

Time-Resolved Coherent Photoelectron Spectroscopy of Quantized Electronic States on Metal Surfaces

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Time-resolved two-photon photoemission in combination with the coherent excitation of several quantum states was used to study the ultrafast electron dynamics of image-potential states on metal surfaces. For a (100) surface of copper, the spectroscopy of quantum beats made previously unresolved high-order states (quantum number $n \geq 4$) experimentally accessible. By exciting electrons close to the vacuum level, electron wave packets could be created and detected that described the quasi-classical periodic motion of weakly bound electrons. They traveled more than 200 Å away from the surface and oscillated back and forth with a period of 800 femtoseconds.

Photoelectron spectroscopy has developed into one of the most versatile and successful tools for surface studies. Particularly attractive features of this technique are the high surface sensitivity associated with the low escape depth of the photoelectrons and the capability of angle-resolved photoemission to completely characterize electronic states in energy and momentum space (1). Recently, these features have been combined with ultrafast laser excitation for direct time-domain investigations of electron dynamics at surfaces (2). Here, we demonstrate another facet of this powerful technique, the investigation of coherence phenomena in real time. In contrast to experimental methods that rely merely on intensities, coherent spectroscopies offer the unique capability of accessing not only the amplitudes but also the phases of the wave functions of interest (3). This technique dramatically increases the amount of information that one is able to obtain about the temporal evolution of fast processes.

In this report, we discuss the dynamics of image-potential states, that is, the quantized excited states of electrons that exist in front of many metal surfaces (4, 5). Using femtosecond time-resolved two-photon photoemission (2PPE), we observed the interference between the wave functions of neighboring eigenstates and the quasi-classical motion of electron wave packets created by the coherent superposition of several quantum states. Recently, the imaging of the static charge density of related surface electronic (ground) states in real space with the scanning tunneling microscope

has attracted considerable interest (6); the present results reveal the dynamical evolution of excited electrons in real time.

Image-potential states are conceptually rather simple. An electron at a distance z in front of a conducting metal surface experiences an attractive force $F(z) = -e^2/(2z)^2$ identical to that produced by a positive (mirror image) charge at a distance z inside the metal (Fig. 1A). If the metal has a band gap (in z direction) near the vacuum level $E_{\text{vac}} \equiv 0$, then an electron below E_{vac} may be trapped in the potential well formed by the Coulomb-like attractive image potential $V(z) = -e^2/4z$ and the repulsive surface barrier (4). The resulting quantized electronic states form a Rydberg series with energies E_n

$$E_n = \frac{-0.85 \text{ eV}}{(n + a)^2}, \quad n = 1, 2, \dots \quad (1)$$

converging toward the vacuum energy, where the influence of the surface potential on the binding energy $E_B = -E_n$ is approximated by a quantum defect $0 \leq a \leq 0.5$. Experimentally, image-potential states have been studied with 2PPE on many metal surfaces including surfaces covered with adsorbates and metallic overlayers (5, 7–11). One photon with energy $\hbar\omega_a$ ($\hbar$ is Planck's constant h divided by 2π and ω is the photon frequency times 2π) excites an electron out of an occupied state below the Fermi energy E_F into the image-potential state n . A second photon with energy $\hbar\omega_b$ excites the electron to an energy above E_{vac} (Fig. 1). The electron leaves the surface, and its kinetic energy $E_k = \hbar\omega_b + E_n$ is measured. Because the wave functions of image-potential states are mainly located in the vacuum above the surface, the lifetimes associated with image states can be significantly longer than those of electronic excitations

in the metal (11, 12). For Cu(100) and Ag(100) surfaces, lifetimes between 30 and 40 fs have been reported for the $n = 1$ state from the measurements of line-widths (5) and early time-resolved experiments (8). Theoretically, the overlap of the wave functions $|n\rangle$ with the bulk electronic states, and thus the lifetime τ_n , is expected to scale as n^3 (4). A sufficiently long decay time of the excited state population is essential for the experimental observation of the coherent phenomena described below.

