

MULTI-DIMENSIONAL FEMTOSECOND-LASER INDUCED DYNAMICS OF CO ON METALS:

ACCOUNTING FOR ELECTRONIC FRICTION AND SURFACE MOTION WITH COMBINED MODELS

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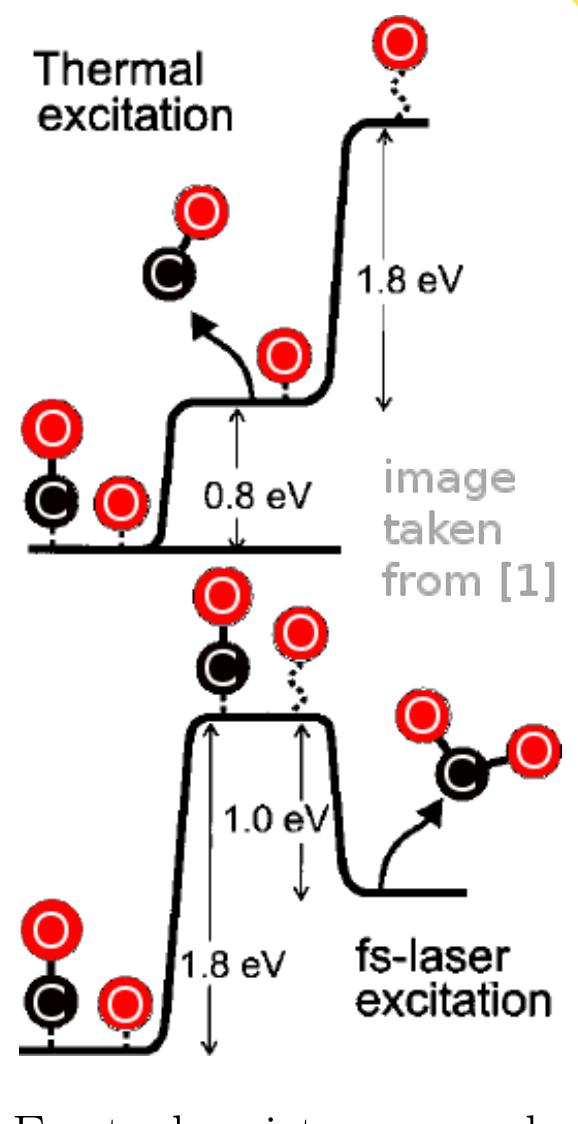
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Introduction

Motivation

- Aim: gain precise understanding of adsorbate bonding on metals
⇒ Important for Catalysis



- Why femtosecond(fs)-lasers?
- produce non-equilibrium 2-T-states
⇒ different than normal heating

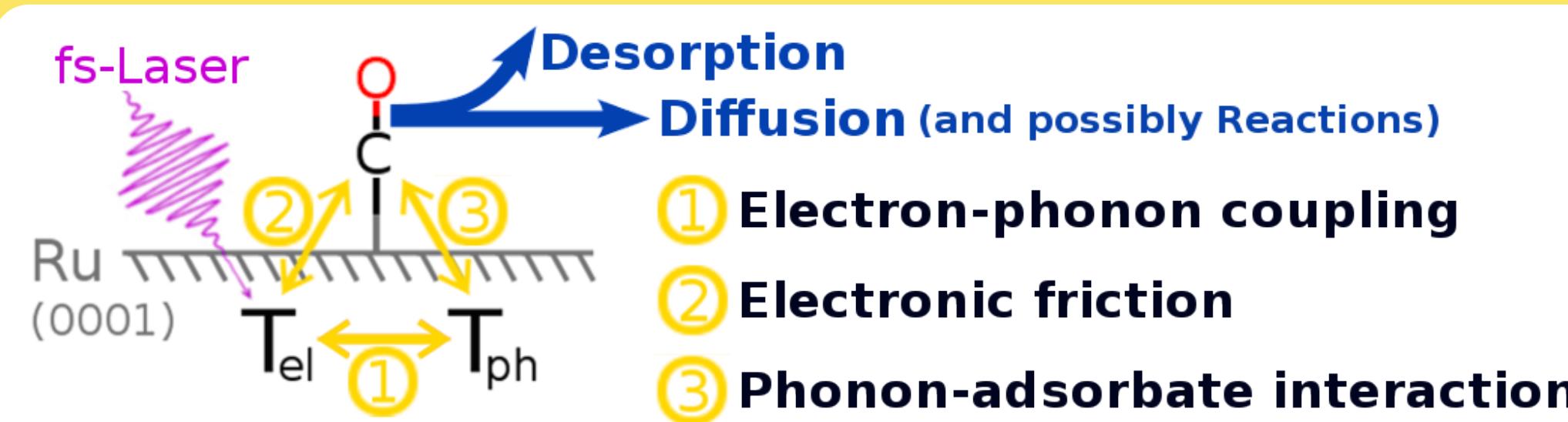
- further tool besides STM and scattering
- direct future applications possible
⇒ "femtochemistry"[1]

