

## MO 22: Biomolecules

Time: Thursday 11:00–12:30

Location: F 107

MO 22.1 Thu 11:00 F 107

**Influence of bulged nucleotides on the overall structure of RNA junctions - Precise structural modeling via single molecule FRET** — ●SASCHA FRÖBEL, HAYK VARDANYAN, SIMON SINDBERT, STANISLAV KALININ, CHRISTIAN HANKE, HOLGER GOHLKE, and CLAUS A. M. SEIDEL — Heinrich-Heine-Universität Düsseldorf, Germany

Recently, our group presented a powerful method for the determination of biomolecular structures via Förster resonance energy transfer (FRET) called *FRET-restrained high-precision structural modeling* [1]. The technique is based on single molecule FRET measurements of dye labeled biomolecules freely diffusing in solution. By explicitly considering dye position distributions the accuracy of the extracted distance information and of the final structural models is increased significantly.

Here, *FRET-restrained high-precision structural modeling* is applied to three structurally related RNA three-way junctions. The molecules differ by the number of unpaired nucleotides at the junction region, referred to as *bulges*. Starting with a fully Watson-Crick paired molecule, the influence of a two- and a five-nucleotide bulge on the overall structure is investigated. Changing the bulge size leads to clearly distinct structures, which reveals the strong influence of this structural element on helix orientations. Apparently, this influence is stronger than that of the secondary structure next to the junction region.

[1] S. Kalinin, T. Peulen, S. Sindbert, P.J. Rothwell, S. Berger, T. Restle, R.S. Goody, H. Gohlke and C.A.M. Seidel, *Nature Methods* **9**, 1218-1225 (2012).

MO 22.2 Thu 11:15 F 107

**The Hydrogen Bonding in Vitamin C: A Puzzle Disentangled** — ISABEL PEÑA<sup>1</sup>, ADAM M. DALY<sup>1</sup>, CARLOS CABEZAS<sup>1</sup>, SANTIAGO MATA<sup>1</sup>, CELINA BERMÚDEZ<sup>1</sup>, AMAYA NIÑO<sup>1</sup>, JUAN C. LÓPEZ<sup>1</sup>, JOSÉ L. ALONSO<sup>1</sup>, and ●JENS-UWE GRABOW<sup>2</sup> — <sup>1</sup>Universidad de Valladolid, Valladolid, Spain — <sup>2</sup>Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany

Vitamin C is a gamma-lactone ring where up to eleven intramolecular hydrogen bonds are feasible, establishing three different types of hydrogen bonding. This hydrogen bonding puzzle can stabilize a myriad of low-energy conformers; high-level ab initio computations predict up to 17 conformers within 900 cm<sup>-1</sup>.

There is still no conclusive experimental information on the spatial nature of the hydrogen bonding network that governs the molecule's five degrees of conformational freedom. The only gas phase experiments of any vitamin have been limited to photoelectron spectra of vitamins A and D.

Supersonic-jet Fourier transform microwave (FTMW) spectroscopy is unrivalled in discerning amongst conformers due to the high resolution that is making it sensitive to even subtle structural changes. Here, we used a broadband FTMW instrument called IMPACT (in-phase/quadrature-phase-modulation passage-acquired-coherence technique) in combination with LASER ablation to overcome the vaporization difficulties of vitamin C - using the third harmonic (355nm) of a ps-LASER. Notably, this IMPACT-FTMW implementation offers the well-known sub-Doppler resolution of a coaxial arrangement.

MO 22.3 Thu 11:30 F 107

**Microwave spectroscopy of trimethylgermanium iodide: Internal dynamics of a highly flexible molecule** — ●DAVID SCHMITZ<sup>1</sup>, ALVIN SHUBERT<sup>1</sup>, THOMAS BETZ<sup>1</sup>, WOLFGANG JÄGER<sup>2</sup>, and MELANIE SCHNELL<sup>1</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Hamburg, and Max-Planck-Institut für Kernphysik, Heidelberg — <sup>2</sup>Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

The internal rotations of the three methyl groups of trimethylgermanium iodide ((CH<sub>3</sub>)<sub>3</sub>GeI) give rise to a complex splitting pattern in its microwave rotational spectrum. The understanding and correct interpretation of this pattern provides information not only about the internal motion, but also about the molecular structure, tunneling pathways, and the electron distribution within the molecule.

This contribution will present the interpretation of our measurements performed with three different microwave spectrometers with different spectral resolutions and covering different frequency regions.

A group-theoretical approach was used to make assignments to the

spectra and understand the splitting pattern. Furthermore, ab initio calculations were performed in order to model the potential energy surface and investigate tunneling pathways. Finally, the results were compared with prior studies on trimethylgermanium chloride ((CH<sub>3</sub>)<sub>3</sub>GeCl) and trimethylgermanium bromide ((CH<sub>3</sub>)<sub>3</sub>GeBr).

