Time-resolved photoelectron spectoscopy from *h*-BN/Ni(111)

Matthias Hengsberger

Physik-Institut der Universität Zürich

International Seminar on Strong Correlations and Angle-Resolved Photoemission Spectroscopy CORPES 07 - MPIPKS Dresden

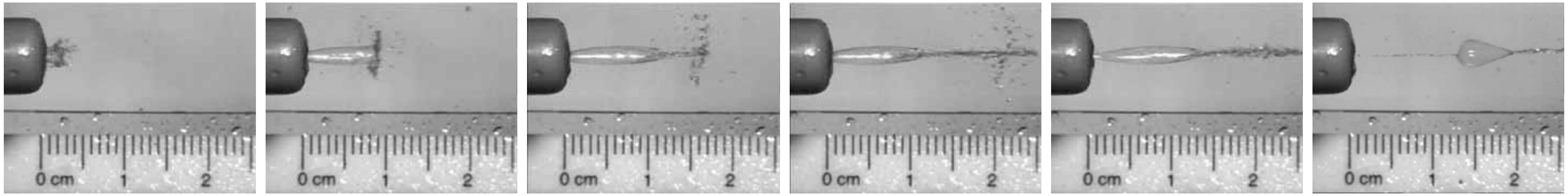
May 8, 2007

outline

- goal and approach of time-resolved experiments
- time-resolved two-photon photoelectron spectroscopy
- population decay and dephasing times
- our system: *h*-BN/Ni(111)
- observation and modeling of resonance and coherence effects
- probe for magnetic order
- conclusion

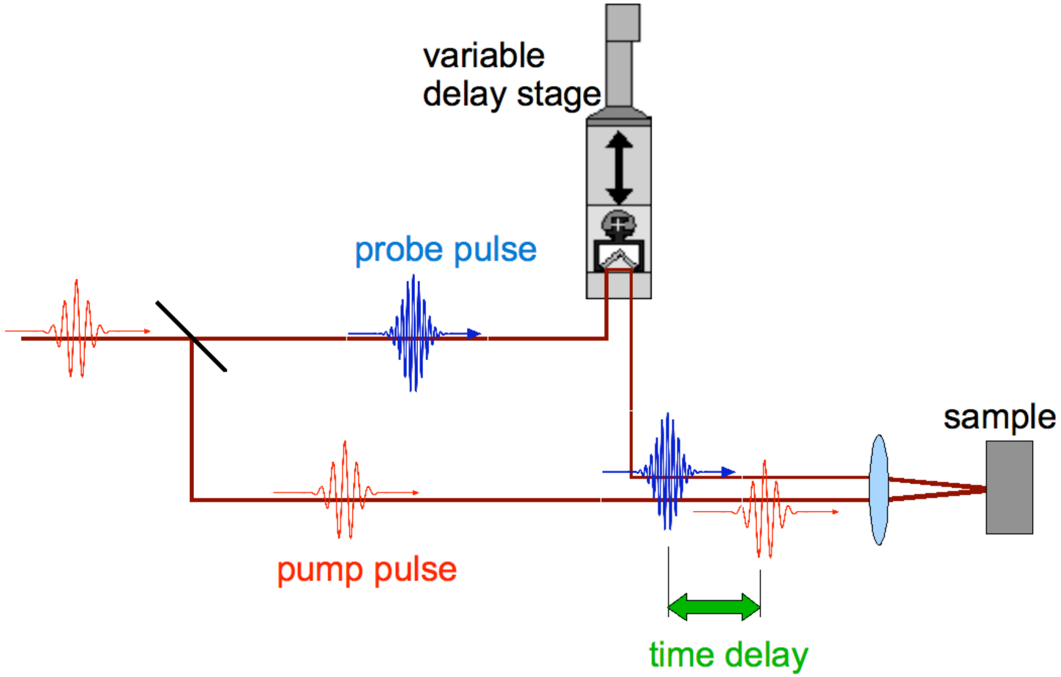
motivation for real-time measurements

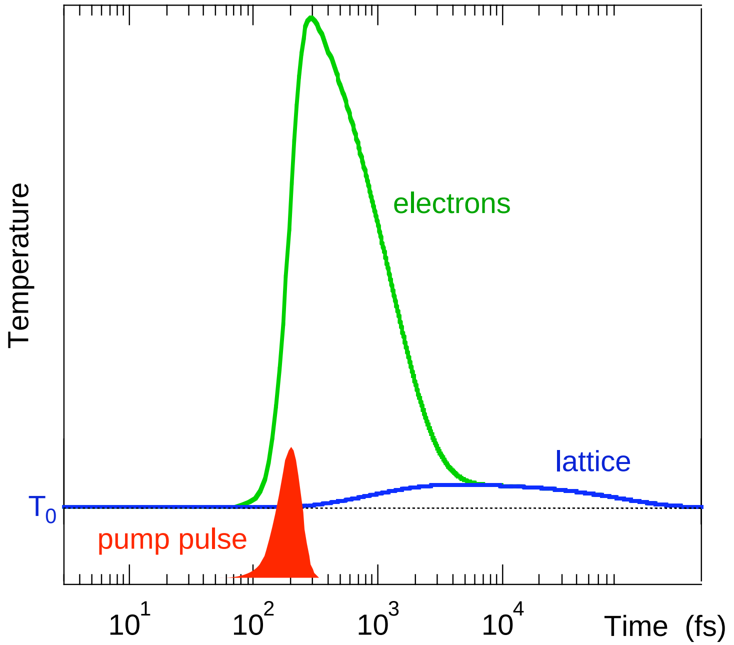
- measure physical observables in real time
- idea: direct measurement of relevant time scales, e.g. in relaxation processes
- such measurements are complementary to spectroscopy, where time scales are *indirectly* deduced
- requirement: temporal resolution in the order of the relevant timescale… “an ultrafast camera”



pulsed water jet - high speed movie
total time about 0.5 ms
source: http://www.iwf.de/Navigation/Projekte/LNW/Stroboskop/index.jsp

pump-probe scheme



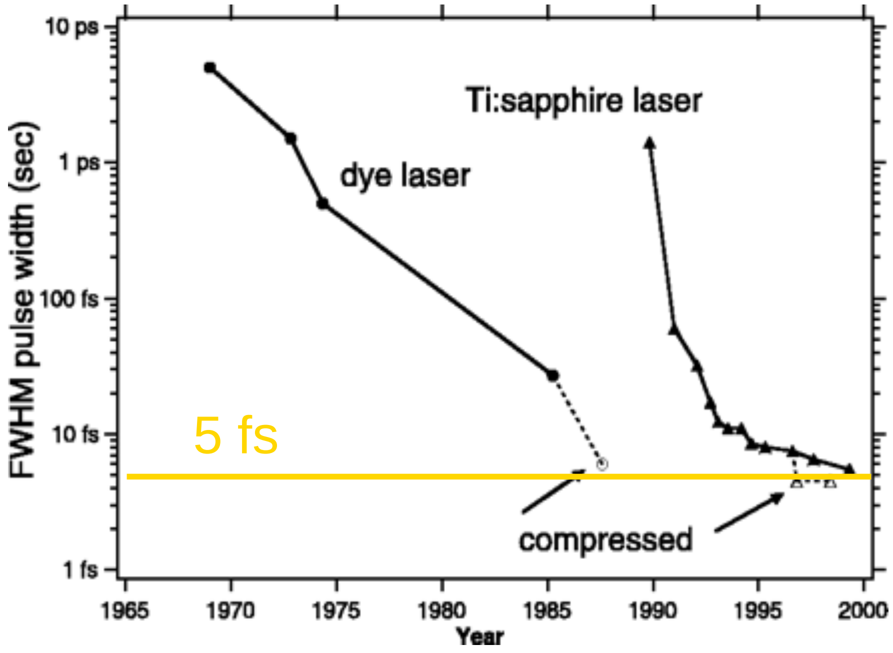


observable: f. ex. photoelectrons generated by probe pulse
time resolution: cross-correlation of pump and probe pulses
temporal jitter: none here

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

generation of light pulses: state-of-the-art

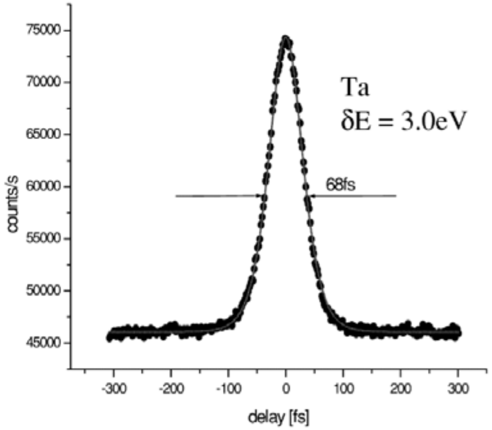
approaching the physical limit for near-IR radiation from a laser:



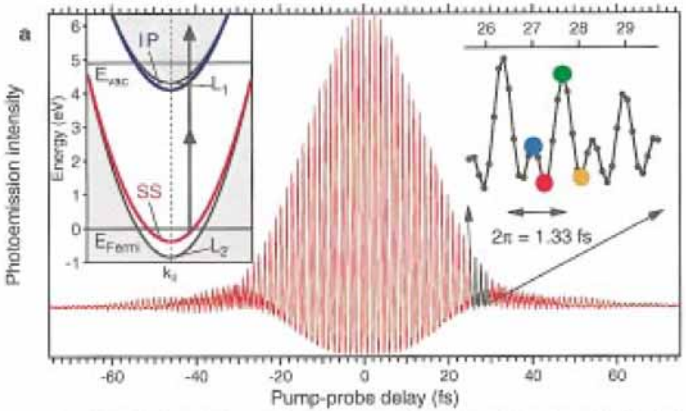
at 800 nm: 1 cycle = 2.7 fs!

Steinmeyer et al., Science 286, 1507 (1999)
Corkum, Nature 403, 845 (2000)

typ. resolution in photoemission experiments nowadays: 10-150 fs



Bauer and Aeschlimann, J. El. Spec. 2002



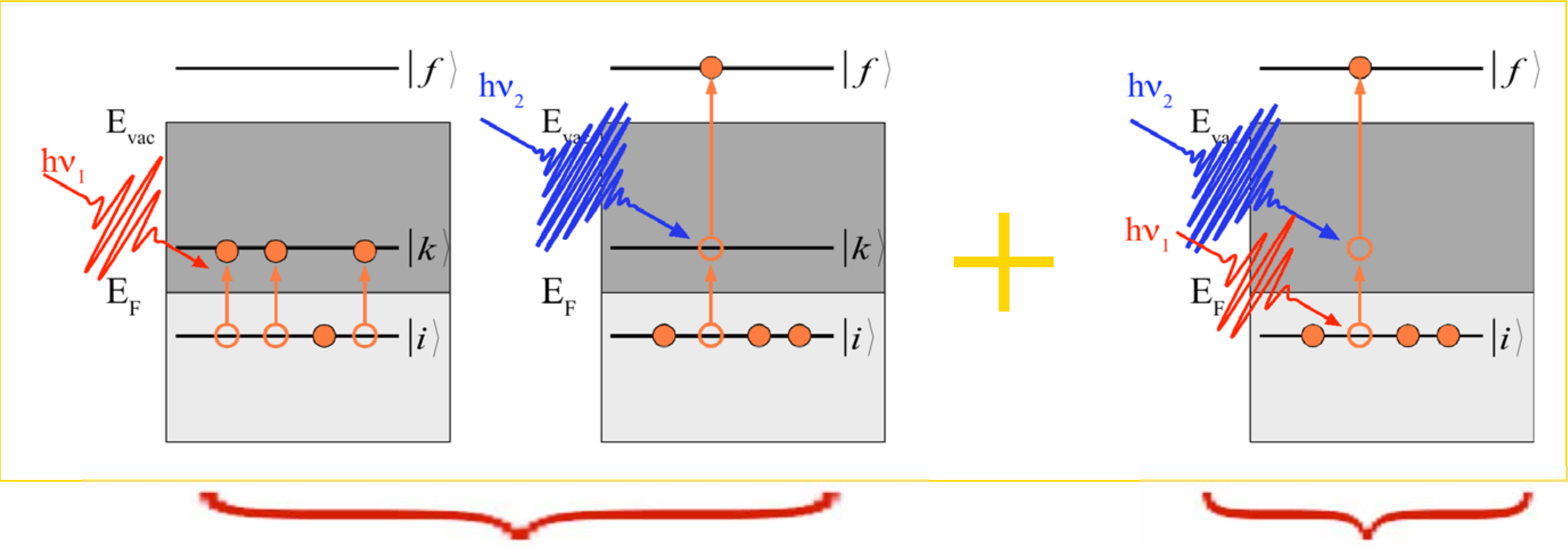
Petek et al., Phys. Rev. Lett. 79, 4649 (1997)
Hattori et al., Jpn. J. Appl. Phys. 39, 4793 (2000)

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

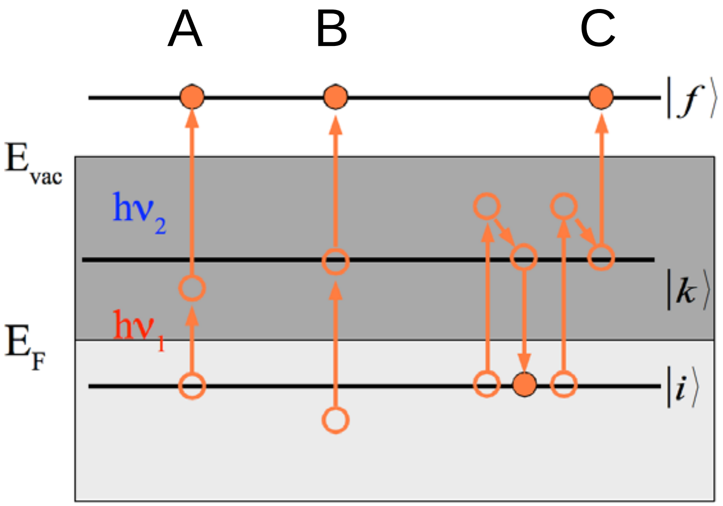


transitions ***i→k→f***:
probe unoccupied intermediate states
$E_F < E_{\boldsymbol{k}} < E_{vac}$
$h\upsilon_1, h\upsilon_2 < \phi < h\upsilon_1 + h\upsilon_2$

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

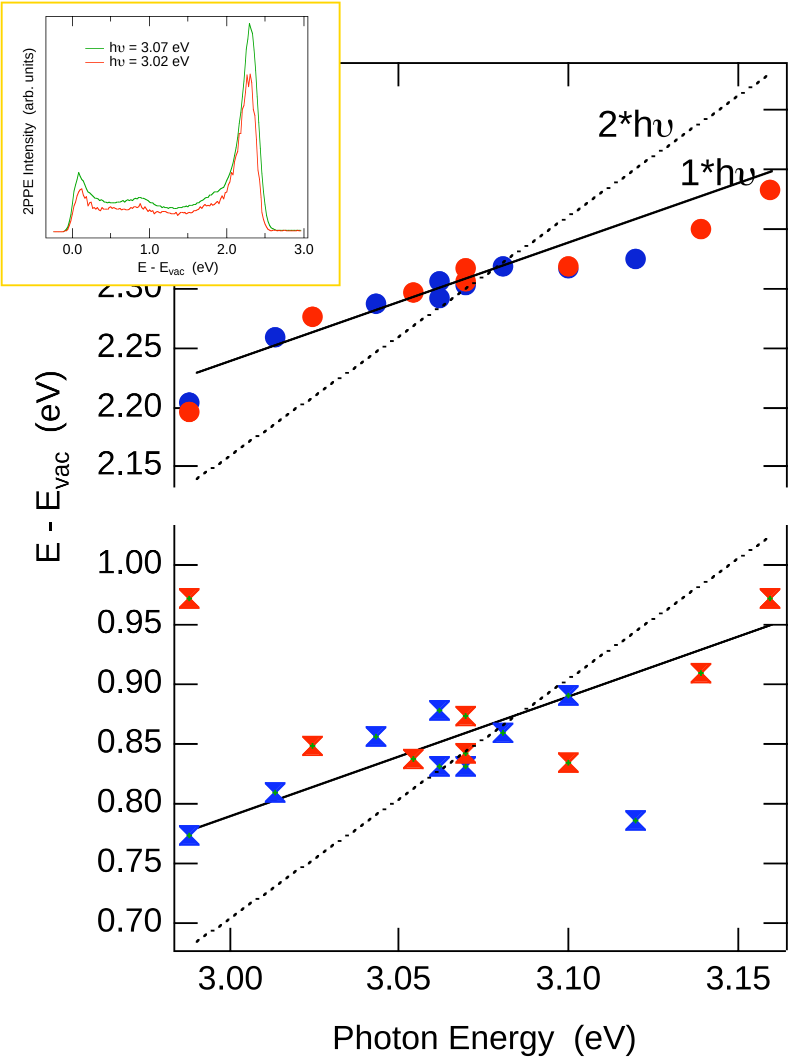
spectra for different photon energies:



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)

