Watching phonons getting all excited during O_2 dissociation at Pd(100)

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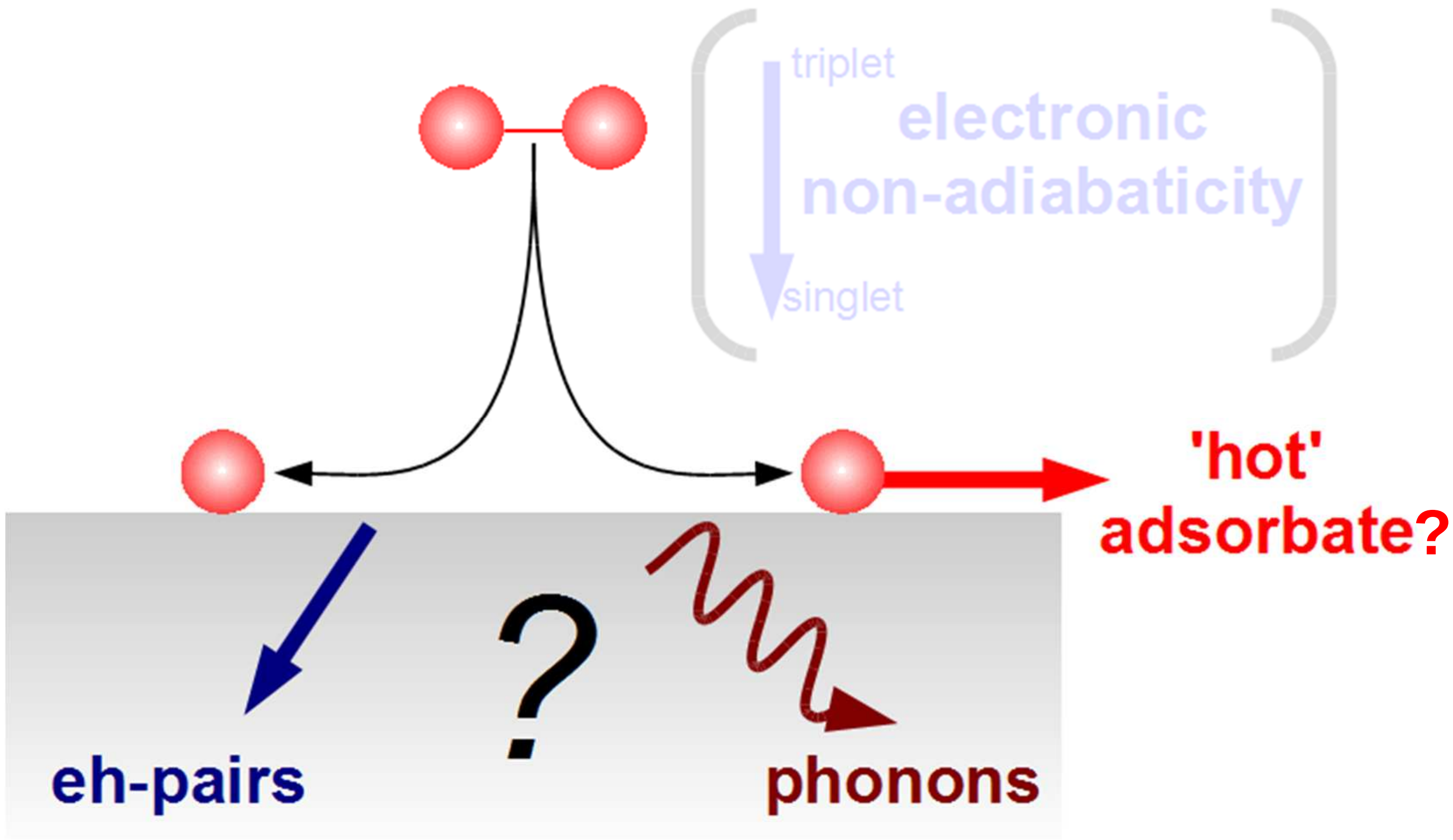
Energy dissipation at surfaces



Showcase O_2/Pd(100): 2.6eV adsorption energy released !
(at GGA/PBE level)

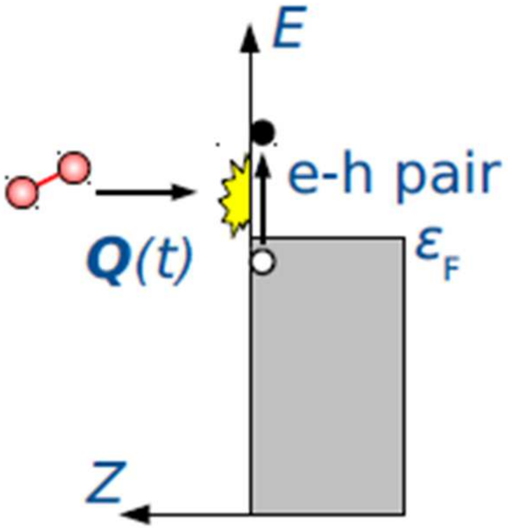
e-h pair excitation: Time-dependent perturbation theory

