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

accounting for electronic friction and surface motion with combined models

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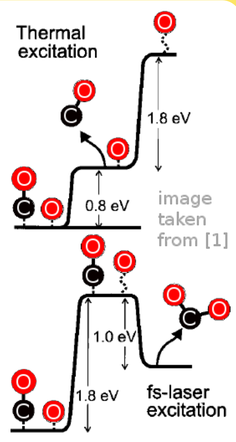
Introduction

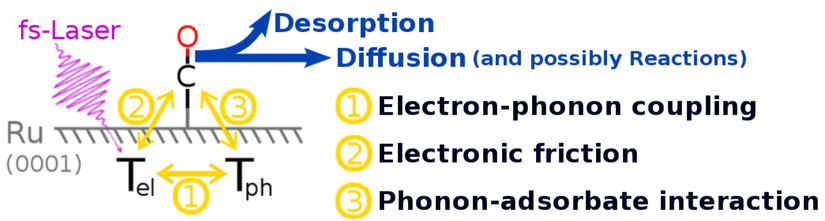
Motivation

- **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

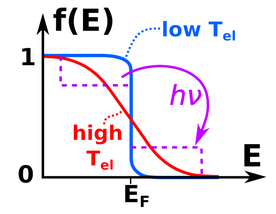
How do fs-Lasers affect Adsorbate-Metal Systems?



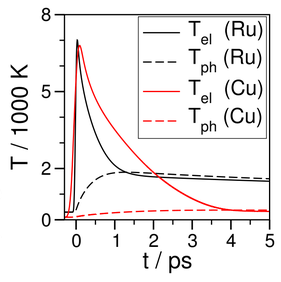
- only **electrons** of metal **absorb laser**
- **electron-hole pairs** thermalize fast ⇒ **"hot"** Fermi-Dirac-distribution
- electrons transfer energy to ion lattice, via ① **electron-phonon coupling**
- **equilibration within ps-timescale**

⇒ 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

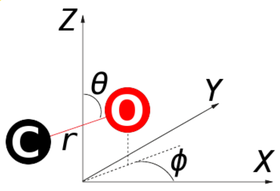


Fermi-Dirac-Distribution



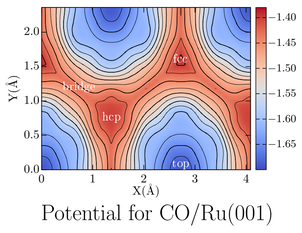
Models and Methods

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

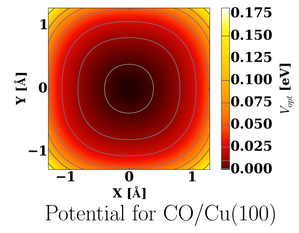


The six dimensions of CO

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

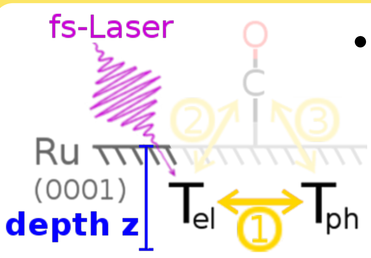


Potential for CO/Ru(001)



Potential for CO/Cu(100)

Two-Temperature Model (2TM)[6]



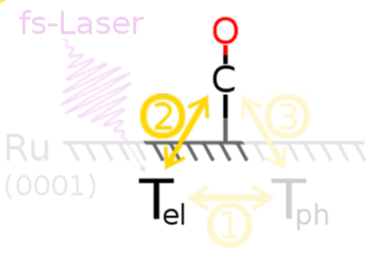
- simulates **interaction** of **electrons** with **phonons** and **laser** ⇒ **gives T_{el} and T_{ph} as $f(z,t)$**

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

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

- electron and phonon heat capacities C_{el} and C_{ph}
- elec. heat conductivity κ
- elec.-phonon coupling g
- laser source term S(z,t)

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

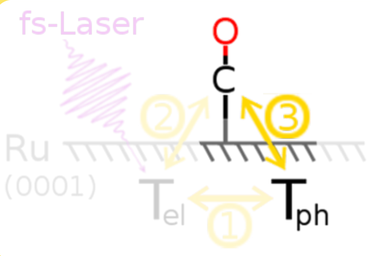


- the **Langevin equation** of motion, a **stochastical** differential equation:

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

- describes **movement of CO** and **interaction with electron-hole pairs** (friction and excitation)
- **Local Density Friction Approx.** (LDFA): *ab-initio* model that gives **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)

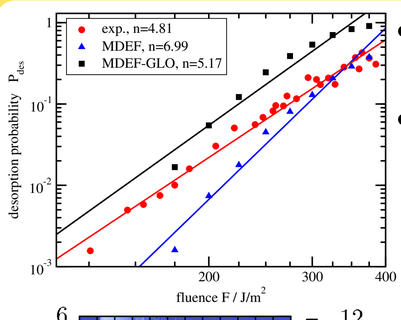
Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[9]