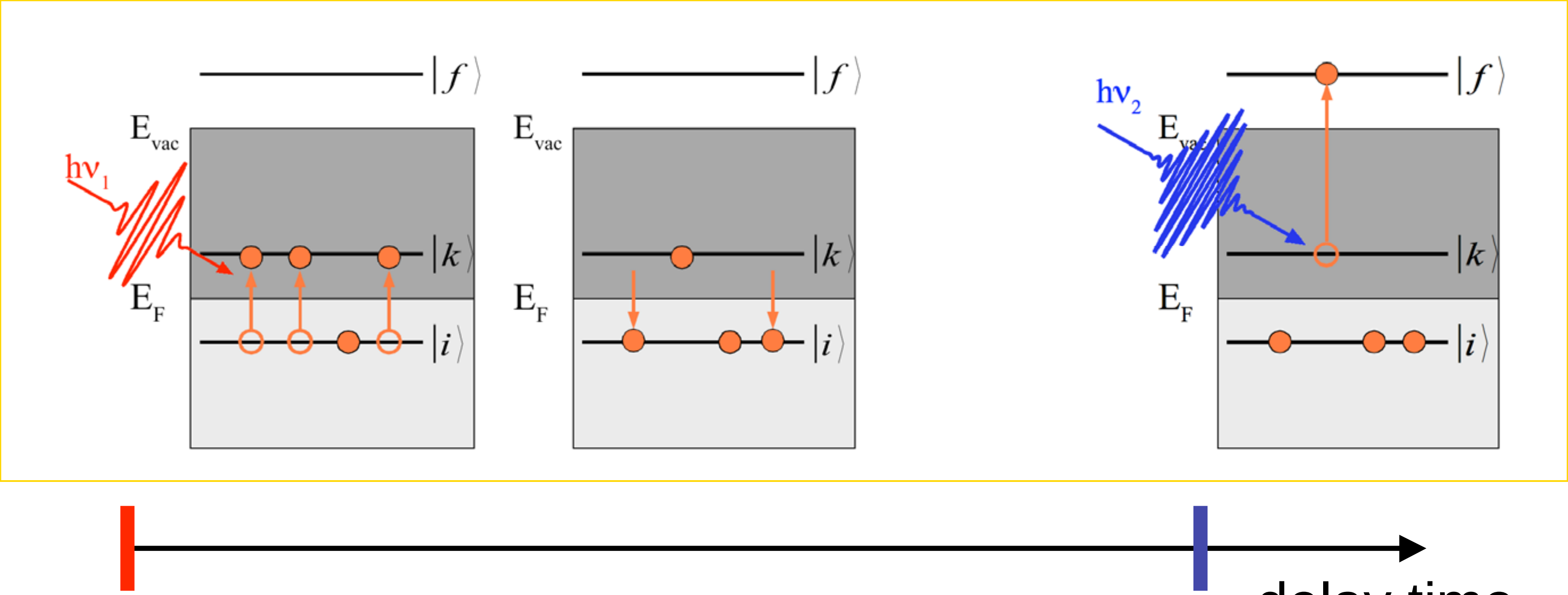


see e.g. Giessen et al., PRL 55, 300 (1985)
W. Steinmann, Appl. Phys. A 49, 365 (1989)

time-resolved 2PPE

- introduce variable time delay between first and second pulse

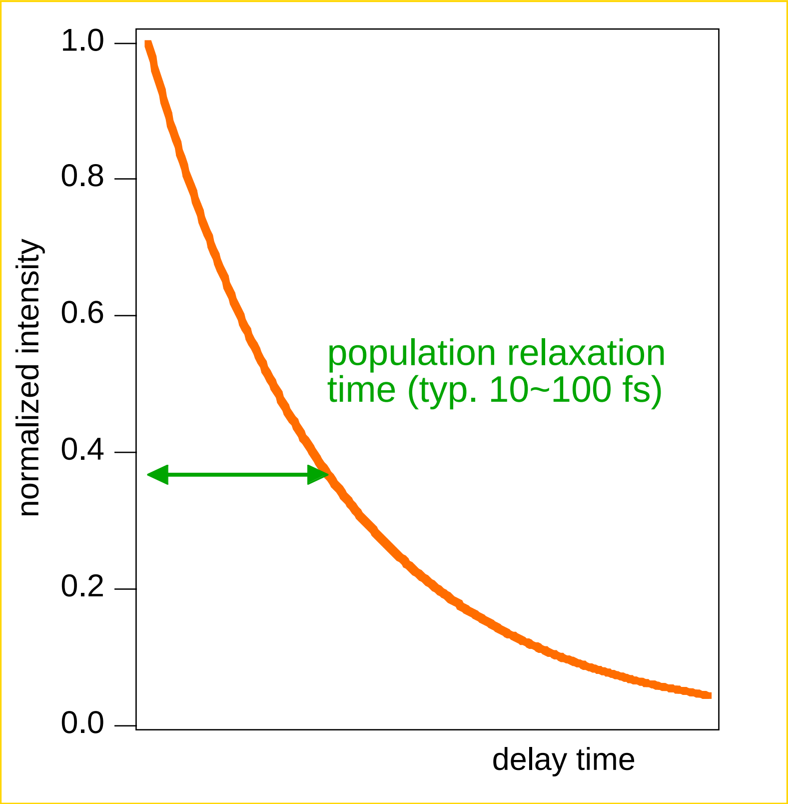
- in case of intermediate state, the excited population decays exponentially with a typical time constant τ after the first pulse

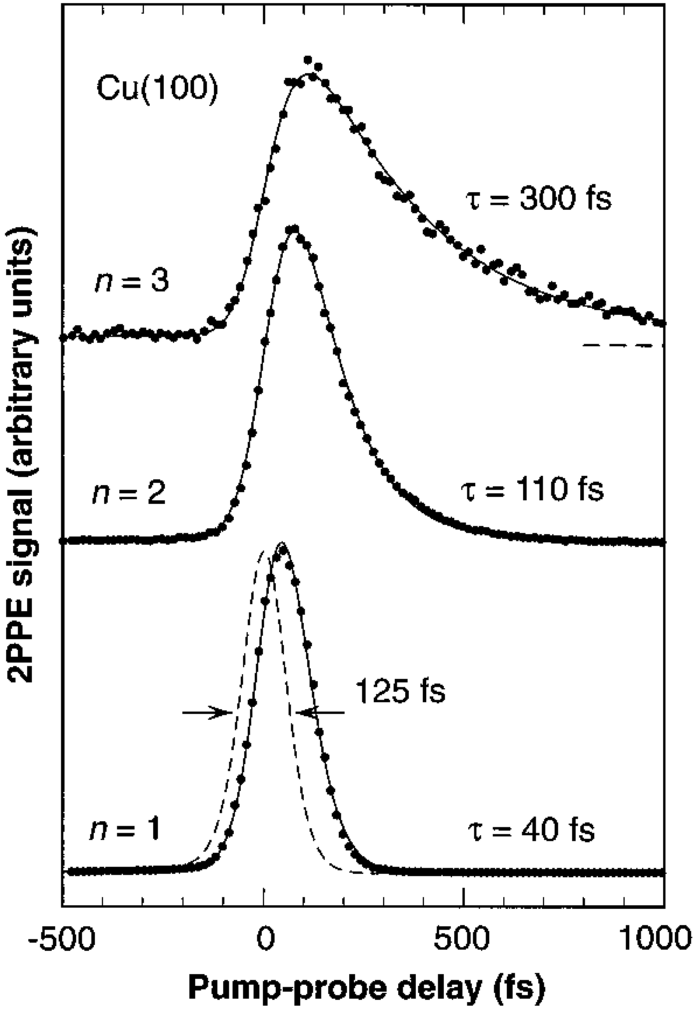


delay time

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





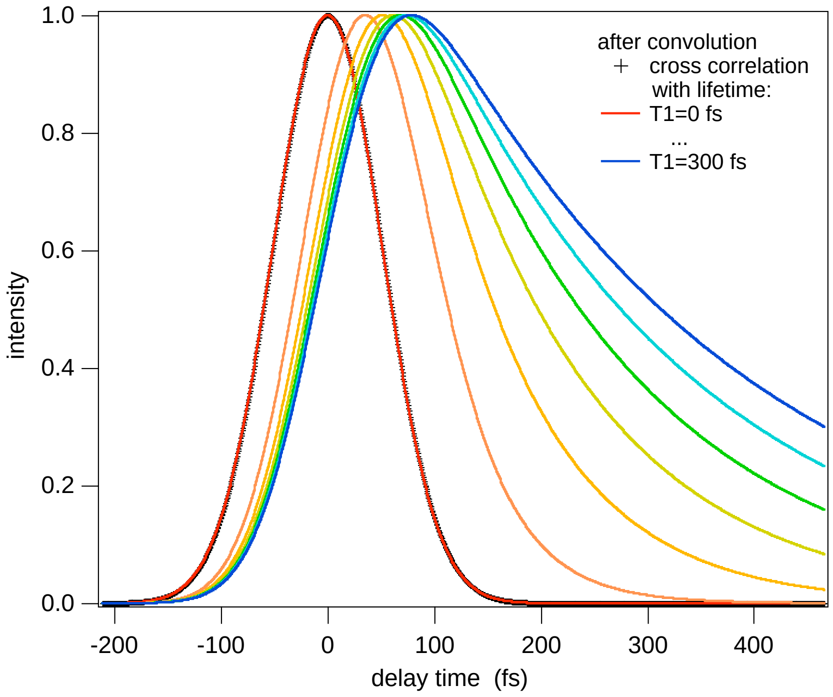
Höfer et al., Science 277, 1480 (1997)

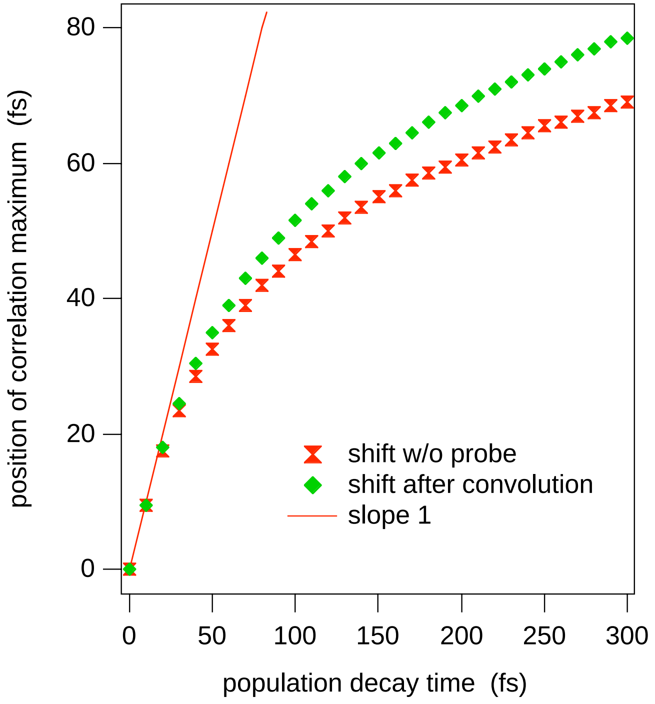
shift of cross-correlation maximum

solution of the differential eqn. for excited state population:

$$\frac{dN_2}{dt}(t) = RI_{\mathrm{pump}}(t) - \frac{N_2(t)}{\tau}$$

and convolution with probe pulse yields a transient with shifted maximum.



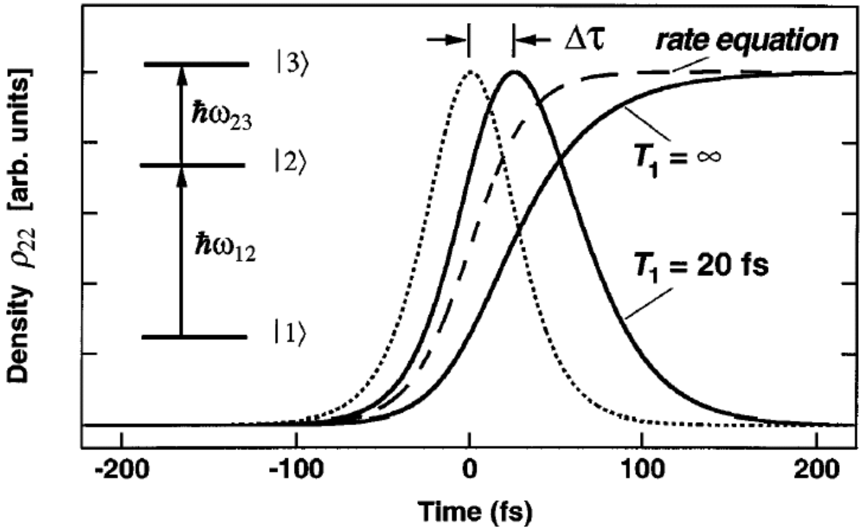


→ measurement of the population decay time of the intermediate state

e.g. Velic et al., J. Chem. Phys. 109, 9155 (1998)

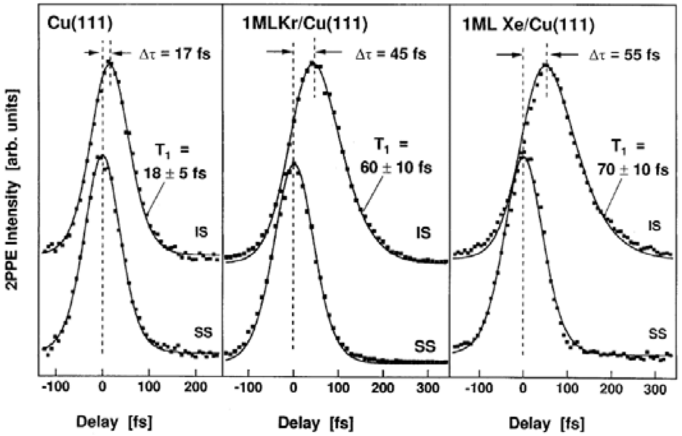
lifetimes show up as shifts of the correlation maxima

in case of a real intermediate state:
population decay time ("lifetime")
causes exponential tail
and
shift of maximum of transient

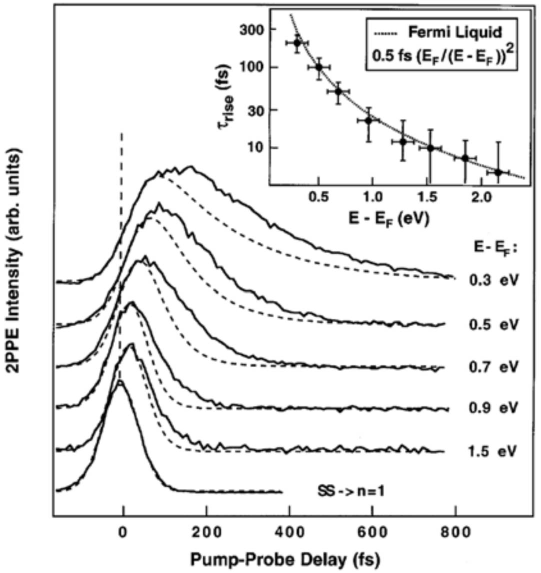


Hertel et al., Phys. Rev. Lett. 76, 535 (1996)
J. Vac. Sci. Techn. A15, 1503 (1997)

- image states on noble gas layers



- lifetime as function of energy



comparing spectral linewidth and lifetime

peak width in spectra typically several 100 meV = "lifetime" of 5 fs
observed lifetimes often 10…300 fs…?

additional decay term, observable only in phase-senstive experiments:
phase decay or *dephasing* (decay of optical coherence), caused by
- finite lifetime of photohole
- quasi-elastic scattering in the intermediate state

mathematical model: density-matrix formalism (optical Bloch equations)

$$\frac{d\rho_{22}}{dt} = \frac{\mu_{12}\varepsilon(t)}{2i\hbar}(\tilde{\rho}_{12} - \tilde{\rho}_{21}) - \frac{\rho_{22}}{T_1}$$

$$\frac{d\tilde{\rho}_{12}}{dt} = \frac{\mu_{12}\varepsilon(t)}{2i\hbar}(\rho_{22} - \rho_{11}) + \left(i(\omega_{12} - \omega) - \frac{1}{T_2}\right)\tilde{\rho}_{12}$$

$$\tilde{\rho}_{12} = \rho_{12}\exp[-i(\omega_{12} - \omega)t]$$

population decay
("energy relaxation")
"pure" dephasing

$$T_2 = (1/2T_1 + 1/T_2^*)^{-1}$$

T_2 related to linewidth in spectra

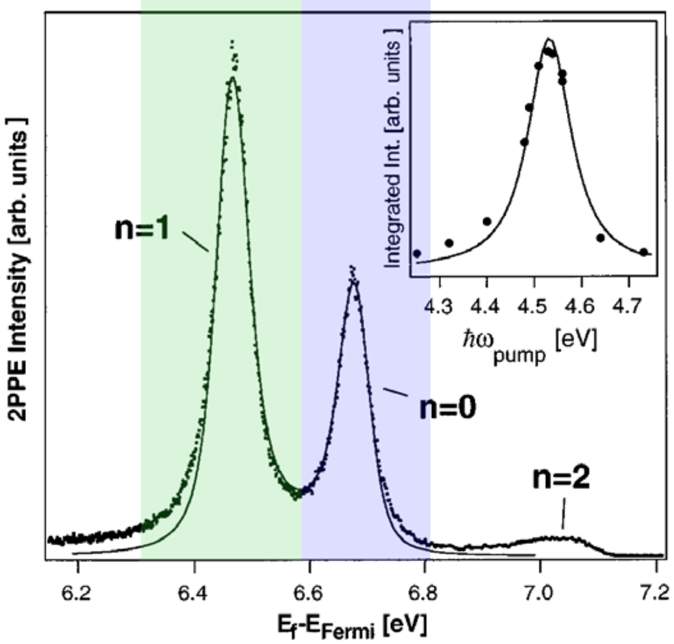
Hertel et al., Phys. Rev. Lett. 76, 535 (1996)
Boger et al., Phys. Rev. B 65, 075104 (2002)

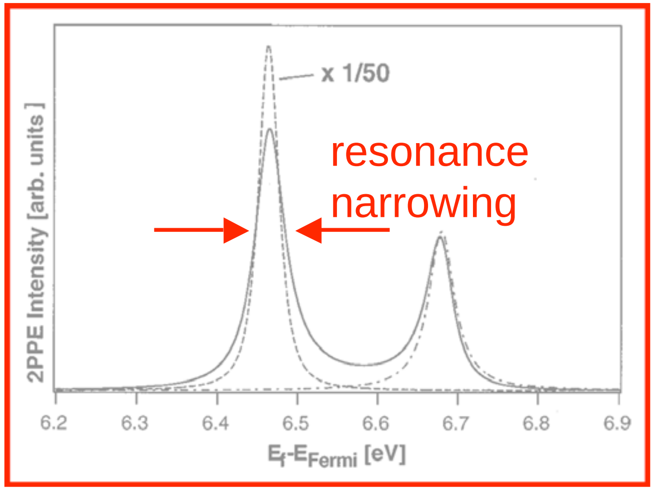
description of the 2PPE spectrum

assumptions: density matrix formalism
("optical Bloch equations" or "Liouville-von Neumann formalism")
analytic solution of **cw** case for 3-level system, i.e. *no time dependence*

$$I_{2\mathrm{PPE}}(\hbar\omega_f) \propto T(\hbar\omega_f)\cdot W_{if}(\hbar\omega_f) = T(\hbar\omega_f)\cdot\frac{|(\boldsymbol{\mu}_{ik}\cdot\mathbf{e}_{\mathrm{pump}})(\boldsymbol{\mu}_{kf}\cdot\mathbf{e}_{\mathrm{probe}})|^2}{8\cdot\hbar^4}\cdot\left[\boxed{\frac{2\Gamma^*_{ik}\Gamma^*_{kf}/\Gamma_k+\Gamma^*_k}{(G_{ik}{}^2+\Omega_{ik}{}^2)(G_{kf}{}^2+\Omega_{kf}{}^2)}}+\boxed{\frac{\Gamma^*_f}{(G_{ik}{}^2+\Omega_{ik}{}^2)(\Gamma^{*2}_{if}+\Omega_{if}{}^2)}}+\boxed{\frac{\Gamma^*_i+4\Gamma^*_i\Gamma^*_f(\Gamma^*_i+\Gamma^*_k+\Gamma^*_f+\Gamma_k/2)/(G_{ik}{}^2+\Omega_{ik}{}^2)}{(\Gamma^{*2}_{if}+\Omega_{if}{}^2)(G_{kf}{}^2+\Omega_{kf}{}^2)}}\right]$$

