Sticking in the Physisorption Well: Influence of Surface Structure

S. Andersson and M. Persson
Department of Applied Physics, Chalmers University of Technology, S-412 96, Göteborg, Sweden

(Received 20 October 1992)

We demonstrate by D_2 nozzle beam experiments on cold Cu(111), Cu(100), and Cu(110) surfaces that the substrate surface structure profoundly influences the sticking and trapping of particles in the physisorption well. Comparison with theoretical calculations reveals that this is caused by structure-specific differences in the particle-phonon coupling and the collision processes that control the lateral propagation of particles trapped in quasibound states.

PACS numbers: 68.35.Ja, 79.20.Nc, 82.65.Pa

Depending on the nature of the interaction, sticking of a gas-phase particle on a solid surface can occur in a number of ways and a given gas-surface combination may show totally different behaviors depending on initial conditions. This is beautifully illustrated by the adsorption of H_2 on copper surfaces, where for low incident kinetic energies the particle can physisorb on a cold surface while at higher energies dissociation becomes increasingly probable [1]. This activated dissociation is a complex dynamical process involving dramatic rearrangements of the electronic distribution and of the nuclear positions. A precise knowledge of the potential energy surface governing the H_2-Cu dissociation dynamics is not at hand and contact between theory and experiment will mostly concern gross features and be of a qualitative nature.

Sticking of H_2 in the physisorption well, on the other hand, does not only represent a comparatively simpler case, but may also, in several aspects, serve as an important model of sticking into a highly mobile, weakly adsorbed molecular precursor. Established methods exist to determine accurate physisorption interaction potentials. This has been done for a number of noble metal crystal surfaces using results from diffraction and selective adsorption measurements [2]. The electronic configuration does not change in a significant way on adsorption, coupling to electronic excitations is expected to be very weak [3], and the energy transfer occurs through the phonon system of the solid lattice. Hence the conditions regarding the physisorption dynamics appear sufficiently clear and we should be able to explore complex matters like the one we address in this work: Will the sticking of a gas-phase particle in the physisorption well depend on the surface structure of a given substrate and if so can the present theory give us an accurate physical picture of the observed behavior, even at a quantitative level?

In this Letter we show, with specific reference to the systems D_2 on Cu(111), Cu(100), and Cu(110), that the trapping and sticking in the physisorption well are profoundly affected by the surface structure. We find that the normal incidence sticking probability on Cu(110) is surprisingly much larger than on the other two surfaces and that this is caused by structure-specific differences in the particle-phonon coupling including *umklapp* processes. The laterally averaged interaction potential varies only a little with the crystal face and affects the sticking probability marginally. The corrugated part of the potential depends strongly on the crystal face, however, and has important influence on the trapping-sticking process at larger angles of incidence. We have previously proposed [4] that sticking at off-normal incidence, apart from possible contributions due to selective adsorption resonances, can be described as a process where particles enter bound or quasibound states of the potential well via phonon emission. In the former case the particle has obtained energy $\epsilon < 0$ and is stuck while in the latter case it is trapped with $\epsilon > 0$ and will propagate along the surface and may ultimately stick via further energy loss to the phonons or scatter back into the gas phase via diffraction. The experiments we discuss here provide an adequate test of the validity of this model since the probability for diffraction will vary substantially with the crystal face. We find that dynamics calculations based on these assumptions account in an excellent way for the experimental observations.

The sticking experiments reported here were performed in the limit of zero coverage via partial monolayer desorption in a cryopumped ultrahigh vacuum (UHV) chamber operating at a base pressure of 2×10^{-11} Torr. We have been using nozzle beams of H_2 and D_2 gases with an optimum energy spread of $\sim 10\%$ and an angular divergence of 0.29°. The initial sticking probability, S_0, was measured at fixed angle of incidence for ~ 40 beam energies in a repetitive cycle. Care was taken to keep the beam pulse time sufficiently short so that any influence of collisions with preadsorbed molecules did not contribute to S_0 in a significant way. The sticking measurements were complemented with background measurements using a shutter in the UHV chamber to block the molecular-beam path. For D_2 we found that such background influence was negligible. The copper specimens were cleaned *in situ* by standard methods involving argon-ion bombardment and heating cycles and could be cooled to < 10 K using helium as a cryogen and they were heated resistively. The apparatus, specimen preparation, and experimental procedure have been described in more detail elsewhere [4].

