Principle: Stroboscopic investigation of motion and structural changes

Goal: Microscopic understanding of elementary processes at surfaces

Application of femtosecond laser spectroscopy
Outline

Introduction
- Why femtosecond laser pulses?
- Example: photochemistry of vision

Generation of femtosecond laser pulses
- Laser basics and mode locking

Femtochemistry
- Vibrational wave packet dynamics

Surface femtochemistry
- Electron and phonon mediated pathways

Non-linear optics as a probe of surface dynamics
- Vibrational sum-frequency generation spectroscopy
Why femtosecond spectroscopy?

**Time scales of chemical reactions:**

Temporal evolution from reactants to products:
- Dynamics of the transition state

Typical timescale: 10-100 fs

![Diagram showing the transition state and energy levels](image)

- Need femtosecond laser pulses for direct observation in time domain
Example: photochemistry of vision

How do we see?

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

Rhodopsin

Retinal

11-cis

all-trans

$cis$-$trans$ isomerization
Hirarchy of time scales

Optical absorption changes during reaction cycle

Ultrafast conformational changes

de-protonation

thermal relaxation

Study time-resolved changes of optical absorption spectrum
Pump-probe spectroscopy

**Basic concept to resolve processes on ultrafast time-scales**

Time resolution is determined by pulse duration
Primary step of vision

Primary step (cis-trans isomerization) of Retinal must occur within 200 fs!

How can this process be so fast?

"Vibrational coherent wave packet motion"
History of time resolution

Break through by development of pulsed laser sources

A.H. Zewail

Nobel prize 1999

Break through by development of pulsed laser sources
Development of short laser pulses

pulse duration (s)

Year

Ruby Laser

Q-switched

Nd-Lasers

ML-Lasers

Dye Lasers

CPM

Ti-Si

Pulse Compression

4.5 fs


„mode locking“

„Titanium Sapphire“
Properties of ultrashort laser pulses

Short pulse: Electrical field $E(t) = \varepsilon(t) \cos(\omega_0 t + \phi)$ with envelope $\varepsilon(t)$

- Pulse width $\tau_P$
- FWHM of $\varepsilon(t)$
- Phase $\omega_0 t + \phi(t)$
- Frequency $\omega(t) = \omega_0 + d\phi(t)/dt$
- Chirp $d^2\phi(t)/dt^2$
- Bandwidth $\Delta\nu$
- Time bandwidth product $\Delta\nu \cdot \tau_P \geq c_B$ (transform limit)
- Chirp: $\frac{d^2\phi}{dt^2} \neq 0$
- Normal dispersion (e.g. glass) $d\omega/dt < 0$

**Electric field, time dependent carrier frequency, and spectral amplitude of an upchirped pulse.**
A generic ultrafast laser consists of a broadband gain medium, a pulse-shortening device, and a resonator.
LASER: Stimulated emission

Example: Four level laser (Nd:YAG)

Population inversion

Titanium-sapphire laser

Fig. 1.7. Simplified energy level diagram of a four-level laser
Resonator modes:

Longitudinal modes: \( \nu_n = n \frac{c}{2 \eta d} \)

Stability:

\[ g_2 = 1 - \frac{d}{R_2} \]

\[ g_1 g_2 = 1 \]

Condition for a stable resonator:

\[ 0 \leq g_1 g_2 \leq 1 \]

Fig. 1.16. Stability diagram for a laser cavity. The shaded areas define the set of values of the cavity parameters \( g_1 \) and \( g_2 \) for which the cavity is unstable [1.5]
Synchronization of laser modes:

One mode: \[ E(t) = E_0 \exp\left[i\omega_0 t + i\phi \right] \]

All modes: \[ E(t) = \sum_{m} E_m \exp\left[i(\omega_0 + \Delta\omega) t + i\phi_m \right] \]

Constant phase between modes \[ \varphi_m - \varphi_{m-1} = \alpha \] („mode-locked“)

**Frequency domain:**

**Temporal structure:**

\[ \Delta t = \frac{1}{\Delta \nu} \]

Fig. 9.2a,b. Signal of a non-mode-locked laser. In the frequency domain (a) the intensities \( I(\nu) \) of the modes have a Rayleigh distribution about the Gaussian mean and the phases are randomly distributed. In the time domain (b) the intensity has the characteristic of thermal noise.