G_{ij}, $\Gamma_{ij}{}^*$ dephasing
Ω detuning

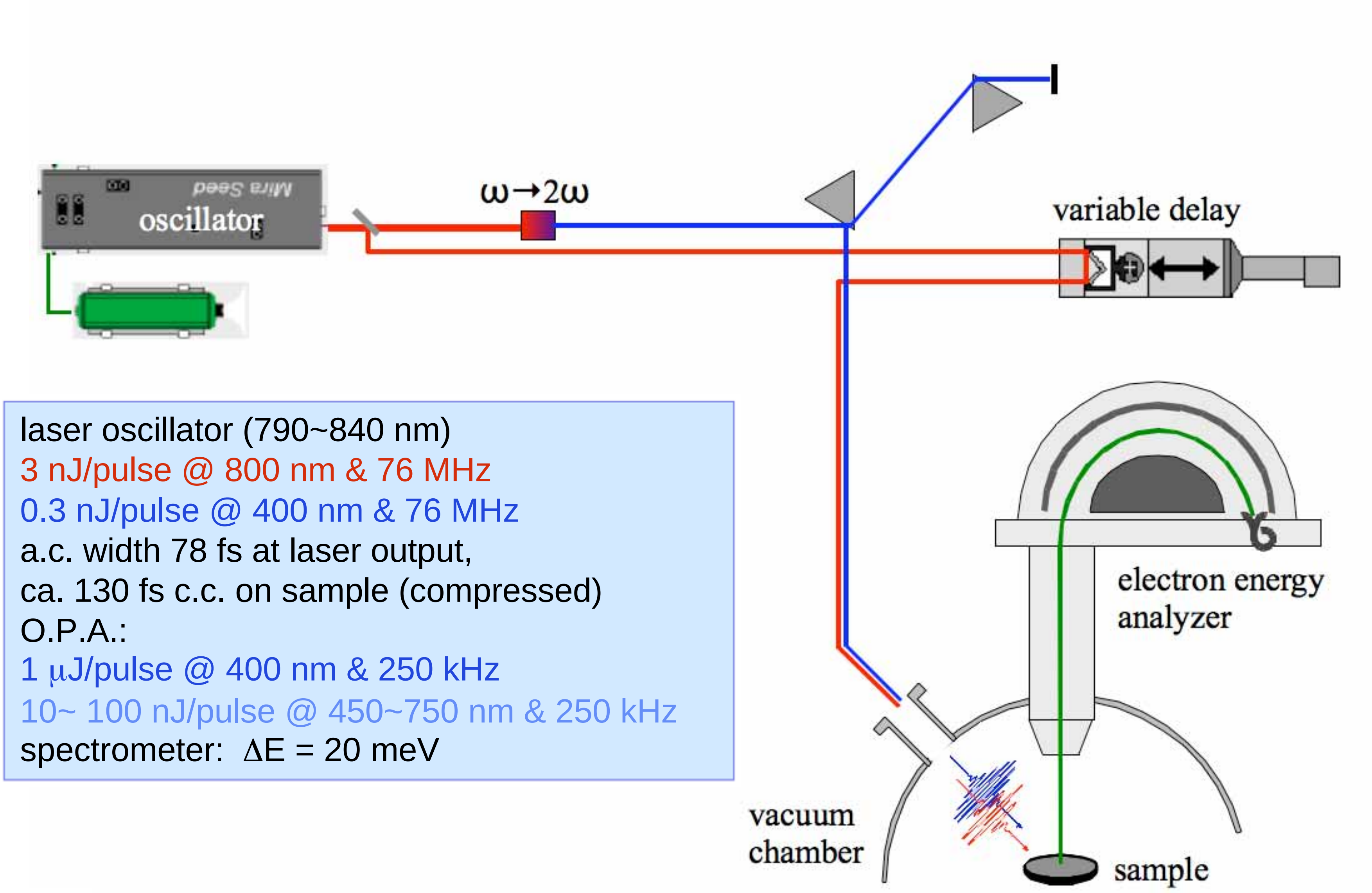




intermediate state peak k
initial state peak i
resonance peak $i \rightarrow k$

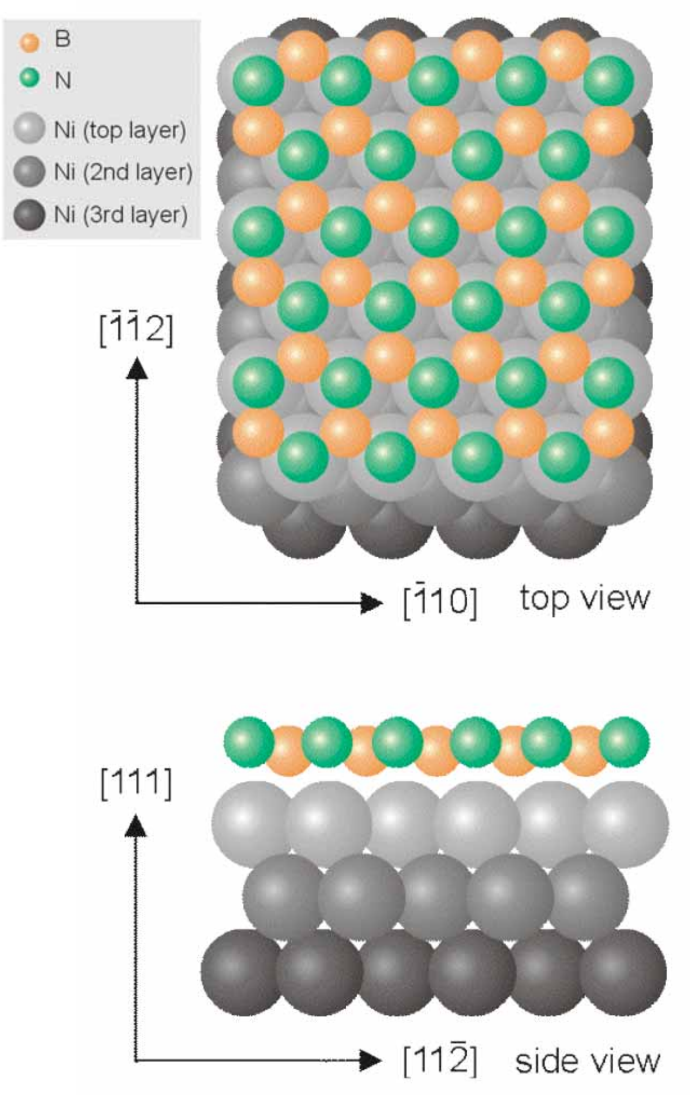
Wolf et al., Phys.Rev.B 59, 5926 (1999)

typical setup: our laboratory



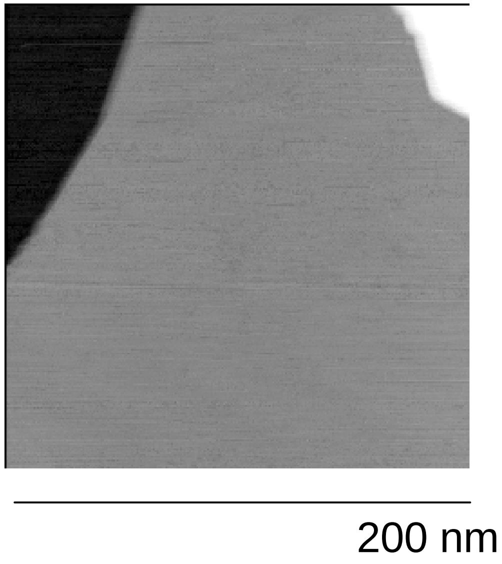
laser oscillator (790~840 nm)
3 nJ/pulse @ 800 nm & 76 MHz
0.3 nJ/pulse @ 400 nm & 76 MHz
a.c. width 78 fs at laser output,
ca. 130 fs c.c. on sample (compressed)
O.P.A.:
1 μJ/pulse @ 400 nm & 250 kHz
10~ 100 nJ/pulse @ 450~750 nm & 250 kHz
spectrometer: ΔE = 20 meV

h-BN on Ni(111)

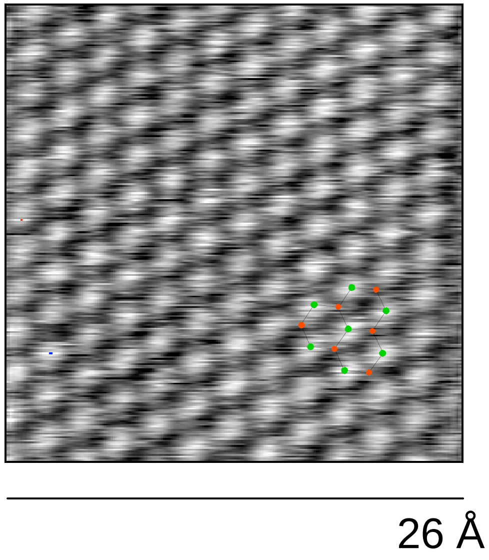


- perfect monolayer growth on Ni(111)
- upon exposure to ~100 L of borazine
- good match of lattice constant
- atomic and electronic structure well known

recipe by Nagashima et al., PRB 51, 4606 (1995)



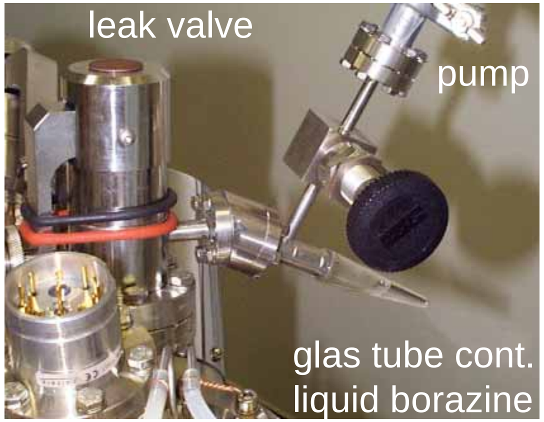
I=1nA, V=0.1V



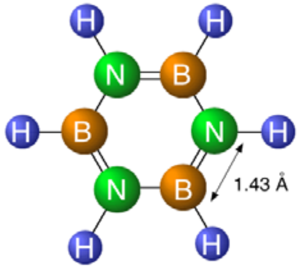
I=9nA, V=-23mV

Auwärter et al., Surf. Sci. 429, 229 (1999)

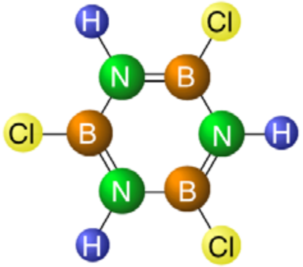
film preparation



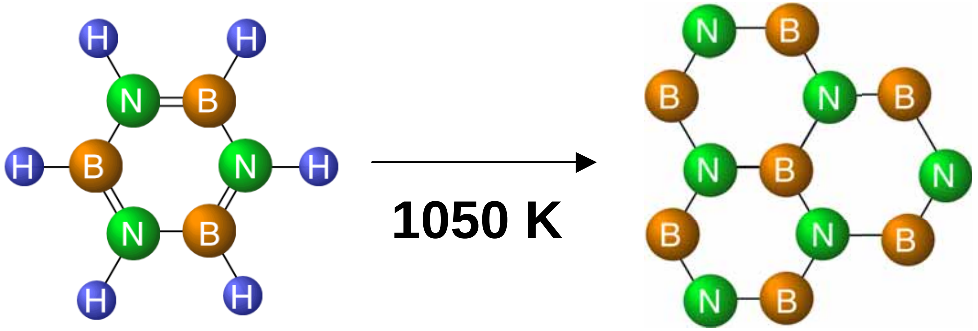
glas tube cont. liquid borazine



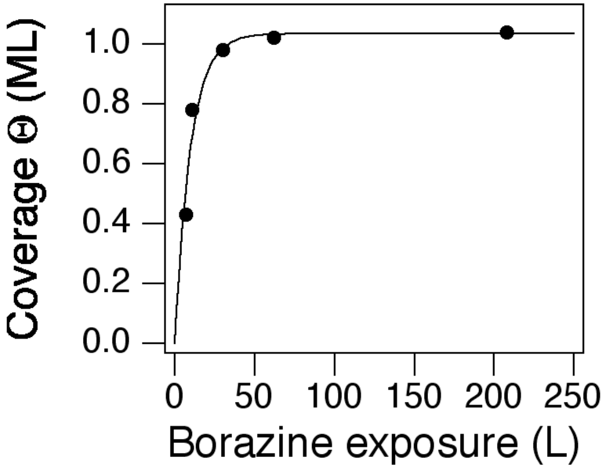
borazine
$(BN)_3H_6$



trichloroborazine
$(BCl)_3(NH)_3$



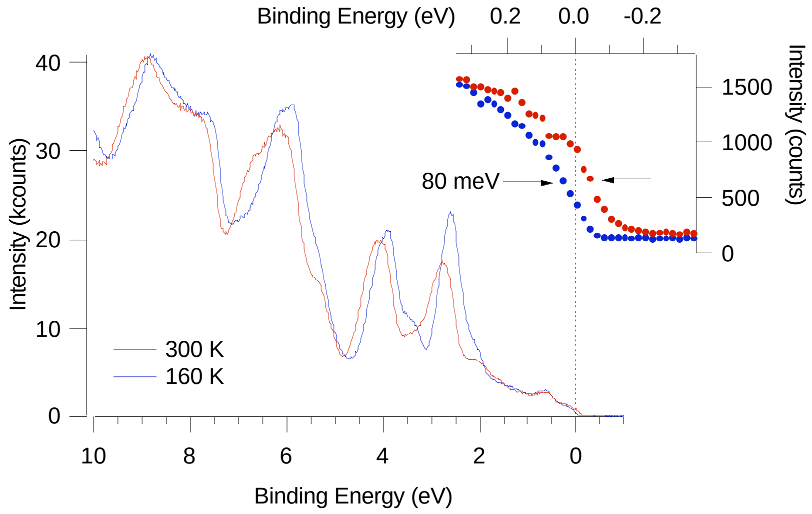
Borazine+Ni(111) **_h_-BN on Ni(111)+3H_2**

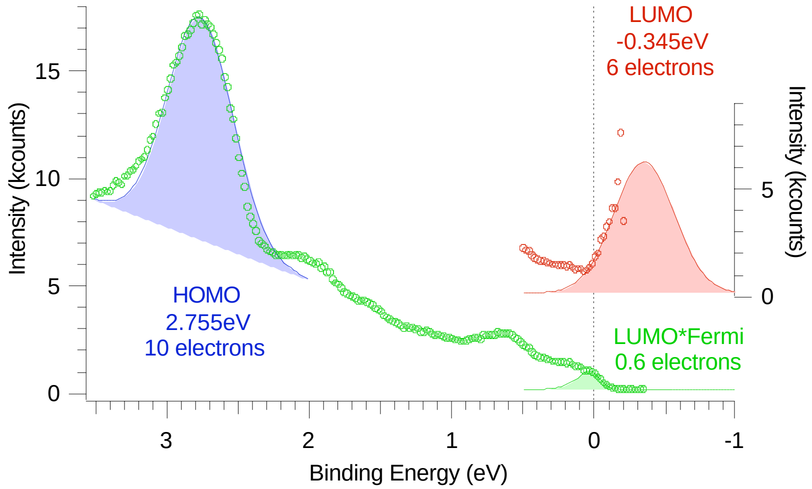


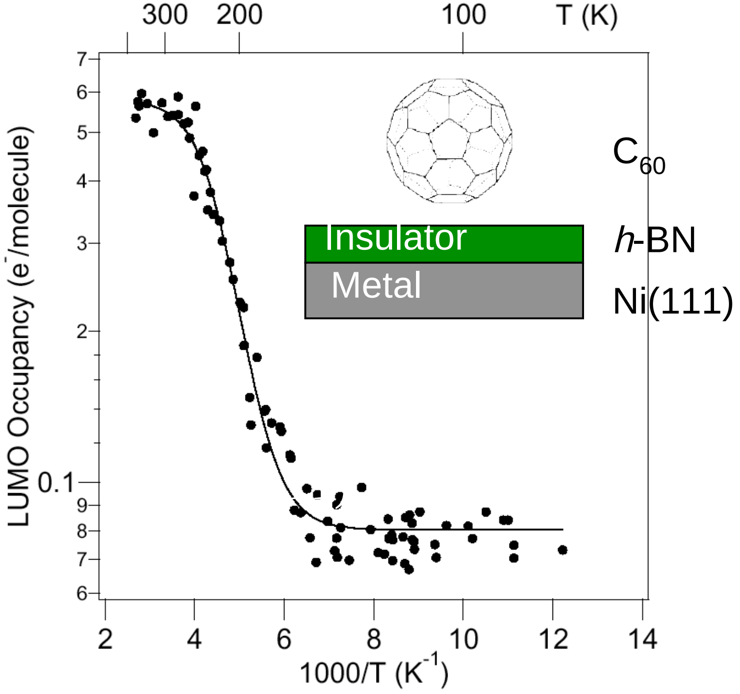
recipe: Nagashima et al., PRB 51, 4606 (1995)
W. Auwärter, PhD thesis U Zurich (2003)

