Photoemission from Physisorbed Xenon: Evidence for Lateral Interactions

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(Received 18 July 1978)

A marked splitting of the $5p_{3/2}$ peak in the uv photoemission spectrum of physisorbed Xe is observed for the first time. The splitting depends on the concentration in the adlayer, becoming apparent just before maximum coverage is reached. The lateral interactions responsible for this effect also produce a strong dispersion of the $5p$ levels.

One starting point in the investigation of the factors governing the adsorption behavior of gases on metal surfaces is physical adsorption, or physisorption. Physisorption energies are typically a few tenths of an eV implying a very weak, van der Waals interaction between the adlayer and the metal. Chemisorption energies range from 0.5 to 5.0 eV, depending on the strength of the chemical bond formed with the surface. Physisorption systems thus offer the opportunity to extract certain general effects in adsorption and to study them in a situation unhindered by strong interactions with the substrate. Using this philosophy we investigate in this paper the uv photoemission spectrum of the system Xe/Pd(100). Various measurements[1-3] on physisorbed xenon have shown that, whereas the spin-orbit splitting of the $5p$ levels and their intensity ratio correspond to those in the gas phase, the $5p_{3/2}$ peak is considerably broadened with respect to the $5p_{1/2}$. Waclawski and Herbst,[1] and later Herbst,[4] have attributed this effect to an unresolved doublet resulting from the splitting of the $5p_{3/2}$ hole state in the crystal field of the substrate-atom cores. Matthew and Devey,[5] as well as Antoniewicz,[6] have pointed out, on the other hand, that this model requires unreasonably large positive charges on surface atoms in order to produce the observed splitting. The latter authors have used an image-charge screening model,[7] which predicts a different relaxation shift for the component states of the degenerate $5p_{3/2}$ level. The two explanations predict exactly the opposite energetic ordering of the two split levels in the spectrum. Our angle-resolved photoemission results from the Xe/Pd(100) system confirm that the $5p_{3/2}$ level is indeed marginally broader at low coverages, but show that a considerably stronger splitting occurs at higher coverages. This effect already becomes apparent at approximately three-quarters coverage and we attribute it to a direct lateral interaction, namely, the overlap of $5p$ orbitals on neighboring Xe atoms. The same lateral interaction leads to strong dispersion effects with both the $5p_{1/2}$ and the two split $5p_{3/2}$ levels changing in energy up to 0.5 eV with varying polar emission angle. We suspect that in earlier experiments[1-3] measurements were performed at high coverage and that a certain degree of ordering was present on the surface. Under these conditions it is clear that the combination of strong splitting and dispersion in an angle-integrated experiment such as that of Waclawski and Herbst would be the main cause of the observed broadening.

The measurements were performed in an angle-resolving photoelectron spectrometer (Vacuum Generators) using He I radiation ($\hbar\omega = 21.2$ eV). The experimental geometry has been described previously.[8] The Pd(100) single crystal was prepared by standard techniques[9] and mounted such that the plane of emission corresponded to the [011] azimuth. It was possible to cool the crystal to ~80 K using liquid N_2 or even lower using liquid He. The formation of the ordered xenon overlayer[10] could be checked with LEED (low-energy electron diffraction).

The growth of the spin-orbit–split $5p$ levels as a function of coverage for a particular angular configuration is shown in Fig. 1. At low coverages the $5p_{3/2}$ level is found to be ~0.1 eV broader than the $5p_{1/2}$ level, which may be attributed to one of the mechanisms described above. As the coverage increases the $5p_{1/2}$ level becomes narrower, with the FWHM (full width at half-maximum) reducing from 0.50 (±0.05) eV to 0.30 (±0.05) eV. Accompanying this effect is the appearance of a shoulder on the $5p_{3/2}$ level at lower ionization energy, which first becomes apparent at a coverage between 0.30 and 0.35. There is already evidence in LEED for ordering in the adlayer at this coverage. The splitting is strongest at the maximum coverage of 0.44,[11] where the extra LEED features from the two orthogonal domains of the xenon hexagonal close-packed structures are clearly visible. We attribute this splitting to a direct bonding interaction between the adsorbate atoms. A further consequence of this

