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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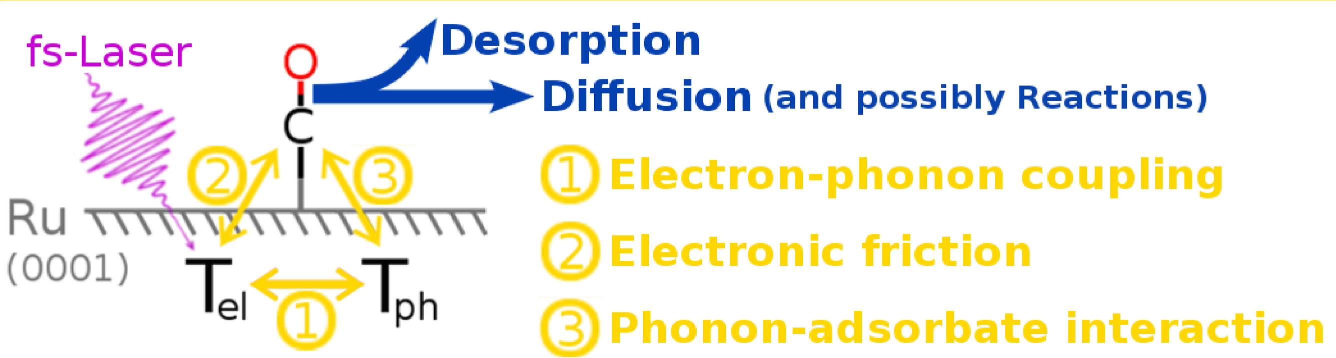
Introduction

Motivation

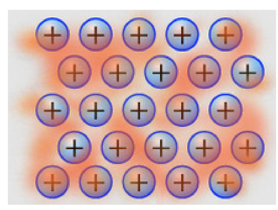
- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
  - allow for investigations on small timescales
  - open up new processes compared to heating (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

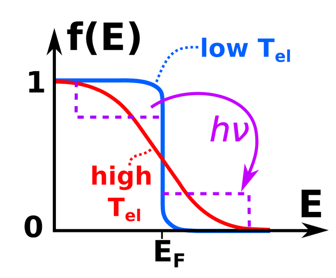
How does fs-laser-irradiation affect metal surfaces?

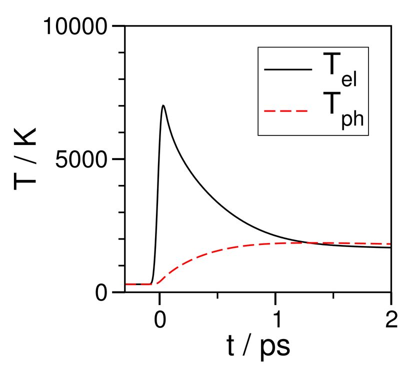


- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron hole pairs thermalize quickly
  $\Rightarrow$ "hot" Fermi-Dirac-distribution (after $\sim$10 fs)
- electrons transfer part of energy to ion lattice, via ① electron-phonon coupling (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)





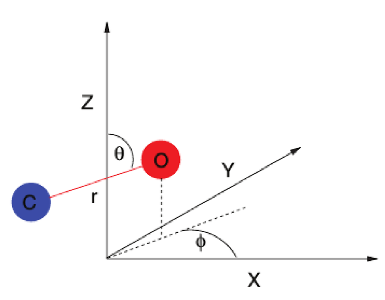


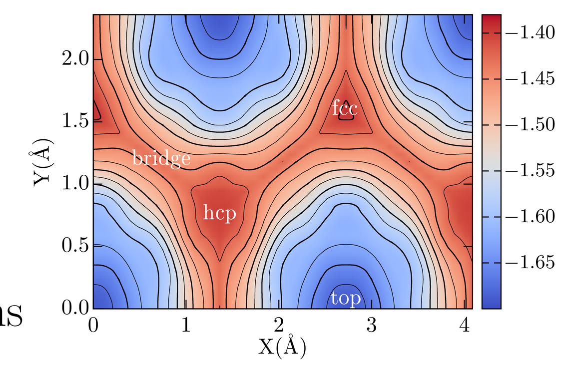
Models and Methods

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

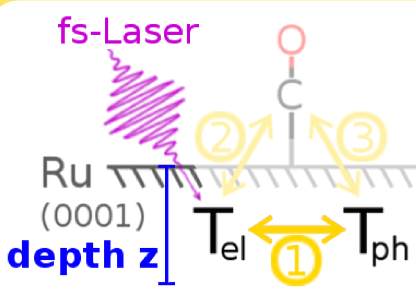
- Basis for dynamics: precomputed PES from DFT (rPBE + D2)
  - all 6 dimensions of the adsorbate
  - analytical PES and gradients $\Rightarrow$ very fast

  $\Rightarrow$ 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]



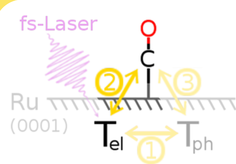
- describes interaction of metal with laser, using two differential equations:

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

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

- calculates T_{el} and T_{ph} as $f(z,t)$ from laser parameters and material properties:
  - laser wavelength λ (affects penetration depth into material)
  - (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]

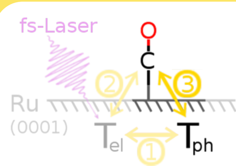


- Langevin equation of motion:

$$m_k\frac{d^2\underline{r}_k}{dt^2} = -\underline{\nabla}_k V(\underline{r}_1,\underline{r}_2) - \eta_{\mathrm{el},k}(\underline{r}_k)\frac{d\underline{r}_k}{dt} + \underline{R}_{\mathrm{el},k}(t).$$

- describes interaction of electron-hole-pairs with molecule

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



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