motivation: charge transfer across the monolayer

C_{60}/*h*-BN/Ni: temperature dependence of LUMO occupation





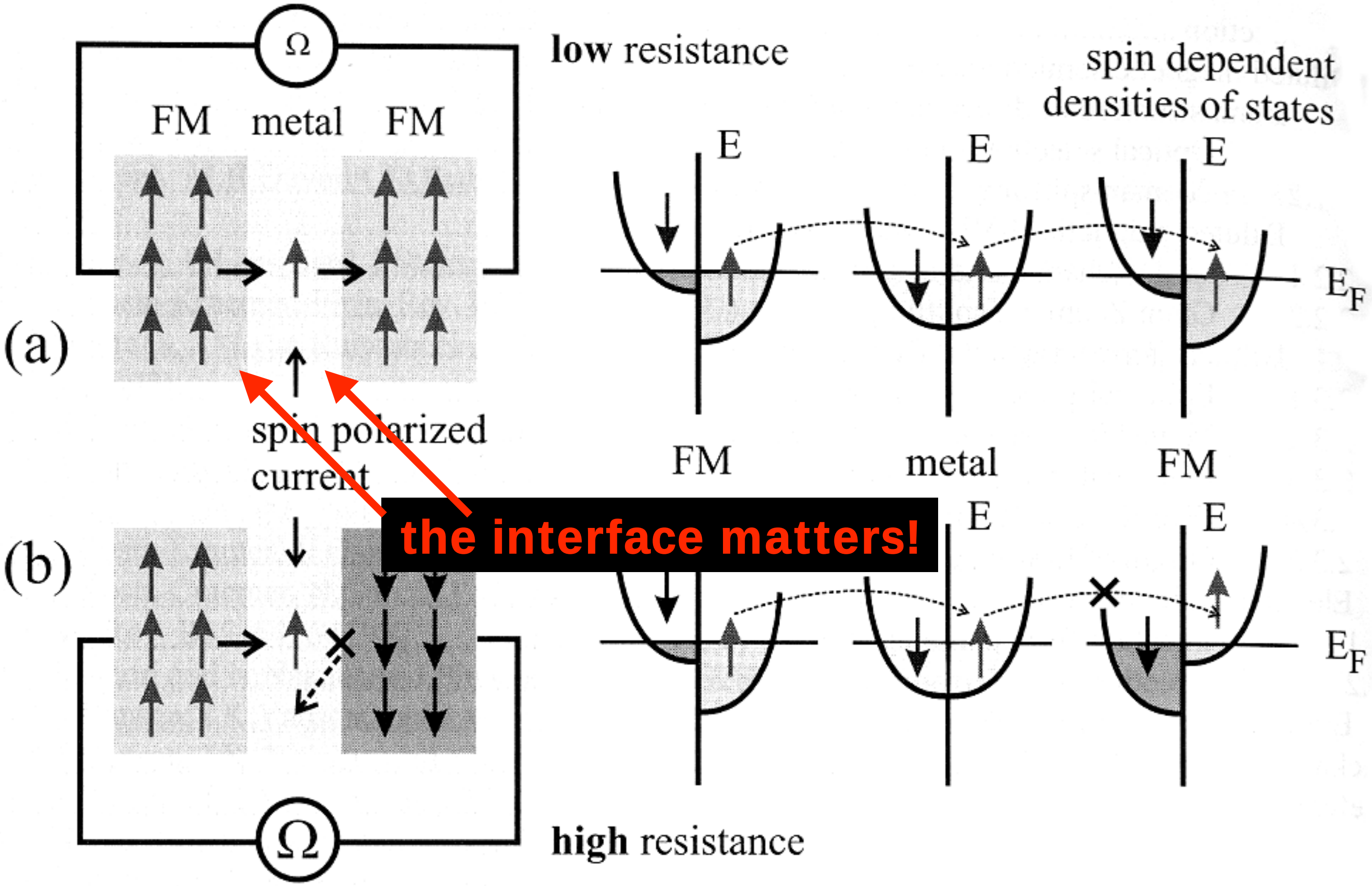


UPS, *h*ν = 21.22 eV, normal emission

Muntwiler et al. Phys. Rev. B 71, 241401 (2005)

long-term motivation: spin-injection

resistance varies as function of ferromagnetic alignement

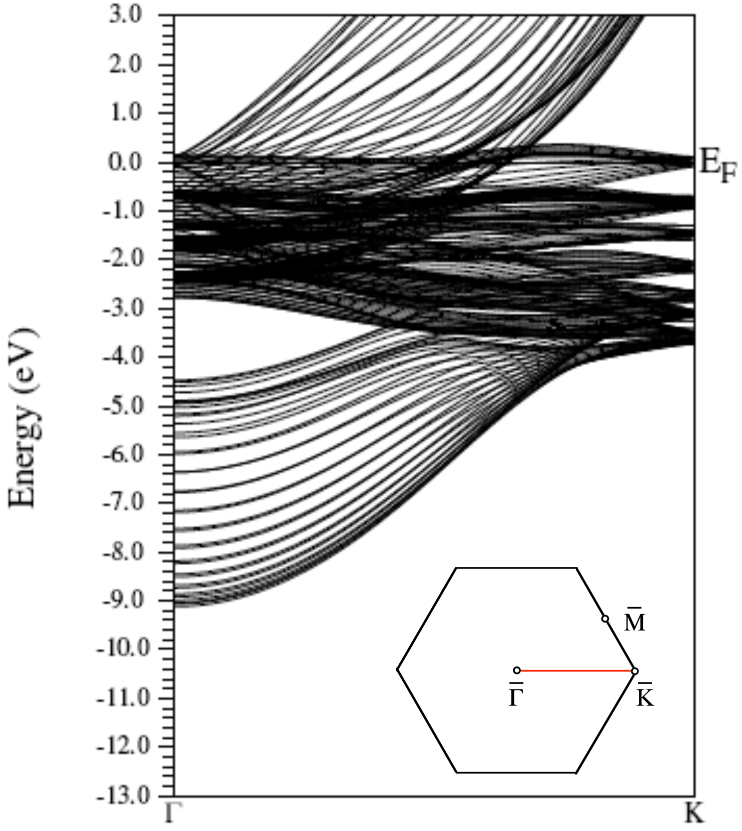


the interface matters!

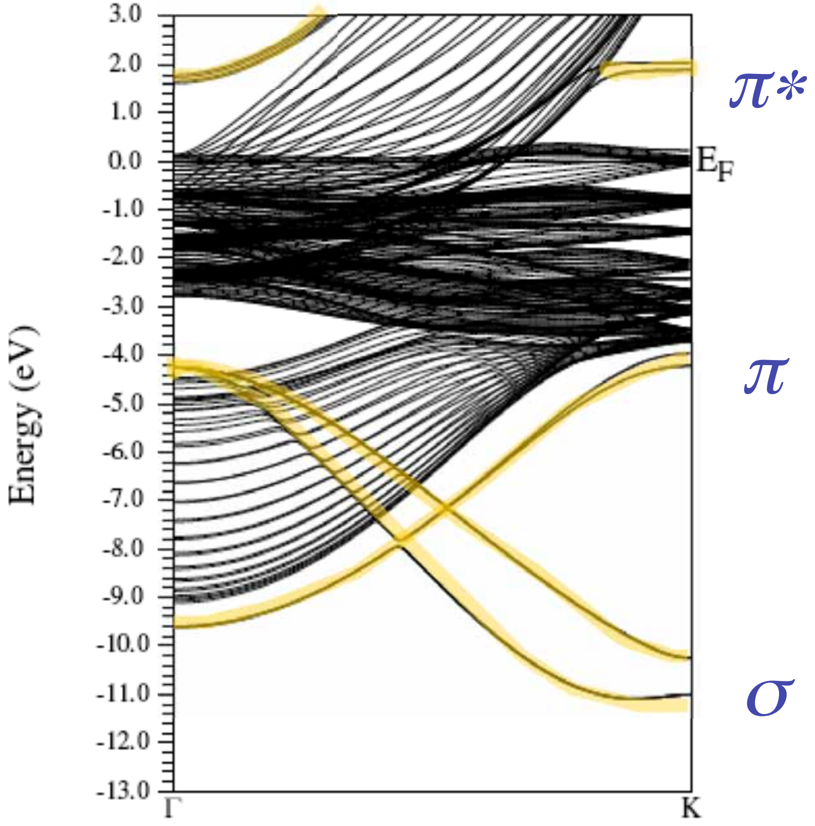
Illustration by B. Beschoten

the band structure of *h*-BN/Ni(111)

Ni (111)



h-BN/Ni (111)

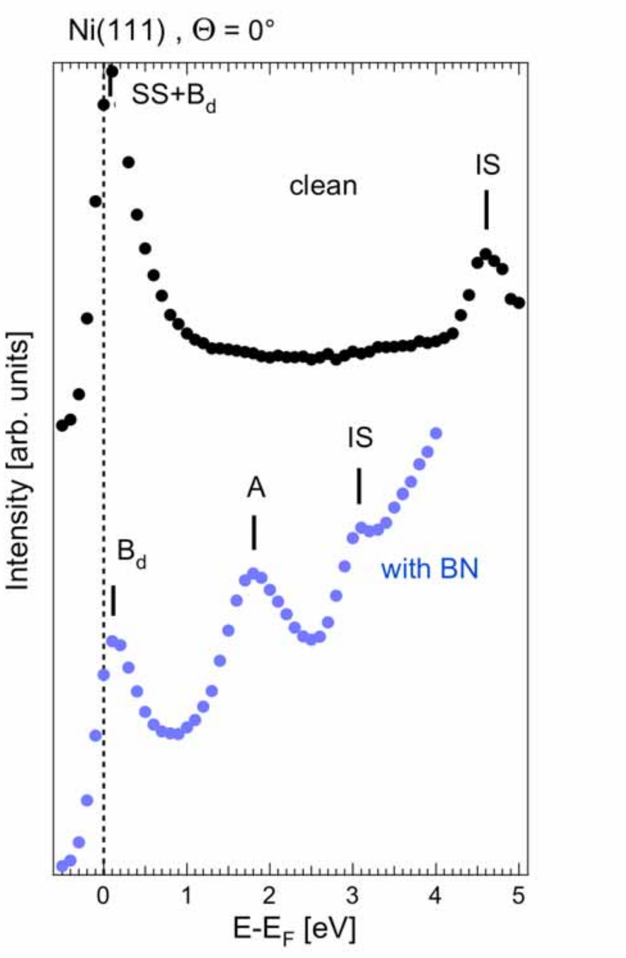


occupied band structure understood - what about conduction bands ?

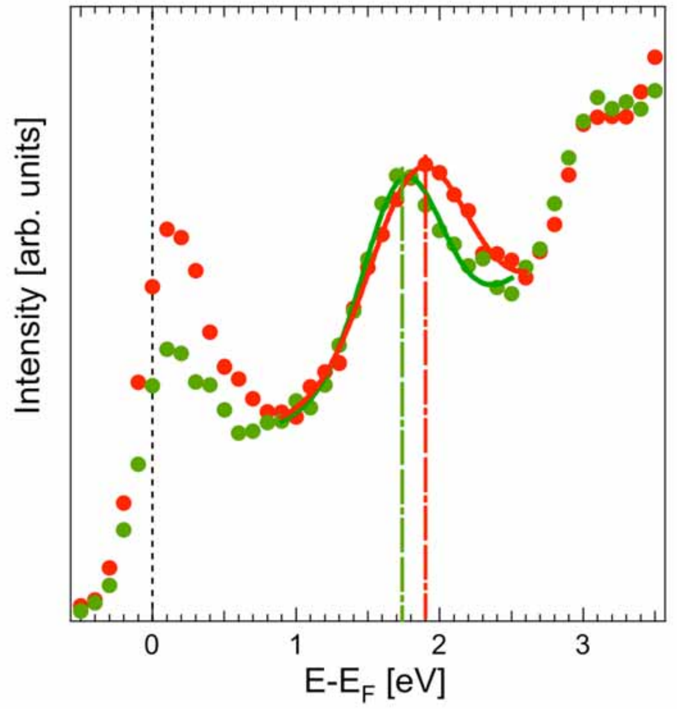
19 layer slab calculations, Grad & Blaha (TU Vienna)
Grad et al., Phys. Rev. B 68, 085404 (2003)
photoemission: W. Auwärter, PhD thesis U Zurich 2003

spin-resolved inverse photoemission

normal incidence spectra (hv=9,5 eV)



spin-resolved data

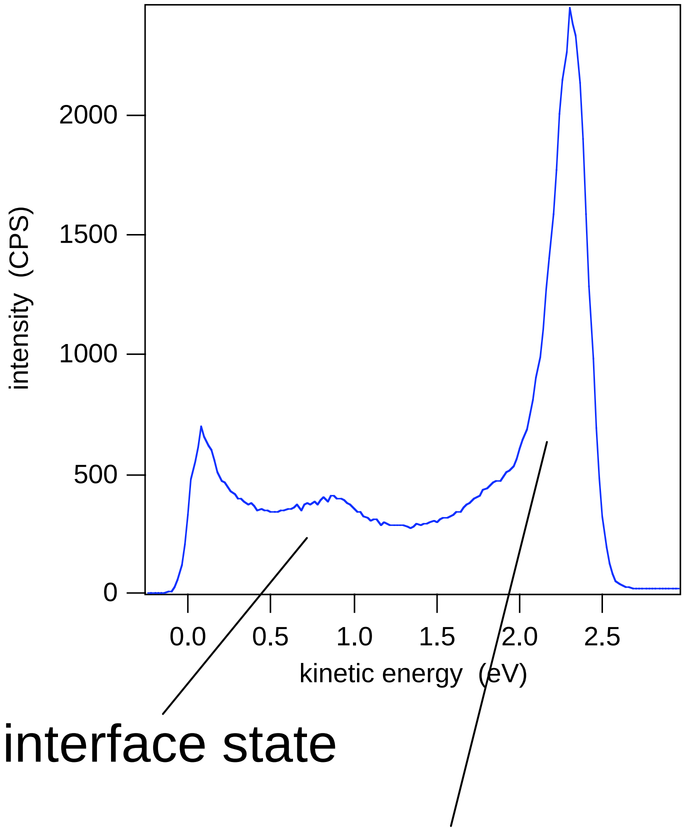


interface state (A): 1.7 eV above EF
exchange splitting 150 ±50 meV
effective mass 1.1 ±0.2 m_0

experimental setup see Donath, Surf. Sci. Rep. 20, 251 (1994).
K. Zumbrägel, diploma thesis, U Münster, 2007.
K. Zumbrägel et al., in preparation (2007)

2PPE: normal emission spectra

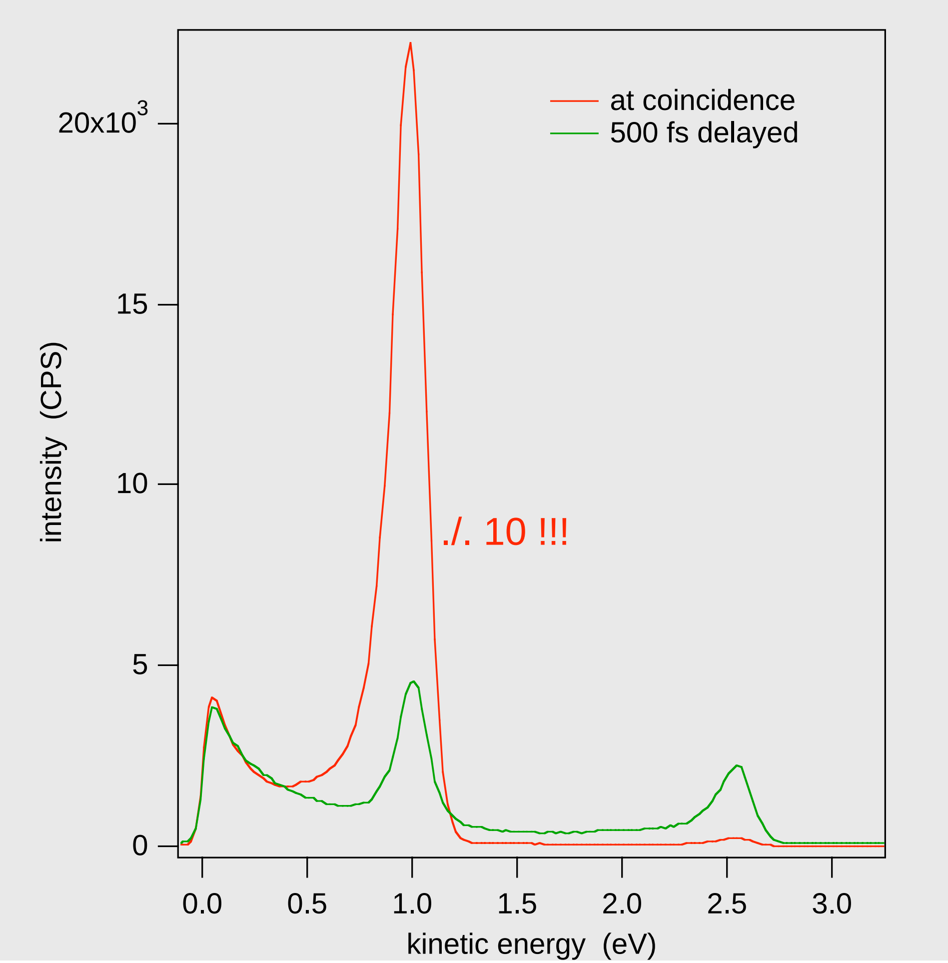
single-colour (400 nm)



interface state

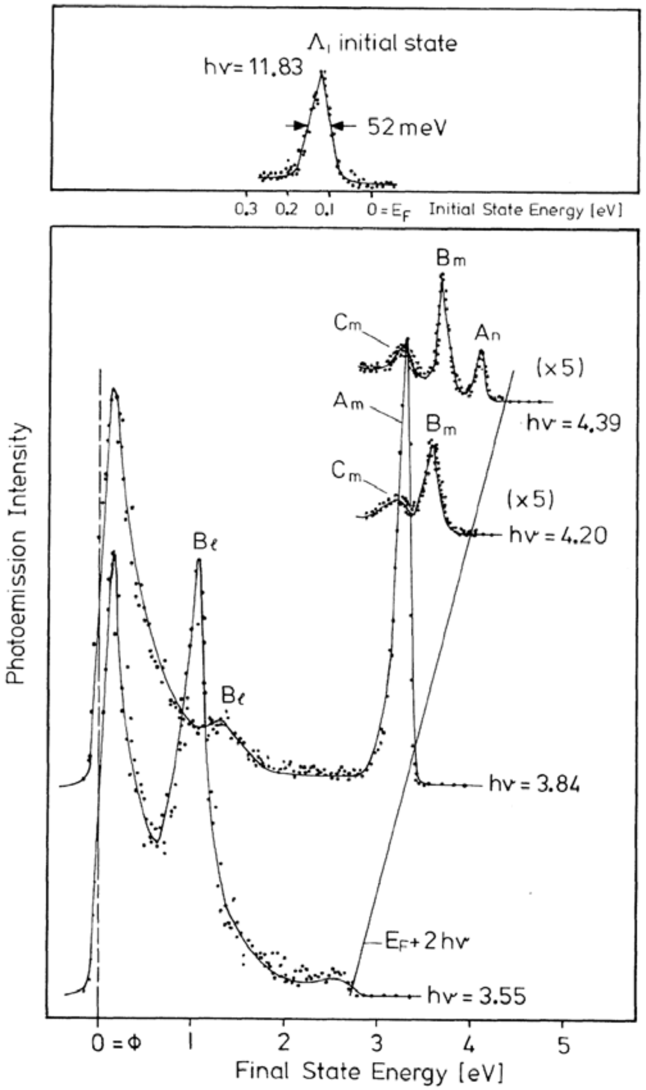
image potential state

pump: 796 nm; probe: 398 nm



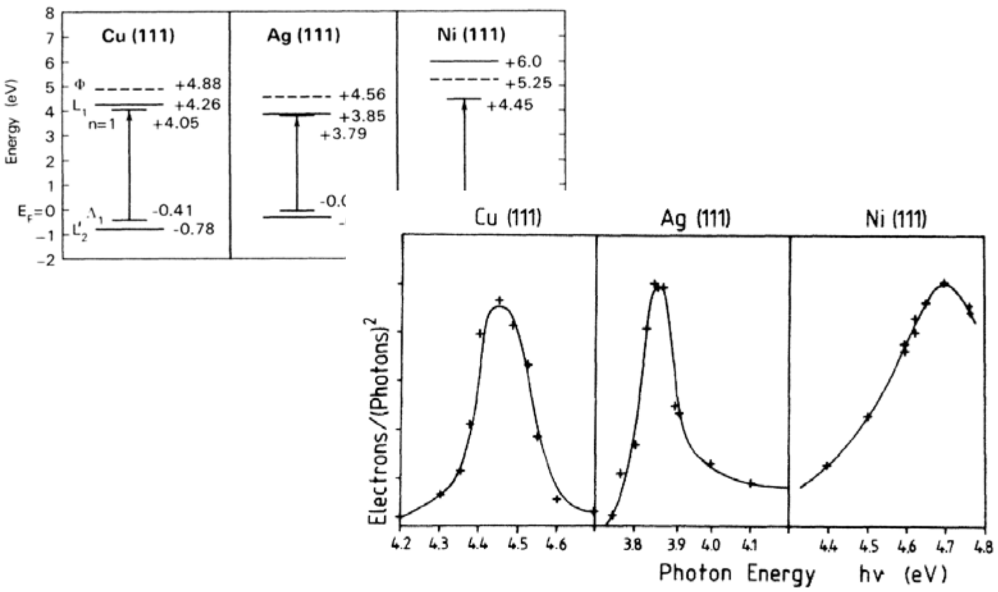
⇒ interface state peak increased by 2-3 orders of magnitude!

