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

Supporting Information

Solvation Dynamics and Energetics of Intramolecular Hydride Transfer Reactions in Biomass Conversion

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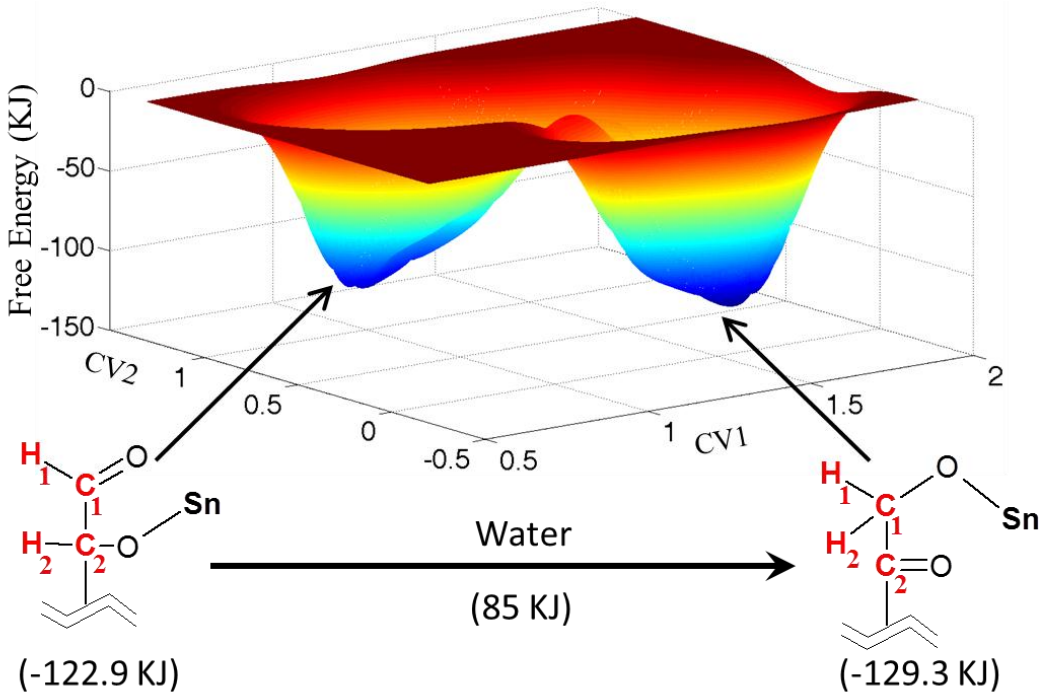

Figure S1: Metadynamics calculated free energy landscape for the hydride transfer from C_2 to C_1 in the presence of explicit, quantum mechanically treated water molecules. Structures corresponding to two minima in the free energy surface are shown. Only the metal centre of the catalyst is shown for clarity purpose. The free energy barrier in the reaction step is shown below the arrow and free energies of the system before and after the hydride transfer are shown in parentheses. Refer to Fig. 1c for the definition of collective variables CV1 and CV2. It has to be noted that, unlike Fig. 2b in the main text, water molecules in this case are given lesser time to relax along the CPMD–metadynamics trajectory.

