Supporting Information

Hot-electron effects during reactive scattering of H_2 from Ag(111): the interplay between mode-specific electronic friction and the potential energy landscape

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I. Neural network representation of the electronic friction tensor

The tensorial friction ($\mathbf{\Lambda}$) differs from the scalar potential energy or electron density in that it has a matrix form and is directionally-dependent on molecular coordinates. In other words, several symmetry equivalent molecular configurations with regard to the invariant potential energy or isotropic friction coefficient would have totally different friction tensor elements. This feature immediately makes it difficult for the extension of any standard methodology for potential energy surface (PES) construction to representing the friction tensor as a function of molecular geometry. The key to solve this issue is to find a unique relationship between the molecular geometry and the friction tensor.

To this end, we choose to fit the elements of the friction tensor in Cartesian coordinates inside an irreducible triangle in the surface unit cell, whose three vertices correspond to the top, fcc, and hcp sites, respectively, as depicted in Fig. 1b. In this triangle, each friction tensor element is symmetry unique with an one-to-one mapping to a molecular geometry, thus posing no problems for fitting. As the first step, we transform the coordinates and corresponding friction tensors into this triangle. This can be done by first translating a data point with the molecular center outside the unit cell into the cell, followed by a series of reflections illustrated in Fig. 1b.[1] Here, $\mathbf{U_1}$, $\mathbf{U_2}$, and $\mathbf{U_3}$ are the corresponding transformation matrices, respectively. Subsequently, we can use any regular interpolation approach for constructing PESs to accurately represent the relationship between the molecular geometry and each element of the friction tensor in this symmetry unique triangle. In this work, we take advantage of the high fidelity of neural networks, in which the six Cartesian coordinates of the H_2 molecule and each individual friction element are set as the input and output, respectively. Since the friction tensor is a symmetric matrix, only the upper triangular elements $\mathbf{\Lambda}_{ij}\,(i \le j)$ are to be determined in practice.

Similar mapping schemes have been successfully applied in constructing PESs for gas-surface systems using either NNs[2-4] or modified Shepard interpolation,[1] where the data were all transformed into a subspace taking advantage of the surface symmetry. One drawback of these PESs is that the gradient of potential energy (*i.e.* force) may not be continuous at the boundary, resulting in non-conservation of total energy when running classical trajectories. However, this is not a problem when representing friction tensor as we only need values of friction coefficients but no gradients in the generalized Langevin equation.

Once the fitting is done, it is straightforward to calculate the friction tensor when the molecule is in the triangle. However, we need the following procedure back-and-forth to evaluate the friction tensor at any point outside the triangle. (1) We find the symmetry equivalent geometry of that point in the irreducible triangle. (2) We calculate each individual NN interpolated friction coefficient at the symmetry equivalent geometry. (3) We take the inverse transformations with $\mathbf{U}_3^{-1}$, $\mathbf{U}_2^{-1}$, and $\mathbf{U}_1^{-1}$ on the combined full 6×6 friction tensor to recover the corresponding friction tensor associated with the original geometry.

II. Quasi-classical trajectory calculations

Quasi-classical trajectory (QCT) calculations with and without electronic frictions were performed using the VENUS code[5] heavily modified by us. The trajectories were initiated with H_2 above the Ag(111) surface (Z=8.0 Å) and its internal coordinates and conjugate momenta were sampled semi-classically for given vibrational and rotational quantum numbers v and j.[6] Only the (v=2, j=0) state of H_2 and D_2 molecules with normal incidence were considered in this work. The initial lateral positions of the molecules were selected randomly covering the unit cell and orientations were randomly distributed. The integration time step was set to be 0.10 fs using Beeman's third-order algorithm.[7] The molecule was considered dissociated on the surface when the H-H distance is larger than 2.5 Å, while non-reactive if it is scattered back beyond 8.1 Å above the surface. For scattered molecules, the vibrational action number v was determined by Einstein−Brillouin−Keller (EBK) semi-classical quantization,[8] and rotational quantum number j by the quantum mechanical expression for rotational angular momentum $J = \sqrt{j(j+1)}\hbar$. As in Ref. 9, the standard histogram binning was imposed. The dissociation and scattering probabilities were calculated as the ratio of the number of reactive trajectories (N_r) and the total number of trajectories (N_t), and that of the number of trajectories with specific v and j (N_{vj}) and the number of scattered trajectories (N_s), respectively. Our definition follows the convention as in recent experimental[10] and theoretical[11] studies. It should be noted, however, that the scattering probability was defined in Ref. 9 as N_{vj}/N_t, which might have a small effect at low incident energies but apparently tends to yield lower values at higher incident energies because more molecules would indeed dissociate.

