# Competition between Electron and Phonon Excitations in the Dynamics of Nitrogen Atoms and Molecules at Metal Surfaces


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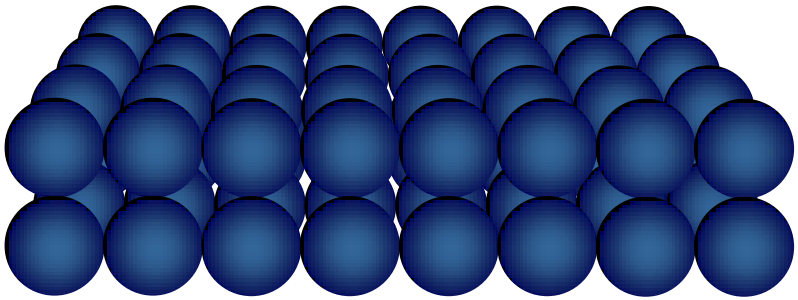
# Energy loss in reflection (and adsorption) processes

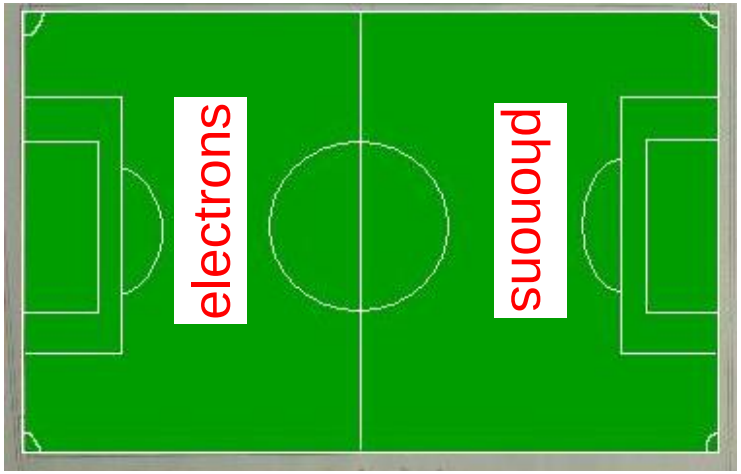
reflection



adsorption



Two channels are relevant:
- phonon excitations
- electronic excitations

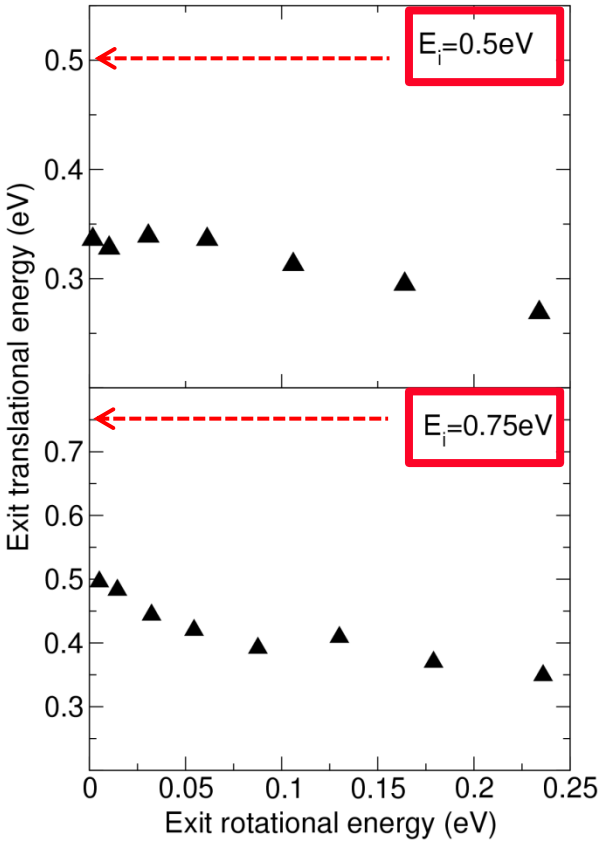



**Gas/surface dynamics**: Adiabatic → Non adiabatic
**Theory**: Ground state → Excited states

# Energy loss of reflected molecules: $N_2$ on W(110)

## Experimental conditions

- $T_s$=1200K
- $T_{rot}$ <5K (J=0)
- Normal incidence and detection



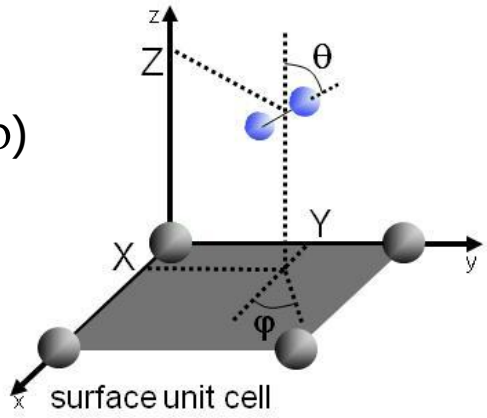

▲ **Experimental data** by Hanisco and Kummel, J.Vac.Sci.Technol. A 11 ,1907 (1993)

# Dynamics of diatomic molecules on metal surfaces: Theory

## First step: Calculation of the PES

### Calculation of the Potential Energy Surface (PES)

- adiabatic approximation
- frozen surface approximation $\Rightarrow$ **6D PES**: V(X, Y, Z, r, $\theta$, $\varphi$)




### 6D PES construction

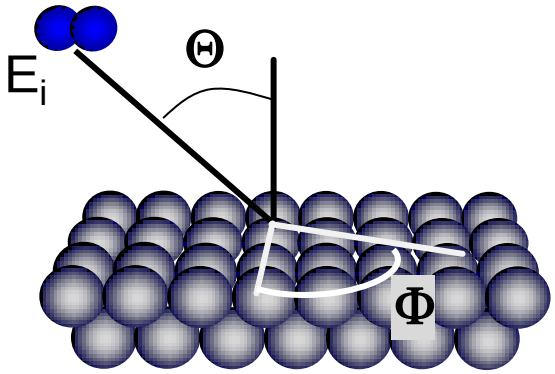
- extended set of DFT energy values, V(X, Y, Z, r, $\theta$, $\varphi$ )
- interpolation of the DFT data: Corrugation reducing procedure (CRP)

