(Brief) Review of the techniques and of recent progress in laser-based photoelectron spectroscopy

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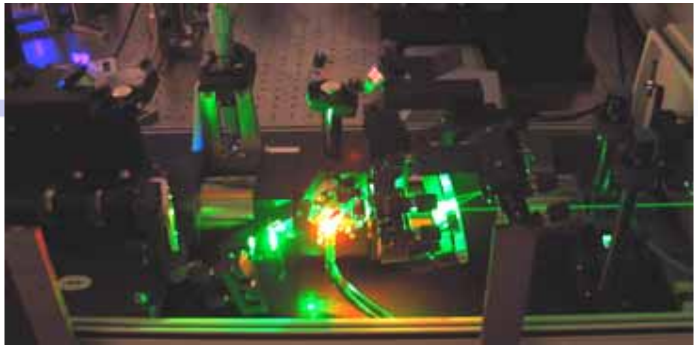
outline



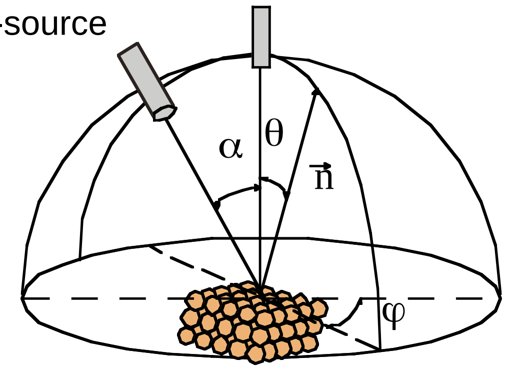
Short history of photoemission with laser light sources:

- spectroscopy of occupied and unoccupied states
- time-resolved experiments: dynamics of hot electrons
- two-photon photoemission
- extreme time resolution: attosecond dynamics
- extreme energy resolution and "bulk sensitivity"
- conclusion

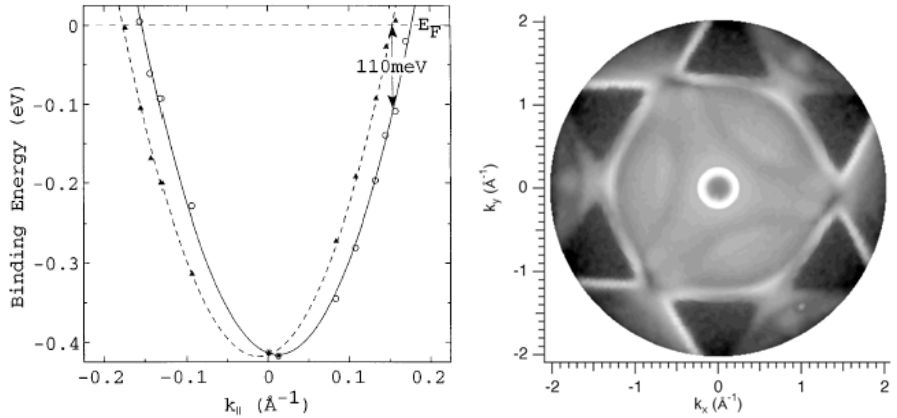
spectroscopy of occupied and unoccupied states

- (angle-resolved) multi-photon photoemission
- how to disentangle contribution of the various states
- spectroscopy at high momentum resolution
- transition dipole moment
- technical issue: space-charge effects

angle-resolved photoelectron spectroscopy

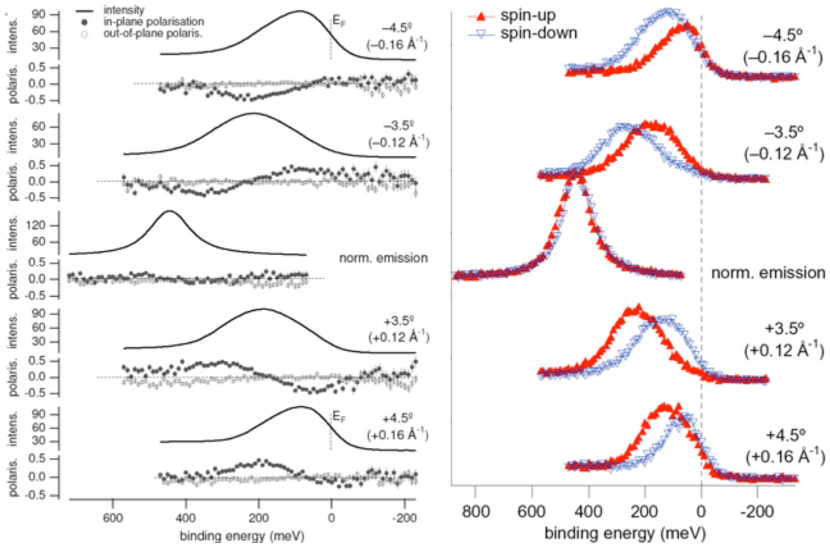


band structure E(k) and Fermi surface k(E_F)



hυ = 5 eV ~ 1 keV
(up to 8 keV for angle-integrated PES)

spin-resolved dispersion



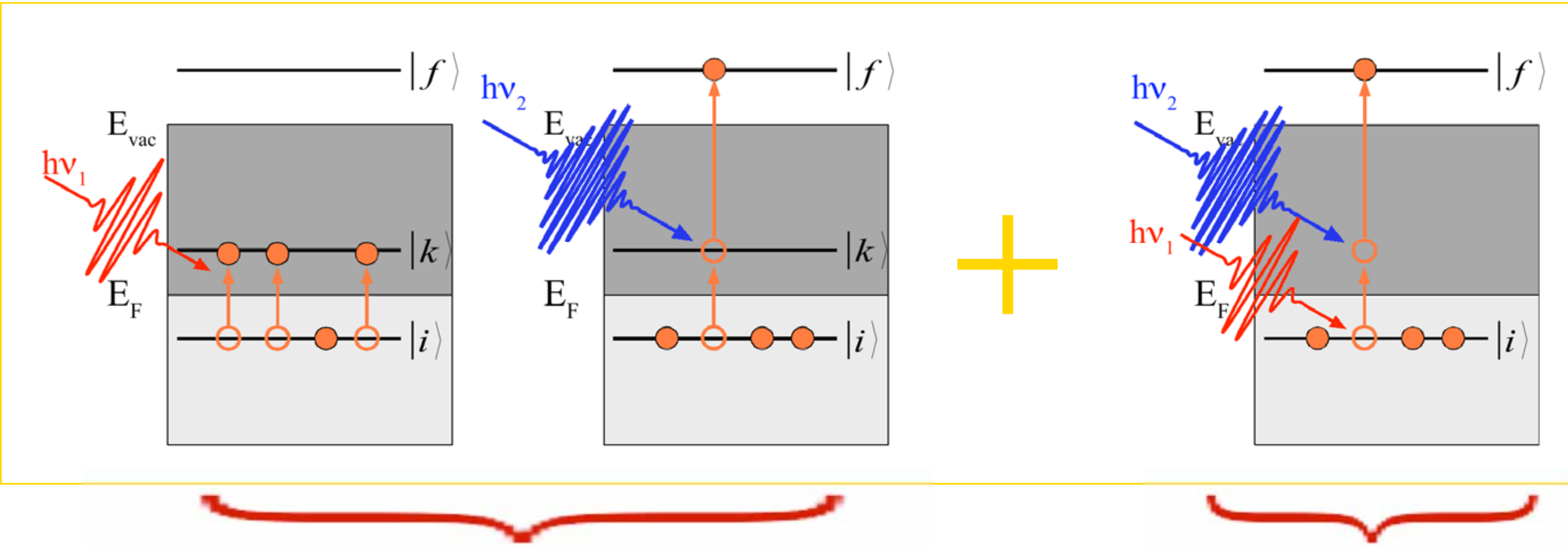
measurement:
photoelectron current as function of
1. kinetic energy → binding energy $E-E_F$
2. emission angle → momentum **k**
3. spin → spin polarization $\mathbf{P}_S$

photoelectron spectroscopy with pulsed laser light

→ advantage of pulsed light sources: high peak intensity

→ reasonable cross-sections for multi-photon processes:

2PPE or two-photon-photoemission

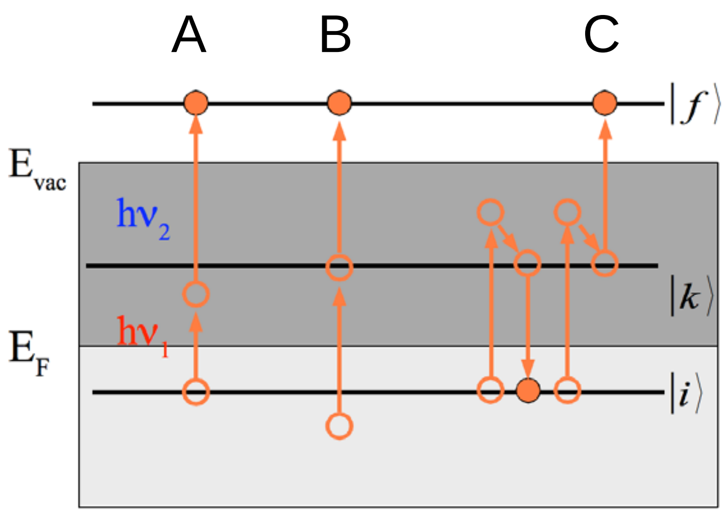


transitions ***i→k→f*** :
probe unoccupied intermediate states
$E_F < E_{\boldsymbol{k}} < E_{vac}$
$h\upsilon_1, h\upsilon_2 < \phi < h\upsilon_1 + h\upsilon_2$

transitions ***i→f*** :
probe occupied initial states
$h\upsilon_1 + h\upsilon_2 - \phi < E_{\boldsymbol{i}} - E_F < 0$

on how to disentangle initial and intermediate states

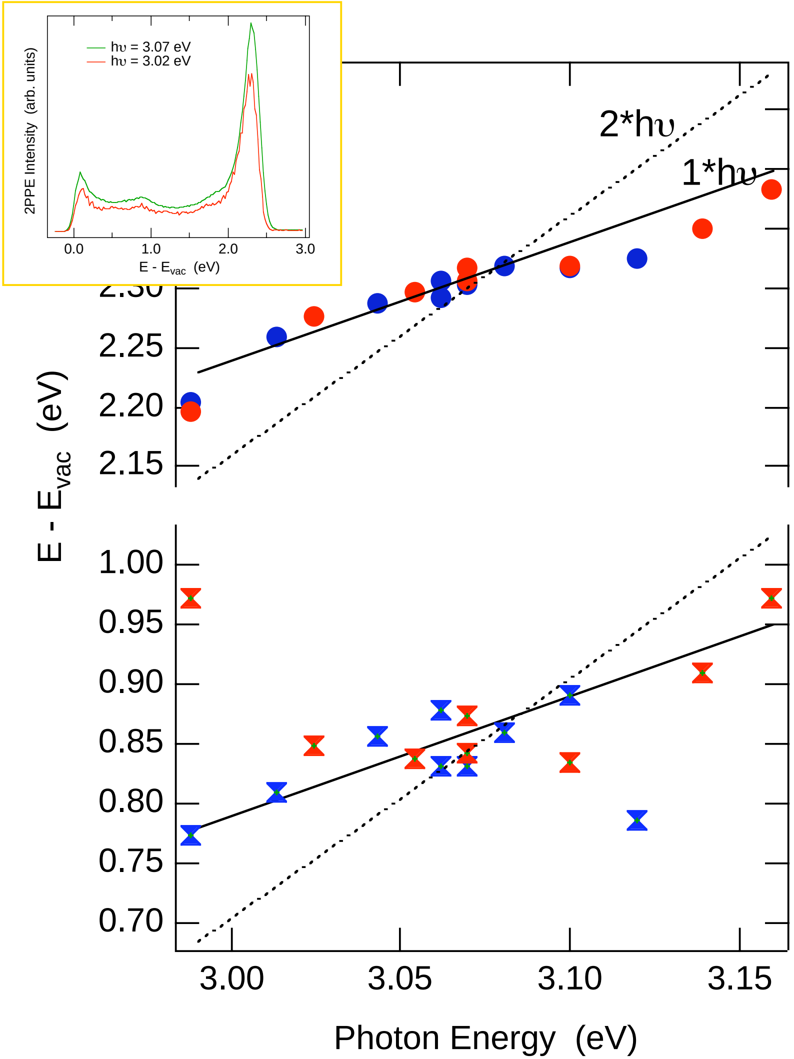
spectra for different photon energies:



A initial state features move with $h\upsilon_1 + h\upsilon_2$

B intermediate state peaks move with $h\upsilon_2$

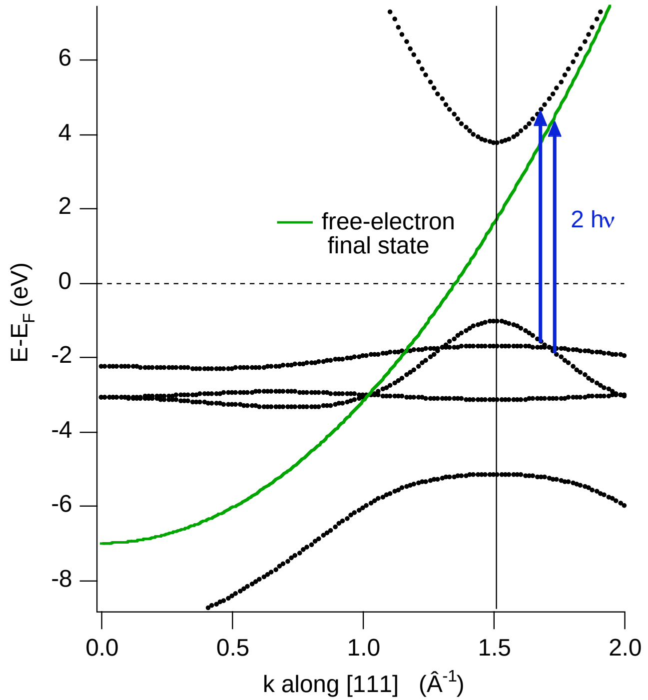
C "energy pooling" do not move (Auger-like process)



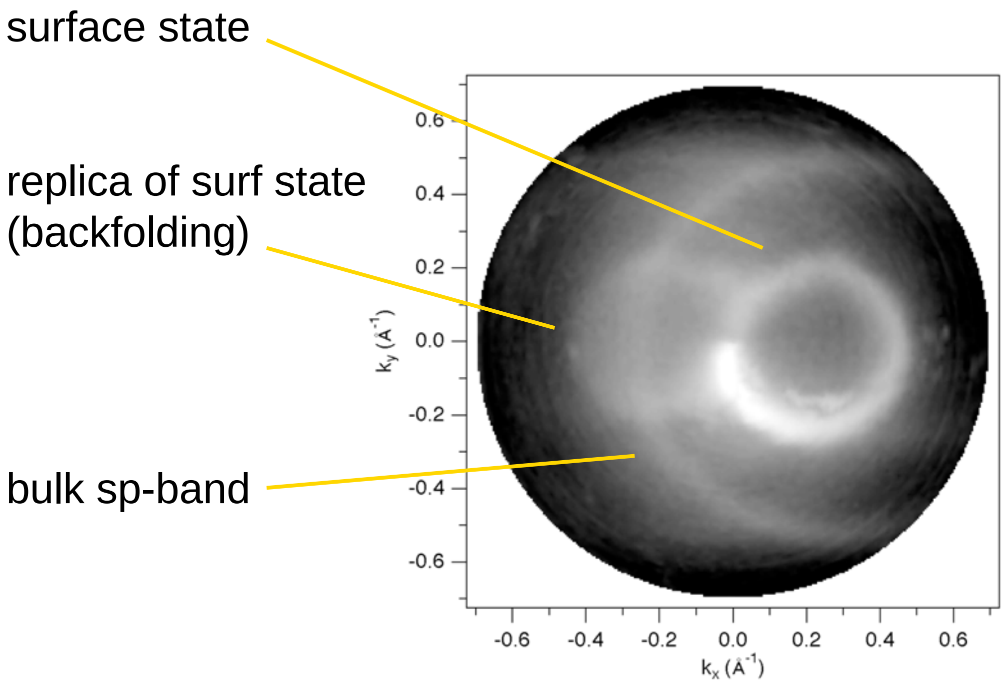
see e.g. Giessen et al., PRL 55, 300 (1985)
W. Steinmann, Appl. Phys. A 49, 365 (1989)

angle-resolved 2PPE

- assuming free-electron final state model (not trivial at low energy!)
- band- and Fermi surface mapping possible by scanning reciprocal space
- condition: no intermediate state available!



