Electronic Supplementary Information:

Stereodynamics of Adiabatic and Non-adiabatic Energy Transfer in a Molecule Surface Encounter

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Supplementary Figs

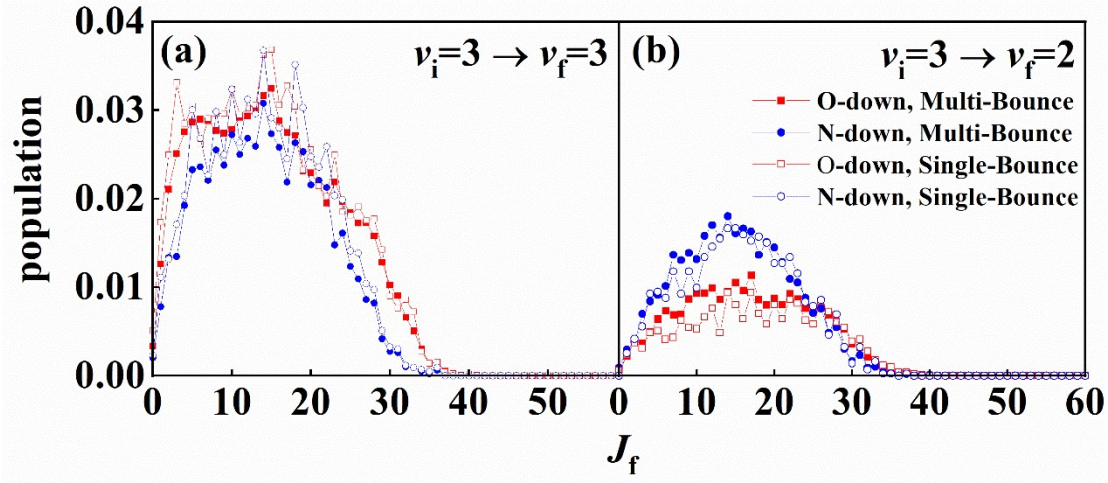

Fig. S1. Comparison of rotational state distributions of vibrationally elastic (v_f=3) and inelastic (v_f=2) scattering of NO(v_i=3) from Au(111), resulted from multi-bounce (filled) and single-bounce (open) trajectories calculated by molecular dynamics with electronic friction (MDEF) using Kohn-Sham orbital-dependent friction (ODF), at E_i = 0.27 eV for N-first (blue) and O-first (red) orientations.

