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Crystal-face dependence of physisorption potentials

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We have measured a crystal face dependence of the physisorption energies for H_2 and D_2 interacting with the Cu(111), Cu(100), and Cu(110) surfaces. The trend of potential-well depths, $D_{111} < D_{100} < D_{110}$, is the opposite of that predicted by existing theory. We argue that a larger binding energy for an open crystal face is a consequence of the face-dependent electron-density profiles and their dynamical response, in particular, the influence on the attractive van der Waals interaction.

The interactions between chemically inert adsorbates and metal surfaces have been understood by analogy with the theory of noble gas atom-atom interactions. The total potential energy is approximated as a sum of two contributions—a long range van der Waals attraction, arising from adsorbate-substrate electron correlation and a short range repulsion, introduced by the overlap of the metal Bloch electron tails and the valence electrons of the adparticle. Potentials for He and H_2 physisorption on simple and noble metals have been calculated[1–5] and found to give bound-state energies and scattering intensities in quantitative agreement with experimental observations. These potentials form shallow minima located rather far outside the surface plane of ion cores, in the dilute density of spilling out metal electrons. Theoretical calculations are then conveniently carried out within the jellium model of the metal substrate[6] which implies that the electronic properties related to the detailed surface ionic structure are not accounted for explicitly. It was noted, however, that the repulsive potential branch is very sensitive to the substrate electron work function[1] which varies by typically 10% between dense and open crystal faces of a given substance. Calculations for H_2 adsorption on low-index Al surfaces,[4] accounting for the differences in work functions of the different faces, predict appreciable changes in the H_2 physisorption energies. Established experimental methods exist that could detect this effect and such measurements should provide a critical test of whether a work function correction to the potential is an adequate means to account for the physisorption properties of real crystal faces.

Whereas binding energies for physisorbed species may be determined from desorption or isosteric heat of adsorption measurements, for light adsorbates, a more direct, accurate, and elegant method exists which allows determination of even fine details of the interaction. This is to determine the resonance structure of the elastic backscattering which arises because of a degeneracy between the incident state and a state of selective adsorption. The particle is then trapped in the surface well, but with enhanced parallel kinetic energy or rotational energy or both.

Using selective adsorption measurements we show, with specific reference to the systems H_2 and D_2 on Cu(111), Cu(100), and Cu(110), that the physisorption potential exhibits a clear crystal-face dependence. The measured potential-well depth *increases* by ~ 10% from Cu(111) to Cu(110). Using existing theory we find that the calculated well depths, on the other hand, are *reduced* by ~ 20% because of a *reduction* in the work function by ~ 10%. The difference between theory and experiment is quite remarkable—opposite trends for the physisorption energies and the values diverge by as much as 30% for different crystal faces of the *same substance.* We suggest that this discrepancy is associated with electronic properties related to the surface ion core structure which affect not only the work function and hence the repulsive potential but also the position of the van der Waals reference plane[7] and thereby the attractive potential. Our argument is based on an important observation concerning the face-dependent electron-density profiles of metal surfaces[8] which were found to be strongly influenced by the surface ionic structure. A crucial feature is that the centroid of induced surface charge depends drastically on the exposed crystal face and the attractive van der Waal potential, which is sensitive to this quantity, will increase for the more open faces. We find that this effect more than compensates for the opposing behavior caused by the face-specific work function dependence of the repulsive potential and that the resulting influence of the surface ionic structure on the physisorption energies is compatible with the sequence of well depths we have measured for H_2 on low-index Cu surfaces.

The selective adsorption measurements reported here were performed in a cryopumped ultrahigh vacuum chamber operating at a base pressure of 2×10^{-11} Torr. Using H_2 and D_2 nozzle beams with an optimum energy spread of about 10% and an angular divergence of 0.29°, we sweep the primary beam energy, ϵ_i, and record the specular beam intensity, I_{00}, for fixed polar, θ_i, and azimuthal angles of incidence. From these scans we determine the energies of the resonance features. Families of resonance positions are mapped out by repeating the procedure for a range of θ_i values.

