Pump-Probe Surface Chemistry at LCLS

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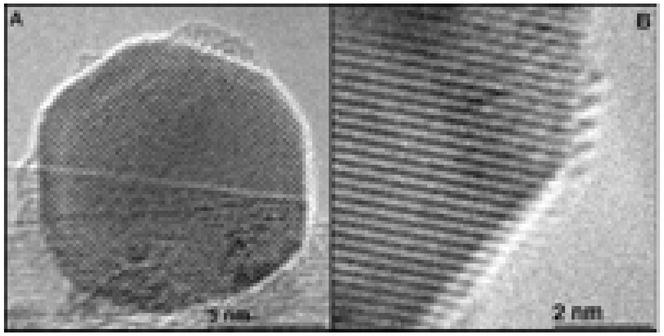
- Alan Luntz, Palo Alto, previous IBM
- Alec Wodtke, University of California, Santa Barbara
- Tony Heinz, Columbia University
- Hvrjo Petek, University of Pittsburg
- Dave Nelson, Livermore National Laboratory
- Hendrik Bluhm, Lawrence Berkeley National Laboratory
- Howard Padmore, ALS, Berkeley
- Martin Wolf, Frei Universität, Berlin, Germany
- Wilfred Wurth, DESY, Germany
- Andrew Hogdson, University of Liverpool, UK
- Geoff Thornton, Manchester University, UK
- Tony Hansson, Stockholm University, Sweden

Surface Chemistry

- 80% of all important chemical reactions takes place on interfaces
- Catalytic processes is the largest chemical industry
- Energy technology, fuel cells, splitting of water by solar
- Environmental science
- Semiconductor technology
- Biosurfaces

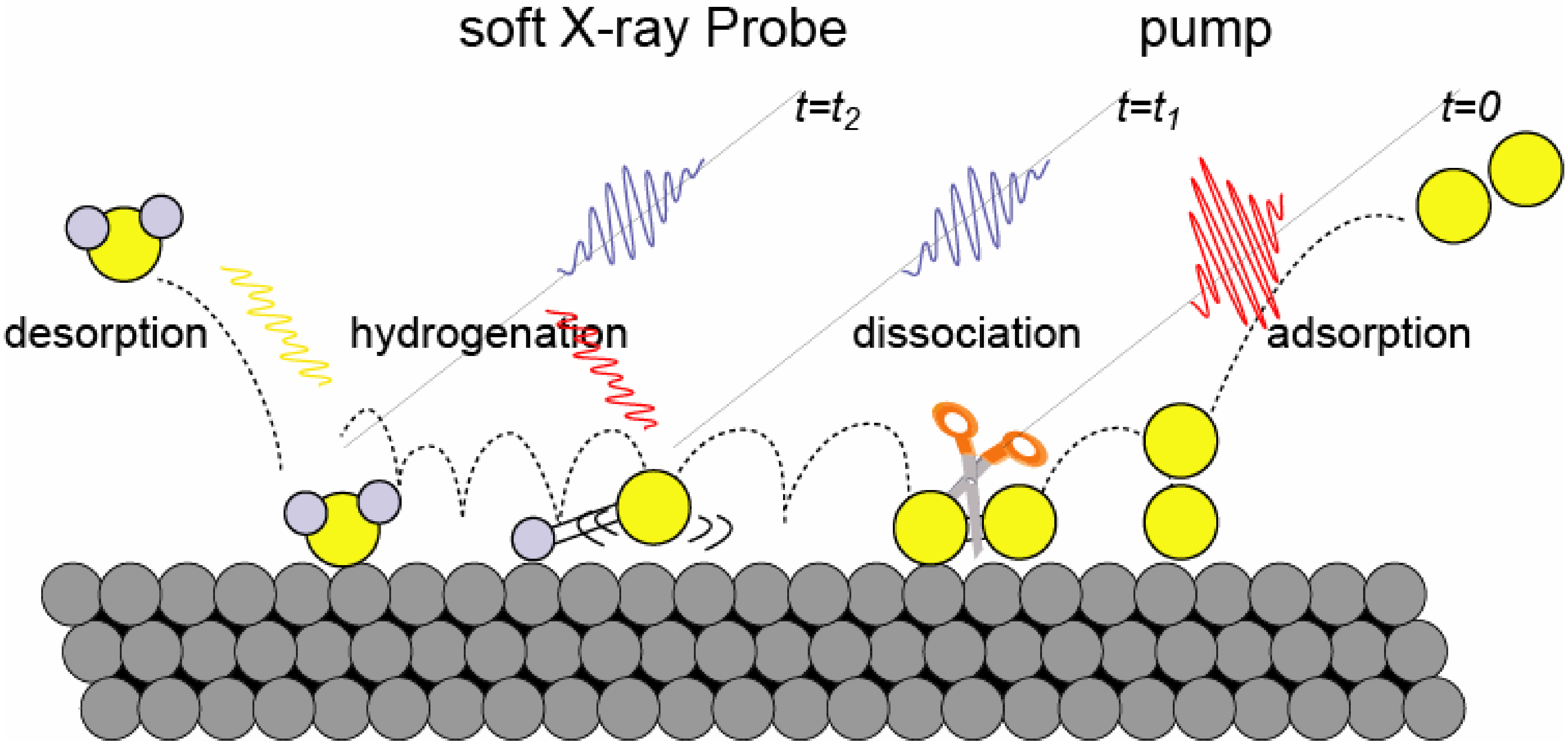
$N_2 + 3H_2 \leftrightarrows 2NH_3$ Haber-Bosch Process



Hansen et.al. Science 294, 1508 (2001)

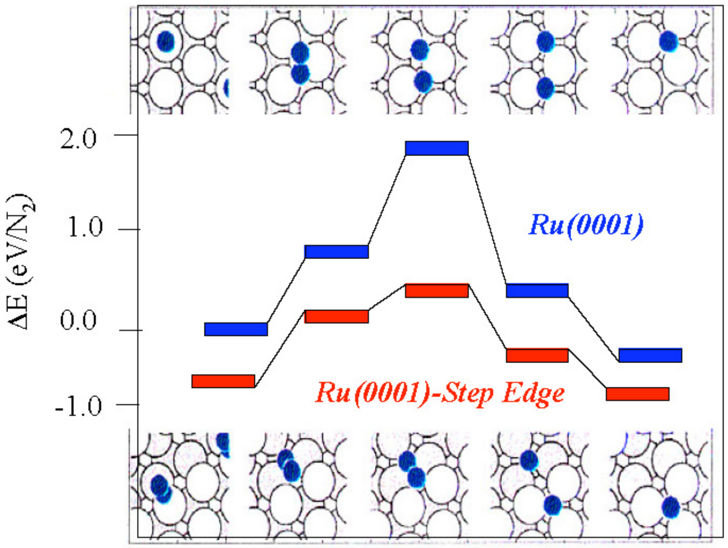
- The most important invention in the 20th century
- Saved 2 billion peoples life
- Consumes 2% of all energy in the world
- Fe and Ru catalyst
- Dissociation of N_2 rate limiting

Elementary Surface Reactions



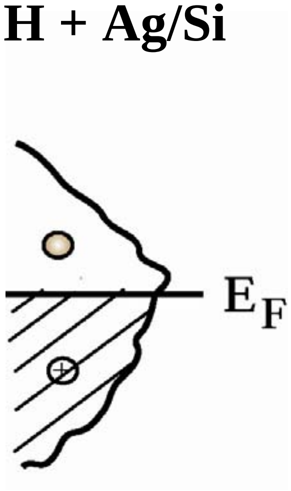
Non Adiabatic Processes

DFT theory



hot electrons from chemistry:

- **exoelectrons**
  Cl_2 + K, NO(v=15) + Cs/Au
- **vibrational de-excitation**
  --adsorbates: CO/Cu
  --scattering: NO/Au, H_2/Cu
  --associative desorption: N_2/Ru
- **chemicurrent**
  H + Ag/Si

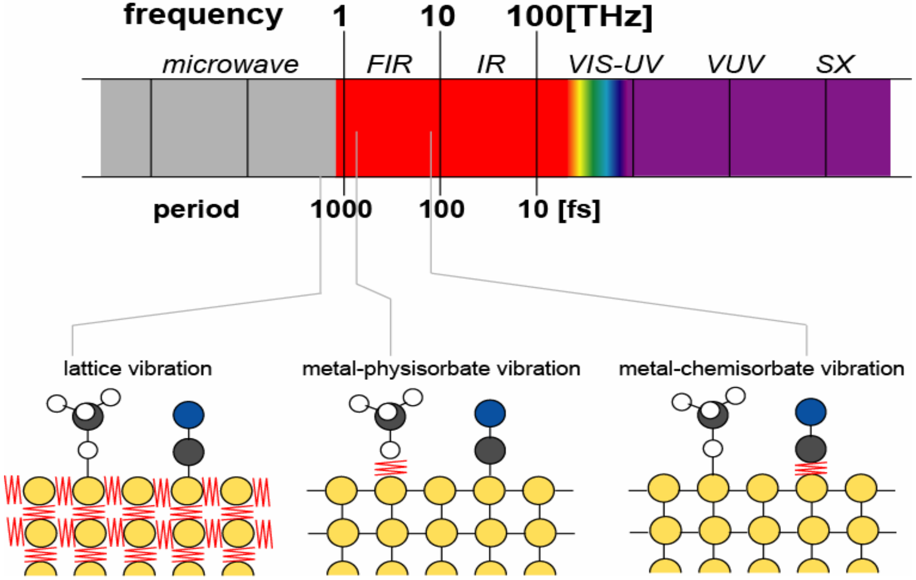


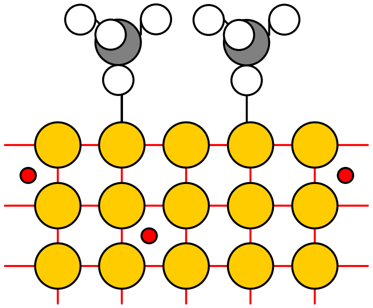
e-h pair excitations?
Energy Transfer

Pump

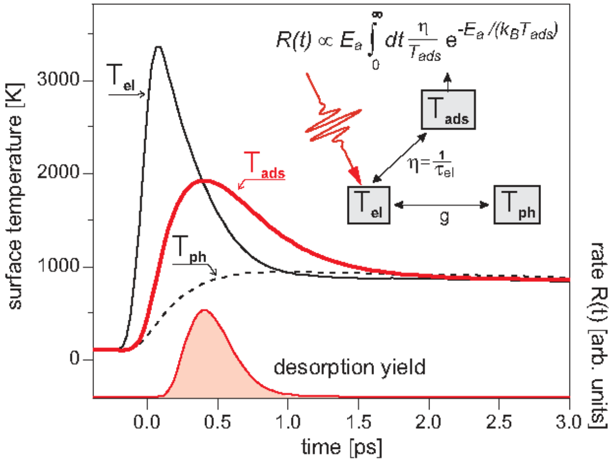
Temperature jump
via
1) Electron-hole pair excitation,
2) Phonon excitation,

