Experimental Determination of the Turning Point of Thermal Energy Helium Atoms above a Cu(001) Surface

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The effective height of CO islands above a Cu(001) surface has been determined to be 2.3 Å from six interference maxima in the energy dependence of a specularly scattered He beam. Calculations of the He-CO-Cu potential and a best fit of the data show that the He-Cu(001) potential, recently predicted by Chizmeshya and Zaremba, must be shifted outwards by 0.64 ± 0.2 Å. Since the position of this potential is based on the electron spillout predicted by the jellium model, its use in the case of Cu(001) must be re-examined.

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The potential between an atom and a metal surface is of fundamental importance for understanding a wide range of gas surface interactions. Accurate experimental data are only available for relatively few systems [1], and the problem has aroused considerable theoretical attention. The most successful approach, as exemplified by the recent extensive calculations of Chizmeshya and Zaremba (CZ) for the rare gases on the low index faces of Cu, Ag, and Au [2], goes back to the pioneering study of Zaremba and Kohn [3]. In this model the potential is treated as a superposition of a short range repulsive and a long range attractive potential. The positions of these potentials are determined, respectively, by the edge of the jellium background z_B [3], which is assumed at a distance $\frac{1}{2}d$ above the outermost plane of atoms with interlayer spacing d, and by the position of the reference plane z_{vdW} for the van der Waals potential. Any uncertainties in their locations will have a direct effect on the potential.

In the present experiments we have determined for the first time the position at which a helium atom is reflected from a metal surface in order to compare directly with the predicted range of the potential. To measure the position of the helium atom turning point we create islands of known height and distance above the outer plane of atoms. The height difference between the islands and the uncovered surface is determined by observing interferences in the specularly scattered intensity of a helium atom beam as a function of incident energy. Atoms scattered from the top of the islands and from the clean surface have a relative phase difference given by

$$\Delta\phi = \Delta k_z h + \alpha(\Delta k_z), \qquad (1)$$

where Δk_z is the change in the perpendicular component of the helium atom wave vector that occurs on scattering from two hard wall surfaces with height difference h. The additional phase shift introduced by the differences in the attractive wells and corrugations of the two surfaces is accounted for by the phase factor α. For the specular direction Δk_z is given by $2k_i \cos\theta_i$, where k_i is the magnitude of the incident wave vector and θ_i is the incident angle. As the incident energy is varied, constructive interference and maxima in the intensity occur for $\Delta\phi = 2n\pi$ and minima occur for $(2n + 1)\pi$, where $n = 0, 1, 2, \ldots$. The quantity α is expected to be small as long as the kinetic energy of the incident helium atom is large compared to the attractive well depth, which is typically of the order of 6 meV for metal surfaces [1,2,4]. For a given He surface potential model α may be calculated and the predicted positions of specular intensity maxima and minima compared with experimental data.

Islands of $c(2 \times 2)$ CO on Cu(001) were chosen since it is well established from low-energy electron diffraction spectroscopy (LEED) [5], electron-energy-loss spectroscopy (EELS) [6], and near-edge x-ray-absorption fine structure spectroscopy (NEXAFS) [7,8] experiments that the weakly chemisorbed molecules (binding energy 0.58 eV [9]) have their axis perpendicular to the surface at "top" sites with a C-Cu spacing of 1.90 ± 0.1 Å and a C-O spacing of 1.15 ± 0.1 Å [5,8,10]. For the bare Cu(001) surface not detectable He diffraction peaks could be observed, indicating a surface corrugation of less than 1×10^{-3} Å. The 96° fixed angle helium atom scattering apparatus and the Cu(001) cleaning procedure are described elsewhere [9,11]. The measurements are performed by measuring the specular intensity as a function of the time of flight, as the incident energy is increased linearly with time from 5.4 ($k_i = 3.2$ Å^{-1}) to 130 meV ($k_i = 15.8$ Å^{-1}) by ramping the temperature of the helium beam source. The time of flight coordinate is then transformed to Δk_z. This technique has the advantage that the velocity resolution is determined only by the time of flight apparatus components and is not limited by the velocity spread of the beam [12]. CO chemisorbs on a Cu(001) surface at temperatures below 170 K [10]. For a surface temperature of 120 K and for coverages of $\theta > 0.12$ monolayer (ML), where the $c(2 \times 2)$ saturation structure corresponds to $\theta = 0.5$, sharp oscillations in the specular intensity as a function of Δk_z were observed. They indicate the formation of single layer islands of adsorbate. Figure 1 shows clearly