The crystal surfaces were oriented with respect to the direction of the incident molecular beam so that at off-normal incidence the scattering plane comprised the surface normal and the $[11\bar{2}]$ direction [Cu(111)], the [010] direction [Cu(100)], and the [001] direction [Cu(110)] in the surface plane. The Cu(110) crystal has also been investigated in the $[1\bar{1}0]$ direction which is along the dense atom rows. The accuracy of these alignments was better than 0.5° as determined from diffraction measurements around the scattering plane. The sticking measurements have for all crystals been complemented with resonance-specular scattering (selective adsorption) and diffraction measurements using both H_2 and D_2 beams. These data have been analyzed following standard physisorption theory [5] to give the angular and lateral average interaction potential, V_0, the angular average lateral corrugation potential, V_1, and the lateral average angular potential, V_2. In this way we have a good handle on the potential energy surfaces that govern the D_2-Cu surface collision process under study. These results will be discussed in detail elsewhere but the data which have been used in the theoretical calculations presented below will be summarized in that context.

Experimental observations for the sticking of D_2 molecules on the copper (111), (100), and (110) surfaces are shown in Fig. 1 [6]. The top and bottom panels show measurements of the initial sticking coefficient, S_0, versus incident energy, ϵ_i, at normal incidence, $\theta_i = 0°$, and glancing incidence, $\theta_i \sim 60°$, respectively. These data reveal several specific features challenging any theoretical description of the sticking process: (i) At normal incidence, we observe that S_0, at all energies, is substantially larger for Cu(110) than for Cu(111) and Cu(100) which behave rather similarly. (ii) At glancing incidence, S_0 for Cu(110) begins at a higher level for low ϵ_i and falls off more quickly with ϵ_i than for Cu(100) and Cu(111), the latter displaying the slowest falloff. (iii) The glancing incidence sticking data for Cu(111) and Cu(100) fall off slowly with ϵ_i as compared to the corresponding normal incidence data.

The glancing incidence data also exhibit peaks related to selective adsorption resonances. We have previously discussed such sticking resonances in some detail [4] and just remark that the strength of resonances involving diffraction events depends strongly on the surface structure via the corrugation potential.

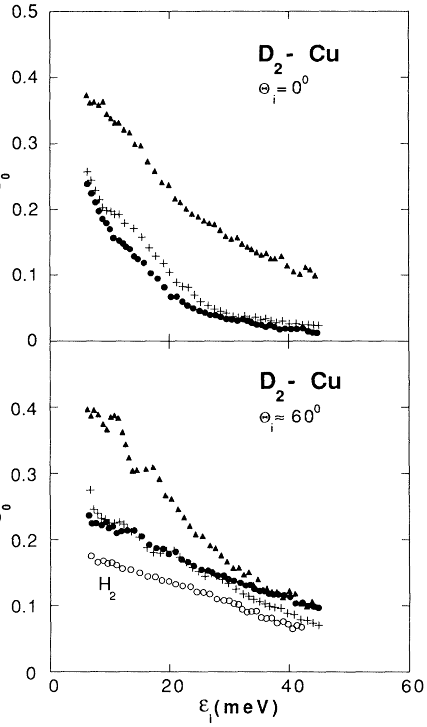

FIG. 1. Initial sticking probability S_0 vs molecular-beam energy ϵ_i of D_2 on Cu(111) (●), Cu(100) (+), and Cu(110) (▲) at 0° and ~ 60° (61°, 62°, and 61°, respectively) angle of incidence. o's give the results for H_2 on Cu(111) at 58° angle of incidence.

