

MULTI-DIMENSIONAL FEMTOSECOND-LASER INDUCED DYNAMICS OF CO ON METALS:

ACCOUNTING FOR ELECTRONIC FRICTION AND SURFACE MOTION WITH COMBINED MODELS

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Introduction

Motivation

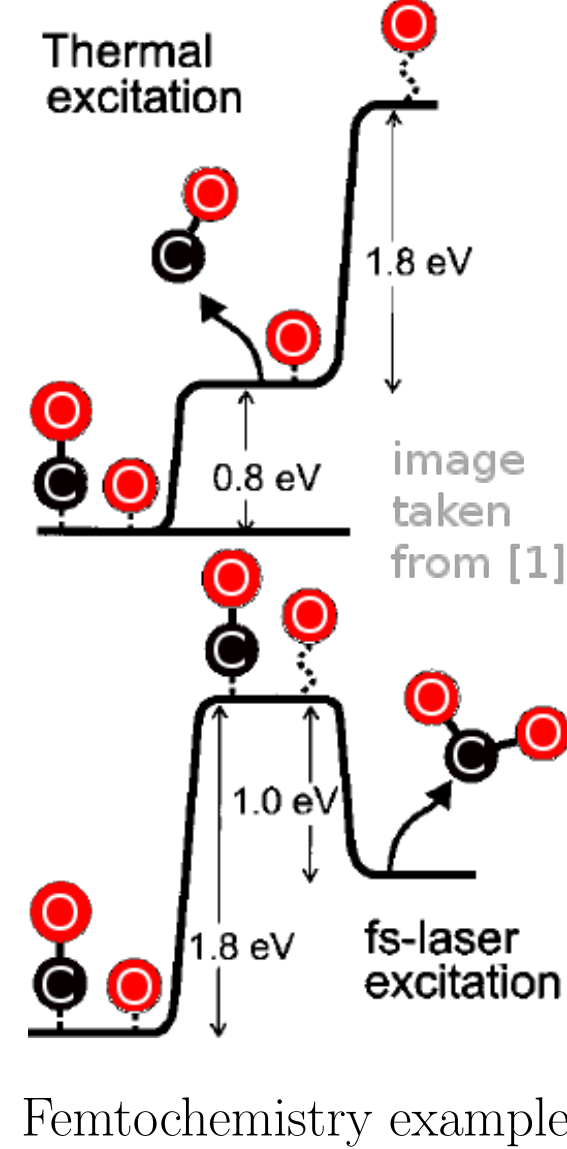
- **Aim:** gain **precise understanding** of **adsorbate bonding** on metals
⇒ Important for **Catalysis**

- **Why femtosecond(fs)-lasers?**

- **produce** non-equilibrium **2-T-states**
⇒ **different than** normal **heating**
- further **tool** besides STM and scattering
- **direct** future **applications** possible
⇒ “**femtochemistry**”[1]