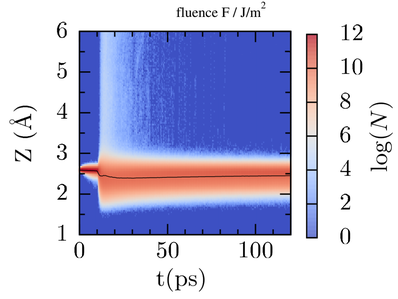
- influence of **phonons** effectively **modeled** (**augments frozen surface**)
- **entire surface** understood as **3D oscillator** (coords. $\underline{r}_s$, mass of one atom)
- **coupling** to molecule **via shifting**: $V_{GLO}(\underline{r}_C,\underline{r}_O;\underline{r}_s) = V(\underline{r}_C-\underline{r}_s,\underline{r}_O-\underline{r}_s)$
- 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

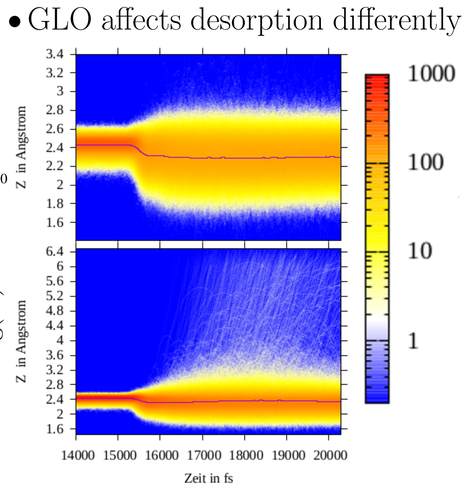
Desorption



- **fluence dependence** of desorption yield close to experiment (Ru)
- GLO affects desorption differently

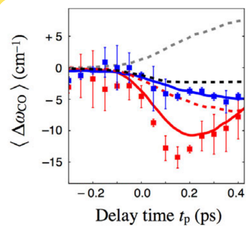


Ru (with GLO)

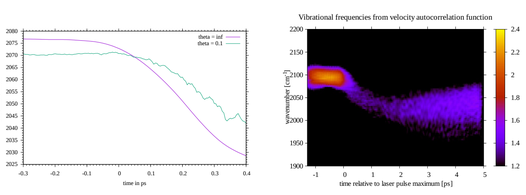


Cu (top with GLO, bottom w/o)

CO-stretch Vibration (Data for Cu)

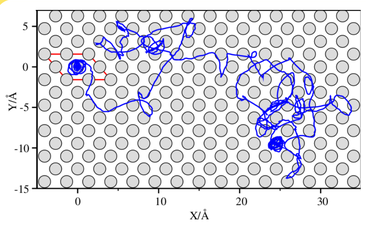


SFG-experiment[3]

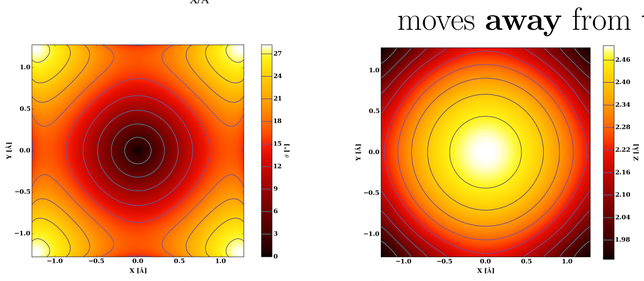


from our dynamics

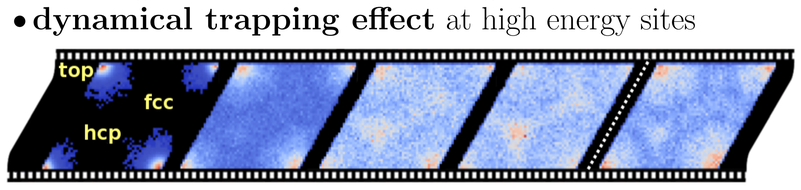
Diffusion



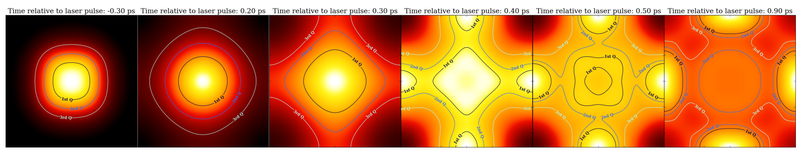
- **typical trajectory** (Ru): **vibration** around top and **hops between top sites**
- **increase** in **θ-angle** and **decrease of Z** when CO moves **away** from **top**



- **dynamical trapping effect** at high energy sites



CO XY-"heat map" on Ru (timescale several ps), molecules favor hcp site after pulse



CO XY-"heat map" on Cu (timescale below one ps), molecules favor bridge site after pulse

Conclusions

- **system: CO** on **Ru(001) or Cu(100)**
- **full-dimensional (6D)** simulation of dynamics driven by **fs-laser irradiation**
- **first principles**, no "free" parameters
- accounting for **1) electronic friction** and excitation by hot electron-hole pairs (via LDFA and the Langevin approach) and **2) substrate motion** (via GLO)
- detailed time- and space-resolved insights

Outlook

- better description of electronic friction: **η_{el} as $f(T_{el})$** and going **beyond LDFA** ⇒ Long term goal: **friction tensors**[10]
- further **2TM improvements**, consider **non-equilibrium lattice (NLM)**[11]
- directly model **SFG influence** by explicitly including **excitation** from **IR-pulse**
- **larger super cells** for other **coverages** and **intermolecular interaction**
- simulate **more complex systems**: hydrocarbons; coadsorbate CO + H or O

References

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