why ultrafast dynamics?

BLACK BOX

electrical energy

light

electrical energy

light
How do we see?

Example: photochemistry of vision

Rhodopsin

Eye

Rods and Cones

Retina

Lens

Sclera

Cornea

Pupil

Iris

Ciliary body

Optic nerve

Transmembrane helices

Bilayer membrane

Rhodopsin

Retinal

11-cis

cis-trans isomerization

Rod cells: A single rod contains $10^8$ rhodopsins (renewed every 10 days throughout a person’s life)

Retinal

all-trans

http://www.fhi-berlin.mpg.de/pc/electronodynamix
ultrafast processes in excited solids

adapted from Petek & Ogawa,


solids and interfaces exhibit various fundamental processes on atto- to picosecond timescales
femtoseconds

- $10^{-15}$ s: processor speed
- $10^{-10}$ s: flash
- $10^{-5}$ s
- 1 s
- $10^5$ s: month
- $10^{10}$ s: end of last ice age
- $10^{15}$ s: age of universe
pump-probe experiment
outline

- introduction: elementary excitations in solids
- charge carrier dynamics in metals and semiconductors
- surface femtochemistry
coupling of electrons, spins, and phonons

elementary scattering processes and energy flow:

- electron-electron scattering
- electron-phonon coupling, $\tau_{e-ph}$
- electron-magnon coupling, $\tau_{e-magn}$
- spin-lattice relaxation, phonon-magnon scattering

$h \nu (~eV)$

http://www.fhi-berlin.mpg.de/pc/electrondynamix
elementary excitations

- single (quasi)-particle excitations:
  - *e.g.* photoholes, injected excess electrons, ...

- two-particle excitations:
  - *e.g.* excitons, Cooper pairs, ...

- collective excitations:
  - *e.g.* magnons, plasmons, phonons, polariton, ...

![Spin wave diagram](http://www.fhi-berlin.mpg.de/pc/electrondynamix)
electron thermalization

at high excitation densities: description by distribution function and time evolution, e.g., according Boltzmann equation

electrons in a metal

fs-laser excitation

t = 0

transient electron distribution function
(assuming rapid decay of coherence)

elementary processes:
  - electronic polarization
  - dephasing/ optical absorption
  - electron thermalization
  - cooling by e-ph coupling, heat transport

http://www.fhi-berlin.mpg.de/pc/electronodynamix
electron thermalization

at high excitation densities: description by distribution function and time evolution, e.g., according Boltzmann equation

\[ f(E) = \frac{1}{e^{\frac{E - E_F}{kT_{el}}} + 1} \]

elementary processes:
- electronic polarization
- dephasing/ optical absorption
- electron thermalization
- cooling by e-ph coupling, heat transport

transient electron distribution function
(assuming rapid decay of coherence)

W.S. Fann, R. Storz, H.W. K. Tom, J.Bokor PRB 46 (1992), 13592
photoabsorption in a metal

elementary scattering processes:

① electron-electron scattering
② electron-phonon, electron-magnon scattering, ....

lifetime of an excited electron above the Fermi sea

- Fermi liquid theory (Landau 1957)
- solution for homogeneous electron gas, self energy (Quinn & Ferell 1958)

screened Coulomb interaction:

\[ W(q, \omega) = \frac{V_q}{\varepsilon(q, \omega)} \]
screening in metals

\[ \tau \sim \omega_p^{-1} \]

\((10^{-16} \text{ s in metals})\)
quasiparticles

fundamental concept in condensed-matter physics:

system of interacting real particles acts as if it were composed of weakly interacting fictitious bodies (quasiparticles)

bare particle + ‘cloud’ of other particles = quasiparticle

one many-body problem $\Rightarrow$ multiple one-body problems
Interactions between quasiparticles limit how long the corresponding quantum states retain their identity, i.e., the lifetime of the excitation.

In combination with the velocity, this lifetime determines the mean free path, a measure of the interaction in the solid.

