8 Time-resolved two-photon photoemission

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8.1 Basics of two-photon photoemission

In this chapter time resolution will be introduced to photoemission experiments. This means not just a series of regular photoemission measurements to monitor the changes of a sample with time. In two-photon photoemission the time delay between the two photons is an additional experimental parameter which can be controlled with femtosecond resolution, i.e., on a time scale relevant for electronic processes. At the same time, the introduction of the second photon leads to the participation of an additional electronic state in the energy diagram for photoemission.

8.1.1 Energy diagram

In Figure 8.1 the transition from initial state $|1\rangle$ to an intermediate state $|2\rangle$ after the absorption of the photon with energy $h\nu_a$ is shown. The second photon of energy $h\nu_b$ excites the electron out of the intermediate state into the final state $|3\rangle$. If the final state energy $E_3$ is above the vacuum energy $E_{vac}$, the electron might leave the surface and its kinetic energy $E_{kin}$ is measured with an electron energy analyzer. Obviously, the initial state has to be occupied, i.e., its energy $E_1$ should be below the Fermi energy $E_F$. The intermediate state on the other hand has to be empty at first. In most cases it is desirable to keep the photon energy $h\nu_a$ below the work function $\Phi = E_{vac} - E_F$, because this constitutes the threshold for one-photon photoemission. This applies also to the other photon, because processes with the role of the two photons interchanged are possible as well.

8.1.2 Energy-resolved spectroscopy

The spectrum sketched at the right of Fig. 8.1 shows a peak at the final state energy $E_3$. The cutoff at kinetic energy zero corresponds to the vacuum level $E_{vac}$ of the sample. Electrons with the highest energy after the absorption of the photons with energies $h\nu_a$ and $h\nu_b$ appear at kinetic energy $E_{max} - E_{vac} = h\nu_a + h\nu_b - \Phi$. These limits are familiar from regular photoemission spectroscopy and can be used to determine the work function from the width of the spectrum. Similarly, the momentum $k_\parallel$ of the electron parallel to the surface is conserved for single-crystal surfaces. For electrons emitted at an angle $\vartheta$ with respect to the surface normal one obtains $h k_\parallel = \sqrt{2mE_{kin}} \sin \vartheta$. Umklapp processes would add reciprocal lattice vectors of the surface to the momentum conservation, but play usually no role in two-photon photoemission. One has to keep in mind that the kinetic energies are generally quite...
low. The requirement that both photons should have energies below the work function leads to maximum kinetic energies less than the work function, i.e., usually below 5 eV. One consequence is a very limited accessible $k_{\parallel}$ range. Most two-photon-photoemission experiments are performed at normal emission. This geometrical restriction permits the use of a negative bias voltage (typically a few Volts) at the sample in order to accelerate the electrons into the analyzer. At the low kinetic energies obtained without bias the transmission of most analyzers drops significantly and magnetic fields have to be shielded very carefully.

### 8.1.3 Time-resolved measurements

The two-photon photoelectron spectroscopy discussed in the previous section does not exploit the time delay between the two photons and it has been tacitly assumed, that the time delay is fixed. The time-resolved mode of two-photon photoemission is performed at fixed kinetic energy and the delay between the two photons is scanned. The first photon pumps the intermediate state and the second photon probes the population of this state. Such measurements are shown in Fig. 8.2 for the first two image-potential states (see Sec. 8.4.2) on Cu(001) and one recognizes a rapid increase of the emission rate followed by an exponential decay with pump-probe delay $T_d$. The time constant for the decay indicates the lifetime of the selected intermediate state. The increase of the signal and the delay zero are determined by the temporal shape of the photon pulses. Their cross correlation can be obtained from measurements.
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at energies where the lifetime at the energy of the intermediate state is much shorter than the pulse durations. For the spectra in Fig. 8.2 the cross correlation has a full width at half maximum of 60 fs. For identical photon energies $h\nu_a = h\nu_b$ the cross correlation becomes symmetric (autocorrelation) and pump and probe pulses cannot be distinguished. For identical polarization of the two photon beams the autocorrelation is dominated by interference effects (see Fig. 8.7).

State-of-the-art lasers used for two-photon photoemission can produce pulses of some 10 fs. This time scale is comparable to the lifetime of electronic excitations at surfaces. The shift of the measured signal relative to the time zero obtained from the cross correlation is a good approximation for lifetimes shorter than the pulse widths [1, 2].
The time-resolved measurement mode presumes that the energy of the intermediate state is independent of the time delay. This is usually fulfilled, but should be checked by measuring energy-resolved spectra for a few selected time delays. An example for such a series of spectra is shown in Fig. 8.3 for image-potential states (see Sec. 8.4.2) on Cu(001). The spectra are normalized to same height and the intensity variation with time delay can be inferred from Fig. 8.2. The energy position of the peaks is indeed independent of the delay. The change of linewidth with delay will be discussed in Sec. 8.2.