resonant excitation channels are known in 2PPE



transient population density of intermediate image potential states may be very high:

→ resonant direct transition



Giesen et al., Phys. Rev. Lett. 55, 300 (1985) and
Phys. Rev. B 33, 5241 (1986)
Steinmann, Appl. Phys. A 49, 365 (1989)

dispersion on resonance at 796 nm

log intensity scale

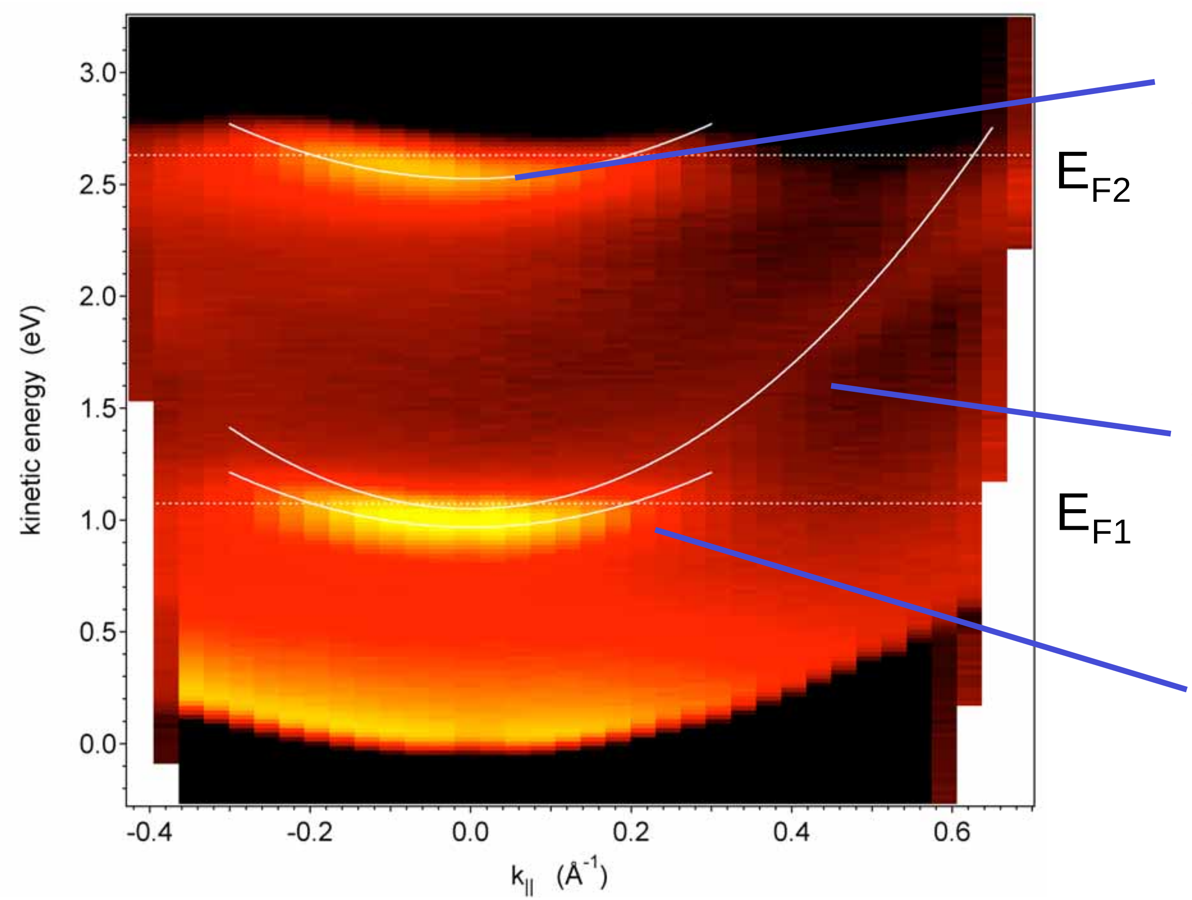


image state
excited with $2h\upsilon$

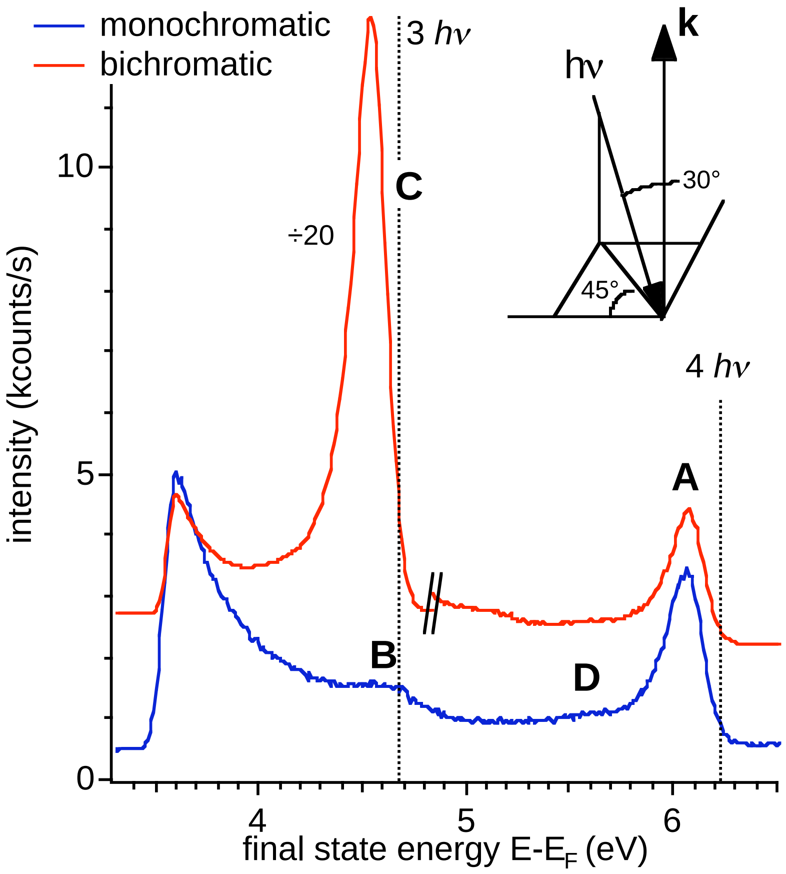
conduction band
excited with $2h\upsilon$

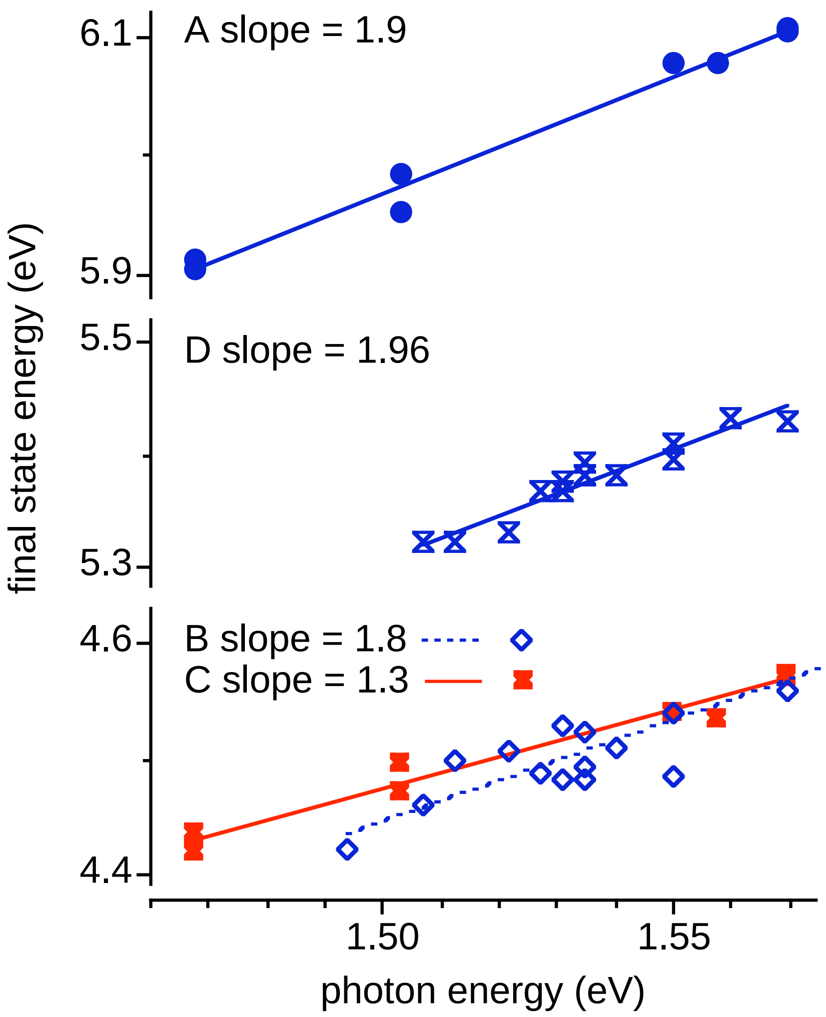
image state
excited with $1h\upsilon$

$h\nu = 1.558$ eV

Muntwiler et al., Phys. Rev. B 75, 075407 (2007)

photon energy dependence





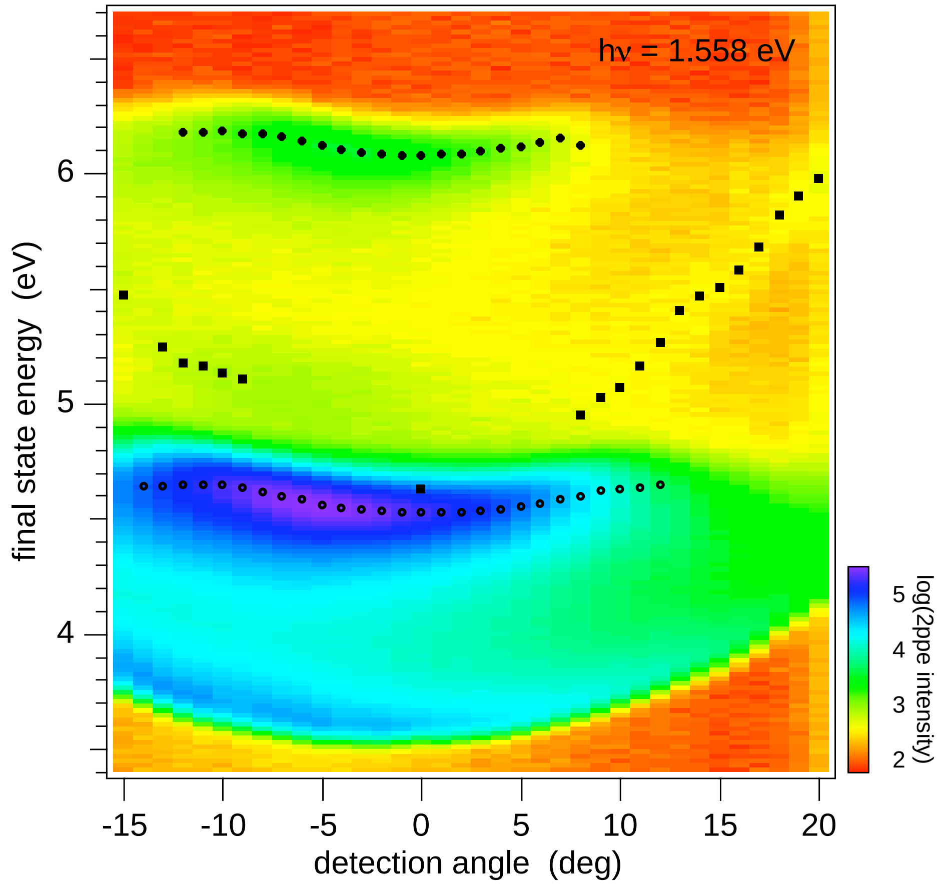
A - image state (blue-blue)

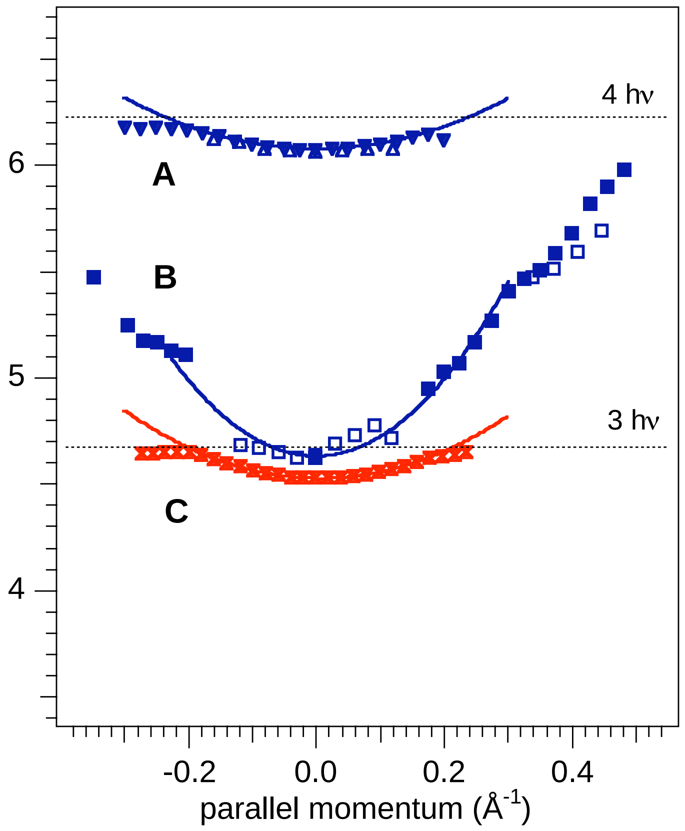
B - interface state (b-b)

C - resonance (r+b)

D - indirect transition from Ni-B bond?

band mapping





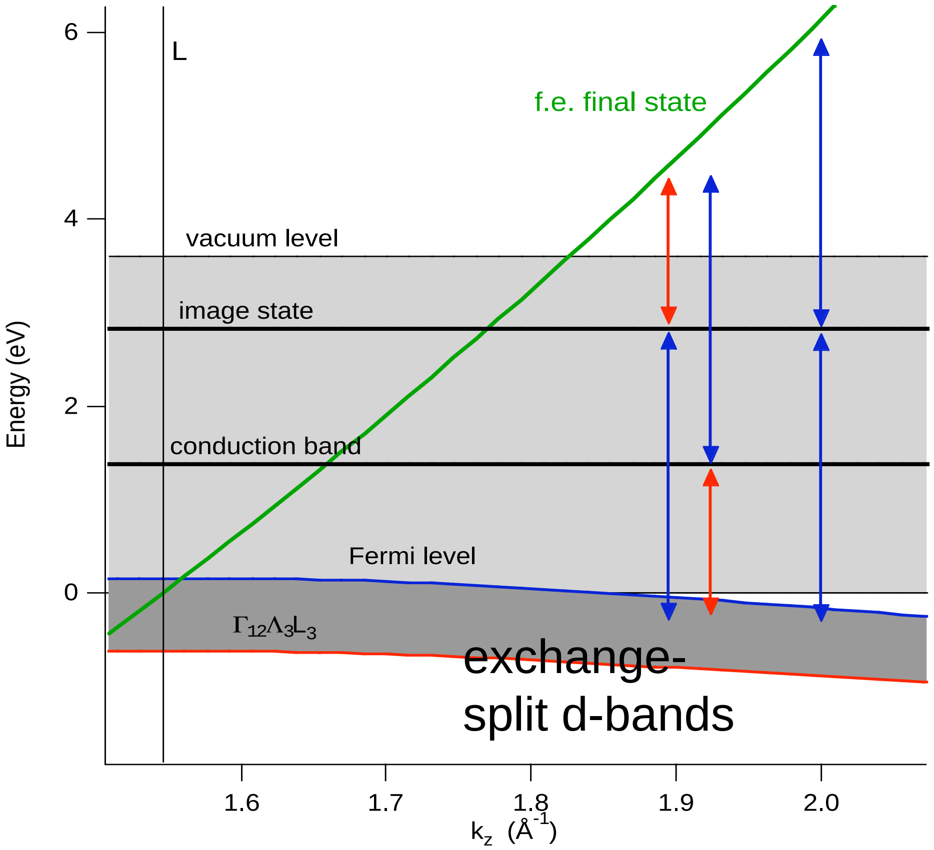
A m* = 1.43, $E_0 = E_{vac}$-650 meV = E_F+2.95 eV

