

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

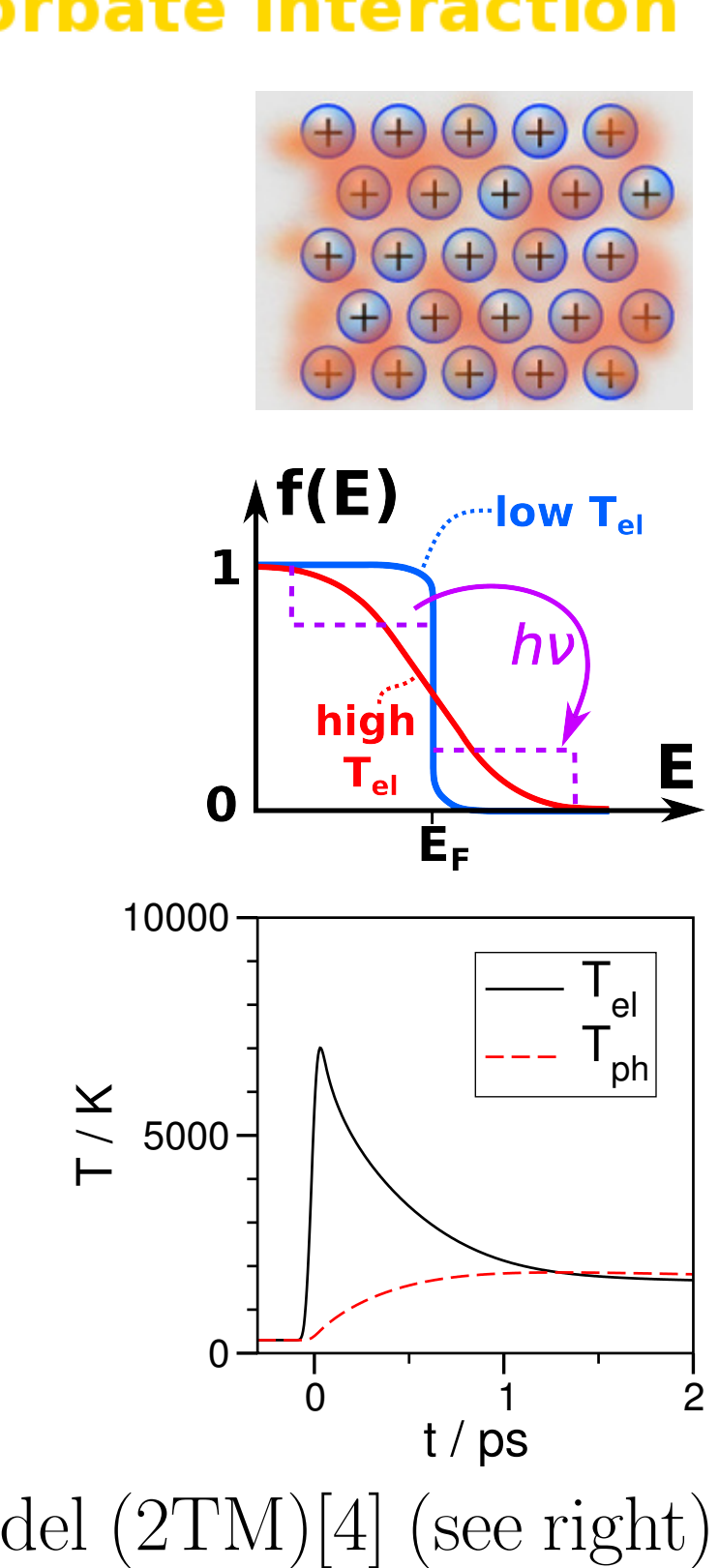
③ Phonon-adsorbate interaction

- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron-hole pairs thermalize quickly
⇒ “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

