from that for hydrogen which was reported in Refs. 4 and 6, but we will postpone a discussions of the reasons for this difference to a future paper. We will refer to a particular adsorption state below in terms of the temperature of the peak in the thermal-desorption spectrum.

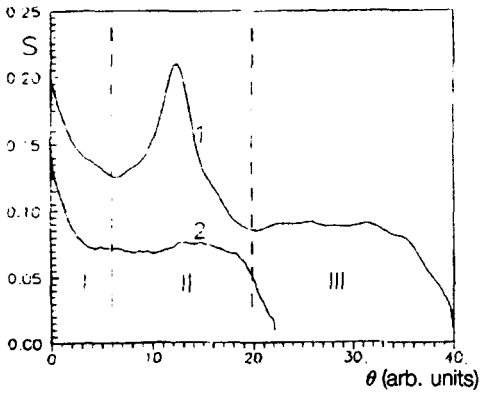


FIG. 2. Sticking probability versus the degree of surface coverage. 1— D_2 ; 2— H_2 . 1) D_2 ; 2) H_2 . $T_s = 5$ K, $T_g = 200$ K.

In the first stage we see an extremely rapid decrease in S , which is characteristic of Langmuir adsorption. In this case, a molecule incident on an occupied position is reflected back into vacuum, and direct dissociative chemisorption occurs at a vacant position. The results of Refs. 10 and 11 also indicate a Langmuir mechanism for the adsorption of hydrogen and deuterium in the initial stage of adsorption on W(110). In the thermal-desorption spectrum for this stage we observe primarily a peak corresponding to the atomic state of deuterium (550 K). The capacity of the 550 K state corresponds to¹⁴ $\theta \approx 0.5$. The molecular state with $T_d = 60$ K, which was discussed in Refs. 4 and 6, contains a relatively small amount of deuterium.

In the second stage, S increases significantly and then goes through a maximum. At the beginning of the second stage in the thermal-desorption spectrum, a peak corresponding to a second state of atomic adsorption at 410 K appears and reaches saturation approximately at the maximum of curve 1. In parallel with the increase in this peak, there is an increase in the peak representing a state of molecular adsorption at 15 K. On the descending part of the $S(\theta)$ curve for the second stage, the 15-K state reaches saturation, and an 8-K state appears. We believe that this 15-K state acts as a prestate for adsorption in the atomic state at 410 K. We interpret the $S(\theta)$ behavior in the second stage as the result of the onset of a mechanism of adsorption through an extrinsic prestate. In this case

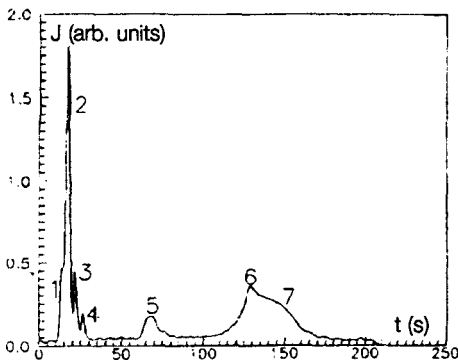


FIG. 3. Spectrum of the thermal desorption of D_2 ; adsorption at $T_s = 5$ K to the point of saturation. Here T_d is the temperature of the desorption peak (K). 1—5; 2—8; 3—15; 4—60; 5—150; 6—410; 7—550.

a molecule incident on an occupied position is capable of migrating to a vacant position and becoming adsorbed there. An unexpected result is the increase in S instead of the usual stabilization. We believe that the reason for this increase is that a weakly bound, physically adsorbed phase of deuterium at 15 K accumulates on the surface, and the collision of an incident molecule with a weakly bound molecule which has already been adsorbed is accompanied by a transfer of kinetic energy far more effective than in a collision with a clean surface or with a surface covered with tightly bound atomic deuterium. The sticking probability for the molecule increases sharply at this point. A similar increase in the sticking probability with the degree of surface coverage is observed for a variety of adsorption systems.^{3,7,13,14} The decrease in the sticking probability after the maximum can be explained on the basis that (first) in this stage there is no longer the possibility of a drainage of molecules into an atomic layer and (second) the 15-K state has a limited capacity. Lutsishin¹¹ also concluded that a prestate is involved in the formation of the atomic phase of hydrogen adsorption at $\theta > 0.5$.

