Wave-Packet Excitation and Quantum-Beat Spectroscopy of Image-Potential States

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ABSTRACT
The ultrafast dynamics of electrons in image-potential states on a Cu(100) surface is studied by means of femtosecond time-resolved two-photon photoemission (2PPE). By coherently exciting several eigenstates of the Rydberg series we observe periodic oscillations of the 2PPE signal as a function of the delay time between pump and probe pulses. These quantum beats allow us to determine the spacing of high-order states (quantum number \( n \geq 4 \)) that are difficult to resolve by conventional electron spectroscopy. The superposition of several states around \( n = 7 \) creates an electron wave packet that describes the quasi-classical periodic motion of weakly bound electrons. Its distance from the surface is reflected in the strength of the photoemission signal. The electron is observed to move about 100 atomic distances away from the surface and oscillates back and forth with a period of 800 femtoseconds. The results demonstrate the power of coherent laser spectroscopy for surface studies.

Keywords: Ultrafast surface dynamics, time-resolved two-photon photoemission, coherent spectroscopy, electron wave packets, quantum beats

1. INTRODUCTION
The properties of electrons at surfaces and interfaces of solid materials control diverse phenomena such as the performance of semiconductor devices and photochemical reactions at surfaces. Recent advances in ultrafast laser technology have enabled to study some of the underlying fundamental dynamics in real time. A particular powerful experimental technique is time-resolved two-photon photoemission (2PPE).\textsuperscript{1–9} A short pump laser pulse excites an electron into an intermediate state, a subsequent probe pulse emits it into the vacuum. The kinetic energy \( E_{\text{kin}} \) as well as the angle \( \theta \) at which the electron leaves the surface are measured and yield the information about its intermediate state.

\[ E_{\text{kin}} = \hbar \omega_{\text{b}} - (E_{\text{vac}} - E_{i}), \quad \hbar k_{\parallel} = \sqrt{2mE_{\text{kin}}} \sin \theta \]  

In these expressions \( \hbar \omega_{\text{b}} \) denotes the photon energy of the probe pulse, \( E_{\text{vac}} \) the vacuum energy and \( m \) the electron mass. \( E_{i} \) and \( k_{\parallel} \) are, respectively, the energy and parallel momentum of the electron which determine its intermediate state if it is confined to a surface. By performing a 2PPE experiment as a function of delay time \( t \) between pump and probe pulses one obtains \( E_{i}(t) \) and \( k_{\parallel}(t) \) and is thus able to follow the relaxation behavior of excited electrons in real time. This technique has been applied with great success to study electron dynamics at the surfaces or near-surface regions of semiconductors and metals over the past decade.\textsuperscript{1–6}

Here, we discuss an extension of this scheme which is possible by exploiting coherence phenomena. In addition to energy and momentum, an excited state is characterized by the phase of its wave function. In the common 2PPE experiment, that merely relies on the measurement of intensities, this phase information is lost. One possibility to recover it, is to control the time delay between pump and probe pulse with interferometric precision.\textsuperscript{7,8} Another possibility is to prepare a coherent superposition of energetically separated states by the pump pulse. Provided that the initial phase relationship is not lost by rapid dephasing processes, the quantum interference between the states will be visible in the intensity of the photoemission signal from the delayed probe pulse. In this article, we give a somewhat extended account of our recently reported investigations of image-potential states where we demonstrated the latter scheme.\textsuperscript{9}
Image-potential states are a class of normally unoccupied electronic states that exist at the surfaces of many single-crystal metals.\textsuperscript{10–12} An electron at a distance $z$ in front of a metal surface induces an electric dipole field and experiences an attractive force $F(z) = -e^2/(2z)^2$, identical to the one produced by a positive image charge at $-z$ inside the metal (Fig. 1A). If the metal has a band gap near the vacuum energy (in the direction perpendicular to the surface) then an electron below $E_{\text{vac}}$ may be trapped in the potential well consisting of the Coulomb-like attractive image potential $V(z) = -e^2/4z$ and the repulsive surface barrier.\textsuperscript{10} The resulting quantized electronic states form a Rydberg series with energies $E_n$ converging towards the vacuum energy.

$$E_n = E_{\text{vac}} - 0.85\text{ eV}/(n + a)^2, \quad n = 1, 2, \ldots$$

(2)

In this equation the influence of the surface potential on the binding energy is approximated by a quantum defect $0 \leq a \leq 0.5$. In the following all energies will be conveniently referred to the vacuum energy $E_{\text{vac}} \equiv 0$.

