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Monte Carlo simulations of hydrogen adsorption on the W(110) and Mo(110) surfaces

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Abstract. Kinetics of low-temperature hydrogen and deuterium adsorption on W(110) and Mo(110) surfaces have been studied by the "real-time" Monte Carlo simulations. Recently reported qualitative dependence of the adsorption characteristics on variation of the H_2 flux is described in terms of the dynamical equilibrium between incident and desorption fluxes and improved conditions for accommodation for the hydrogen molecules at high incident fluxes. The role of the intrinsic precursor state in hydrogen dissociative adsorption is analyzed.

PACS. 82.65.+r Surface and interface chemistry; heterogeneous catalysis at surfaces – 02.50.Ng Distribution theory and Monte Carlo studies – 82.20.Wt Computational modeling; simulation

1 Introduction

On a transition metal surface, hydrogen can be adsorbed either with dissociation of the molecules with subsequent atomic chemisorption or, at low temperatures, into relatively weakly bound physisorption states [1–10]. Activation energy for the dissociative chemisorption of hydrogen on W(110) and Mo(110), as indicated by increase of the sticking probability with decreasing energy of molecules in incident hydrogen beams [9], is small if any, which implies possibility of the atomic chemisorption even at low (5 K) temperatures. After completion of the atomic monolayer, further hydrogen adsorption is accomplished in a molecular form. In other words, the molecular monolayer is formed over the completed layer of chemisorbed hydrogen atoms [1,8–10]. The coverage θ can be defined in terms of the number of hydrogen molecules per adsorption site at the W(110) or Mo(110) surface, that is, $\theta = 0.5$ corresponds to a complete atomic monolayer. The largest hydrogen coverage that can be obtained at $T = 5$ K, in dynamical equilibrium with impinging hydrogen flux, is about $\theta = 1.5$, which corresponds to formation of a complete molecular monolayer. This behavior is in contrast to the subsequent growth of several physisorbed monolayers, as reported for rare gases at low temperatures [11].

In the dissociative chemisorption, extrinsic and, probably, intrinsic precursor states play an important role [4–7,12–17]. These intermediate states can be qualitatively described in terms of capturing the molecule into potential well near the surface, and therefore may be related to temporal molecular physisorption. One may easily imagine the temporal capturing of a molecule in the potential well when the molecule cannot dissociate, because the proper surface site is occupied by another adsorbed atom. Being captured in this extrinsic precursor state, the molecules can, with high probability, move along the surface. Eventually, the molecule can occur above a vacant site at the surface, that is, in the intrinsic precursor state. Then the molecule can dissociate, with chemisorption at this site of one of the two atoms and, in neighborhood, of the other one. However, the molecule also can be desorbed from the precursor state, which distinguishes this model from that of direct dissociative chemisorption [18–21]. Thus, macroscopic kinetics of adsorption will depend upon the relationship between rates of the dissociative chemisorption and molecular desorption, as well as of the surface diffusion and molecular flux.

Existence of intrinsic precursor states has been a subject of some controversy. In the case of strongly activated chemisorption, with a large activation energy, as for hydrogen adsorption on simple and noble metals [11,21,22], intrinsic precursor states can be directly observed due to presence, at the surface, of both atomic and molecular species even at very low coverages. Obviously, the molecular physisorption state can serve as a precursor for subsequent dissociative chemisorption. In contrast, when the dissociative adsorption of hydrogen occurs with impinging molecules of very low energy, evidence of the existence of the intrinsic molecular precursor states is only indirect [1–3,8–16]. Furthermore, determination of the state of adsorbed molecules in very low coverage limit is fraught with difficulties.

