fs-laser-driven dynamics of CO on Ru(0001)

a computational study using electronic friction (MDEF) and the generalized Langevin oscillator (GLO)

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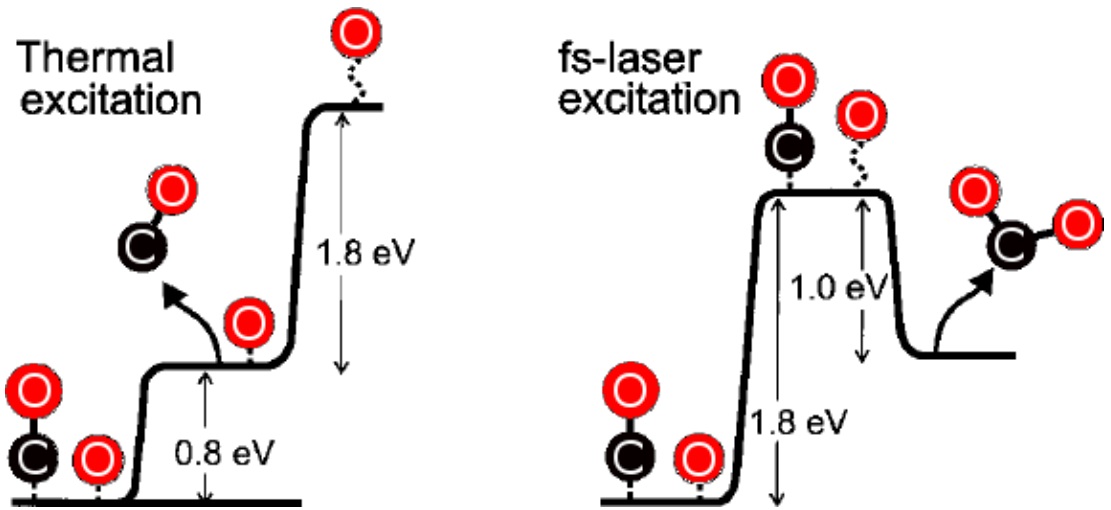
General motivation

Why investigate fs-laser-driven surface dynamics?

- gain fundamental understanding of adsorbate bonding
  $\Rightarrow$ additional tool besides scattering experiments
- possible direct application in catalysis: “femtochemistry”
  $\Rightarrow$ new reaction pathways opened up by fs-lasers



CO/O-coadsorbate @ Ru(0001)

M. Bonn *et al.*, SCIENCE 1999

Specific motivation for the CO/Ru-System

CO/Ru system important for catalysis

e. g. Fischer-Tropsch synthesis

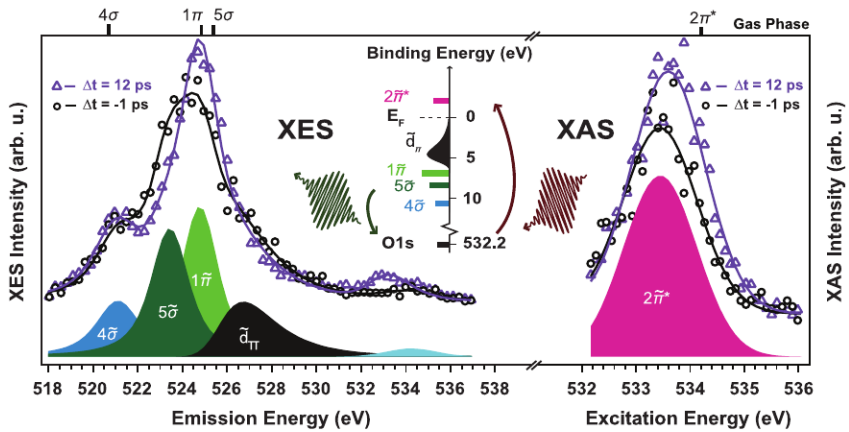
Experimentally well studied system

- especially regarding fs-laser irradiation e.g. Bonn, SCIENCE 1999 and Funk J. CHEM. PHYS 2000 (Ertl group - chemistry Nobel prize 2007).
- recently, time resolved x-ray spectra (XAS and XES) $\Rightarrow$ “movie” of changes in orbital DOS

