MO 15 Biomolecules II

Zeit: Freitag 17:00–18:45 Raum: HU 2097

MO 15.1 Fr 17:00 HU 2097

Non-Adiabatic Effects on Peptide Vibrational Dynamics Induced by Conformational Changes — •Burkhard Schmidt, Jens Antony, and Christof Schütte — Freie Universität, Institut für Mathematik II, Arnimallee 2-6, 14195 Berlin

Quantum dynamical simulations of vibrational spectroscopy have been carried out for glycine dipeptide (CH3-CO-NH-CH2-CO-NH-CH3). Conformational structure and dynamics are modeled in terms of the two Ramachandran dihedral angles of the molecular backbone. Potential energy surfaces and harmonic frequencies are obtained from electronic structure calculations at the DFT (B3LYP/6-31+G(d)) level. The ordering of the energetically most stable isomers (C7 and C5) is reversed upon inclusion of the quantum mechanical zero point vibrational energy. Vibrational spectra of various isomers show distinct differences, mainly in the region of the amide modes, thereby relating conformational structures and vibrational spectra. Conformational dynamics is modeled by propagation of quantum mechanical wave packets. Assuming a directed energy transfer to the torsional degrees of freedom, transitions between the C7 and C5 minimum energy structures occur on a sub-picosecond timescale (700 ... 800 fs). Vibrationally non-adiabatic effects are investigated for the case of the coupled, fundamentally excited amide I states. Using a two state-two mode model, the resulting wave packet dynamics is found to be strongly non-adiabatic due to the presence of a seam of the two potential energy surfaces. Initially prepared adiabatic vibrational states decay upon conformational change on a timescale of 200 ... 500 fs with population transfer of more than 50

MO 15.2 Fr 17:15 HU 2097

Structural identification of gas-phase biomolecules using IR spectroscopy — •Joost M. Bakker[1,2], Isabelle Compagnon[1], Gert von Helden[2], Jos Oomens[1], and Gerard Meijer[2] — [1]FOM Institute for Plasma Physics Rijnhuizen, Nieuwegein, The Netherlands — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

For biologically relevant molecules, the primary structure can nowadays be obtained in a rather routine fashion, making use of techniques such as mass spectrometry and electrophoresis. The secondary and higher orders structures, i.e. the three dimensional structure, of such systems are much harder to obtain, however. Since the secondary structure is a decisive factor in the biological function of the species, it is of great interest to study the fundamental interactions that determine the shape of the molecule. In gas-phase experiments the influences of a solvating medium are eliminated, so a careful study of these inter- and intramolecular interactions is possible.

Here, we present results of studies of gas-phase biomolecules using infrared (IR) ion-dip spectroscopy. Using this double-resonance technique, IR spectra of cold, well defined structural conformers can be measured. IR excitation of the molecules of interest is performed with mid-IR radiation (5–40 μm) produced by the Free-Electron Laser for Infrared eXperiments (FELIX) in Nieuwegein, the Netherlands, followed by UV ionization. Among systems that are studied are small tryptophan containing peptides, the gas-phase nucleobase pair guanine-cytosine and a model di-saccharide: lactose.

MO 15.3 Fr 17:30 HU 2097

Solvation of Protonated Biomolecular Building Blocks: IR spectra of Protonated Imidazole Clusters — •Horia-Sorin Andrei, Nicola Solca, and Otto Dopfer — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Imidazole (Im) is a principal building block of many bioorganic compounds, such as the DNA bases adenine (A) and guanine (G) and the amino acid histidine (His). Because of its high proton affinity, Im is often protonated even at physiological pH values and acts in many enzymatic processes as a proton shuttle. Here, we report on IR spectra and quantum chemical calculations of ImH^+-$(H_2O)_n$ clusters to evaluate the properties of ImH^+ under controlled microhydration conditions. Additional spectra recorded for ImH^+-L_n with L=Ar, N_2, and CH_4 yield detailed information about the acidity of the NH protons of ImH^+ in both nonpolar and polar environments.

