Femtosecond-laser induced dynamics of CO on Ru(0001): New insights from a hot-electron, electronic friction model including surface motion

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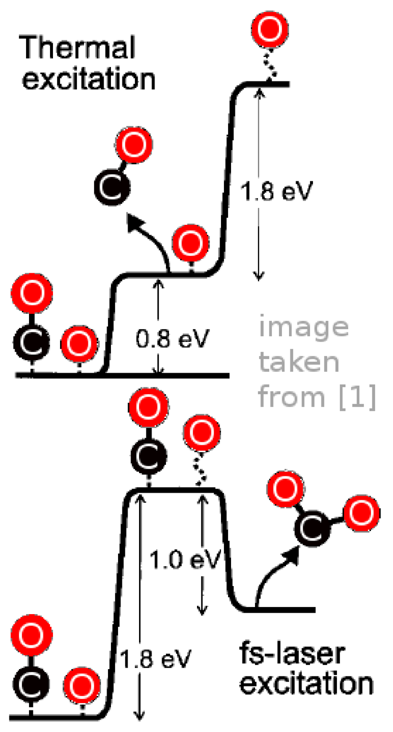
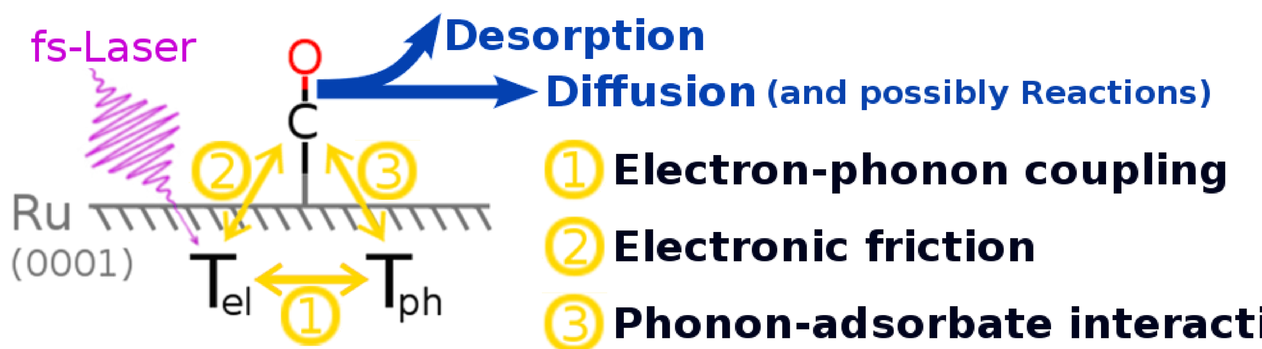
Introduction

Motivation

- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers ⇒ very valuable tool
  - allow for investigations on small timescales
  - open up new processes compared to heating or "normal" lasers ⇒ femtochemistry, e.g.[1]:
  - may enable specific control over catalytic reactions ⇒ photocatalysis
- specific motivation for system CO/Ru(0001)
  - experimentally well studied regarding fs-laser irradiation, e.g. [2, 3]
  - fulldimensional *ab-initio* potential recently developed in our group[4]
  - details of this indicate interpretation of experiment [3] may be wrong



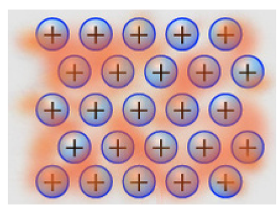
How does fs-laser-irradiation affect metal surfaces?

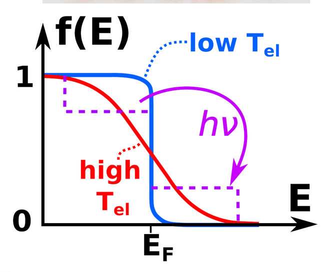


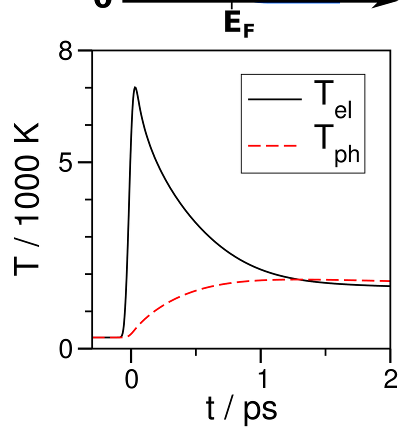
1. **Electron-phonon coupling**
2. **Electronic friction**
3. **Phonon-adsorbate interaction**

- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron-hole pairs thermalize quickly ⇒ "hot" Fermi-Dirac-distribution (after ∼10 fs)
- electrons transfer part of energy to ion lattice, via (1) **electron-phonon coupling** (phonons = lattice vibrations; quasi-particles)
  - electrons couple to phonons as their fast movement causes "shockwaves" in ion lattice
  - equilibration process completes after ∼1 ps

⇒ Thus, with fs-lasers, two different temperatures:
  - T_{el} - electron temperature
  - T_{ph} - phonon temperature
- electron-hole pairs and phonons both couple to adsorbed molecule





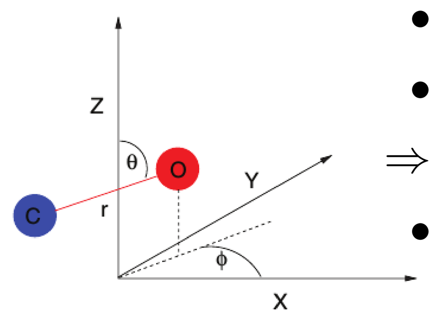


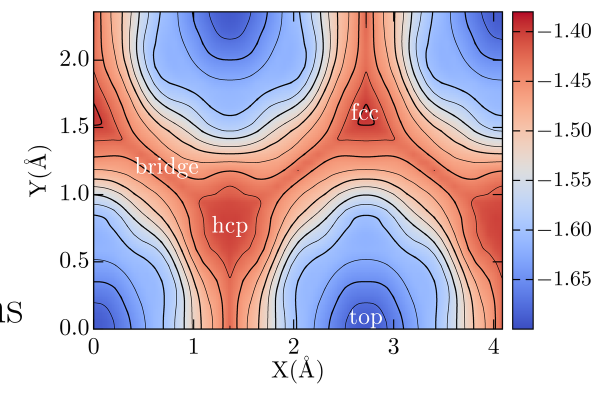
Models and Methods

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 and length of trajectories can be large
  - downsides: – surface atoms frozen ⇒ no phonons
    – had to be constructed first





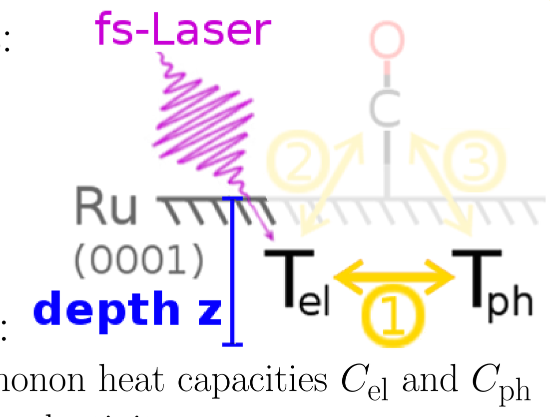
Two-Temperature Model (2TM)[5]

- describes interaction of metal with laser, using two differential equations:

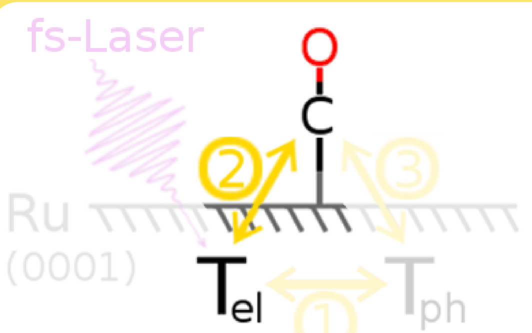
$$C_{\mathrm{el}}\frac{\partial T_{\mathrm{el}}}{\partial t} = \frac{\partial}{\partial z}\kappa\frac{\partial}{\partial z}T_{\mathrm{el}} - g(T_{\mathrm{el}} - T_{\mathrm{ph}}) + S(z,t),$$