Concerning some of the observations listed above we may suggest intuitive physical explanations. The importance of a trapping-sticking process and its dependence on elastic backdiffraction could rationalize the observations expressed in points (ii) and (iii). The origin of the differences in magnitude of the sticking probability with crystal face is less obvious. The laterally averaged H_2-Cu interaction potential, V_0, varies only marginally with crystal face as can be seen in the top panel of Fig. 2. The phonon excitation probability is related to this potential, and will on this ground alone be rather similar in the three cases. The difference must clearly be traced to the phonon spectra [7]. They are not so different, however, and the mechanism must be more subtle. It turns out that the crucial factor is the specific coupling to the phonons which depends on the ion core locations. The classical turning point, z_t, of a low-energy D_2 molecule lies a distance from the surface plane that is comparable with the surface lattice spacing. Hence the molecule interacts with several neighboring surface atoms, the Armand effect [8], and the coupling normal to the surface is dominant. The effect of this on the coupling between the particle and single phonons, including *umklapp* processes, is well expressed via the spectral function

$$C(\omega) = \sum_{\mathbf{G}} \int_{\rm SBZ} \frac{d^2Q}{A_{\rm SBZ}} e^{-(\mathbf{Q}+\mathbf{G})^2/Q_c^2} \frac{\hbar \rho_{zz}(\mathbf{Q},\omega)}{2m\omega}, \tag{1}$$

where ρ_{zz} is the projected local density of states and m is the substrate atom mass. The momentum cutoff $Q_c = \sqrt{\lambda/z_t}$ lies well within the surface Brillouin zone of area $A_{\rm SBZ}$ [9], and λ is the exponent in the repul-

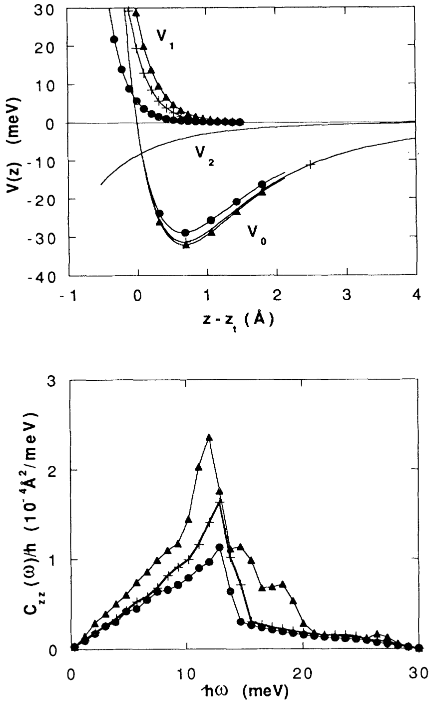

FIG. 2. The top panel displays the physisorption interaction potential for H_2 on Cu(111) (●), Cu(100) (+), and Cu(110) (▲). $V_0(z)$ is the lateral and angular averaged potential, $V_1(z)$ and $V_2(z)$ are the minimum-to-maximum variation of the angular averaged corrugation potential and the laterally averaged angular potential, respectively, at a fixed distance from the surface. The position z of the molecular center of mass is given with respect to the classical turning point z_t at $\epsilon_i = 0$. The bottom panel shows the calculated spectral function $C(\omega)$ vs phonon energy $\hbar\omega$ for Cu(111) (●), Cu(100) (+), and Cu(110) (▲).

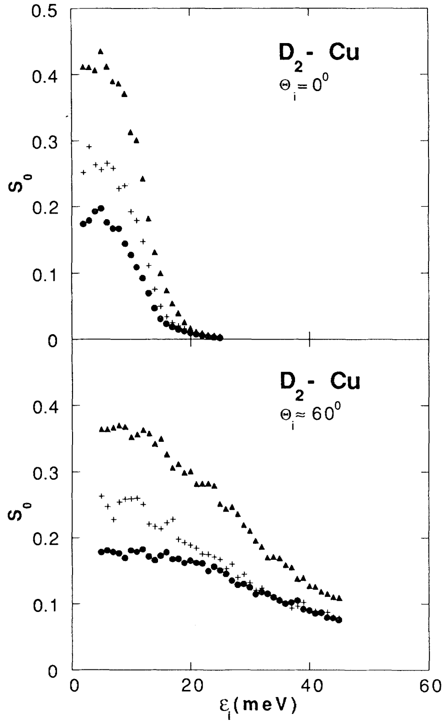

FIG. 3. Single-phonon DWBA calculations of the initial sticking probability S_0 vs particle energy ϵ_i of D_2 on Cu(111) (●), Cu(100) (+), and Cu(110) (▲) at 0° and ~ 60° (61°, 62°, and 61°, respectively) angle of incidence.

