Influence of the Local Surface Structure on the 5*p* Photoemission of Adsorbed Xenon

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(Received 24 May 1979)

This Letter analyzes peaks in ultraviolet photoemission spectra due to the $5p_{3/2}$ and $5p_{1/2}$ levels of Xe atoms adsorbed on various surfaces. The binding-energy shifts are used to distinguish between (a) Pd- and Pt-like adsorption sites on Pd-Pt surfaces, (b) the 5×1 and 1×1 modification of an Ir(100) surface, and (c) step sites and terrace sites on a stepped Ru(0001) surface. The findings are ascribed to local work-function effects and to initial- and final-state orbital energy effects. Xe atoms are thus a very sensitive, local, surface probe.

Originally the interaction between rare gas atoms and a solid surface was ascribed to mere van der Waals or dispersion forces (physisorption). These interaction energies should be rather unspecific and of comparable magnitude with the bonding forces in solid rare gases. Low-energy electron-diffraction (LEED) investigations tend to support this assumption, since frequently the formation of hexagonally close-packed layers is observed.[1-3] With the system Xe/W(110) even preadsorption of oxygen did not influence the sequence of LEED patterns.[4] Only a substrate-lattice-induced orientation of the hcp xenon overlayer as a whole has been observed in some cases.[1,5]

Doubt of the validity of this unspecific interaction model arose, for example, from the magnitude of work-function changes and adsorption energies observed with xenon adsorption on different metals and different crystal faces of the same metal, respectively.[6] Discussion of partial charge transfer between a xenon atom and the metal surface according to Mulliken's charge-transfer, no-bond (CTNB) model[7] led to better agreement between theoretical and experimental adsorption energies.[6] Quite recently the first direct experimental evidence for true electronic interaction was demonstrated for the system Xe/Pd(110) by means of ultraviolet photoelectron spectroscopy (UPS).[8] Furthermore, on the same Pd(110) surface Xe atoms exhibited a surprisingly high sensitivity to coadsorbed species like oxygen and carbon monoxide.[9] This effect manifested itself in the photoemission spectra, where the Xe $5p_{3/2}$ and $5p_{1/2}$ ionization levels were significantly shifted on the energy scale with respect to the Fermi level E_F as a function of the amount of coadsorbate.

The present communication demonstrates with three examples the pronounced influence of the substrate structure on the photoemission spectra of Xe adsorbed on (1) PtPd surfaces, (2) the reconstructed (5×1) and the unreconstructed (1×1) surface of Ir(100), and (3) a stepped Ru(0001) surface. The experimental setup has been described in detail earlier.[8,10] Figure 1 shows UP (He I) spectra of a Pd(110) surface containing different amounts of evaporated Pt. All spectra were recorded in an ambient Xe atmosphere at 100 K. The maxima arising from the Xe $5p_{3/2}$ and Xe $5p_{1/2}$ levels are located (with respect to E_F) at 6.2 and 7.35 eV on clean Pd(110) (spectrum *d*) and at 5.1 and 6.4 eV with a surface completely covered by Pt (spectrum *a*). The latter values are identical to those found with compact Pt(111).[9,11] For intermediate alloyed surfaces, spectrum *b* is clearly composed of two sets of Xe 5*p* peaks shifted by ~0.7 eV with respect to each other (note the reduced minimum between the peaks !) and spectrum *c* shows an intermediate shift. It is obvious to associate the two xenon states (spectrum *b*) with xenon atoms being adsorbed at Pd- and Pt-like adsorption sites, respectively. The separation of the Xe 5*p* spectra on both pure metal surfaces is 1.1 eV, strongly suggesting the operation of the different work functions: $\varphi_{\text{Pd}}{}^{\text{clean}} \approx 5.0$ eV, $\varphi_{\text{Pt}}{}^{\text{clean}} \approx 6.0$ eV. However, as no precise values of the absolute work functions φ for both surfaces are available, it is not clear whether $\Delta\varphi$ gives the full explanation of the observed Xe peak separation. Nevertheless it is evident that such measurements provide a *local* probe of the surface structure.

An Ir(100) surface offers an elegant way to prepare *in situ* two different surface structures on the same bulk substrate, i.e., the unreconstructed (1×1) structure with a "normal" square surface geometry and the reconstructed (5×1) structure which exhibits hexagonal atomic arrangement.[12,13] The work function of the (1×1) surface exceeds that of the (5×1) surface by 150 meV.

