# 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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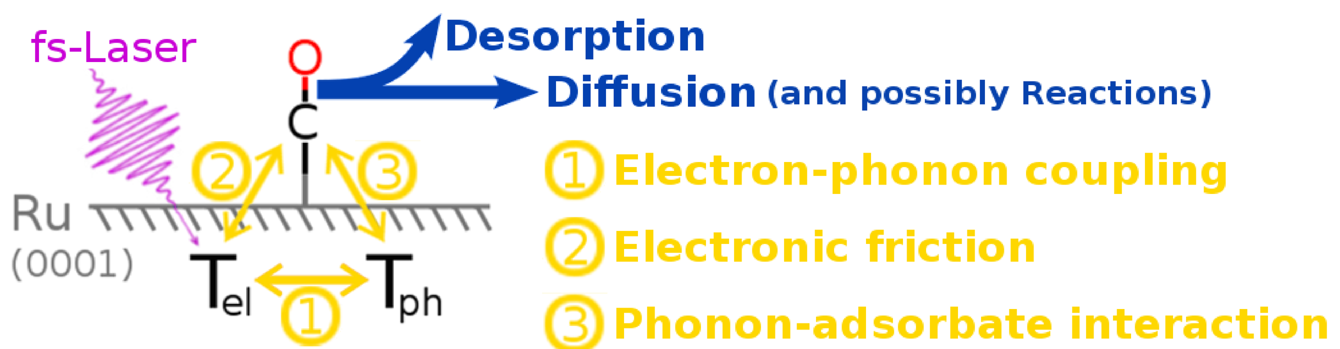
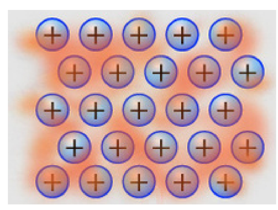
## Introduction

### Motivation

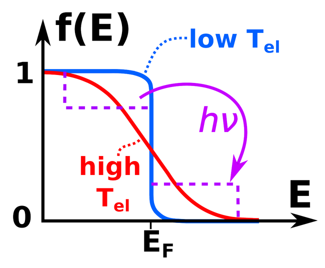
- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
  - allow for investigations on small timescales
  - open up new processes compared to heating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

### How does fs-laser-irradiation affect metal surfaces?



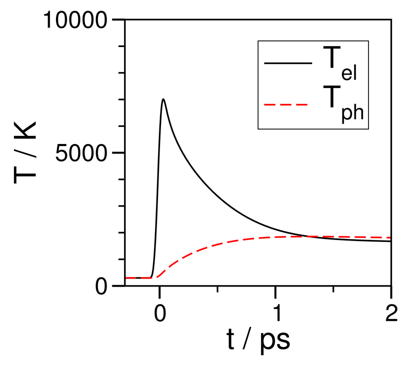



- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron hole pairs thermalize quickly
  ⇒ "hot" Fermi-Dirac-distribution (after ∼10 fs)




- 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

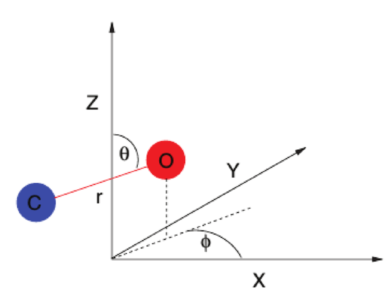



- can be simulated using a Two-Temperature Model (2TM) [1] (see right)

## Models and Methods

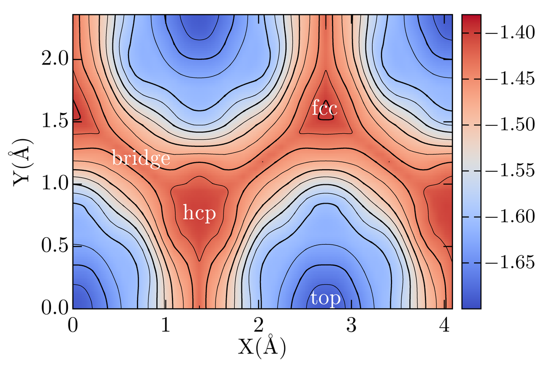
### Six-dimensional Potential Energy Surface (6D PES)

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

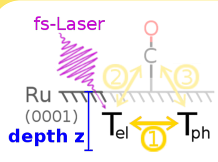



- all 6 dimensions of the adsorbate
- analytical PES and gradients ⇒ very fast

⇒ 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

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

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

- calculates $T_{el}$ and $T_{ph}$ as $f(z,t)$ from laser parameters and material properties:
  - laser wavelength $\lambda$ (affects penetration depth into material)
  - (effective) absorbed fluence $F$ (energy/area)
  - pulse duration $\tau$ (all three appear in the "source term" $S(z,t)$)
  - electron and phonon heat capacities $C_{el}$ and $C_{ph}$
  - electron heat conductivity $\kappa$
  - electron-phonon coupling constant $g$

### 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).