Supporting Information for:

The Role of Tensorial Friction in Nonadiabatic Energy Loss at Metal Surfaces

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Section I. Computational Details

a) TDPT Calculations

In the quasistatic (zero-frequency) limit, eq. 2 in the manuscript for the friction tensor becomes:

$$\Lambda_{ij} = \pi\hbar \sum_{k,\nu,\nu'} \left\langle \psi_{k\nu} \middle| \frac{\partial}{\partial R_i} \psi_{k\nu'} \right\rangle \left\langle \psi_{k\nu'} \middle| \frac{\partial}{\partial R_j} \psi_{k\nu} \right\rangle (e_{k\nu'} - e_{k\nu}) \delta(e_{k\nu'} - e_{k\nu}) (f(e_{k\nu}) - f(e_{k\nu'})),$$

where $f(e_i)$ is the population of the e_i KS state according to Fermi-Dirac statistics.
In this work we represent the electronic structure in a local atomic orbital basis. Hereby we expand molecular states by linear combination of basis functions:

$$|\psi_{k\nu}\rangle = \sum_a C_{k\nu}^a |\varphi_{k\nu}^a\rangle,$$

wherein the basis functions are formally defined as Bloch-like generalized basis functions. As in the original derivation by Head-Gordon and Tully [1] we can thereby re-express the nonadiabatic coupling elements through the generalized eigenvalue problem as:

$$\left\langle \psi_{k\nu} \middle| \frac{\partial}{\partial R} \psi_{k\nu'} \right\rangle \approx \frac{C_{k\nu}^a \left(\frac{\partial}{\partial R} H_k^{ab} - e_F \frac{\partial}{\partial R} S_k^{ab} \right) C_{k\nu'}^a}{e_{k\nu'} - e_{k\nu}},$$

where $H_k^{ab} = \langle \varphi_k^a | H_k | \varphi_k^{ab} \rangle$ and $S_k^{ab} = \langle \varphi_k^a | \varphi_k^b \rangle$.
The delta function is approximated with a finite width (see main text) Gaussian function centered around the Fermi level.

b) LDFA Calculations

In order to compare the TDPT results with LDFA, we used the formulation of the rate described in eq (8) of Ref. 2:

$$\Gamma = \frac{3\hbar}{m r_s^2} \sqrt[3]{\frac{4}{9\pi}} \sum_{l=0}^{\infty} (l+1) sin^2 (\delta_{l+1} - \delta_l),$$

where r_s is the Wigner-Seitz radius associated with the electron density ρ: $r_s = \sqrt[3]{\frac{3}{4\pi\rho}}$,
$\delta_l = \delta_l(r_s)$ are the tabulated phase shifts associated with the angular momentum quantum number l at a particular radius r_s. We used the density created by the clean Pd(100) surface at the corresponding Cartesian positions of the hydrogen atom (LDFA-IAA method). The tabulated phase shifts are taken from Ref. 3 and interpolated to arrive at the value at a desired r_s.

c) Delta function approximation

Equation (2) in the main text includes the Dirac delta function, which is in the present work approximated as a Gaussian function. The width of the Gaussian is an empirical parameter, which in the reported results was chosen to be 0.6 eV. This finite width

transforms a discrete state spectrum into a continuous Density-of-States (DOS). This is a standard approach in Brillouin zone sampling, as first introduced by Methfessel and Paxton [4]. The width, however, does not significantly impact the lifetime: changing the Gaussian width from 0.2 to 1.0 eV leads to lifetime variations of about 15% at the chosen Monkhorst-Pack [5] *k*-point grid of 20x20x1.

Section II. Cartesian friction tensor of H on Pd(100) surface

In order to demonstrate the correlation of the symmetry of the friction tensor with the symmetry of the PES, we plotted each Cartesian component of the friction tensor along the minimum energy path (See Fig. 2, main manuscript).

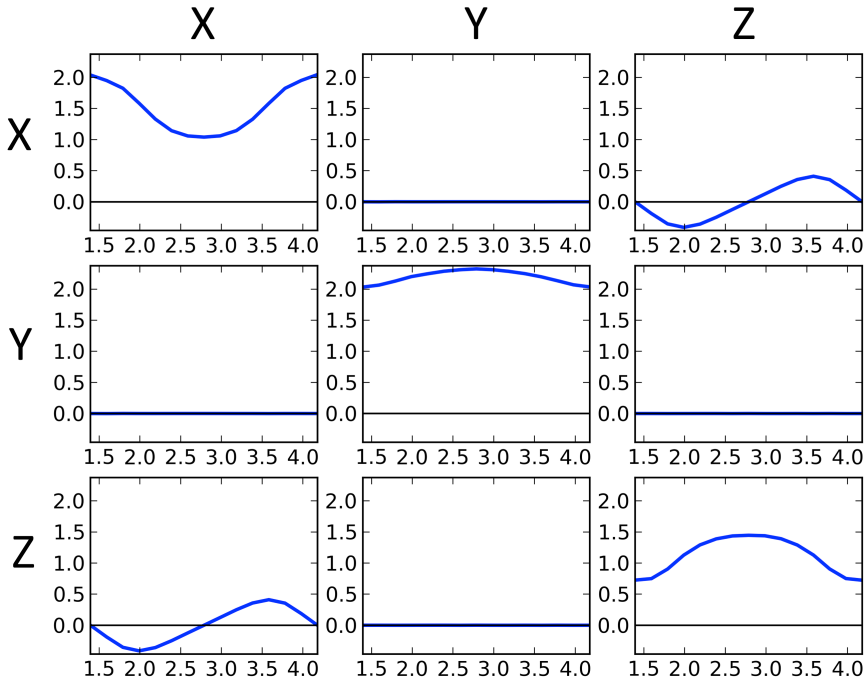

Figure S1. Cartesian components of the friction tensor (1/ps) as a function of the reaction coordinate along the minimum energy path (in Angstrom distance from the x-axis origin of the unit cell) described in Fig. 2 of the main manuscript.

