

MO 15 Molecular Clusters II

Zeit: Montag 16:30–18:45

Raum: H10

MO 15.1 Mo 16:30 H10

Effiziente globale Optimierung: Von Clusterstrukturen bis zur Proteinfaltung — ●BERND HARTKE — Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstr. 40, 24098 Kiel

Mit stochastisch-heuristischen globalen Optimierungsmethoden [1,2] konnten wir unvoreingenommene Strukturvorschläge für Solvatationscluster der Alkali-Kationen machen [3]. Simulationen der IR-Spektren der besten Strukturen stimmen hervorragend mit experimentellen Spektren überein [4] und werden von MD-Simulationen bei experimentell relevanten Temperaturen bis 150 K gestützt. Daraus ergibt sich eine neue Hypothese zur Begründung magischer Zahlen in diesen Systemen [5].

Kürzlich konnten wir unsere Methoden auch auf das verwandte Problem der Proteinfaltung ausdehnen [6]. In ersten Anwendungen konnten wir nicht nur Testsysteme, sondern auch reale Proteine aus der Protein-datenbank PDB erfolgreich falten.

[1] B. Hartke, *J. Comput. Chem.* 20 (1999) 1752.

[2] B. Hartke, *Angew. Chem.* 114 (2002) 1534.

[3] F. Schulz und B. Hartke, *Chem. Phys. Chem.* 3 (2002) 98.

[4] F. Schulz, B. Hartke und J. Lisy, Manuskript in Vorbereitung.

[5] F. Schulz und B. Hartke, *Theor. Chem. Acc.* 114 (2005) 357.

[6] F. Koskowski und B. Hartke, *J. Comput. Chem.* 26 (2005) 1169.

MO 15.2 Mo 16:45 H10

Spektroskopie an kleinen Wasser-Clustern mit Synchrotronstrahlung — ●SILKO BARTH¹, VOLKER ULRICH¹, SANJEEV JOSHI¹, AXEL REINKÖSTER² und UWE HERGENHAHN¹ — ¹Max-Planck-Institut für Plasmaphysik, EURATOM Assoziation, Boltzmannstr. 2, 85748 Garching — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Wir haben die Ionenausbeute von kleinen Wasser-Clustern entlang der Sauerstoff-K-Kante mit Flugzeit-Massenspektroskopie bestimmt. Unsere Ergebnisse können mit Absorptions-Messungen an flüssigem Wasser und an Eis verglichen werden. Die Messungen an flüssigem Wasser wurden in einer neueren, viel diskutierten Arbeit als Hinweis auf eine drei- statt vierfache Koordination der Wassermoleküle in der Flüssigkeit interpretiert [1]. Unsere Spektren zeigen eine Mischung der Charakteristika von flüssigem Wasser und Volumen-Eis.

Wir haben weiterhin das erste Ionisationspotential von $(\text{H}_2\text{O})_N$ mit $N = 2 \dots 5$ bestimmt.

[1] Ph. Wernet *et al.*, *Science* 304, 995 (2004).

MO 15.3 Mo 17:00 H10

Spectroscopic Characterization of Proton Wires: IR Spectra of Microsolvated Protonated Ethanol Chains — ●OTTO DOPFER and NICOLA SOLCA — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Proton transfer, proton transport, and proton pumps are fundamental chemical and biological phenomena. Detailed understanding of these processes at the molecular level requires knowledge of the potential energy surface describing the proton wire. Mass spectrometric, spectroscopic, and quantum chemical characterization of proton-bound complexes under isolated or controlled microsolvation conditions provide the most direct access to this potential, yielding valuable information on the mobility of excess protons in solution. The present work reports IR photodissociation spectra [1] of size-selected protonated ethanol complexes of the type $(\text{EtOH})_m\text{H}^+\text{-Ln}$, with $L=\text{Ar}$ and N_2 , $m=1-4$, and $n=0-5$. The IR spectra provide detailed information on the degree of delocalization of the excess proton along the ethanol chain as a function of the length of the chain (m), the type of solvent (L), and the degree of solvation (n) [2,3]. Significantly, the symmetry of the proton bridge (Zundel or Eigen type) is found to depend sensitively on the symmetry of the microsolvation environment. Moreover, the acidity of the terminal OH groups decreases with the length of the chain. Density functional calculations support the interpretation derived from the spectroscopic data.