Fig. 9.2a,b. Signal structure of an ideally mode-locked laser. The spectral intensities (a) have a Gaussian distribution, while the spectral phases are identically zero. In the time domain (b) the signal is a transform-limited Gaussian pulse.
Multimode Interference and Mode-Locking

Mode-locking

(a) Single Mode

(b) Two Modes

“2 beam interference“

(c) 8 Modes, Random phases

(d) 8 Modes Phases = 0 at t = 0

Fresnel representation

\[ N \text{ Modes with } E_i = E_0 \sin \omega_i t \]

Frequency separation \( \omega_i - \omega_j = \Delta \omega \)

Laser resonator frequency \( \omega = \frac{2\pi c}{2L} \)

\[ E = N \cdot E_0 \]

\[ \Delta t = \Delta t = \frac{2\pi}{m \Delta \omega} \]

\[ \theta = \frac{2\pi}{\Delta \omega} \]

\[ \theta = 2\pi \]

Fig. 3.2. Fresnel representation of \( m \) modes. The sum of the vectors represents the amplitude of the field inside a laser cavity at different times, when all the modes are supposed to be in phase at time \( t = 0 \) (see text)
non-linear optical Kerr effect

Induced polarization in non-linear optical medium

\[ P(\omega) = \varepsilon_0 \chi(\omega) E = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \ldots \]

Linear optics: \( n_0 = \sqrt{\varepsilon} = \sqrt{\varepsilon_0 (1+4\pi \chi^{(1)})} \)

Non-linear optics: \( n = n_0 + n_2 I(t,x) \)

Longitudinal and transversal Kerr effect

1) self phase modulation

2) self focussing "Kerr lens"

\[ dn = n_2 I(x)L \]
Kerr lens mode-locking and dispersion

Kerr Lens Mode-locking (KLM)

Example: Ti:Sa laser

Pulse broadening due to dispersion

Prism compressor (GVD compensation)

\[
\frac{d^2 I}{d\lambda^2} = 4L \left\{ \left[ \frac{d^2 n}{d\lambda^2} + \frac{2n - \frac{1}{n^3}}{ \left( \frac{dn}{d\lambda} \right)^2} \right] \sin \beta - 2 \left( \frac{dn}{d\lambda} \right)^2 \cos \beta \right\}
\]
Measurement of pulse duration

interferometric autocorrelation

Charakteristische Pulsparameter:

Halbwertsbreite (Zeitlicher Verlauf)
Spektrum des Laserpulses
Phase $\varphi(t)$ bzw. $\varphi(\omega)$

auto correlation $I(\tau) = \int \left[ E(t) + E(t + \tau) \right]^2 dt$

Beispiel: Titan-Saphir Laser

$\Delta \lambda = 105 \text{nm}$

$\tau = 8 \pm 0.5 \text{fs}$

$\tau \Delta \nu = 0.38 \pm 0.03$
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- Vibrational sum-frequency generation spectroscopy
Real-time probing of chemical reactions

Basic principle: Spectroscopic snapshots on the timescale of nuclear motion
'locking of chemical reactions'

Example: Photodissosiation along repulsive potential energy surface

Femtosecond transition state spectroscopy

---

Photofragmentation of a triatomic molecule such as ICN is shown schematically here. The velocity of fragments is typically 1 km per second, in 100 fs the distance spanned is 1 Å. [Adapted from M. Rosker, M. Dantus, and A. H. Zewail, Science, 241, 1200 (1988).]
Real-time probing of chemical reactions II

Real-time femtosecond probing of "transition states" in chemical reactions


Example: photodissociation |ICN -> ICN* -> I + CN

FIG. 2. Similar to Fig. 1, but more detailed schematic diagram, appropriate to a quasiadiabatic molecule AB, showing the several "windows" to the potential $V_i$ for the probe laser detuned successively to the red by amounts $\Delta_i$ ($i = 0, \sigma, \beta, \text{and} \gamma$)., corresponding to $R^* = \infty, R^* \beta, R^* \gamma, \text{and} R^* \sigma$, as shown. Note that the upper potential, $V_0$, is assumed to be flat for $R > R^* \gamma$.