required power:
5mJ per pulse at 800nm





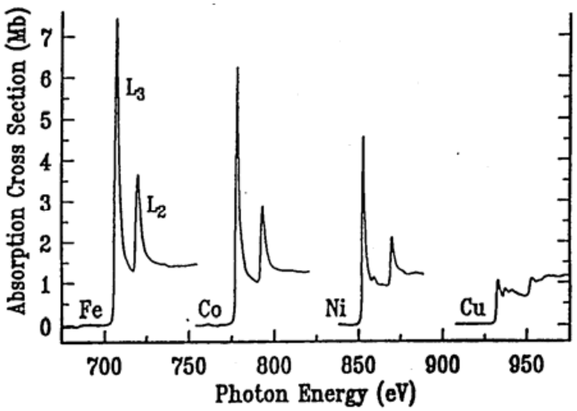
non-adiabatic vibronic-coupling



A. Luntz

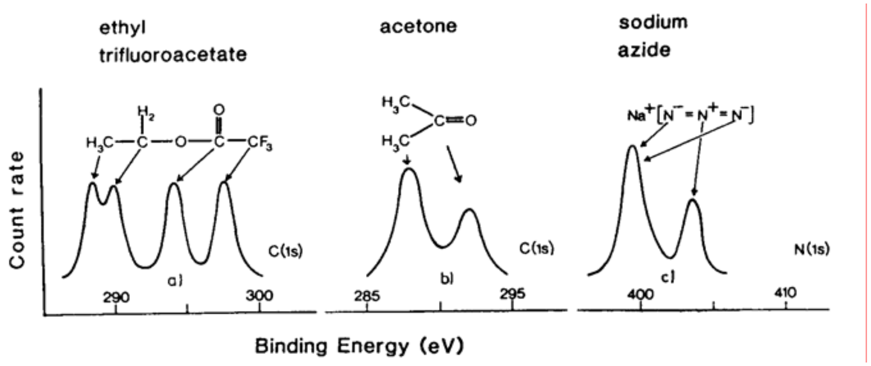
Atom Specific Probe

Element Sensitive



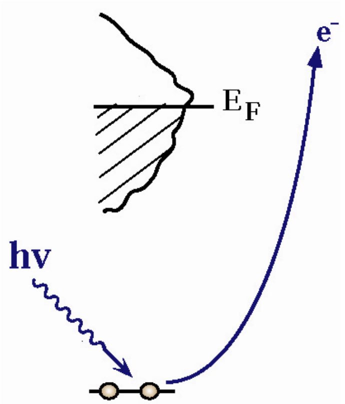
Stöhr et.al

Chemical Shifts

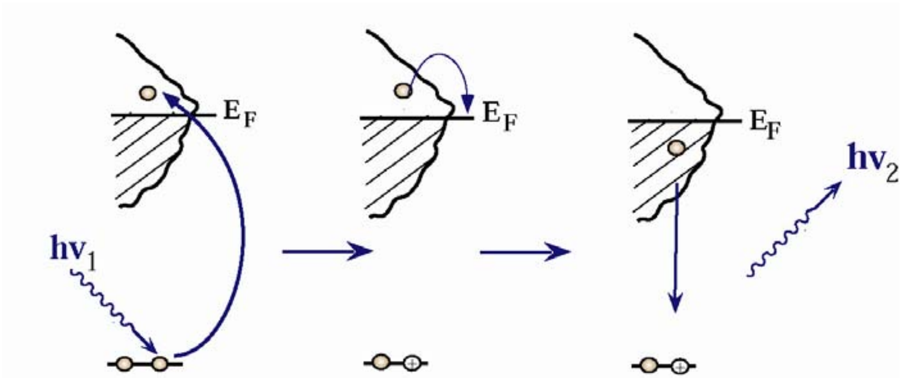


Hufner, Photoelectron Spectroscopy

Spectroscopies based on Fixed Incident Photon Energy

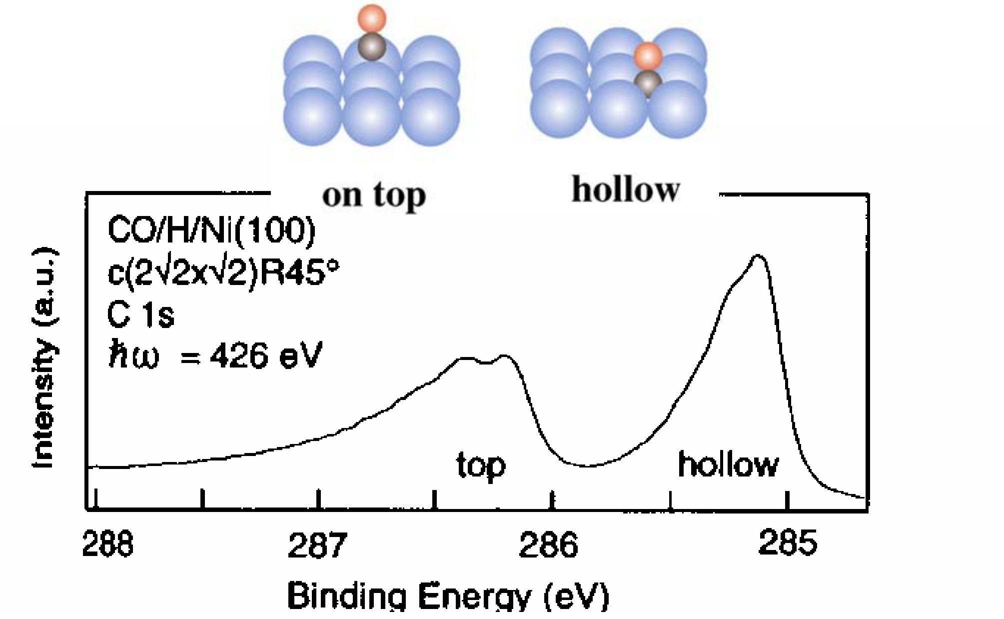


Core Level Photoelectron Spectroscopy

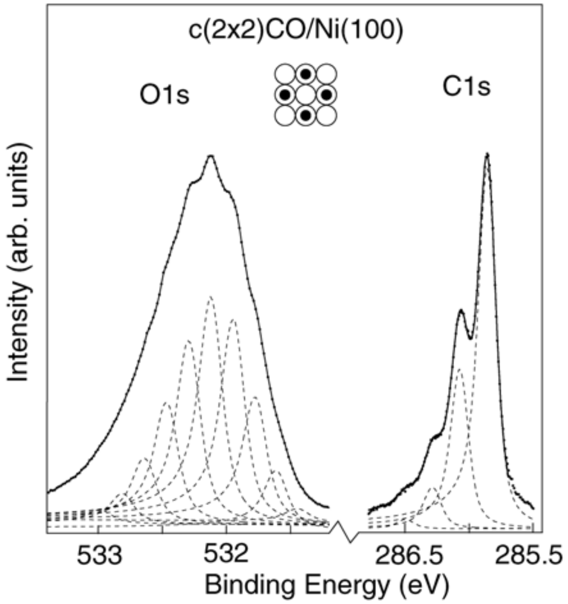


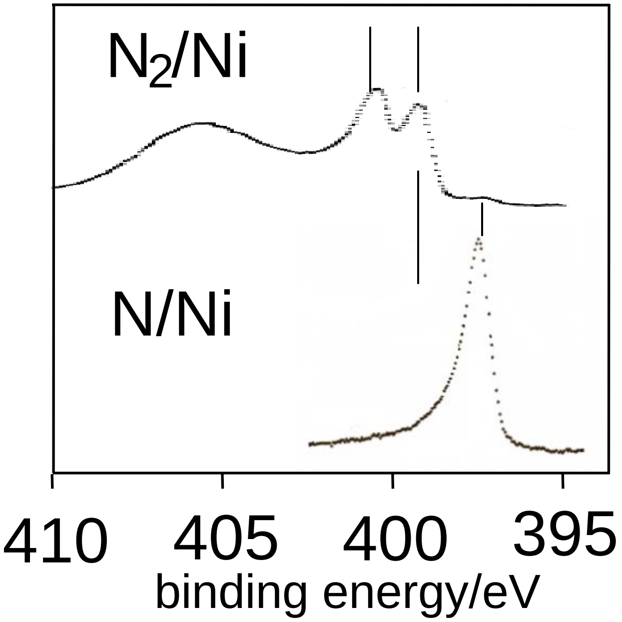
X-Ray Emission Spectroscopy

Core Level Shifts and Geometry



J. El spec. **126**, 3 (2002)

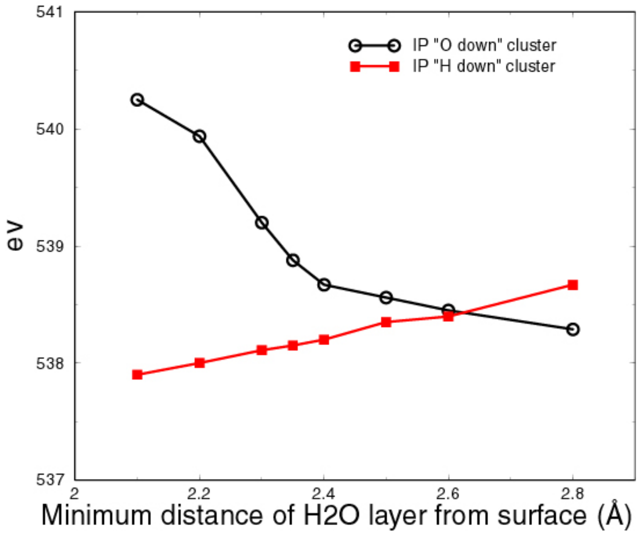




ΔE

1.5 eV

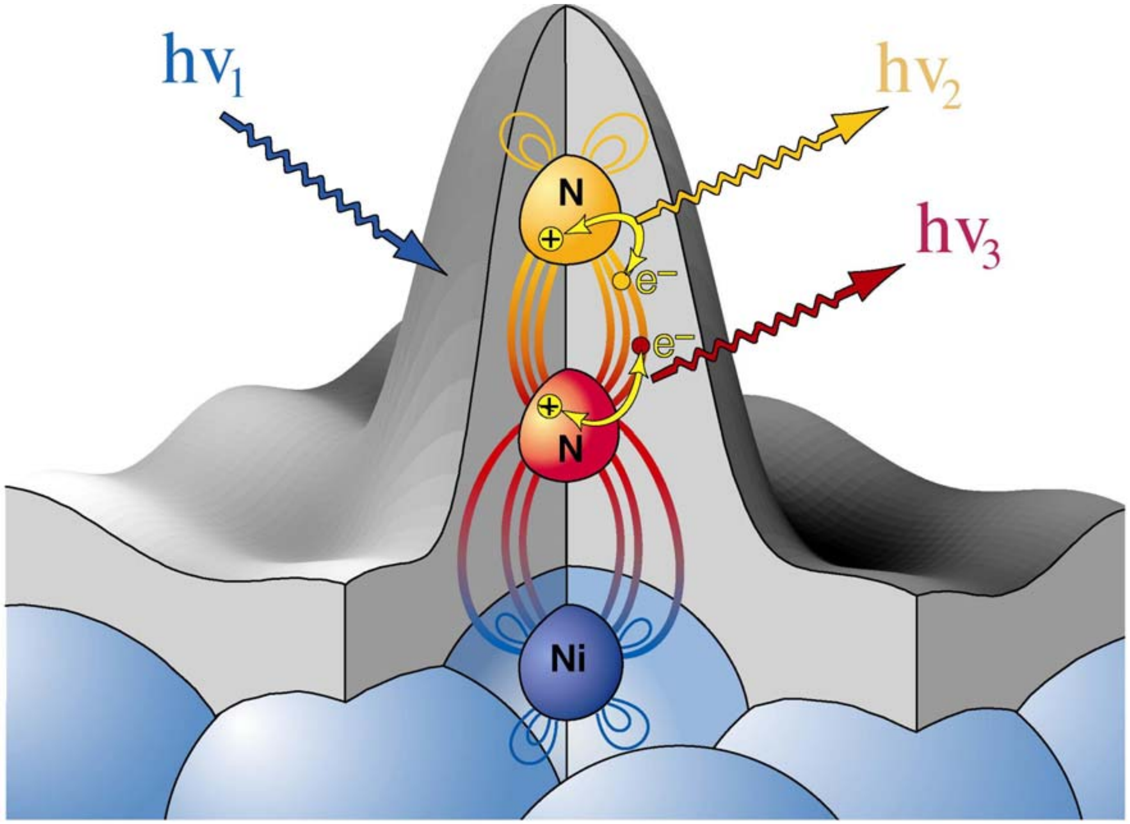
2.0 eV

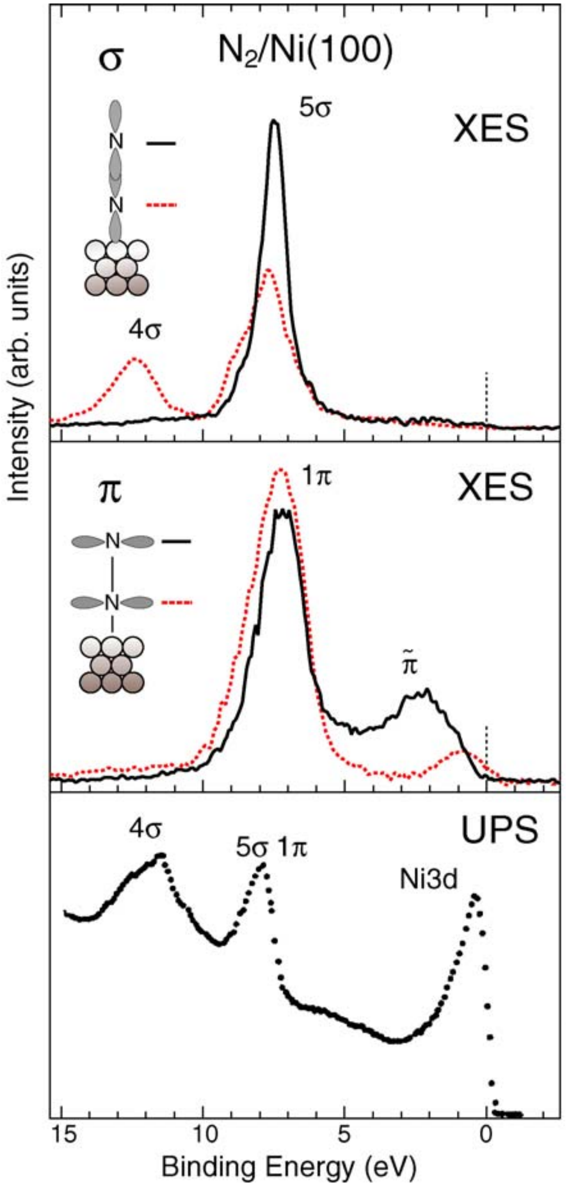