**lifetime-determining factors:**

- initial state (energy, momentum)
- final state (“phase space”)
- screening (response function)
outline

- introduction: elementary excitations in solids
- charge carrier dynamics in metals and semiconductors
- molecule dynamics at surfaces
image potential states at metal surfaces

Echenique & Pendry (1978)
classical image potential:

\[ V(z) = E_{\text{vac}} - \frac{e^2}{4z} \]

binding energy (Rydberg series):

\[ E_n = E_{\text{vac}} - \frac{0.85 \text{ eV}}{(n + a)^2}, \quad (n = 1, 2, \ldots) \]

\[ a = (1 - \phi_c / \pi) / 2 \quad \text{(quantum defect)} \]
probing the energy levels: photoemission

- photoelectron spectroscopy:
  - absolute binding energies
  - surface sensitivity
  - UHV conditions

真空能级 $E_{\text{vac}}$
费米能级 $E_{\text{F}}$
价电子能级
核心能级
工作函数 $\Phi$

2PPE spectroscopy

2-photon photoelectron spectroscopy
experimental setup I
laser setup

Verdi V18
Micra < 40 fs, 4 nJ/pulse @ 76 MHz

RegA 9050
< 40 fs, 3 μJ/pulse @ 300 kHz

stretcher

compressor

NOPA
< 20 fs,

OPA 9450
< 60 fs,

200 nm
275 nm
400 nm
800 nm
480-700 nm
240-350 nm

http://www.fhi-berlin.mpg.de/pc/electronodynamix
2PPE of image potential states

Berthold et al., PRL 88, (2002) 056805

courtesy: Ulrich Höfer, Marburg
time-resolved 2PPE of image potential states

\[ E_B = \hbar \omega_b - E_{\text{kin}} \]

\[ E_{\text{Vac}} \]

\[ h \omega_b \]

\[ |2> \]

\[ |1> \]

\[ E_{\text{kin}} \]

\[ n=1 \]

\[ n=2 \]

\[ n=3,4,\ldots \]

[Graph showing binding energy vs. pump-probe delay]
time-resolved 2PPE of image potential states

- direct measurement of the lifetime using 2PPE
- excellent agreement with many-body theory (GW approximation)


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ferromagnetic surfaces: spin splitting

origin: different density of states of majority and minority electrons

Passek et al., PRL 75, 2746 (1995)
Aeschlimann et al., PRL 79, 5158 (1997)
spin-, angle-, and energy-resolved 2PPE

example: 3ML Fe film on Cu(100)

Schmidt et al., PRL 95, 107402 (2005)
spin-dependent image state lifetimes

Passek et al., PRL 75, 2746 (1995)
Aeschlimann et al., PRL 79, 5158 (1997)
Schmidt et al., PRL 95, 107402 (2005)
Magnon-enhanced intraband scattering

Schmidt et al., PRL 95, 107402 (2005)
• potential step at the surface: electrons leaking into the vacuum
• band bending & adsorption: change of surface dipole
zincoxide: a promising challenge

- **inorganic semiconductor: ZnO**
  - wide band gap semiconductor
  - transparent
  - high carrier mobility
  - room temperature luminescence
  - wurtzite structure
  - two polar, one non-polar
  - low-index surface

Is the pristine ZnO(10-10) surface stable?

- hydrogen termination probable
- potential metalicity of the ZnO(10-10) surface:
  
  Wang et al., PRL 95, 266104 (2005)
hydrogen termination

Fermi edge

downward shifted CBM

secondary cut off

http://www.fhi-berlin.mpg.de/orpc/electronfundamix
time-resolved spectroscopy

Tisdale et al., JPC C 112, 14682 (2008)

\[ \tau = 225 \pm 15 \text{ fs} \]

\[ \frac{I_{pk}}{I_{bg}} = 1.90 \]

Intensity (cts/sec x 10^3)

Pump-probe delay (fs)

