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

Supporting information for:

The Reaction Mechanism of Polyalcohol Dehydration in Hot Pressurized Water

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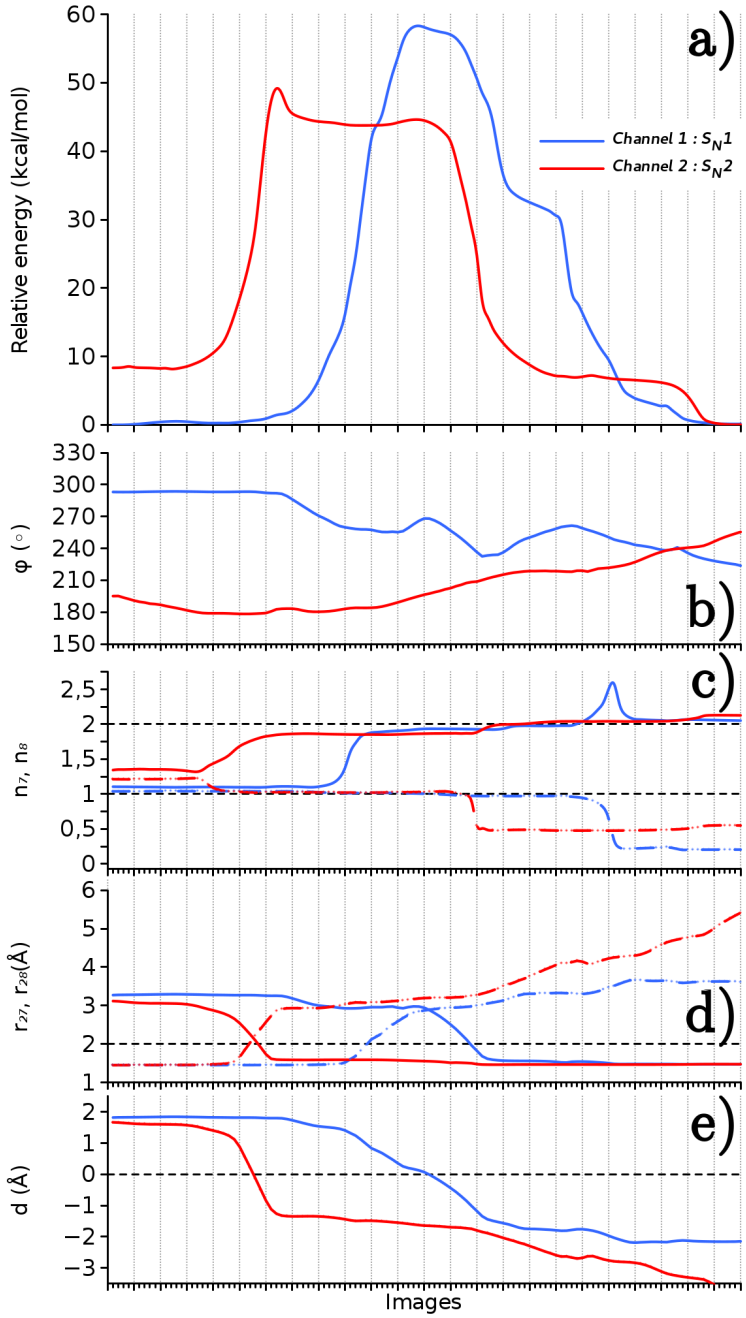

Figure S1: The change along the $HDO(H_2O)_4H^+$ minimum energy paths, Channels 1 (blue) and 2 (red), obtained from the PBE/SV(P) calculations. (a) The relative energy, and the structural variables (b) ϕ, (c) n_7 (solid line) and n_8 (dashed line), (d) r_{27} (dashed line) and r_{28} (solid line), and (e) d. The barriers of the S_N1 channel (blue) and the S_N2 channel (red) are 58 and 45 kcal/mol, respectively.