Phys.Rev.Lett. **89**, 276102 (2002)

X-ray Emission Spectroscopy

Atom specific probing



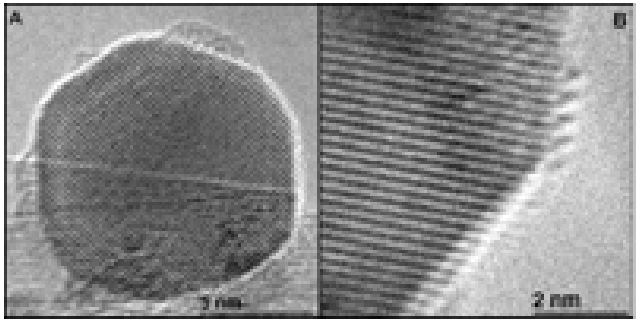


Phys. Rev. Lett. **78** (1997) 2847, *Surf. Sci. Reps.* **55** (2004) 49.

Femtosecond Chemistry

Haber-Bosch

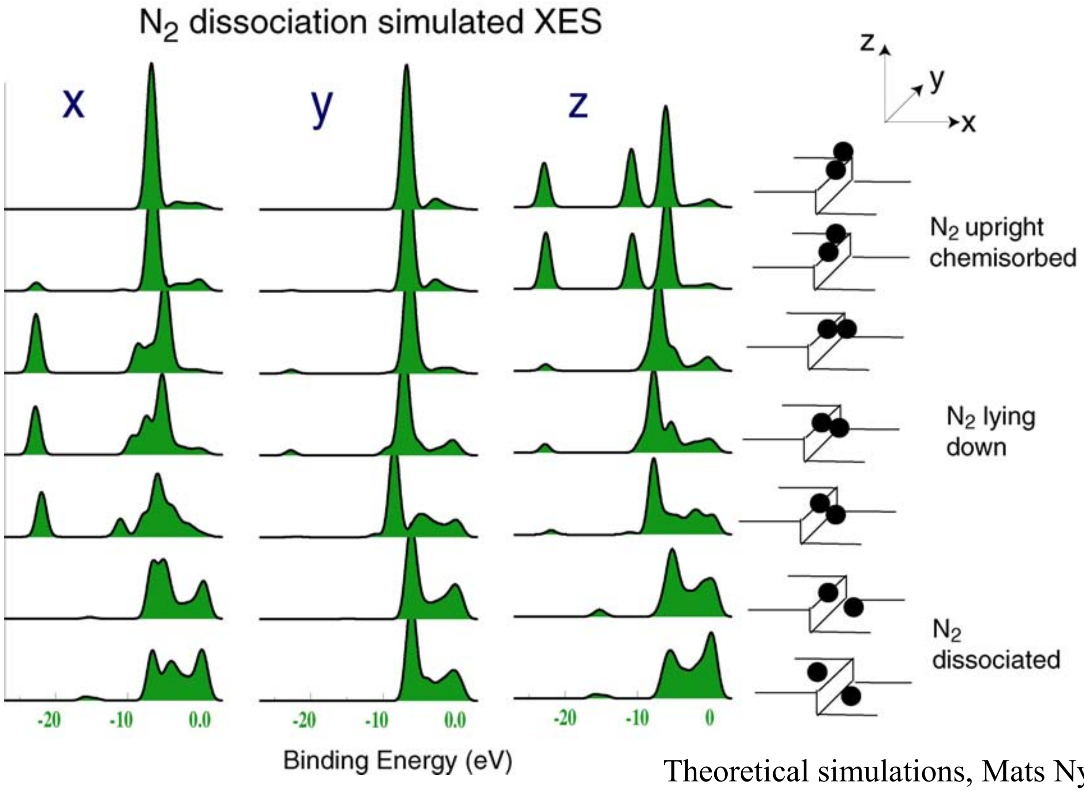
$N_2 + 3H_2 \rightarrow 2NH_3$



Hansen et.al. Science 294, 1508 (2001)

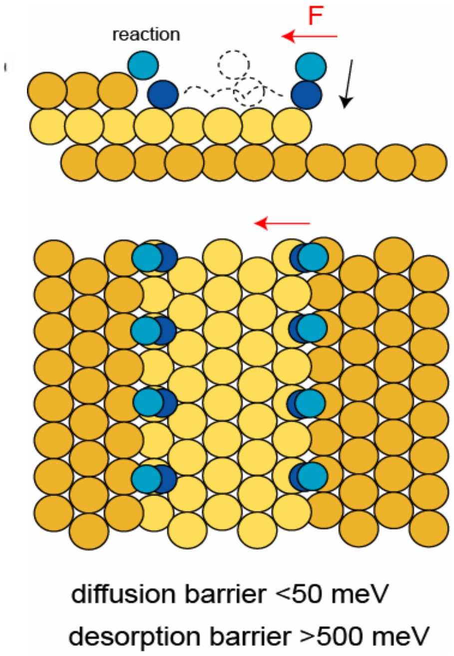
New Ru Catalyst

Active site at steps



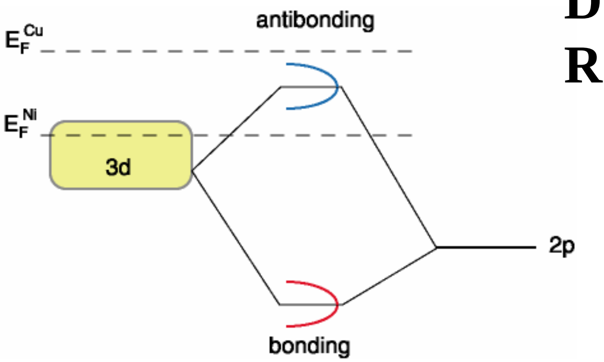
Both N atoms

Theoretical simulations, Mats Nyberg,
Stockholm University

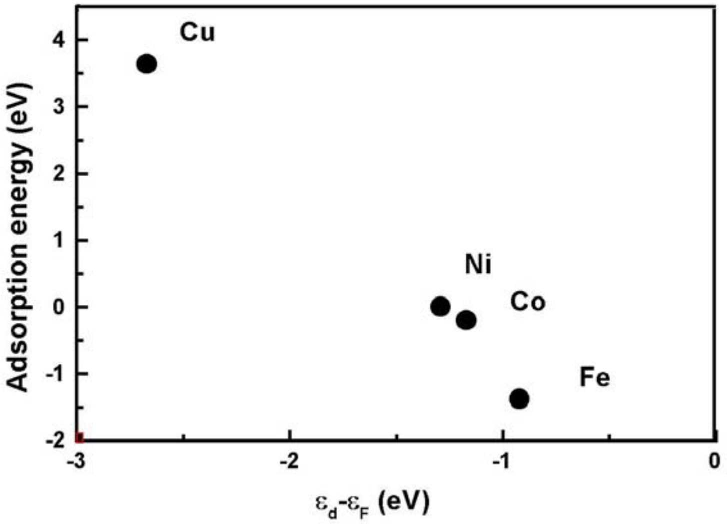


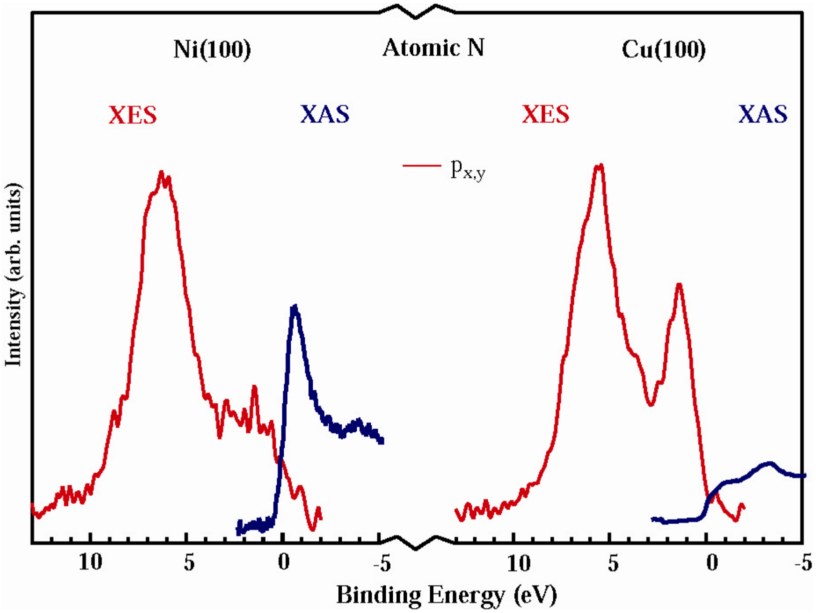
Potential First Experiment

Population of hot electrons on adsorbate
Antibonding states
Desorption
Reaction N +H ⟶ NH



Non Resonant Excited XES





Nilsson et. al, *Catal. Lett.* **100**, 111 (2005)

