MO 11: Biomolecules

Time: Tuesday 14:00–16:00 Location: V38.02

MO 11.1 Tue 14:00 V38.02

The Sugar Ribose - Structural Complexity in the Gas Phase — E. J. Cocinero[1], P. Écija[1], F. Basterretxea[1], J. A. Fernández[1], F. Castaño[1], A. Lesarri[2], and •J.-U. Grabow[3] — [1]Universidad del País Vasco, Bilbao, Spain — [2]Universidad de Valladolid, Valladolid, Spain — [3]Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany

Sugars are cellular energy fuels, metabolic intermediates, mediators of cellular interactions and structural building blocks. Recently sugars moved into the focus of the quest for prebiotic building blocks in the interstellar medium as tracer for the construction of molecular complexity. However, sugars are structurally complex and elusive to experimental methods: the C5 D-aldose sugar, ribose, was only elucidated by X-ray crystal diffraction in 2010, but the structural information is biased by crystal packing forces. NMR methods conducted in condensed phases yield only solvent-averaged indirect structures.

In textbooks ribose is usually depicted as a β-furanose, predominant in ribonucleosides, ARN, ATP and other biochemically relevant derivatives. But is β-furanose the native form of free ribose? In order to solve these questions we conducted a rotational study of ribose combining FTMW spectroscopy in supersonic jets with ultrafast UV laser vaporization. We could detect six low-energy conformers, all belonging to the pyranose motif; in energetic order: cc-β-pyr $^1C_4$, cc-β-pyr $^4C_1$, c-β-pyr $^1C_4$, c-α-pyr $^1C_4$, cc-α-pyr $^1C_4$, c-α-pyr $^4C_4$. As given, the method also allows for unambiguous distinction between different orientations - clockwise/counterclockwise - of the hydroxyl groups.

MO 11.2 Tue 14:15 V38.02

Monitoring Potential Molecular Interaction Pathways between Adenine and Amino Acids (Gly, Lys, Arg) Using Raman Spectroscopy and DFT Modeling — •Patrice Donfack[1], Shweta Singh[1,2,4], Sunil K. Srivastava[1,3,4], Sebastian Schlücker[4], Phool C. Mishra[2], Birendra P. Asthana[2], and Arnulf Materny[1] — [1]Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany — [2]Department of Physics, Banaras Hindu University, Varanasi 221005, India — [3]Department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalaya, Main Campus, Koni, Bilaspur-495009, India — [4]Fachbereich Physik, Universität Osnabrück, Barbarastraße 7, D-49076 Osnabrück, Germany

In this contribution, we report on Raman spectroscopy and DFT calculations on binary mixtures of adenine with the amino acids Gly, Lys, and Arg at varying molar ratios. We have observed specific changes in the Raman bands of adenine due to the presence of the amino acids. While this is less apparent in the adenine/Gly system, in for Lys or Arg consistent changes are observed in the adenine bands that involve the amino (-NH_2) moiety and the ring N-7 and N-9. Conclusions can be drawn on the interactions between adenine and Lys or Arg proving to be sensitive to both protonation and hydrogen bonding properties. A clear indication is provided that whether the adenine interacts with an amino acid strongly depends on the chemical structure of the latter. DFT calculations have been carried out to further elucidate realistic interaction schemes of adenine with the amino acids.

MO 11.3 Tue 14:30 V38.02

Excited states lifetimes of riboflavin derivatives in solution — •Yvonne Schmitt[1], Madina Mansurova[2], Wolfgang Gärtner[2], and Markus Gerhards[1] — [1]TU Kaiserslautern,Physikal.&Theoret. Chemie,67663 Kaiserslautern — [2]MPI für Bioanorganische Chemie, 45470 Mülheim a. d. Ruhr

Riboflavin has a wide spread field of applications in biology. It reaches from human beings where it is a part of the FAD and FMN, to animals where it is part of the so called cryptochromes and plants in which it supports the execution of photosynthesis. From the spectroscopic point of view riboflavin has interesting features because it can exist in three redox states and different electronic states with different structures. The free rotating ribitiyl chain can lead to different isomers and it is in discussion if these different build ups of riboflavin are important for its functionality. To characterize different electronic states and structures of the molecule infrared, absorption, fluorescence and fluorescence lifetime measurements are applied in addition to quantum mechanical calculations. In this contribution the attention is turned to derivatives of riboflavin since riboflavin exists in nature mostly in a modified form. The electronically excited states and their lifetimes are characterized in different solvents and compared to the spectroscopic features of pure riboflavin.

MO 11.4 Tue 14:45 V38.02

IR-MPD and H-/D-exchange studies on aspartame (Asp-Phe-OMe) and Asp-Phe — •Lars Barzen[1], Christine Merkert[1], Fabian Menges[1], Yevgeniy Nosenko[1], Gereon Niedner-Schatteburg[1], Philippe Maitre[2], and Jean-Michel Ortega[2] — [1]TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany — [2]CLIO/LCP, Université Paris-Sud 11, 91405 Orsay Cedex, France

Aspartame (Asp-Phe-OMe), which is a well known sweetener, and its unprotected analog Asp-Phe have been investigated in the gas phase in the form of protonated cations, of deprotonated anions and of alkali metal cation adducts. We recorded infrared multiphoton dissociation (IR-MPD) spectra of protonated and deprotonated aspartame and Asp-Phe in the range of 2200 - 3900 cm^{-1} by a Laservision IR-OPO system and of protonated and deprotonated aspartame in the range of 600 - 1800 cm^{-1} through application of the Free Electron Laser (FEL) CLIO in Orsay, Paris. For the protonated and deprotonated species and for the alkali metal ion adducts (Li-Cs) of both peptides the most stable structures and IR-spectra have been calculated at DFT level (B3LYP//cc-pVDZ/Stuttgart RSC 1997) and have been compared with respect to their alkali binding sites. H-/D-exchange studies of the protonated and of the alkali metal attached species (Li-K) with ND_3 in our 7-T-Bruker-FT-ICR mass spectrometer give information on the number of easily accessible / available acidic protons and therefore help to elucidate the structure of these molecules. These results are compared to the calculated minimum structures.

