Abstract

Solute-induced retardation of water dynamics probed directly by THz spectroscopy

The dynamics of water surrounding a solute is of fundamental importance in chemistry and biology. The properties of water molecules near the surface of a bio-molecule have been the subject of numerous, sometimes controversial experimental and theoretical studies, with some suggesting the existence of rather rigid water structures around carbohydrates and proteins [Pal, S.K, Peon, J., Bagchi, B., Zewail, A.H., (2002), *J. Phys. Chem. B* **106**, 12376-12395]. Hydrogen bond rearrangement in water occurs on the picosecond time scale, so relevant experiments must access these times. Here, we show that THz spectroscopy can directly investigate hydration layers. By a precise measurement of absorption coefficients at 2.3 THz and 2.9 THz we could determine the size and the characteristics of the hydration shell. The hydration layer around a carbohydrate (lactose) is determined to extend to (5.13 ± 0.24) Å from the surface corresponding to ca. 123 water molecules, beyond the first solvation shell. Accompanying molecular modeling calculations support this result and provide a microscopic visualization. The observed increase of the THz absorption of the water in the hydration layer is explained in terms coherent oscillations of the hydration water and solute. Simulations also reveal a slowing down of the hydrogen bond rearrangement dynamics for water molecules near lactose, which occur on the picosecond time scale. Further studies on solvated proteins yield an even larger dynamic hydration layer. The measurements reveal a more complex response of the water solvation dynamics on the solute. THz spectroscopy is shown to be a sensitive tool to detect solute induced changes in the water network.