

Laser-driven dynamics of CO on Ru(0001)

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

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30. November 2016

1 Introduction

- Motivation - in general and system specific
- First impressions of fs-laser-driven dynamics

2 Models and methods

- Foundations: 6D potential and two-temperature model
- Electronic friction: non-adiabatic coupling approximated
- The generalized Langevin oscillator (GLO)
- “Half-time”: short summary (and time for any first questions)

3 Results

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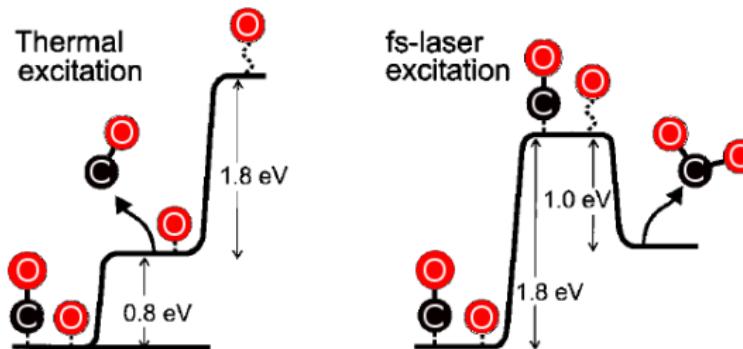
3

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 investigating CO/Ru(0001)

CO/Ru(0001) system important for catalysis, e.g.:

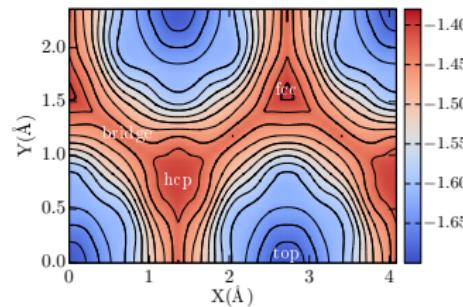
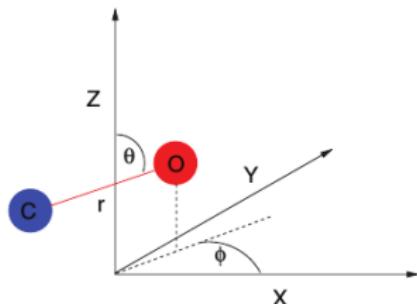
- Fischer-Tropsch synthesis
- exhaust gas converters (systems with similar metals)

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).
- desorption kinetics: large prefactors ⇒ still not understood
- recently, time resolved x-ray spectra (XAS and XES)
⇒ “movie” of changes in orbital density of states
 - Dell'Angela *et al.*, *Science* 2013

Further specific motivation for investigating CO/Ru

Füchsel *et al.*, *JChemPhys* 2014



Important prior theory work was done at our group

Füchsel *et al.*, *JChemPhys* 2014

- Development of a potential energy surface (PES)
 - from over 90 000 DFT points!
 - all 6 dimensions of the adsorbate
 - very fast because preconstructed
- ⇒ **enables large-scale dynamics!**

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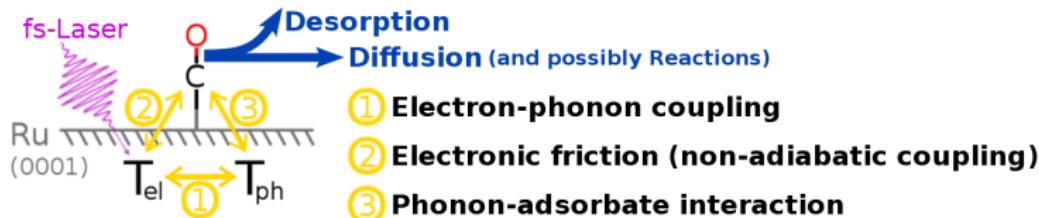
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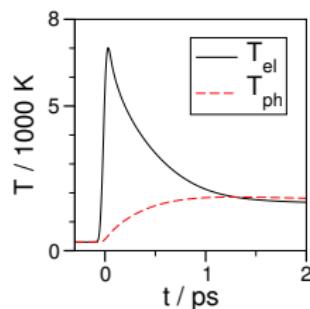
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What happens after fs-laser excitation of the metal?



