Attosecond dynamics and the dielectric response of metallic surfaces

Luca Castiglioni
Department of Physics
University of Zurich, Switzerland

Photocathode Physics for Photoinjectors (P3)
Santa Fe, NM, USA - October 15-17, 2018
1. Attosecond delays in photoemission from metallic surfaces

What are the contributions to the observed delays?
What is the origin of the strong energy dependence?

2. Optical fields at metallic surfaces

What is the screening response?
Can we measure the effective field at the surface?
Can the screening be reduced by using nano-structures or thin films?
ETH Zürich
Ultrafast Laser Physics
Reto Locher
Matteo Lucchini
Lamia Kasmi
Lukas Gallmann
Ursula Keller

Universität Zürich
Surface Physics
Pavel Kliuiev
Kay Waltar
Michael Greif
David Becker-Koch
Matthias Hengsberger
Jürg Osterwalder

Paul-Scherrer Institut
Lab. Micro- and Nanotech.
Johannes Haase
Jeroen van Bokhoven

Chiba University
Condensed Matter Theory
Peter Krüger

DESY
FLASH BL 3
Thorsten Golz
Ekaterina Zapolnova
Rui Pan
Nikolas Stojanovic

X-ray optics
Sasa Bajt

Swiss Light Source (SLS)
Matthias Muntwiler
1. Attosecond photoemission delays from metallic surfaces

\[ \tau_{\text{Surf}} = \frac{\Delta \phi \text{Surf}}{2\omega_0} = \tau_{\text{Wig}} + \tau_{\text{transp}} + \tau_{\text{cc}} \]
Temporal aspects of the photoelectric effect

The photoelectric effect was first observed from metallic surfaces and was crucial in the development of modern physics.

Early statements about the dynamics reached from instantaneous to intensity-dependent.

Modern understanding of electronic structure largely owing to photoelectron spectroscopy.

Attosecond dynamics in metals

- **Plasma frequency** in metals typically $>10^{15}$ Hz, thus characteristic timescale of purely electronic effects (e.g. dynamical screening) on the order of attoseconds.
- **Electron transport** on atomic length scales ($\sim 4$ Å lattice constant) and typical conduction band group velocities on attosecond timescale.
Temporal aspects of the photoelectric effect

The photoelectric effect was first observed from metallic surfaces and was crucial in the development on modern physics.

Early statements about the dynamics reached from instantaneous to intensity-dependent.

Modern understanding of electronic structure largely owing to photoelectron spectroscopy.

Attosecond dynamics in metals

- Plasma frequency in metals typically $>10^{15}$ Hz, thus characteristic timescale of purely electronic effects (e.g. dynamical screening) on the order of attoseconds.
- Electron transport on atomic length scales ($\sim 4$ Å lattice constant) and typical conduction band group velocities on attosecond timescale.
Temporal aspects of the photoelectric effect

The photoelectric effect was first observed from metallic surfaces and was crucial in the development of modern physics. Early statements about the dynamics reached from instantaneous to intensity-dependent. Modern understanding of electronic structure largely owing to photoelectron spectroscopy.

Attosecond dynamics in metals

- Plasma frequency in metals typically >10^{15} Hz, thus characteristic timescale of purely electronic effects (e.g. dynamical screening) on the order of attoseconds.
- Electron transport on atomic length scales (~4 Å lattice constant) and typical conduction band group velocities on attosecond timescale.

From femto- to attoseconds

High-harmonic generation (HHG)
Leads to attosecond pulse trains (APT)
Small relative delays observed in photoemission from W(110)

W(110) VB vs. 4f

$\Delta t = 110$ as

escape depth and inelastic scattering:

\[ W(110) \]
\[ \text{VB vs. 4f} \]
\[ \Delta t = 110 \text{ as} \]

transport and interlayer interference:
Zhang and Thumm, PRL 102, 123601 (2009)
Kazansky and Echenique, PRL 102, 177401 (2009)

resonant bulk vs. surface emission

Initial state localization:
Zhang and Thumm, Phys Rev. A 84, 065403 (2011)
**W(110): VB vs. 4f**  \[ \Delta \tau = 110 \pm 70 \text{ as} \]  

**Mg(0001): VB vs. 2p**  \[ \Delta \tau = 0 \pm 20 \text{ as} \]  
**temporal broadening of WP**  \[ \Delta \tau = 111 \pm 50 \text{ as (WO}_3\text{)} \]  
\[ \Delta \tau = 71 \pm 56 \text{ as (Au)} \]

“Conventional” pumpe-probe technique to study **dynamics of excited states** and out-of-equilibrium populations.
**2PPE** to study the energetics and dynamics of unoccupied states such as image potential states.

