

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 Floß¹, Peter Saalfrank¹, Gernot Fuchsels³, Ivor Lončarić⁴, and J. I. Juaristi^{4,5,6}

¹Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany

²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

³Universiteit Leiden, Gorlaeus Laboratories, Einsteinweg 55, 2333 Leiden, The Netherlands

⁴Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain

⁵Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain

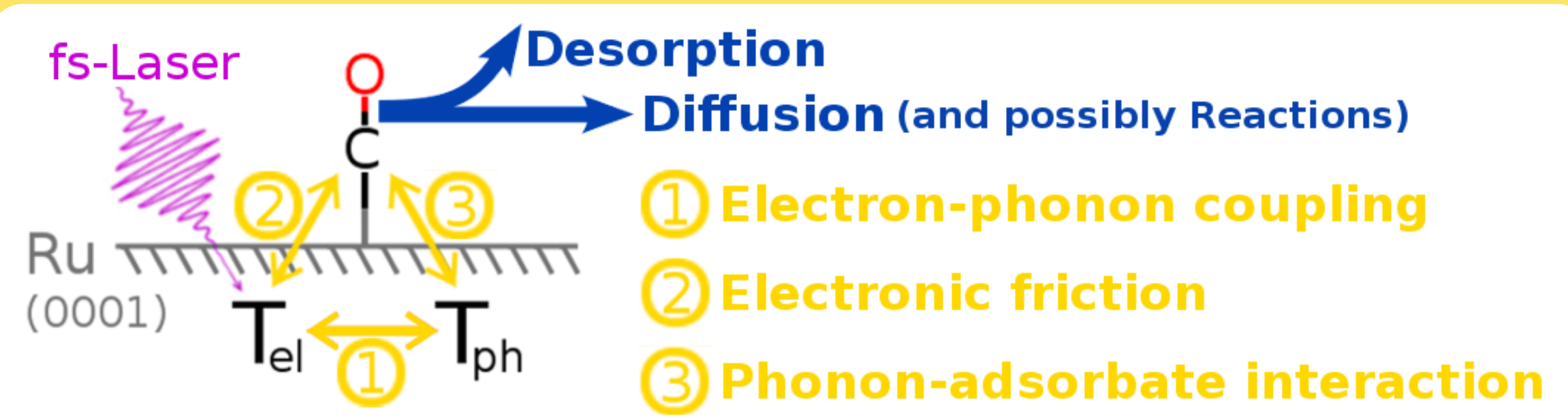
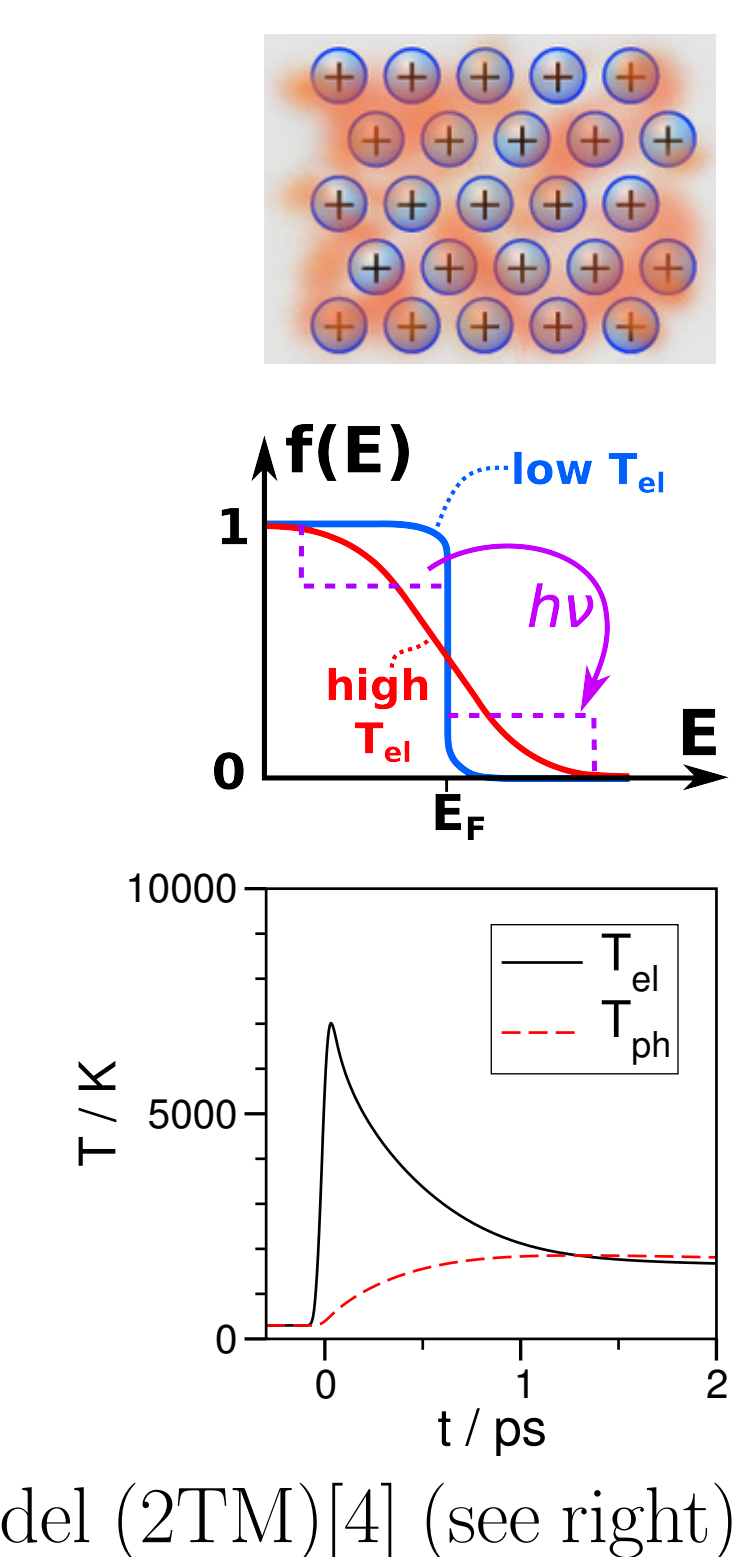
⁶Donostia International Physics Center DIPC, P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain

