"Modern Methods in Heterogeneous Catalysis Research" - WS 04/05

Time-resolved Studies of Surface Reactions

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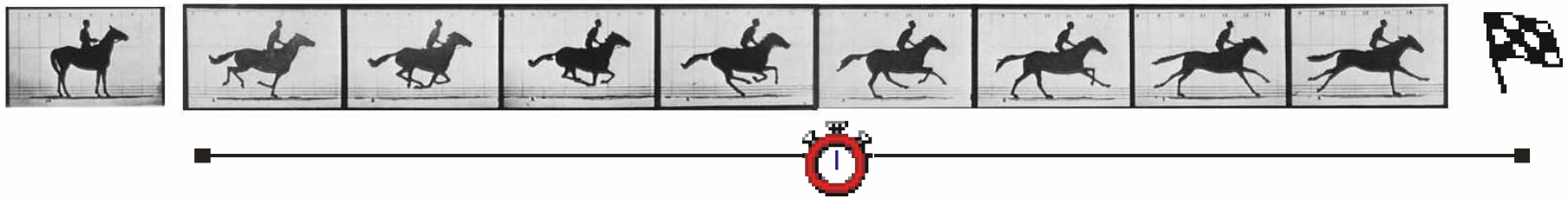
structure dynamics



kinetics

E. Muybrigde 1887

Goal: Microscopic understanding of coupling between electronic excitations and nuclear degrees of freedom

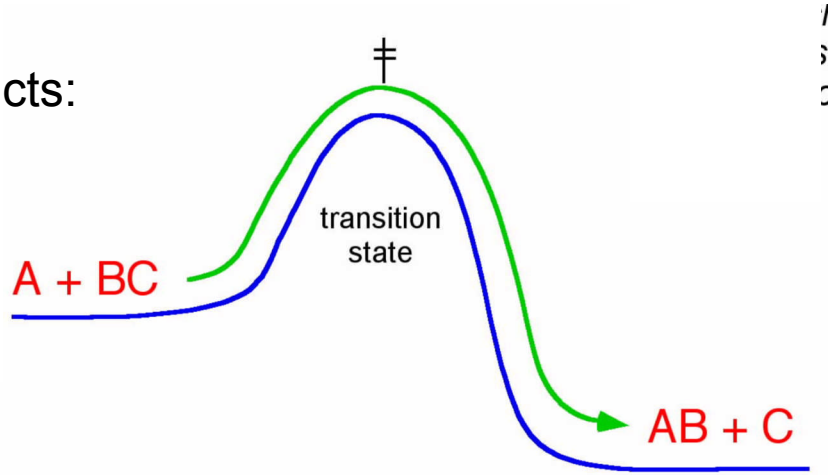
→ Application of femtosecond laser spectroscopy

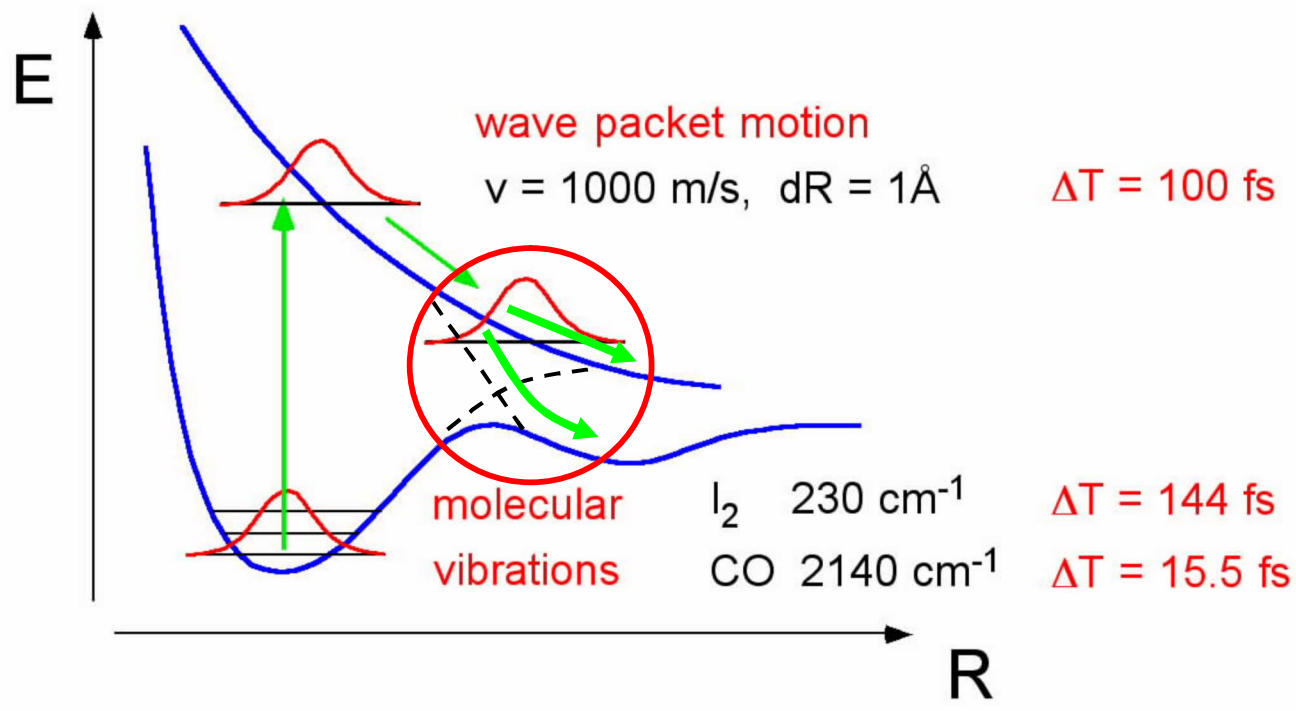
Timescales of chemical reactions

Temporal evolution from reactants to products:

→ Dynamics of the transition state

Typical timescale: 10-100 fs



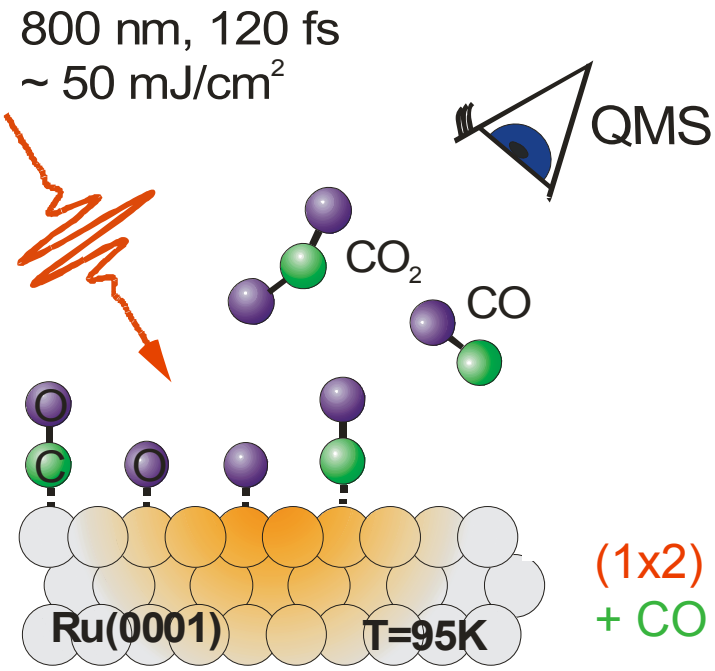


→ Key concept: Dynamics on Born-Oppenheimer potential energy surface

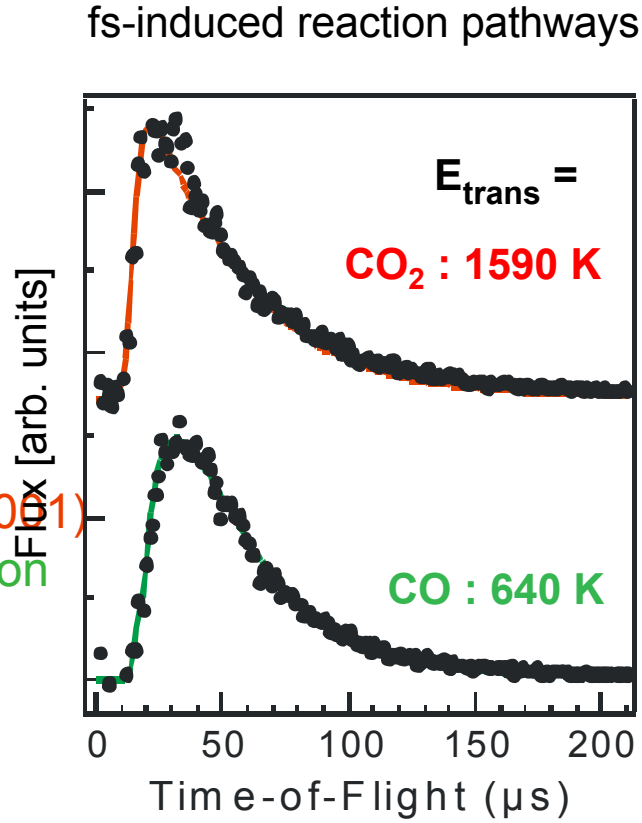
→ Non-adiabatic coupling between electronic states near (avoided) crossings

Motivation: fs-laser-induced chemistry

Example: CO Oxidation on Ru(001) competes with CO desorption (UHV conditions)



(1x2) - O/Ru(001)
+ CO saturation



$$2\,CO_{ads} + O_{ads} \xrightarrow{h\nu} CO\uparrow + CO_2\uparrow$$

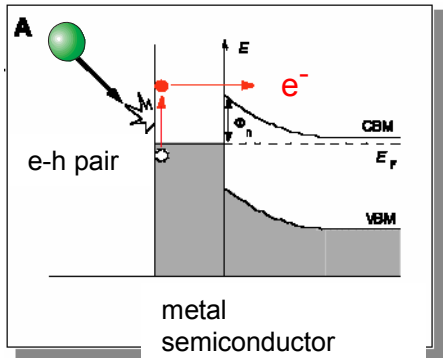
$$2\,CO_{ads} + O_{ads} \rightarrow CO\uparrow$$

→ New reaction pathway is „switched on“ upon fs excitation

Outline

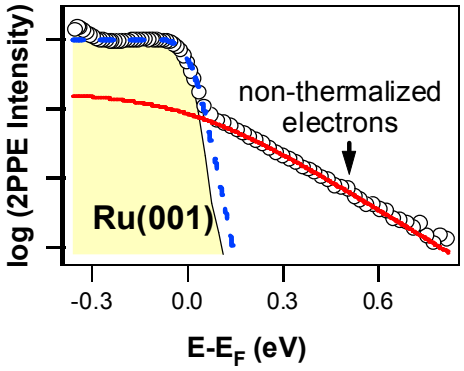
Introduction

→ Non-adiabatic processes at surfaces



Electron thermalization in metals

→ Test of the two-temperature model



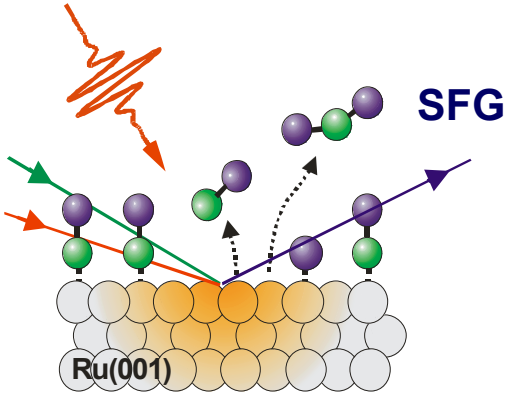
Surface femtochemistry

→ Electron and phonon mediated pathways

→ Isotope effects and electronic friction model

Non-linear optics as a probe of surface dynamics

→ Vibrational sum-frequency generation spectroscopy

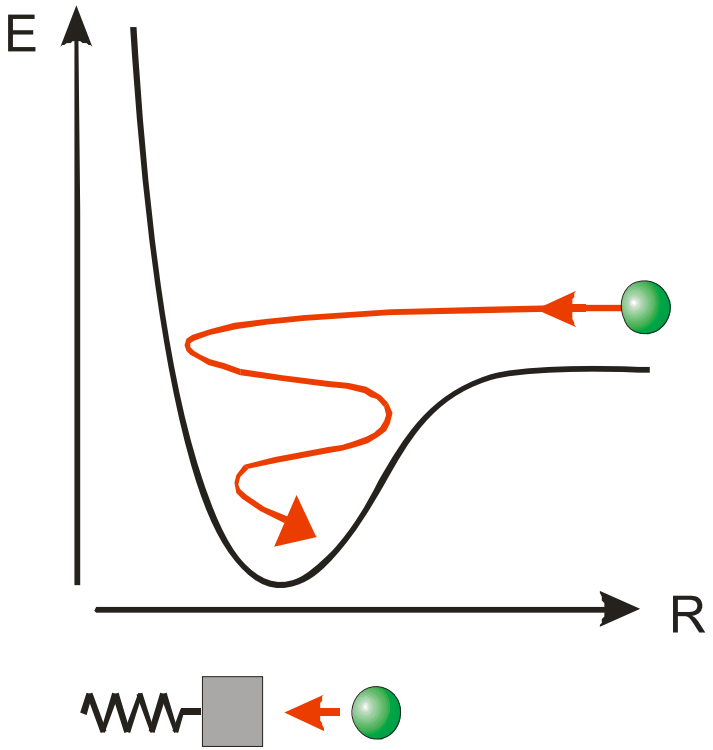


Electron dynamics thin ice layers on metals

Gas surface interaction

Role of non-adiabatic processes in surface reactions ?

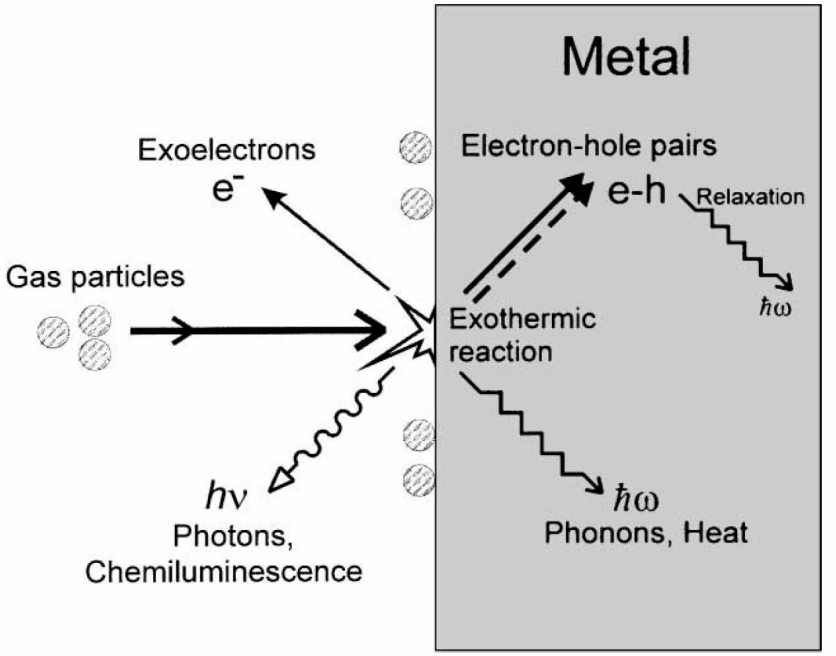
Example: Adsorption at a metal surface



„forced-oscillator model“

→ Energy dissipation via phonon excitation

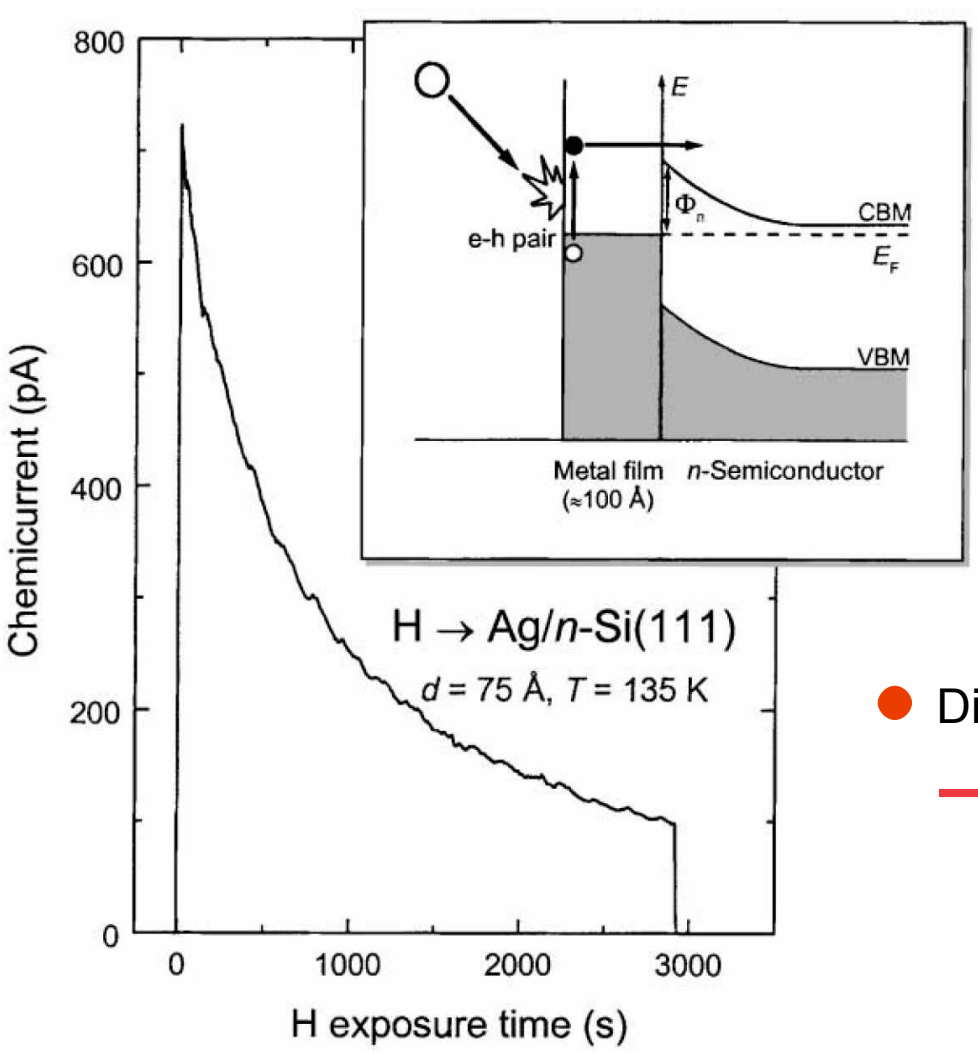
Question: Coupling between nuclear (vibrational) motion of adsorbate and electronic excitations ?



- Exothermic reactions at metal surfaces

→ Coupling to electron-hole pair excitations in the substrate

Chemicurrents



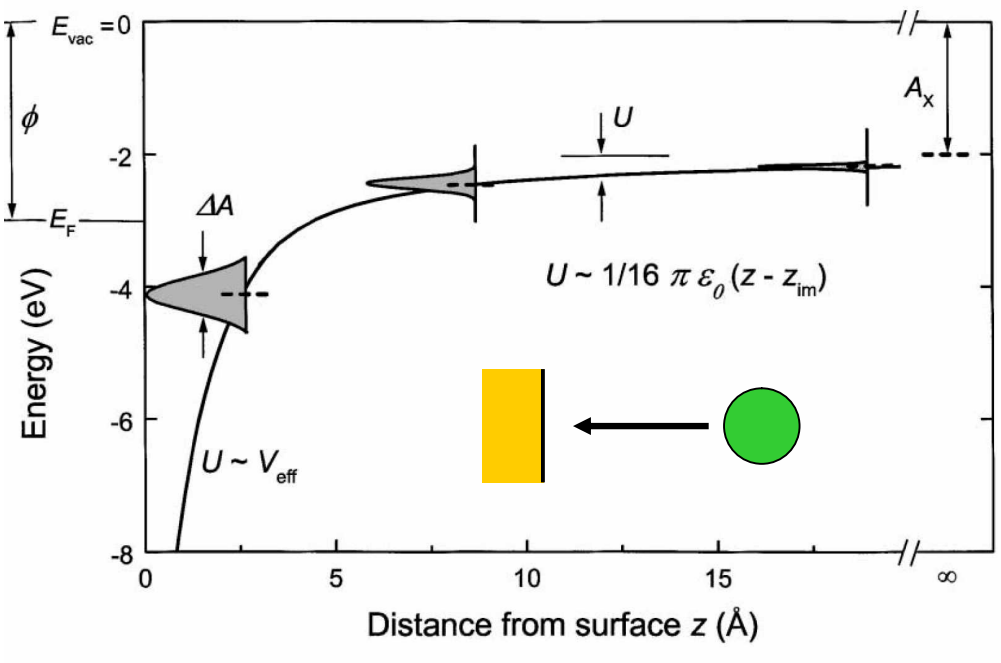
- Adsorption on thin metal film
- Charge separation across small Schottky barrier
  → Chemicurrent
- Current provides lower limit of excitation probability

- Direct observation of e-h pair excitation
  → Evidence for non-adiabatic coupling between adsorbate motion electronic excitations

See review article by H. Nienhaus, Surf. Sci. Rep. **45**, 3 (2002)

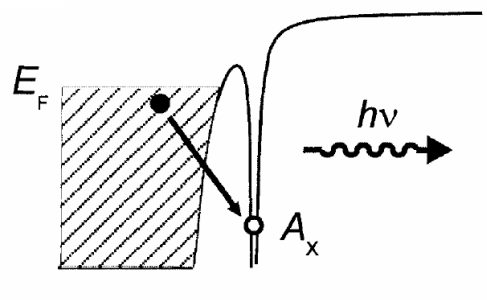
Chemicurrents: Mechanism

Newns-Anderson model

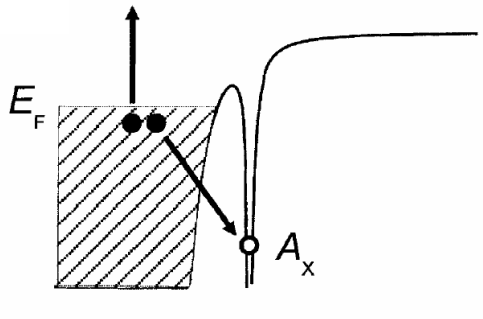


- Unoccupied affinity level is pulled down by adsorbate surface interaction
  - → broadening of resonance linewidth
  - → adsorbate substrate charge transfer

Chemiluminescence



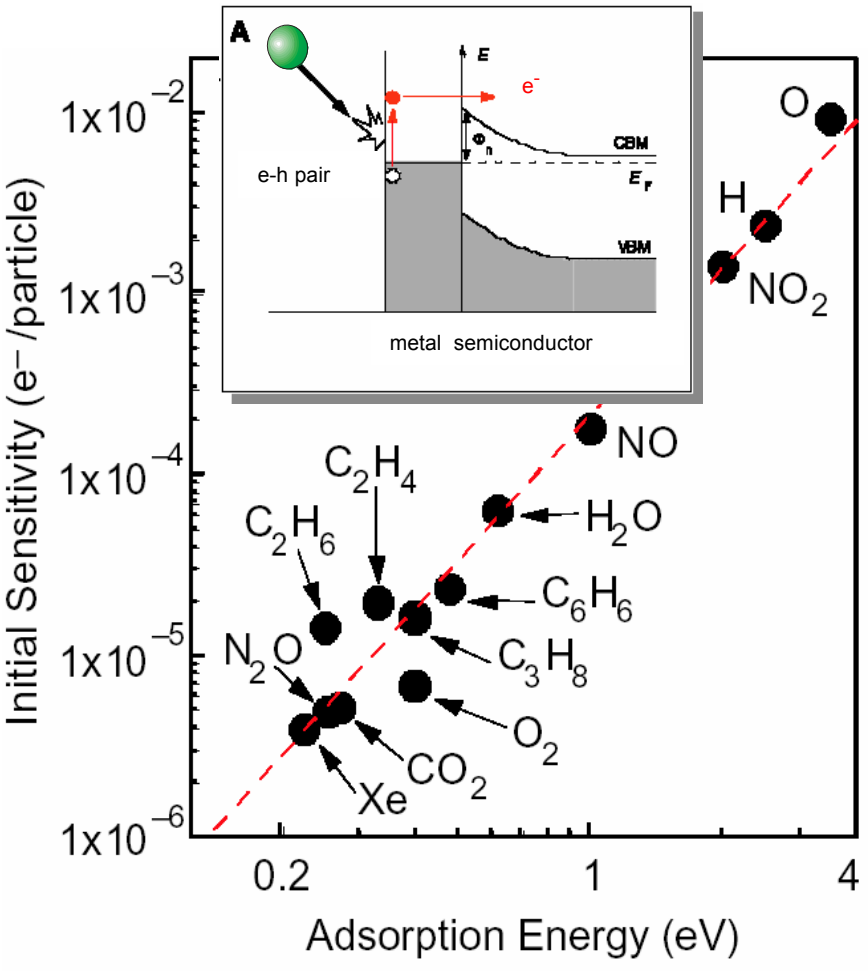
Exoelectron emission



- Filling of hole below E_{Fermi} by substrate electrons
  - → *e-h* excitation:
    - chemicurrent
    - exoemission
  - → luminescence

Electronic excitations at surfaces

Gergen *et.al.*, Science **294**, 2521 (2001)



- Chemicurrent observed for various adsorbates

  → electronic excitations play maior role in gas surface interaction

- Energy dissipation via e-h pair excitation („electronic friction“)

- Feasibility of reverse process?