Due to their conceptual simplicity image-potential states are ideally suited to study the physics of electrons in two dimensions. Because the wave functions of image-potential states are mainly located in the vacuum in front of the surface, the lifetimes associated with image states can be significantly longer than those of electronic excitations in the metal.\textsuperscript{3,4} For the surfaces of Cu(100) and Ag(100) lifetimes between 30 and 40 fs have been reported for ($n = 1$)-state from the measurements of linewidths\textsuperscript{11} and early time-resolved experiments.\textsuperscript{13} Theoretically, the overlap of the wave-functions $|n\rangle$ with the bulk electronic states and thus the lifetime $\tau_n$ is expected to scale like $n^3$.\textsuperscript{10} A sufficiently long decay time of the excited state population is essential for the experimental observation of the coherent phenomena described below. On the other hand, the reduced overlap of the high-$n$ states with the metal makes their excitation and detection with 2PPE experimentally difficult.

**Figure 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 (non-shaded 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 square of the wave functions of the lowest three states is shown. (B) Energy-resolved 2PPE spectrum obtained after excitation with photons $\hbar \omega_a$ and $\hbar \omega_b$ as described in the text. (From Ref. 9).
2. EXPERIMENTAL

The experimental setup consisted of an 80-MHz femtosecond Ti:sapphire laser system that generated infrared (IR) pulses of 45-70 fs duration. Frequency-tripled ultraviolet (UV) pulses from this laser with pulse durations between 75 and 95 fs and a photon energy of $\hbar \omega_a = 4.7 \text{ eV}$ were used for the excitation step as indicated in Fig. 1B. 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 ultra-high vacuum chamber used for the present experiments have been described elsewhere.\(^{11}\) It should be emphasized that the high repetition rate of the laser and the long-term stability of the experimental setup are crucial for the present investigation of higher-order image-potential states ($n \geq 4$).

3. DYNAMICS OF LOW-$N$ STATES

Typical energy-resolved 2PPE spectra obtained from Cu(100) at room temperature are displayed in Fig. 1A. They show three well-separated peaks corresponding to the emission from the image states $n = 1, 2, 3$ and a shoulder arising from $n \geq 4$. For these measurements the delay between UV and IR pulses was adjusted to maximize the signal from the ($n = 1$)-state. The 2PPE intensity was recorded as function of the analyzer energy. The effect of the variable delay between the UV and IR pulses is demonstrated by the sequence of spectra plotted in Fig. 2A. As expected the intensity of the first image-potential is seen to decay the fastest. Some signal from the $n = 3$ state and its shoulder persist even at delays as high as 800 fs.

![Figure 2](image)

**Figure 2.** (A) Energy-resolved 2PPE spectra obtained for different time delays between the UV pump and the IR probe pulses. For positive delays the UV excitation pulse preceded the IR probe pulse. (B) 2PPE-cross-correlation traces obtained for the three lower image-potential states of Cu(100). The dashed line marks the cross-correlation from the Cu(111) reference in the absence of a resonant intermediate state. The spectral width of the pump pulse is indicated by $\Delta E$ in the excitation scheme to the right.
For quantitative measurements of the decay rates, the time-domain experiments were performed by setting the electron analyzer to a fixed electron energy and recording 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, in the absence of resonant intermediate states, we recorded the direct 2PPE signal from the occupied surface state of a Cu(111) sample which was mounted on the same holder. The results plotted in Fig. 2B show that the finite lifetimes of the electrons excited to the images states \( n = 1, 2, 3 \) of Cu(100) lead to a shift and asymmetric broadening of the correlation traces as compared to the Cu(111) reference. The deduced decay times are \( \tau_1 = 40 \pm 6 \text{ fs} \), \( \tau_2 = 110 \pm 10 \text{ fs} \) and \( \tau_3 = 300 \pm 15 \text{ fs} \). A detailed discussion of the relaxation dynamics of these low-\( n \) states will be published elsewhere. For the following it is important to note two observations. 1) The lifetimes \( \tau_n \) increase significantly with the quantum number \( n \) as expected theoretically. 2) A comparison of the lifetimes with the spectral linewidths \( \Gamma/2 = \bar{\hbar}/T_2 \) are indicative of dephasing times \( T_2 \) that are only slightly shorter than twice the decay time \( T_1 \) of the population in the image states. This suggests that, in principle, coherent phenomena arising from the simultaneous excitation of more than one state should be observable. For a pulse duration of the excitation pulse of 95 fs this does not occur for the well separated low-lying image states (Fig. 2A).

