

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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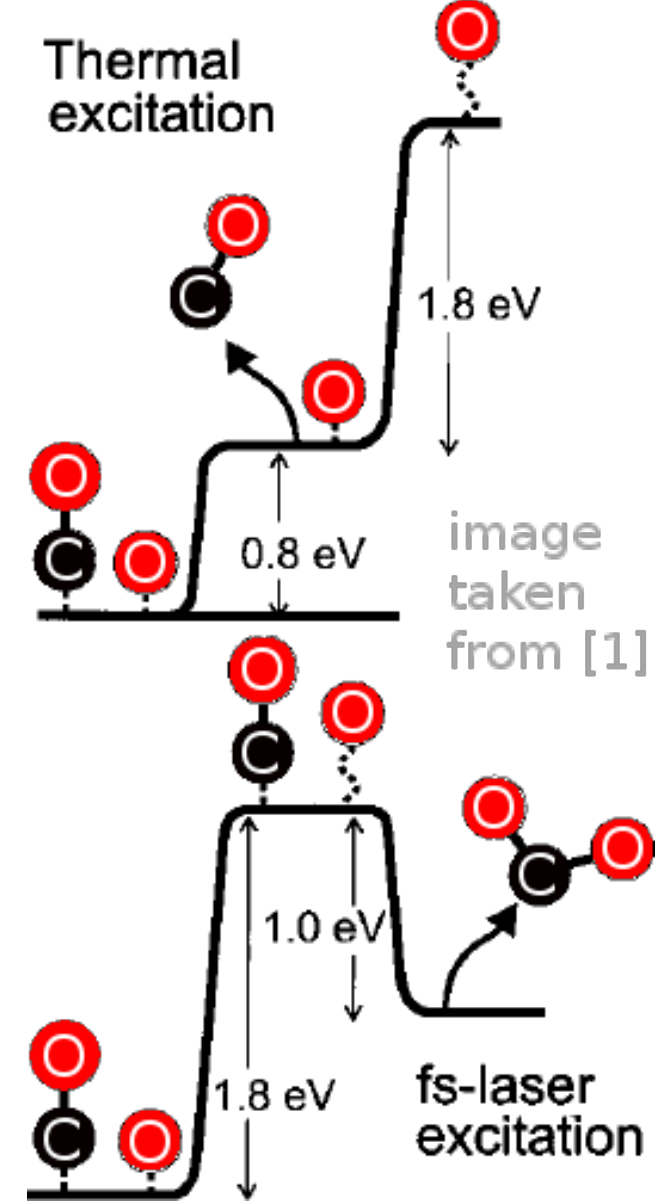
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Introduction

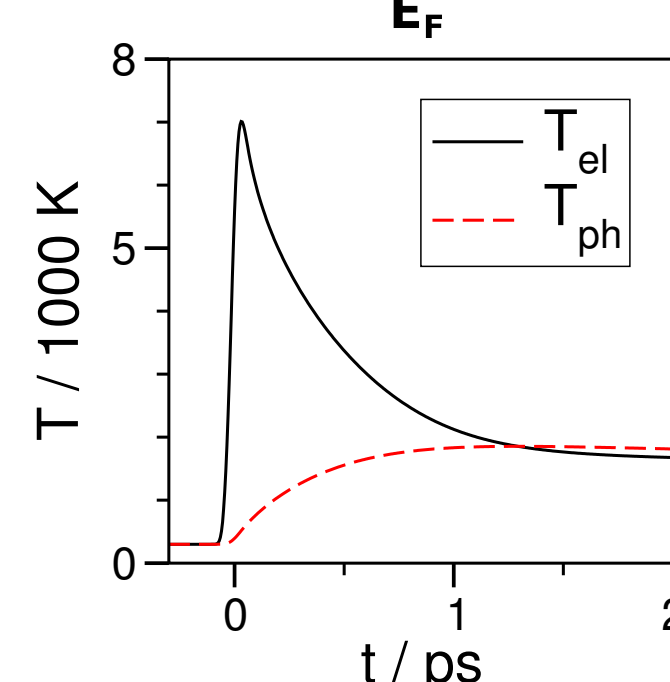
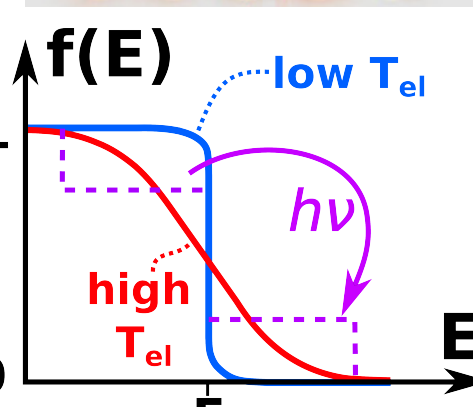
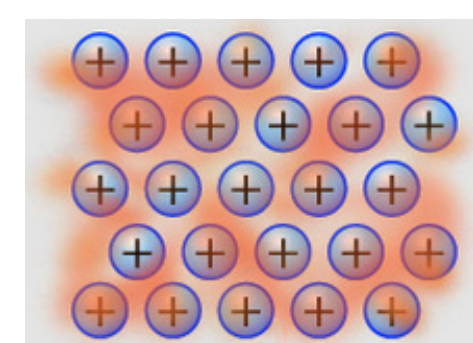
Motivation

