Two-Dimensional Localization of Electrons at Interfaces

R. L. Lingle, Jr., D. F. Padowitz, R. E. Jordan, J. D. McNeill, and C. B. Harris
Department of Chemistry, University of California, Berkeley, California 94720
and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 26 July 1993)

Evidence for electron localization in 2D at metal-dielectric interfaces is reported. A nondispersive peak, derived from the image-potential state and observed in angle-resolved two-photon photoemission, is assigned to localized excess electrons. The image electron on alkane monolayers is a free electron. Bilayers of chain or ring alkanes show both localized and delocalized states; electrons are localized on trilayer *n*-pentane. Bilayers and trilayers of neopentane show no localization. Our results link the geometry of adlayer molecules with localization of excess electrons at interfaces.

PACS numbers: 73.20.Dx, 71.50.+t, 79.60.Jv, 79.60.Ht

Electrons at interfaces exhibit novel phenomena of both fundamental interest and widespread technological importance. For example, both weak and strong localization phenomena have been observed for electrons in disordered two-dimensional systems [1]. Although transport measurements are effectively used to study localization, few methods are available to directly characterize the single particle states populated by an electron at an interface. In this paper the excited state energy levels of a metal-dielectric interface have been studied in order to develop a microscopic understanding of the behavior of electrons in complex media. We have grown molecular-thickness layers of various alkanes on the Ag(111) surface and have measured the energies and effective masses of excess electrons at these interfaces by angle-resolved two-photon photoemission (TPPE). Initial studies established the effectivness of this technique for studying electrons bound to a bare metal surface by the image potential [2], while recent experiments have addressed the case of metal-adsorbate systems [3-6]. Image-potential states on surfaces provide a nearly ideal system in which to study the physics of an electron in two dimensions [7]. Using a TPPE instrument with exceedingly good sensitivity and energy resolution [4], this investigation demonstrates the application of angle-resolved TPPE as a new probe of electron localization in 2D systems. This technique forms a bridge between band structure measurements and transport studies of localization phenomena.

The details of the angle-resolved TPPE spectrometer have been given elsewhere [4,5]. TPPE probes the normally unoccupied electronic levels at an interface by populating those levels with one laser pulse and photoemitting from the same levels with a second pulse. Molecular layers were grown by either dosing the cold Ag(111) crystal or using the temperature and pressure to reversibly control the layer growth under equilibrium conditions. These studies include layers of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, and neopentane (2,2-dimethylpropane). The experiments reported here were done at sample temperatures in the range of 80 to 200 K, depending on the adsorbate. Layer-by-layer growth of the adsorbate can be identified and monitored *in situ* by TPPE [4]. Figure 1 shows the TPPE spectrum for $k_\parallel = 0$ (emission normal to the surface) for the $n=1$ image-potential state that persists when the Ag(111) surface is covered with different adlayer thicknesses of neopentane and *n*-pentane. The parameter $k_\parallel$ is the electron wave vector in the plane of the surface.

The dispersion data for the $n=1$ image electron as a function of layer thickness are best illustrated by comparing *n*-pentane/Ag(111) with neopentane/Ag(111). For a bare surface, the electron has parabolic dispersion and effective mass 1.3 times greater than that of a free elec-

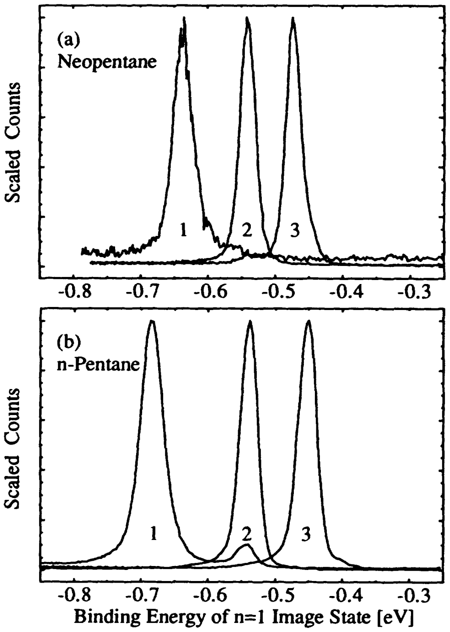

FIG. 1. The $n=1$ image-potential peak in the TPPE spectrum shifts to smaller binding energy (higher photoelectron kinetic energy) as successive layers of dielectric material are adsorbed. The image-potential states form a Rydberg series of hydrogenic levels and persist on many adsorbate-covered metal surfaces [4,5]. The binding energy of the $n=1$ image state on bare Ag(111) is -0.77 eV. The monolayer peak in (b) is accompanied by a small bilayer peak, illustrating the *in situ* monitoring of layer growth. Curve heights have been scaled.