Potential Program

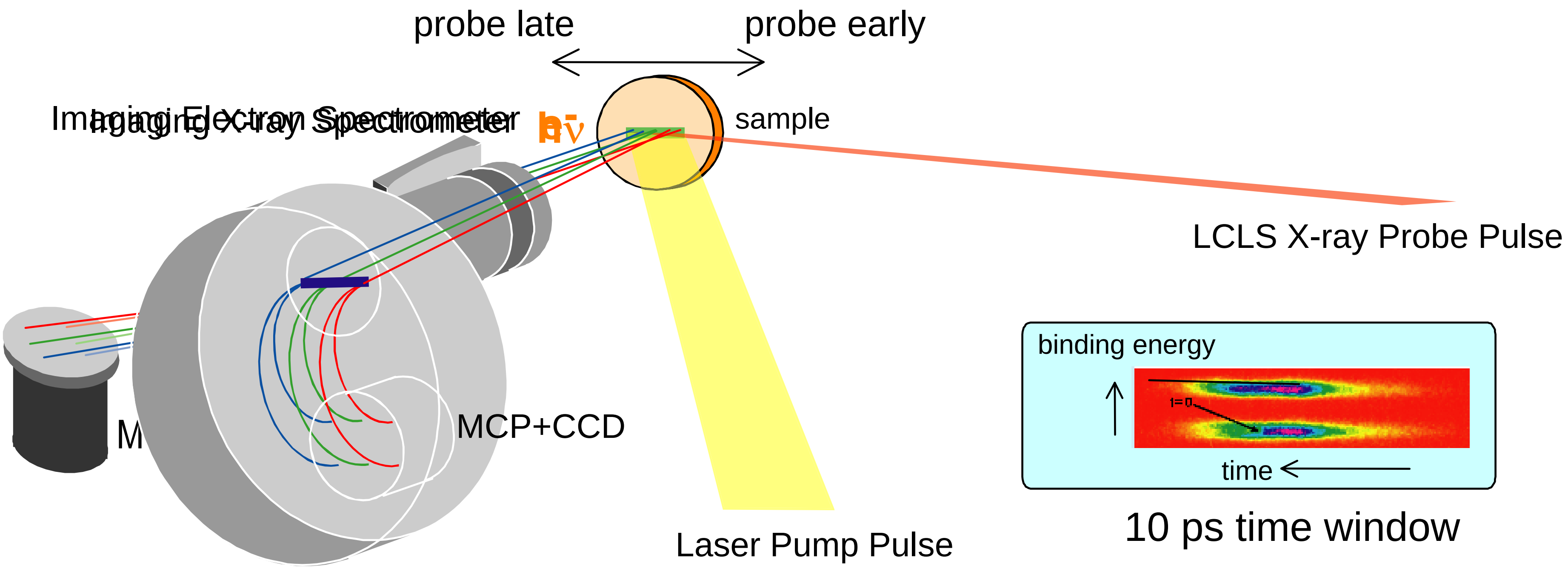
Catalysis

- N_2 Dissociation and N hydrogenation on Ni, Fe and Ru, **Ammonia Synthesis**
- O_2 Dissociation and O hydrogenation on Ni, Pt, **Fuel Cell Hydrogen**
- O Recommendation to O_2 on Ni, Pt and RuO_2, **Electrolysis Hydrogen**
- CH_4 dissociation and activation, **Steam Reforming Hydrogen**
- CO oxidation with O on Ru and Pt, **Exhaust Catalysts**
- CO and NO to CO_2 and N_2 on Rh, **Exhaust Catalysts**
- CO_2 and H_2 to methanol on Cu, **Methanol Synthesis**
- CO and H_2O on Cu, **Water Gas Shift for Hydrogen**

Other

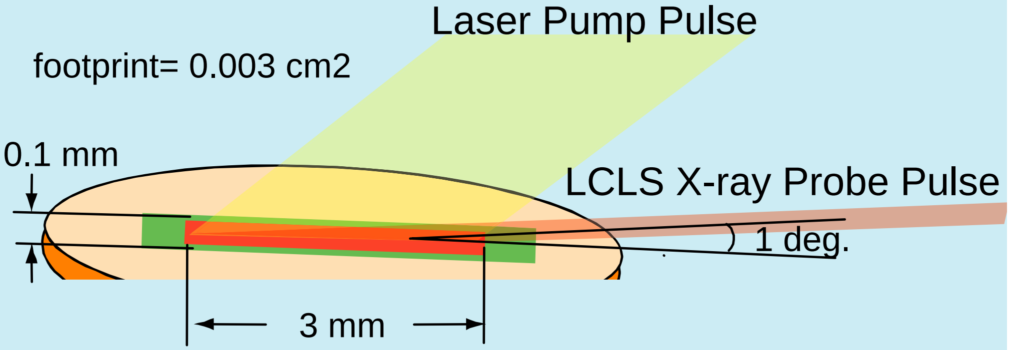
- Carrier Dynamics in semiconductors, **Solar Cell**
- TiO_2 photocatalysis, **Water Splitting for Hydrogen**
- Redox processes at environmental interfaces, **Environmental Science**
- Solvated electrons, **Radiation Chemistry**

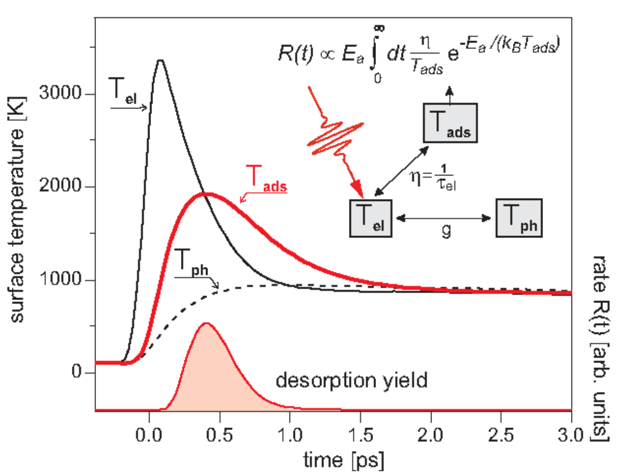
Measures complete time history around t=0 in single shot

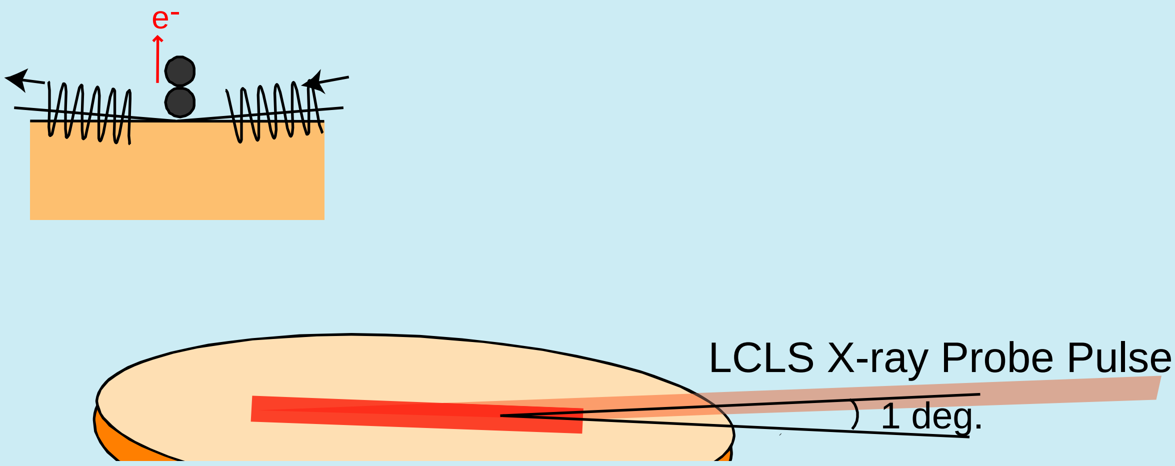


10 ps time window

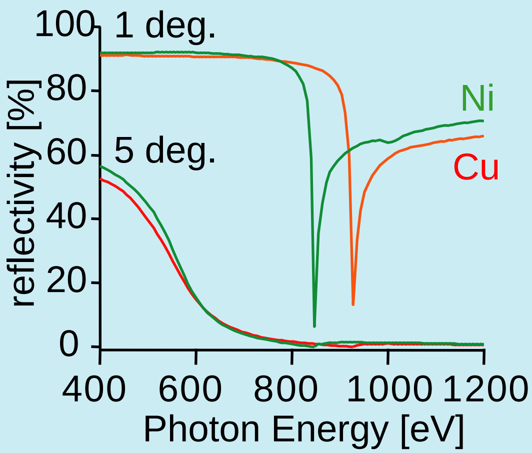
required laser power: 1-10 μJ/pulse

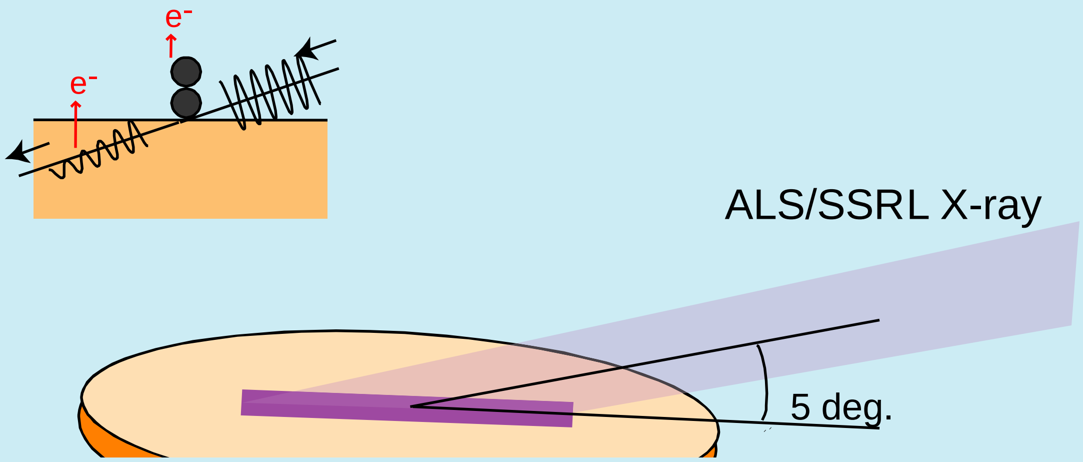






X-ray interaction with matter calculator
http://www-cxro.lbl.gov/optical_constants/





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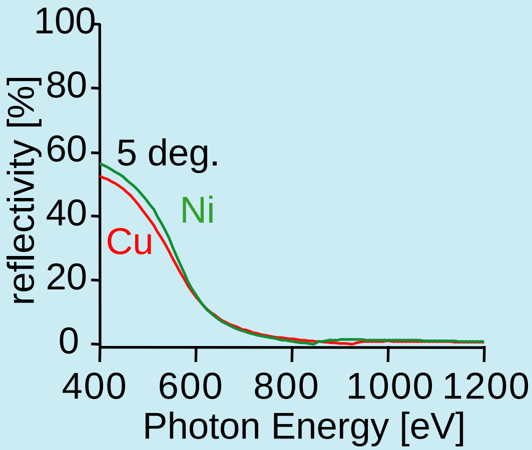


Count rate: ALS/SSRL and LCLS

ALS/SSRL: 10^{13} photons/sec

600 sec accumulation is necessary for XES!

LCLS: 10^{13} photons/shot

= 10^{15} photons/sec

6 sec accumulation for XES!

Radiation damage: ALS/SSRL and LCLS

Without scanning, the sample is seriously damaged!

ALS/SSRL

Several shots seriously damage the sample.

LCLS

Scanning is necessary: 10 micron/sec

ALS/SSRL

Scanning is necessary: 10 micron/shot =1 mm/sec.