References

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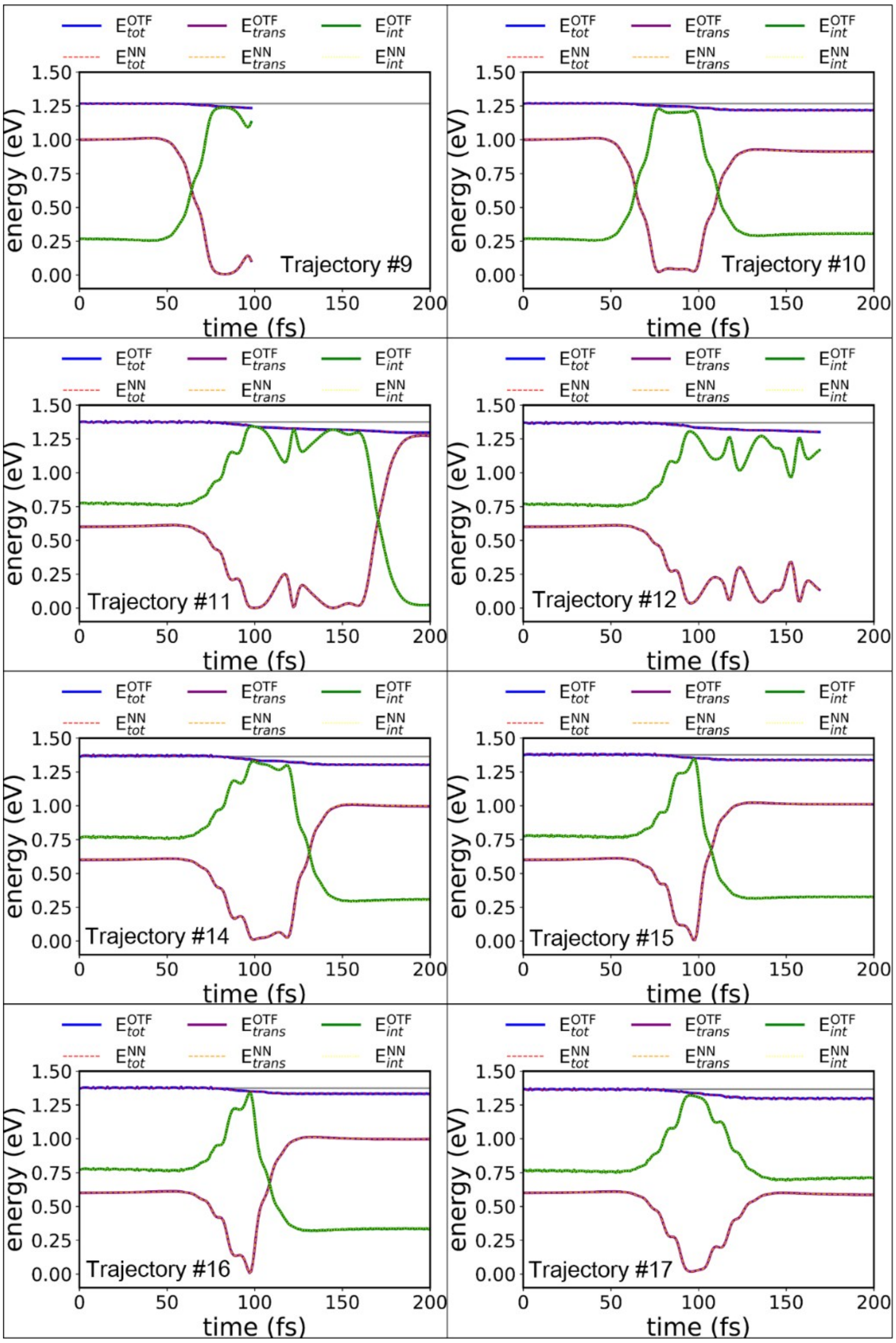