---

**Cu(100)**

$E_B = 40 \text{ meV}$

---

**2PPE**

$h\nu_1, h\nu_2 < \phi < h\nu_1 + h\nu_2$

---

**tr-PES**

$h\nu_1 < \phi < h\nu_2$

---

**tr-PES** to study excitation and relaxation of hot electrons in a topological insulator

**FIG. 1 (color online).** (a) Transient photoemission intensity time traces as a function of delay for 2PPE, measured using 22 and 78 eV photons. The feature labeled 1 appears to be populated before time-zero. Feature 1(c) returns to its equilibrium value, and the BVB electrons and metallic surface are decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

To understand the coupled dynamics of bulk and surface states, we first focus on the energetic region of the EDCs associated with the BVB and BCB. After excitation, a FD distribution with increased temperature is observed and attributed to scattering of photoexcited electrons with electrons in the cold Fermi sea. We attribute this feature to scattering of photoexcited electrons within the integration windows indicated in the subsequent discussion.

At negative delay, the distribution decays exponentially with a time constant 70(20) fs and results from a direct optical transition pumped by 2PPE with an energy of 19 eV. Its decay toward negative delays indicates that the lower-lying BCB and SS have negligible population.

Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

At negative delay, the distribution decays exponentially with a time constant 70(20) fs and results from a direct optical transition pumped by 2PPE with an energy of 19 eV. Its decay toward negative delays indicates that the lower-lying BCB and SS have negligible population.

Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.

After 2 ps the SS and BCB populations have significantly decayed and energetically relaxed towards the bottom of the conduction band. By fitting each EDC with a Fermi-Dirac (FD) distribution, we extract an electronic temperature as a function of delay, shown in Fig. 1(b). At negative delays there is a well-defined FD distribution at the Fermi edge. Intriguingly, this BCB population is accompanied by a persistent population in the SS, but only energetically below the first image potential state (IPS). Note that we confine our fit to delays after Δτ = –6 fs, and thus the IPS relaxation is decoupled from the SS and bulk band dynamics which are the focus of this Letter, and we can safely disregard it for the remaining discussion.
Pump-probe vs. RABBITT (streaking)

Reconstruction of **Attosecond Beating By Interference of Two-Photon Transitions**

**RABBITT and streaking**

These **sub-cycle resolved experiments** with attosecond resolution probe the dynamics of quasi-bound continuum states.

**Pump: XUV APT**
(Attosecond pulse train)
**Probe: fs IR**

\[ I = \cos(2\omega \tau + \phi_{q+1} - \phi_{q-1} + \phi(\text{atomic, } q+1) - \phi(\text{atomic, } q-1)) \]

Reconstruction of Attosecond Beating By Interference of Two-Photon Transitions

\[ P_{2q} \propto |M^{(a)} + M^{(e)}|^2 \]
\[ = |M^{(a)}|^2 + |M^{(e)}|^2 + 2|M^{(a)}||M^{(e)}| \cos[\arg(M^{(a)*}M^{(e)})] \]

\[ \Delta \Phi_{2q} = \Delta \theta_{2q} + \Delta \phi_{2q} \]

\[ SB_{2q} \sim \cos \left( 2\omega_0 \tau - \Phi_{2q} \right) = \cos \left( 2\omega_0 \tau - \Delta \theta_{2q} - \Delta \phi_{2q}^A \right) \]

\[ \frac{\Delta \phi_{2q}^A}{2\omega_0} = \tau_{2q}^{A} = \tau_{2q}^{Wig} + \tau_{2q}^{cc} \]

Paul et al., Science 292, 1689 (2001)
Dahlström et al., Chem. Phys. 414, 53 (2013)
Yakovlev et al., PRL 105, 073001 (2010)
Interferometric pump-probe spectroscopy in two foci (targets)

Differential pumping and interferometric stability

Interferometric stability required over long beam path.

Solely differential pumping between HHG generation (20 mbar) and surface target (< 5e-10 mbar)

RABBITTTs on noble metal surfaces

- Clear sub-cycle dynamics in all three metals.
- Replicas of valence band are spectrally resolved.
- Background due to secondary electrons and above threshold photoemission (ATP) depends on the work function.
RABBITT in two targets: Ar/Ag(111)
RABBITT in two targets: Ar/Ag(111)
RABBITT in two targets: Ar/Ag(111)

\[ SB_{2q} \sim \cos \left( 2\omega_0 \tau - \Delta \theta_{2q} - \Delta \varphi_{2q}^{Ar} + 2\varphi_0 \right) \]

\[ SB_{2q} \sim \cos \left( 2\omega_0 \tau - \Delta \theta_{2q} - \Delta \varphi_{2q}^{Surf} + 2\varphi_0' \right) \]

Optica. 2, 405 (2015)
A “crude” 3-step model

1. XUV excitation
2. Wavepacket propagation / transport
3. Interaction with IR probe field

\[ \tau_{\text{surf}} \equiv \frac{\Delta \phi_{\text{surf}}}{2\omega_0} = \tau_{\text{Wig}} + \tau_{\text{transp}} + \tau_{\text{cc}} \]