4. QUANTUM BEAT SPECTROSCOPY

The situation already becomes different when a somewhat shorter UV pulse duration is used and the energy analyzer is set to detect two-photon photoemission corresponding to a binding energy slightly below the \( n = 3 \) state. Results obtained for a pump pulse duration \( \tau_{UV} = 75 \text{ fs} \) and a binding energy \( E_B = -E_i = 70 \text{ meV} \) are plotted in Fig. 3. The data show an overall decay of the intensity as a function of the pump-probe delay on a timescale that is similar to the relaxation time of the \( n = 3 \) state. This overall decay is superimposed by weak oscillations with a periodicity of 115 fs that is clearly revealed after a smoothly decaying curve is subtracted from the data.

**Figure 3.** 2PPE cross correlation trace obtained for a binding energy that is slightly less than that of the \( n = 3 \) state using an excitation pulse of 75 fs duration and a 45-fs IR probe pulse. The weak coherent admixture of the \( n = 4 \) state leads to periodic oscillations of the 2PPE signal as a function of pump-probe-delay.
This experiment represents a variant of the well known quantum beat spectroscopy of closely adjacent states. Our 75-fs pump pulses have a bandwidth of 30 meV (measured full width at half maximum) and are thus able to coherently excite more than one eigenstate of the Rydberg series. In the simple case of the coherent excitations of two levels \( n \) and \( n+1 \) the oscillations reflect the beating between the corresponding wavefunctions \( \Psi_n(t) = |n\rangle \exp(-i\omega_n t) \) and \( \Psi_{n+1}(t) = |n+1\rangle \exp(-i\omega_{n+1} t) \), with \( \omega_n = E_n/\hbar \). Provided there is no loss of coherence, the 2PPE intensity \( I(t) \) long after the pulse will be given by

\[
I(t) \propto |a_n(t)\Psi_n(t) + a_{n+1}(t)\Psi_{n+1}(t)|^2 \tag{3}
\]

\[
I(t) \propto a_n^2 + a_{n+1}^2 + 2a_na_{n+1}\cos(\omega_{n,n+1} t) \tag{4}
\]

with the (exponentially) decaying coefficients \( a_n(t) \) and \( a_{n+1}(t) \) and a beat frequency of \( \nu_{n,n+1} = \omega_{n,n+1}/2\pi = (E_{n+1} - E_n)/\hbar \). The beating period of 115 fs in Fig. 3 corresponds to an energy difference of 36 meV.

The quantum beats become much more pronounced when the energy analyzer is set to detect electrons with yet smaller binding energies. An example corresponding to a binding energy \( E_B \approx 40 \text{ meV} \) is displayed in Fig. 4. In this case the almost transform-limited 95-fs sech\(^2\) pump pulse (bandwidth 14 meV) predominantly excites electrons into the \( n = 4 \) and the \( n = 5 \) states. The beating period observed for short delays is \( 2\pi/\omega_{4,5} = 230 \text{ fs} \) corresponding to an energy difference between the states \( \Delta E_{4,5} = 17.8 \text{ meV} \). After 2 ps most of the population in the \( n = 4 \) state

![Figure 4](image)

