

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]
 - details of this indicate interpretation of experiment [2] may be wrong

How does fs-laser-irradiation affect metal surfaces?

1 Electron-phonon coupling
2 Electronic friction
3 Phonon-adsorbate interaction

• metals: ion lattice plus quasi-free electron gas

• visible light is absorbed only by the electrons

• produced electron hole pairs thermalize quickly
 \Rightarrow “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

\Rightarrow Thus, with fs-lasers, two different temperatures:

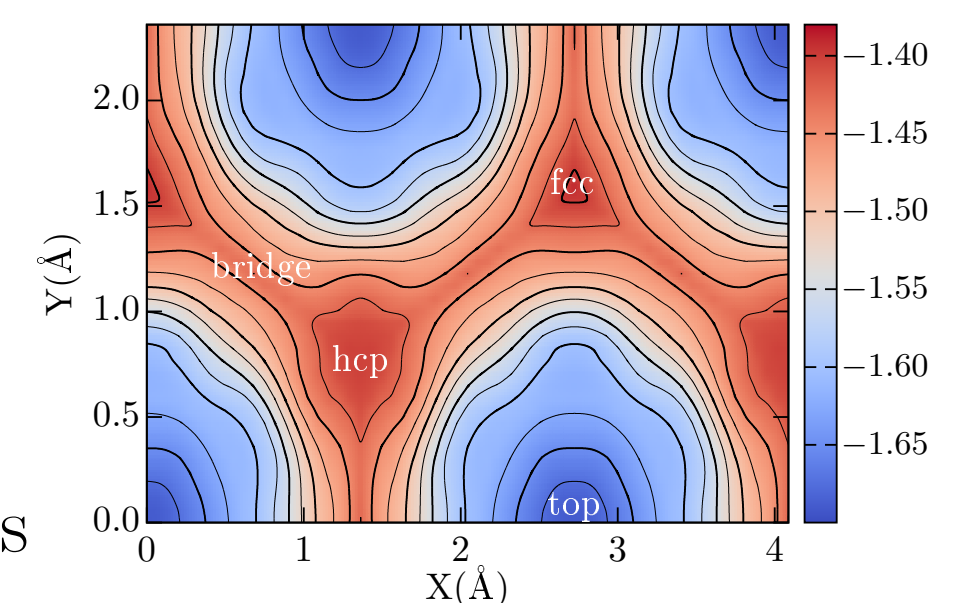
- T_{el} - electron temperature
- T_{ph} - phonon temperature

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

Models and Methods

Six-dimensional Potential Energy Surface (6D PES)[3]

- Basis for dynamics: precomputed PES from DFT (rPBE + D2)
 - all 6 dimensions of the adsorbate
 - analytical PES and gradients \Rightarrow very fast \Rightarrow number and length of trajectories can be large
 - downsides: – surface atoms frozen \Rightarrow no phonons
 - had to be constructed first



Two-Temperature Model (2TM)[4]

- consists of two coupled differential equations:

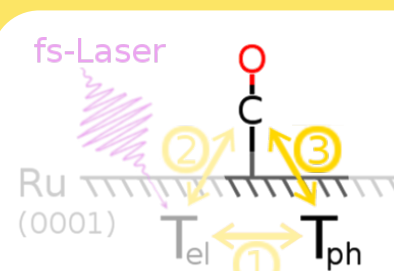
$$C_{el} \frac{\partial T_{el}}{\partial t} = \frac{\partial}{\partial z} \kappa \frac{\partial T_{el}}{\partial z} - g(T_{el} - T_{ph}) + S(z, t),$$
- describes interaction of the metal surface and laser

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

Electronic Friction: Langevin Dynamics[5] and Local Density Friction Approximation (LDFA)[6]

$$m_k \frac{d^2 r_k}{dt^2} = -\nabla_k V(r_1, r_2) - \eta_{el,k}(r_k) \frac{dr_k}{dt} + \underline{R}_{el,k}(t).$$

Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[7, 8, 9]



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