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Observation of above-threshold multiphoton photoelectric emission from image-potential surface states

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Subpicosecond laser pulses have been applied to investigate multiphoton photoemission from single-crystal Pt(111) surfaces. Image-potential surface states on the Pt(111) surface give rise to sharp resonant enhancements in the multiphoton photoemission spectrum which allow for unambiguous identification of above-threshold peaks.

The phenomenon of above-threshold ionization (ATI) has been extensively studied in atomic and molecular photoionization, but how the optical physics which leads to ATI (ponderomotive effect) influences the photoelectric effect from solids has received comparably little attention. Two studies of above-threshold photoemission (ATP) from polycrystalline metal surfaces have recently been reported with moderate[1] or poor[2] energy resolution. In both experiments, ATP effects were identified via the detection of electrons with energy greater than the minimum multiphoton photoeffect energy, $E_{\min}=n_0h\nu-\Phi$, where n_0 is the minimum number of photons of energy $h\nu$ necessary to overcome the work function Φ. However, the spectacular series of peaks, separated by $h\nu$, characteristic of ATI from atoms was not observed at all in Ref. 2, and only suggested in the spectra reported in Ref. 1, due to poor energy resolution.

In this experiment we study the intensity dependence of the multiphoton photoemission spectrum from the clean, single-crystal Pt(111) surface. The unique feature of this sample is that it is known to possess[3] a special class of surface electronic states known as image-potential states. These states arise due to the fact that an electron outside a metal surface can be bound to its image charge, forming a Rydberg series of states converging on the vacuum level. These states have the character of a one-dimensional hydrogen atom with a potential in the z direction of $V(z)=e^2/4z$, hence a binding energy for the first excited state of approximately $\frac{1}{16}$ Ry$=0.85$ eV, where Ry is the Rydberg constant. Measured image-state binding energies for a variety of materials and crystalline orientations actually range[4,5] from 0.4 to 1.0 eV due to the departure of the crystal dielectric constant from unity as well as the details of the electron wave-function phase shift upon reflection at the metal-surface-potential discontinuity.[6] The binding energy of the $n=1$ (first excited) image state on Pt(111) has been reported[4] as 0.63 eV.

When present, image states have a dramatic influence on multiphoton photoemission spectra.[7] They provide a very strong intermediate-state resonant enhancement, giving rise to exceptionally sharp features in the photoelectron spectrum, even when there are no sharp initial-state features below the metal Fermi level. This property has made it possible for us to clearly and unambiguously identify sharp peaks in the photoemission spectrum with energy greater than $E_{\min}$ as arising due to ATP. Furthermore, due to the extremely simple hydrogenic nature of the image-state wave functions, the phenomenon of ATP involving image states is highly amenable to a fundamental theoretical analysis.

A Pt(111) single-crystal sample was held under UHV conditions (10^{-10} Torr), and cleaned using sputter-anneal cycles until a sharp low-energy electron-diffraction pattern was obtained. A dual-jet synchronously pumped dye laser operating at 680 nm wavelength (1.84 eV photon energy) was amplified by an excimer-pumped dye laser amplifier to produce pulses of 100 μJ energy and 500 fs duration at a repetition rate of 100 Hz. The 1.84-eV light was used for the multiphoton photoemission study. Electron energy spectra were recorded by a time-of-flight spectrometer capable of processing multiple electrons for each laser shot. Unless specified otherwise, all the spectra were taken in the normal-emission direction.

Multiphoton photoemission spectra were measured from the Pt(111) surface for both s- and p-polarized light. Figure 1 is the photoemission spectrum for p-polarized light at an intensity of 15 GW/cm^2. The work function[4] of Pt(111) is 5.9 eV, and so it takes at least four photons to excite photoelectric emission. With the same incident pump intensity, it was found that the number of photoelectrons produced by the p-polarized light was about 10

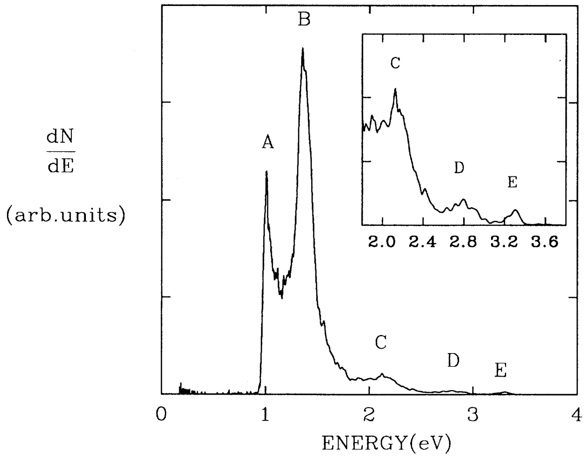

FIG. 1. Multiphoton photoemission spectrum from a Pt(111) single-crystal surface. The laser intensity was 15 GW/cm^2.