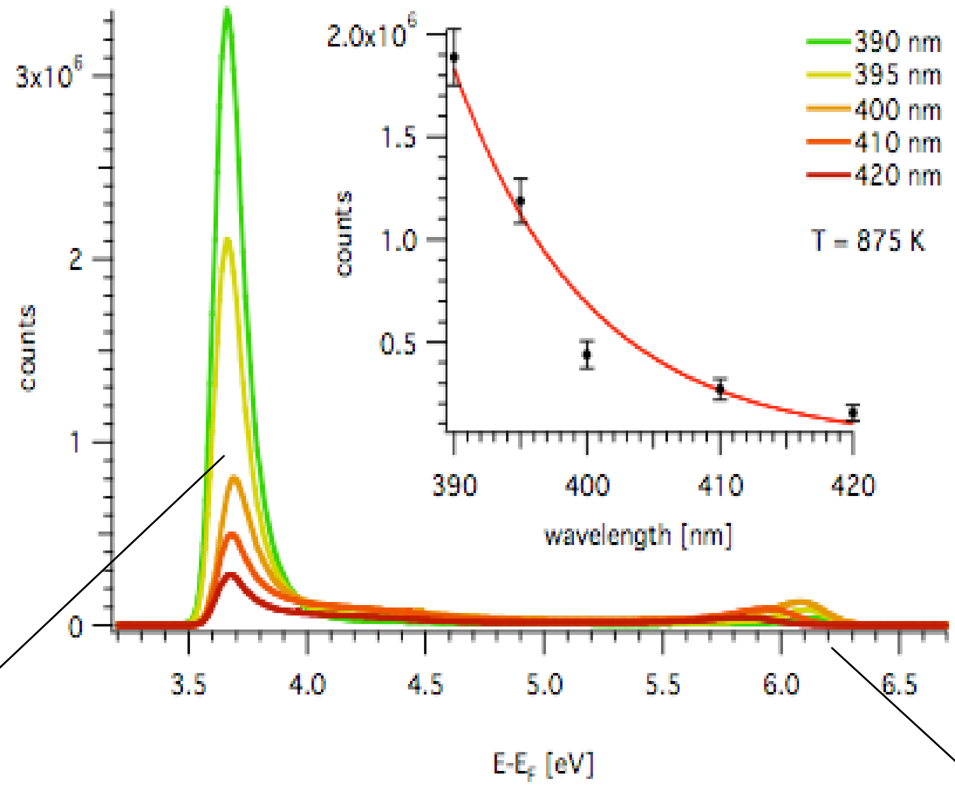
ex: Fermi surface of vicinal Cu(443)
hυ=3.08 eV, T=200 K



M. Hengsberger, F. Baumberger et al., unpublished

cross-section: one- vs. two-photon photoemission

- direct comparison at high temperature (845 K)
- sample workfunction 3.6 eV, photon energy 3.15 eV



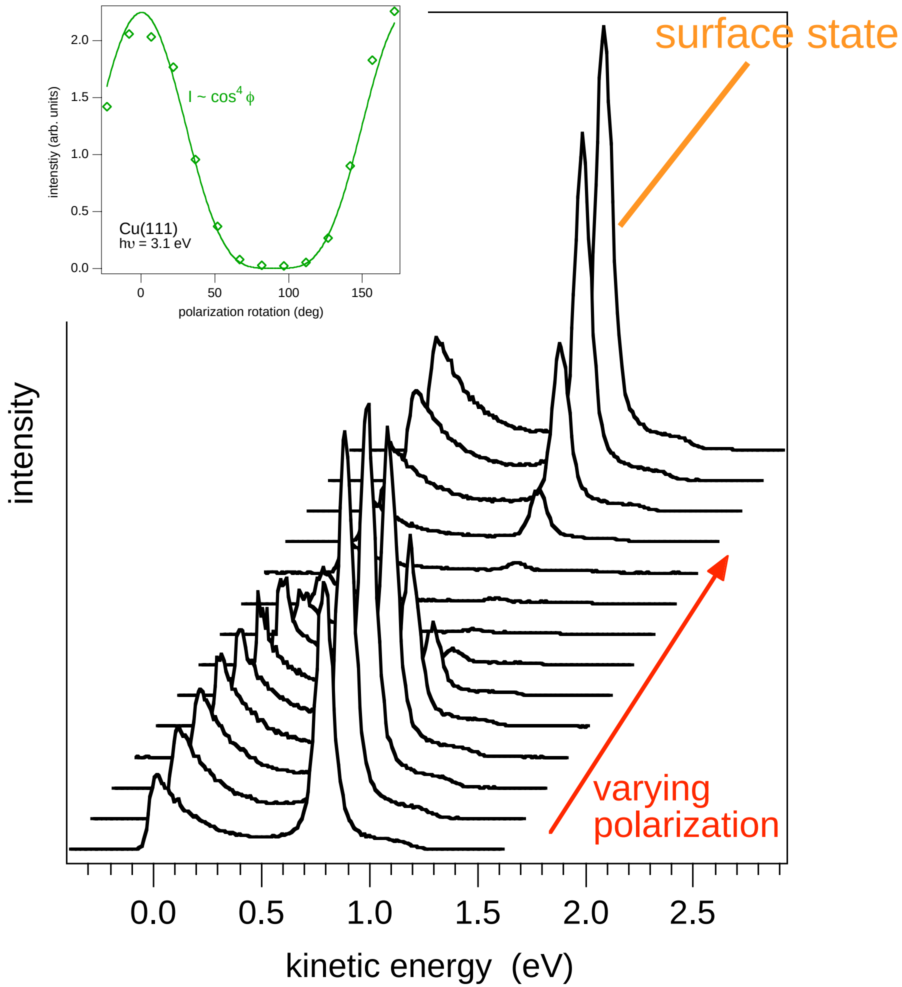
Boltzmann tail
~400 meV above E_F!

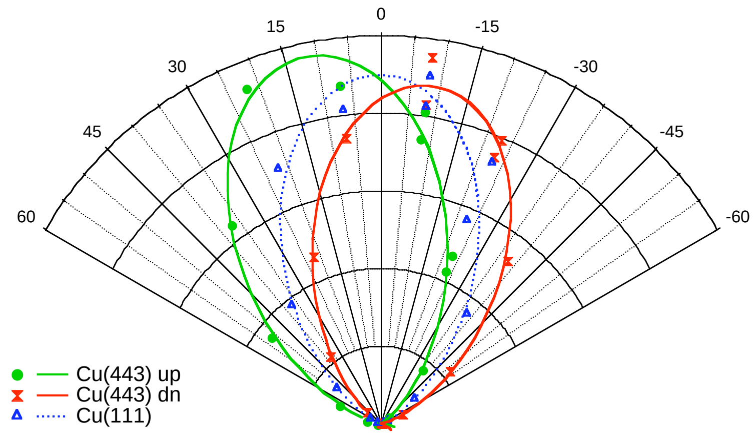
resonant 2PPE transition

D. Leuenberger, Master Thesis, U Zürich 2007

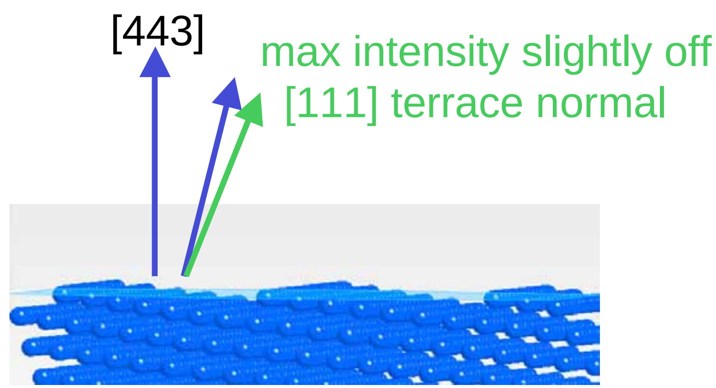
polarization dependence: transition dipoles

2PPE spectra taken as function of linear light polarization from Cu(443) and Cu(111)





orientation of transition dipoles yields information about state symmetries

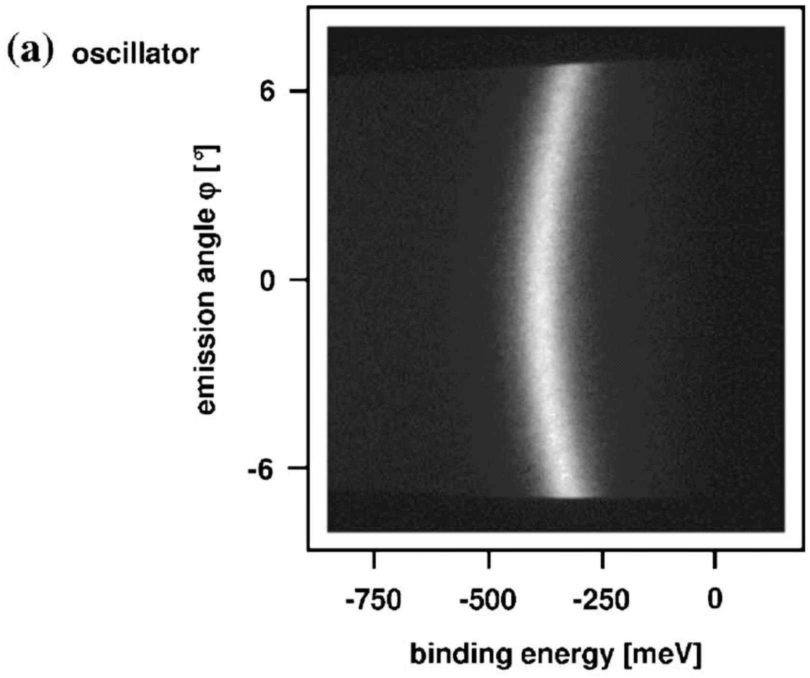


M. Hengsberger, F. Baumberger et al.
see e.g. Wolf et al., Phys. Rev. B 59 (1999)

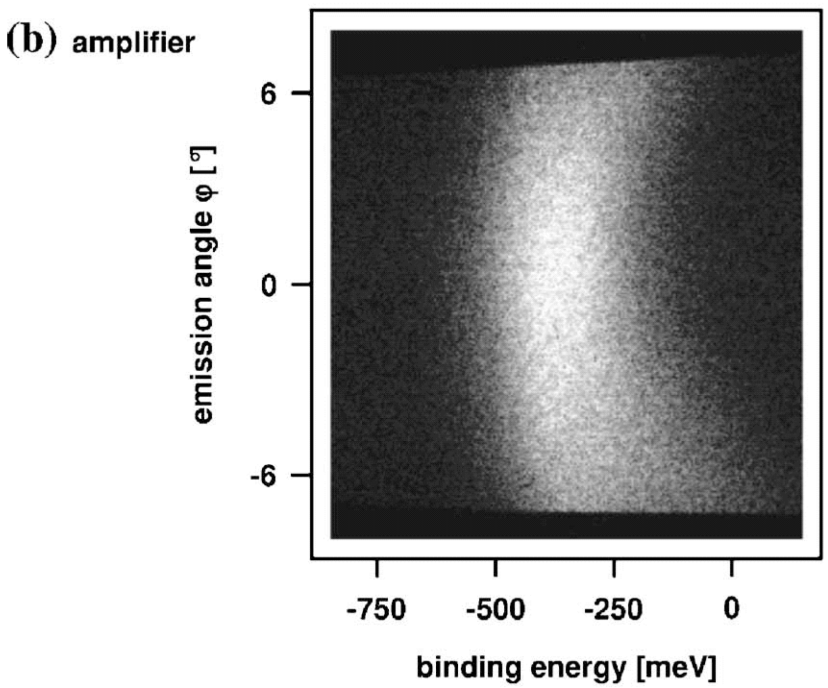
a parenthesis: (space-charge problems

- many electrons within one single 100 fs-pulse interact
- distortions of energy spectrum and angular distribution

high repetition rate, low pulse energy



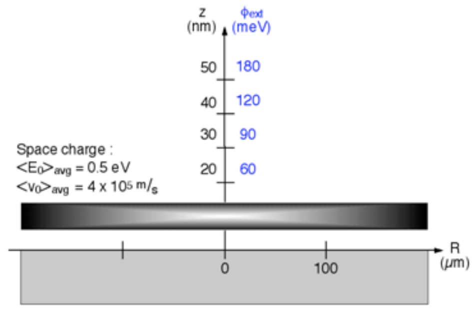
low repetition rate, high pulse energy



laser-PES: Passlack et al., J. Appl. Phys. 100, 024912 (2006)
for synchrotron experiments see Zhou et al., J. El. Spec. Rel. Phen. 142, 27 (2005)

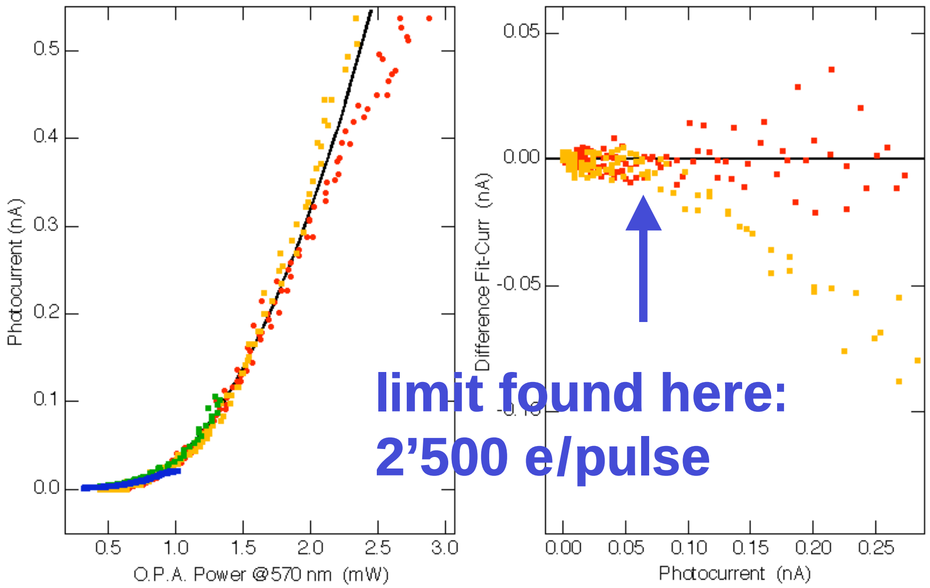
simple model: space charge in pulsed experiments

emission of thousands of photoelectrons within typ. 100 fs leads to significant space charge
current of the order of mA !



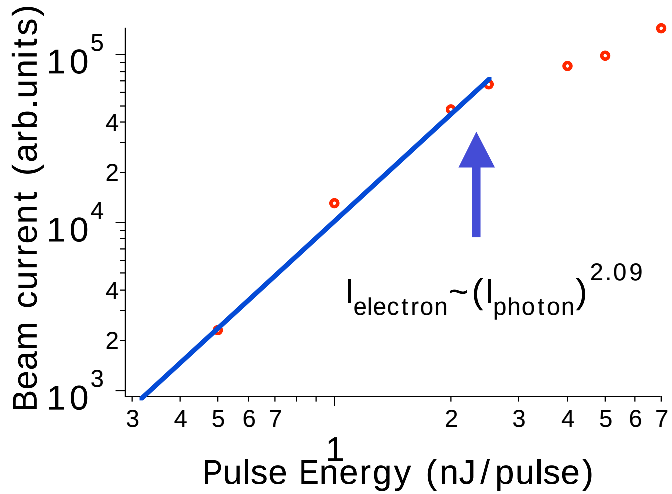
first observation: decreasing efficiency of the PE process

