Sticking of Molecular Hydrogen on a Cold Cu(100) Surface

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Using nozzle beams of n-H_2, p-H_2, n-D_2, and o-D_2 gases, with incident energies and angles in the ranges 20–75 meV and 30°–70°, we have measured the initial sticking probability, S_0, on a cold (~ 15 K) Cu(100) surface. S_0 comprises a smooth background and a series of peaks with maxima occurring when the incident energy equals a rotational excitation energy. We argue that background and structure arise primarily from parallel-momentum–nonconserving phonon processes during the initial collision.

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With specific reference to the system H_2 or D_2 on Cu(100), we address several matters concerning the sticking of a gas-phase particle incident at a metal surface. They are the following: (i) the relative importance of electronic and vibrational substrate degrees of freedom in dissipating the incident kinetic energy; (ii) the role of internal degrees of freedom such as molecular rotations; and (iii) the relevance of a description in terms of an initial trapping step.

The Cu(100) surface physisorbs H_2 at low temperatures[1] and displays weak diffraction features[2] characteristic of a flat surface. This has suggested a picture of sticking whereby an initial parallel-momentum–conserving process traps the particle at the surface, with probability T. Then only the normal component of the energy $\epsilon_i^z = \epsilon_i \cos^2\theta_i$, where θ_i is the angle of incidence, need be dissipated or converted to rotational or vibrational energy on impact. Most sticking calculations refer to T and it is often assumed, sometimes tacitly, that most trapped particles eventually stick. The sticking probability, S_0, is then essentially equal to T and determined primarily by the normal energy ϵ_i^z. In addition, rotational conversion should be governed by the resonant condition

$$\epsilon_i^z = \epsilon_{j'j} - \epsilon_n, \tag{1}$$

where $\epsilon_{j'j}$ are the rotational excitation energies of the molecule and ϵ_n the bound-state energies of the surface well.

We pointed out previously[3] that the observed dependence of the sticking probability, S_0, on the rotational populations of gas-phase molecules is hard to reconcile with such a model because the matrix elements governing rotational conversion are too small, a conclusion that has since been reaffirmed.[4] We proposed that rotational trapping may occur as a result of collisions with impurities or surface defects which break translational invariance parallel to the surface and couple strongly to rotations. Subsequent experiments with nozzle beams, described below, have not confirmed this suspicion, however. Instead they suggest a picture of sticking processes on the bare surface that is at once intriguing and surprisingly simple. We find no evidence for an initial parallel-momentum–conserving trapping step and conclude that most sticking events involve transfer to the solid of the full particle energy, ϵ_i, on initial collision. We argue that (i) phonon processes dominate the sticking; (ii) coupling to the phonon system is essentially local with full relaxation of parallel-momentum conservation; and (iii) rotational excitation influences the sticking primarily via a resonant enhancement of the particle-phonon coupling. These conclusions are drawn from measurements of the initial sticking probability, S_0, when nozzle beams of n-H_2, n-D_2, p-H_2, and o-D_2 strike a Cu(100) surface at energies between 20 and 75 meV and incident angles between 30° and 70°. Here, n-H_2 and n-D_2 refer to beams having thermal rotational distributions characterized by the nozzle temperature, while p-H_2 and o-D_2 refer to converted gases with predominantly even-j rotations. The most important features of the data from the point of view of the above conclusions are (i) striking isotope effects; (ii) the primacy of the total energy, ϵ_i, rather than the normal energy, ϵ_i^z; and (iii) the occurrence of more or less symmetric peaks in $S_0(\epsilon_i)$ for ϵ_i close to the rotational excitation energies $\epsilon_{j'j} = [j'(j'+1) - j(j+1)]B$, with B the rotational constant of the molecule ($B_{H_2} = 7.3$ meV and $B_{D_2} = 3.7$ meV).

The apparatus[5] consisted of H_2 nozzle beams shaped by skimmers in three differentially turbopumped chambers. The gas was expanded from a 10-μm-diam nozzle at temperatures between 100 and 1200 K (combining liquid-nitrogen cooling and resistive heating). An H_2 (D_2) pressure of 1.1 (1.5) bars produced adequate beam intensities with an energy spread $\sim 20\%$ and an angular divergence of 0.25°. The beam expanded to a diameter of 5 mm and covered almost the entire sample surface. This minimizes the influence of lateral diffusion of adsorbed molecules. p-H_2 and o-D_2 beams were produced via on-line conversion of the normal gases by use of a nickel-silicate catalyst kept at 25 K. Beam intensities were determined with a rotatable stagnation arrangement (1.5° angular resolution) equipped with a calibrated ionization gauge. Beam energies and the relative rotational populations of normal and converted gases were obtained by the performance of diffraction measurements using the same detection arrangement. The sticking and diffraction experiments were performed in a cryopumped UHV system[6] with the Cu(100) sample mounted so that the scattering plane comprised the normal and the [010] direction in the surface.

