Review

Quasi-elastic scattering of electrons in image-potential states

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Abstract

Image-potential states provide a model system to study electron scattering at surfaces. With time-, energy- and angle-resolved two-photon photoemission quasi-elastic intraband and resonant inter-band scattering processes can be identified and resolved. The scattering sources are related to phonons and to imperfections of the surface such as defects and steps.

Keywords: Surface electronic phenomena; Angle-resolved photoemission; Two-photon photoemission; Surface states; Image-potential states; Femtosecond dynamics

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1. Introduction

Image-potential states are a well-known class of states at metal surfaces and form a series of free-electron-like bands [1,2]. With increasing quantum number $n$ the probability density moves away from the surface and the interaction with electrons and atoms at the surface decreases. For perfect surfaces at low temperatures electron–electron interaction with surface and bulk electrons causes decay of the excited electronic state by inelastic intra- and interband scattering [3]. For real surfaces scattering by phonons or defects, e.g. adatoms or steps, provide additional scattering channels, which lead to small or negligible change of energy. These quasi-elastic scattering processes are the topic of this contribution. Possible processes are illustrated in Fig. 1 for particles in real space and more accurately for electronic states in an energy diagram. In process A, the electron is scattered elastically from an image-potential state to a bulk state. This leads to a decrease of the population in the image-potential state and can be detected by time-resolved two-photon photoemission. Experimentally, it has been found for scattering by adatoms [4] and contributes to the asymmetry of scattering at step edges [5,6]. Process A will not be discussed in detail in the present paper. The most simple scattering process leads just to a change of direction, i.e. momentum, parallel to the surface and is illustrated as process B in Fig. 1. This intraband scattering does not change the population in the image-potential band and can therefore not be detected in usual time-resolved two-photon photoemission measurements. The phase change in the scattering event, however, increases the linewidth or destroys quantum beats as will be shown in Section 2. The series of image-potential bands offers always the elastic scattering between different bands as an additional possibility. Section 3 discusses this case of resonant interband scattering where a large momentum transfer parallel to the surface is accompanied by a change of the wave function perpendicular to the surface. This process is particularly effective at steps as indicated in Fig. 1 and leads to

![Fig. 1. Defect-induced scattering processes for image-potential states in real space (left) and in an energy diagram (right).](image-url)
a biexponential decay in time-resolved two-photon photoemission measurements due to the markedly different lifetimes of different image-potential states.

2. Intraband scattering processes

Any scattering process changes the momentum of the particle and should therefore lead to an exchange of energy between the scattering partners. The energy difference of the particle before and after the interaction can be small compared to the experimental energy resolution and it is convenient to call such a scattering process ‘quasi-elastic’. Inelastic scattering processes can be easily detected by the change in energy of the particle or the loss of population of a particular state with well-defined energy. A quasi-elastic scattering event of a quantum-mechanical particle can be seen in a phase change of the time evolution of its wave function. This dephasing process (or more precisely pure dephasing) should be distinguished from decay processes which also lead to the loss of phase coherence. The identification of the dephasing in image-potential states by time- and energy-resolved two-photon photoemission (2PPE) will be exemplified for clean metal surfaces in Section 2.1. Scattering of electrons in image-potential states by phonons and defects involves small energy transfer and will be discussed in Sections 2.2 and 2.4, respectively. Inelastic scattering by coupling to molecular vibrations is the topic of Section 2.3.

2.1. Linewidths and quantum beats of clean surfaces

Electrons in image-potential states can interact a priori with any real particle or quasiparticle excitation at the surface. On a perfect surface the interaction with the atoms including their valence electrons is described by the crystal potential. Its main influence is the creation of the band gap necessary to support image-potential states and it determines their energy relative to the vacuum level [1,2]. The electron–electron interaction has two implications on the electrons excited into image-potential states: (i) Screening of the charge by the metal electrons leads to the image potential and is taken into account by the energies of the image-potential states. (ii) Inelastic electron–electron scattering is responsible for the finite lifetime of the image-potential states. The last process may lead to energy changes small compared to the experimental energy resolution. The purpose of this section is to introduce the basic concepts of how to extract the dephasing rate from time- and energy-resolved two-photon photoemission data. The clean Cu(001) surface serves as an example and we will show that dephasing plays only a minor role for this surface.