(b)

Lifetime (fs)

\[ E - E_{CBM} (\text{eV}) \]
time-resolved spectroscopy

- fast initial dynamics
- slow relaxation (~100 ps)
time-resolved spectroscopy

Tisdale et al., JPC C 112, 14682 (2008)

\[ \tau = 225 \pm 15 \text{ fs} \]

\[ I_{pk}/I_{bg} = 1.90 \]
summary

Further reading:

- introduction: elementary excitations in solids
- charge carrier dynamics in metals and semiconductors
- molecule dynamics at surfaces

http://www.fhi-berlin.mpg.de/pc/electronodynamix
outline

- introduction: elementary excitations in solids
- charge carrier dynamics in metals and semiconductors
- molecule dynamics at surfaces
timescales of chemical reactions

temporal evolution from reactants to products:

- dynamics of the transition state
- goal: microscopic understanding of elementary steps and dynamics of energy transfer

- femtosecond laser pulses for direct observation in time domain
- key concept: dynamics on Born-Oppenheimer potential energy surfaces
- breakdown of the BO approximation near (avoided) crossings

- non-adiabatic coupling between different electronic states
surface reactions and heterogeneous catalysis

heterogeneous catalysis:
- reduced reaction barrier at surfaces
- prominent examples:
  - automotive catalyst
  - ammonia synthesis

chemical reactions typically occur in the electronic ground state
role of electronic excitations?

dissociative adsorption
rate-limiting step:

dissociative desorption
goal: microscopic understanding of surface reactions
femtochemistry at metal surfaces

ultrafast energy redistribution after optical excitation of a metal surface

fs-laser pulse

- optically thin monolayer
- substrate-mediated excitations dominate

coupling to adsorbate vibrations induces reaction

reminder: fs-laser excitation in metals

fs-laser excitation of electrons in a metal

dephasing / optical absorption

elementary processes:
electronic polarization
cooling by e-ph coupling, heat transport
electron thermalization

transient electron distribution function
(assuming rapid decay of coherence)

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

coupling to adsorbate motions

fs-laser excitation of electrons in a metal

DIET - Desorption Induced by Electronic Transitions
DIMET - Desorption Induced by Multiple Electronic Transitions

\( \tau \sim 1-10 \text{ fs} \)

* MGR model (Menzel, Gomer, Redhead)
reaction mechanism

**Electron-mediated**

- Reaction coordinate
- Reaction coordinate

**Phonon-mediated**

- adsorbate
- substrate

How to distinguish?
2-pulse correlation

How to distinguish electron and phonon mediated mechanism?

$T_{el}$ and $T_{ph}$ for 2 pulse excitation with time delay $\Delta t$

- Phonon-mediated: slow response
- Electron-mediated: fast response

![Graphs showing surface temperature and reaction yield over pulse-pulse delay](http://www.fhi-berlin.mpg.de/p/lectronodynamix)
experimental setup II

"Feulner cup" detector

Ti:sapphire oscillator + amplifier
- 4 mJ, 110 fs, 20-400 Hz, 800 nm

QMS ionisation volume

QMS

H₂/D₂

CCD

2 equally intense pulses

pulse profile diagnostics

http://www.fhi-berlin.mpg.de/pc/electrodynamix
H+H recombinative desorption

\[ Y = A \exp \left(-\frac{E_a}{k_B T}\right) \]

\[ \langle E_{\text{kin}} \rangle / 2k_B \]

\[ \text{H}_2: 2100 \text{ K} \]

\[ \text{D}_2: 1700 \text{ K} \]
2-pulse correlation

Coupled heat baths with $T_{el}$, $T_{ph}$, $T_{ads}$

Rate $\sim e^{-E_a/k_b T_{ads}}$

Two-Temperature Model

Brandbyge et al., PRB 52, 6042 (1995)

H$_2$ yield [a.u.] vs. pulse-pulse delay [ps]

