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
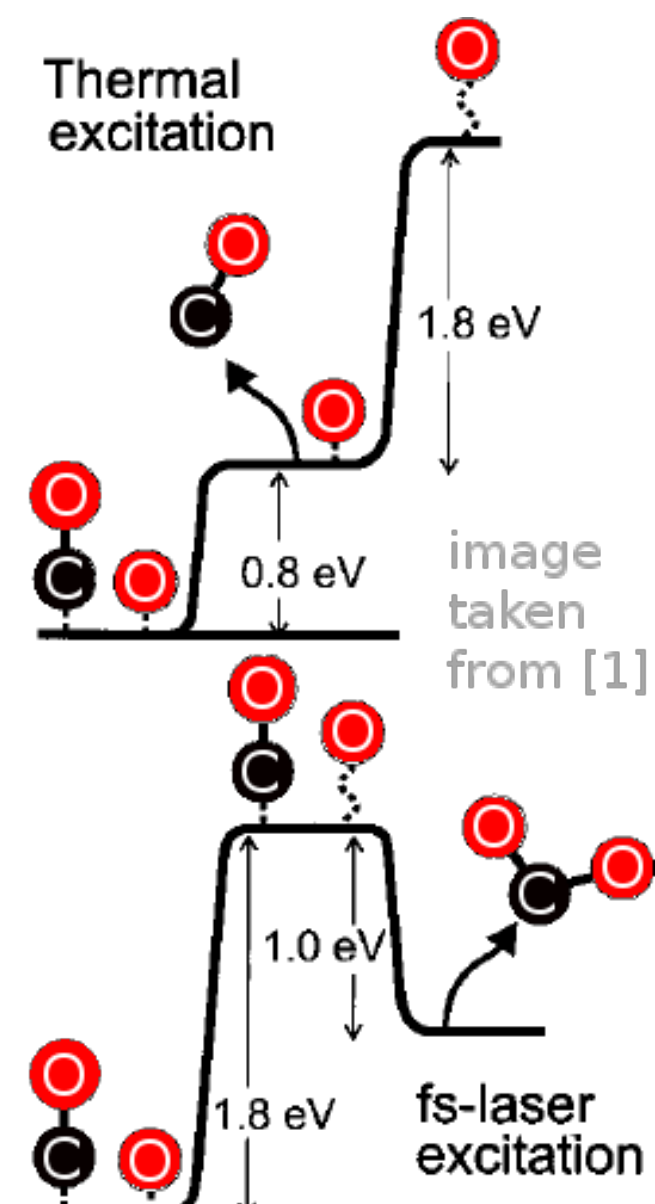

How does fs-laser-irradiation affect metal surfaces?

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 ①electron-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
- can be simulated using a Two-Temperature Model (2TM)[5] (see right)
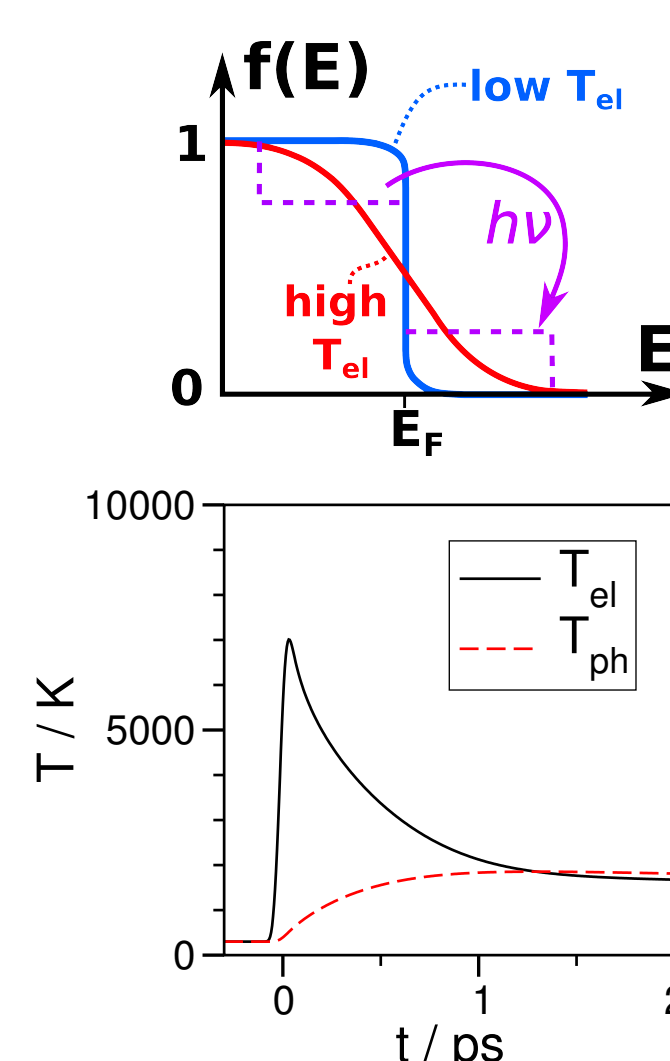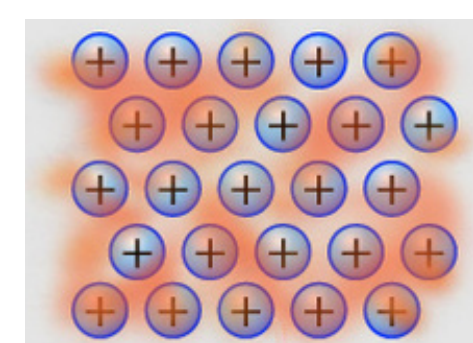
Models and Methods