In Figure S1 we show all matrix elements of the Cartesian friction tensor. We can see that the friction tensor is completely diagonal in the high-symmetry points (hollow: first and last points and bridge: middle point at 2.75 Å). As the hydrogen atom leaves the hollow site, the off diagonal *xz* component of the tensor starts growing. It reaches zero again at the saddle point. The non-diagonal *xz* component is negative during the motion uphill to the saddle point and is positive while moving downhill to another minimum.

Section III. Simulation of the CO internal stretch dynamics on the Pd(100) surface

We used the Langevin dynamics equation (eq. 1, main manuscript) to simulate the dynamics of the internal stretch of the CO molecule adsorbed at the equilibrium top site. For this one dimensional problem, we interpolated the potential energy surface and the internal stretch normal mode component of the friction tensor (shown as lifetime in Fig S2 A) over 121 points for the CO bond length within ± 0.15 Å from the equilibrium value (1.164 Å). Forces, positions, and velocities were propagated according to the Leapfrog algorithm. We only consider energy loss due to the electronic friction term and neglect the random fluctuating term.

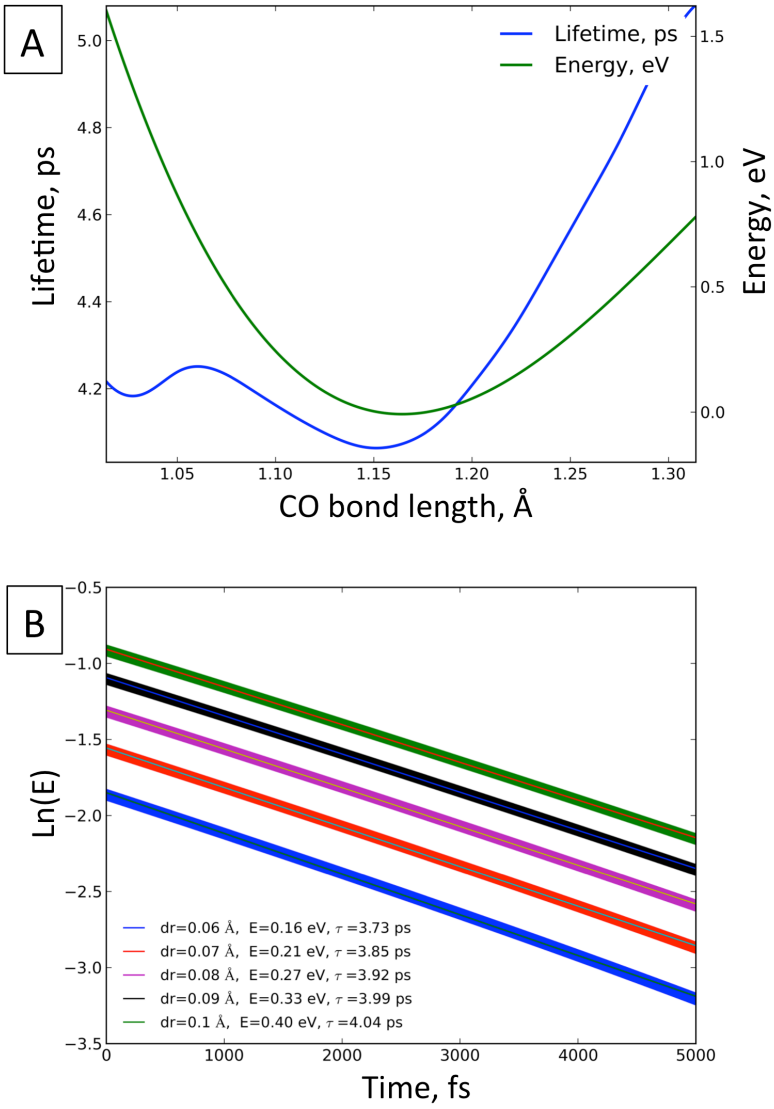

Figure S2. Langevin dynamics for the CO internal stretch: (A) interpolated potential energy surface (right y-axis) and the internal stretch normal mode component (left y-axis)

of the friction tensor (ps) and (B) logarithm of the total energy (in eV) as a function of simulation time (in fs) for different initial stretch displacements.

We then monitored the dissipation of the total energy of the oscillator as a function of time for various values of initial stretch of the CO bond. The lifetimes were then calculated through the slope of the logarithm of the total energy under the assumption of exponential energy decay. The resulting lifetimes varied about 10% with the extent of bond stretch ranging between 0.06-0.10 Å. The vibrational energy of the CO internal stretch calculated from the harmonic approximation is 0.25 eV, which corresponds to the lifetime of 3.92 ps (Figure S2, B). This value is in good agreement with the static value calculated using TDPT (4.07 ps).

Section IV. References.

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