Details of the time resolved x-ray experiment

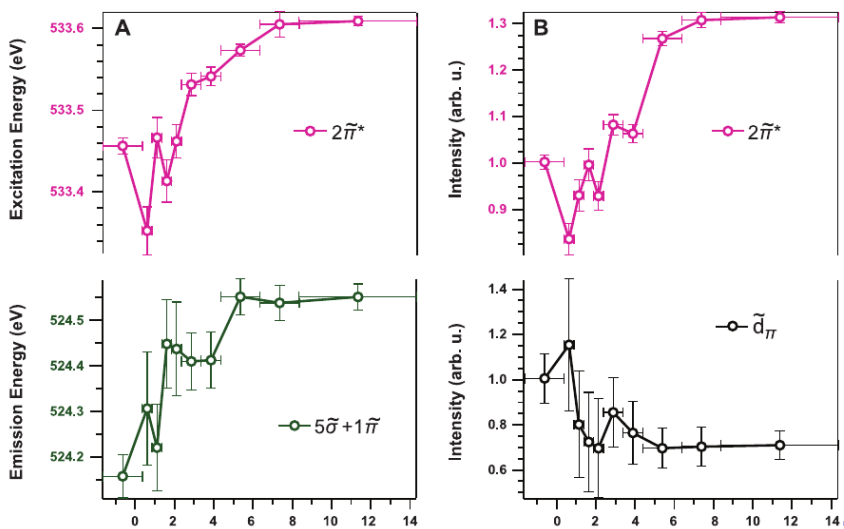
What was done?

- pump: *vis*-fs-laser
- probe: x-ray free electron laser (K edge of O-atom)



What is observed?

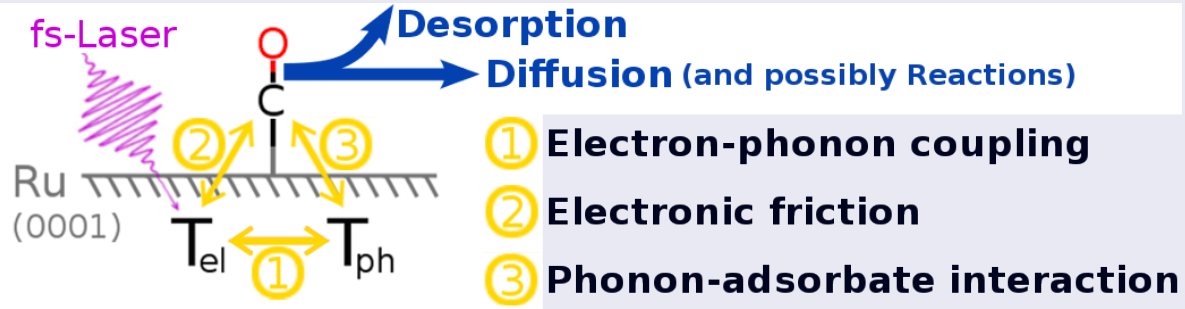
- orbital density of states
- energies shift towards gas-phase values of CO
- intensities change
  - $2\tilde{\pi}^*$ increase by $\sim 30\%$
  - $\tilde{d}_\pi$ decrease by $\sim 30\%$
  - Participator peak appears



What happens after fs-laser excitation of the metal?

Coupling between three different kinds of degrees of freedom:

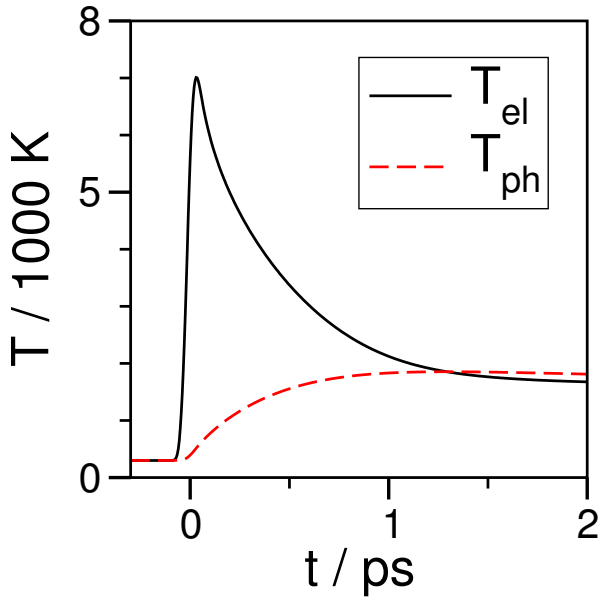
- electron gas (T_{el})
- lattice vibrations (T_{ph})
- adsorbate movement (T_{ads})



Two-Temperature Model

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

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



Laser-Driven Diffusion