Coupling between 3 kinds of degrees of freedom:

- electron gas (T_{el})
 - initially absorbs laser energy
 - low heat capacity \Rightarrow high T_{el} ($\approx 5\text{-}10 \text{ kK}$)
- lattice vibrations (T_{ph})
 - thermalization with electrons: ps time scale \Rightarrow fs-laser causes two distinct temperatures!
- adsorbate movement (T_{ads})



Details of the time-resolved x-ray experiment

Dell'Angela *et al.*, *Science* 2013 (experimental part by Nilsson group, SLAC/LCLS, Stanford)

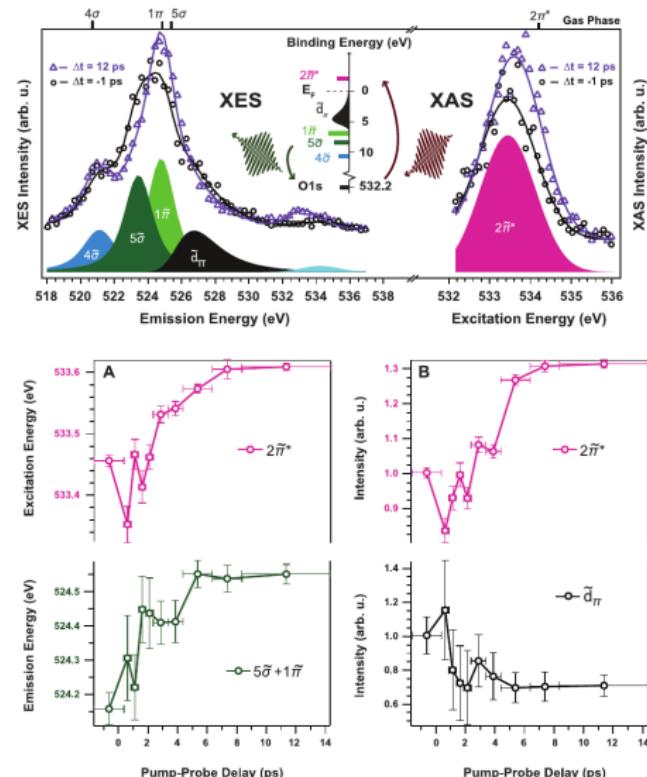
What was done?

- pump: *vis-fs-laser*
- probe: x-ray free e^- laser
 - K-edge of O-atom

What is observed?

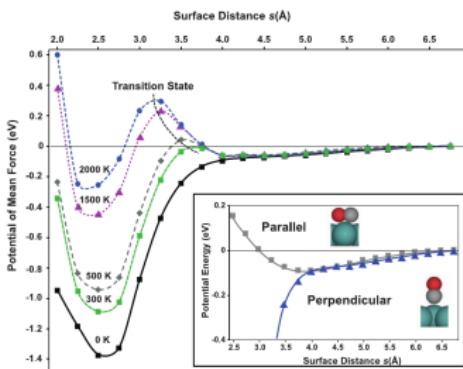
- orbital density of states at O
- energies shift towards gas-phase values of CO
- intensities change
 - $2\tilde{\pi}^*$ \Rightarrow increase by $\sim 30\%$
 - \tilde{d}_π \Rightarrow decrease by $\sim 30\%$
 - participant peak appears

⇒ physisorbed precursor(?)



