Multi-dimensional Femtosecond-laser induced dynamics of CO on metals:

accounting for electronic friction and surface motion with combined models

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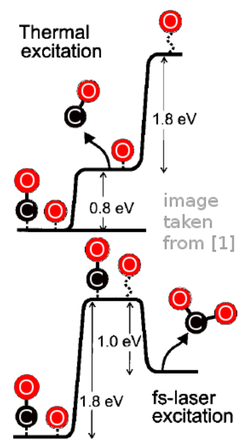
Introduction

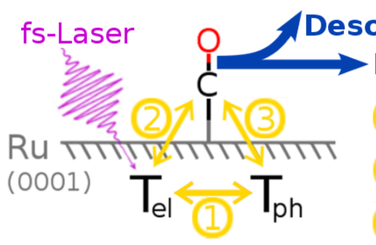
Motivation

- **Aim:** gain more **precise understanding** of **bonding** between **adsorbates** and **metals**
  ⇒ Fundamentally important for **Catalysis**
- **Why femtosecond(fs)-lasers?**
  - **cause** highly non-equilibrium **2-T-states**
    ⇒ **different** processes **than** from **heating**
  - further **tool besides STM** and **scattering**
  - **direct** future **applications** possible
    ⇒ **"femtochemistry"**[1]
- **Why** study **CO/Ru(001)** or **CO/Cu(100)**?
  - both are well studied **model systems**
  - recently, interesting **fs-laser experiments**[2][3]
  - moreover, significant **progress** in **theory** for both systems[4][5]
    ⇒ Very accurate (**ab-initio** based) **6-dim. potentials** available
  - also: **theory** has to **start small!** Anyhow, in future **possible** to **describe bigger systems with** the herein **presented methods**



example for femtochemistry

How do fs-lasers affect adsorbate-metal systems?

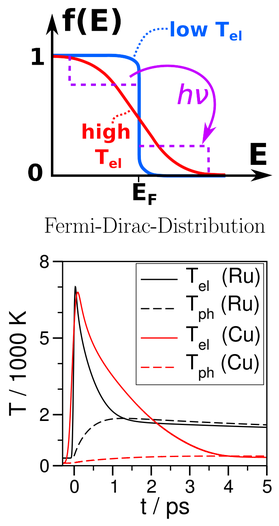


① **Electron-phonon coupling**
② **Electronic friction**
③ **Phonon-adsorbate interaction**

- **laser** is **absorbed by metal electrons** only
- produced **electron-hole pairs** thermalize quickly ⇒ **"hot"** Fermi-Dirac-distribution
- **electrons transfer** part of **energy** to ion **lattice**, via ① **electron-phonon coupling**
- **equilibration** complete **within ps**-timescale

⇒ **Thus**, with **fs-lasers two temperatures**:
- T_{el} - electron temperature
- T_{ph} - phonon temperature

- **both couple to adsorbed molecule**
- described by **Two-Temperature Model** [6]



Fermi-Dirac-Distribution

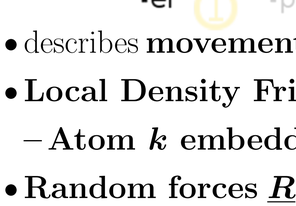
Models and Methods

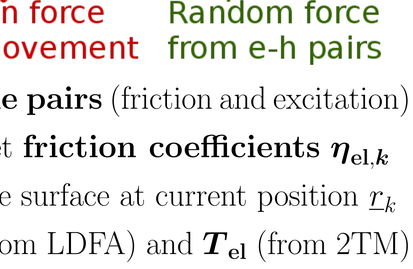
Six-dimensional Potential Energy Surface (6D PES)[4]

- Basis for dynamics: **precomputed PES** from DFT (rPBE + D2)
  - **all 6 dimensions** of the adsorbate
  - **analytical** PES and gradients ⇒ **very fast**

⇒ **number**, length of **trajectories** can be **large**

- **downsides**: – surface frozen ⇒ **no phonons**
  – had to be constructed first





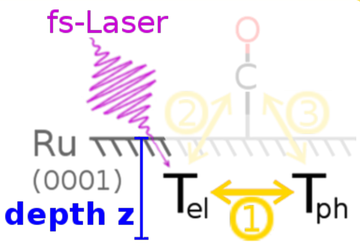
Potential for CO/Ru(001)

