Laser-driven dynamics of CO on Ru(0001)

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

Robert Scholz

AG Saalfrank
Institut für Chemie
Universität Potsdam

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Outline

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 maybe time for a few questions)
3. Results and discussion
   - Overview of computational settings
   - Laser-driven diffusion and desorption
   - Physisorbed precursor states?
4. Summary and Outlook

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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 ($n\,CO + 2n\,H_2 \rightarrow$ Alkane/Alkene/Alkohole + H_2O)
- exhaust gas converters (cars, power plants, etc.)

Experimentally well studied system

- especially regarding fs-laser irradiation:
  - e.g. Bonn *et al.*, *Science* 1999; Funk *et al.*, *JChemPhys* 2000
  - (both Ertl group $\Rightarrow$ chemistry Nobel prize 2007).
- desorption kinetics: large prefactors $\Rightarrow$ still not understood
- recently, time resolved x-ray spectra (XAS and XES) $\Rightarrow$ "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 preconstucted

$\Rightarrow$ **enables large-scale dynamics!**

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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 ⇒ high T_{el} (≈5-10 kK)
- lattice vibrations (T_{ph})
  - thermalization with electrons: ps time scale
    ⇒ 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 $\sim 30\%$
  - $\tilde{d}_\pi \Rightarrow$ decrease by $\sim 30\%$
  - participator peak appears

$\Rightarrow$ physisorbed precursor(?)

Details of the accompanying theory

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

Dell'Angela *et al.*, *Science* 2013

Scholz *et al.*, *PhysRevB* 2016

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More facts about the potential energy surface (PES)

How was it constructed?

- GGA-level (RPBE) with VdW-correction (D2)
- (2x2) cell with 1 CO ⇒ 14 atoms, 0.25 ML coverage
  - all 6 dimensions of adsorbate ⇒ surface atoms frozen
- interpolation with cubic splines and corrugation reducing procedure (CRP)
  - atomic potentials temporarily substracted ⇒ smoother intermittent potential, interpolates better
- slightly newer PES: C_{3v}- instead of C_{6v}-symmetry
  - differences between hcp and fcc sites not neglected

Two-temperature model (TTM)

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

$$C_{\mathrm{ph}} \frac{\partial T_{\mathrm{ph}}}{\partial t} = g(T_{\mathrm{el}} - T_{\mathrm{ph}}).$$

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Different approaches to non-adiabatic coupling

Langevin dynamics + electronic friction

- fastest method ⇒ suited for multi-dimensional dynamics
- good approximation for weak non-adiabatic coupling

The Langevin equation

A stochastic differential equation

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

Langevin equation within IAA (independent atom approx.)

- friction coefficient of Atom k: $\eta_{\mathrm{el},k}(\underline{r}_k) \Rightarrow$ dissipation
  - derived from local density friction approximation (LDFA) $\Rightarrow$ individual atom (again IAA) in free electron gas
  - $\eta_{\mathrm{el},k}(\underline{r}_k)$ dependent on electron density of bare surface
- random force $\underline{R}_{\mathrm{el},k}(t) \Rightarrow$ fluctuation
  - Gaussian white noise
  - describes excitation by hot electron-hole pairs
  - proportional to: $\eta_{\mathrm{el},k}(\underline{r}_k)$ and $T_{\mathrm{el}}(t)$

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Generalized Langevin Oscillator

$$m_s \frac{d^2 \underline{r}_s}{dt^2} = \underbrace{-\underline{\nabla}_s V(\underline{r}_1 - \underline{r}_s, \underline{r}_2 - \underline{r}_s)}_{\text{Force due to PES}} \underbrace{- m_s \underline{\underline{\Omega}}^2 \underline{r}_s}_{\text{Harmonic oscillator}} \underbrace{+ m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_g}_{\text{Coupling to ghost oscillator}}$$

$$m_s \frac{d^2 \underline{r}_g}{dt^2} = \underbrace{-m_s \underline{\underline{\Omega}}^2 \underline{r}_g}_{\text{Harmonic oscillator}} \underbrace{+ m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_s}_{\text{Coupling to surface oscillator}} \underbrace{- \eta_{\mathrm{ph}} \frac{d\underline{r}_g}{dt}}_{\text{Friction force}} \underbrace{+ \underline{R}_{\mathrm{ph}}(T_{\mathrm{ph}})}_{\text{Random forces}}$$

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Example trajectory
(in this case without GLO-model)

Heating of DOFs Z and θ

Fluence-dependence of desorption yield P_{des}

Power-law

- $P_{\mathrm{des}} = A \cdot F^n$
- not exactly

Differences in exp.

- coverage:

$\Rightarrow$ 0.68 ML (max.)

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No population of physisorbed state in our dynamics

As is to be expected from negligible barrier in potential of mean force (PMF)

Why are the entropic barriers of the PMFs so different?

Because separability assumption fails clearly

- if introduced for our PMF ⇒ barrier of similar heigth!
- expectable, because X/Y and θ strongly coupled

Dynamical trapping: alternative/additional explanation?

Suprising patterns in XY-distribution

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

Is there a physisorbed precursor state nevertheless?

Dynamical trapping can't explain all observations

- XAS of hcp-site computed: $2\pi^*$-intensity not increased
- participator peak not explained by any XY-redistributions
  $\Rightarrow$ Existence of physisorbed state very likely
- but nevertheless not stable for Ru(2x2):CO models
  $\Rightarrow$ probably stabilized by CO-CO-interactions

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