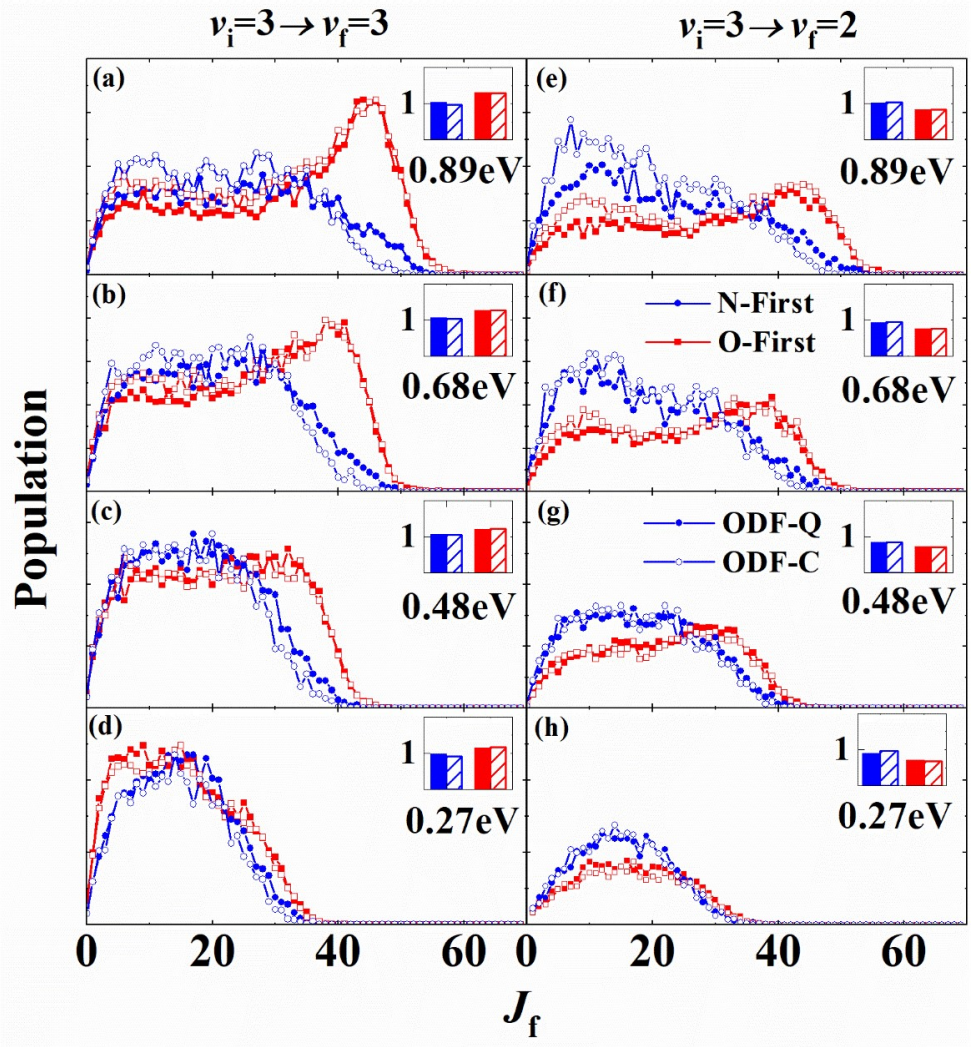

Fig. S2. Comparison of theoretical final rotational state distributions of vibrationally elastic (v_f=3) and inelastic (v_f=2) scattering of NO(v_i=3) from Au(111) with E_i ranging from 0.27 to 0.89 eV for N-first (blue) and O-first (red) orientations obtained by MDEF simulation with ODF using quantum angular distributions (ODF-Q, filled) and classical angular distribution (ODF-C, open). The inset shows the ratio of the final vibrational state population with N-first (blue) and O-first (red) orientation relative to that with the isotropic orientation.