The sticking probability at zero coverage, S_0, was deduced from the initial slope of the work-function change, $\Delta\phi$, with normalization to values at monolayer saturation. $\Delta\phi$ was measured with a tracking electron-beam retardation method[5,7] with simultaneous monitoring of the specular scattering intensity. The monolayer saturation densities required for the normalization were determined via separate desorption experiments to be $[0.75\ (0.65)]\times 10^{15}/\mathrm{cm}^2$ for D_2 (H_2). These figures, and therefore the absolute sticking coefficients, are uncertain by up to 20%. Relative values, however, are accurate to an estimated 5%. The relation between $\Delta\phi$ and the coverage was measured via partial monolayer desorption.

Figures 1 and 2 summarize a set of measurements of S_0 with incident angle $\theta_i = 60°$ and incident energies ϵ_i between 20 and 75 meV. Data are shown for thermal rotational populations (n-H_2, n-D_2; full circles) and the converted gases (p-H_2, o-D_2; open circles).[8] In each case, S_0 falls off with ϵ_i but shows structure near the rotational excitation energies $\epsilon_{j'j}$. The connection between the structure and molecular rotations is confirmed by the enhancement (suppression) of peaks corresponding to even (odd) j on going from the thermal to the converted gases. All structures are consistent with the selection rule $j' = j+2$, indicating the absence of magnetic interactions. At other angles of incidence between 30° and 70°, the same behavior was found except for an overall scaling $\sim 1/\cos\theta_i$. The beam-detection arrangement did not permit a check of this scaling for normal or grazing incidence.

A direct comparison between H_2 and D_2 is complicated by the rotational structure. Using the data for n- and p-H_2 (n- and o-D_2) together with the known rotational populations we estimate backgrounds that represent roughly the sticking of "spherical" molecules. The backgrounds, S_0^B, are shown in Figs. 1 and 2 (full lines) and their ratio, $S_0^B(D_2)/S_0^B(H_2)$, is plotted in Fig. 3. The ratio displays steplike features close to $\epsilon_i = \epsilon_D$ and $2\epsilon_D$, where $\epsilon_D \simeq 30$ meV is the highest Cu phonon energy. Simple models of the coupling to harmonic phonons[9] predict that for a light (mass m) particle the weight of an n-phonon event is $\sim m^n$. The structure in Fig. 3 is thus suggestive of a switch from one- to two-phonon and two- to three-phonon events as the incident energy increases. If the backgrounds were due to electron-hole sticking, the structure and magnitude of the isotope effect are hard

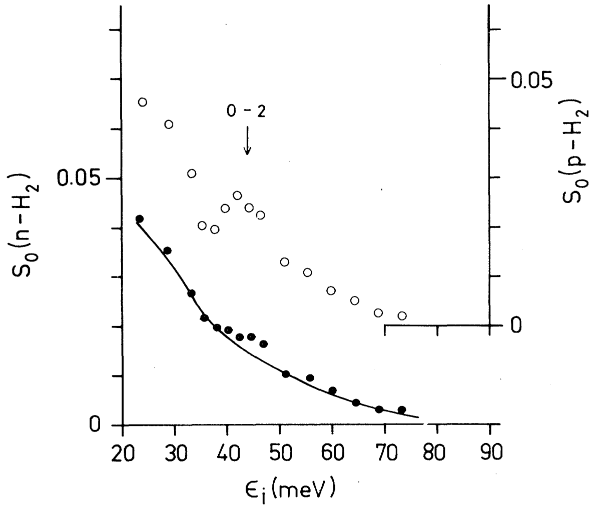

FIG. 1. Initial sticking coefficient, S_0, of n-H_2 (full circles) and p-H_2 (open circles) on a cold (~ 15 K) Cu(100) surface vs molecular-beam energy, ϵ_i. The angle of incidence was $\theta_i = 60°$ with respect to surface normal. The solid line shows an estimated background with the effect of rotations removed.

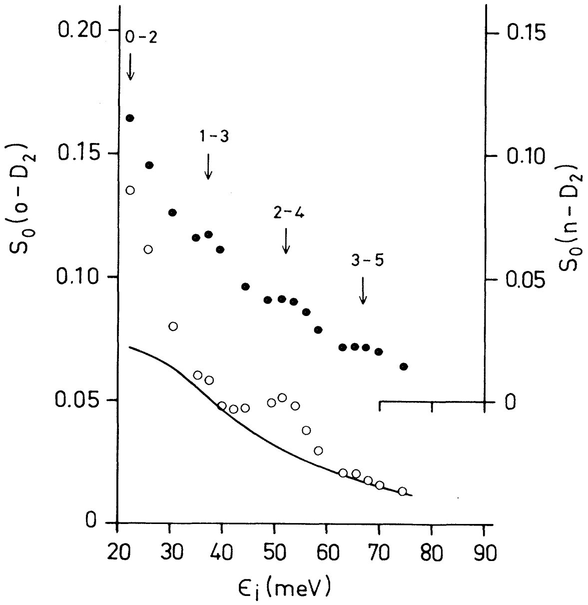

FIG. 2. Same as Fig. 1 but for n-D_2 (full circles) and o-D_2 (open circles).

