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

Robert Scholz[1,2], Gereon Floß[1], Peter Saalfrank[1], Gernot Füchsel[3], Ivor Lončarić[4], and J. I. Juaristi[4,5,6]

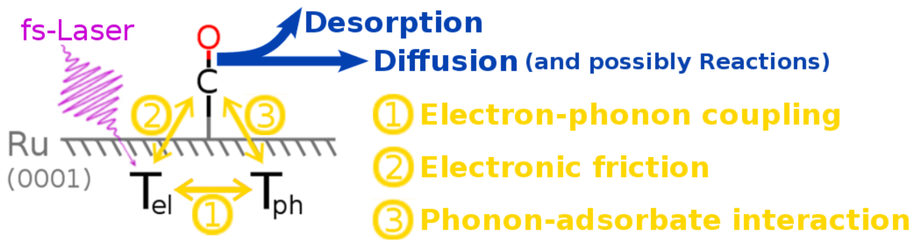
[1]Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany
[2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany
[3]Universiteit Leiden, Gorlaeus Laboratories, Einsteinweg 55, 2333 Leiden, The Netherlands
[4]Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain
[5]Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[6]Donostia International Physics Center DIPC, P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain

Introduction

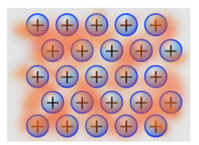
Motivation

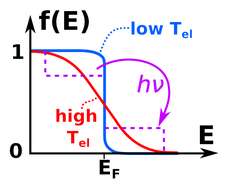
- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
  - allow for investigations on small timescales
  - open up new processes compared to heating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

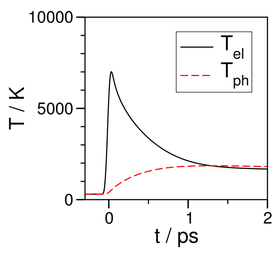
How does fs-laser-irradiation affect metal surfaces?



- 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)

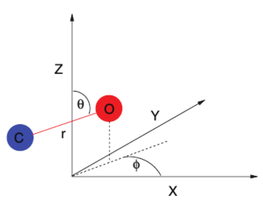
Models and Methods

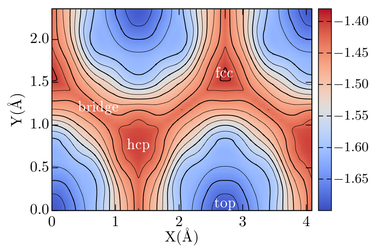
Six-dimensional Potential Energy Surface (6D PES)

- 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)

- calculates T_{el} and T_{ph} from material constants and laser parameters e.g.:
  - penetration depth (dependent on laser wavelength and material)
  - pulse duration
  - effective absorbed fluence (energy/area)

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).