MO 11: Biomolecules 1

Time: Wednesday 14:00–15:45 Location: BEBEL HS213

MO 11.1 Wed 14:00 BEBEL HS213

Probing Protonation Sites of Isolated Flavin Molecules via IR Spectroscopy — •Alan Günther[1], Judith Langer[1], Giel Berden[2], Jos Oomens[3], and Otto Dopfer[1] — [1]Institut für Optik und Atomare Physik , Hardenbergstr. 36, 10623 Berlin, Germany — [2]Radboud University Nijmegen, Institute for Molecules and Materials, FELIX facility, Toernooiveld 7, 6525 ED Nijmegen — [3]University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands

Infrared spectra of the isolated protonated flavin molecules lumichrome, lumiflavin, riboflavin (vitamin B2), and the biologically important cofactor of blue-light receptors flavin mononucleotide are measured in the fingerprint range (600-1850 cm^{-1}) by means of IR multiple photon dissociation (IRMPD) spectroscopy. Using density functional theory calculations, the geometries, relative energies, and linear IR absorption spectra of several low energy isomers have been calculated. Comparison of the calculated IR spectra with the measured IRMPD spectra reveals that the N10 substituent at the isoalloxazine ring influences the protonation site of the flavin. Lumichrome with a hydrogen substituent is only stable as N1 hydrogenated tautomer and protonates at N5 of the pyrazine ring. The presence of the sugar unit in riboflavin leads to protonation at N1 of the pyrimidinedione moiety, and methyl substitution in lumiflavin stabilizes the tautomer which is protonated at O2. In contrast, flavin mononucleotide occurs as both the O2 and N1 protonated tautomers. The frequencies and relative intensities of the two C=O stretch vibrations in protonated flavins serve as reliable indicators for their protonation site.

MO 11.2 Wed 14:15 BEBEL HS213

Rotational Spectrum of 4-Aminobenzonitrile - Nuclear Quadrupole Coupling Constants of Two Chemically Distinct Nitrogen Atoms — •Thomas Betz[1,2,3], Sabrina Zina[1,2,3], Jack B. Graneek[1,3], and Melanie Schnell[1,2,3] — [1]Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, D-22761 Hamburg — [2]The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, D-22761 Hamburg — [3]Center for Free-Electron Laser Science, Notkestrasse 85, D-22607 Hamburg

4-aminobenzonitrile belongs to the class of para-substituted benzonitriles, which evoked attention because some representatives display double-fluorescence effects. In 4-aminobenzonitrile this has not been observed and this study aims to improve the understanding of the underlying principles.

The rotational spectrum between 2 and 8.5 GHz of this molecule in the gas phase is reported. Due to the two chemically distinct nitrogen atoms the observed transitions show a complex hyperfine structure. From the determination of the nuclear quadrupole coupling constants, information on the electronic environment of these atoms could be inferred. The results are compared to related molecules and indicate a reason for the absence of double-fluorescence effects in 4-aminobenzonitrile.

MO 11.3 Wed 14:30 BEBEL HS213

Histidine-cation interaction and microsolvation from first principles — •Markus Schneider[1], Volker Blum[1,2], Carsten Baldauf[1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]MEMS, Duke University, Durham, U.S.A.

Protein-cation interactions play a crucial role in shaping the three-dimensional structure of protein. Of special importance here is the histidine side chain that is, among other examples, involved in the metal cation complexation by the Alzheimer Aβ peptide. Our work aims for understanding the binding of cations by histidine as well as its effect on the peptide structure from first principles. However, the first critical point is the appropriateness of the chosen level of theory for quantitative predictions of such interactions. To that end, we focus on the effect of microsolvation, with either Zn^{2+} or a H_2O molecule or both in competition, on the protonation state of the His sidechain. We first assemble a large ensemble of possible conformations from empirical force field calculations. Then, we use these conformations to benchmark the performance of density-functional theory based methods against high-level coupled-cluster calculations. In particular, we assess the PBE generalized gradient approximation as well as the PBEh and B3LYP hybrid density functionals, all of them corrected for long-range dispersion with either the pairwise Tkatchenko-Scheffler scheme or a newly developed many-body dispersion scheme (MBD∗).

MO 11.4 Wed 14:45 BEBEL HS213

Elucidating the Building and Breaking of Hydrogen Bonds: Two color delay dependent IR probing of torsional isomerization — •Johannes Lang, Maximilian Gaffga, Fabian Menges, Kevin Muller, Werner Thiel, and Gereon Niedner-Schatteburg — Technische Universität Kaiserslautern, Germany

Infrared multiple-photon dissociation (IR-MPD) spectroscopy can be used to characterize organometallic complexes in the gas phase [1]. Here, we investigate a flexible arrangement of a single Ag(I) center with two suitable ligands via IR MPD spectroscopy and density functional theory (DFT) based calculations. Bands of at least two isomers can be assigned in the experimental spectrum. These bands correspond to NH—O or CH—O stabilized rotational conformers, in which the Ag(I) ion serves as a pivot. Delay dependent two color IR-MPD measurements elucidate changes of the relative isomer population. We characterize rotational barriers, the change of vibrational frequencies and IR intensities along the isomerization pathway by DFT based calculations [2].