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

⇒ get T_{el} and T_{ph} as $f(z,t)$ from laser parameters and material properties:
- laser wavelength λ (affects penetretion depth into material)
- (effective) absorbed fluence F (energy/area)
- pulse duration τ (all three appear in the "source term" $S(z,t)$)
- electron and phonon heat capacities C_{el} and C_{ph}
- electron heat conductivity κ
- electron-phonon coupling constant g



Electronic Friction: Langevin Dynamics[6] and Local Density Friction Approximation (LDFA)[7]

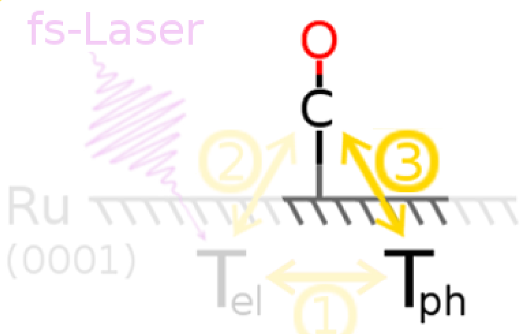


- Langevin equation of motion, a stochastical differential equation:

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

- describes movement of CO on the PES and interaction with electron-hole pairs (friction and excitation)
- Local Density Friction Approx. (LDFA): most simple model to calculate 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 $\underline{R}_{\mathrm{el},k}$: gaussian white noise, dependent on both $\eta_{\mathrm{el},k}$ (from LDFA) and T_{el} (from 2TM)
  - justified by the 2. fluctuation dissipation theorem [11], which relates friction and thermal movement

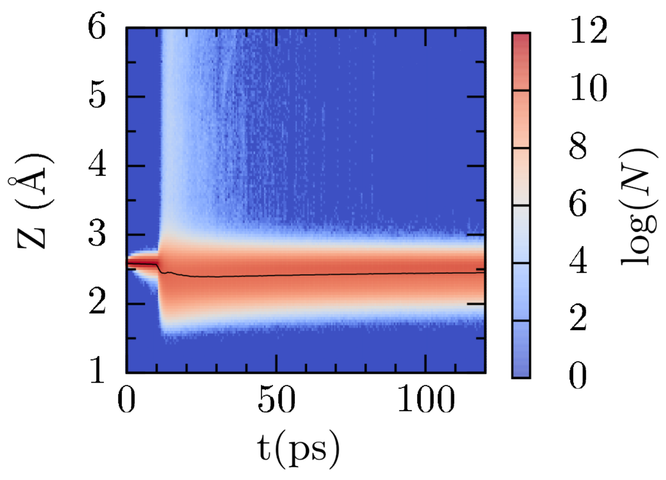
Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[8, 9, 10]



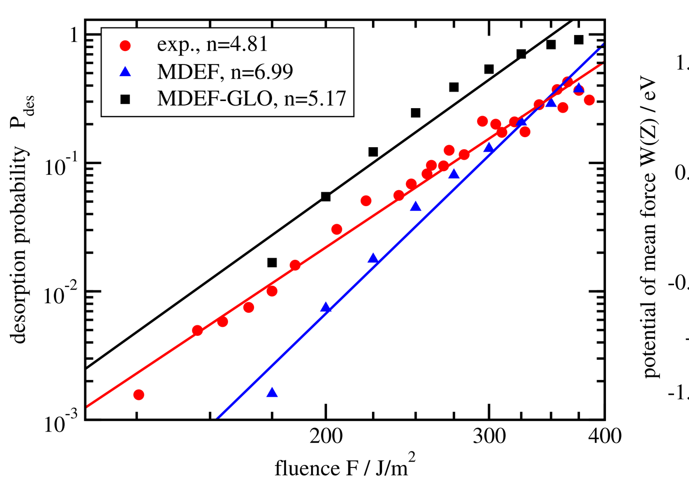
- influence of phonons modeled in an effective way (augments frozen surface)
- entire surface understood as 3D oscillator (coordinates $\underline{r}_s$, mass $m_s = m_{\mathrm{Ru}}$)
- coupling to molecule via shifting: $V_{\mathrm{GLO}}(\underline{r}_{\mathrm{C}},\underline{r}_{\mathrm{O}};\underline{r}_s) = V(\underline{r}_{\mathrm{C}} - \underline{r}_s, \underline{r}_{\mathrm{O}} - \underline{r}_s)$
- additionally coupled to ghost oscillator $\underline{r}_g$ to model influence of the bulk
  - ghost oscillator is subject to friction η_{ph} and random forces $\underline{R}_{\mathrm{ph}}(T_{\mathrm{ph}})$