0031-9007/94/72(14)/2243(4)$06.00

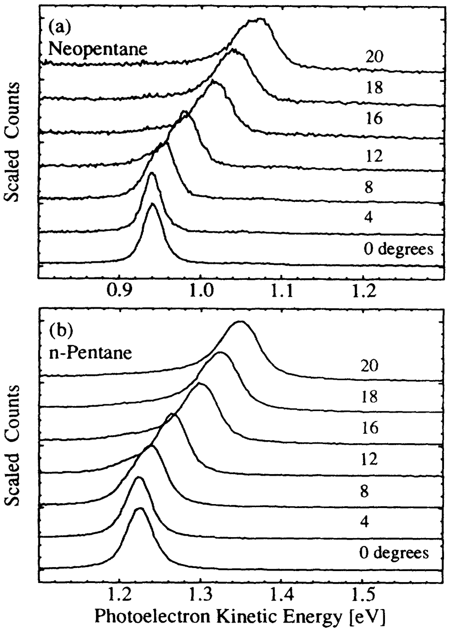

FIG. 2. Monolayer dispersion. Angle-resolved TPPE measures the band structure of the $n=1$ image-potential state which persists in the presence of a monolayer of *n*-pentane or neopentane on Ag(111). The image electron in either case has an effective mass ratio of 1, indicating a free electron. Curve heights have been scaled.

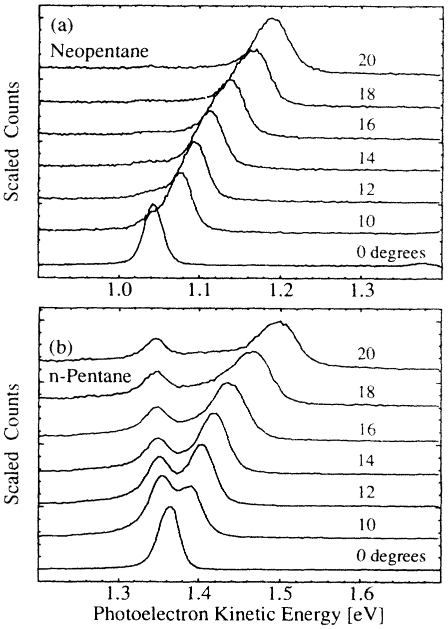

FIG. 3. Bilayer dispersion. A nondispersive feature (interpreted as a localized electron state) is prominent in (b) for the *n*-pentane bilayer, while the parabolically dispersing band (extended electron state) dominates the bilayer spectrum of neopentane. Curve heights have been scaled.

tron, $m^*/m_e = 1.3 \pm 0.1$. For *any* physisorbed alkane *monolayer* we have studied, the effective mass of the image electron is reduced to that of a free electron, $m^* \approx m_e$. This is evident in Fig. 2 where the monolayer spectra for the neopentane and *n*-pentane are almost identical. However, *a bilayer* of cyclohexane or *any* straight-chain alkane studied shows a nondispersive feature (i.e., the energy of the photoelectron does not depend on angle) in addition to the parabolically dispersing feature, as shown in Fig. 3(b) for the *n*-pentane bilayer. The nondispersive peak dominates the TPPE spectrum of a *trilayer* of *n*-pentane in Fig. 4(b), leaving only a trace of the parabolic band. On the other hand, the bilayer and trilayer spectra of neopentane show that the parabolic band remains the dominant feature in the spectrum. The parabolically dispersing bands in the bilayers and trilayers of any straight-chain alkane or cyclohexane show effective masses which are again greater than that of a free electron, unlike the monolayer results. These all have $m^*/m_e = 1.2 \pm 0.1$, whereas neopentane maintains free electron dispersion, $m^* \approx m_e$, for both the bilayers and trilayers. Furthermore, the $n=2$ state of the image-potential Rydberg series does not show a nondispersive feature for any of the alkane bilayers for which $n=2$ dispersion is measurable.

We attribute the nondispersive feature in these spectra to localized electron states, in contrast to electrons in extended states characterized by dispersive bands. (We