Figure S1. Comparison of the total, internal and translational energies as a function of time for eight representative trajectories computed with the on-the-fly MDEF simulation (OTF, solid lines)[12] and those with the simulation based on the interpolated friction tensor (NN, dotted lines), under the same initial conditions. The trajectory numbering corresponds to that was given in Ref. 12 with H_2 in both the ground and first excited states (#9 and #10 correspond to v=0, the rest to v=1).

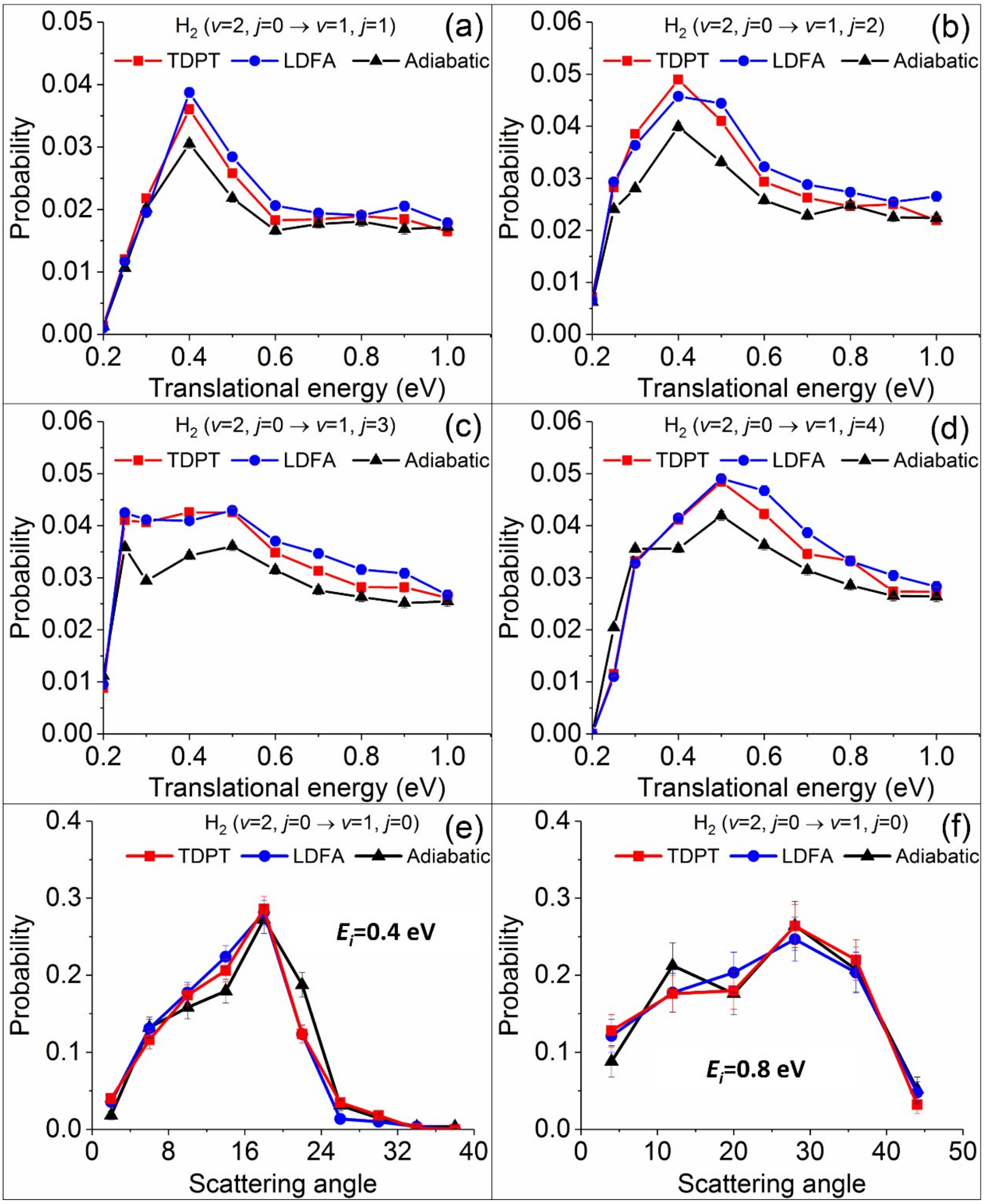

Figure S2. State-to-state scattering probabilities from H$_2$(v=2, j=0) to (a) H$_2$(v=1, j=1), (b) H$_2$(v=1, j=2), (c) H$_2$(v=1, j=3), (d) H$_2$(v=1, j=4), and