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

accounting for electronic friction and surface motion with combined models

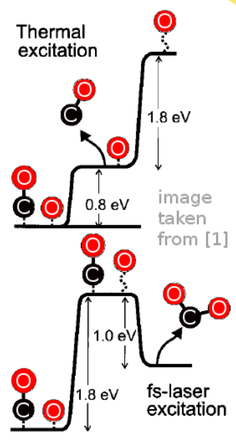
Robert Scholz[1], Peter Saalfrank[1], Ivor Lončarić[2], Jean Cristophe Tremblay[3], Gernot Füchsel[3], and Gereon Floß[1]

[1]Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany
[2]Ruđer Bošković Institute, Div. of Theor. Physics, Bijenička cesta 54, 10000 Zagreb, Croatia
[3]Freie Universität, Inst. für Chemie und Biochemie, Takustr. 3, 14195 Berlin, Germany

Introduction

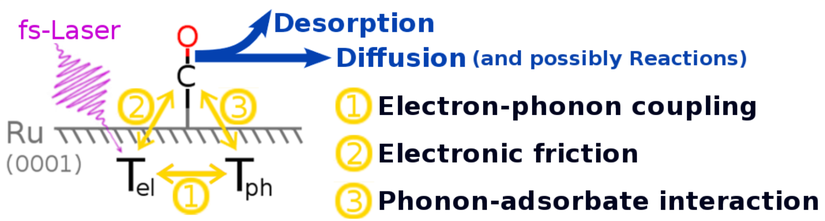
Motivation

- **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

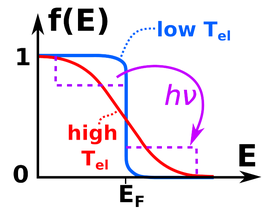
How do fs-Lasers affect Adsorbate-Metal Systems?



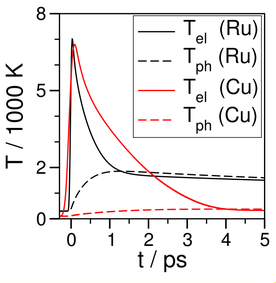
- only **electrons** of metal **absorb laser**
- **electron-hole pairs** thermalize fast ⇒ **"hot"** Fermi-Dirac-distribution
- electrons transfer energy to ion lattice, via ① **electron-phonon coupling**
- **equilibration within ps-timescale**

⇒ 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

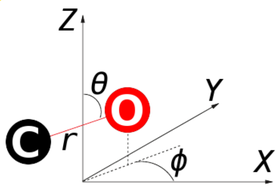


Fermi-Dirac-Distribution



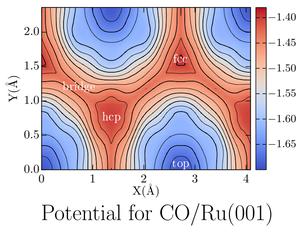
Models and Methods

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

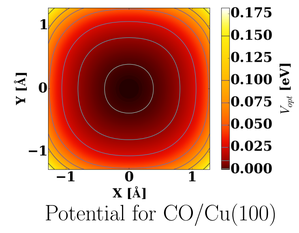


The six dimensions of CO

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

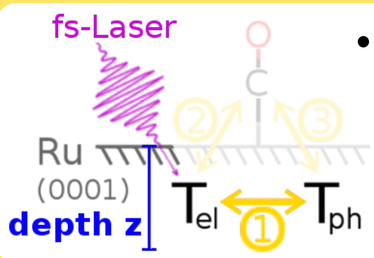


Potential for CO/Ru(001)



Potential for CO/Cu(100)

Two-Temperature Model (2TM)[6]



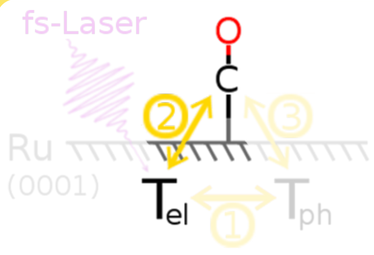
- simulates **interaction** of **electrons** with **phonons** and **laser** ⇒ **gives T_{el} and T_{ph} as $f(z,t)$**

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

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

- 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]

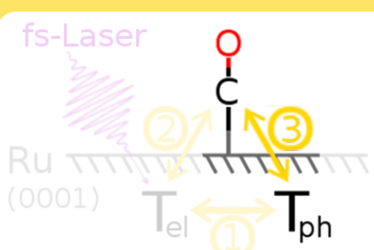


- the **Langevin equation** of motion, a **stochastical** differential equation:

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

- 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)

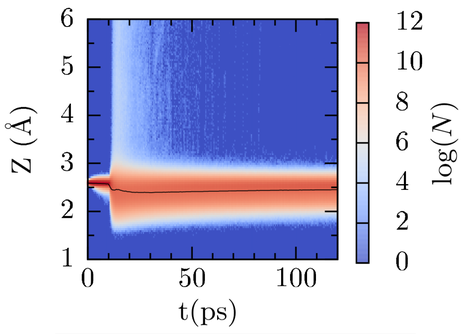
Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[9]



