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Biological Chemistry and Molecular Recognition
Ion Chemistry

Exploring Non-Covalent Solute-Solvent Interactions in the Gas Phase

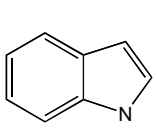
Non-covalent interactions between polypeptides and proteins play a major role in determining the chemical and physical behaviour of these biomolecular polymers. Indeed, a delicate balance between intramolecular interactions and solvation has a significant impact on whether or not many biomolecules exhibit biological, and ultimately physiological, activity. As such, learning more about the nature of these non-covalent interactions and the influence they exert on molecular conformation is an important and topical area of chemical investigation.

A central aim of this project is to understand how non-covalent hydrogen bonding interactions determine molecular and electronic structure and thereby affect physical and chemical behaviour in small, micro-solvated molecules of biological relevance. The project will employ laser spectroscopic techniques together with our recently developed, novel liquid microjet technologies to explore intra- and inter-molecular interactions within small "template" biomolecules isolated as micro-solvated clusters within the gas phase. The "template" molecules will serve as model systems in the development of experimental strategies for interrogating larger molecular systems of direct biochemical interest.

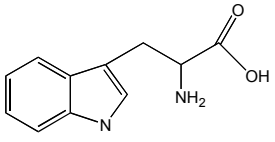
Solutions of "template" biomolecules, including indole, tryptophan, tryptamine and phenylalanine will be introduced to the high vacuum via a liquid microjet. An infrared laser pulse (generated by Raman shifting the fundamental output of a Nd:YAG laser) focused onto the liquid jet will desorb the biomolecular solute from solution into the gas phase. The biomolecules do not absorb the IR radiation, rather the water solvent absorbs this light (via the first overtone of the condensed-phase O-H stretch) and is rapidly heated (in ~7 ns). The resulting thermal shock wave desorbs the intact solute molecules. The extent of solvation of the gas-phase biomolecules is expected be a strong function of the IR laser power, and hence the desorption shock wave.

A second (tunable) UV laser pulse will ionize the intact biomolecules once they are isolated in gas phase. The photoions will be accelerated from the "source" chamber into a time-of-flight (TOF) mass spectrometer. Structural information will be obtained for the "bare" parent ions as well as "micro-solvated" cluster ions by monitoring photoion yields as a function of the laser ionization wavelength.

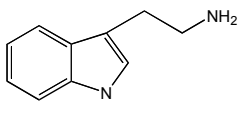
This project offers the possibility of undertaking advanced molecular modeling activities, including *ab initio* molecular orbital, density functional, semi-empirical and force-field theoretical approaches to aid in the interpretation of experimental results.



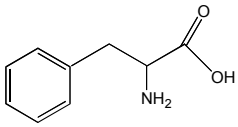
Indole



Tryptophan



Tryptamine



Phenylalanine

References

1 W. L. Holstein, M. R. Hammer, G. F. Metha and M. A. Buntine, *Int. J. Mass Sprectrom.,* **207** (2001) 1-12.