Applied Physics Report No. 95-29

Physisorption energies: Influence of surface structure

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(January 30, 1996)

Abstract

The crystal face dependence of the physisorption energies for H_2 and D_2 interacting with low-index faces of Al and Cu has been measured. The effect is pronounced for Al. The data show that the (111) and (110) faces of Al display similiar potential well-depths, larger by 40 % than the well-depth for the intermediate (100) face. We discuss this surprising result in the light of conventional theoretical models and show, in particular, that these fail to take account of important non-asymptotic effects in the face dependent electron density profiles.

In analogy to inert atom - atom interactions, the interactions between chemically inert adsorbates and metal surfaces can be thought of as a competition between a long range van der Waals attraction and a short range Pauli repulsion. The former devolves from a correlation effect and falls off at large distances like z^{-3}, and the latter is due to the overlap of the metal Bloch orbitals tails in the selvedge with the occupied orbitals of the adparticle. The interactions of He and H_2 and simple and noble metal surfaces have been calculated [1–5] and found to give bound-state energies and scattering intensities in quantitative agreement with experimental observations. The resulting potential wells form shallow minima located rather far outside the surface plane, as defined by the lattice of ion cores, where the contours of the electronic distribution have flattened out to a considerable extent. This allows as a first approximation the use of the jellium model of the metal [6], within which lateral variations due to discrete nature of the ionic lattice are ignored. In the jellium model, in particular, the He- and H_2- surface interactions are independent of crystal face.

The simplest way of including a face sensitivity is via the dependence of the Pauli repulsion on the substrate electron workfunction [1]. This can vary by, typically, 10 % between dense and open faces of a given crystal. Changes in the work function influence the electron spill-out at the surface and hence the overlap of orbitals. Calculations for H_2 adsorption on low-index Al surfaces [4] that take account of the differences in work functions of the different faces (renormalized jellium model) predict a small but systematic face dependence of the interaction with larger workfunction faces having larger well-depths.

Using selective adsorption measurements we show, for the systems H_2 and D_2 interacting with low-index surfaces of Al and Cu, that the physisorption potential does, in fact, exhibit a clear crystal face dependence. The trend of potential-well depths, D, differ for the two metals. For Cu, we observed a rather small face sensitivity, with the well-depths following the sequence $D_{111} < D_{100} < D_{110}$. This correlates in a simple manner with the degree of close packing of the crystal faces, but in the opposite way to that suggested by the renormalized jellium model. This finding has been reported previously [7]. For Al a much larger face-sensitivity is found with no simple correlation between well-depth and closeness of surface packing. Specifically, $D_{100} < D_{111} < D_{110}$. The measured well-depth actually *increases* by about 40% on going from Al(100) to Al(110) , while Nordlander et al. [4] predicted a $\sim 10\%$ *reduction* that correlates with the smaller (110) workfunction. This qualitative discrepancy in two cases, and in particular for the case of Al, where both theory and experiment show a relatively large effect, suggests that the renormalized jellium model does not contain the essential elements of the face-senstivity. In this paper, we elaborate on the measurements that allow this conclusion and discuss elements of the theory that might account for the discrepancies.

Measurements of the physisorption well parameters were performed in a cryopumped ultra-high vacuum chamber operating at a base pressure of 2×10^{-11} Torr. The crystal targets were kept at 80 K during the selective adsorption measurements and their surfaces were oriented so that the scattering plane, defined by the incident and specular particle beams, comprised the surface normal and the $[11\bar{2}]$ direction (Al(111)), the [011] direction (Al(100)), the [001] direction (Al(110)) in the surface plane. These alignments were found to be accurate within 0.5° as determined from diffraction measurements around the scattering plane. The x-ray aligned ($< 0.2°$) and polished aluminium specimens were prepared *in situ* by standard methods involving cycles of low-energy argon-ion sputtering and heating to 775K. This procedure produced clean and well-ordered (111) and (100) surfaces as revealed by high-resolution electron energy loss spectroscopy and elastic H_2 scattering. H_2 diffraction measurements revealed a substantial amount of disorder on the (110) surface as previously observed in elastic He atom scattering studies [8]. We found, however, that the ordered (110) domains produced coherent scattering of adequate quality for the selective adsorption measurements. Preparation of the Cu surfaces, the measurement procedure and a more detailed description of the apparatus have been presented elsewhere [9].