To be captured into the precursor state, the impinging molecule transfers or exchanges kinetic energy to the substrate. Presumably, this energy can be transferred to the

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crystal lattice through phonon production. By adopting a classical treatment of the molecule, the scattering probabilities can be roughly estimated both for one-phonon and many-phonon processes [17,22–24]. However, for typical energies of hydrogen molecules in the molecular beam (25 meV), the related wavelength should be about the lattice period of the transition metal surface, which results in pronounced diffraction [23,25]. Hence, scattering of the hydrogen molecules demands quantum mechanics for a realistic description, which, to-date, is available only for a one-phonon process [23–25]. This complexity precludes an evaluation of the initial sticking coefficient with the accuracy that is required for comparison with experiment.

The concept of the intrinsic precursor state has been recently questioned from the viewpoint of results of calculations of the 6D potential energy surfaces [26–32] for hydrogen on Pd(100) and W(100) [28–31]. Within this model, the increase of the initial sticking coefficient with decreasing the energy of impinging hydrogen molecules was explained by diminishing rotation, which, due to improved "steering", facilitates adoption of the "best" orientation of the molecule at the surface for symmetry allowed bond-breaking and chemisorption. This mechanism explains the experiment without involving intrinsic precursor states, so it was suggested that the precursor model should be abandoned. However, as follows from these and other [18–21] calculations, hydrogen molecules have a high mobility along the surface thus spending considerable time in vicinity of the surface [19,20]. This implies, again, the model of precursor states with a high mobility of molecules captured into these states.

Investigations of hydrogen adsorption on W(110) and Mo(110) surfaces at low temperatures (5 K) have revealed a strong dependence of kinetics parameters of adsorption on the molecular flux [10]. This dependence is very pronounced when the second (that is, molecular) layer is formed. In particular, increase of the flux results in strong increase of both the sticking coefficient and saturation coverage reached at dynamical equilibrium conditions. For the W(110) and Mo(110) surfaces, the $S(\theta)$ dependences for hydrogen adsorption, obtained at $T = 5$ K, are found to be qualitatively different, as discussed in more detail below.

These experiments were conducted under dynamical quasi equilibrium conditions, which allows one, at least in principle (though not in practice [33]), to explore equilibrium thermodynamics [11,17,22,24,34] for interpretation of the results. Direct evaluation of the sticking probability, however, is quite involved, and thus could provide only a qualitative description of the kinetics. For example, different approximations for evaluation of degrees of freedom for adsorbed molecules lead to quite different values ($10^{13} \div 10^{19}$) of the obtained frequency factors ν (pre-exponent) in the Polanyi-Wigner desorption equation [34,35]. Furthermore, various models predict also a strong coverage dependence of the factor for different rate processes in adsorbed overlayers [34]. In absence of more rigorous evaluations, it is also possible to explore a simple semi-empirical estimation of $\nu \sim \mathrm{kT/h} \sim 10^{12}$ [35], which also can provide agreement between calculated and experimental TPD spectra. It should be noted here, that activation energies, within such an approximation, can be estimated only with respect to chosen value of ν.

Fortunately, the characteristics of hydrogen adsorption on the W(110) and Mo(110) allows for implementation of the lattice gas model to gain the statistical description. Indeed, the saturation coverage ($\theta = 0.5$, as defined in the number of molecules) for the chemisorbed hydrogen atoms within the first monolayer suggests that each adsorption site at the surface is occupied by just one atom. Furthermore, the largest molecular coverage in the second monolayer that can be obtained at equilibrium with incident flux, again corresponds just to one adsorbed molecule per adsorption site at the surface [36]. It should be noted here that such introduced lattice of adsorption sites does not imply any particular geometry (actual positions of the atom and molecule at the surface), but only suggests equivalence of the adsorption sites.

Kinetics of molecular hydrogen adsorption on the W(110) and Mo(110) was studied earlier by means of the Monte Carlo simulations in the "real time mode" [36]. With obtained values of desorption activation energies, the calculated TPD spectra were in good agreement with experiment. It was found also that small (0.1 meV) repulsive lateral interaction between adsorbed hydrogen molecules was essential for a correct explanation of $S(\theta)$ dependences on the molecular flux.