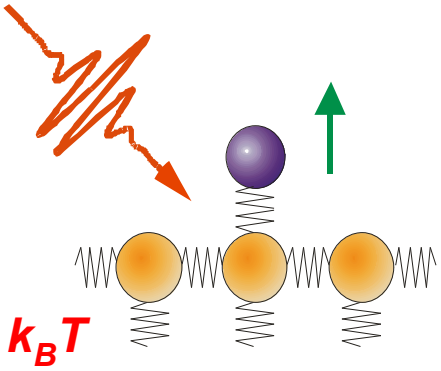
  → chemical reactions driven by electronic excitations

Laser induced surface dynamics

Question: How does laser excitation induce surface reactions ?

Thermal activation

→ Phonon driven process (in electronic ground state)



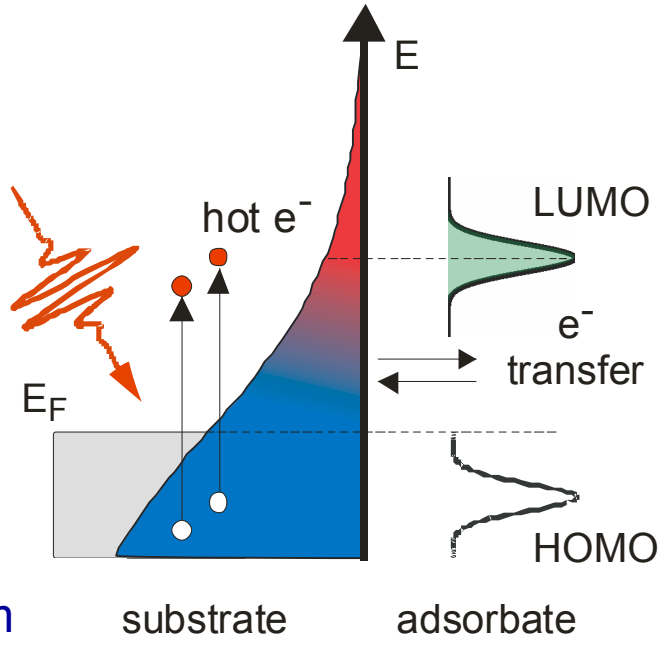
Electronic excitations and charge transfer

→ Chemical bonding implies electronic coupling between „adsorbate“ and substrate

→ Electron stimulated desorption and surface photochemistry

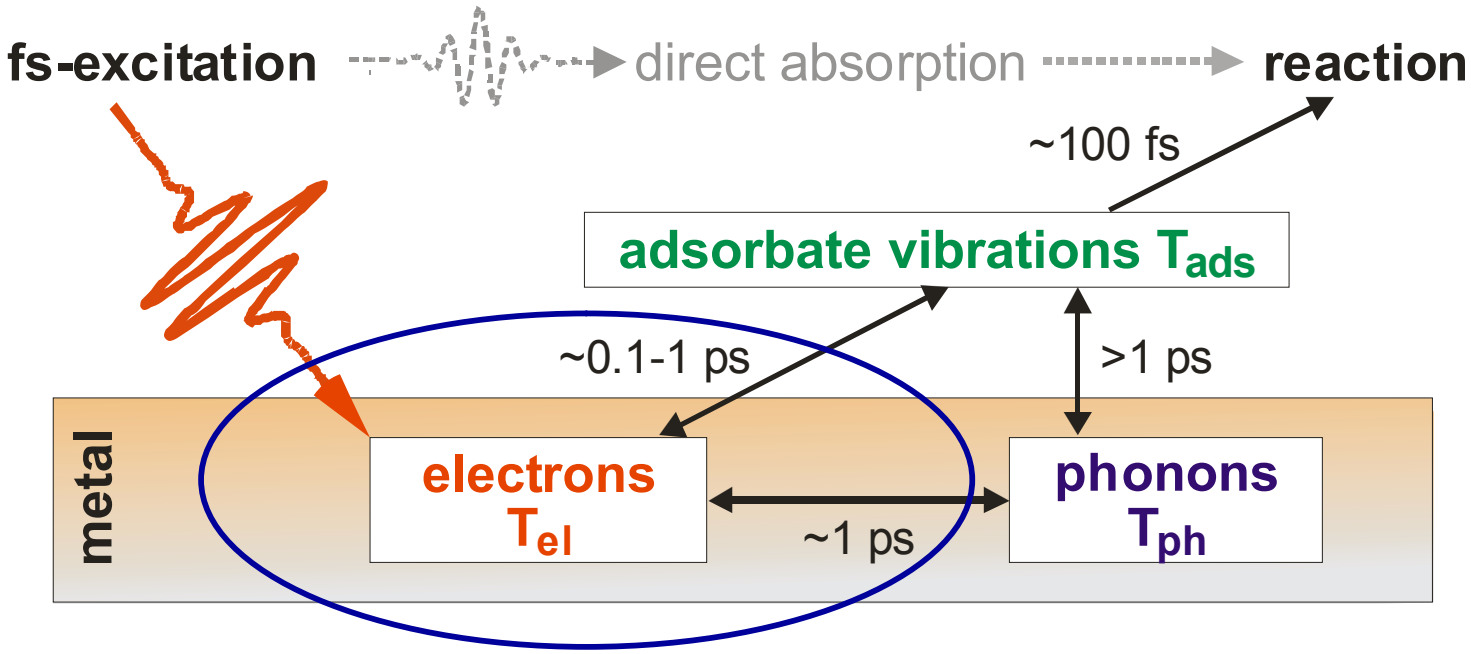
→ Vibrational relaxation at metals by electron-hole pair excitation

→ Energy transfer by coupling between electronic and nuclear degrees of freedom



Optical excitation of metal surfaces

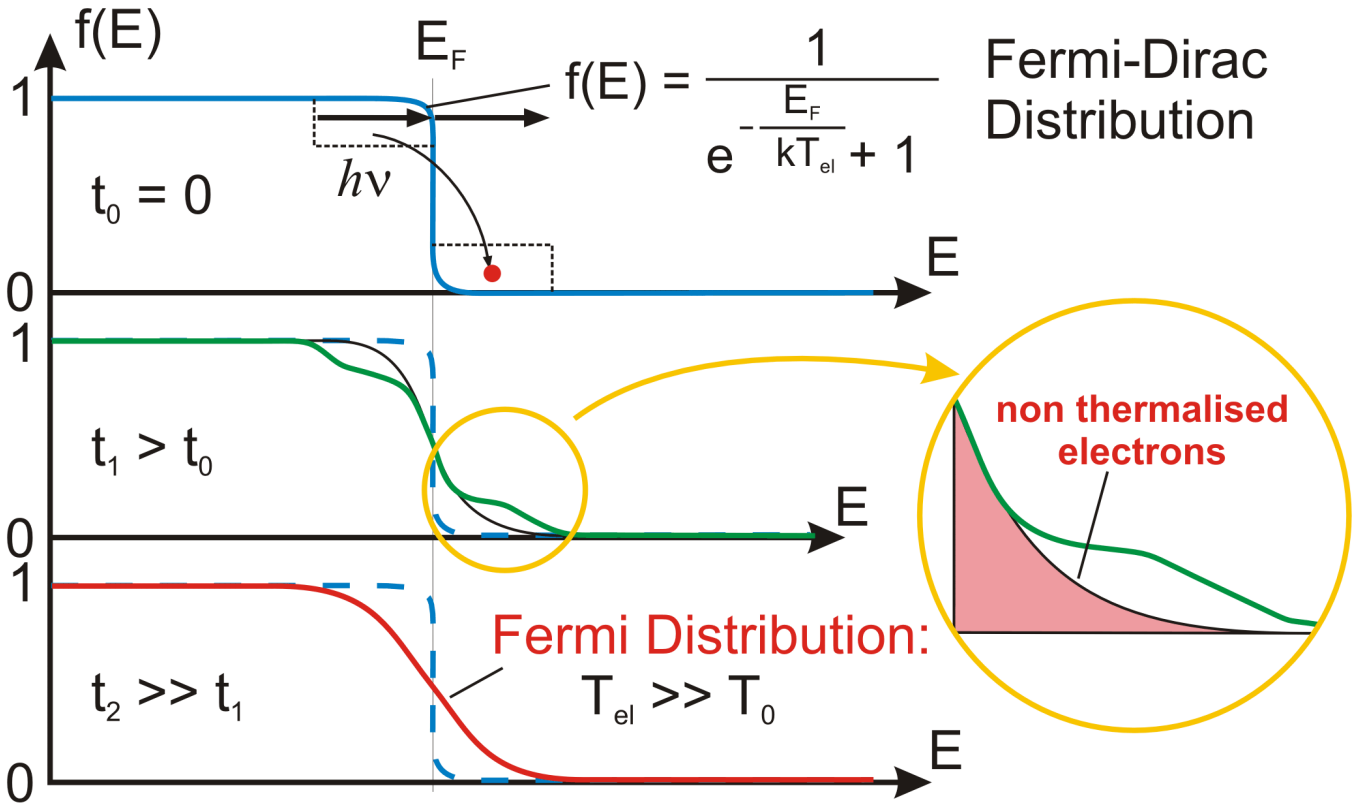
Mechanism and timescales of energy transfer after optical excitation



- Photoabsorption in a metal substrate creates a transient non-equilibrium electron distribution
- Relaxation to phonon and adsorbate vibrational excitation
- Primary step: Electron thermalization and cooling

Electron thermalization dynamics in metals: Test of the two-temperature model using 2PPE

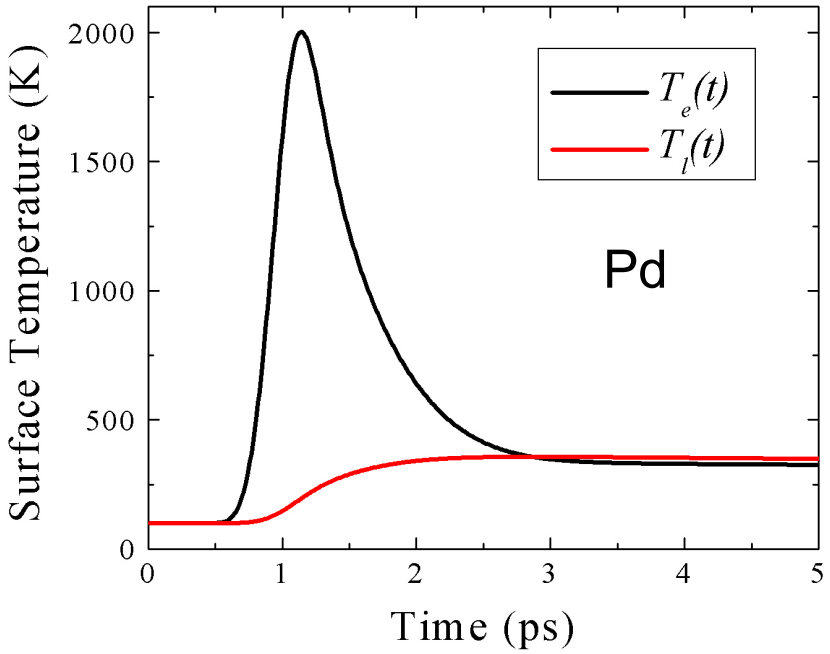
Electron dynamics in metals following optical excitation

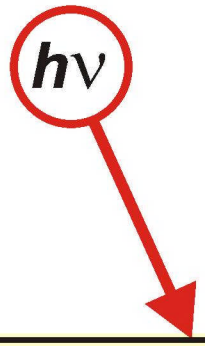


W.S. Fann, R. Storz, H.W. K. Tom, J.Bokor PRB **46** (1992), 13592

The two-temperature model

- Model assumes two heat baths for electrons and phonons: $C_{el} >> C_{ph}$
- Nearly thermal (Fermi-Dirac) distribution for electrons
- Coupled diffusion equation for T_{el} and T_{ph}





$$C_{\mathrm{el}}(T_{\mathrm{el}})\,\frac{\partial T_{\mathrm{el}}}{\partial t} = \nabla(\kappa \nabla T_{\mathrm{el}}) - g(T_{\mathrm{el}} - T_{\mathrm{ph}}) + S(z,t)$$

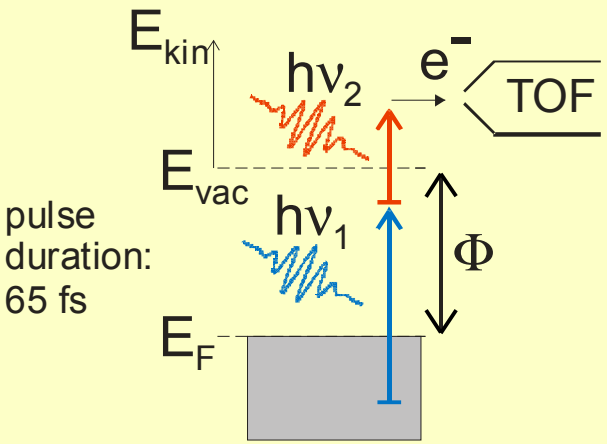
$$C_{\mathrm{ph}}(T_{\mathrm{ph}})\,\frac{\partial T_{\mathrm{ph}}}{\partial t} = g(T_{\mathrm{el}} - T_{\mathrm{ph}})$$

z

Time-resolved two-photon photoemission

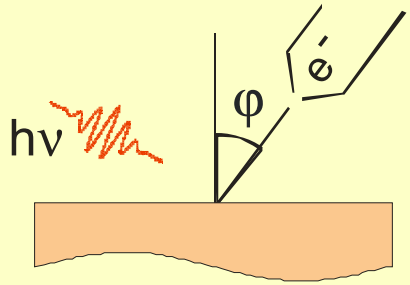
- How to probe electron thermalization and cooling ?

energy- and time-resolution:

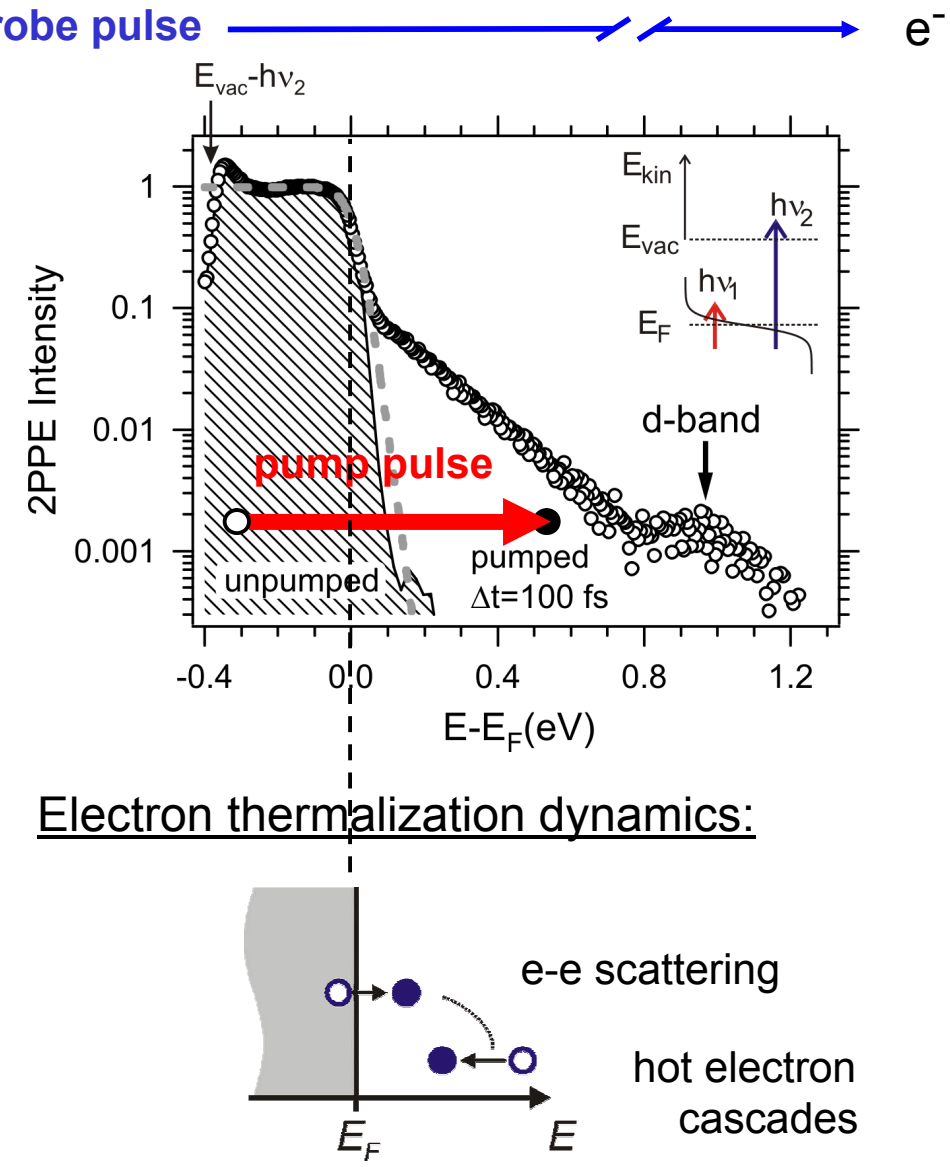


$$E - E_F = E_{kin} + \Phi - h\nu_2$$

momentum resolution:

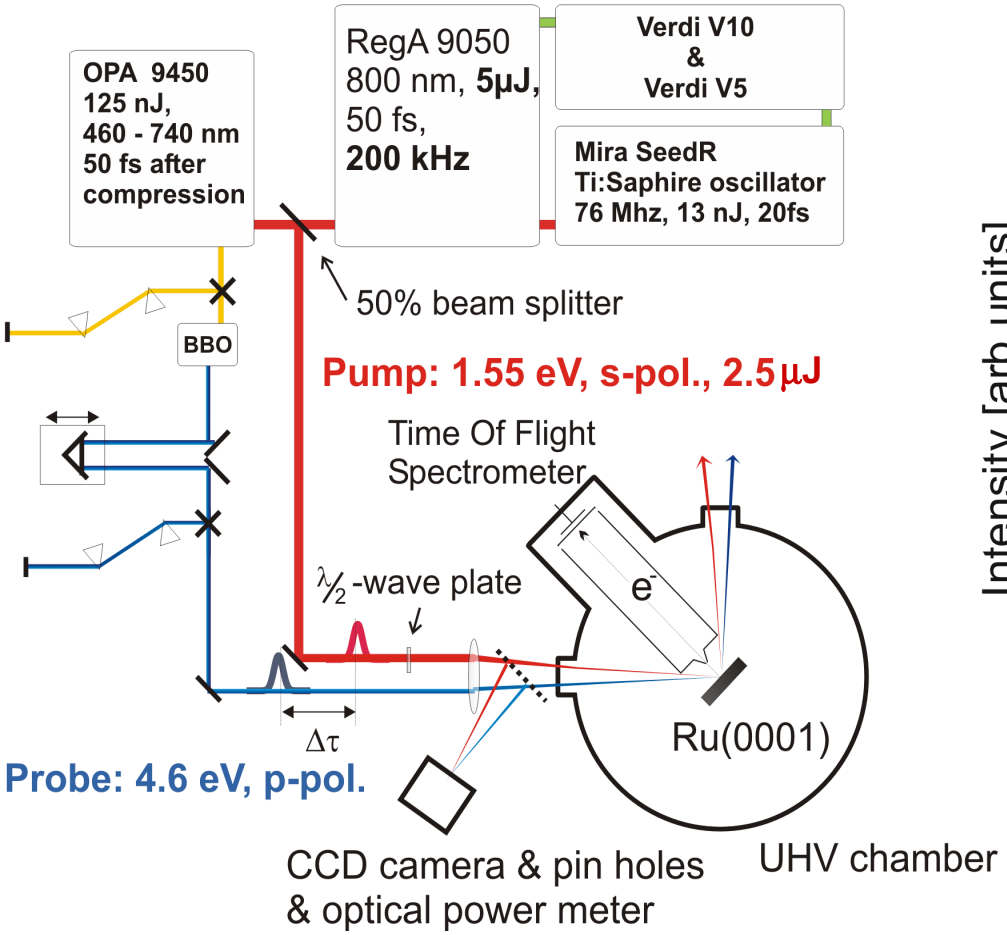


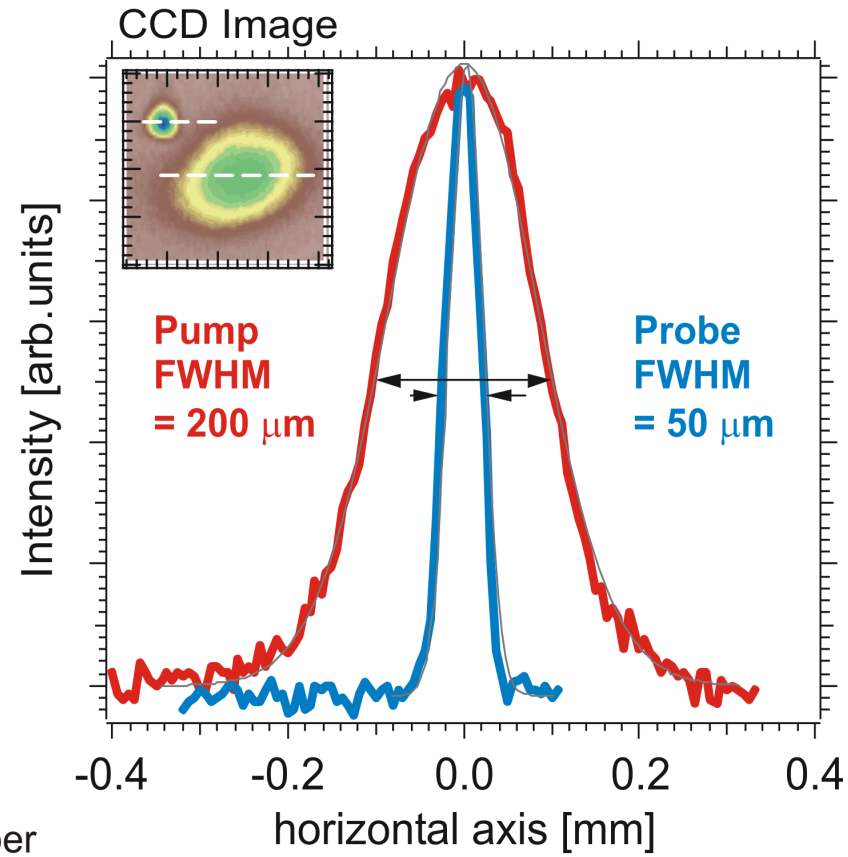
$$k_{||} = \sin\varphi\sqrt{2mE_{kin}}/\hbar$$



