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

accounting for electronic friction and surface motion with combined models

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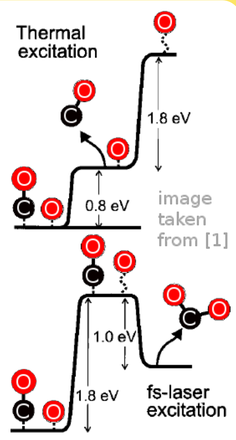
Introduction

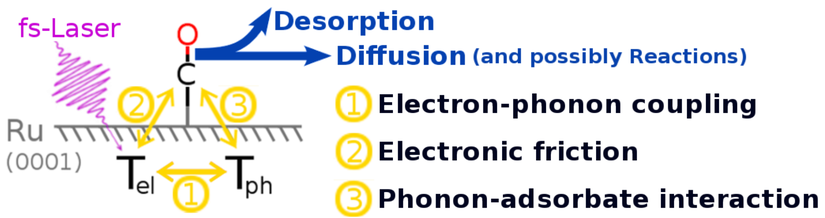
Motivation

- **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

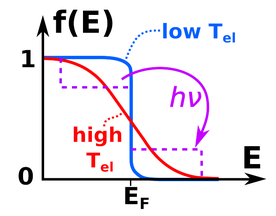
How do fs-lasers affect adsorbate-metal systems?



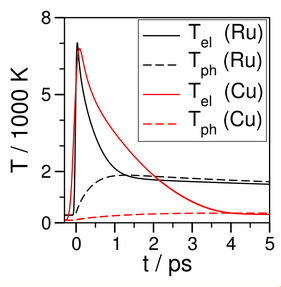
- only **electrons** of metal **absorb laser**
- **electron-hole pairs** thermalize fast ⇒ **"hot"** Fermi-Dirac-distribution
- electrons transfer energy to ion lattice, via ① **electron-phonon coupling**
- **equilibration within ps-timescale**

⇒ 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



Fermi-Dirac-Distribution



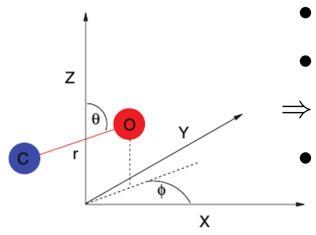
Models and Methods

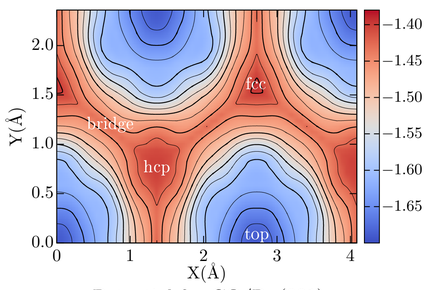
Six-dimensional Potential Energy Surface (6D PES)[4]

- 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





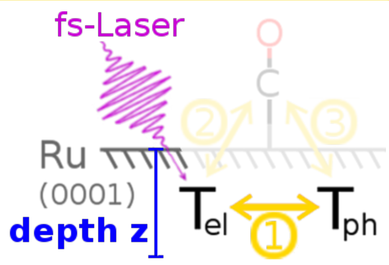
Potential for CO/Ru(001)

Two-Temperature Model (2TM)[6]

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

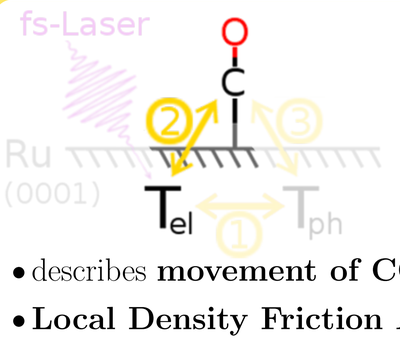
$$C_{\mathrm{el}}\frac{\partial T_{\mathrm{el}}}{\partial t} = \frac{\partial}{\partial z}\kappa\frac{\partial}{\partial z}T_{\mathrm{el}} - g(T_{\mathrm{el}} - T_{\mathrm{ph}}) + S(z,t),$$

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



⇒ **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]