Figure 2 exhibits UP(He I) spectra for both modifications of the clean and xenon-covered Ir(100) surfaces. The xenon $5p_{3/2,1/2}$ maxima are

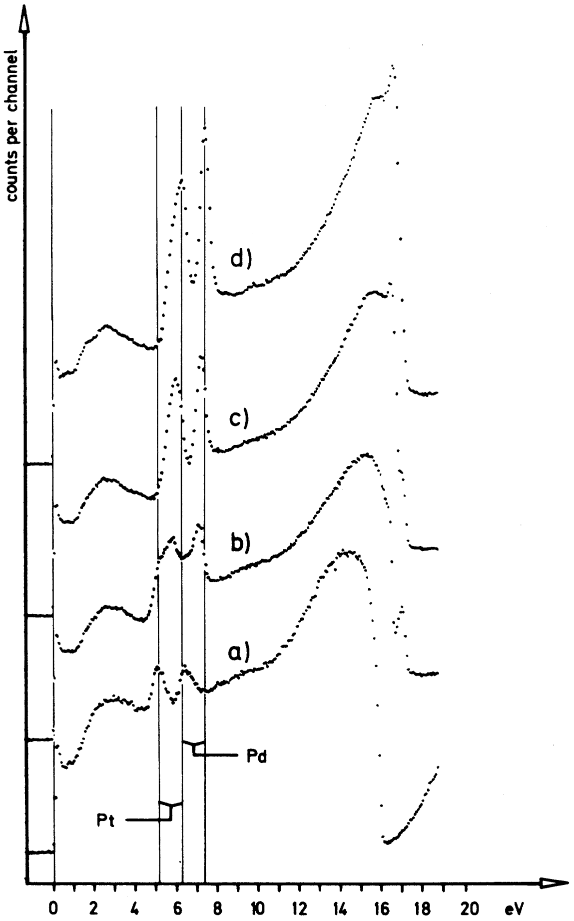

FIG. 1. UP (He I) spectra of xenon-covered PtPd surfaces. (a) Pd(110) surface heavily Pt covered at 100 K (Auger electron spectorscopy probing about four layers deep indicated only a small remaining Pd signal), (b) Pt/Pd(110) surface of (a) after a short flash up to 100 °C, (c) Pt/Pd(100) surface of (a) after a short flash to 200 °C and (d) Pd(110) surface of (a) after heating up to 400 °C. On the as-prepared surfaces xenon was adsorbed at 100 K and an ambient pressure of (a) 5×10^{-6} Torr, (b) 5×10^{-8} Torr, (c) 1×10^{-7} Torr, and (d) 1×10^{-7} Torr Xe.

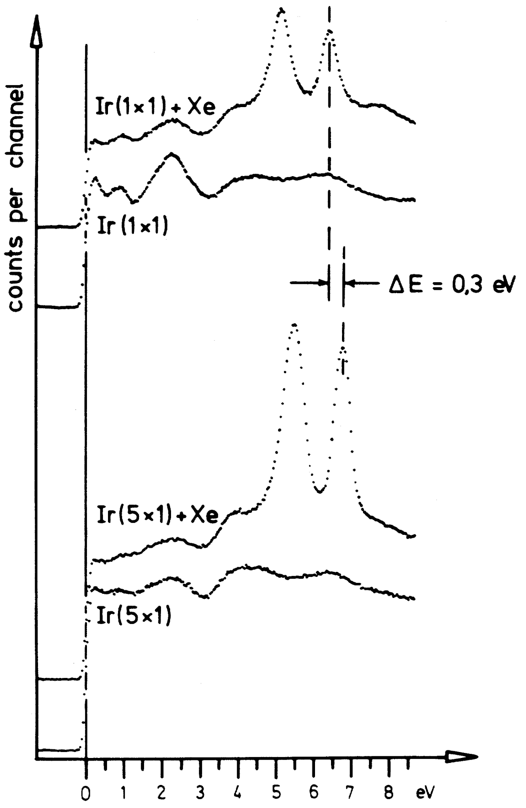

FIG. 2. Expanded UP (He I) spectra of the clean and xenon covered (1×1) and (5×1) surface structures of Ir(100). Xe adsorption at 100 K and 5×10^{-6} Torr Xe.