For fixed photon energy, two-photon photoemission measurements depend on two parameters: kinetic energy of the electrons and time delay between the pump and probe laser pulses. A set of energy spectra is plotted in Fig. 2 on a binding energy scale relative to the vacuum level. Data were obtained from a Cu(001) surface for various pump–probe delays. The peak positions for the image-potential states \( n = 1 \) and \( 2 \) are independent of the delay. This is a prerequisite for meaningful time-resolved measurements of the decay rate. However, there is a considerable change in the width of the peaks. The linewidth (full width at half maximum) is plotted in Fig. 3 as a function of pump–probe delay. It decreases linearly from negative time delay (probe before pump) and reaches a constant value for long delays. These observations can be explained by modeling the two-photon photoemission process in the Liouville–von-Neumann formalism [7–9]. The density-matrix
description leads to the optical Bloch equations [10] which can be solved analytically for certain limiting cases [11,12]. The decay and dephasing rates $\Gamma$ and $\Gamma^*$ are introduced ad hoc into these equations without modeling the underlying microscopic scattering processes. The resulting lineshape can be described very well by a Lorentzian convoluted

Fig. 2. Two-photon photoemission spectra for the image-potential states on Cu(001) for different pump–probe delays taken with $3\hbar\omega = 4.46$ eV pump and $\hbar\omega = 1.49$ eV probe pulses.

Fig. 3. Linewidth for the $n = 1$ and 2 image-potential states (circles and squares, respectively) on Cu(001) compared to the results of numerical calculations for Gaussian and hyperbolic-secant laser pulses (solid and dashed lines, respectively). Adapted from [11].
by a Gaussian function. The latter accounts for the experimental parameters such as the energy resolution of the analyzer and the spectral bandwidth of the laser pulses. The Lorentzian represents the intrinsic linewidth and contains information about the dephasing rate and depending on the delay also the decay rate. For the one-step process of direct photoemission the intrinsic linewidth contains the sum of decay and dephasing rates, which cannot be separated directly in the experiment. For the identification of the contributions of phonons or defects to the linewidth one has to vary the temperature or defect density, respectively.

The distinction of two-photon photoemission lies in the fact that we probe a time-dependent population of the intermediate state \([11]\). If the laser pulses are longer than the lifetime of the involved states the intrinsic linewidth is given approximately by the sum of decay and twice the dephasing rate \((\Gamma + 2\Gamma^*)\) \([12]\). For comparable time scales, the time dependence includes the temporal shape of the pump pulse and the decay of the excited electron. The decay is assumed to be exponential after the pump pulse is over. This is illustrated in Fig. 3 where calculations are compared to the data extracted from spectra as shown in Fig. 2. The parameters decay and dephasing rates as well as the widths of pump and probe pulses match the values obtained by independent measurements \([11]\). For long delays the linewidth is determined by twice the dephasing rate \((2\Gamma^*)\) and spectral width of the laser pulses. The decay rate \(\Gamma\) does not contribute to the linewidth for Gaussian-shaped laser-pulse envelopes in two-photon photoemission \([11]\). This is in contrast to one-photon photoemission which proceeds from a constant initial-state population. From the almost identical linewidth for both image-potential states at long delays (see Fig. 3) we can immediately deduce almost identical dephasing rates for the \(n = 1\) and \(2\) image-potential states. From a comparison with the measured decay rate (obtained as \(\Gamma = \hbar/\tau\) from the measured lifetime \(\tau\)) we conclude that the dephasing rates are negligible for the Cu(001) surface \([13]\). Fig. 3 presents also the results of calculations for laser pulses with a hyperbolic-secant envelope as dashed lines \([11]\). The agreement with the experimental data is worse for negative delays. This proves the Gaussian envelopes of the used laser pulses as confirmed for the infrared laser pulses by measurements of the autocorrelation function \([14]\).

For the higher image-potential states \((n \geq 3)\) a linewidth analysis is not feasible in practice. The states are difficult to resolve in the energy domain because their separation is small compared to the energy resolution of the analyzer and the bandwidth of the femtosecond laser pulses. However, the large spectral bandwidth leads to the coherent excitation of several image-potential states as discussed in \([16]\). For the \(n = 3\) and \(4\) states on Cu(001) the resulting quantum beats are shown in Fig. 4. The data consist of exponentially decaying oscillations of the 2PPE-signal superimposed on an exponential decay due to the finite lifetime of the involved states. The respective function is convoluted by a Gaussian to take the pulse envelope of the probe pulse into account. The decay of the oscillation is a direct visualization of the loss of phase coherence between the two states \([17]\). In the example shown in Fig. 4 the oscillations decay only slightly faster than the population of the \(n = 3\) state. This indicates that scattering processes that would dampen the oscillations in addition to the decay of the population in the \(n = 3\) and \(4\) states are of minor importance. For well-prepared Cu(001) surfaces dephasing is thus negligible for image-potential states with high as well as low quantum numbers.

