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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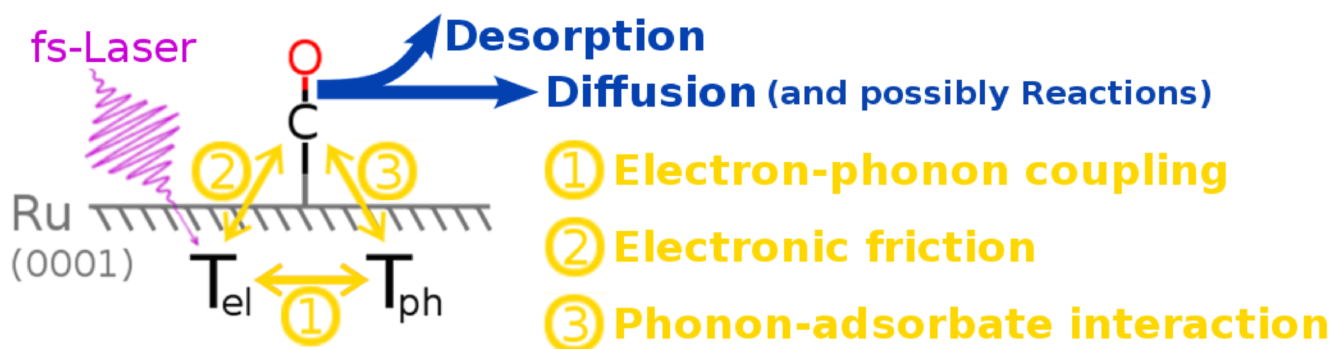
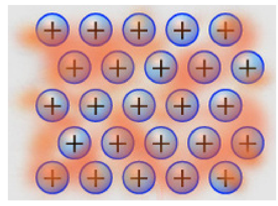
Introduction

Motivation

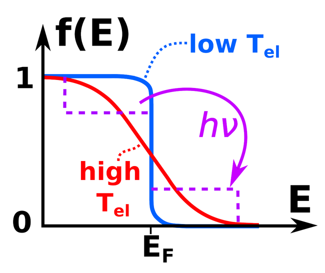
- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
  - allow for investigations on small timescales
  - open up new processes compared to heating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

How does fs-laser-irradiation affect metal surfaces?

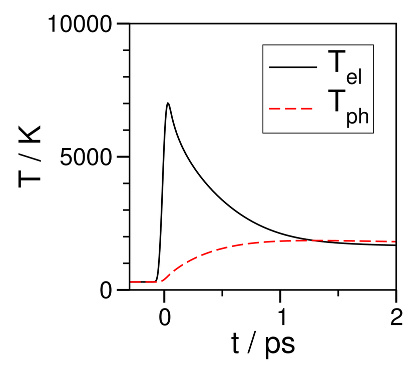




- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron hole pairs thermalize quickly ⇒ "hot" Fermi-Dirac-distribution (after ∼10 fs)



- 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

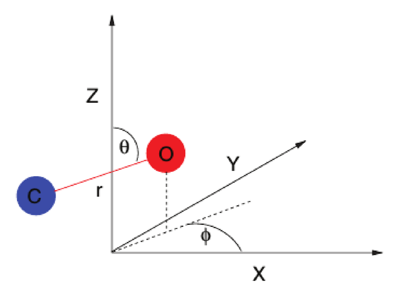


⇒ Thus, with fs-lasers, two different temperatures:
  - T_{el} - electron temperature
  - T_{ph} - phonon temperature
- can be simulated using a Two-Temperature Model (2TM) [1] (see right)

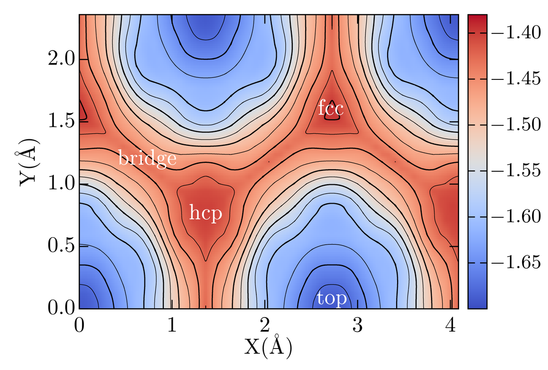
Models and Methods

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
- calculates T_{el} and T_{ph} from laser parameters, e.g.:
  - pulse duration
  - effective absorbed fluence F (energy/area)
  - laser wavelength (affects penetretion depth into material)
- and from material properties

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

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

Electronic Friction: LDFA and Langevin Dynamics

Inclusion of Phonons: GLO-model

References

[1] S. I. Anisimov, B. L. Kapeliovich, and T. L. Perel'man, *Sov. Phys.-JETP* **39**, 375 (1974).

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