Experimental setup

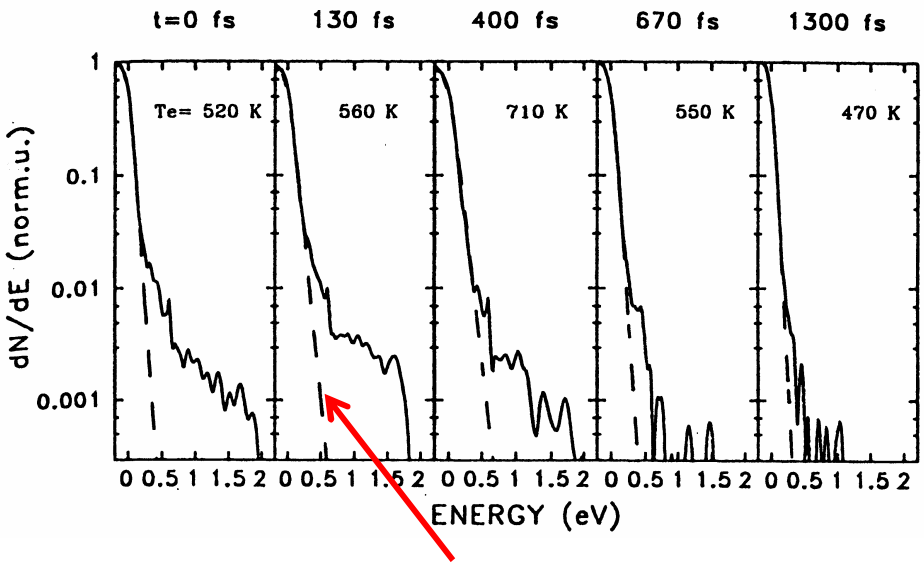
Femtosecond time-resolved two-photon photoemission spectroscopy





Electron thermalization in gold

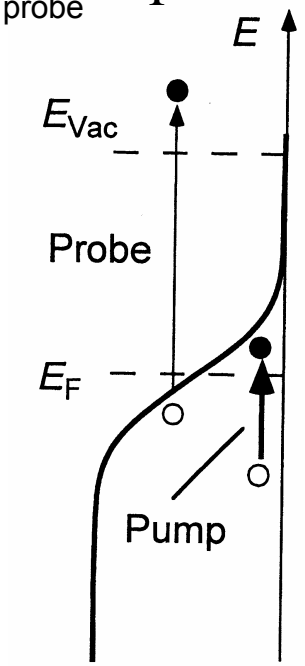
Pump fluence: 120 μJ/cm^2



Fermi-Dirac distribution

- Method:

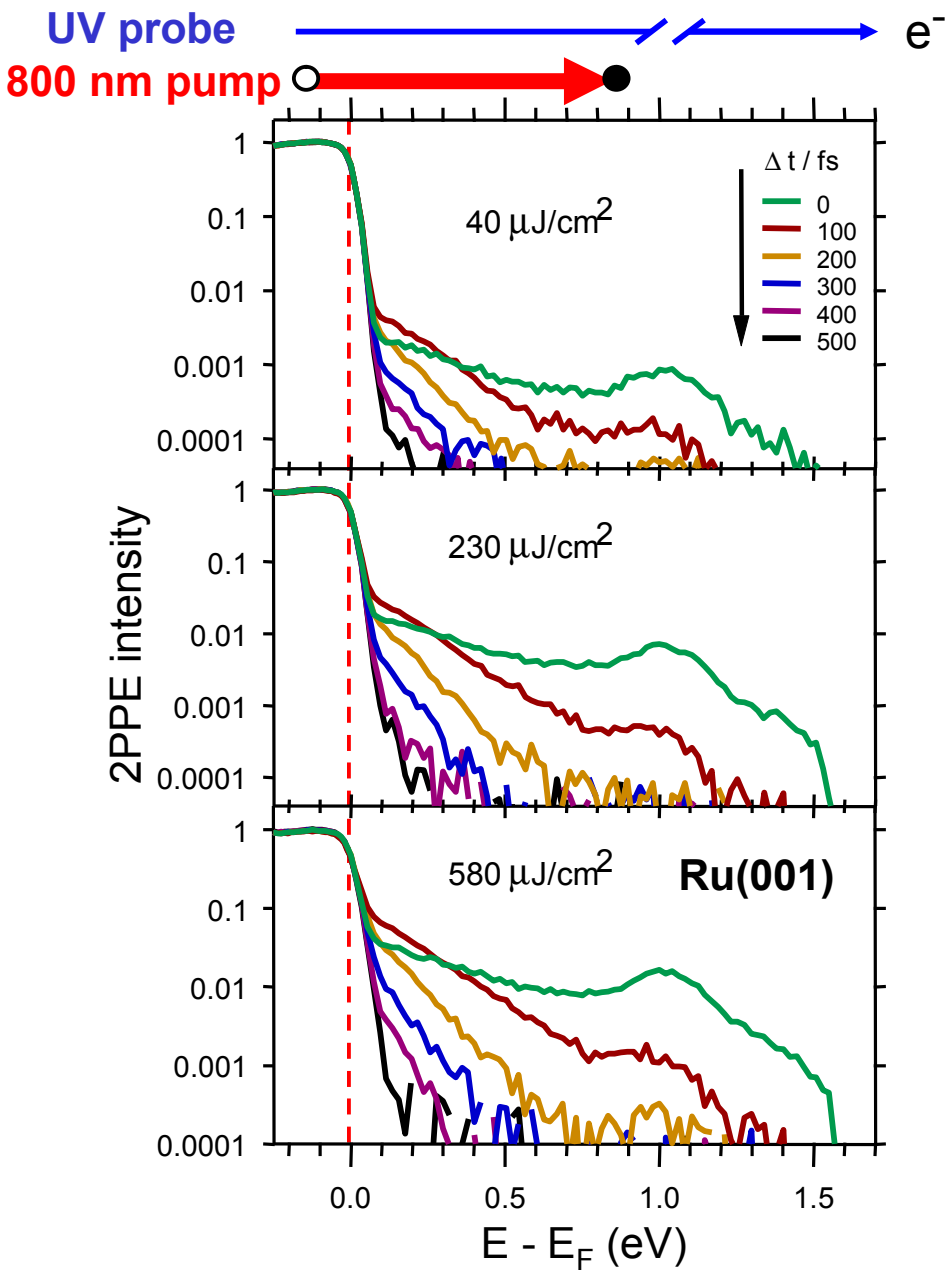
  time-resolved photoemission with $h\nu_{probe} > \Phi$



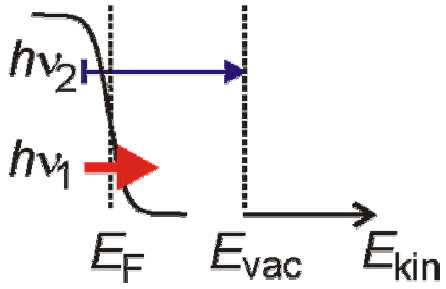
W. S. Fann, R. Storz, H.W.K. Tom, J. Bokor, *Electron thermalization in gold*, Phys. Rev. **B 46**, 13592 (1992)

- Electron thermailization occurs faster with increasing excitation density

Time-resolved 2PPE from Ru(001)

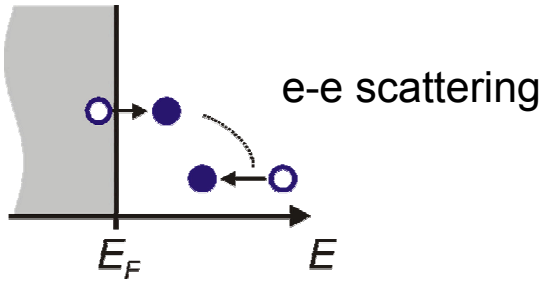


Pump-probe scheme:



probing electron dynamics around E_{Fv}

1) Electron thermalization:

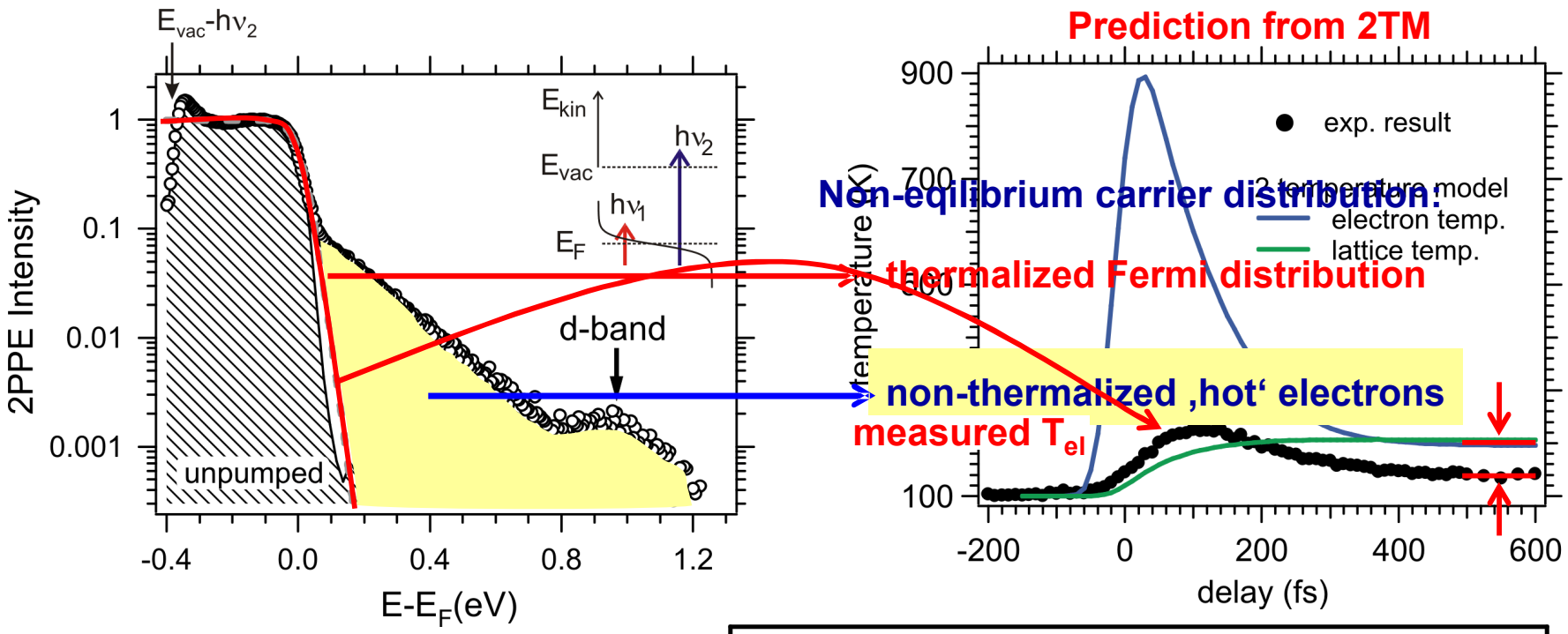


2) Relaxation by e-ph scattering

3) Energy transport in the bulk

Lisowski *et al.*, Appl. Phys. A **78**, 165 (2004)

Analysis of electron distribution



Comparison with 2TM:

- Assume thermalized distribution for electrons and phonons
- Thermalized electrons carry only minor fraction of excess energy
- 2TM over-estimates final T_{el}

Two Temperature Model (TTM):

transport e-ph coupl. opt. exc.

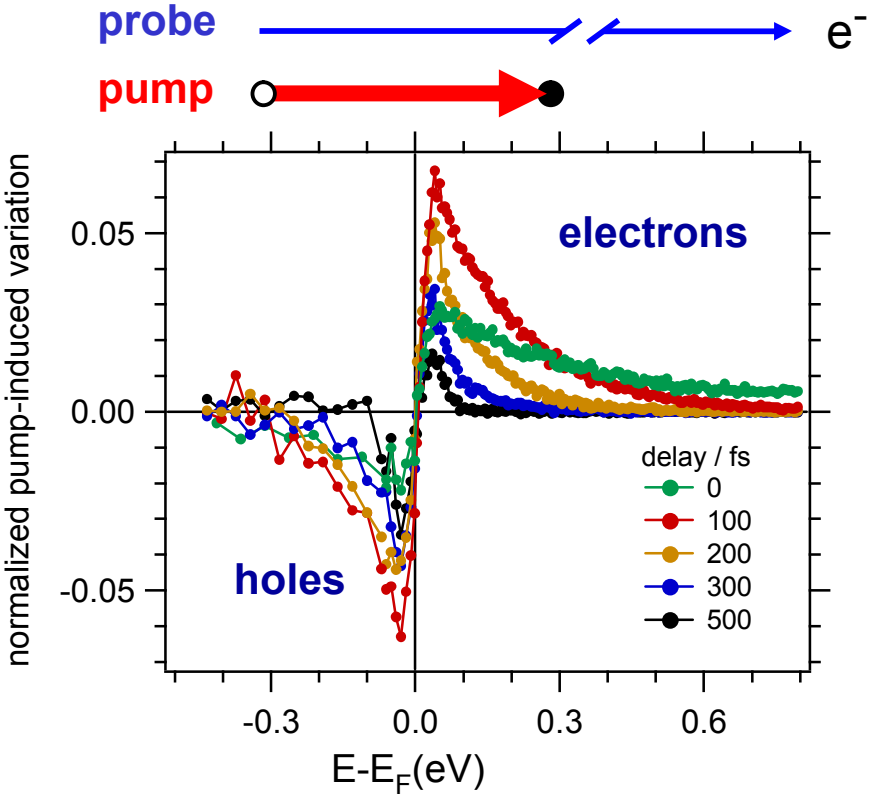
$$C_{el}(T_{el})\frac{\partial T_{el}}{\partial t} = \nabla(\kappa \nabla T_{el}) - H(T_{el}, T_{ph}) + S(z,t)$$

$$C_{ph}(T_{ph})\frac{\partial T_{ph}}{\partial t} = H(T_{el}, T_{ph})$$

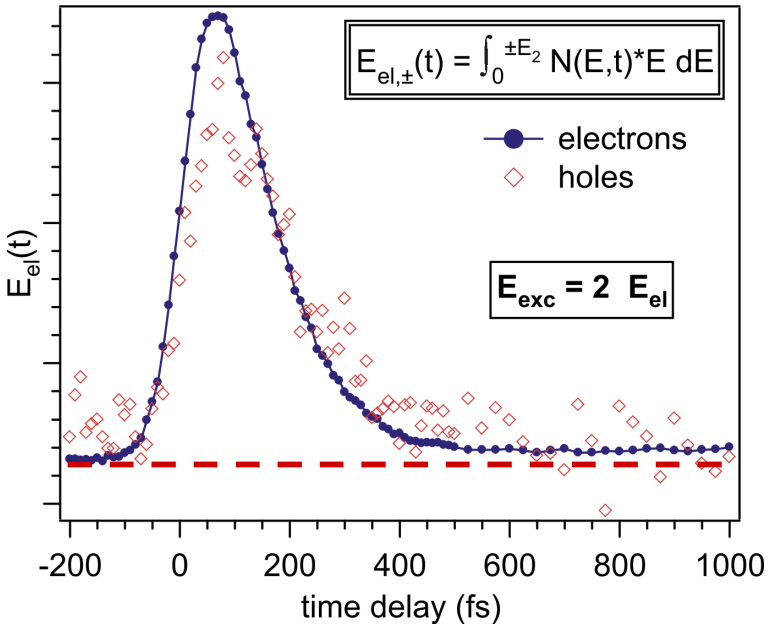
$H(T_{el},T_{ph})$: thermal electron distributions
Debye model for phonons

Anisimov et.al., Sov. Phys. JETP 39, 375 (1974)

Dynamics of electrons and holes



Excess energy of electrons + holes

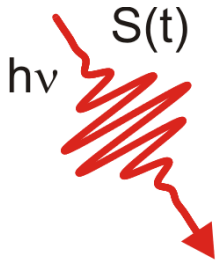


Pump induced changes of electron distribution:

- Highly symmetric electron and hole distributions for *all* delays due to nearly constant DOS around E_F
- Dynamics of electrons and holes can be treated equivalently
- Ultrafast relaxation (much faster compared to noble metals, e.g Au: 1-2 ps)

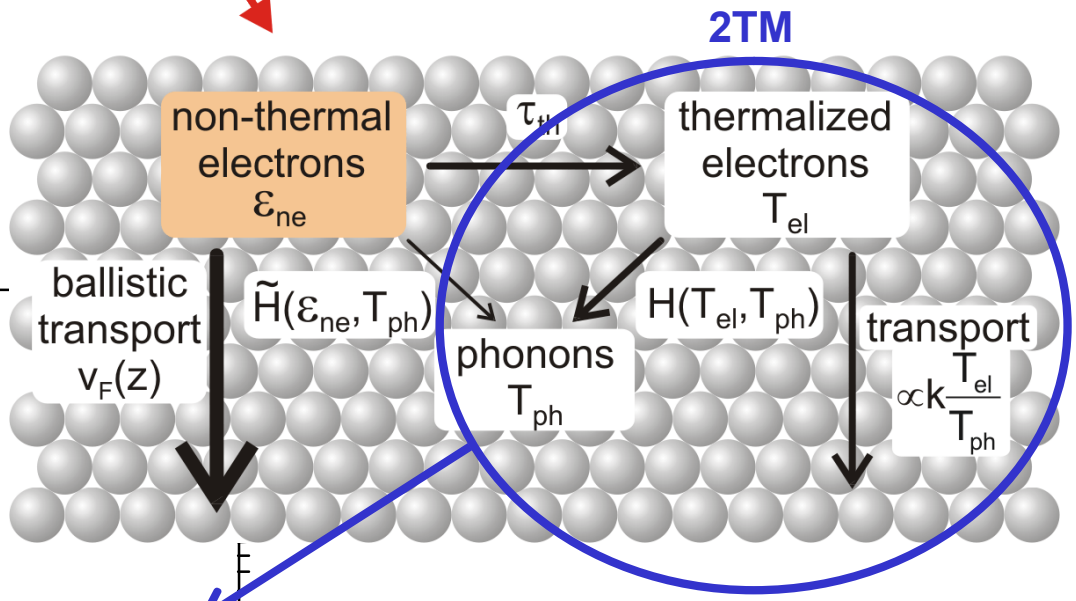
Extended heat bath model

Goal:
Understanding the role of non-thermalized electrons

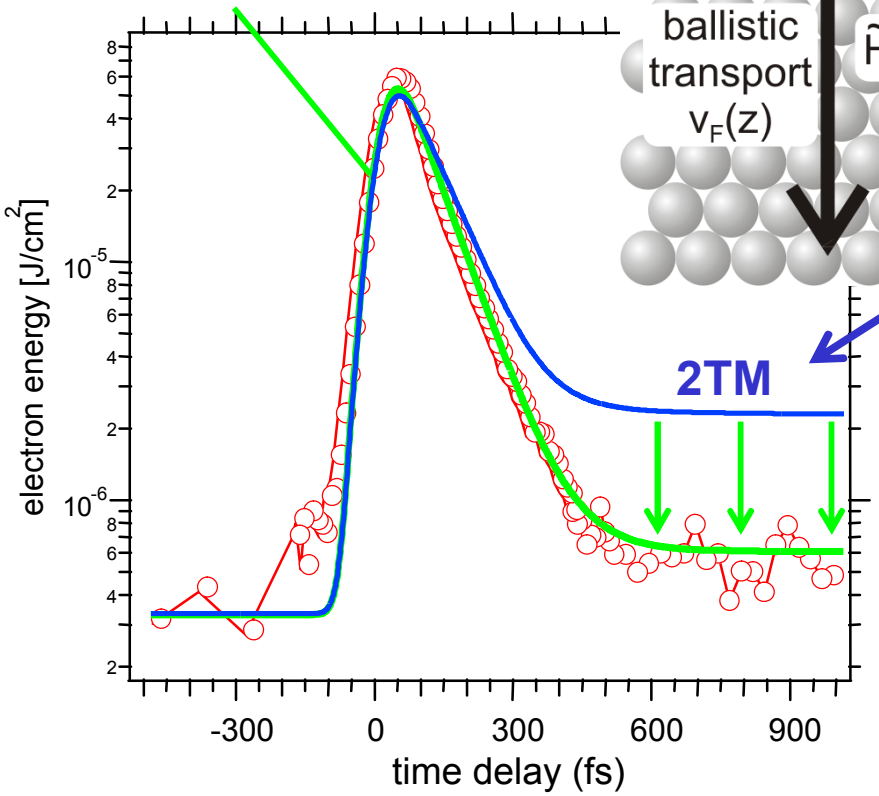


Extension of two temperature model

Appl. Phys. A **78**, 165 (2004)



Extended model including ballistic transport



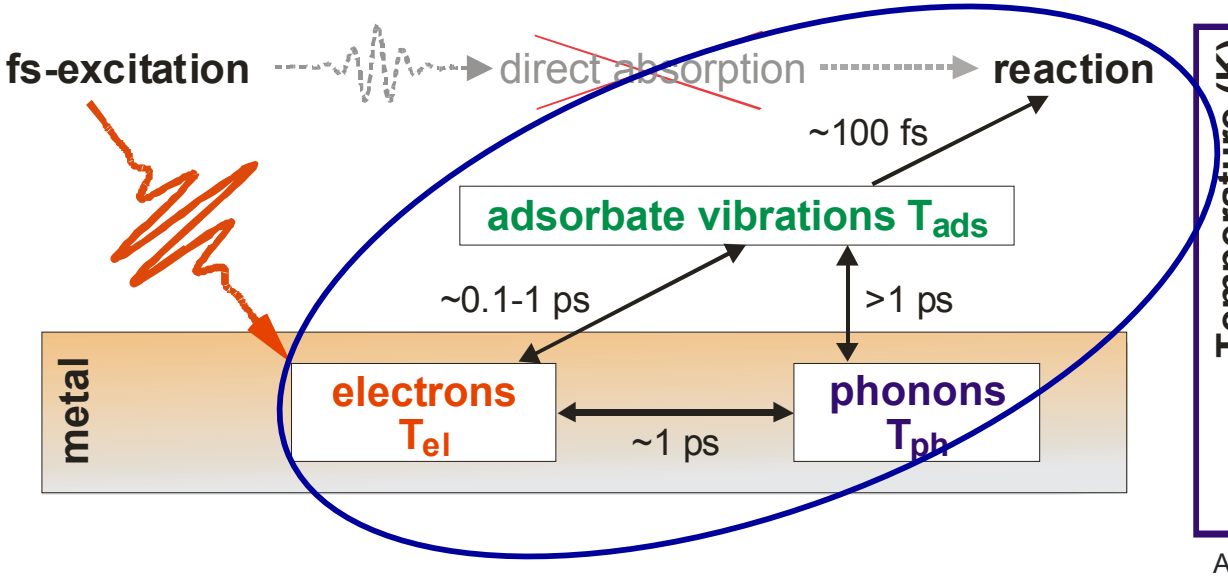
→ 2TM underestimates rate of energy flow into the bulk

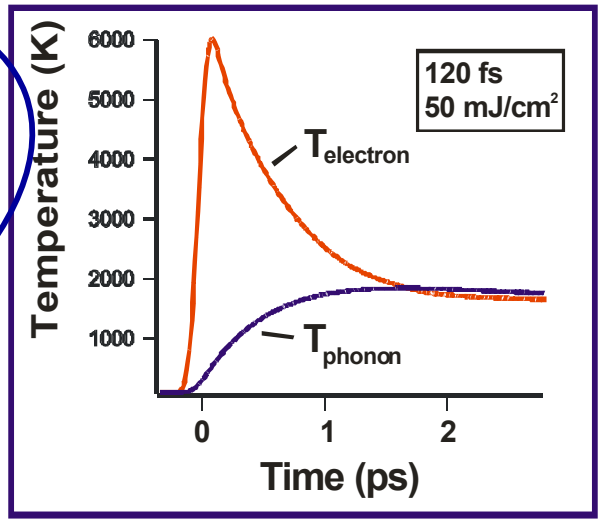
→ efficient ballistic transport of non-thermal electrons

→ however, peak energy is described reasonable well by both models

Femtochemistry at metal surfaces

Mechanism and timescales of energy transfer after optical excitation





Anisimov, et al. Sov. Phys. JETP **39**, 375 (1974)

→ substrate-mediated excitation mechanism dominates

→ **transient non-equilibrium between e**lectrons and phonons: $T_{el} >> T_{ph}$

→ new reaction mechanism?

