

# **“Hot” adatoms hopping: Phononic dissipation & equilibration dynamics from first-principles**

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Exothermic surface chemical reactions may easily release several electron volts of energy. This challenges first-principles based dynamical simulations to account for adequate energy dissipation channels. Focusing on phononic dissipation, a novel embedding scheme for metallic substrates allows for energy to be dissipated out of a quantum-mechanically described reaction zone and into a computationally undemanding, yet reliably described, extended bath [1]. In the application to oxygen dissociation over Pd(100) this predicts “hot” dissociation fragments traveling ballistically over several lattice constants as a consequence of non-immediate energy transfer to the metal surface. This raises fundamental questions when considering the short-range transient mobility measured experimentally for the similarly exothermic O<sub>2</sub>/Pd(111) reaction [2]. Here, we elucidate phononic dissipation within the (111) as compared to the (100) surface and explain the small net displacement by revealing randomized trajectories of hyperthermal hops between neighboring hollow sites due to scattering by the strongly corrugated chemisorption potential. We therefore invalidate the simplistic physical picture implying a minimal number of hops for small adatom separations and anticipate further paradigm shifts required to accommodate such “hot chemistry”, for example, in our current understanding of heterogeneous catalysis.

## **References:**

- [1] J. Meyer, K. Reuter, *Angew. Chem. Int. Ed.* **53**, 4721-4724 (2014).
- [2] M.K. Rose, A. Borg, J.C. Dunphy, T. Mitsui, D.F. Ogletree, M. Salmeron, *Surf. Sci.* **561**, 69-78 (2004).