

# OPTISCHE KONTROLLE UND SPEKTROSKOPIE DISSIPATIVER PROZESSE AN GRENZFLÄCHEN

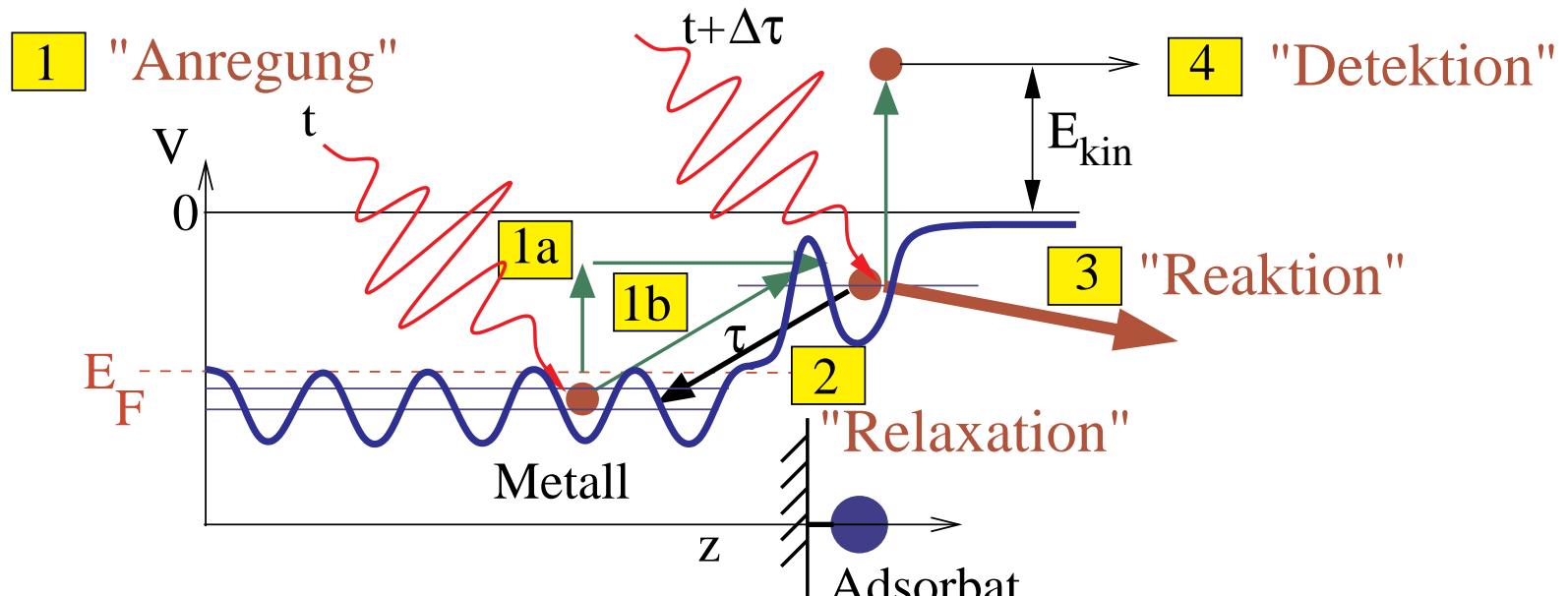


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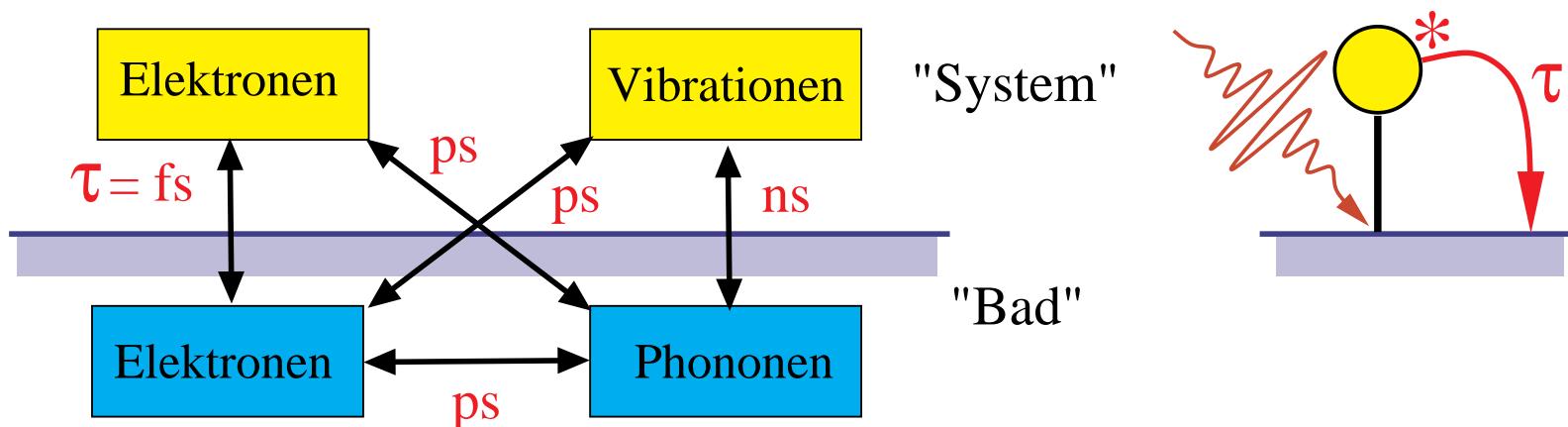
Universität Potsdam

# Ultraschnelle photoinduzierte Prozesse an Grenzflächen

- “Generische Situation”