Ag cathode,
light: 570 nm, 140 fs, fluence ~60 µJ/cm²



limit found here: 2'500 e/pulse

Au cathode,
light: 400 nm, 100 fs, fluence ~6 µJ/cm²

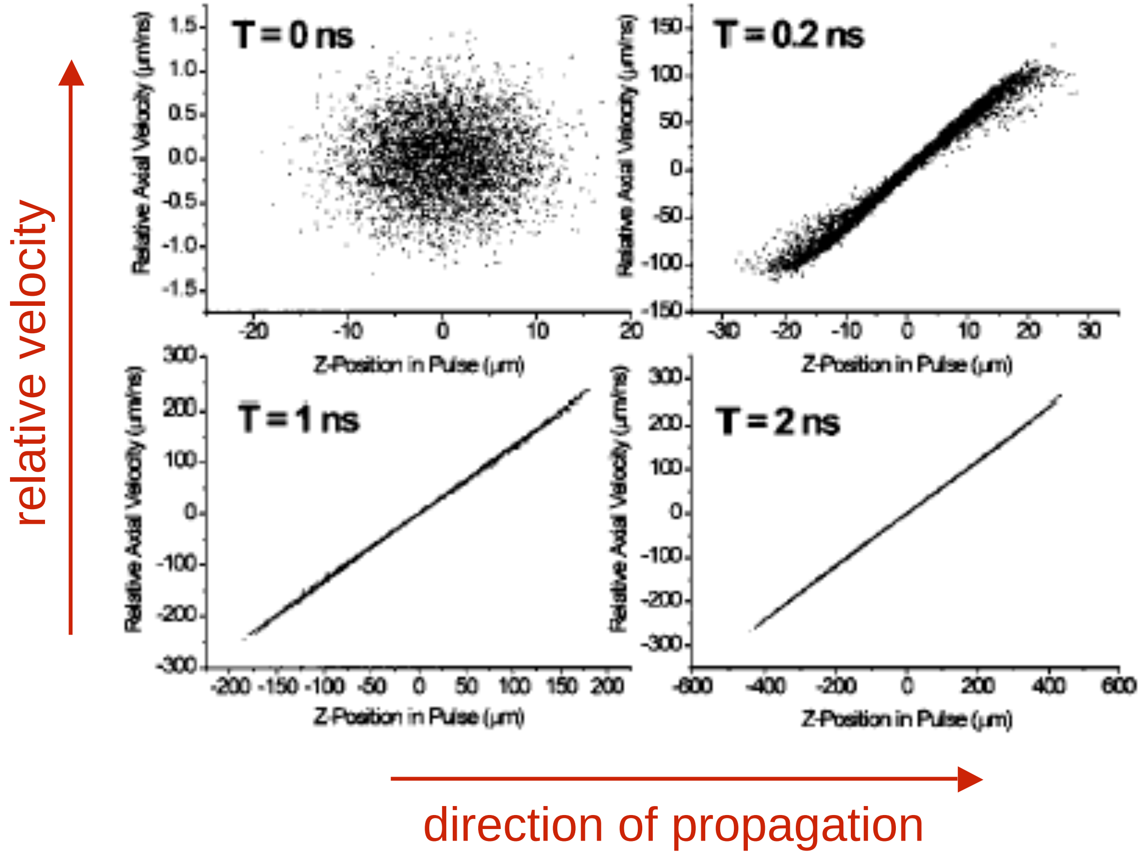


C. Cirelli, Ph.D. thesis, U Zürich 2006

space charge : chirp during drift

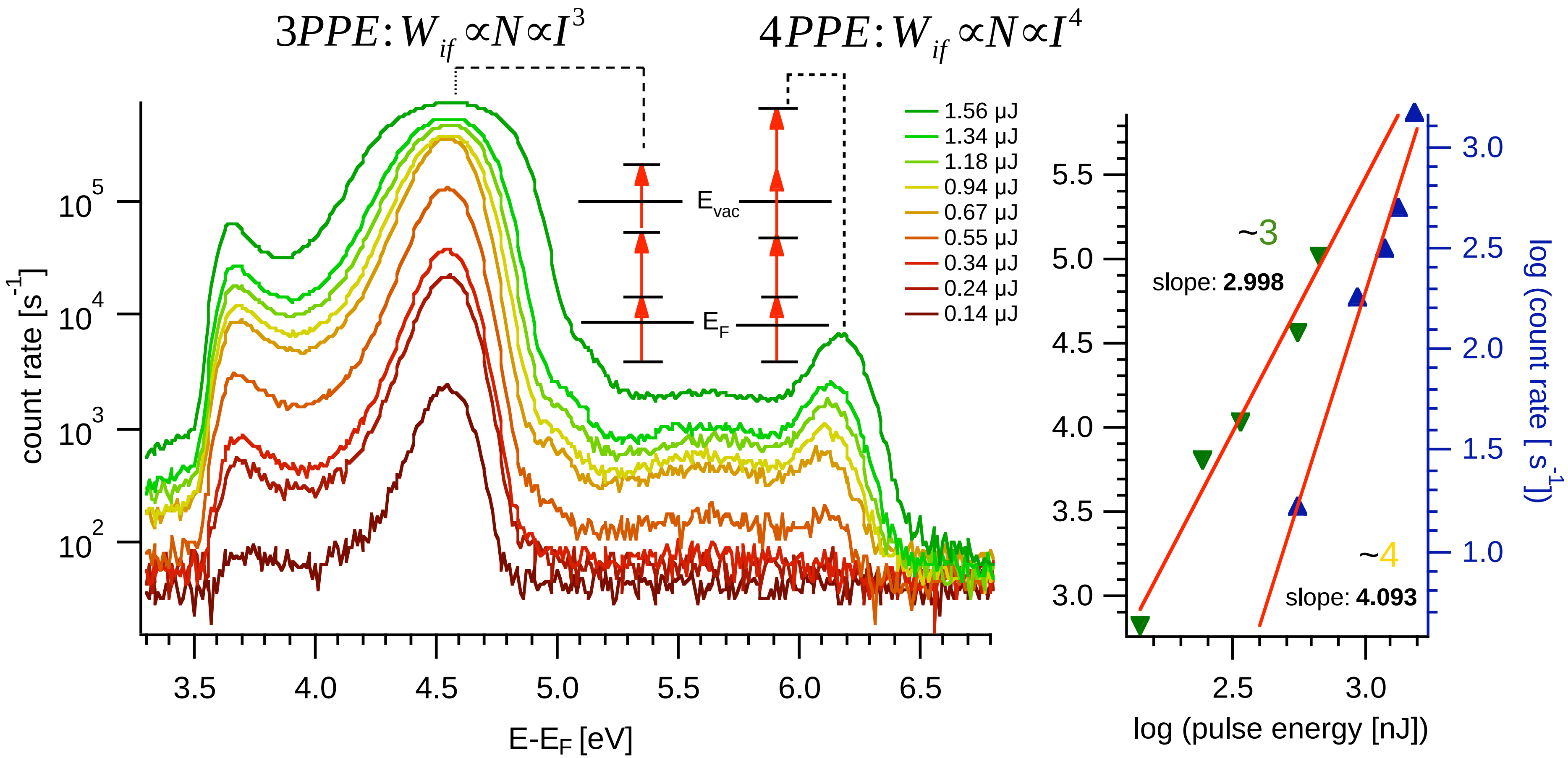
numerical solution of the equation of motion of a N-electron pulse:

Siwick et al., J Appl. Phys. 92, 1643 (2002)



multi-photon PE at high laser intensities

- laser: regenerative amplifier, fluence about 4 mJ/cm^2, hν=1.55 eV
- sample: h-BN/Ni(111)
- higher order transition (3PPE) and (4PPE)

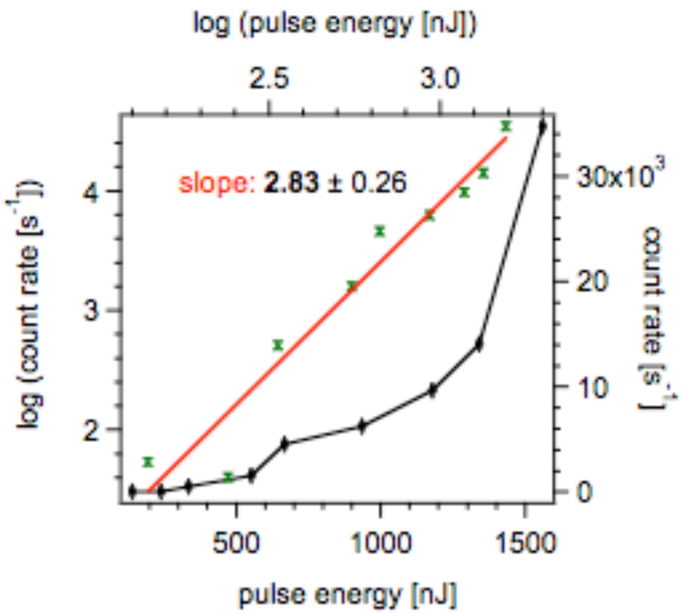


Surface Physics Group, Physics-Institute, U Zurich

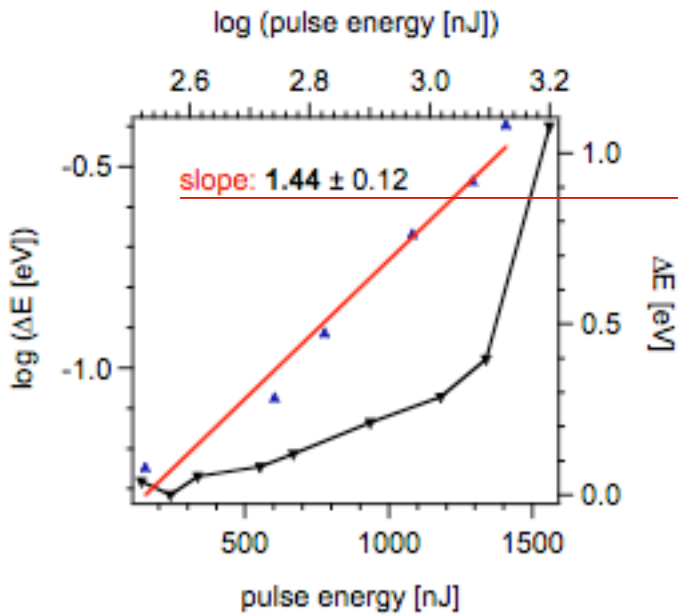
space charge induced broadening) - parenthesis closed

$$3PPE \Rightarrow N \propto I^3$$

$$\Delta E \cong v_0 \left(\frac{me}{\varepsilon_0 \pi r_0} \right) \sqrt{N} \propto I^{3/2}$$



yield at secondary cut-off (3PPE)
= measure of total electron yield



spectral width of 3PPE transition

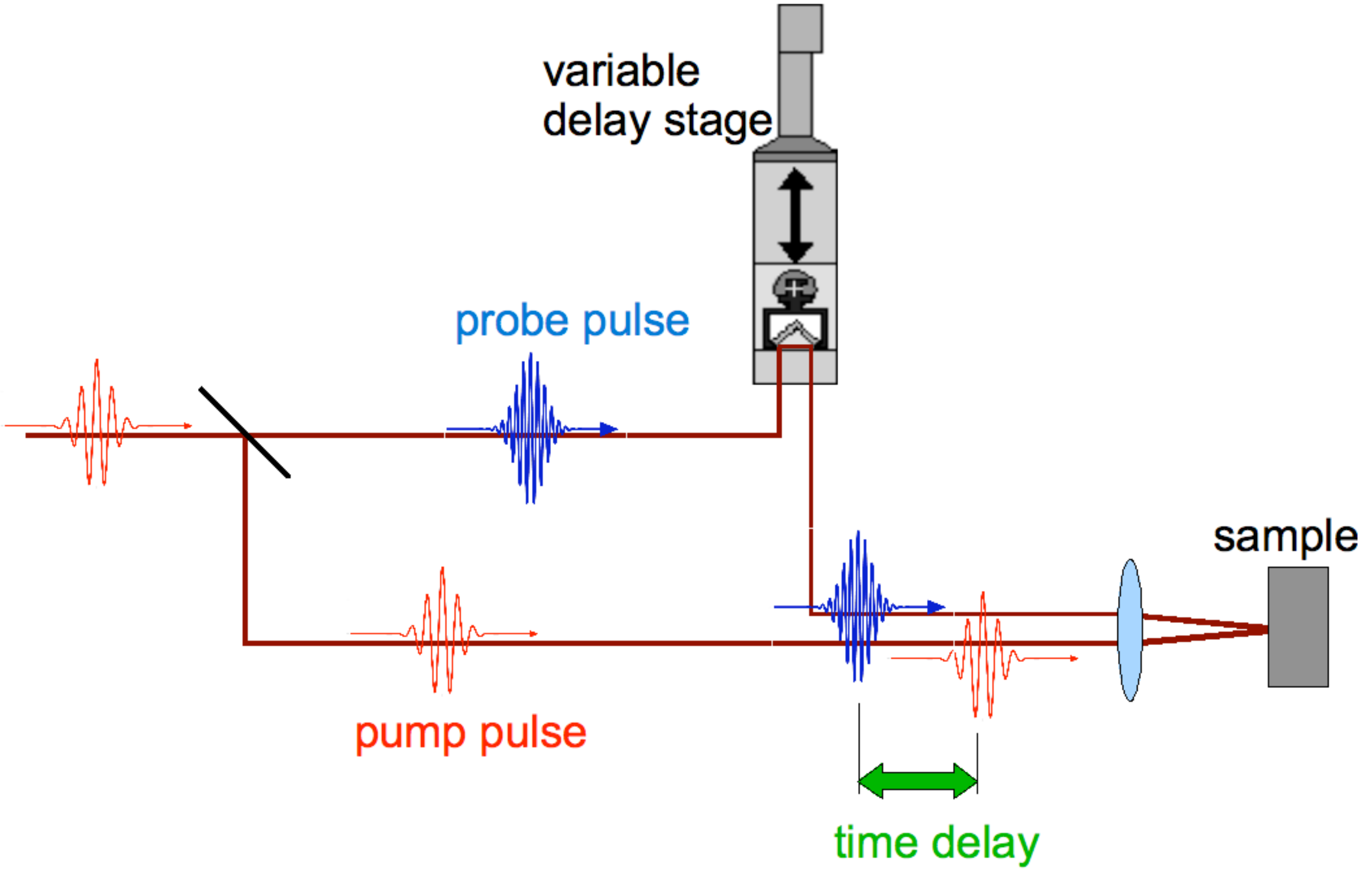
broadening scales with square root of the number of electrons (photocurrent)
in agreement with Passlack et al., J. Appl. Phys. 100, 024912 (2006)

D. Leuenberger, Master Thesis, U Zürich, 2007

time-resolved experiments: dynamics of hot electrons

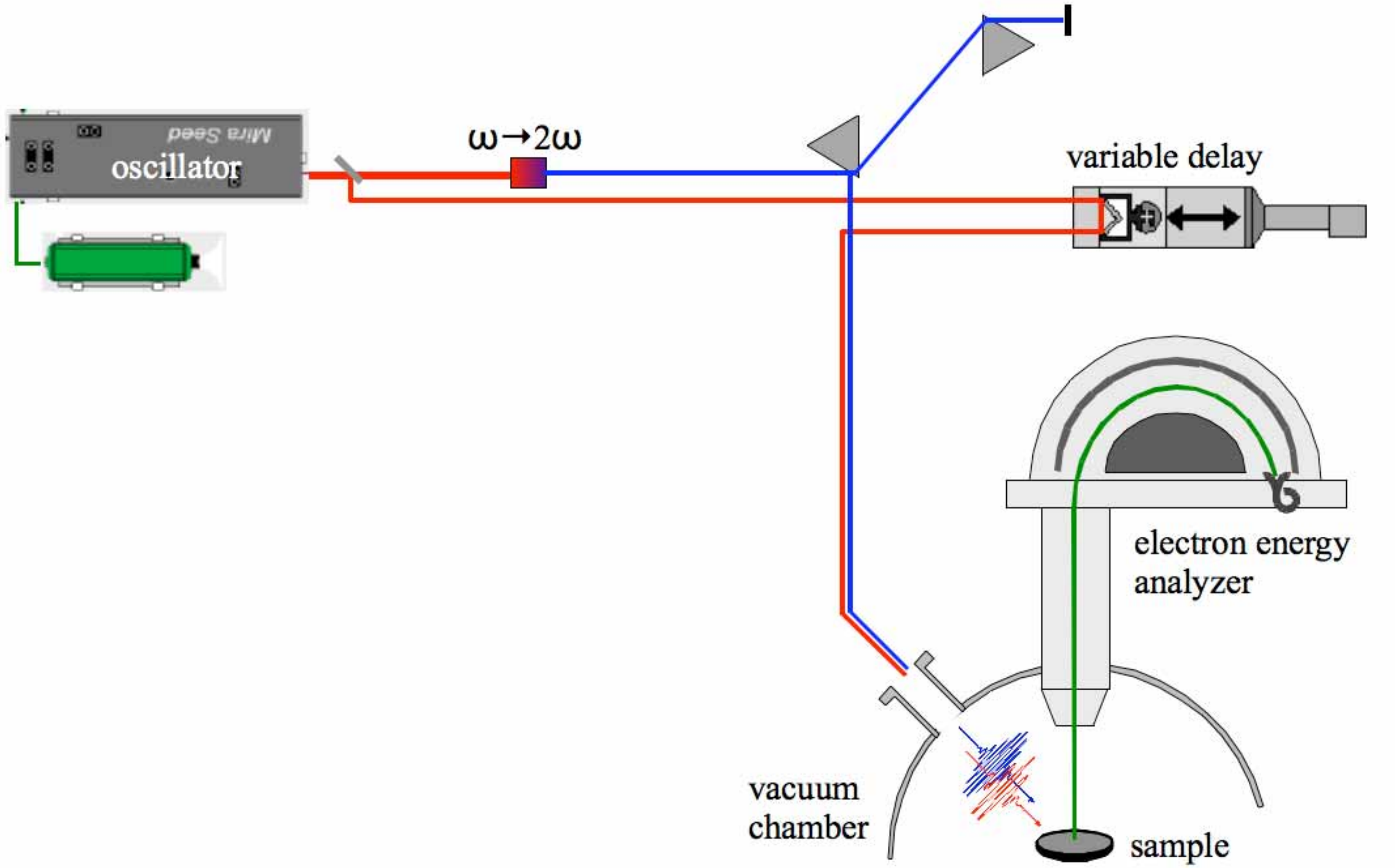
- study of lifetimes of excited states
- high excitation density
- (thermo-)dynamics of the hot electron gas
- timescales of electron-electron and electron-phonon scattering

pump-probe scheme



observable: f. ex. photoelectrons generated by probe pulse
time resolution: cross-correlation of pump and probe pulses
temporal jitter: none here