B m* = 0.43, $E_0 = E_F$+1.51 eV

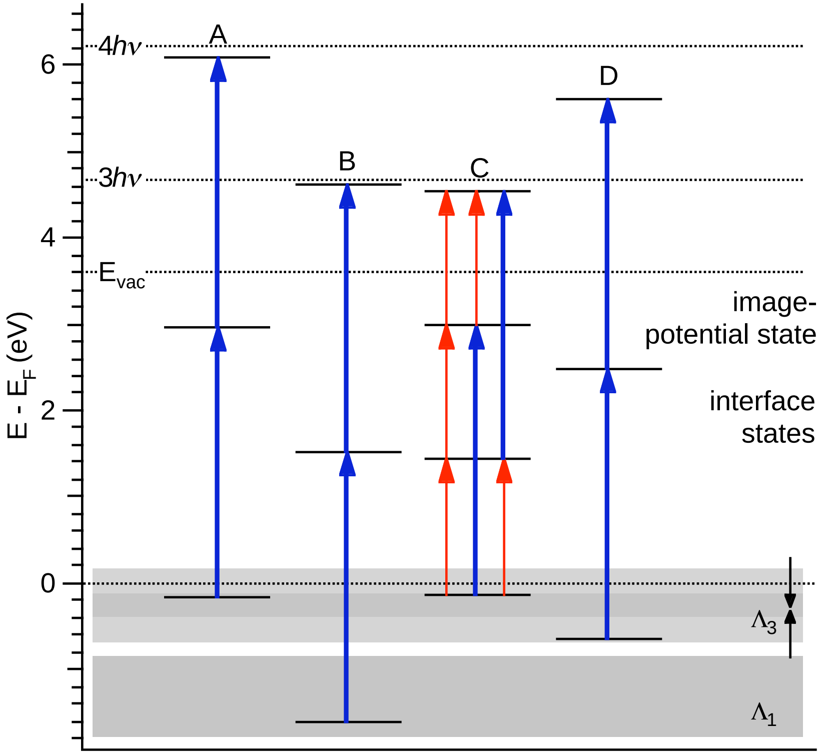
C m* = 1.1, $E_0 = E_F$ +1.4eV

Muntwiler et al., Phys. Rev. B 75, 075407 (2007)

resonance as result of two excitation pathways



exchange-
split d-bands

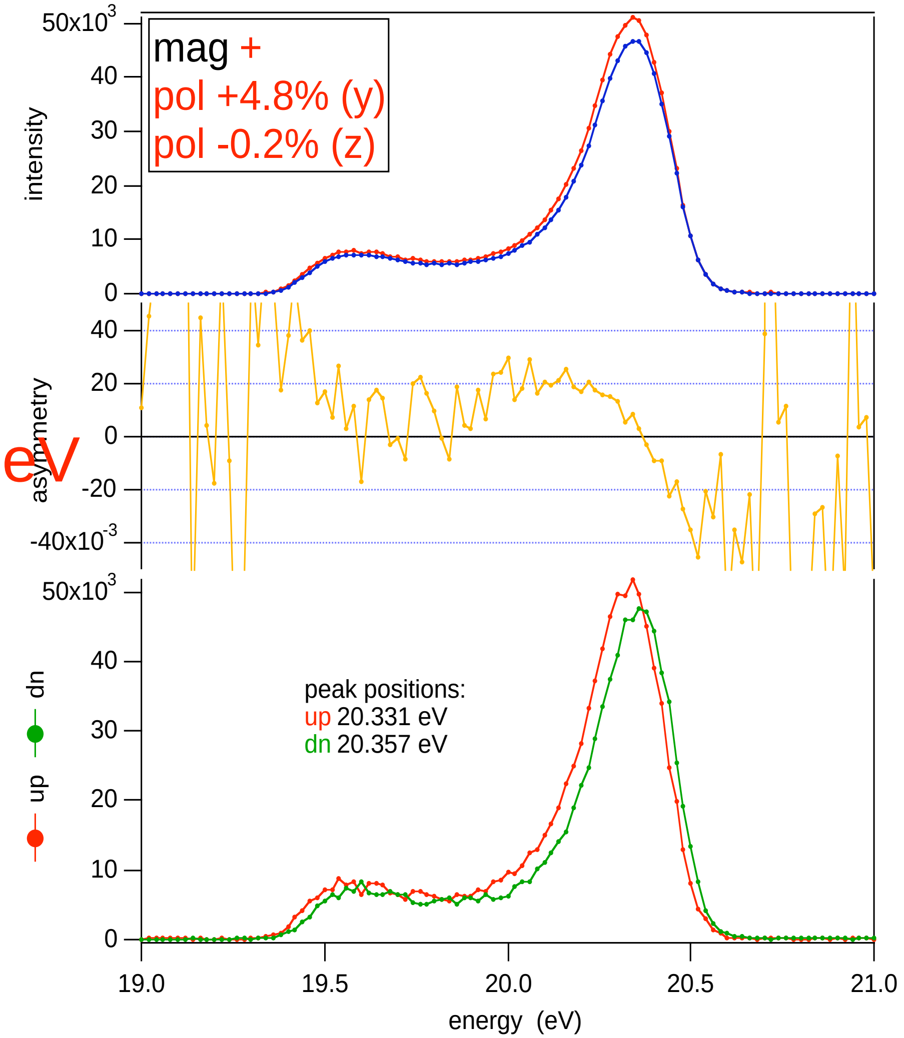


spin-resolved 2PPE at λ = 794 nm

remanent sample magnetization 20%
Sherman function of Mott detectors 14%
⇒ very low spin signal !

100% magnetized sample:

- 25% polarization (**majority**)
- splitting of resonant peak 26 meV



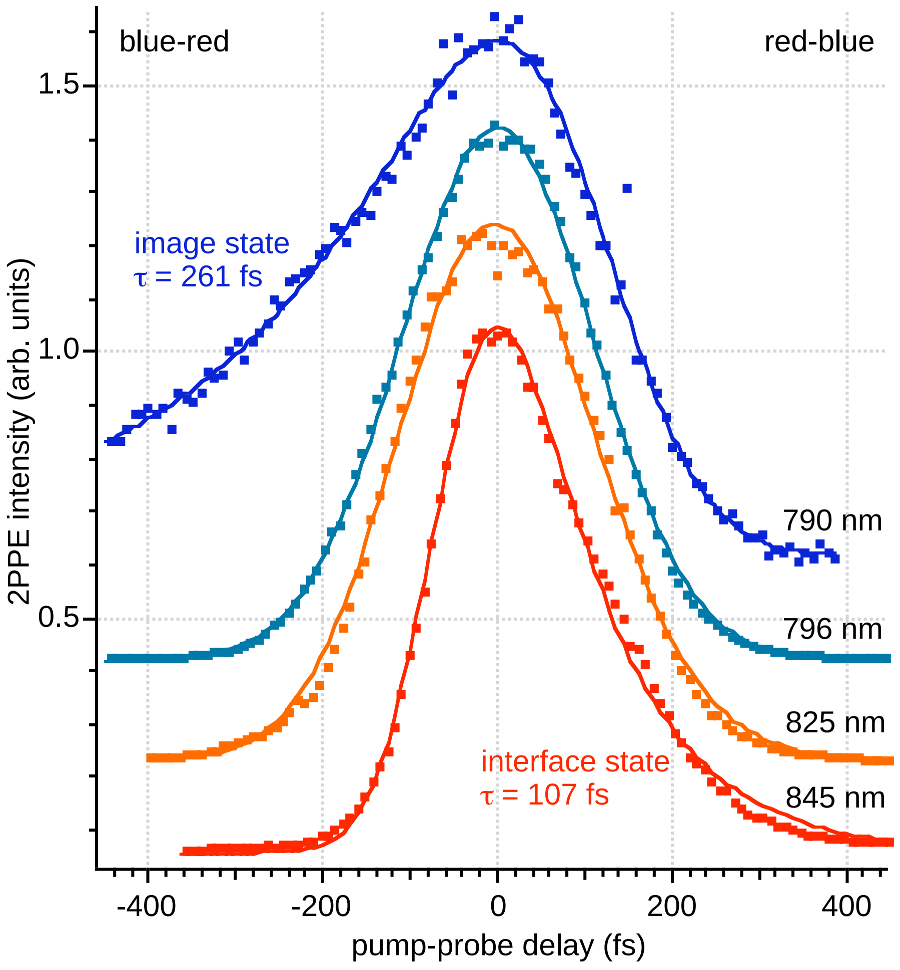
M. Hengsberger et al.,
US-provisional patent (filed July 2005)
Int. patent no. WO2007/006168A1 (2007)

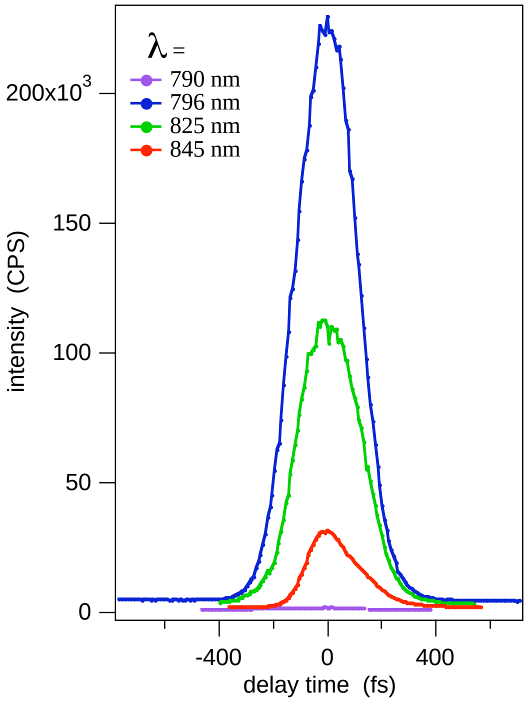
summary: spectroscopy

state/peak	method	band bottom (eV)	effective mass (m_0)	exchange splitting (meV)
interface state	theory (DFT) inv. PE 2PPE	1.7 1.7 1.51	0.73 1.1 ±0.2 0.43 ±0.1	100 150 ±50 --
image potential state	theory (DFT) inv. PE 2PPE	-- E_{vac} - 0.6 E_{vac} - 0.65	-- 1.46 ±0.5 1.43 ±0.2	-- -- > 36 (*)
resonant peak	theory (DFT) inv. PE 2PPE	-- -- 4.63 (final state)	-- -- 1.12 at delay 0	-- -- 26

(*) deduced from temperature-dependent data (see later)
theory (DFT calculations): Grad et al., Phys. Rev. B68, 085404 (2003)

correlation traces as function of photon energy



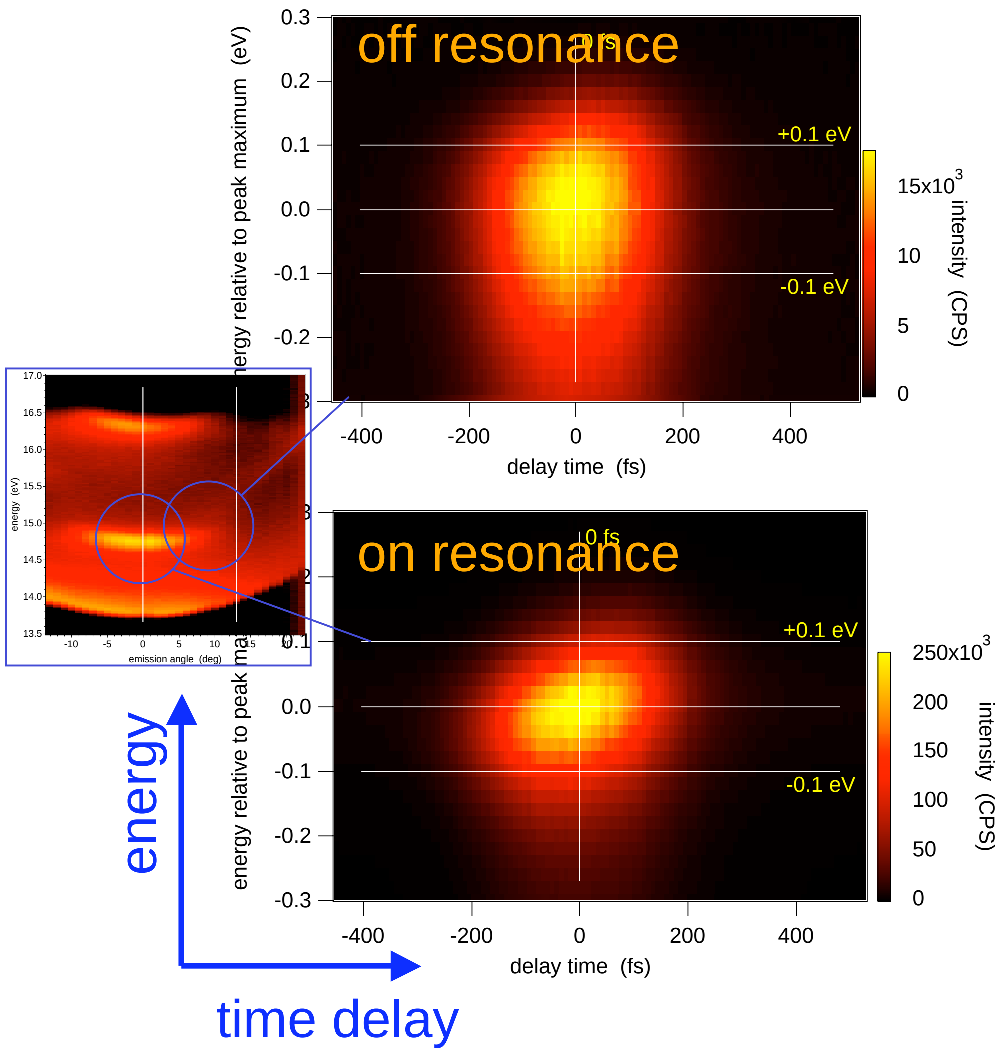


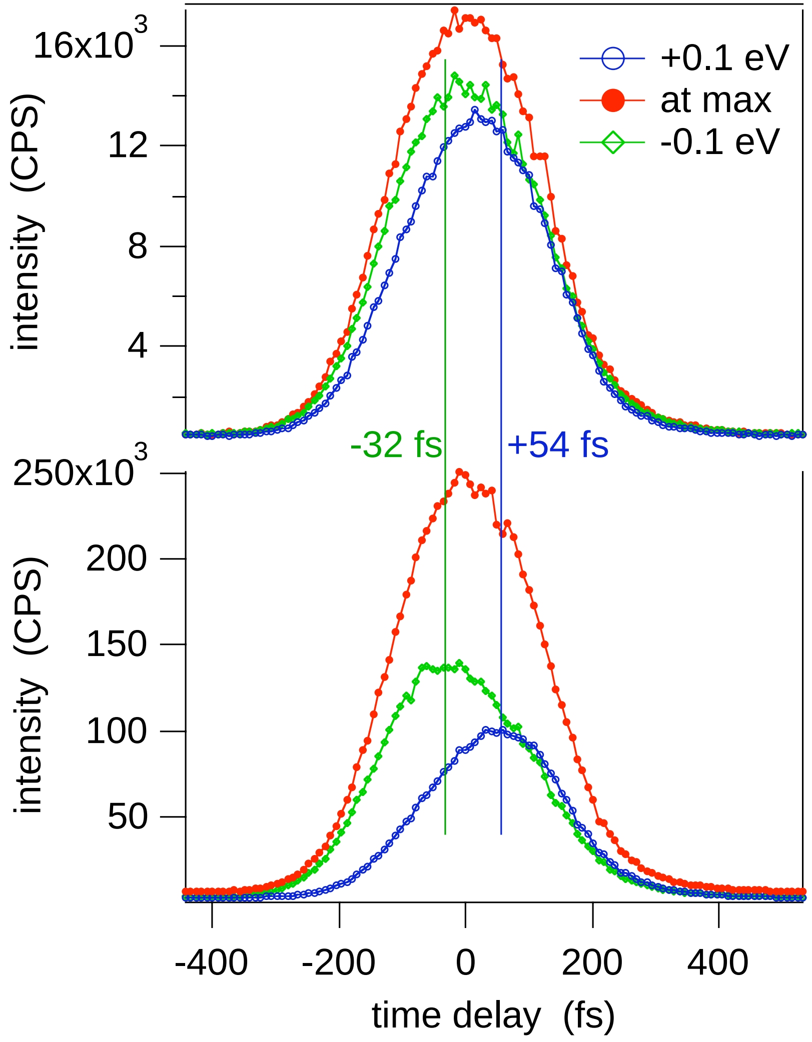
⇒ two different processes: blue after red and red after blue

⇒ in resonance, cross-correlation almost symmetric !

Muntwiler et al., Phys. Rev. B 75, 075407 (2007)

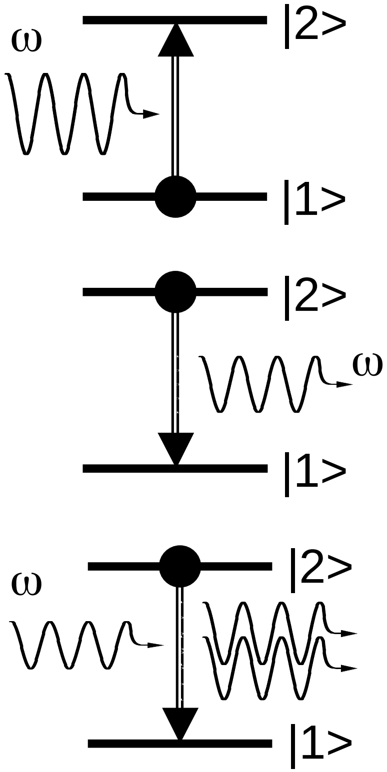
can we see lifetime-related shifts in correlation curves ?