separated by 280 meV between the two surfaces; again for the surface with the higher work function the adsorbate emission occurs at lower binding energy. However, it is to be noted that the peak shift (0.28 eV) is about twice as large as the work-function difference (0.15 eV). Again the local character of this effect can be demonstrated: By proper thermal treatments surfaces with work functions between the two limiting cases can be prepared. The corresponding photoemission spectra allow identification of adsorption on local patches with either (1×1)- or (5×1)-like configuration of the surface atoms.[14]

Figure 3 shows the influence of local surface condition even more pronounced: This figure displays spectra over the energy range of the Xe peaks for different xenon exposures of a stepped Ru(0001) surface. At low coverages Xe $5p_{3/2}$ and Xe $5p_{1/2}$ peaks emerge at 6.4 and 7.6 eV, respectively. With increasing coverage, an additional set of Xe $5p_{3/2,1/2}$ peaks develops at 5.6 and 6.9 eV, hence, shifted to lower binding energy (with respect to E_F) by 0.8 eV as compared with the low-coverage Xe state. At saturation coverage the high-coverage xenon state (Xe II) is about ten times as intense as the persisting low-coverage xenon state (Xe I). From separate measurements,[15] it follows that the adsorption energy as well as the dipole moment of the Xe I state are considerably larger than the corresponding quantities of the Xe II state. These findings together with the step density on the RU(0001) surface (as deduced from LEED) strongly suggest identifying Xe I and Xe II with atoms adsorbed at step sites and on terrace sites, respectively.

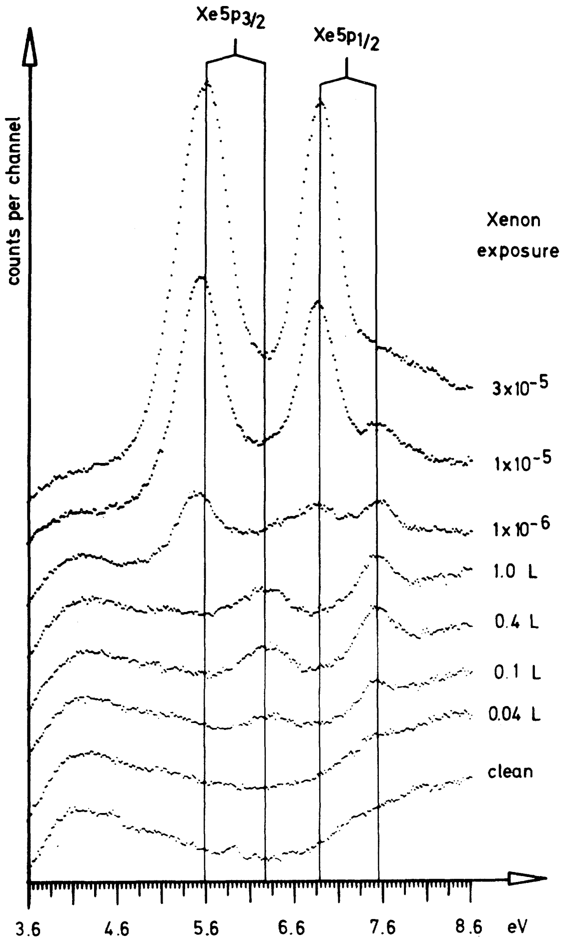

FIG. 3. $5p_{3/2}$ and $5p_{1/2}$ photoemission (He I) features of xenon adsorbed on a stepped Ru(0001). Xe adsorption at 100 K and the indicated exposures (1 L $=10^{-6}$ Torr sec).

Explanation of the multipeaked spectra found in the three examples described above in terms of band-structure effects within the Xe overlayer[16] may be excluded, because the features persist far below monolayer coverage.

Comparison of the different values for the binding energies (with respect to the *Fermi level*) of the Xe $5p$ levels shows that the numbers may differ by as much as 1.3 eV [Xe I/Ru(0001) − Xe/Pt(111)]. In order to decide whether these variations of the ionization potentials are characteristic for the respective adsorption situation the ionization potentials of adsorbed xenon have to be compared with those of gaseous xenon (12.1 and 13.4 eV with respect to the vacuum level, respectively). Taking into account that a photoemission experiment probes the difference between final-state orbital energies ϵ_f and initial-state orbital energies ϵ_i leads to

$$V_{I,\,\mathrm{gas}}=V_{I,\,\mathrm{ad}}+\varphi+\Delta(\epsilon_f-\epsilon_i), \tag{1}$$

where $\Delta(\epsilon_f-\epsilon_i)=(\epsilon_f^{\,\mathrm{ad}}-\epsilon_i^{\,\mathrm{gas}})-(\epsilon_i^{\,\mathrm{ad}}-\epsilon_i^{\,\mathrm{gas}})$ accounts for the difference of these energies in the gas phase and the adsorbed layer, respectively. φ is the work function of the clean substrate surface. Hence, a comparison of $V_{I,\mathrm{ad}}$ values measured for different surface conditions on the basis of Eq. (1) is reduced to variations of φ, ϵ_f, and ϵ_i.