Analysis of repulsive excited state PES

"Clocking of chemical reactions"
Real-time probing of chemical reactions III

Wave packet dynamics in reactive systems: \( \text{NaI} \rightarrow [\text{Na} \cdot \cdot \text{I}]^* \rightarrow \text{Na} + \text{I} \)


Landau-Zener picture

\( P_{\text{LZ}} \sim 0 \)

\( P_{\text{LZ}} \sim 1 \)

The Landau-Zener formula,

\[
P_{\text{LZ}} = \exp \left\{ -\frac{4\pi^2}{\hbar \nu (E_J)} \frac{V_{01}^2}{dR} \left| V_{\infty} - V_{11} \right| \right\}
\]

predicts that the probability of a molecule jumping from one potential surface to another is a function of the relative velocity of the particles at the crossing region.

“Coherent wave packet motion”

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- Electron and phonon mediated pathways

Non-linear optics as a probe of surface dynamics
- Vibrational sum-frequency generation spectroscopy
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
**fs-laser-induced chemistry at surfaces**

**Example:** CO oxidation versus desorption on Ru(001) single crystal surface

800 nm, 120 fs
\[ \sim 50 \text{ mJ/cm}^2 \]

![Diagram showing fs-induced reaction pathways](image)

Co-adsorption of O+CO on Ru(001) (UHV conditions)

\[
2 \text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \xrightarrow{h\nu} \text{CO} \uparrow + \text{CO}_2 \uparrow
\]

\[
2 \text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO} \uparrow + kT
\]

New reaction pathway is "switched on" upon fs excitation
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

Energy transfer to phonons and adsorbate vibrational excitation

Primary step: Electron thermalization and cooling
Electron thermalization dynamics in metals probed with 2PPE and the two-temperature model

Electron dynamics in metals following optical excitation

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

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: \( C_{\text{el}} \gg C_{\text{ph}} \)
- Nearly thermal (Fermi-Dirac) distribution for electrons
- Coupled diffusion equation for \( T_{\text{el}} \) and \( T_{\text{ph}} \)

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

\[
C_{\text{ph}}(T_{\text{ph}}) \frac{\partial T_{\text{ph}}}{\partial t} = g(T_{\text{el}} - T_{\text{ph}})
\]
Time-resolved two-photon photoemission

- How to probe electron thermalization and cooling?

energy- and time-resolution:

\[ E_{\text{kin}} = h \nu_1, \hspace{1cm} h \nu_2 \]

momentum resolution:

\[ k_\parallel = \sin \varphi \sqrt{2mE_{\text{kin}}/\hbar} \]

UV probe pulse \( \rightarrow e^- \)

Electron thermalization dynamics:

- Hot electron cascades
- e-e scattering

Energy and time-resolution:

- Pulse duration: 65 fs
- Momentum resolution:

Electron vacuum energy: \( E_{\text{vac}} \)

Pump pulse

TOF

2PPE Intensity

- Unpumped
- Pumped \( \Delta t = 100 \text{ fs} \)
Experimental setup

Femtosecond time-resolved two-photon photoemission spectroscopy

- **Pump**: 1.55 eV, s-pol., 2.5 μJ
- **Probe**: 4.6 eV, p-pol.

**Equipment**
- OPA 9450: 125 nJ, 460 - 740 nm, 50 fs after compression
- RegA 9050: 800 nm, 5 μJ, 50 fs, 200 kHz
- Verdi V10 & Verdi V5
- Mira SeedR: Ti:Sapphire oscillator, 76 MHz, 13 nJ, 20 fs

**Experimental Layout**
- 50% beam splitter
- Time Of Flight Spectrometer
- Ru(0001)
- CCD camera & pin holes & optical power meter
- UHV chamber

**Intensities**
- Pump FWHM = 200 μm
- Probe FWHM = 50 μm
Electron thermalization in gold

W. S. Fann, R. Storz, H.W.K. Tom, J. Bokor, 
*Electron thermalization in gold,* 

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

Pump fluence: 120 $\mu$J/cm$^2$

- Electron thermalization occurs faster with increasing excitation density
Time-resolved 2PPE from Ru(001)