[Busnengo et al., JCP 112, 7641 (2000)]

# Dynamics of diatomic molecules on metal surfaces: Theory

## Second step: Dynamics in the PES

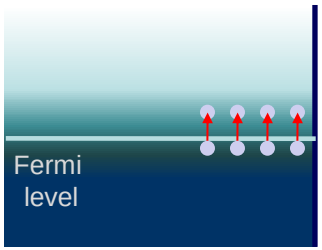
### Classical trajectory calculations: Monte Carlo sampling



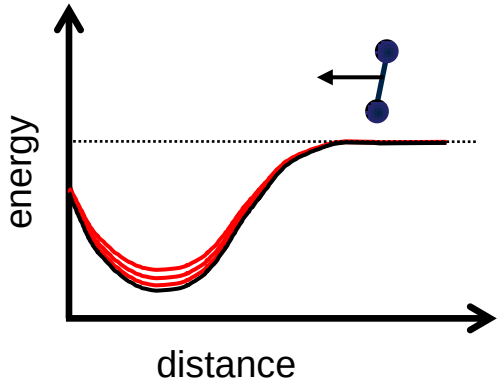

- incidence conditions are fixed: ($E_i$, Θ)
- sampling on the internal degrees of freedom: (X, Y, θ, φ) and on Φ (azimuthal angle of trajectory)

# description of electronic excitations by a friction coefficient

a continuum of low-energy electronic excitations
is available at the metal surface
and the PES is just shifted in energy




metal surface




## classical equations of motion

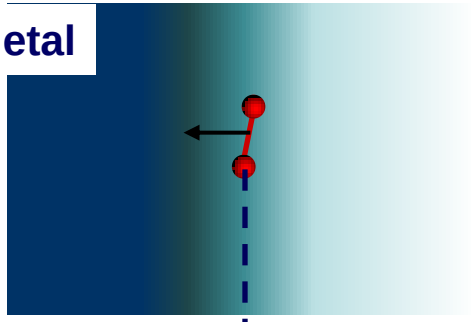
for each atom "*i*" in the molecule

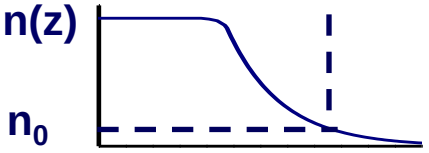
$$m_i(d^2r_i/dt^2) = -dV(r_i,r_j)/d(r_i) - \eta(r_i)(dr_i/dt)$$

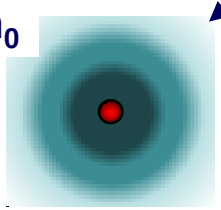
adiabatic force: 6D DFT PES

friction coefficient

## friction coefficient: effective medium approximation



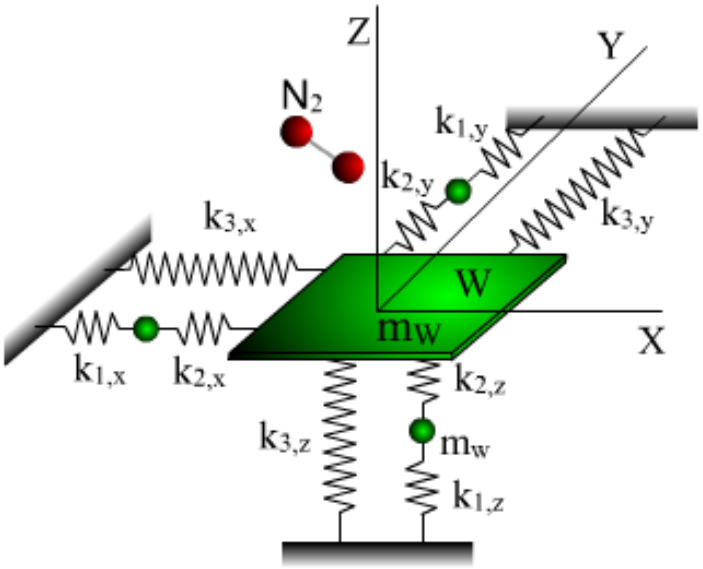

$$\eta = n_0 k_F \sigma_{tr}(k_F)$$

effective medium:
FEG with electronic density $n_0$

Juaristi *et al.*, PRL 100, 116102 (2008)

# energy dissipation channels: phonon excitation

## Generalized Langevin Oscillator (GLO) model




- Surface motion is described in terms of a single 3D harmonic oscillator with a 3x3 frequency matrix.
- Coupling between the molecule and the surface phonons is described by a space rigid shift of the 6D PES.
- Dissipation and thermal fluctuations are included with the help of a ghost 3D oscillator, subject to damping and random forces.