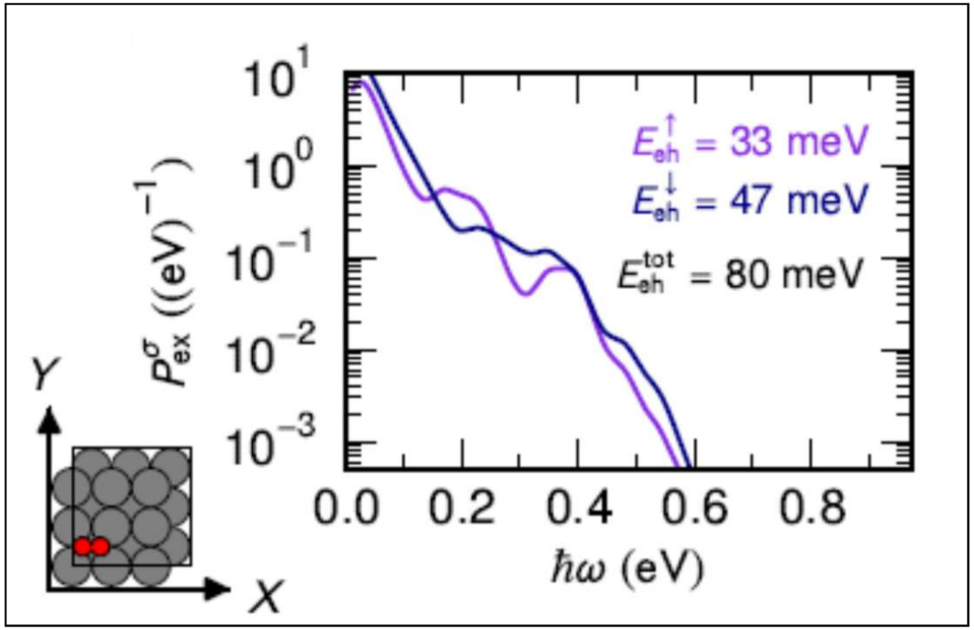
$$h^\sigma(t) \approx h_{(0)} + v^\sigma(Q(t))$$

M. Timmer and P. Kratzer,
Phys. Rev. B 79, 165407 (2009)

$$p_{ij}^\sigma(t) = \frac{1}{i\hbar} \langle \varepsilon_j^\sigma | v^\sigma(Q(t)) | \varepsilon_i^\sigma \rangle \exp\left(\frac{i}{\hbar} (\varepsilon_j^\sigma - \varepsilon_i^\sigma)\, t \right)$$

$$\tilde{P}_{\mathrm{ex}}^\sigma(\hbar\omega) = \sum_{ij} \left| \int_{-\infty}^{+\infty} \mathrm{d}t\, p_{ij}(t) \right|^2 \delta\left(\hbar\omega - (\varepsilon_j^\sigma - \varepsilon_i^\sigma)\right) \qquad E_{\mathrm{eh}}^\sigma = \int_0^{+\infty} \mathrm{d}\varepsilon\, \varepsilon\, P_{\mathrm{ex}}^\sigma(\varepsilon)$$





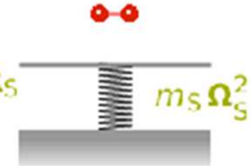
J. Meyer
and
K. Reuter,
New J. Phys.
13, 085010 (2011)

Phonon energy sinks „from the shelf“

- surface oscillator (SO) J. C. Polanyi and R. J. Wolf, *J. Chem. Phys.* **82**, 1555 (1985).

☺ easily coupled to frozen surface potential: $V_{6D}^{SO} = V_{6D}(\mathbf{R}_{6D} - \mathbf{R}_S) + \frac{1}{2} m_S \mathbf{R}_S \mathbf{\Omega}_S^2 \mathbf{R}_S$

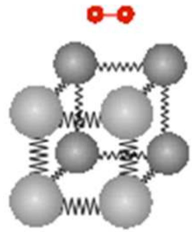
☹ minimalistic Einstein approximation for substrate degrees of freedom



- generalized Langevin equations J. C. Tully, *J. Chem. Phys.* **73**, 1975 (1980).

☺ in principle large bath included in ansatz: $H = H_{bath} + H_{sys} + H_{int}$

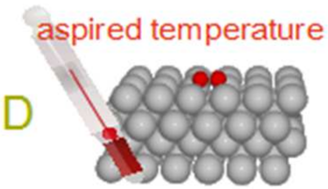
☹ ***but:*** in practice harmonic solid **and** approximations when integrating out bath degrees of freedom



- thermostats e.g. M. E. Tuckerman and G. J. Martyna, *J. Phys. Chem. B* **104**, 159 (2000).

☺ modified EOM allowing to sample ***NVT*** statistical properties via MD

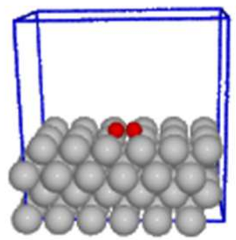
☹ ***but:*** single trajectories lose physical meaning



- *ab-initio* MD (AIMD) e.g. A. Groß, *Phys. Rev. Lett.* **103**, 246101 (2009).

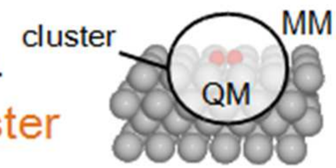
☺ substrate mobility described at *ab-initio* quality

