Question: How can we catch the motion of objects?

Stroboscopic investigation of motion and structural changes

...a fast camera is enough!
Introduction

- Non-adiabatic processes at surfaces: Chemicurrents

Surface femtochemistry

- Surface dynamics with electronic friction
- Example: Associative desorption of H₂ from Ru(0001)

Time-resolved probe of structural dynamics

- Femtosecond laser spectroscopy
- Time-resolved x-ray diffraction
- Non-thermal melting and coherent phonon excitation
- Time-resolved photoelectron spectroscopy

Attosecond laser spectroscopy

- High harmonic and attosecond pulse generation
- Electron streak camera and Auger decay
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
Gas surface interaction

Role of non-adiabatic processes in surface reactions?

Example: Adsorption at a metal surface

- Coupling between nuclear motion of adsorbate and electronic excitations?

E

| R |

„forced-oscillator model“

- Energy dissipation via phonon excitation

- Coupling to electron-hole pair excitations in the substrate

exothermic adsorption

gas particles

hv

exo-electrons

phonons, heat

metal substrate
Chemicurrents

- Adsorption on thin metal film
- Charge separation across small Schottky barrier
  - 
- Current provides lower limit of excitation probability
- Direct observation of e-h pair excitation
  - Evidence for non-adiabatic coupling between adsorbate motion electronic excitations

Chemicurrents in gas-surface interaction

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

- Chemicurrent observed for various adsorbates
- Electronic excitations play an important role during adsorption

- Energy dissipation via e-h pair excitation
- Mechanism of e-h pair excitation?
Mechanism

**Newns-Anderson model**

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

- Filling of hole below $E_{\text{Fermi}}$ by substrate electrons
  - $e-h$ excitation:
    - Chemicurrent
    - Exoelectron emission
  - Chemiluminescence
Electronic friction

Newns-Anderson picture provides a mechanism for electronic friction

- vibrational damping at metals
- surface femtochemistry

Electronic friction of adsorbates

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

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: $T_{el} \gg T_{ph}$
- Non-thermal reaction mechanism: separation of time scales of energy flow
**Reaction mechanism**

- **fs-laser excitation**
- **electron-mediated energy flow**

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

- Electron thermalization: \( \tau_{\text{thermalization}} \ll 100 \text{ fs} \)

- MGR model (Menzel, Gomer, Redhead)

## Experimental Investigations

### Desorption:
- NO and O₂/Pd
- CO/Cu, CO/Pt
- O₂/Pt
- CO/NiO

### Reactions:
- CO + O₂/Pt
- CO + O, C + O, H+H/Ru

### Systems

- 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
- Isotope effects

Misewich, Loy, Heinz
Tom, Prybyla
Ho
Mazur
Stephenson, Richter, Cavanagh
Bonn, Wolf, Ertl
Zacharias, Al-Shamery, Freund
Domen
associative H$_2$ desorption from H/Ru(0001)

Femtosecond laser induced desorption of H$_2$ by 100 fs, 10 mJ/cm$^2$ pulses

Remarkably high translational energy ($<E_{\text{trans}}>/2k \sim 2000$ K)

2 pulse correlation measurements

- Ultrafast response indicates coupling to hot electron transient

![Diagram showing pulse correlation measurements with a focus on phonon-mediated and electron-mediated responses.](image)

- FWHM = 1.1 ps

- **H$_2$**

- **exp. data**

- phonon-mediated: slow response
- electron-mediated: fast response
**Electronic friction model**

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

Rate $\sim e^{-\frac{E_a}{k_BT_{ads}}}$

- Electronic 1D friction model proves:
  - 2-pulse correlation
  - fluence dependence
  - isotope effects

**Electronic 1D friction model**

$\eta_{el} = \tau_{el}^{-1}$

$\int \frac{\eta_{el}}{T_{ads}} \exp(-\frac{E_a}{k_BT_{ads}})$

Friction coefficient

Activation energy

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

**H$_2$**

FWHM = 1.1 ps

Heat diffusion

Two-Temperature Model
Energy partitioning within the D$_2$ product

Resonance Enhanced Multiphoton Ionization (REMPI)