LCLS

A large sample size is beneficial

10 micron/shot scan rate

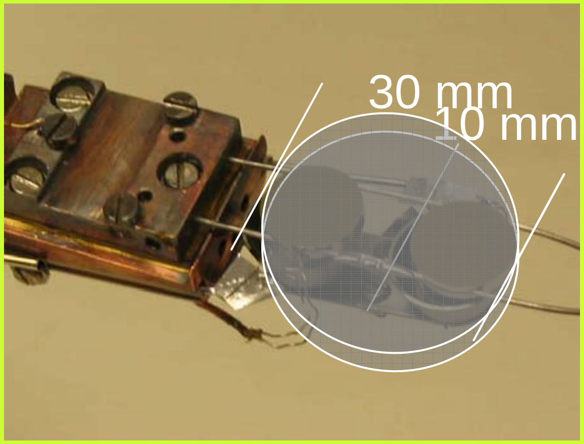
2000 shots accumulation

Improve spectrometer 50

10 x statistic as ALS/SSRL

but in 100 time frames

Need to prepare a large sample

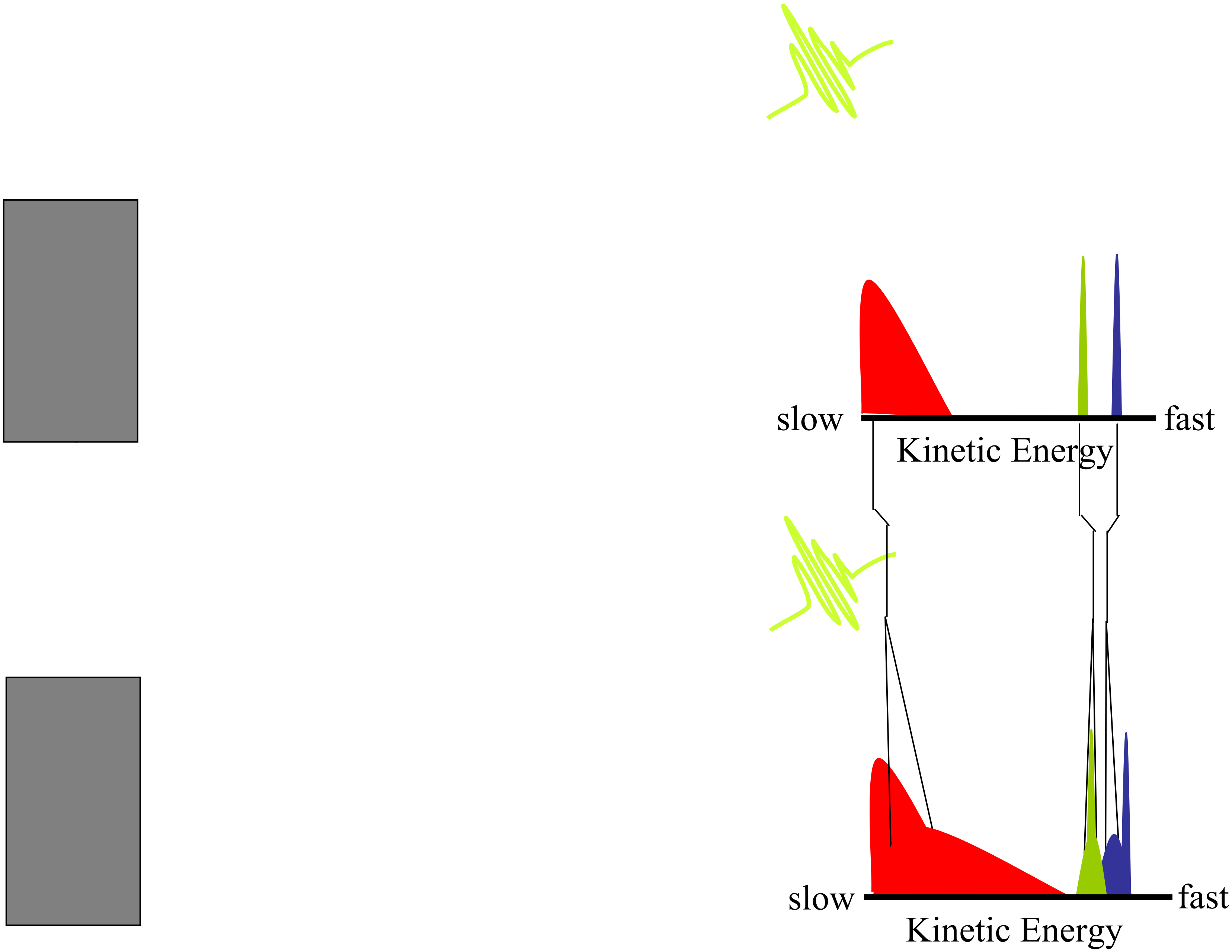


2000
shots

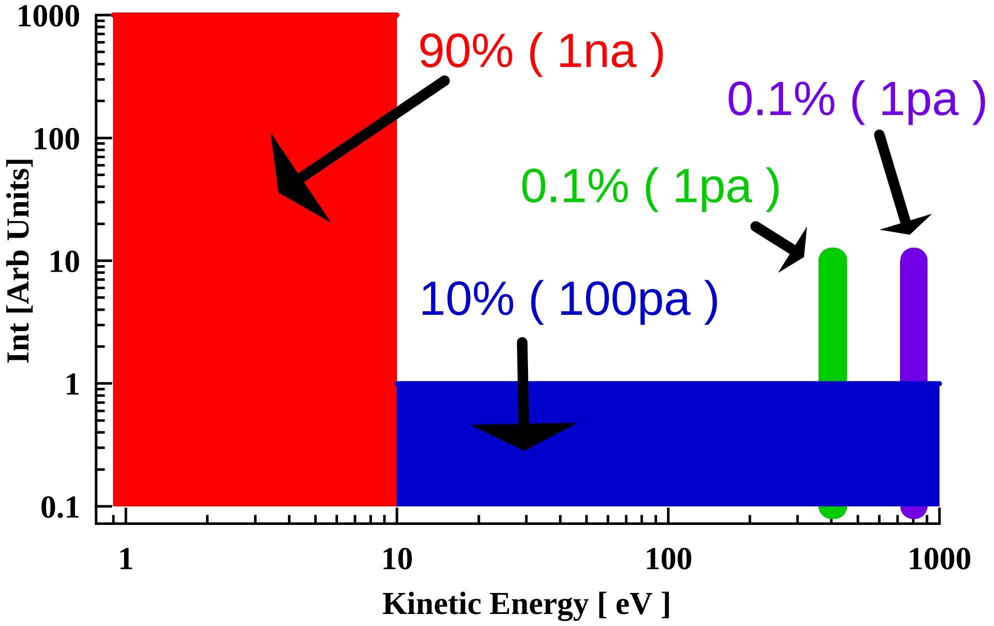
laser

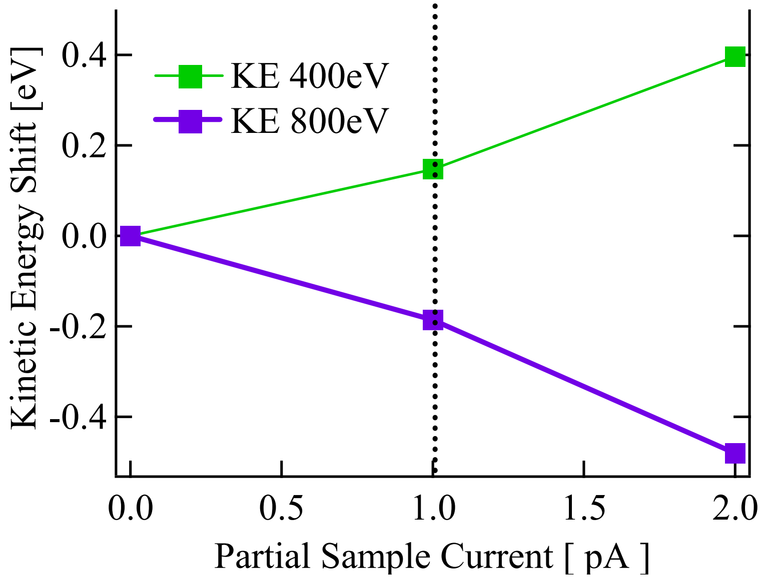
LCLS

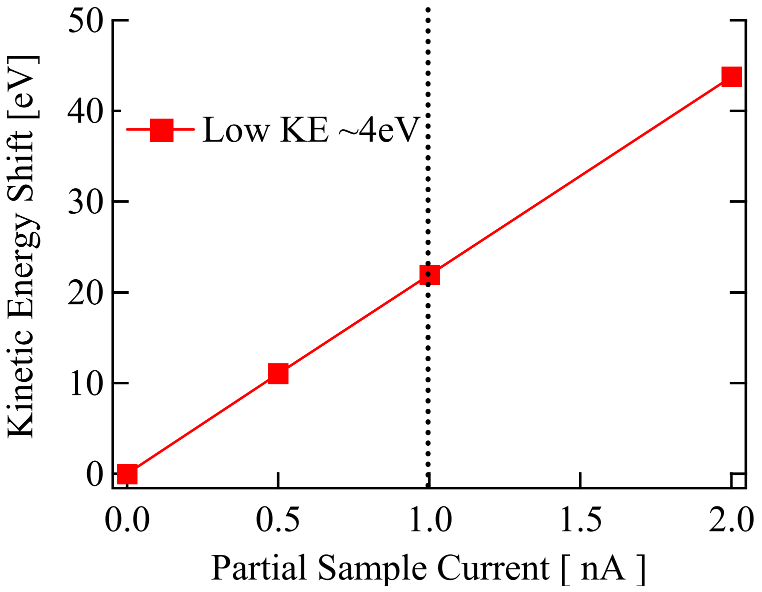
Space Charge Effect: Kinetic Energy Shift and Broadening