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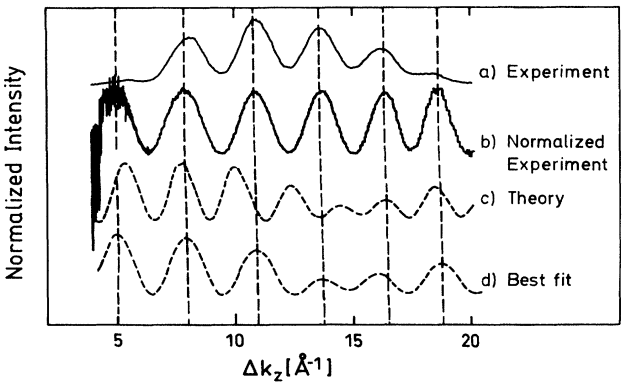

FIG. 1. Specular intensity of helium atoms scattered from islands of CO ($T = 120$ K, $\theta \approx 0.2$) on a Cu(001) surface as a function of perpendicular momentum transfer to the surface. Curve *a* gives the raw experimental data while *b* shows the measured data smoothed by an experimental envelope function. Curve *c* shows theoretical results for an interaction potential obtained as a linear superposition of He-CO gas phase potentials modified for the surface interaction, and using the He-Cu(001) potential calculated by Chizmeshya and Zaremba [2,4]; see text. In curve *d* the origin of the CZ potential has been shifted outwards by 0.64 Å, providing a much better fit. Note that the spacing in *b* decreases with increasing Δk_z, reflecting differences in the steepness of the repulsive potentials.

six maxima in the specular intensity as a function of Δk_z for $\theta = 0.2$ measured along the $\langle 100 \rangle$ azimuth. From the detailed analysis given below it is found that the maxima correspond to $\Delta\phi = 4\pi$ to 14π. From the positions of the strongest peaks for $\Delta\phi = 6\pi$ to $\Delta\phi = 12\pi$ and neglecting the second term on the right in Eq. (1) an effective height $h_{\text{eff}} = 2.3 \pm 0.05$ Å is determined.

The CZ potential for He-Cu(001) is a sum of a repulsive potential $V_R(z)$ given by [2]

$$V_R(z) = V_0(1 + \gamma_z)\, e^{-\gamma z}, \tag{2}$$

and an attractive van der Waals potential $V_{\text{vdW}}(z)$ given by

$$V_{\text{vdW}}(z) = \frac{C_{\text{vdW}}}{(z - z_{\text{vdW}})}\, f_2[\gamma(z - z_{\text{vdW}})], \tag{3}$$

where ($V_0 = 1.487$ eV, $\gamma = 2.718$ Å^{-1}) and $C_{\text{vdW}} = 0.227$ eV Å^3, and f_2 is the Tang-Toennies damping function [2,4]. The potential has a minimum of $\epsilon = 5.76$ meV at a distance $z_m = 3.00$ Å above the jellium edge, which is situated at $z_B = 0.814$ Å above the top layer of Cu. The jellium edge location includes the small charge neutrality correction (-0.0881 Å) of Nordländer and Harris [13].