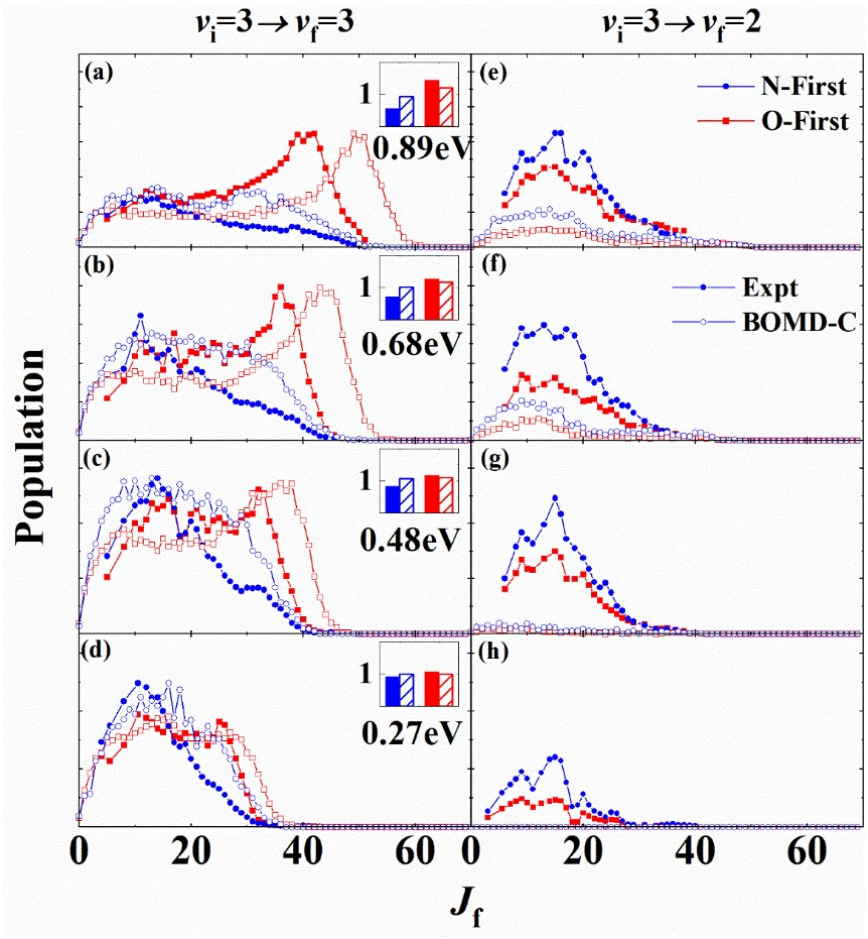

Fig. S3. The same as Fig. S2 but for the comparison of results of the experiment (filled) and adiabatic Born Oppenheimer molecular dynamics (BOMD) simulations using classical angular distribution (BOMD-C) (open). At each E_i, calculated rotational state distributions in both channels are multiplied by the same factor so that the highest theoretical peak matches the highest experimental one. Note that the ratio of the final vibrational state population with N-first (blue) and O-first (red) orientation relative to that with the isotropic orientation is not shown in the vibrationally inelastic channel because the population is so low that the statistics are poor and the result is not meaningful.

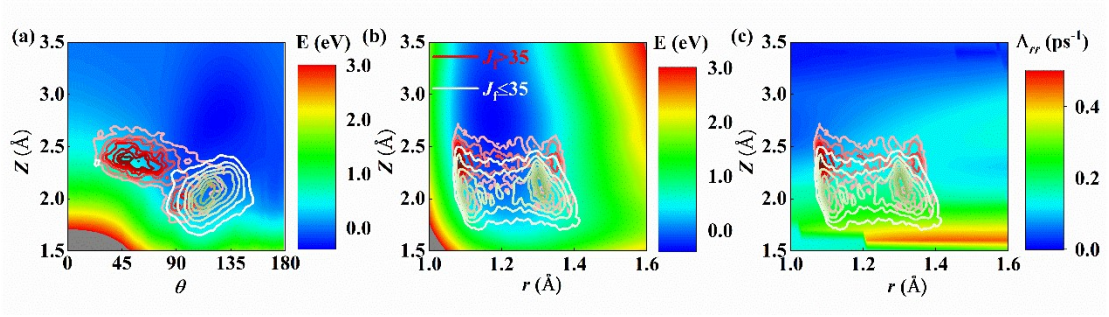

Fig. S4. Contour plots of the NO geometries of the closest approach to the surface for ODF-C trajectories scattered to $J_f \leq 35$ (white) and $J_f > 35$ (red) with E_i =0.89 eV. (a) values of the NO center-of-mass altitude above the surface (Z) and the orientational angle (θ) are shown superimposed on a 2D cut of the NN-PES (colors). (b) values of Z and NO bond length (r) are shown superimposed on a 2D cut of the NN-PES (colors). (c) the trajectory inner turning points are shown superimposed on the NN-ODF diagonal element (Λ_{rr}) as a function of Z and r (colors) (panel c). Note that the 2D cut of the NN-PES is obtained with all other coordinates optimized on the PES and the surface configuration fixed at the adsorption state.