### 8.1.4 Variation of photon energy

In regular photoelectron spectroscopy the variation of the photon energy leads to the constant initial or constant final state spectroscopy, depending on the particular state under investigation. In two-photon photoemission there are in addition intermediate states and two different photons. A constant intermediate state spectroscopy \( E_2 = \text{const.} \) could be done in different ways (cf. Fig. 8.1):

- Tune \( h\nu_a \) at fixed \( h\nu_b \) and \( E_{\text{kin}} \).
- Tune \( h\nu_b \) and \( E_{\text{kin}} \) at fixed \( h\nu_a \).
- Tune \( h\nu_a, h\nu_b \) and \( E_{\text{kin}} \).

Similarly constant initial \( (E_1 = \text{const.}) \) and final \( (E_3 = \text{const.}) \) state spectroscopies could be done in a variety of modes. All these modes play no role in practice, because the photon energy of femtosecond lasers is rather difficult to tune. In addition, the delay between the two laser pulses has to be controlled very carefully. This makes a continuous variation of the photon energies for spectroscopic purposes infeasible.

Measurements at several discrete photon energies are, however, important in order to identify a particular peak in a spectrum as initial, intermediate, or final state:

- The energy of a final state should obviously not depend on either photon energy \( h\nu_a \) or \( h\nu_b \).
- The intermediate state is emitted after absorption of photon with energy \( h\nu_b \). Its kinetic energy should therefore change proportional to the change \( \Delta h\nu_b \). Because \( h\nu_a \) and \( h\nu_b \) might switch their role as pump and probe pulses, the change of kinetic energy could also be \( \Delta h\nu_a \). This process would correspond of course to a different intermediate state energy [3]. It should be noted, that the sequence of the excitations may be determined also from time-resolved measurements [4]. If \( h\nu_b \) is absorbed before \( h\nu_a \), the exponential decay appears at negative delays (see Fig. 8.10).
- An initial state is excited directly by two photons. Consequently the change of the kinetic energies is given by the sum \( \Delta h\nu_a + \Delta h\nu_b \).

An example for the photon energy dependence of initial and intermediate states is given in Fig. 8.4 for Cu(111) at 100 K [5, 6]. The \( n = 0 \)-peak which shows the stronger variation with photon energy corresponds to the well-known occupied surface state (see also Sec. 8.4.1) on Cu(111) and is an initial state. The other peak shows less variation and is an \( n = 1 \)
image-potential state (see Sec. 8.4.2) which is populated as intermediate state. At the photon energy $h\nu_a = 4.536$ eV a resonant excitation from the surface to the image-potential state occurs [7, 8]. This resonance enhancement cannot be seen in Fig. 8.4, because the spectra are normalized to same height.

The considerations of identifying initial, intermediate and final states by a variation of the photon energy apply strictly only to surface states which show no dispersion with momentum perpendicular to the surface. For transitions between bulk bands the energies of both involved bands change with photon energy in a way determined by the bulk band structure. This might lead to changes of the kinetic energy not covered by the cases listed in the previous paragraph. The observation of bulk bands by two-photon photoemission will be discussed in Sec. 8.3.1.

8.1.5 Experimental setup

The basic requirements for a two-photon-photoemission experiment are a light source and an electron energy analyzer. The main difference to a regular photoemission experiment rests in the light source which has to be intense enough to stimulate the second-order photoemission process. This involves pulsed lasers in all cases. A typical setup is shown in Fig. 8.5. A Ti:sapphire laser pumped by an all solid-state laser emitting green light produces pulses at 1.55 eV photon energy with pulse durations down to 12 fs at a repetition rate of 86 MHz. These pulses are frequency-doubled by second-harmonic generation and the third harmonic is generated by sum-frequency generation in non-linear optical crystals. The photon energies $h\nu_a$ and $h\nu_b$.
$h\nu_a$ are usually based on a common fundamental laser frequency. Deriving the two laser pulses from the same laser source is essential for recombining the pulses with femtosecond precision on the sample for time-resolved experiments. The ultimate time-resolution is obtained by interferometric control of the delay stage to a fraction of the wavelength [9]. Interference occurs only for identical photon energies $h\nu_a = h\nu_b$ and polarization. For best performance of the experiment a good characterization of the laser pulses is necessary (see following Sec. 8.2 and Ref. [10]). This involves pulse compression by prism pairs such as shown in Fig. 8.5 and measurement of the autocorrelation and spectrum of the laser pulses (not shown). The proper characterization of the cross correlation or autocorrelation can, however, only be done by measuring the photoemission or second harmonic signal from the sample [1, 9, 11].