**Figure 4.** Quantum beats observed after the coherent excitation of image-potential states with quantum numbers \( n = 4, 5, 6 \) (\( E_B \approx 40 \text{ meV} \)). (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 \( E_a(t) \) 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 \( \nu_{45} = (E_5 - E_4)/\hbar \) and \( \nu_{56} = (E_6 - E_5)/\hbar \) between the excited states. (B) Relative population of the individual levels resulting from the calculation and corresponding decay times \( \tau_n \). 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. (From Ref. 9).
has decayed. The oscillations now reflect the interference of the amplitudes in \( n = 5 \) and the weakly excited \( n = 6 \) state that persist at these delays (\( 2\pi/\omega_{5,6} = 430\,\text{fs}; \Delta E_{5,6} = 9.6\,\text{meV} \)). In general, the Fourier transform of the raw data with the smooth exponential decay subtracted directly yields the various beating frequencies. This is shown in the upper right corner of Fig. 4. The two main frequency components are 4.3 and 2.3 THz which yield energy differences of 17.5 meV and 10.0 meV, respectively. The deduced values are slightly higher than the theoretical energy in the upper right corner of Fig. 4. The two main frequency components are 4.3 and 2.3 THz which yield energy data with the smooth exponential decay subtracted directly yields the various beating frequencies. This is shown part of the figure displays the calculated population in the states

It must be emphasized that the accurate spectroscopy of these states in energy-domain would require a resolution in the meV-range which is difficult to achieve experimentally. In the literature of image-potential states, e.g., the best energy resolution has been reported by Padowitz et al.\(^{17}\) With a time-of-flight electron analyzer these authors were able to resolve the \( n=4 \)-state of Xe/Ag(111). With quantum beat spectroscopy, closely separated lines can even be resolved in cases where inhomogenous broadening of a whole set of levels would principally prevent their spectral resolution. 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. Briefly, an initial state \( |0\rangle \) is coupled to several excited states \( |n\rangle = |1\rangle \ldots |2\rangle \) by the pump pulse which are then coupled to a final state \( |f\rangle \) by the probe pulse. The decay of the excited states is taken into account by lifetimes \( \tau_n \) of the population in each state. In order to limit the number of free parameters the following approximations are made for the present application: 1) Dephasing without population decay (pure dephasing) is neglected. 2) Power laws are assumed for lifetimes \( \tau_n \propto (n+a)^3 \) and coupling strength \( \frac{\hbar}{\Delta}(n|\mu_{ab}|0) \propto (n+a)^{-3} \). 3) All energies of excited states are assumed to be given by eq. (2). 4) The coupling of the excited states to the continuum by the probe pulse is approximated by a weighted projection of the coherent superposition of excited states into the continuum and convolution with the envelope of the probe pulse. A Gaussian analyzer transmission function and a power law for the emission probability \( \frac{\hbar}{\Delta}(f|\mu_{ab}|n) \propto (n+a)^{-3} \) is used to describe the detection probability. 5) An important effect to obtain close quantitative agreement with the experiment is the availability of a continuum of initial states in the conduction band of the metal and the finite energy resolution of the electron analyzer. It is taken into account by performing the calculation for different initial states and by incoherently summing up the obtained intensities.

A fit of the model calculation with excited states from \( n = 4 \ldots 8 \) taken into account is shown in Fig. 4A. Apart from a trivial scaling factor, the fit has only three variable parameters, the lifetime \( \tau_4 \), the quantum defect \( a \) and the mean binding energy of the detected states \( E_B \). Although the latter is fixed by the experiment, we observed that the modelling is more sensitive to this parameter than the accuracy with which we could control it experimentally (\( \pm 10\,\text{meV} \)). In view of the approximations involved and the few variable parameters in the fit, the agreement between experiment and theoretical model is excellent and confirms the validity of the theoretical description. The deduced quantum defect is \( a = 0.15 \). The lifetime of the \( n = 4 \) state is \( \tau_4 = 630\,\text{fs} \), only slightly smaller than the 690 fs that are obtained by extrapolating from \( \tau_3 = 300\,\text{fs} \) using the \( (n+a)^3 \) power law. The observed slight deviations of the level spacing from the behaviour predicted by eq. (2) as well as the exact dependences of the lifetimes of the image states on the quantum number are related to the details of the electronic structure of the surface.\(^{11}\) The lower part of the figure displays the calculated population in the states \( n = 4, 5, 6 \) that mainly contribute to the measured intensity. The lifetimes are likely to be the longest that have ever been observed for an electronic excitation on a bare metal surface. For example, \( \tau_4 = 630\,\text{fs} \) corresponds to a Lorentzian linewidth \( \Gamma \simeq 1\,\text{meV} \). Of course, the long lifetimes are associated with weak overlap with bulk electronic states. The resulting low excitation cross sections have prevented the time-resolved detection of states beyond \( n = 2 \) and the energy-resolved detection of states beyond \( n = 4 \) in previous experiments.\(^{11–13,17}\)