- S. A. Adelman
*J. of Chem. Phys. 71, 4471 (1979).*

- John C. Tully
*J. of Chem. Phys. 73, 1975 (1980).*

- **H. F: Busnengo et al.**
***Phys. Rev. B 72, 125411 (2005)***

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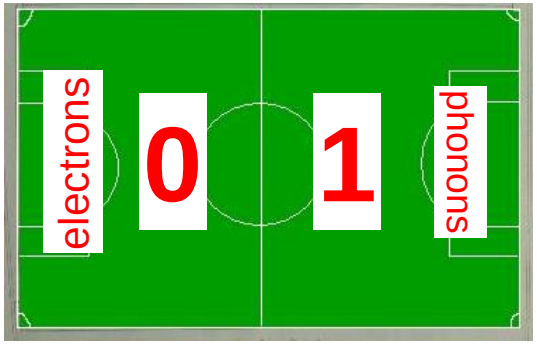
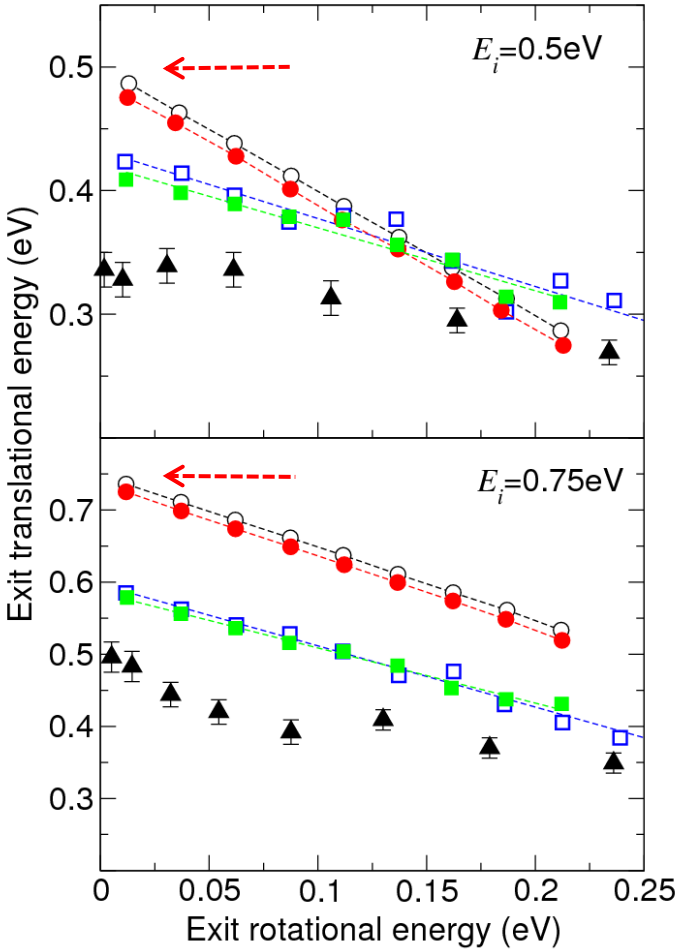



▲ **Experimental data** by Hanisco and Kummel J.Vac.Sci.Technol. A 11 ,1907 (1993)

adiabatic

electronic friction

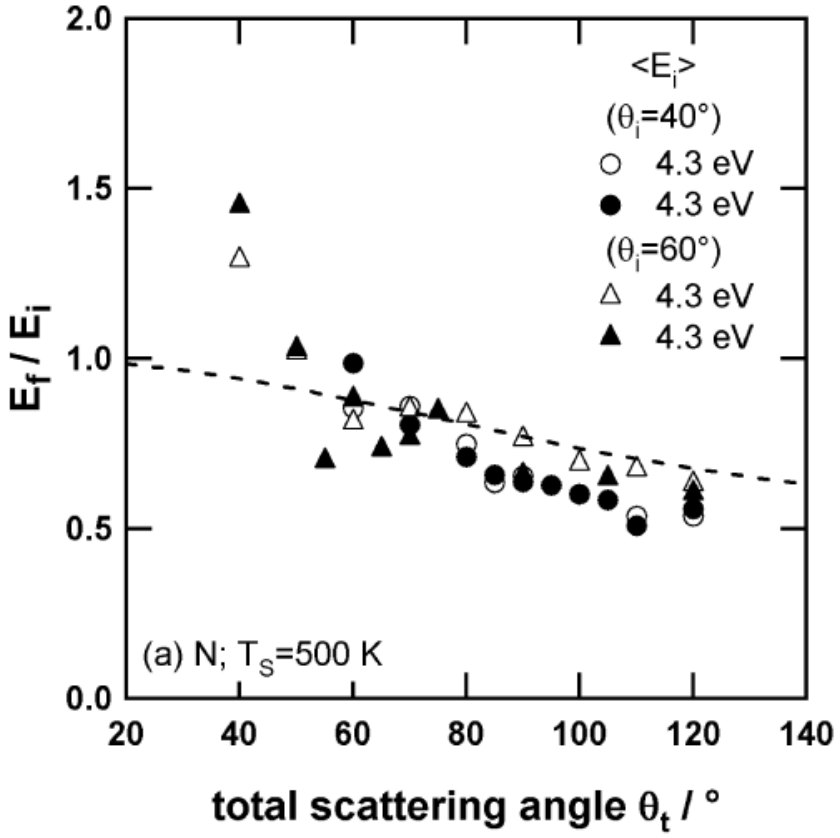
phonons

phonons + friction

Phonon excitations are responsible for most of the energy transfer observed experimentally

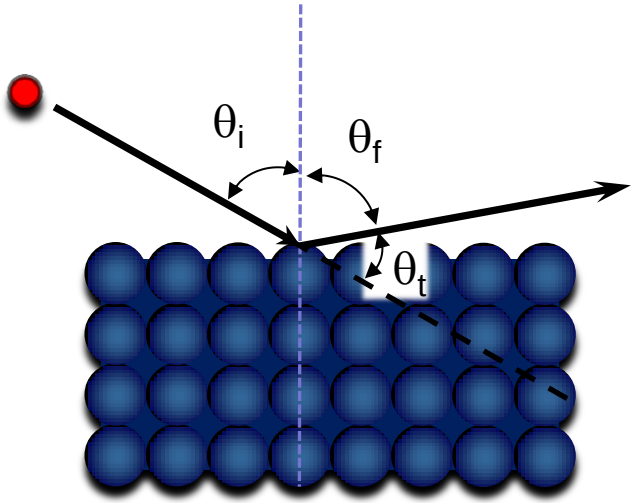
Martin-Gondre *et al.*, Phys. Rev. Lett. 108, 096101 (2012)