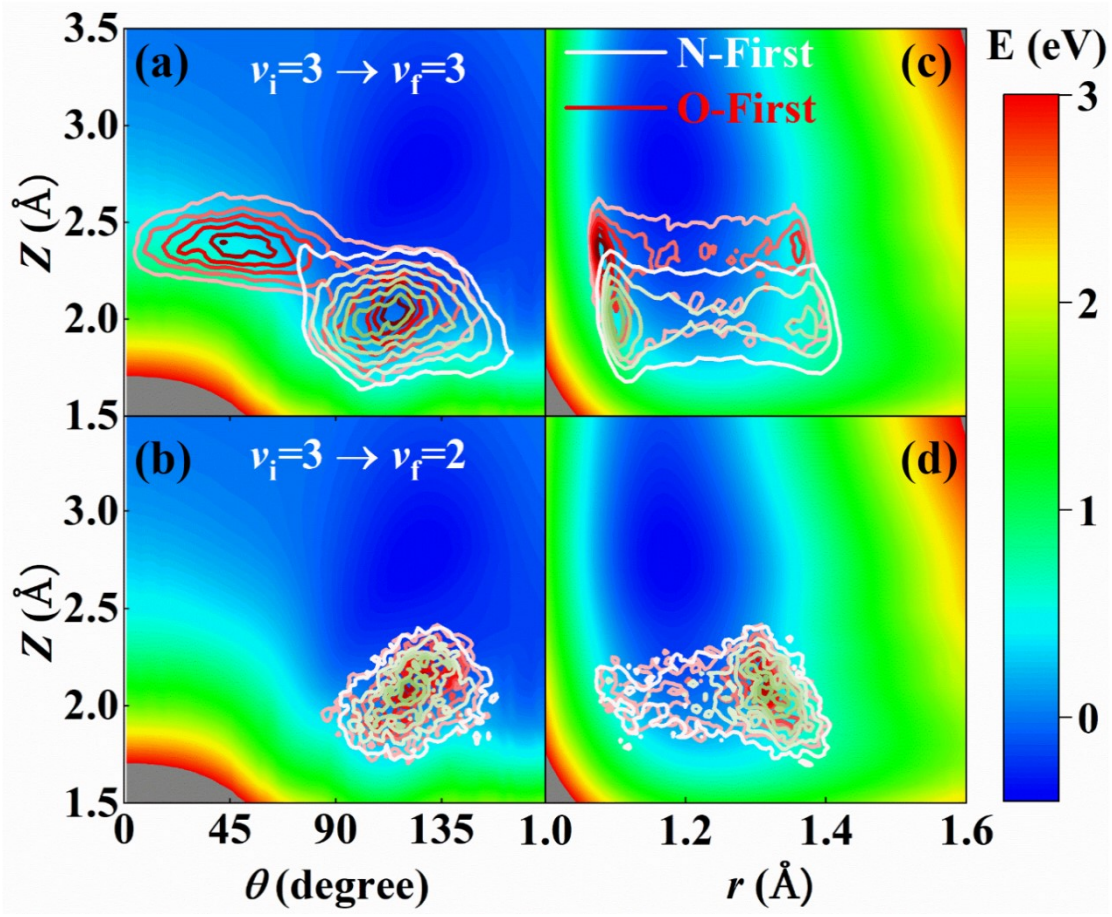

Fig. S5. Contour plots of the NO geometries of the closest approach to the surface with initial N-first (white) and O-first (red) orientations in BOMD-C trajectories scattered to v_f=3 (top two panels) and v_f=2 (bottom two panels) with E_i =0.89 eV. (a-b) values of the NO center-of-mass altitude above the surface (Z) and the orientational angle (θ) are shown superimposed on a 2D cut of the NN-PES (colors). (c-d) values of Z and NO bond length (r) are shown superimposed on a 2D cut of the NN-PES (colors). Note that the 2D cut of the NN-PES is obtained with all other coordinates optimized on the PES and the surface configuration fixed at the adsorption state.