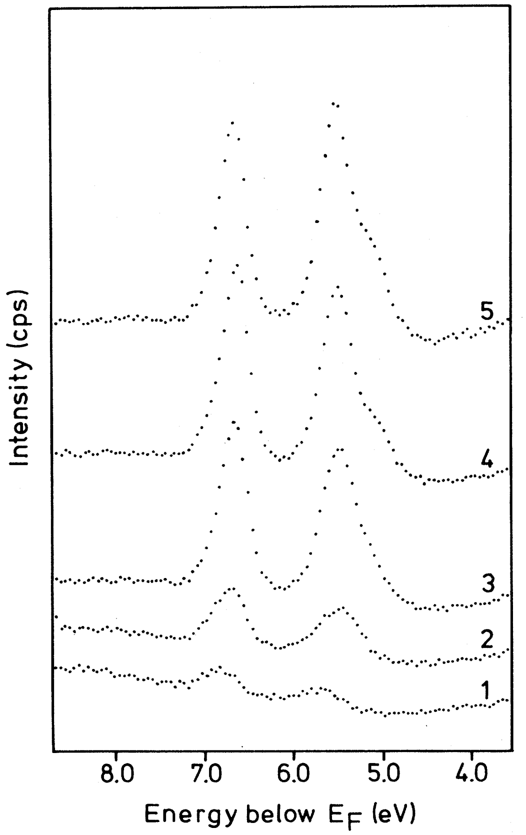

FIG. 1. Coverage dependence of the Xe $5p$ peaks in the photoemission spectrum of xenon physisorbed on Pd(100). Coverages as estimated from peak areas: 1, 0.04; 2, 0.11; 3, 0.32; 4, 0.38; 5, 0.44 (maximum coverage, 5.8×10^{14} atoms cm^{-2}). Angle of incidence $\alpha = 60°$, polar angle of emission $\theta = 20°$, ΓH, He I, and surface ≈80 K.

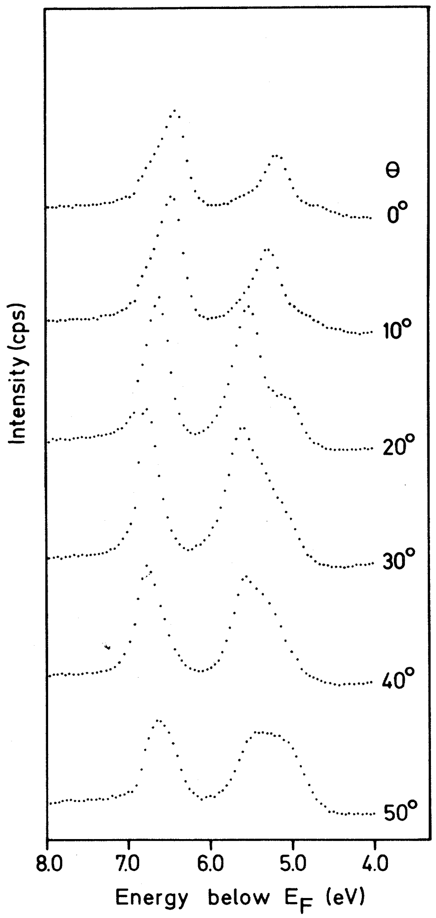

FIG. 2. Polar-angle dependence of emission from a hexagonal xenon monolayer on Pd(100). $\alpha = 60°$, ΓH, He I, and surface ~70 K.

lateral interaction is the dispersion effect shown in Fig. 2. This dependence of initial-state energy on $k_{\parallel}$, the wave-vector component parallel to the surface, is direct evidence for the bandlike character of the Xe $5p$ levels at high coverage. Because the resulting band structure is two-dimensional, photoemission polar angular distributions such as that of Fig. 2 enable us, in principle, to map out directly the surface Brillouin zone (SBZ).[12] The SBZ's of the two orthogonal domains are shown in Fig. 3 (top) in relation to the azimuthal directions of the crystal. The ΓH direction, which corresponds to the [011] azimuth, is unique in that it is the same in both SBZ's and was therefore chosen for the present investigation. At $\theta = 0°$ (Γ point) in Fig. 2 five peaks are observed in the spectrum. The two shoulders at 6.8 and 5.5 eV show no dispersion, whereas the $5p_{1/2}$ peak at 6.4 eV and the two split $5p_{3/2}$ peaks at 5.1 and 4.6 eV shift to higher ionization energies as θ is increased. Elsewhere[13] we demonstrate how the two high-ionization-energy shoulders can be due to a breakdown of $k_{\parallel}$ conservation: Because the xenon overlayer is out of registry with the substrate, waves reaching the detector via reflection at the Pd substrate are excited incoherently. Thus for a given $k_{\parallel}$ of the final state many nonequivalent points of the Xe SBZ contribute to the spectrum, producing two peaks in which the effect of dispersion is averaged out. On these two broad features are superimposed the three sharp peaks from direct emission.

