

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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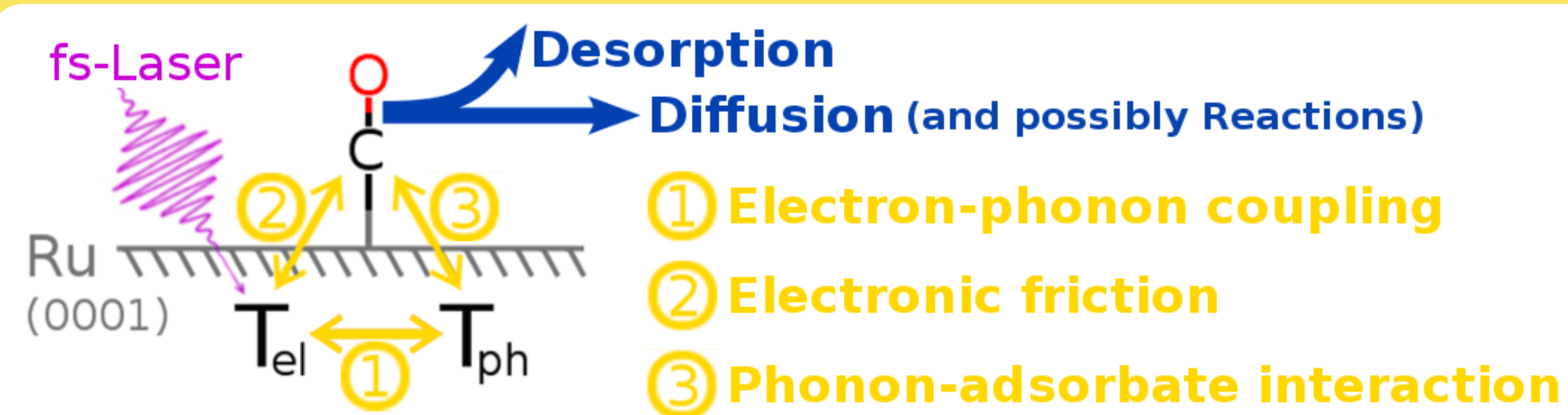
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Introduction

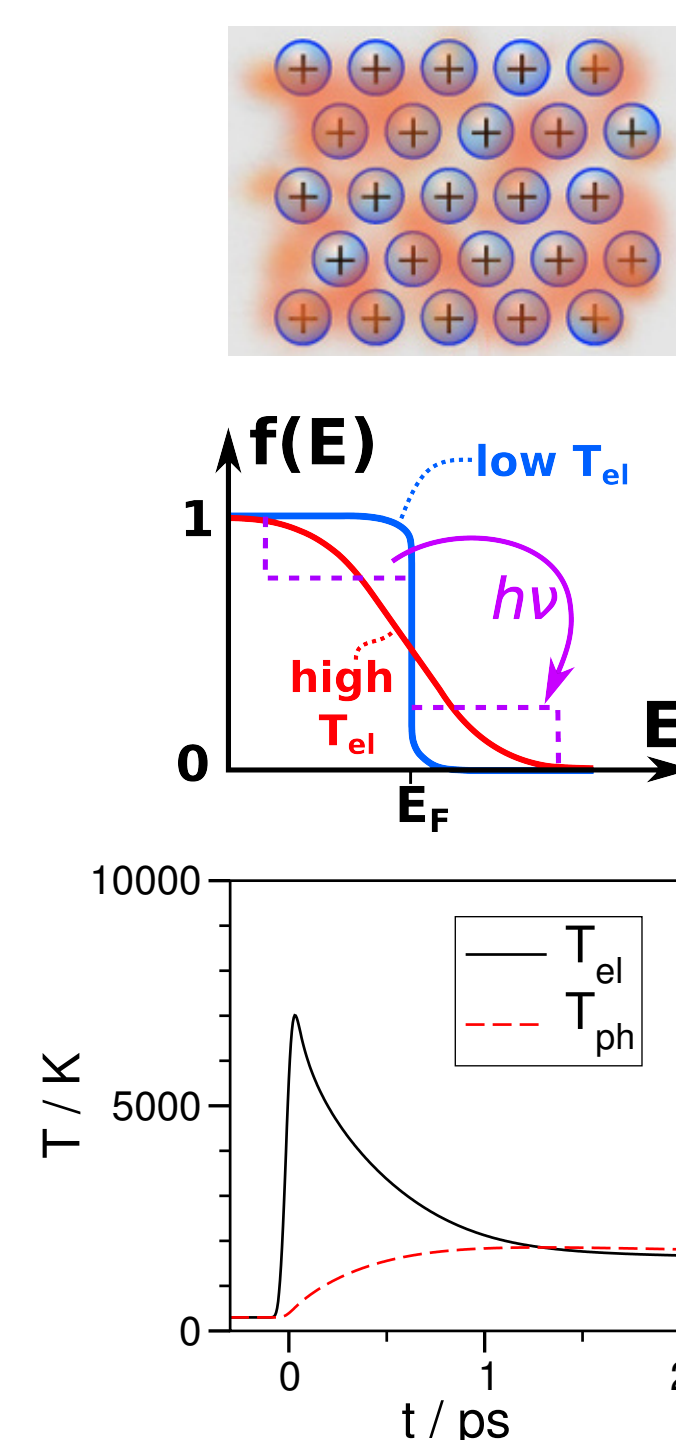
Motivation

- 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 ~ 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:

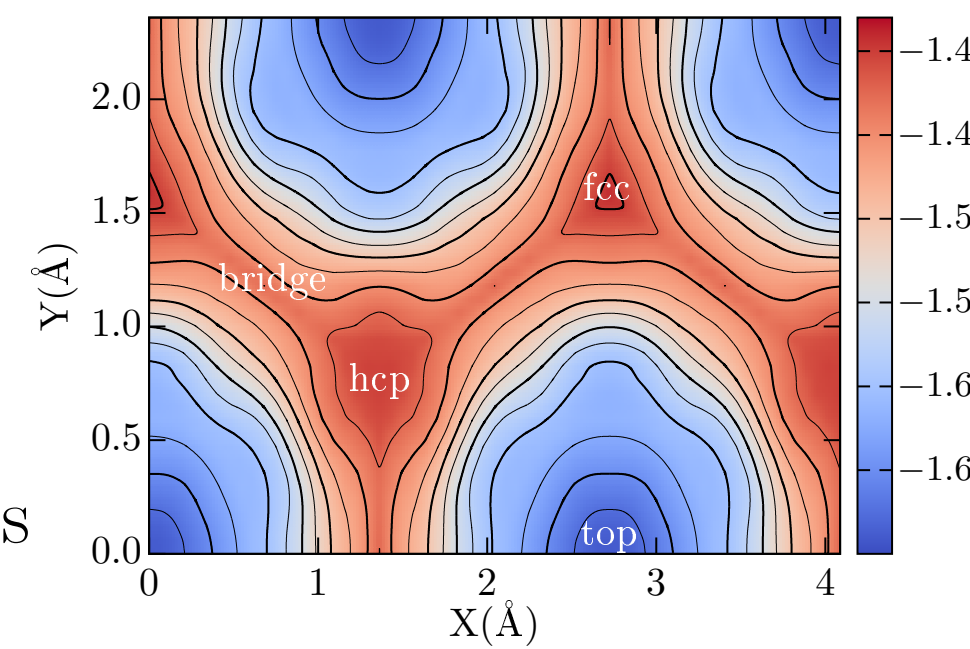
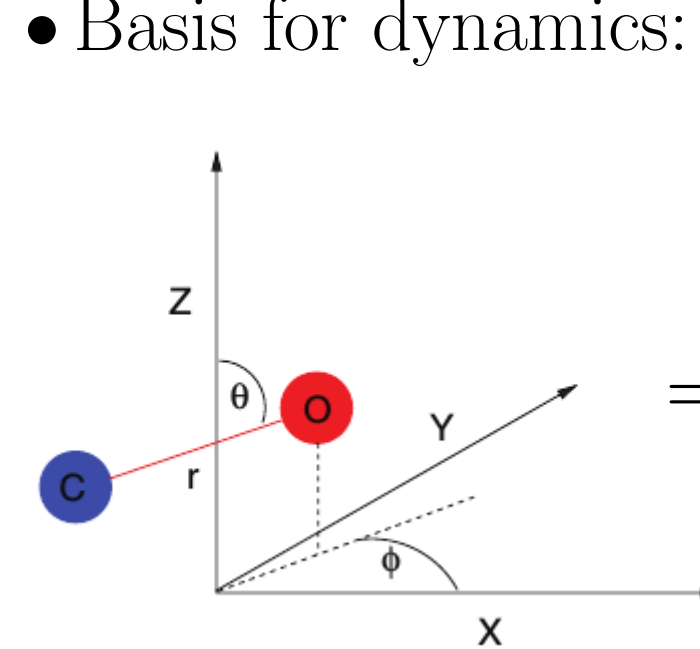
- T_{el} - electron temperature
- T_{ph} - phonon temperature

- 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]