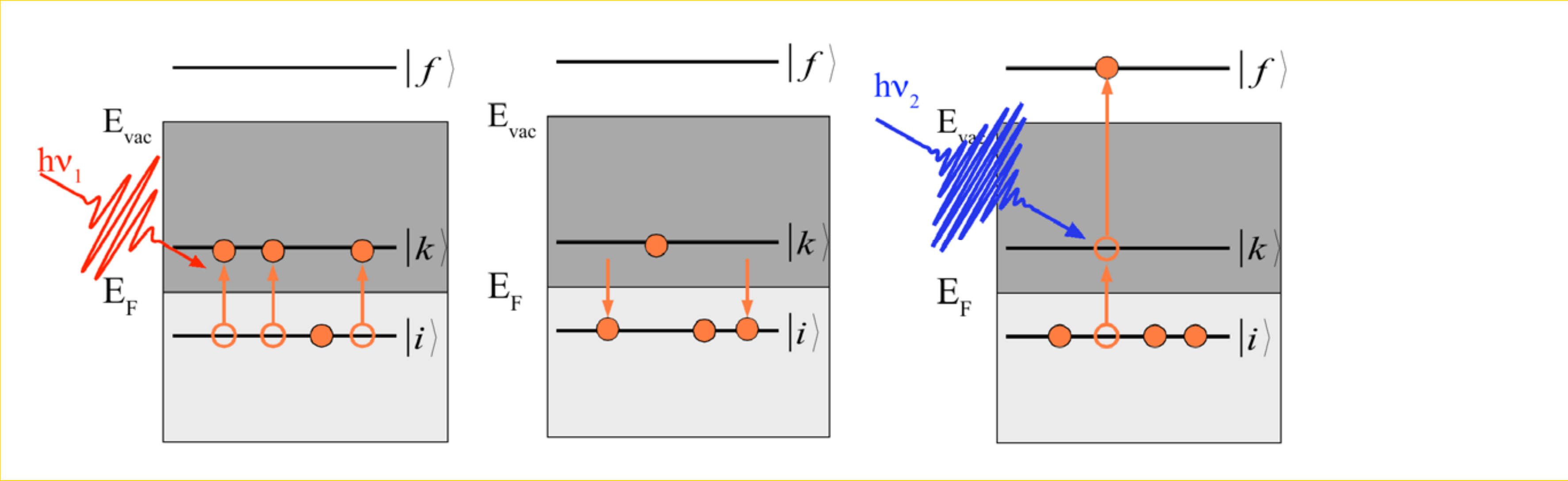
typical setup: our laboratory



time-resolved 2PPE

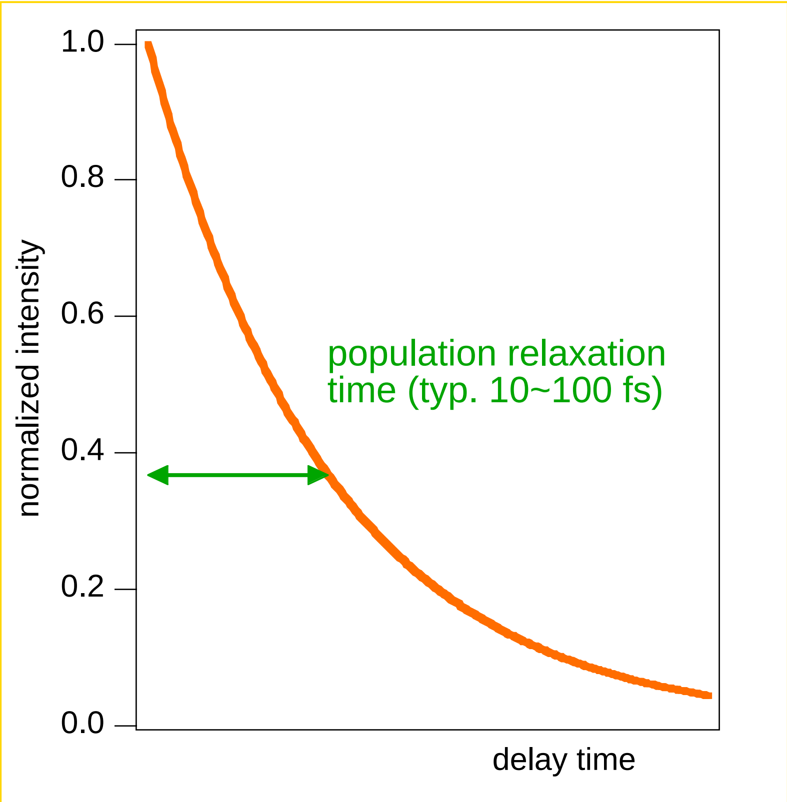
→ introduce variable time delay between first and second pulse

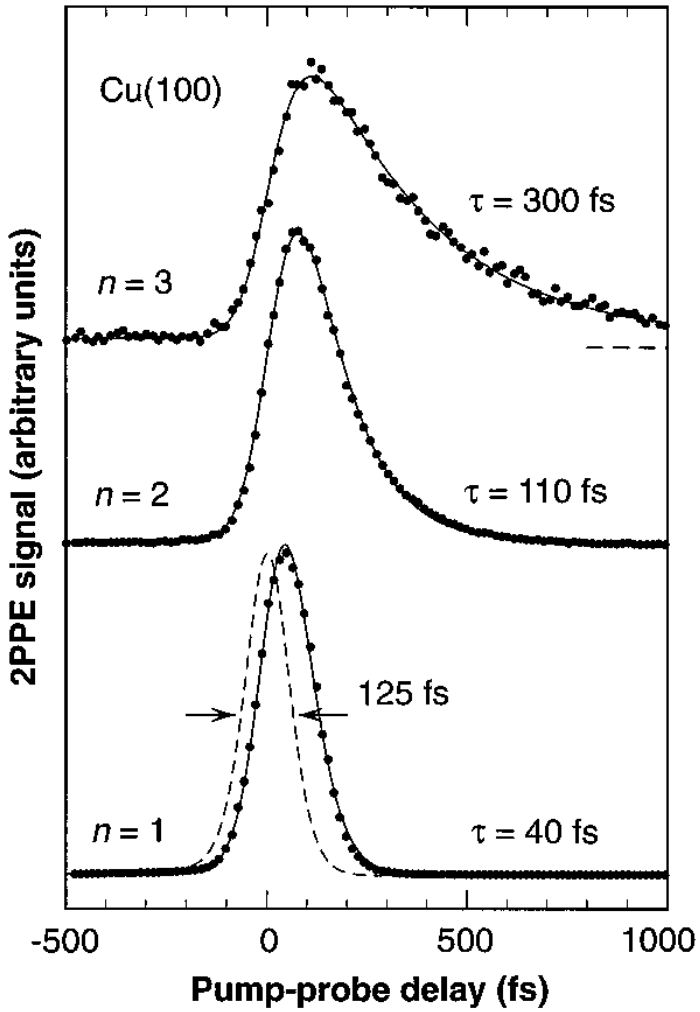
→ in case of intermediate state, the excited population decays exponentially with a typical time constant τ after the first pulse



extracting lifetimes from the transient intensities

if temporal pulse profiles (or cross-correlation) are known, the transients can be deconvoluted
→ direct access to decay constant

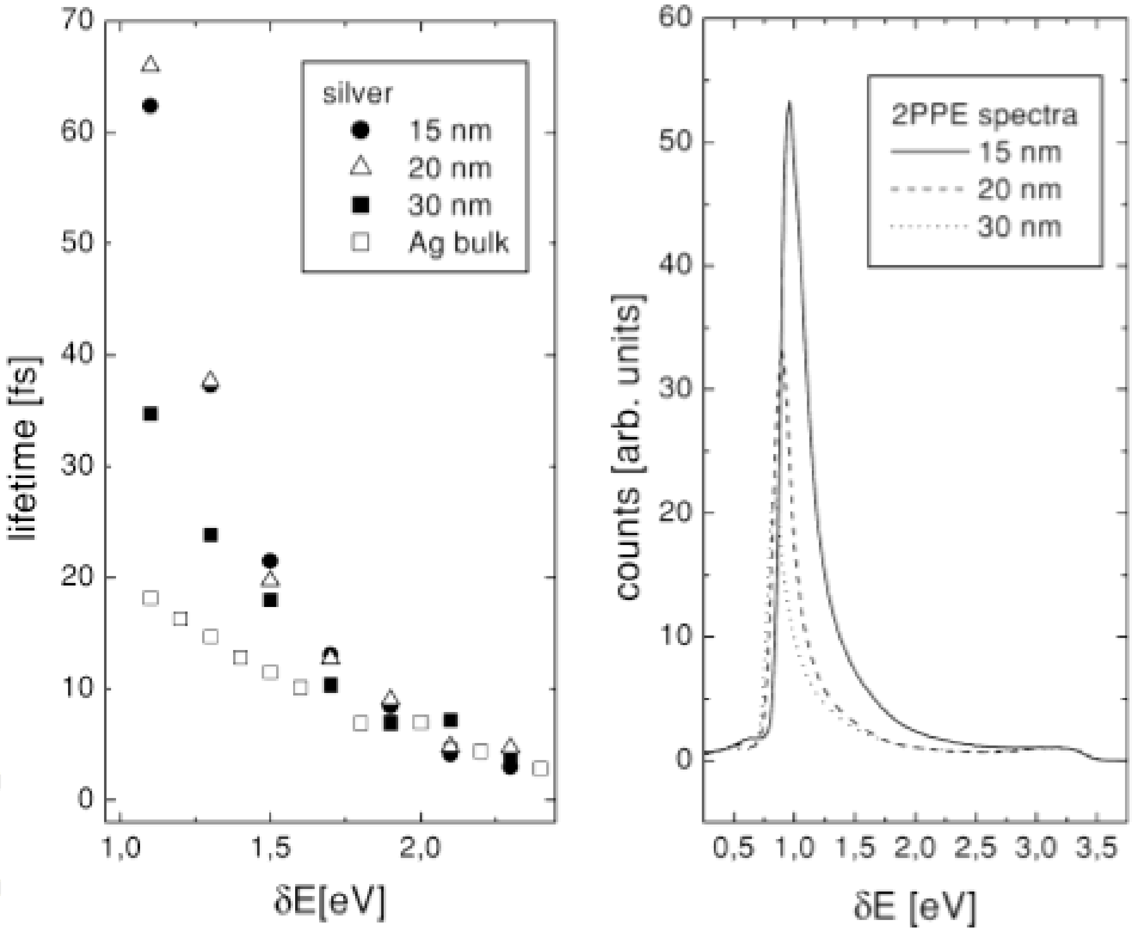




Höfer et al., Science 277, 1480 (1997)

effects of hot carrier diffusion

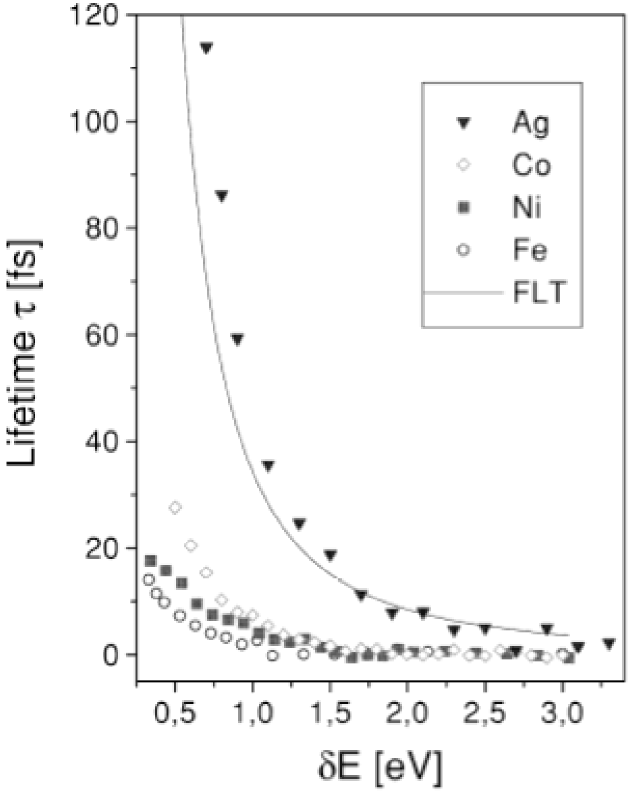
excited carriers diffuse towards bulk: apparently faster population decay
solution: thin film samples



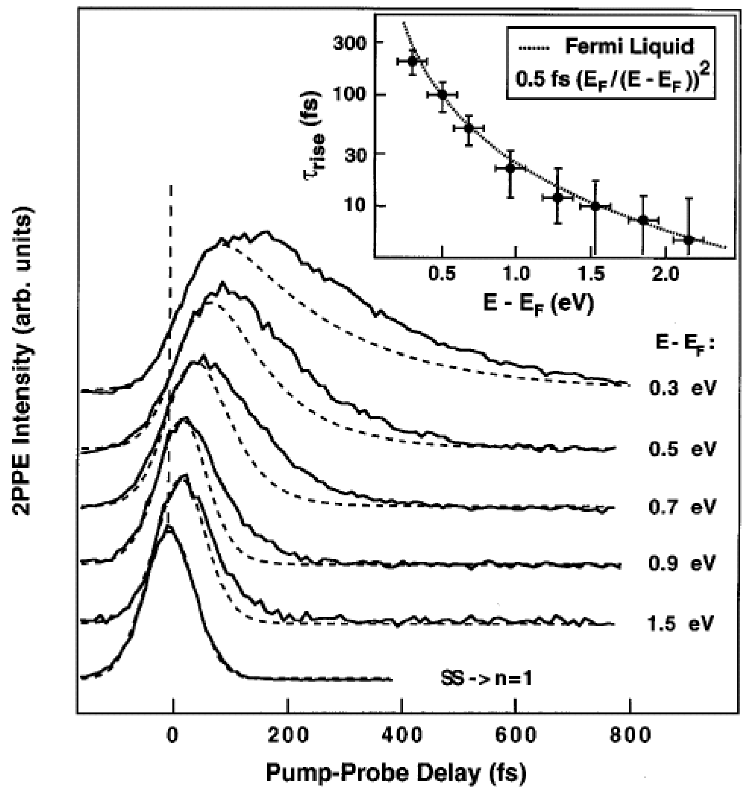
M. Aeschlimann et al.,
Appl. Phys. A 71, 1 (2000)

Auger-like cascade processes

in the secondary tail of 2PPE spectra, long lifetimes can be observed from states indirectly filled “from above” by inelastic scattering of highly excited electrons → Fermi-liquid like behaviour



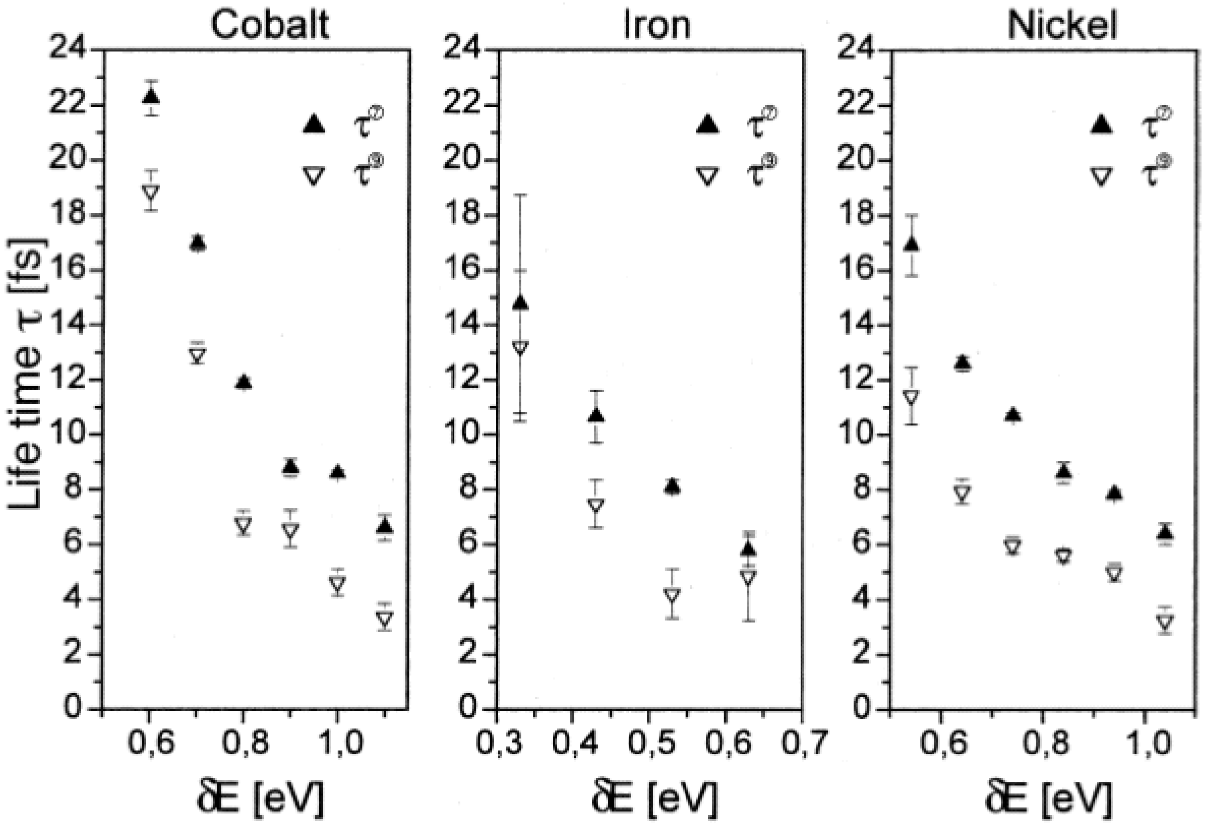
Aeschlimann, Appl. Phys. A 71, 1 (2000)