- by non-thermal activation
- by separation of time scales of energy flow

Surface femtochemistry

Systems

- **NO and O_2/Pd**
- **CO/Cu**
- **CO/Pt**
- **O_2/Pt**
- **CO/NiO**
- **CO + O_2/Pt**
- **CO + O/Ru, H+H/Ru**

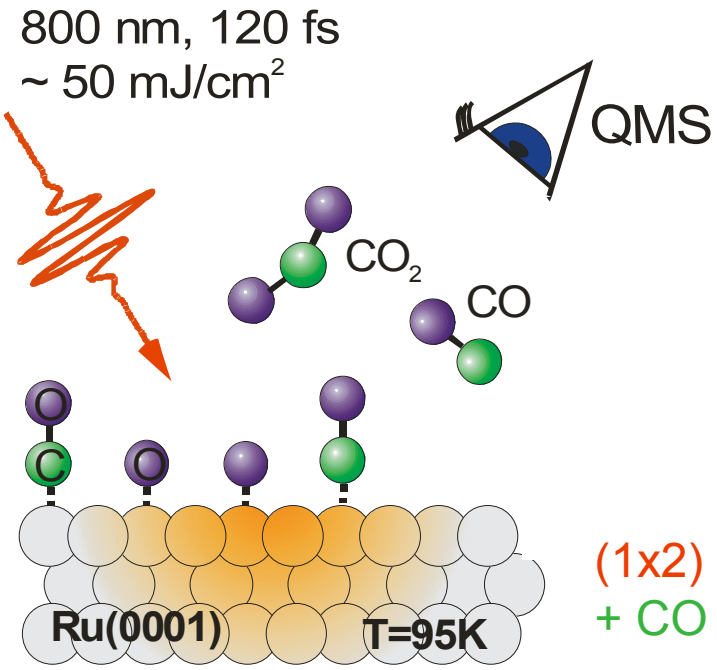
Misewich, Loy, Heinz
Tom, Prybyla
Ho
Mazur
Stephenson, Richter, Cavanagh
Bonn, Wolf, Ertl
Zacharias, Al-Shamery
Domen

Experimental Investigations

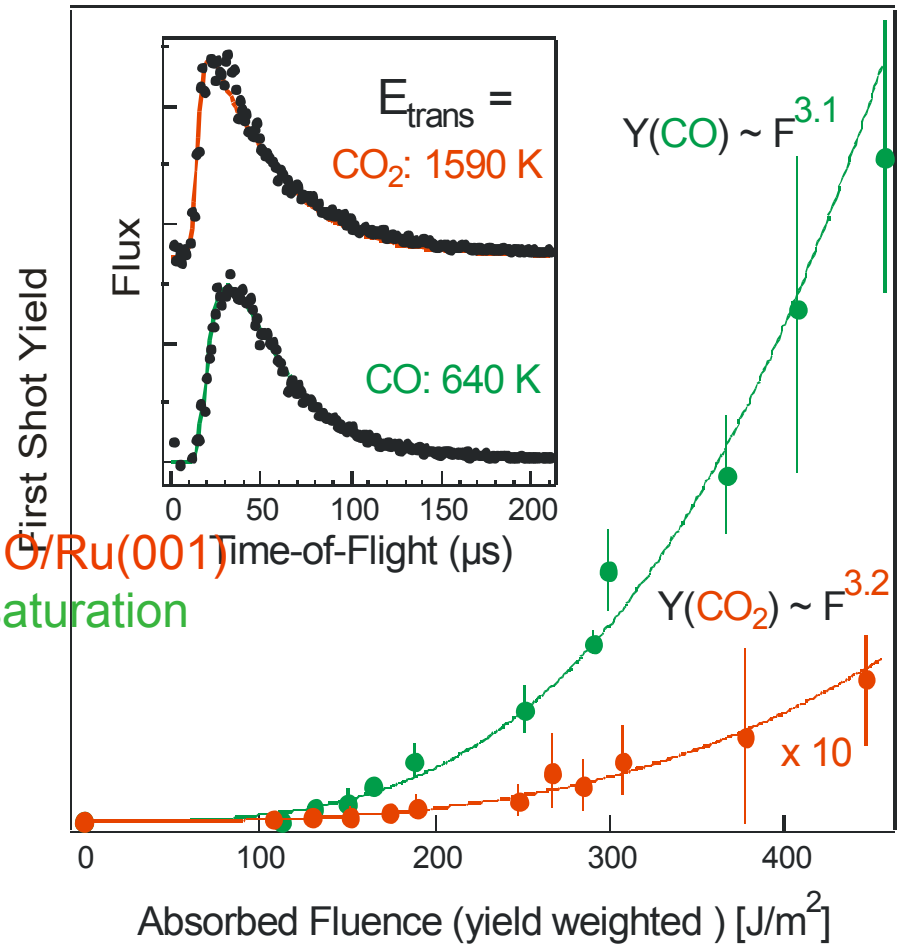
Yield
Fluence dependence
Translational energy
Vibrational energy
Rotational energy
Ultrafast dynamics
Influence of laser pulse duration
Influence of photon energy
Dependence on adsorption site
Dependence on coverage
Competitive reaction pathways

Example I: Desorption and oxidation of CO on Ru(001)

Oxidation of CO impossible under equlilibrium conditions



(1x2) - O/Ru(001)
+ CO saturation



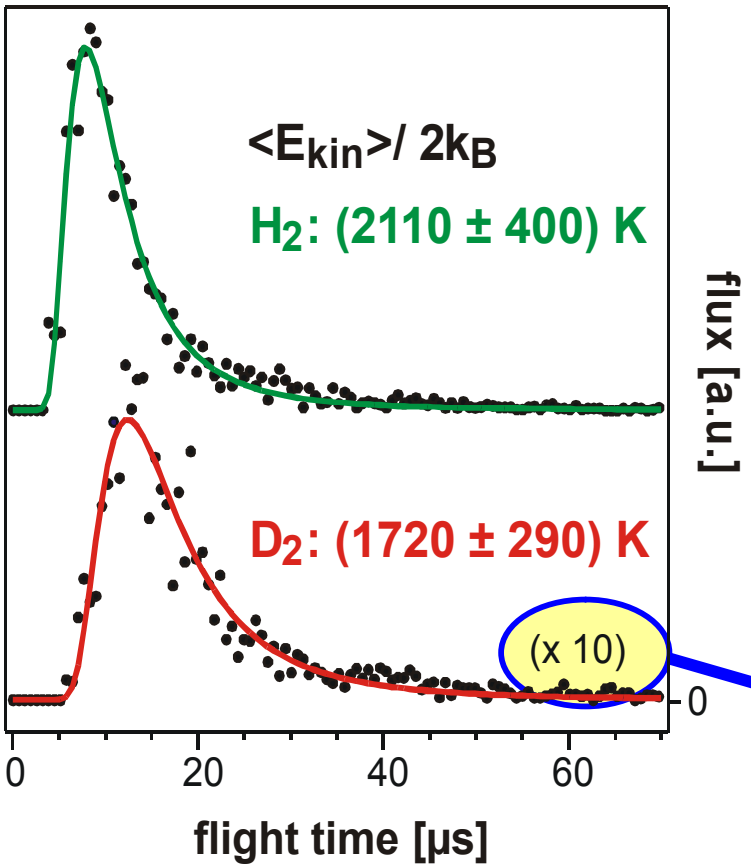
$$2\,CO_{ads} + O_{ads} \xrightarrow{h\nu} CO\uparrow + CO_2\uparrow$$

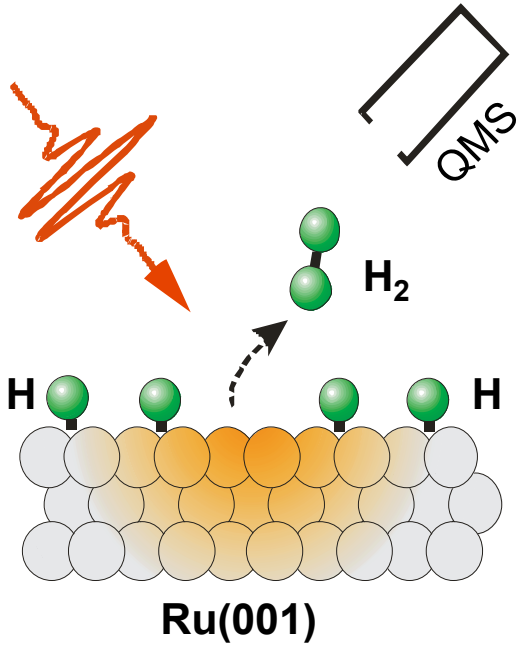
$$2\,CO_{ads} + O_{ads} \rightarrow CO\uparrow$$

→ New reaction pathway upon fs excitation

Example II: Recombinative desorption of H_2 on Ru(001)

H_2 formation induced by fs laser excitation of H/Ru(001)





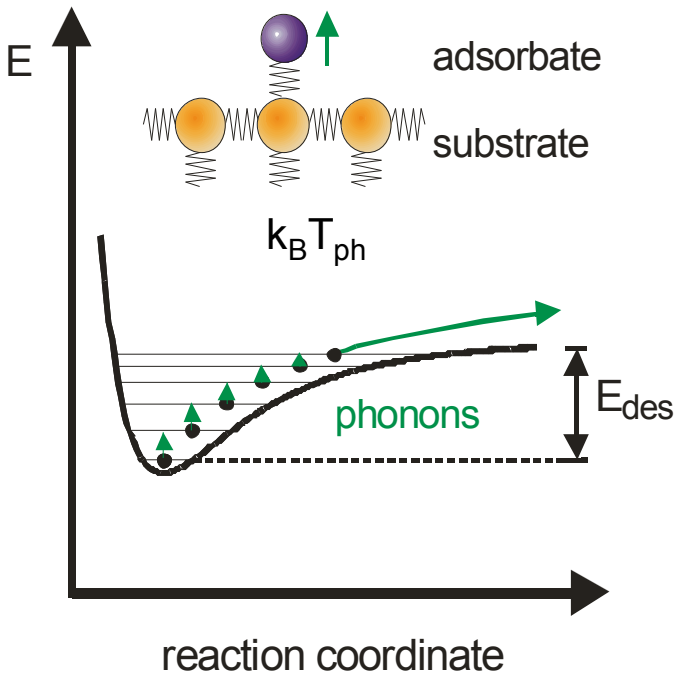
Full monolayer of H/Ru(001)

$$\frac{\text{Yield } (H_2)}{\text{Yield } (D_2)} = 10 \pm 2.4$$

- High translational temperature of desorbing species
- Pronounced isotope effects in H_2/D_2 yield

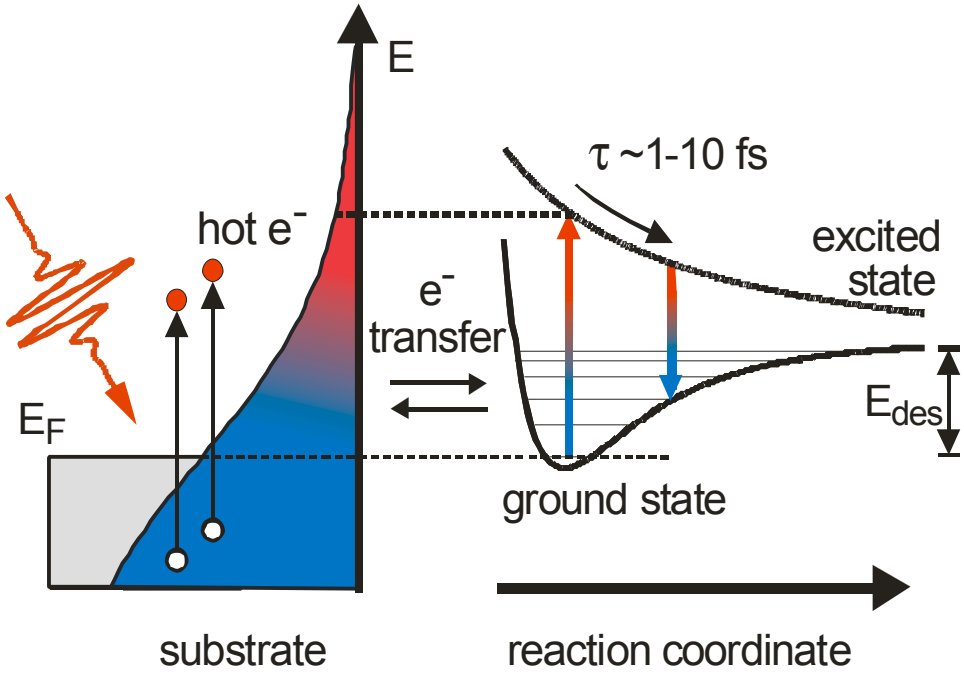
Reaction mechanisms

Phonon-mediated



Electron-mediated

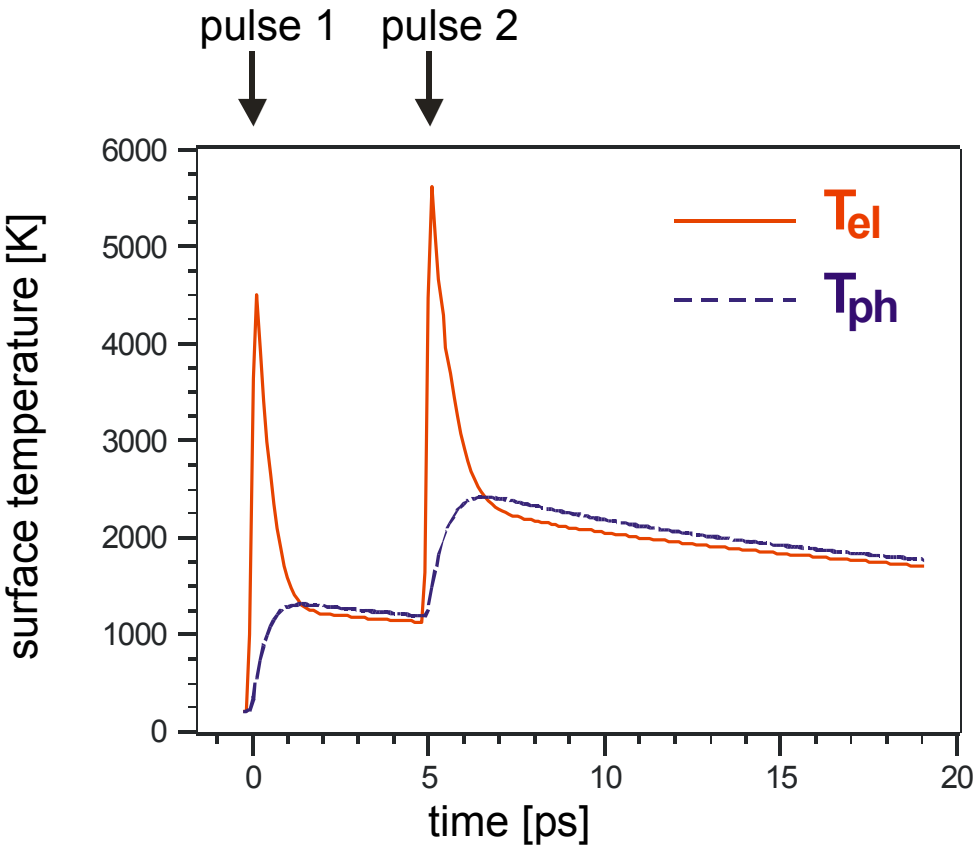
DIMET - Desorption Inducded by Multiple Electronic Transitions

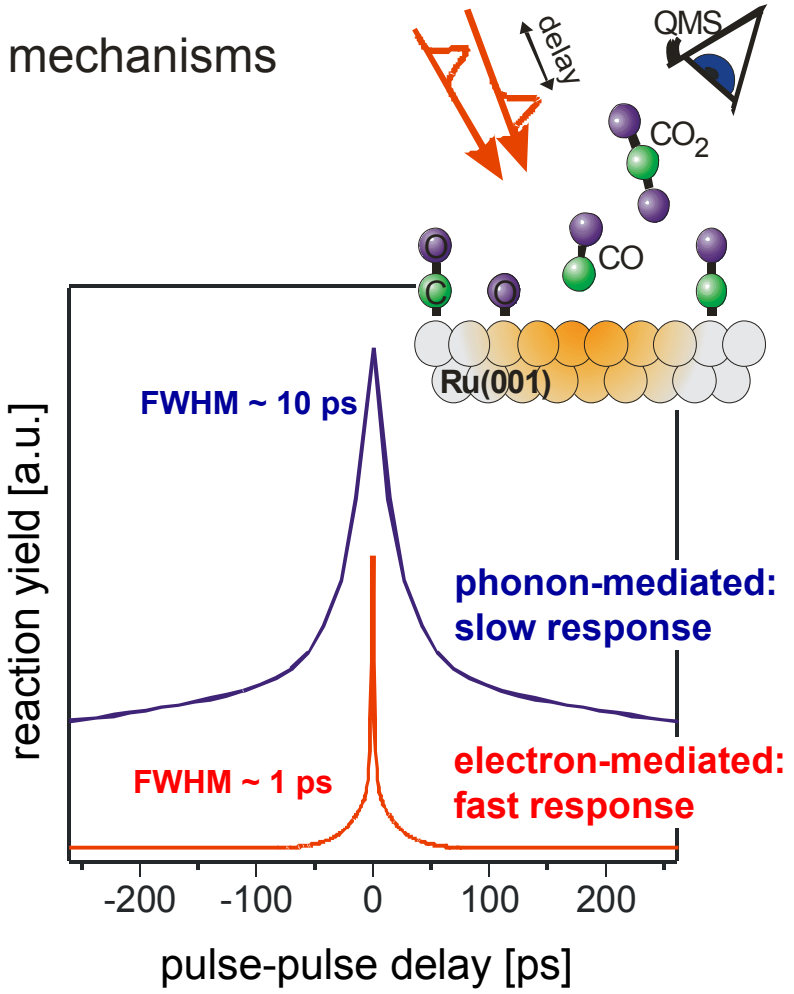


→ **How to distinguish?**

Temperature profiles and 2-pulse correlation

Goal: Discerning electron and phonon driven mechanisms



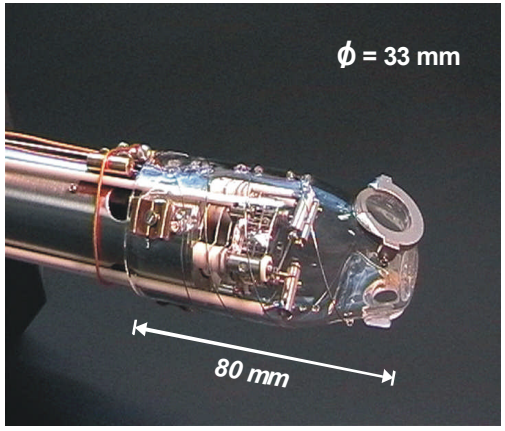


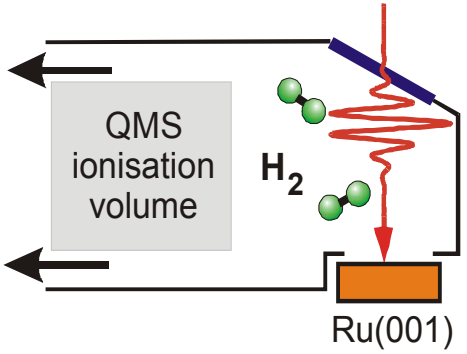
→ Two-pulse correlation measurement of the reaction yield allows to distinguish between the two reaction mechanisms!

