MO 24: Biomolecules 2

Time: Friday 14:00–15:30 Location: BEBEL SR144

MO 24.1 Fri 14:00 BEBEL SR144

IRMPD spectra of metal-lumichrome ionic complexes — •Pablo Nieto[1], Alan Günther[1], Sophie Seidenbecher[1], Judith Langer[1], Giel Berden[2], Jos Oomens[2], and Otto Dopfer[1] — [1]Institut für Optik und Atomare Physik Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany — [2]Radboud University Nijmengen Institute for Molecules and Materials, FELIX facility, Toernooiveld 7, 6525 ED Nijmengen, The Netherlands

Flavins are a fundamental class of biomolecules with a lumichrome (LC) chromophore. This family of molecules is involved in many important biological processes. To understand these phenomena at the molecular level, spectroscopic studies of isolated flavins and their complexes are required. We report IRMPD spectra of mass selected Me^{q+}-LC (Me^{q+}= Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+} and Ag^+) ionic complexes in the fingerprint range (800-1900 cm^{-1}) recorded in a FT-ICR-MS ion trap coupled to the free electron laser FELIX. In the liquid phase, flavins preferently bind to positions at N5 and O4 [2]. In contrast, the additional O2 binding site was identified in our experiments. Furthermore, the spectra for Li^+ and Ag^+ are very similar, suggesting that both ions have comparable binding energies to LC. Finally, Mg^{2+} ions form strongly-bound Mg^{2+}-$(LC)_2$ complexes in a T-shaped structure. The large IRMPD linewidth (>15 cm^{-1}) due to the ion temperature (300 K) poses a limitation to these experiments. This limitation will be overcome with our new apparatus equipped with an ESI source and a cryogenic 22-pole ion trap (4 K) where single photon absorption spectroscopy will be carried out.

MO 24.2 Fri 14:15 BEBEL SR144

The α-Helix Motif in β-Peptides — Franziska Schubert[1], Kevin Pagel[1], Mariana Rossi[1,2], Stephan Warnke[1], Gert von Helden[1], Volker Blum[1,3], •Carsten Baldauf[1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Physical and Theoretical Chemistry, University of Oxford, U.K. — [3]MEMS, Duke University, Durham, U.S.A.

The natural α-helix motif is important in protein-protein recognition and binding. Its imitation by non-natural peptides may open route to modulators of protein interactions. In order to identify the prominent α-helix-motif also in β-peptides, we compare the conformational preferences of peptides Ac-$(Xaa)_6$-$LysH^+$, with Xaa being the α-amino acid alanine (peptide Pα) or its β-equivalent homo-alanine (peptide Pβ) that contains one more methylene unit than the α-building block. Such polyalanine-peptides were developed by Jarrold and co-workers to form α-helices in the gas phase.[1] Conformational space of Pα and Pβ was sampled globally by force field replica-exchange molecular dynamics (REMD) and then refined locally by *ab initio* REMD with the PBE functional corrected for long-range dispersion. Pα is found to be mostly α-helical in the gas-phase at 300K.[2] Considering harmonic free energy corrections for Pβ, we find helical and non-helical conformers in the low free-energy regime. Helices are strongly stabilized by vibrational free energy. The combination of simulations with vibrational spectra and collision cross sections provides the first evidence for the α-helix motif in β-peptides. [1] Hudgins, Ratner, Jarrold: JACS 120, 12974 (1999); [2] Rossi, Scheffler, Blum: JPCB 117, 5574 (2013).

MO 24.3 Fri 14:30 BEBEL SR144

Two color enhanced IRMPD spectroscopy of mononuclear Ag(I)/Cu(I)-Bispyridine-complexes — •Joachim Hewer, Maximilian Gaffga, Yevgeniy Nosenko, and Gereon Niedner-Schatteburg — Technische Universität Kaiserslautern, Germany

Mass spectrometry and IR spectroscopy in combination enable us to investigate isolated ionic species without interference form solvents, lattices or adsorbates. Utilizing a two laser setup, resonant two color IRMPD (infrared multi photon dissociation) is capable of enhancing fragmentation efficiencies, thus revealing vibrational bands, which may be hardly observable by single color IRMPD.[1][2] We report studies on a set of mononuclear transition metal complexes $[HP\text{-}M\text{-}AP]^+$ (HP = 2-Hydroxypyridine, 3-Hydroxypyridine; AP = 2-Aminopicoline; M = Ag, Cu), which serve as model systems for intramolecular energy transfer across the metal center. Our investigations elucidate the internal vibrational redistribution (IVR) process as a function of the frequency, intensity and time delay of the applied nanosecond IR pulses. The specific fragmentation behavior provides some insight into vibrational mode couplings beyond ergodicity.