5. ELECTRON WAVE PACKETS

As the level spacing of the image-potential states decreases with increasing quantum number \( n \), their population with a 95-fs pulse leads to the coherent superposition of 5 or more states. A discussion of the resulting effects in terms of quantum beats would be very complicated and not useful for the understanding of 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 \( R_n(a,z) \) multiplied by \( z \) and expanded by a factor of 4.\(^{10}\) The coherent excitation of several
states in the vicinity of some central state \( \bar{n} \) out of the initial state localized at the surface creates a wave packet

\[
\Psi_{WP}(z, t) = \sum_{n} a_{n} z R_{n}^{z=0}(z/4) e^{-i\omega_{n} t}
\]  

(5)

The temporal and spatial evolution of the probability \(|\Psi_{WP}(z, t)|^{2}\) resulting from calculated coefficients \(a_{n} \propto (n + a)^{-3}\) is displayed in Fig. 5 for two cases. In the case of the superposition of three levels in the vicinity of \( \bar{n} = 5 \) by a 95-fs pulse the probability \(|\Psi_{WP}(z, t)|^{2}\) concentrates at a distance of \( \sim 90 \text{ Å} \) from the surface (Fig. 5A). There, it exhibits only weak temporal modulations that are opposite in phase to the much more pronounced modulations close to the surface. This example corresponds to the quantum beat experiment shown in Fig. 4. The spatial dynamics of the wave packet is negligible for the description of this experiment. When the same pulse excites image-potential states in the vicinity of \( \bar{n} = 7 \), five levels \( (n = 5, \ldots, 9) \) appreciably contribute to the total amplitude. The wave packet now exhibits a much more dramatic spatial dynamics. The probability of locating the electron oscillates back and forth from the surface (Fig. 5B).

For the further discussion it is instructive to note that in the classical limit the orbiting period of an electron is given by

\[
T_{n} = \frac{2\pi}{(\omega_{n+1} - \omega_{n})}
\]

A Taylor expansion of \(\omega_{n} \propto n^{-2}\) around the central frequency \(\omega_{\bar{n}}\) then becomes

\[
\omega_{n} = w_{\bar{n}} + \frac{2\pi}{T_{\bar{n}}} \Delta n - \frac{2\pi}{(\bar{n}/6)T_{\bar{n}}}(\Delta n)^{2} + \ldots
\]  

(6)

where \(\Delta n = n - \bar{n}\). When only the harmonic term of eq. 6 is considered, then the wave function 5 can be written in terms of product of a fast oscillating contribution that is not observable in the experiment and a term with a periodicity of the classical revolution time \(T_{\bar{n}}\)

\[
\Psi_{WP}(z, t) = e^{-i\omega_{\bar{n}} t} \sum_{n} a_{n} z R_{n}^{z=0}(z/4) \exp \left[ -2\pi i \left( \frac{\Delta n t}{T_{\bar{n}}} + \ldots \right) \right].
\]  

(7)