sive part of V_0. Small $\mathbf{Q} + \mathbf{G}$ are favored through $C(\omega)$ and this is precisely the virtue of the Cu(110) surface which has significantly smaller $\mathbf{Q}$ and $\mathbf{G}$ vectors in one surface direction. This has a clear effect, as can be seen in the lower panel of Fig. 2, where $C(\omega)$ for Cu(110) is larger than for the other two surfaces over most of the phonon bandwidth. We remark that the difference in the linearly increasing low-energy range derives from the *umklapp* processes. From these observations we expect that the energy transfer to the Cu(110) phonon system should be more efficient in a corresponding manner.

The "standard" theory of sticking in the quantum regime is based on the distorted-wave Born approximation (DWBA) and has been described in many recent papers [4, 10]. Single-phonon DWBA calculations of the normal incidence sticking probability for D_2 on the three copper surfaces are shown in the top panel of Fig. 3. The calculations reveal, in the low-energy range where single-phonon processes dominate, the same relative trend as observed in the experimental data in Fig. 1. S_0 for Cu(110) is substantially larger than for Cu(111) and Cu(100). The difference between Cu(111) and Cu(100) derives from differences in $C(\omega)$ and V_0 both acting to give a larger S_0 for Cu(100). The quantitative agreement between experiment and theory, at low ϵ_i, is somewhat fortuitous since the DWBA calculations are carried out in a perturbative way. This is acceptable for Cu(111) and Cu(100) where experiment and theory agree on a sticking probability of ~0.2 in the low-energy range. It is obvious from the data in Fig. 1 and Fig. 3 that a single-phonon theory is only adequate at low incident particle energies. For energies > 10 meV the experimental data show much larger sticking probabilities than the theory. This is due to multiphonon processes which in principle can be included by higher-order perturbation theory in the DWBA calculations [11]. We have not exploited this possibility in the present work but we will present a thorough discussion of multiphonon effects in another context [12]. Here we just note that the strength of a multiphonon process is essentially determined by a self-convolution of the single-phonon excitation probabilities. These are larger for Cu(110) than for (111) and (100) and as a consequence the difference in the normal incidence sticking probabilities is enhanced at higher energies.

In the glancing incidence case we know that single-phonon processes dominate the energy transfer over the whole energy range. This is manifested via the observed isotope ratio for H_2 and D_2 sticking, which stays approximately constant, $S_0(D_2)/S_0(H_2) \sim 1.4$, over the range of incident energies [12]. This behavior is exemplified for Cu(111) in the bottom panel of Fig. 1. Single-phonon DWBA calculations for D_2 sticking at glancing incidence on the three copper surfaces are summarized in the bottom panel of Fig. 3. These calculations include particles trapped into quasibound states via phonon emission and account for the partitioning of these particles into a fraction that reverts to the gas phase via diffraction and another fraction that sticks via further energy loss to the phonon system [13]. The diffraction process was introduced in the calculations via the corrugation potential V_1 which is shown in the potential summary of Fig. 2. The corrugation strength V_1 was estimated by tuning to the experimentally observed intensity of the first-order Bragg beams from the three crystal surfaces [12]. While V_0, as noted above, varies only weakly with crystal face, V_1 varies substantially; the open (110) surface being the most corrugated and the dense (111) surface the least. When we compare the DWBA calculations displayed in Fig. 3 with the corresponding experimental data in Fig. 1 we find good agreement over the range of incident energies for all crystal faces. The falloff of S_0 with energy has the correct trend; slowest for Cu(111) and most quickly for Cu(110). Incidentally we note that the result for Cu(111) is almost identical to the pure trapping situation, i.e., backdiffraction into the gas phase of particles trapped into quasibound states is sufficiently weak so that sticking via further phonon emission is the dominant process. For Cu(110) the deviation from pure trapping is substantial; S_0 is reduced by a factor of ~ 2 at $\epsilon_i =$ 40 meV. This is caused by enhanced backdiffraction of particles that initially were trapped on this more corrugated surface. The larger S_0 at low ϵ_i for Cu(110) has the same physical origin as discussed in relation to the normal incidence data, i.e., the specific coupling to the phonon system including *umklapp*.