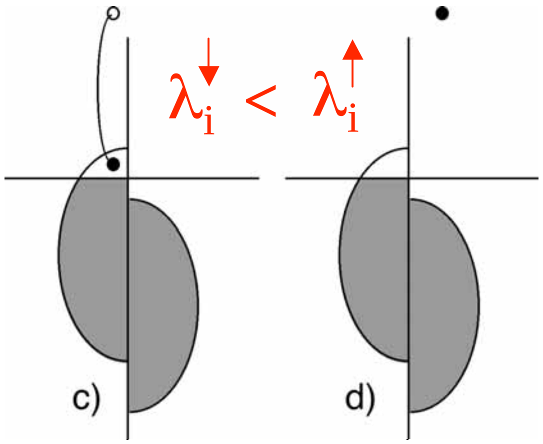


Hertel et al., Phys.Rev. Lett. 76, 535 (1996)

spin-dependent lifetimes

lifetimes and mean-free path depend on number of available empty states
→ minority spin carriers have shorter lifetimes (important for spintronics)

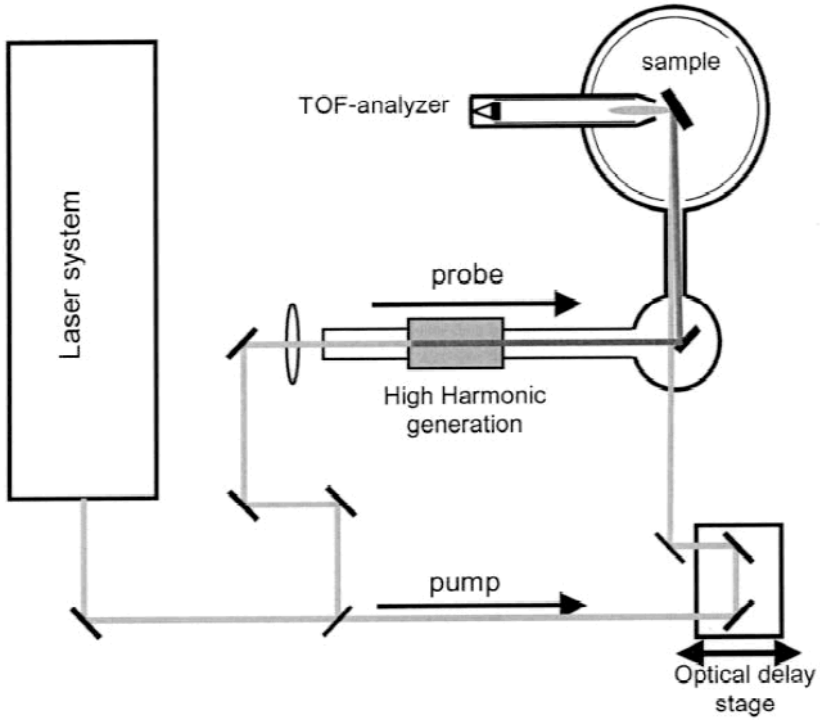


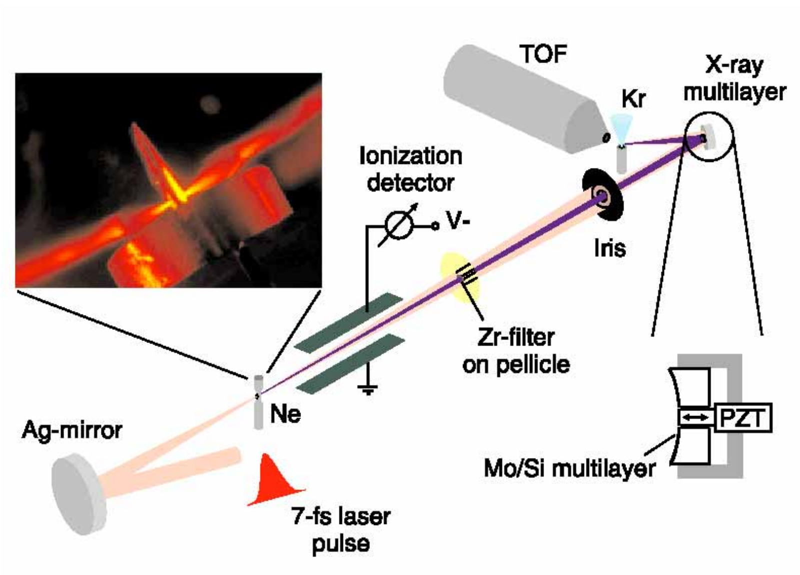


Bauer and Aeschlimann, J.El.Spec. 2002
more recently: Schmidt et al., Phys. Rev. Lett. 95, 107402 (2005)

time-resolved *one*-photon photoemission

consists of triggering a system by a pump pulse and probing with a vuv-probe pulse (1PPE process) - vuv-pulses are produced by high-harmonic generation

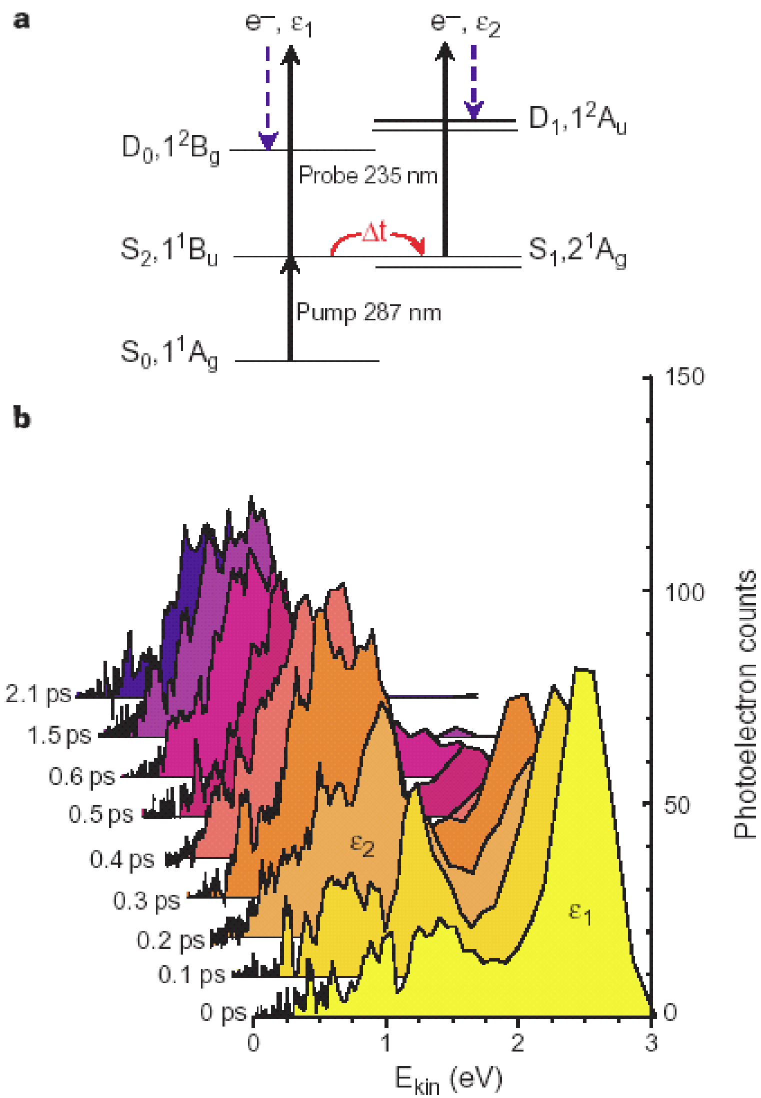




Bauer and Aeschlimann, J.El.Spec. 2002

M. Drescher et al., Science 291, 1923 (2001)

time-resolved 1PPE from molecules (gas phase)



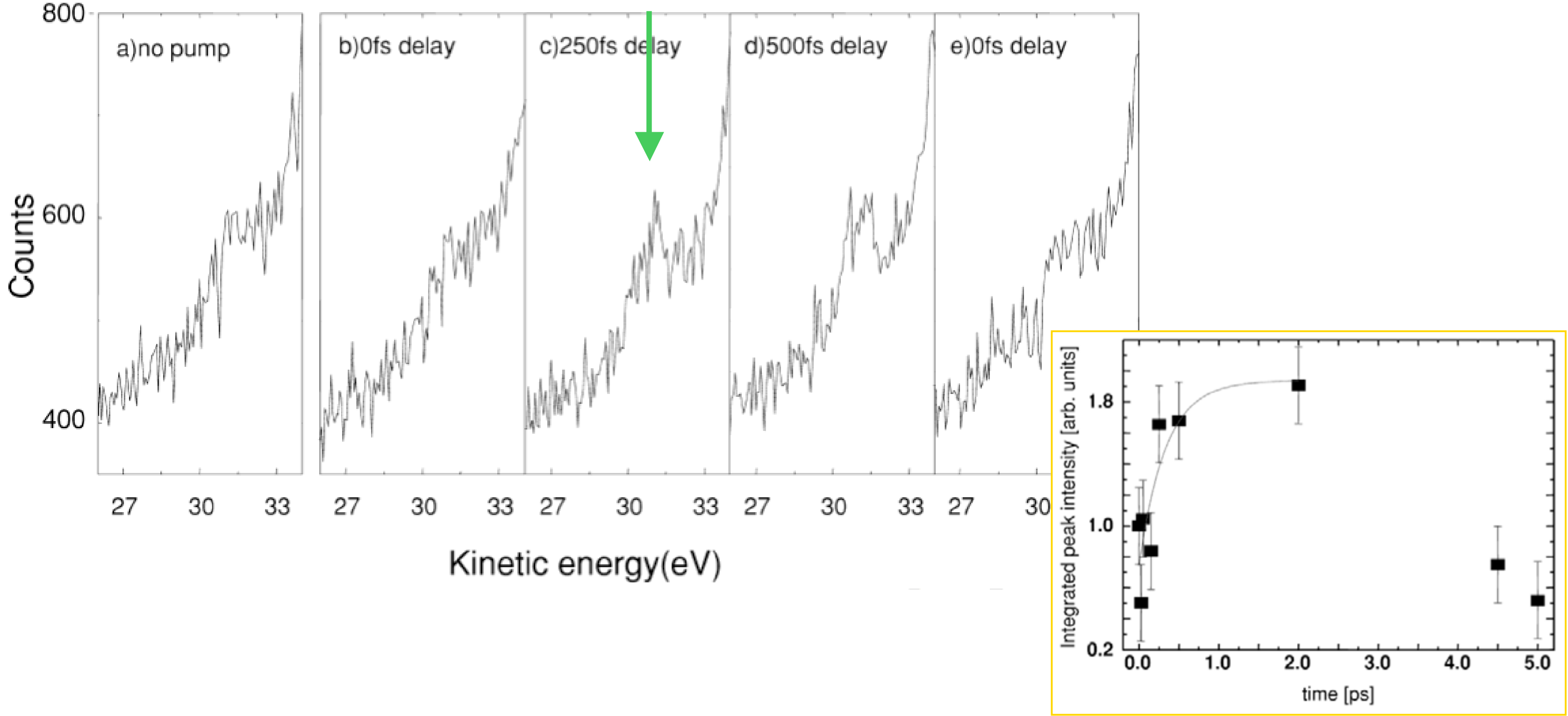
chemical reaction kinetics in gas phase observed by 1PPE:

ultrafast cis-trans conversion in all-trans-2,4,6,8-decatetraene $C_{10}H_{14}$ promoted by vibrational motion (*photoisomerization*)

V. Blanchet et al., Nature 401, 52 (1999)

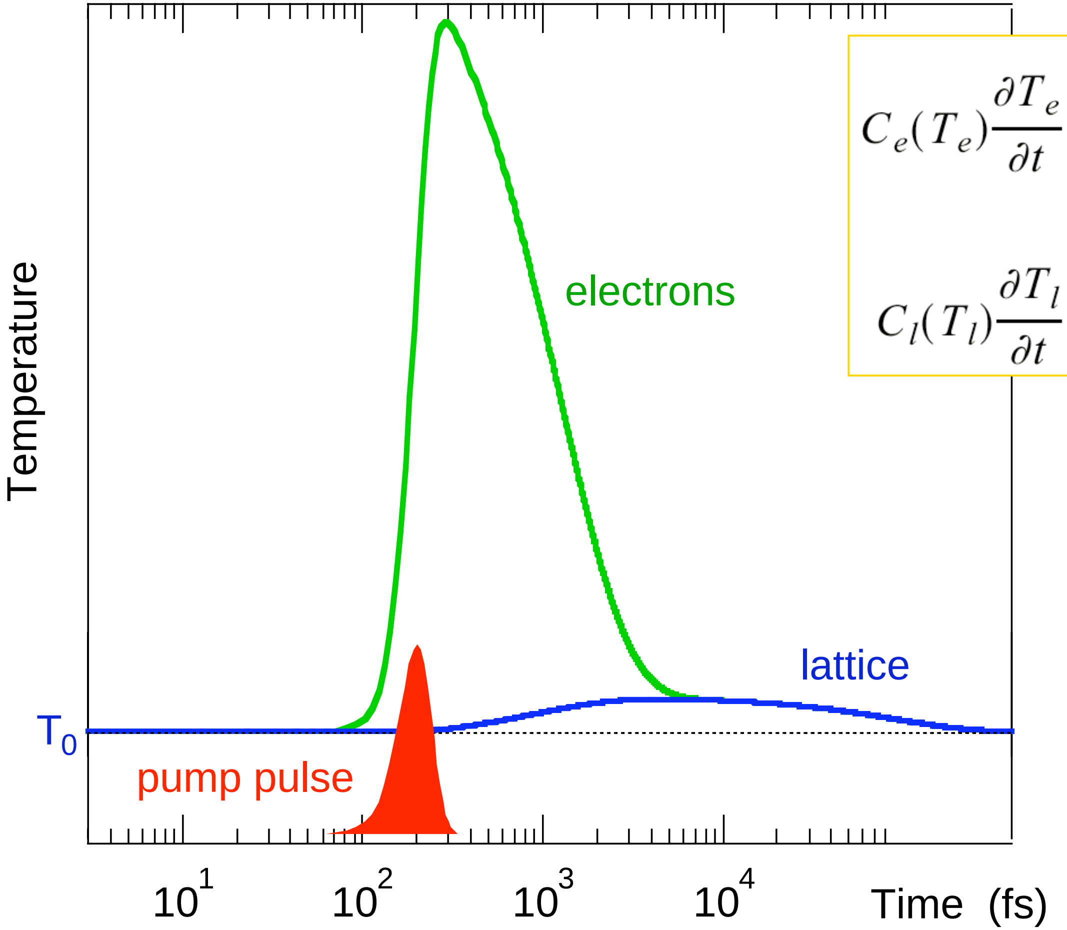
chemical reaction kinetics on surfaces

O2/Pt(111) at 77 K (high harmonic H27, 42 eV)
oxygen is excited by hot electron transfer from substrate and changes orientation (550 fs, transient peroxo phase), reflected in peak at 6 eV



M. Bauer et al., Phys. Rev. Lett. 87, 025501 (2001)

light-solid interaction: what happens after pump pulse ?



two-temperature model

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z}\left(\kappa \frac{\partial}{\partial z} T_e\right) - g(T_e - T_l) + S(z,t)$$

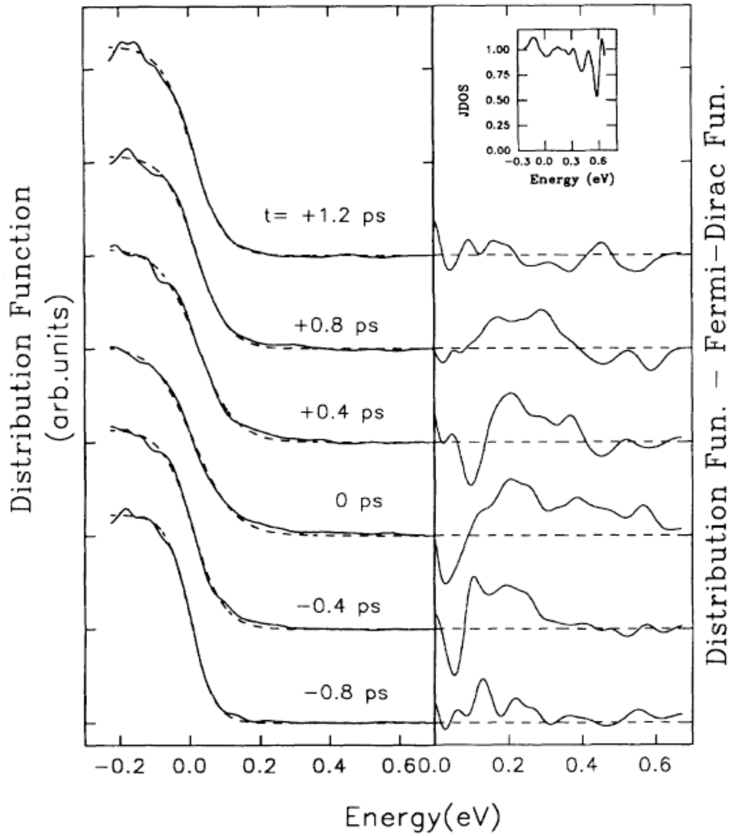
$$C_l(T_l)\frac{\partial T_l}{\partial t} = g(T_e - T_l).$$