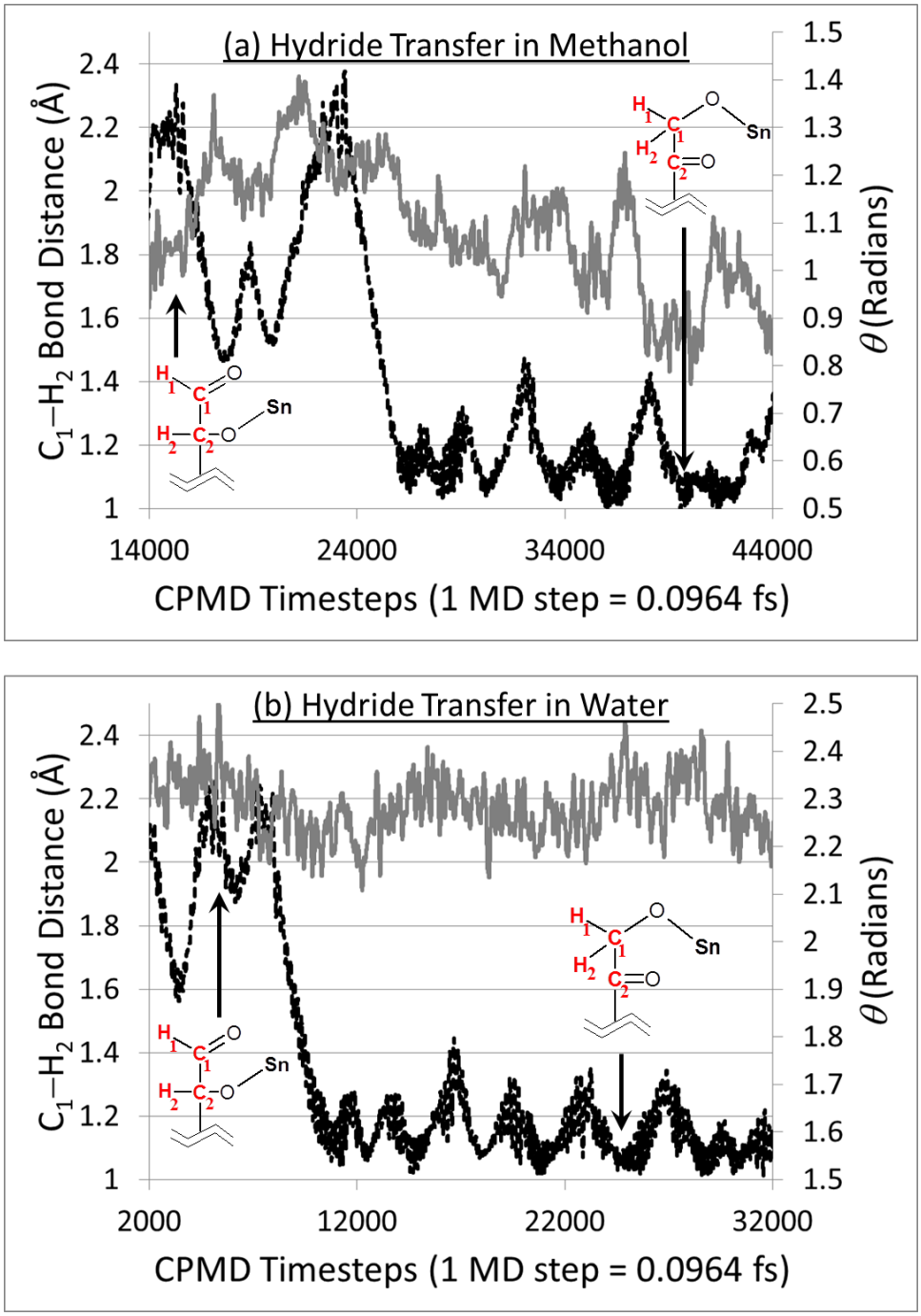

Figure S2: Variation in the orientation of the solvent dipole vector with respect to *x*–axis (or the angle that the solvent dipole vector makes with the *x*–axis of the simulation cell) during the hydride transfer step in the CPMD–metadynamics trajectory. (a) Methanol as the solvent, and (b) Water as the solvent. The C_1–H_2 bond distance along the trajectory is also shown as a dotted line.