The main advantage of Ti:sapphire laser systems over excimer-laser-pumped dye lasers is the high repetition rate. Previous systems had comparable output power, but were limited by space-charge effects [12]. At high repetition rate a few electrons are emitted per laser pulse and no space charge can develop. Employing Ti:sapphire lasers the count rate could be increased by four orders of magnitude over previous systems [13] with the added bonus of time resolution in the femtosecond regime.

A reduction of the repetition rate below 1 MHz is necessary if the electron energy analysis is done by time-of-flight detection [14, 15]. The energy resolution for such a system can compete with hemispherical analyzers, because the kinetic energies of the electrons are rather low and consequently the flight times are quite long. The ultimate performance of any detection system is limited by the number of electrons which can be registered per laser pulse [16]. Hemispherical analyzers with several channeltrons as shown in Fig. 8.5 are best in combination with high-repetition-rate lasers. At low repetition rate, time-of-flight detection has the advantage of registering for each laser pulse all electrons with any kinetic energy.

Some two-photon-photoemission experiments combining lasers and synchrotron light sources have been reported [17]. The pulse length of the electron bunches in the synchrotron limits the time resolution and the synchronization between laser and synchrotron constitutes a difficult task [18]. However, such experiments might become more important in the future with the construction of new free-electron-laser sources. It is interesting to note that the laser sources for two-photon photoemission provide more photons per second than a state-of-the-art synchrotron beam line albeit typically at lower photon energies.

Figure 8.5: Experimental setup for two-photon photoemission.
8.2 Theoretical description of two-photon photoemission

Two-photon photoemission involves the absorption of two photons and the two optical transitions are treated usually as independent consecutive processes. The matrix elements can be obtained according to the well developed theories for regular photoemission. The energy and momentum conservation have been exploited already in Sec. 8.1. An analysis of two-photon-photoelectron spectra using the obvious extension of the one-step model of photoemission [19] has not been done so far. There are a few aspects in the two-photon-photoemission process which are absent in regular photoemission and will be discussed in this section.

8.2.1 Coupling between electron and hole

In regular photoemission the optical transition couples to a free-electron wave function in vacuum. This holds also for the second transition in two-photon photoemission. The first optical transition in contrast occurs between two bound states, because the intermediate state has an energy below the vacuum level. This opens the possibility for a coupling between the initial-state hole $|1\rangle$ and the intermediate-state electron $|2\rangle$ and the formation of an exciton. Such effects have been predicted for the transition between the occupied surface state and the $n = 1$ image-potential state on Cu(111) shown in Fig. 8.4 [20]. An experimental verification is still lacking since the lifetime of this exciton is only a few femtoseconds and the energy shift is only a few meV. For semiconductors [21], molecular adsorbates [22, 23] or insulators [24] excitonic effects might be more important. One interesting aspect would be the lifting of momentum conservation by the spatial localization of the exciton [21, 22].

8.2.2 Phase coherence

In a time-resolved two-photon-photoemission experiment the pulse duration can be comparable to the time scale of the temporal quantum-mechanical evolution of the involved states. This can be stated in different ways depending on the particular circumstances:

- The lifetime is long compared to the pulse duration, or equivalently,
- the linewidth is narrow compared to the spectral bandwidth of the laser pulses.
- The energy differences of some states are comparable to the spectral bandwidth.

These statements apply also to the absorption of a single photon, but the time resolution in two-photon photoemission leads to particular effects which makes the phase coherence of the quantum-mechanical time evolution accessible. Note, that this refers not to the (spatial or temporal) coherence of the laser light which is described by the electric field. Coherence effects between the two laser pulses occur only for identical photon energies and polarization state. These lead to some special effects discussed in Ref. [9]. The formal description in this situation is identical to the one outlined here, if the interference of the photon fields is incorporated.