Dipole-allowed transitions
We consider all dipole-allowed transitions that lead to interfering quantum paths $2q+1$ and $2q-1$.

\[ s \quad d \quad g \]

\[ (m = 0) \quad (m = 0, \pm 1, \pm 2) \quad (m = 0, \pm 1, \pm 2) \]

Optica. 2, 405 (2015)
Wigner delay as a consequence of scattering phase shift

\[ \Psi_{\text{in}}(r,t) \propto \int_0^{+\infty} dE |A(E)| e^{i(-kr-Et)} \]

\[ \Psi_{\text{out}}(r,t) \propto \int_0^{+\infty} dE |A(E)| e^{i(kr-Et+\eta(E))} \]

scattering phase shift: \( \eta(E) \)

Wigner time-delay:

\[ t_W = \frac{d\eta(E)}{dE} \]

Wigner, Phys. Rev. 98, 145 (1955)
Model based on scattering calculations

- Valence band serves as initial states, *i.e.* 4d (Ag), 5d (Au)
- Dipole-selection rules and multiplicities applied
- Scattering of plane wave expanded into spherical harmonics
- Scattering potential: linearized-muffin-tin-orbitals (LMTO)
Electron transport

Ballistic electron transport

- Single site ($z = \lambda$): 250 as
- Summation over $z$: 150 as

Effective transport time

Inelastic-mean free path from literature
Group velocities: fitting to free electron final states
Summation over emission sites (20 layers)
Delay contributions

- Atomic delays (Wigner & cc): +/- 20 as
- Transport: 100-200 as

\[ \tau_{\text{Surf}} = \frac{\Delta \varphi_{\text{Surf}}}{2\omega_0} = \tau_{\text{Wig}} + \tau_{\text{transp}} + \tau_{\text{cc}} \]
**Experimental delays**

\[ \tau_i(E_{\text{kin}}) = \frac{\lambda(E_{\text{kin}})}{v_g(k_{\parallel}, k_{\perp}^{(i)})} \]

**RABBITTs on noble metal surfaces**

- Delays vary non-monotonically with energy.
- Largest contribution from final state.
- Wavepacket propagation.
- Lifetime/delay depends only on inelastic mean-free path and group velocity.


Optica. 2, 405 (2015)
RABBITT on Cu(111)

Resonance

Optica. 4, 1492 (2017)

(a) Norm. intensity (b) $\phi$ (°) (c) XUV Photon energy (d) Electron energy (e) Phot. energy (f) Delay (fs) (g) Delay (fs)
RABBITT on Cu(111)

Chen et al. PNAS, E5300 (2017)

Resonance
2.

Optical fields at metallic surfaces
Ingoing and outgoing IR pulses form a transient grating above the surface.

Can the E-field at attosecond timescales and atomic length scales still be correctly described by macroscopic Fresnel equations?
RABBITT at different incidence angles of the light but equivalent positions in momentum space.
Comparison of calibrated photoemission delays at 15° and 75°

Experimental phase shifts are in agreement with Fresnel!

PRL 115, 137401 (2015)
Interaction of photoelectron wavepacket with IR probe-field happens right at the surface (z=0). This precise localisation is important for the correct interpretation of attosecond delays.
TFz screening on Pt nanostructures

FLASH BL3 (THz)

THz pump - XUV probe

XUV: 151 eV (< 80 fs), p-pol
THz: 1.5 - 2.0 THz, s-pol
THz screening on Pt nanostructures

Pt(111)/YSZ/Si(111) thin films

**Pt thin film:**
Small *sub-wavelength* Pt islands with (111) faces on THz-transparent substrate.
Pt islands large enough to resemble electronic structure of bulk Pt.
THz screening on Pt nanostructures

(a) Pt(111) thin film

(b) E [10^6 V/m]

(c) Pt(111) bulk

(d) E [10^6 V/m]
1. Attosecond delays in photoemission

- RABBITT and streaking allow study of electron dynamics on an as timescale.
- Photoemission delays dominated by electron transport.
- Enhanced lifetime of resonant transition due to lower group velocity. Photoemission final state matters!

2. Optical fields at metallic surfaces

- “attosecond metrology” allows for probing of effective fields at surfaces.
- Fresnel equations (i.e., Maxwell) remain valid on atomic length- and timescales.
- Different screening behaviour of bulk metals and thin films.
Interaction of a single attosecond pulse (SAP) with an IR field

Relative delay $\tau$ between the two states
Interaction of an attosecond pulse train (APT) with an IR field

\[ \text{vac} \]

\[ |f_1\rangle \]

\[ |f_2\rangle \]

\[ |1\rangle \]

\[ |2\rangle \]
Pulse reconstruction from ARPES data

kinetic energy [eV]