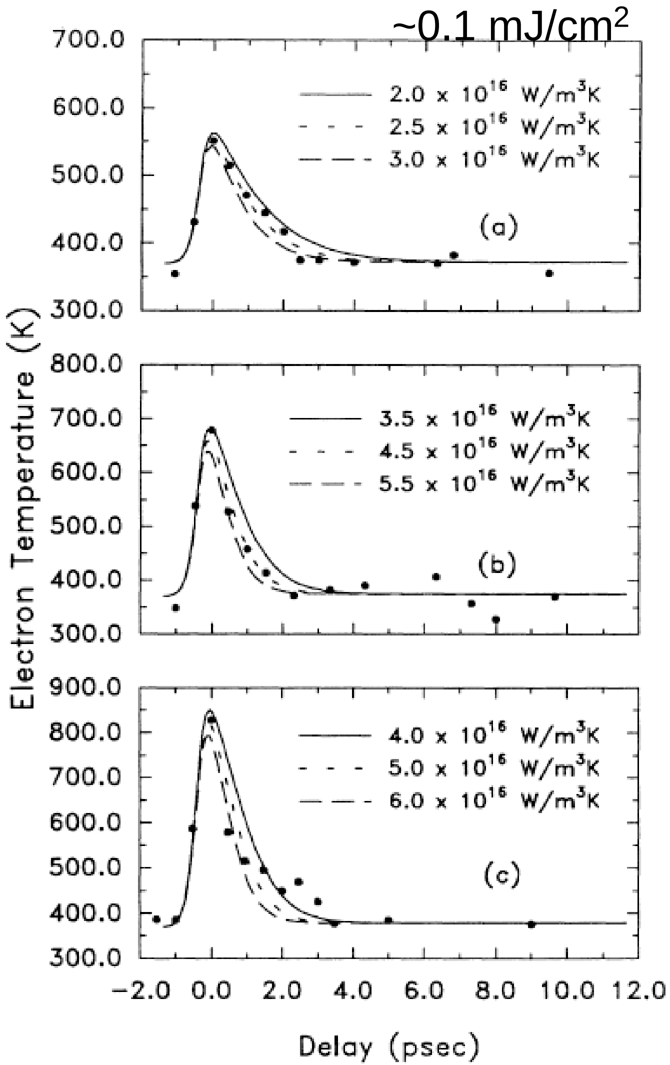
e-e interaction: 1-100 fs
e-ph interaction:
 optical phonons > 500 fs
 acoustic phonons 1-10 ps

e.g. M. Bonn et al., Phys. Rev. B 61, 1101 (2000)

measurement of electron (thermo-)dynamics

after thermalization of hot-electron distribution (thermodynamic equilibrium after ca. 100 fs), the Fermi edge can be used as ultrafast electron thermometer

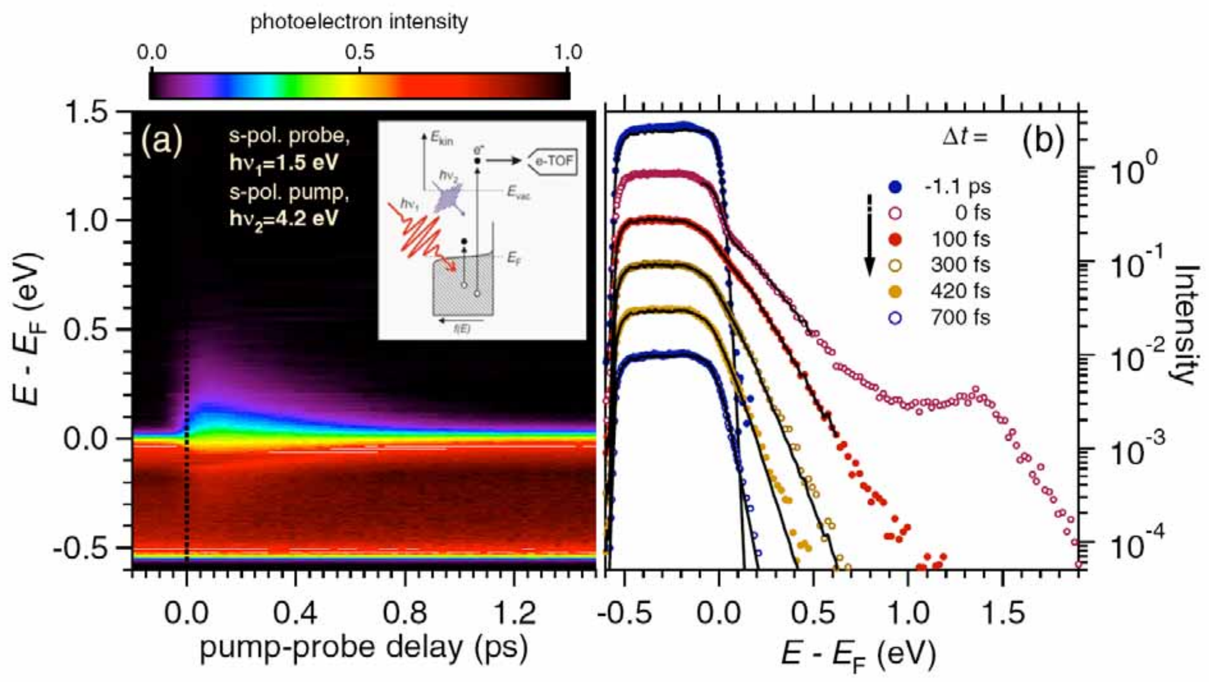




Fann et al., Phys. Rev. Lett. 68, 2834 (1992)

time-resolved photoelectron spectroscopy

- electrons promoted into unoccupied states by pump pulse
- thermodynamic equilibrium (Fermi-Dirac distribution) within 100 fs
- energy dissipation by scattering events:
  - electron-electron interaction, typ. 10-100 fs
  - optical phonons typ. 500-1000 fs
  - acoustic phonons typ. 1-10 ps

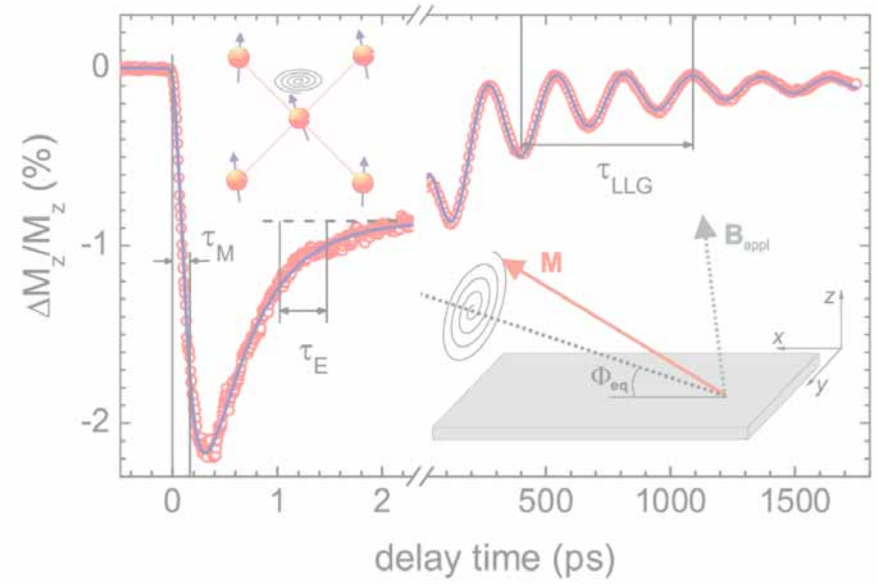


Bovensiepen, J. Phys.: Cond. Mat. 19, 083201 (2007)

example: ultrafast demagnetization

- macroscopic magnetization significantly reduced (>50%) after absorption of an intense laser pulse in thin nickel films
Beaurepaire et al., Phys. Rev. Lett. 76, 4250 (1996)

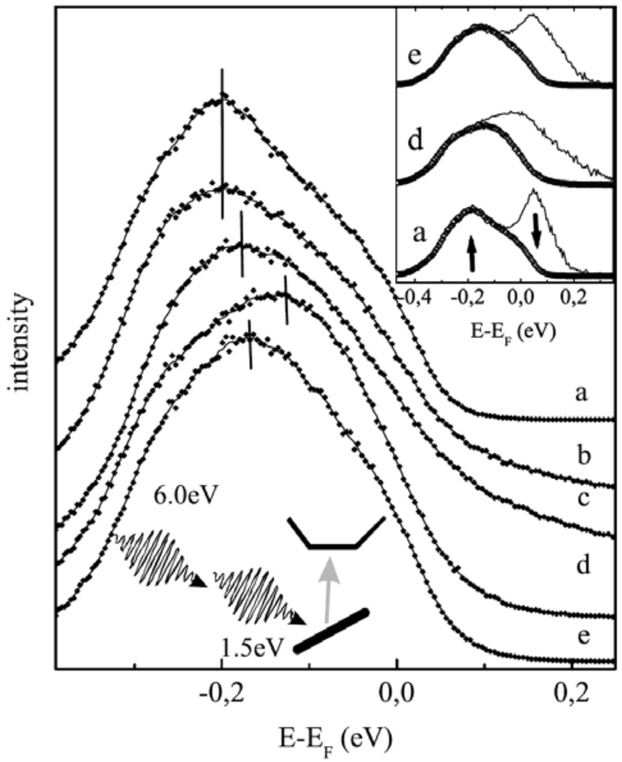
- mostly magneto-optical measurements
- electron gas from equilibrium:
- **Kerr effect still representative of magnetization?**

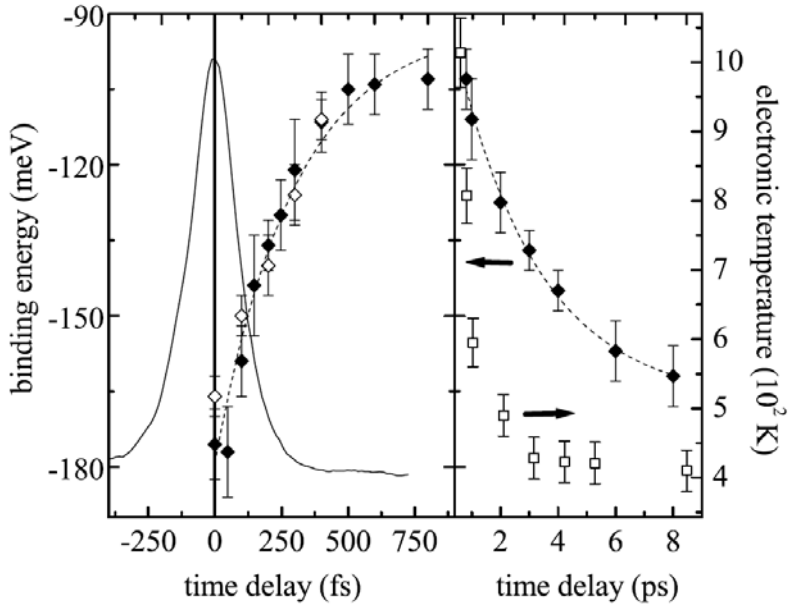


Koopmans et al., Phys. Rev. Lett. 95, 267207 (2005)

TR-PES and ultrafast demagnetization

time-resolved photoemission: exchange splitting vanishes within 300 fs





Rhie et al., Phys. Rev. Lett. 90, 247201 (2003)

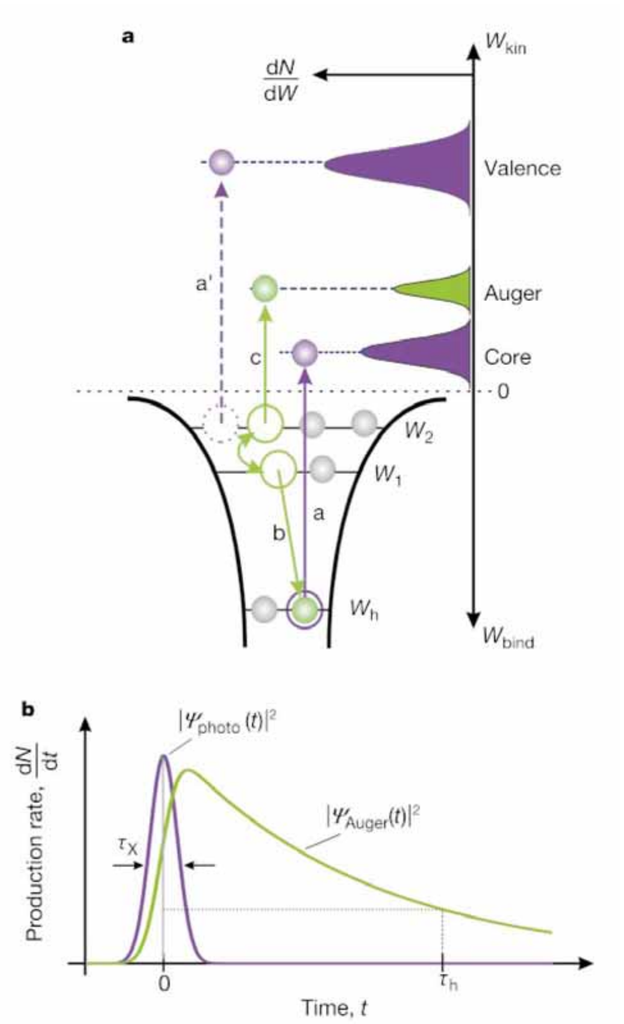
further experiments:
Gd(0001)/W: Bovensiepen et al., Phys. Rev. Lett. 95, 137402 (2005) TR-MOKE
J. Phys.: Cond. Mat. 19, 083201 (2007) TR-PES
Co/Cu(001): Cinchetti et al., Phys. Rev. Lett. 97, 177201 (2006) TR-PES

extreme time resolution: attosecond dynamics

- broad-band laser light: ultrashort pulses
- high-harmonic generation
- how to perform an "attosecond experiment"
- case study: photoemission vs. Auger excitation
- approaching the timescale of the photoemission process?