The interaction of the laser fields with the electronic states $|k\rangle$ leads to a superposition

$$|\Psi\rangle = \sum_k c_k(t)|k\rangle.$$  \hspace{1cm} (8.1)
In the absence of the laser fields the time dependence \( c_k(t) \) would be given by

\[
c_k(t) = c_k^0 e^{-t/2\tau_k} e^{i\phi_k(t)} e^{iE_k t/\hbar}
\]

with \( c_k^0 = c_k(0) \). (8.2)

The exponential decay is described by the lifetime \( \tau_k \) and the energy \( E_k \) determines the quantum-mechanical phase. The term containing \( \phi_k(t) \) describes additional changes of the phase. Such phase-breaking events are (quasi-)elastic scattering of the electron with no or negligible change of energy or population \( |c_k(t)|^2 \). The experiment samples the population of the final state \( |c_3(t)|^2 \) and this quantity depends on both laser fields, and in particular on the time delay between pump and probe pulse, as can be inferred from Eq. (8.1). The sampling of a time-dependent population of the intermediate state \( |2\rangle \) by the excitation with photon \( h\nu_b \) into the final state \( |3\rangle \) is the essential difference to regular photoemission which probes a constant population in the initial state \( |1\rangle \).

For the calculation one has to introduce the Hamilton operator \( \hat{H}_0 \) of the unperturbed system which obeys \( \hat{H}_0 |k\rangle = E_k |k\rangle \). The photons are described in the dipole approximation by the time-dependent electric fields \( \vec{E}(t) = \vec{E}_a(t) + \vec{E}_b(t) \) leading to an interaction operator \( \hat{V} \) with only off-diagonal matrix elements \( V_{kl} \propto \langle l | \vec{E} \cdot \vec{p} | k \rangle \) and the momentum operator \( \vec{p} \).

The solution of this problem may be done by perturbation theory up to fourth order in the electric fields [25]. The Liouville-von-Neumann equations [26] are basically equivalent and more convenient, because the density matrix \( \hat{\rho} \) contains the population \( \rho_{33} = |c_{33}(t)|^2 \) directly:

\[
\frac{\hbar}{i} \frac{d}{dt} \rho_{kl} = \frac{1}{\hbar} \left[ \hat{H}_0 + \hat{V}, \hat{\rho} \right]_{kl} - \Gamma_{kl} \rho_{kl}
\]

(8.3)

The damping matrix \( \hat{\Gamma} \) is introduced phenomenologically to describe the decay of population and phase included in Eq. (8.2). The matrix elements are real and can be written as [27]

\[
\Gamma_{kl} = \frac{1}{2} (\Gamma_k + \Gamma_l) + \Gamma_{kl}^*, \quad \text{with} \quad \Gamma_{kl}^* = \Gamma_{lk}^* \quad \text{and} \quad \Gamma_{kk}^* = 0.
\]

(8.4)

The decay rates \( \Gamma_k \) are directly related to the lifetimes \( \tau_k = \hbar/\Gamma_k \), whereas the dephasing rates \( \Gamma_{kl}^* \) describe the breaking of the phase relation between states \( |k\rangle \) and \( |l\rangle \).

The system of differential equations (8.3) can be solved numerically. It may be simplified by retaining only terms with photon energies close to the energy differences between the states. For this case, only the envelopes of the electric fields have to be considered. The resulting optical Bloch equations [26] may be solved analytically in certain limiting cases [8, 10, 28] for a three level system. Instead of discussing solutions of the optical Bloch equations in detail, some of the more surprising features will be illustrated by selected results.

The description of regular photoemission spectra by two-level optical Bloch equations yields the familiar result of a Lorentzian convoluted with the spectrum of the laser pulse [10]. The Lorentzian width contains a sum of decay and dephasing rates, which cannot be separated. One- and two-photon photoemission start from a constant initial-state population, but the two-photon process samples a time-dependent intermediate-state population with the second photon. This time dependence changes upon tuning the photon energy on or off resonance for a transition between discrete initial and intermediate states. In Fig. 8.4 the linewidth at resonance \( (h\nu_b = 1.512 \text{ eV}) \) is narrower than the linewidth observed for each state off resonance.
8.2 Theoretical description of two-photon photoemission

This has been observed also using 15 ns laser pulses [6]. A simple interpretation based on the multiplication of two Lorentzian lineshapes convoluted with a Gaussian apparatus function gave a satisfactory fit to the data [6, 27]. Using the optical Bloch equations for infinitely long pulses, the experimental lineshape can be described quite well and values for the decay and dephasing rates of the surface and image-potential state can be obtained [8].

The linewidths of the peaks observed in the energy-resolved spectra of Fig. 8.3 are plotted in Fig. 8.6 as a function of pump-probe delay. A constant value is reached for long delays, whereas a linear increase is obtained towards negative delays. This surprising behavior can be explained quantitatively by calculations with a three-level system of optical Bloch equations.