In the present work we extend the real-time Monte Carlo model to the case of dissociative adsorption, aiming justification of existing physical models for hydrogen adsorption on transition metal surfaces. In particular, the role of precursor states in the hydrogen dissociative chemisorption on the W(110) and Mo(110) surfaces is in focus of our study.

2 The model of hydrogen adsorption

Qualitative description of adsorption can be obtained by considering the motion of hydrogen molecules in one-dimensional potential of transition metal surface, using the HyperChem code, which suggests several options for treating the potential: (i) molecular mechanics, that is, Newton mechanics with classical forces; (ii) semi-empirical (SE) potentials which explore "universal" adjusted parameters for overlap integrals; (iii) ab initio (Hartree-Fock), and (iv) density functional theory calculations. Thus, interaction with the model surface can be described in terms of classical molecular mechanics (MM) or quantum mechanics. In the latter case, the semi-empirical (SE) approximation (in spite of a rather rough approximation and only limited justification of the parameters for transition metals) is believed to be sufficient to provide reasonable estimations of involved interactions. Within the MM approach, a hydrogen molecule is considered as a classical particle in the van der Waals potential near the surface, while SE potential accurately accounts for electronic structure and therefore allows for simulation of dissociation as well.

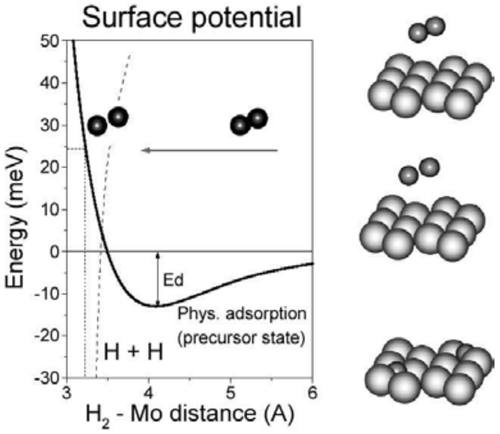

Fig. 1. Potential energy of a hydrogen molecule near the Mo(110) surface, evaluated by the molecular mechanics method (solid line). Attractive side of the potential for a hydrogen atom, estimated with the semi-empirical quantum mechanics method, is denoted by a dashed line. At the temperature of the gas $T_g = 300$ K, average energy of incident hydrogen molecules is about 25 meV, which is well above the activation energy for dissociative chemisorption. The "tail" of the surface electrons leaking into vacuum can cause dissociation of the hydrogen molecule as illustrated by snapshots, obtained in the course of molecular dynamics simulations.

The potential of interaction of the hydrogen molecule with the fragment of the Mo(110) surface, calculated by using classical molecular mechanics, is shown in Figure 1. Near the surface, the van der Waals interaction attracts the molecule until, at certain distance from the surface, the molecule reaches the "tail" of substrate electrons leaking into vacuum. This results in repulsion of the molecule from the surface and can lead to its reflection. However, the molecule can lose kinetic energy (for instance, into excitation of phonons in the substrate [17,22–24]) and thus can be captured in the potential well near the surface, as expected in the case of physisorption. The depth of the minimum of the potential for hydrogen molecule at the Mo(110) surface is found to be about 15 meV, which implies that the physisorbed molecular layer can be stable only at low (liquid helium) temperatures of the substrate.

With molecular dynamics method (MD), the process of physisorption can be simulated (in present work, using the HyperChem code) to provide an illustration of movement of hydrogen molecules in the one-dimensional potential near the surface. Energy of impinging hydrogen molecules is about 25 meV, which corresponds to the 300 K temperature of the flux (see Fig. 1), and therefore, in absence of energy exchange with the surface, these molecules will reflect at various angles. However, energy dissipation can be accounted for by introducing the "constant temperature" mode which simulates the equilibration of the system (to avoid uncontrollable increase of speed, it is assumed that after each series of scattering events the molecule is cooled down to the surface temperature which is about 4 K). Then, with properly adjusted parameters, physisorption of hydrogen molecules on the Mo(112) surface can be readily simulated.

