Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Density Functional Based Simulations of Proton Permeation of Graphene and Hexagonal Boron Nitride : Supplementary Information

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Fig. S1 and S2 show the projected density of states (PDOS) of the electronic spectra of graphene and h-BN for selected points in Fig. 2 of the main text.
The PDOS are calculated with a Gaussian broadening of 0.01 Ha and the Fermi energy taken is taken as E=0. Note that when the proton is 1 Å above the surface, the unoccupied H state enters the occupied part of the spectrum, signalling the formation of a covalent bond.

Fig. S1) PDOS for **graphene** with a proton in the center of the hexagon (left) and 1 Å above the surface (right). Filled (open) curves show the occupied (unoccupied) part of the spectrum.

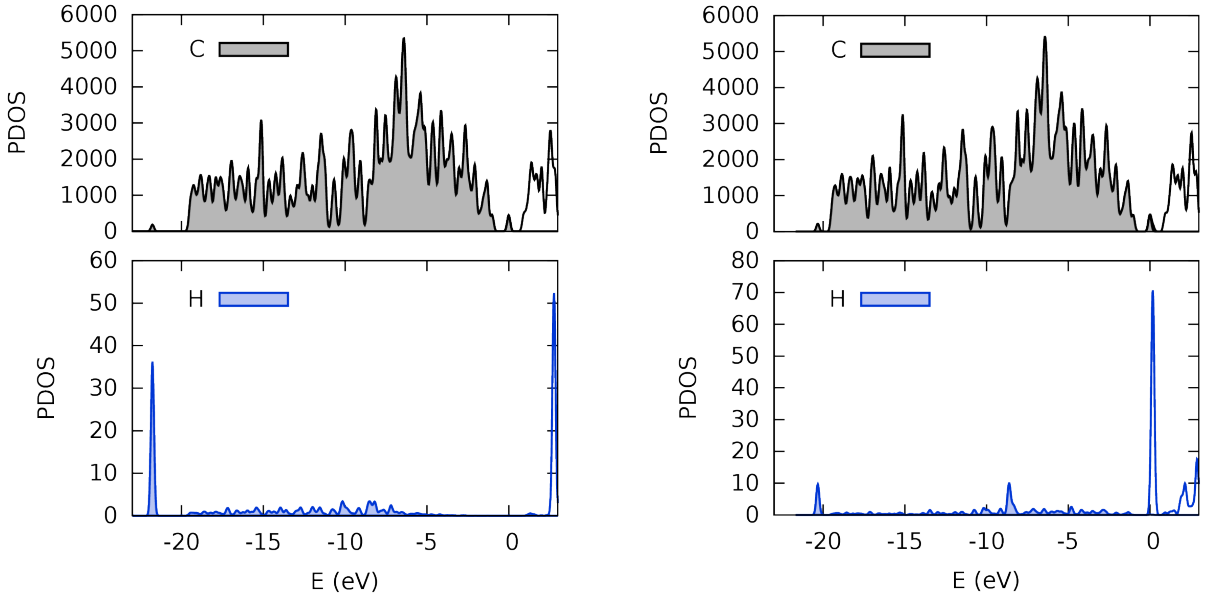

Fig. S2) Projected density of states (PDOS) for **h-BN** with a proton in the center of the hexagon (left) and 1 Å above the surface (right). Filled (open) curves show the occupied (unoccupied) part of the spectrum.

