

fs-laser-driven dynamics of CO on Ru(0001)

a computational study using electronic friction (MDEF) and
the generalized Langevin oscillator (GLO)

Robert Scholz

Institut für Chemie
Universität Potsdam

30. November 2016

1 Introduction

- Motivation

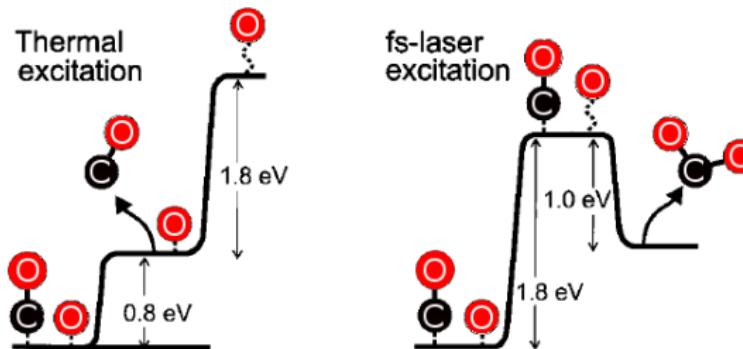
2 models and methods

3 results

General motivation

Why investigate fs-laser-driven surface dynamics?

- gain fundamental understanding of adsorbate bonding
⇒ additional tool besides scattering experiments and STM
- possible direct application in catalysis: “femtochemistry”
⇒ new reaction pathways opened up by fs-lasers



CO/O-coadsorbate @ Ru(0001)

M. Bonn *et al.*, Science 1999

Specific motivation for the CO/Ru-System

CO/Ru system important for catalysis

e. g. Fischer-Tropsch synthesis

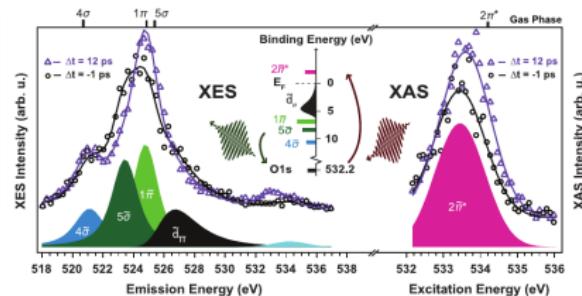
Experimentally well studied system

- especially regarding fs-laser irradiation e.g.:
Bonn *et al.*, *Science* 1999; Funk *et al.*, *JChemPhys* 2000
(both Ertl group - chemistry Nobel prize 2007).
- recently, time resolved x-ray spectra (XAS and XES)
⇒ “movie” of changes in orbital DOS

Details of the time-resolved x-ray experiment

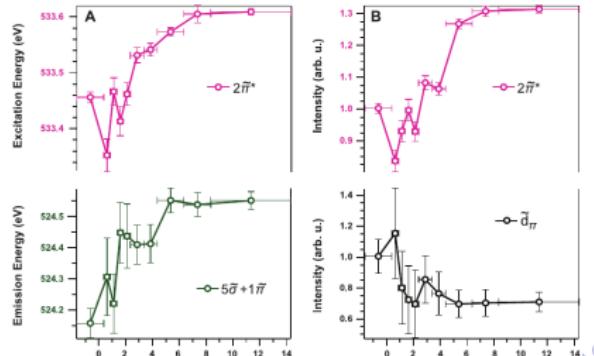
What was done?

- pump: vis-fs-laser
- probe: x-ray free electron laser (K edge of O-atom)



What is observed?

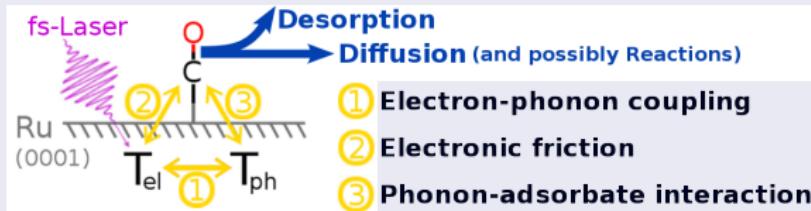
- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
 - $2\tilde{\pi}^*$ \Rightarrow increase by $\sim 30\%$
 - \tilde{d}_π \Rightarrow decrease by $\sim 30\%$
 - participator peak appears



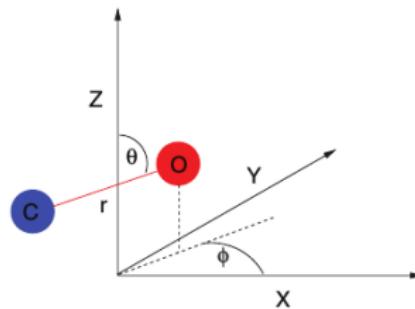
What happens after fs-laser excitation of the metal?

