

Solvation of simple solutes in water: structural details of the hydrophobic interaction

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Abstract

The hydrophobic interaction is a major stabilizing force in biological molecules and their interactions. The thermodynamic signatures of phenomena such as protein folding or aggregation show these processes to be entropy driven. However, the hydrogen bond itself has a strong enthalpic component and well studied geometric constraints. The majority of experimental structural biology approaches specifically suppress the water signal (NMR) or detect only specific, highly ordered water molecules (X-ray crystallography). Molecular dynamics simulation provides complete atomic resolution for both the solute and solvent, and we use geometric approaches to understand the effects of simple hydrophobic solutes on the surrounding water solvent. The effects of a variety of small solutes on hydrating water molecules have been measured in terms of radial and spatial distributions and measurements of orientation preferences. Our simulation solutes vary from the small, slightly soluble methane molecule, to cyclohexane, benzene, and finally buckminsterfullerene (C_{60}), a meso-scale sphere (diameter ≈ 1 nm). Our results indicate that van der Waals forces are primarily responsible for water structure at the hydrophobic surface. Water density in the first and second hydration shells as well as water-water interactions both within and between shells have been characterized. In the first hydration shell, water density and water-water hydrogen bonded contacts are enhanced. Between the first and second hydration shells, hydrogen bonded contacts are reduced, with interactions predominately occurring at longer distances and higher hydrogen bond angles. We describe triangular arrangements of three water molecules, where the first is hydrogen bonded to the second, the second is hydrogen bonded to the third, and the first and third form a longer-range, non-hydrogen bonded contact. Water "triangles" in the first hydration shell of methane and C_{60} are arranged to minimize the net water dipole near the surfaces of both solutes, reducing the total energy of the system.