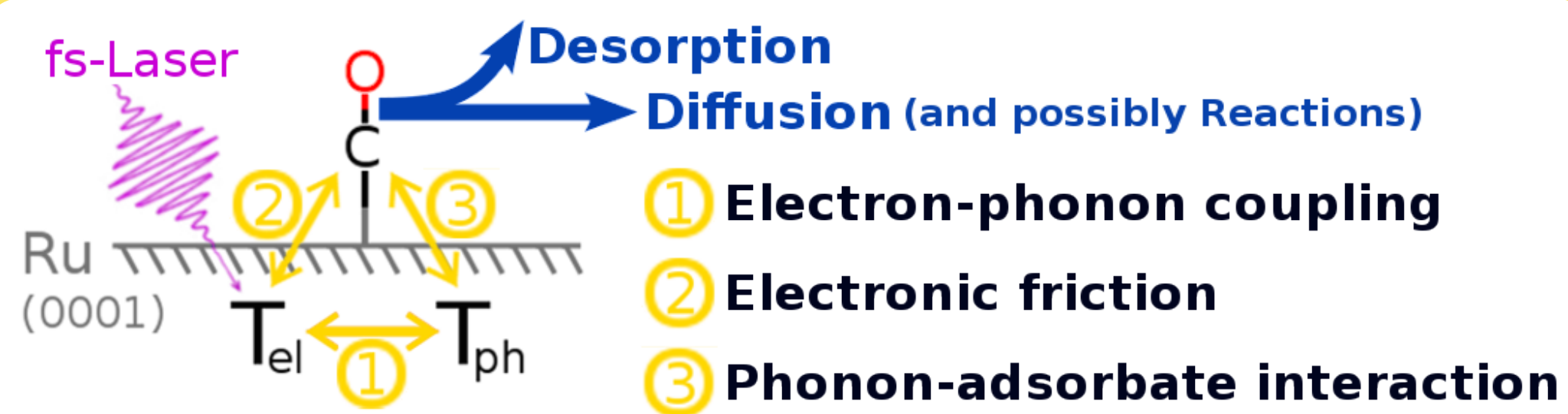
- **Why CO/Ru(001) and CO/Cu(100)?**

- both are well studied **model systems**
- recently, interesting **fs-laser experiments**[2][3]
- also, **ab-initio** based **6-dim. potentials** available [4][5]



Femtochemistry example

How do fs-lasers affect adsorbate-metal systems?

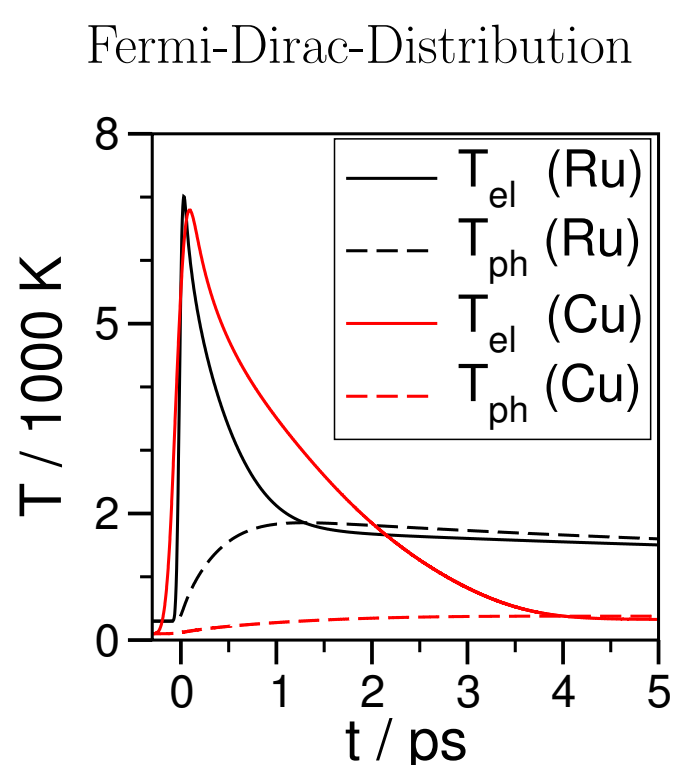
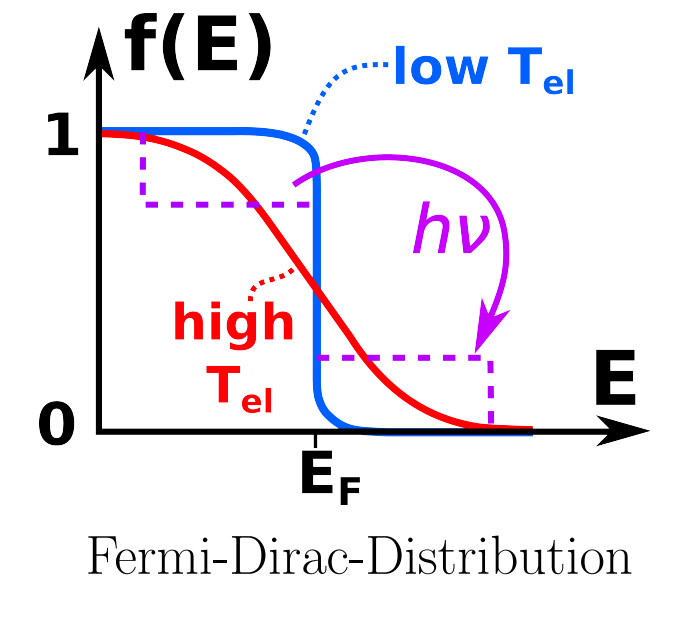


- only **electrons** of metal **absorb** laser

- **electron-hole pairs** thermalize fast
⇒ “**hot**” Fermi-Dirac-distribution

- electrons transfer energy to ion lattice, via ① **electron-phonon coupling**

- **equilibration** within **ps-timescale**



⇒ Thus, for few ps **two temperatures**:

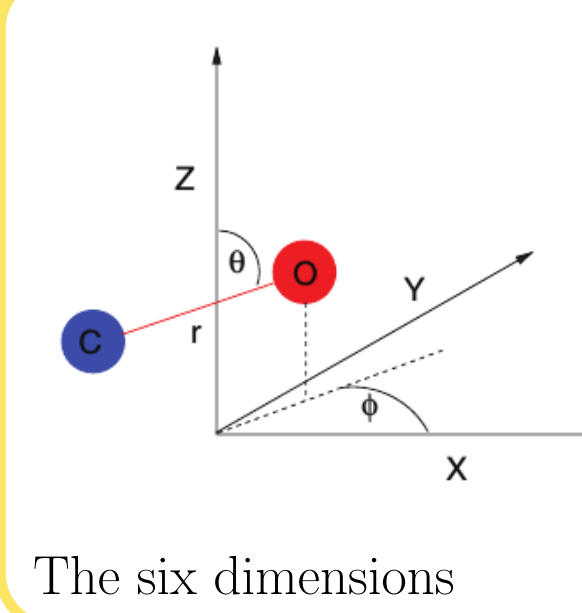
- T_{el} - electron temperature
- T_{ph} - phonon temperature

- both can **couple** to adsorbed **molecule**

- low electron heat **capacity** ⇒ T_{el} higher

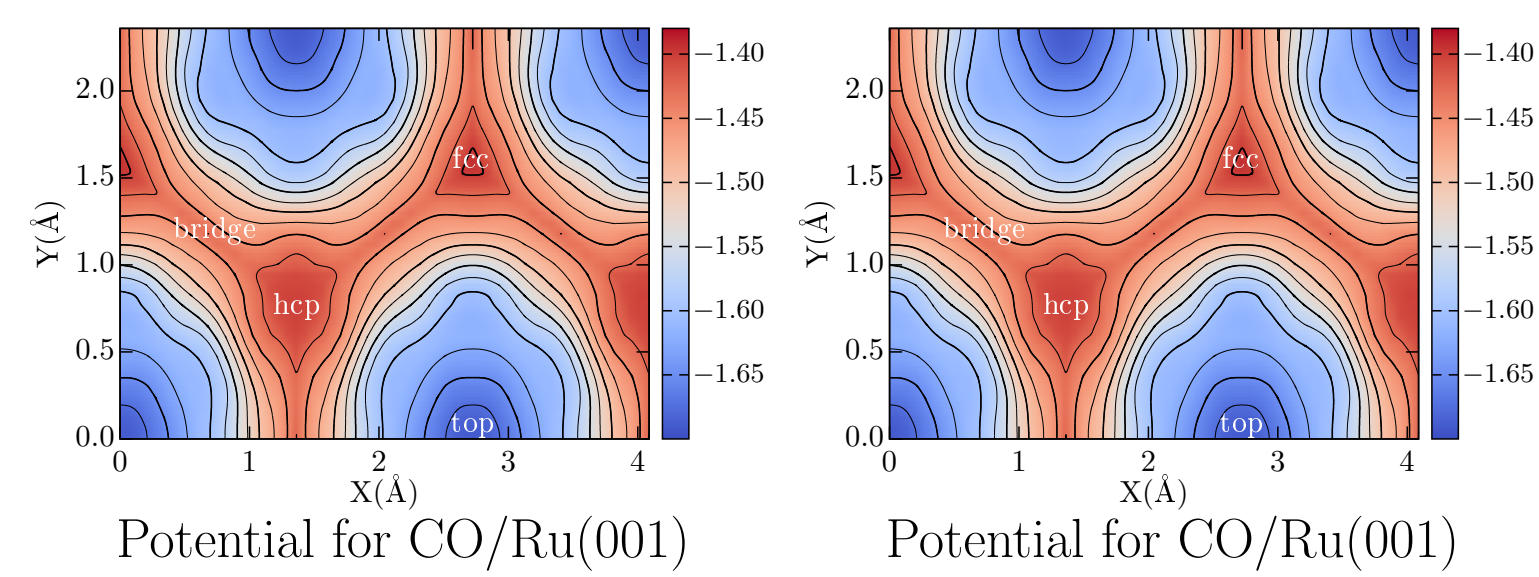
Models and Methods

Basis of the Dynamics: the Six-dimensional Potential Energy Surfaces (PES)[4][5]