Another example for the dependence of the lineshape on pump-probe delay is shown in Fig. 8.7. Using two identical photon beams the delay can be controlled interferometrically with subwavelength resolution. Two-photon photoemission spectra for the occupied surface state on Cu(111) (see Fig. 8.4 and Sec. 8.4.1) taken for in and out of phase conditions between the two electric fields show different lineshapes and energy positions [29]. In these experiments not only the phase of the wave function but also of the photon fields is important. This opens the possibility of a coherent control of the excitations.

In the last example the temporal phase of the wave function enters directly. If the energy separation of intermediate states is comparable to the bandwidth of the laser pulses, several states can be excited coherently. The optical Bloch equations have to be solved including several intermediate states [13, 30]. When the pump pulse is over, the intermediate state pop-
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Phase delay between both pulses
- $2\pi$ pulses
- $2\pi - \pi$ pulses
- $2\pi - \pi/2$ pulses
- $2\pi + \pi/2$ pulses
- Single pulse excitation

Surface state $k = 0.15 \text{ Å}^{-1}$

Figure 8.7: Top: Interferometric two-photon photoemission signal for the occupied surface state on Cu(111) as a function of pump-probe delay. Bottom: Spectra taken for in and out of phase conditions between pump and probe pulses (after Ref. [9]).

The last term oscillates with a frequency which depends on the energy difference of the coherently excited states. These oscillations are damped by the lifetimes of the states and
the loss of phase coherence described by the dephasing rates $\Gamma_{kl}$. The average population decays exponentially with time constants $\tau_k$ as indicated by the first term of Eq. (8.5). An experimental illustration is given in Fig. 8.8 for image-potential states (see Sec. 8.4.2) on Cu(100) \cite{2, 13}. The oscillatory and exponential contributions can be separated and show different time constants for decay. Thus the decay and dephasing can be identified directly and assigned to different scattering processes.

A coherent control of the quantum beats could be achieved by adding a *chirp* to the laser pulses, i.e., manipulating the arrival time of the different spectral components while maintaining the spectrum of the pulse. One could then excite the $n = 4$ state before the $n = 3$ state and shift the phase of the quantum-beat pattern. Such effects have not yet been observed in two-photon photoemission, but have been used to control chemical reactions by feedback-optimized phase-shaped femtosecond laser pulses \cite{31}.

### 8.3 Bulk properties

This section deals with two-photon photoemission involving bulk states. Because electron spectroscopies are always surface sensitive, it is not easy to identify specific bulk features in two-photon photoemission spectra. In particular, the bulk-sensitive region at high kinetic energies known from regular photoemission is not accessible here. The discussion is divided between the observations of bulk states and the properties of hot electrons excited by femtosecond laser pulses in the sample.

#### 8.3.1 Direct bulk transitions

The first report of transitions of bulk states by two-photon photoemission identified an unoccupied state at 1.48 eV above $E_F$ on Cu(001) \cite{32}. It was observed by a resonance from the occupied $X_5$ state (top of the d-bands) and assigned to the $X_4'$ point, the edge of the sp-band.
gap at X. Later inverse photoemission measurements locate a surface resonance at 1.4 eV above $E_F$ [33], which might reverse the assignment of the bulk transition to a surface state.

The second example also involves a reinterpretation of a previous result. In the pioneering work of Giesen et al. [34] an unoccupied state 1.92 eV above $E_F$ was found for Ag(111) which could not be satisfactorily explained by any surface- or bulk-band-structure calculations. A later study showed, that there is no intermediate state involved, and assigned the transition to a two-photon excitation between two bulk sp-bands [35]. The dispersion of the bands in the relevant energy range leads to a photon-energy dependence mimicking an intermediate state. A similar direct transition between sp-bands has also been identified for Cu(111) [36].

These two examples show that the observation of a peak at a fixed intermediate state energy as a function of photon energy is not sufficient to assign the peak to a bulk or surface state. However, one can use the fact familiar from regular photoemission, that only bulk bands show a dispersion perpendicular to the surface and consequently with photon energy. Consequently, a transition which does not exhibit a constant initial, intermediate, or final state energy must involve bulk bands. Several examples for this behavior have been found on the Si(100) surface and assigned to various transitions between bulk bands [37]. The agreement between experiment and bulk band structure calculations is far from perfect. The strong intensity variations with photon energy [38, 39] leave the possibility of a reinterpretation.