The H_2 and D_2 nozzle beams had an optimum energy spread of about 10 % and an angular divergence of 0.29°. For fixed polar, θ_i, and azimuthal angles of incidence, we sweep the primary beam energy, ϵ_i and record the specular beam intensity, I_{00}. The energies of the resonance features are determined from these scans and families of resonance positions are mapped out by repeating the procedure for a range of θ_i values. The condition for a resonance associated with a surface reciprocal lattice vector $\mathbf{G}$ and with rotational transitions $j \rightarrow j'$ of energy $\epsilon_{jj'}$ is

$$\epsilon_i = \epsilon_n + \epsilon_{jj'} + \frac{\hbar^2}{2m}(\mathbf{K}+\mathbf{G})^2 \tag{1}$$

where ϵ_n is the bound state energy and $\mathbf{K}$ is the wavevector component parallel to the surface of the incident beam. The resonant transitions and the bound state energies are determined by fitting the experimental resonance dispersion curves to calculated dispersion relations as described previously [7]. The assignments can be checked by changing the azimuthal angle of incidence and by using para-H_2 and ortho-D_2 beams in combination with the normal species.

The result of this analysis is summarized in Fig. 1 where the measured bound level energies for p-H_2 and n-D_2 interacting with the aluminium (111), (100) and (110) surfaces are plotted versus the mass reduced level number $\eta = (n+\frac{1}{2})/\sqrt{m}$. This mode of display is used because data for H_2 and D_2 should then fall on a common curve [10]. Clearly, this condition is well satisfied for the level sequences plotted in Fig. 1a. To obtain estimates of the well-depths, D, the curves are fitted to a third order polynomial which is then extrapolated to $\eta = 0$. Since the nozzle beams are composed predominantly of $j = 0$ molecules, the level energies refer to the rotationally averaged interaction. The measured sequence of physisorption well-depths for H_2 and D_2 interacting with low-index Al surfaces is accordingly: 37.4 meV, 28.3 meV and 40.4 meV for the (111), (100) and (110) surfaces, respectively. The corresponding measurements for Cu have been presented elsewhere [7] and the observed sequence of well-depths is listed in Table I together with the values for Al.

The observation of similar well-depths for the most close-packed and most open Al faces, larger by as much as 40% than the well-depth for the intermediate (100) face is quite surprising and certainly not anticipated. In analyzing selective adsorption data, questions as to uniqueness of assignment can arise because of the possibility of absent features in the data devolving from *e.g.* more deep lying levels. In the present case, we note that no assignment of the selective adsorption features observed for the (100) face could be made on the basis of physisorption potentials corresponding to well-depths between 30 and 50 meV. This is detailed in Fig. 1b where we show three plots of the data for Al(100) that assume different assignments of levels and give different well-depths. The middle curve corresponds to a well-depth of around 40 meV, which is of the expected magnitude given the (111) and (110) results. However, the data for H_2 and D_2 do not fall on a common curve and the discrepancies are much larger than can be accounted for by experimental errors in the resonance levels (estimated to be around 0.2 meV) or by violation of the scaling law [10]. Thus, in spite of the similarity of the well-depth to those of the (111) and (110) faces, the middle curve is incompatible with the data. The upper curve does display accurate scaling behaviour, but the well-depth of 56 meV would imply a desorption temperature significantly larger than the observed value of 10-15 K [11]. Thus the well-depth assignment of 28.3 meV for Al(100) is the only one that is compatible with the available data.

We now discuss the calculation of physisorption potentials using recent theoretical prescriptions [4,12]. Within this calculational scheme the laterally and rotationally averaged physisorption potential involves the superposition of repulsive and attractive contributions V_R and V_{VW}, respectively. The repulsive branch is determined from the shift of the metal one-electron energies by the molecule. This contribution may be calculated by perturbation theory in a pseudo-potential description of the molecule and is, in a jellium model, given by,

$$V_R(z) = \int_0^{\epsilon_F} d\epsilon_z n(\epsilon_z; z) \langle\langle v_{ps} \rangle\rangle. \tag{2}$$

