

# 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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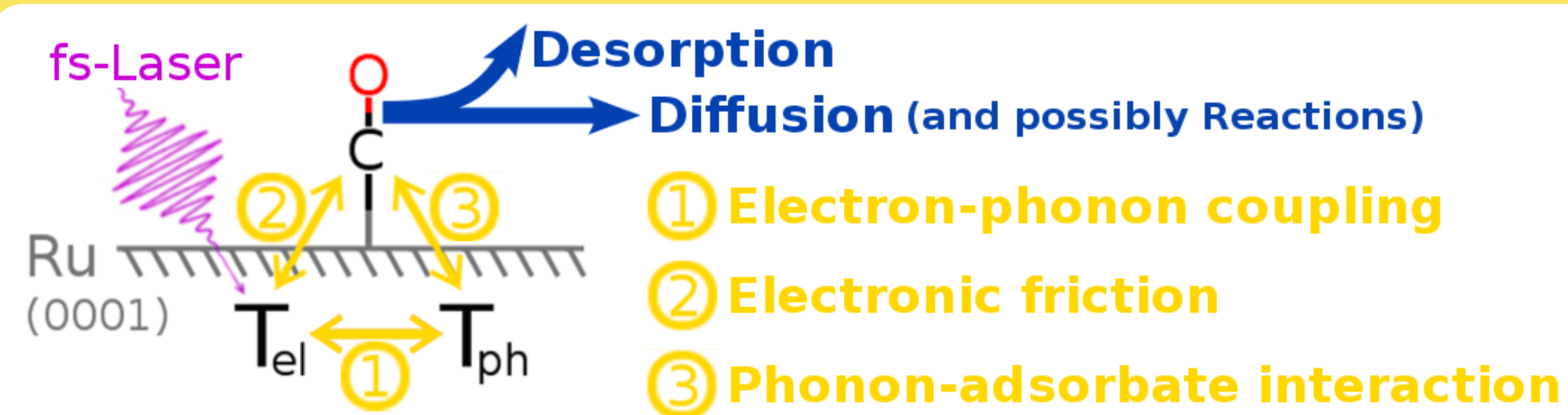
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## Introduction