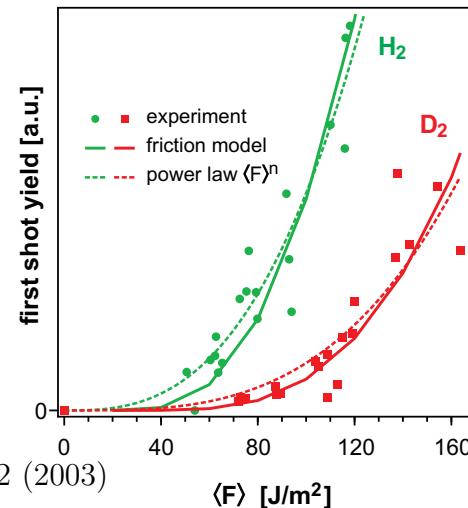
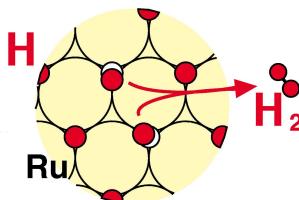
- “Dissipation”



# UP 1: Kontrolle der Dynamik von UV-/VIS-angeregten Adsorbaten durch IR-Schwingungspräparation

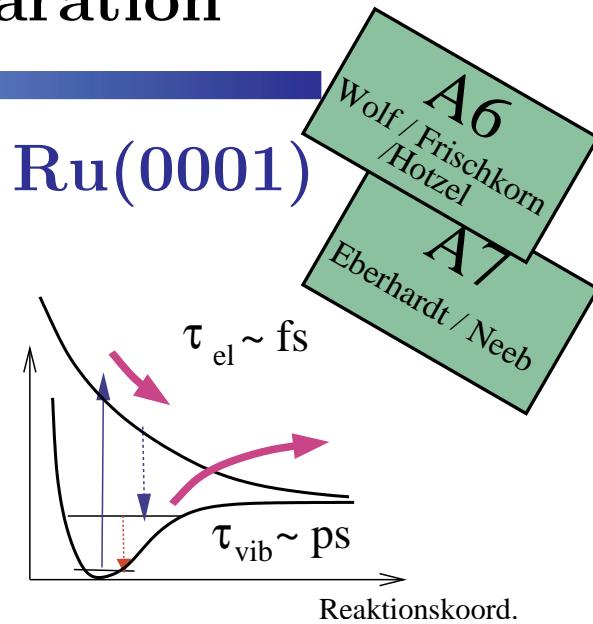
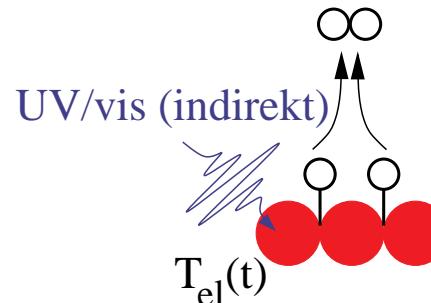
## • UP 1A: Assoziative Desorption von H<sub>2</sub> von Ru(0001)