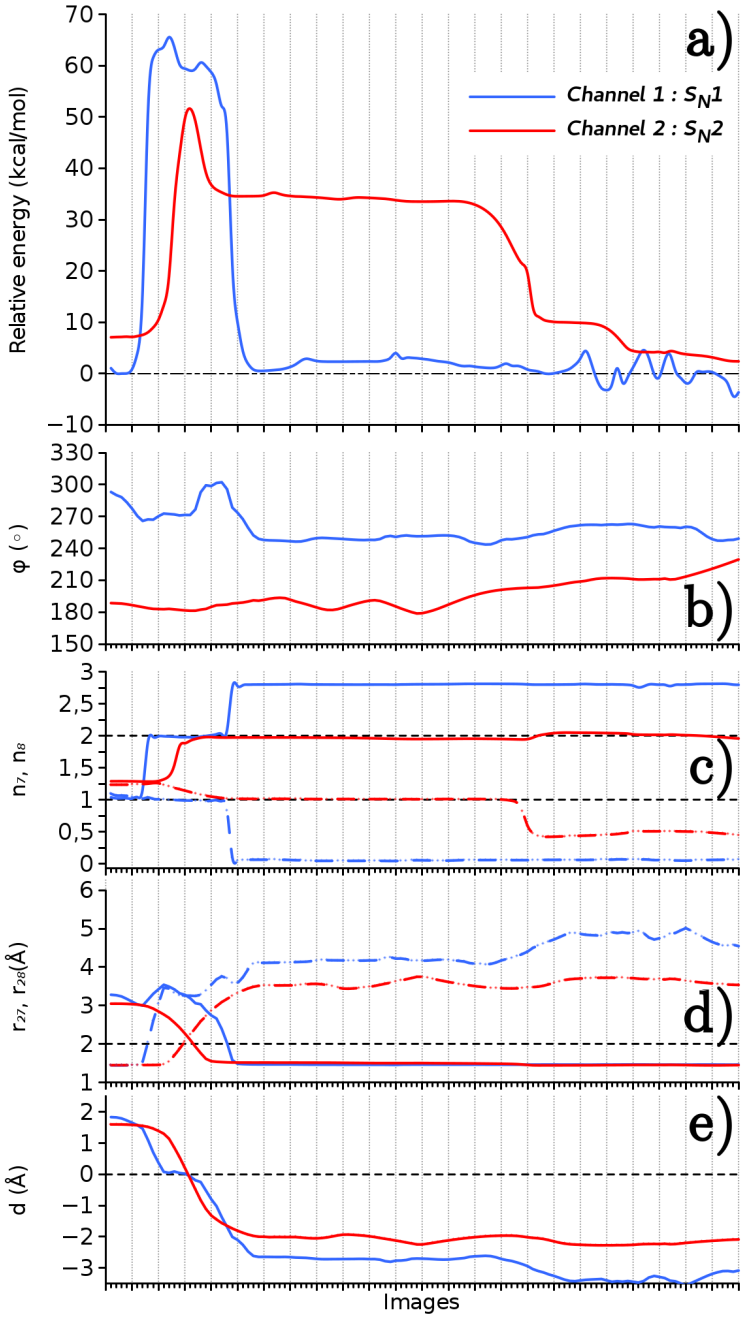

Figure S2: The change along the $HDO(H_2O)_6H^+$ minimum energy paths, Channels 1 (blue) and 2 (red), obtained from the RIMP2/SV(P) calculations. (a) The relative energy, and the structural variables (b) ϕ, (c) n_7 (solid line) and n_8 (dashed line), (d) r_{27} (dashed line) and r_{28} (solid line), and (e) d. The barriers of the S_N1 channel (blue) and the S_N2 channel (red) are 66 and 41 kcal/mol, respectively.

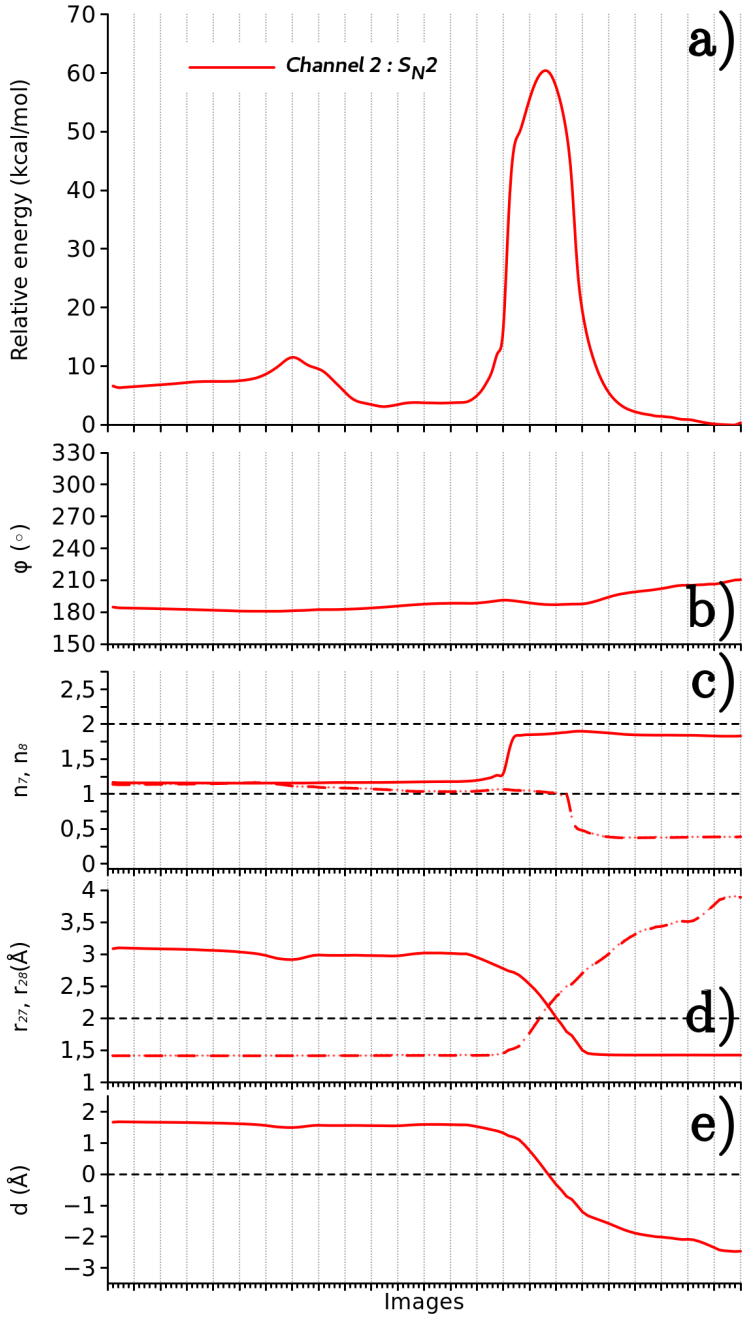

Figure S3: The change along the $HDO(H_2O)_6$ minimum energy path, Channels 2 (red), obtained from the PBE/SV(P) calculations. (a) The relative energy, and the structural variables (b) ϕ, (c) n_7 (solid line) and n_8 (dashed line), (d) r_{27} (dashed line) and r_{28} (solid line), and (e) d. The barriers of the S_N2 channel without and extra proton is 57 kcal/mol.

