Two-Photon Photoemission and the Dynamics of Electrons at Interfaces

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ABSTRACT

A new instrument for angle-resolved two-photon photoemission with exceptional sensitivity and energy resolution has allowed a detailed examination of the interaction of image-state electrons with adsorbates. In addition to measuring the electrostatic properties of molecular-thickness films, the technique serves as a probe of adsorbate growth modes, and provides new opportunities to explore the dynamics of electrons in well-controlled two-dimensional systems.

1. TWO-PHOTON PHOTOEMISSION

1.1 Comparison of photoelectron spectroscopies

Two-photon photoemission is a new method for measuring the normally unoccupied or excited electronic states of a surface. The high intensity of laser light allows a non-linear process in which one photon excites an electron from an occupied level into an unoccupied level and a second photon then ejects the electron from this excited state. As in conventional photoemission spectroscopy, the energy of the ejected electron is measured and the difference between the electron's energy and the known energy of the photon establishes the energy of the bound state. Both the photon energy and the energy of the electron can be determined to high precision so that excellent energy resolution is possible.^{1,2}

Band structure can be determined in two-photon photoemission just as in angle-resolved photoemission spectroscopy.^{3,4} For a well-ordered surface the momentum of an electron parallel to the surface ($k_{\parallel}$) is conserved (modulo a reciprocal lattice vector) during photoemission. Measuring the angle of photoemission along with the photoelectron energy yields the energy of the bound state as a function of its parallel momentum. This establishes the dispersion of the excited states.

Two-photon photoemission can be time resolved to explore excited state dynamics. If the arrival of the second photon is delayed, the excited state will decay before the electron can be photoemitted. By measuring the photoelectron signal as a function of the time delay, the lifetime of the excited state can be directly measured.²

The older technique of inverse photoemission also measures unoccupied electronic levels. A monoenergetic beam of electrons is scattered from the surface. A small fraction of the electrons drop into the unoccupied states, emitting a photon in the process. The energy of the emitted photon is used to establish the energy of the bound state. Difficulties in analyzing emitted light in the vacuum UV limited most earlier inverse photoemission work to energy resolution of about 700 meV.⁵ This has been improved in the past several years, but is still much poorer than the resolution of two-photon photoemission.

Inverse photoemission is indifferent to the lifetime of the state into which the electron drops. The lifetime only appears in the line width, with the usual complications of inhomogeneity and phase relaxation. Inverse photoemission may be more sensitive to very short-lived excited states than the current generation of two-photon photoemission spectrometers. A more subtle distinction is that two-photon photoemission prepares a excited state of the N electron system, while inverse photoemission adds an electron to form an $N+1$ electron system. If screening of the hole created by two-photon

photoemission is rapid and complete, as it is for metals, there is little difference in the energies of the N and $N+1$ electron states.

1.2 Two-photon photoemission spectrometers

The two-photon process requires high intensity light in the near UV. In some cases two-photon photoemission has been done with a combination of laser and synchrotron radiation. Many two-photon photoemission experiments make use of low-repetition rate, high powered lasers to generate sufficient near UV light. Eximer pumped dye lasers and high harmonics of amplified Nd:YAG have been used.^{1,2} A difficulty with these systems is the large electron flux from each laser pulse. Space charge due to the high density of electrons can smear the energy distribution and degrade resolution.

We have taken a different approach. Instead of the 10-100 Hz repetition rate lasers commonly used, we employ a CW mode locked Nd:YLF and synchronously pumped dye laser to generate 6 picosecond pulses at a 2 MHz repetition rate. Only one electron is detected per 10^3 laser pulses, so space charge is eliminated while maintaining kHz electron count rates. In addition, picosecond pulses permit simple and precise determination of the electron energy by measuring the time-of-flight of the electrons. Electrons around 1 eV traverse a 10 cm flight path in a few hundred nanoseconds. This is 10^5 times longer than the initial laser pulse, giving a theoretical resolution limit of 0.01 meV. Provided the flight tube is free of stray fields, the practical limit on the energy resolution in this instrument is the timing electronics, which give a resolution of about 5 meV. Our system is also equipped for angle-resolved detection for band structure and dispersion measurements.^{6,7} Figure 1 shows a diagram of the instrument and a photoelectron time-of-flight spectrum for the $n=1$ image state of Ag(111) acquired in 100 seconds.