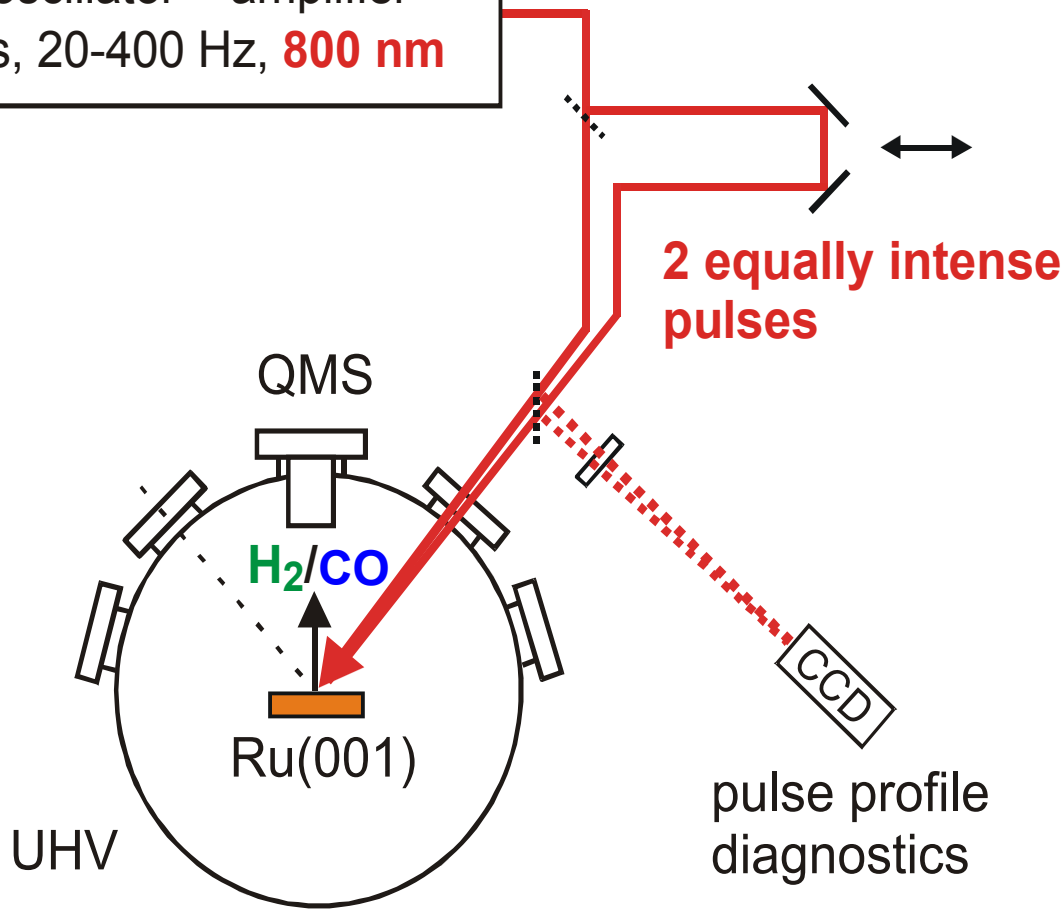
Experimental setup

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

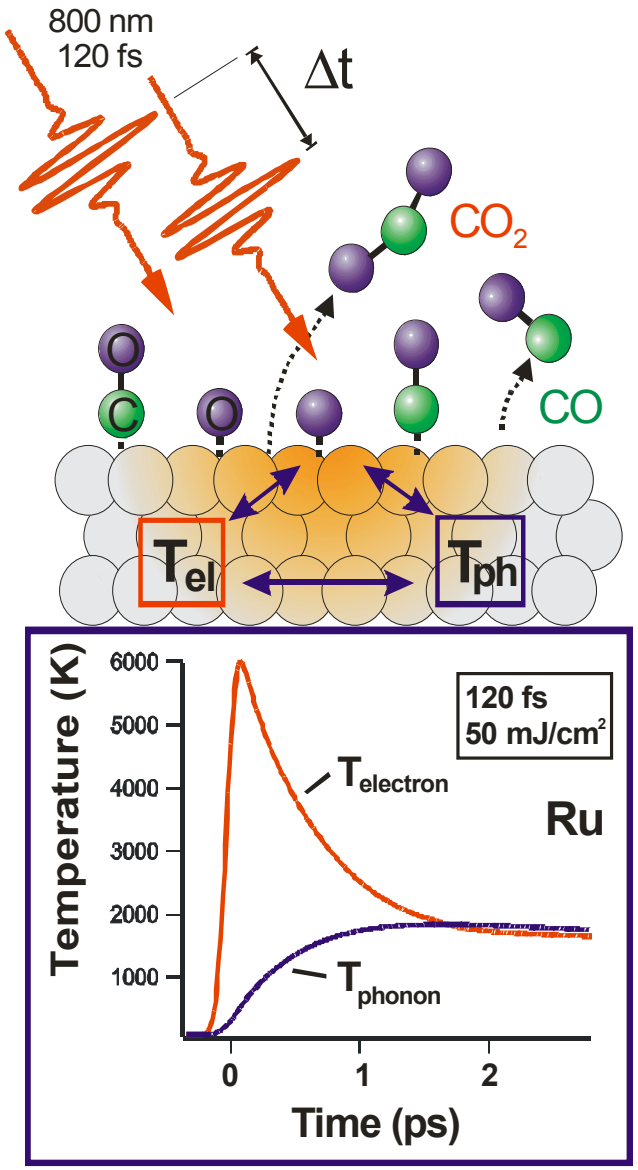
"Feulner cup" detector



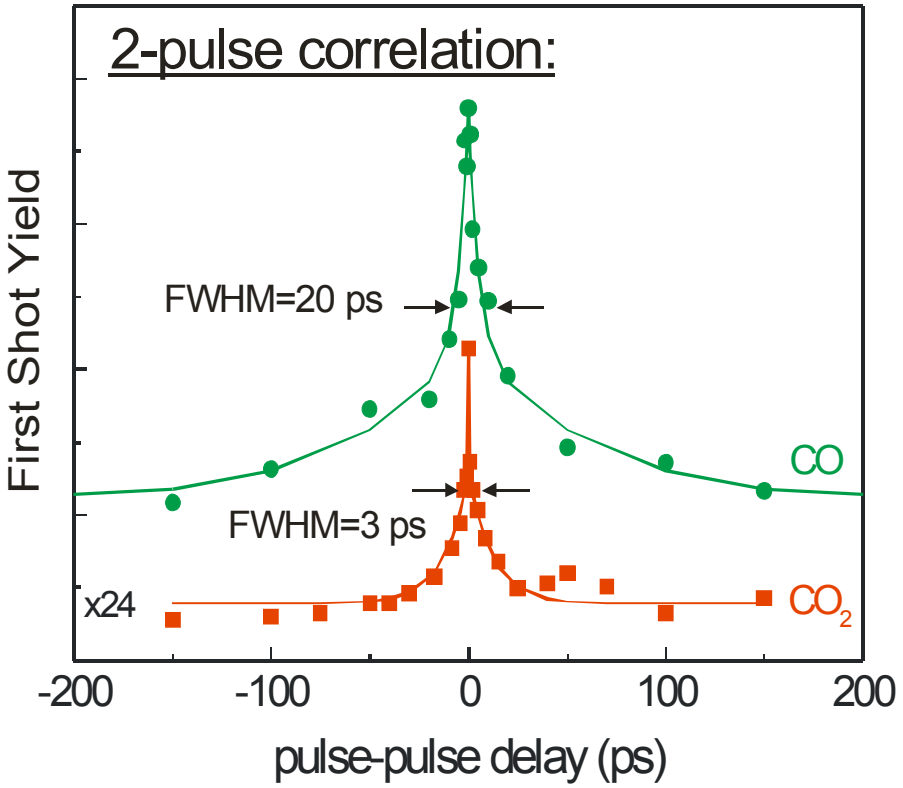




2-pulse correlation measurements



Goal: discriminate between electron and phonon mediated mechanism

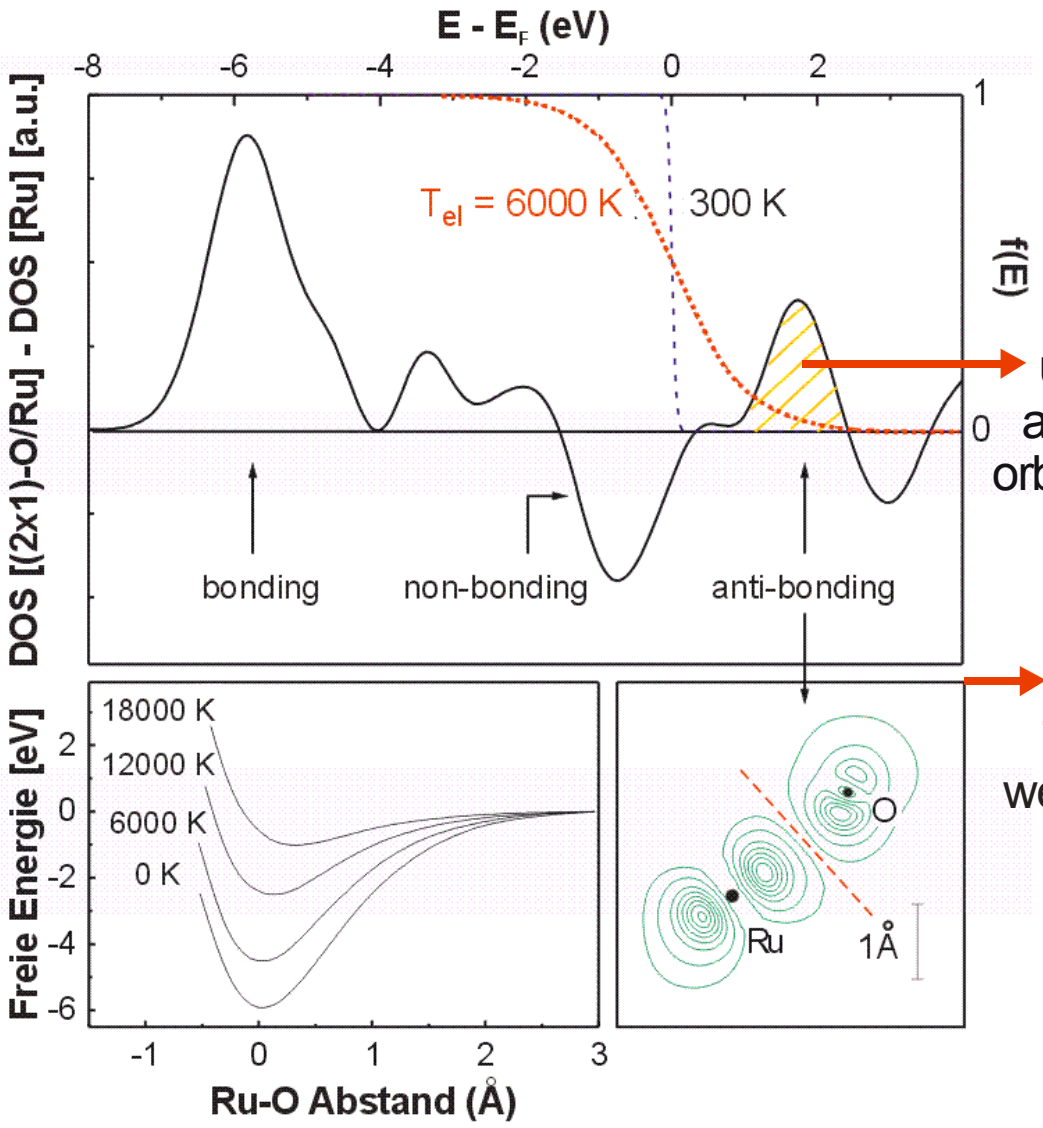


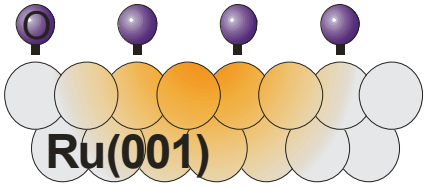
Desorption: phonon-mediated

Oxidation: hot electron-mediated

DFT calculations

C. Stampfl, M. Scheffler, FHI Berlin





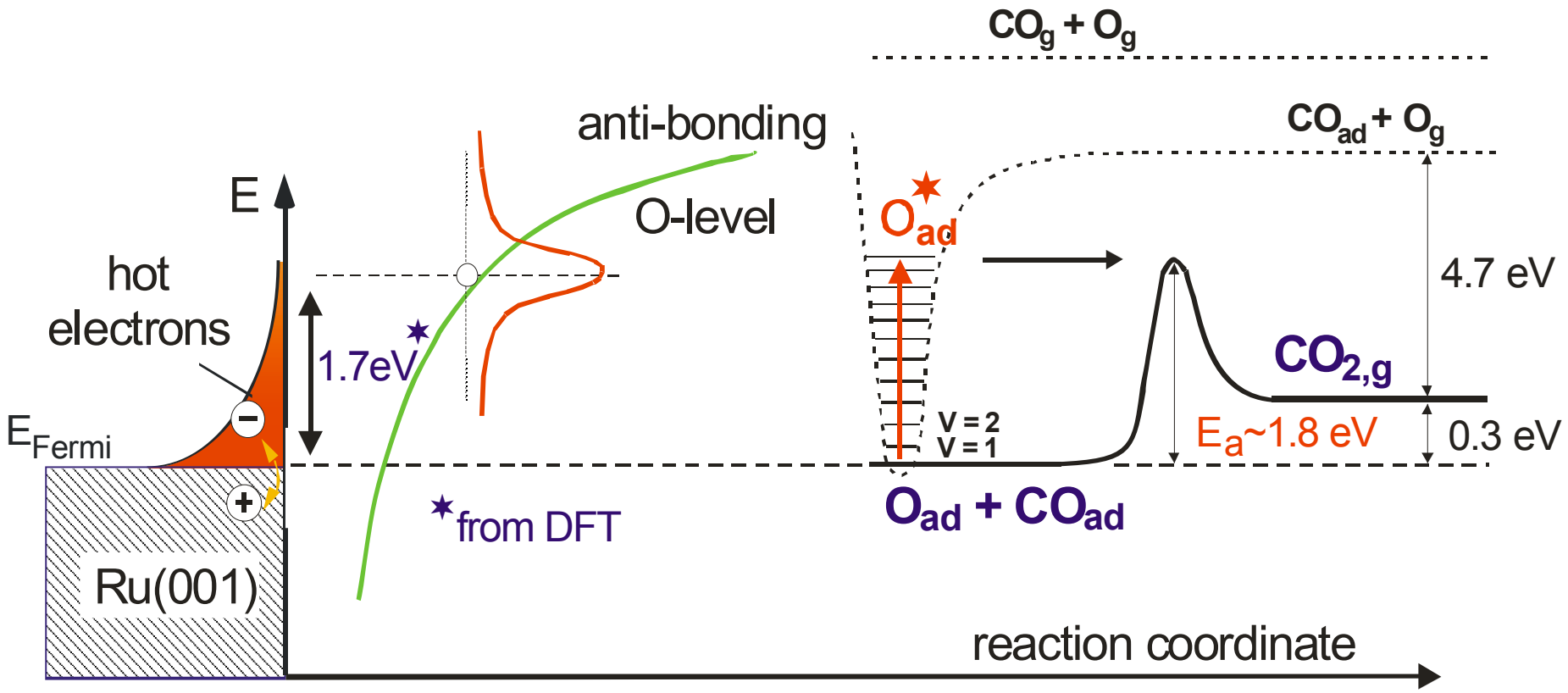
unoccupied anti-bonding orbital ~1.7eV above E_F

increasing T_{el} leads to weakening of Ru-O-Bond

Hot electron-induced activation of the O-Ru bond

Mechanism for CO oxidation

Hot electron mediated vibrational excitation of the O-Ru bond

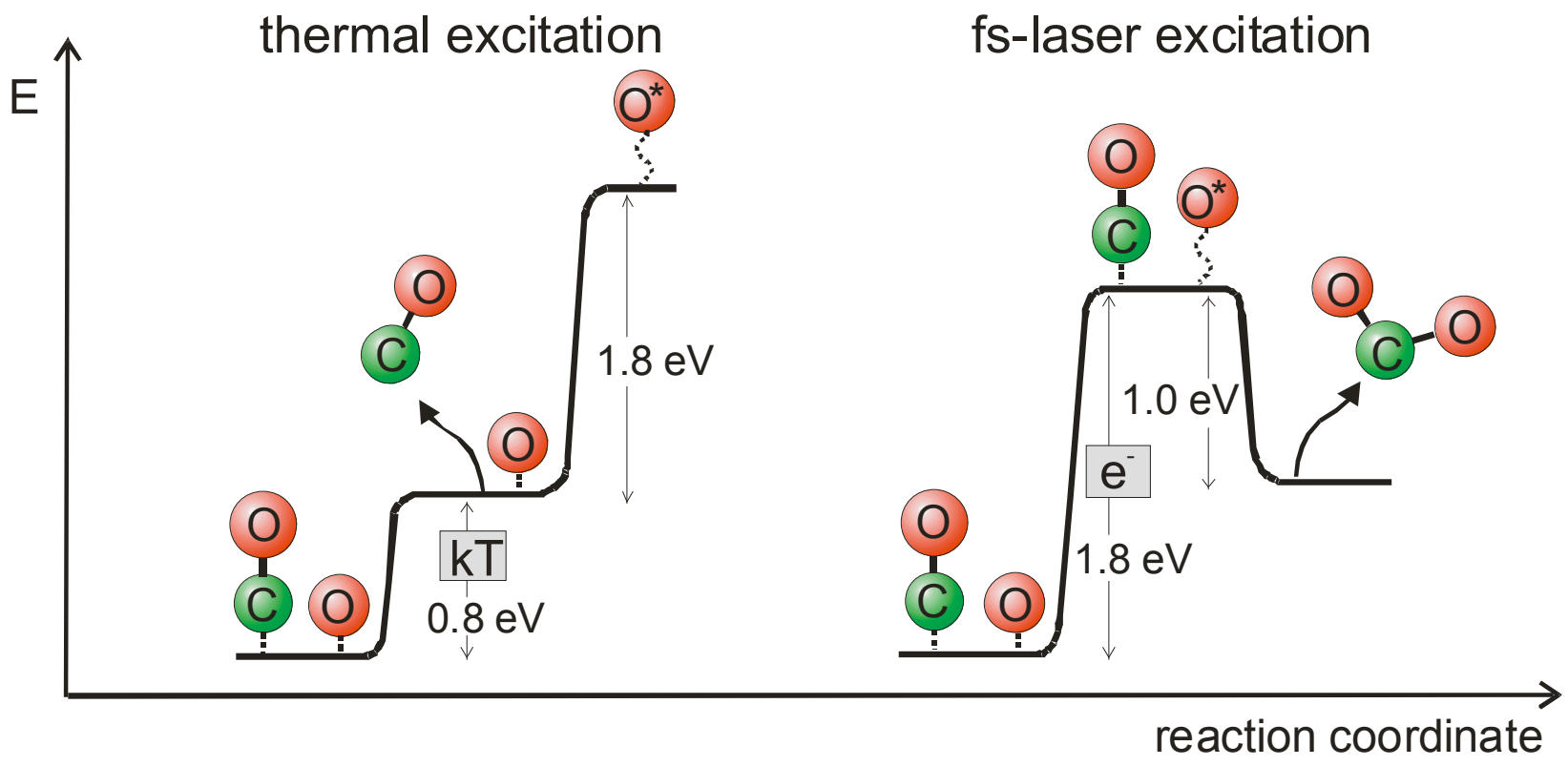


Non-adiabatic energy transfer from electronic excitations to adsorbate coordinate

M. Bonn et al, Science **285**, 1042 (1999)

Discussion

Reaction pathways for thermal versus femtosecond excitation

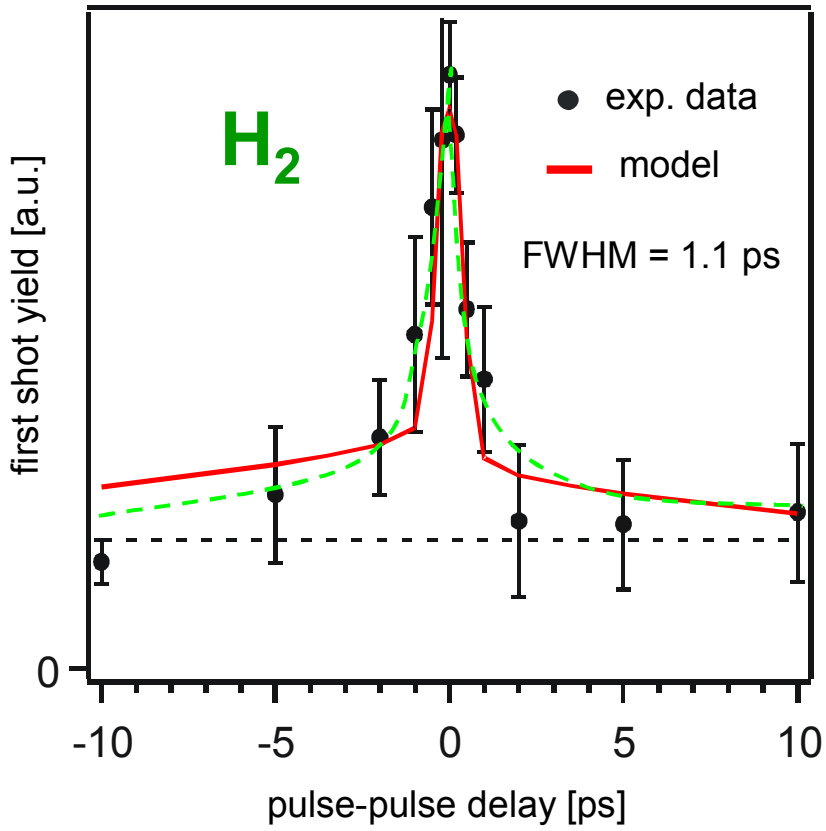


Under thermal excitation the CO has desorbed before oxygen is activated

→ Seperation of time scales opens new reaction pathway

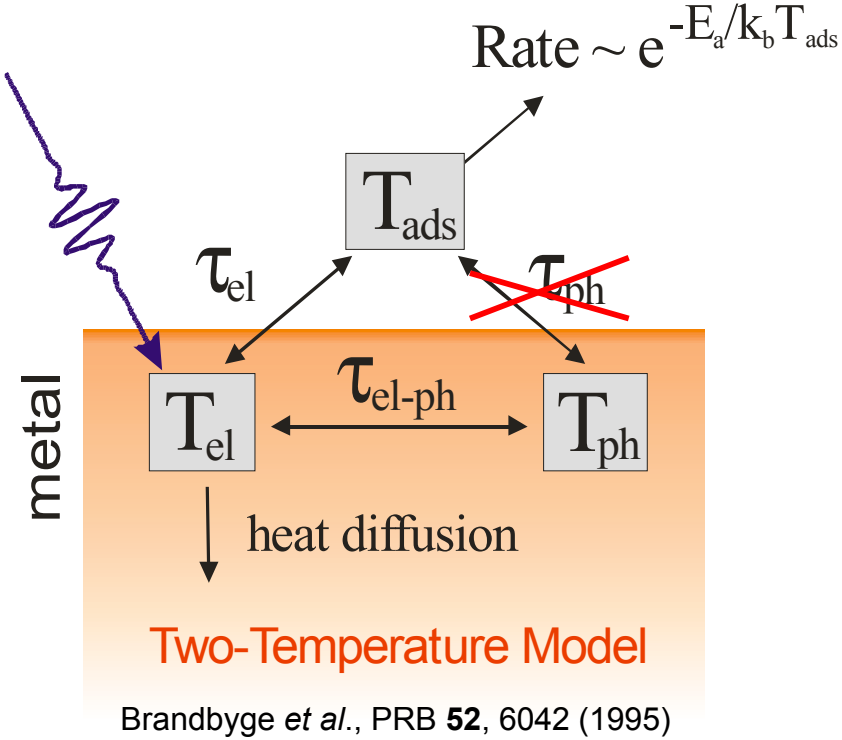
2PC of laser-induced H_2 formation

- Ultrafast response indicates coupling to hot electron transient



- Coupled heat baths: T_{el}, T_{ph}, T_{ads}

  Coupling rates: $\tau_{el}^{-1}, \tau_{ph}^{-1}, \tau_{el\text{-}ph}^{-1}$.