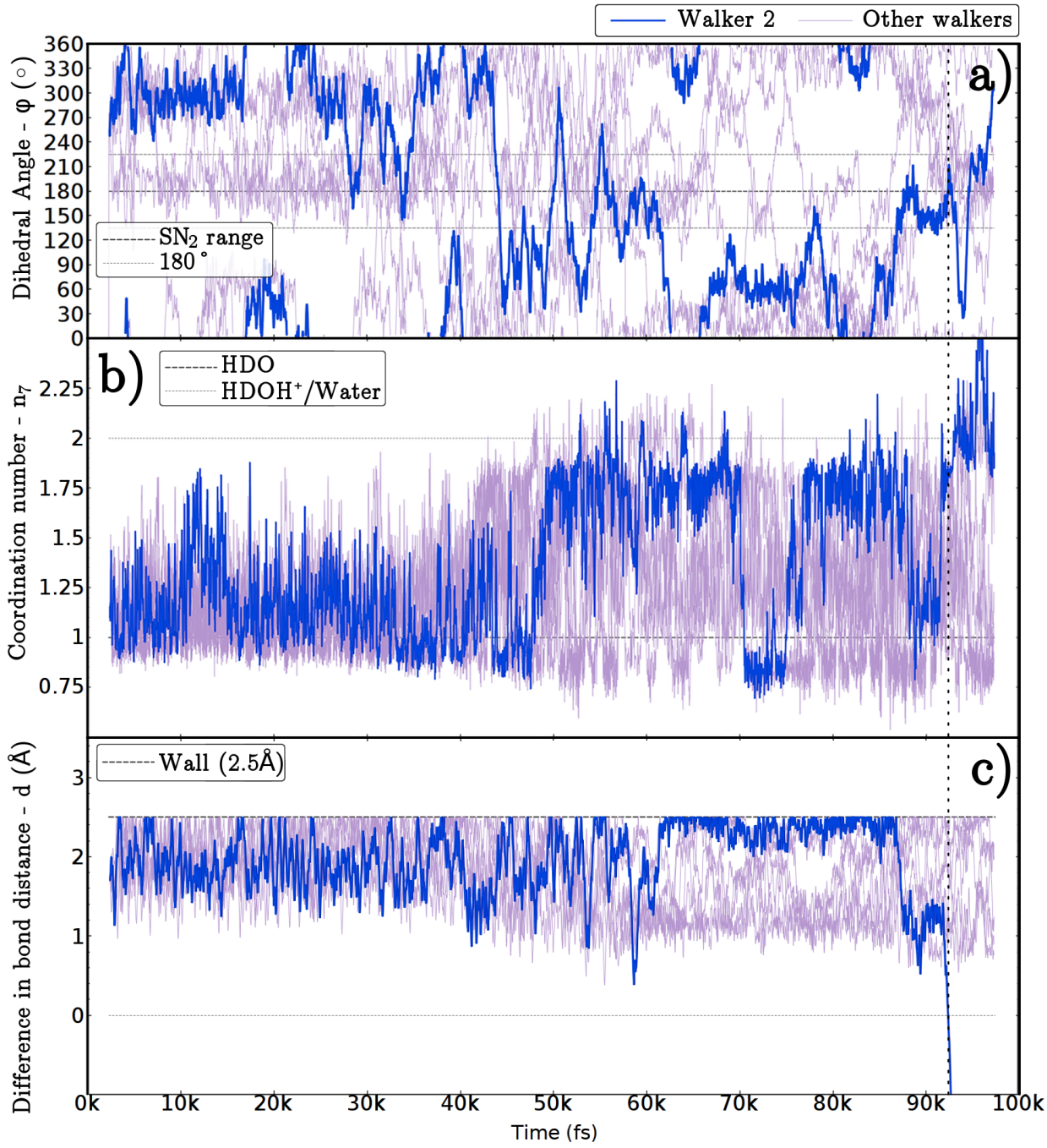

Figure S4: The evolution of three collective variables, (a) ϕ (b), n_7 and (c) d, of the respective walkers obtained from the PBE/PW metadynamics calculations of aqueous solution. All the walkers are shown in purple, except Walker 2 highlighted in blue which has first lead to the reaction. Walker 2 crossed the transition state at 92 ps marked by the dotted line. In (a), the region in which S_N2 can occur (135°–225°) is marked by dashed lines. In (b), the values of neutral HDO ($n_7 = 1$) and protonated HDO ($n_7 = 2$) are marked by dashed lines. In (c), the restriction wall used in metadynamics at $d = 2.5$Å and the region of transition state $d = 0.0$ Å are marked by dashed lines.