The azimuthal angle has been kept fixed in these measurements and the crystal surfaces were oriented so that the scattering plane, defined by incident and specular beams, 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

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crystal was also investigated in the 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 copper specimens were cleaned *in situ* by standard methods involving argon-ion bombardment and heating cycles and cooled to 80 K using liquid nitrogen as a cryogen and they were heated resistively. We have presented a more detailed description of the apparatus, specimen preparation, and experimental procedure elsewhere.[9]

Figure 1 displays a set of selective adsorption measurements for Cu(111). The resonant transitions and the bound-state energies, ϵ_n, are determined via the fitted kinematical resonance dispersion curves. The condition for a resonance associated with a surface reciprocal lattice vector $\mathbf{G}$ and with rotational transition $j \rightarrow j'$ is $\epsilon_i = \epsilon_n + \epsilon_{jj'} + \hbar^2(\mathbf{K}+\mathbf{G})^2/2m$ where $\epsilon_{jj'}$ is the rotational excitation energy and $\mathbf{K}$ is the wave-vector component parallel to the surface of the incident beam. The transitions in Fig. 1 involve a first order $\mathbf{G}$ vector apart from a $0 \rightarrow 2$ rotational transition for D_2 to a level at -19.0 meV. The p-H_2 and n-D_2 nozzle beams used are, at the beam temperatures of concern, composed predominantly of $j = 0$ molecules (>90% for p-H_2 and about 60% for n-D_2). The measured level energies hence refer to the angular averaged interaction potential.

The result of this analysis for the copper (111), (100), and (110) surfaces is summarized in Fig. 2 where the measured bound-state energies for H_2 and D_2 are plotted versus the mass-reduced level number $\eta = (n+\frac{1}{2})/\sqrt{m}$. This method, of molecular physics,[10] provides an elegant tool to decide if a particular level assignment is compatible with a single gas-surface potential for the two hydrogen isotopes. The data for H_2 and D_2 should then fall on a common curve, a condition that is satisfied for the level sequences plotted in Fig. 2. The curves are well represented by third order polynomical fits and these yield, for $\eta = 0$, the potential-well depths, D, which we have listed in Table I.

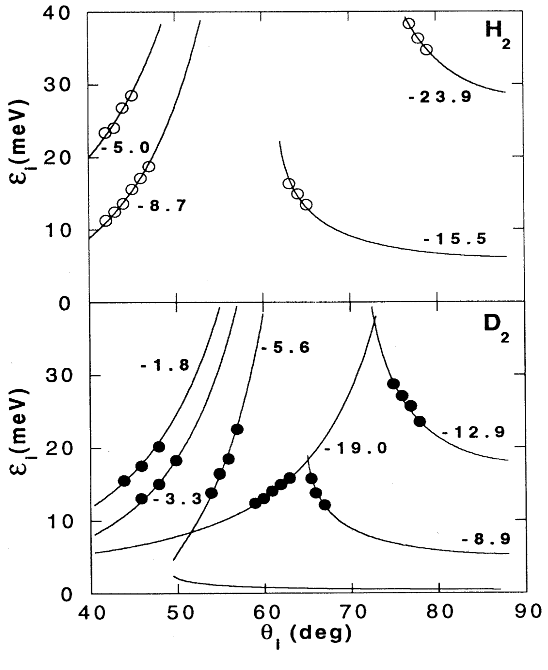

FIG. 1. Dispersion relations for selective adsorption resonances of H_2 and D_2 scattered from Cu(111). Open (full) circles denote resonance energies, ϵ_i, vs incident angle θ_i observed for p-H_2 (n-D_2) nozzle beams. The solid curves are fitted kinematical dispersion relations denoted by the appropriate bound-state level energies in meV.