- Why CO/Ru(001) and CO/Cu(100)?
- both are well studied model systems

- recently, interesting fs-laser experiments[2][3]

- also, ab-initio based 6-dim. potentials available [4][5]

How do fs-Lasers affect Adsorbate-Metal Systems?

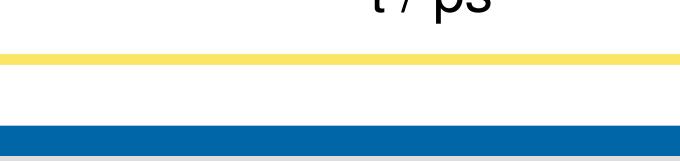
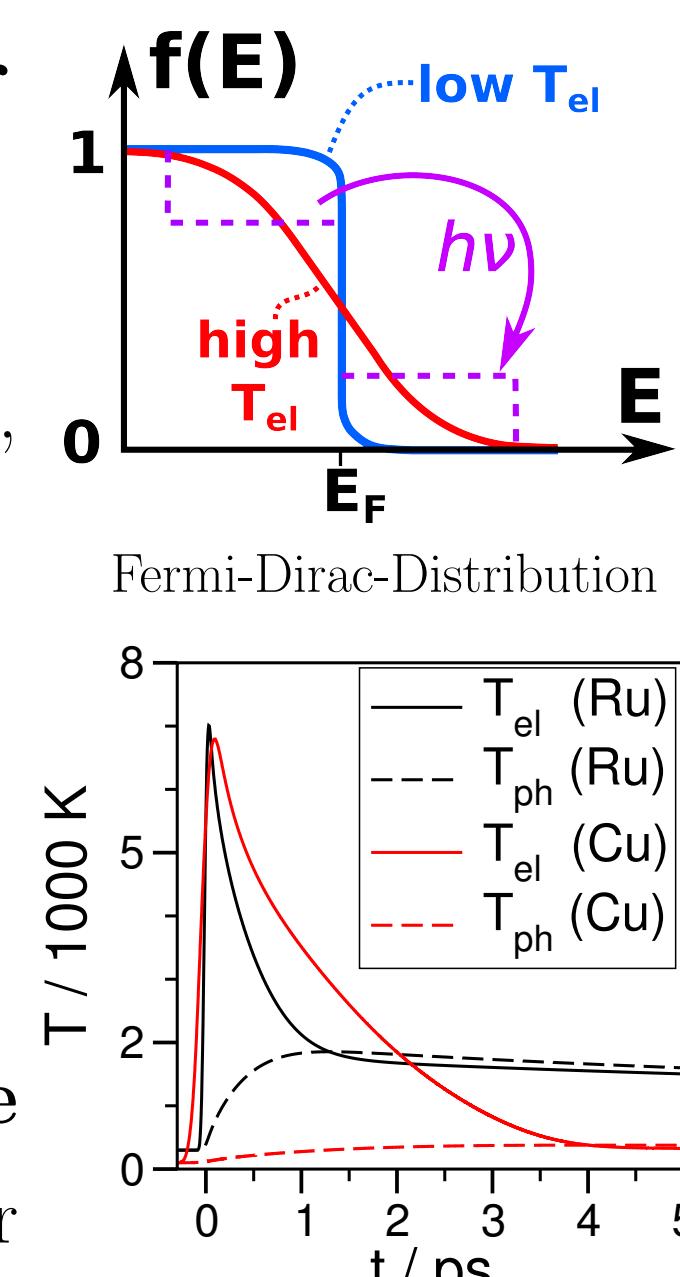


