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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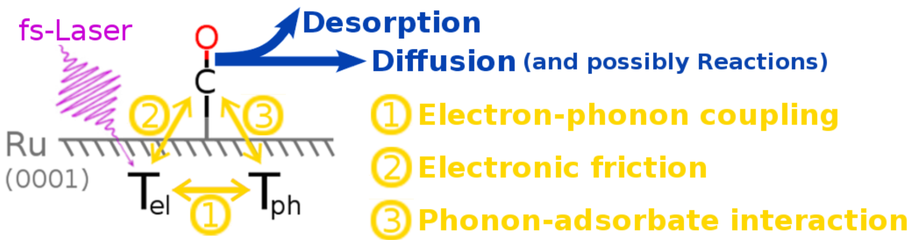
Introduction

Motivation

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

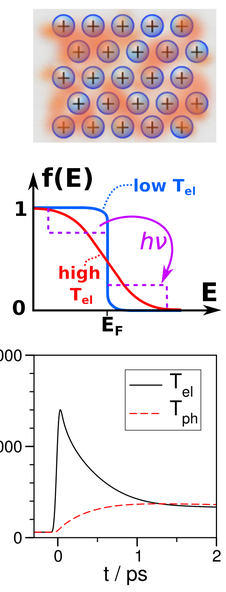
How does fs-laser-irradiation affect metal surfaces?



- 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

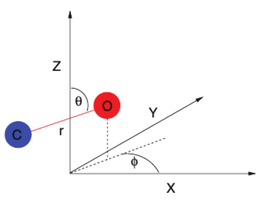
- can be simulated using a Two-Temperature Model (2TM) [4] (see right)



Models and Methods

Six-dimensional Potential Energy Surface (6D PES)

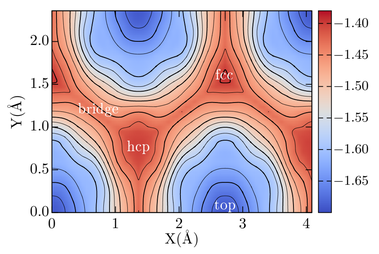
- Basis for dynamics: precomputed PES from DFT (rPBE + D2)



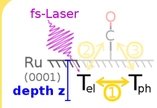
  - all 6 dimensions of the adsorbate
  - analytical PES and gradients ⇒ very fast

⇒ number and length of trajectories can be large

  - downside: surface atoms frozen ⇒ no phonons



Two-Temperature Model (2TM) [4]



- consists of two coupled differential equations: $C_{\mathrm{el}}\frac{\partial T_{\mathrm{el}}}{\partial t} = \frac{\partial}{\partial z}\kappa\frac{\partial}{\partial z}T_{\mathrm{el}} - g(T_{\mathrm{el}} - T_{\mathrm{ph}}) + S(z,t)$,
- describes interaction of the metal surface and laser $C_{\mathrm{ph}}\frac{\partial T_{\mathrm{ph}}}{\partial t} = g(T_{\mathrm{el}} - T_{\mathrm{ph}})$.
- calculates 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: LDFA and Langevin Dynamics

Inclusion of Phonons: GLO-model

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