Introduction

Motivation

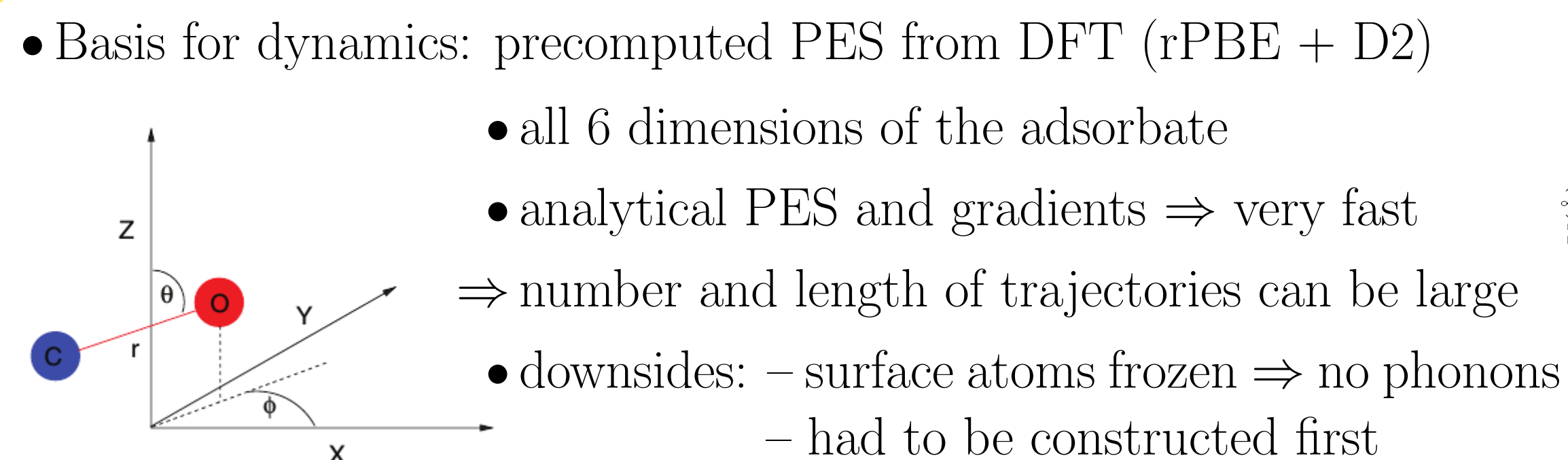
- research on small molecules adsorbed to metals is important for:
 - catalytic applications
 - fundamental understanding of bonding
- femtosecond(fs)-lasers are a valuable tool for such research as they
 - allow for investigations on small timescales
 - open up new processes compared to heating (femtochemistry)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