- only electrons of metal absorb laser
- electron-hole pairs thermalize fast
⇒ "hot" Fermi-Dirac-distribution
- electrons transfer energy to ion lattice, via ① electron-phonon coupling
- equilibration within ps-timescale

⇒ Thus, for few ps two temperatures:

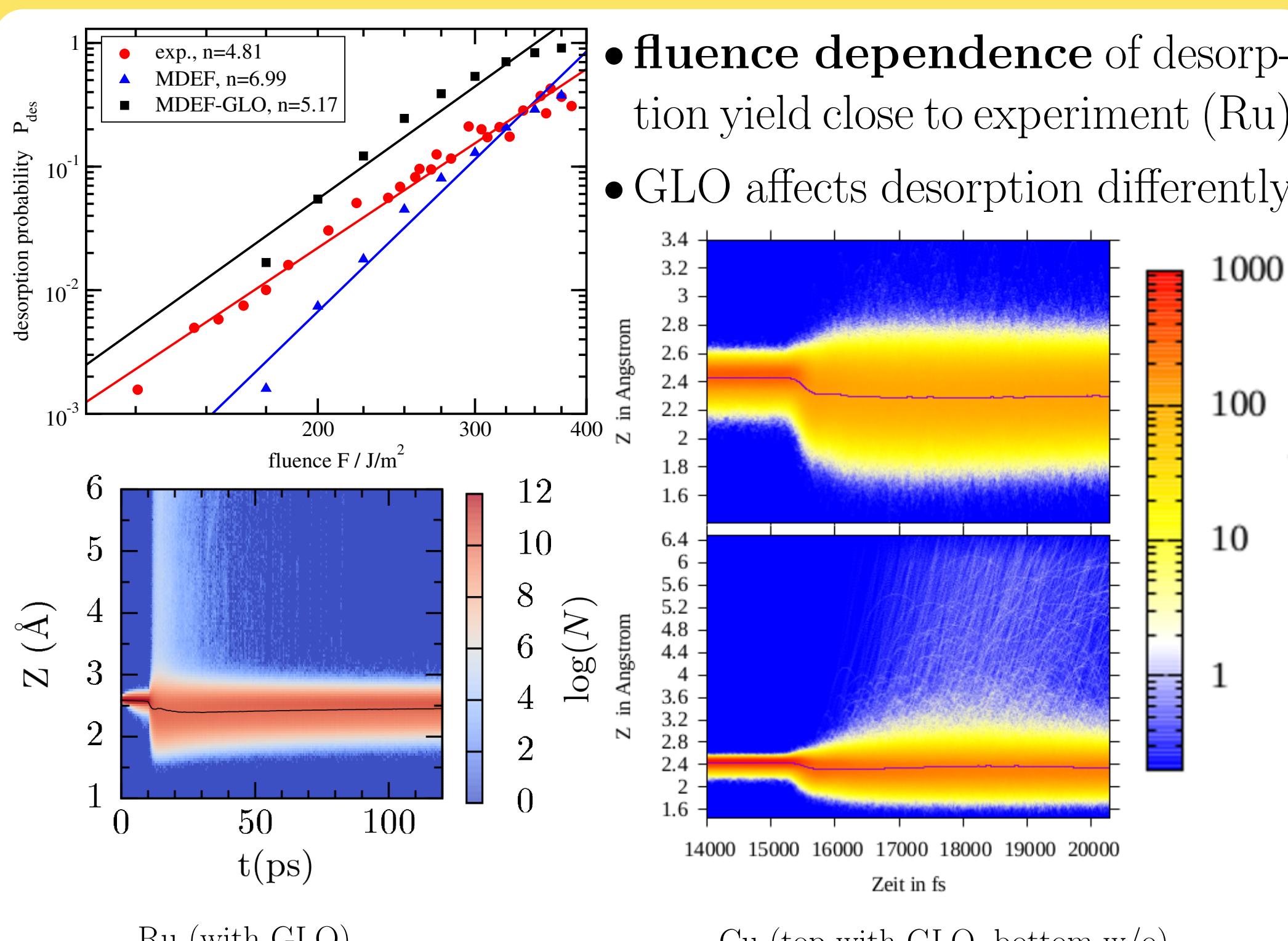
- T_{el} - electron temperature
- T_{ph} - phonon temperature