# A different system: Atomic N on Ag(111)



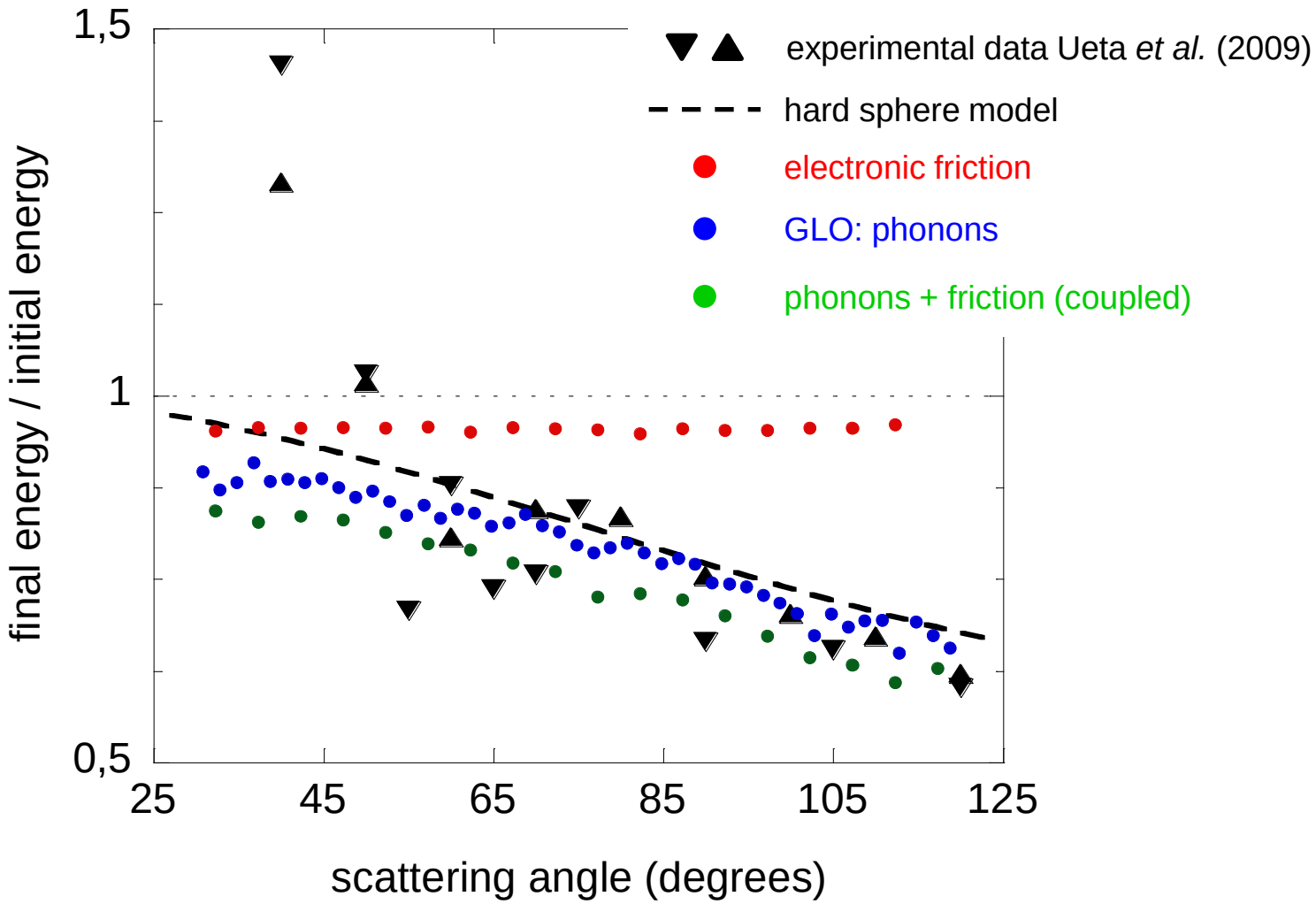

Effusive beam of N atoms with <$E_i$>=4.3eV

Scattering angle: $\theta_t=180-(\theta_i+\theta_f)$

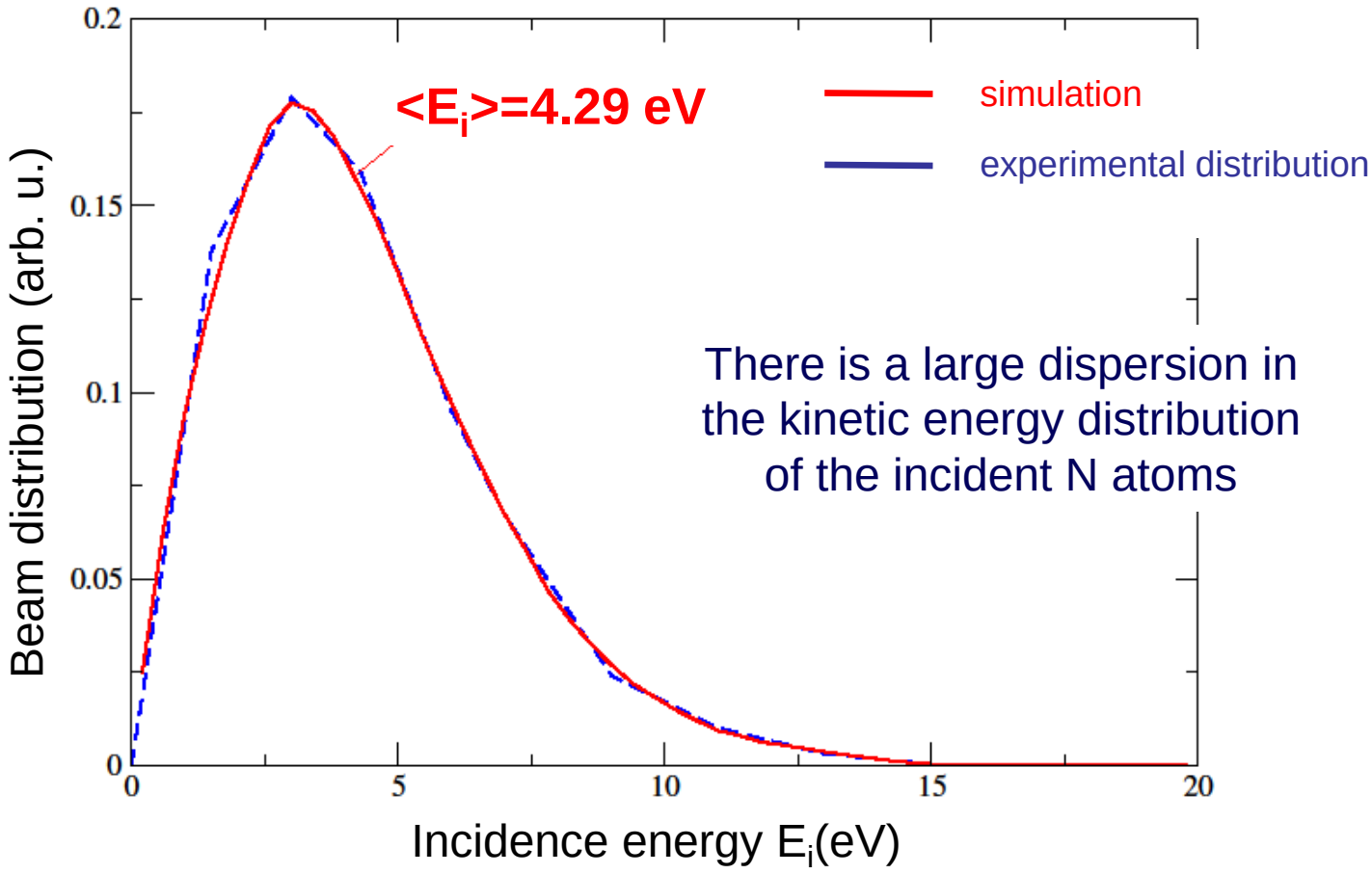



