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Time and angle resolved photoemission spectroscopy using femtosecond visible and high-harmonic light

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Abstract. The angle resolved photoelectron spectroscopy (ARPES) has emerged as a leading technique in identifying static key properties of complex systems such as the electronic band structure of adsorbed molecules, ultrathin quantum-well films or high temperature superconductors. We efficiently combined ARPES by using a two-dimensional analyzer for parallel energy (E) and momentum (kₚ) detection with femtosecond time-resolved spectroscopies. Using time and angle resolved two photon photoemission (2PPE) with visible light pulses, the hot electron dynamics in complex electronic structures are directly accessible by means of angle resolved hot electron lifetime mapping. Furthermore, femtosecond ARPES spectra recorded with high harmonic generation (HHG) light pulses are presented, showing the potential of this technique for future investigations of surface dynamics and photo-induced phase transition processes.

1. Introduction

Two photon photoemission (2PPE) is one of the most important techniques to study femtosecond electron dynamics of solids and surfaces. Over the last years, a huge number of experiments have been done to study the relaxation dynamics of excited electrons. Examples include investigations of various different elements (e.g. Ag, Au [1], transitions metals Ta [2], Ru [3], Mo and Rh [4], ferromagnetic 3d metals Fe, Co and Ni [5]), surface-adsorbate systems [6][7][8][9][10][11] and scattering dynamics in model-like image potential states ([12] and references therein). Particularly angle resolved 2PPE contributed to an identification of the different electron-electron and electron-phonon scattering processes [13][14][15][16]. Typically, conventional electron analyzers were used to record the energetic spectrum at a specific angle and for measurement of the complete data a rotation of the sample was necessary. Güdde et al. have shown that the ARPES technique can efficiently be combined with femtosecond time-resolved 2PPE by using a two-dimensional analyzer for parallel energy and momentum detection (TAR-2PPE) [17]. In this paper, we introduce the concept of evaluating and visualizing femtosecond electron dynamics by (E,kₚ) lifetime mapping. By this means,
a rather complete view of hot electron dynamics in complex electron systems accompanied by a sub-
femtosecond relative temporal resolution can be achieved. A typical example is given in section 3, 
showing the inelastic lifetimes of a Cs* resonance state on Cu(111) as a function of E and k||.

Furthermore, time resolved IR-pump X-ray-probe photoemission can also be extended to the 
momentum space by the use of state-of-the-art 2D photoelectron spectrometers [18]. The ultrafast 
dynamics in complex systems associated, for instance, with the nuclear motion or a photo induced 
phase transition after intense laser irradiation (IR-pump) provide valuable information on fundamental 
physical properties. These ultrafast dynamics can now be mapped by the measurement of the transient 
electronic band-structure E(k||) as function of time using femtosecond time-resolved high-harmonic 
light (X-ray probe). In particular, by recording the energy distribution as well as the momentum 
distribution of the photoemitted electrons, a rather complete characterization of the different steps 
involved in these processes becomes possible. An example of an angle resolved photoemission 
spectrum of a Pt(111) surface recorded with femtosecond high-harmonic light pulses is shown in 
section 4.

2. Experimental setup
The angle-resolved photoemission and two-photon photoemission studies were conducted using a 150 
cm hemispherical energy analyzer (SPECS Phoibos 150). This two-dimensional detector is able to 
record the electron emission spectra between ± 7 or ± 13 degrees without rotating the sample. The 
laser system used for the time-resolved two-photon photoemission experiments (2PPE) is a mode-
locked Ti:sapphire laser, pumped by 6.9 W from a diode pumped all-solid state laser system (800 nm, 
82 MHz repetition rate, 23 fs pulse width, energy of 15 nJ per pulse). The output of the Ti:sapphire 
laser is frequency doubled in a 0.2 mm thick beta barium borate (BBO) crystal to produce pulses of hv 
= 3.1 eV with a pulse width of 30 fs (determined from autocorrelation measurements in 2PPE from the 
Shockley surface state of the Cu(111) surface). A typical work function Φ of the investigated surfaces 
between 3.5 eV and 4.5 eV allows for photoemission within a two-step excitation process, permitting 
the direct spectroscopic access to intermediate excited states between Fermi edge and vacuum level. In 
a conventional stroboscopic pump-probe configuration, it also enables us to probe the decay dynamics 
of the excited state population at a temporal resolution of a few femtoseconds.