In order to understand the spectra of Fig. 2 we address ourselves to the bonding scheme at the Γ point. Similar to the situation in gas-phase photoemission the $5p$ orbitals are spin-orbit split: Because of the interaction of the spin magnetic

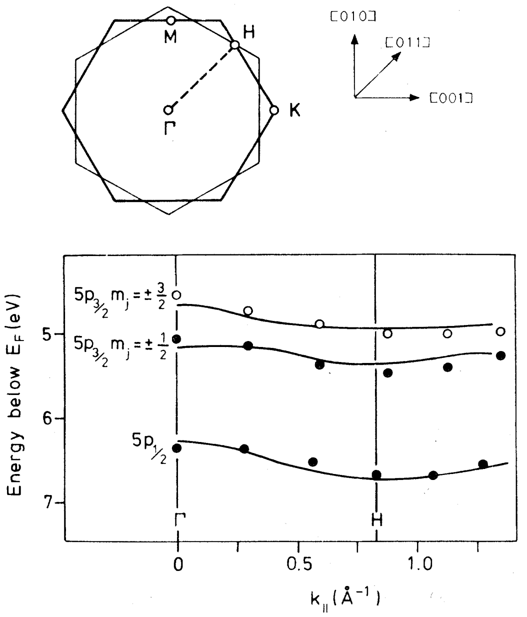

FIG. 3. Above: The superimposed SBZ's of the two orthogonal domains of the hexagonal xenon overlayer together with the azimuthal directions of the crystal. Below: Tight-binding band structure for an isolated, hexagonal xenon monolayer together with the experimental results of Fig. 2.

moment with the orbital motion of the electron, two different levels are produced depending on whether the spin and orbital angular momenta are parallel or antiparallel. The energy of the parallel $p_{3/2}$ state with four electrons is higher than that of the antiparallel $p_{1/2}$ state with two electrons. At the Γ point the symmetry is C_{6v}, for which there are only two-dimensional representations of the corresponding double group.[14] The $p_{3/2}$ states will consequently show a twofold splitting in the xenon field, regardless of the nature of the interaction. The observation of dispersion indicates, however, that a direct overlap of $5p$ wave functions on neighboring xenon atoms takes place, when the adlayer is sufficiently close-packed in an ordered array. As well as the $5p_{1/2}$ band there will therefore be two bands derived from $5p_{3/2}$ states and consisting of overlapping $m_j = \pm\frac{1}{2}$ orbitals and of overlapping $m_j = \pm\frac{3}{2}$ orbitals without mixing. m_j is the magnetic quantum number of the total angular momentum of the single-electron atomic states. If a two-dimensional Bloch function with $k_{\parallel} = (0, 0)$ is constructed using a hexagonal array of $m_j = \pm\frac{1}{2}$ orbitals, which have both p_z and p_x, p_y character, the resulting band consists of a mixture of bonding and antibonding contributions. The $m_j = \pm\frac{3}{2}$ orbitals are, however, pure p_x, p_y in origin and lead to a $m_j = \pm\frac{3}{2}$ band which is entirely of antibounding character in the xenon layer. The ($p_{3/2}$, $m_j = \frac{3}{2}$)-derived Bloch state will therefore have the highest energy in the whole Brillouin zone. We show elsewhere[13] using the analysis of normal-emission spectra at variable angle of incidence[8,15] that this assignment is indeed correct: The peak at 5.1 eV is $5p_{3/2}$, $m_j = \pm\frac{1}{2}$ and the peak at 4.6 eV $5p_{3/2}$, $m_j = \pm\frac{3}{2}$. The strict labeling of these bands is, however, only valid at the Γ point. Away from the Γ point the symmetry is reduced (the ΓH direction in the SBZ, for example, has no symmetry at all) and the $m_j = \pm\frac{3}{2}$ and $m_j = \pm\frac{1}{2}$ bands will mix. Despite this lowering of symmetry still only three constituent bands are expected from the $5p$ states, because, under the conditions of the experiment, the Kramers degeneracy will not be lifted.

