PROBING HYDROGEN BOND NETWORK VIBRATIONS IN CARBOHYDRATE SOLVATION SHELLS AT THZ FREQUENCIES

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We have employed THz spectroscopy to study properties of the hydrogen bond network of water directly, whose collective vibrational modes are known to be resonant in this frequency range. A table-top THz spectrometer with a p-Germanium laser source emitting 2W pulses, was used to perform measurements on strongly absorbing aqueous solutions of different carbohydrates. The high output power of the laser source in combination with a difference setup enabled us to determine changes of the solution's absorption coefficient due to increasing carbohydrate concentration with high precision. The acquired data were modeled with an approach assuming a random distribution of the solvated molecules[a]. The model allows for the extraction of the absorption coefficent of solvation shell water as well as the actual size of the solvation shell. We find a general increase of the absorption coefficent in the solvation shell that we ascribe to a retardation of water dynamics on picosecond timescales as found by molecular dynamics simulations. The range of this effect or the actual thickness of the solvation shell as probed by our method lies between 3.7 Å for the monosaccharide glucose and 6.5 Å for the disaccharide trehalose[b]. These results indicate that the solvation shell of a carbohydrate molecule not only consists of the first layer of water molecules but also includes the second layer and may even involve a third one as in the case of trehalose. The strength of the effect we observe in THz absorbance strongly correlates with the number of hydrogen bonds formed between the solute molecule and the solvent. We therefore conclude that they provide the link between the solute and its solvation shell, forcing the solvating water to change its dynamical properties.

[a] U. Heugen, G. Schwaab, E. Bründermann, M. Heyden, X. Yu, D.M. Leitner, and M. Havenith **PNAS** 2006, vol. 103, no. 133, 12301-12306

[b] M. Heyden, G. Niehues, U. Heugen, D.M. Leitner, and M. Havenith ***JACS*** 2008, *accepted*