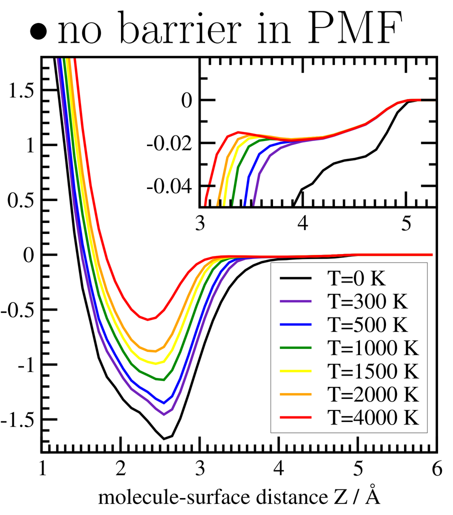
Results

Desorption

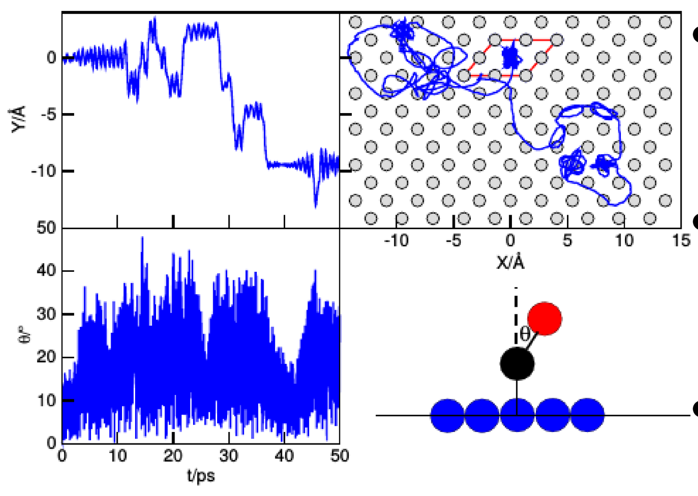


- desorption mainly during first 50 ps
- fluence dependence of desorption yield close to experiment
- no "precursor state" as suggested by [3]
- no barrier in PMF



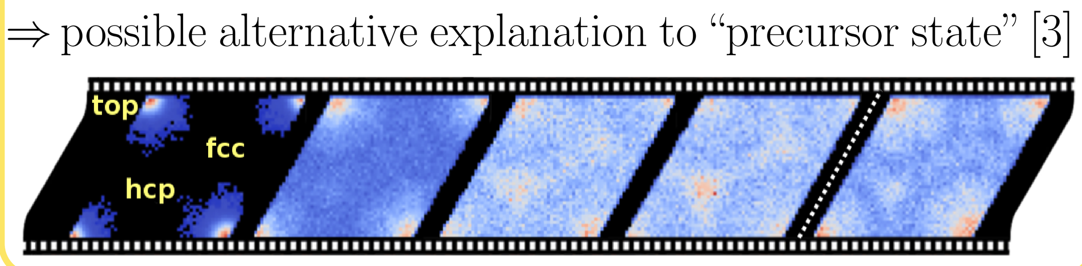


Diffusion



- 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

⇒ possible alternative explanation to "precursor state" [3]



Conclusions

- 6D Langevin dynamics of CO on Ru(0001)
- 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

- calculation of RIXS spectra currently performed
- employ better electonic friction (beyond LDFA)
- enhance 2TM with electron-electron-scattering
- simulate other coverages (here only 0.25ML)
- include interaction between adsorbate molecules

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