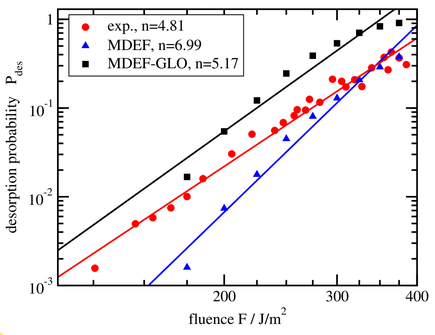
- influence of **phonons** effectively **modeled** (**augments frozen surface**)
- **entire surface** understood as **3D oscillator** (coords. $\underline{r}_s$, mass of one atom)
- **coupling** to molecule **via shifting**: $V_{GLO}(\underline{r}_C,\underline{r}_O;\underline{r}_s) = V(\underline{r}_C-\underline{r}_s,\underline{r}_O-\underline{r}_s)$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

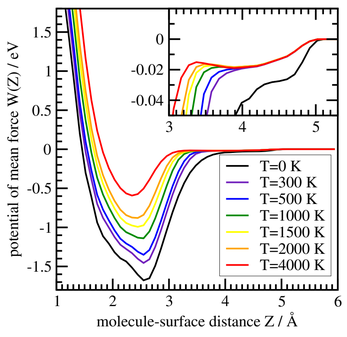
Results

Desorption (Data for Ru)

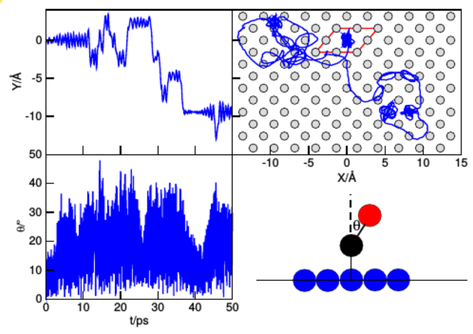


- desorption mainly during first 50 ps
- fluence dependence of desorption yield close to experiment
- no barrier in PMF

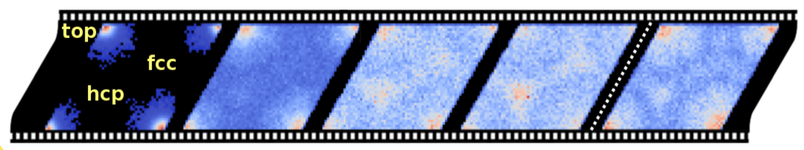




Diffusion (Data for Ru, but Cu similar)

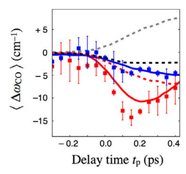


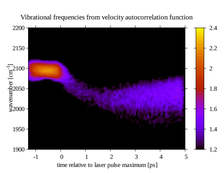
- typical trajectory: hops between top sites and vibration
- increase in θ-angle when CO moves away from top
- overall, very large diffusion
- also, nonisotropic diffusion behaviour observed:
- dynamical trapping effect at hcp site predicted



Vibrations (Data for Cu)

- Frequency-shift from time-resolved SFG





- Preliminary results from our dynamics

Conclusions

- **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

[1] M. Bonn, S. Funk, Ch. Hess, D.N. Denzler *et al.*, *Science* **285**, 1042 (1999).
[2] M. Dell'Angela, T. Anniyev, M. Beye, R. Coffee *et al.*, *Science* **339**, 1302 (2013).
[3] K. Inoue, K. Watanabe, T. Sugimoto *et al.*, *Phys.Rev.Lett.* **117**, 186101 (2016).
[4] G. Füchsel, J.C. Tremblay, and P. Saalfrank, *J.Chem.Phys.* **141**, 094704 (2014).
[5] R. Marquardt, F. Cuvelier, R.O. Olsen *et al.*, *J.Chem.Phys.* **132**, 074108 (2010).
[6] S.I. Anisimov, B.L. Kapeliovich and T.L. Perelman, *Sov.Phys.-JETP* **39**, 375 (1974).
[7] M. Head-Gordon and J.C. Tully, *J.Chem.Phys.* **103**, 10137 (1995).
[8] J.I. Juaristi, M. Alducin, R. Díez Muiño *et al.*, *Phys.Rev.Lett.* **100**, 116102 (2008).
[9] H.F. Busnengo, M.A. Di Césare, W. Dong *et al.*, *Phys.Rev.B* **72**, 125411 (2005).
[10] R. J. Maurer, M. Askerka, V. S. Batista, J. C. Tully *Phys.Rev.B* **94**, 115432 (2016).
[11] L. Waldecker, R. Bertoni, R. Ernstorfer, J. Vorberger *Phys.Rev.X* **6**, 021003 (2016).