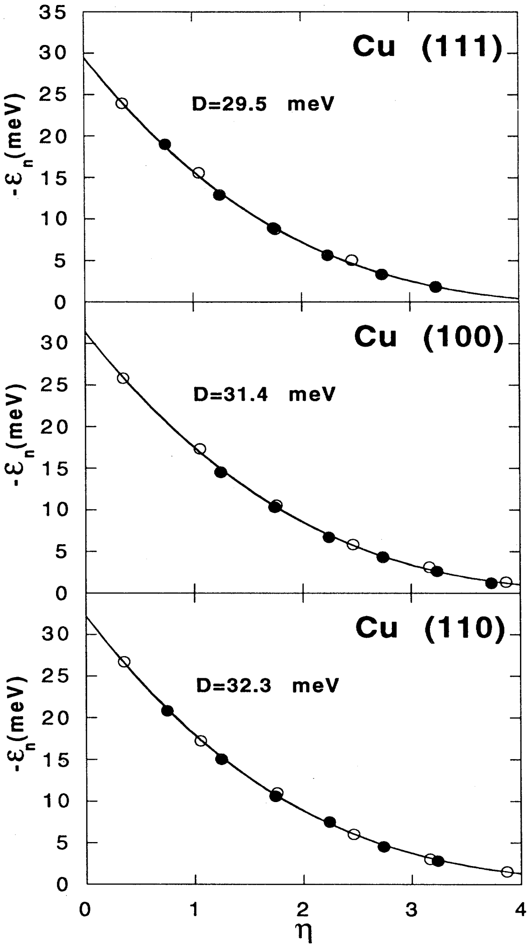

FIG. 2. Bound-state level energies, ϵ_n, vs mass reduced level number, $\eta = (n+\frac{1}{2})/\sqrt{m}$, measured for p-H_2 (○) and n-D_2 (●) beams interacting with three low-index Cu surfaces. The solid curves represent third order polynomial fits to the experimental data and give, for $\eta = 0$, the well depths D.

We have related the measured physisorption energies to potentials which we derive using recent theoretical prescriptions.[4,11] Within this calculational scheme the lateral and angular average physisorption potential involves the superposition of repulsive and attractive contributions V_R and V_{VW}, respectively, whose functional forms are given by

$$V_R(z) = V_0 \exp(-\alpha z), \tag{1}$$

$$V_{VW}(z) = -\frac{C_{VW}}{(z - z_{VW})^3} f(k_c(z - z_{VW})), \tag{2}$$

TABLE I. Physisorption potential-well depths for H_2 on Cu surfaces; D and D_1 (D_2) are measured and calculated values, respectively. The experimental work function values Φ are from Ref. 16. The potential parameters V_0 and α for Cu(110) and $k_c = 0.47a_0^{-1}$ are from Ref. 4 while $C_{VW} = 4.54a_0^3$ eV and $z_{VW} = 0.41a_0$ are from Ref. 11.

Cu	(111)	(100)	(110)
D (meV)	29.5	31.4	32.3
D_1 (meV)	31.7	26.0	24.6
D_2 (meV)	29.2	31.6	32.2
$\delta z_{VW}(a_0)$	−0.09	0.20	0.28
Φ (eV)	4.94	4.59	4.48
V_0 (eV)	5.15	5.60	5.74
α (a_0^{-1})	1.26	1.22	1.21

where z is the normal distance of the H_2 bond center from the jellium edge. In the attractive branch, the van der Waals constant, C_{VW}, and reference plane origin, z_{VW}, depend on the dielectric properties of the substrate and adsorbate. The function f describes the saturation of $V_{VW}(z)$ as the distance $z - z_{VW}$ becomes comparable with the extent of the molecule. In the repulsive branch, the range parameter, α, depends primarily on the substrate work function, Φ, and is approximately given by $2\sqrt{2\Phi}$, which is twice the decay constant of a Fermi surface electron wave function with its wave vector, $\mathbf{k}_F$, normal to the surface. The amplitude parameter, V_0, depends, for a given adsorbate, on the work function, the precise form of the surface potential, and the density of electrons at the selvedge.

The repulsive potential is clearly very sensitive to the metal electron spill out. In the theoretical calculations this is determined from the Lang-Kohn jellium model of a metal surface.[6] It was noted, however, that this model did not reproduce the metal work functions with sufficient accuracy. In order to overcome the problem, a renormalization scheme was suggested[1] where the jellium one-electron potential is adjusted by using the experimental work function values. The sensitivity of the physisorption potential to the work function is the direct cause to the changes in physisorption energies for H_2 on the different Al surfaces.[4] A surface with a higher Φ value has a smaller amplitude of metal electron wave functions at the position of the molecule leading to a smaller overlap and less repulsion than a surface with a lower Φ.

The potential-well depth for H_2 adsorbed on Cu(110) was calculated previously[4] and we have used the parameters for this system to derive values for H_2 on Cu(111) and Cu(110) by adjusting V_0 and α to account for the differences in work functions.[12] The calculated well depths, D_1, the work function values, and the relevant potential parameters are listed in Table I. We find that a 10% reduction in Φ from Cu(111) to Cu(110) reduces D_1 by ~20%. Considering that we are dealing with crystal faces of the same substance, it is remarkable that the measured and calculated physisorption potentials give opposite trends for the sequences of well depths, diverging by as much as 30%.