Coupling between three different kinds of degrees of freedom:

- electron gas (T_{el})
- lattice vibrations (T_{ph})
- adsorbate movement (T_{ads})

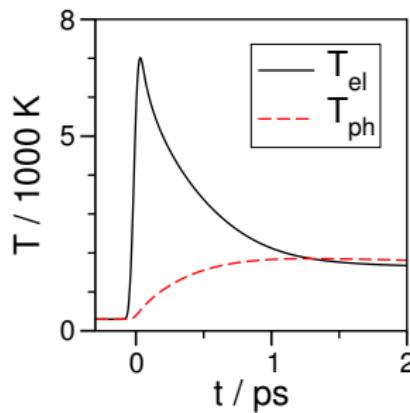


Ab-initio-based, full-dimensional (6D) potential energy surface (PES)

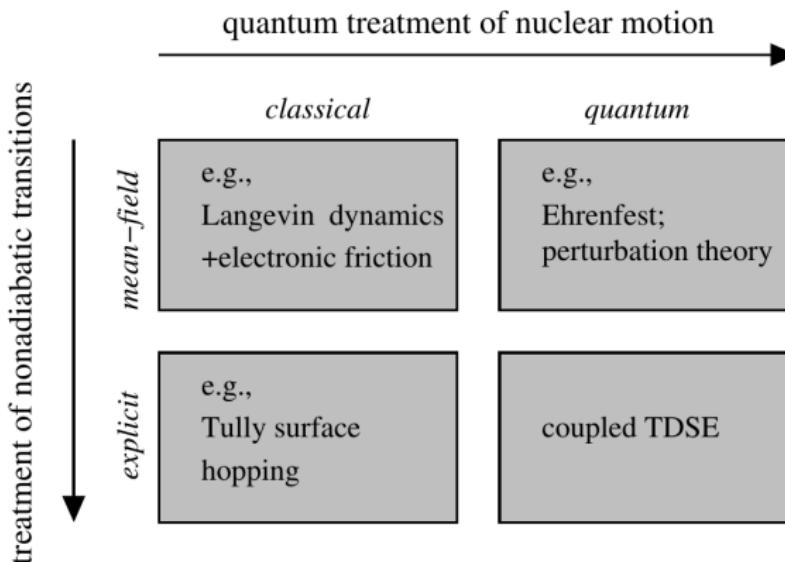


Two-Temperature Model

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



Non-adiabatic coupling



Langevin Dynamics

$$\underbrace{m_k \frac{d^2 \underline{r}_k}{dt^2}}_{\text{Force on Atom } k} = \underbrace{-\nabla_k V(\underline{r}_1, \underline{r}_2)}_{\text{Force due to PES}} - \underbrace{\eta_{\text{el},k}(\underline{r}_k) \frac{d\underline{r}_k}{dt}}_{\text{Friction force slows movement}} + \underbrace{R_{\text{el},k}(t)}_{\text{Random force from e-h pairs}}.$$

- $R_{\text{el},k}(t)$ = Gaussian white noise
 - describes excitation by hot electron-hole pairs
 - dependent on: $\eta_{\text{el},k}(\underline{r}_k)$ and T_{el}

Local density friction approx. plus independent atoms

Generalized Langevin Oscillator

$$m_s \frac{d^2 r_s}{dt^2} = -\underbrace{\nabla_s V(r_1 - r_s, r_2 - r_s)}_{\text{Force due to PES}} - m_s \underline{\underline{\Omega}} r_s + m_s \underline{\underline{\Lambda}}_{gs} r_g$$

Harmonic oscillator Coupling to ghost oscillator

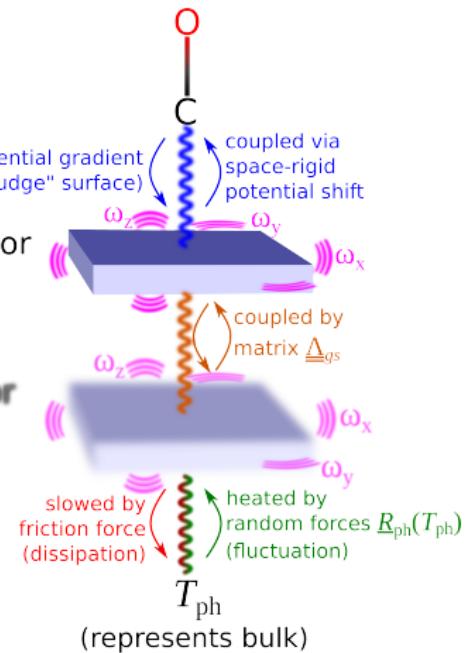
$$m_s \frac{d^2 r_g}{dt^2} = -m_s \underline{\underline{\Omega}} r_g + m_s \underline{\underline{\Lambda}}_{gs} r_s - \eta_{ph} \frac{dr_g}{dt} + R_{ph}(T_{ph})$$