On the other hand, the electrons from the substrate leak out into the vacuum and can attach to the molecules, captured in precursor states, thus leading to dissociation [2,37–39] with subsequent chemisorption of hydrogen atoms. This process, obviously, requires a quantum mechanical approach to obtain accurate values of the potential near the surface, probabilities of dissociation and chemisorption, and critical distance from the surface, at which a hydrogen molecule will dissociate. Such calculations are extremely involved if a rigorous description is required, but for a qualitative illustration of the dissociative hydrogen adsorption can be performed (with the HyperChem code) by means of molecular dynamics simulations. Thus, with semi-empirical approximation and using "unrestricted Hartree-Fock" method for the hydrogen molecule, pretty snapshots of the process have been obtained, as shown in the right part of the Figure 1.

Obviously, these simulations should be considered only as an illustration, which, nonetheless, allows for elucidation of some interesting features of the adsorption-desorption process for hydrogen on the Mo(110) surface. Thus, the distance from the surface which corresponds to beginning of the dissociation of the hydrogen molecule is about 3.5 Å, that is just corresponds to repulsion branch of the classical MM potential in the left part of the Figure 1. It seems very probable that electrons from the surface can penetrate into the molecule and partly fill antibonding state thus causing the dissociation. After the dissociation, hydrogen atoms adsorb in bridge sites at the Mo(110) surface, as is seen in the last snapshot in Figure 1.

As stated above, to some extent, the physisorption of hydrogen molecules can be considered as a precursor state for subsequent chemisorption. Then, being temporary captured into the precursor state, a molecule can be either desorbed or chemisorbed. Relative rates (or probabilities) of these two channels, as well as the efficiency of accommodation of the molecules in the physisorbed state, determine the sticking coefficient for chemisorption.

Under conditions used in experiments for dynamical molecular adsorption of hydrogen [8–10], the rate of adsorption can be presented as

$$\frac{dn}{dt} = F - k(n,T)F - n\nu \exp(-E_{eff}/k_B T) \qquad (1)$$

where n is the concentration of molecules on the surface, F is the flux of incident hydrogen molecules which are reflected from the surface with probability $k(n,T)$. Desorption flux here is in the Polanyi-Wigner form with the frequency factor $\nu = 10^{13}$ s^{-1} [40–42]. Effective desorption activation energy includes also variation of the depth of the Van-der-Waals potential well E_d [41–43]] due to lateral interaction U [44–46], that is, $E_{eff} = E_d - U$.

To avoid introducing further parameters into the model, desorption energies E_{eff} for hydrogen molecules in the intrinsic and extrinsic precursor states were assumed to be the same (possible difference between these energies should not be very pronounced and thus will not affect substantially the adsorption kinetics). In particular, present Monte Carlo simulations of a dissociative hydrogen adsorption explore parameters, which have been found to be relevant for adsorption of molecular hydrogen [36] in the second layer (that is, over the complete atomic monolayer). This implies, in agreement experiment [8–10], that the dissociative chemisorption should be much faster and therefore almost completed before the molecular layer starts to form.

The adsorption rate can be expressed also in terms of sticking probability for impinging molecules as $S(n,T) \times F$, which defines the sticking coefficient for dynamical process at the surface under impinging molecular flux F. More convenient for analysis is related term $S(\theta)$, where the molecular coverage is defined as $\theta = n/n_0$ and n_0 is the concentration of adsorption sites, 1.4×10^{15} cm^{-2} in the case of W(110) or Mo(110) surface.

Evaluation of $S(\theta)$ requires estimation of several involved factors such as lateral and adsorption interactions, accommodation of incident molecules and their mobility at the surface. This is just the case when Monte Carlo simulations, providing a transparent description of the net dynamical process of adsorption, may be successfully applied. Adopting a lattice gas model and choosing explicitly necessary parameters, the simulations are straightforward and allow a justification of a presumed physical model through the computer experiment.