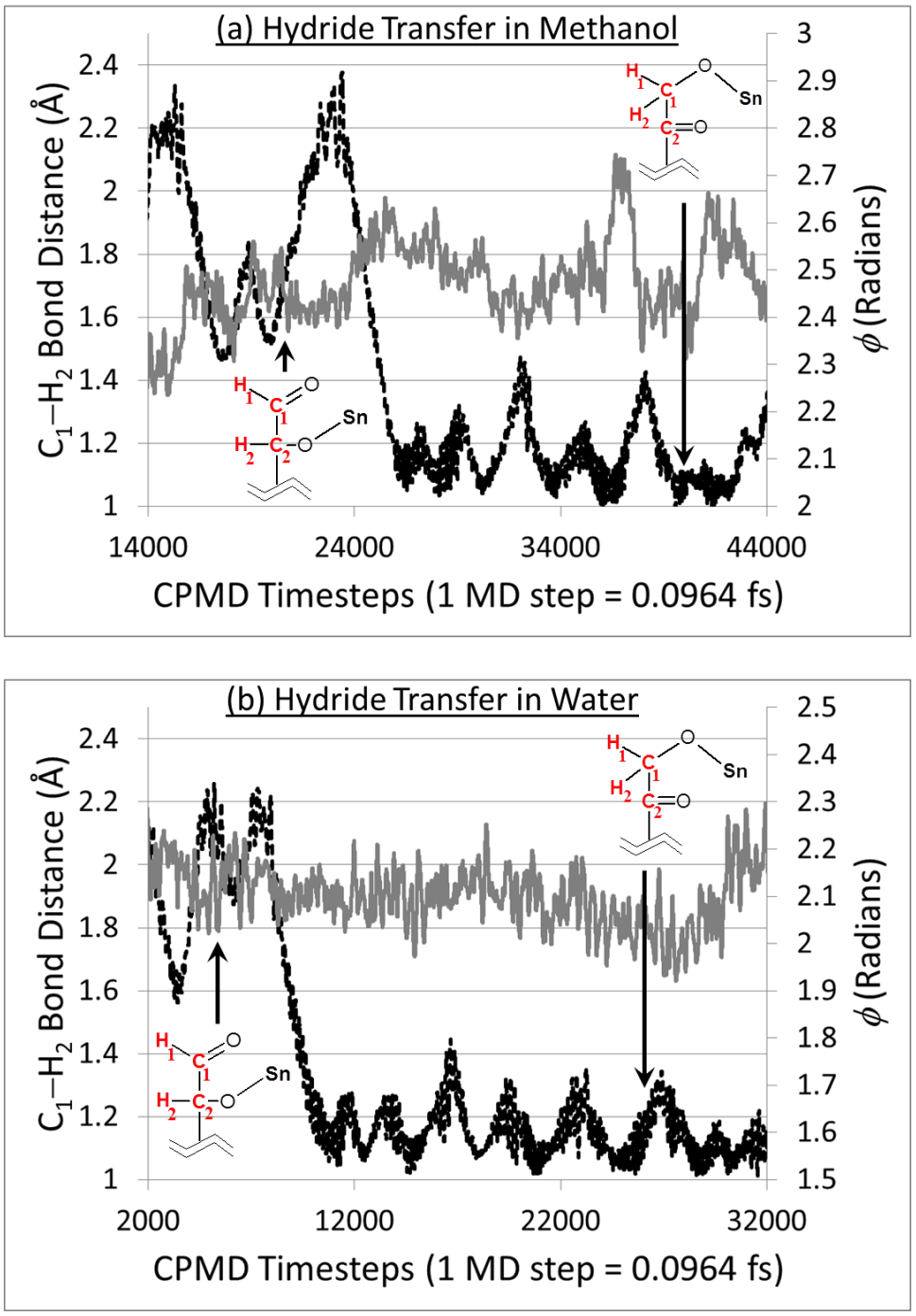

Figure S3: Variation in the orientation of the solvent dipole vector with respect to *y*–axis (or the angle that the solvent dipole vector makes with the *y*–axis of the simulation cell) during the hydride transfer step in the CPMD–metadynamics trajectory. (a) Methanol as the solvent, and (b) Water as the solvent. The C_1–H_2 bond distance along the trajectory is also shown as a dotted line.