[1] O. Dopfer, *Int. Rev. Phys. Chem.* 22, 437 (2003). [2] N. Solca and O. Dopfer, *J. Am. Chem. Soc.* 126, 9520 (2004). [3] N. Solca and O. Dopfer, *J. Phys. Chem. A* 109, 6147 (2005).

MO 15.4 Mo 17:15 H10

Excited state hydrogen transfer in aminopyridine dimer: details of the reaction coordinate — ●THOMAS SCHULTZ, HANS-HERMANN RITZE, ELENA SAMOYLOVA, VALORIS REID SMITH, INGOLF VOLKER HERTEL, and WOLFGANG RADLOFF — Max Born Institut, Max Born Str. 2A, 12489 Berlin, Germany

The doubly hydrogen-bonded aminopyridine dimer (APd) resembles a Watson-Crick base pair and served as model system for a theoretically predicted hydrogen-transfer process in the excited state. We characterized this reaction experimentally by femtosecond pump-probe ionization spectroscopy. The reaction rate $(1.2-1.8) \times 10^{10} \text{ s}^{-1}$ varied non-monotonously with the excitation energy and showed a considerable H/D isotope effect. Based on our observations and ab initio calculations, we propose an excited state reaction pathway with a rate determining barrier for the H-transfer. The cluster structure appears to be a crucial factor determining the occurrence and rate of the H-transfer reaction. This may explain why the corresponding reaction was not observed for the adenine-thymine base pair, which adopts a non-Watson-Crick structure in the gas phase.

MO 15.5 Mo 17:30 H10

Mass-selected Gas Phase Infrared Spectroscopy of $\text{NH}_4^+(\text{NH}_3)_n$ ($n=0-7$) — ●GABRIELE SANTAMBROGIO¹, MATHIAS BRÜMMER¹, SARA FONTANELLA¹, YONGGANG YANG², OLIVER KÜHN², and KNUT R. ASMIS³ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Molekülphysik, Faradayweg 4-6, 14195 Berlin, Germany

The hydrogen bond interaction is key in understanding the structure and properties of water and biomolecules. However, our understanding of strong, low-barrier hydrogen bonds and their central role in enzyme catalysis, biomolecular recognition, proton transfer across biomembranes and proton transport in aqueous media remains sketchy.

Here we present results on the infrared photodissociation spectroscopy of gas phase mass selected $\text{NH}_4^+(\text{NH}_3)_n$ ($n=0-7$) in the region between 600 and 2000 cm^{-1} . The ammonia umbrella mode is observed at 1300 cm^{-1} for $n=1$ and is monotonically red-shifted down to 1100 cm^{-1} for $n=7$. Its position is a measure for the strength of the hydrogen bonds and shows evidence for closing of the first solvation shell after $n=4$. The threefold degenerate antisymmetric stretch mode of the ammonium ion is observed around 1500 cm^{-1} . Its degeneracy is lifted upon solvation until a symmetric solvation shell is reached for $n=4$. Only the $n=1$ cluster is predicted to exhibit strong hydrogen bonding and evidence or a shared proton mode is found at 750 cm^{-1} for $n=1$. Surprisingly, we also find such spectral signatures for some of the larger cluster ions.