H. Ueta, M. A. Gleeson, and A. W. Kleyn
*J. Phys. Chem. A* ***113****, 15092 (2009)*

# Atomic N on Ag(111)



# *Effusive* beam of N atoms on Ag(111)



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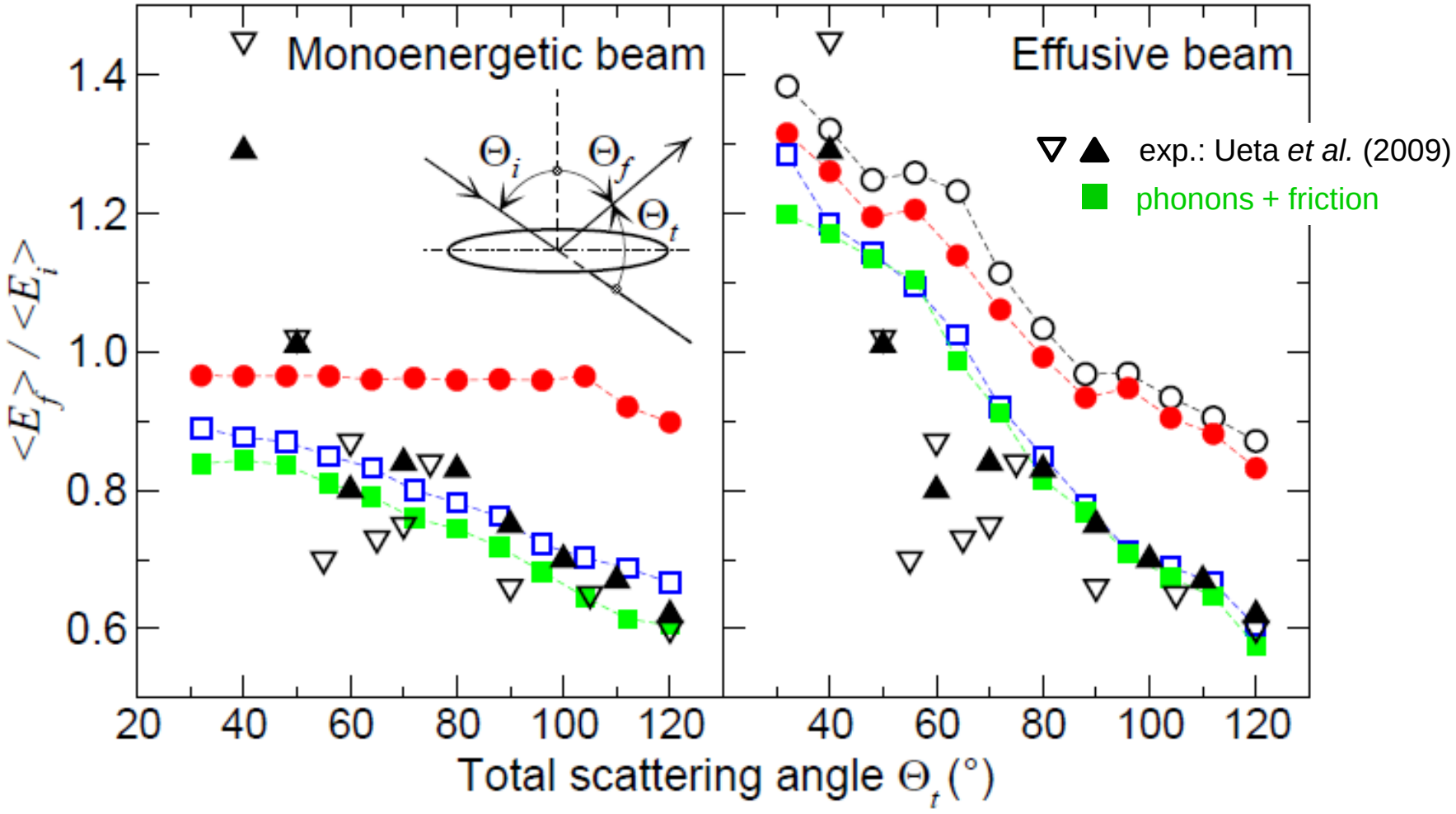