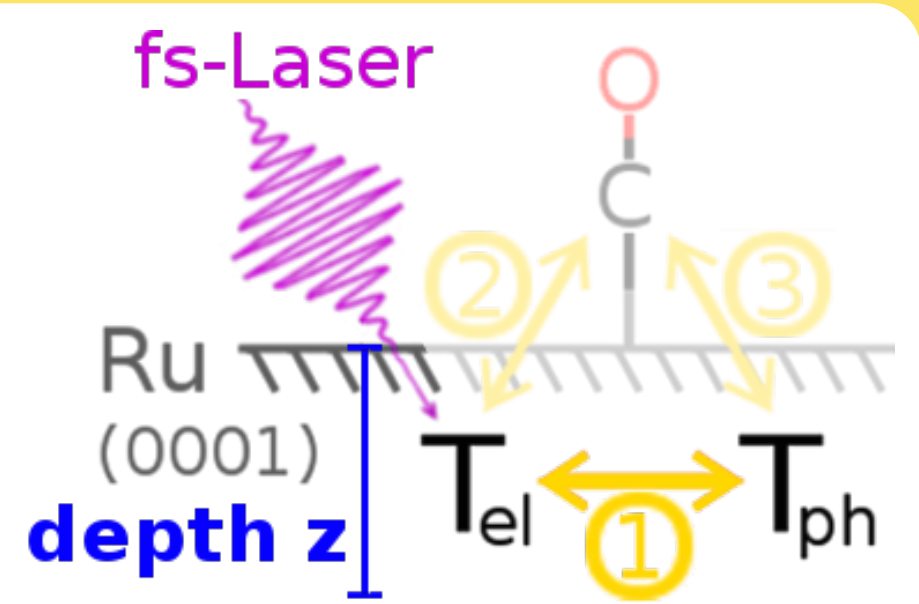
- describes interaction of metal with laser, using two differential equations:

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

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

\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)
- (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



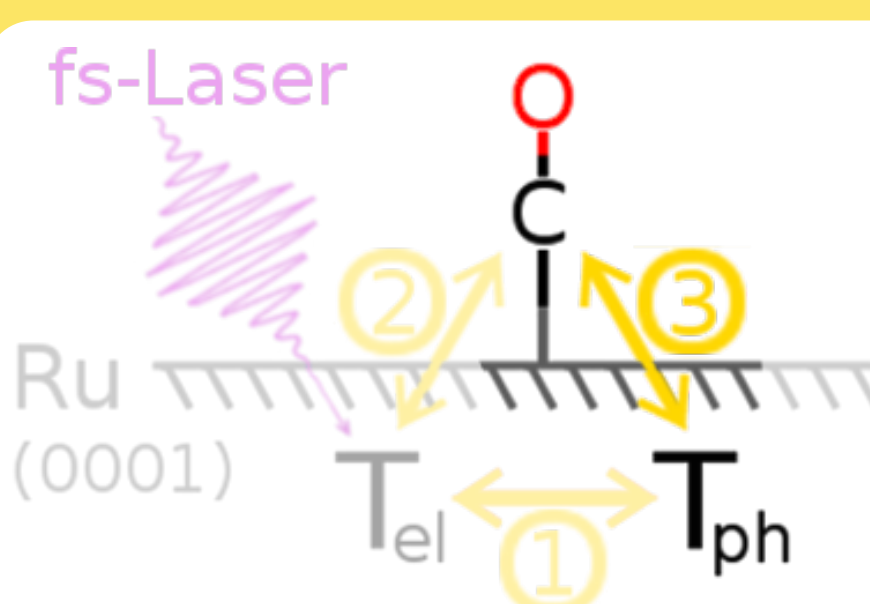
Electronic Friction: Langevin Dynamics[5] and Local Density Friction Approximation (LDFA)[6]

- Langevin equation of motion, a stochastic differential equation:

$$m_k \frac{d^2 r_k}{dt^2} = \underbrace{-\nabla_k V(r_1, r_2)}_{\text{Force on Atom } k} - \underbrace{\eta_{el,k}(r_k)}_{\text{Force due to PES}} \frac{dr_k}{dt} + \underbrace{R_{el,k}(t)}_{\text{Friction force slows movement}} + \underbrace{R_{el,k}(t)}_{\text{Random force from e-h pairs}}$$

- 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 $\eta_{el,k}$

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



References

- [1] S. Funk, M. Bonn, D. N. Denzler, C. Hess, M. Wolf and G. Ertl, *J. Chem. Phys.* **112**, 9888 (2000).
- [2] M. Dell’Angela, T. Anniyev, M. Beye, R. Coffee, A. Föhlisch et al., *Science* **339**, 1302 (2013).
- [3] G. Fuchsels, J. C. Tremblay, and P. Saalfrank, *J. Chem. Phys.* **141**, 094704 (2014).
- [4] S. I. Anisimov, B. L. Kapeliovich, and T. L. Perel’man, *Sov. Phys.-JETP* **39**, 375 (1974).

- [5] M. Head-Gordon and J. C. Tully, *J. Chem. Phys.* **103**, 10137 (1995).

- [6] J. I. Juaristi, M. Alducin, R. Díez Muiño, H. F. Busnengo and A. Salin, *Phys. Rev. Lett.* **100**, 116102 (2008).

- [7] S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976).

- [8] J. C. Tully, *J. Chem. Phys.* **73**, 1975 (1980).

- [9] H. F. Busnengo, M. A. Di Césare, W. Dong, and A. Salin, *Phys. Rev. B* **72**, 125411 (2005).