We have also performed a simple tight-binding band-structure calculation for the hexagonal xenon layer which reproduces the main features of the observed results. Only two-center integrals and next-nearest-neighbor interactions were taken into account. Matrix elements were calculated numerically. Figure 3 shows the energy of the bands along the ΓH direction of the SBZ plotted together with the experimental values of Fig. 2. The theory not only puts the $m_j = \pm\frac{3}{2}$ band at the highest energy, as it must; it also reproduces well the extent of the dispersion. This agreement indicates that the bonding interaction takes place primarily between xenon atoms directly and not via the substrate. This is hardly a surprising result in an adsorption system as weak as Xe/Pd; it does, however, give us some idea of the importance of the direct through-space interaction in adsorbate band formation in chemisorption systems, where attention in recent years has focused mainly on the interaction with the substrate. The present results have a second important consequence: The contribution of image-charge screening to the observed splitting is not as important as hitherto supposed. This does not necessarily mean that this form of relaxation is unimportant, merely that there is essentially no difference in relaxation energy between the two valence states involved.

We thank K. Kambe and N. V. Richardson for useful discussion and the Deutsche Forschungsgemeinschaft for funding. The interest and support of H. Gerischer and K. Molière are also gratefully acknowledged.

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[12] As in all photoelectron experiments the recorded energy spectrum corresponds to the hole state. Thus in fact we measure hole dispersion and, only by inference, the electron dispersion in the initial state. This approximation is essentially Koopmans's theorem.

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Direct Determination of Lifetime and Energy Dispersion for the Empty Δ_1 Conduction Band of Copper

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(Received 6 July 1978)

We present an accurate determination of the energy dispersion (E vs k) and the first direct determination of the energy-dependent lifetime $\Gamma(E)$ of well-defined excited Bloch states in a crystal. Using angle-resolved photoemission for Cu(100), we find that the lifetime broadening increases from $\Gamma = 1.2$ eV (6×10^{-16} sec) to 1.8 eV (4×10^{-16} sec) for Δ_1 conduction-band states ranging 10.5 to 13.5 eV above the Fermi level. The measured dispersion (~2% accuracy) shows a reduced effective mass ($m^*/m_0 = 0.90-0.94$) which is related to self-energy effects.

X-ray and ultraviolet photoelectron spectroscopy studies have yielded substantial information about occupied energy bands—e.g., densities of states—in the last decade. Indeed, angle-resolved studies at low photon energies $\hbar\omega \lesssim 100$ eV have recently yielded rather accurate energy dispersions (E vs k) for occupied valence bands,[1-5] and promise an even better future. However, much less is known about the energy-band dispersions of empty conduction bands well above the Fermi level E_F. Usually, it has been necessary to assume either that specific theoretical one-electron models are valid[3] or that a simple nearly-free-electron–band picture is valid.[4]

Even less is known about the lifetime of electrons in excited states well above E_F. These lifetimes are important since they determine such basic quantities as the electron mean free path (i.e., spatial escape depth) and the momentum broadening δk, which determines the limiting momentum resolution of angle-resolved photoemission.[6] The principal sources of information about lifetimes have been escape-depth measurements of electron attenuation through an overlayer.[7] Such measurements have determined energy-dependent mean free paths which are averaged over many crystal directions, since polycrystalline samples have been used. Also, there are often serious questions of inaccuracies due to inhomogeneities—e.g., island growth—because very thin overlayer films must be used.[7]

In this paper, we present an accurate determination of the energy dispersion E vs k as well as a direct determination of the lifetime broadening $\Gamma(E)$ for excited Bloch states in the lowest empty conduction band along Δ in Cu. Using angle-resolved normal photoemission from Cu(100) with continuum synchrotron radiation, we have directly determined the spectral distribution [i.e., Lorentzian distribution of width $\Gamma(E)$] of these excited Bloch states. For this method, the only required assumption is that there exists a smooth E-vs-k dispersion relation for the final states involved. For energies between 10.5 and 13.5 eV above E_F, we find that the energy broadening Γ increases from 1.2 eV FWHM (full width