Martin-Gondre *et al.*, Phys. Rev. Lett. 108, 096101 (2012)

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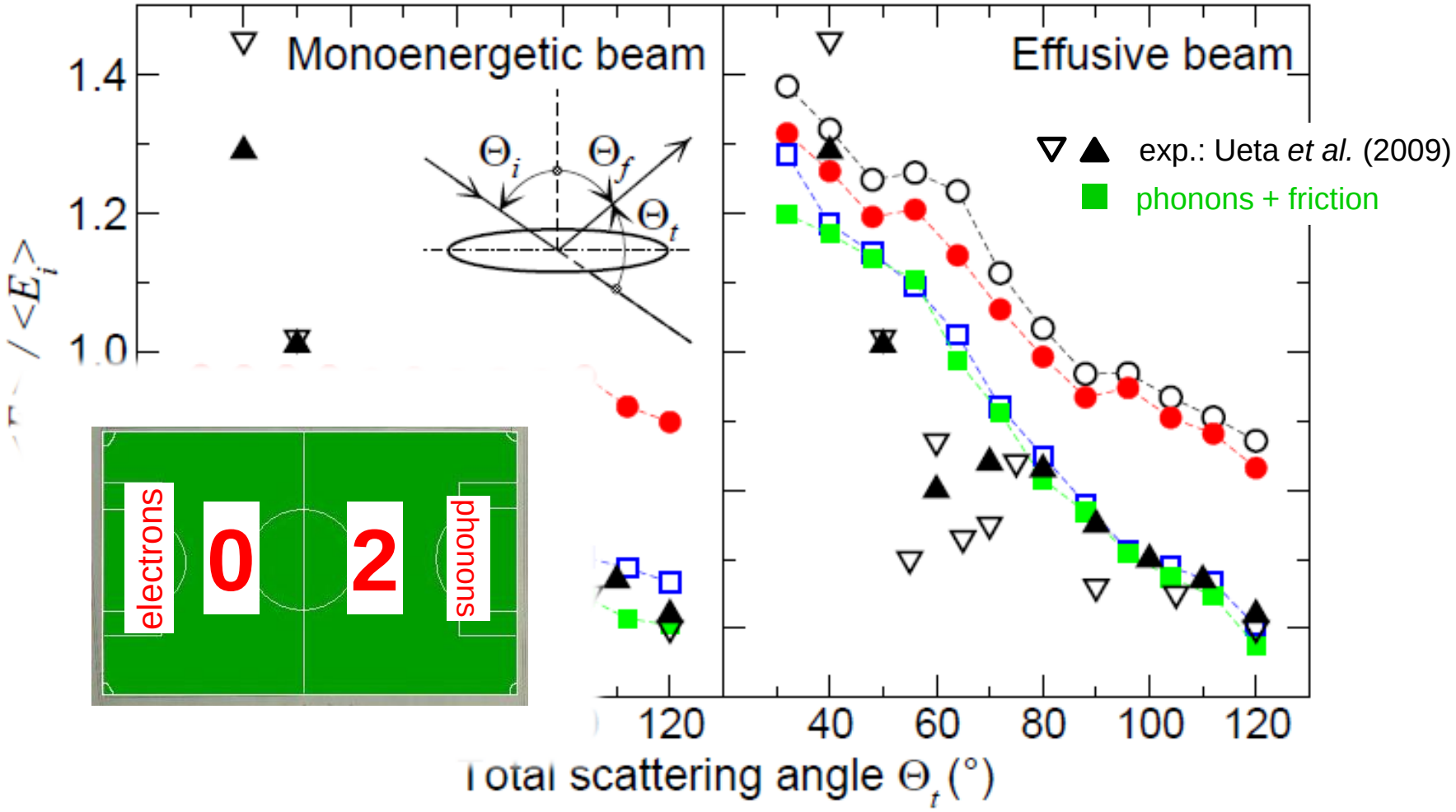
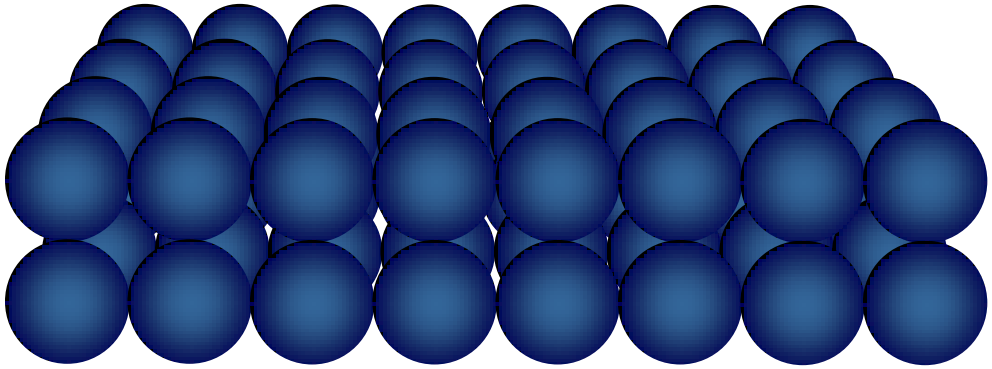