Here $n(\epsilon_z; z)$ is the local density of metal electron states with perpendicular energy ϵ_z at the normal distance z of the H_2 bond center from the jellium edge, and ϵ_F is the Fermi energy. The double average of the molecular pseudopotential is defined as,

$$\langle\langle v_{ps} \rangle\rangle = \int \frac{d^2 k_{||}}{A} \int \frac{d\Omega_{\hat{n}}}{4\pi} \langle \mathbf{k}_{||}, \kappa | v_{ps}(\hat{n}) | \mathbf{k}_{||}, \kappa \rangle, \tag{3}$$

where the matrix element of $v_{ps}(\hat{n})$, at a molecular orientation $\hat{n}$, is between inhomogenous plane waves with parallel wave vectors $\mathbf{k}_{||}$ and a decay constant κ determined by the value of the metal potential, $v_m(z)$, and the normal energy ϵ_z. A is the area of the range of the integration of $\mathbf{k}_{||}$ that is limited by its maximum possible value $\sqrt{2m(\epsilon_F - \epsilon_z)}$. The resulting $\langle\langle v_{ps}\rangle\rangle$ depends weakly on ϵ_z, and has a z-dependence through the surface potential, $v_m(z)$. The local density of states, $n(\epsilon_z; z)$, falls off exponentially away from the surface, which results in an exponentially repulsive potential $V_R(z)$. The face dependence of $V_R(z)$ will show up predominantly via the behaviour of $n(\epsilon_z; z)$.

The attractive branch, V_{VW}, derives from the van der Waal attraction and is represented via the functional form,

$$V_{VW}(z) = -\frac{C_{VW}}{(z - z_{VW})^3} f(k_c(z - z_{VW})) \tag{4}$$

where C_{VW} is the van der Waals constant, z_{VW} is the reference plane position, and the function f describes the saturation of $V_{VW}(z)$ as the distance $z - z_{VW}$ becomes comparable with the extent of the molecule. C_{VW} and z_{VW} depend on the dielectric properties of the substrate and adsorbate. The expression for z_{VW} involves also a surface quantity; the centroid of the surface charge, $d(iu)$ induced by an external frequency dependent field. Among these parameters only z_{VW} is expected to be face dependent.

In the theoretical calculations of the crystal face dependence of the physisorption potential, Nordlander *et al.* [4] proposed to neglect the crystal surface dependence of the van der Waals attractive branch and to treat only the repulsive branch. This was done using the "renormalized jellium model" proposed by Zaremba and Kohn [1]. The jellium potential is renormalized so as to reproduce the measured workfunction and the position of the ionic background edge is adjusted to preserve charge neutrality. The calculated well-depths, D_{RJM}, listed in Table I display the expected correspondence with the trend of workfunctions, Φ.

The strong disagreement even in trend with the experimental well-depths, D, listed in Table I indicates that the renormalized jellium model fails to describe the salient features of the face dependence. The argument that this devolves only from the repulsive branch, whose overall magnitude depends on the asymptotic fall off of the density, which depends directly on Φ, would seem not to be correct.

In fact, both aspects of this argument are incorrect. Firstly, the face dependence of the attractive branch is not negligible. This branch falls off like $(z - z_{VW})^{-3}$ [13] and the origin parameter, z_{VW}, depends on a surface quantity; the centroid of surface charge induced by an external frequency dependent field. Andersson and Persson [7] found that the observed well-depth sequence for the faces of Cu could be explained as a result solely of the sensitivity of the parameter z_{VW} to crystal face. Secondly, as we now show, the common assumption that the electron density trend in the selvedge can be deduced from the workfunction turns out to be incorrect.

Fig. 2 shows plots of the laterally averaged density profiles, $n(z)$, outside an Al surface for the three cases (111), (100) and (110). In Fig. 2a the density profiles are obtained using the Zaremba-Kohn procedure. As noted in Table I, the magnitude of the densities in the selvedge follow the work function trend. Figure 2b shows self-consistently calculated density profiles obtained within a model where the ion-cores in the surface region are represented by laterally averaged Ashcroft pseudopotentials [15]. The surface ion-core layers were placed in their bulk positions except for the two outermost (110) planes which were shifted in accordance with experimental observations [16]. This model is one-dimensional with respect to the ion-core layers and retains much of the computational simplicity of the jellium model. It should be more accurate for the close packed faces and least accurate for the open (110) face where lateral electron redistribution may be significant. The calculated values of the workfunction are 4.19, 4.30, and 3.84 eV, displaying the same trend as the experimental values listed in Table I. The density profiles, however, do not reflect these values in a simple manner. In the region where the H_2 physisorption interaction has its minimum ($z \sim 4a_0$), the (110) surface has by far the highest density (which is consistent with the lower work function) but the high workfunction (100) surface has larger density than the (111) surface, displaying a reversal of trend. The reason for this is that the behaviour of the density in this region is governed by near-field effects [17] and not by the asymptotic fall-off of the density, which sets in only for $z > 12$ a_0.