The six dimensions

- **precomputed** with DFT (GGA)
- all **six dimensions** of the adsorbate
- **analytical** ⇒ **very fast**
⇒ **many trajectories** possible
- but: surface frozen ⇒ **no phonons**



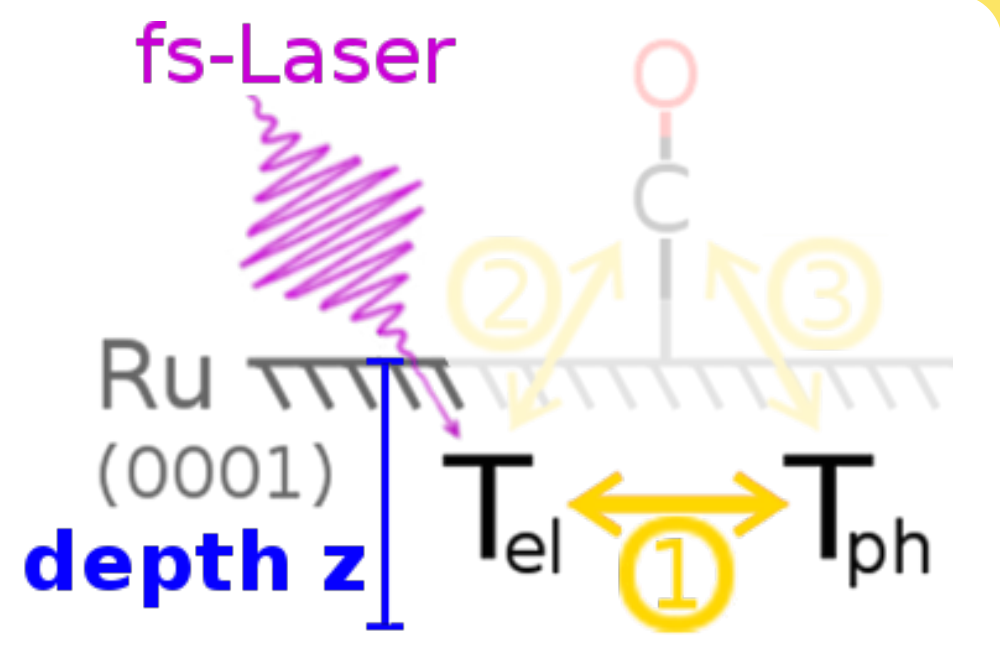
Two-Temperature Model (2TM)[6]

- describes **interaction** of **electrons** with **phonons** and **laser**

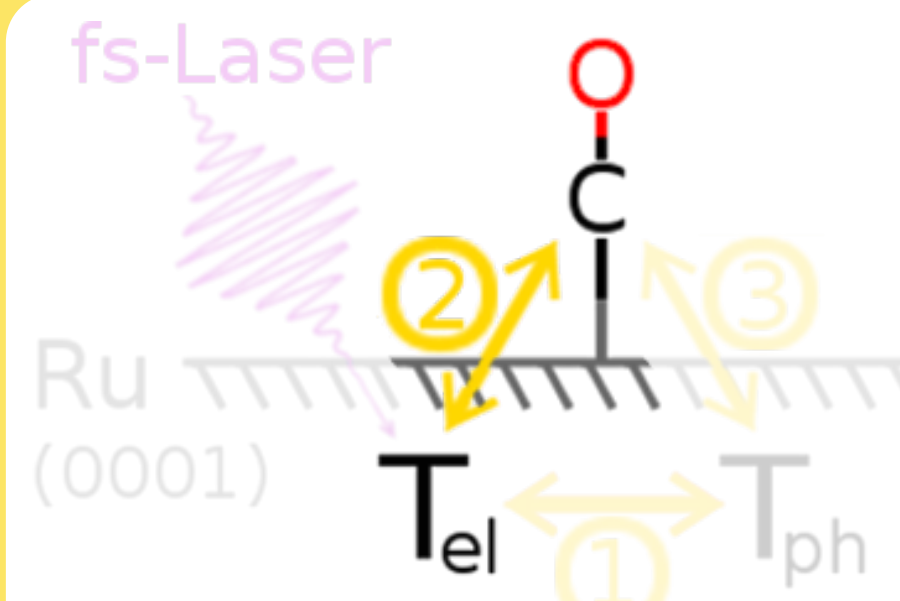
$$C_{el} \frac{\partial T_{el}}{\partial t} = \frac{\partial}{\partial z} \kappa \frac{\partial}{\partial z} T_{el} - g(T_{el} - T_{ph}) + S(z, t),$$