Details of the accompanying theory

still Dell'Angela *et al.*, *Science* 2013 (theory part by Nørskov group, SUNCAT, Stanford)



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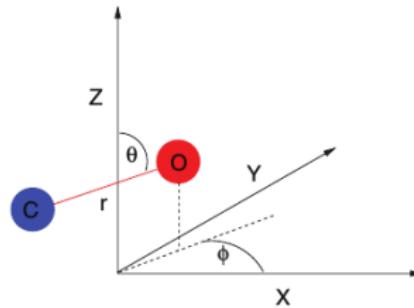
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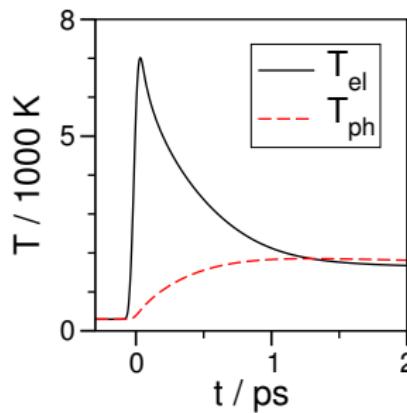
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Ab-initio-based, full-dimensional (6D) potential energy surface (PES)



Two-Temperature Model (TTM)

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



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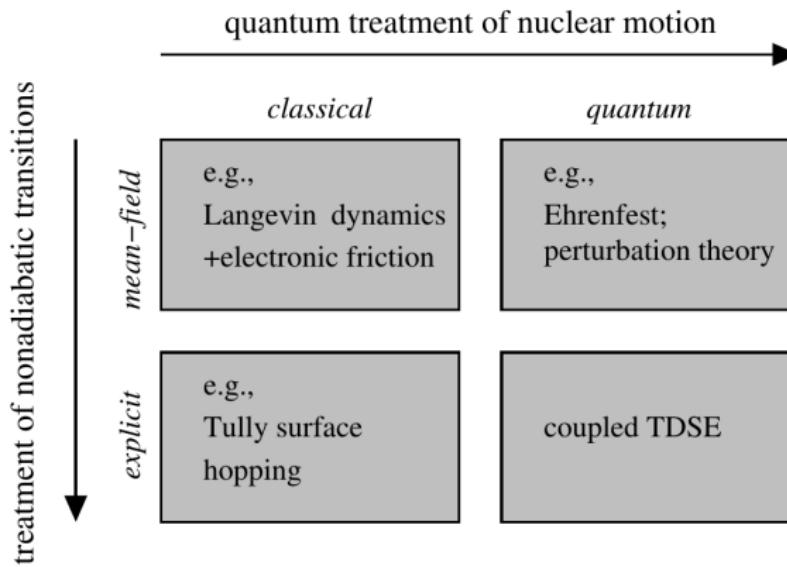
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Different approaches to describe non-adiabatic coupling



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

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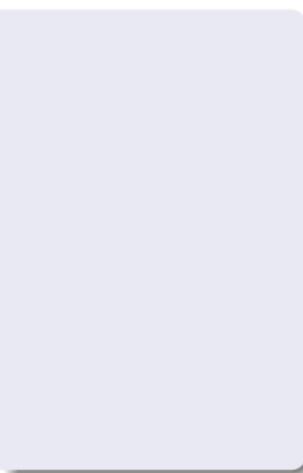
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Generalized Langevin Oscillator