scattering angular distributions from H$_2$(v=2, j=0) to H$_2$(v=1, j=0) at incidence energies (E_i) of 0.4 eV (e) and 0.8 eV (f), obtained without (black triangles) and with electronic friction by LDFA (blue circles) and TDPT (red squares).

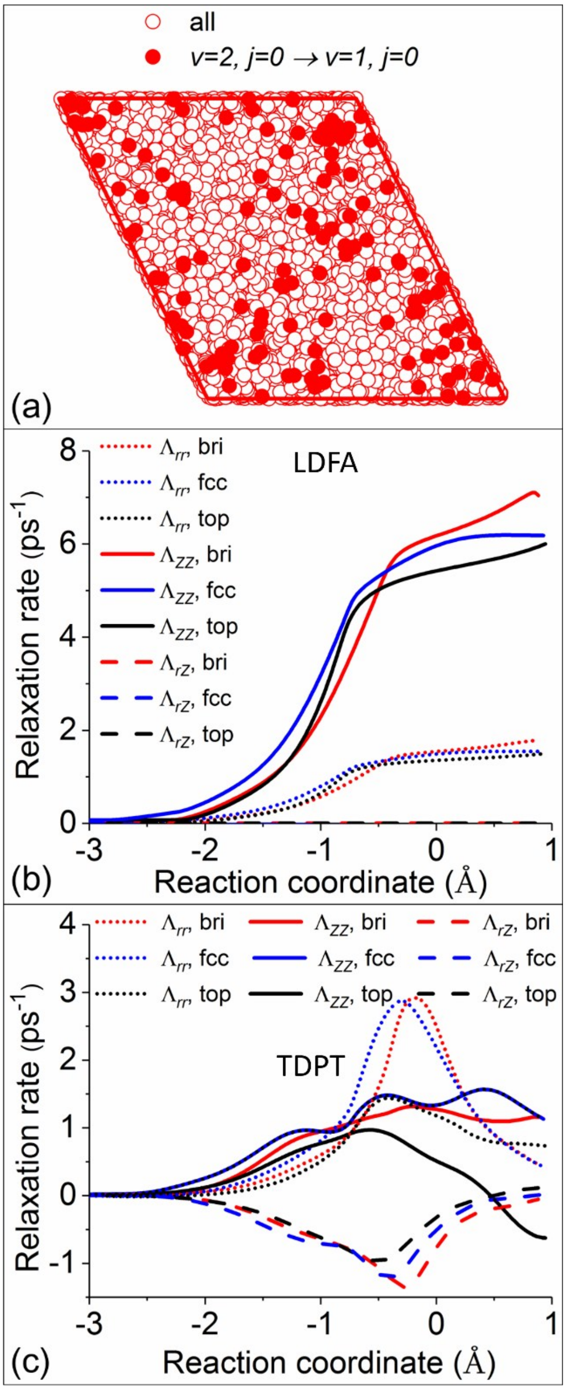

Figure S3. (a) Distribution of initial positions in the unit cell of all scattered trajectories (open circles) and those with vibrational deexcitation from H_2(v=2, j=0) to H_2(v=1, j=0) (solid circles). Comparison of several LDFA (b) and TDPT (c) friction coefficients in internal coordinates (Λ_{rr}, Λ_{ZZ}, and Λ_{rZ}) in the H_2+Ag(111) system along the reaction paths over the top, bridge, and fcc sites.