The experimental setup consisted of a 80-MHz Ti:sapphire laser system that generated infrared (IR) pulses of 70-fs duration. Frequency-tripled 95-fs ultraviolet (UV) pulses from this laser were used for the excitation step ($\hbar\omega_a = 4.7 \text{ eV}$). The photoelectrons were emitted by the fundamental IR pulses ($\hbar\omega_b = 1.57 \text{ eV}$) and were detected in a hemispherical analyzer with an energy resolution of 30 meV and an angular acceptance of $\pm 0.6^\circ$ about the surface normal. The preparation of the Cu(111) and Cu(100) samples and details of the ultrahigh-vacuum chamber have been described elsewhere (5). The samples were kept at room temperature. Typical energy-resolved 2PPE spectra of Cu(100) obtained for zero delay between the UV

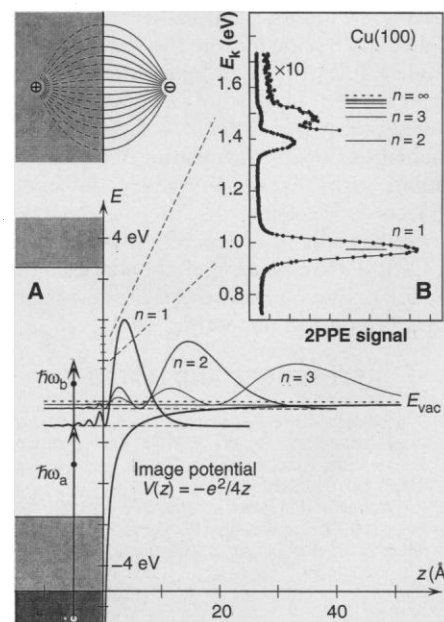


Fig. 1. (A) Electric field and potential energy diagram of an electron in front of a Cu(100) surface ($z = 0$). The potential well formed by the sp band gap (unshaded area in the metal) and the Coulomb tail leads to a series of discrete hydrogen-like electronic states that extend into the vacuum ($z > 0$). The squares of the wave functions of the lowest three states are shown. (B) Energy-resolved 2PPE spectrum obtained after excitation by photons of energy $\hbar\omega_a$ and $\hbar\omega_b$.

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and IR pulses (Fig. 1B) show three well-separated peaks corresponding to emission from the image-potential states $n = 1, 2$, and 3 and a shoulder arising from $n \geq 4$.

For the time-domain experiments, we set the electron analyzer to a fixed electron energy and recorded the 2PPE intensity as a function of the variable delay between the UV pump and the IR probe pulses. To measure the true cross-correlation between pump and probe pulses, we recorded the direct 2PPE signal from the occupied surface state of a Cu(111) sample (11) that was mounted on the same holder. The finite lifetimes of the electrons excited to the image states $n = 1, 2$, and 3 of Cu(100) led to a shift and asymmetric broadening of the correlation traces as compared to the Cu(111) reference (Fig. 2). The deduced decay times— $\tau_1 = 40 \pm 6$ fs, $\tau_2 = 110 \pm 10$ fs, and $\tau_3 = 300 \pm 15$ fs—increase significantly with n , as expected theoretically.

Under the present experimental conditions, the measured 2PPE intensity from each of the levels $n = 1, 2$, and 3 simply reflects the temporal evolution of the population of a single quantum state. Coherent phenomena arising from the simultaneous excitation of more than one state did not occur for the widely separated low- n image-potential states. When states with $n \geq 4$ were excited, the bandwidth of our 95-fs pump pulses (14-meV full width at half

maximum) became comparable to the energy separation of the states of the Rydberg series, and the coherent excitation of more than one eigenstate became possible, resulting in a different dynamical behavior of these electrons.