☹ affordable supercell sizes (**PBC**s!) limits description of phonons

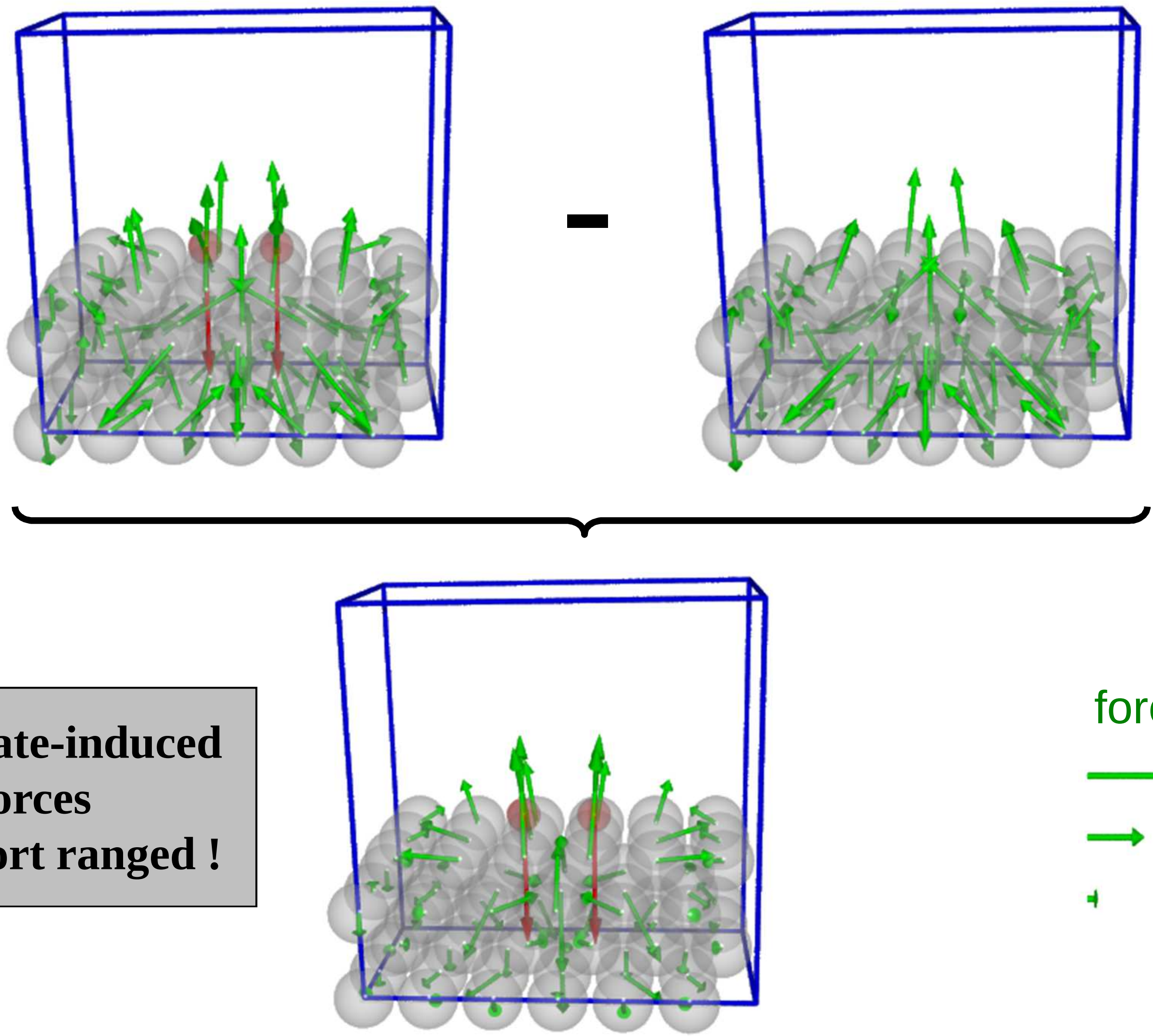


- QM/MM embedding e.g. C. Bo and F. Maseras, *Dalton Trans.* **2911** (2008).

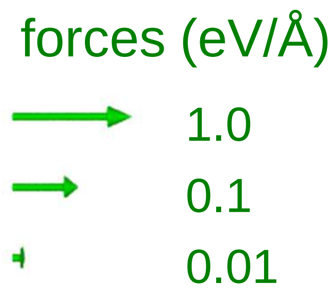
☹ metallic band structure cannot be mimicked by feasibly large cluster



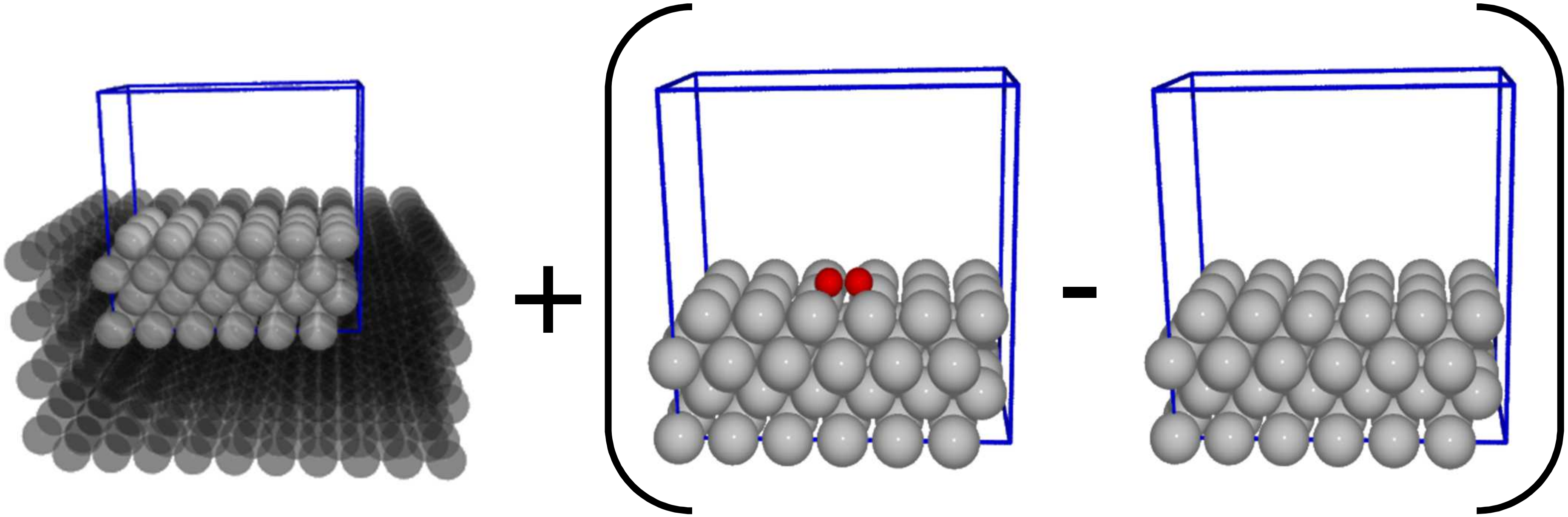
Exploiting locality: Elastic vs. chemical forces



Adsorbate-induced forces very short ranged !