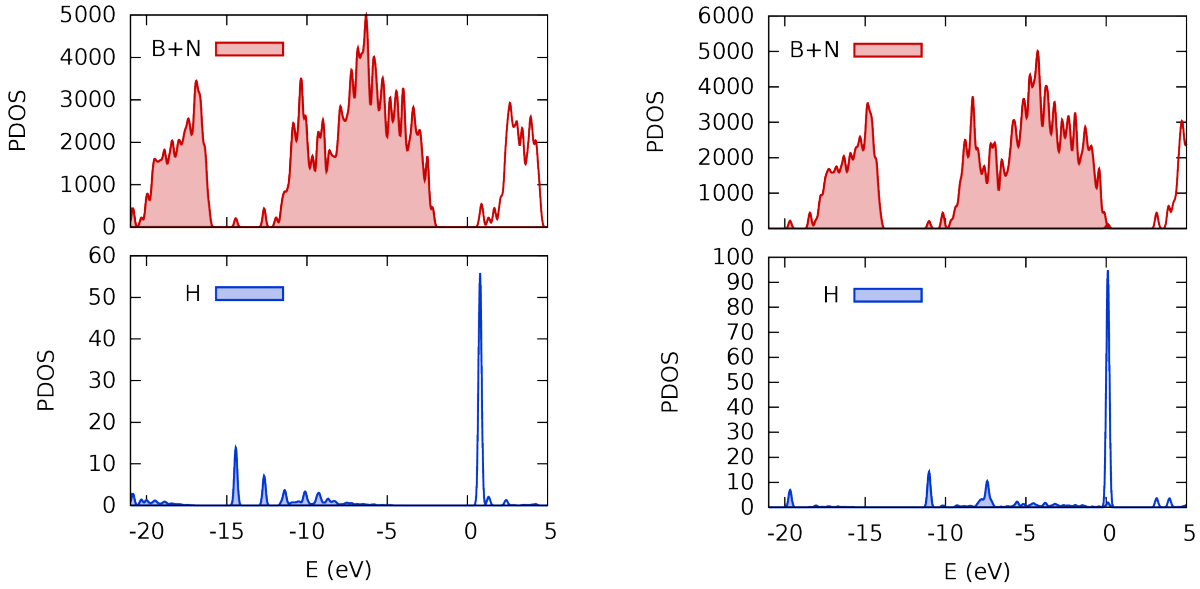

Table S1) Statistics corresponding to figure S1 and S2.
N(X) = ∫ PDOS(X) f(E) dE, where f(E) the Fermi-Dirac distribution with T=300K.

	N(C)	N(H)	Total
graphene + proton at z=0 Å	1151.13	0.87	1152
graphene + proton at z=1 Å	1151.36	0.64	1152
	N(B+N)	N(H)	Total
h-BN + proton at z=0 Å	1151.24	0.76	1152
h-BN + proton at z=1 Å	1151.40	0.60	1152

Fig. S3) Mulliken population analysis of the H nuclei for the frames shown in the main text. The H nuclei are coloured by their respective Mulliken population. The atoms being forced during the steered molecular dynamics simulation have a gray transparent background added. All H projected MP values are between 0.77 and 0.96 e^-.

