Ultrafast excited state dynamics in low-dimensional materials probed by time-resolved ARPES

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Coupling between the various degrees of freedom
**Pump pulse**: creates non-equilibrium state

**Probe pulse**: monitors photoinduced dynamics at variable time delays

Energy and momentum resolution:

\[ E_{kin} = \hbar \omega - E_b - \Phi \]

\[ \hbar k_\parallel = \sqrt{2m_e E_{kin} \cdot \sin \alpha} \]
Transient electronic structure probed by trARPES

Snapshots of the electronic structure for different time delays:

Record 'movies' of photoinduced changes of the electronic band structure $E(k_x,k_y,\Delta t)$

see e.g. F. Schmitt et al., Science 321, 1649 (2008)
Physics of quasi 2D materials

Charge density wave formation:

Metal to insulator transitions:

Spin-valley-layer correlation:

Main interactions:
- Electron-phonon coupling
- Coulomb correlations
- Excitonic effects
- Spin-orbit coupling

Prototypical systems:
- TaS$_2$
- TiSe$_2$
- TbTe$_3$
- MoS$_2$
- WSe$_2$
Why ultrafast spectroscopy?

(my biased view)
Phase transitions and ultrafast dynamics

- Phase transitions in solids (near equilibrium)
- Ultrafast photoexcitation (non-equilibrium)

What can be learned from bringing the system out of equilibrium?

- Timescale to induce a transition to a non-equilibrium state
- Spectroscopy of such excited states and 'new' phases
- Timescale for the return to equilibrium

Scattering processes in excited states

Hierarchy of timescales of ultrafast processes in solids

Example: e-e scattering

Elementary scattering processes in metals:

1. electron-electron scattering

2. low energy excitations:
   - electron-phonon scattering
   - electron-magnon scattering

Note that electrons and ions in solids are screened by surrounding charge density

- screened Coulomb interaction
- concept of „quasiparticles“
Photoinduced phase transitions

- Hierarchy of timescales of ultrafast processes in solids

- Mechanistic understanding from ultrafast dynamics:
  - Timescale to induce the transition to a different phase
  - Probe the dynamics of the order parameter (e.g. gap closing)

Example: Metal-Insulator transition
Momentum dependent scattering in excited states

- Intervaly scattering of optically excited carriers in semiconductors

- Enhanced Spin Hall effect in GaAs

- Spin- and Valleytronics in TMDCs
  R. Bertoni et al., arXiv:1606.03218
Orbital tomography in 2D adsorbate layers

Molecular orbital reconstruction from photoelectron angular distributions

**Pentancene/Ag**


What about ultrafast dynamics and excited states?
Orbital tomography in 2D adsorbate layers

What about ultrafast dynamics and excited states?

► Challenge: From understanding of static electronic structure…

…to dynamics of electronic excitations and charge transfer.

► Examples: Excited states, singlet/triplet conversion, electron-nuclear coupling, interfacial charge transfer, phase transitions & more…

► Ultimate goal: Excited state structural dynamics and microscopy
A brief
(incomplete & biased)
history of
time-resolved photoemission
Time-resolved ARPES: ..the early days

We report the first use of angle-resolved ultraviolet-photoemission spectroscopy to study electron dynamics in the picosecond time domain on a photoexcited semiconductor surface. Transient population in a normally unoccupied surface state on InP(110) was directly observed. The band minimum for this state was found to lie at \( \bar{\Gamma} \) and the surface-band dispersion near \( \bar{\Gamma} \) (effective mass) was measured along two surface symmetry directions.

harmonic generation in Xe (\( h\nu = 10.5 \) eV)

InP surface state: decay on 100 ps time scale
Surface Intervally Scattering on GaAs(110):
Direct Observation with Picosecond Laser Photoemission

R. Haight and J. A. Silberman
IBM T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 11 October 1988)

Angle-resolved laser photoemission investigations of the laser-excited GaAs(110) surface have revealed a previously unobserved valley of the C3 unoccupied surface band whose minimum is at $\bar{X}$ in the surface Brillouin zone. Electron population in this valley increases only as a result of scattering from the directly photoexcited valley at $\bar{\Gamma}$. With high momentum resolution, we have isolated the dynamic electron population changes at both $\bar{\Gamma}$ and $\bar{X}$ and deduced the scattering time between the two valleys.
Femtosecond Studies of Image-Potential Dynamics in Metals