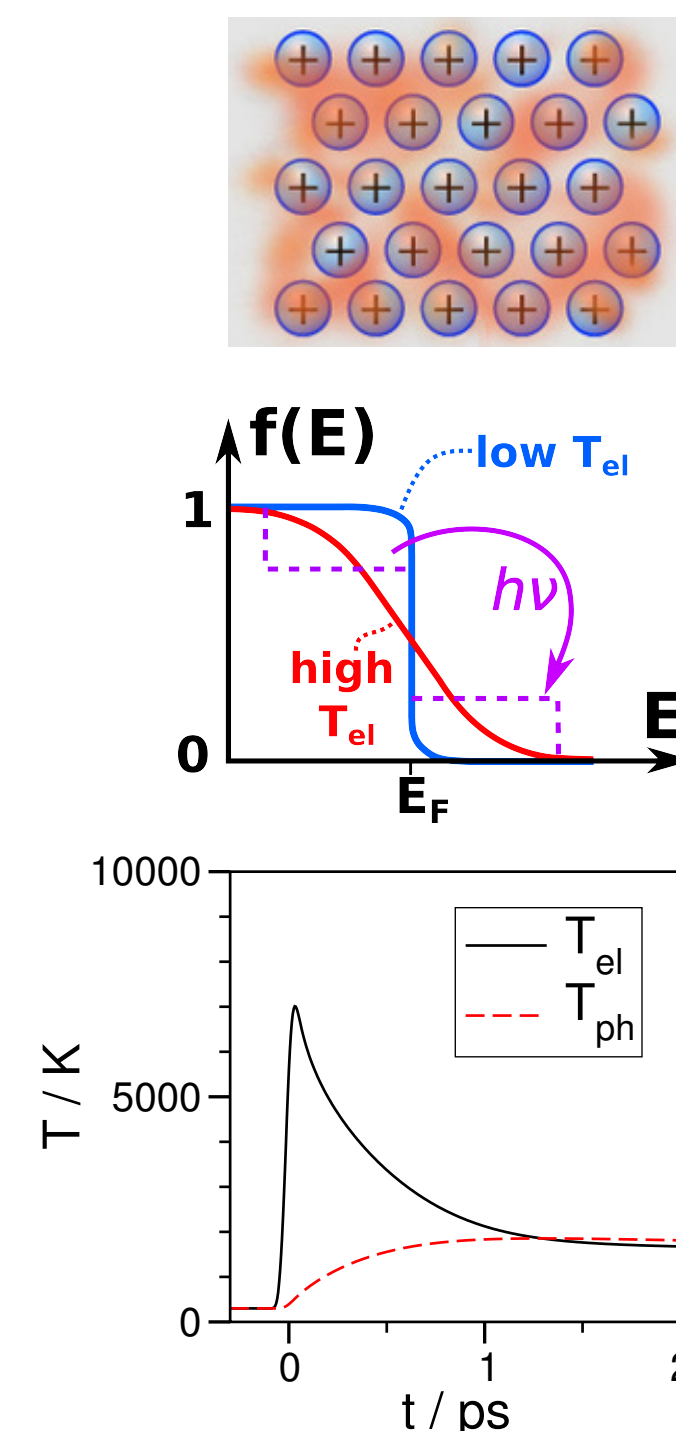
### Motivation

- 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?



- 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  $\sim 10$  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  $\sim 1$  ps



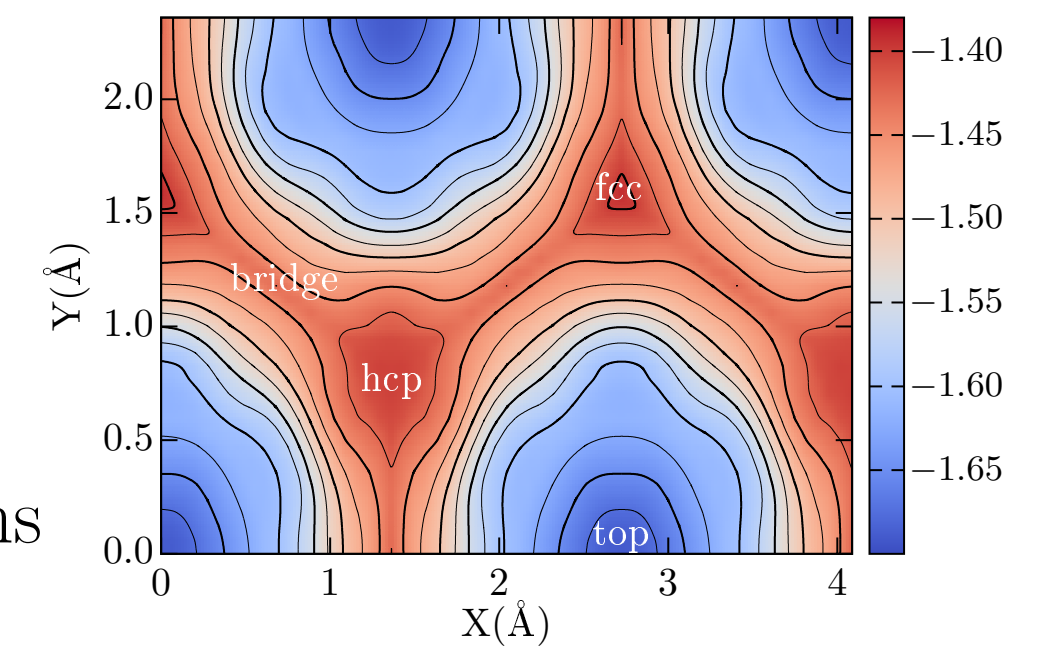
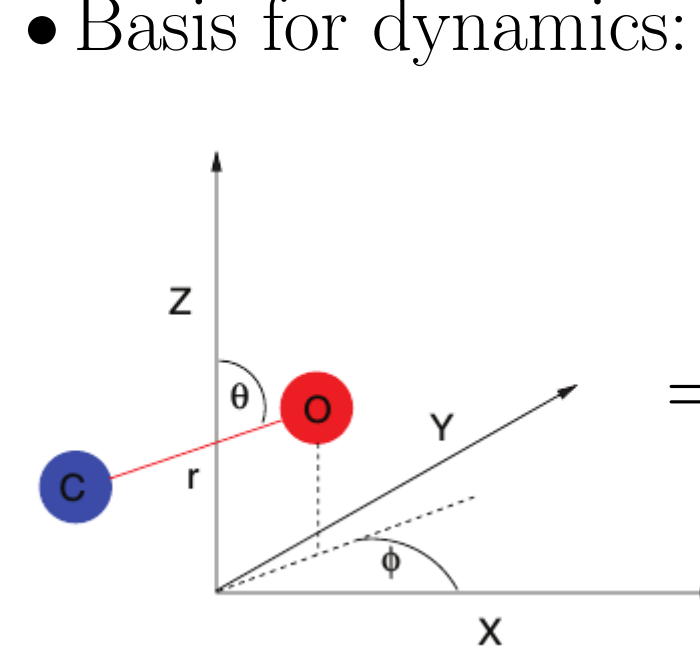
$\Rightarrow$  Thus, with fs-lasers, two different temperatures:

- $T_{el}$  - 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]

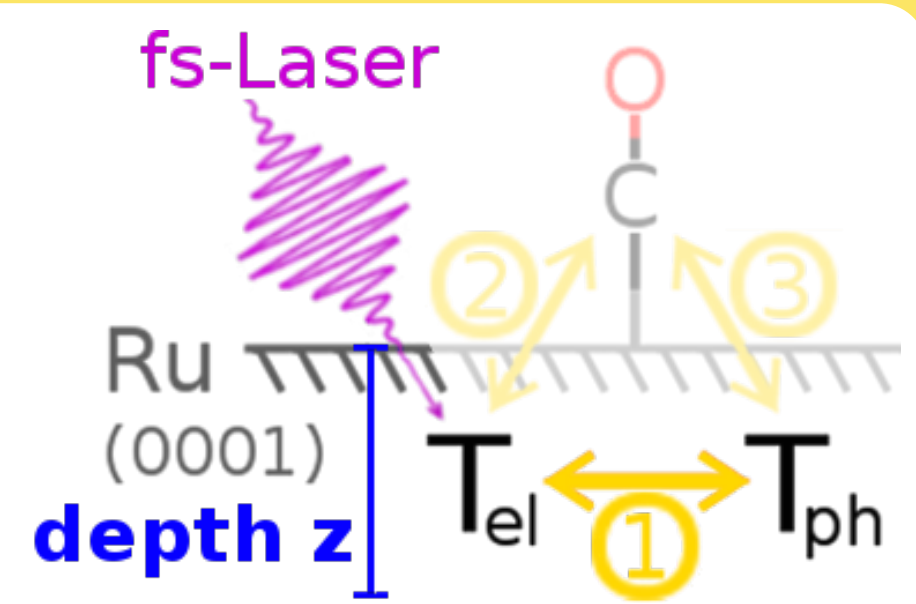
- describes interaction of metal with laser, using two differential equations:

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

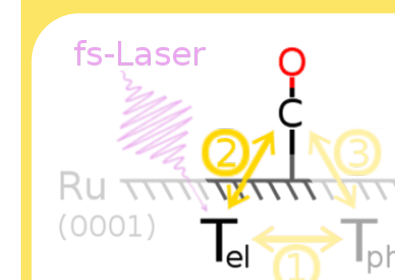
$$C_{ph} \frac{\partial T_{ph}}{\partial t} = g(T_{el} - T_{ph}).$$

$\Rightarrow$  get  $T_{el}$  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  $g$



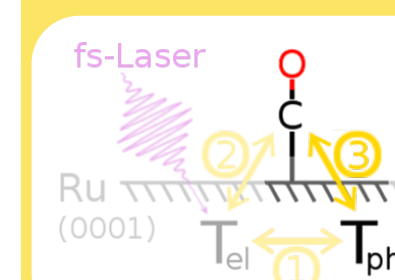
### Electronic Friction: Langevin Dynamics[5] and Local Density Friction Approximation (LDFA)[6]



- Langevin equation of motion:
- describes interaction of electron-hole-pairs with molecule

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

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



## References

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