FWHM = 1.1 ps

http://www.fhi-berlin.mpg.de/pc/electronodynamix
Energy transfer by coupling between adsorbate vibration and metal electrons

Electronic friction: hot electrons, \( E_{\text{Fermi}} \) level

Coupling rate \( \eta \approx \frac{1}{\tau_{\text{el}}} \sim \frac{1}{M} \)

- energy transfer by coupling between adsorbate vibration and metal electrons
- example: CO desorption from Cu(100)

Struck et al., *PRL* 77, 4576 (1996)

\[ Y \sim <F>^3 \]
2-pulse correlation

yield weighted fluence (J/m^2)

isotope ratio Y(H_2)/Y(D_2)

2-pulse correlation

origin of isotope effect: DIMET

H_2 vs D_2

lifetime $\tau$ (~ 1–10 fs)

electronically excited PES

ground state PES of substrate-adsorbate-complex

Ru-H/D distance

http://www.fhi-berlin.mpg.de/pc/electronodynamix
real-time probing of vibrational dynamics

- so far: only the (desorbing) reaction products probed
  → surface-sensitive non-linear optics (SHG, SFG):
  direct look inside the excited adlayer
vibrational spectroscopy

IR absorption spectroscopy (FTIR)
- background
- IR detection
- optical linear technique

vibrational sum-frequency generation (SFG)
- no background
- visible detection
- sensitivity: 0.001 ML
- short pulses: time resolution
- surface/interface sensitive

Pot. Energy

v=0
v=1
v=2

C-O distance

5 mm + 800 nm = 690 nm
vibrational SFG spectroscopy

second order non-linear optical process

\[ P^{(2)}_{\omega_{SFG}} = \chi^{(2)}_{\omega_{SFG}} E_{\omega_{IR}} E_{\omega_{VIS}} \]

→ surface sensitive method: SFG is symmetry forbidden in isotropic (bulk) media (dipole approximation)

time-resolved SFG as molecule-specific probe of surface reactions

- no background
- visible detection
- sensitivity: 0.001 ML
- short pulses: time resolution
- surface/interface sensitive

http://www.fhi-berlin.mpg.de/pc/electronodynamics

5 mm + 800 nm = 690 nm

IR

SFG

Vis

Pot. Energy

C-O distance

v=0

v=1

v=2
broadband IR vibrational SFG spectroscopy

spectrally broad fs-IR pulse + spectrally narrow VIS upconversion pulse

experimental setup III

Ti:sapphire oscillator + amplifier
4 mJ, 800 nm, 110 fs, 20-400 Hz,

OPG/OPA (TOPAS)
2.5-10 μm, 20-30 μJ

pump pulse

pulse shaper
FWHM 7 cm⁻¹, 7 μJ

narrow band
VIS pulse
tunable
IR pulse

spectrometer
CCD camera
multi-channel detection

Ru(001)

SFG probe
time-resolved SFG of CO/Ru during desorption

- pronounced transient red shift
- linewidth broadening
- decrease of intensity

**problems:**
- dipole-dipole coupling in the adlayer
- small concentration of "products"

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Bonn et al., *PRL* 84, 4653 (2000)

T = 340 K, F = 55 J/m²

CO yield (a.u.)

Pump-Probe delay
-4.5 ps
-2.0 ps
-1.5 ps
-1.0 ps
-0.5 ps
0.5 ps
3.0 ps
23.0 ps
68.0 ps
168.0 ps

SFG intensity (a.u.)

IR wavenumber (cm⁻¹)

CO/Ru(001)

fs pump
optical probe

VIS
IR
CO
SFG

CO/Ru(001)
time-resolved SFG of CO/Ru during desorption

**calculation:**
- thermal excitation of frustrated translation
- anharmonic coupling to CO stretch mode

**low fluence:** good fit

**high fluence:**
- excitation and coupling to higher frequency modes

strong redshift indicates: frustrated rotation dominantes

summary

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