Experiment<sup>1</sup>

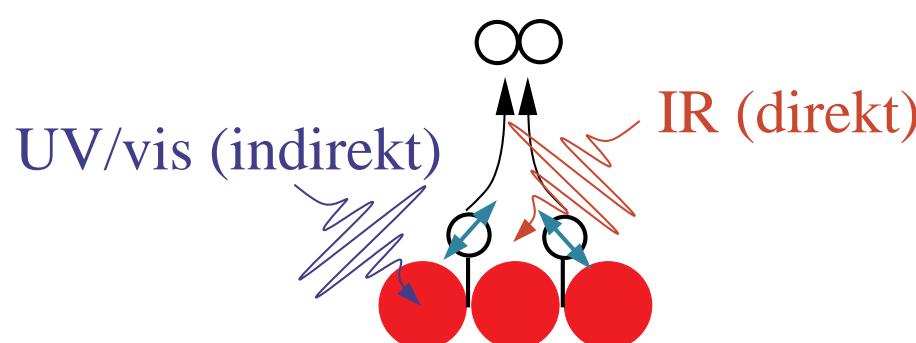


<sup>1</sup> Wolf et al., PRL **91**, 226102 (2003)

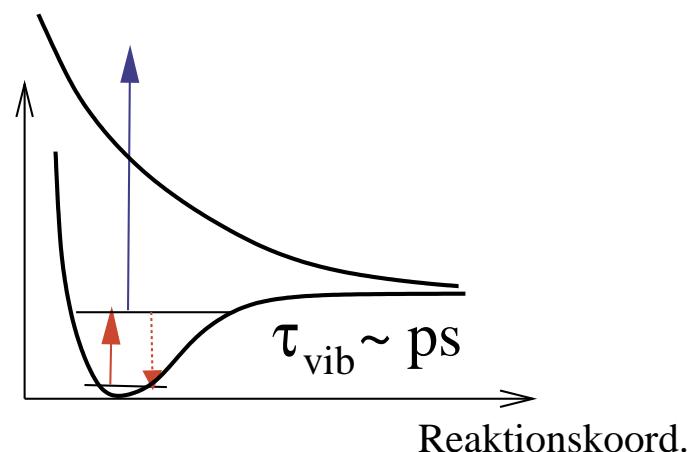
Modell



## • Ziel: Kontrolle durch IR-Vibrationspräparation<sup>2</sup>



<sup>2</sup> Paramonov, P.S., JCP **110**, 6500 (1999)



# UP 1A: Assoziative Desorption von H<sub>2</sub>/Ru(0001)

- (Optimale) Kontrolle der IR-Anregung

Populationen: Dichtematrixtheorie<sup>1</sup>

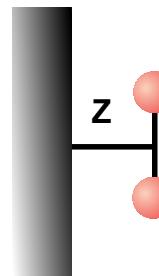
$$\frac{\partial \rho_{nn}}{\partial t} = \sum_p^N \underbrace{[-\frac{i}{\hbar} (V_{np}(t)\rho_{pn} - \rho_{np}V_{pn}(t))]}_{\text{System-Feld}} + \underbrace{(\Gamma_{np}\rho_{pp} - \Gamma_{pn}\rho_{nn})}_{\text{Dissipation}}$$