The small dephasing for the clean Cu(001) surface leads to the following conclusions: (i) The amount of defects or steps is rather small. (ii) The influence of phonons is negligible
because the overlap of the image-potential states with bulk bands is minimal for states close to the center of the band gap [13]. (iii) The contribution of electron–electron scattering events with small energy transfer is low because no final states are available at the bottom of the image-potential bands. For parallel momentum $k_{\parallel} \neq 0$ intraband scattering is possible [18].

Generalizing the lesson learned from Cu(001), the dephasing rate should be rather low for metal surfaces with negligible amounts of impurities and defects. A small overlap with bulk states reduces electron–phonon scattering which provides the main quasi-elastic scattering channel on a perfect surface and will be the topic of Section 2.2. Electron–electron scattering with bulk or surface electrons is predominantly inelastic and described by the lifetime. For clean metal surfaces the intrinsic linewidths should therefore be identical to the decay rates $\hbar/\tau$ in particular at low temperatures. However, the linewidths measured previously with low-repetition-rate nanosecond laser systems are usually larger than decay rates obtained from time-resolved spectroscopy [19]. The contributions from the bandwidth of the laser pulses can be neglected for nanosecond pulse durations. The discrepancy to the former data [2] is therefore most likely attributable to poorer statistics, limited analyzer resolution, and longer measurement times. The latter could lead to surface contamination which would result in dephasing. Because most of these measurements were done at room temperature dephasing by phonon scattering contributes also to the linewidth. From energy-resolved spectra with femtosecond pulse lengths the intrinsic linewidth has to be determined with care because of the effects presented in Figs. 2 and 3.

2.2. Phonon-induced broadening

Quasi-elastic scattering by phonons depends on the number of excited phonons which is for high temperatures proportional to the absolute temperature $T$. The resulting dephasing shows up in an increase of the linewidth with temperature. Two-photon photoemission spectra from a Cu(111) sample are shown in Fig. 5 for temperatures between 25 and
460 K [20]. The two peaks correspond to the $n = 1$ image-potential state and the occupied surface state ($n = 0$). The peaks shift significantly with temperature, attributed mainly to the variation of the band gap due to the thermal expansion of the lattice [20]. More interesting in the present context is the change of the linewidth with temperature. The spectra of Fig. 5 were modelled by three-level optical Bloch equations using experimentally derived lifetimes for the $n = 1$ image-potential state. The obtained dephasing rates plotted in Fig. 6 increase for both states linearly with increasing temperature. Above 400 K, a significant deviation is found for the $n = 1$ state because the energy of the state is degenerated with bulk bands in this temperature range [20]. The concomitant larger penetration into the bulk leads to an increased coupling with bulk phonons and results in an increase of the dephasing rate.

The slope of the linear increase of the dephasing rate with temperature is commonly described by the electron–phonon mass-enhancement parameter $\lambda = \Gamma_{\text{e-ph}}^*/2\pi k_B T$ [21]. The value $\lambda = 0.14 \pm 0.02$ derived for the occupied surface state ($n = 0$) in 2PPE is in excellent agreement with the results of photoemission experiments [22–24]. For the $n = 1$ image-potential state the parameter $\lambda$ has a smaller value of $0.06 \pm 0.01$ compared to the occupied surface state. The explanation for this observation lies in the smaller penetration of the wave function into the bulk for the $n = 1$ state compared to the $n = 0$ state [20].

An extrapolation to $T = 0$ K yields dephasing rates of 40 and 14 meV for the $n = 0$ and $n = 1$ states. This indicates a significant amount of defects even on Cu(111) surfaces prepared according to the state of the art. For the occupied surface state an agreement of the
intrinsic linewidth from photoemission experiments with scanning tunneling spectroscopy measurements on perfect sample areas and theoretical calculations is obtained only, if data are taken within a few minutes after sample preparation [24, 25]. Theoretical calculations of the electron–phonon coupling for the occupied surface state on Cu(111) are in excellent agreement with the experimental data [24]. Results for the \( n = 1 \) image-potential state are not available. The parameter \( \lambda \) can be expected to be rather small as calculated for \( n = 1 \) states of Na/Cu(111) [26] and of the (001) surfaces of Cu and Ag [27]. The latter observation is attributed to the small overlap with bulk bands for image-potential states near the center of the band gap [13].