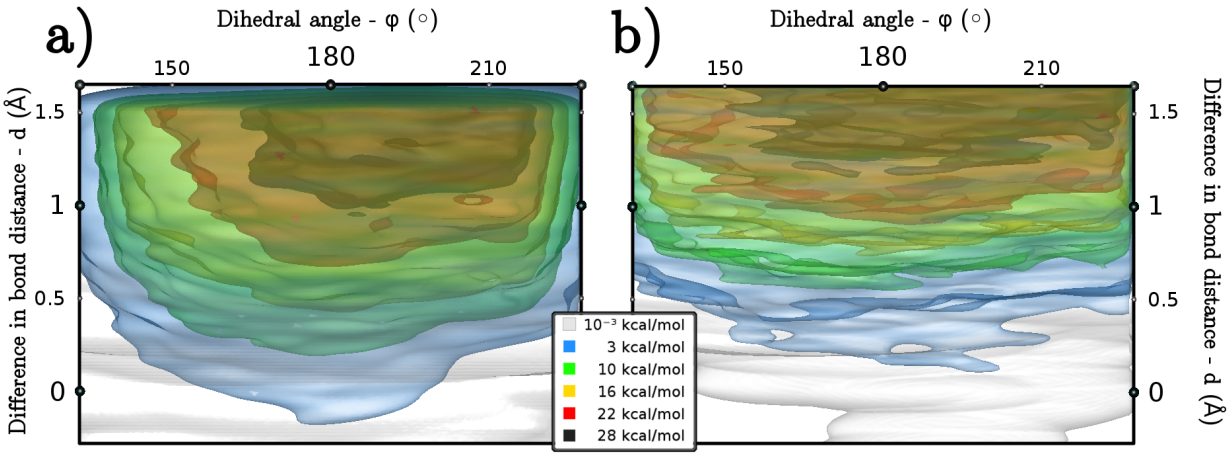

Figure S5: Three-dimensional free energy surface of (a) $x = 4$ and (b) $x = 6$ in the HDO microsolvated model with respect to d, ϕ and n_7, obtained from the PBE/SV(P) metadynamics calculations. The views are in a direction parallel to n_7.

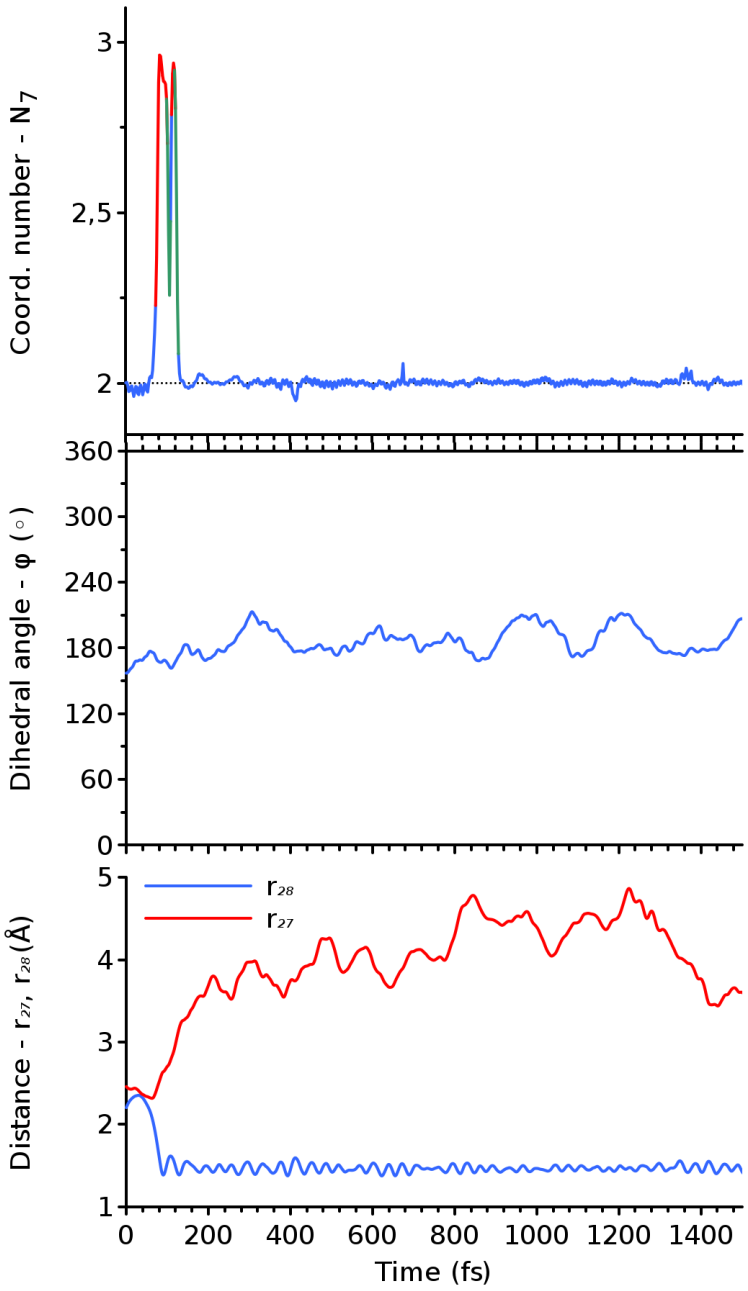

Figure S6: The change of structural variables N_7 (top panel), ϕ (middle panel) and r_{27} and r_{28} (bottom panel) along a backward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_7 indicates the position of an excess proton. It is red when O_7 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