Optimale Kontrolle

$$J = \text{Sp} [\hat{W} \hat{\rho}(t_f)] + \text{N.B.}$$

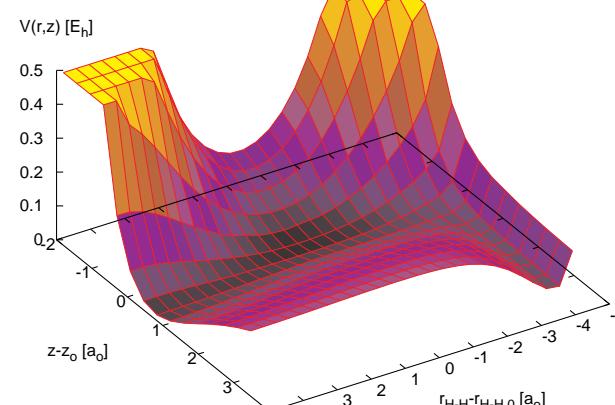
- Clusterrechnungen

Koordinaten

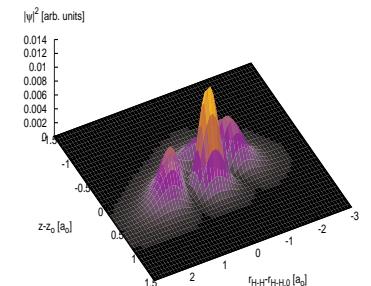
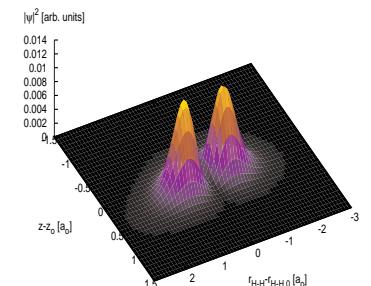
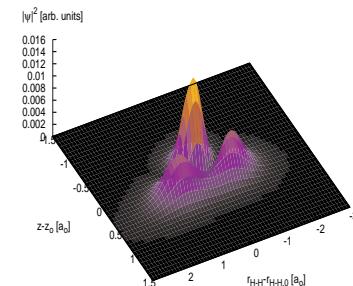
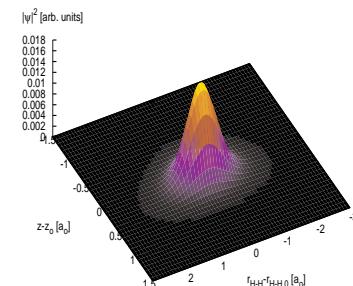


Potential

(Ru<sub>13</sub>H<sub>2</sub>, B3LYP)



Schwingungswellenfunktionen

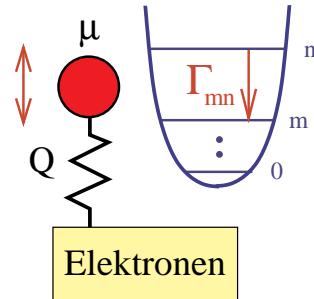


<sup>1</sup> Prog. Surf. Sci. **62**, 239 (1999)

$\omega_{\parallel} = 80 \text{ meV}; \omega_{\perp} = 135 \text{ meV}$

# UP 1: IR-Anregung im dissipativen System

- **Vibratorische Übergangsraten  $\Gamma_{mn}$**



## Tully-Methode<sup>1</sup>

$$\Gamma_{01} = \frac{\pi\hbar}{\mu} \text{Sp} [\mathbf{P}(E_F) \mathbf{G} \mathbf{P}(E_F) \mathbf{G}]$$

$$\mathbf{G} = \mathbf{H}' - E_F \mathbf{S}'$$

## Erweiterungen

$$\Gamma_{mn} = \frac{2\pi}{\hbar} \sum_f \left| \langle m | e_f | \hat{T}_{nuc} | n | e_i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega_{mn})$$