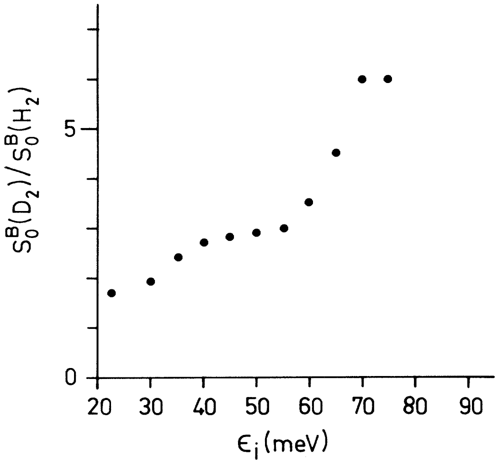

FIG. 3. Ratio of backgrounds $S_0^B(D_2)/S_0^B(H_2)$ (solid lines in Figs. 1 and 2) vs beam energy.

to explain. Since H_2 is lighter it travels faster than D_2 for the same energy and so should give rise to greater electronic nonadiabaticity. Theoretical calculations[10] showed a $m^{-1/2}$ dependence and, furthermore, that electron-hole sticking is negligible where no chemical interaction is involved. We conclude that the backgrounds are due to sticking via phonon excitation.

A general expression for the sticking coefficient in terms of state-to-state transition rates $W_{i\to f}$ is

$$S_0 \sim (1/\sqrt{\epsilon_i}\cos\theta_i)\sum_f{}' W_{i\to f}, \tag{2}$$

where the sum runs over all final states with the particle bound to the surface and the prefactor arises from normalization to the incoming current. The data described above indicate that the prefactor already gives essentially the entire dependence on θ_i (at least, in the range 30°–70°). Thus the sum over transition rates must depend only on the total energy.[11] This is hard to understand on the basis of an initial trapping step and subsequent thermalization of trapped particles. For instance, the model of Stiles and Wilkins,[4] where single-phonon processes are treated via the elastic continuum model and the distorted-wave Born approximation (DWBA), leads to an approximate scaling of the trapping coefficient, T, with ϵ_i^z.[12] Over the range of ϵ_i^z shown in Fig. 1, 5–19 meV, T varies relatively slowly[4] and clearly has little to do with the observed sticking behavior. At the highest energy shown, for instance, T is more than 20 times the measured values of S_0. If, within the same model, the sum in (2) is assumed to refer only to negative-energy particles in the final state, then the one-phonon sticking probability vanishes near $\epsilon_i \simeq \epsilon_D$, where Fig. 3 suggests that two-phonon processes take over. The data would therefore seem to indicate a criterion for sticking whereby the full incident energy is absorbed by the phonon system on initial collision.

The insensitivity of the sum of transition rates in (2) to the incident angle implies that particles which stick "see" a surface that is "rough" on an atomic scale. This would appear to be in conflict with the observation of a strong specular peak and very weak diffraction features in the coherently scattered fraction, which shows the behavior expected of an almost flat surface. A possible resolution of the conflict might be that incoherent events reflect a roughness induced by the molecule-surface interaction, an effect that is absent in the DWBA. A simpler explanation might be that whereas the strength of a given diffraction beam depends on a particular Fourier component of the potential, the sticking coefficient involves a sum over all components. In their DWBA calculations for He/W, Stutzki and Brenig[12] report that a flat-surface approximation (neglect of umklapp) was wrong by a factor of 3, while a purely local particle-lattice coupling reproduced the correct trapping probability within 15%. This result may be potential specific, and, in any event, only indirectly relevant to our data, which for the most part refer to higher-order phonon processes. Nevertheless, the primacy of the total energy, ϵ_i, in the data does point to a local interaction with the lattice, of whatever origin, and nonconservation of parallel momentum for sticking events.