Figure 5. Calculated temporal evolution of wave packets created by the coherent superposition of several image-potential states for two cases. (A) Superposition of three levels in the vicinity of \( \bar{n} = 5 \) by a 95-fs pulse. The probability \(|\Psi_{WP}(z, t)|^{2}\) concentrates at a distance of \( z \sim 90 \text{ Å} \) from the surface exhibits only a weak temporal modulation. (B) Superposition of image-potential states centered around \( \bar{n} = 7 \) created by the same excitation pulse. The dynamics of the wave packet resembles the classical motion of an electron that oscillates in the image potential with a period of 800 fs. The maximum distance is \( \sim 200 \text{ Å} \) away from the surface. (For the sake of clarity the finite lifetime and dephasing of the image-potential states have not been taken into account in the calculation of \(|\Psi_{WP}(z, t)|^{2}\).
**Figure 6.** Wave-packet excitation of weakly bound image-potential states centered around $\bar{n} = 7$ ($E_B \approx 15$ meV). Thick lines in the main panel 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. In order to reveal the main features the effect of the incoherent summation over different excitations due to the limited energy resolution has been neglected. The inset shows the corresponding temporal and spatial evolution of the created coherent state for the first 2 ps. (After Ref. 9).

Fig. 5B shows that immediately after the excitation ($t \leq 0.1$ ps $\ll T_{\bar{n}}$) the electron has a high probability of being located close to the surface. $|\Psi_{WP}|^2$ exhibits the minima and maxima typical for the Laguerre polynomials that constitute the individual eigenfunctions $|n\rangle$ which according to eq. (7) all add in phase. As time progresses the individual $|n\rangle$'s get out of phase and the center of mass of $|\Psi_{WP}|^2$ moves away from the surface. After $t = T_{\bar{n}}/2 \approx 0.4$ ps the wavefunction of neighbouring states are added with opposite signs. The amplitudes near the surface have completely disappeared and $\Psi_{WP}$ describes an electron located almost 200 $\AA$ away from the surface. Then the processes repeat itself with a period of $T_{\bar{n}} \approx 0.8$ ps. Due to the significant dispersion of the levels described by the higher terms in the Taylor expansion (6) this repetition is not exact and the electron becomes delocalized for $t_p > 2$ ps (not shown).

Results corresponding to such a situation were obtained by performing 2PPE experiments for a binding energy of $E_B \approx 15$ meV. The excited eigenstates are centered around $\bar{n} = 7$. The data displayed in Fig. 6 show a strong correlation feature at delay zero and oscillations that persist for more than 3 ps. The smooth line is the result of the density matrix calculation with intermediate states between $n = 4$ and $n = 15$ taken into account. In order to reveal the main features the effect of the incoherent summation over different excitations due to the limited energy resolution has been neglected. Nevertheless, the calculation qualitatively reproduces the main experimental features quite well.

A comparison of the temporal evolution of the wave packet reproduced in the inset of Fig. 6 and the 2PPE
intensity shows that the second laser pulse probes the localization of the oscillating electron. The distance of the wave packet from the surface is reflected in the strength of the 2PPE-signal. The minima at \( t = 1.1 \) and 1.6 ps as well as the maxima at 0.9 fs 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 14 meV of the excitation pulse). For this reason, not all of the detected photoelectrons originate from the coherent excitation of the same intermediate levels.

Qualitatively, the detection of the wave packet motion by the probe pulse can be understood from the fact that far away from the surface the electron is nearly free and cannot absorb a photon. Only if it is close to the surface, the metal is able to provide the necessary momentum for photon absorption. Quantitatively, the larger photoemission matrix-element close to the surface is related to the strongly varying potential \( \nabla_z V \).

The created electron wave packets have an analogue in the Rydberg wave packets of atomic physics. For future surface investigations it should be remarked that, quite generally, wave packets that reflect the motion of a particle may 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 \( T_\tau \approx 800 \text{ fs} \). Computer simulations of Rydberg wave packets have shown that such a relationship between pulse duration and classical orbit time may generally be expected to lead to the "best" wave packets.

### 6. CONCLUSIONS

In the present investigation, 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 Cu(100) surface it was demonstrated that the spectroscopy of quantum beats makes 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 describe the quasi-classical periodic motion of weakly bound electrons. Of course, time-resolved coherent photoelectron spectroscopy is not limited to the study of 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. The ability to probe the evolution of the wave function of a dissociative or desorptive electronic state in real time is expected to open new avenues also in the examination of adsorbed species. Of particular interest in this context could be the photochemistry of weakly coupled but aligned and ordered molecular layers on oxidized surfaces or the coherent control of photostimulated adsorbate reactions on spacer layers.

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### REFERENCES