QM/Me embedding



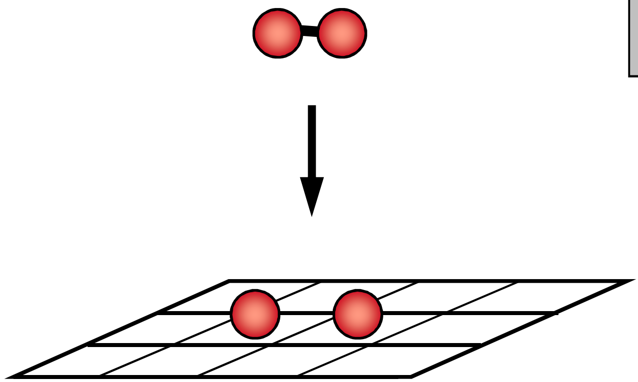
Large-scale MM MD … with additional QM-force contributions

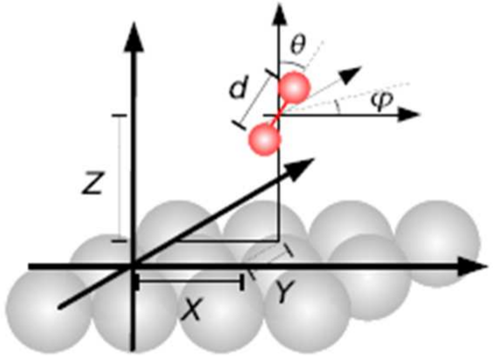
DFT-parametrized MEAM
50x50x50 Pd atoms
LAMMPS
S. J. Plimpton, J. Comp. Phys. 117, 1 (1995)

DFT GGA/PBE
6x3x4 (or 8x3x4) slabs
CASTEP
S.J. Clark *et al.*, Z. Kristallogr. 220, 567 (2005)

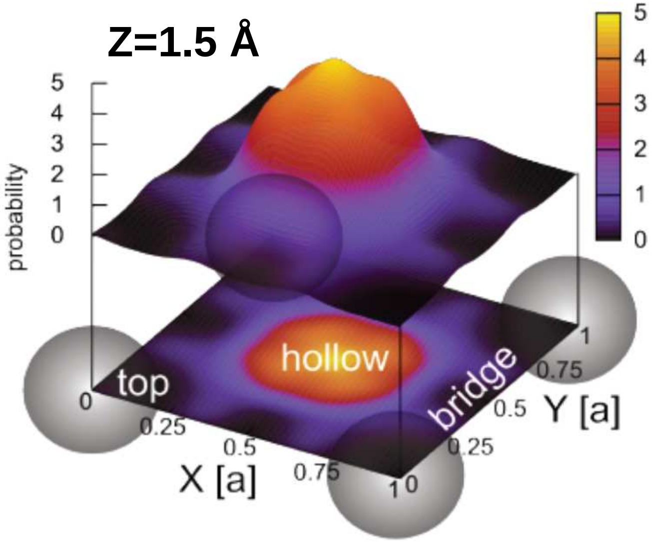
Forget Markov: Hot adatoms are alive!

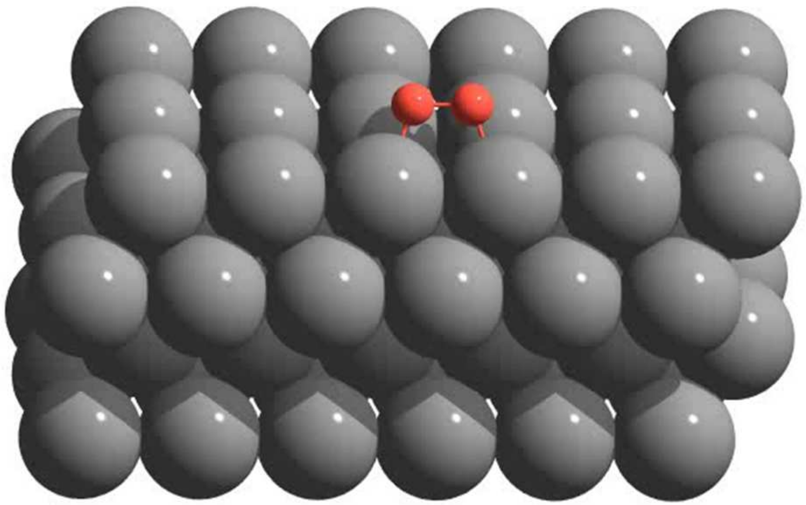
$$k = \tilde{S}_{\circ}(T)\frac{pA_{\mathrm{uc}}}{\sqrt{2\pi m k_{\mathrm{B}} T}}$$





