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論 文 要 旨
THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

Non-covalent bonds play important roles in biological systems. For example, DNA base pairs include intermolecular interactions and van der Walls interactions support the stability of DNA double strand. Because of the importance of the non-covalent interactions, they attract attention from many researchers. Most of researches have been conducted in solution phase because it is regarded as the mimic environment of the biological systems. However, in the solution phase, it is very difficult to investigate the non-covalent interactions because of disturbance of water. For example, if we want to investigate the intermolecular interactions between a neurotransmitter and its receptor, it is very difficult to distinguish the interactions between the neurotransmitter and the receptor and the interaction with water. Thus, in the present study, we used gas phase spectroscopic technique, particularly, supersonic jet spectroscopic technique. By this method, all hot molecules are cooled down by supersonic jet cooling process and the molecules including the weak non-covalent interactions are trapped into each local minimum. By applying advanced double resonance laser spectroscopic techniques, it is possible to investigate each conformer of the target molecule including the non-covalent interactions. Furthermore, because biomolecules have several H-bond donors and acceptors, it is natural to think that it is possible to apply the supersonic jet spectroscopic technique to investigate the biomolecules. However, in order to measure the biomolecules, one problem, non-volatility of the biomolecules, should be overcome. If we heat a meat, we can obtain a steak but proteins never be evaporated. In order to overcome the problem, recently, laser desorption technique was developed. Instead of the heating, laser is irradiated to the sample then the sample is vaporized by the desorption procedure. With aid of it, we investigated bio and bio-relevant molecules including the non-covalent interactions.

In the present study, laser desorption supersonic jet technique was used to investigate the target molecules. In order to observe the conformer selected UV spectra, UV-UV hole-burning (HB) spectroscopy was applied. With aid of this method, it was possible to indicate 0-0 transitions of each conformer and assign their vibronic bands. In addition, in order to assign the observed conformers, conformer selected IR spectra were also measured by IR dip spectroscopy by replacing the UV burn laser to IR laser.

10 conformers of Homophenylalanine (HPhe), phenylalanine (Phe) analogue molecule, were found by UV-UV HB spectroscopy and their structures were assigned by IR dip and UV absorption spectra with aid of quantum chemical calculations in both S_0 and S_1. It shows the combination of simulated IR and UV spectra is powerful to assign flexible molecules.

Six conformers of Ac-HPhe-Gly-Gly-NH_2 were found by UV-UV HB spectroscopy and assigned by conformer selected IR spectra together with quantum

chemical calculations. It was demonstrated that the most stable conformer of Ac-Phe-Gly-Gly-NH_2 having β-turn - β-turn structure disappears in Ac-HPhe-Gly-Gly-NH_2 due to the strength of NH-π interaction. It suggests that the elongation of the side chain influences the conformation due to the interaction between the aromatic ring and the chain.

Four conformers of adrenaline, which is one of the most famous neurotransmitters, and two conformers of its mono-hydrated cluster were identified by UV-UV HB spectroscopy and structures of the observed species were assigned by comparing with experimental results and theoretical calculations. We found that the most stable conformer of adrenaline is changed due to the enhancement of the π H-bond induced by the attachment of the water molecule. When the water molecule is attached to adrenaline, the water molecule pushes the NH group of adrenaline toward the aromatic ring thus their distance becomes shorter. It suggests that water influences the conformation of adrenaline significantly.

A complex of catechol, a part of adrenaline, and SIVSF-NH_2 peptide, a mimic of its receptor, was measured by laser desorption supersonic jet technic. REMPI spectrum was successfully measured by monitoring the parent mass of the complex and IR dip spectrum was also measured to assign the observed conformer. It is expected that it will allow us to understand molecular recognition in neuro system at molecular level.

We also measured acetaminophen, an enzyme inhibitor, by laser desorption supersonic jet technique and found four species by the UV-UV HB spectroscopy. From the analysis, acetaminophen has two conformers and each conformer gives two independent transitions starting from the most stable $0a_1$ and the hot 1e internal rotational levels.

We can conclude that both inter- and intramolecular interactions play important roles on conformations of biomolecules, reduction of conformers, changing their structures and modification of the stability among conformers. Particularly, in both Ac-HPhe-Gly-Gly-NH_2 and mono-hydrated adrenaline, it was demonstrated that the intramolecular NH-π interaction plays a very important role to stabilize such conformations.