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

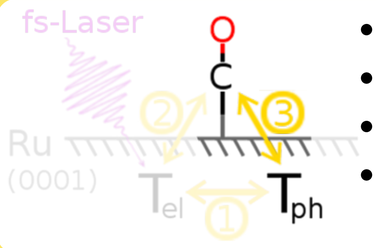
Electronic Friction: Langevin Dynamics[7] and Local Density Friction Approximation (LDFA)[8]

- Langevin equation of motion, a stochastical differential equation:

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

- 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 $\underline{r}_k$
- **Random forces $\underline{R}_{el,k}$**: white noise, **dependent on** both $\eta_{el,k}$ (from LDFA) and T_{el} (from 2TM)
  – justified by **2. fluctuation dissipation theorem**[9] (relating friction and thermal movement)

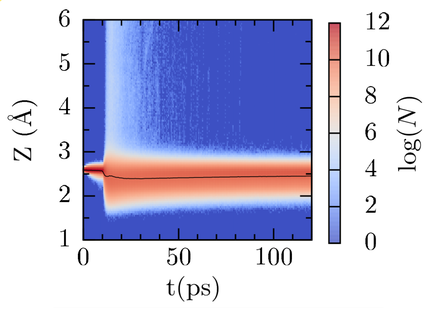
Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[10]



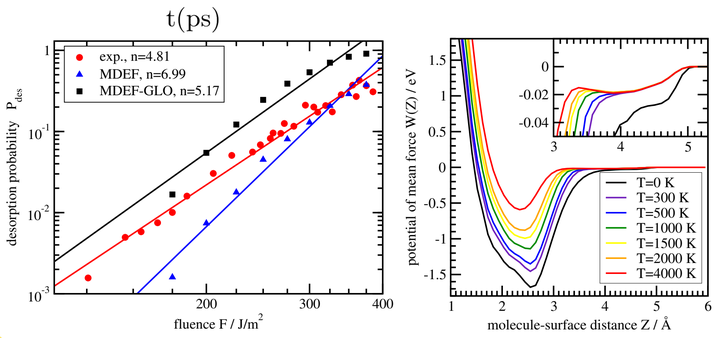
- influence of **phonons** effectifely **modeled** (**augments frozen surface**)
- **entire surface** understood as **3D oscillator** (coords. $\underline{r}_s$, mass 1 atom)
- **coupling** to molecule **via shifting**: $V_{GLO}(\underline{r}_C,\underline{r}_O;\underline{r}_s) = V(\underline{r}_C-\underline{r}_s,\underline{r}_O-\underline{r}_s)$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

Results

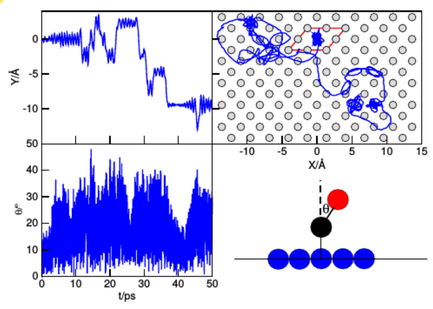
Desorption (Data for Ru)



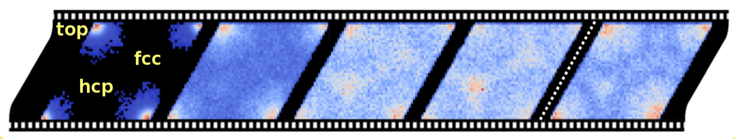
- desorption mainly during first 50 ps
- fluence dependence of desorption yield close to experiment
- no barrier in PMF



Diffusion (Data for Ru, but Cu similar)

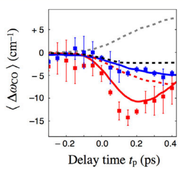


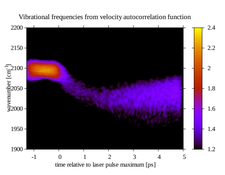
- typical trajectory: hops between top sites and vibration
- increase in θ-angle when CO moves away from top
- overall, very large diffusion
- also, nonisotropic diffusion behaviour observed:
- dynamical trapping effect at hcp site predicted



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 desorp directly

Outlook

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

References

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