MO 22.4 Thu 11:45 F 107

**Structural investigations on isolated alanine containing peptides with FT-IR spectroscopy in combination with DFT calculations** — ●MANUEL ZIMMER, SEBASTIAN KRUPPA, and MARKUS GERHARDS — TU Kaiserslautern, Fachbereich Chemie Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Due to the direct correlation between structure and functionality of biomolecules the structural investigation of proteins and peptides as well as their amino acid building blocks are of great scientific interest. IR spectroscopy combined with theoretical calculations provides a powerful tool to determine structural preferences of biologically relevant molecules. Thus, this strategy was applied to the protected alanine peptides Ac-Ala<sub>n</sub>-OMe (n=1-4). For comparison with IR spectra recorded in a heatable gas cell possible isomers of the different alanine peptides as well as their IR modes were calculated by DFT and DFT-D3 calculations (B3LYP/TZVP). The application of Grimme dispersion corrections to a stepwise elongated alanine chain allows a systematic investigation of the dispersion influence on the peptide structures. For increasing peptide chain lengths folded structures are energetically favored. This is much more pronounced in calculations including dispersion corrections. It is also observed that dispersion corrections show significantly different results at a chain length of n ≥ 3. From comparison of calculated with experimental IR frequencies it can be deduced that stretched and folded structures can coexist in the gas phase.

MO 22.5 Thu 12:00 F 107

**Broadband Microwave Spectroscopy of Biologically Relevant Complexes in the Gas Phase** — ●SABRINA ZINN<sup>1,2</sup>, THOMAS BETZ<sup>1,2</sup>, DAVID SCHMITZ<sup>1,2</sup>, V. ALVIN SHUBERT<sup>1,2</sup>, and MELANIE SCHNELL<sup>1,2</sup> — <sup>1</sup>Center for Free-Electron Laser Science, Hamburg — <sup>2</sup>Max-Planck-Institut für Kernphysik, Heidelberg

A new broadband microwave spectrometer, designed for structural investigation of biologically relevant complexes in the gas phase, is presented. In nature, molecular recognition processes often initiate the formation of complexes. An interesting example are Lectins responsible for cell-cell recognition, in which the aromatic moieties of the protein interact with carbohydrates on the cell surface. In our experiments, this recognition process is modeled by forming complexes with aromatic molecules such as benzene, indole, or tryptophan and monosaccharides like glucose, galactose, or fructose.

The rotational spectra of these systems will be recorded with the new Chirped-Pulse Fourier-Transform Microwave spectroscopy (CP-FTMW) method. With this technique, rotational spectra can be measured in a very short time, allowing several complexes to be probed and to investigate the role of different substituents. This technique will be combined with a laser desorption source to bring fragile molecules, for example the monosaccharides, into the gas phase. The analysis of the rotational spectra will give direct insights into the structure of the molecular complexes and will lead to a better understanding of the recognition process, the molecular forces involved and the influence of functional groups and steric effects.

MO 22.6 Thu 12:15 F 107

**Metalated Hoogsteen binding in a nucleobase pair mimic by two-color IR dissociation spectroscopy** — YEVGENIY NOSENKO, FABIAN MENGES, CHRISTOPH RIEHN, and ●GEREON NIEDNER-SCHATTEBURG — FB Chemie und Forschungszentrum OPTIMAS, TU Kaiserslautern, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Deutschland

Two Ag<sup>+</sup> ions, deprotonated 1-methylthymine (1MT-H)- and 1,3-dideaza-adenine (DDA) self-assemble in methanolic solution to a cationic [(Ag)<sub>2</sub>(1MT-H)(DDA)]<sup>+</sup> complex. This stoichiometry identifies in the course of electrospray ionization mass spectrometry. We compare one- and two-color IR Multiple Photon Dissociation spectra (1000-4000 cm<sup>-1</sup>) of trapped complexes with calculated DFT spectra in order to assign vibrational bands and to identify the silver coordi-

nation pattern. This approach reveals two structurally and energetically close isomers that resemble a metalated Hoogsteen-like binding motif invoking metallophilic interaction amongst the adjacent silver ions,[1] which has recently been postulated for a Hoogsteen-type double helix containing 18 contiguous Ag<sup>+</sup> mediated base pairs between 1,3-dideaza-2'-deoxyadenosine and thymidine comprising two Ag<sup>+</sup> ions

per base pair.[2] A two color IR/IR double resonance scheme proved in particular useful to observe the weakly absorbing or weakly fragmenting vibrational bands.[1] References: [1] Y. Nosenko, F. Menges, C. Riehn and G. Niedner-Schatteburg, submitted to PCCP. [2] D. Megger, C. Guerra, J. Hoffmann, B. Brutschy, F. Bickelhaupt and J. Müller, Chemistry-a European Journal, 2011, 17, 6533