R. W. Schoenlein and J. G. Fujimoto

Department of Electrical Engineering and Computer Science and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

G. L. Eesley and T. W. Capehart

Physics Department, General Motors Research Laboratories, Warren, Michigan 48090
(Received 28 September 1988)

We report the first time-resolved studies of image-potential states on Ag(100). Femtosecond ultraviolet-pump and visible-probe techniques are combined with two-photon photoemission spectroscopy to measure transient photoemission spectra with femtosecond resolution. The lifetime of the $n=1$ image-potential state on Ag(100) is observed to be several tens of femtoseconds.

pulse width 55 fs
A brief history of time-resolved photoemission:

Advent of Ti:sapphire lasers in the 90s:
fs time-resolved 2PPE spectroscopy

M. Aeschlimann, H. Petek, C.B. Harris, Th. Fauster, U. Höfer, MW,..
The drosophila: Image potential states

Time and angle-resolved two-photon-photoemission spectroscopy

Electron dynamics in image potential states

Time and angle-resolved two-photon-photoemission spectroscopy


Courtesy: U. Höfer
Ferromagnetic surfaces: Spin-dependent lifetimes

Example: 3ML Fe film on Cu(100)

pronounced spin dependence!

M. Weinelt & coworkers, PRL 95, 107402 (2005)
Ferromagnetic surfaces: Spin-dependent lifetimes

Origin: different density of states of majority and minority electrons

M. Weinelt & coworkers, PRL 95, 107402 (2005)
Lifetimes of electronic excitations in metals

e-e scattering is mediated by screened Coulomb interaction $W$


Inelastic linewidth: ($GW$ approximation)

$$\Gamma = \tau^{-1} = 2 \sum_{f} \int d\vec{r} \int d\vec{r}' \phi_{i}^{*}(\vec{r}) \phi_{f}(\vec{r}') \text{Im} [-W(\vec{r}, \vec{r}; \omega)] \phi_{i}(\vec{r}') \phi_{f}(\vec{r}).$$

Factors that determine lifetime:

- Initial state (Energy, momentum)
- Final state (“phase space”)
- Screening (response function)
A brief history of time-resolved photoemission:

Beyond single particle excitations employing higher excitation densities:
Electron thermalization and phase transitions
Time-resolved photoemission spectroscopy

“ARPES from a laser excited sample”

Fermi-Dirac Distribution:
\[ f(E) = \frac{1}{e^{\frac{E - E_F}{kT_{\text{el}}} + 1}} \]

\( t_0 = 0 \)
\( t_1 > t_0 \)
\( t_2 >> t_1 \)

non thermalised electrons

probes:
- 6 eV, 90 fs
- 1.5 eV, 55 fs

pump:
- 1.5 eV, 55 fs

W.S. Fann, R. Storz, H.W. K. Tom, J.Bokor PRB 46 (1992), 13592
Electron thermalization in Gadoninium

Transient electron temperature

\[ T_{\text{Fermi-Dirac}} \]

\[ T_{\text{e}} \]

\[ T_{\text{i}} \]

\[ h\nu \]

\[ \text{non-thermal e}^- \]

\[ \Delta t < 100 \text{ fs} \]

Two temperature model fits time evolution of electron distribution

Thermalized electron distribution established within \[ \Delta t < 100 \text{ fs} \]
Example Gd(0001): electronic structure

Gd surface state

Gd(0001) surface exhibits exchange-split d$_{z^2}$ surface state

$\uparrow$ time-resolved photoemission

S. Blügel & coworkers
Separation of surface electronic structure and distribution function: 
⇒ time-resolved population, line width, and binding energy

Parameters: \( E_{S\uparrow} \) and \( E_{S\downarrow} \) + linewidth \( \Gamma_S \)

already determined by s-pol. probe
Analysis assumes that we measure populations

Common assumptions:
• Constant matrix elements
• Static bandstructure and DOS
• No experimental artifacts (space charge, …)

...however, seems to work not too bad...
Charge density wave formation

Are materials with a half filled valence band always metals?