The gas phase He-Co potential is well characterized both theoretically and experimentally. The theoretical potential of Thomas, Kraemer, and Diercksen [14] (hereafter referred to as the TKD potential) has been shown to give good agreement with the experimental inelastic He-CO scattering cross sections and differential cross section measurements [15]. Further, an excellent fit to diffusion and viscosity data for He/CO gas mixtures was achieved [16,17] by this potential with an additional small 0.75% inward contraction of the radial function in the zeroth order term of the Legendre polynomial expansion. The scattering measurements and the transport data are sensitive to the position of the potential zero and its repulsive part, respectively, but are relatively insensitive to the form of the potential well. A potential produced by fitting recent IR absorption data on ^{3}He-CO and ^{4}He-CO van der Waals dimers gives a potential zero position that agrees well with that of the TKD potential, whereas the attractive part of the potential is 23% larger than the TKD potential [18]. Since the repulsive part of the He-CO potential is the most important in the current context, we take the TKD potential (with the minor correction to give the "POT11" potential proposed in [17]) as the basis for our He-CO potential, but scale the attractive part so as to fit the well depth derived from the IR data.

For CO adsorbed on a Cu(001) surface the CO electronic distribution is slightly affected by adsorbate-substrate binding. As a result, the position of the repulsive part of the potential of the adsorbed CO with the incoming He atom may be changed with respect to that of free CO. This effect has been checked in *ab initio* Hartree-Fock calculations on free CO and on Cu_nCO, $n = 1, \ldots, 34$ cluster models representing the CO/Cu(100) system [19–21]. The results show that the electronic charge distribution well above the CO adsorbate (above its oxygen center) decays exponentially with distance and that the actual charge and its decay length are very close to that of the free CO distribution. In particular, at distances corresponding to the turning point of the helium atom, the CO electronic charge density for CO adsorbed on Cu(001) is identical within 1% to that of free CO. It may therefore be safely concluded that there is no significant change to the repulsive part of the He-CO potential.

Modifications to the van der Waals potential due to the presence of image charges on the surface and the change in polarizability of the adsorbed CO molecule are discussed in detail by Lovrić and Gumhalter in [22], and in Table III of [22] the relevant coefficients are given for the He-CO-Cu interaction. It is interesting to note that by increasing the attractive part of the TKD He-CO potential by 23% so as to fit the IR data on He-CO clusters, the attractive part of the TKD is brought into almost exact agreement with the van der Waals potential predicted by Lovrić and Gumhalter in [22] for the He-free CO interaction.

A simple pairwise addition of He-CO interactions at the surface is justified by the weak lateral CO-CO interactions as determined from the small dispersion of the CO frustrated translational mode in the densely packed, $\theta = 0.5$ layer [11]. Figure 2 shows that the resulting potential

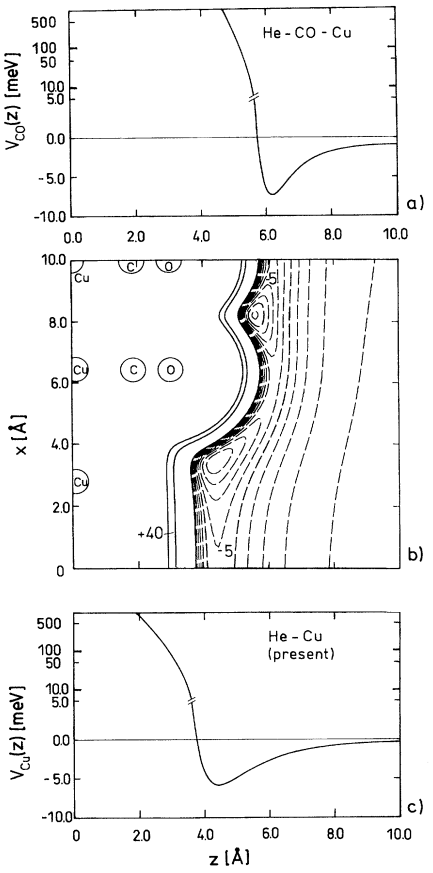

FIG. 2. (a) The theoretical He surface potential energy modified for the surface interaction as a function of distance, z, from the surface above a CO molecule. (b) Potential contours of the He-CO-Cu(001) interaction potential at the edge of a CO island in the ⟨100⟩ direction with the origin of the potential of Chizmeshya and Zaremba shifted outwards by 0.64 Å to fit the experimental data. The dashed lines show negative potential contours and have a spacing of 1 meV, and the solid lines show positive potential contours with a spacing of 40 meV. (c) The potential energy curve for the clean Cu(001) surface determined in the present work.