3 Monte Carlo simulations

It is reasonable, for purposes of Monte Carlo simulations of adsorption, to take values of initial sticking coefficients S_0 from experimental data [8–10]. The sticking probability for hydrogen and deuterium on the clean W(110) surface increases with decreasing gas temperature, that is, energy of impinging molecules [9]. According to results of these experiments, in the present work we have adopted $S_0 = 0.3$ for hydrogen on W(110) at surface temperature $T = 5$ K and the gas temperature $T_g = 300$ K, and $S_0 = 0.28$ for hydrogen and $S_0 = 0.33$ for deuterium on the Mo(110) surface at $T_g = 100$ K.

Desorption activation energies for hydrogen and deuterium at the Mo(110) and W(110) surfaces have been evaluated by comparison of results of the real-time Monte Carlo simulations for molecular hydrogen adsorption with experimental data for coverage dependence of sticking under various hydrogen fluxes [36]. In particular, for hydrogen on the Mo(110) surface, the activation energy E_d is found to be of 14.4 meV, which is in good agreement with the value derived from molecular dynamics simulations (cf. Fig. 1). This activation energy corresponds to the highest peak of 5 K in TPD spectrum, and therefore the related low-temperature state should be the most important, among the other states found for hydrogen on the Mo(110) surface [10], for the competition between incident and desorption fluxes. For deuterium on Mo(110), $E_d = 14.6$ meV. For hydrogen and deuterium on the W(110) surface, desorption activation energies are 14.6 meV and 14.8 meV, respectively.

In the case of dissociative chemisorption, the model must explicitly account for the probability of dissociation of a molecule, captured in the intrinsic precursor state [48], as well as the mobility (surface diffusion) of the molecules, which can move the molecule into an intrinsic precursor state. Hence, the molecule in intrinsic precursor can be either desorbed with probability $W_d = \nu \exp(-E_d/k_BT)$ per second or chemisorbed with dissociation with probability $W_{diss} = \nu \exp(-E_{diss}/k_BT)$ per second, whereas the molecule in extrinsic precursor (above already occupied site at the surface) can be either desorbed or moved, by means of the surface diffusion, into neighboring lattice site which can be, in turn, either of extrinsic or intrinsic type. It is implied that the frequency factor $\nu = 10^{13}$ s^{-1} is the same for desorption and dissociation rates. Hence, the probabilities of desorption and dissociation are controlled by E_d and E_{diss} that can be derived from the best fit of results of the Monte Carlo simulations at low coverages to experimental $S(\theta)$ dependences at various hydrogen molecular fluxes.

When an impinging molecule occurs above the lattice site that has been already occupied by another molecule, the dissipation of energy is facilitated due to perfect mass match between colliding molecules as compared to the collision with a substrate surface atom. This improved accommodation is modeled by allowing the impinging molecule to find a vacant neighboring site, at which physisorption of the molecule is very probable (actually, it is implied that the probability of sticking in this case is unity). In contrast, the interaction between hydrogen molecule and W surface, covered by a monolayer of atomic hydrogen, can be attributed to the interaction between the molecule and the W–H complex, rather than to interaction between the hydrogen molecule and the chemisorbed hydrogen atom. A hydrogen atom, which adsorbs at a relatively deep in-bridge position, is strongly bounded with the tungsten atoms thus forming a kind of a rigid molecule, and therefore there is a mass mismatch between these surface molecules and impinging hydrogen.

The number of adsorption sites taken for simulations should be sufficient to provide a reasonable statistics. Chosen in the present study 36×30 matrix (for W(110), the related surface area is about 100×100 Å) with periodic boundary conditions is found to be sufficient for these purposes [36]. Thus, on increasing the number of lattice sites, no noticeable changes in the kinetics of adsorption were detected. To diminish the random statistical scattering of data, values of sticking coefficients and coverage were averaged over several (typically, 10) courses of simulations with different starting values of series of pseudo random numbers.