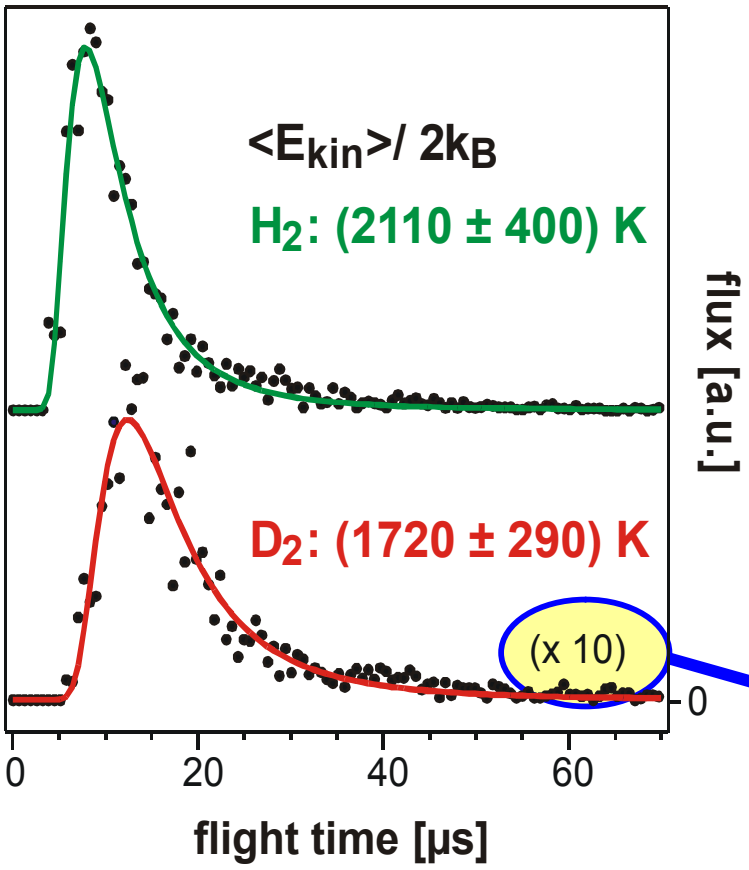
Brandbyge *et al.*, PRB **52**, 6042 (1995)

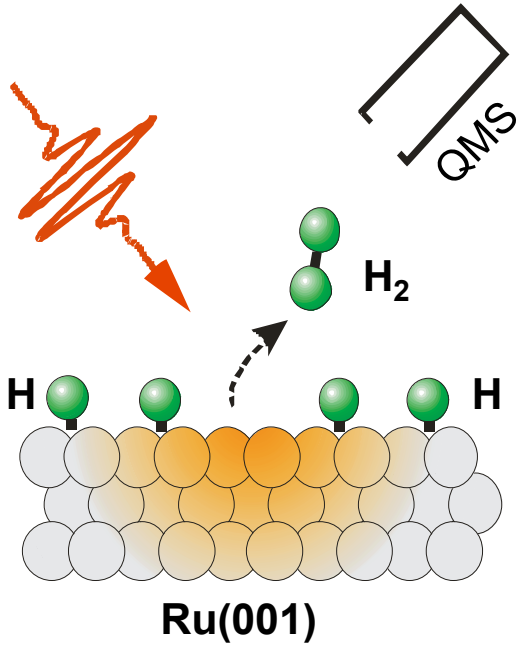
→ Electronic friction model yields: E_a = 1.35 eV and τ_{el} = 180 fs for H_2

(τ_{el} = 360 fs for D_2)

Isotope effect in recombinative desorption

H_2 formation induced by fs laser excitation of H/Ru(001)





Full monolayer of H/Ru(001)

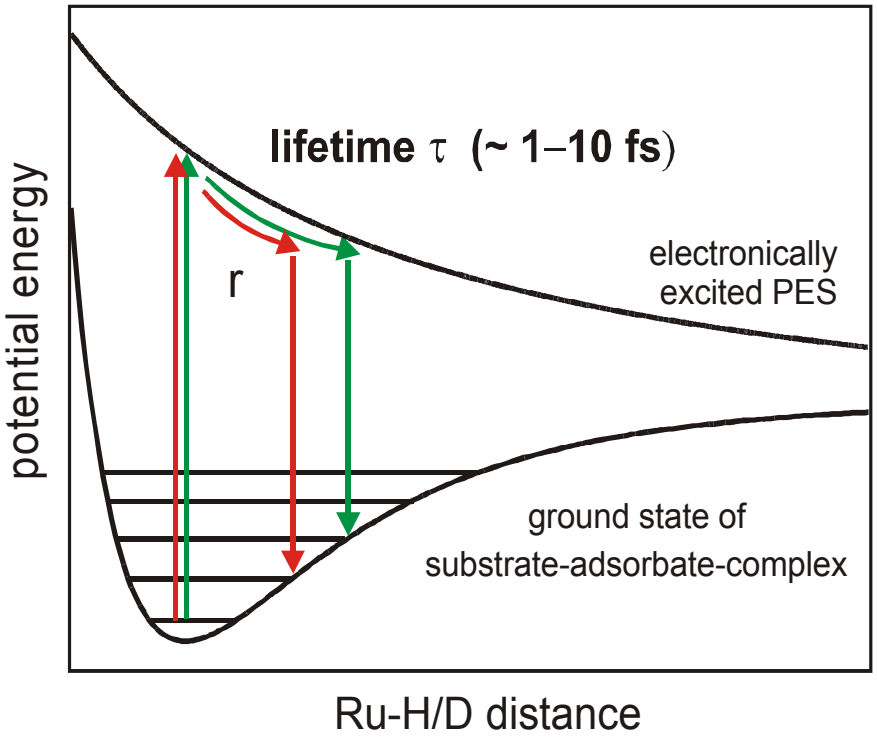
Isotope effect

$$\frac{\text{Yield } (H_2)}{\text{Yield } (D_2)} = 10 \pm 2.4$$

- Pronounced isotope effects in H_2/D_2 yield

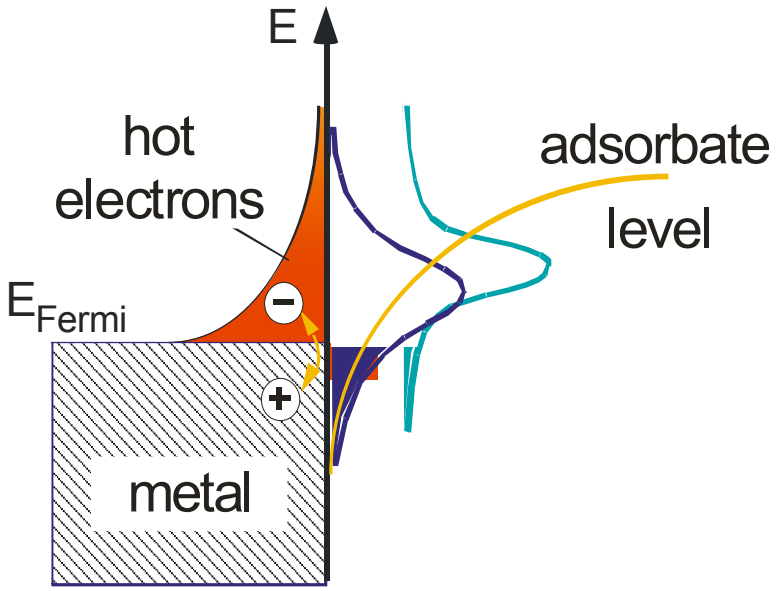
Isotope effect and electronic friction model

- Origin:
  - mass-dependent distance traversed on excited PES
  - lighter adsorbate starts moving more rapidly



- Electronic friction:

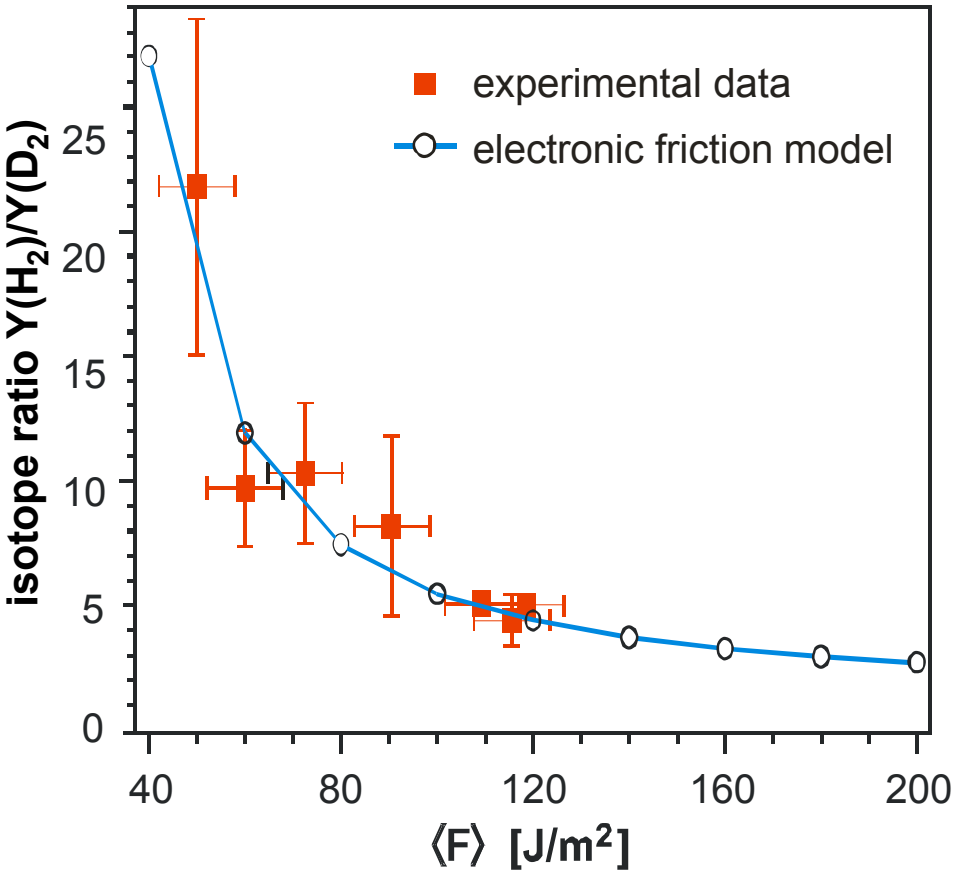
Energy transfer by coupling between adsorbate vibration and metal electrons

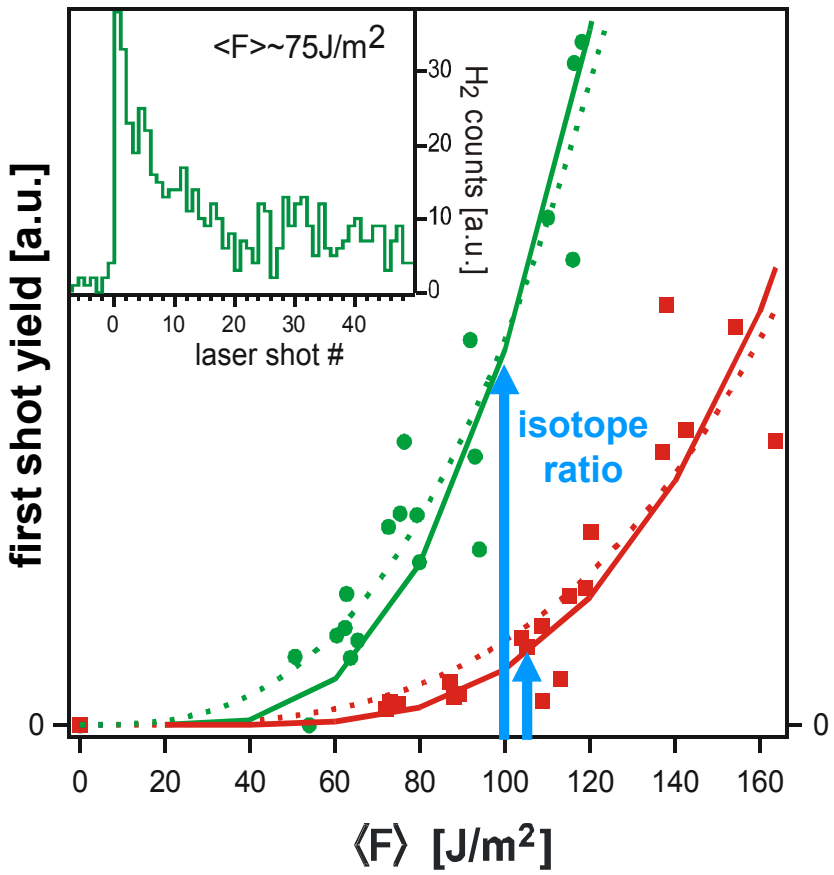


Coupling rate $\eta = \frac{1}{\tau_{el}} \sim \frac{1}{M}$

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

Fluence dependence: isotope ratio and first shot yield





Electronic friction model* simultanously describes:

- 2-pulse correlation
- fluence depedence of yield and isotope ratio

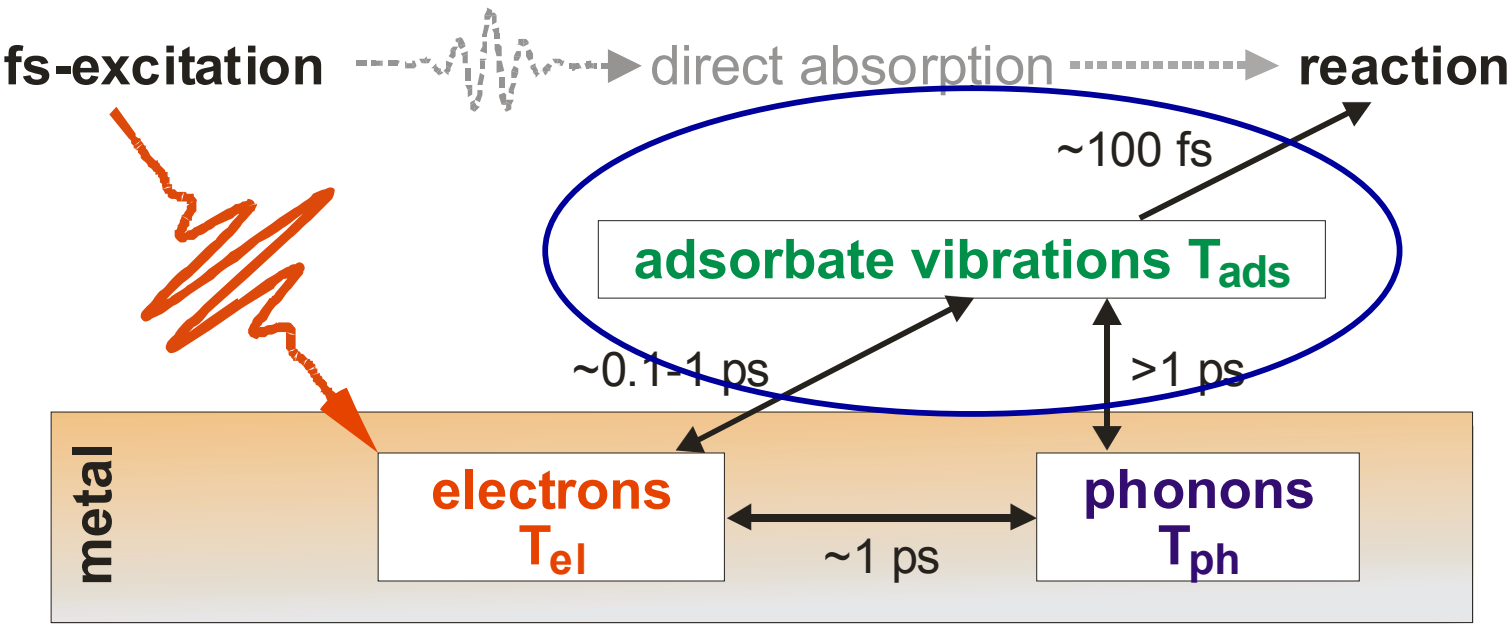
* Brandbyge *et al.*, PRB **52**, 6042 (1995)

exp. data — model — power law fit

→ $Y(H_2) \sim \langle F \rangle^{2.8}$ and $Y(D_2) \sim \langle F \rangle^{3.2}$

Real-time probing of vibrational dynamics

Goal: Probe suface reactions directly in the time domain

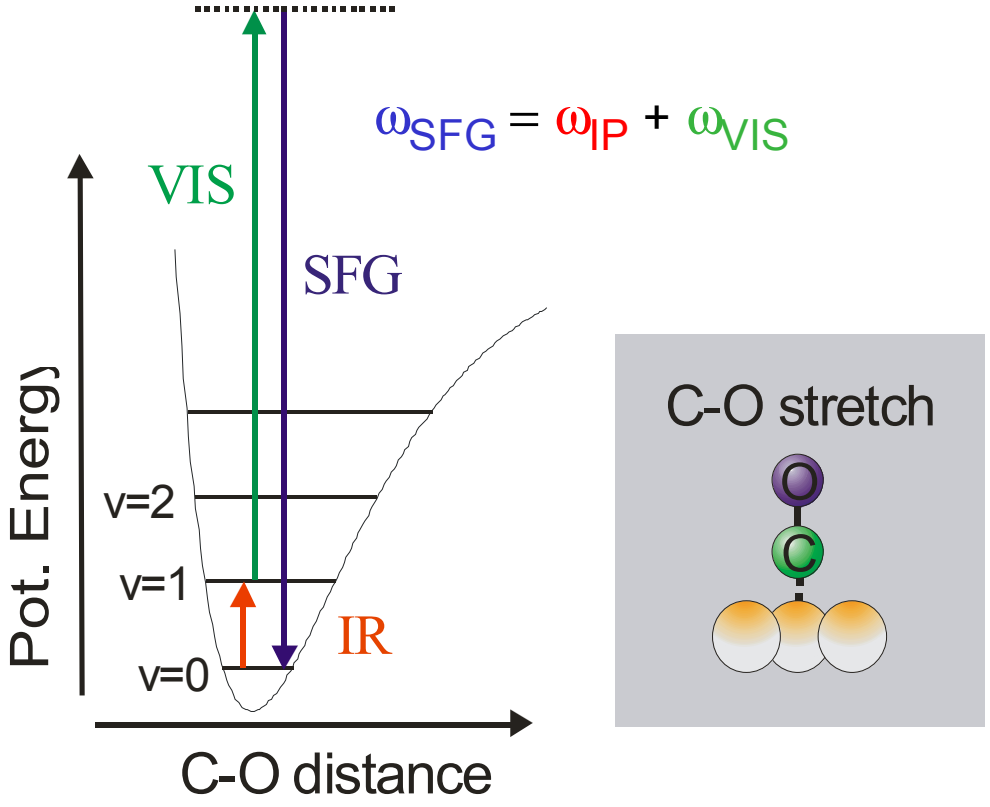


→ So far probed only the (desorbing) reaction products

→ Use surface sensitive non-linear optics (SHG, SFG) to obtain a direct look inside the excited adlayer

Vibrational spectroscopy: Sum-frequency-generation

Principle of sum-frequency generation (SFG):



- Second order non-linear optical process

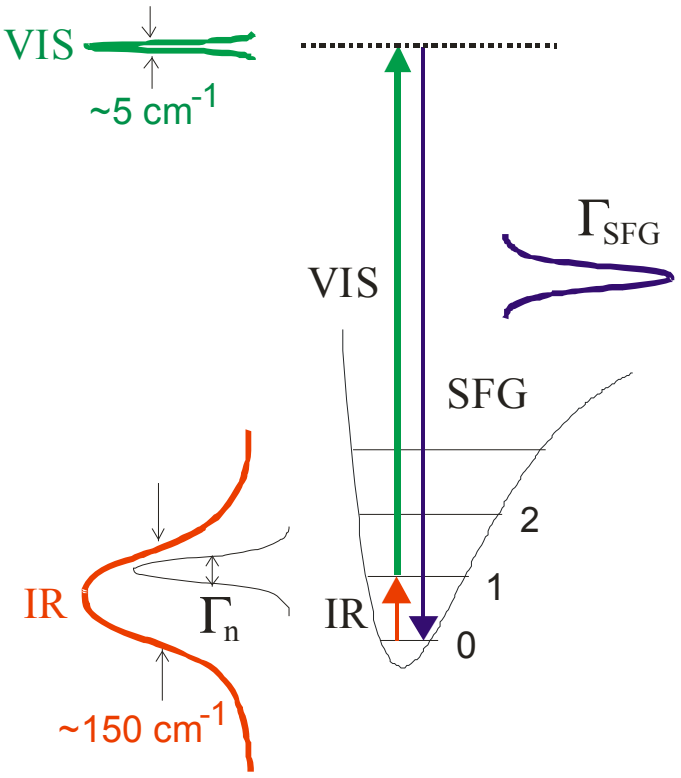
$$\mathbf{P}^{(2)}_{\omega_{SFG}} = \chi^{(2)}_{\omega_{SFG}} \mathbf{E}_{\omega_{IR}} \mathbf{E}_{\omega_{VIS}}$$

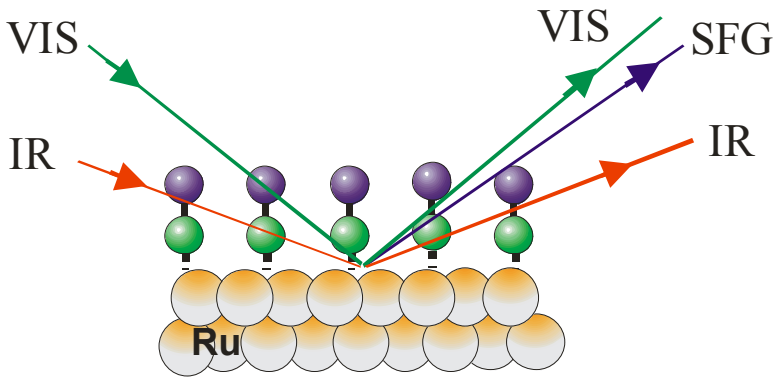
- Surface sensitive method: SFG is symmetry forbidden in isotropic (bulk) media (in dipole approximation)