The work function corrected potential can evidently not provide a physical explanation of the experimentally observed sequence of H_2 physisorption energies. We argue that the difference between experiment and theory is associated with electronic properties related to the surface ionic structure which affect not only the work function and hence the repulsive potential but also the position of the van der Waals reference plane and thereby the attractive potential. We will give grounds for our argument below but following this line of reasoning we have determined shifts, δz_{VW}, of the van der Waals reference plane origin required to adapt the calculated well depths to the experimental data. The calculated potentials were adjusted via a least square fit to the experimental bound-state energies. The corresponding well depths, D_2, are listed in Table I together with the shifts δz_{VW}. We find that the measured sequence, D, is well reproduced by an outward shift of $0.37a_0$ from Cu(111) to Cu(110).

Our argument for a crystal-face-dependent position of the van der Waals reference plane is based on an important observation made by Monnier *et al.*[8] in their theoretical treatment of the face-dependent electron density profiles of metal surfaces. They found that the profiles are often not jelliumlike but depend strongly on the exposed crystal face. For a given metal the most densely packed face has the tightest density profile, while conversely the least densely packed face has the most spread out profile. This behavior will, at least qualitatively, influence the repulsive potential in the same manner as the work function correction discussed above.

The crucial feature found in these calculations is a drastic shift of the centroid of induced surface charge with crystal face. The centroids are, for example, located $1.08a_0$, $1.83a_0$, and $2.57a_0$ outside the jellium edge for the Al(111), (100), and (110) faces, respectively. This quantity, $d(0)$, is equal to the static limit of the frequency dependent centroid of induced surface charge, $d(iu)$, which enters into the expression for z_{VW}.[7] An approximate formula for $d(iu)$ is given by[11,13,14]

$$d(iu) = \frac{d(0)\lambda\omega_p^2}{\lambda\omega_p^2 + d(0)u^2}, \tag{3}$$

where ω_p is the jellium plasma frequency and λ is determined from the static electron-density profile.[15] Using the calculated profiles for the Al faces[8] and the same dielectric properties as in previous calculations of the van der Waals reference plane position for H_2 on Al,[11] we find that $z_{VW} \approx 0.58d(0)$ for all three faces and hence shifts from $0.63a_0$ for Al(111) to $1.06a_0$ for Al(100) and $1.50a_0$ for Al(110). These large shifts affect the corresponding physisorption energies dramatically. The previously calculated well depths for H_2 on Al(111), (100), and (110) (Ref. 4) are 30.4, 32.3, and 27.6 meV, respectively. These values were obtained for $z_{VW} = 0.85a_0$. If we use the face-dependent z_{VW} values listed above, keeping all other parameters the same as in Ref. 4, we arrive at a remarkably different sequence of well depths 23.8, 40.0, and 58.4 meV. We note that the trend is the same as we observe experimentally for H_2 on the Cu faces, i.e., the largest well-depth is found for the open crystal face.

The electron-density profiles and the induced charge distributions for the Al crystal surfaces were calculated using a pseudopotential method.[8,15] Corresponding calculations for Cu surfaces have not been carried out and would presumably, because of the Cu 3*d* shell, require another theoretical approach. We have therefore obtained estimates of the van der Waals reference plane origin for the Cu surfaces using the values derived for the corresponding Al faces. The calculated values of z_{VW} for H_2 on Cu and Al are $0.41a_0$ and $0.85a_0$, respectively.[11] The ratio is ~ 0.5 and we arrive at an outward shift of z_{VW} by $0.45a_0$ from Cu(111) to Cu(110). Such an increase in the value of the van der Waals reference plane origin would, as we found above, increase the physisorption potential-well depth for Cu(110) enough to reverse the trend caused by the face-specific work function dependence.

In conclusion we have found that the physisorption energies of an inert adsorbate interacting with metal crystal surfaces will be larger for an open face than for a densely packed face of a given substance. This behavior can be understood from the face-dependent electron-density profiles and their dynamical response, which for the open crystal face cause the van der Waal attractive contribution to the physisorption potential to increase more than the Pauli repulsive contribution does.

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