The “real-time” scale, which is important for a direct comparison of results of simulations for $S(\theta)$ with experiments, performed at various molecular fluxes, has been introduced as follows. For the time t, the number of molecules impinging the surface at a given flux (that is, exposition) can be expressed in terms of a fraction of a monolayer. Then, the hydrogen exposition can be related to the number of adsorption attempts with respect to the number of the sites at the model surface. For example, one "adsorption cycle" [36,48,49] of 108 adsorption attempts corresponds to the exposition of 0.1 ML (the monolayer is represented by the window of $36 \times 30 = 1080$ adsorption sites), or to the real time of 1 second under the flux of 1.4×10^{14} molecules/(cm^2 s).

The adsorption of hydrogen molecules at the lattice sites is followed by their rearrangement (through "surface diffusion") with account for the lateral interaction and temperature-driven fluctuations (the entropy terms). This model is usually explored in the framework of the Monte Carlo simulations of the orderdisorder transitions in thin films (see, e.g., [50,52]). Briefly, a randomly chosen particle is moved to a neighboring site with probability exp($-\Delta E/kT$). The energy difference caused by this displacement is calculated with regard to the lateral interaction with other molecules that currently occupy neighboring adsorption sites. In the case of a gain in energy ($\Delta E < 0$) due to the displacement, or when calculated probability exceeded a random number, the displacement is accomplished, while otherwise rejected. Usually, after 5–10 such displacements per particle, the dynamical equilibrium in the film is achieved, which can be controlled by evaluation of total energy (in equilibrium, the free energy approaches minimum while the total energy fluctuates about certain main value that depends on temperature). For low temperatures, this procedure gives ordered structures whereas for higher temperatures, fluctuations result in the film disordering [50–52].

Hence, in the present work, the net adsorption-desorption process is simulated in a real-time mode using proper values of fluxes (expressed in terms of the monolayer fractions) of incident and desorbing molecules, which allows a direct comparison with kinetics characteristics derived from experiments on hydrogen and deuterium adsorption. General scheme of the simulations with suggested algorithm may be summarized as follows:

1. the first step is adsorption into precursor states. A random site at the surface can be (i) vacant ; (ii) occupied by a chemisorbed hydrogen atom, and (iii) occupied by a molecule. In cases (i) and (ii), which correspond to physisorption in intrinsic and extrinsic precursors, respectively, the molecule can be adsorbed with probability S_0. In contrast, in the case (iii), energy exchange with the surface is facilitated due to mass match between colliding molecules, and therefore a unity probability of capturing in a vacant neighboring site is adopted. If there is no vacant nearest neighbor sites, this adsorption attempt is rejected;
2. being captured into the intrinsic precursor state, the molecule can either dissociate with probability W_{diss} (then hydrogen atoms occupy two vacant sites in the chemisorbed layer) or desorb with probability W_{des};
3. the molecules in extrinsic precursor states can accomplish several jumps to neighboring vacant sites, which simulates the surface diffusion. If, along the diffusion, the molecule occurs in the intrinsic precursor, it can dissociate (as in the case (i)).

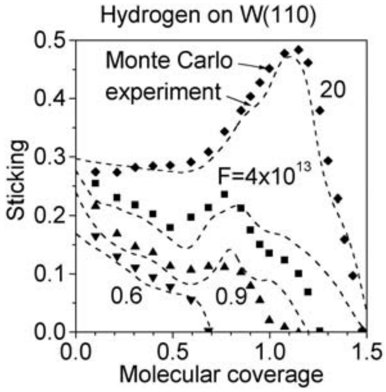

Fig. 2. Results of Monte-Carlo simulations of hydrogen adsorption on the W(110) surface (shown by symbols) for various values of the H_2 flux. For comparison, experimental dependences taken from reference [10] for the fluxes $F = 0.6 \times 10^{13}$ cm^{-2} s^{-1} (1), 0.9×10^{13} cm^{-2} s^{-1} (2), 4×10^{13} cm^{-2} s^{-1} (3), and 20×10^{13} cm^{-2} s^{-1} (4) are shown by dashed lines.