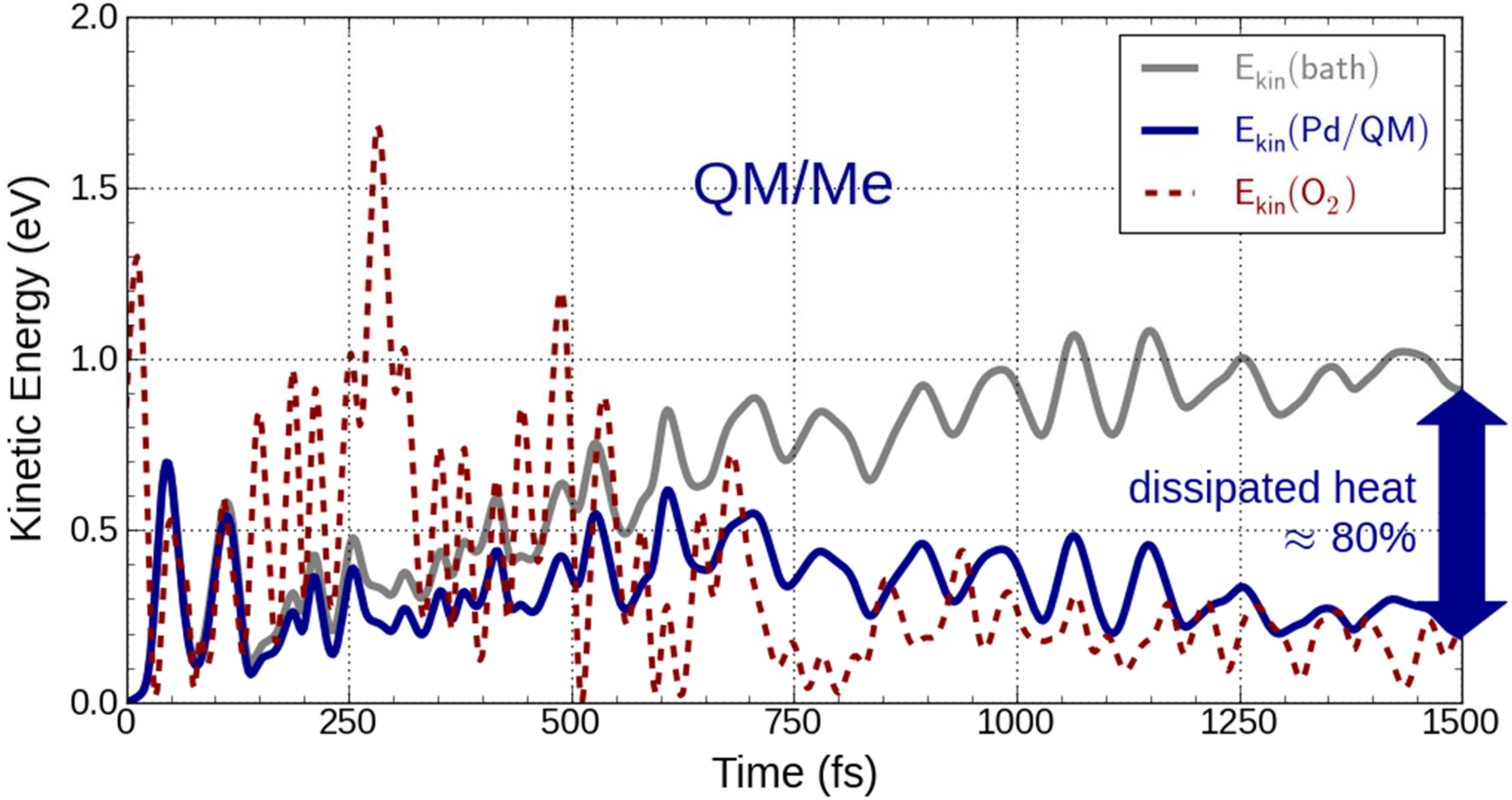
$V_{\mathrm{fsa}} = (X, Y, Z, d, \theta, \varphi)$