- One-dimensional metallic system with a half filled band can be unstable against lattice distortion \( \rightarrow \text{Peierls instability} \)

\[
E_k = \frac{\pi}{2a} \quad \text{for} \quad a \rightarrow 2a
\]

\[
E_F = \frac{\pi}{a} \quad \text{for} \quad a \rightarrow 2a
\]

- \( \rho(r) \): charge density wave

- \( \tilde{a} = 2a \):

- Note: wave vector \( 2k_F = \frac{\pi}{a} \) fulfills Bragg reflection condition ("nesting")

\[
\begin{align*}
E & \quad k_F = \frac{\pi}{2a} \\
E_F & \quad k_F = \frac{\pi}{a} \\
\end{align*}
\]

\[
\begin{align*}
E & \quad k_F = \frac{\pi}{\tilde{a}} \\
E_F & \quad \text{opening of gap} \\
\end{align*}
\]
Mechanisms of insulator-metal transitions

Mott insulator

- Bandwidth $W$
- Coulomb repulsion $U$

$U/W > 1$

Mott transition (at low $T$)

electronic mediated transition

Charge density wave

- Electronic vs. elastic energy
- Half-filled band $\rightarrow$ metal
- Filled sub-band $\rightarrow$ insulator

transition mediated by ion motion
Dynamics of a photoexcited Mott insulator: TaS$_2$

1) Coherent CDW mode:

2) Ultrafast collapse of the electronic gap:

Ultrafast dynamics of photoexcited Mott phase

- Ultrafast transfer of spectral weight into the gap (gap collapse < 50 fs)
- Continuous recovery ($\tau_H = 680$ fs)
  \[ \Rightarrow \] inconsistent with (Peierls type) coupling to CDW mode

Time-resolved photoemission: \( T = 30 \text{ K} \)

„insulating phase“ @30 K

\( T = 30 \text{ K} \)
\( h\nu_{\text{pump}} = 1.5 \text{ eV} \)
\( h\nu_{\text{probe}} = 6.0 \text{ eV} \)
normal emission

Time-resolved photoemission: $T = 30$ K

beating between two modes

LHB peak shift (meV)

Frequency (THz)

Bulk

Surface

see Demsar et al., PRB 66, R041101

A case study: Photoinduced insulator-to-metal transition in tri-tellurides (RTe₃)
CDW amplitude mode probed by 6eV trARPES
What can be learned by bringing the system out of equilibrium?

Exploit separation of timescales between different processes:

- Timescale to induce the transition to a different phase
- Probing the dynamics of the order parameter (e.g. gap closing)
Tri-Tellurides – a model CDW system

Tight-binding model: Te 5p orbitals coupled by $t_\parallel$ und $t_\perp$

Diamond shaped Fermi surface

Curvature of bands $\propto$ ratio $t_\perp/t_\parallel$

**Goal:** Probe dynamics of electronic structure directly by time-resolved ARPES

Ultrafast electronic melting of CDW state: TbTe$_3$

- Snapshots of electronic structure $E(k)$ at different time delays:

- Delayed collaps of CDW gap (>100 fs) after photodoping

CDW transition requires nuclear motion ➔ excitation of amplitude mode
Dynamics of photoinduced transition implies a “Peierls type” scenario

Can we directly measure the order parameter (gap size)?
Time-resolved Fermi surface: DyTe$_3$

- Gapped area and metallic pocket well resolved with pTOF
- Excellent agreement with 7eV ARPES data and tight-binding model

Simultaneous mapping of $k_x$, $k_y$, $E_{kin}$ versus time delay $\Delta t$

Time-resolved Fermi surface: DyTe$_3$

- Gapped area and metallic pocket well resolved with pTOF
- Excellent agreement with 7eV ARPES data and tight-binding model

Dynamics:
- Collapse of the large gap within ~150 fs
- Recovery of metallic Fermi surface (FS)
- Heavy oscillations of intensity near FS

Simultaneous mapping of $k_x$, $k_y$, $E_{kin}$ versus time delay $\Delta t$
Dynamics along the Fermi surface

Transients of electronic bandstructure near the gap:
Dynamics of occupied and unoccupied bands

$k_{\text{perpendicular}}$ $k_{\text{parallel}}$
Dynamics of the gapped region: DyTe₃