We conclude by summarizing our observations into a general picture regarding the role of the substrate surface structure on the sticking of a gas-phase particle in the physisorption well: (i) The sticking probability at normal incidence will be larger for an open lattice with a larger unit cell than for a close-packed lattice with a smaller unit cell, because smaller momentum transfers are favored by the momentum cutoff in the particle-phonon coupling. (ii) At glancing incidence, trapping is prevalent and the sticking probability for a close-packed weakly corrugated surface lattice is close to the pure trapping limit. (iii) On the open surface the initially trapped particles are more likely to revert to the gas phase via diffraction and the sticking probability will fall off more quickly with increasing particle energy than for a close-packed weakly corrugated surface.

We thank J. Harris for useful discussions concerning this work. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

---

[1] For a review see, *Dynamics of Gas-Surface Interactions*, edited by C. T. Rettner and M. N. R. Ashfold (Royal Society of Chemistry, London, 1991).

[2] J. Perrau and J. Lapujoulade, Surf. Sci. **121**, 341 (1982); C.-F. Yu, K. B. Whaley, C. S. Hogg, and S. J. Sibener, Phys. Rev. Lett. **51**, 2210 (1983); J. Chem. Phys. **83**, 4217 (1985); U. Harten, J. P. Toennies, and Ch. Wöll, J. Chem. Phys. **85**, 2249 (1986); M. Chiesa, L. Mattera, R. Musenich, and C. Salvo, Surf. Sci. **151**, L145 (1985); S. Andersson, L. Wilzén, and M. Persson; Phys. Rev. B **38**, 2967 (1988); L. Wilzén, F. Althoff, S. Andersson, and M. Persson, Phys. Rev. B **43**, 7003 (1991).

[3] K. Schönhammer and O. Gunnarsson, Phys. Rev. B **22**, 1629 (1980).

[4] S. Andersson, L. Wilzén, M. Persson, and J. Harris, Phys. Rev. B **40**, 8146 (1989).

[5] P. Nordlander, C. Holmberg and J. Harris, Surf. Sci. **152**, 702 (1985); **175**, L753 (1986).

[6] Scattering off the (110) surface along the dense atom rows ([1$\bar{1}$0]) results in large differences in selective adsorption but the trapping-sticking behavior is influenced only moderately. This is a consequence of the importance of out-of-plane diffraction processes. A detailed account of these observations will be presented in Ref. [12].

[7] The phonon spectral functions were calculated using a method based on a central nearest-neighbor force constant model with no modifications in the surface region. These spectra will be discussed in Ref. [12].

[8] G. Armand and J. R. Manson, Surf. Sci. **80**, 532 (1979).

[9] V. Bortolani, A. Franchini, N. Garcia, F. Nizzoli, and G. Santoro, Phys. Rev. B **28**, 7358 (1983); V. Celli, G. Benedek, U. Harten, J. P. Toennies, R. B. Doak, and V. Bortolani , Surf. Sci. **143**, L376 (1984).

[10] F. O. Goodman, Surf. Sci. **92**, 185 (1980); **111**, 279 (1981); J. Stutzki and W. Brenig, Z. Phys. B **45**, 49 (1981); M. D. Stiles and J. W. Wilkins, Phys. Rev. Lett. **54**, 595 (1985); V. Buch, J. Chem. Phys. **91**, 3788 (1989).

[11] G. Armand and J. R. Manson, Phys. Rev. B **43**, 14 371 (1991).

[12] M. Persson and S. Andersson (to be published).

[13] The partitioning of the trapped particles on the different crystal surfaces was calculated using the Monte Carlo technique detailed in Ref. [4] but with the difference that S_0 has been calculated by considering their escape probabilities.