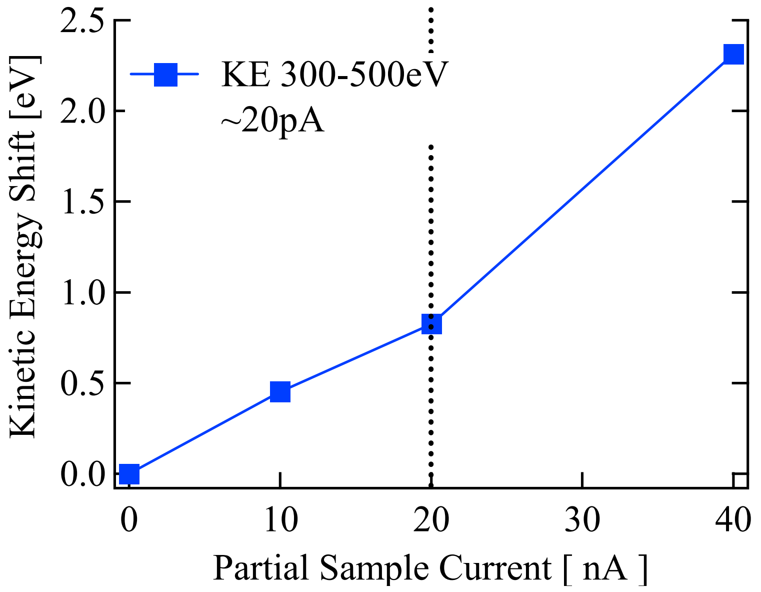


Energy Shift @ 10mm

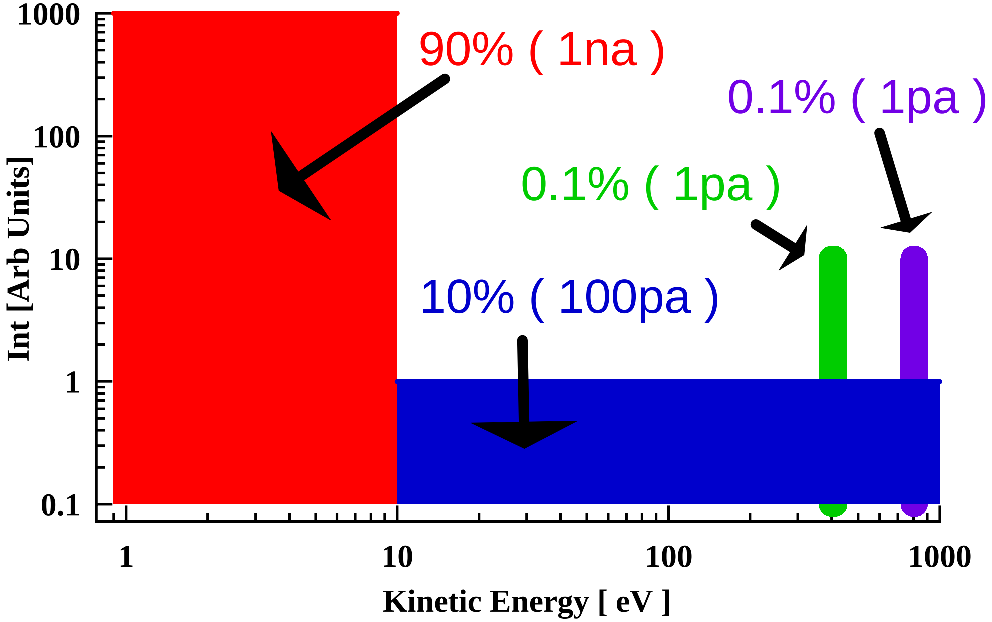


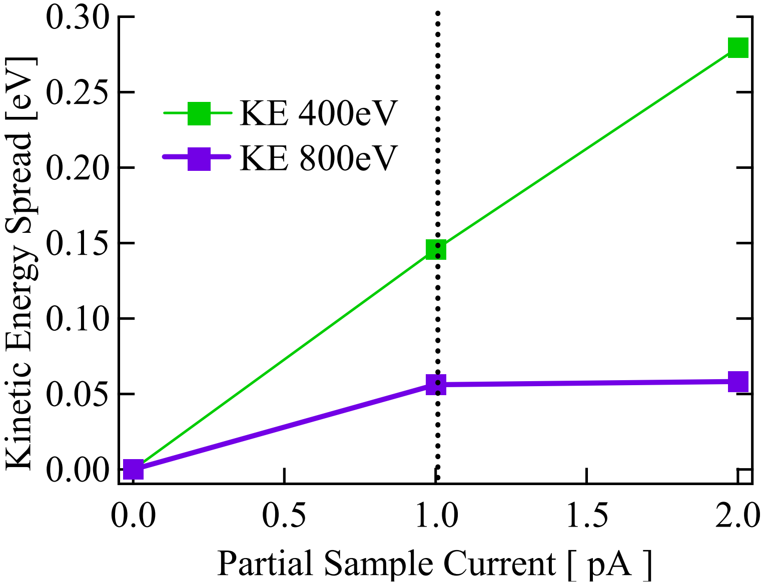


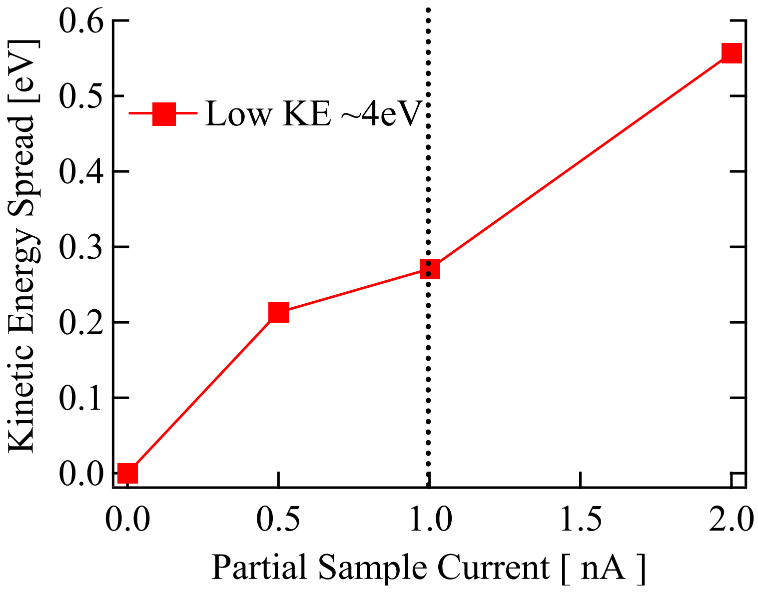


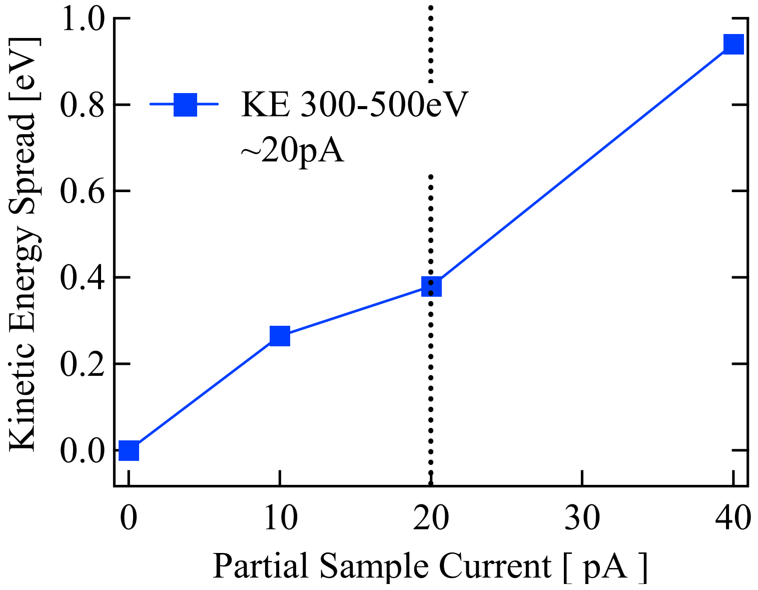


Energy Broadening @ 10mm









Space Charge Summary

- Experiments are **feasible at < 1nA**

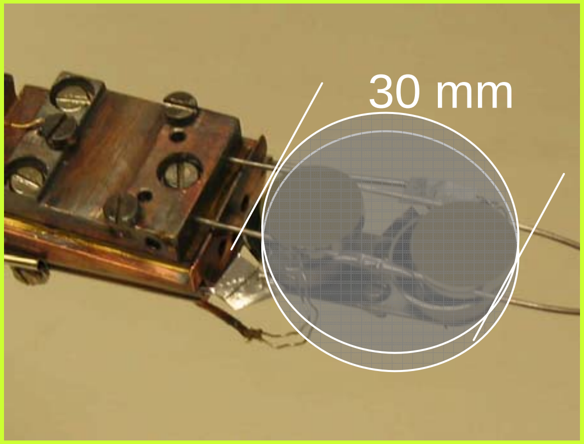
- Low KE => Energy Shift
- Same KE => Energy Broadening

- **1nA**: ~ **20eV** Eshift ~ **0.6eV** Ebroad
- **0.1nA**: ~ **2eV** Eshift ~ **0.1eV** Ebroad

Estimated PES count rate

5000 emitted electrons per shot in spectral region with 0.1 nA
10% detection efficiency, polarized light, Scienta spectrometer, R4000
500 electrons per shot in spectral region
50 time frames gives 10 counts per shot
1 counts on peak per shot and time frame with 1 eV FWHM

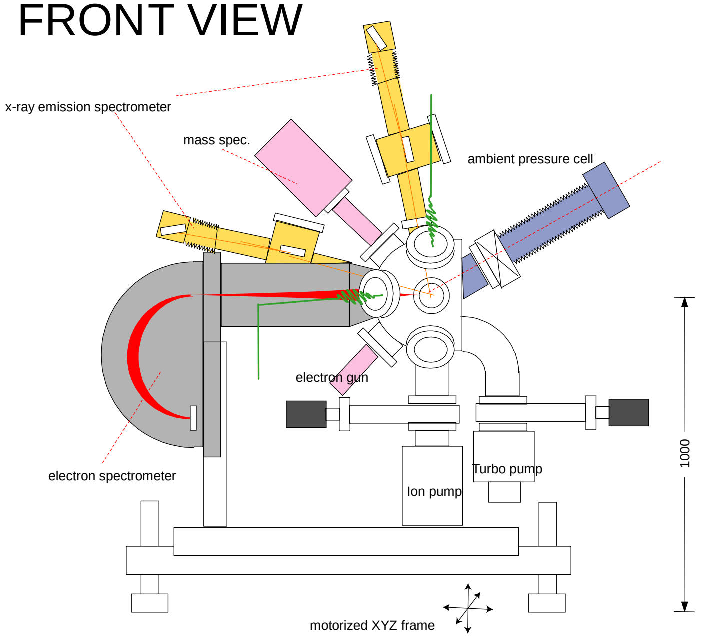
2000 counts on spectral peak
with 50 simultaneous times
in one surface preparation



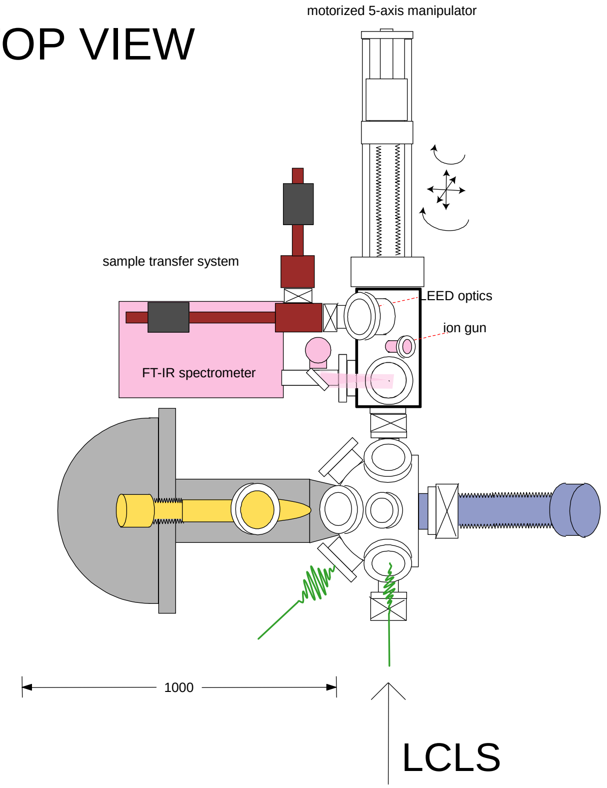
2000
shots

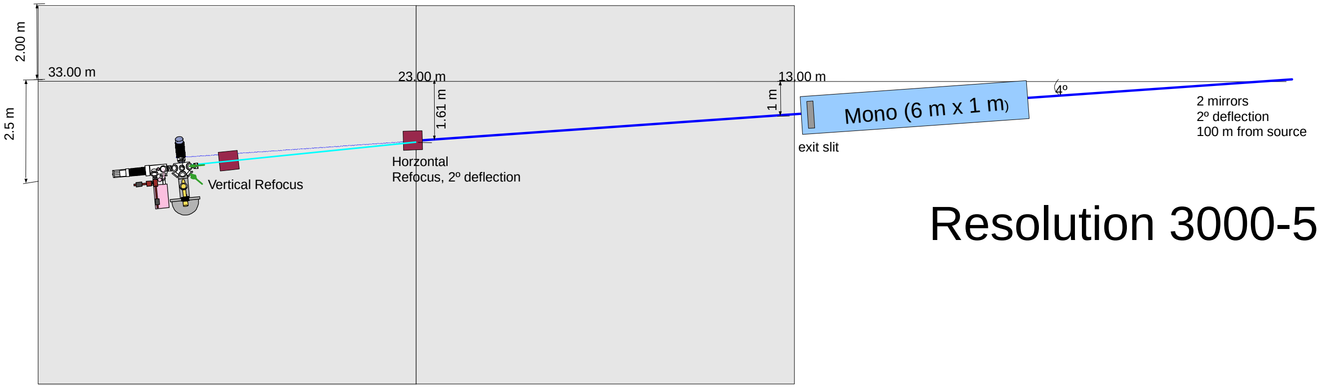
+ In reality electrons will be emitted in larger angle spread than assumed

