Resonant Sticking at Surfaces

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On the basis of data taken for H_2 and D_2 beams impinging on a cold Cu(100) target, it is argued that the sticking of a light inert quantum particle at a metal surface occurs predominantly via resonant processes involving quasibound states. A resonance line in the sticking coefficient is expected whenever the incident particle energy nears a threshold for inelastic scattering from a long-lived local mode.

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The sticking of an incident particle with kinetic energy ϵ_i on a solid lattice is easy to visualize if classical mechanics is valid. The particle follows a unique trajectory determined by the initial conditions and the interactions and its initial impact drives a wave front into the lattice. If the energy carried away by the wave front exceeds ϵ_i the particle is irreversibly stuck. If this energy is less than ϵ_i the particle may escape on rebound or be trapped temporarily, in which case its fate depends on subsequent energy exchange with the lattice. These effects have been demonstrated explicitly in molecular-dynamics calculations.[1-3]

In quantum mechanics, the sticking process is less easy to describe. The conventional picture[4-6] assumes a clean separation of adparticle and target lattice with the particle motion governed by Hamiltonian $H_p = T_p + V_p(\mathbf{x}_p)$, comprising kinetic energy and a "stiff lattice" potential. For a molecule, T_p and $\mathbf{x}_p$ include center-of-mass and relative coordinates. The sticking coefficient is assumed to be related to the rate at which particles transfer from scattering to bound states of H_p by exciting phonons of the target lattice.

Recently, we demonstrated that the sticking coefficients of H_2 and D_2 on a cold Cu (100) surface display structure associated with molecular rotations.[7] A peak in the sticking coefficient was found when the incident energy, ϵ_i, approaches a free molecular rotation energy. Rotational structure is predicted by the conventional picture,[6] but the peaks occur at energies associated with the rotationally mediated selective adsorption resonances characteristic of coherent elastic, or Mössbauer, scattering where the lattice recoils as a rigid unit. These energies depend strongly on incident angle and the level structure of the Hamiltonian H_p and do not correlate at all with the locations of the observed structure.

The purpose of this paper is to present new data for incident energies well within the phonon band which demonstrate conclusively that the sticking of an inert quantum particle does not occur via direct phonon excitation with the particle "falling into a bound state of the well," as the conventional picture assumes, but via resonant processes involving quasibound states of the compound lattice. Such processes have long been known to dominate the cross section for low-energy neutron capture by nuclei.[8] As in the neutron+nucleus case, the relevant quasibound states are features of the many-body Hamiltonian describing lattice plus adparticle and are not to be confused with the "one-body" selective adsorption resonances that characterize the coherent elastic scattering. Experimentally, the quasibound states that give rise to a substantial sticking are found to occur near thresholds for inelastic scattering from sharp local modes. We suggest that they correspond to subthreshold levels where the adparticle is very loosely bound.

The data on which these conclusions are based were taken with use of nozzle beams of H_2 and D_2 impinging on a cold Cu (100) target at incident energies, ϵ_i, in the range 3 to 70 meV and with incident angle, θ_i, between 30° and 70°. The experimental equipment and measurement procedure have been described briefly[7] and further details will be given elsewhere. The extension of the data to low incident-particle energies was achieved by seeding of the beams with a noble gas. Ne was chosen because its low physisorption energy of ~ 10 meV prevents its accumulating on the target at a temperature ~ 10 K. The zero-coverage sticking coefficient of H_2 or D_2 was measured by determination of the initial slope of the work function change as the nozzle beam was turned on. The use of different seedings established energy ranges where the seed gas had no marked influence on the sticking of H_2 and D_2. Measurements with unseeded D_2 beams

down to energies of ~ 8 meV were possible with use of liquid helium as a coolant. These gave the same sticking coefficients as the seeded beams throughout the region of overlap. Data taken by use of beams having thermal rotational populations and catalytically converted beams with only even-j particles were used to construct approximately the sticking behavior that would be displayed by a beam composed solely of $j=0$ molecules.