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- 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)
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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
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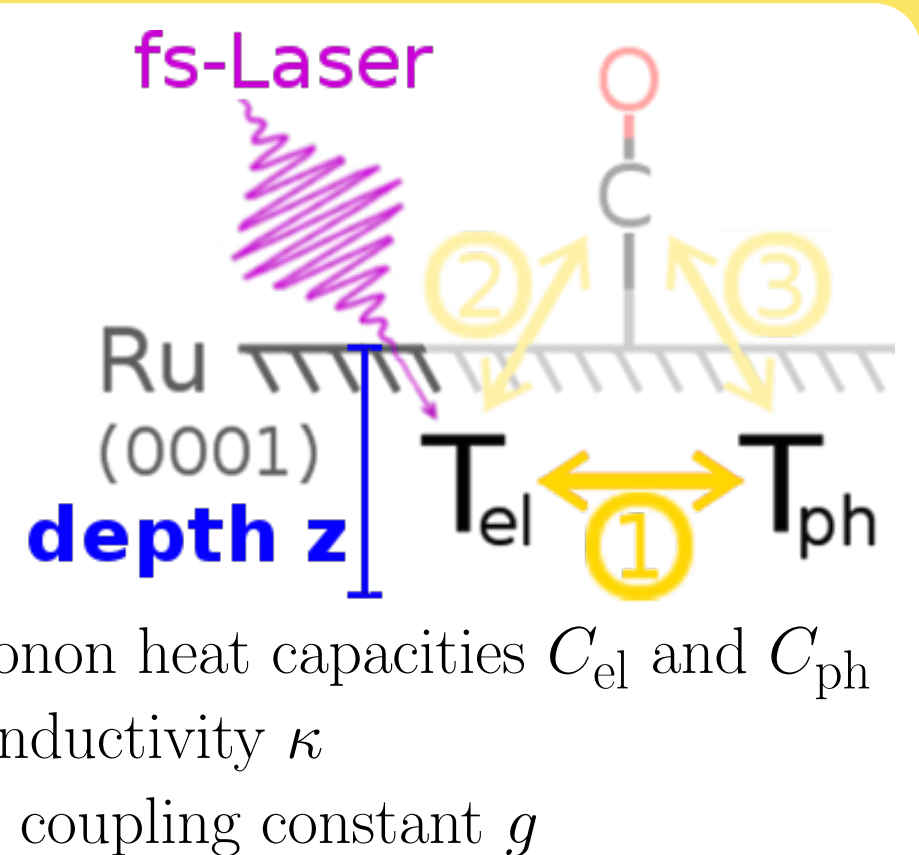
Two-Temperature Model (2TM)[4]