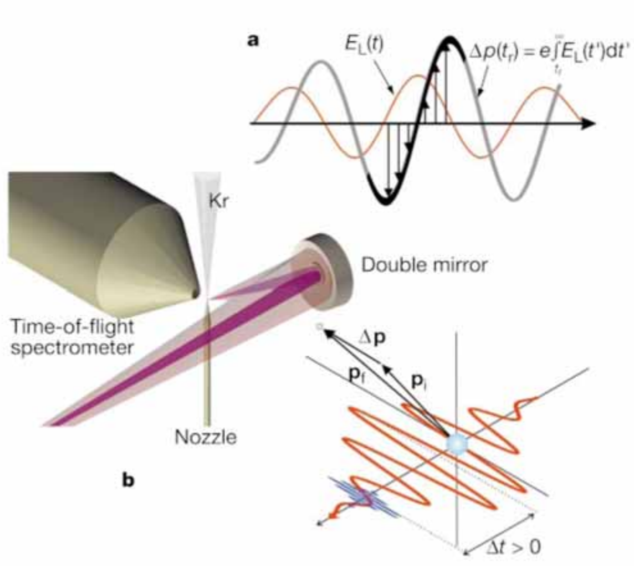
extreme time resolution: techniques

idea of the experiment:
measure timescale of Auger excitation after photoemission process



sampling technique:

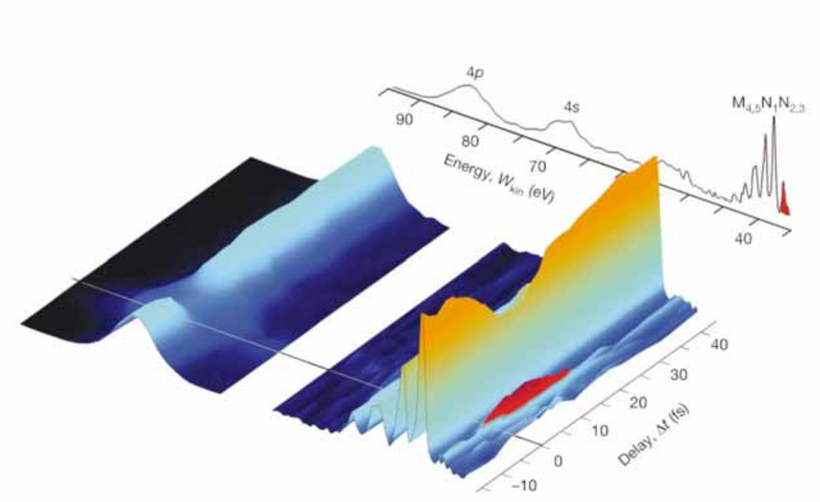
- emitted electrons experience acceleration depending on the phase and amplitude of the light field (5 fs, 800 nm)
- integration of the action over the light pulse duration leads to spectral shift and broadening depending on photohole lifetime

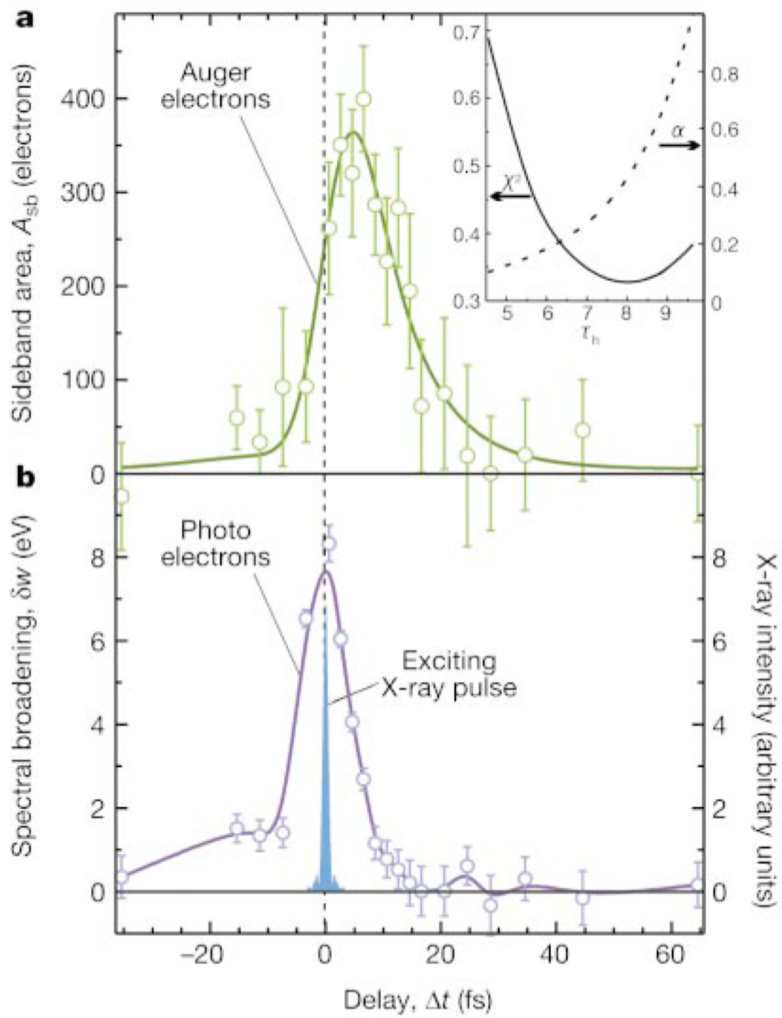


Drescher at al., Nature 419, 803 (2002)

extreme time resolution: core hole lifetime

4p vs $M_{4,5}N_1N_{2,3}$





results:

Auger electron emission delayed

→ Auger M d5/2 core hole lifetime 7.9 fs

→ photoelectrons (4p) follow pulse shape of the NIR pulse and give clock zero

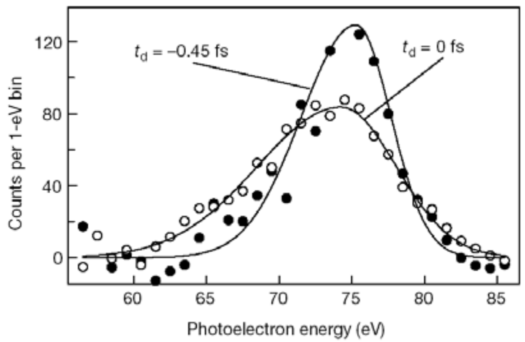
Drescher at al., Nature 419, 803 (2002)

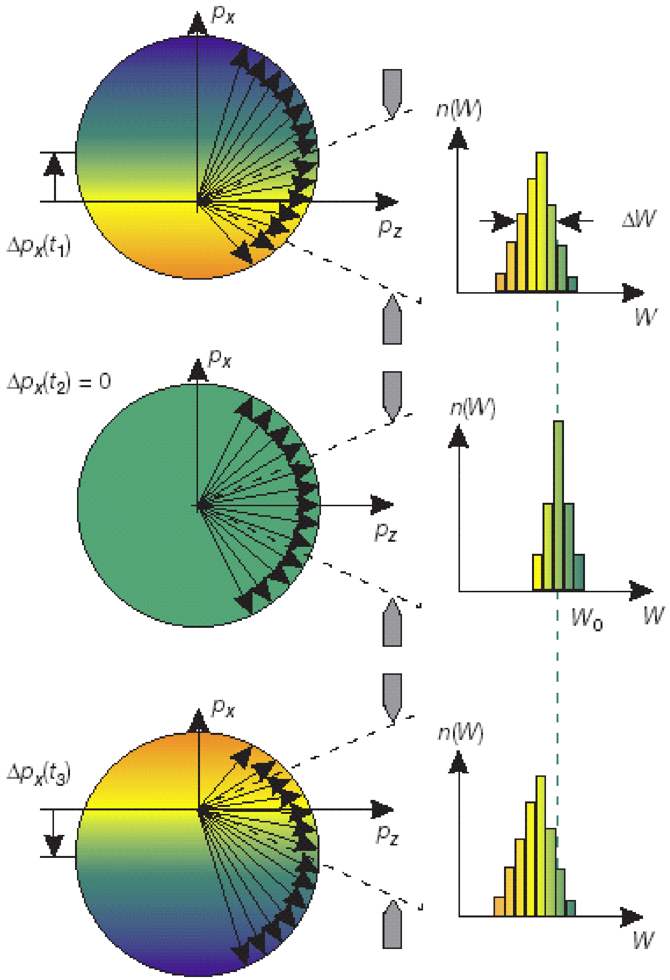
towards fundamental timescale of the photo-effect

experiment:
x-ray photoemission spectra (hυ=90 eV) from atomic Kr in presence of a strong infrared light field

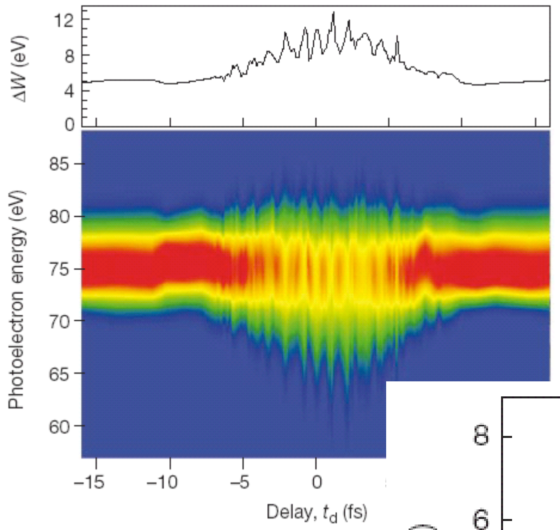
momentum transfer from light field depends on phase of the field at instance of “birth” of the photoelectron

result:
mapping of the phase of the IR field through the Kr photoemission signal





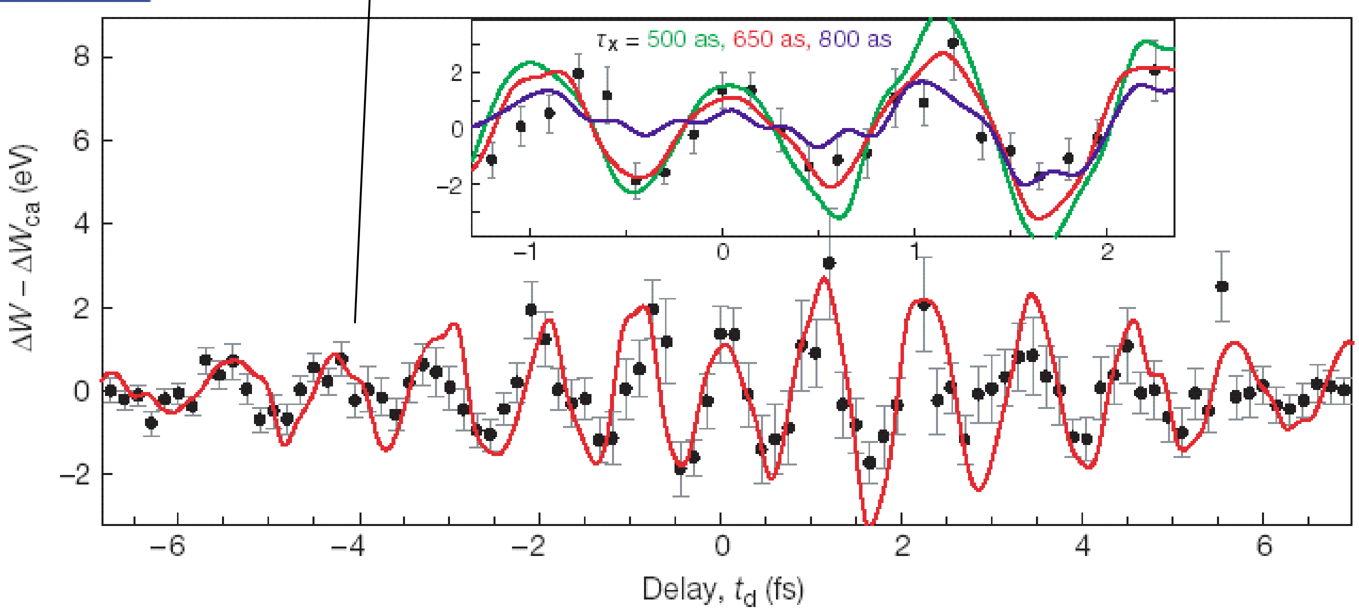
result: the current world record



x-ray pulse width 650 as

100 as = 10^{-16} s = 30 nm delay length (!)

phase of the 800 nm light pulse

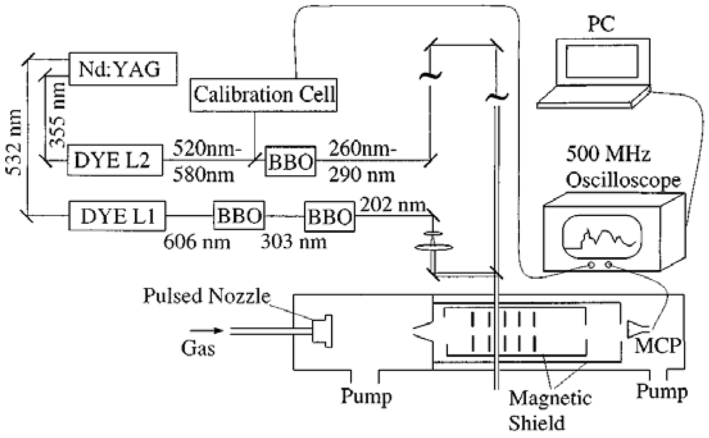


Hentschel et al., Nature 414, 509 (2001)

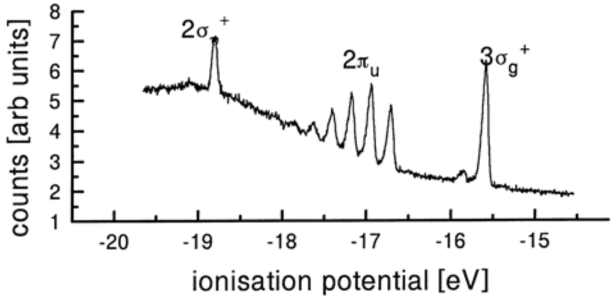
extreme energy resolution and "bulk sensitivity"

- narrow-band laser light sources
- time-of-flight analyzers
- state-of-the art experiments
- universal curve: how to measure "bulk data"

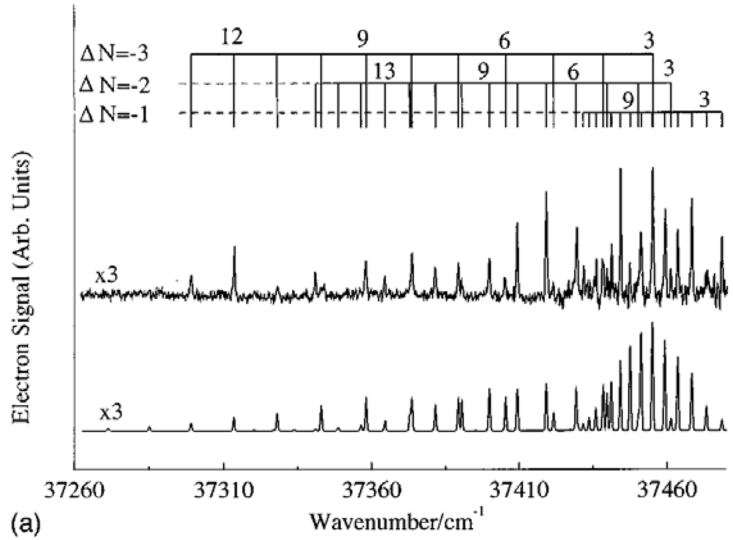
ZEKE PES = zero electron kinetic energy PES



- standard: vibrational modes in gas phase



- high-resolution spectroscopy: rotational modes (here ammonia)

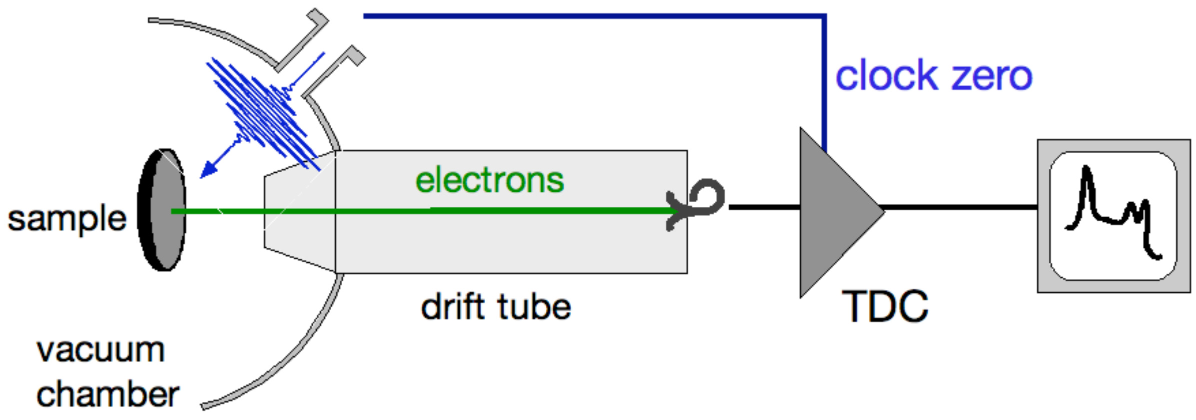


laser pulse: 5 ns, 6.13 eV, 200-300 μJ/pulse
detection: time-of-flight,
electron mutliplier and 500 MHz oscilloscope
energy resolution: 0.6 cm^{-1} = 75 μeV!
but close to kinetic energy zero
(threshold ionization)

total x range: 480 cm^{-1} = ~60 meV

Signorell et al., J. Chem. Phys. 106, 6523 (1997)

laser combined with time-of-flight detector (TOF)