[1] Y. Nosenko, F. Menges and C. Riehn, G. Niedner-Schatteburg, PCCP, 2013, 8171-8178.

[2] M. Gaffga, J.I. Lang, F. Menges, K. Muller, W. Thiel, G. Niedner-Schatteburg, 2013, manuscript in preparation.

MO 24.4 Fri 14:45 BEBEL SR144

Infrared Photodissociation Spectroscopy of Microsolvated β-phenethylamine Cation Complexes in the Gas Phase — •Markus Schütz, Aude Bouchet, Alexander Klemt, and Otto Dopfer — Institut für Optik und Atomare Physik, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Neurotransmitters have important biological functions and play an important role in human behaviour. The molecule β-phenethylamine (PEA) is the simplest aromatic biogenic ethylamino neurotransmitter. It acts as a backbone of numerous hallucinogen substances and as a model for more complex neurotransmitters. Infrared photodissociation (IRPD) spectra of the Ar- and H_2O-tagged PEA cation complexes are recorded to study the conformation and microsolvation in nonpolar and polar environment. Comparison with simulated vibrational spectra from density functional theory allows for the assignment of different isomers and reveals some surprising insights into geometrical structures.

MO 24.5 Fri 15:00 BEBEL SR144

Gas-Phase Spectroscopy of Conformer-Selected Proteins — •Stephan Warnke, Kevin Pagel, and Gert von Helden — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Mass spectrometry (MS) is a key technique to investigate biomolecules in the gas phase and many methods are available to obtain mass/charge ratios with very high accuracy. In combination with gas-phase spectroscopy, information about the molecules' composition and local structure can be obtained. However, the overall 3-dimensional structure of the molecule cannot be investigated with these methods alone - even though their knowledge is crucial for the understanding of intra- and inter- molecular interactions as well as the function of the molecule in the living organism. Additionally, peptides and proteins can coexist in a multitude of different conformations in the gas phase and is is not clear in how far this structural heterogeneity does affect the above mentioned methods. A technique that is sensitive to the higher order structure of gas-phase ions is ion mobility spectrometry (IMS). In IMS the absolute (angle averaged) collision cross section and, thus, the effective size of the ion is determined. When molecules coexist in different conformations, they can be separated in space and time to allow for experiments on both mass/charge as well as shape/charge selected biomolecular ions.

In this talk, first results of spectroscopic experiments on mass/charge and conformer selected gas-phase proteins will be presented.

MO 24.6 Fri 15:15 BEBEL SR144

Binding motifs of a microsolvated neurotransmitter: IR spectroscopy of Ar-tagged protonated phenylethylamine and its water clusters — •Aude Bouchet, Markus Schütz, and Otto Dopfer — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

The characterization of the three-dimensional structure of biologically relevant molecules, the role played by inter- and intramolecular interactions, especially with water which is the ubiquitous solvent in biological media, and their ability to form charged groups, are key issues to be addressed to deepen the understanding of recognition phenomena at the molecular level in biological environments. Biomolecules are generally not neutral in physiological medium, but protonated or zwitterionic. The conformation of these charged molecules and their solvation shell is thereby modified compared to neutral species. Here, vibrational spectroscopy, associated with quantum chemical calculations, has been applied on a protonated neurotransmitter, phenylethylamine (H^+PEA), and its water clusters isolated in the gas phase. The results obtained on the Ar-tagged H^+PEA show that a strong intramolecular $NH\cdots\pi$ interaction induces conformational locking of the monomer into a folded structure. Monohydrated H^+PEA reveals

that a very stable inclusion structure is experimentally generated, in which the water molecule is inserted between the positively charged amino group and the phenyl moiety of H^+PEA. This ligand acts both as an hydrogen bond acceptor ($NH\cdots O$) and hydrogen bond donor ($OH\cdots\pi$). A second isomer, for which the water is H bonded to a "surface" NH group is also found.