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

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

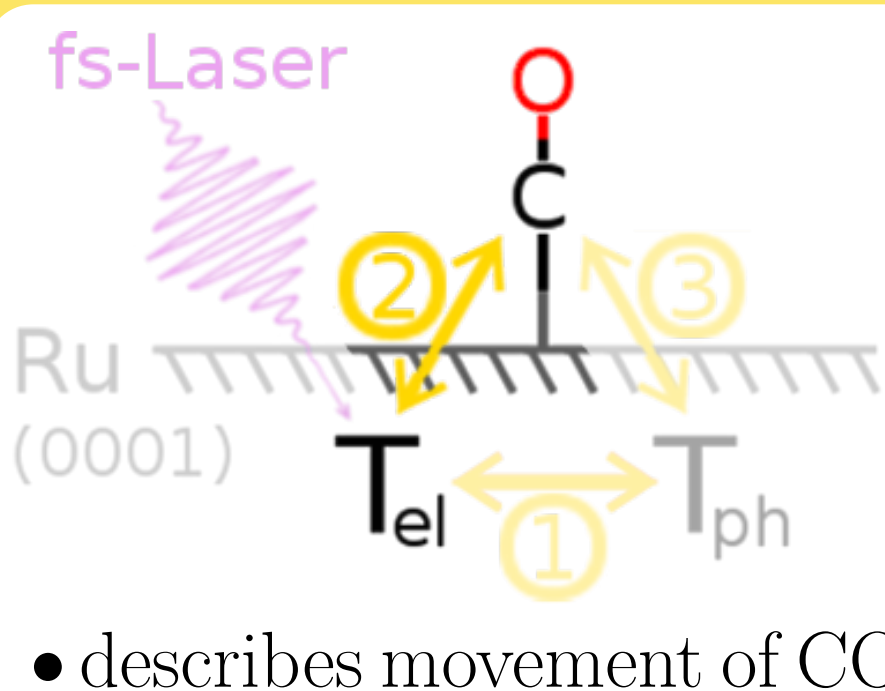
$$C_{ph} \frac{\partial T_{ph}}{\partial t} = g(T_{el} - T_{ph}).$$

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

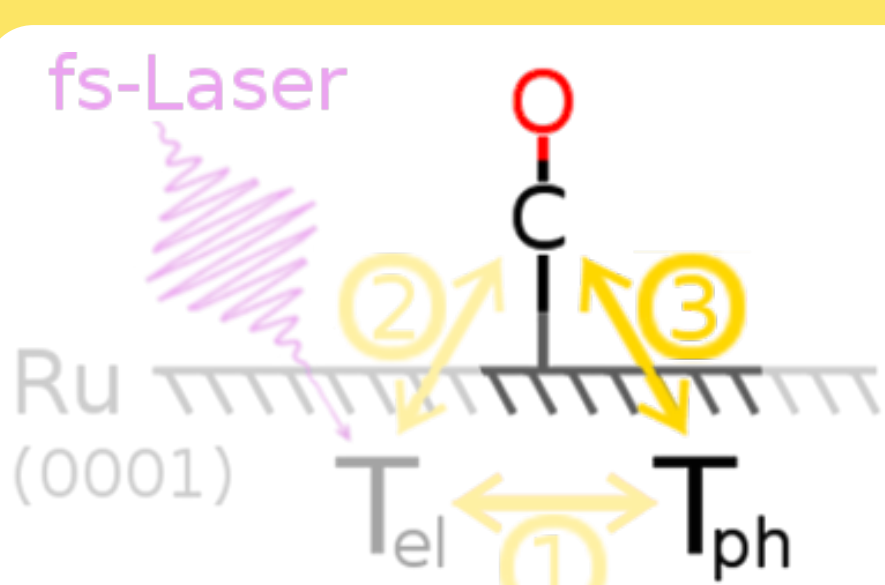
- laser wavelength λ (affects penetration depth into material)
 - (effective) absorbed fluence F (energy/area)
 - pulse duration τ (all three appear in the “source term” $S(z, t)$)
 - electron and phonon heat capacities C_{el} and C_{ph}
 - electron heat conductivity κ
 - electron-phonon coupling constant g
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Electronic Friction: Langevin Dynamics[5] and Local Density Friction Approximation (LDFA)[6]

- Langevin equation of motion, a stochastic differential equation:

$$m_k \frac{d^2 r_k}{dt^2} = \underbrace{-\nabla_k V(r_1, r_2)}_{\text{Force on Atom } k} - \underbrace{\eta_{el,k}(r_k)}_{\text{Force due to PES}} \frac{dr_k}{dt} + \underbrace{R_{el,k}(t)}_{\text{Random force from e-h pairs}}$$
 - describes movement of CO on the PES and interaction with electron-hole pairs (friction and excitation)
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Inclusion of Phonons: Generalized Langevin Oscillator(GLO)-model[7, 8, 9]

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