- both can couple to adsorbed molecule
- low electron heat capacity ⇒ T_{el} higher

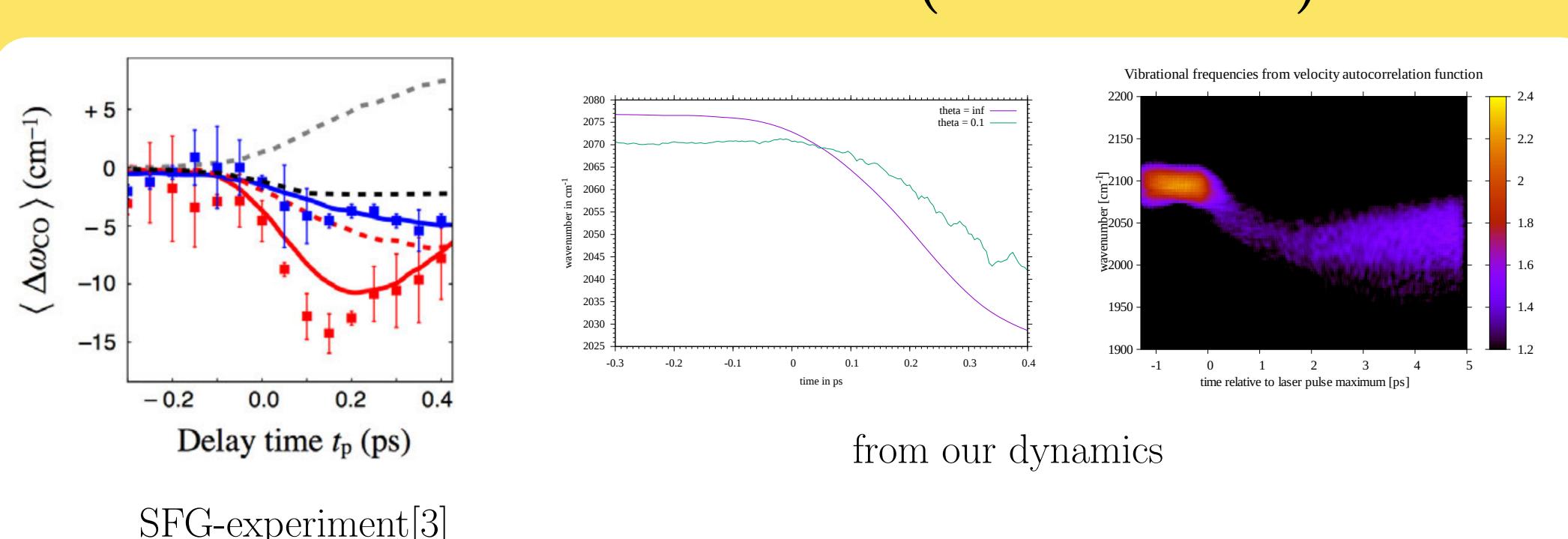


Results

Desorption



CO-stretch Vibration (Data for Cu)