The identification of transitions involving bulk bands can obviously be quite difficult in two-photon photoemission spectroscopy. This explains the lack of time-resolved measurements for bulk states. A notable exception might be the identification of a saddle point in the band structure of graphite through an anomaly in the lifetimes of hot electrons [40].

### 8.3.2 Lifetimes of hot electrons

A short high-intensity laser pulse creates a large number of electronic excitations in a sample. The electrons or holes are generated within the penetration depth of the light which is typically considerably larger than the escape depth of the electrons in a two-photon photoemission experiment. The excited (hot) electrons rapidly lose energy by scattering with the other electrons which are available at high density in a solid. The transfer of energy to the lattice via electron-phonon coupling occurs much slower on a time scale of ps.

The Fermi-Dirac distribution of the electron gas can be seen directly at the high-energy end of a regular photoemission spectrum. Using laser pulses with high intensity to heat the electron gas, the rise of the electron temperature and the cooling by the lattice was observed [41]. For photon energies within a few $kT$ below the work function one-photon photoemission processes might still be observable at the low-energy end of the electron spectrum. Only the exponential tail of the Fermi-Dirac distribution is visible and the temperature of the electron gas can be measured [12]. If one- and two-photon processes are visible in a spectrum, the relative intensity of these processes can be estimated to $10^4 \ldots 10^5$ [12]. In order to distinguish between one- and two-photon processes, it can be helpful to measure the intensity dependence of the spectral features. For identical photons $h
u_a = h\nu_b$ the electron signal depends linearly or quadratically on the laser intensity for one- and two-photon processes, respectively. When two different photons are used, one may use the disappearance of the two-photon features, if either of the two laser beams is blocked or a suitable time delay is introduced. Note that
Fig. 8.9: Two-photon photoemission spectra (linear scale at the bottom) and relaxation times of hot electrons (logarithmic scale at the top) from Cu(111) for various photon energies (after Ref. [42]).

processes involving two photons from a single laser pulse can be identified only by intensity variation, if they cannot be excluded by energy considerations (see Sec. 8.1.2). Choosing the photon energies $h\nu \ll \Phi$ ensures that only two-photon photoemission processes are observed. Examples for spectra obtained at a Cu(111) sample are shown at the bottom of Fig. 8.9. The energy scale refers to an intermediate state which leads to opposing shifts of the vacuum edge (left) and the Fermi edge (right) with photon energy. The energy distribution of hot electron decreases monotonically with energy. The superimposed peak shifting parallel to the Fermi edge corresponds to emission from the top of the d-bands at constant initial-state energy. The relaxation time obtained at the respective intermediate-state energies is plotted at the top of Fig. 8.9 on a logarithmic scale. The dependence follows roughly the prediction $\propto (E - E_F)^{-2}$ from Fermi-liquid theory [43]. The deviations around 1.5 eV are
presumably due to secondary electrons arising from the Auger decay of d-holes [42, 44, 45]. The lifetime of d-holes is longer than the hot-electron lifetime at the respective energy [45] leading to an apparent increase of the observed relaxation time. The decay of the hot electrons themselves also leads to the generation of secondary electrons which appear at low kinetic energies. This intrinsic process makes the determination of lifetimes close to $E_F$ difficult and can be reduced by using low photon energies [46]. In many studies this requires a lowering of the work function by suitable adsorbates [42, 44, 47]. There seems to be a negligible influence by the adsorbates on the measured lifetimes.

The last observation proves that mainly the properties of the hot electrons in the bulk are measured by these time-resolved two-photon photoemission experiments. The large penetration depth of the light compared to the escape depth of the electrons suggests that transport effects might influence the data. Some electrons from deeper layers can travel into the sampled volume near the surface while on the other hand some electrons leave the surface region. These effects can be modeled using ballistic transport [48] or bulk band structure calculations [42]. The latter method is able to explain the differences observed for various low-index copper surfaces [49]. A more direct proof of the transport effect is given by the dependence of hot-electron lifetimes on thickness of thin noble-metal films [50].

All these experiments show that in the absence of specific intermediate states time-resolved two-photon photoemission is able to obtain valuable information on the lifetime of hot electrons in the bulk, if secondary electrons and transport effects are taken into account. This applies also for (111) surfaces of noble metals where a band gap exists for emission in the measurement direction normal to the surface. Apparently, scattering associated with the emission process ensures that electrons from the whole Brillouin zone reach the detector. This ensures that the experiment samples the complete distribution of hot electrons in the bulk and explains the good agreement of the measured lifetimes with simple free-electron models based on Fermi-liquid theory.