The high intensity laser system is a commercial 1 kHz multipass Ti:sapphire amplifier 
(Quantronics, Odin) pumped by the second harmonic of a Q-switched Nd:YLF (yttrium lithium 
fluoride laser (Quantronics, model 527) and seeded by a sub-20 fs Ti:sapphire oscillator (KML-MTS 
kit). At an average power of 1.4 W, the amplifier produces 35 fs laser pulses with a central wavelength 
of 800 nm. The p-polarized amplifier output is split into pump and probe pulses, with 20% of the 
incident beam power in the pump pulse required for time-resolved experiments (not used in this 
study). The remaining 80% of the femtosecond laser light is used for the generation of the high 
harmonic probe pulse for photoelectron spectroscopy. This light is focused into an argon-gas-filled 
capillary (HHG light source) to generate ultrashort EUV pulses with energies up to 45 eV. A double 
mirror monochromator consisting of two multilayer mirrors selects a single harmonic out of the 
discrete UV spectrum at a center photon energy of 41.85 eV. Furthermore, in order to focus the EUV 
light onto the sample surface, the second multilayer mirror is a concave mirror with a radius of 
curvature of 1 m. Residual light from the laser fundamental and low harmonics is filtered by a 200 nm 
thick aluminium film supported by a nickel mesh (Lebow) at the exit of the monochromator. More 
details are described in [18].

The Cu(111) crystal has been cleaned by repeated Ar+ sputtering (10 min, 500 V) and annealing 
cycles (15 min, 800 K) prior to the experiments. The Pt(111) crystal was cleaned by repetitive 
sputtering (10 min, 800 eV), annealing (flash to 1000°C) and oxidation/reduction cycles. The surface 
quality was checked by thermal desorption spectroscopy (TDS) and photoemission characteristics. The 
Cs was deposited from a resistive heated getter source (SAES getters).
3. E(k∥) hot electron lifetime mapping with time-resolved 2PPE

3.1. Principle scheme of time- and angle-resolved 2PPE

Figure 1 shows the principle scheme of the time- and angle-resolved 2PPE experiment (TAR-2PPE). 2PPE E(k∥) photoemission maps are recorded as a function of pump-probe delay. From this image series pump-probe correlation traces for each pixel or each point of the energy E vs. momentum k∥ space can be extracted. Depending on the investigated system and the nature of excitation (mono- or bichromatic, cross- or autocorrelated, phase-resolved or -averaged), the extracted correlation traces contain specific information on the hot electron dynamics as inelastic lifetimes and/or dephasing times. The parallel data acquisition in this scheme enables a significant improvement of time resolution by detecting lifetime differences between different states or different electron excitations, as will be discussed below.

![Figure 1: Principle scheme of the time and parallel angle resolved 2PPE experiment: E(k∥) photoemission maps are recorded at different temporal delays between the femtosecond pump and probe laser pulse. From this image series pump-probe correlation traces for each pixel can be extracted. In an autocorrelation measurement, the FWHM of these traces can be taken as a qualitative measure for the probed ultrafast electron dynamics.](image)

3.2. Hot electron dynamics of a Cs-adsorbate resonance state on Cu(111)

At low Cs coverage, Cs adsorbs on a metal as a positive ion [19][20] (see also a discussion in [10] and references therein). The long-lived Cs* resonance state is associated with the transient capture of an electron by the Cs+ adsorbate. The Cs* resonance is a hybrid of the Cs 6s and 6p atomic orbitals, mainly in the \( m = 0 \) symmetry subspace \([8][9][10][21]\) (\( m \) is the projection of the electron angular momentum along the atomic axis perpendicular to the surface). Due to the presence of a surface-projected band gap on the (111) surfaces of noble metals, the charge transfer between the adsorbate and the substrate is severely hampered, leading to long lifetimes of up to tens of femtoseconds \([6][7][8][9][10]\). The resonance energy \( E_{\text{Res}} \) is about 3 eV above the Fermi energy, almost independent of noble metal species and surface orientation \([22][23]\). With increasing Cs-coverage, the resonance...
energy shifts towards the Fermi energy, a behavior arising from the interaction between the excited Cs* state and the dipole layer formed by the surrounding alkali adsorbates.