The (ground state) $\epsilon_i^{\,\mathrm{ad}}$ values are determined by the specific bonding interaction between a xenon atom and its adsorption site. This interaction via prevalent dispersion forces and some chemisorptive bonding contribution may vary from site to site as is, in fact, suggested by the different adsorption energies detected on different metals, on different faces of the same metal,[6] and at terrace sites as compared with step sites on the Ru(0001) surface.[15] An effect due to variation of ϵ_i upon $V_{I,\,\mathrm{ad}}$ is therefore expected. $\epsilon_f^{\,\mathrm{ad}}$ energies in turn are determined by the interaction of the hole state with the electron gas of the metal substrate. The resulting relaxation effects therefore again depend on the local dielectric properties of the surface.

Finally one has to consider that the work function is only a macroscopic average quantity. The actual local value φ_{local} at an inhomogeneous surface, for instance at the step sites of our Ru(0001) surface, at the crystallographically different surface patches of the partially reconstructed Ir(100) surface, or at the two-component PtPd surfaces, may deviate appreciably from the macroscopic φ. The extent to which the more conceptional splitting into work-function, final-state, and initial-state effects is justified cannot be decided at the moment, since no experimental possibility to distinguish between these contributions is available.

Horn and Bradshaw[16] have been able to measure the UPS spectra of xenon in the gas phase, adsorbed on Pd(100), and in the bulk state in one and the same spectrometer with respect to a common reference level, i.e., the Fermi level of the Pd sample, which enabled them to account for the work-function contribution of the substrate. However, this holds only for a uniform macroscopic work function but not for variations of φ on the microscopic scale. Horn and Bradshaw also pointed to the unsolved problem of separating $\Delta\epsilon_i$ and $\Delta\epsilon_f$ contributions to the measured ionization potentials.[16]

Apart from these difficulties the present results demonstrate that UPS data from adsorbed Xe atoms provide a sensitive tool for probing local surface inhomogeneities. In particular, it is suggested that this technique can be used in selective adsorption studies to identify surface compositions of multicomponent systems. The weakness of the xenon-metal bond and the low temperature to be applied guarantee that no adsorption-induced segregation will occur. As demonstrated in the case of the Ir(100) surface which reconstructs only in the topmost atom layer,[17] the xenon adsorption method should also give the surface composition of the outermost atomic layer only.

Financial support of this work by the Deutsche Forschungsgemeinschaft Sonderforschungsbereich 128 is gratefully acknowledged.

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Temperature Dependence of the Shear Modulus and Melting of the Two-Dimensional Electron Solid

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(Received 30 April 1979)

The temperature dependence of the shear modulus μ in the two-dimensional electron solid has been determined in a computer simulation. It is found that at low temperatures T, μ decreases linearly with increasing T. A sharp drop of μ together with the onset of electron diffusion in the range $140 > \Gamma > 120$, where $\Gamma = e^2(\pi n_s)^{1/2}/k_B T$, suggestes a melting point consistent with the experiment by Grimes and Adams. The results presented here are consistent with recent theories of dislocation-mediated melting in two dimensions.

In a recent experiment, Grimes and Adams[1] have observed the formation of a two-dimensional (2D) electron solid for electrons on the surface of liquid helium. They find a melting temperature T_m which we write as $\Gamma_m \simeq 137 \pm 15$, where $\Gamma = (\pi n_s)^{1/2} e^2/k_B T$ and n_s is the areal electron density.

A theoretical estimate for the melting point of this system has first been given by Platzman and Fukuyama.[2] They use a self-consistent phonon theory to calculate the effects of phonon-phonon interactions and find an instability in the transverse mode at $\Gamma = 2.8$ which they identify with the melting point.

More recently, an estimate for Γ_m has been given by Thouless,[3] based on the theory of dislocation-mediated melting, which was proposed by Kosterlitz and Thouless,[4] and analyzed in greater