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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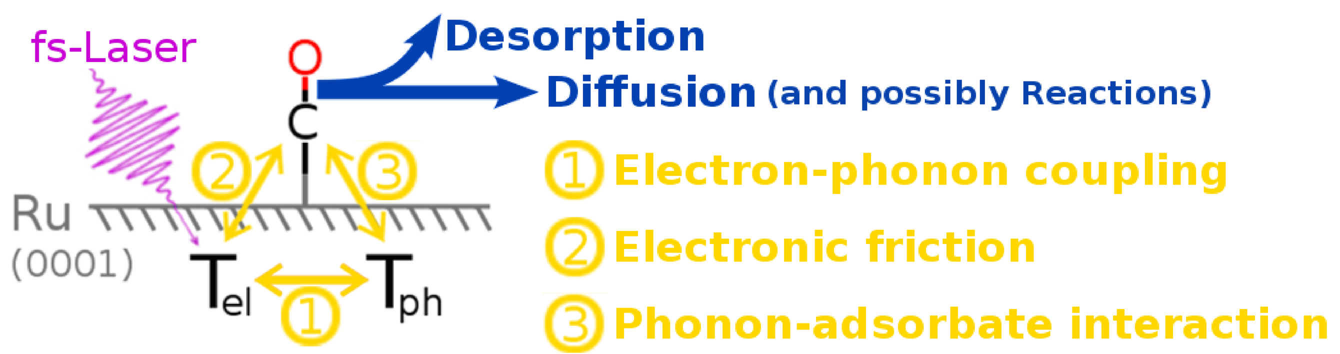
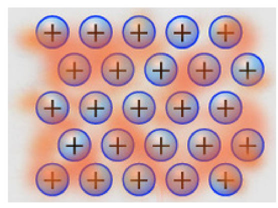
Introduction

Motivation

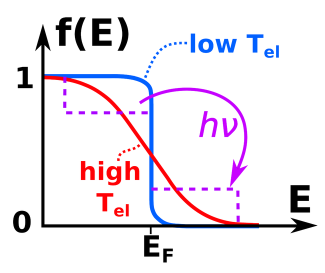
- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
  - allow for investigations on small timescales
  - open up new processes compared to heating (femtophotochemistry)
  - may enable specific control over catalytic reactions (photocatalysis)

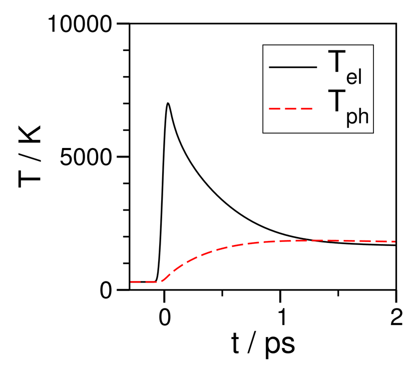
How does fs-laser-irradiation affect metal surfaces?





- 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



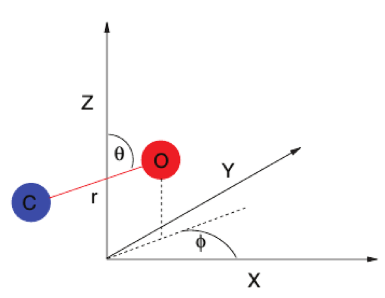


⇒ Thus, with fs-lasers, two different temperatures:
  - T_{el} - electron temperature
  - T_{ph} - phonon temperature
- can be simulated using a Two-Temperature Model (2TM) [1] (see right)

Models and Methods

Six-dimensional Potential Energy Surface (6D PES)

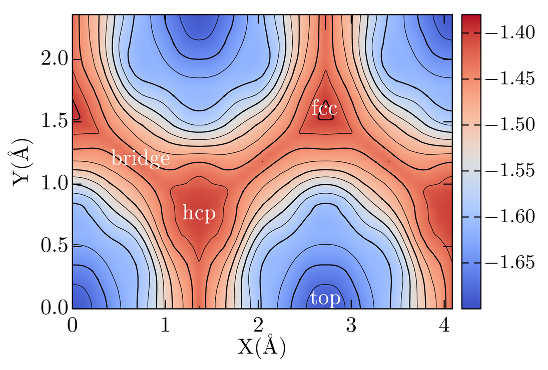
- Basis for dynamics: precomputed Potential Energy Surface (PES)



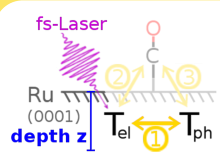
- all 6 dimensions of the adsorbate
- analytical PES and gradients ⇒ very fast

⇒ number and length of trajectories can be large

- downside: surface atoms frozen ⇒ no phonons



Two-Temperature Model (2TM) [1]



- consists of two coupled differential equations:
- describes interaction of the metal surface and laser

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

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

- calculates T_{el} and T_{ph} from laser parameters and material properties e.g.:
  - 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

References

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[2] M. Dell'Angela, T. Anniyev, M. Beye et al., *Science* **339**, 1302 (2013).