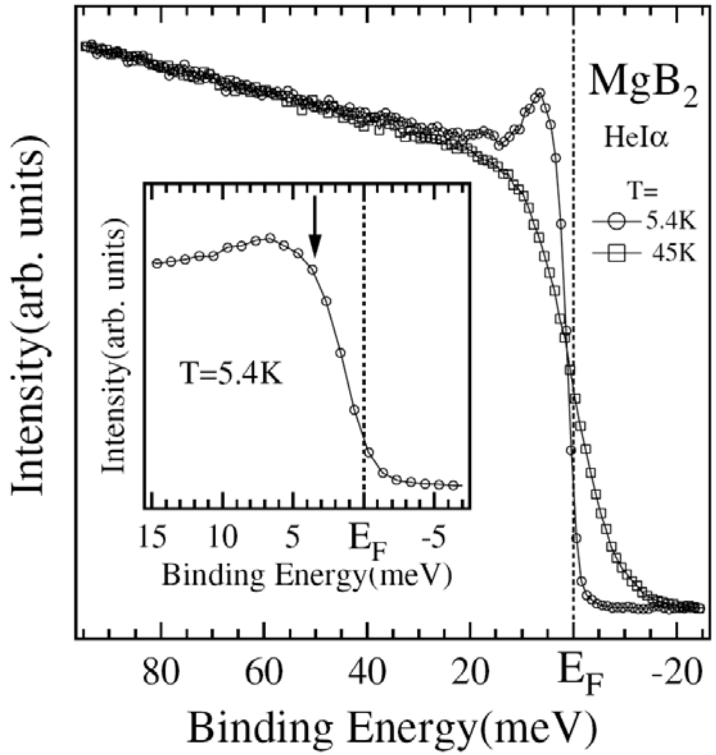


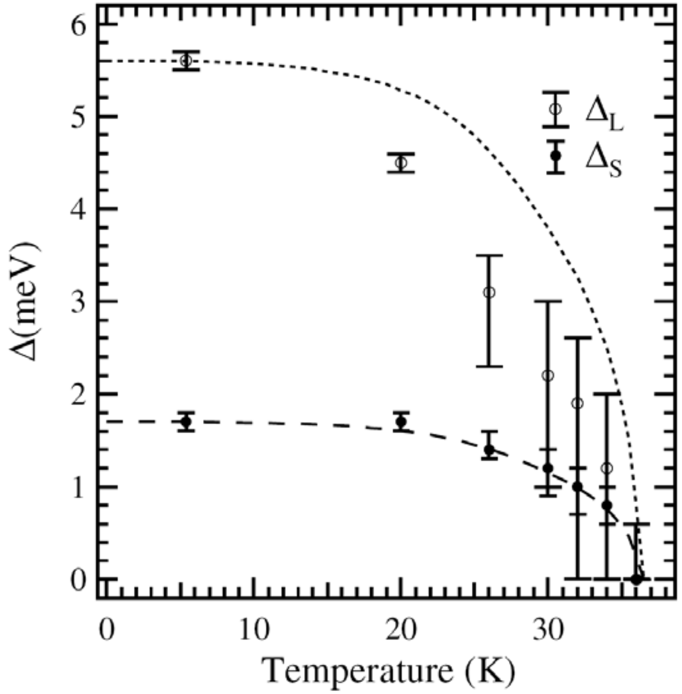
- TOF resolution limited by TDC: currently about 250 ps possible
- 2 eV kinetic energy = 8.4×10^5 m/s, drift tube of 0.5 m -> about 0.5 μs flight time
- TOF resolving power $\Delta t/t = \Delta v/v = 0.5\ \Delta E/E = 5 \times 10^{-4}$
- energy resolution TOF = $10^{-3} * E_{kin}$ = 2 meV
- spectral width of the exciting laser at photon energy of 8 eV: pulse duration 100 ps or 20 μeV (transform limit) - negligible

for PES with time-of-flight detection
see e.g. Karlsson et al., Rev. Sci. Instr. 67, 3610 (1996)

current state-of-the-art with conventional light source

- high-flux microwave-driven He discharge lamp
- hemispherical electrostatic analyzer
- exp. resolution 2-4 meV, sample temperature down to ~ 4K

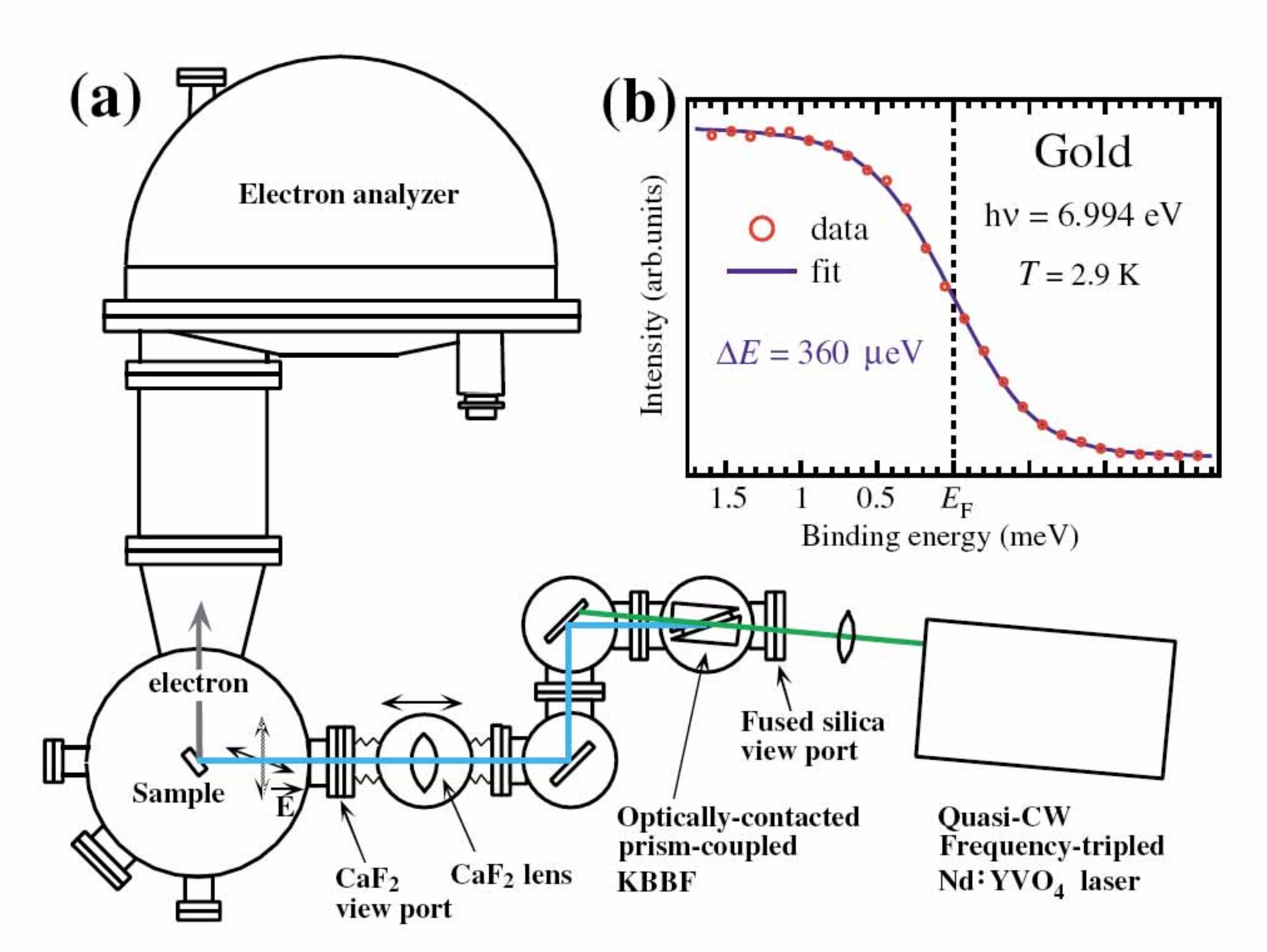




Tsuda et al., Phys. Rev. Lett. 87, 177006 (2001)
Physica B 312-313, 666 (2002)

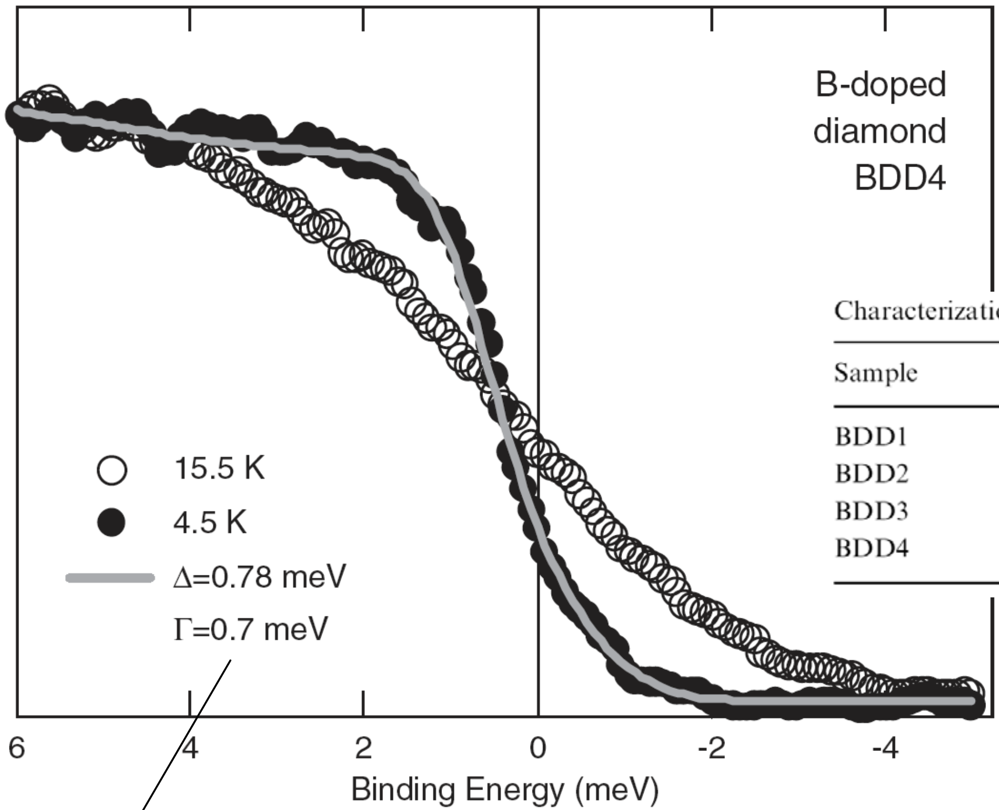
ultrahigh resolution with lasers

laser: 6.994 eV + Scienta R4000 spectrometer, ΔE = 360 μeV



Kiss et al., Phys. Rev. Lett. 94, 057001 (2005)

superconduction gap in boron-doped diamond



Characterization of the B-doped diamond samples

Sample	n_B (cm^{-3})	Electrical property	Synthesis
BDD1	3.5×10^{19}	Insulating	HTHP (single)
BDD2	1.75×10^{20}	Weakly insulating	CVD (poly)
BDD3	6.53×10^{21}	SC, $T_c = 5$ K	CVD (poly)
BDD4	8.37×10^{21}	SC, $T_c = 6.6$ K	CVD (single)

exp. energy resolution 700 μeV

Ishizaka et al., Sci. Techn. Adv. Mat. 7, S17 (2006)

new aspects of the interpretion at low photon energy

PRL 96, 017005 (2006) PHYSICAL REVIEW LETTERS week ending 13 JANUARY 2006

Laser Based Angle-Resolved Photoemission, the Sudden Approximation, and Quasiparticle-Like Spectral Peaks in $Bi_2Sr_2CaCu_2O_{8+\delta}$

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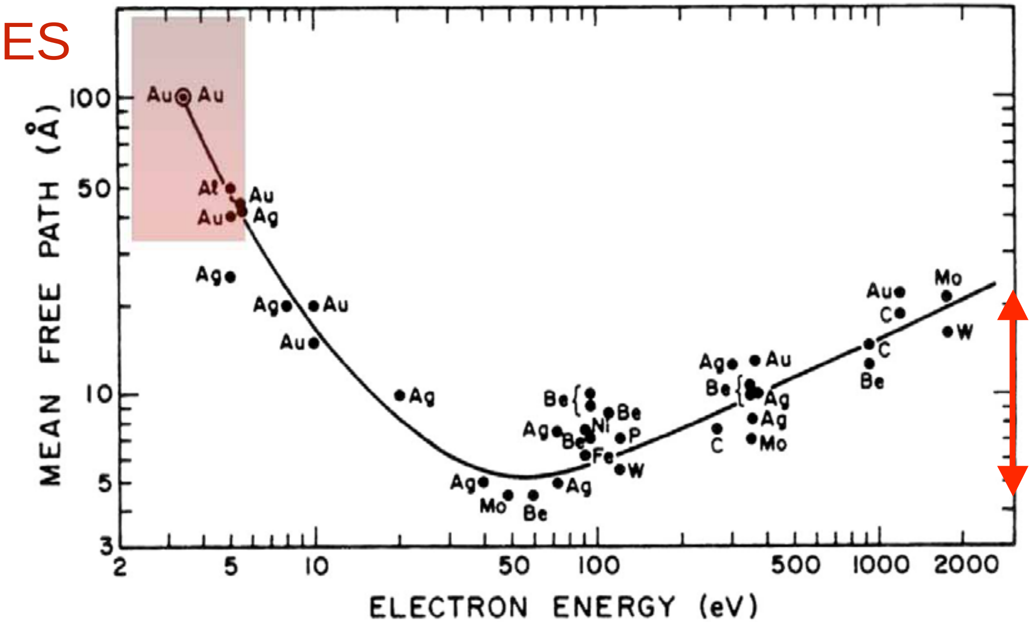
laser-PES

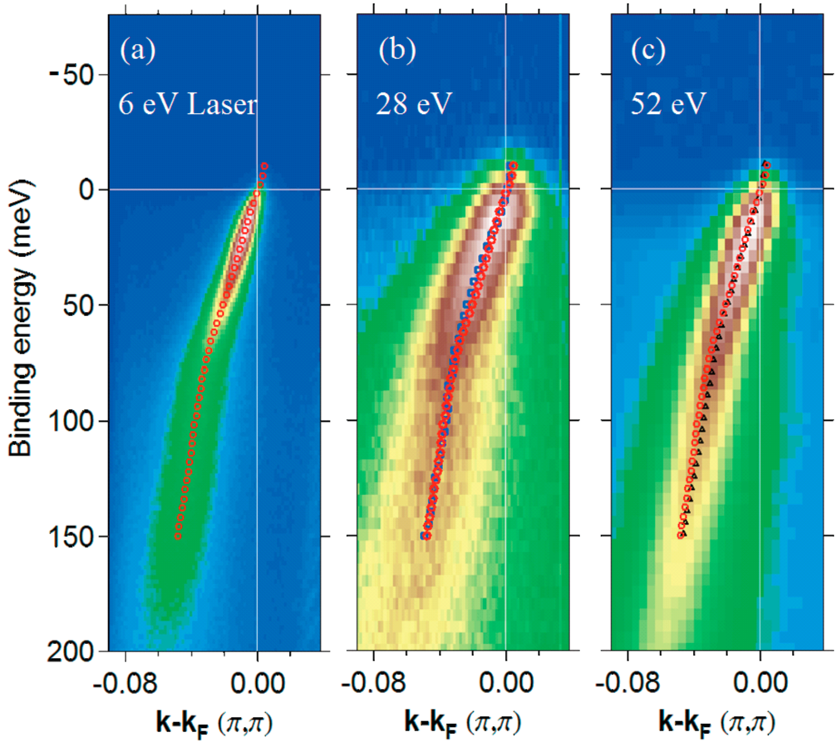


VUV-PES: escape depth: 4~20 Å

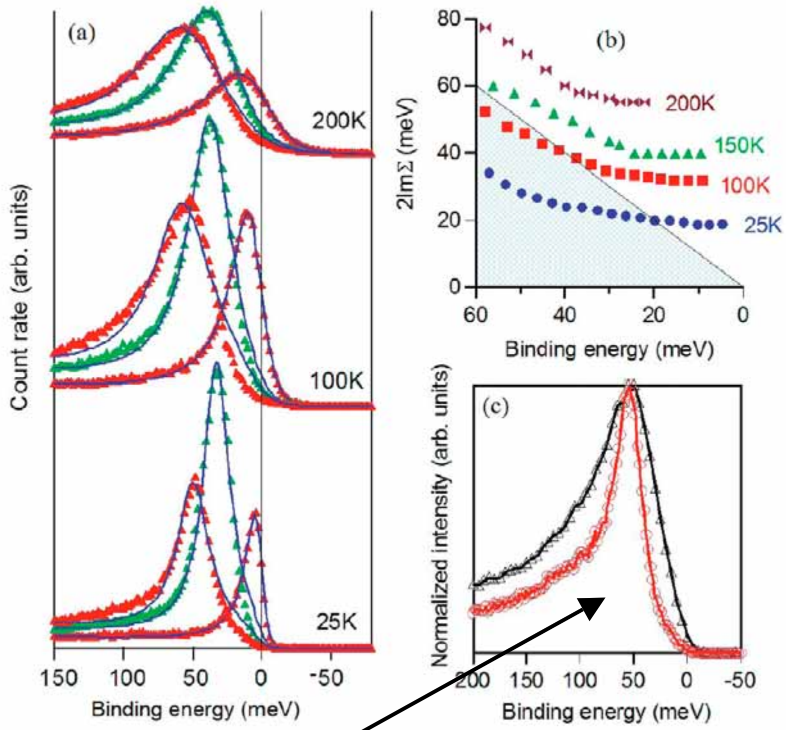
- bulk sensitive measurements at low kinetic energy
- problem: sudden approximation still valid?
- required for current interpretation of photoemission spectra

quasi-particle spectra at low energy

- ✓ pragmatic answer: sudden approximation apparently valid
- ✓ obervation of sharp quasi-particle peaks



dispersion cuts along nodal direction
at T=25 K



comparison laser/synchrotron (52 eV)

Koralek et al., Phys. Rev. Lett. 96, 017005 (2006)

take-home message

- **lasers had huge impact on photoelectron spectroscopy:**
  - temporal resolution (femto- and attoseconds)
  - study of matter far from thermodynamic equilibrium
  - ultrahigh energy resolution possible
  - “cheap” way of performing bulk-sensitive high-resolution measurements

- **new challenges:**
  - experiment: space-charge problems
  - higher photon energies for high-flux narrow-band sources
  - theory: validity of the sudden approximation
  - theory: inclusion of coherence effects (talk tomorrow)

- **dream:** combine femtosecond with spatial nanometer resolution:
  - … using photoemission microscope
    Chelaru et al., Phys. Rev. B 73, 115416 (2006)
  - … using laser and STM
    Takeuchi et al., Appl. Phys. Lett. 85, 3268 (2004)

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