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

⇒ get T_{el} and T_{ph} as $f(z, t)$ from laser parameters and material properties



Electronic Friction: Langevin Dynamics[7] and Local Density Friction Approximation (LDFA)[8]



- Langevin equation of motion, a stochastic differential equation:

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

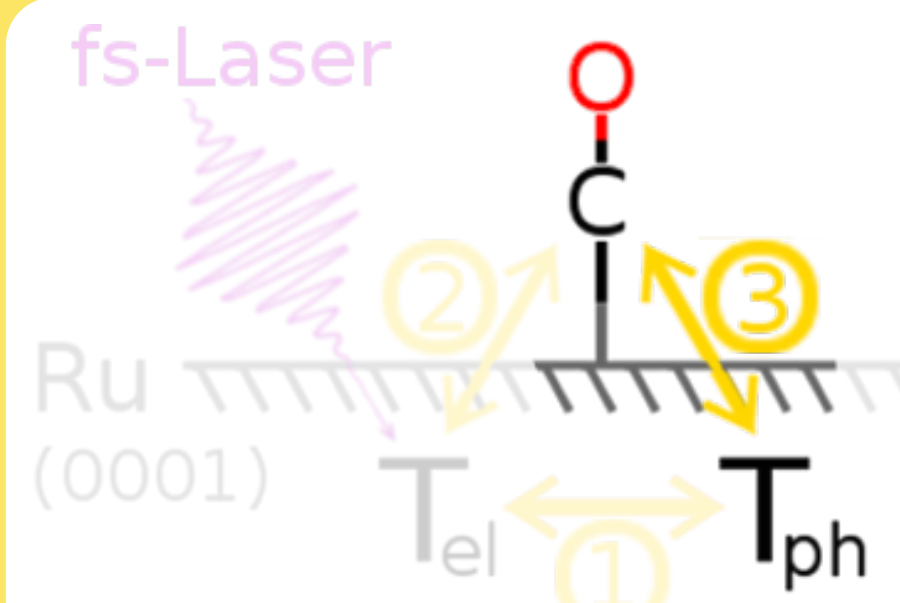
- describes **movement** of CO and **interaction** with **electron-hole pairs** (friction and excitation)

- **Local Density Friction Approx.** (LDFA): simple **model** to get **friction coefficients** $\eta_{el,k}$

- Atom k embedded in **free electron gas** with density of bare surface at current position \mathbf{r}_k

- **Random forces** $\mathbf{R}_{el,k}$: white noise, **dependent** on both $\eta_{el,k}$ (from LDFA) and T_{el} (from 2TM)

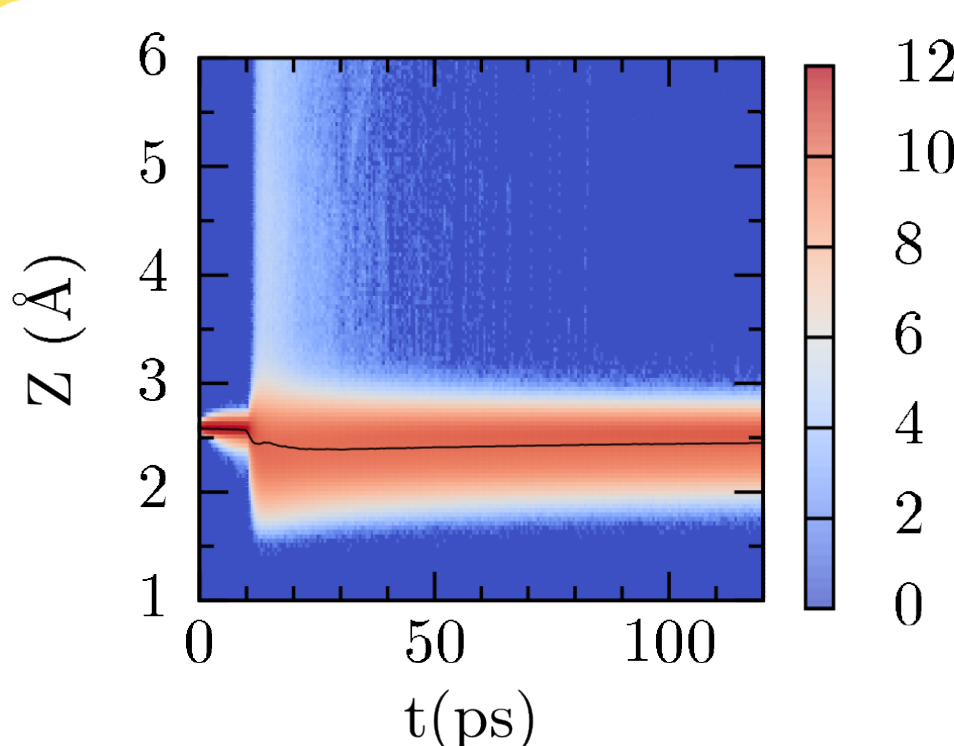
Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[9]