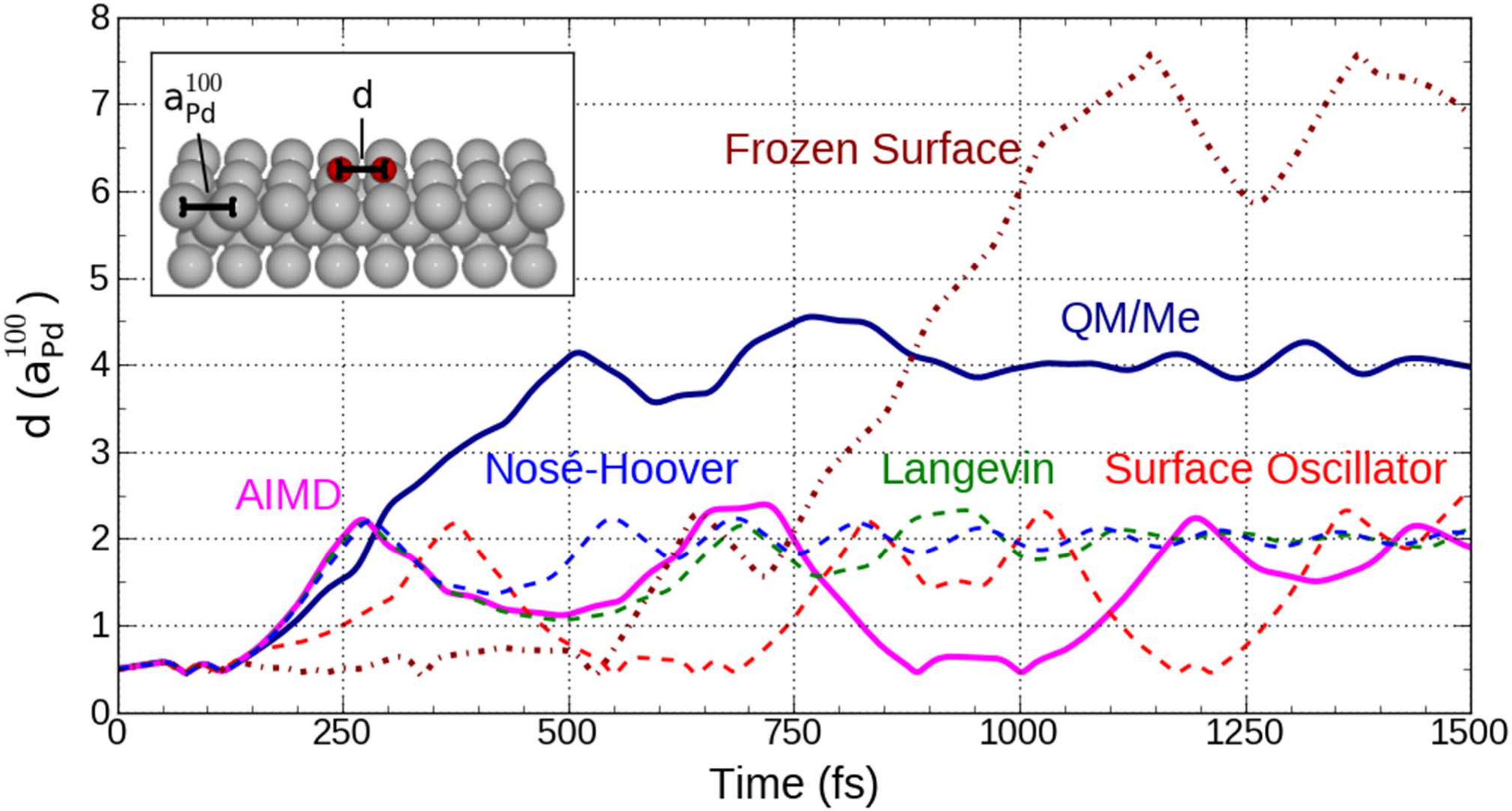
J. Meyer and K. Reuter, in preparation

Energy dissipation out of QM region



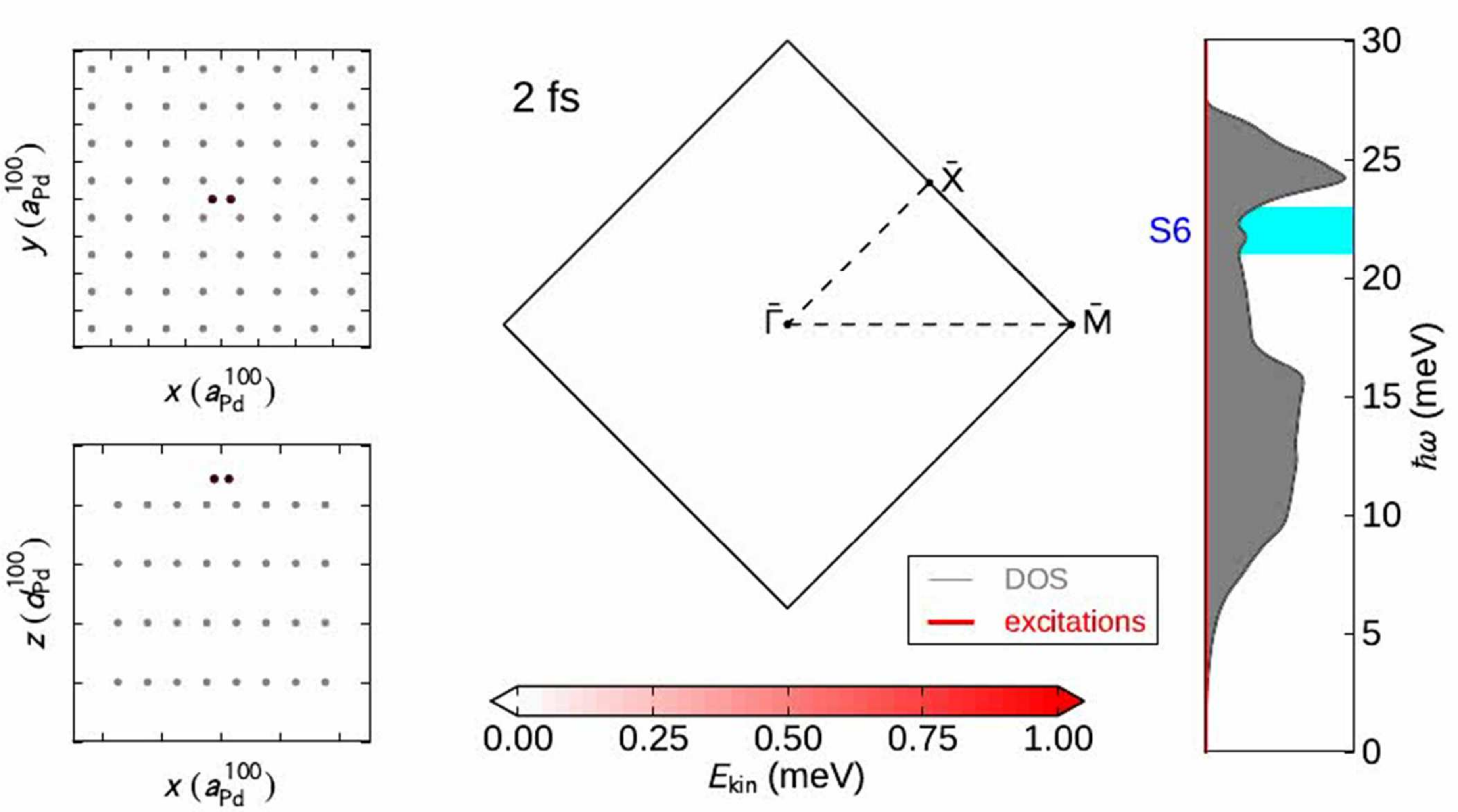
Dominant fraction of released energy is dissipated out of QM-region on picosecond timescale