MO 15.6 Mo 17:45 H10

IR spectrum of the ethyl cation: nonclassical versus classical structure — ●HORIA-SORIN ANDREI, HANNES KUCHELMEISTER, NICOLA SOLCA, and OTTO DOPFER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The competition between classical and nonclassical geometries is a fundamental issue for hydrocarbon molecules. The ethyl cation (C_2H_5^+ , protonated ethen) represents the most simple example for protonation of a $\text{C}=\text{C}$ double bond. Calculations predict the nonclassical structure to be slightly more stable than the classical structure. However, spectroscopic evidence for this conclusion is still lacking. The present work reports IR photodissociation spectra [1] of size selected clusters of the ethyl cation with Ar and N_2 . The IR spectra recorded in the CH stretching range provide detailed information on the degree of delocalization of the excess proton between the two C atoms. Significantly, the structure of the additional proton depends sensitively on the microsolvation environment. Whereas Ar is a negligible perturber, leaving C_2H_5^+ in the most stable nonclassical geometry, the stronger interaction with N_2 induces a switch from a nonclassical to a classical C_2H_5^+ ion core. The latter ligand appears to form a weak covalent bond to one C atom of the ethyl cation. The interpretation of the IR spectra is supported by rotational line profile simulations and ab initio calculations.

[1] O. Dopfer, *Int. Rev. Phys. Chem.* 22, 437 (2003).

MO 15.7 Mo 18:00 H10

Das Phenanthren-Anion und seine Wassercluster — ●MARTIN TSCHURL, STEFAN GILB und ULRICH BOESL — Department Chemie der TU München, Physikalische Chemie 1

Die Elektronenaffinität (EA) ist eine der fundamentalen thermodynamischen Größen eines Moleküls. Sie spielt z.B. eine wichtige Rolle bei Reduktionsprozessen und beim Elektronentransfer.

Die Photodetachment-Photoelektronenspektroskopie [1] ist eine der Methoden, mit denen sich die Elektronenaffinität sehr genau bestimmen lässt.

Das Ausbleiben von Phenanthren-Anionen im Massenspektrometer stellt ein Indiz für eine negative oder sehr geringe EA des Moleküls dar. Durch stufenweise Anlagerung von Wassermolekülen und eine von Schiedt et al. [2] eingeführte Extrapolationsmethode erhärtet sich dieser Verdacht. Zusätzlich kann hier etwas über das Solvatationsverhalten von Anionen gelernt werden. Der Vergleich zwischen theoretischen Berechnungen und Messergebnissen untermauert getroffene Annahmen. Zuletzt wird noch der Brückenschlag zwischen der EA und dem Reduktionspotential der Moleküle gewagt.

[1] U. Boesl, W.J. Knott, Mass. Spec. Rev. 67 (1989) 171.

[2] J. Schiedt, W.J. Knott, K. Le Barbu, E.W. Schlag, R. Weinkauff, J. Chem. Phys. 113 (2000) 9470.

MO 15.8 Mo 18:15 H10

Electronic excitation in the benzonitrile dimer: The intermolecular structure of the benzonitrile dimer in the S_0 and S_1 state determined by rotationally resolved electronic spectroscopy. —

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The benzonitrile dimer is an interesting example for a homo dimer. The rotationally resolved UV spectra of the electronic origin of the benzonitrile dimer has been measured. The benzonitrile dimer was found to be of C_{2h} symmetry in the S_0 and S_1 state. From the inertial parameters, the N...H-distance was found to be 236 pm in the electronic ground state and 232 pm in the electronic excited state.

MO 15.9 Mo 18:30 H10

IR and UV spectra of the gas-phase benzene dimer — ●UNDINE ERLEKAM, MARCIN FRANKOWSKI, GERT VON HELDEN, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

The benzene dimer is a simple prototype system to get insight into dispersive interactions between aromatic molecules.

We investigate the benzene dimer via two-colour Resonance Enhanced Multi Photon Ionization (REMPI) and mass-selective Infrared (IR) ion dip spectroscopy in the C-H-stretch region. Benzene clusters are formed and internally cooled in a supersonic jet expansion. A few ns before UV excitation and ionization, the molecular beam is interrogated by a tunable IR laser. If the IR photons are resonant with a vibration in the complex, population is transferred into a vibrationally excited state, leading to a reduction of the ion signal. By recording the ion yield while tuning the IR wavelength, the IR spectrum is obtained.

UV and IR spectra of (C_6H_6) , $(C_6H_6)_2$ and $(C_6H_6)(C_6D_6)$ will be presented. $(C_6H_6)(C_6D_6)$ forms two isomers having different UV excitation as well as IR spectra. Surprisingly, the relative population of the two different isomers depends extremely on experimental conditions.