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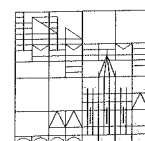
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Book of Abstracts

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S6-P08: Understanding water dynamics near topologically complex solutes using simulation

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The structural and dynamic properties of solutes in water (e.g. conformational fluctuations of proteins, conformation of disaccharides) are known to depend on the properties of water of hydration. Our understanding of the connection between solute and solvent properties is at present incomplete, however, because the structural and dynamic properties of water of hydration in turn are affected by solute chemistry and topology. Here we report a study on the least understood aspect of the properties of water of hydration: their dependence on solute topology. Using classical all-atom molecular simulations, we investigate water near disaccharides in explicit solvent. Disaccharides were chosen for this work because they are small, and so allow for detailed study, but already show the topological and chemical complexity characteristic of large biomolecules. We find that water of hydration translates and rotates more slowly than in the bulk, and that the observed slow down of local water populations correlates with increases in local hydrophobicity. We also find that water may interact differently with identical functional groups depending on the chemistry and topology of neighboring groups, in line with recent observations on proteins

We rationalize these observations by investigating the mechanism of hydrogen bond exchange (water rotation) for waters within the sugar first solvation shell. In the bulk, water rotation occurs through large, fast, angular jumps involving bifurcated hydrogen bond intermediates. The rotational slow down of water near topologically simple solutes relative to bulk can be predicted using transition state theory, by accounting for the decrease in the accessible volume of the transition state and changes in the enthalpy of the hydrogen bonds. In contrast, accounting for these two factors fails to predict the slow down of water near our topologically complex solutes. We show that this failure arises from unexpected broadening of the transition state associated with rotation of water near complex solutes.