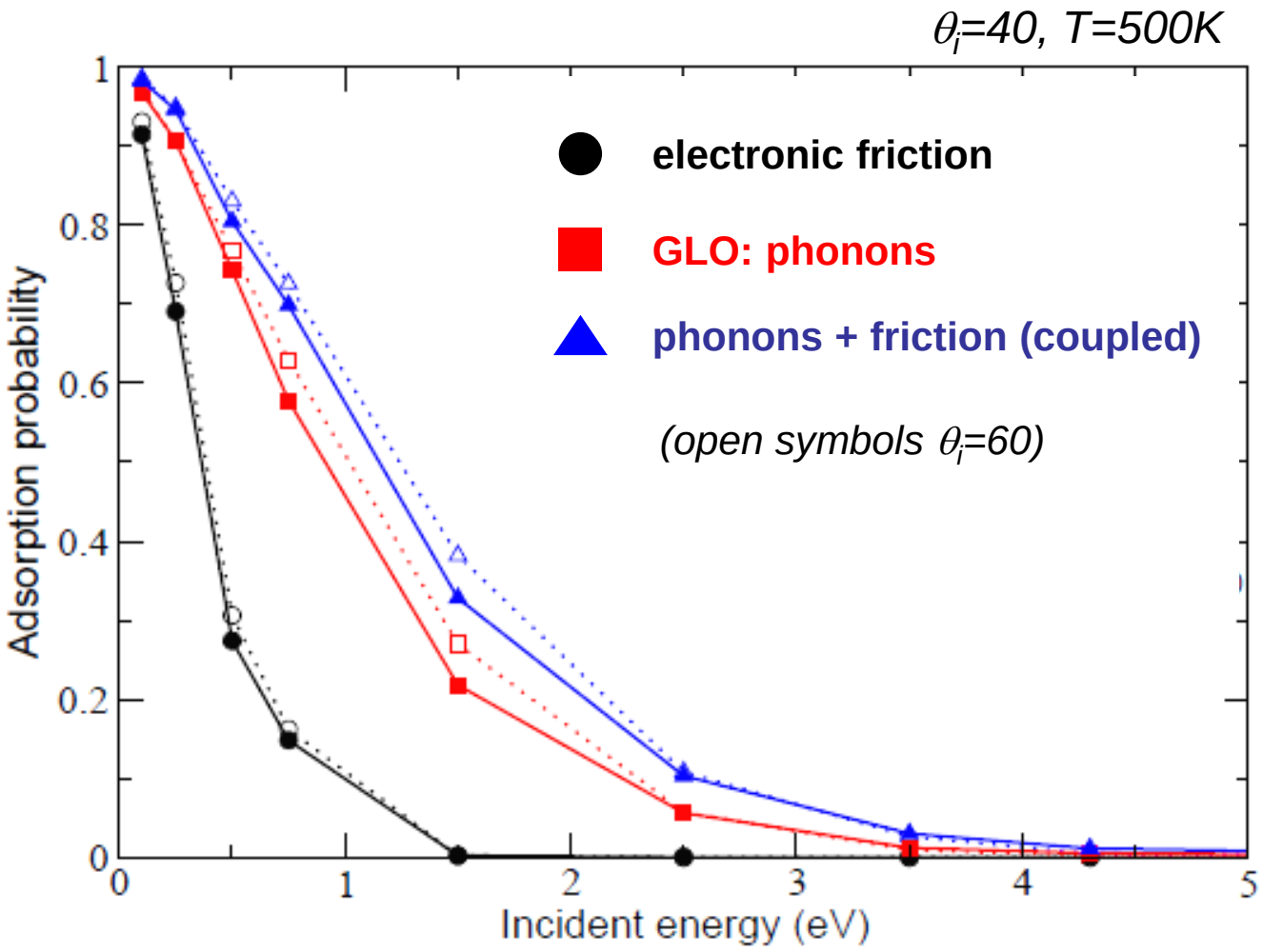

Martin-Gondre *et al.*, Phys. Rev. Lett. 108, 096101 (2012)

# Energy dissipation channels in atomic adsorption at metal surfaces

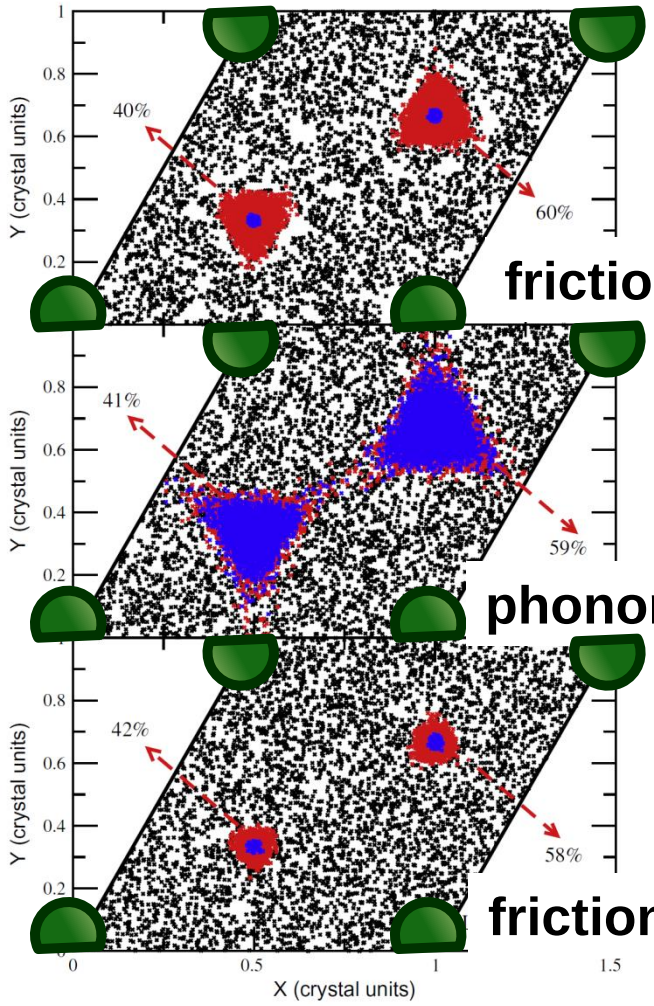
Initial kinetic energy is transferred to the surface