1.3 Applications

To date, two-photon photoemission has been applied most extensively to the surface states of semiconductors⁸⁻¹³ and to the image-potential states of metal surfaces. The image-potential states are a particularly interesting class of surface states in which an electron is bound largely outside the surface. A charge outside a perfect conductor produces a polarization at the surface which appears as an equal and opposite charge inside the conductor. This gives rise to an attractive potential with a simple Coulombic form, and a series of bound states similar to that of a hydrogen atom. The image states of metal surfaces have been extensively studied by two photon-photoemission, particularly by Steinmann and coworkers.¹ The paper by R. M. Osgood in this volume gives an account of some recent work on image states on metal surfaces.

We have performed extensive studies on the effects of non-metallic adsorbates on the image potential states of metals. The electron in the image state is a "test charge" - sensitive to the local electrostatic properties of the adsorbate layer. In addition, this provides a new probe of the structure and growth of adsorbate layers. The nature of this probe, based on surface electrostatics and the energy of a bound electron, may be intrinsically more sensitive to variations in the adsorbate layer than standard electron scattering methods.¹⁴

Perhaps most interestingly, we can study the dynamics of the electron itself. Angle-resolved two-photon photoemission gives the dispersion or effective mass of the electron moving in the surface plane. We find scattering and localization of the electron depending on the composition and thickness of adsorbate layers.^{14,15}

2. ELECTRONS AT INTERFACES

2.1 Image states and electrons in reduced dimensions

The image potential is a generic feature of interfaces. A charge near an interface polarizes the two media unequally, which results in an electrostatic potential. This image potential is important in electron transport across interfaces, Schottky or tunneling barriers. For materials in vacuum, the image potential supports bound states which are confined to the region of the surface, as mentioned above. The potential which binds the electrons to the surface is effectively one-dimensional. The bound state wave functions are localized hydrogenic states in the direction normal to the surface, but are delocalized plane

Fig. 1. Two-photon photoemission spectrometer based on a high-repetition-rate laser and time-of-flight analysis of photoelectron energy. The bottom figure is a photoelectron spectrum of the $n=1$ image state of Ag(111). This spectrum was acquired in 100 seconds.

waves in the surface plane. In the simple hydrogenic model, the electron is completely free in the surface plane. Prior to quantum wells, electrons in image states on a liquid He surface were the experimental paradigm for the 2-D electron gas.

Compared to the other surface states of metals, the image states are unusual in their location outside the surface, the resulting long lifetimes, and in the simple pattern of their energy levels. By observing changes in the image states of a metal surface as various molecules are adsorbed in well-defined layers, we have a precisely controlled system to explore the dynamics of electrons in 2-D and the development of an interface. We can examine the interaction of the excited electron with well-characterized adsorbate films of selected composition and controlled thickness, molecular layer by layer. The behavior of electrons in these 2-D systems can be related to the problems of excess electrons in condensed media.

A further step is suggested in a recent paper which reports the observation of 1-D image states at step edges.¹⁶

2.2 The influence of adsorbates

The image electrons are a few angstroms outside the surface, certain to interact in interesting ways with adsorbates. Perhaps the single most remarkable fact is that the image state does persist in the presence of adsorbates, and often remains recognizable for many layers. We have found that image states continue to be observable for adsorbed alkali metals, rare gases, and simple hydrocarbons.¹⁴ The image state is well defined for the C_5 - C_8 alkanes we have studied, while benzene, naphthalene, hexene, and perfluorocyclohexane all seem to quench the image state. Chemisorbed thiols and sulfur on Ag(111) give weak image states. We found no distinct image state for water on Ag(111) and a similar result has been found for Ag(100). Other workers have observed the quenching of image states by oxygen.^{17,18}

In the case of water, the surface may simply be too rough to support sharp image states. Water wets silver poorly and probably grows in 3-D clusters or crystallites rather than layers.¹⁹ For the alkenes, we expect that low-lying electronic excitations may provide relaxation pathways that shorten the lifetime of the image electrons. This would both reduce the two-photon signal and broaden the peak, so the residual image state might be difficult to see.

Electronic excitations of the adsorbed molecules themselves, seen in inverse photoemission and in electron energy loss spectroscopy, have not yet been identified in two-photon photoemission. This is most likely due to rapid energy and charge transfer to the metal. These states are expected to become visible when shorter laser pulses and higher intensities are used.

Fig. 2. Spatial extent of wave functions for image-potential states of a metal surface (in the hydrogenic approximation) compared to the thickness of a layer of Xe atoms.