The relative numbers of attempts of adsorption, dissociation, desorption and diffusion is controlled by introducing the real-time scale, as detailed above. After the adsorption-diffusion-desorption cycle is accomplished, the sticking probability is determined as the ratio of the number of adsorbed molecules to the number of impinging atoms.

Results of simulations of dynamical hydrogen adsorption on the W(110) surface are presented in Figure 2 for several values of the H_2 flux that were used in the experiments [10]. As seen from comparison with experimental plots (shown by dashed lines), $S(\theta)$ dependences, simulated with parameters $E_d = 14.6$ meV and $E_{diss} = 14.0$ meV, do reproduce the main features of the kinetics of hydrogen adsorption on the W(110) surface. In particular, calculated plots resemble the increase of the sticking for high H_2 fluxes as well as the increase of dynamically equilibrated coverages with increasing the flux. Both these features result from changing proportion between incident and desorption fluxes (see Eq. (1)) as well as from improved accommodation for the hydrogen molecules at high incident fluxes. Indeed, when a molecule impinges another (previously adsorbed) molecule at the surface, due to a perfect match of masses, the energy transfer must be very efficient thus facilitating the capturing of the molecule into the physisorption state.

It is important that agreement between the simulated and experimental $S(\theta)$ dependences is achieved over the total coverage range and for all hydrogen molecular fluxes. Such an agreement, at coverages up to 0.5, can be reached only with account for the intrinsic precursor states. This statement has been justified by simulations without allowing for a molecule to be captured into intrinsic precursor, which the condition is equal to canceling the probability of desorption from this state. No dependence of the sticking coefficient on the flux of impinging hydrogen molecules at low coverages has been found in these control simulations, in contradiction with experiment. Hence, the dependence of the sticking coefficient on impinging flux is a result of competition between the incident and desorption fluxes and therefore appears only when there is the desorption flux from the states of molecular adsorption, that is, precursor states.

Although these results of simulations do support the concept of hydrogen adsorption through precursor states, this does not imply that a direct dissociative chemisorption of hydrogen on the W(110) surface is impossible. Apparently, both mechanisms should be valid, while only the chemisorption through precursor states can lead to the dependence of sticking on the flux of hydrogen molecules.

For hydrogen adsorption on the Mo(110) surface, the dependence of sticking coefficient on coverage is qualitatively different from those for H_2 on W(110) and for deuterium on Mo(110) (Fig. 3). It is only for hydrogen on the Mo(110) that there appears a picturesque drop of sticking at $\theta = 0.5$ (which corresponds to a complete monolayer of chemisorbed hydrogen atoms). What is the origin of this dramatic difference? The answer may be found by comparing characteristic desorption temperatures for these systems. Thus, for hydrogen on the Mo(110), the main TPD peak for molecular desorption is only slightly above 5 K that is the surface temperature at which the adsorption kinetics was studied [1,8–10]. In contrast, corresponding desorption peaks in TPD spectra for hydrogen on W(110) and deuterium on Mo are at 6 K and 10 K, respectively [8–10]. Hence, for hydrogen on the Mo(110) surface at $T = 5$ K, desorption flux must be substantial, whereas for deuterium on Mo(110), as well as for H_2 on W(110), it should be small.

For hydrogen adsorption on the Mo(110) surface, the best fit to the experimental $S(\theta)$ dependences (Fig. 3) has been obtained with $E_d = 14.4$ meV and $E_{diss} = 14.2$ meV. For deuterium, the desorption activation energy was $E_d = 14.8$ meV (which relates to the characteristic desorption temperature of 10 K [36]). We underscore that the qualitative difference in the coverage dependence of sticking of hydrogen on the Mo(112) and W(112) surfaces has been reproduced in the Monte Carlo simulations with the only difference (0.2 meV) in the activation energies for desorption and dissociative adsorption. Such a small difference in desorption energies follows directly from TPD experiments [8–10] and resembles temperatures of main peaks of hydrogen molecular desorption.