The resulting sticking coefficients, $S(\epsilon_i,\theta_i)$, are shown in Fig. 1 for $3<\epsilon_i<70$ meV and for $\theta_i=60°$ and 40° (D_2 only). $S(\epsilon_i,\theta_i)$ shows pronounced structure at characteristic energies that are independent of θ_i. As the D_2 data illustrate, changing θ_i effected only an overall scaling of S, i.e., for $30°<\theta_i<70°$,

$$S(\epsilon_i,\theta_i)\simeq S(\epsilon_i)/\cos\theta_i. \quad (1)$$

The higher-energy structures in $S(\epsilon_i)$, at ~ 21 and 42.5 meV for D_2 and H_2 respectively, are the $j=0\rightarrow 2$ rotational resonance peaks. Also shown in Fig. 1 are reconstructions of the sticking coefficients in the higher energy range that D_2 beams having only $j=2$ particles would display (dashed lines). The rotational structure then occurs at ~ 52 meV, corresponding to the $j=2\rightarrow 4$ molecular rotation. In addition to the rotational peaks, $S(\epsilon_i)$ displays two other features: a prominent lower-energy peak centered at $\epsilon_i\simeq 12$ meV and a broad structure at $\epsilon_i\sim 30$ meV. These features occurred at the same value of the incident energy irrespective of angle of incidence, rotational composition, or whether the impinging particles were H_2 or D_2.

Conclusive evidence that the data in Fig. 1 refer to sticking on the flat surface is presented in Fig. 2, where we show the elastic specular reflectivity, $I_{00}/I_0\equiv I(\epsilon_i)$, of D_2 from the Cu (100) surface. If the sticking were occurring at steps or impurities, which do not contribute to $I(\epsilon_i)$, then this and $S(\epsilon_i)$ would show no correlation. As can be seen, the contrary is the case and all structure in $S(\epsilon_i)$ is faithfully mirrored in $I(\epsilon_i)$, though the rotational dip is less pronounced because the reflectivity data refer to thermal rotational populations.[9] Also shown in Fig. 2 are the specular reflectivities of He and Ne particles from the same surface. The He reflectivity displays a prominent feature at ~ 10 meV, with a hint of fine structure, and also shows a clear dip at ~ 28 meV that is barely discernible in the D_2 reflectivity. This suggests that the helium sticking coefficient, which could not be measured because the binding energy is too small to prevent desorption at the lowest attainable surface temperature of ~ 10 K, would show similar behavior

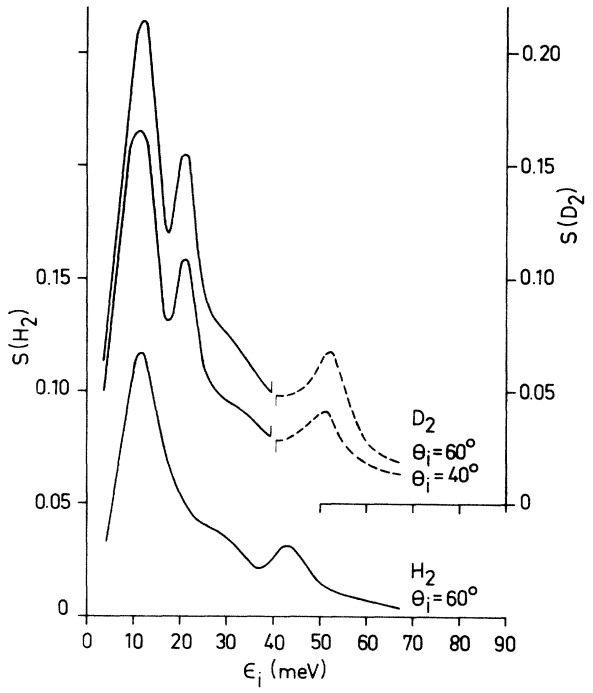

FIG. 1. Sticking coefficients of H_2 and D_2 on a Cu (100) surface (temperature ~ 10 K) as functions of incident beam energy, ϵ_i, and for incident angles $\theta_i=60°$ and 40° (D_2 only). Full lines correspond to incident beams with only $j=0$ molecules. Dashed lines correspond to D_2 beams with only $j=2$ molecules. The curves were constructed by use of raw data taken for beams with thermal rotational populations and converted beams having only even j.