2.3. Phonon-induced inelastic scattering

Theoretical calculations show that phonons with large momentum may also scatter between different surface bands [26]. Although the energy change associated with this interband scattering is small, it is not quasi-elastic in the sense introduced above because it changes the population of the state under scrutiny. Similar to the resonant interband scattering discussed in Section 3 such processes cannot be distinguished from other inelastic decay processes, unless it is possible to identify the scattered electrons in the final state. Up to now, corresponding experiments have not been reported.

Of course, also the inelastic nature of phonon-induced intraband scattering can become experimentally observable. Whereas small energy and momentum changes are accessible only due to the corresponding dephasing, as discussed above, sufficiently large energy...
transfers caused by multiple scattering events or by high energetic phonons become visible in terms of a population change. An experimental result that has been interpreted in such a way is the intraband relaxation of image-potential state electrons observed by Hotzel et al. for 1 ML of N\(_2\) on Xe spacer layers on Cu(111) \[28\].

The decoupling of the N\(_2\) layer from the copper substrate reduces the relevant electronic states to two bands as sketched in the inset of Fig. 7: a partially occupied band \(n = 0\) related to the occupied surface state on the clean Cu(111) surface and an image-potential band \(n = 1\). Due to the different effective masses of these bands, excitations between these bands are for a given photon energy only possible at well-defined parallel momentum \(k_\parallel\). States at lower energies in the band are therefore populated after inelastic scattering from higher lying states. The associated time-resolved two-photon photoemission measurements are shown in Fig. 7. For \(k_\parallel = 0.15\) Å\(^{-1}\) the signal increases immediately with the pump pulse and decays with a time constant of 0.6 ps. At the bottom of the band at \(k_\parallel = 0\) the intensity increases on a time scale of 0.6 ps and has a lifetime of 1.6 ps. Rise and decay times between the quoted values are found for intermediate parallel momenta.

The obvious interpretation is intraband relaxation of the electrons towards the bottom of the band. It is observed in the decay of the higher lying states as well as the related filling of lower lying states by cascading electrons. Hotzel et al. \[28\] proposed that the scattering processes are due to a coupling of the electrons in image-potential states to nuclear degrees of freedom in the N\(_2\) layer such as hindered rotations (librations). Corresponding calculations of intraband decay rates were found to be in good agreement with the experimental findings \[28\]. A significant contribution of electronic scattering processes mediated by bulk states was excluded by Hotzel et al. It should be added in this context that the \(k_\parallel\)-dependence of the lifetimes for clean and Ar-covered Cu(100) \(\tau(k_\parallel = 0)/\tau(k_\parallel = 0.15\) Å\(^{-1}\) \(= 1.3\) is significantly weaker than that of the data shown in Fig. 7 \[18,29\]. Although neither

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**Fig. 7.** Cross-correlation traces of the \(n = 1\) peak measured at different \(k_\parallel\) on 1 ML N\(_2\)/1 ML Xe/Cu(111) with photon energies of \(h\nu_{\text{pump}} = 4.28\) eV, \(h\nu_{\text{probe}} = 2.14\) eV (solid lines). Dotted line: cross-correlation function of the pulses. Going from \(k_\parallel = 0\) to \(k_\parallel = 0.15\) Å\(^{-1}\) the \(n = 1\) lifetime decreases from 1.6 ± 0.4 ps to 0.62 ± 0.1 ps, while the finite rise behavior, which is very pronounced at \(k_\parallel = 0\), completely disappears. (From \[28\]).
experimental nor theoretical values for electron-mediated intraband scattering are known for Cu(111), it seems unlikely that it could lead to as strong an intraband decay as observed for the N₂/Xe/Cu(111) system.

For semiconductors the electron and phonons couple via deformation potential scattering [30]. This process has been studied in detail for surface states on the Si(100) surface [31–33]. Electrons resonantly excited to the unoccupied dangling-bond band with an excess energy of about 350 meV scatter via phonon emission on a time scale of 50 fs and reach the band bottom in 1.5 ps.