2.2.1 Binding energy

The image potential is pinned to the vacuum level. Adsorption changes the work function and so the vacuum level moves relative to the Fermi energy. The resulting shift in the position of the image states relative to the Fermi level been observed in inverse photoemission.²⁰ This does not correspond to a change in the binding energy of the image state. Changes in the image state's binding energy due to adsorption are beyond the resolution of inverse photoemission and were not reported until our work.

The simplest case we have studied is that of a monolayer of Xe on Ag(111). After corrections for the contact potential produced by the work function change, the monolayer appears to reduce the binding energy of the $n=1$ image state by about 100 meV. This is seen in Fig. 3. This can be considered as screening of the image potential, or a measure of the "dielectric strength" of the monolayer. Of course such a term is not well defined since the electron is not in a homogeneous medium; the extent of the wave function exceeds the monolayer thickness.

2.2.2 Effective mass

A free electron exhibits parabolic dispersion $E = \hbar^2 k^2 / 2m_e$. The dispersion of the image state on a metal surface differs slightly from the free electron due to the band structure of the metal. As $k_{||}$ changes, the position and width of the projected gap changes and this changes the binding energy E_b of the image state.²¹ Total energy becomes $E = E_b(k_{||}) + \hbar^2 k_{||}^2 / 2m_e$, consequently, the image state on a real metal shows an effective mass differing from that of a free electron. For Ag(111) the effective mass of the $n=1$ image state is $m^* = 1.35 m_e$, greater than that of a free electron.⁷

When the surface is covered by a monolayer of Xe, the effective mass becomes $1.00 m_e$; once again a free electron. The dispersion is shown in the bottom of Fig. 3. Part of the change, but not all, can be attributed to the decrease in work function, which shifts the image state relative to the Ag levels. The remaining difference suggests that the penetration of the $n=1$ wave function into the metal is reduced either by the electron being excluded from the Xe layer or being moved away from the surface. The unsurprising conclusion is that the Xe reduces the electron's interaction with the metal.

Similar results, with varying degrees of screening, are found for Kr and Ar monolayers. Bilayer Xe is not so simple. In bulk Xe, the conduction band minimum is 0.5 eV below the vacuum level. For the bilayer there may be features due to the emergence of the Xe band structure interacting with the image state. The photoemission peaks have not yet been assigned.

2.3 Where is the electron?

Lacking detailed knowledge of the potential we cannot know *a priori* what the wave function will be on the adsorbate covered surfaces. How far does the electron penetrate into the adsorbate? Is it localized primarily at the metal-adsorbate interface or does it move to the adsorbate vacuum interface? The answer surely depends on the nature of the adsorbate. In the thought experiment of placing a new layer of metal on the surface, the image state moves outside the adsorbate. This may be the general behavior for adsorbates with a large dielectric constant.

For lower dielectric strength adsorbates, whether the electron penetrates the layer or is excluded by it may depend on the adsorbate's electron affinity. If the electron affinity of the adsorbate is large, the electron may be pulled inside the adsorbed layer, at least for sufficient thicknesses. For bulk Xe crystals the conduction-band minimum (the affinity level or V_0) is about 0.5 eV below the vacuum level. For sufficiently thick Xe, we believe the electron would move inside the adsorbate layer, bound at the metal-Xe interface. Within the film the image potential is asymptotic to the conduction band minimum, which plays the role of the vacuum level for an electron in bulk Xe. A second, weaker image potential would exist at the Xe-vacuum interface and so electrons might be bound at both interfaces.

The first monolayer is unique: it is in direct contact with the metal. There will be charge redistribution and the molecules of the first layer become polarized. The charge redistribution upon adsorption is related to the work function change; the direction and extent of polarization varies for different adsorbates. Lang and Williams' classic calculation of adsorbates on jellium gives a buildup of electron density between the Xe core and the metal.²²⁻²⁴ This should shift the image plane away

Fig. 3. $n=1$ image state binding energy and dispersion on clean and Xe-monolayer covered Ag(111).

from the metal, but need not completely exclude the electron from the Xe layer. Lang's calculation was for an isolated atom, the band structure of 2-D adsorbate layer must also be considered.

2.4 Growth morphology and phase diagrams of adsorbates

The effect of increasing doses of adsorbate are seen in the top of Fig. 4. As the surface coverage of cyclohexane increases a remarkable series of peaks occurs. The multiple peaks at a given dose are evidence for partial layer growth (Stranski-Krastanov or Frank-Van der Merwe growth). Evidently the surface is covered by patches of a few discrete thicknesses at each dose. As the dose increases, the earlier peaks decrease and new peaks grow in at lower binding energies. If the layer is carefully annealed we can get a single peak corresponding, for instance, to a complete bilayer. If the surface was not wet by the cyclohexane and 3D crystallites formed (Volmer-Weber growth) we would expect discrete peaks.