The recorded 2PPE intensity corresponding to a binding energy of $E_B \approx 40$ meV (Fig. 3A) shows an overall decay of the intensity on a time scale of roughly 1 ps, modulated by strong oscillations. This experiment represents a variant of the well-known quantum-beat spectroscopy of closely spaced states (3). In the simple case of coherent excitation of two levels $|n\rangle$ and $|n+1\rangle$, the oscillations reflect the beating between the corresponding wave functions $\Psi_n(t) = |n\rangle \exp(-i\omega_n t)$ and $\Psi_{n+1}(t) = |n+1\rangle \exp(-i\omega_{n+1} t)$. Provided there is no loss of coherence, the 2PPE intensity $I(t)$ long after the pulse is given by

$$I(t) \propto |a_n(t)\Psi_n(t) + a_{n+1}(t)\Psi_{n+1}(t)|^2 \quad (2a)$$

$$\propto a_n^2 + a_{n+1}^2 + 2a_n a_{n+1} \cos(\omega_{n,n+1} t) \quad (2b)$$

with the (exponentially) decaying coefficients $a_n(t)$ and $a_{n+1}(t)$ and a beat frequency of $\nu_{n,n+1} = \omega_{n,n+1}/2\pi = (E_{n+1} - E_n)/h$ ($h = 4.136$ eV fs).

For $E_B \approx 40$ meV, the 95-fs pump pulse predominantly excites electrons into the $n = 4$ and $n = 5$ states. The beating period observed for short delays is $\nu_{4,5}^{-1} = 230$ fs (Fig. 3A), corresponding to an energy difference between the states $\Delta E_{4,5} = h\nu_{4,5} = 17.8$ meV. After 2 ps, most of the population in the $n = 4$ state has decayed. The oscillations now reflect the interference of the amplitudes in the $n = 5$ state and the weakly excited $n = 6$ state that persist at these delays ($\nu_{5,6}^{-1} = 430$ fs; $\Delta E_{5,6} = 9.6$

meV). In general, the Fourier transform of the raw data directly yields the various beating frequencies (Fig. 3A, inset). The two main frequency components are 4.3 and 2.3 THz, which yield energy differences of 17.8 and 9.6 meV, respectively. The deduced values are slightly higher than the theoretical energy differences expected from Eq. 1 with the quantum defect $a = 0.21$ that reproduces the experimental binding energy for the $n = 1$ state. Similar results have been obtained for a Ag(100) surface. It must be emphasized that accurate spectroscopy of these states in the energy domain would require a resolution in the millielectron volt range, which is difficult to achieve experimentally (13). Additionally, time-resolved coherent spectroscopy is able to provide information about the relaxation behavior of the electrons in these states.

A density matrix formalism has been used to quantitatively model excitation, decay, and interference of the image-potential states in a unified way (14). Figure 3B displays the resulting temporal evolution of the population in the states $n = 4, 5$, and 6. The deduced lifetimes are extremely long for an electronic excitation on a bare metal surface. For example, $\tau_4 = 630$ fs corresponds to a Lorentzian linewidth $\Gamma \approx 1$ meV. This value of τ_4 is only slightly smaller than the value of 690 fs obtained by extrapolating from $\tau_3 = 300$ fs using the n^3 power law, confirming previous theoretical predictions (4). The long lifetimes of high-order image-potential states are associated with weak overlap with bulk electronic states. The resulting low-excitation cross sections have prevented previous time-resolved measurements of states beyond $n = 2$ (8).

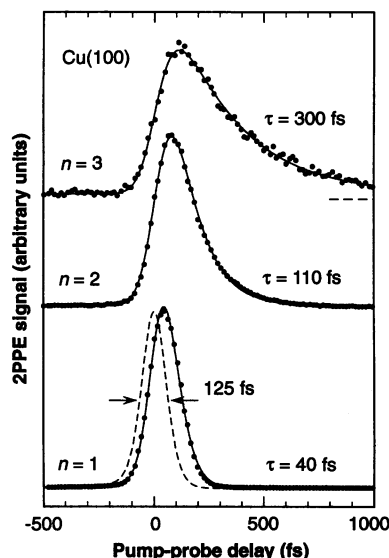
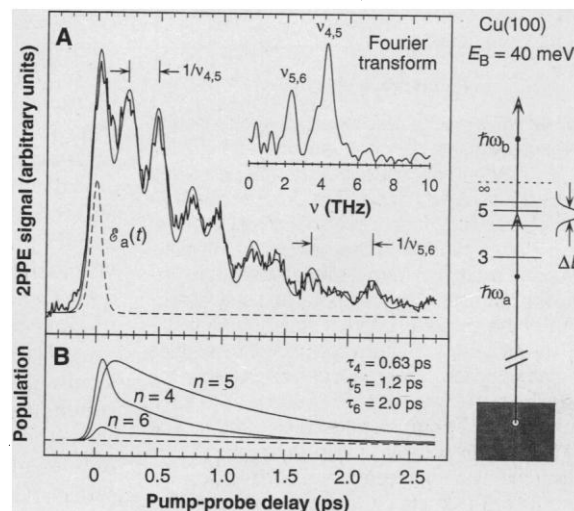