### 2.4. Influence of defects

Defects are a major source for quasi-elastic scattering at surfaces. They interrupt the periodicity of the surface and quasi-free-electron motion of the electrons parallel to the surface is disturbed. The simplest process would be elastic scattering by the defect. This changes the direction but not the energy of the electron in the image-potential state as indicated by process B in Fig. 1.

Early energy-resolved two-photon photoelectron spectroscopy observed already an increase of the linewidth of image-potential states with adsorbate coverage for several systems [2,34–36]. However, these studies could not distinguish between inelastic decay and quasi-elastic scattering-induced by the adsorbates. The combination with time-resolved measurements is needed to separate the different processes for image-potential states.

![Fig. 8. Influence of Cu adatoms on the quantum beats on Cu(001). The inset shows the decay rate of the average population as a function of decay rate of the oscillations for Cu and CO on Cu(001). (Adapted from [15]).](image-url)
As a first illustration for defect scattering we show in Fig. 8 time-resolved two-photon photoemission data for small amounts of Cu adatoms and CO molecules on Cu(001) [15,17,37]. In the quantum-beat spectroscopy of the $n = 3$ and $4$ image-potential states the decay of the population is caused by inelastic scattering, whereas the oscillations are dampened in addition also by quasi-elastic scattering events which change the temporal phase of the wave functions. Fig. 8 shows that CO has almost no influence on the lifetime, but destroys the oscillations very effectively. On the other hand does a small concentration of Cu adatoms decrease the lifetime dramatically. In the inset of Fig. 8 a quantitative comparison of the decay of the oscillations to the one of the population is presented. For CO as well as Cu a significant contribution of dephasing is found.

The same behavior as for the higher image-potential states shown in Fig. 8 is found for the $n = 1$ and $2$ image-potential states. Fig. 9 shows a series of spectra as a function of CO coverage on Cu(001). Already at low CO exposures a strong increase of the linewidth relative to the clean surface can be seen immediately from the raw data. For the $n = 1$ image-potential state a comparison of the intrinsic linewidth with the decay rate measured in time-resolved experiments is shown in Fig. 10. The analogous data for Cu on Cu(001) are also included. The results for the $n = 1$ state are quite similar to the ones shown in the inset of Fig. 8 for the $n = 3$ and $4$ states. In these plots the adsorbate coverage does not enter explicitly, because the decay and dephasing rates are compared for the same

![Fig. 9. Series of energy-resolved 2PPE spectra as a function of CO exposure (from [37]).](image)
sample preparation. For Cu the coverages are almost an order of magnitude lower than for CO [37,38].

The reason for the relatively strong dephasing caused by CO molecules compared to Cu adatoms is not completely understood yet. A good starting point for a theoretical modeling might be the distinction between attractive and repulsive scattering potentials presented by the adsorbates to the electrons in the image-potential states [15].

The decay and dephasing rates for different systems can be compared by looking at the ratio between these rates. Such an evaluation is shown in Fig. 11 as a function of binding energy. For the clean surfaces decay exceeds dephasing in all cases. The Cu(001) surface (not shown in Fig. 11) was discussed already in Section 2.1 and only upper bounds for the dephasing rates can be given [13]. The temperature dependence of the dephasing for Cu(111) was the topic of Section 2.2. The almost equal strength of decay and dephasing for the \( n = 1 \) image-potential state on Cu(111) is most likely attributed to disorder in the step separation [39,40].

For CO and Cu on copper substrates the change of the respective rates with coverage is given in Fig. 11. By taking the ratio any differences in coverage or morphology cancel. All adsorbate systems lead to a decrease of the ratio compared to the clean substrates. This indicates that disorder on the surface favors quasi-elastic over inelastic scattering. For Cu on Cu(001) decay is comparable or larger than dephasing, while for CO on Cu(001) dephasing dominates. Assuming that decay and dephasing occurs by scattering

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**Fig. 10.** Decay rate of the average population as a function of intrinsic linewidth for the \( n = 1 \) image-potential state for small amounts of Cu and CO on Cu(001). (Adapted from [37,38]).
events close to the surface, one would expect the ratio to be independent of the quantum number of the image-potential state [15]. For CO on Cu(001) the ratio increases with binding energy while the opposite trend with a small variation is observed for the other systems. Further experimental studies of other adsorbate systems and substrates are necessary to understand this behavior.