### 8.4 Surface properties

The previous section showed that the lifetimes of electronic excitations in the bulk are usually quite short which makes time-resolved two-photon photoemission a surface-sensitive technique. Electrons coupled only weakly to the bulk can be found as surface states and in particular as image-potential states. Loosely bound adsorbates might also have long-lived states which are potentially important for photochemical reactions. One common feature of all these surface-related states is the absence of dispersion perpendicular to the surface which unambiguously makes them pure initial or intermediate states. The different types of states will be the topic of the final section of this chapter.

#### 8.4.1 Surface states

On semiconductor surfaces the broken bonds lead to a rearrangement of the geometric and electronic structure which in most cases results in occupied and unoccupied dangling bond states separated by a band gap. Electrons in the lowest conduction band states (bulk or surface) can decay only by recombination with a hole. This process is quite unlikely and may
lead to rather long lifetimes of the respective states. The time scale of the relaxation of higher excited electrons might lead to a delayed filling of the conduction band minima. These processes are qualitatively similar to the generation of secondary electrons in metals as discussed in the previous section and can result in complex electron dynamics [39]. The work on semiconductor surfaces has been reviewed by Haight [51].

On metals a variety of surface states are well known from photoemission and inverse photoemission studies. Only states near the center of the surface Brillouin zone are accessible by two-photon photoemission, because of the low kinetic energies used. This restricts the studies mainly to close-packed surfaces. For Ag(111), Cu(111), and Au(111) the surface states have been observed by two-photon photoemission (see Figs. 8.4, 8.7 and Ref. [12]). Owing to the large work function three-photon photoemission has been employed on Pt(111) to excite the occupied surface state [52]. In time-resolved experiments occupied states show the cross correlation between pump and probe pulses and do not yield any interesting information on the electron dynamics. For Pd(111) the surface state is unoccupied and its lifetime has been determined [4]. The experimental data are shown in Fig. 8.10 on a semilogarithmic scale. The occupied surface state \((n = 0)\) is pumped by the IR pulse and probed by the UV pulse. The population follows the cross correlation (solid dots) for positive delays and persists towards negative delays, when the UV pulse follows the IR pulse. The opposite behavior is displayed by the \(n = 1\) image-potential state (see Sec. 8.4.2) which is pumped by the UV pulse. From
data obtained over a dynamic range of several orders of magnitude one can extract the lifetime directly from the exponential decay of the intensity (straight lines in the semilogarithmic plot of Fig. 8.10) at delay times where the laser pulses show negligible intensity in the cross correlation (solid dots in Fig. 8.10). The results are confirmed by fits using the optical Bloch equations [4].

### 8.4.2 Image-potential states

Time-resolved two-photon photoemission was illustrated in the previous sections using examples involving image-potential states [12, 62–64]. The image force acting on an electron in front of a metal surface can be derived from a long-range Coulomb-like potential as illustrated in Fig. 8.11. A band gap in the band structure may impede the penetration of the electron into the metal along the direction of the motion. This results in a series of bound states with binding energies relative to the vacuum level of approximately 1/16 of the values in the hydrogen atom. Figure 8.11 shows the wave functions of the first two image-potential states on Cu(001) which hardly penetrate into the metal and have maxima several Ångstroms away from the surface [62]. These states are only weakly coupled to the metal which leads to lifetimes matching the current experimental possibilities. The corresponding measured lifetimes are listed in Table 8.1 for normal emission ($k_\parallel = 0$). The data compilation shows the $n^3$ dependence of the lifetime for large quantum numbers $n$ [62, 65]. The importance of the band gap can be seen for Cu(111) where the first image-potential state has a longer lifetime than the second, which lies outside the band gap [15, 56]. The ab initio theoretical description of image-potential states is fairly complex due to the long-range potential arising from the screening in a many-body sys-
Figure 8.12: Binding energies (left) and lifetimes (right) for image-potential states as a function of Xe coverage on Ru(0001). The solid lines show the result of a tunneling model, the dashed lines correspond to a continuum model (after Ref. [60]).

tem. However the agreement between calculated and experimental values for binding energies and lifetimes is remarkably good [4, 43, 61].