# Energy dissipation channels in the adsorption of N atoms on Ag(111)



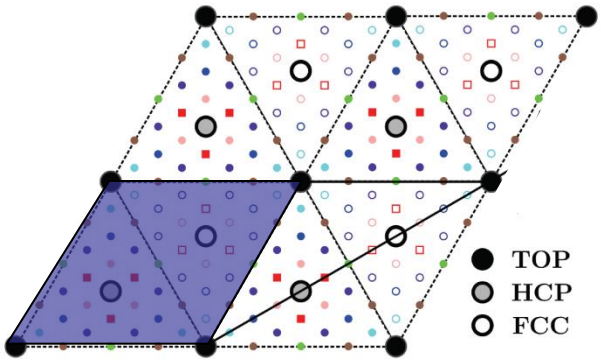
# Time evolution of energy dissipation channels in the adsorption of N atoms on Ag(111)




$E_i$=100 meV, $\theta_i$=40, T=500K

- **Initial position of adsorbed N atoms**
- **Final position of adsorbed N atoms (after 10 picoseconds)**
- **Final position of adsorbed N atoms (after 20 picoseconds)**

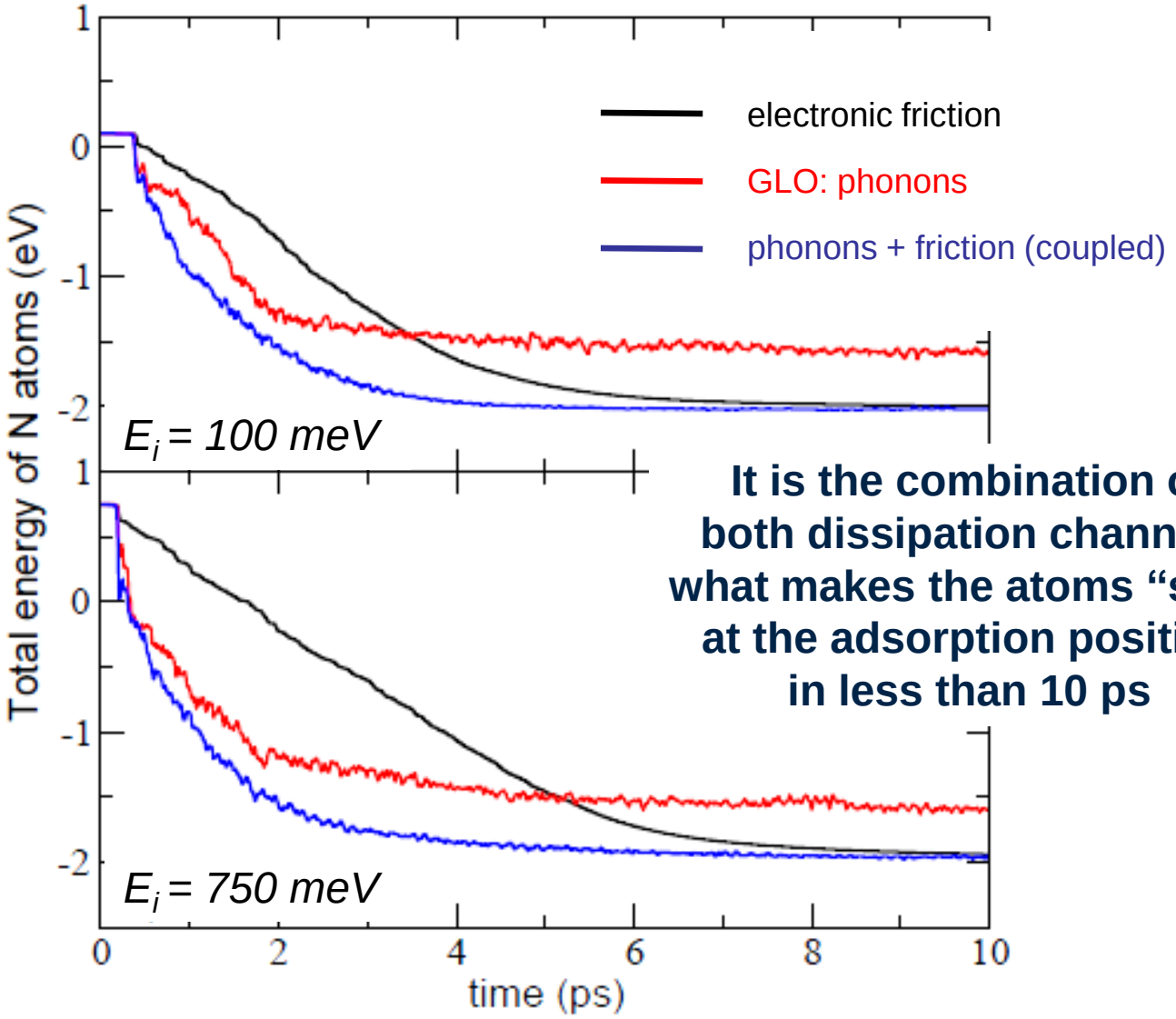
**Ag(111)**



# Adsorption of N atoms on Ag(111): Time scale of the dissipation

$\Theta_i = 40$

$T = 500K$




**It is the combination of both dissipation channels what makes the atoms "stop" at the adsorption position in less than 10 ps**

# Conclusions

- Phonon excitations are responsible for most of the energy transfer between Nitrogen and metal surfaces (at least in the systems studied so far).

- The contribution of phonon and electron excitations to the energy transfer is roughly additive.

- Electronic friction is an additional channel able to accelerate the accommodation process of adsorbates at metal surfaces.


# thank you for your attention

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