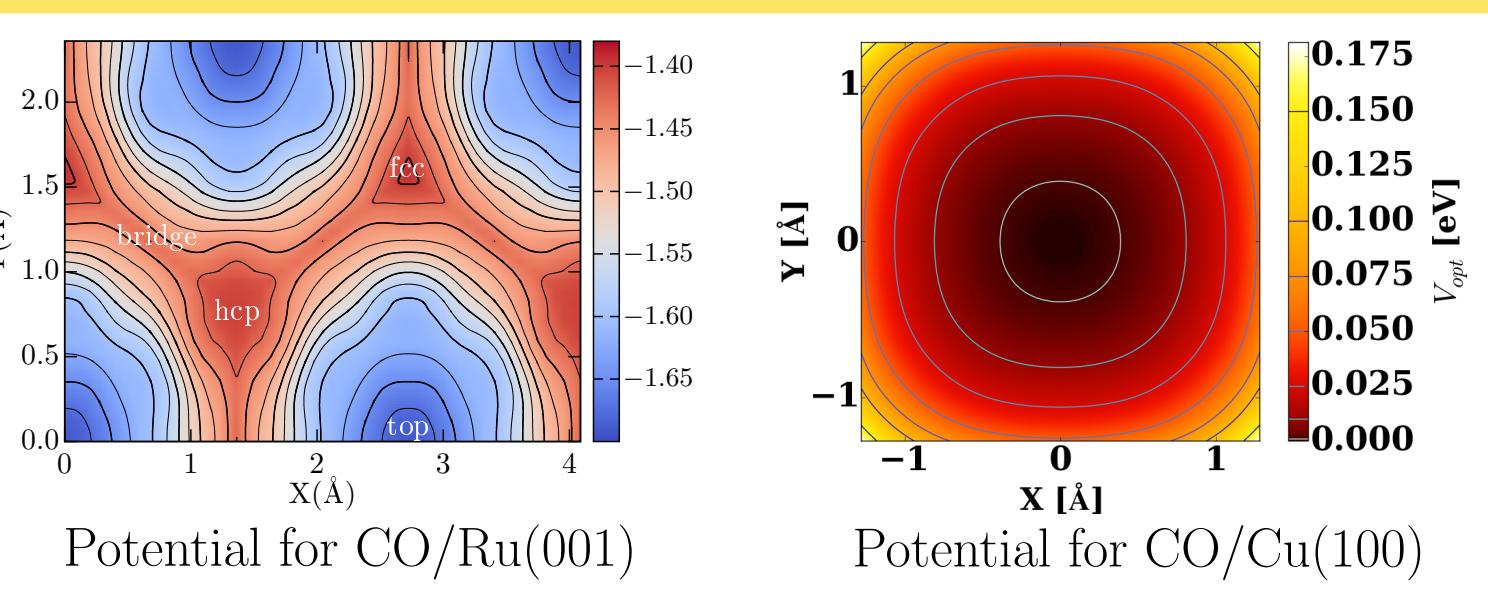


Models and Methods

Basis of the Dynamics: the Six-dimensional Potential Energy Surfaces (PES)[4][5]

The six dimensions of CO

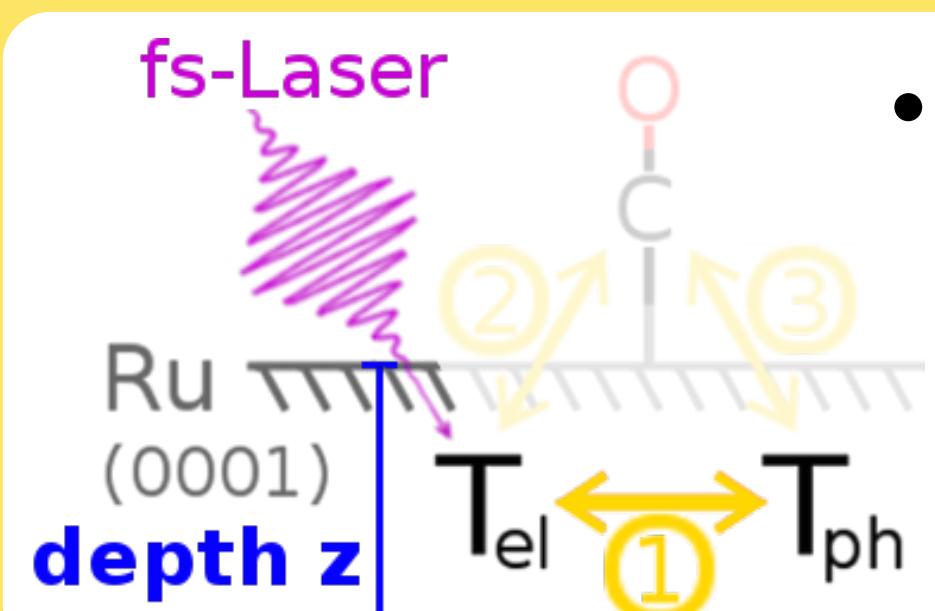
- precomputed with DFT (GGA)
- all six dimensions of the adsorbate
- analytical ⇒ very fast
- many trajectories possible



