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

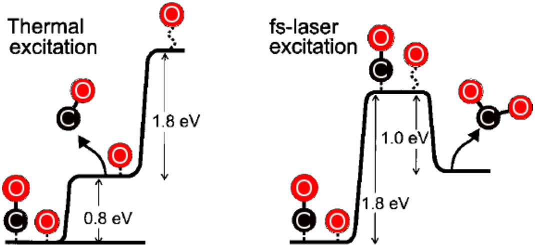
30. November 2016

Gliederung

General motivation

Why investigate fs-laser-driven surface dynamics?

- gain fundamental understanding of adsorbate bonding
  $\Rightarrow$ additional tool besides scattering experiments and STM
- possible direct application in catalysis: “femtochemistry”
  $\Rightarrow$ 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, SCIENCE 1999 and Funk J. CHEM. PHYS 2000 (Ertl group - chemistry Nobel prize 2007).
- recently, time resolved x-ray spectra (XAS and XES) $\Rightarrow$ “movie” of changes in orbital DOS

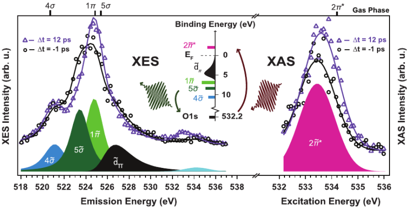
Details of the time-resolved x-ray experiment

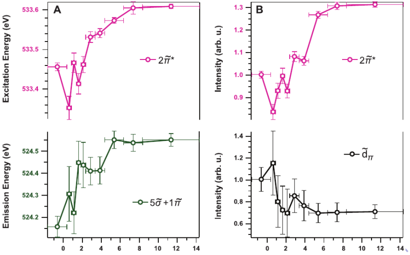
What was done?

- 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 $\sim 30\%$
  - $\tilde{\mathrm{d}}_\pi \Rightarrow$ decrease by $\sim 30\%$
  - participator peak appears

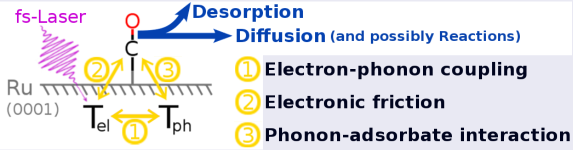




What happens after fs-laser excitation of the metal?

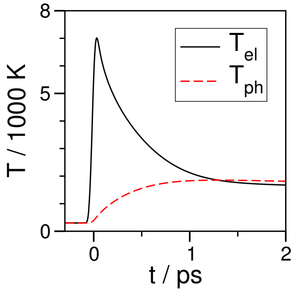
Coupling between three different kinds of degrees of freedom:

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

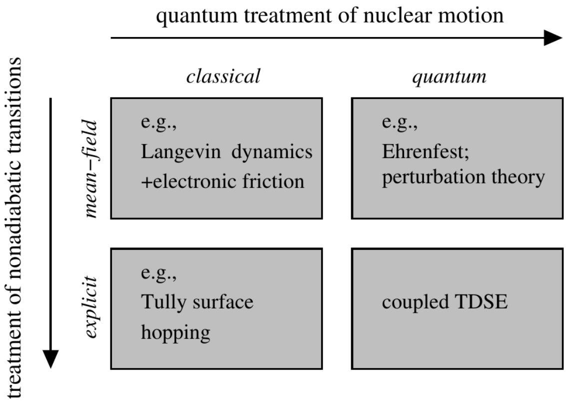


Two-Temperature Model

$$
\begin{aligned}
C_{\mathrm{el}}\frac{\partial T_{\mathrm{el}}}{\partial t} &= \frac{\partial}{\partial z}\kappa\frac{\partial}{\partial z}T_{\mathrm{el}} - g(T_{\mathrm{el}} - T_{\mathrm{ph}}) + S(z,t), \\
C_{\mathrm{ph}}\frac{\partial T_{\mathrm{ph}}}{\partial t} &= g(T_{\mathrm{el}} - T_{\mathrm{ph}}).
\end{aligned}
$$



Non-adiabatic coupling



Langevin Dynamics

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

- $R_{\mathrm{el},k}(t)$ = Gaussian white noise, dependent on:
  - $\eta_{\mathrm{el},k}(\underline{r}_k)$
  - and T_{el}

Local density friction approx. plus independent atoms

Laser-Driven Diffusion