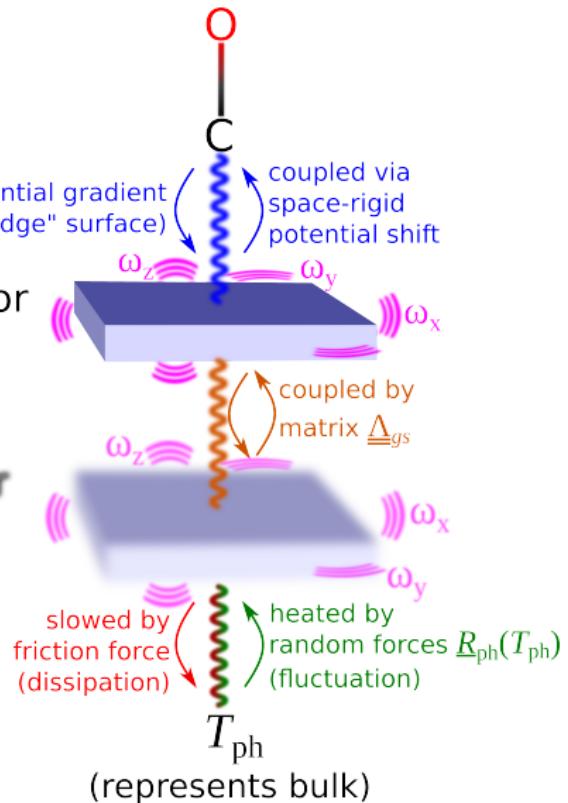
Surface oscillator

both oscillate in the 3 dimensions x, y, z

Ghost oscillator

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

$$m_s \frac{d^2 r_g}{dt^2} = -m_s \underbrace{\underline{\underline{\Omega}}^2 r_g}_{\text{Harmonic oscillator}} + m_s \underbrace{\underline{\underline{\Lambda}}_{gs} r_s}_{\text{Coupling to surface force oscillator}} - \eta_{ph} \frac{dr_g}{dt} + R_{ph}(T_{ph})$$