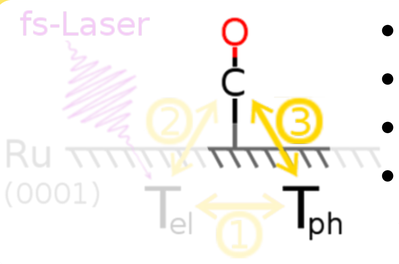


- Langevin equation of motion, a stochastical differential equation:

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

- describes **movement of CO** and **interaction with electron-hole pairs** (friction and excitation)
- **Local Density Friction Approx.** (LDFA): simple **model** to get **friction coefficients $\eta_{\mathrm{el},k}$**
  – **Atom k embedded in free electron gas** with density of bare surface at current position $\underline{r}_k$
- **Random forces $\underline{R}_{\mathrm{el},k}$**: white noise, **dependent on** both $\eta_{\mathrm{el},k}$ (from LDFA) and T_{el} (from 2TM)
  – justified by **2. fluctuation dissipation theorem**[9] (relating friction and thermal movement)

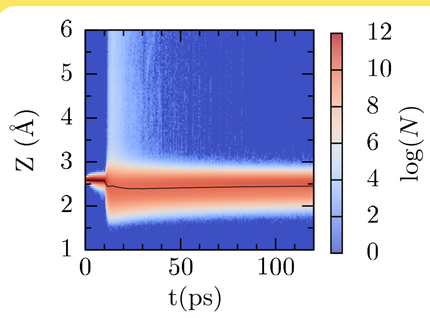
Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[10]



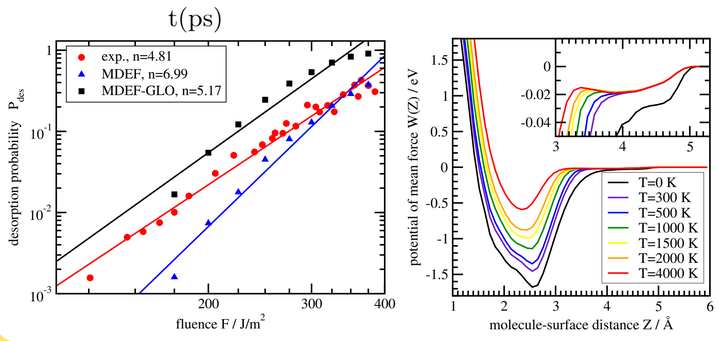
- influence of **phonons** effectifely **modeled** (**augments frozen surface**)
- **entire surface** understood as **3D oscillator** (coords. $\underline{r}_s$, mass 1 atom)
- **coupling** to molecule **via shifting**: $V_{\mathrm{GLO}}(\underline{r}_C,\underline{r}_O;\underline{r}_s) = V(\underline{r}_C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

Results

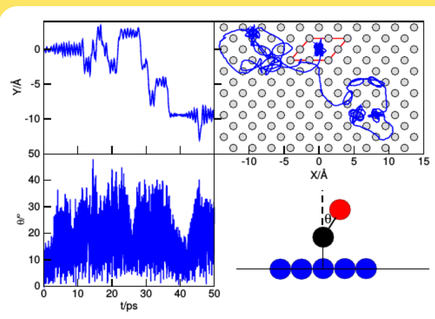
Desorption (Data for Ru)



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

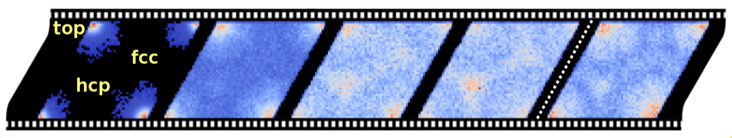


Diffusion (Data for Ru, but Cu similar)



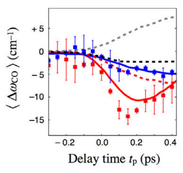
- typical trajectory: hops between top sites and vibration
- increase in θ-angle when CO moves away from top
- overall, very large diffusion

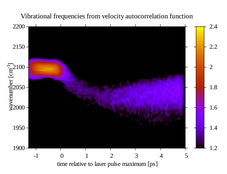
- also, nonisotropic diffusion behaviour observed:
- dynamical trapping effect at hcp site predicted



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 ($\eta(T_{\mathrm{el}})$ 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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