**Pump-probe scheme:**

1) **Electron thermalization:**

2) **Relaxation by e-ph scattering**

3) **Energy transport in the bulk**

Extended heat bath model

Goal:
Understanding the role of non-thermalized electrons

Extension of two temperature model

Extended model including ballistic transport

Goal:
Understanding the role of non-thermalized electrons

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

2TM

Femtochemistry at metal surfaces

Mechanism and timescales of energy transfer after optical excitation

- Substrate-mediated excitation mechanism dominates
- Transient non-equilibrium between electrons and phonons: $T_{el} >> T_{ph}$
- New reaction mechanism?
  - by non-thermal activation
  - by separation of time scales of energy flow

Reaction mechanisms

**Phonon-mediated**

- $k_B T_{ph}$
- Adsorbate
- Substrate
- Reaction coordinate $E$
- Desorption energy $E_{des}$

**Electron-mediated**

- $E_F$
- Excited state
- Ground state
- Electron transfer
- Reaction coordinate $E$
- $\tau \sim 1-10$ fs

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

---

**How to distinguish?**
Desorption induced by multiple electronic transitions

J. A. Misewich, T. F. Heinz, and D. M. Newns
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598-0218
(Received 28 January 1992)

**Fig. 1.** Two-pulse correlation data as a function of pulse delay $\tau$ of the weak excitation pulse with respect to the strong pulse. (a)–(c) The experimental desorption yields of NO for different pulse-pair fluences: (a) 1.7 and 1.8 mJ/cm$^2$, (b) 1.6 and 2.2 mJ/cm$^2$, and (c) 1.3 and 3.0 mJ/cm$^2$. (d)–(f) Calculations of the exponentiated peak electronic (solid symbols) and lattice temperatures (open symbols), as discussed in the text, for the conditions corresponding to (a)–(c), respectively.

**Fig. 2.** (a) DIMET $n_{ex} = 2$ excitations
(b) DIMET with $n_{ex} = 20$ from a stochastic trajectory simulation.

see also Brandbyge et al., PRB 52, 6042 (1995)
<table>
<thead>
<tr>
<th>Systems</th>
<th>Experimental Investigations</th>
</tr>
</thead>
<tbody>
<tr>
<td>• NO and O$_2$/Pd</td>
<td>Yield</td>
</tr>
<tr>
<td>• CO/Cu</td>
<td>Fluence dependence</td>
</tr>
<tr>
<td>• CO/Pt</td>
<td>Translational energy</td>
</tr>
<tr>
<td>• O$_2$/Pt</td>
<td>Vibrational energy</td>
</tr>
<tr>
<td>• CO/NiO</td>
<td>Rotational energy</td>
</tr>
<tr>
<td>• CO + O$_2$/Pt</td>
<td>Ultrafast dynamics</td>
</tr>
<tr>
<td>• CO + O/Ru, H+H/Ru</td>
<td>Influence of laser pulse duration</td>
</tr>
<tr>
<td>Misewich, Loy, Heinz</td>
<td>Influence of photon energy</td>
</tr>
<tr>
<td>Tom, Prybyla</td>
<td>Dependence on adsorption site</td>
</tr>
<tr>
<td>Ho</td>
<td>Dependence on coverage</td>
</tr>
<tr>
<td>Mazur</td>
<td>Competitive reaction pathways</td>
</tr>
<tr>
<td>Stephenson, Richter, Cavanagh</td>
<td>Isotope effects</td>
</tr>
<tr>
<td>Bonn, Wolf, Ertl</td>
<td></td>
</tr>
<tr>
<td>Zacharias, Al-Shamery</td>
<td></td>
</tr>
<tr>
<td>Domen</td>
<td></td>
</tr>
</tbody>
</table>
Example I: Desorption and oxidation of CO on Ru(001)

Oxidation of CO impossible under equilibrium conditions

2 CO + O → CO↑ + CO2↑

800 nm, 120 fs
~ 50 mJ/cm²

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

New reaction pathway upon fs excitation

E_{trans} = CO2: 1590 K
CO: 640 K

Y(CO) ~ F^{3.1}
Y(CO2) ~ F^{3.2}

Absorbed Fluence (yield weighted) [J/m²]

First Shot Yield

Time-of-Flight (µs)

Flux
Example II: Recombinative desorption of H₂ on Ru(001)

H₂ formation induced by fs laser excitation of H/Ru(001)

Full monolayer of H/Ru(001)

QM

H₂: (2110 ± 400) K

D₂: (1720 ± 290) K

flux [a.u.]

flight time [µs]