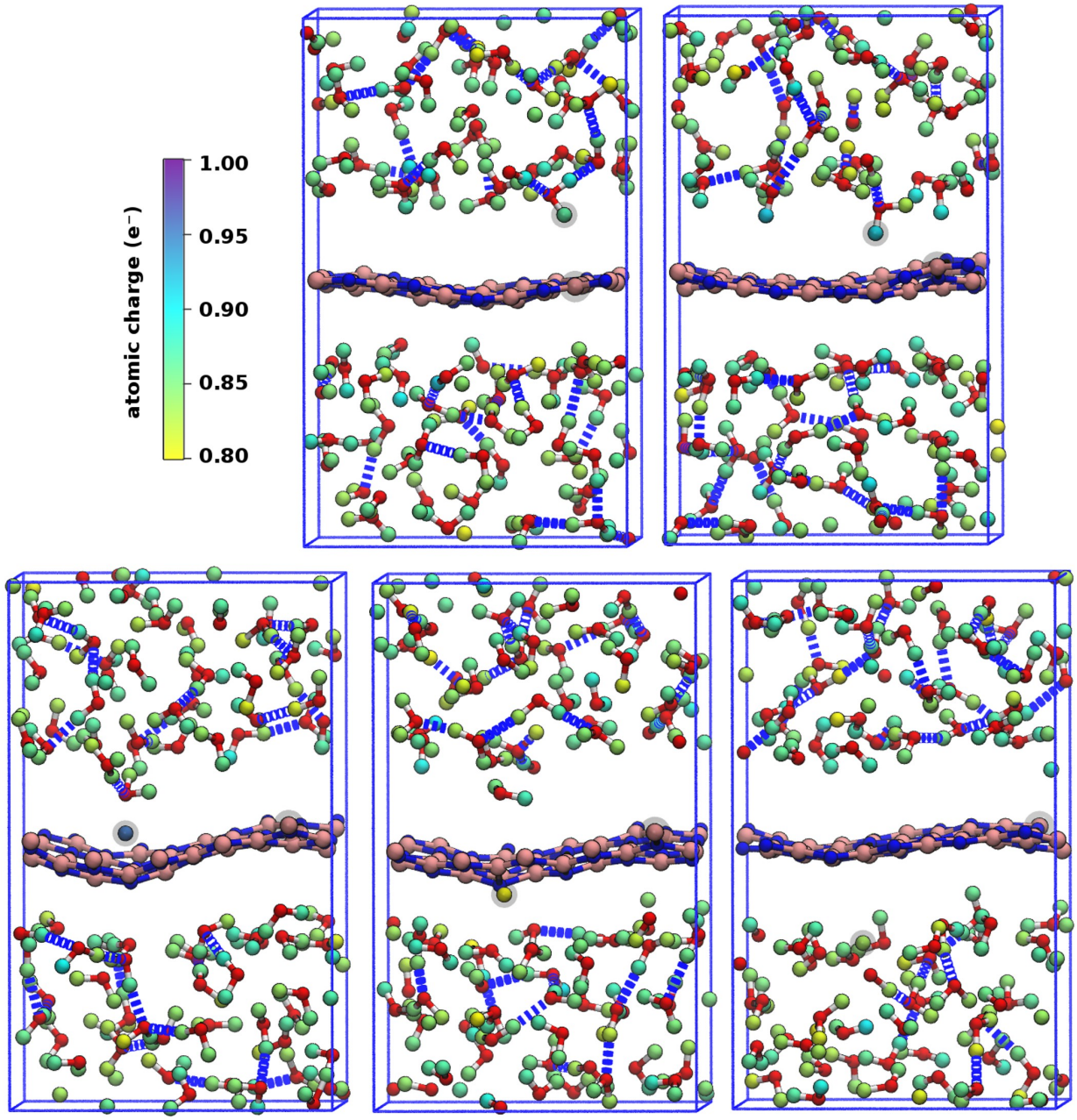

Table S2) Statistics of the Mulliken Population (MP) analysis from Fig. S3.
N(X) = sum of the atomic charges of atoms of type X
Total = N(H) + N(O) + N(B) + N(N)

	MP(biased H)	N(H)	N(O)	N(B) + N(N)	Total
Frame a	0.87	150.65	553.37	239.98	944
Frame b	0.91	150.78	553.45	239.76	944
Frame c	0.95	150.79	553.91	239.31	944
Frame d	0.80	150.89	553.62	239.49	944
Frame e	0.83	150.99	553.01	240.00	944

Fig. S4a) Steered Molecular dynamics for proton permeation of h-BN. The top panel shows collective variable (ξ) and its derivation from the (moving) target value (ξ_t). The middle panel shows the evolution of the distance between the H nucleus and the nearest O atom. The bottom panel shows the evolution of the SMD performed work (W(t)) and the potential energy (E_{pot}). The gray highlighted area shows the range from which the barrier can be estimated, which is between the OH bond breaking and the slipping.
This plot corresponds to Fig. 4f in the main text with κ = 10 eV/Å².