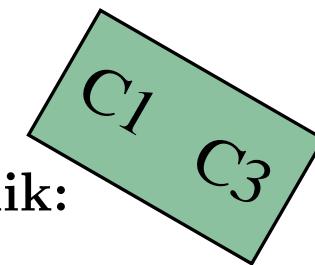
$$\langle m | e_f | \hat{T}_{nuc} | n | e_i \rangle = -\frac{\hbar^2}{\mu} \left\langle m | T_{fi}^{(1)}(Q) | \frac{\partial n}{\partial Q} \right\rangle_Q$$

**Aspekte:**  $T_{fi}^{(1)} = \langle e_f | \frac{\partial e_i}{\partial Q} \rangle_r = T_{fi}^{(1)}(Q)$

Anharmonizität; höhere Vibrationsniveaus;  $|e_f\rangle$

- **UP 1B: Selektive IR-Anregung in CO/Cu(100)**

Mode			
Symmetrie	e	e	a <sub>1</sub>
$\omega$ (cm <sup>-1</sup> )	4	357	372
$\tau_{vib} = \Gamma_{01}^{-1}$ (ps)	108	2.3	8.2



## Dynamik:

Multi Configurational Time

Dependent Hartree

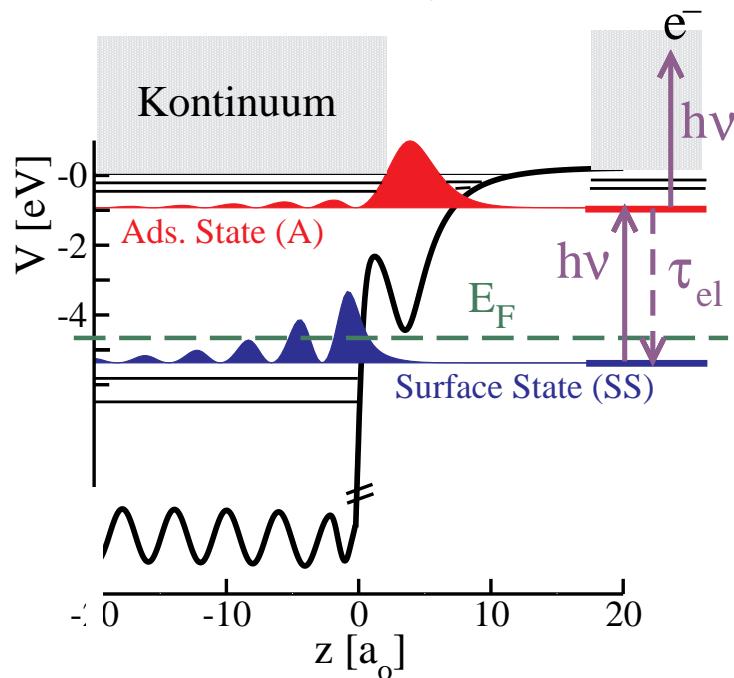
61D WP-Propagation: Nest, Meyer, JCP **119**, 24 (2003)

<sup>1</sup> Tully et al., PRB **46**, 1853 (1992)

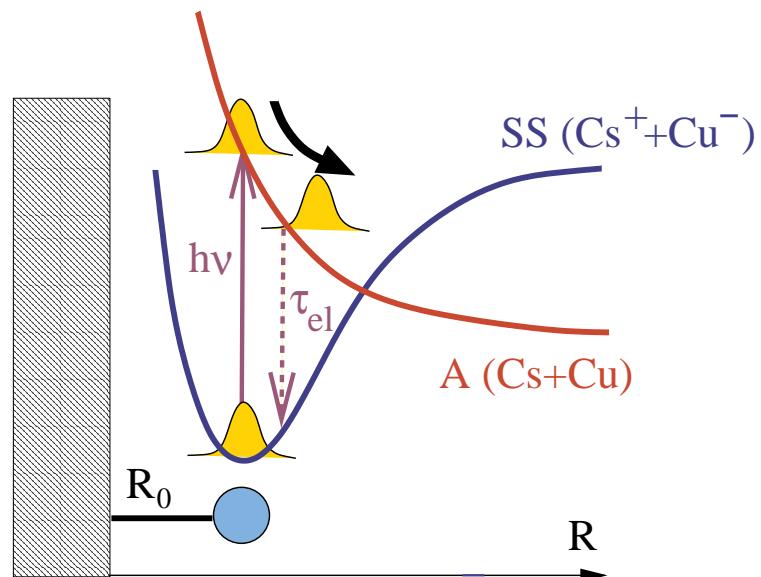
# UP 2: Kontrolle und Spektroskopie der Elektronen- und Kerndynamik von Cs/Cu(111)