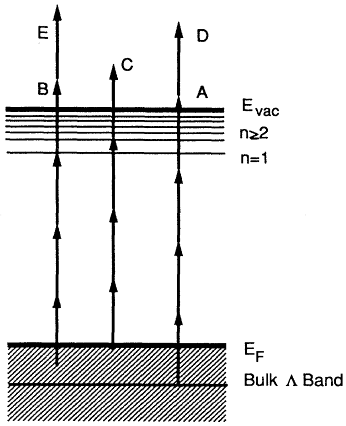

FIG. 2. Schematic energy-level diagram depicting the various multiphoton processes leading to each of the labeled peaks in the spectra.

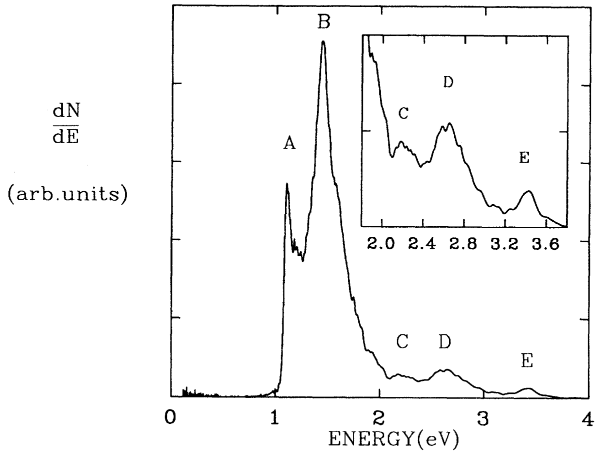

FIG. 3. Multiphoton photoemission spectrum taken under the identical conditions as those of Fig. 1, except that the laser intensity was increased to 30 GW/cm^2.

times more than with s-polarized light. The difference in absorption for s- and p-polarized light is only 10% and cannot explain this substantial difference of the photoelectron yield. However, the result can be understood by recognizing that the various structures in the p-polarized spectrum are due to the resonant enhancement of the multiphoton photoemission by image states (refer to Fig. 2). Since the dipole moment for image-state excitation is perpendicular to the surface, the probability of excitation with s-polarized light is zero.[7] On the other hand, p-polarized light can couple the image state with both bulk initial states and free-electron final states in the vacuum. Peak B at 1.36 eV in Fig. 1 is assigned as three-photon-resonant, four-photon photoemission via the $n=1$ image-potential state. In addition to the polarization dependence, this assignment is confirmed by the sharpness of the peak, which has a full width at half maximum of 100 meV, the extreme sensitivity of the peak strength to surface cleanliness, and the angular dependence of the peak signal. Since the potential for electrons outside the surface of a metal is nearly one dimensional, the electrons are nearly free in the direction parallel to the surface, and, indeed, the effective mass in the parallel direction for image-state bands has been measured to be nearly unity for many materials and crystalline faces.[8] This leads to a dispersion of the image-state bands upward in energy with increasing parallel momentum. This leads to a shift of the image-state peaks upward in energy as the emission angle moves away from the normal direction, and this is indeed what was observed.

The broader peak C at 2.15 eV is assigned as three-photon-resonant, four-photon photoemission via $n>2$ image states. This assignment is based on the strength of the peak which is even more sensitive to the surface quality than peak B as well as its position, which is close to the vacuum level. In addition to these four-photon resonances, there are weaker structures, D at 2.8 eV and E at 3.3 eV. We attribute these peaks to above-threshold five-photon processes based on their high kinetic energy as well as their intensity dependence. Notice that the separation between the peaks B and E is close to one photon energy.

In Fig. 3, we show the photoelectron spectrum taken at twice the intensity as that used in Fig. 1, namely, 30 GW/cm^2. The $n=1$ peak B now appears blueshifted from 1.44 to 1.36 eV, and the spectral width is broader than the low intensity case. The broadening can be due to space-charge broadening of the spectrum coming from the higher density of charge being emitted from the surface on each shot, or it may possibly be due to ponderomotive effects. Similar effects have been observed in the subpicosecond above-threshold ionization of atoms.[9] The weak features D and E in Fig. 1 become more prominent and, more importantly, the relative strength of the D and E peaks compared to the B and C peaks increases dramatically in the higher intensity spectrum of Fig. 3, as compared to the lower intensity spectrum of Fig. 1.

On the basis of its width, 500 meV, and relative energy, we assign the 2.8-eV peak D to five-photon, above-threshold photoemission from the highest bulk valence band[10] of Λ symmetry. Four-photon photoemission from this bulk band would be above the photoelectric threshold, but lies below the 1-eV cutoff of the spectrometer. Feature A represents the high-energy edge of this peak.

In summary, we have studied above-threshold multiphoton photoelectric emission from a well-characterized, single-crystal surface. Image-potential surface states on the Pt(111) surface give rise to sharp resonant enhancements in the multiphoton photoemission spectrum, which allow for unambiguous identification of above-threshold peaks. The relative simplicity of the image-state wave functions should allow a detailed theoretical analysis of the influence of ponderomotive effects on the photoelectric effect from metal surfaces.

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