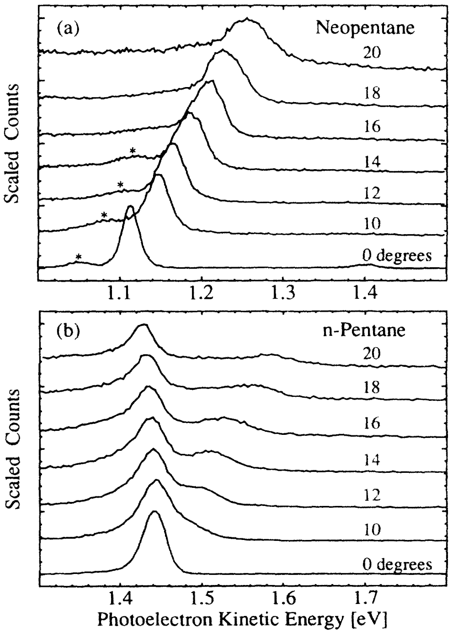

FIG. 4. Trilayer dispersion. The delocalized state continues to dominate the neopentane spectrum. The trend of the nondispersive feature (localized state) becoming more prominent in the *n*-pentane spectrum as layer thickness increases is clearly established. The features marked * in (a) are due to small patches of bilayer interspersed with trilayer. Curve heights have been scaled.

speak here of localization and delocalization in the plane of the surface; the image potential obviously binds the electron near the surface in the z direction.) Free-electron-like states show parabolic bands, which are characterized by an effective mass m^* with dispersion $E(k_\parallel)=\hbar^2k_\parallel^2/2m^*+E_0$. The extreme opposite case is that of a spatially localized electron. For a laterally localized state, $k_\parallel$ is not a good quantum number. Instead, the localized state is a superposition of many $k_\parallel$ plane wave states, the coefficients of which are given by the spatial Fourier transform of the localized wave function. Photoelectrons emitted from a localized state can be ejected over a range of angles. However, the energy is not a function of $k_\parallel$, so angle-resolved TPPE will yield a flat energy band as a function of angle.

We have extensively studied metal-alkane interfaces, investigating the effects of different preparation methods and annealing procedures on localization. However, the only two parameters that control the appearance of the nondispersive peak are the layer thickness and the identity of the adsorbate. The obvious effect of layer thickness is illustrated by the increasing prominence of the nondispersive feature in Figs. 2(b), 3(b), and 4(b). This effect is probably due to increasing overlap of the image electron wave function with the adlayer as thicker layers are grown. This interpretation is confirmed by the fact that the $n=2$ states (not shown) do *not* show a nondispersive feature while the corresponding $n=1$ states do. The hydrogenic model for an image-potential electron on a bare metal predicts that the expectation value of the distance z from the surface is 3 Å for the $n=1$ wave function compared to 13 Å for the $n=2$ wave function [8]. In comparison, a layer of cyclohexane is approximately 3 Å thick.

The importance of adsorbate chemical identity for determining whether or not excess electrons are localized in the plane of the interface is obvious from the contrasting spectra for neopentane and n-pentane in Figs. 3 and 4. The different interfacial electronic structures we observe are probably not due to differences in gross adlayer morphology, since ordered films result in each case. Low energy electron diffraction studies of straight-chain alkanes and cyclohexane adsorbed on Ag(111) [9] have shown that the monolayer ordered domain sizes are on the order of 100 Å. Ordered multilayers grow in the same structure as the ordered monolayer in most cases. The nearly spherical neopentane probably adsorbs in hexagonal layers.

In proposing a plausible mechanism for excess electron localization, we note that the $n=1$ image electron is increasingly constrained to reside inside the molecular layer as the thickness increases from monolayer to trilayer. It is now generally accepted for many classes of Hamiltonians that localized electronic states (for which the wave-function envelope decays exponentially) exist in two-dimensional systems for any amount of disorder [10]. On this basis alone, we might expect that excess electrons at an alkane/Ag(111) interface should be localized on the length scale of the ordered domain size. However, the data point to localization on a smaller length scale.

We note from Figs. 3(b) and 4(b) that the highest momentum electrons observable with our current apparatus ($k_\parallel \approx 0.32$ Å^{-1} at 20°) participate in the formation of the localized state. Higher momentum plane wave states have shorter de Broglie wavelengths and sense fewer defects per wavelength. Therefore the de Broglie wavelength associated with the electrons of highest momentum, ≈ 20 Å, sets a rough *upper limit* on the lateral spatial extent of the localized states. Thus defects which persist in the *ordered* adlayer domains probably provide enough disorder to enforce localization on a length scale significantly smaller than the domain size, provided that the individual adlayer molecules couple strongly to an excess electron.

We suggest that differences in coupling strength between an excess electron and the various adsorbate species lead to delocalized states for neopentane and localized states otherwise. For some atomic and molecular scatters the phase shifts due to interaction with the attractive and repulsive parts of the electron-molecule pseudopotential roughly cancel one another over a range of energies. A medium comprised of such constituents will appear more or less transparent to an excess electron. This effect is the basis for well-developed theories explaining the high electron mobilities in some rare gas fluids [11,12] and is responsible for delocalized states and high electron mobility in liquid neopentane [13]. Thus an excess electron will be largely insensitive to structural imperfections in the neopentane layers.