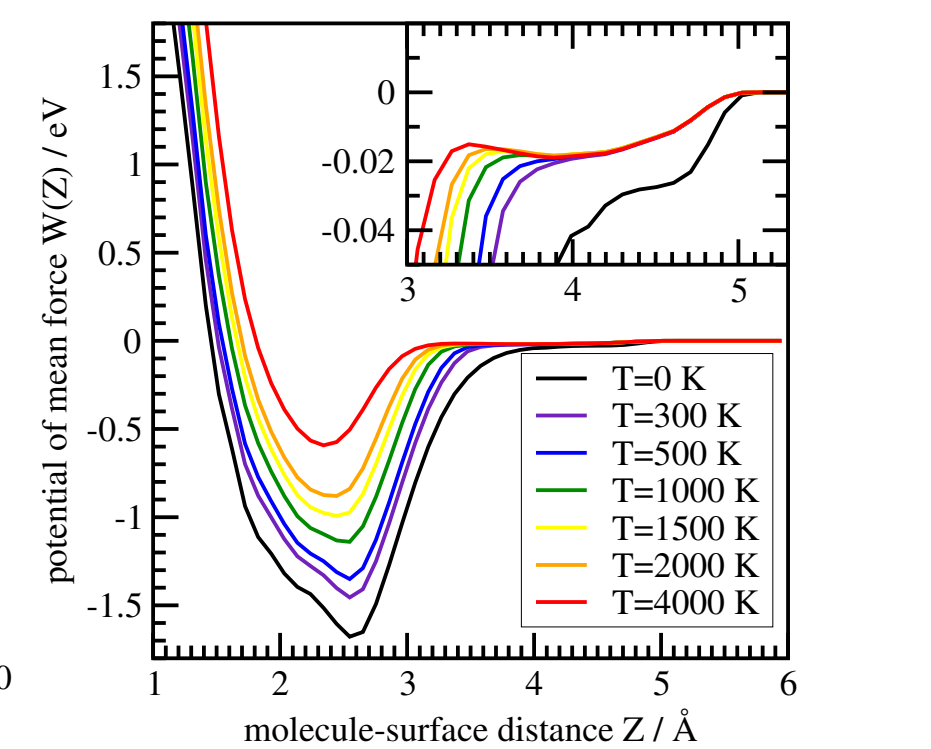
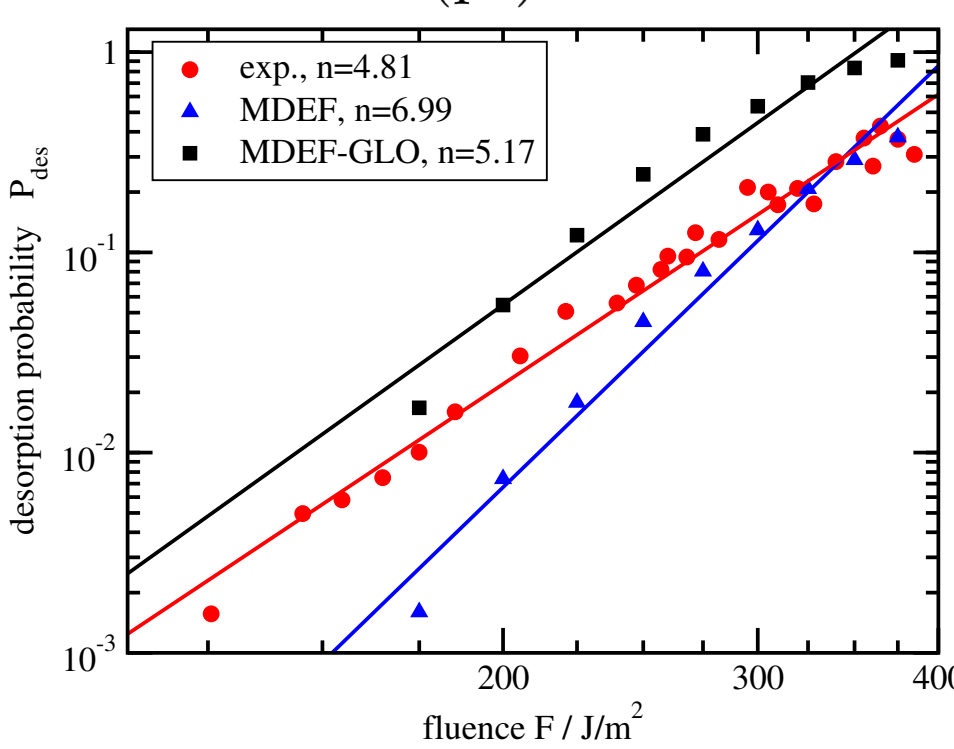
- influence of **phonons** effectifely **modeled** (**augments frozen surface**)
- **entire surface** understood as **3D oscillator** (coords. \mathbf{r}_s , mass 1 atom)
- **coupling** to molecule **via shifting**: $V_{GLO}(\mathbf{r}_C, \mathbf{r}_O; \mathbf{r}_s) = V(\mathbf{r}_C - \mathbf{r}_s, \mathbf{r}_O - \mathbf{r}_s)$
- additionally coupled to **ghost oscillator** \mathbf{r}_g , **models** influence of **bulk**
– ghost oscillator is subject to friction η_{ph} and random forces $\mathbf{R}_{ph}(T_{ph})$