Potential for CO/Ru(001)

Potential for CO/Cu(100)

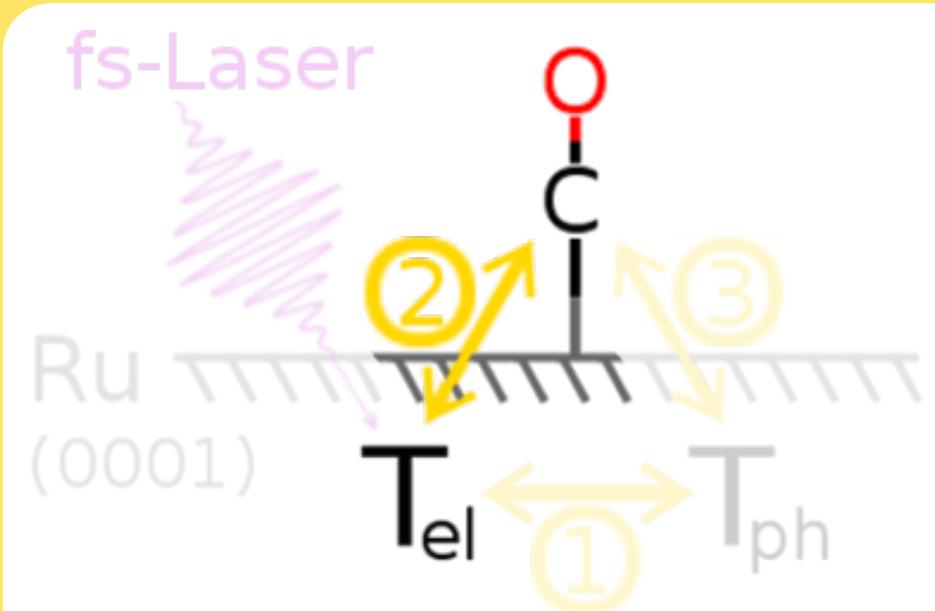
Two-Temperature Model (2TM)[6]



$$\begin{aligned} \text{simulates interaction of electrons with phonons and laser} &\Rightarrow \text{gives } T_{el} \text{ and } T_{ph} \text{ as } f(z, t) \\ C_{el} \frac{\partial T_{el}}{\partial t} = \frac{\partial}{\partial z} \kappa \frac{\partial}{\partial z} T_{el} - g(T_{el} - T_{ph}) + S(z, t), \\ C_{ph} \frac{\partial T_{ph}}{\partial t} = g(T_{el} - T_{ph}). \end{aligned}$$

- electron and phonon heat capacities C_{el} and C_{ph}
- elec. heat conductivity κ
- elec.-phonon coupling g
- laser source term $S(z, t)$

Electronic Friction: Langevin Dynamics[7] and Local Density Friction Approximation (LDFA)[8]



- the Langevin equation of motion, a stochastical differential equation:

$$m_k \frac{d^2 r_k}{dt^2} = -\nabla_k V(r_1, r_2) - \eta_{el,k}(r_k) \frac{dr_k}{dt} + R_{el,k}(t).$$