- Population of the unoccupied upper CDW band
- Collapse of CDW gap within ~200 fs
- Transient formation of continuous “metallic” band dispersion
- Fitting to tight binding band structure
Dynamics of the CDW band gap

Conclusion:

- **Insulator-to-metal transition** (lower CDW band shifts above $E_F$)
- **However, CDW gap never closed completely** (even at high fluence)

**Origin:** enhanced nesting in excited state

Tight-binding model: reduced $t_\perp$
Mode analysis of gap modulation

- 3 pulse experiment: "Pump – Reexcite – Probe"

- Antiphase modulation of both CDW bands: Beating of two modes at 2.23 and 1.77 THz which modulate the gap size

Second (3x weaker) pump pulse re-populates upper CDW band to be probed by trARPES

Conclusion II: At least two modes modulate the CDW gap (oder parameter), indicating a complex dynamics in the excited state.
Discussion: CDW amplitude mode

Schematic sketch of the CDW potential energy surface

- CDW order parameter remains finite in photoexcited state
- Multiple phonon modes modulate the CDW gap

Photoinduced insulator-to-metal transition in TiSe$_2$
Electron-hole fluctuations and amplitude mode probed by HHG based XUV trARPES
**Goal**: Probing transient electronic structure of solids throughout $k$-space

$k$-space access to full Brillouin zone

Desired parameters of trARPES photon source:

- Sufficient photon energy to **access full Brillouin zone**, i.e. $h\nu > 10$ eV
- High repetition rate providing **good counting statistics**, i.e. $>100$ kHz
- **Time resolution**: from few fs to several 10 fs pulse duration
- Flexibility in time-bandwidth product: **Adapted** energy resolution
Example: trARPES using HHG in the lab

M. Bauer, K. Rossnagel, L.Kipp, Univ. Kiel)

**Pump**
- $\hbar \omega = 1.59 \text{ eV}$
- $F_{\text{abs}} \leq 8 \text{ mJ/cm}^2$
- 3 kHz rep rate

**Probe**
- $\hbar \omega = 43 \text{ eV}$
- $\Delta \tau \approx 30 \text{ fs}$
- $\Delta E < 500 \text{ meV}$
- Flux $\approx 10^9 \text{ photons/s}$

High harmonic generation (Argon)

EUV multilayer mirrors

concept from H. Kapteyn & M. Murname
Ultrafast dynamics of the “complete” Brillouin zone

$\text{TiSe}_2$

$T = 115\ \text{K}$

$\hbar\omega = 43\ \text{eV}$

$\nu_{\text{rep}} = 3\ \text{kHz}$

$F_{\text{abs}} \approx 5\ \text{mJ/cm}^2$

M. Bauer & coworkers

*Nature* 471, 490 (2011)
**Time-domain classification of PIPT mechanisms**

**Approach: “learning by destroying”**

![Graph showing photon density and drop time](image)

1T-TiSe$_2$

strongly fluence-dependent gap closing time

\[
\tau_{\text{quench}} \approx \frac{2\pi}{\omega_{\text{plas}}} = 2\pi \sqrt{\frac{\varepsilon_0 \varepsilon_\infty m_e^*}{e^2 n_e}} \propto n_e^{-\frac{1}{2}}
\]

⇒ excitonic insulator behavior

pump pulse excitation

\[
\begin{align*}
\tau &= \mathcal{O} \left( \frac{\hbar}{t_{\text{hop}}} \right) \\
\tau &= \mathcal{O} \left( \frac{2\pi}{\omega_{\text{plas}}} \right) \\
\tau &= \mathcal{O} \left( \frac{\pi}{\omega_{\text{amp}}} \right)
\end{align*}
\]

Metal insulator transition in TiSe$_2$

1T-TiSe$_2$

van der Waals gap

Below the $T_c$:
2x2 PLD and CDW phase

Excitonic insulator?