The bottom of Fig. 4 shows the phase diagram for n-octane obtained in this fashion. We see evidence for the order-disorder transition within the first monolayer, and subsequent formation of multilayers. This is in good agreement with low-energy electron diffraction.²⁵ The spectra for cyclohexane show some hysteresis with temperature. We examine the evolution of the spectrum with coverage as the sample is heated or cooled under a constant backing pressure of cyclohexane. One peak which appears just after monolayer coverage during cooling does not disappear upon heating in the same order it formed. This suggests a metastable phase.

2.5 Rydberg series and local vacuum levels

As in hydrogen, the image-potential states form a Rydberg series, converging to the vacuum level.²¹ The higher Rydberg states, $n=2,3,\dots$ move rapidly away from the surface and are increasingly independent of the surface details. We can observe the $n=2,3$ and sometimes higher states. As expected, these states are less affected by low adsorbate coverages. In Fig. 8 for cyclohexane, we have expanded the $n=2,3$ peaks and see that they are unaffected by the first few layers of adsorbate. Only after 3-4 adsorbate layers do we begin to see splitting of the $n=2$ peak.

The convergence of the Rydberg series to the local vacuum level is robust. Model calculations indicate that the convergence is rapid for wide variation of potentials. The higher states are far from the surface and little affected by a few adsorbate layers. This allows a very accurate determination of the vacuum energy if only a few of the higher states can be observed. If we observe the $n=3$ state, we can determine the vacuum level to within 10 meV. This is independent of work function measurements.

2.5 Localization

The image state on a monolayer of alkanes shows a parabolic dispersion with an effective mass roughly that of a free electron. A striking change occurs for two layers of n-alkanes: a new, non-dispersive feature appears in addition to the normally dispersing peak. For three layers almost all of the photoemission intensity is in the non-dispersive feature. The non-dispersive peak can be considered to have an infinite effective mass; these electrons are no longer free in the surface plane.

If electrons are elastically scattered after being ejected from the bound state, they would lose $k_{||}$ information and appear at all angles. At any angle the resulting spectrum is the same k -averaged density-of-states. This is well known where photoemission occurs through a disordered surface layer such as an oxide. The feature we see does not resemble this typical density-of-states artifact, which is very broad in energy. The energy of our non-dispersing feature is sharp and very close to that of the dispersing peak at surface normal or $k_{||}=0$. Comparing bilayers to monolayers, we see that the emission at normal is greatly enhanced at the expense of emission at higher angles. The electrons are pooling at the bottom of the band; extensive relaxation may be occurring before photoemission. We tried in several ways to intentionally increase the disorder of the adsorbate layer, which should be all too easy, but no difference in the relative intensity of the non-dispersive peak was seen.

Figure 5 compares mono-, bi-, and trilayers of n-pentane and neopentane. In sharp contrast to n-pentane, neopentane does not show a non-dispersive peak. This is consistent with experiments on electron mobility in liquids. These show that

Fig. 4. Two-photon photoemission spectra for cyclohexane at increasing doses and a phase diagram constructed from similar data for n-octane at constant backing pressure and varying surface temperature.

Fig. 5. Dependence of electron localization on layer thickness and composition: $n=1$ image state dispersion for monolayer (top), bilayer (middle), and trilayer (bottom) n-pentane and neopentane.

mobility is greatest in solvents whose molecules are spherical such as methane. The polarizability of non-spherical molecules is anisotropic, which leads to scattering of the electrons and reduces mobility. It is quite possible that the same effects are being seen in our 2-D solid as in bulk liquids. The detailed mechanism of localization is under continued study.

2.6 Time-resolved dynamics

The most promising application of two-photon photoemission is in pump-probe measurements to directly resolve the evolution of excited states. Bokor, Haight, and others have used time-resolved two-photon photoemission to study the lifetimes of excited states of semiconductor surfaces.⁸⁻¹⁰ Lifetimes of image states on bare metals have been measured.²⁶ Time-resolved measurements have yet to be performed on adsorbate systems. These will soon provide direct measurements of the time required for electron relaxation and localization in well-characterized 2-D and 1-D systems.

3. ACKNOWLEDGMENTS

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