Results

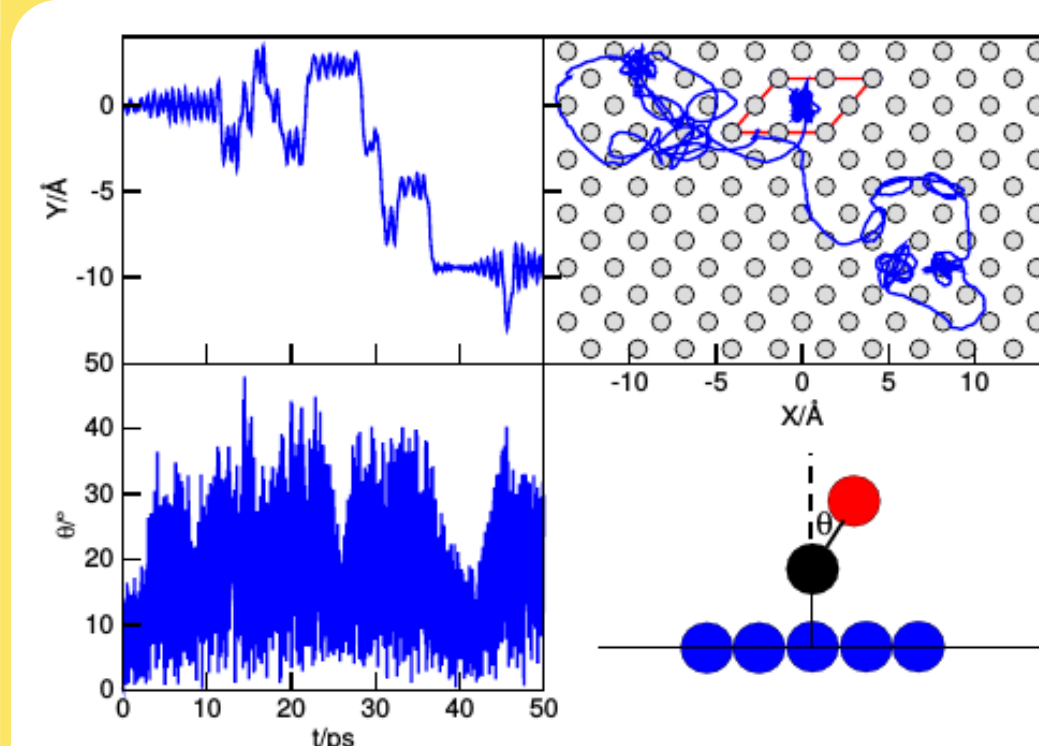
Desorption (Data for Ru)



- desorption mainly during first 50 ps
- fluence dependence of desorption yield close to experiment
- no barrier in PMF