FRONT VIEW



TOP VIEW





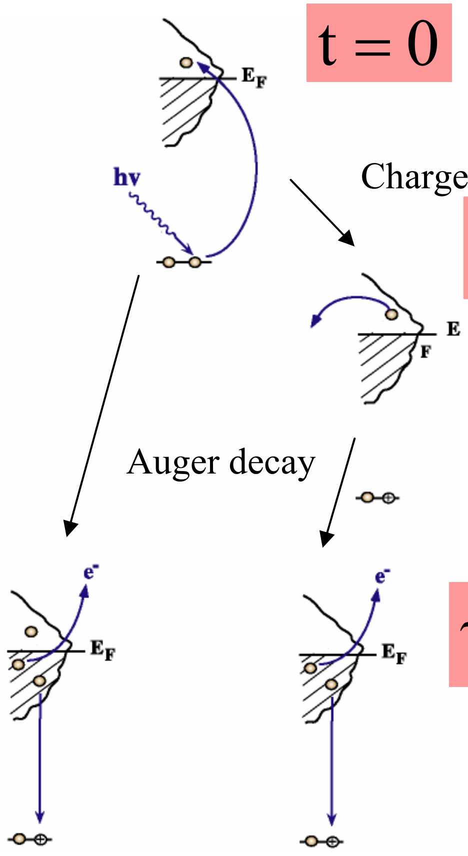
Resolution 3000-5000

Acknowledgement

- Hirohito Ogasawara-SSRL
- Dennis Nordlund-SSRL
- Alan Luntz-Palo Alto

Core Hole Clock Method

Probing charge transfer processes on a femtosecond timescale



$t = 0$

Charge transfer

τ_{CT}

Auger decay

$t = \tau$

$\tau_{Ar2p} = 5.5 \mathrm{x} 10^{-15} \mathrm{s}$

+1 Spectator final state

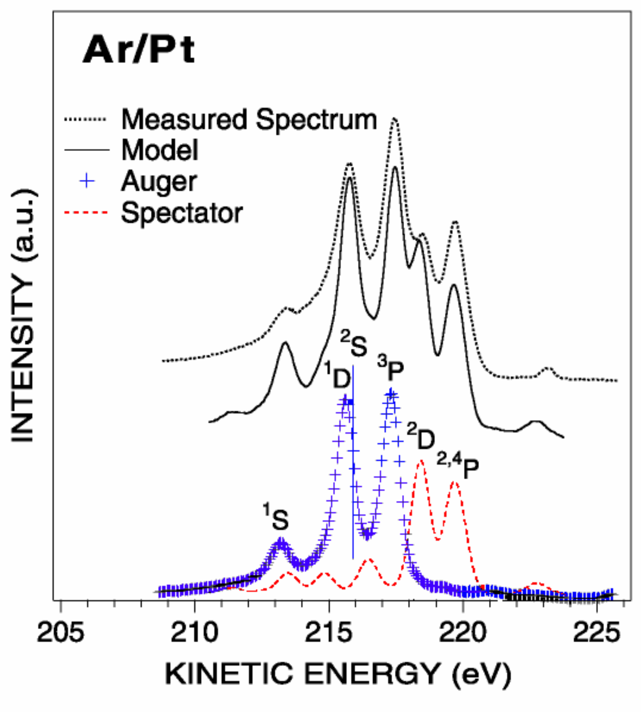
46%

+2 Auger final state

54%

$$P_{CT} = \left(1 + \tau_{CT} / \tau_{Ar2p}\right)^{-1}$$

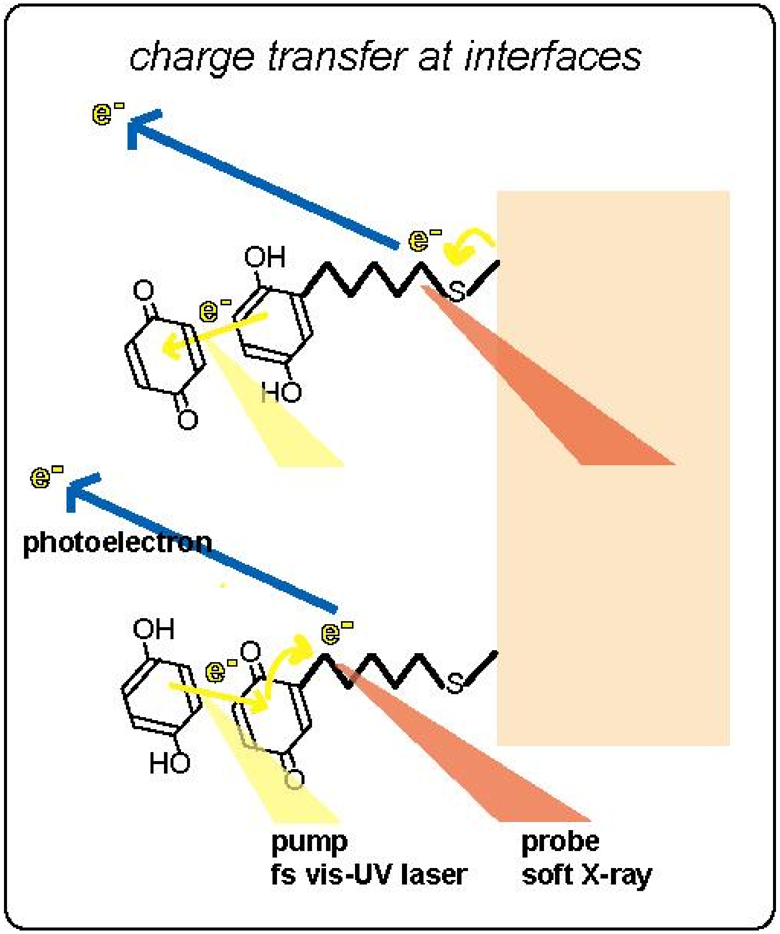
$\tau_{CT} = 4.7 \mathrm{x} 10^{-15} \mathrm{s}$

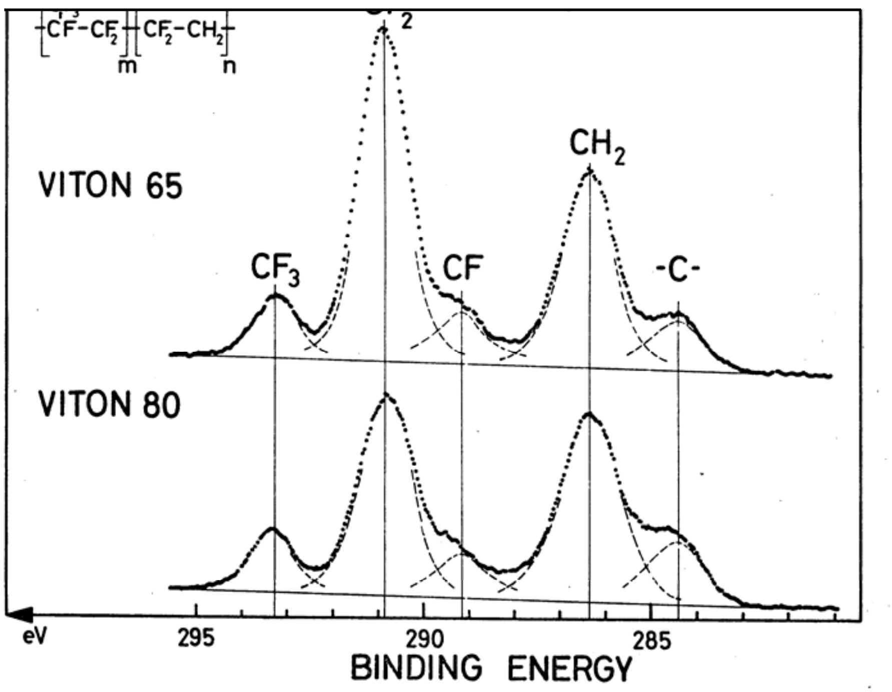


Karis et. al. Phys. Rev. Lett. 76, 1380 (1996)

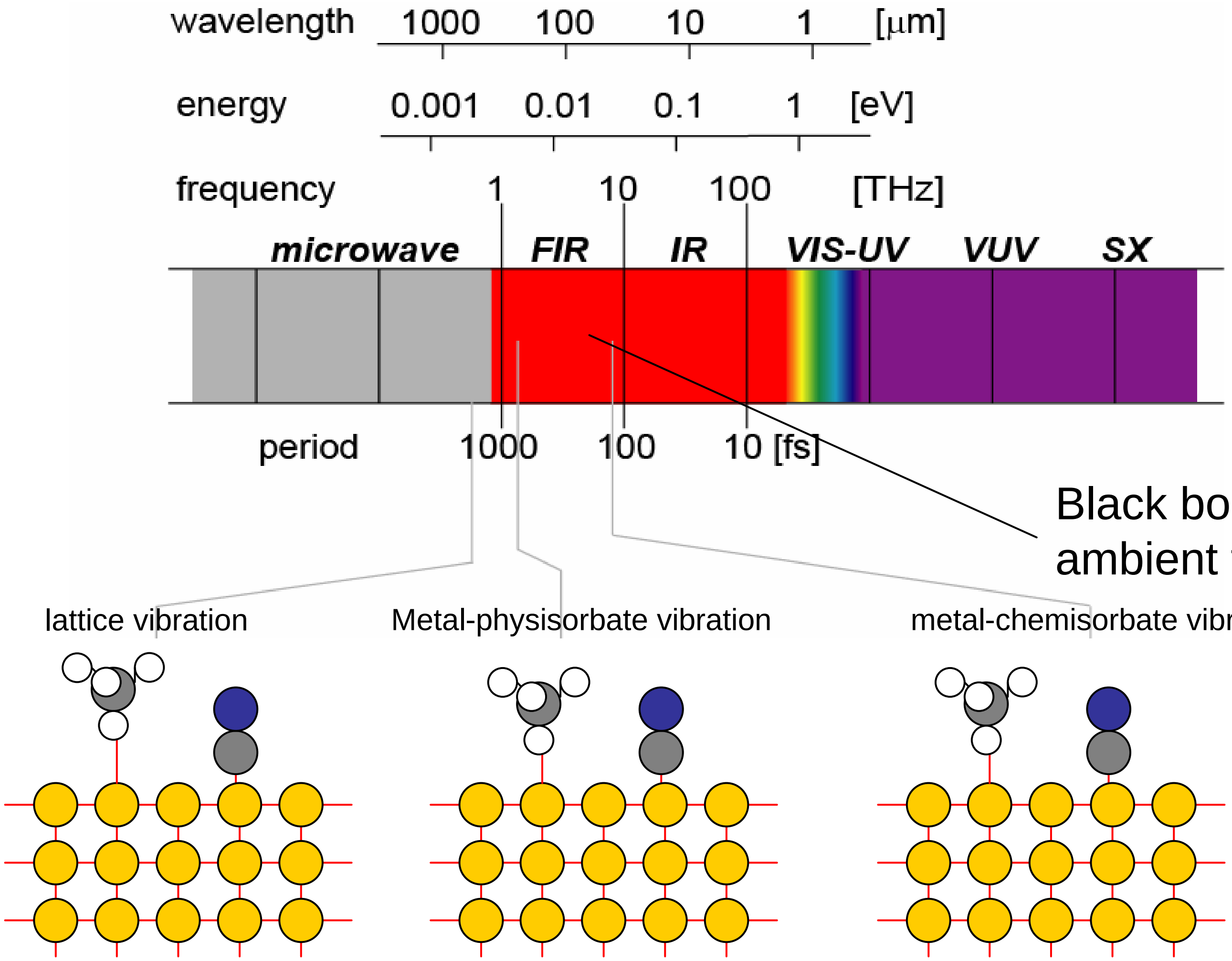
Sandell et. al. Surf. Sci. 429, 309 (1999)