Figure 2(a) shows a 2D E(k ||) photoemission map recorded with 2PPE with hν = 3.1 eV for Cu(111) covered with approximately 0.03 ML of Cs. The data was recorded at room temperature. Clearly visible in the spectrum is the Cs 6s-6p resonance state at a kinetic energy around Ekin = 1.55 eV (note that the energy scale given in Figure 2(a) refers to the kinetic energy of the electrons after the photoemission process). The parallel momentum covered by ± 7° emission angle of the analyzer at Ekin = 1.55 eV is ± 0.078 Å⁻¹.

To visualize the dependence of the electron dynamics on energy E and momentum k ||, 2D autocorrelation maps AC_FWHM(E,k ||) are created, which consist of rectangular areas ΔE*Δθ that are color coded corresponding to the measured FWHM of the autocorrelation traces for a certain kinetic energy and emission angle. A reasonable choice of ΔE and Δθ has to be done in comparison to the experimental energy- and angle-resolution and with respect to the achievable time-resolution. Figure 2(b) shows such a AC_FWHM(E,k ||) intensity map corresponding to the 2PPE spectrum in Figure 2(a) with ΔE = 50 meV and Δθ = 0.7° in comparison to 20 meV and 0.2° experimental resolution. An improvement of time-resolution and a smoothing of the extracted AC_FWHM values was achieved by semi overlapping of the rectangular areas with nearest neighbours, however with the trade-off in reduced energy and angle resolution. One can clearly see the signature of the long-lived Cs* resonance state reproduced by an increased broadening of the autocorrelation trace, which here directly corresponds to an increased lifetime of electrons in the Cs-state.
A reasonable quantification of the inelastic lifetimes in the case of the Cs* resonance state can be achieved by solving the Liouville-von Neumann equations for rapid dephasing and following the details given in reference [23][33][34]. By this means, the inelastic lifetimes can be evaluated, and the intensity map $\text{ACFWHM}(E,k_\parallel)$ can be drawn as an inelastic lifetime map $\tau(E,k_\parallel)$ of the excited electrons in intermediate states (see inelastic lifetime scale $\tau$ in Fig. 2(b)) [33].

3.3. Absolute and relative errors of the $\text{ACFWHM}$ values and the extracted lifetimes.

An absolute quantification of the detailed dynamics from 2PPE correlation measurements strongly depends on the deployed technique (auto- or crosscorrelation, mono- or bichromatic, etc.), the specific system under investigation and the reliability of the used evaluation method. The achievable resolution by the measurement itself depends mainly on the used laser pulse-width and statistical errors. Concerning the relative resolution within one $\text{ACFWHM}$ or lifetime map, one has the possibility to trade between energy-, angle- and time-resolution. However, the relative error caused by technical reasons is much lower compared to the error of the absolute value of the complete dataset: the parallel data acquisition of all the different $(E,k_\parallel)$-values ensures that most of the systematic errors affect the collected data in the same way. Errors (e.g. drift of the laser intensity) that broaden or narrow one of the extracted correlation traces will either broaden all or narrow all the other extracted correlation traces in the same image-dataset, too. This enables a high reliability and relative time-resolution in comparative studies down in the sub-femtosecond regime.

4. Angle resolved X-ray pump-probe spectroscopies using high-harmonics

In comparison to femtosecond light sources in the visible and VUV regime for time-resolved ARPES [24], the use of high harmonic light has three main advantages. (1) The high photon energies delivered by the HHG source extend the information accessible by time-resolved photoemission experiments to much deeper lying electronic states, even into the regime of classical core level spectroscopy [25]. (2) The use of intense femtosecond pump pulses in time-resolved photoemission experiments often gives rise to an additional electron background in the kinetic energy range up to about 10 eV, resulting from multiphoton photoemission processes and strong field-effects by the pump pulse itself [26][27][28][29]. Therefore, to extract the relevant photoemission signal out of this (pump-induced) background, a significantly higher photon energy (and consequently electron kinetic energy) delivered by a HHG source is desirable. (3) Finally, for a given acceptance angle of the energy analyzer, the use of high