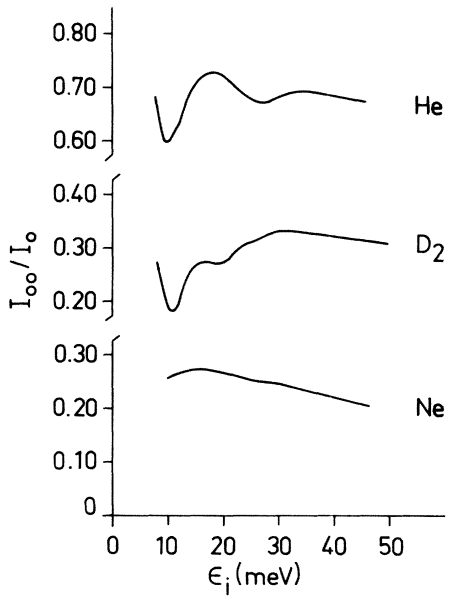

FIG. 2. Specular reflectivity of He, D_2, and Ne from a Cu (100) surface (temperature ~ 90 K) as a function of incident energy, ϵ_i, and with incident angle $\theta_i=60°$. I_0 and I_{00} are respectively the intensities of the incident and specularly reflected beams. The absolute values of I_{00}/I_0 are slightly uncertain.

to that of D_2, with the rotational peaks absent. The Ne reflectivity, on the other hand, is rather featureless.

As background to our interpretation of these data we consider the behavior of the sticking coefficient that would be expected in the conventional picture. For simplicity, we ignore all rotational structure and restrict ourselves to low incident energies. As ϵ_i is lowered below the phonon band edge (~ 30 meV) and into the band, more and more phonons have sufficient energy to transfer the particle to the well. Thus S should increase with decreasing ϵ_i with a saturation towards lower energies because the particle cannot be transferred below the ground state of the well (~ 18 meV). The only structures that can arise are edges that mark the opening of a new channel for single-phonon events, e.g., the onset of transfer to a particular bound level via Rayleigh phonon excitation. This behavior is found in explicit calculations,[5,6] which do not show the sharp peak at ~ 12 meV with strong fall-off to low energies that characterizes the measured sticking coefficient in this energy range.[10] Furthermore, whether a "normal energy" (trapping) or "total energy" (sticking) criterion is used, the conventional model does not at all give the observed dependence on incident angle. The data therefore imply a sticking mechanism that lies outside the scope of this model.

In seeking an alternative explanation we are guided by the similarity between the data of Fig. 1 and measurements of the neutron capture cross sections by nuclei, which show strong, sharp resonant features.[8] These were long ago attributed to the existence of quasibound states in the continuum of the compound nucleus. When the free-neutron kinetic energy approaches a quasibound-state energy, this state is excited and can decay either by reemitting the neutron or via radiative neutron capture. The result is a resonant enhancement of the coupling between the neutron and photon continua, as was shown by Breit and Wigner,[11] who were able to explain the sharp structure in the neutron-capture cross sections in detail.

Transposing their analysis to the surface case, we suppose that the system H_2-Cu(100) possesses a group of essentially equivalent quasibound states at positive energy ϵ_0 that do not interact with each other but decay either by desorbing the H_2 or by emitting phonons into the bulk, with consequent capture of the H_2. The sticking coefficient would then be given by the rate of decay of an initial scattering state resulting from the indirect coupling to the phonon continuum, normalized tc the incident current. A straightforward calculation gives the result

$$S(\epsilon_i,\theta_i) \sim \frac{h^2\bar{n}}{2m_p\epsilon_0\cos\theta_i}\frac{\Gamma_p\Gamma_{\rm ph}}{(\epsilon_i-\epsilon_0)^2+\Gamma^2}, \qquad (2)$$

where Γ is the half-width of a quasibound state, $\Gamma_{\rm ph}$ and Γ_p are the partial widths due to phonon creation and particle emission, m_p is the particle mass, and $\bar{n}$ is an inverse area that depends on the spectral weight of the compound states. (For independent oscillators, $\bar{n}$ is just their surface density.)

Several assumptions and approximations are involved in the derivation of (2), which is intended to be illustrative rather than quantitative. Nevertheless, it is evident that the main features of the data are consistent with a sum of contributions of this form, including the dependence on incident angle [Eq. (1)]. This results from the normalization to the incoming current and relies on the assumption that the decay of a quasibound state via desorption is isotropic over the half space. The resonant attenuation of the specular reflectivity, $I(\epsilon_i,\theta_i)$, is also given by (2) but with the partial width $\Gamma_{\rm ph}$ replaced by the total width, Γ, in the numerator. The theory thus accounts qualitatively for the mirror structure in the reflectivity. A crude estimate of the isotope effect for H_2/D_2 predicted by (2) can be obtained as follows. Comparison of the overall strengths of the 12-meV sticking line (Fig. 1) and the corresponding dip in the reflectivity (Fig. 2) suggests that $\Gamma \sim \Gamma_{\rm ph} \gg \Gamma_p$. In this limit the peak in the sticking coefficient has amplitude $S_{\max} \sim m_p^{-1}\Gamma_p/\Gamma_{\rm ph}$. If we assume that matrix elements depend on m_p only weakly, the mass dependence of $\Gamma_p/\Gamma_{\rm ph}$ is that of the ratio of the free-particle and free-phonon densities of states. Thus $S_{\max} \sim m_p^{1/2}$, a somewhat weaker dependence than observed, but with the correct sign.