It should be noted also that, at $T = 5$ K, the dependences of sticking coefficient on coverage for deuterium and hydrogen on the W(110) surface are similar (see Figs. 2 and 3). At this temperature, which is substantially lower than those corresponding to the molecular phase peaks in TPD spectra for both hydrogen and deuterium, desorption is relatively small and therefore small increase in activation energy does not lead to pronounced changes of the $S(\theta)$ dependences.

Within a simple one-dimension model of the surface potential (see Fig. 1) one can expect that decrease in the depth of the minimum in the potential plot for physisorption, that is, in E_d, will be followed by an increase in the activation energy for chemisorption. Thus, in comparison with W(110), the depth of the minimum for Mo(110) appears to be less for 0.2 meV, while the activation energy for chemisorption increases for 0.2 meV. Obviously, this small difference in the depth for the potentials should be attributed to difference in electronic structure for W(110) and Mo(110) surfaces (recall that lattice constants for W and Mo are almost identical). The dominant role of d electrons, for which the degree of localization determines the net density of electrons leaking into vacuum, is evident. Thus, $5d$ electrons in W extend to a substantially longer distance than $4d$ electrons of Mo, and therefore should be more active in sense of probability of the dissociative attachment [37–39] to hydrogen molecules captured in intrinsic precursor states. More extended electronic "tail" leads also to increase in work function for the W(110) as compared to the Mo(110) surface, which can be described in terms of increasing power of the double electrical layer. This feature may result in a stronger polarization of a physisorbed hydrogen molecule and therefore in increase of the depth of the potential.

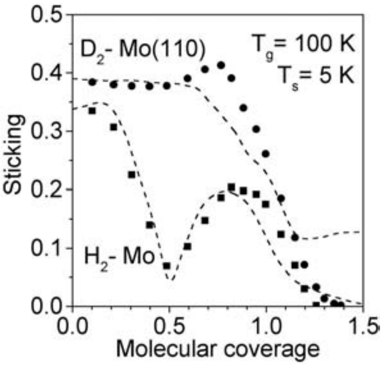

Fig. 3. Experimental (dashed lines) [9] and Monte Carlo (symbols) dependences of the sticking coefficient on coverage for hydrogen and deuterium on the Mo(110) surface. The surface temperature is $T = 5$ K and the temperature of hydrogen in the gas phase is $T_g = 100$ K.

It should be noted that suggestions in references [1,8–10] regarding the different kinetics of hydrogen adsorption on W(110) and Mo(110), interpreted as a result of different rates of surface diffusion [53], do not contradict the present suggestions. Probably, both desorption and diffusion rates are responsible for kinetics of adsorption at low temperatures. In the present work, surface diffusion was treated as "fast" (that is, without any barrier), and therefore the role of difference of the diffusion rates could not be revealed.

4 Conclusion

The results of the Monte Carlo simulations of the kinetics of hydrogen and deuterium adsorption on the W(110) and Mo(110) surfaces support the concept of precursor states and clarify the role of these states in kinetics of dissociative adsorption. The net process of adsorption under impinging flux of hydrogen molecules can be understood within the framework of a simple intuitive picture which includes also enhanced accommodation probability for the molecules that collide with previously adsorbed molecules, surface diffusion of molecules, and lateral interaction, which result in the dependence of hydrogen coverages on the flux at dynamical equilibrium.

The simulations reveal a major importance, among other factors, of the desorption activation energy with regard to the temperature of the surface. It is a small (0.2 meV) difference in the desorption energies for hydrogen and deuterium on the Mo(110) surface that result in qualitative difference of dependences of sticking at 5 K. It should be expected therefore that at lower temperatures, 2–3 K, which will essentially decrease the desorption of hydrogen, this difference will become less important, and the $S(\theta)$ dependences for hydrogen and deuterium on Mo(110) will be similar, unless the quantum diffusion plays significant role in these processes.

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