Harmonic oscillator Coupling to surface force oscillator Friction Random forces

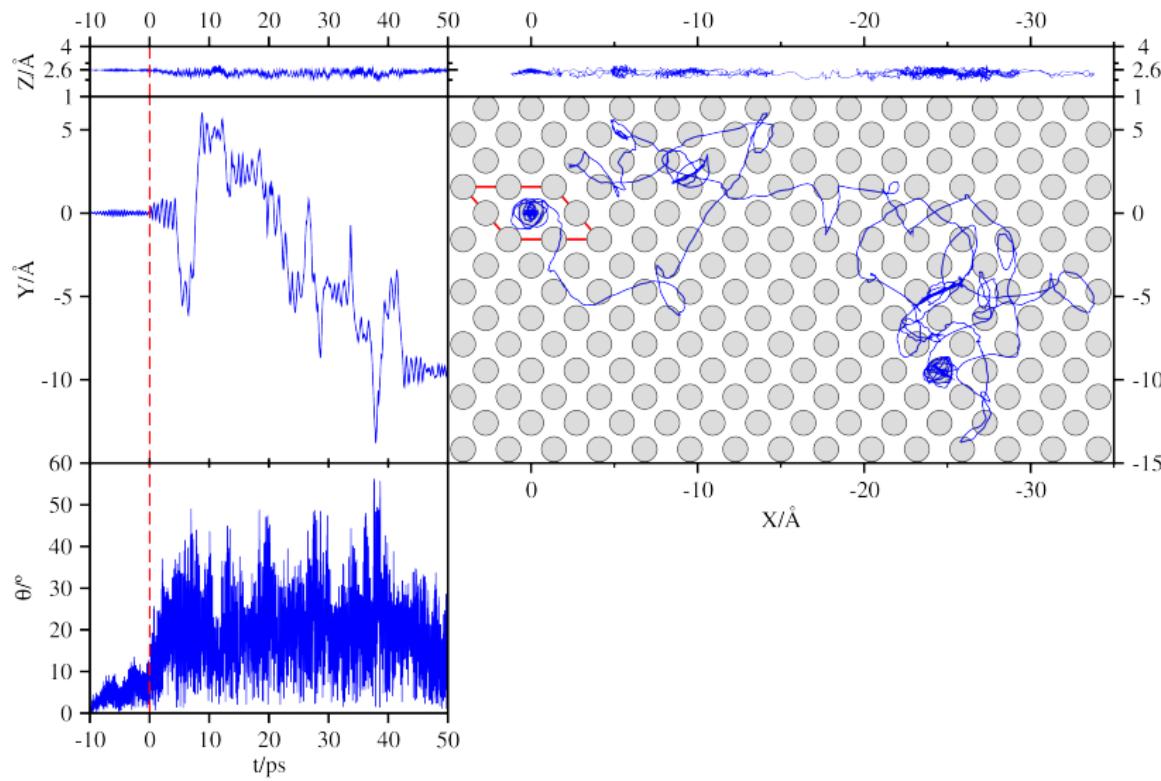
Surface oscillator

both oscillate in the
3 dimensions x, y, z

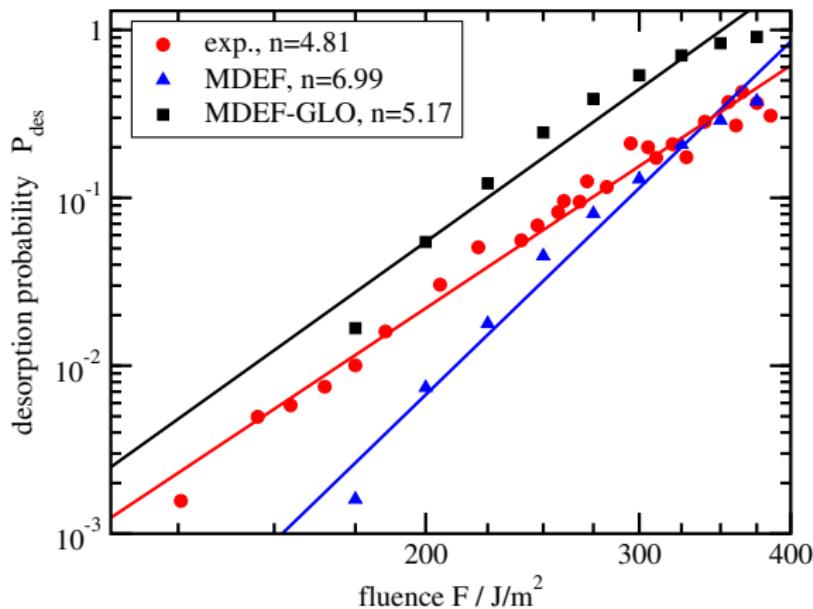
Ghost oscillator



Laser-Driven Diffusion



Fluence-dependence of desorption yield P_{des}



Anisotropic diffusion + dynamical trapping