Yield (H₂)  
Yield (D₂)  
= 10 ± 2.4

- High translational temperature of desorbing species
- Pronounced isotope effects in H₂/D₂ yield
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

QMS
H\textsubscript{2}/D\textsubscript{2}
CCD
pulse profile diagnostics

"Feulner cup" detector

80 mm

Ru(001)

QMS ionisation volume

H\textsubscript{2}

UHV

H\textsubscript{2}/CO
2-pulse correlation measurements

Goal: discriminate between electron and phonon mediated mechanism

2-pulse correlation:

\[ \text{First Shot Yield} \]

\[ \text{FWHM}=3 \text{ ps} \]

\[ \text{FWHM}=20 \text{ ps} \]

\[ \Delta t \]

\[ \text{Desorption: phonon-mediated} \]

\[ \text{Oxidation: hot electron-mediated} \]
DFT calculations

C. Stampfl, M. Scheffler, FHI Berlin

Ru(001)

unoccupied anti-bonding orbital ~1.7 eV above EF

increasing $T_{ei}$ 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

Under thermal excitation the CO has desorbed before oxygen is activated.

Separation of time scales opens new reaction pathway.
Electronic friction model

- **Electronic friction:**
  
  *Energy transfer by coupling between adsorbate vibration and metal electrons*

  \[ \eta = \frac{1}{\tau_{el}} \sim \frac{1}{M} \]

What is “electronic friction”?

*Example: Change of electric resistivity in a thin metal film upon Xe adsorption*

Fig. 8.2. (a) The damping (caused by electronic excitations) of the translational motion of the adsorbate layer (right) can be related to the adsorbate-induced increase in film resistivity by a change of reference frame (left). (b) The Xe-induced resistivity change \( \Delta R \) of a thin silver film. From [8.11].

2PC of laser-induced H₂ formation

- Ultrafast response indicates coupling to hot electron transient

- Coupled heat baths: $T_{el}$, $T_{ph}$, $T_{ads}$
  
  Coupling rates: $\tau_{el}^{-1}$, $\tau_{ph}^{-1}$, $\tau_{el-ph}^{-1}$.

**Electronic friction model** yields: $E_a = 1.35 \text{ eV}$ and $\tau_{el} = 180 \text{ fs}$ for H₂

  ($\tau_{el} = 360 \text{ fs}$ for D₂)
Isotope effect in recombinative desorption

H₂ formation induced by fs laser excitation of H/Ru(001)

- Full monolayer of H/Ru(001)
- QMS

\[
\frac{\text{Yield (H}_2\text{)}}{\text{Yield (D}_2\text{)}} = 10 \pm 2.4
\]

- Pronounced isotope effects in H₂/D₂ yield

\( <E_{\text{kin}}>/ 2k_B \)

H₂: (2110 ± 400) K

D₂: (1720 ± 290) K

flight time [µs]

flux [a.u.]

\( (\times 10) \)
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*

\[ \eta = \frac{1}{\tau_{el}} \sim \frac{1}{M} \]

*Coupling rate*

Brandbyge *et al*., PRB **52**, 6042 (1995)
**Fluence dependence: isotope ratio and first shot yield**

Electronic friction model* simultaneously describes:
- 2-pulse correlation
- fluence dependence of yield and isotope ratio

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

\[ Y(H_2) \sim \langle F \rangle^{2.8} \quad \text{and} \quad Y(D_2) \sim \langle F \rangle^{3.2} \]
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  - Vibrational sum-frequency generation spectroscopy
Real-time probing of vibrational dynamics

Goal: Probe surface reactions directly in the time domain

- fs-excitation
- direct absorption
- reaction

- adsorbate vibrations $T_{ads}$
  - $\sim 100 \text{ fs}$
  - $\sim 0.1-1 \text{ ps}$
  - $>1 \text{ ps}$

- electrons $T_{el}$
  - $\sim 1 \text{ ps}$
- phonons $T_{ph}$

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
sum-frequency generation (SFG)

Background-free, visible detection
Sensitivity: $10^{-3}$ ML
Short pulses: time resolution
Surface specific

IR absorption spectroscopy (FTIR)

C-O stretch

Pot. Energy

C-O distance

5 $\mu$m + 800 nm = 690 nm

IR

VIS

SFG

With background, IR detection optical linear technique

Background-free, visible detection
Sensitivity: $10^{-3}$ ML
Short pulses: time resolution
Surface specific
Principle of sum-frequency generation (SFG):