On the other hand, the straight-chain alkanes and cyclohexane have electron-molecule pseudopotentials which couple a low-energy excess electron strongly to these molecules [14]. For cases with strong coupling, the defects in the otherwise ordered adlayer can readily lead to localized states in accordance with the aforementioned prediction of 2D localization theory. These differences in coupling strengths are intimately related to the molecular geometries. For the alkanes, the coupling strength depends primarily on the degree to which an excess electron scatters off of the electron density of the C-C bonds [14]. Neopentane presents mainly methyl groups on its scattering surface, hiding the electron density associated with the C-C bonds on the inside of the molecule. However, the straight-chain or cyclic alkanes expose the electron density associated with C-C bonds to an incoming excess electron.

Additional evidence suggesting that the nondispersive feature is due to a localized electronic state is found by comparing our results with excess electron mobility data for nonpolar liquids. The excess electron mobility of liquid neopentane is 2 to 3 orders of magnitude higher than for n-alkanes or cyclohexane [15]. We suggest that the correlation of low excess electron mobility in the liquid with localization at the interface corroborates our interpretation, although we emphasize that we are not aware of an analytical result directly relating electron effective mass to mobility for quasi 2D systems.

Confirmation that the adlayer electronic structures differ with molecular geometry is provided by the already noted fact that the effective mass of the *delocalized* excess electron is different for neopentane than for the aspherical alkanes. This independently establishes that the electronic structures of metal-alkane interfaces differ for the two classes of adlayer constituents. This is consistent with our assignment of the nondispersive peak as a feature of the intermediate state rather than an artifact due to scattering during photoemission.

In conclusion, we have studied the structure of the unoccupied electronic levels at metal-dielectric interfaces and found both localized and delocalized states. The data suggest a correlation between molecular geometry and the spatial extent of the excess electron wave function which may be applicable to other interfacial systems. This is the first work to observe localization of excess electrons at an interface as a nondispersive feature in angle-resolved photoemission. The method (TPPE) presented here for the study of localization is general and should also be applicable to many different interfaces.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

---

[1] T. Ando, A. B. Fowler, and F. Stern, Rev. Mod. Phys. **54**, 437 (1982); G. Bergmann, Phys. Rep. **107**, 1 (1984); N. Fortier and R. R. Parsons, J. Phys. C **20**, 565 (1987); P. W. Adams and M. A. Paalanen, Phys. Rev. Lett. **61**, 451 (1988).

[2] W. Steinmann, Appl. Phys. A **49**, 365 (1989), and references therein.

[3] D. Rieger, T. Wegehaupt, and W. Steinmann, Phys. Rev. Lett. **58**, 1135 (1987).

[4] D. F. Padowitz, W. R. Merry, R. E. Jordan, and C. B. Harris, Phys. Rev. Lett. **69**, 3583 (1992).

[5] W. R. Merry, R. E. Jordan, D. F. Padowitz, and C. B. Harris, Surf. Sci. **295**, 393 (1993).

[6] R. Fischer, S. Schuppler, N. Fischer, Th. Fauster, and W. Steinmann, Phys. Rev. Lett. **70**, 654 (1993).

[7] D. Straub and F. J. Himpsel, Phys. Rev. Lett. **52**, 1922 (1984); K. Giesen, F. Hage, F. J. Himpsel, H. J. Riess, and W. Steinmann, Phys. Rev. Lett. **55**, 300 (1985); P. M. Echenique and J. B. Pendry, Prog. Surf. Sci. **32**, 111 (1990); P. Leiderer, J. Low Temp. Phys. **87**, 247 (1992), and references therein.

[8] W. R. Merry, Ph.D. dissertation (Department of Chemistry, University of California, Berkeley, 1992), pp. 12–14.

[9] L. E. Firment and G. A. Somorjai, J. Chem. Phys. **69**, 3940 (1978).

[10] E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett. **42**, 673 (1979).

[11] D. F. Coker, B. J. Berne, and D. Thirumalai, J. Chem. Phys. **86**, 5689 (1987); G. J. Martyna and B. J. Berne, J. Chem. Phys. **88**, 4516 (1988).

[12] J. Lekner, Phys. Lett. **27A**, 341 (1968); J. A. Jahnke, L. Meyer, and S. A. Rice, Phys. Rev. A **3**, 734 (1971); D. Hsu and D. Chandler, J. Chem. Phys. **93**, 5075 (1990).

[13] B. J. Berne, Department of Chemistry, Columbia University (private communication).

[14] Z. H. Liu and B. J. Berne, J. Chem. Phys. **99**, 9054 (1993).

[15] A. O. Allen, National Standards Reference Data Series—58 (U.S. GPO, Washington, DC, 1976).