Force on Atom k

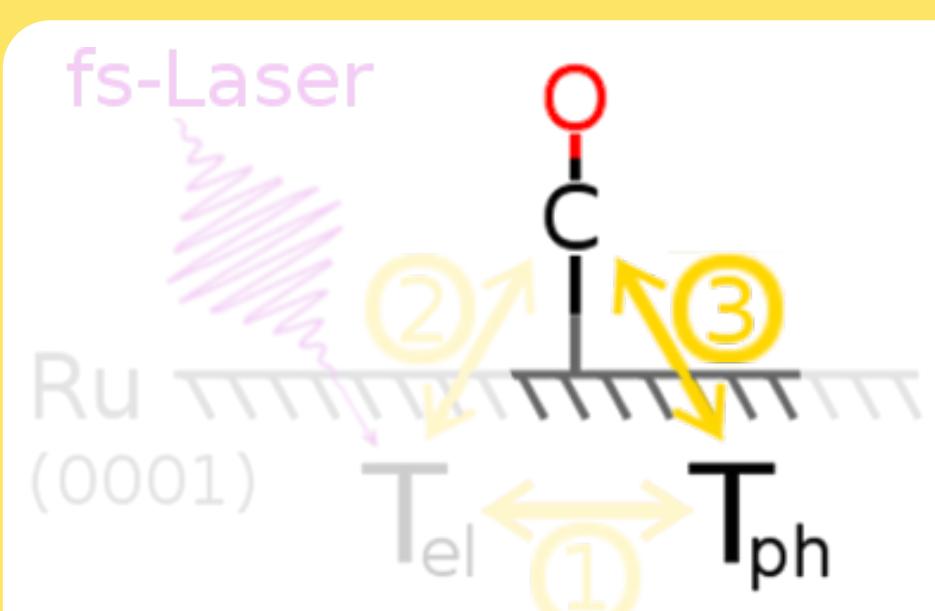
Force due to PES

Friction force slows movement

Random force from e-h pairs

- describes movement of CO and interaction with electron-hole pairs (friction and excitation)
- Local Density Friction Approx. (LDFA): ab-initio model that gives friction coefficients $\eta_{el,k}$
- Atom k embedded in free electron gas with density of bare surface at current position r_k
- Random forces $R_{el,k}$: white noise, dependent on both $\eta_{el,k}$ (from LDFA) and T_{el} (from 2TM)

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



- influence of phonons effectively modeled (augments frozen surface)
- entire surface understood as 3D oscillator (coords. r_s , mass of one atom)
- coupling to molecule via shifting: $V_{GLO}(r_C, r_O; r_s) = V(r_C - r_s, r_O - r_s)$
- additionally coupled to ghost oscillator r_g , models influence of bulk
- ghost oscillator is subject to friction η_{ph} and random forces $R_{ph}(T_{ph})$

Conclusions

- system: CO on Ru(001) or Cu(100)
- full-dimensional (6D) simulation of dynamics driven by fs-laser irradiation
- first principles, no "free" parameters
- accounting for 1) electronic friction and excitation by hot electron-hole pairs (via LDFA and the Langevin approach) and 2) substrate motion (via GLO)
- detailed time- and space-resolved insights