We turn now to the rotational structure. In earlier work[3] we interpreted the influence of rotation in terms of conversion of incident kinetic energy to rotational energy in a trapping step, with defects or impurities playing a major role, and subsequent decay of the rotation with the particle remaining in the well. The present data are hard to reconcile with this interpretation. Exhaustive investigations eliminated defects as a major factor. Furthermore, no marked change of results was observed as a result of exposure to the ambient conditions. We are therefore satisfied that both the background and the structure in the data refer to sticking on the bare Cu(100) surface. In the seeking of an alternative role for the rotations, three features seem to be of importance. Firstly, the rotational structures in Figs. 1 and 2 are more or less symmetric peaks and not edges. (A crude "falling-into-the-well" picture would allow rotational conversion for $\epsilon_{j'j} - U < \epsilon_i < \epsilon_{j'j}$, where U is the well depth of $\simeq 22$ meV.[2]) Secondly, the peaks occur when the total energy, ϵ_i, equals a rotational excitation energy. This indicates that the matrix elements responsible for the rotation are characteristic of a "rough" surface. Thirdly, the rotational structure shows a striking isotope effect. On taking account of the relative rotational populations in the beams and of the Gaunt factors governing rotational transition, we estimate that the 2-4 structure for o-D_2 is $\sim$ 6 times stronger than the 0-2 structure for p-H_2. Since these transitions have roughly the same energy, the large effect points to a strongly massdependent coupling.

These features suggest an intimate connection between rotational structure and phonon excitation. We picture this as follows. A classical oblate particle can transmit momentum and energy to the phonons via its translational motion *and* its spin. An increase in the spin energy at the expense of translational energy during impact can delay the particle, giving the lattice time to carry away sufficient energy to cause sticking. One might thus expect the spin degree of freedom to enhance the sticking probability. When the spin is quantized it would not be unreasonable if the effect occurs most readily when the available energy in the system, ϵ_i, and a rotational excitation energy are equal.[13] The result would then be a rotationally mediated resonant enhancement of the phonon excitation probability. A theoretical treatment of this problem is not straightforward. In particular, the Born series would seem to be a poor starting point, though one would doubtless find resonant behavior in high order as a result of virtual excitation of rotations. Currently, we can offer no explicit theoretical support for our interpretation, which must therefore be regarded as speculation. It is, however, the only interpretation we have found that is not contradicted by the data.

In summary, we end up with a picture of the sticking of H_2 and D_2 on Cu(100) at low temperature that is perhaps surprising but nevertheless remarkably simple. The sticking does not occur in several steps, with trapping on impact and subsequent dissipation, but as a result of the initial collision with the lattice. If this results in transfer of energy ϵ_i to the phonons the particle is irreversibly stuck, regardless of its subsequent behavior. Particles which trap initially but retain sufficient energy to escape do so with high probability.[14] Rotational excitation is an important effect but contributes via the resonant enhancement of the phonon excitation probability rather than an initial trapping via translational-to-rotational conversion. These conclusions imply that the interaction "experienced" by particles which stick has a quite different nature from that deducible from the coherent fraction,[15] a point that has been made previously on theoretical grounds.[9]

This discussion refers only to a restricted range of incident energies and angles. At lower energies than we have been able to measure and at grazing incidence, trapping processes may be more important. In addition, we note that as molecules collect on the surface the sticking coefficient was found to increase markedly because of molecule-molecule collision. This behavior and further details concerning the above will be presented in a future paper.

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[1] S. Andersson and J. Harris, Phys. Rev. Lett. **48**, 545 (1982).

[2] J. Lapujoulade and J. Perreau, Phys. Scr. **T4**, 138 (1983).

[3] S. Andersson and J. Harris, Phys. Rev. B **27**, 9 (1983).

[4] M. D. Stiles and J. W. Wilkins, Phys. Rev. Lett. **54**, 595 (1985).

[5] This newly constructed apparatus will be described in detail elsewhere.

[6] Ambient pressure of 3×10^{-11} Torr. Details concerning cleaning and cooling of the sample have been given in Refs. 1 and 3.

[7] This technique, which caused no obstruction of the molecular beam, turned out to be quite sensitive and fast; 0.5-meV rms noise level at 0.3-s time constant.

[8] The desorption probability has been estimated to be at least 1 order of magnitude smaller than the smallest S_0 shown in the figures.

[9] See, for example, H. D. Meyer, Surf. Sci. **104**, 117 (1981).

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

[11] The dissociation probability of N_2 on W(110) also depends on the total rather than normal energy [D. J. Auerbach, H. E. Pfnür, C. T. Rettner, and J. E. Schaegel, J. Chem. Phys. **81**, 2515 (1984)]. Because of the fundamentally different interaction, this dependence may be of different origin than that for H_2- physisorption on Cu(100).

[12] J. Stutzki and W. Brenig, Z. Phys. B **45**, 49 (1981).

[13] Reference 1 showed that the $\epsilon_{j'j}$ correspond also to long-lived excitations of the physisorbed state.

[14] Possibly due to collisions with steps.

[15] A similar conclusion follows from the insensitivity of the dissociation probability of HD on W(110) to selective adsorption [C. T. Rettner, L. A. DeLouise, J. P. Cowin, and D. J. Auerbach, Chem. Phys. Lett. **118**, 355 (1985)].