Finally, in the third stage of the adsorption, we see a stabilization of the D_2 sticking probability, followed by a decrease in this probability to zero, as is typical of adsorption through a prestate. In the thermal-desorption spectrum in this state we see an increase in the 8-K desorption peak. At the very end of the process, a knee, which we attribute to the 5-K adsorption state, arises on the leading edge of this peak. We believe that the latter state is the prestate for adsorption into the 8-K molecular state.

We can attribute, largely arbitrarily, the different adsorption states to different adsorption monolayers. We can then say that a saturated film of deuterium on W(110) at 5 K consists of three layers, with the beginnings of a fourth: the 550-K and 410-K atomic states correspond to the first layer, the 15-K molecular state corresponds to the second layer, the 8-K molecular state corresponds to the third, and, finally, the 5-K state corresponds to the fourth layer, which is filled to only a small extent under these conditions.

Also shown in Fig. 2 is a $S(\theta)$ curve for H_2 adsorption on the W(110) surface for $T_s \approx 5$ K and $T_g = 200$ K. We note the following quantitative and qualitative differences between the curves for deuterium and hydrogen: 1) The H_2 sticking probability is substantially smaller than that for D_2 at all values of θ , including the case of a clean surface. This result is evidence in favor of a phonon mechanism for the dissipation of the energy of the incident molecule. 2) In the case of H_2 , the Langmuir adsorption is followed by the onset of a stabilization of S , with barely discernible indications of a maximum. 3) During H_2 adsorption, the surface becomes saturated at values of θ much lower than in the D_2 case. In the H_2 case, a stable weakly bound state corresponding to the third stage of the $S(\theta)$ curve for D_2 apparently does not form at $T_s \approx 5$ K.

We are inclined to believe that the main reasons for these large differences in the sticking probabilities of deuterium and hydrogen are the difference between the masses of these isotopes and the associated difference between the quantum-mechanical properties of the physically adsorbed molecules. Since the level of zero-point vibrations in a physically adsorbed potential well for the heavier deuterium molecules is considerably lower on the energy scale than the level for hydrogen, there may be associated consequence of importance to the mechanism of adsorption through an extrinsic prestate. In the first place, the lifetime of a molecule in the adsorbed state with respect to desorption and thus the surface concentration at a given temperature in the case of deuterium may be con-

siderably larger. Second, surface diffusion, which makes a vacant position accessible during adsorption through a prestate, is considerably slower in the D_2 case than in the H_2 case.

We believe that it is for this reason that in the H_2 case, in contrast with the D_2 case, there is no accumulation of physically adsorbed molecules in the second stage (Fig. 2). These physically adsorbed molecules lead to a more effective dissipation of the energy of the incident molecules and to an increase in the sticking probability. The H_2 molecules which are incident and which are trapped in a physically adsorbed state migrate very rapidly to vacant regions on the surface, and the equilibrium concentration of these molecules is low. The third stage of the adsorption is not realized in the case of hydrogen at $T_s \approx 5$ K, because of the high level of zero-point vibrations.

Let us summarize the results of this study. The behavior of the sticking probability S for D_2 as a function of the degree of surface coverage θ on the W(110) surface at $T_s \approx 5$ K is complicated and extremely unusual. The primary distinguishing feature is a sharp maximum. The sharp increase in S with increasing θ is attributed to the accumulation of weakly bound, physically adsorbed D_2 molecules on top of a layer of atomic deuterium. The collisions of these molecules with incident D_2 molecules are accompanied by an effective dissipation of energy and a capture. In the case of H_2 adsorption, this effect is not observed. We believe that the reason for this difference between the adsorption of D_2 and H_2 is a difference in quantum-mechanical properties: the position of the level of zero-point vibrations in the physically adsorbed well.

In the initial stage, during the formation of the 550-K atomic adsorption state, we observe a Langmuir adsorption mechanism for both D_2 and H_2 . Later, as θ increases, adsorption through an extrinsic prestate becomes predominant. Because of the differences between the quantum-mechanical properties of D_2 and H_2 , mentioned above, a larger number of stationary adsorption states are realized in the former case at $T_s \approx 5$ K.

The initial sticking probability for D_2 (~ 0.2) turns out to be considerably larger than that for H_2 (~ 0.15), indicating a phonon mechanism for the dissipation of the energy of the incident molecule.

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