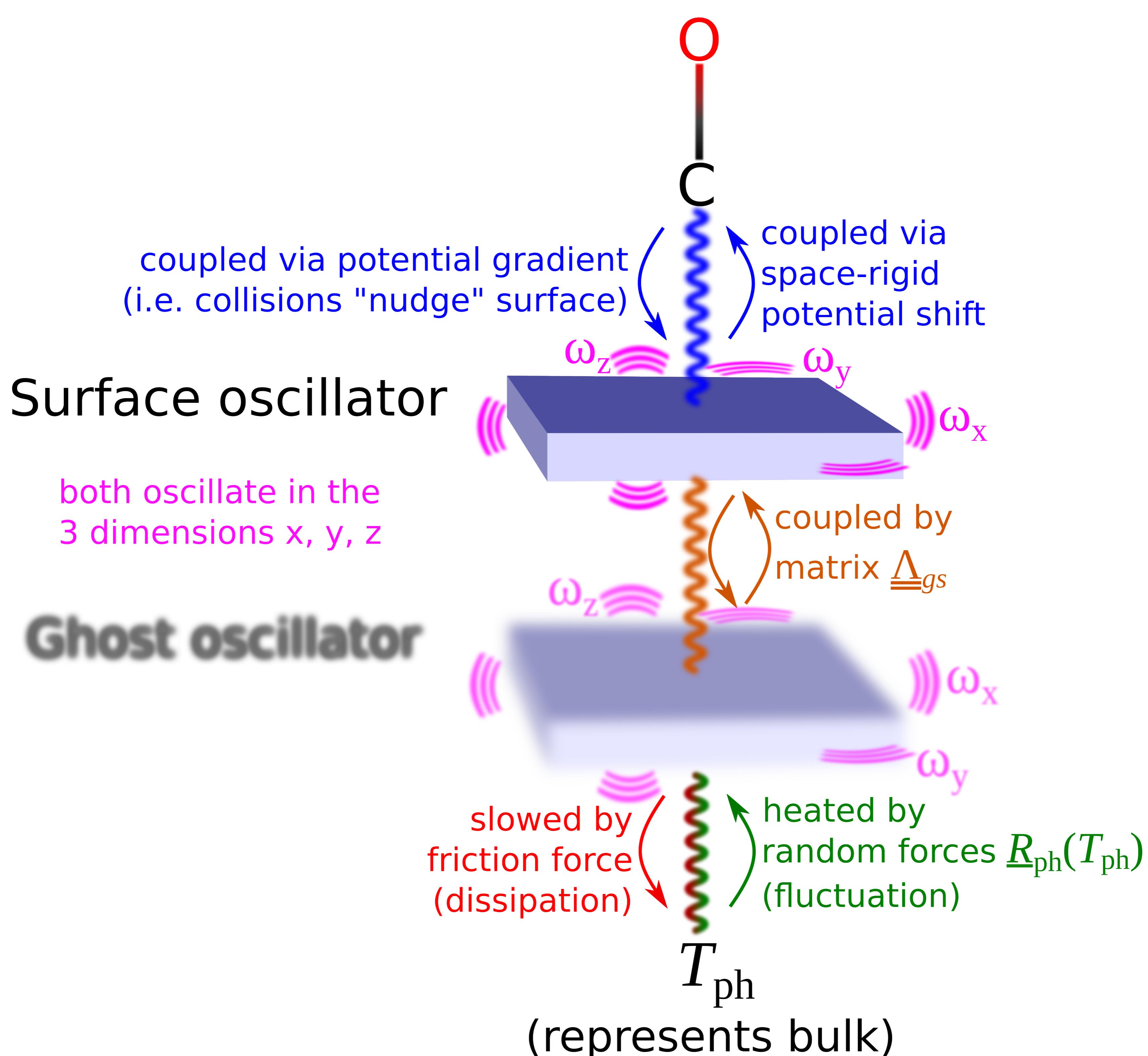
Outlook

- better description of electronic friction: η_{el} as $f(T_{el})$ and going beyond LDFA ⇒ Long term goal: friction tensors[10]
- further 2TM improvements, consider non-equilibrium lattice (NLM)[11]
- directly model SFG influence by explicitly including excitation from IR-pulse
- larger super cells for other coverages and intermolecular interaction
- simulate more complex systems: hydrocarbons; coadsorbate CO + H or O

References

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More details on the GLO model



- Equations of motion for surface oscillator \underline{r}_s and ghost oscillator \underline{r}_g :

$$m_s \frac{d^2 \underline{r}_s}{dt^2} = \underbrace{-\nabla_s V(\underline{r}_1 - \underline{r}_s, \underline{r}_2 - \underline{r}_s)}_{\text{Force due to PES}} - m_s \underline{\underline{\Omega}}^2 \underline{r}_s + m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_g$$

Force due to PES Harmonic oscillator Coupling to ghost oscillator

$$m_s \frac{d^2 \underline{r}_g}{dt^2} = \underbrace{-m_s \underline{\underline{\Omega}}^2 \underline{r}_g}_{\text{Harmonic oscillator}} + \underbrace{m_s \underline{\underline{\Lambda}}_{gs} \underline{r}_s}_{\text{Coupling to surface oscillator}} - \underbrace{\eta_{ph} \frac{d \underline{r}_g}{dt}}_{\text{Friction force}} + \underbrace{R_{ph}(T_{ph})}_{\text{Random forces}}$$

Harmonic oscillator Coupling to surface oscillator Friction force Random forces

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