YES, even two shifts!

optical excitation : rate equations



absorption:
probability Bw
(w= photon density)

spontaneous emission:
probability A

stimulated emission:
probability Bw

⇒ rate equations

(1) level population $N_1 + N_2 = N$

(2) transition rates

$$dN_1/dt = -dN_2/dt = N_2 A + (N_2 - N_1) Bw$$

yield general solution for excited state population N_2 [assuming $N_1(0)=N$] :

$$N_2(t)/N = \left\{1 - \frac{(A+Bw)}{A+2Bw}\right\}\left\{1 - e^{-(A+2Bw)t}\right\}$$

if spontaneous emission neglected :

$$N_2(t)/N = \tfrac{1}{2}\left\{1 - e^{-2Bw\,t}\right\} \xrightarrow[t\to\infty]{} \frac{1}{2}$$

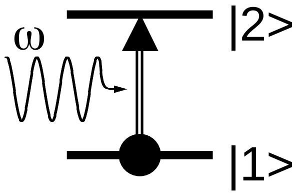
where $2Bw = \alpha F(t) = \alpha \int_{-\infty}^{t} d\tilde{t}\; I(\tilde{t})$

key parameter : intensity !

see e.g. R. Loudon "The Quantum Theory of Light",
Oxford University Press (1973)

density matrix formalism

(or : Liouville-von Neumann in 2PPE community)



describe system by density matrix

Schrödinger picture (time-dependent wave function)

wave function : density matrix formalism :

$$|\psi\rangle = C_1(t)\,|1\rangle + C_2(t)\,|2\rangle \qquad \rho \equiv |\psi\rangle\langle\psi| = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}\begin{pmatrix} C_1^* & C_2^* \end{pmatrix} = \begin{pmatrix} C_1C_1^* & C_1C_2^* \\ C_1^*C_2 & C_2C_2^* \end{pmatrix}$$

$|C_1(t)|^2$ probability of being in lower state $= \rho_{11}$

$|C_2(t)|^2$ probability of being in excited state $= \rho_{22}$

$\boxed{C_1(t)C_2^*(t) = C_1^*(t)C_2(t) \text{ coherent superposition state } = \rho_{12} = \rho_{21}^*}$

this state is created by interaction with radiation

$\langle \mathbf{A} \rangle$ $= \mathrm{Tr}(\rho\mathbf{A})$

example : macroscopic polarization = off-diagonal elements

$$P = N\langle\mu_{12}\rangle = N\,\mathrm{Tr}(\mu_{12}\rho) = N\mu_{12}(\rho_{12} + \rho_{21}) = 2N\mu_{12}\,\mathrm{Re}\{\rho_{12}\}$$

optical Bloch equations : 1.) ansatz

optical Bloch equations = eqns. of motion of density matrix

starting from Liouville equation $\dot{\rho} = -\frac{i}{\hbar}[\mathbf{H}, \rho]$

where $\mathbf{H} = \mathbf{H_0} + \mathbf{V} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \mu_{12} \cdot \mathbf{E}(t) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

introduce (phenomenologically) decay of states by inserting imaginary energy terms $\Rightarrow$ leads to exponential decay in probability amplitudes :

$$\mathbf{H} + \mathrm{i}\Gamma = \mathbf{H_0} + \mathrm{i}\Gamma + \mathbf{V} = \begin{pmatrix} \mathrm{E}_1 & 0 \\ 0 & \mathrm{E}_2 \end{pmatrix} + \mathrm{i} \begin{pmatrix} \Gamma_1 & 0 \\ 0 & \Gamma_2 \end{pmatrix} + \mu_{12} \cdot \mathbf{E}(\mathrm{t}) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

we obtain the equation of motion with the convention Γ=1/T :

$$\boxed{\dot{\rho} = -\frac{1}{2}[\Gamma, \rho] - \frac{\mathrm{i}}{\hbar}[\mathbf{H}, \rho]}$$

optical Bloch equations : 2.) decay & relaxation

⌦ population decay or "energy relaxation" - "longitudinal relaxation time"

recombination by (usually radiative) decay - inelastic process

$$\dot{C}_i = \ldots - \tfrac{1}{2}\Gamma_i C_i \quad \Rightarrow \quad C_i(t) \propto \exp\left\{ - i/\hbar\, E_i t - \tfrac{1}{2}\Gamma_i t \right\}$$

since $\rho_{ij} = C_i^* C_j$ it follows that

$$\dot{\rho}_{ij} = \ldots - \Gamma_{ij}\,\rho_{ij} \quad \text{with} \quad \Gamma_{ij} = \tfrac{1}{2}\left(\Gamma_i + \Gamma_j\right)$$

⌦“pure" dephasing : addit'nl decay of off-diagonal elements

interaction with environment (quasi-elastic processes) causes fluctuations of resonance frequency:

$$\omega(t) = \omega_0 + \delta\omega(t) \;:\; \text{integrate and take ensemble average}$$

$$\Rightarrow \left\langle \exp\left\{ -i \int d\tilde{t}\, \delta\omega(\tilde{t}) \right\} \right\rangle = (\text{...a lot of algebra...}) \; = e^{-\Gamma_{ph} t}$$

⌦ yields an effective transverse decay rate

$$\boxed{\Gamma_{12}^{T} = \tfrac{1}{2}\left(\Gamma_1 + \Gamma_2\right) + \Gamma_{ph} \overset{\text{often}}{=} \frac{1}{2T_1} + \frac{1}{2T_2} + \frac{1}{T_{12}^*}}$$

optical Bloch equations : 3.) final set of equations

combining hamiltonian and decay terms yields:

$$\dot{\rho}_{11} = -\Gamma_1 \rho_{11} + \frac{i}{\hbar} \mu_{12} \cdot \mathbf{E}(t)\left(\rho_{12} - \rho_{21}\right) \qquad (1)$$

$$\dot{\rho}_{22} = -\Gamma_2 \rho_{22} - \frac{i}{\hbar} \mu_{12} \cdot \mathbf{E}(t)\left(\rho_{12} - \rho_{21}\right) \qquad (2)$$

$$\dot{\rho}_{12} = -\Gamma^{T}_{12} \rho_{12} - i\omega_0 \rho_{12} - \frac{i}{\hbar} \mu_{12} \cdot \mathbf{E}(t)\left(\rho_{22} - \rho_{11}\right) \qquad (3)$$

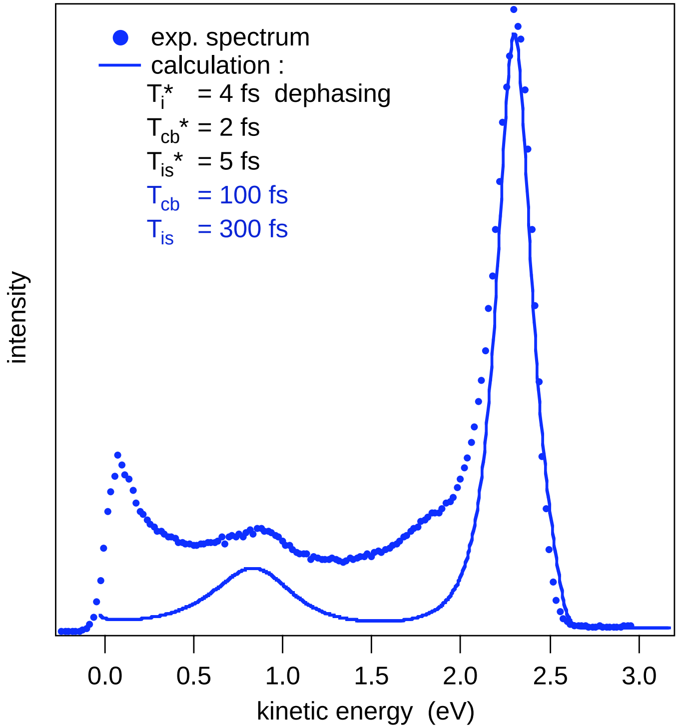
with $\Gamma^{T}_{12} = \frac{1}{2}\left(\Gamma_1 + \Gamma_2\right) + \Gamma_{ph}$ and $\hbar\omega_0 = E_2 - E_1$

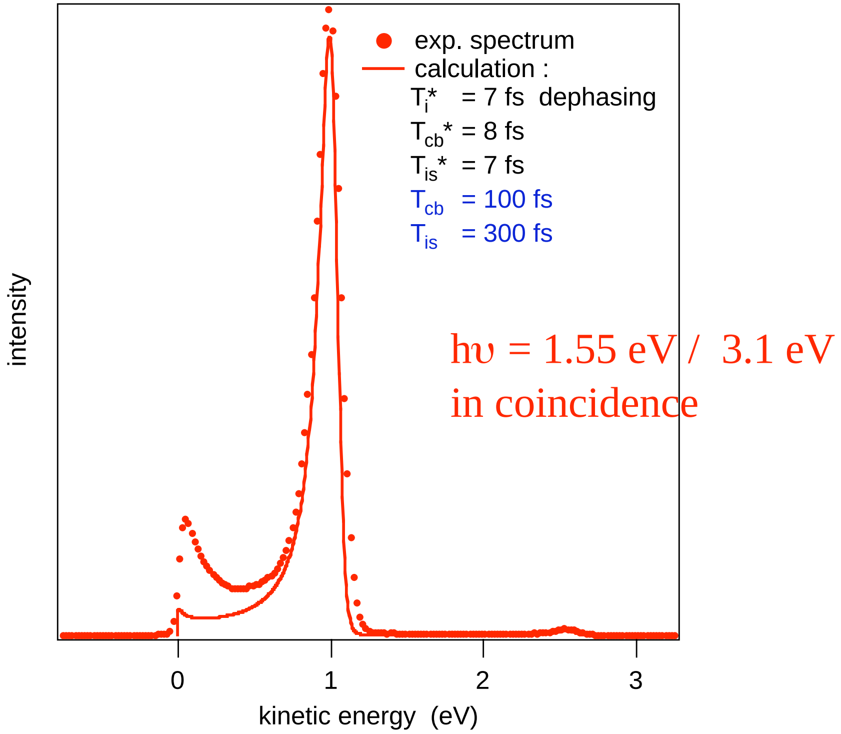
and $\mathbf{E}(t) = \frac{1}{2}\left(\hat{\mathbf{E}}(t) + \hat{\mathbf{E}}^{*}(t)\right)$

optical Bloch equations (OBE)

first calculations: optical Bloch equation, cw case

- based on : Wolf et al., Phys. Rev. B 59, pp 5926-35 (1999)
- c.f. S. Mukamel, *Principles of nonlinear optics*, Oxford U Press 1995
- 4-level system (initial and final state continua, 2 discrete intermediate states), including RWA, cw approximation (no time dependence), analytical solution



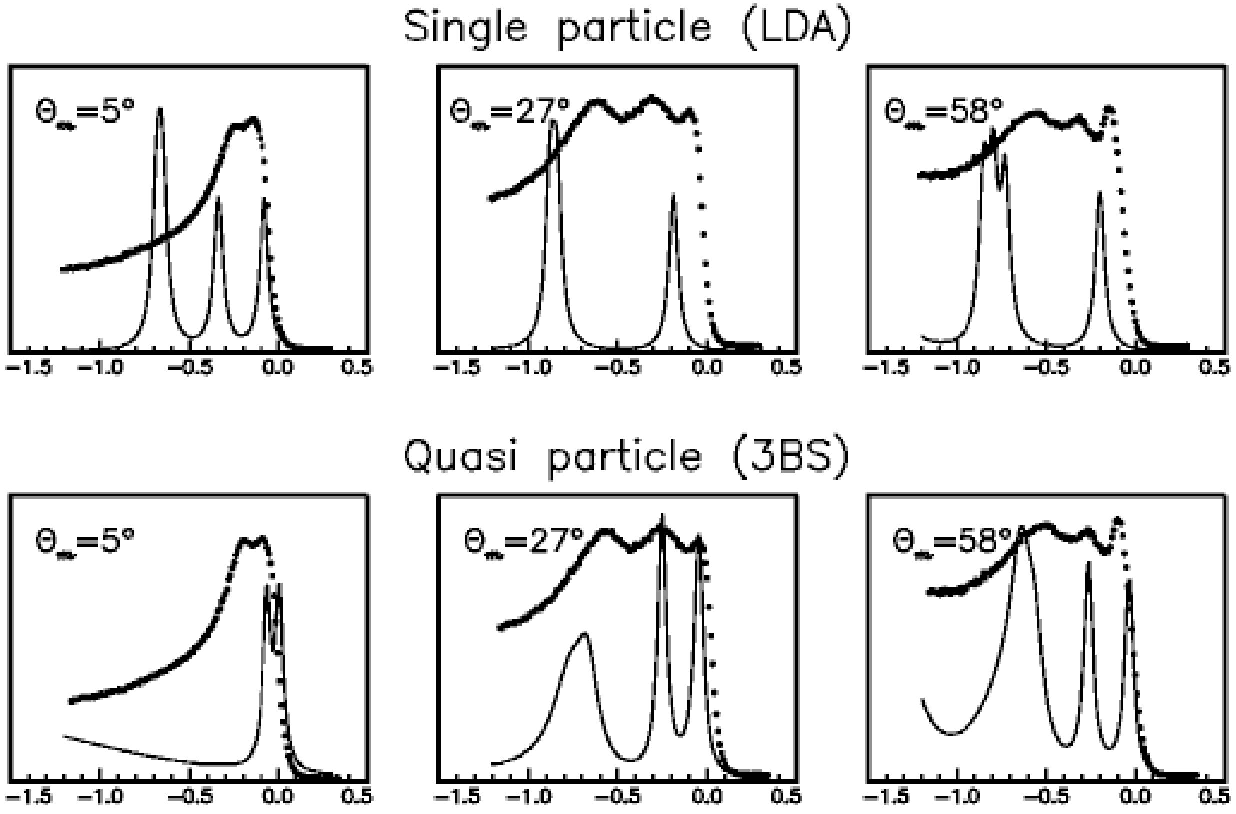


hυ = 1.55 eV / 3.1 eV
in coincidence

population decay times 100 and 300 fs
dephasing times typically 2~ 8 fs

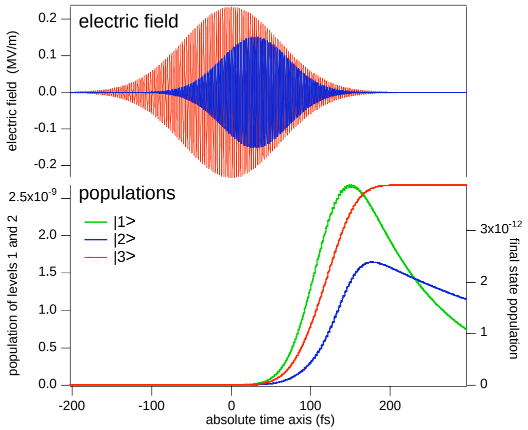
dephasing dominated by photohole lifetime

broad peaks in conventional photoemission spectra (21.2 eV):
→ photohole lifetimes of a few femtoseconds



from: F. Manghi et al., PRB 59, R10409 (1999)

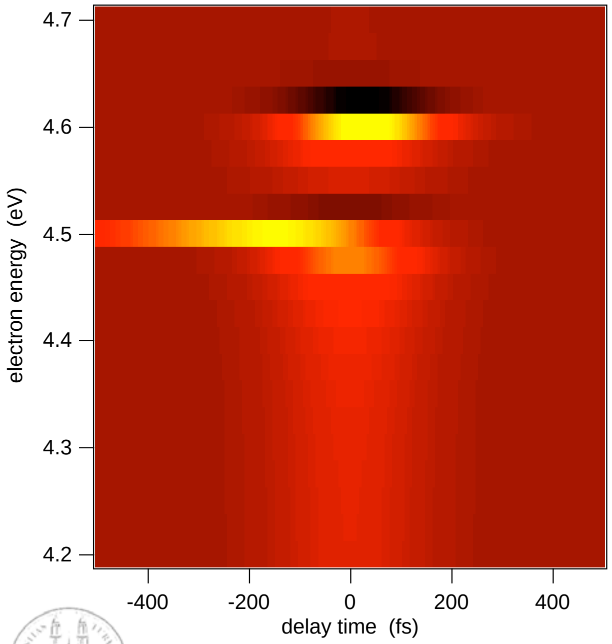
dynamical calculations: solving the Optical Bloch Eqns.



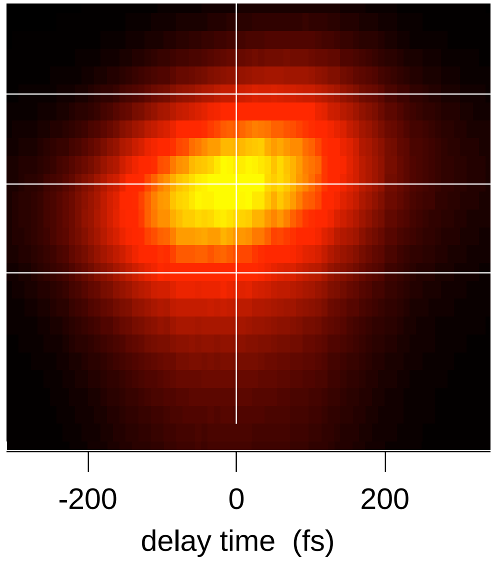
- ➢ semi-classical ansatz for electric field
- ➢ solve set of 9-10 coupled differential equns.
- ➢ integration over absolute time axis (left)

- ➢ temporal shifts and broadening due to dephasing reproduced

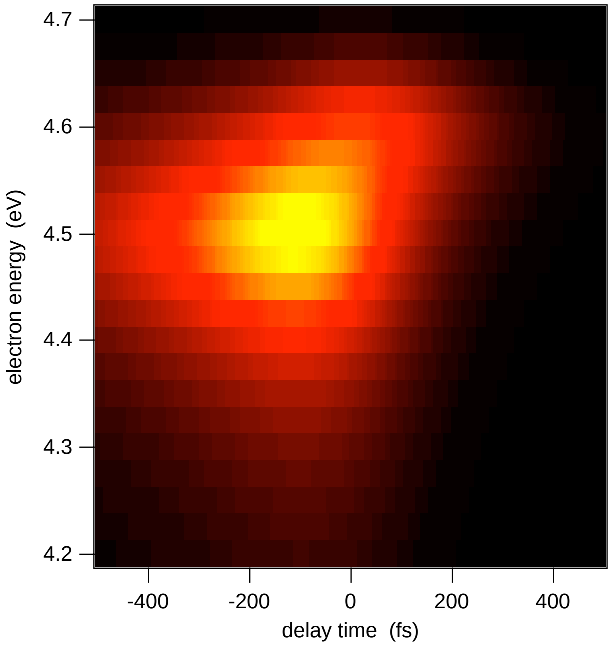
very long dephasing time (1 ps)



exp. (λ=800 nm)



dephasing 8 fs

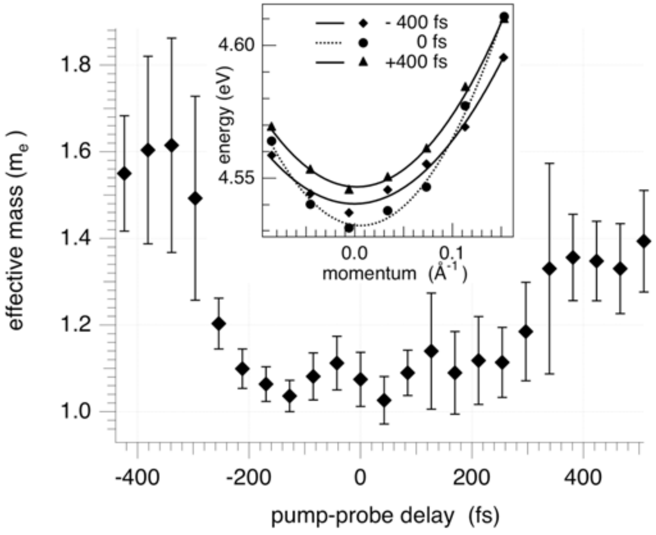


summary: time-resolved measurements

- very long lifetimes found in two-colour experiments:
  - interface state 107 fs (in close proximity to metal!)
  - image potential state 261 fs - can be understood within dielectric continuum model (Lingle et al., Chem. Phys. 205, 191 (1996))