- research on small molecules adsorbed to metals is important for:
 - catalytic applications
 - fundamental understanding of bonding
- femtosecond(fs)-lasers \Rightarrow very valuable tool
 - allow for investigations on small timescales
 - open up new processes compared to heating or “normal” lasers \Rightarrow femtochemistry, e.g. [1]:
 - may enable specific control over catalytic reactions \Rightarrow photocatalysis
- specific motivation for system CO/Ru(0001)
 - experimentally well studied regarding fs-laser irradiation, e.g. [2, 3]
 - fulldimensional *ab-initio* potential recently developed in our group [4]
 - details of this indicate interpretation of experiment [3] may be wrong



How does fs-laser-irradiation affect metal surfaces?

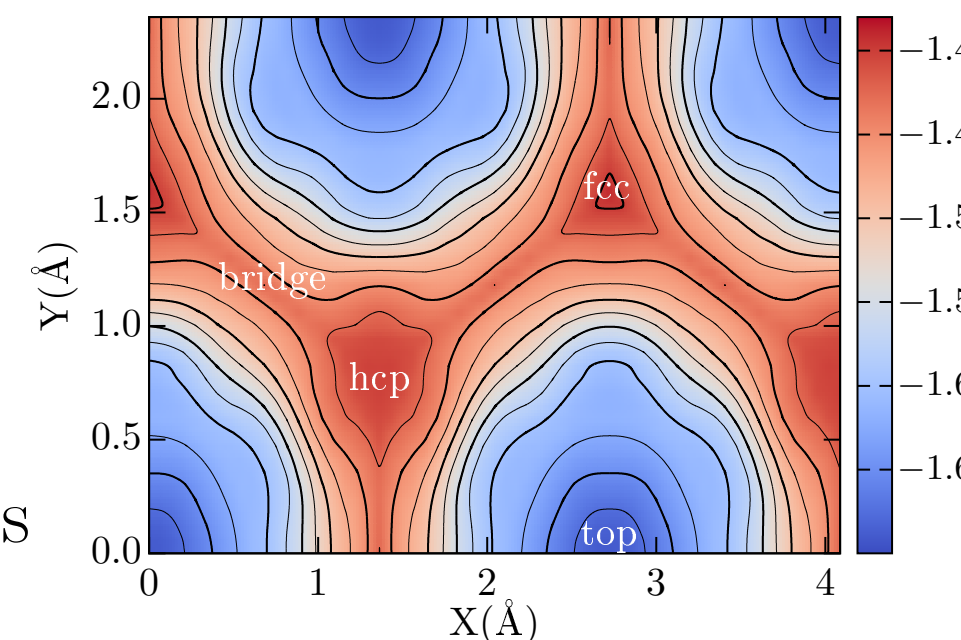
- fs-Laser** \Rightarrow **Desorption** **Diffusion** (and possibly Reactions)
- ① **Electron-phonon coupling**
② **Electronic friction**
③ **Phonon-adsorbate interaction**
- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron-hole pairs 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) [5] (see right)



Models and Methods

Six-dimensional Potential Energy Surface (6D PES) [4]

- 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) [5]

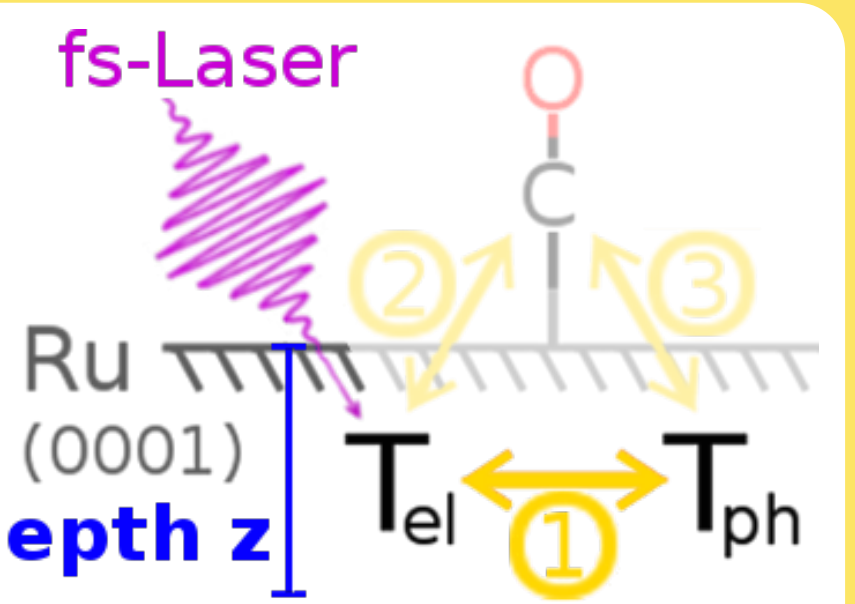
- describes interaction of metal with laser, using two differential equations:

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

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

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

- laser wavelength 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 [6] and Local Density Friction Approximation (LDFA) [7]

- Langevin equation of motion, a stochastic differential equation:

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

Inclusion of Phonons: Generalized Langevin Oscillator (GLO)-model [8, 9, 10]

- 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

Desorption

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Diffusion

References

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