→ Time-resolved SFG as molecule specific probe of surface reactions

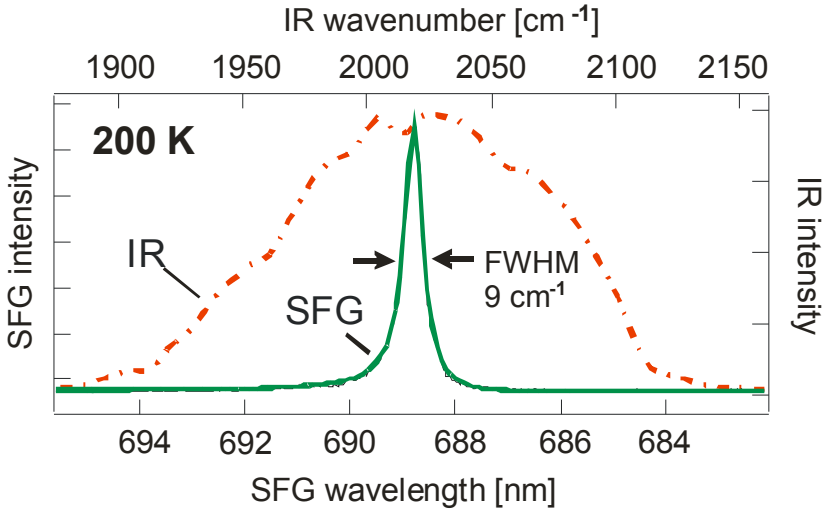
Broadband IR vibrational SFG spectroscopy

Vibrational spectroscopy without tuning the IR frequency





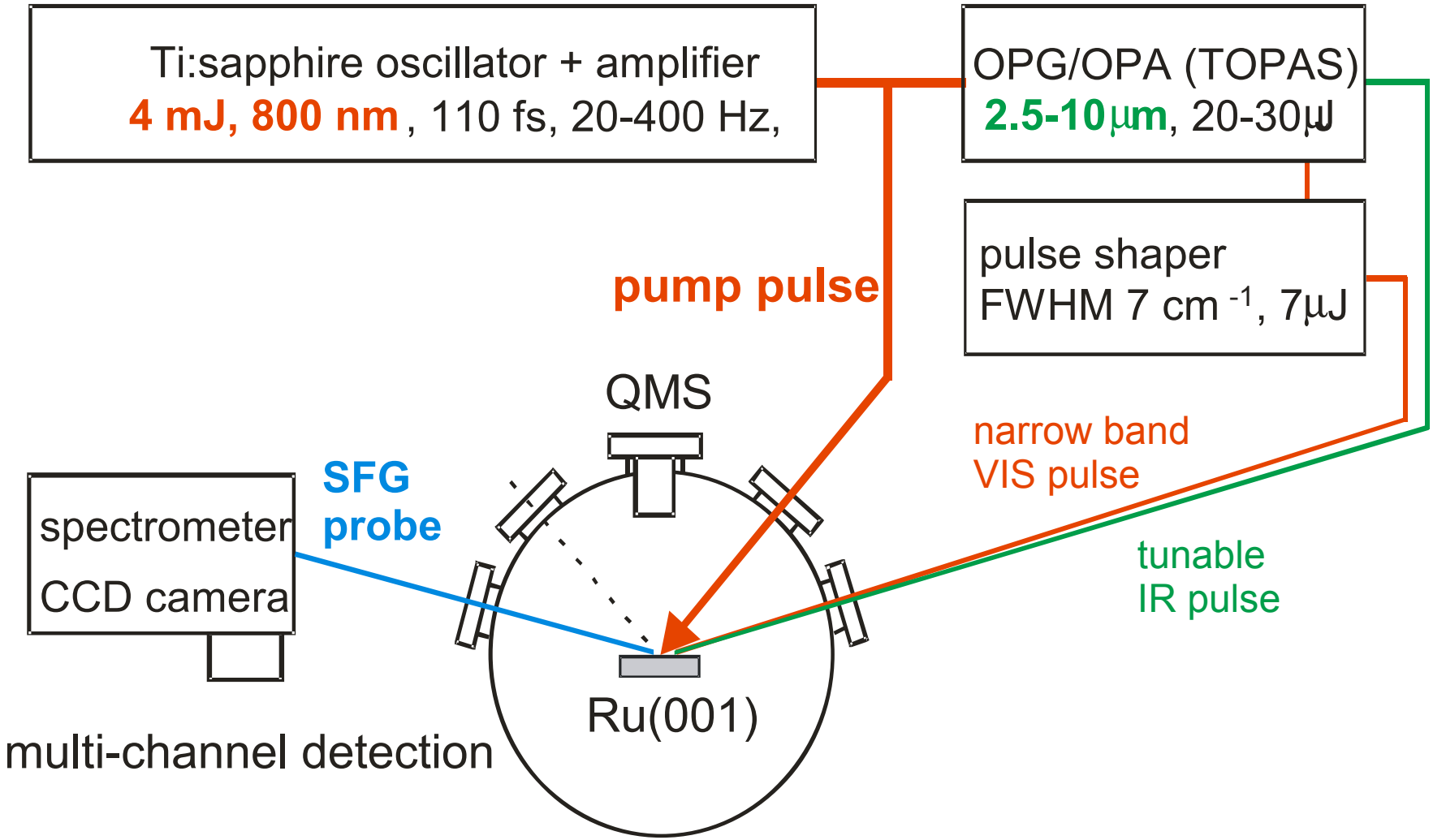
SFG spectrum (√3x√3)-CO/Ru(001)



→ Use spectrally broad fs- IR pulse with spectrally narrow VIS upconversion pulse

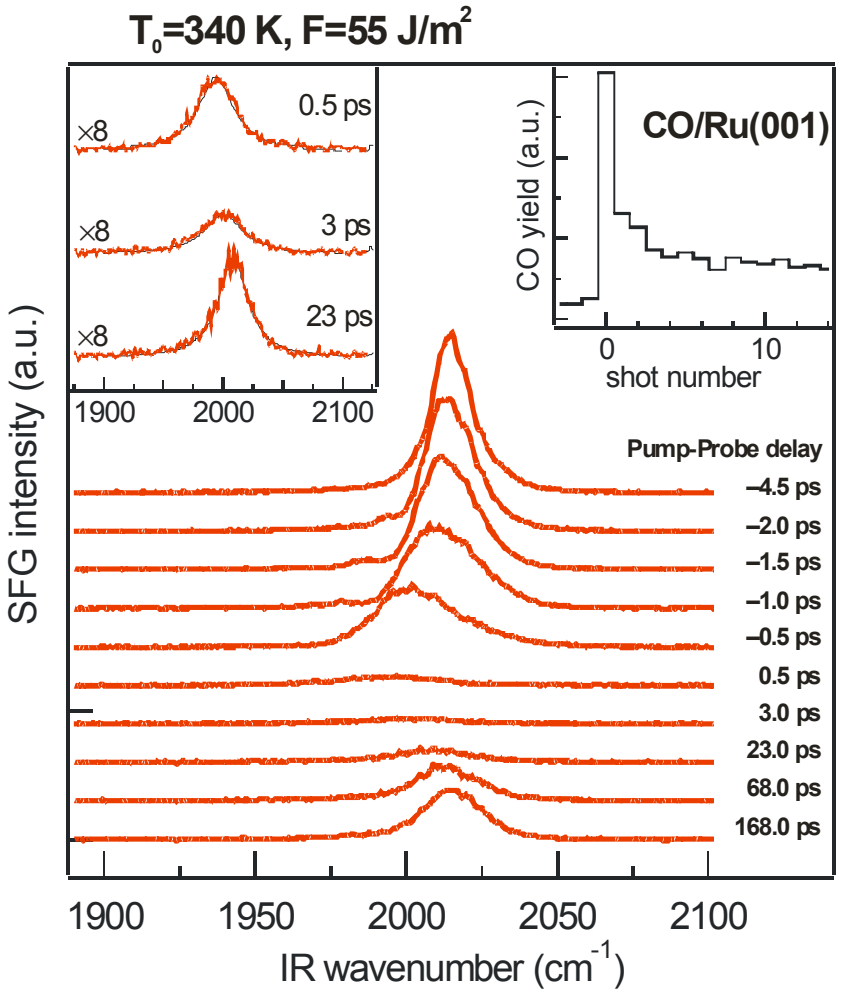
L.J. Richter *et al.*, Opt. Lett. **23**, 1594 (1998).

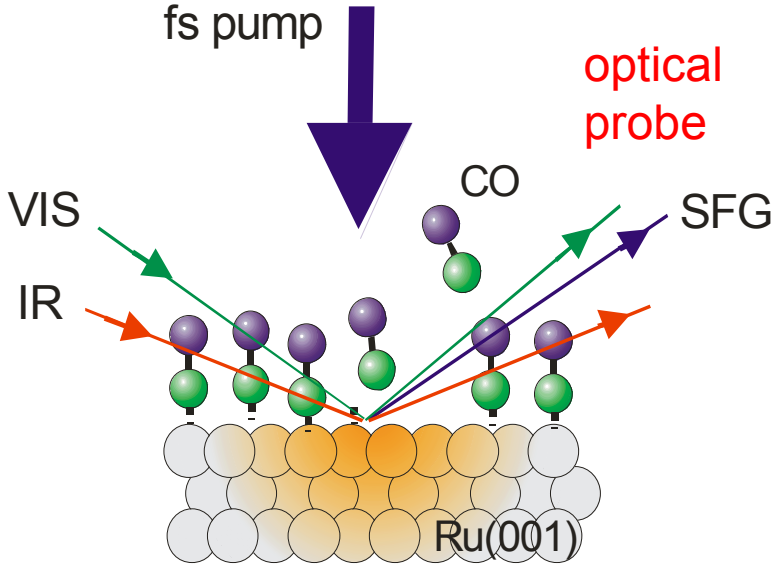
SFG experimental setup



Time-resolved SFG of CO/Ru during desorption

Spectroscopic snapshots of the CO stretch mode





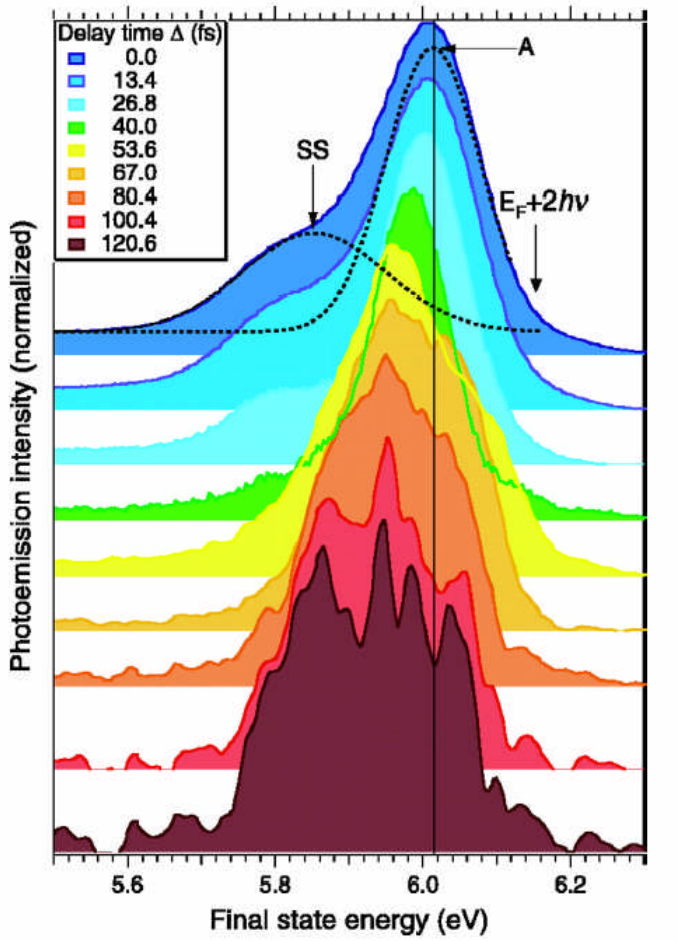
- Pronounced transient red shift, linewidth broadening and decrease of intensity
- Problems:
  Dipole-dipole coupling in the adlayer and small concentration of „products“

M. Bonn *et al,* Phys. Rev. Lett **84**, (2000) 4653

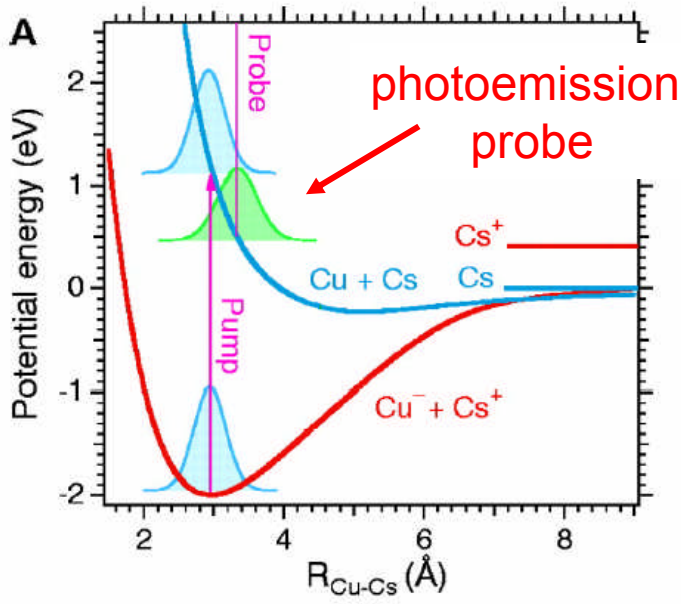
Real-time probing of surface reactions: 2PPE

Snapshots of excited electronic states during evoltution of wavepacket

Time-resolved 2PPE spectra



‚Desorption' of Cs/Cu(111)



Time-resolved 2PPE of Cs 6s-6p_z state:

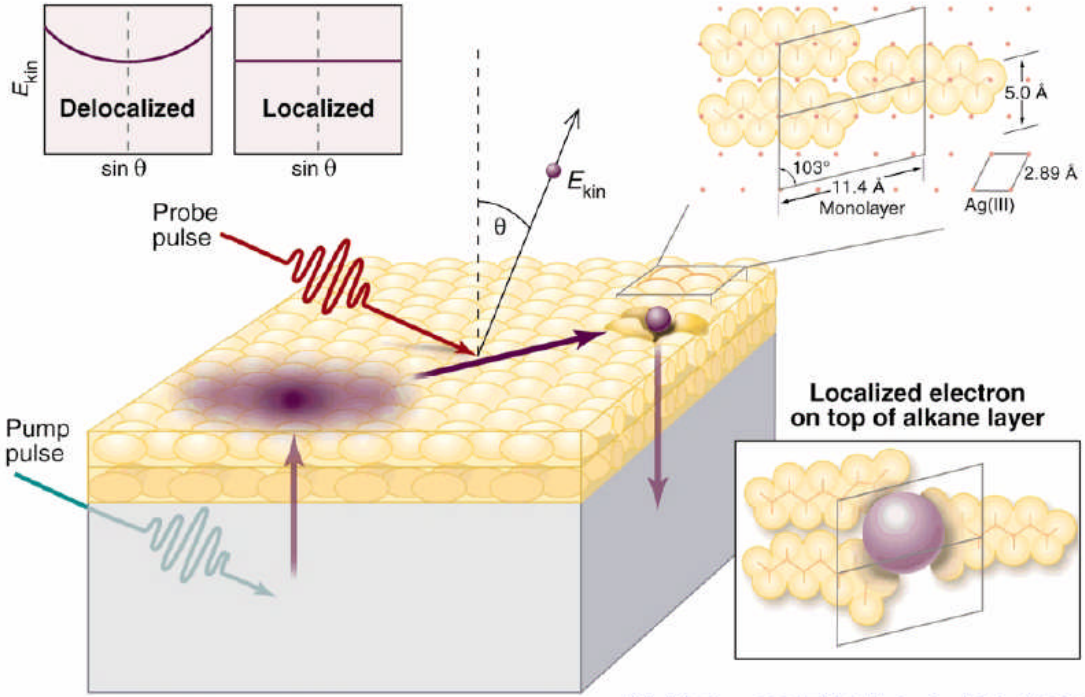
- (Long) lifetime $\tau_r = 50\,\text{fs}$
- Shift in 150 fs: $\Delta E = -0.2\,\text{eV}$

$\Rightarrow$ Cs-Desorption: $\Delta R_{Cu-Cs} = 0.3\,\text{Å}$

[Petek, Weida, Nagano & Ogawa, SCIENCE **88**, 1402 (2000)]

Electron localization in adsorbate layers

[Ge, Harris *et al.*, SCIENCE **279**, 202 (1998)]



[U. Höfer, SCIENCE **279**, 190 (1998)]

Dynamics of "small polaron"

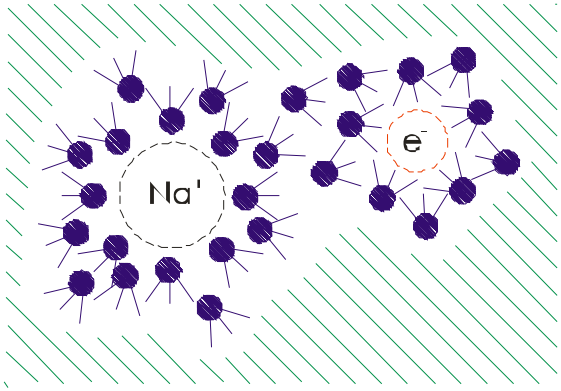
- Classical theory problem
  - Landau (1933)
  - Pekar (1954)
  - Holstein (1955)
  - Marcus (1956)
- Related phanomena:
  - Solvatated Electron
  - Conducting polymers
  - High-T_c superconductors
  - Photosynthesis

→ Electron localization and solvation in polar adsorbate overlayers

Solvated electrons in polar liquids

Brief history:

- Davy (1808) reports blue ammonia containing compounds
- Weyl (1863) discovers a blue solution of Na in liquid ammonia
- Kraus (1908) attributes the blue color to trapped electrons surrounded by NH_3 molecules
- Ogg (1940) develops first model for solvated electrons
- Hart & Boag (1962) discover the hydrated electron in water



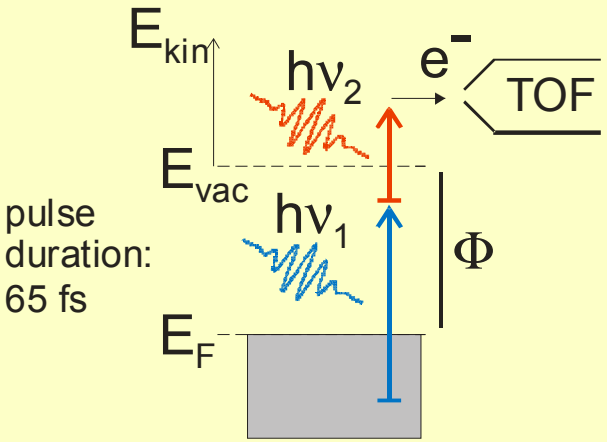
Optical absorption spectrum

Schindewolf, Angew. Chemie **80**, (1968) 165

Courtesy: C.P. Schulz, MBI Berlin

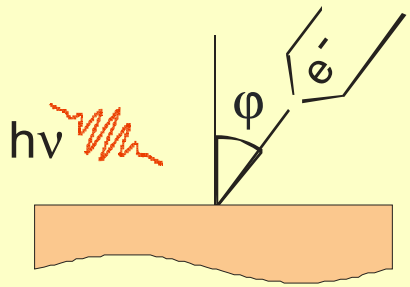
Time-resolved two-photon photoemission

energy- and time-resolution:



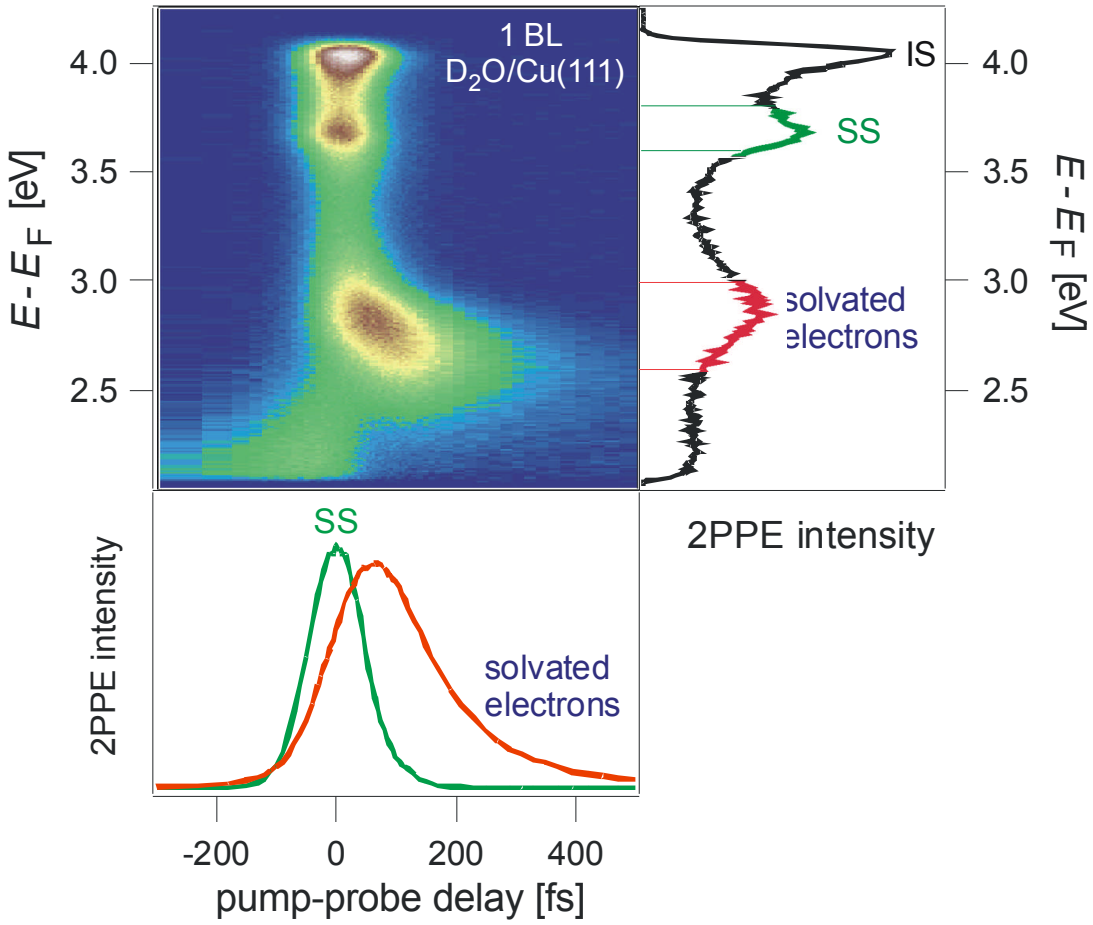
$$E - E_F = E_{kin} + \Phi - h\nu_2$$

momentum resolution:



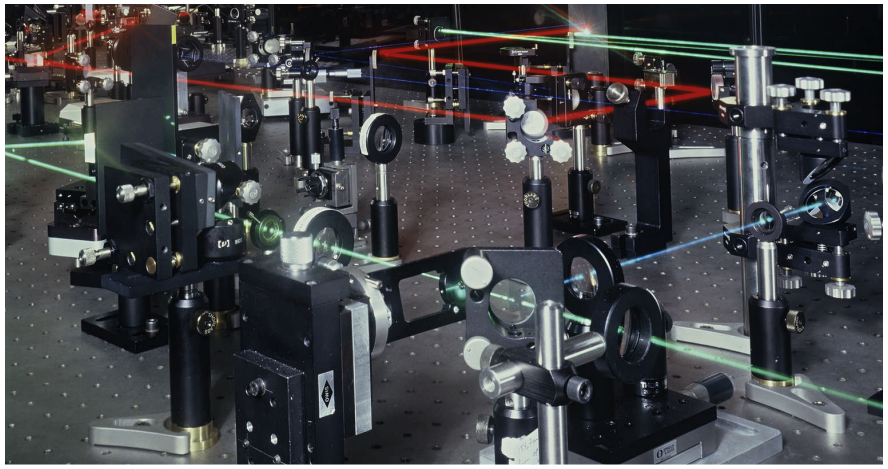
$$k_{||} = \sin\varphi\sqrt{2mE_{kin}}/\hbar$$

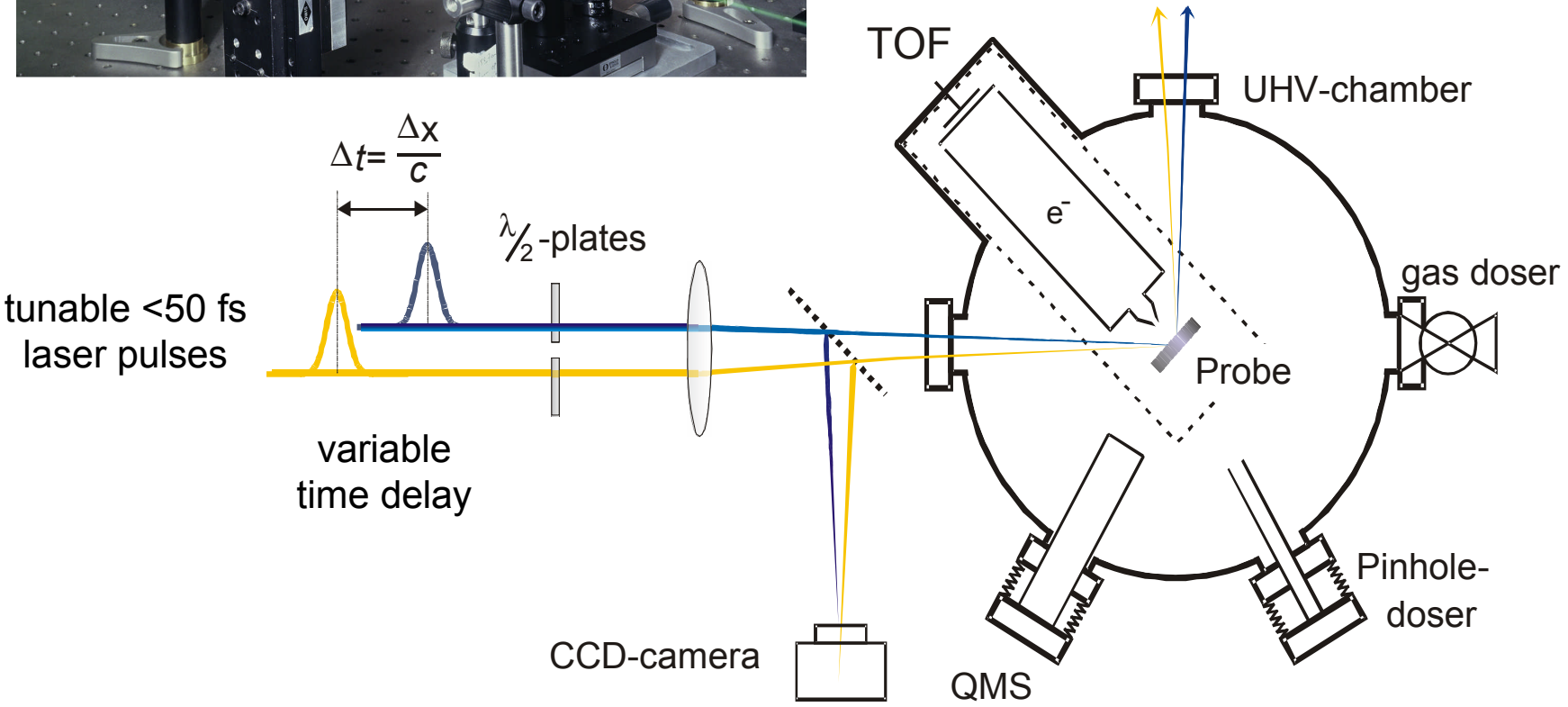
2PPE spectra as a function of time delay



→ analysis of solvation and localization dynamics using time- and angle-resolved 2PPE

2PPE experiment

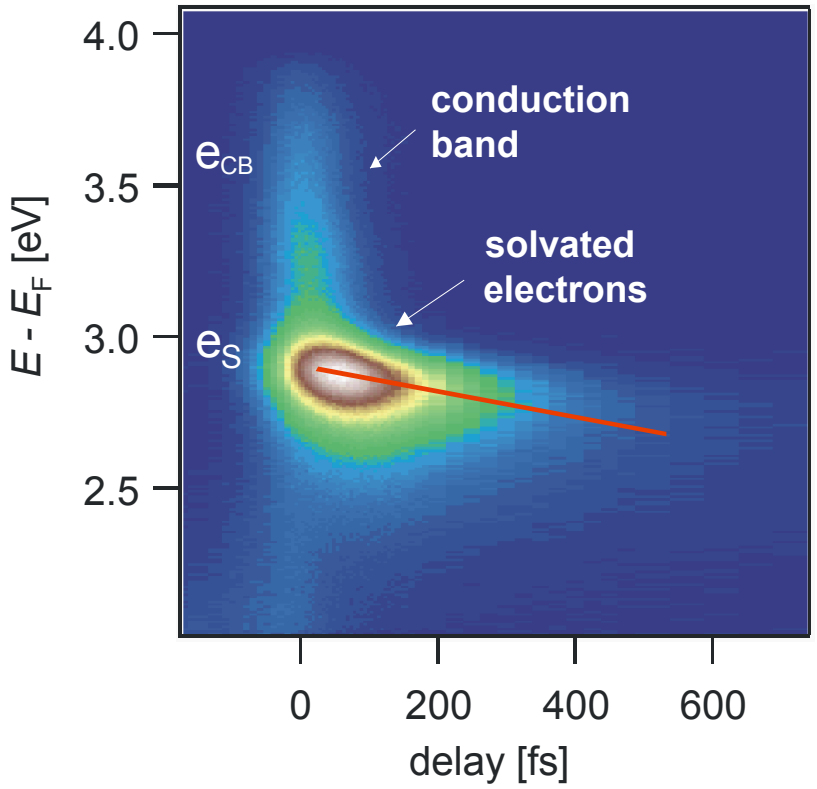




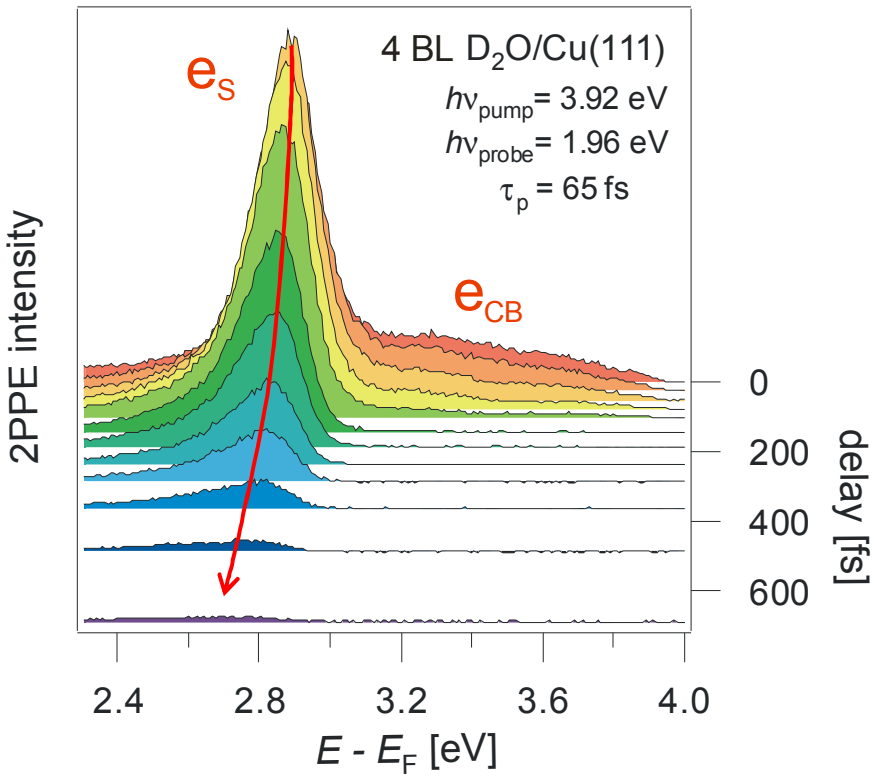
Part I: Electron transfer dynamics in D_2O/Cu(111)

Dynamics of photoinjected electrons in multilayers of amorphous ice

two-photon-photoemission



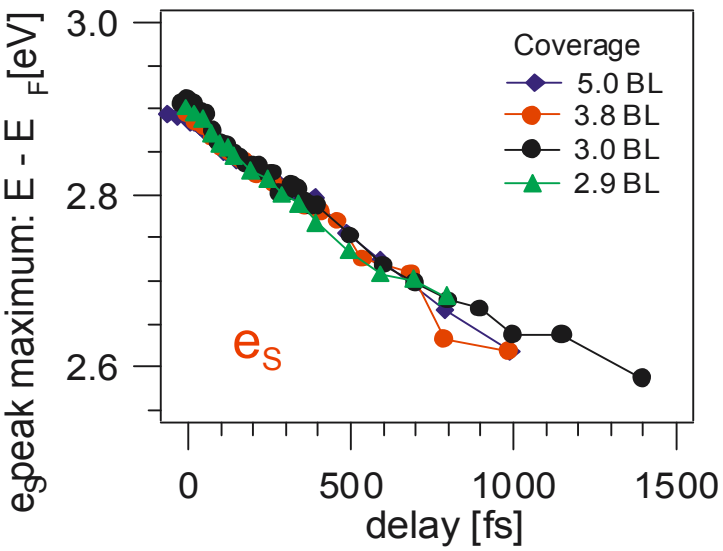
time-resolved spectra



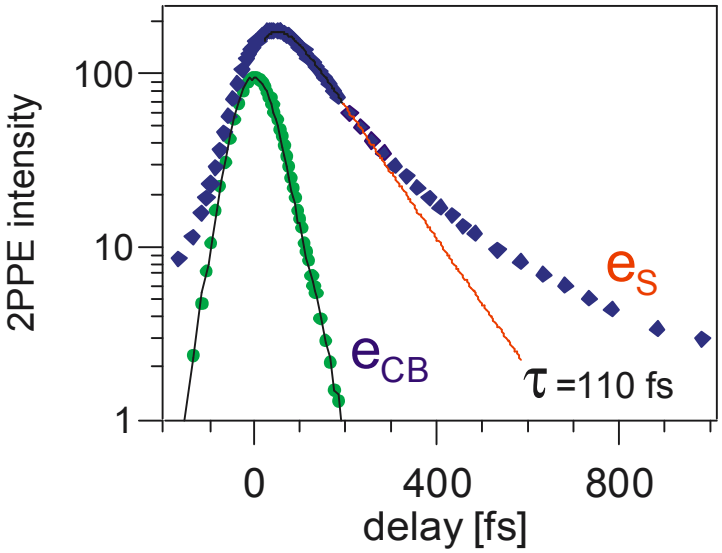
- Ultrafast relaxation within experimental time resolution (e_{CB} -> e_S)
- Stabilisation of localized electronic state (e_S) on time scale of 0.1-1 ps

Energetic stabilization and population decay

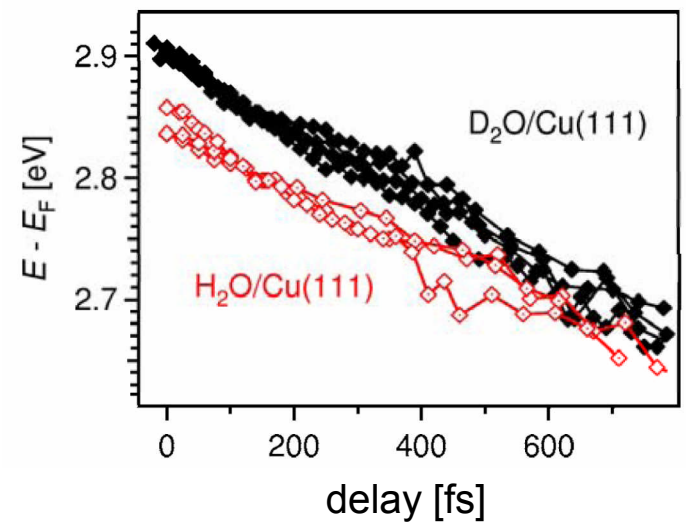
peak shift



population



isotope effect



e_{CB}: population decay within pulse width

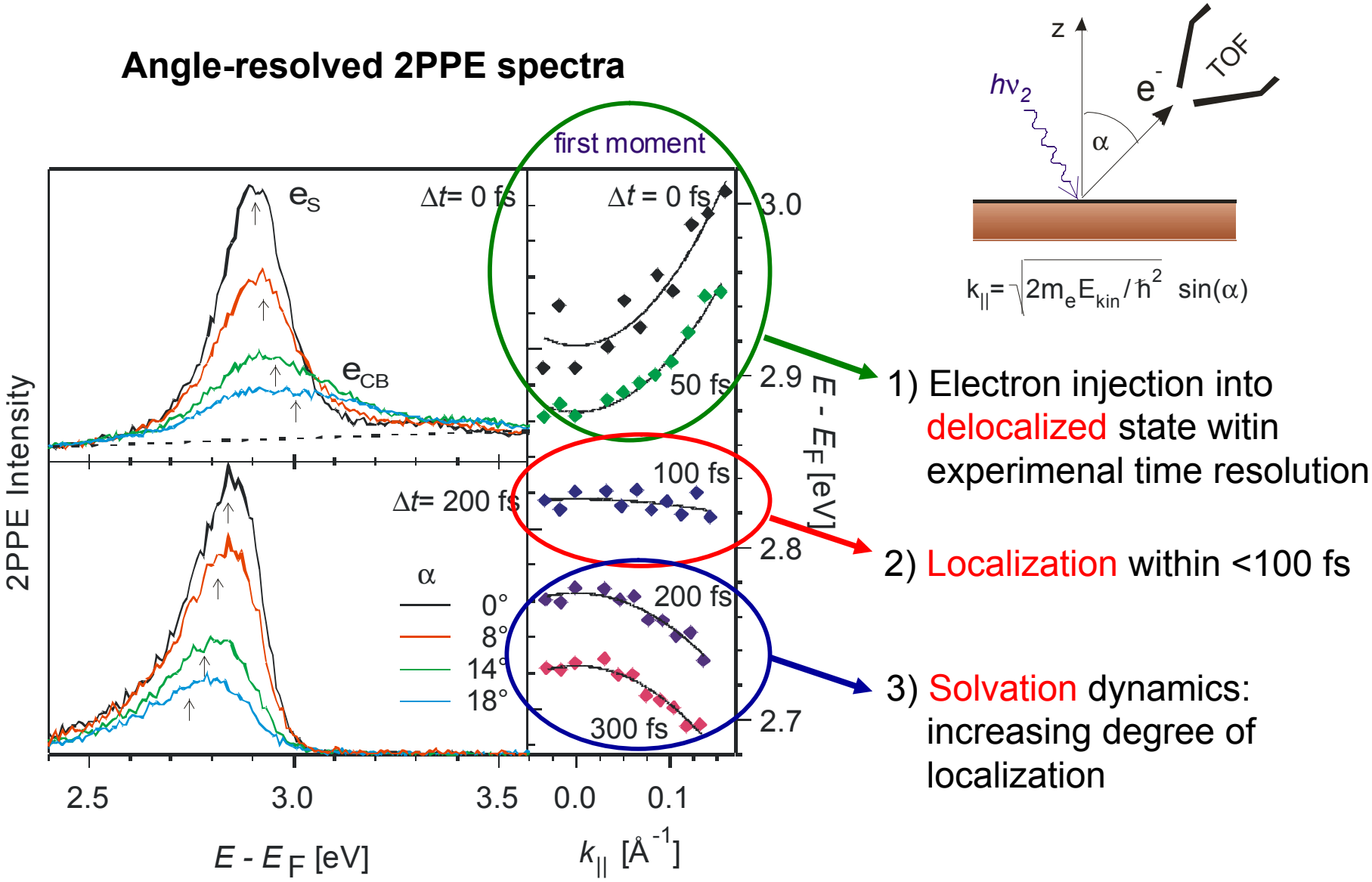
e_S: energetic stabilization 300 meV/ps, non-exponential decay t >100fs

Isotope effects:

very similar stabilization rate for H_2O and D_2O

~50 meV shift due to different band gap/ orientational disorder

Dispersion and localization dynamics



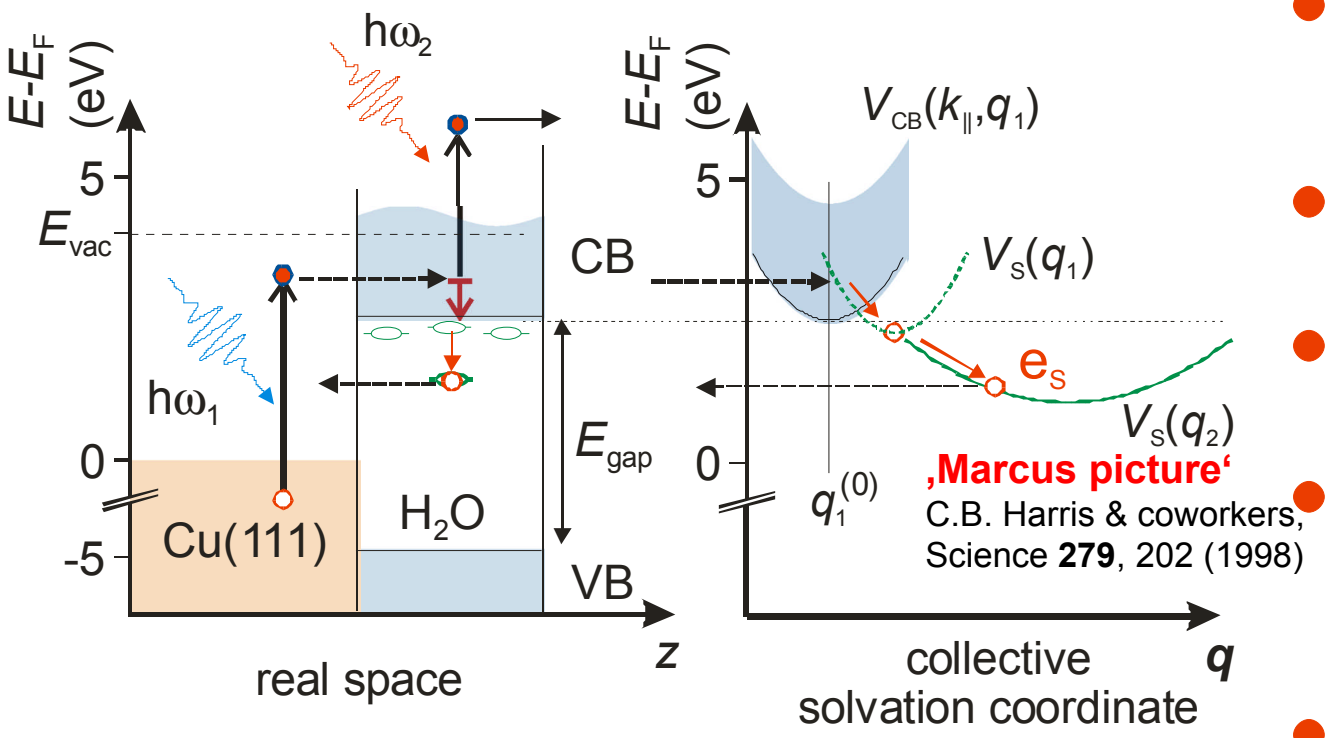
1) Electron injection into delocalized state witin experimenal time resolution

2) Localization within <100 fs

3) Solvation dynamics: increasing degree of localization

Mechanism

Electron transfer, localization and solvation dynamics in H_2O/Cu(111)



‚Marcus picture'
C.B. Harris & coworkers, Science **279**, 202 (1998)

- Electron transfer into the conduction band (CB) of the ice layer
- Relaxation to the bottom of CB (τ<50 fs)
- Localization into pre-cursor states of the ice
- Solvation: Stabilization and energy transfer into collective solvent modes; + increasing localization
- Competing process: Electron transfer back to the metal substrate

- Open Questions

  Influence of structure and coverage on solvation dynamics ?

  Nature of the solvation site: internal versus surface states ?

Gahl et al, PRL **89**, (2002)

Summary

Introduction

→ Non-adiabatic processes at surfaces: Chemicurrents

Electron thermalization in metals

→ Test of the two-temperature model

Surface femtochemistry

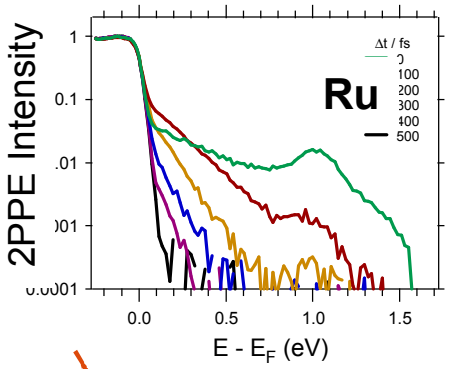
→ Electron and phonon mediated pathways

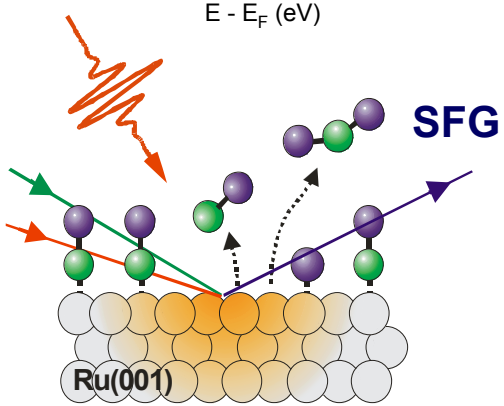
→ Isotope effects and electronic friction model

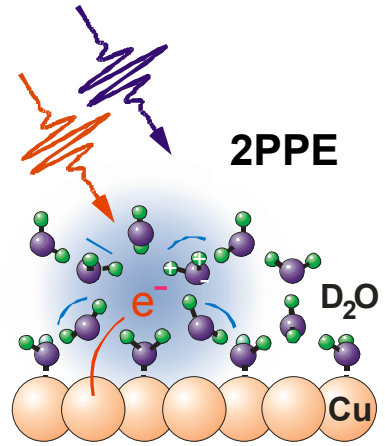
→ Vibrational sum-frequency generation spectroscopy

Electron dynamics thin ice layers on metals

→ Electron injection, localization and solvation







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