Femtosecond-laser induced dynamics of CO on Ru(0001): New insights from a hot-electron, electronic friction model including surface motion

Robert Scholz[1,2], Gereon Floß[1], Peter Saalfrank[1], Gernot Füchsel[3], Ivor Lončarić[4], and J. I. Juaristi[4,5,6]

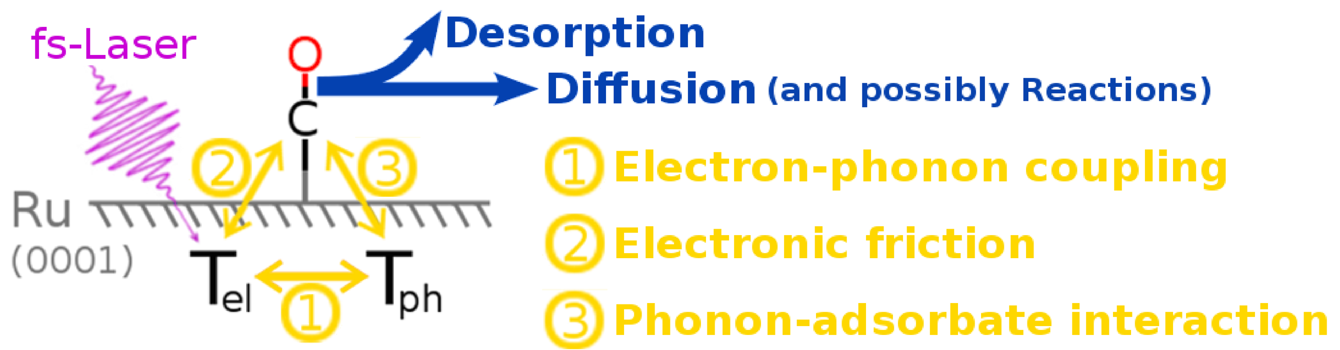
[1]Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany
[2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany
[3]Universiteit Leiden, Gorlaeus Laboratories, Einsteinweg 55, 2333 Leiden, The Netherlands
[4]Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain
[5]Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[6]Donostia International Physics Center DIPC, P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain

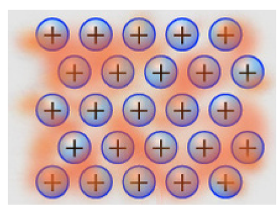
Introduction

Motivation

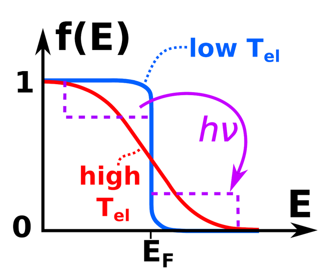
- research on small molecules adsorbed to metals is important for:
  - catalytic applications
  - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
  - allow for investigations on small timescales
  - open up new processes compared to heating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

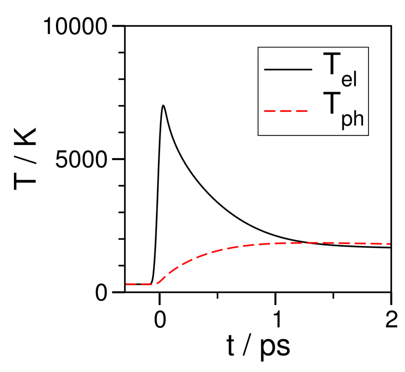




- metals: ion lattice plus quasi-free electron gas
- visible light is absorbed only by the electrons
- produced electron-hole pairs thermalize quickly
  ⇒ "hot" Fermi-Dirac-distribution (after ∼10 fs)



- 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

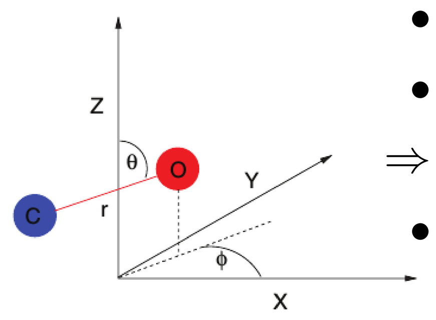


⇒ Thus, with fs-lasers, two different temperatures:
  - T_{el} - electron temperature
  - T_{ph} - phonon temperature
- can be simulated using a Two-Temperature Model (2TM)[4] (see right)

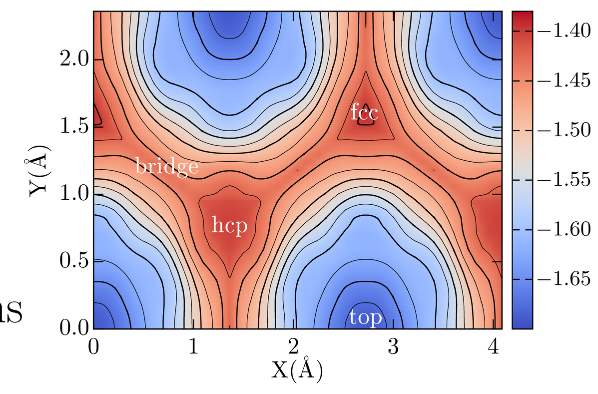
Models and Methods

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

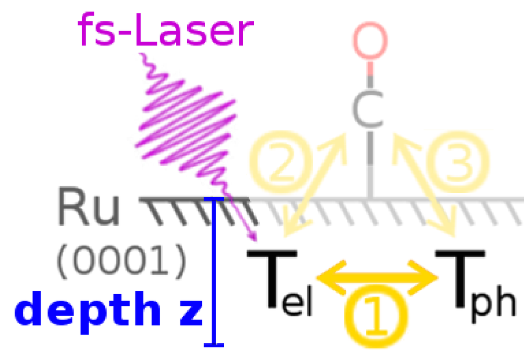


Two-Temperature Model (2TM)[4]

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

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

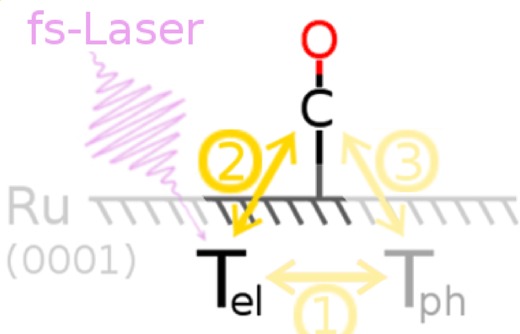
$$C_{ph}\frac{\partial T_{ph}}{\partial t} = g(T_{el} - T_{ph}).$$



⇒ 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]

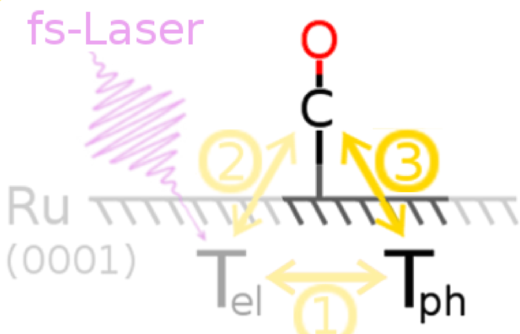


- Langevin equation of motion, a stochastical differential equation:

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

- 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 $\eta_{el,k}$ and T_{el}

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



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