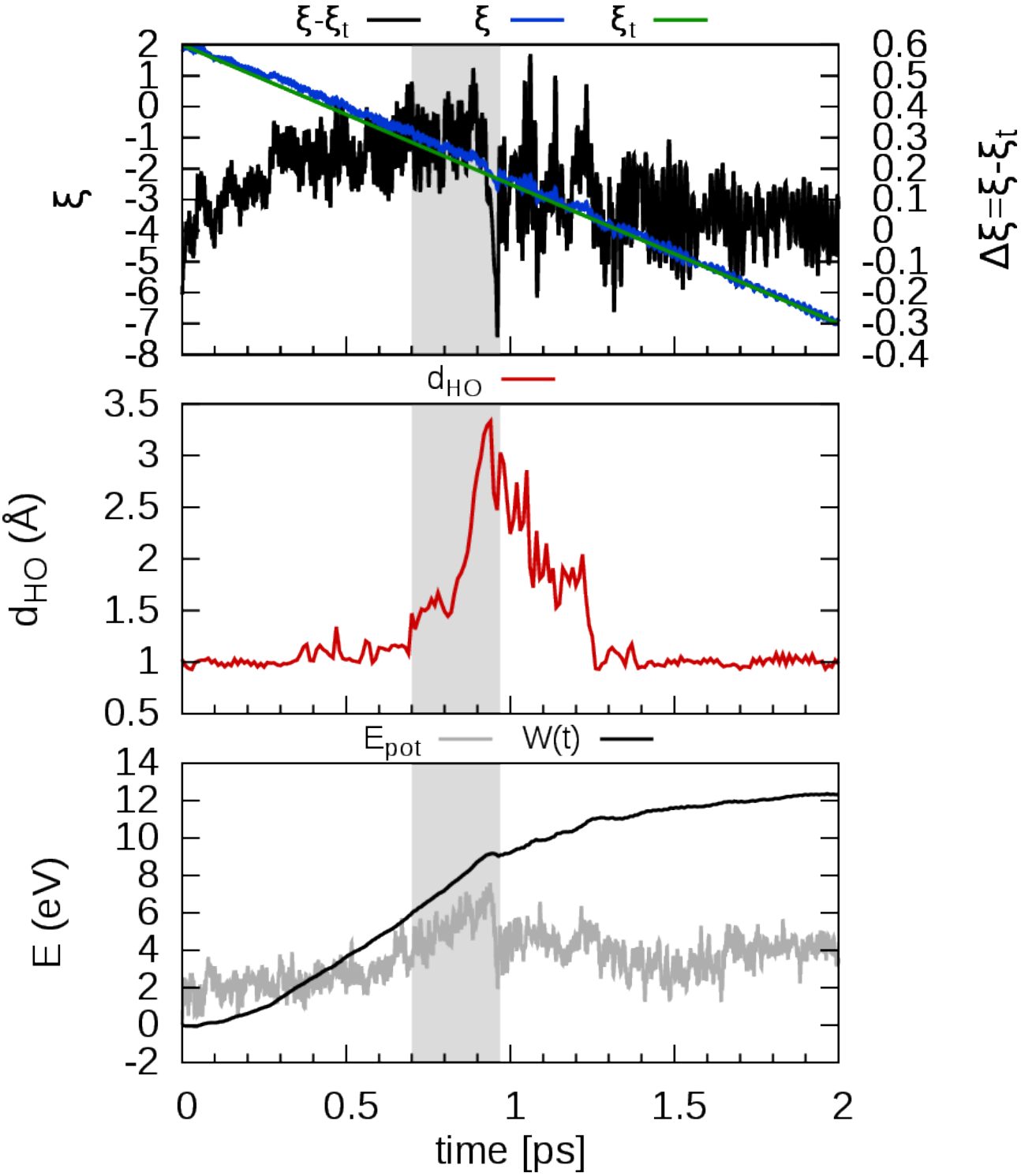

Fig. S4b) Continuation of Fig. S4a on a larger timescale, illustrating the multiple transitions.