MO 15.4 Fr 17:45 HU 2097

Excited state H-transfer and conical intersections in 2-aminopyridine: A model for DNA base pairs — •Thomas Schultz, E. Samoylova, W. Radloff, and I.V. Hertel — Max-Born-Institut Berlin, Max-Born Strasse 2a, 12489 Berlin, Germany

2-Aminopyridine (2AP) dimer allows the investigation of basic photochemical reaction mechanisms in hydrogen bonded chromophores. Time resolved ionization spectroscopy revealed nanosecond excited state lifetimes for the 2AP monomer and larger clusters ($2AP_{n\geq 3}$), but a remarkably accelerated excited state relaxation (τ = 65 ps) for the H-bound dimer. This fast relaxation was assigned to an excited state H-transfer and subsequent relaxation via conical intersections to the electronic ground state. Calculated cluster structures indicated that the H-transfer occurs only in near-planar doubly H-bound structures. The same process may occur in the Watson-Crick base pair guanine-cytosine and could thus contribute to the photochemical stability of DNA.

MO 15.5 Fr 18:00 HU 2097

Excited state dynamics of a PYP chromophore model system explored with ultrafast infrared spectroscopy — •Anwar Usman, Omar F. Mohammed, Karsten Heyne, Jens Dreyer, and Erik T. J. Nibbering — Max Born Institut, Max Born Strasse 2A, D-12489 Berlin, Germany

Ultrafast mid-infrared spectroscopy enables the determination of dynamically evolving structures by monitoring vibrational marker modes. We perform ultrafast polarization sensitive visible pump-infrared probe spectroscopy on deprotonated trans-S-phenyl-thio-p-hydroxycinnamate, a model compound for photoactive yellow protein. We derive structural information from the observed bleach signals by comparison of the experimental frequency positions and anisotropies with results from quantum chemical calculations. The electronically excited state decays with 8 ps or 15 ps time constants for 1:1 or 10:1 DMSO:buffer, respectively, with a quantum yield for isomerization product formation less than 5

MO 15.6 Fr 18:15 HU 2097

Excited state dynamics of isolated DNA bases and base pairs — •Elena Samoylova, Th. Schultz, W. Radloff, H.-H. Ritze, and I.V. Hertel — Max-Born Institut Berlin, Max-Born-Str. 2A, D-12489 Berlin, Germany

We describe excited state dynamics of adenine$_n$ and thymine$_n$ clusters (n=1,2,3) with femtosecond pump-probe mass and electron spectroscopy. The clusters were excited with 250-272 nm pulses and ionized with 800 nm. The monomers decay to the electronic ground state through the $n\pi^*$ state with time constants of 1 ps for adenine and 6.5 ps for thymine. A similar relaxation pathway is found in thymine clusters. In contrast to this, time-dependent signals of adenine dimer suggest an additional relaxation channel via the $\pi\sigma^*$ state that is much faster ($<$ 50 fs). The dynamics of the adenine-thymine heterodimer indicate both relaxation channels described above. Different isomers may contribute to the cluster signals observed in our gas phase experiments. A new experimental approach combining hole burning method with femtosecond time-resolved spectroscopy is suggested to resolve this issue.

MO 15.7 Fr 18:30 HU 2097

Excited state dynamics in the solvated DNA base adenine — •Valoris Reid Smith, E. Samoylova, H. Lippert, H.-H. Ritze, W. Radloff, I.V. Hertel, and Th. Schultz — Max-Born-Institut Berlin, Max-Born Strasse 2a, 12489 Berlin, Germany

The extraordinary robustness of DNA with respect to damage by the harmful UV components of sunlight may have been crucial to the development of life on earth. The structural complexity of DNA hinders an understanding of the underlying photophysical processes. To simplify the analysis, we studied the isolated DNA base adenine, and microsolvated water clusters thereof by femtosecond time resolved spectroscopy and photoelectron photoion coincidence measurements. Two competing relaxation pathways were identified: (a) $\pi\pi^*$ to $n\pi^*$ internal conversion followed by a picosecond relaxation back to the ground state and (b) $\pi\pi^*$ to $\pi\sigma^*$ internal conversion followed by ultrafast relaxation to the ground state.

In Adenine-water clusters, the $\pi\pi^*$ to $\pi\sigma^*$ process dominated the ob-

served reaction dynamics. This was explained by the lowering of the $\pi\sigma^*$ state energy in the water clusters. In the Adenine$(H_2O)_2$ cluster, an additional process leads to a yet unidentified state with a very long lifetime.