MO 11.5 Tue 15:00 V38.02

IR/UV investigations of isolated β-turn and β-sheet peptides — •Kirsten Schwing[1], Thomas Schrader[2], and Markus Gerhards[1] — [1]TU Kaiserslautern, Physikal. und Theoret. Chemie, 67663 Kaiserslautern — [2]Universität Duisburg-Essen, Organische Chemie, 45117 Essen

Due to the direct correlation between structure and functionality of biomolecules the structural investigation of peptides is of great scientific interest. Beyond the influence from the peptide environment intrinsic properties as amino acid sequence and secondary structure are of high importance for conformational preferences. The latter can be studied in molecular beam experiments with combined IR/UV spectroscopy as well as DFT calculations. This strategy is applied to two tripeptide models containing the aromatic amino acids phenylalanine and tyrosine (Ac-Phe-Tyr(Me)-NHMe and Boc-Phe-Tyr(Me)-NHMe). Both species prefer β-turn-structures energetically favoured by aromatic $\pi...\pi$ interactions, whose impact on the stability of secondary structures has been revealed for biological systems. Further important secondary structure motifs are β-sheets, whose formation in the brain tissue is involved in the pathogenesis of different neurodegenerative diseases. Here we describe the first IR/UV analysis of an isolated hetero dimer in a molecular beam. The chosen systems Ac-Val-Tyr-NHMe and Ac-Ala-Ala-Ala-OMe can form different binding motifs as isolated monomer species but the hetero dimer gives a clear evidence of a β-sheet arrangement indicating driving forces for specific structural preferences in isolated peptides.

MO 11.6 Tue 15:15 V38.02

Light triggered peptide folding: Beta-hairpin formation on the nano to microsecond timescale. — •Andreas Deeg[1], Michael Rampp[1], Tobias E. Schrader[1], Jose Pfizer[2], Luis Moroder[2], and Wolfgang Zinth[1] — [1]BioMolecular Optics, University of Munich, Germany — [2]Max-Planck-Institut für Biochemie, Martinsried, Germany

The formation of secondary structure elements like alpha-helices or beta-hairpins are still a matter of intense scientific interest. We have investigated the folding mechanism of a beta-hairpin structure with a model peptide containing two amino acid strands connected by an azobenzene switch in the centre. The peptide forms a beta-hairpin when the azobenzene is in the cis conformation and a random structure

for azobenzene in trans [1]. Recently the light triggered unfolding of the beta-hairpin has been investigated and the unfolding was observed within 3ns [2]. In this contribution the folding of the peptide was studied by time resolved vibrational spectroscopy on the nano to microsecond timescale for different temperatures. We observed strongly temperature dependent single exponential folding dynamics on the 10-100 microsecond timescale. A folding mechanism and an energy landscape, consistent with our data are discussed.

[1] S.-L Dong, Chem.Eur.J. 12, 1114-1120 (2006)
[2] T.E. Schrader, PNAS 104, 15729-15734 (2007)

MO 11.7 Tue 15:30 V38.02

Rotationally resolved electronic spectroscopy of a flexible biomolecule: melatonine — •Michael Schmitt[1], Christian Brand[1], W. Leo Meerts[2], and David W. Pratt[3] — [1]Heinrich-Heine-Universität Düsseldorf — [2]Radboud University Nijmegen — [3]University of Pittsburgh

Rotationally resolved electronic spectra of two origin bands of melatonin have been analyzed using an evolutionary strategy approach. From a comparison of the *ab initio* calculated structures of energy selected conformers to the experimental rotational constants, one band could be shown to be due to a gauche structure of the side chain, while the other band is due to an anti structure. Both bands show a splitting from the three-fold internal rotation of the methyl rotor in the N-acetyl group of the molecules. From a torsional analysis we additionally were able to determine the barriers of the methyl torsion in both electronic states. The electronic nature of the lowest excited singlet state could be determined to be L_b (as in the chromophore indole) from comparison to the results of *ab initio* calculations.

MO 11.8 Tue 15:45 V38.02

Multiplex-CARS microspectroscopy as a tool for fast characterisation of ligno-cellulosic biomass — •Christoph Pohling[1], Christian Brackmann[2], Tiago Buckup[1], Annika Enejder[2], and Marcus Motzkus[1] — [1]PCI, Uni Heidelberg, Germany — [2]Dep. of Chemical and Biological Engineering, Chalmers University, Göteborg, Sweden

Wood biopolymers such as cellulose and lignin have strong potential to replace petroleum-based sources for synthesis of chemicals and materials. This development requires efficient characterization of these renewable raw products, especially in industrial processing where measurement speed is an important factor. Raman microspectroscopy detects sample components probing molecular vibrations. However, the method is time consuming and a pixel dwell time of 500 ms is often necessary in case of biological samples. In this work acquisition time has been reduced using the non-linear Raman-based technique multiplex coherent anti-Stokes Raman scattering (MCARS) microscopy. Wood samples have been investigated using a data acquisition time of 60 ms per pixel and MCARS provided excellent image contrast, background-free chemical imaging and quantitative results. Data analysis using the maximum entropy method (MEM) gave Raman-equivalent data on sample composition and polarization control of the excitation beams provided additional information on the molecular orientation of the wood fibers. In total, MCARS turned out to be a very suitable tool for material characterization, providing rapid imaging with quantitative measures of sample composition and structural information.