This overall good correspondence with the data is compelling evidence that the sticking of a weakly interacting quantum particle on a lattice proceeds preferentially via formation of quasibound states. It remains to consider the nature of these states. An important hint is provided by calculations of the local density of harmonic phonon levels at crystal surfaces which shows sharp, almost singular structures near band edges.[12] The structure arises because the dispersion relations are very flat so that the modes are essentially local. The most prominent structures are associated with flat surface-phonon bands. For Cu(100) these are estimated to fall in the energy range 11–14 meV.[13] The pronounced structure in the sticking coefficient at ~ 12 meV thus falls near *thresholds* for inelastic scattering from these local surface modes. Similarly, the broad 30-meV structure coincides with thresholds for exciting modes of local character close to the bulk band edge.[12] Finally, the rotational peaks fall near the thresholds for rotational excitation of the H_2 or D_2.

This association of all structures in $S(\epsilon_i)$ with threshold conditions for exciting sharp local modes, either of the target or the internal degrees of freedom of the particle, may imply that the quasibound states have to do with threshold resonance. At threshold the delay time of the specular beam diverges because the system

cannot decide through which channel it should exit. However, slight downshifts of the peaks and the fact that the minima in the He and D_2 reflectivities occur at slightly different energies suggest that the states are in fact subthreshold. Their hallmark is then a loosely bound adparticle with a long excursion distance in the van der Waals tail of the interaction. This implies a very weak coupling between the two subsystems so that the total Hamiltonian will have a sharp level whenever either of the subsystem Hamiltonians displays one. This need not be the case if the subsystems are in strong contact.[14]

We conclude with some brief remarks. (i) Dispersion of the nozzle beams has a marked influence on the data of Fig. 1 and may obscure some fine structure. Rough fits using (2) on the assumptions that each peak represents a single quasibound state and that the beam dispersion is Lorentzian gave resonable agreement for the main features and estimated intrinsic widths ~ 4, 2, and 2 meV for the 12-, 21- (D_2), and 42.5-meV (H_2) structures, respectively. These figures may have little meaning, however, and measurements with an improved energy resolution are clearly necessary. (ii) The large values of S at local-mode thresholds should not be thought of as implying that a strong inelastic scattering from these modes would be observed above threshold. In fact, the recovery of the reflectivity above threshold indicates that this scattering is very weak. Equation (2) shows that the resonant sticking coefficient at peak depends only on the *ratio* of coupling strengths to the two continua, not their absolute values. (iii) Though resonant sticking is probably the dominant mechanism for light particles that interact weakly, this will not be the case for massive particles or for strong interactions, where matrix elements for normal processes are large. Resonance lines can only be expected when these matrix elements, which determine the widths, are very small.[15] The almost flat reflectivity curve of Ne (Fig. 2) suggests that this condition is no longer fulfilled for the more massive particle.

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[8]See, for example, J. E. Lynn, *The Theory of Neutron Resonance Reactions* (Clarendon, Oxford, 1968).

[9]The same is true for H_2 which demonstrates that the structure in $I(\epsilon_i)$ is not due to interference effects.

[10]This low-energy falloff is not due to reflection from the attractive branch of the interaction, which plays a role only at extremely low energies.

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[14]The inadequacy of a "stiff-lattice" treatment in this regard has been stressed by T. R. Knowles and H. Suhl, Phys. Rev. Lett. **39**, 1417 (1977). The inequivalence between the quasibound states that lead to sticking and selective-adsorption resonances has a parallel in neutron capture, where it has long been known that mean field theories, which ignore the detailed response of the target nucleons to the incoming neutron, fail spectacularly.

[15]The assumption of pairwise forces is likely to lead to overestimates of these matrix elements because conduction-electron screening has been neglected. This may be the reason why model calculations (e.g., Refs. 5 and 6) give too-large values for the sticking coefficient for H_2-Cu due to direct phonon excitation.