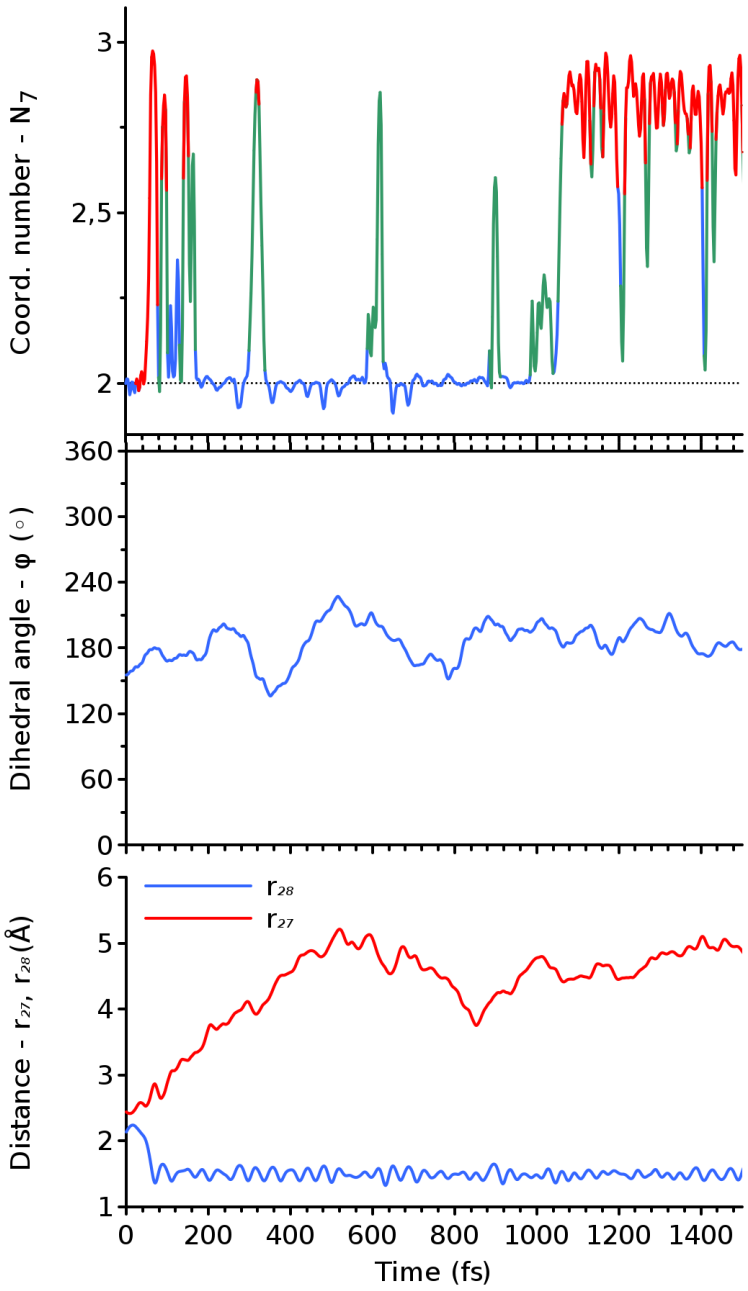

Figure S7: The change of structural variables N_7 (top panel), ϕ (middle panel) and r_{27} and r_{28} (bottom panel) along a backward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_7 indicates the position of an excess proton. It is red when O_7 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