References:

[1] Nosenko, Y., et al., Physical Chemistry Chemical Physics, 2013. 15(21): p. 8171-8178.

[2] Gaffga, M., Lang, J.I., Menges, F., Muller, K., Thiel, W., Niedner-Schatteburg, G., manuscript in preparation. 2014.

MO 11.5 Wed 15:00 BEBEL HS213

Femtosecond 2D-IR spectroscopy of SCN - a vibrational probe for protein dynamics — •Daniela Kern-Michler, Luuk van Wilderen, Henrike M. Müller-Werkmeister, and Jens Bredenbeck — Institut für Biophysik, Gothe Universität / Frankfurt am Main

Novel vibrational probes like nitrile, azide or thiocyanate (SCN) groups [1] are useful to obtain dynamic and site-specific information in proteins. We measured steady-state and time-resolved infrared (IR) spectra of methylthiocyanate (MeSCN) in various solvents with different polarities and H-bonding character to characterize the SCN moiety as an infrared label. To demonstrate the applicability in a protein, we introduced a $S^{13}C^{15}N$ group into bovine hemoglobin (Hb) [2].The central SCN stretch frequency depends on the solvent properties, making SCN a suitable probe for its local environment. In addition, we measured time-resolved two-dimensional infrared (2D-IR) spectra of $S^{13}C^{15}N$ in Hb, which hint at local structural rearrangements on an ultrafast timescale. The low central frequency observed in the protein compared to MeSCN indicates that the label is not hydrogen bonded, although we measure a shorter vibrational lifetime (T1) than for MeSCN. The rich molecular detail the label provides on its local surroundings, combined with its relatively long T1 (34 ps), makes the SCN vibration thus a promising IR label to resolve protein dynamics.

[1]Lindquist et al. (2009) PCCP,11 (37), 8105-8380 [2] Fafarman et al. (2006). JACS,128, 13356-13357 [3] Kim et al. (2013) Chem. Rev.113 (8), pp 5817-5847

MO 11.6 Wed 15:15 BEBEL HS213

Ultrafast pump-probe spectroscopy on the initial photoreaction of bathy-phytochrome Agp2 of *Agrobacterium tumefaciens* reveals transient protonation processes — •Patrick Singer[1], Sybille Wörner[2], Tilman Lamparter[2], and Rolf Diller[1] — [1]Dept. of Physics, Univ. Kaiserslautern, 67663 Germany — [2]Dept. of General Botany, KIT, 76131 Germany

Plant photomorphogenesis is regulated by the photoreceptor phytochrome, a light controlled protein in plants, bacteria and fungi. Photoinduced interconversion between a thermally stable red absorbing state Pr and the biologically active far red absorbing state Pfr is initiated by light absorption of the open chain tetrapyrrole bilin chromophore, undergoing a rapid isomerization reaction (femtosecond timescale)[1]. In this study we investigate Agp2 from *A. tumefaciens*, which fundamentally differs from common phytochromes in its photodynamic properties caused by a thermally (in-)stable (Pr)Pfr ground state (bathy-phytochrome). Previous investigations reveal protonation/deprotonation of the Pr chromophore with an unusually low pKa = 7.85 (pKa > 11 in common phytochromes)[2]. We performed transient UV/Vis pump-probe spectroscopy on the fs-time scale in different buffer-conditions (H_2O/D_2O; pH6 - pH9) to investigate spectral and kinetic properties of the primary photoreaction of the Pr state. Transient measurements reveal two fast decaying intermediate species dependent on buffer condition. The results are discussed in context of chromophore protonation processes. [1]C. Schumann et al. Biophys.J. 94 3189-3197(2008) [2]B. Zienicke et al. JBC 288 31738-31751(2013)

MO 11.7 Wed 15:30 BEBEL HS213

Ultrafast Spectroscopic Studies of Cyclic Tetrazolium Cell Dyes and their Photoproducts

— •Florian Kanal, Domenik Schleier, Nina Schopf, and Patrick Nuernberger — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Tetrazolium salts are cyclic dyes which are commonly used for testing cell viabilities by detecting formazans as their enzymatically metabolised ring-open forms. The influence of light is often ignored in these assays, although for some tetrazolium salts photochemical reduction to formazans has been reported.

The ultrafast photochemistry of two of the most prominent tetrazolium salts, 2,3,5-Triphenyl-tetrazolium chloride (TTC) and 3-(4,5-Dimethyl-2-thiazolyl)-2,5-diphenyl-tetrazolium bromide (MTT) was investigated in alcoholic and different pH-valued aqueous solutions by ultrafast spectroscopy. Both compounds yield the formazan via reaction channels involving different short-living ring-open and -closed structures within few nanoseconds either in alcoholic (TTC) or in basic (MTT) solution.

Depending on the solvent, TTC-formazan shows either the formation of a bicyclic radical or huge conformational changes in the formazan skeleton upon long-time irradiation. In contrast, the ultrafast dynamics of TTC- and MTT-formazan are almost unaltered if the solvent is changed. As only the primary steps of both reactions take place on an ultrafast time-scale, involvement of a long-living state is most likely for the final product formation.