The repulsive branch of the physisorption interaction is determined essentially by $n(z)$, and the modified electron density profiles obtained from our pseudopotential model would, retaining the assumption that the attractive branch displays no face-dependence, predict the sequence of well-depths $D_{111} > D_{100} > D_{110}$. Specifically, we find that the face dependence of V_R due to these profiles gives well-depths of 39.6 , 29.5 and 23.0 meV for the (111), (100) and (110) faces, respectively. Including the face-dependence of V_{VW} that results from the origin parameter z_{VW} in the manner of Liebsch [12], but with the modified density profiles [18], changes the calculated well-depths to 30.7, 28.9 , and 27.7 meV for (111), (100) and (110), respectively. The ordering of the two close-packed faces is as found experimentally; though the difference is rather small because the face-dependencies of V_R and V_{VW} work against each other in a delicate manner, but the value for the (110) surface is much smaller than found experimentally.

Tentatively, therefore, we can attribute the apparently anomalous finding that $D_{100} < D_{111}$ to near-field effects. The well-depths follow the trend in electron density in the relevant region and this is not governed by the workfunction. The anomalous behaviour of D_{110} is not explained but this could be due to the failure of the laterally avergaged pseudopotential model for open surfaces.

In conclusion, we have presented measurements of the physisorption well parameters for H_2 and D_2 on the (111), (100) and (110) faces of aluminum and copper. The experimental well-depths are consistently smaller on faces having larger workfunction, a correlation exactly opposite to that expected on the basis that the main origin of the face sensitivity is the Pauli repulsion and that this follows in trend the asymptotic fall-off of the electron density, which is governed by the workfunction. This indicates that the theory needs refinement in order to treat the effect of the crystal structure. We have considered two effects and found them to be important. First, it was shown with the aid of specific calculations for aluminium using pseudopotentials that the repulsive branch of the physisorption well has a crystal face-dependence which depends on near-fields and so does not correlate with the asymptotic behaviour of the electron density. Second, a pronunced face-dependence of the van der Waals branch was revealed by calculating the van der Waals origin for the actual density profiles. These calculations explain the trend for the two most close-packed faces of aluminium but not the behaviour of the open (110) surface. They also reveal a delicate cancellation of terms and a quantitative comparison calls for a theory at a more fundamental level.

Financial support from the Swedish Natural Science Research Council is gratefully acknowledged and for MP also in part by USA's National Science Foundation under grants DMR 91-03466 and 94-07055.

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TABLES

TABLE I. Measured workfunctions, Φ, and well-depths, D. The well-depths D_{RJM} are the calculated values in the renormalized jellium model for Al (Ref. [4]) and Cu ([7]). The workfunctions Φ_{calc} and the well-depths D_{calc} are the calculated values in the laterally averaged pseudo potential model, in which the observed relaxations of the two outermost surface layers are included for the (110) surface [16] and the values for k_c and C_{VW} are the same as in Ref. [4].

	Al			Cu		
	(111)	(100)	(110)	(111)	(100)	(110)
Φ (eV)	4.24^a	4.41^a	4.06^a	4.94^b	4.59^b	4.48^b
Φ_{calc} (eV)	4.19	4.30	3.85			
D (meV)	37.4^c	28.3^c	40.4^c	29.5^d	31.4^d	32.3^d
D_{RJM} (meV)	30.4	32.3	27.6	31.7	26.0	24.6
D_{calc} (meV)	30.7	28.9	27.7			

^{a} Ref. [14], ^{b} Ref. [19], ^{c} this work, and ^{d} Ref. [7]

FIGURES

FIG. 1. Measured bound-state level energies, ϵ_n, versus mass reduced level number, $\eta = (n + \frac{1}{2})/\sqrt{m}$. a) shows plots for p-$H_2$ and n-D_2 beams interacting with three low-index Al surfaces. The solid curves represent third order polynomial fits to the experimental data and give, for $\eta = 0$, the well-depths D. b) shows plots of the data for Al(100) that assume different assignments of the levels.

FIG. 2. Calculated electron density profiles, $n(z)$, of three low-index Al surfaces as a function of the distance from the jellium edge. a) depicts the results for $n(z)$ in the renormalization scheme while b) depicts the corresponding results obtained in the quasi-one dimensional pseudopotential model. n_B is the bulk jellium density corresponding to an electron gas density parameter $r_s = 2.07$.