- scan VUV rovibrational population distribution
- change VUV polarization molecular alignment

cooperation with H. Zacharias (Münster)
Experimental setup

Reaction trigger: fs-laser + state-selective detection: tunable VUV source

- Nd:YAG solid state laser: 800 mJ, 9 ns, 10 Hz, 1064 nm
  - 2ω
  - 4ω
  - dye laser, 80 mJ, 636-660 nm
  - 266 nm
  - 106 - 110 nm λ/2-plate
  - Ti:sapphire oscillator + amplifier: 4.5 mJ, 110 fs, 10-400 Hz
  - 800 nm

VUV conversion efficiency $10^{-6}$

- 532 nm: 330 mJ/pulse
- 266 nm: 4.5 mJ/pulse
- 330 nm: 8.5 mJ/pulse
State-resolved detection of desorbing $D_2$

No Boltzmann-like rotational population distribution

\[
\langle E_{\text{rot}} \rangle = 80 \text{ meV} \\
\langle E_{\text{vib}} \rangle = 100 \text{ meV} \\
\langle E_{\text{trans}} \rangle = 430 \text{ meV}
\]

\( N \sim \exp \left( -\frac{E}{k_B T} \right) \)

**Reaction dynamics**

**Detailed picture of reaction mechanism and energy flow**

- hot electron driven
- coupling times and activation energy
- high translational energy

**Unequal energy partitioning**

\[
\langle E_{\text{trans}} \rangle : \langle E_{\text{vib}} \rangle : \langle E_{\text{rot}} \rangle = 5.5 : 1.5 : 1
\]

predominantly translational excitation

**Molecular alignment**

\[ A_0^{(2)} = 0.3 \]

preferentially helicoper-like

quadrupole alignment parameter \(-1 \leq A_0^{(2)} \leq 2\)

**Energy balance**

\[
\langle E_{D2\_flux} \rangle = 160 \text{ meV} = k_B T_{\text{ads}}^{\text{friction}}
\]

good agreement with 1D friction model

**1D model fits energy balance: Why?**

- multidimensional friction / energy transfer
- PES topology (barrier location)
Theory: Molecular dynamics with electronic friction

Fluctuating forces $F(t)$ by frictional coupling to electron temperature

$$\langle F_i(t) F_i(t') \rangle = 2k_B T_e \eta_{ii} \delta(t-t')$$

(fluctuation dissipation theorem)

Equations of motion:

$$\ddot{\mu}_d = \frac{\partial V}{\partial d} - \eta_{dd} \dot{d} - \eta_{dz} \dot{z} + F_d(t)$$

$$\ddot{\mu}_z = \frac{\partial V}{\partial z} - \eta_{zz} \dot{z} - \eta_{dz} \dot{d} + F_z(t)$$

$$\ddot{\mu}_q = \frac{\partial V}{\partial q} - \eta_q \dot{q} + F_d(t)$$

cooperation with A. Luntz (Odense) and M. Persson (Liverpool)

Head-Gordon & Tully, JCP 103, 10137 (1995)
Friction coefficients and PES

2x2 unit cell for DFT (LDA)

JCP 119, 4539 (2003)

Friction coefficients (TDDFT):

\[ \eta_{\text{dd}}, \eta_{\text{zz}}, -\eta_{\text{dz}} \]

PES:

\[ V^* \approx 60 \text{ meV} \]

reaction path S
“First principle” model: $V_{2D}(z,d)$ AND $\eta(z,d)$ → no adjustable parameter
multi-dimensional friction

small $S$: $\sim$ isotropic coupling

near $V^*$: $\eta_{dd} \approx 3 \eta_{zz}$

$\eta$ [meV ps Å$^{-2}$]

$S$ [Å]

0 < t < 1 ps

- excitation occurs only while electrons are still hot

crucial time span

time evolution

reaction path $S$

origin of unequal energy partitioning ???
Trajectories: dynamics on ground PES

sufficient energy is a prerequisite,
... but not everything

rapid interchange between $z$ and $d$ ("thermalization")

reaction

no reaction

dynamics on ground state PES
Summary I

Introduction

- Non-adiabatic surface dynamics: Chemicurrents

Surface femtochemistry

- Femtochemistry driven by hot electron excitation
- Example: Associative desorption of H$_2$ from Ru(0001)
- Multidimensional dynamics with electronic frictions

Time-resolved probe of structural dynamics

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