Atom specific probing of charge transfer





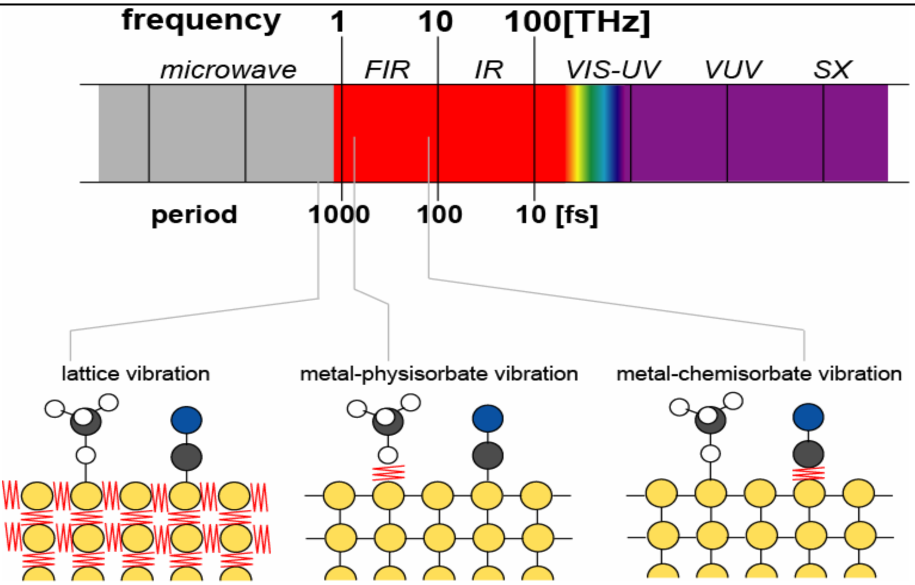
THz radiation and molecular vibration



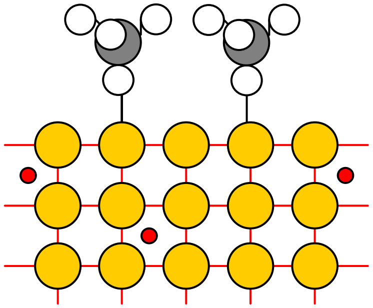
Black body radiation at ambient temperature

THz = Far-IR (~0.01[eV], ~30[μm]) can excite thermal process: lattice vibration, adsorbate-metal vibration.

Temperature jump
via
Electron-hole pair excitation,
Lattice vibration excitation,
….
required power: ~1-10 mJ/pulse



Temperature jump



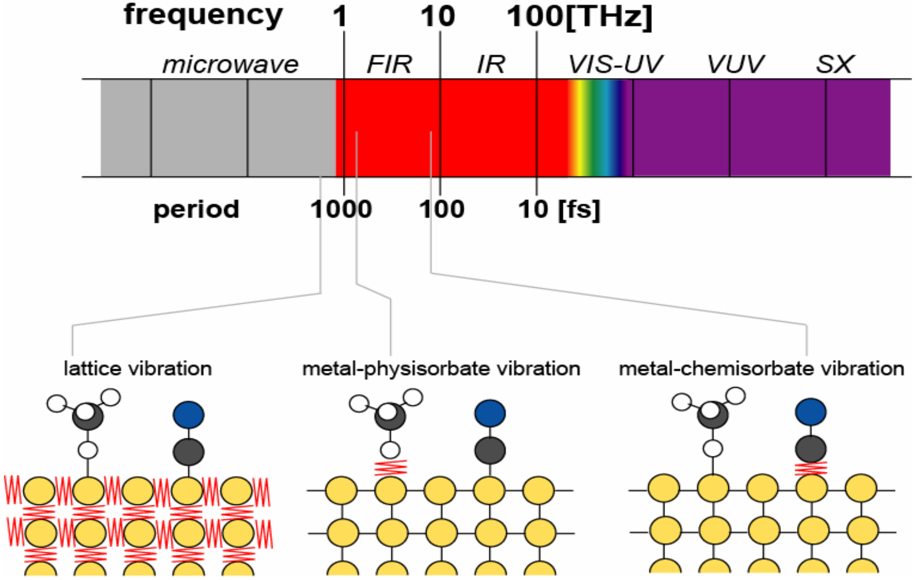
fs laser: hot electron problem

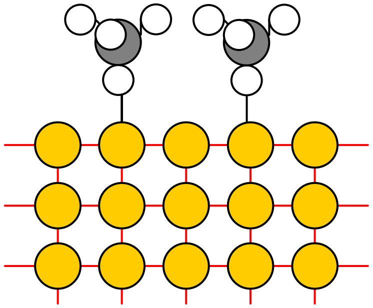
THz: NO hot electron

Temperature jump ensues the motion of adsorbate and stimulates surface chemical reactions.

Temperature jump

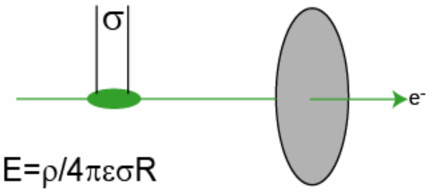
via
Electron-hole pair excitation,
Lattice vibration excitation,
….
required power: ~1-10 mJ/pulse





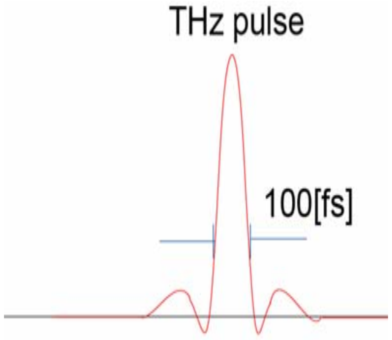
Temperature jump ensues the motion of adsorbate and stimulates surface chemical reactions.

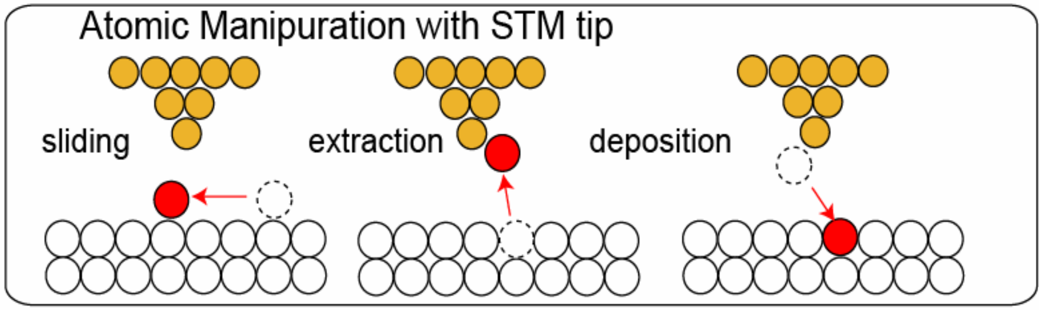
THz radiation and surface chemistry

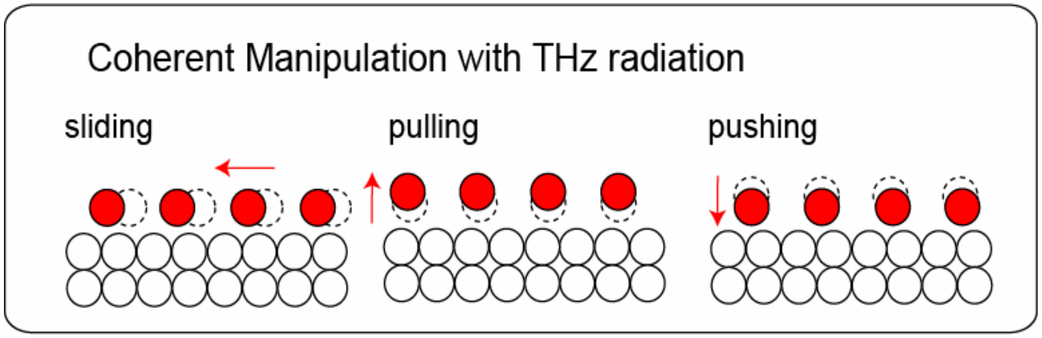


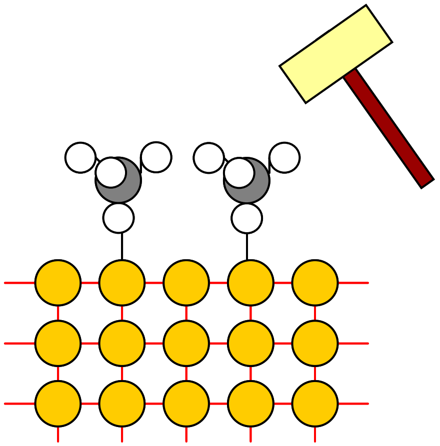
$E = \rho / 4\pi\varepsilon\sigma R$
$= 1nC/(4*3.14*20\mu*100\mu*8.854pF/m)$
$= 4.5GV/m = \underline{0.45\ V/Å}$

~ 0.1-0.3 V/Å





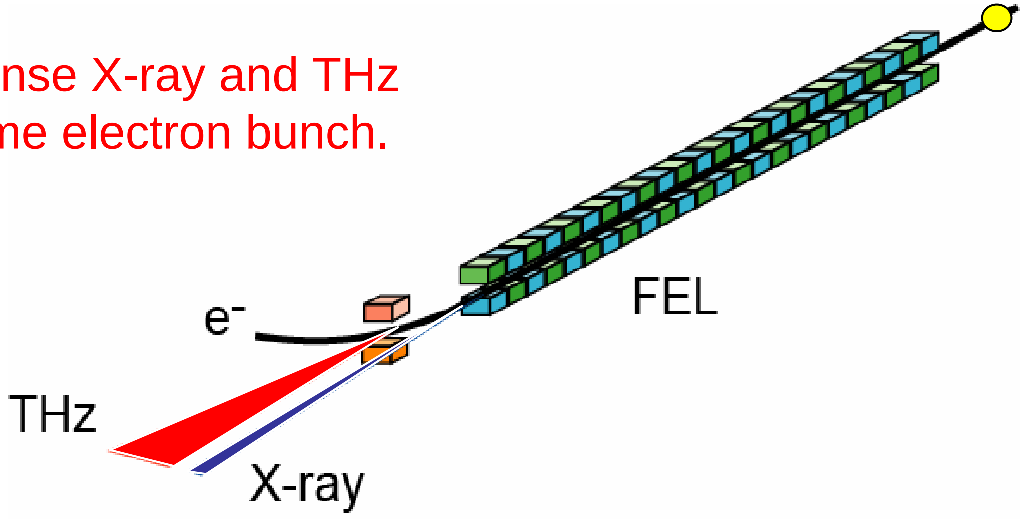


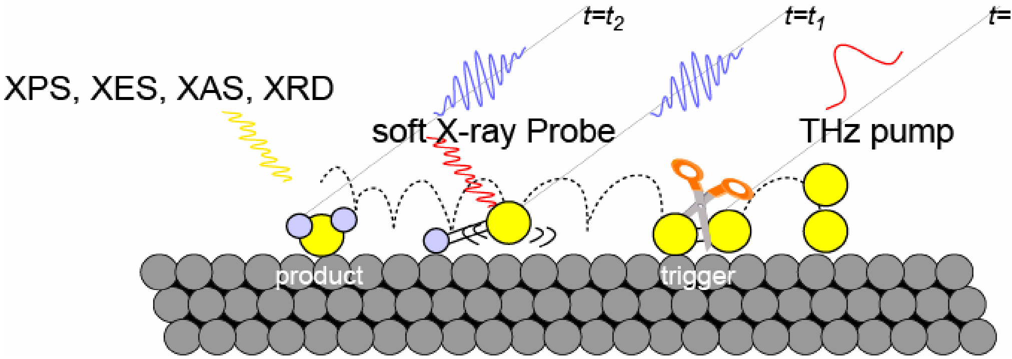


THz electric field ~ Coulomb force between e$^-$ and the nuclei
manipulation of molecule, coherent control molecular motion

How to probe THz induced process

FEL can produce intense X-ray and THz radiation from the same electron bunch.





on-axis radiation, soft X-ray, hard X-ray, off-axis radiation: THz
Pump: THz, **Probe:** XPS, XES, XAS, XRD, IR

Ultrafast processes in water and ice