LASER DESORPTION SUPERSONIC JET SPECTROSCOPY OF HYDRATED TYROSINE

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The structure of tyrosine (tyr) consists of amino-acid chain and phenol, and it has roughly two possible binding sites for water, amino-acid site and phenolic OH site. Investigating how water molecule binds to tyr will give fundamental information for hydrations of peptide and protein. Resonance enhanced multi photon ionization (REMPI) spectrum of tyr-water 1:1 cluster has already been reported by de Vries and co-workers,[a] however, no analysis on the hydrated structures has been reported. In the REMPI spectrum, two clusters of bands are observed; one appears at $\sim$35600 cm^{-1} energy region which is the almost same with 0-0 transitions of tyr monomer,[b] and another is observed at $\sim$300 cm^{-1} lower than the former. Based on the electronic transition energy of phenylalanine and the hydrated clusters,[c] the former is expected to be derived from a structure that water binds to amino acid site. On the other hand, it is plausibly predicted that the latter originates from a structure that water binds to phenolic OH group, because the electronic transition of mono hydrated phenol is $\sim$300 cm^{-1} red-shifted from the monomer.[d] We applied IR dip spectroscopy which can measure conformer selective IR spectra to the tyr-$(H_2O)_1$ clusters by using laser desorption supersonic jet technique to confirm the assignments. Especially in the phenolic OH bound isomer, it was found that the intra molecular hydrogen bond within amino-acid chain, which is far from the water molecule and cannot interact directly with each other, is strengthened by the hydration.

[a] A. Abio-Riziq et al., *J. Phys. Chem. A*, **115**, 6077 (2011).
[b] Y. Shimozono, et al., *Phys. Chem. Chem. Phys.*, (2013) DOI: 10.1039/c3cp43573c.
[c] T. Ebata et al., *Phys. Chem. Chem. Phys.*, **8**, 4783 (2006).
[d] T. Watanabe et al., *J. Chem. Phys.*, **105**, 408 (1996).