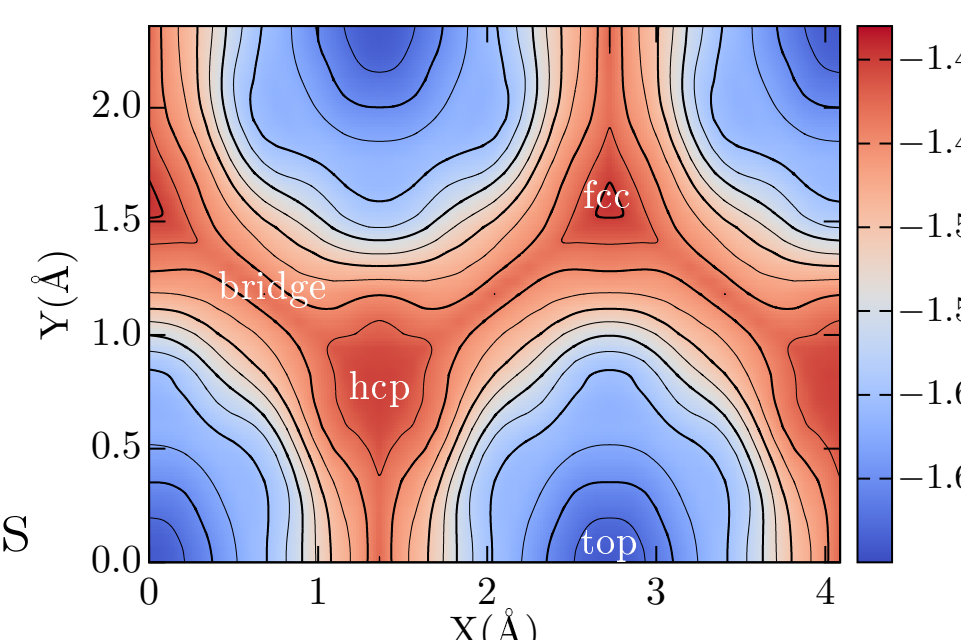
• can be simulated using a Two-Temperature Model (2TM)[4] (see right)



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 ⇒ very fast
- ⇒ number and length of trajectories can be large
- downsides: – surface atoms frozen ⇒ no phonons
– had to be constructed first



Two-Temperature Model (2TM)[4]

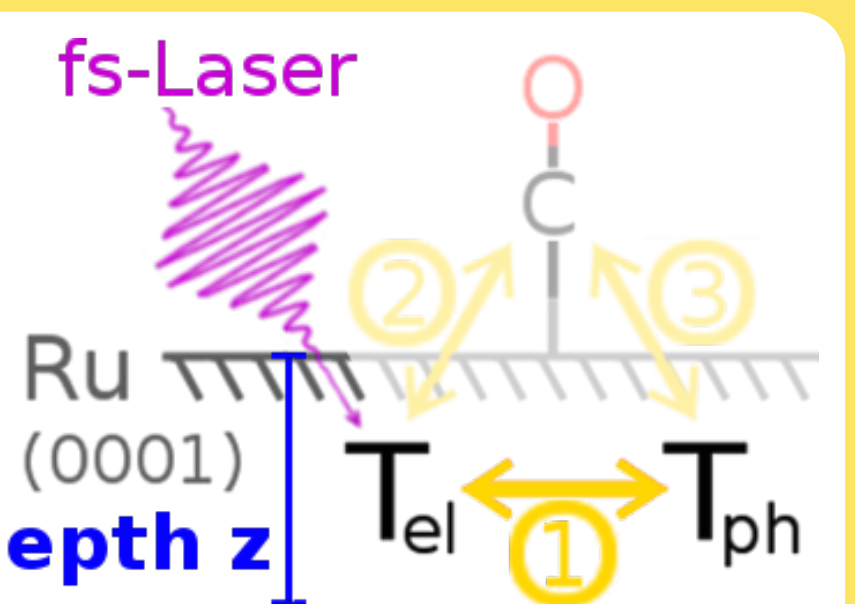
- describes interaction of metal with laser, using two differential equations:

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

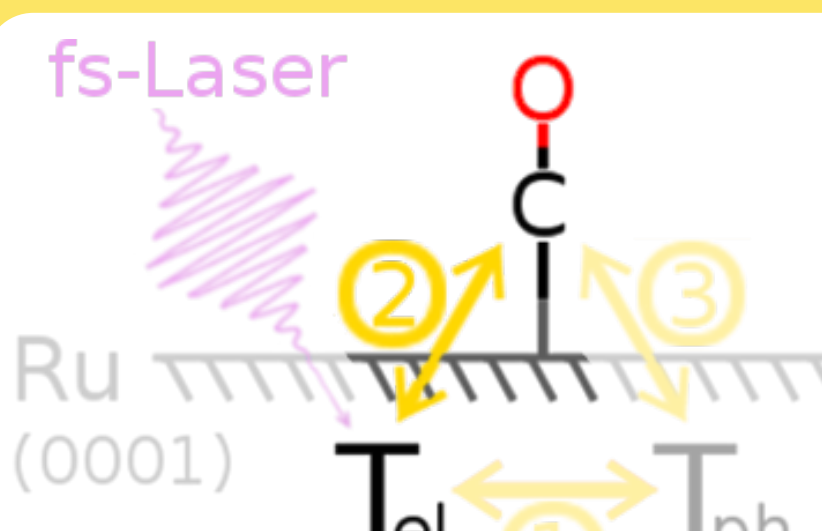
$$C_{ph} \frac{\partial T_{ph}}{\partial t} = g(T_{el} - T_{ph}).$$

⇒ get T_{el} and T_{ph} as $f(z, t)$ from laser parameters and material properties:

- laser wavelength λ (affects penetration depth into material)
- (effective) absorbed fluence F (energy/area)
- pulse duration τ (all three appear in the “source term” $S(z, t)$)
- electron and phonon heat capacities C_{el} and C_{ph}
- electron heat conductivity κ
- electron-phonon coupling constant g



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

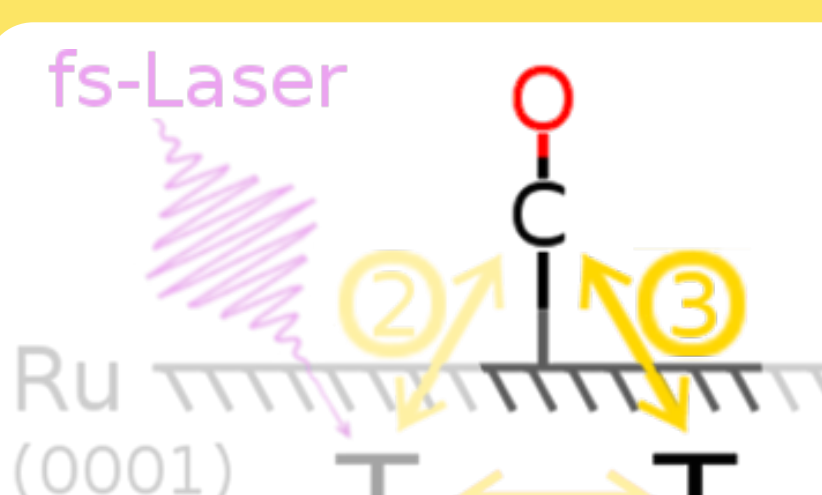


• Langevin equation of motion, a stochastic differential equation:

$$m_k \frac{d^2 \underline{r}_k}{dt^2} = \underbrace{-\nabla_k V(\underline{r}_1, \underline{r}_2)}_{\text{Force on Atom } k} - \underbrace{\eta_{el,k}(\underline{r}_k)}_{\text{Force due to PES}} \frac{d \underline{r}_k}{dt} + \underbrace{\underline{R}_{el,k}(t)}_{\text{Friction force slows movement}} + \underbrace{\underline{R}_{el,k}(t)}_{\text{Random force from e-h pairs}}.$$

- describes movement of CO on the PES and interaction with electron-hole pairs (friction and excitation)
- Local Density Friction Approx. (LDFA): most simple model to calculate friction coefficients $\eta_{el,k}$
 - Atom k embedded in free electron gas with density of bare surface at current position \underline{r}_k
- Random forces $\underline{R}_{el,k}$: gaussian white noise, dependent on both $\eta_{el,k}$ (from LDFA) and T_{el} (from 2TM)
 - justified by the 2. fluctuation dissipation theorem [10], which relates friction and thermal movement

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



- influence of phonons modeled in an effective way (augments frozen surface)
- entire surface understood as 3D oscillator (coordinates \underline{r}_s , mass $m_s = m_{Ru}$)
- coupling to molecule via shifting: $V_{GLO}(\underline{r}_C, \underline{r}_O; \underline{r}_s) = V(\underline{r}_C - \underline{r}_s, \underline{r}_O - \underline{r}_s)$
- additionally coupled to ghost oscillator \underline{r}_g to model influence of the bulk
 - ghost oscillator is subject to friction η_{ph} and random forces $\underline{R}_{ph}(T_{ph})$

Results

References

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