Figure 3. Angle-resolved photoemission spectra of the Shockley surface state and a series of quantum well states of 40 ML Ag/Cu(111) recorded at photon energies of 6 eV (fourth harmonic of the Ti:sapphire oscillator, 4(a)) and 21.22 eV (He I line of a discharge VUV lamp, 4(b)), respectively.
photon energies significantly extends the accessible momentum range of the photoemitted electrons. This last issue is highlighted in Fig. 3, which displays angle-resolved photoemission data of ultrathin silver films (40 ML) on Cu(111) recorded at photon energies of 6 eV (fourth harmonic of the Ti:sapphire oscillator, Fig. 4(a)) and 21.22 eV (He I line of the discharge VUV lamp, Fig. 4(b)), respectively. The plots map the kinetic energy distribution of the photoemitted electrons as function of the emission angle $\theta$. The series of dispersive states visible in both maps are due to the Shockley surface state (topmost feature) and quantum well states (higher binding energy states); the latter are localized within the silver film [30][31][32]. The component of the electron momentum parallel to the surface $k_\parallel$ is conserved in the photoemission process, and for a given emission angle $\theta$ and kinetic energy $E_{\text{kin}}$, its absolute value can be calculated:

$$k_\parallel = \sqrt{\frac{2m_e}{\hbar^2}} E_{\text{kin}} \cdot \sin(\theta).$$

This equation directly implies that for a given analyzer acceptance angle, a higher electron kinetic energy allows for a deeper view into momentum space. The apparent difference in the dispersion of the quantum well states as function of emission angle observed in Figs. 3(a) and 3(b) is a direct consequence of this property. The constant acceptance angle of $\pm 7^\circ$ for both measurements transforms into a $k_\parallel$ interval of about $\pm 0.09 \text{ Å}^{-1}$ for initial state energies close to the Fermi edge at 6 eV excitation ($E_{\text{kin},e} \approx 2 \text{ eV}$) and into a $k_\parallel$ interval of about $\pm 0.25 \text{ Å}^{-1}$ for the same initial states, but for excitation energies of 21 eV ($E_{\text{kin},e} \approx 16 \text{ eV}$). In terms of probing transient changes in $E(k)$ within a time-resolved photoemission experiment, the use of ultrashort XUV pulses instead of UV pulses will obviously extend the accessible states not only with respect to energy but also with respect to momentum.

Figure 4. Photoemission maps of the Pt(111) surface band-structure at finite angle with the He II line (left) and with the $\sim 7$ fs pulsed HHG light source, after selecting the 27th harmonic (right).

Figure 4 shows two photoemission maps of the Pt(111) surface for momentum values between about $\pm 1.5 \text{ Å}^{-1}$. The left spectrum has been recorded with the He II line of the gas discharge lamp with a photon energy of $h\nu = 40.81 \text{ eV}$. The right spectrum is the corresponding photoemission map recorded with the 27th harmonic with an energy of $h\nu = 41.85 \text{ eV}$ and a pulse duration of about 7 fs [25][35]. Both maps are composed from several angle-resolved photoemission measurements and identical analyzer settings have been used, corresponding to an energy resolution of 400 meV. Evident, however, is an overall energy broadening of the photoemission features in the HHG spectrum in comparison to the He II spectrum. This broadening reflects the intrinsic bandwidth of the femtosecond HHG light pulses of about 0.8 eV [18] (time-bandwidth product for Gaussian-shaped and bandwidth-limited pulses $\approx 0.44$).
5. Summary and Outlook
Technically, we combined in an efficient manner the ARPES technique and femtosecond time-resolved 2PPE. Femtosecond band mapping or lifetime mapping gives a powerful tool to investigate hot electron dynamics with a high (relative) time resolution down to the sub-femtosecond regime. The technique opens a new exciting field in time-resolved 2PPE measurements probing the electron dynamics on a much more sophisticated level. E.g. specific questions concerning the relevance of band-structure details (k-localized band-gaps, spin-orbit splitted states, etc.) to the decay of hot electrons can directly be addressed.

Furthermore, we have shown ARPES spectra of Pt(111) recorded with a femtosecond pulsed HHG light source and a state-of-the-art 2D photoelectron spectrometer. In an IR pump - X-ray probe configuration, this extension of ARPES represents a powerful experimental setup, e.g. for the investigations of the dynamics of photo induced phase transitions.

Acknowledgments
This work was supported by the SFB/TRR49 and the DFG GRK 792.

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