Fig. 2. The 2PPE cross-correlation traces obtained for the $n = 1, 2$, and 3 image-potential states of Cu(100). For positive delays, the UV excitation pulse preceded the IR probe pulse. Dots indicate measured data points. The solid lines are the results of density matrix calculations taking into account one intermediate state with a finite lifetime τ , as indicated. The dashed line marks the cross-correlation from the Cu(111) reference in the absence of a resonant intermediate state.

Fig. 3. Quantum beats observed after the coherent excitation of image-potential states with quantum numbers $n = 4, 5$, and 6 ($E_B \approx 40$ meV). (A) The thick curve corresponds to the measured 2PPE signal as function of pump-probe delay. The thin line is the result of the density matrix calculation for the two-photon excitation depicted schematically on the right side of the figure. The dashed line shows the envelope $\mathcal{E}_a(t)$ of the exciting UV pulse. The Fourier transform was obtained after subtraction of a smooth exponential decay from the measured data and directly gives the beating frequencies $\nu_{4,5} = (E_5 - E_4)/h$ and $\nu_{5,6} = (E_6 - E_5)/h$ between the excited states. (B) Relative population of the individual levels resulting from the calculation and corresponding decay times τ_n . The coherent peaks visible for $n = 4$ and $n = 6$ are caused by off-resonant excitation of these levels from the continuum of initial states in the metal.



For a binding energy of $E_B \approx 15$ meV, the excited eigenstates are centered around a mean value of $\bar{n} = 7$ (Fig. 4). The data show a strong correlation feature at delay zero and oscillations that persist for more than 3 ps. A discussion in terms of quantum beats between the states $n = 5, \dots, 9$ that significantly contribute to the measured signal would be complicated and not useful for understanding the dynamics of these weakly bound electrons. Instead, a description in terms of a spatially localized wave packet is more appropriate.

In space representation, the eigenstates $|n\rangle$ of the image potential are given by the s-like radial wave function of the hydrogen atom $R_n^{l=0}(z)$ multiplied by z and expanded by a factor of 4 (4). The coherent excitation of several states in the vicinity of $\bar{n} = 7$ out of the initial state localized at the surface creates a wave packet

$$\Psi_{WP}(z, t) = \sum_n a_n z R_n^{l=0}(z/4) e^{-i\omega_n t} \quad (3)$$

This wave function represents the oscillatory motion of the electron in the image potential in front of the surface. According to the calculated temporal and spatial evolution of the probability $|\Psi_{WP}(z, t)|^2$