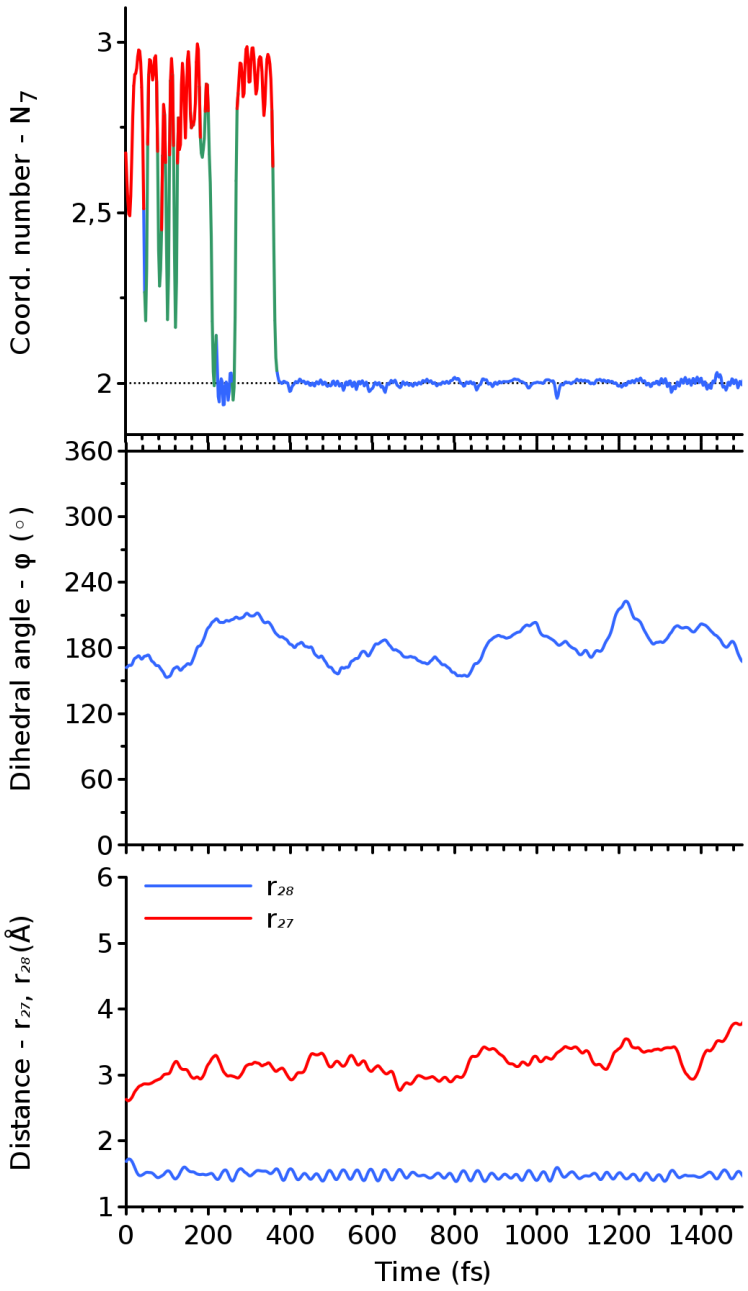

Figure S8: The change of structural variables N_7 (top panel), ϕ (middle panel) and r_{27} and r_{28} (bottom panel) along a backward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_7 indicates the position of an excess proton. It is red when O_7 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

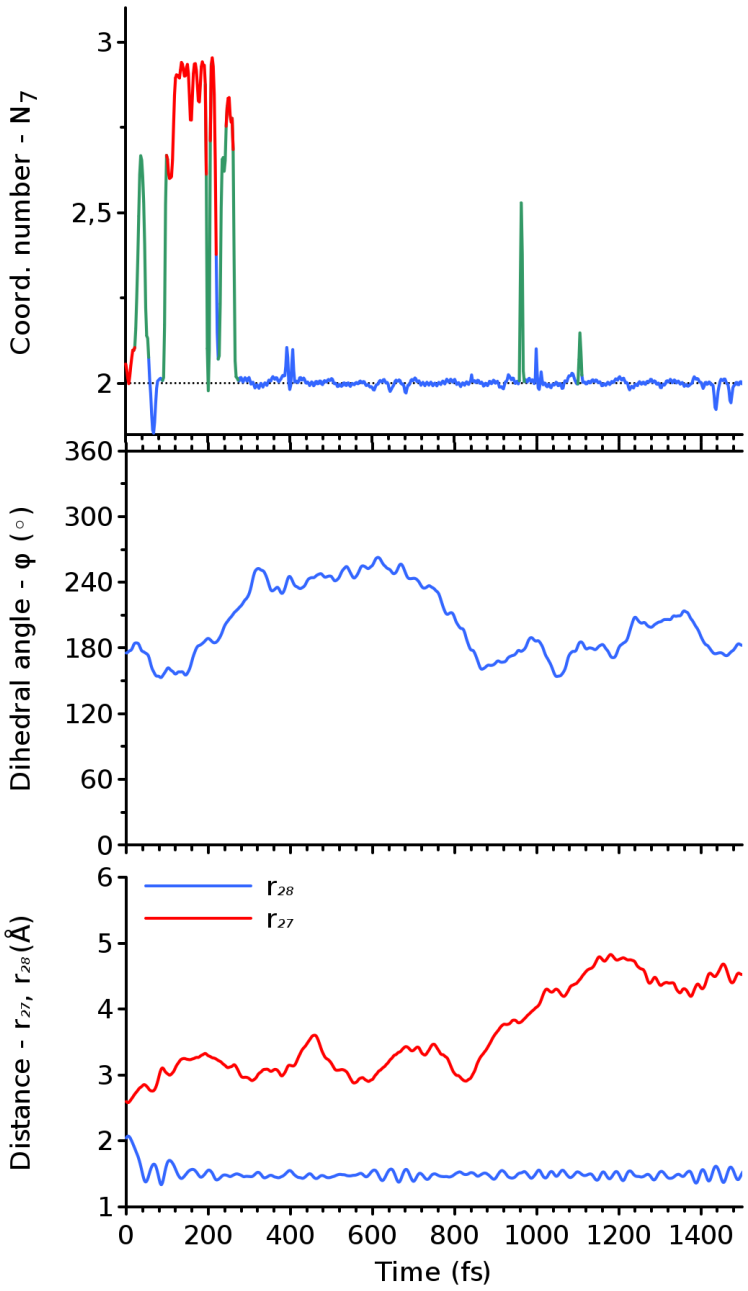

Figure S9: The change of structural variables N_7 (top panel), ϕ (middle panel) and r_{27} and r_{28} (bottom panel) along a backward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_7 indicates the position of an excess proton. It is red when O_7 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

