The THz dance of the protein with the water

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***Abstract*— We show that THz absorption measurements of solvated proteins is a new tool to probe the dynamical hydration shell around biomolecules. The measurement of the concentration dependent changes of the Terahertz absorption coefficient yields information on the solute induced changes of the solvation dynamics, its dependence on protein concentration, and the width of the dynamic hydration layer. The results show the potential of THz spectroscopy to yield answers on these biologically relevant questions.**

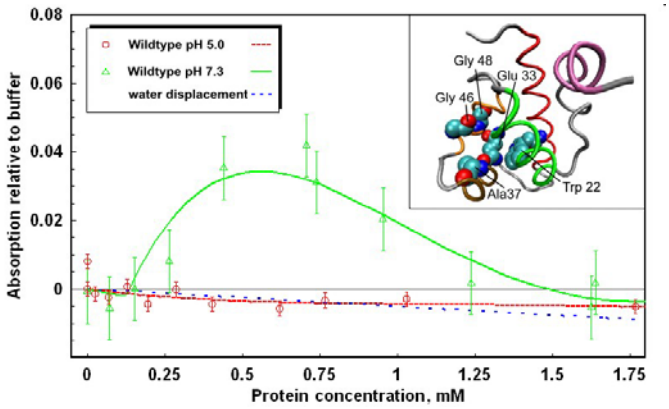
I. Introduction And Background

The focus in protein folding has been very much on the importance of structure, e.g. protein backbone and sidechains. Yet hydration waters make comparable contributions to the structure and energy of proteins. Although the dynamics of the hydration water occurs on the picosecond time scale, 'slaving' to fast solvent modes profoundly is suspected to affect the slower but larger-scale protein motions [1]. In return the protein influences the structure and dynamics of surrounding water molecules [2]. Whereas X-ray and NMR are valuable tools to detect the bound water molecules, they will not provide a clear picture of the changes in the long range solvation dynamics. Fundamental questions of biomolecule hydration include, how far out into the solvent does the biomolecule influence the water network motions, how is the water affected. How are the properties of the hydration water influenced by the separation between protein molecules in solution and how are they influenced by the surface charge and the protein folding? Terahertz spectroscopy is shown to be a powerful tool to directly probe such solute induced changes in the solvation dynamics [3].

II. Results

Using our THz p-type Germanium laser spectrometer we have measured the concentration dependent change of the integral THz absorption coefficient in the spectral range from 2.1-2.8 THz. Solvation of the five helix bundle protein λ^*_{6-85} leads to an unexpected non-monotonic trend in the measured terahertz absorbance as a function of the protein: water molar ratio (see Fig.1). The trend can be explained by overlapping solvation layers around the proteins [4]. Molecular dynamics simulations indicate water dynamics in the solvation layer around one protein to be distinct from bulk water out to about 10 Å. At higher protein concentrations such that solvation layers overlap, the calculated absorption spectrum varies non-monotonically, qualitatively consistent with the experimental observations. The experimental data suggest an influence on the correlated water motion beyond 20 Å, greater than the pure structural correlation length usually measured. Our results, measuring several site specific mutants demonstrate, that the long range hydration layer is protein sequence and pH dependent. Whereas the native wildtype shows the most pronounced effect on the fast water dynamics, the denaturated protein have much less influence on the fast water network motions [5].

Figure 1: Measured integral THz absorption for the protein lambda-repressor as a function of the protein concentration. Displayed is the result for the folded protein (green curve) and partially unfolded protein (red curve). The observed distinct absorption indicates the changes in the dynamical hydration dynamics upon protein folding. For comparison, the dotted line shows the predicted concentration dependence for a THz-transparent ball of the size of the protein.



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978-1-4244-2120-6/08/$25.00 ©IEEE.