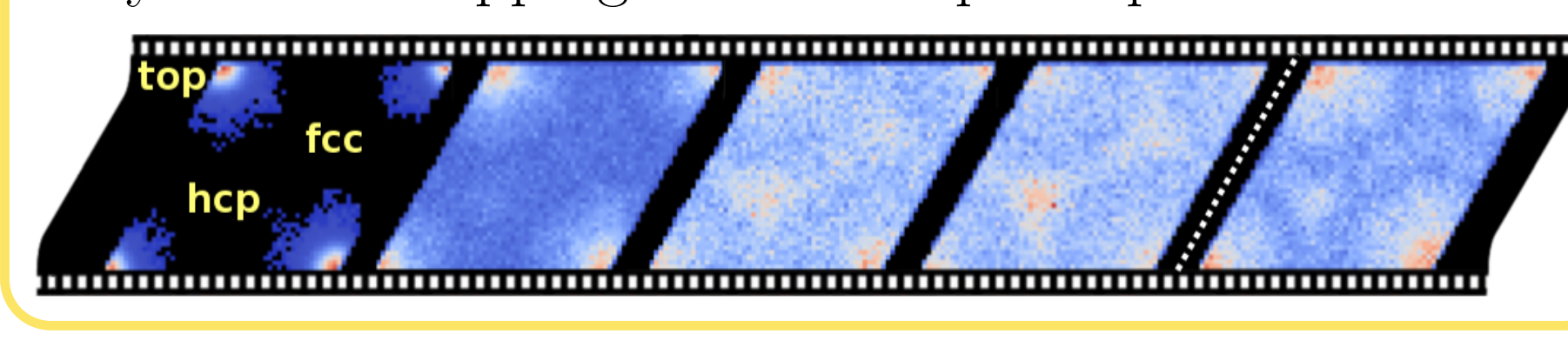


Diffusion (Data for Ru, but Cu similar)



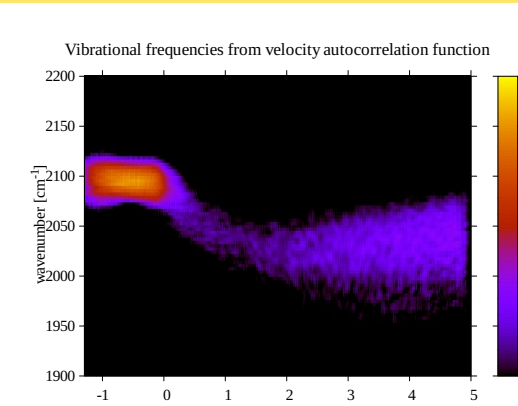
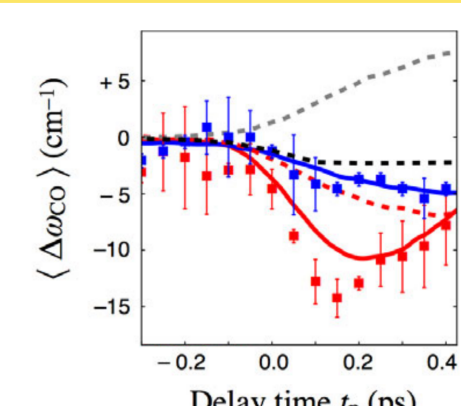
- typical trajectory: hops between top sites and vibration
- increase in θ -angle when CO moves away from top
- overall, very large diffusion

- also, nonisotropic diffusion behaviour observed:
- dynamical trapping effect at hcp site predicted



Vibrations (Data for Cu)

- Frequency-shift from time-resolved SFG



- Preliminary results from our dynamics

Conclusions

- 6D Langevin dynamics of CO on Ru and Cu
- based on first principles, no “free” parameters
- accounting for (via LDFA) electronic friction, hot electron excitation and (via GLO) substrate motion
- allows for detailed time- and space-resolved insights
- no physisorbed state, molecules desorb directly

Outlook

- better electronic friction ($\eta(T_{el})$ and beyond LDFA)
⇒ Long term goal: use tensorial friction (exact)
- non-equilibrium lattice model (NLM) instead 2TM
- simulate other coverages (bigger super cells)
- simulate bigger systems (CO + H; hydrocarbons)
- include interaction between adsorbate molecules

References

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[2] M. Dell’Angela, T. Anniyev, M. Beye, R. Coffee *et al.*, *Science* **339**, 1302 (2013).

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