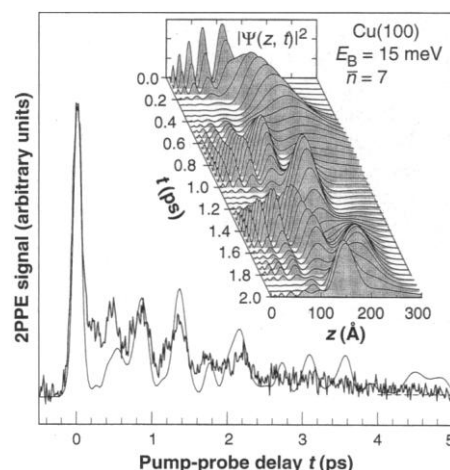


Fig. 4. Wave-packet excitation of weakly bound image-potential states centered around $\bar{n} = 7$ ($E_B \approx 15$ meV). Thick lines indicate the recorded 2PPE signal as function of the delay t of the IR probe pulse with respect to the exciting UV pulse. The smooth thin line is the calculated intensity, assuming excitation from a single initial state. (**Inset**) The corresponding temporal and spatial evolution of the created coherent state for the first 2 ps. The dynamics of the wave packet resembles the classical motion of an electron oscillating in the image potential with a period of 800 fs. The maximum distance from the surface is ~ 200 Å. The 2PPE signal is correlated with the probability of finding the electron close to the surface ($z = 0$). For the sake of clarity, the finite lifetime and dephasing of the image-potential states were not taken into account in the calculation of $|\Psi_{WP}(z, t)|^2$.

(Fig. 4, inset), immediately after excitation the electron has a high probability of being located close to the surface. The probability $|\Psi_{WP}|^2$ exhibits minima and maxima typical of the Laguerre polynomials that constitute the individual eigenfunctions $|n\rangle$, which all add in phase. As time progresses, the individual eigenfunctions shift out of phase, and the center of mass of $|\Psi_{WP}|^2$ moves away from the surface. By factoring out the fast oscillations with the center frequency $\omega_{\bar{n}=7}$ in Eq. 3 and noting that in the classical limit the orbiting period of an electron is given by $T_n = 2\pi/(\omega_{n+1} - \omega_n)$, it is easy to see that after $t = T_{\bar{n}}/2 \approx 0.4$ ps, the wave functions of neighboring states add with opposite signs. The amplitudes near the surface completely disappear, and Ψ_{WP} represents an electron located more than 200 Å away from the surface. The process then repeats itself with a period of $T_{\bar{n}} \approx 0.8$ ps. Because of the significant dispersion of the levels in the Coulomb potential (Eq. 1), this repetition is not exact, and the electron becomes delocalized for $t > 2$ ps.

The second laser pulse probes the localization of the oscillating electron. Far away from the surface, the electron is nearly free and cannot absorb a photon. Only close to the metal is the substrate able to provide the necessary momentum for photon absorption. Quantitatively, the larger photoemission matrix element close to the surface is related to the potential gradient $\nabla_z V(1)$. Comparison of the temporal evolution of the wave function and the 2PPE intensity shows good qualitative agreement. For example, the minima at $t = 1.1$ and 1.6 ps, as well as the maxima at 0.9 and 1.4 ps, are clearly correlated with the wave-packet motion. Deviations between experiment and calculation are mainly caused by the limited energy resolution of the electron analyzer (30 meV, compared to a bandwidth of the excitation pulse of 14 meV). For this reason, not all of the detected photoelectrons originate from the coherent excitation of the same intermediate levels.

The created electron wave packets have an analog in the Rydberg wave packets of atomic physics (15). For future surface investigations, it should be remarked that, quite generally, wave packets that reflect the motion of a particle can be created by short laser pulses if the initial state is well localized and if the laser bandwidth allows coherent excitation of several nondegenerate eigenstates of the system. In our case, only metal electrons in the vicinity of the surface have sufficient overlap with the image-potential states to be excited. The UV pulse duration of 95 fs corresponds to about 10% of the classical period $T_{\bar{n}=7} \approx 800$ fs.

Computer simulations of Rydberg wave packets have shown that such a relation between pulse duration and classical orbit time may generally be expected to lead to the "best" wave packets (15).

Time-resolved coherent photoelectron spectroscopy is not limited to the study of the electron dynamics of clean surfaces. Recently, much insight into the dynamics of gas-phase chemical reactions has been gained with femtosecond time-resolved laser spectroscopy of coherent states (16). The ability to probe the evolution of the wave function of a dissociative or desorptive electronic state in real time is expected to open avenues in the examination of the photochemistry of adsorbates. For chemisorbed species on metal surfaces, both nuclear motion and electronic energy flow typically occur on the femtosecond time scale (17). Therefore, such investigations will generally require shorter pulse durations than those used here for relatively long-lived image-potential states.

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