## • Experimente

### Elektronendynamik



### Kerndynamik



## • Befunde:

- direkte SS  $\rightarrow$  A Anregung,  $\tau_{el} \approx 50$  fs<sup>1</sup>
- 2-Puls-Korrelation: Cs-Bewegung Echtzeit<sup>1</sup>
- Cs/Pt(111): Vibratorisches Wellenpaket<sup>2</sup> (Gd: [3])

<sup>1</sup> Petek et al., Science **288**, 1402 (2000)

<sup>2</sup> Matsumoto et al., CPL **366**, 606 (2002)

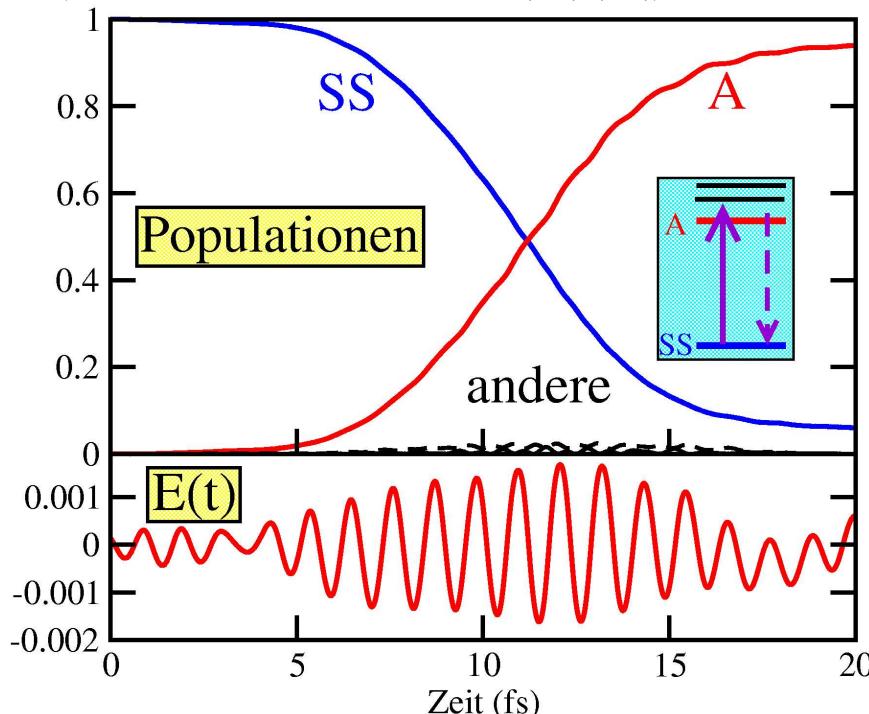
<sup>3</sup> Melnikov et al., PRL **91**, 227403 (2003)

## UP 2: Kontrolle und Spektroskopie der Elektronen- und Kerndynamik von Cs/Cu(111)

- **Ziele:**
  - Kontrolle / Optimierung der elektronischen Anregung
  - Kontrolle / Optimierung der Kerndynamik
  - Detektion von Zwischenzuständen mittels 2PPE
  - Erzeugung eines vibratorischen Wellenpakets?
- **Vorarbeiten: Elektronendynamik ( $SS \rightarrow A$ )**

Optimale Kontrolle<sup>1</sup>:

( $N = 4$ ,  $T = 20$  fs,  $\hat{W} = |A\rangle\langle A|$ )



<sup>1</sup> Ohtsuki et al., JCP **110**, 9825 (1999)

A6  
Wolf / Frischkorn  
/ Hotzel

# Zusammenfassung und Einbindung

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