- time-resolved measurements give further support for two excitation channels in the resonant peak

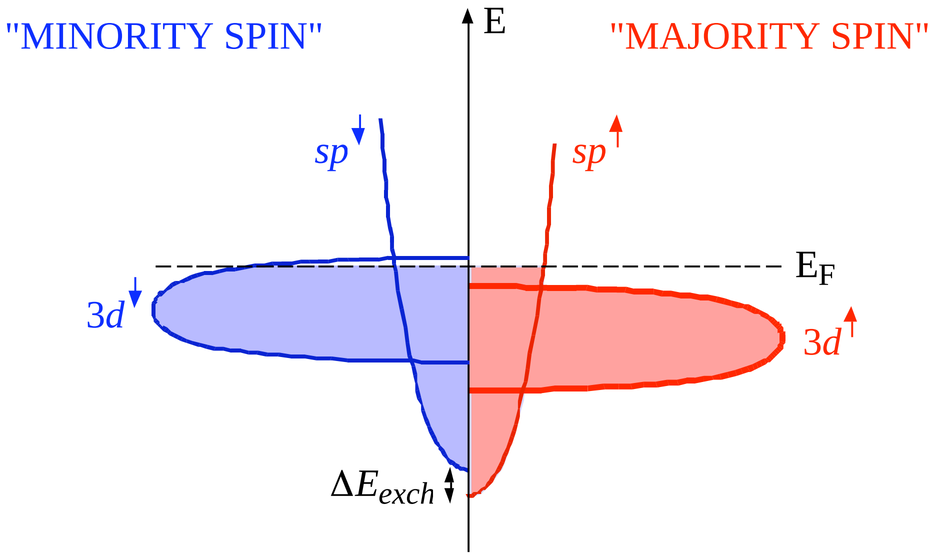
- effective mass of resonant peak changes as function of time delay (not yet understood)

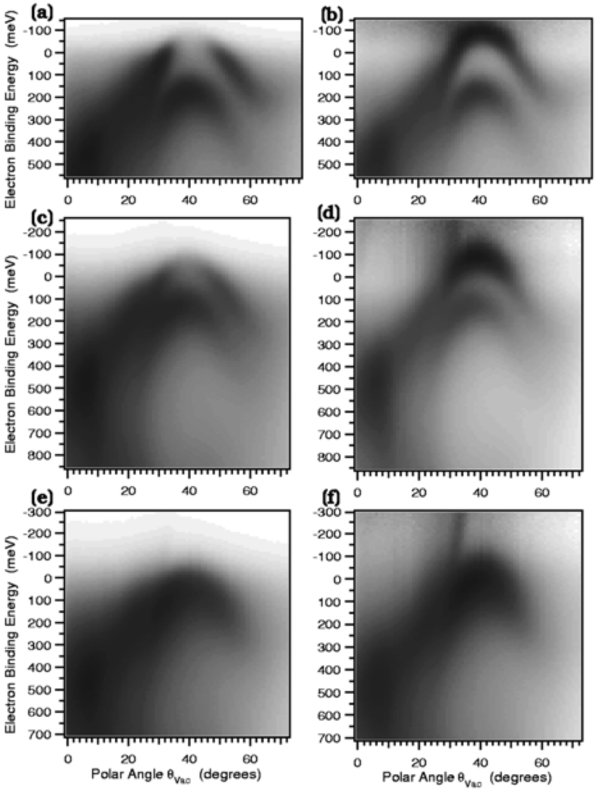


2PPE signal as probe for magnetic order

idea:

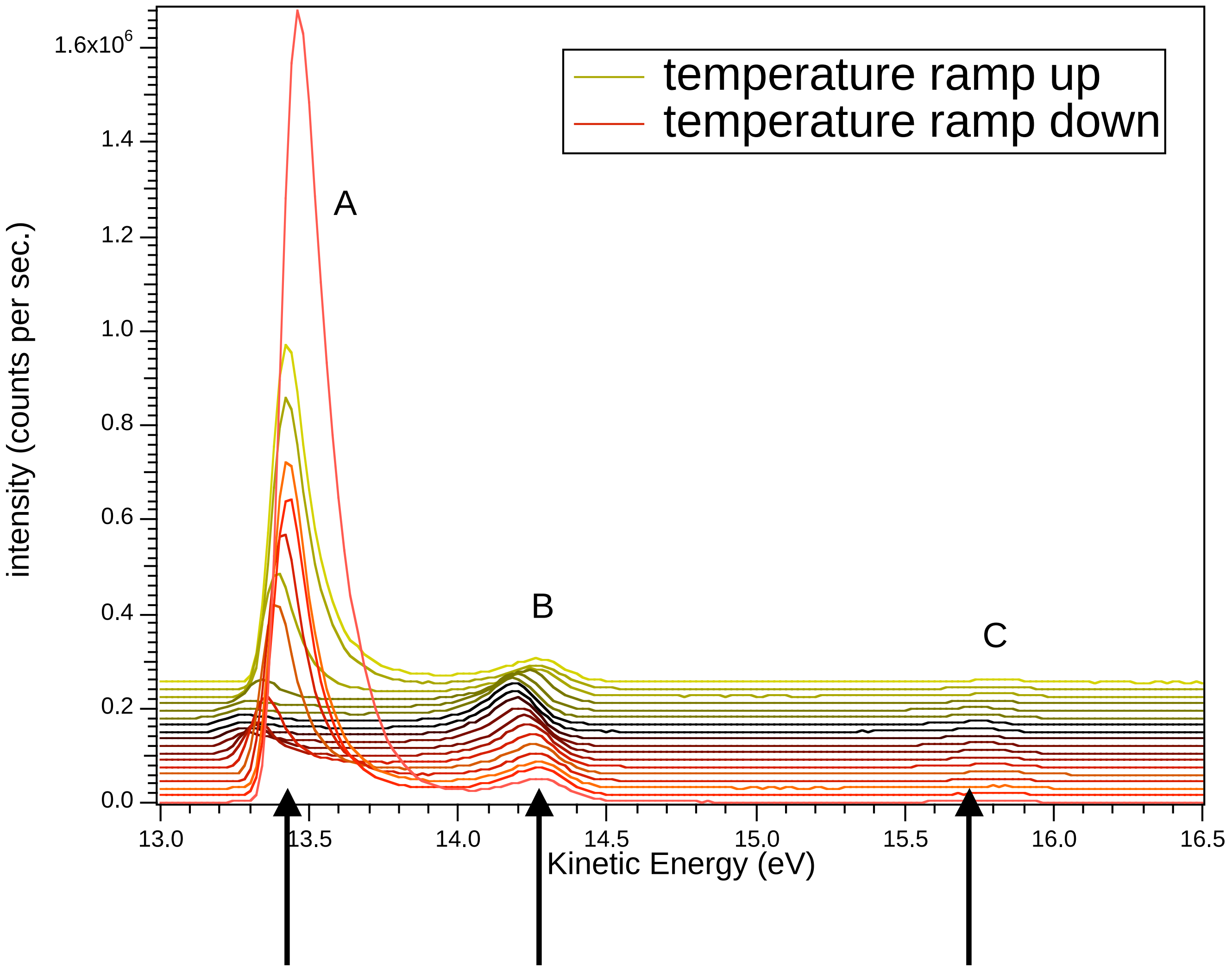
- resonance sensitive to precise band energies
- "detuning" by varying exchange splitting
- sensitivity to magnetic order?
- first test: 2PPE at high temperature…





Kreutz et al, Phys. Rev. B 58, 1300 (1998)

2PPE spectra as function of temperature



secondary
cut-off

red-blue
resonance

image state
(blue-only)

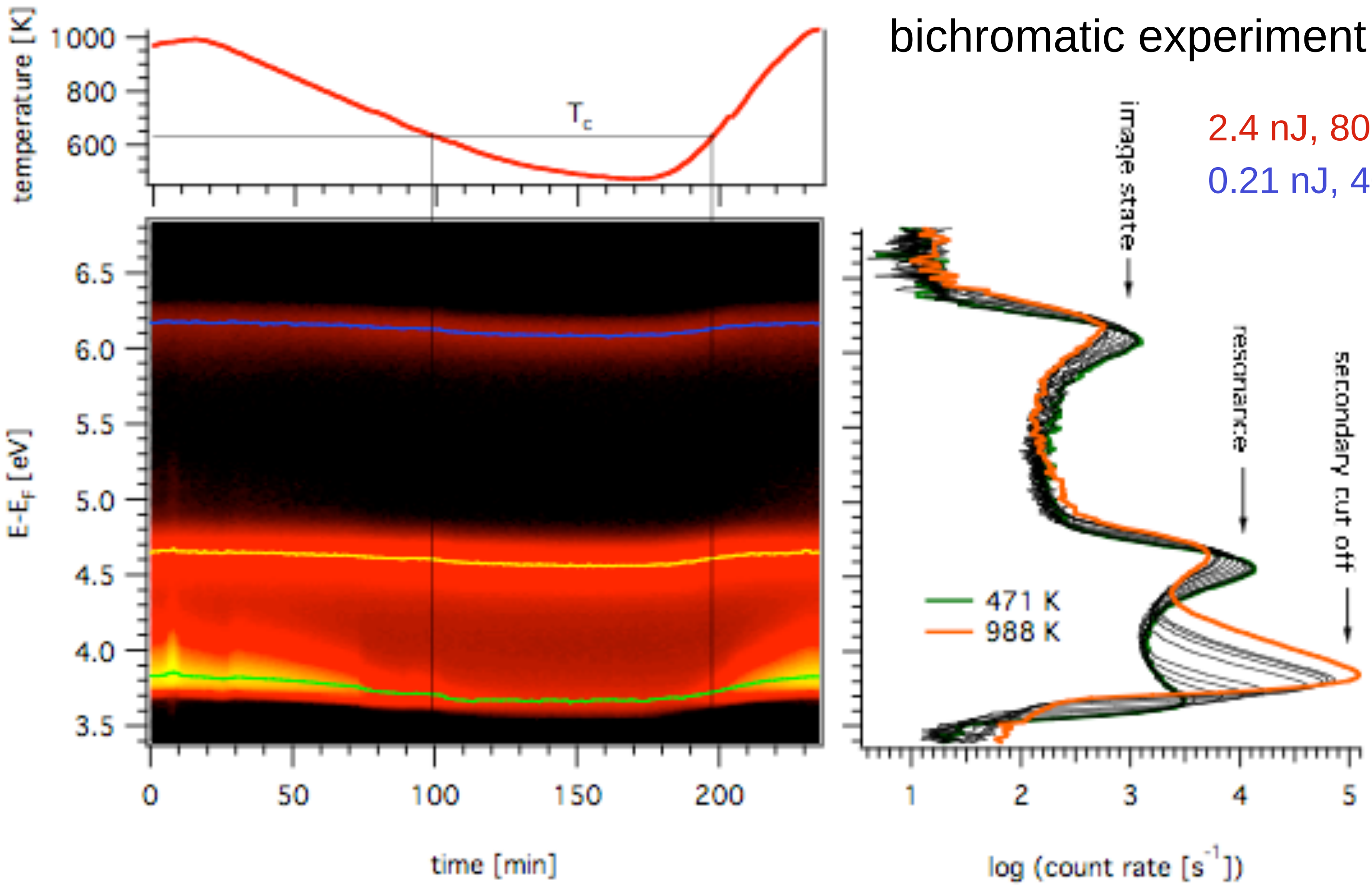
D. Leuenberger
Master Thesis (2006)

spectra as function of temperature

bichromatic experiment

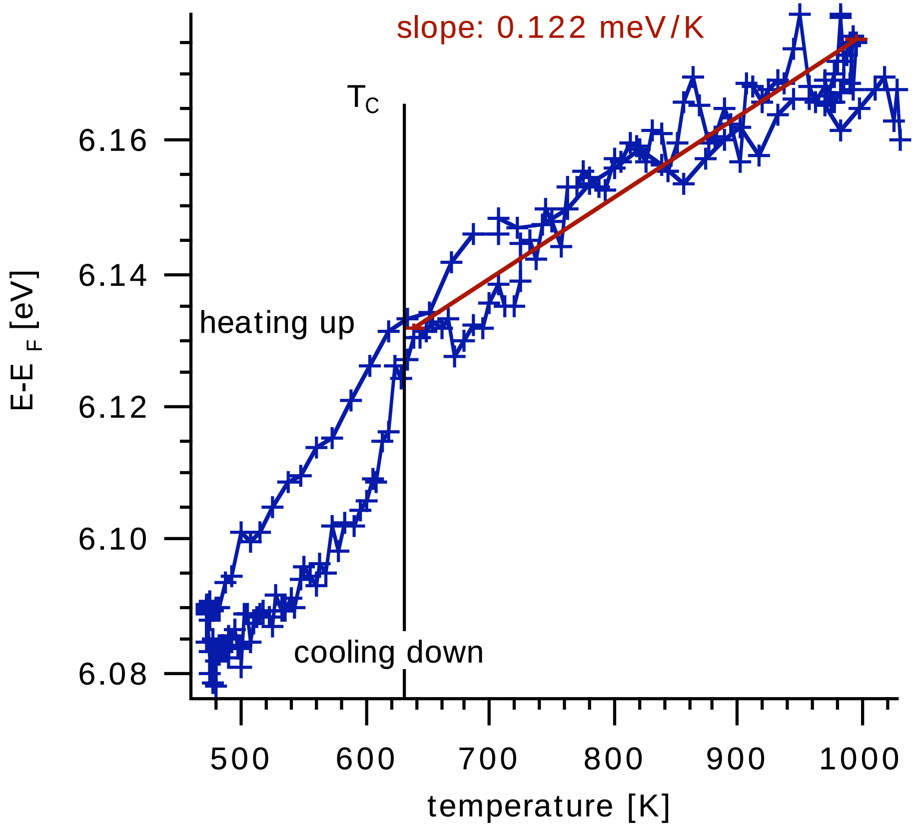
2.4 nJ, 800 nm

0.21 nJ, 400 nm



2PPE transitions across T_c → signature of magnetic phase change?

image potential state position versus temperature

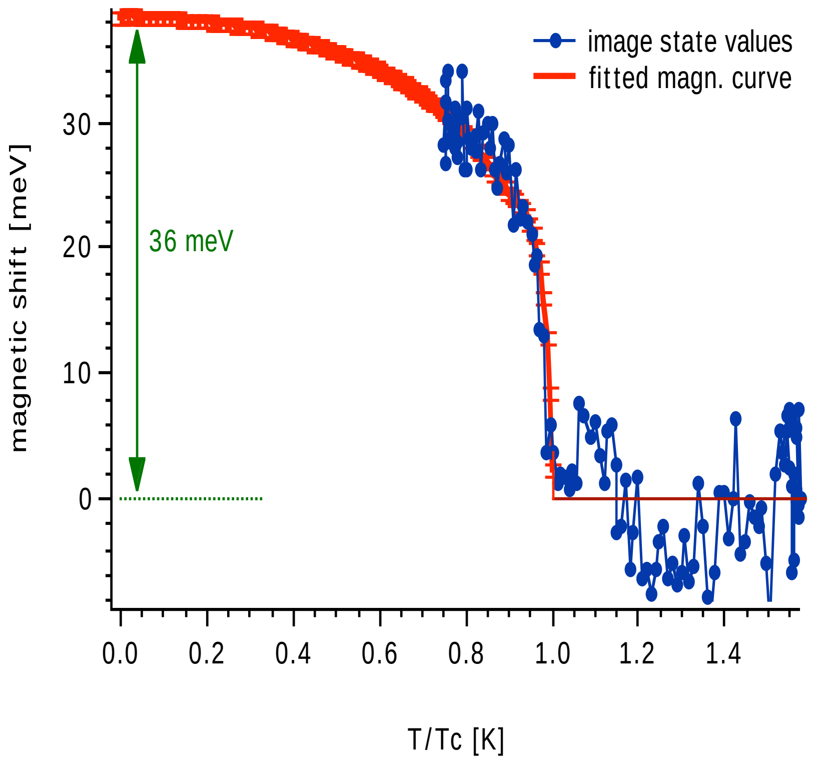


above T_c:
thermal band shift caused by thermal lattice expansion

below T_c:
thermal band shift + magnetic band shift (collapsing exchange splitting)

exchange splitting of image potential state

subtraction of the thermal shifts leads to:



- image potential state dominates peak position
- majority character
- width decreases by 60 meV over same temperature range

→ majority part of the exchange splitting?

agrees with previous measurements for bare Ni:

Fischer *et al.:* ΔE < 40 meV (2PPE); Phys. Rev. B 42, 9717 (1990)

Donath *et al*.: ΔE = 18 meV (IPES); Phys. Rev. Lett. 69, 1101 (1992)

Conclusions : time-resolved 2PPE from *h*-BN/Ni(111)

- huge resonance observed in 2PPE spectra from h-BN/Ni(111)
- resonance is caused by interaction of two transition channels within the h-BN layer
- spectroscopy quite difficult to interpret but in reasonable agreement with DFT and inverse photoemission

- lifetimes of intermediate states are rather long:
  about 107 fs for interface state and 261 fs for image potential state
- transient spectra can be modeled using the framework of Optical Bloch Equations

- resonant peak is partially spin-polarized (~25%, majority)
- new (chemically inert) source for spin-polarized electrons?

- 2PPE spectra show signatures of magnetic phase change at Tc
- exchange splitting of image potential state estimated to be >36 meV

people who contributed

Andrei Dolocan
Claudio Cirelli
Dominik Leuenberger
Hansjörg Neff

Matthias Muntwiler
Martina Corso
Felix Baumberger

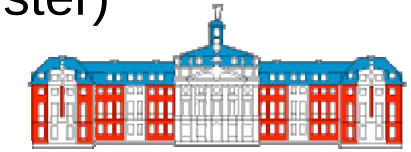
Martin Klöckner
Thomas Greber
Jürg Osterwalder

in collaboration with:

Jorge Lobo-Checa
(PSI & U Zürich, now U Basel)

Wolfgang Schuesslbauer
Thomas Ruchti
(Time-Bandwidth-Products)

C. Eibl, K. Wulff, K. Zumbrägel,
M. Donath (U Münster)



acknowledgments

sample preparation and characterization

Dr. H. Sachdev (U Saarbrücken)
Dr. W. Auwärter (now TU München)

theoretical support

Prof. P. Blaha (TU Wien)

optical setup

Dr. Günter Steinmeyer (formerly ETHZ, now Max-Born-Institut, Berlin)
Prof. Peter Hamm and Dr. Jan Helbing (PCI, U Zürich)

time- and spin-resolved photoelectron spectroscopy

Prof. Helmut Zacharias (U Münster)
Prof. Vladimir Petrov (TU St. Petersburg)

financial support from

Swiss National Science Foundation
University of Zürich