Theoretical calculations of the dephasing and population decay, which is induced by a low coverage of the alkali adsorbates Na or Cs and Cu adatoms, have been done for Cu(100) and Cu(111) surfaces using a wave-packet-propagation method [41–44]. The calculated results for Cu adatoms [41] compare well to the experimental data [14,45] as illustrated in Fig. 12. The results show that the relevant scattering processes can be treated with todays theoretical and calculation methods.

The discussion so far concentrated on low coverages of adsorbates. For higher coverages the adsorbates agglomerate in islands leading to a decrease in the number of scattering centers. For complete layers and ordered structures the quasi-elastic scattering by defects should be minimized as illustrated in Fig. 13 for CO on Cu(001) [17]. Minima in the linewidth are observed for the c(2×2) and the compression structure (see also Fig. 9) while the lifetime stays around 10 fs for exposures >3 L. The sum of all scattering processes represented by the linewidth correlates well with the width of the LEED spots. In homoepitaxial growth RHEED-like oscillations of the linewidth are found for layer-by-layer growth [37]. However, the linewidths for complete overlayers are generally larger than for clean surfaces indicating a noticeable amount of defects and associated scattering.

![Fig. 11. Ratio of decay rate to dephasing rate as a function of binding energy. For adsorbate-covered surfaces the change of the rates with coverage is evaluated.](image-url)
So far we have covered intraband scattering with small energy transfer. Phonons and defects scatter electrons in image-potential states quasi-elastically within the same band. For the case of N₂ overlayers the scattered electrons could be seen leaving the initial-state and reappearing in the final state at lower energy and momentum in the same image-potential band. Most of the conclusions from this section are not specific for image-potential states, because intraband scattering by defects or phonons can occur for any band in the electronic structure at surfaces.
3. Resonant interband scattering

A characteristic feature of image-potential states is the existence of an infinite series of states converging towards the vacuum level. In each state the electron can move freely parallel to the surface. The resulting energy bands do not intersect on a flat surface. For regularly stepped surfaces band crossings occur and energy gaps appear at \( n = 1 \) band intersections \([40]\). For the crossing between \( n = 1 \) and 2 bands no gaps were resolved indicating a small coupling between bands of different quantum numbers and associated wave functions perpendicular to the surface. Although the coupling between different image-potential bands is not seen in the energy dispersion it can be observed in the time-resolved experiments.

Fig. 14 shows time-resolved 2PPE data obtained by Berthold et al. \([46]\) for the \( n = 1 \) image-potential state of Cu(001). They are taken at two different parallel momenta, at the band bottom of the \( n = 1 \) state, \( k_\parallel = 0 \) (\( E_B = 0.60 \) eV) and at \( k_\parallel = 0.33 \text{ Å}^{-1} \) where the \( n = 1 \) binding energy matches the bottom of \( n = 2 \) band (\( E_B = 0.18 \) eV). The intensity is plotted on logarithmic scale and shows good statistics over four orders of magnitude. The lowest curve of Fig. 14 is a reference measurement that was taken with a photon energy below the threshold for excitation of the \( n = 2 \) state. It shows a simple linear decay in the semilogarithmic plot. For photon energies above this threshold the data exhibit a biexponential decay. The short timescale corresponds to the lifetime of the \( n = 1 \) state, whereas the longer timescale matches the value obtained for the \( n = 2 \) state around \( k_\parallel = 0 \).

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Fig. 14. Logarithmic plot of \( n = 1 \) pump-probe traces for various excitation conditions and emission angles (thick lines). The binding energies of \( E_B = 0.60 \) and 0.18 eV are referenced to the vacuum level at \( k_\parallel = 0 \) and correspond to the \( n = 1 \) band bottom at \( k_\parallel = 0 \) and a parallel momentum of \( k_\parallel = 0.33 \text{ Å}^{-1} \), respectively. The computed instrument function has a full width at half maximum of 90 fs (dotted line). Results of numerical simulations described in the text are displayed as thin lines. (From \([46]\)).
The obvious explanation for these findings is the scattering of electrons from the \( n = 2 \) state to the \( n = 1 \) band. Because the lifetime of the \( n = 2 \) state is significantly longer than that of the \( n = 1 \) state, the scattered electrons are seen after the initial population of the \( n = 1 \) band has decayed. The relative intensity of the interband scattering signal is plotted in Fig. 15 as a function of binding energy. The fraction is below 0.5% except for energies around the \( n = 2 \) state where more than 3% are found. Here the electrons can be scattered elastically between the two image-potential bands as sketched in the dispersion plot of the inset of Fig. 15.