CDW amplitude mode?

see also: talk by Selene Mor
HHG-based trARPES with MIR excitation: 1T-TiSe$_2$

$T > T_{CDW}$:

1T-TiSe$_2$

MIR Pumping at 3100nm in CDW phase (30 K)

(performmed @ ARTEMIS 1kHz laser facility in Oxford)
Ultrafast electronic dynamics in TMDCs (WSe$_2$)
Circular dichroism and excited state band mapping probed XUV trARPES
Semiconducting transition metal dichalcogenides

General characteristics: **layered crystals, about 40 different TMDCs**

Examples:
- MoS$_2$
- WSe$_2$

No intra-layer inversion symmetry

**Pronounced excitonic effects:**
- up to several 100 meV binding energy for freestanding monolayers

**Pronounced spin-orbit splitting:**
- up to 500 meV spin splitting in valence band

**Peculiar electronic structure:**
- spin-, valley- and layer degrees of freedom
- pronounced $k$-dependence
Valley and layer dependent spin-orbit splitting in TMDCs

Spin-polarized bands in WSe$_2$

Xu et al., Nature Phys. 10, 343 (2014)
Valley and layer dependent spin-orbit splitting in TMDCs

Spin-polarized bands in WSe$_2$


Xu et al., Nature Phys. 10, 343 (2014)
Experimental access to valley- and layer polarization

1. Layer-sensitivity:
   *elastic mean free path* @ 20 eV

2. Valley-sensitivity:
   *momentum resolved ARPES*

(performe at ARTEMIS 1kHz laser facility in Oxford)
Experimental access to valley- and layer polarization

1. Layer-sensitivity: 
   elastic mean free path @ 20 eV

2. Valley-sensitivity: ARPES

3. Spin-sensitivity: 
   optical excitation with circular polarized light

see talk by Roman Bertoni (Fr 15:20)
Projection of spin-, valley- and layer-polarization on excited states?

→ Intervalley scattering transfers population from 2D to 3D states.
→ These states govern interlayer coupling, transport, …

see talk by Roman Bertoni (Fr 15:20)
**Goal:** Probing transient electronic structure of solids throughout k-space

Desired parameters of trARPES photon source:

- Sufficient photon energy to **access full Brillouin zone**, i.e. \( h\nu > 10 \text{ eV} \)
- High repetition rate providing **good counting statistics**, i.e. >100 kHz
- **Time resolution**: from few fs to several 10 fs pulse duration
- Flexibility in time-bandwidth product: **Adapted** energy resolution

\[
E_{\text{kin}} = \hbar\omega - E_b - \Phi
\]
\[
\hbar k = \sqrt{2m_eE_{\text{kin}}}
\]

**k-space access to full Brillouin zone**

1. BZ
2. BZ

\( h\nu = 6 \text{ eV} \)
\( h\nu = 20 \text{ eV} \)

\( \beta \rightarrow k_x \) image for one angle \( \beta \)

\( \Theta \)

**k-space access examplified for CeTe\(_3\)** at \( h\nu = 6 \text{ eV} \) and \( h\nu = 20 \text{ eV} \).
Development of 500 kHz OPCPA System

Compressed OPCPA output:

- Prism Compressor
  - 20 W @ 500 kHz (40 µJ)
  - @ 790 nm
  - < 20 fs
- Power stability: 0.3%/hr

3 m

SHG

pressure scaling:

HHG

400 nm-driven HHG in Ar: 7th harmonic (at 21.5 eV) >10^{11} photons/s at sample within ~100 meV bandwidth
Occupied bands, K valley WSe$_2$

Excited state mapping in WSe$_2$ ($\Delta t = 50 \text{ fs}$, 3 eV pump, ”full k-space”)

500 kHz HHG-based ARPES

Direct mapping of conduction band (excited states)
Time- and \( k \)-resolved snapshots of excited states

Excited state mapping in WSe\(_2\)  
(\( \Delta t = 50 \text{ fs} \), 3 eV pump, ”full k-space”)

500 kHz trARPES: full k-space picture of transient population of surface band structure
Conclusions

- Time-resolved photoemission provides a powerful tool to probe the dynamics of the transient electronic structure.

- Photoinduced insulator-to-metal transitions: Ultrafast gap collapse and periodic modulation of band structure by CDW amplitude mode in RT₃.

- Spin-, valley- and layer-dependent dynamics in TDMCs probed by 500kHz XUV time-resolved ARPES.

- Perspective: Mechanistic insights from advanced VUV trARPES setups combing selective IR/THz pumping and full k-space access.
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HHG-based trARPES & TMDCs
TaS$_2$
CDW transition in RTe$_3$