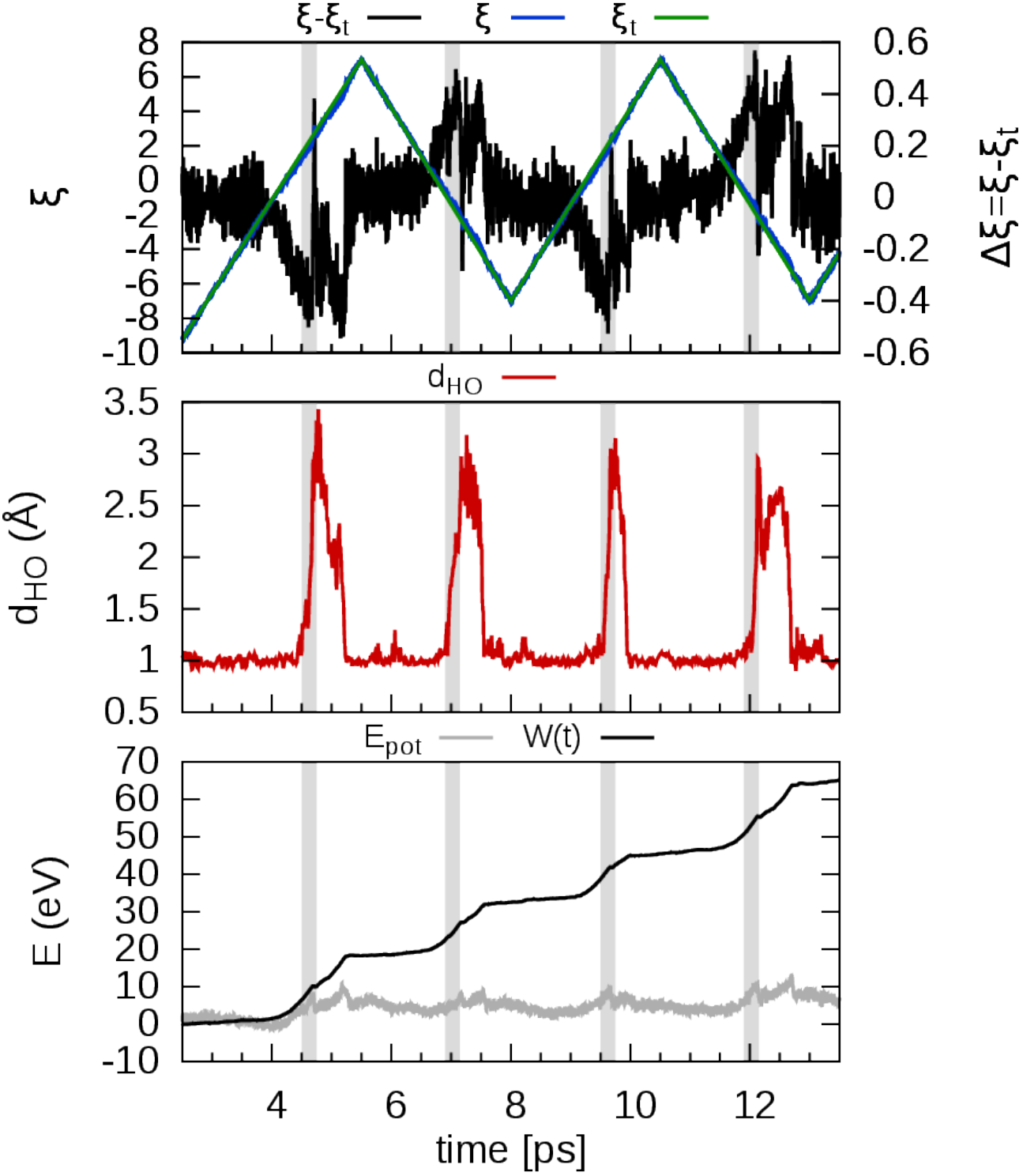

Fig. S4c) Similar to Fig. S4a, only here with κ = 1 eV/Å². In this case the slipping is more more clearly illustrated.