The work by Berthold et al. [46] clearly proved the existence of resonant interband scattering and demonstrated that the relative rates can be deduced quantitatively from 2PPE data with sufficient signal-to-noise ratios. However, the physical origin of the process could not be clarified. Later studies found a much smaller resonant interband scattering signal for a Cu(001) sample [45]. In view of the strong resonant interband scattering on stepped Cu(001) surfaces peaked near the bottom of the \( n = 2 \) band [39] it seems likely that in the original study [46] more steps or defects (\( \approx 0.5% \)) were present than expected for a perfectly oriented (001) sample.

The small interband scattering signal at energies below the \( n = 2 \) state could be explained by resonantly scattered electrons cascading via intraband scattering along the \( n = 1 \) band [18]. At surfaces with steps or adatoms with strong resonant interband scattering [39,45,47,48] the long-lived component at the bottom of the band has similar relative intensity as on the clean surface. The cascade electrons therefore amount to a minor

![Fig. 15. Contribution of the slowly decaying component due to resonant interband scattering from \( n = 2 \) to \( n = 1 \) as a function of \( n = 1 \) binding energy. Vertical dashed lines mark the energetic positions of \( n = 2 \) and 3 at \( k_{\parallel} = 0 \) (from left to right). Inset: measured dispersion of \( n = 1 \). Arrows indicate the resonant interband scattering process. (From [46]).](image-url)
fraction of the signal and the dominating process occurs via electron–electron scattering with bulk electrons.

Resonant interband scattering is particularly notable on stepped surfaces [39]. Fig. 16 shows data for a Cu(119) surface measured in the upstairs (solid circles) and the opposite downstairs (open circles). For the downstairs direction no long-lived component is visible, whereas at 121 meV binding energy the fast decay corresponding to the $n=1$ image-potential state is hard to identify. Resonant interband scattering strongly favors the upstairs direction. For lower binding energies the traces show the quantum beats similar to Fig. 4 indicating contributions from electrons scattered out of the $n=2$ image-potential bands. The oscillations on the Cu(119) surface are much less pronounced compared to the Cu(001) surface indicating a considerable amount of dephasing by the steps or deviations from a regular step periodicity.

The relative intensity of the interband scattering signal is plotted as a function of binding energy in the bottom panel of Fig. 17. Values up to 70% and 25% are found for scattering out of the $n=2$ and 3 bands, respectively. The high percentages are related to the observation of the predominant scattering in the upstairs direction. The resonant interband scattering shows a maximum around 120 meV binding energy. The decay rate of the scattered component (upper panel in Fig. 17) is constant and slightly above the value obtained at the band bottom of the $n=2$ image-potential state. The findings indicate that the resonant interband scattering at stepped surfaces takes place at a well-defined energy

Fig. 16. Time-resolved 2PPE measurements of the $n=1$ image-potential state on Cu(119) as a function of binding energy plotted on a semilogarithmic scale. Spectra are recorded either for $k_\parallel$ running upstairs (solid circles) and downstairs (open circles). Components I–III are indicated by solid lines. (Adapted from [39]).
and momentum. This conclusion is supported by energy-resolved spectra which show a series of peaks for long delays. The scattering takes place at well-defined energies slightly above the band minima [39]. Through the dispersion of the bands these energies are related to a well-defined momentum transfer corresponding to approximately half the reciprocal lattice vector of the step structure.

For single adatoms on a flat surface no preferential scattering direction is expected when the crystal structure of the substrate is disregarded. First experiments have demonstrated interband scattering for Cu adatoms on a Cu(001) surface [45,48]. The process is observed for all energies of the $n = 2$ image-potential band with similar intensity. The absence of a resonant enhancement implies that scattering of image-potential electrons by adsorbate atoms is possible at all energies and the corresponding momenta between the two image-potential bands. This observation is supported by theoretical calculations which show for copper adatoms on copper surfaces that elastic interband transitions occur without restrictions [41].

4. Conclusions

Quasi-elastic scattering processes are important at any surface for any electronic state. Image-potential states provide a unique model system to study the various scattering processes in detail with the available experimental capabilities. The controlled variation of parameters such as temperature and adsorbate or step density permits the identification of the scatterers as phonons, adsorbates or steps. The implications for electron transfer processes at interfaces between substrate surfaces and adsorbates or overlayers are at best recognized, but far from being understood.
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References