Surface states are by their very nature always rather sensitive to adsorption. This holds also for image-potential states which are completely quenched by many adsorbates [14]. However, adsorbates without electronic states close to the vacuum level may be described as a dielectric spacer layer. The modification of the image potential can then be treated by classical continuum electrostatics [60, 66, 67]. For adlayers of noble gases the lifetime increases with layer thickness, because the coupling to metal is reduced. Figure 8.12 shows experimental data for

<table>
<thead>
<tr>
<th>Material</th>
<th>(\tau_1)</th>
<th>(\tau_2)</th>
<th>(\tau_3)</th>
<th>(\tau_4)</th>
<th>(\tau_5)</th>
<th>Refs.</th>
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</thead>
<tbody>
<tr>
<td>C(0001)</td>
<td>40 ± 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[53]</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>7 ± 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[54]</td>
</tr>
<tr>
<td>Cu(001)</td>
<td>40 ± 6</td>
<td>120 ± 15</td>
<td>300 ± 20</td>
<td>630 ± 30</td>
<td>1200 ± 60</td>
<td>[11, 13]</td>
</tr>
<tr>
<td>Cu(119)</td>
<td>15 ± 5</td>
<td>39 ± 5</td>
<td>105 ± 15</td>
<td>200 ± 20</td>
<td>350 ± 40</td>
<td>[55]</td>
</tr>
<tr>
<td>Cu(117)</td>
<td>15 ± 5</td>
<td>39 ± 5</td>
<td>95 ± 15</td>
<td>190 ± 20</td>
<td>350 ± 40</td>
<td>[55]</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>18 ± 5</td>
<td>14 ± 3</td>
<td>40 ± 6</td>
<td></td>
<td></td>
<td>[56, 57]</td>
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<tr>
<td>Cu(775)</td>
<td>18 ± 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[58]</td>
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<tr>
<td>Ag(001)</td>
<td>55 ± 5</td>
<td>160 ± 10</td>
<td>360 ± 15</td>
<td></td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>32 ± 10</td>
<td>≤ 20</td>
<td></td>
<td></td>
<td></td>
<td>[59]</td>
</tr>
<tr>
<td>Ru(0001)</td>
<td>11 ± 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[60]</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>25 ± 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>26 ± 7</td>
<td>62 ± 7</td>
<td></td>
<td></td>
<td></td>
<td>[61]</td>
</tr>
</tbody>
</table>
Figure 8.13: Full width at half maximum of the autocorrelation traces (left panel) and two-photon photoemission spectra (right panel) for a clean and Cs-covered Cu(111) surface. The photon energy is 3.3 eV and the electrons are accelerated by 4 eV to obtain the given kinetic energy in the analyzer (after Ref. [71]).

Xe on Ru(001), but illustrates also the problem of quantitative modelling the results [60]. For adlayers with electronic bands degenerate with the image-potential states a description by a quantum-well model is more appropriate [68, 69, 70].

8.4.3 Adsorbate states

The image-potential states provide a nice model system to study the electron dynamics at a surface with the experimental possibilities available today. With regard to the understanding and possible applications in photochemistry at surfaces it is important to gain access to the decay of electronic excitations at adsorbates or the charge transfer into the substrate. For many systems the relevant time scales are much shorter than the time resolution of two-photon photoemission experiments. Therefore only a few time-resolved studies of adsorbate states have been reported up to now. For C₆F₆ on Cu(111) an unoccupied molecular resonance could be identified and its lifetime was measured as a function of film thickness [70, 72, 73]. For Cs on Cu(111) an alkali-derived resonance is shown in the right panel of Fig. 8.13 at an energy 2.75 eV above $E_F$ [71]. Its lifetime is significantly larger compared to the values obtained on the clean surface as shown by the increased width of the autocorrelation traces (left panel of Fig. 8.13). At low temperatures the electron resides even longer on the Cs atom [74]. This leads to desorption and the bond breaking can be monitored by changes in the electronic structure as a function of time and distance [75, 76].
8.5 Outlook

Time-resolution was introduced to two-photon photoemission about 15 years ago [77, 78]. With the advent of easy to use, high-repetition rate Ti:sapphire lasers the experimental possibilities expanded tremendously. Today it is possible to study more systems in ever more detail. Current work is directed to an understanding of electron scattering processes on a femtosecond time scale with high energy and momentum resolution [22, 66, 79–80]. Continuous progress is made in the development of solid-state and free-electron laser sources as well as improved detection systems. The list of interesting surfaces and adsorbates is far from being exhausted. We are therefore looking into a bright future for time-resolved photoemission with lots of new and surprising physics to come.

Acknowledgements

This work would not have been possible without the excellent contributions from Martin Weinelt and my graduate students. I thank Martin Aeschlimann, Michael Bauer, Pedro Echenique, Ulrich Höfer, Hrvoje Petek, Martin Wolf, and Xiaoyang Zhu for discussions, preprints, and figures. Continuous support from the Deutsche Forschungsgemeinschaft is acknowledged.

References