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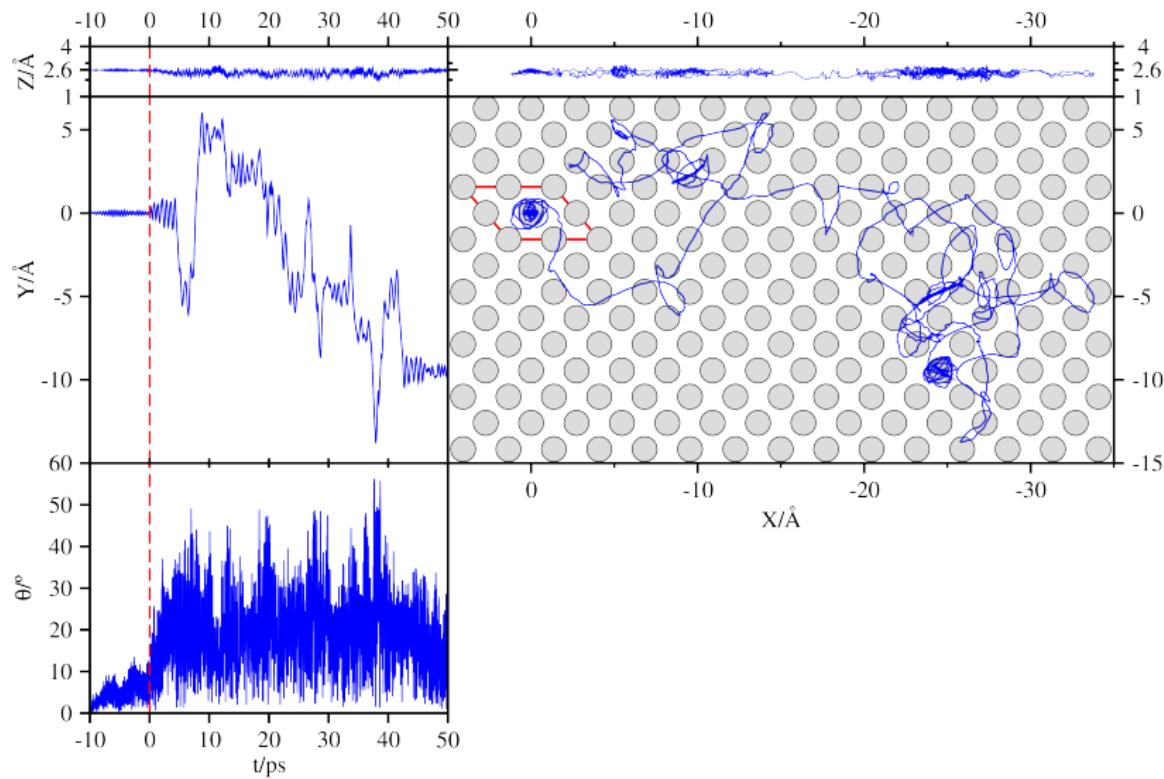
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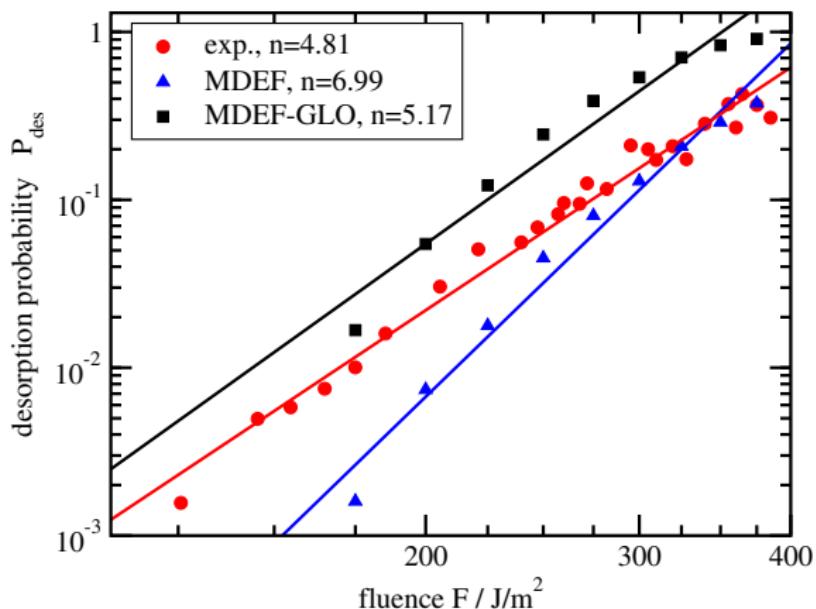
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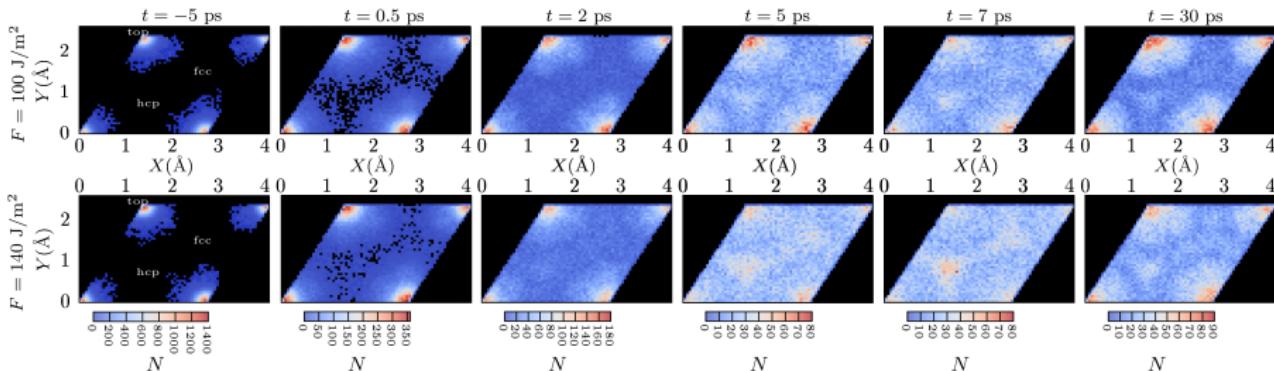
Laser-Driven Diffusion



Fluence-dependence of desorption yield P_{des}



Anisotropic diffusion + dynamical trapping



Surprising patterns in XY-distribution

- preference of **hcp-site** after 5-7 ps, despite it being a local maximum!
⇒ **dynamical trapping** (cf. 30 ps)
- effect dependent on fluence
⇒ consistent with experiment
(weaker “precursor”-signal for lower fluence)

