Study of Hydrogen-Bonding Energetics and Dynamics of Biological Water Using Ultrafast Electronic Spectroscopy

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When water molecules locate near a biological macromolecule such as protein, their properties are known to deviate from those of water molecules in bulk. Those water molecules in the vicinity of protein surfaces are called biological water. Biological water plays crucial roles in the structure, dynamics and function of biological entities including protein-protein and protein-substrate interactions [1]. Therefore, the study of the energetics and dynamics of biological water is an essential step towards better understanding the characteristics of biological phenomena.

At a biological surface, the hydrogen bond of a water molecule among them can be either replaced by that to a hydrophilic protein surface or limited depending on the topology, hydrophobicity, and/or the charged state of the protein surface (and pocket). The hydration dynamics of biological water has been intensively explored, experimentally and theoretically, to show its deceleration compared to the dynamics of bulk water [1-3]. On the other hand, its energetics has been overlooked, which is a key to understand the molecular interactions at biological surfaces.

Here we report the analysis of the hydrogen-bond energy of biological water through chemical kinetics analysis of excited-state proton transfer (ESPT) mediated by a water hydrogen-bond bridge. The fluorescent, non-canonical amino acid, 7-azatryptophan (AW), was used in this study as a probe. The chromophore of AW, 7-azaindole, is well-known for undergoing ESPT catalyzed by a water molecule, for which 7-azaindole competes with other water molecules to form a cyclic hydrogen-bond bridge. The probe is inserted to a coiled-coil protein to selectively probe the water energetics at the surface of the protein [4]. From the measurements of the femtosecond-resolved fluorescence spectra of the fluorescent amino acids installed, the hydration dynamics was also investigated.

References

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