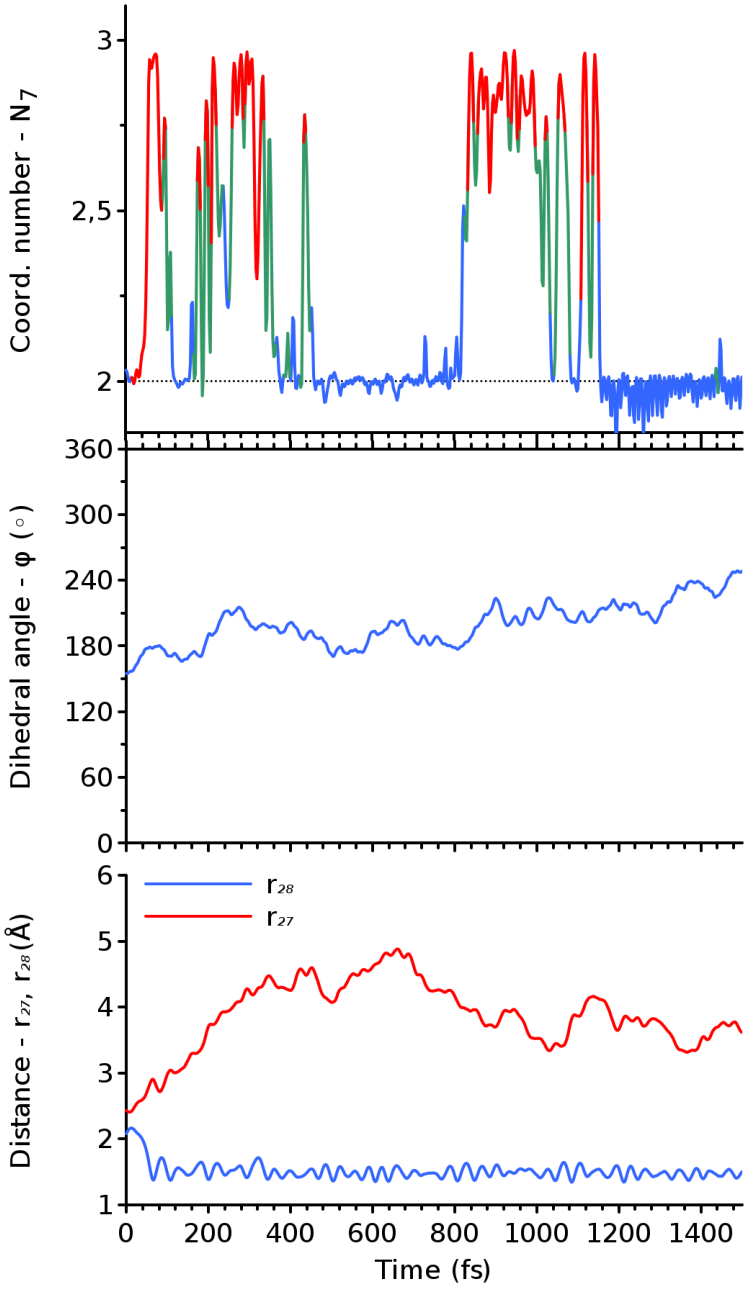

Figure S10: The change of structural variables N_7 (top panel), ϕ (middle panel) and r_{27} and r_{28} (bottom panel) along a backward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_7 indicates the position of an excess proton. It is red when O_7 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

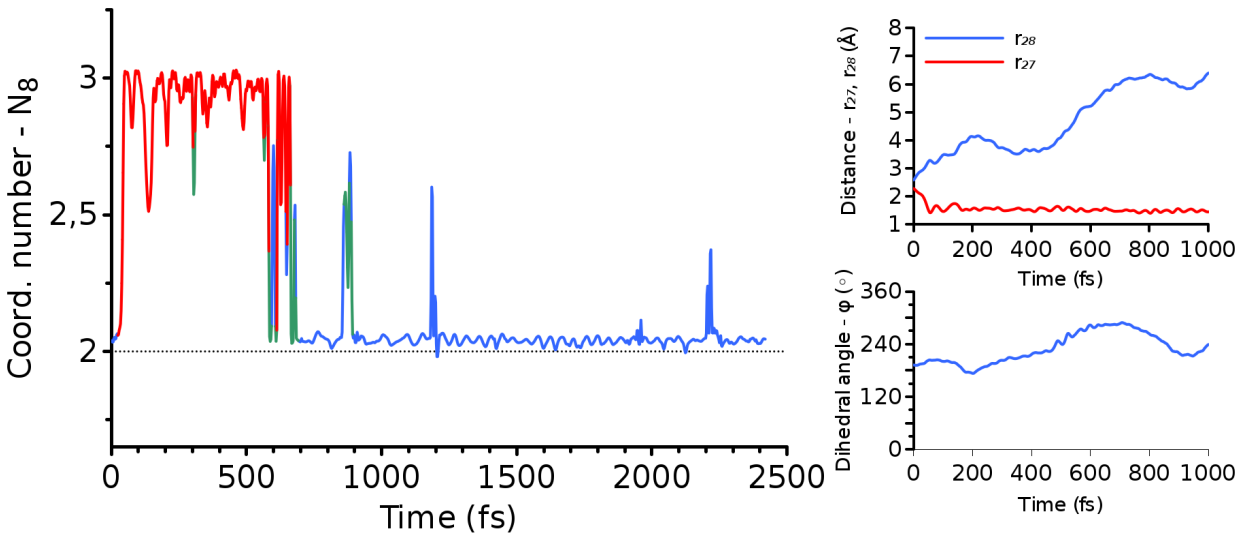

Figure S11: The change of structural variables N_8 (left panel), r_{27} and r_{28} (upper right panel), and ϕ (bottom right panel) along a forward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_8 indicates the position of an excess proton. It is red when O_8 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