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
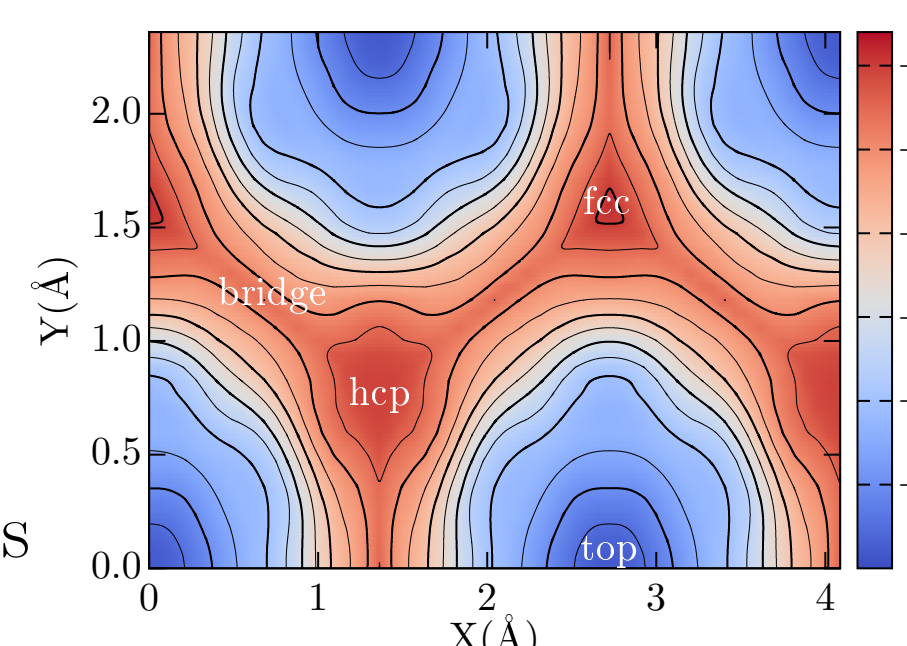
Two-Temperature Model (2TM)[5]

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

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

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

⇒ get T_{el} and T_{ph} as $f(z,t)$ from laser parameters and material properties:
- laser wavelength λ (affects penetration 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
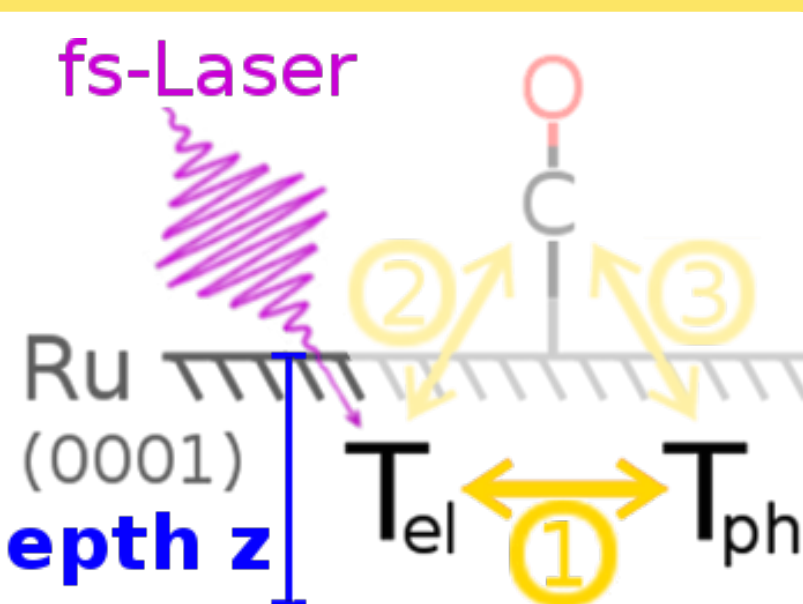
Electronic Friction: Langevin Dynamics[6] and Local Density Friction Approximation (LDFA)[7]

- Langevin equation of motion, a stochastical differential equation:

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

(Force on Atom k)

- 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 $\eta_{el,k}$
  - Atom k embedded in free electron gas with density of bare surface at current position $\underline{r}_k$
- Random forces $\underline{R}_{el,k}$: gaussian white noise, dependent on both $\eta_{el,k}$ (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 $m_s = m_{Ru}$)
- 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 $\underline{r}_g$ to model influence of the bulk
  - ghost oscillator is subject to friction η_{ph} and random forces $R_{ph}(T_{ph})$

Results

Desorption

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References

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