Energy sinks from the shelf - revisited



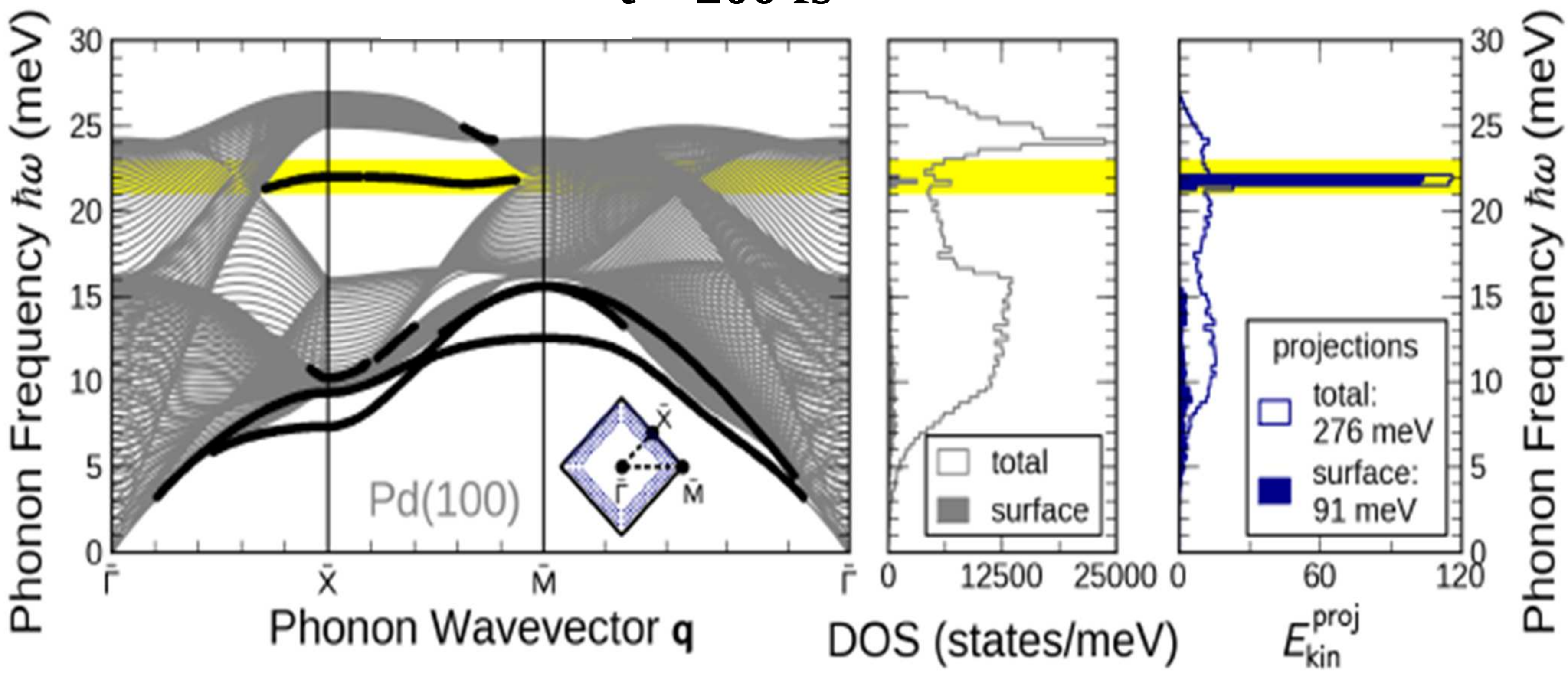
Qualitatively different (hot) adsorbate dynamics (at least for the present trajectory…)