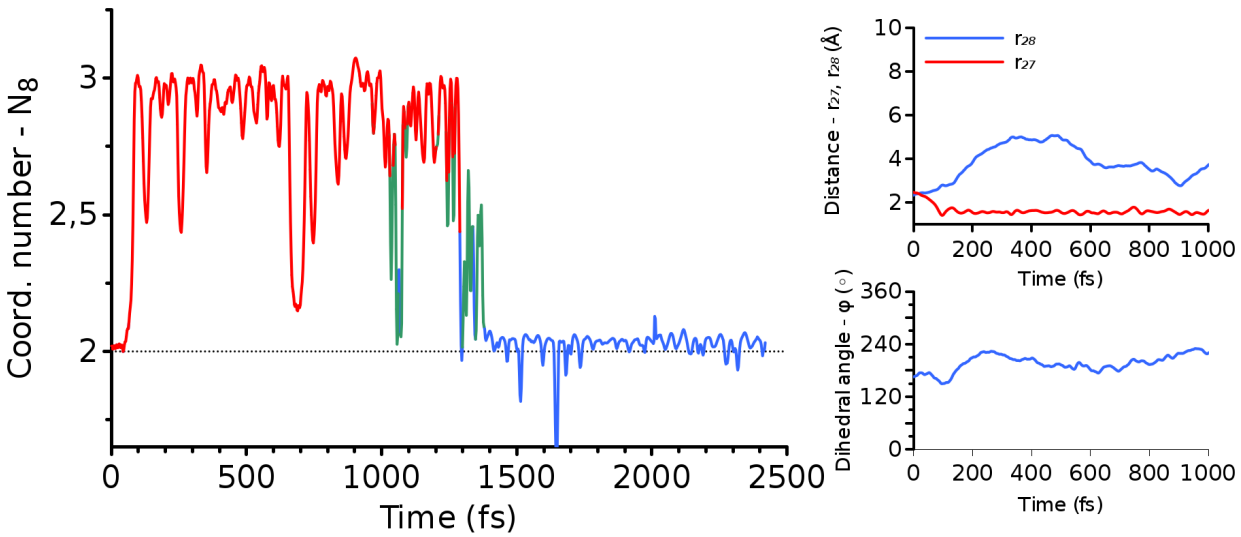

Figure S12: The change of structural variables N_8 (left panel), r_{27} and r_{28} (upper right panel), and ϕ (bottom right panel) along a forward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_8 indicates the position of an excess proton. It is red when O_8 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.

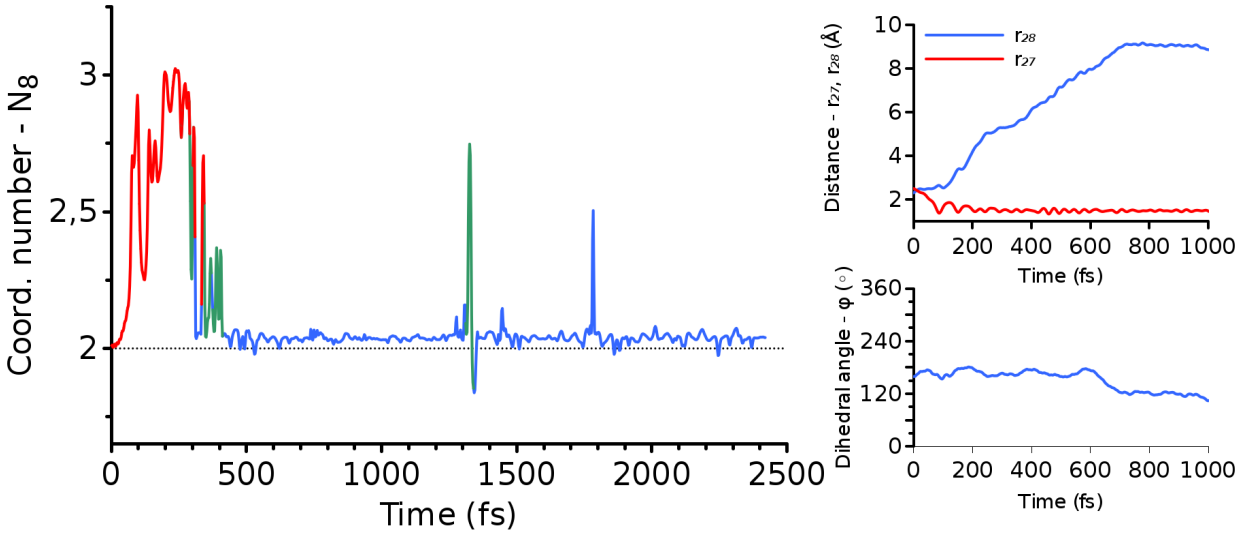

Figure S13: The change of structural variables N_8 (left panel), r_{27} and r_{28} (upper right panel), and ϕ (bottom right panel) along a forward trajectory launched from the point near the transition state obtained from the PBE/PW molecular dynamics calculations of aqueous solution. The color of N_8 indicates the position of an excess proton. It is red when O_8 is protonated, green when a water molecule hydrogen bonded to HDO is protonated, and blue otherwise.