differs between locations above CO islands and above the bare Cu surface. Overall, the potential variation is shallower and its repulsive part steeper above the CO islands compared to the bare Cu surface. In order to estimate this difference and the corrugation-induced phase shift, which together correspond to the second term on the right in Eq. (1), the specular scattering intensity was calculated within the "sudden approximation" (SA) proposed in [23] as a function of Δk_z. This approximation ignores multiple scattering contributions, which are considered separately [24]. The specularly scattered amplitude from a unit cell of the $c(2 \times 2)$ structure was added to that of a corresponding area of the uncovered Cu(001) surface. The latter must be multiplied by a weighting factor that includes the fraction of the surface covered by CO islands and the ratio of the Debye-Waller factors for the two surfaces. Because of the large inelastic scattering cross sections associated with the frustrated translation mode of the CO molecule the Debye-Waller factor for the CO overlayer is expected to be very large [11], and so the weighting factor was set to 0.1 for the calculations shown in Fig. 1. The weighting factor affects only the intensity of the calculated signal, and not the position of the maxima and minima. Note also that the experimental intensities were not corrected for the varying instrument response function.

Figure 1 compares the experimental dependence of the specular intensity on Δk_z with SA predictions. Curve a is the raw data, and curve b is the raw data divided by the observed intensity envelope to assist peak position identification. Curve c is the dependence calculated for the CZ potential for the He-Cu(001) interaction and the TKD He-CO potential modified as described above. Neither the positions nor the spacing of the maxima, especially of those with the most intensity, agree with the experimental data. The predicted positions of the maxima between $\Delta k_z = 5$ Å^{-1} and $\Delta k_z = 20$ Å^{-1} correspond to an effective height of the CO island of $h_{\text{eff}} = 2.9 \pm 0.05$ Å, considerably larger than the value of 2.3 ± 0.05 Å determined directly from curve b as described above. As can be seen from curve d of Fig. 1 a much better fit of the data is obtained by shifting the He-Cu(001) potential outwards by 0.64 Å while keeping the form of the potential the same. The quality of the fit was noticeably degraded by varying the outward shift by ± 0.2 Å, and so this is taken as the experimental error.

The shift of 0.64 ± 0.2 Å determined here is quite consistent with the differences between the CZ potential ($z_m = 3.00$ Å) and two independent calculations. One is a self-consistent-field (SCF) calculation for He interacting with a small cluster of Cu atoms which predicts $z_m = 3.545$ Å [25]. The other is an additive atom potential model for He-Cu(111), which yields $z_m = 3.41$ Å [26]. In an unpublished SCF calculation Chizmeshya also predicted an outward shift of about 1 Å [27]. For Ag(111) and Ag(110) Jónsson and Weare [28] also expect that the jellium model gives values too small by about 1 Å.

In conclusion, our helium atom interference experiments indicate that the effective island height of CO islands above a bare Cu(001) surface is 2.3 ± 0.05 Å. This is to be compared with a value of 2.9 ± 0.05 Å as predicted using He-CO gas phase potentials, modified for effects arising from adsorption, and the CZ He-Cu(001) potential. In order to fit the experimental data the effective origin of the He-Cu(001) potential must be shifted outwards by 0.64 ± 0.2 Å. Thus we conclude that the jellium model cannot provide a reliable method for determining the origin of the repulsive potential for a copper surface. As discussed by Chizmeshya [27] this may have to do with the d core in the transition metals which tends to shift the $4s$ valence shell electron outwards.

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