Watching phonons getting all excited…



The role of surface phonons

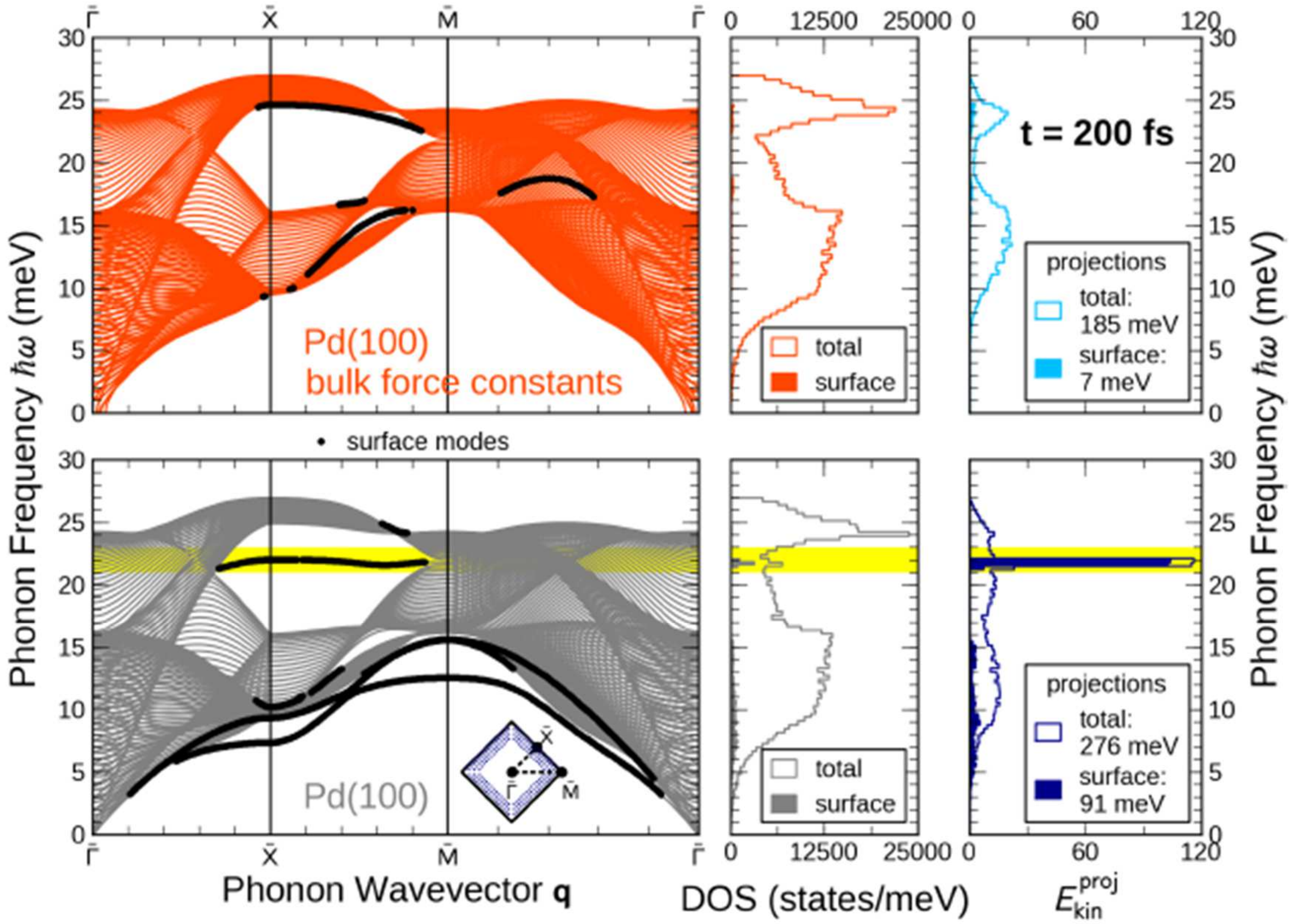
t = 200 fs



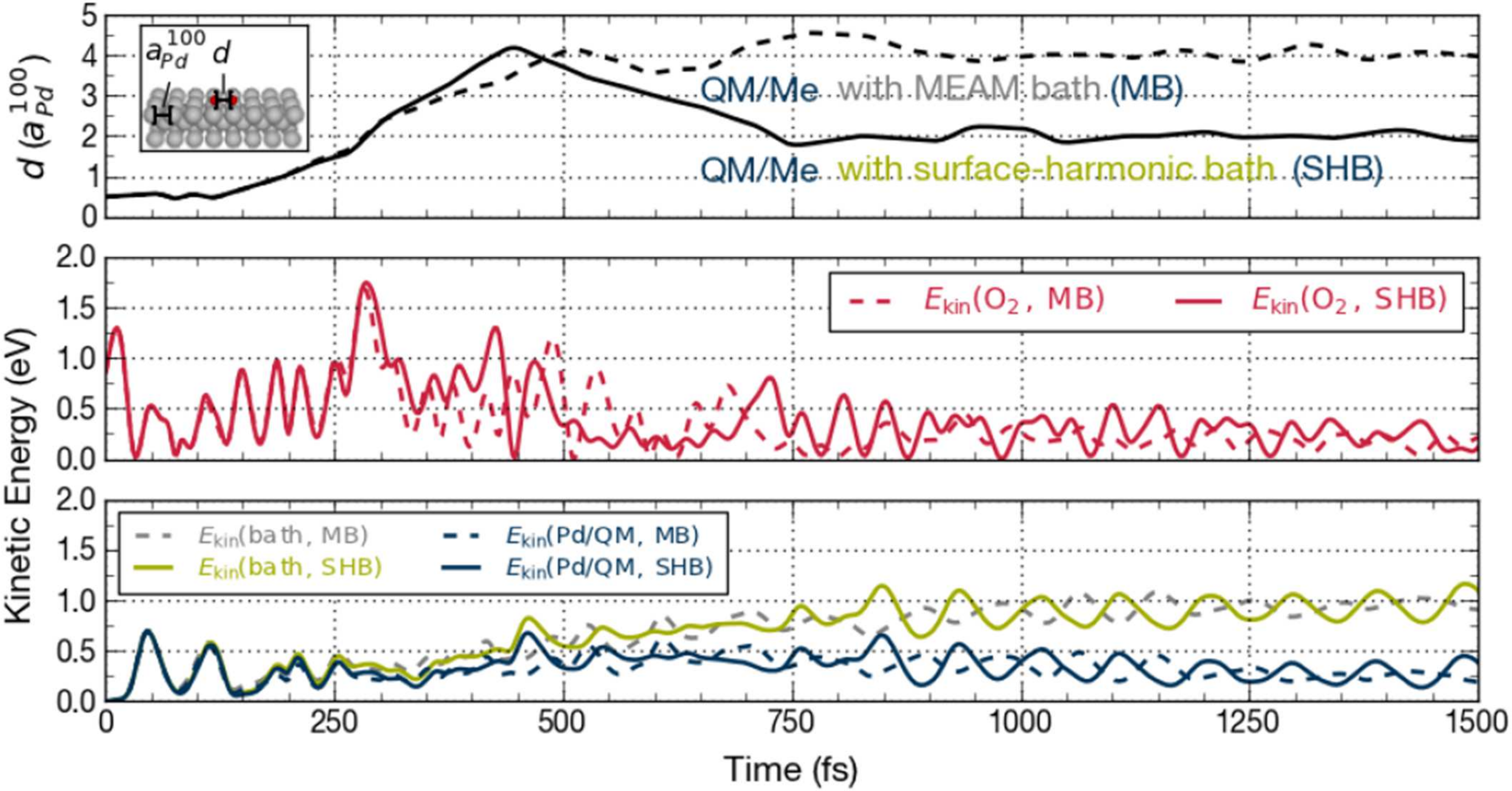
Strong non-equilibrium population of non-Rayleigh surface phonon modes

J. Meyer and K. Reuter, in preparation

When details matter: Substrate without surface phonons



When details matter: Comparison to harmonic substrate



Beat the heat…

QM/Me seamlessly enriches *ab initio* MD at metal surfaces by „correct" (classical) physics of (surface) phonons

- **Counterpart of QM/MM simulations for insulating substrates**
- **Essentially the same computational cost as regular AIMD**

Application to O_2 dissociation at Pd(100) reveals plenty of interesting physics

- **Hot adatom motion over several lattice constants**
- **Dynamics governed by excitation of non-Rayleigh surface phonon modes**
- **Phonon anharmonicity is another important factor (hitherto often neglected in surface dynamic studies)**

DFG

MMM

Frontiers…

- Get more trajectories… (and compare to stochastic theories)
- Trend understanding of electronic non-adiabaticity in surface dynamical processes at metal surfaces
- Coupling of adiabatic vibrational coupling (QM/Me) with electronic non-adiabaticity (el. friction?)