

MO 41 Hauptvorträge

Zeit: Mittwoch 10:40–12:40

Raum: H12

Hauptvortrag

MO 41.1 Mi 10:40 H12

Light and molecules: from structure to function using laser pulses — ●LETICIA GONZÁLEZ — Institut für Chemie und Biochemie, Takustrasse 3, 14195 Berlin

This talk will address the problem of tracking the ultrafast dynamics of light induced reactions in real time and its possible manipulation from the theoretical point of view. The different steps that take place in a chemical reaction, like breaking and forming of bonds, isomerization processes, etc, occur in a femtosecond time regime. Using laser pulses in this time scale, it is possible to follow carefully the movement of the nuclei. Furthermore, today's laser technology has made it possible to shape laser pulses in such a way that a particular nuclear motion can be artificially imprinted, leading to the so-called coherent control of molecular reactions. Using quantum chemistry and wave packet propagations I will illustrate how to use laser light to maneuver the structure and function of polyatomic systems. Specifically, molecular orientation, selective dissociation of molecular bonds, how to separate enantiomers from a racemic mixture, and how to initiate a molecular rotor will be shown.

Hauptvortrag

MO 41.2 Mi 11:10 H12

Ultrafast bimolecular proton transfer in water: from direct exchange to sequential hopping — ●ERIK T. J. NIBBERING¹, OMAR F. MOHAMMED¹, JENS DREYER¹, DINA PINES², and EHUD PINES² — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany — ²Department of Chemistry, Ben Gurion University of the Negev, Beersheva 84125, Israel

Bimolecular acid-base neutralization reactions in aqueous solution involve, according to Eigen and Weller, diffusive motion, and upon formation of the reactive encounter complex, an exchange of a proton. Until now the nature of this encounter pair had not been elucidated. Proton transfer may occur in a tight complex between acid and base directly bound by a hydrogen bond, forming the reaction coordinate. An encounter complex may also involve an acid and base connected via a water bridge [1]. We now have been able to determine the ultrafast proton transfer rates of these tight and loose acid-base complexes with femtosecond infrared spectroscopy. We use the dye stain pyranine as optically triggered acid (photoacid ROH) as a means to follow in real time its reaction with carboxylic bases B⁻. By monitoring infrared-active marker modes we are able, in the case of the loose complexes, to follow the sequential, von Grothuss type, hopping of the proton from the photoacid, through an intermediate water bridge, to the base [2]. The transient spectra of the hydrated proton band indicate a hydronium cation H₃O⁺ stabilized in an Eigen configuration in an ionic complex RO⁻ ··· H₃O⁺ ··· B⁻. [1]. M. Rini et al., Science 301, 349 (2003); J. Chem. Phys. 121, 9593 (2004). [2]. O. F. Mohammed et al., Science 310, 83 (2005).

Hauptvortrag

MO 41.3 Mi 11:40 H12

***o*-Nitrobenzaldehyde: A "Tool" to study Hydrogen Transfer Reactions, Nucleophilic Additions, and Eliminations** — ●PETER GILCH, HILMAR SCHACHENMAYR, WOLFGANG SCHREIER, and STEFAN LAIMGRUBER — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Upon light absorption *o*-nitrobenzaldehyde is transformed into *o*-nitrosobenzoic acid. Although this reaction has first been described more than 100 years ago it is only now that by femtosecond vibrational spectroscopy intermediates of this reaction have been unequivocally identified [1]. The excitation of NBA initiates a hydrogen transfer which within 400 fs results in the formation of a first ground state intermediate - a ketene. This ketene has been observed via femtosecond IR spectroscopy. The ketene is subject to a nucleophilic addition occurring with a strongly solvent dependent reaction time (with time constants of ~ 10 ps – 2 ns). In protic solvents the reaction takes place while the ketene is still vibrationally hot which results in non-exponential kinetics. The product of the addition is characterized by IR and stimulated Raman spectroscopy. It transforms into the final nitroso product via an elimination. Thus, NBA allows to study at least three elementary reaction types of organic chemistry.

[1] S. Laimgruber et al., Angew. Chem. Int. Ed. 44 (2005) 7901.

Hauptvortrag

MO 41.4 Mi 12:10 H12

Peptides and peptide aggregates in the gas phase: what do we learn from isomer selective IR/UV spectroscopy — ●MARKUS GERHARDS — H.-Heine Universität Düsseldorf, Institut für Physikalische Chemie I, Universitätsstraße 26.33.02, 40225 Düsseldorf

Secondary structures play an important role to explain the function of proteins. There are different important binding motifs like β -sheets, α -helices, β -turns or γ -turns. These structures are stabilized by intra- or intermolecular hydrogen bonds. In order to figure out the influence on structure and individual hydrogen bonds upon aggregation with water and to learn more about the driving forces to form secondary structures, isolated di- up to pentapeptides and peptide aggregates are analyzed by mass-, isomer-, and state-selective combined IR/UV techniques, i.e. for each isomer of a given peptide the individual IR spectrum can be recorded in a molecular beam experiment. In combination with force field and ab initio calculations the IR spectra yield the structural binding motif and the strength of the hydrogen bonds. By adding water gradually the influence of a microsolvation shell on the secondary structure can be investigated. Not only water but also templates can form aggregates with peptides. The chosen templates are important to inhibit pathogenic β -sheets, especially the aggregation of templates to a peptide sequence responsible for Alzheimer disease will be discussed.