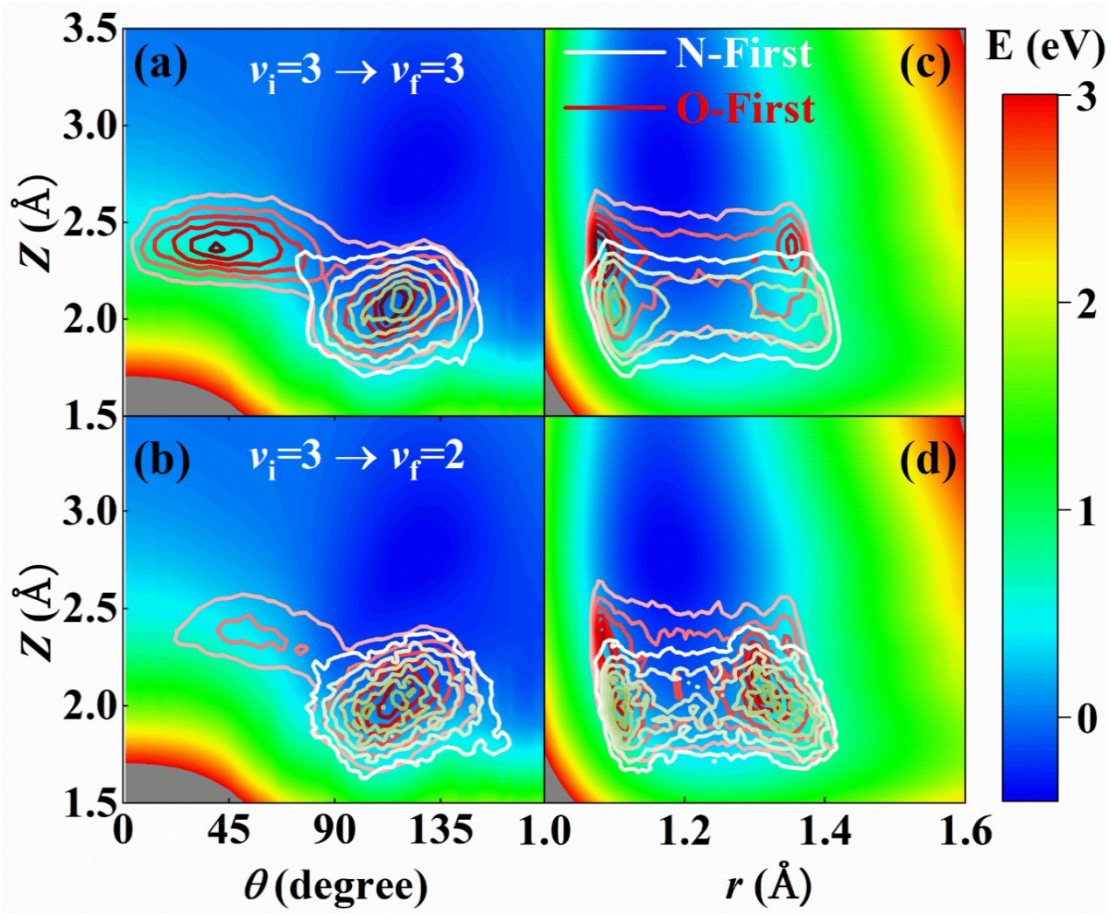

Fig. S6. Similar to Fig. S5 except for ODF-C trajectories.

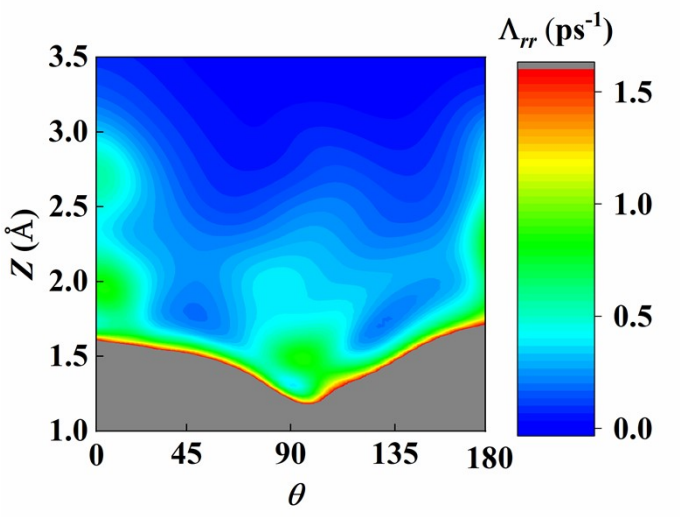

Fig. S7. Contour plot of the NN-ODF diagonal element (Λ_{rr}) as a function of the NO center-of-mass above the surface (Z) and the orientational angle (θ). Note that the 2D cut of the NN-ODF is obtained with all other coordinates and the surface configuration fixed at the adsorption state.