- Second order non-linear optical process

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

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

Time-resolved SFG as molecule specific probe of surface reactions
Broadband IR vibrational SFG spectroscopy

Vibrational spectroscopy without tuning the IR frequency

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

SFG experimental setup

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

OPG/OPA (TOPAS)
2.5-10 \( \mu \text{m} \), 20-30 \( \mu \)J

Tunable IR pulse

Pump pulse

QMS

SFG probe

Pulse shaper
FWHM 7 cm\(^{-1}\), 7 \( \mu \)J

Narrow band VIS pulse

tunable IR pulse

Multi-channel detection

SFG

Ru(001)

Spectrometer

CCD camera
**Example water/Ru(001)**

**Sum-frequency generation (SFG)**

- intrinsically surface sensitive

- SFG signal is enhanced when IR Photon is resonant with vibrational transition

\[
I_{SFG} \propto \left| P^{(2)}(\omega_{SFG}) \right|^2 \propto \left| \chi_S^{(2)}(\theta) \right|^2 I_{IR} I_{VIS} =: \left| \chi_S^{(2)}(\theta) \right|^2 I_{IR} I_{VIS} \\
I_{SFG} \propto |A_{NR}(\theta)| + \sum_q \frac{|A_q(\theta)| \exp(i\phi_q)}{\omega_{IR} - \omega_q + i\Gamma_q} \left| I_{IR} \right|^2
\]

**Example: D\textsubscript{2}O covered and bare Ru(001) surface**

- \(\text{D}_2\text{O multilayers}: \text{free OD resonance}\)

- \(\text{bare Ru}: \text{nonresonant background}\)
Equivalence of spectral- and time-domain measurements

1) Time-resolved SFG: temporally short, spectrally broad IR + VIS-pulse
2) Frequency-resolved SFG: temporally long, spectrally narrow VIS-pulse

SFG spectrum

\[ I \sim e^{-2t/T_2} \]

\[ \Gamma \sim 1/T_2 \]

FID

- IR field
- IR polarization
- VIS field

SFG intensity

- time (ps)
- IR frequency (cm\(^{-1}\))

Linewidth
**IR-broadband SFG: Spectral and time-resolution**

**Frequency domain:**
- VIS, IR, SFG
- CH$_3$CN on Au

**Time domain:**
- IR-VIS delay
- C-N stretch

- Experimental frequency resolution: better than 3 cm$^{-1}$
- Experimental time resolution: better than 150 fs

M. Bonn et al. (Univ. Leiden)
Probing surface inhomogeneities with SFG

Time-domain measurements are particularly sensitive to inhomogeneities in surface adsorption sites due to temporal separation of interferences.
Time-resolved SFG of CO/Ru during desorption

Spectroscopic snapshots of the CO stretch mode

$T_0 = 340 \text{ K}, F = 55 \text{ J/m}^2$

Pronounced transient red shift, linewidth broadening and decrease of intensity

Problems:
- Dipole-dipole coupling in the adlayer
- Small concentration of "products"

Time-resolved SFG of CO/Ru(0001)

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

**Low fluence:** Good fit

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

Strong redshift indicated that frustrated rotation is dominant.
Real-time probing of surface reactions: 2PPE

Snapshots of excited electronic states during evolution of wavepacket

Time-resolved 2PPE spectra

′Desorption′ of Cs/Cu(111)

Time-resolved 2PPE of Cs 6s-6p\textsubscript{z} state:

- (Long) lifetime $\tau_r = 50$ fs
- Shift in 150 fs: $\Delta E = -0.2$ eV
  $\Rightarrow$ Cs-Desorption: $\Delta R_{Cu-Cs} = 0.3$ Å

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

**Introduction**
- Why femtosecond laser pulses?

**Generation of femtosecond laser pulses**
- Laser basics and mode locking

**Femtochemistry**
- Vibrational wave packet dynamics

**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
thanks to

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S. Wagner, C. Frischkorn, Freie Universität Berlin
D. Denzler, S. Funk, C. Hess, and G. Ertl, Fritz-Haber-Institut Berlin
S. Roke, M. Bonn, Leiden University, The Netherlands
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