MO 14: Molecular Clusters

Zeit: Montag 16:30–18:00 Raum: 6D

MO 14.1 Mo 16:30 6D

MD simulations of laser excited clusters — •Thomas Raitza, Heidi Reinholz, and Gerd Roepke — Universität Rostock; Universitätsplatz 3; 18055 Rostock

The measurements of optical properties are relevant for plasma diagnostics. The investigation of reflectivity and absorption of electromagnetic waves in inhomogeneous media will be done with special attention to laser excited clusters. Interaction of cluster systems with intense laser pulses were investigated via MD simulation. Hydrogen and sodium clusters containing 50 - 500 atoms were calculated. Material properties were included using and discussing different pseudo potentials. Comparison to experimental absorption measurements of Kim et al. [1] and to simulations of Belkacem et al. [2], Ditmire et al. [3] and Fennel et al. [4] are shown.

[1] K. Y. Kim, I. Alexeev, E. Parra, and H. Milchberg; *PRL*, **90**, 023401 (2003)

[2] M. Belkacem, F. Megi, and E. Suraud; *Eur. Phys. J. D*, **40**, 247 (2006)

[3] T. Ditmire, T. Donnelly, A. M. Rubenchik, R. W. Falcone, and M. D. Perry; *PRA*, **53**, 3379 (1996)

[4] T. Fennel, G. F. Bertsch, and K.-H. Meiwes-Broer; *Eur. Phys. J. D*, **29**, 367 (2004)

MO 14.2 Mo 16:45 6D

Master Equation Modeling of Phase Transitions in Low Temperature Black-Body Infrared Radiative Dissociation (BIRD) of Hydrated Ions — Stephan J. Reitmeier[1], O. Petru Balaj[2], Mirko Gruber[1], and •Martin K. Beyer[3] — [1]Department Chemie, TU München, Germany — [2]DCMR-Ecole Polytechnique, Palaiseau, France — [3]Insitut für Chemie, TU Berlin, Germany

Black-body infrared radiative dissociation (BIRD) of $V(H_2O)_n^+$, $n = 5$ - 21, was studied with a newly developed temperature-controlled ICR cell in a temperature range of 200 - 300 K. Arrhenius plots of the observed unimolecular rate constants for the loss of water molecules exhibit the expected linear behavior, which confirms that the radiation temperature experienced by the trapped ions actually is the measured temperature of the cell walls. Analysis with the standard master equation modeling of a single reactant well yields activation energies for the loss of water molecules which are significantly lower than those calculated with density functional theory or literature values of the water binding energy to protonated water clusters. Ab initio molecular dynamics simulations of selected cluster sizes reveal that some hydrogen bonds which are present in the equilibrium geometry are broken at elevated temperatures. The energy of those hydrogen bonds is present as latent heat in the clusters, which helps to lower the activation energy of water loss. A multi-well master equation model is developed to describe the population of the different phases in the trapped ensemble of ions. Activation energies derived from single and multi-well master equation modeling are compared.

MO 14.3 Mo 17:00 6D

IR Spectra of Protonated Furan, Pyrrole, and Naphthalene — •Ulrich Lorenz[1], Joel Lemaire[2], Philippe Maitre[2], Maria-Elisa Crestoni[3], Simonetta Fornarini[3], and Otto Dopfer[1] — [1]Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany — [2]Laboratoire de Chimie Physique, UMR8000 CNRS-Université Paris-Sud 11, Faculté des Sciences d' Orsay, Orsay Cedex, France — [3]Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma La Sapienza, Roma, Italy

Infrared Multiple Photon Dissociation (IRMPD) Spectra of protonated furan, pyrrole, and naphthalene are recorded in the 700 to 1800 cm^{-1} range in order to probe the preferred site of protonation. The species are generated by chemical ionization of the corresponding neutral compounds in a ICR mass spectrometer and dissociated employing the free electron laser at the Centre Laser Infrarouge Orsay. The comparison with the linear IR spectra calculated at the B3LYP/6-311G(2df,2pd) level of theory allows for the assignment of the most stable isomers as the carriers of the observed spectral features. The spectrum of protonated naphthalene is discussed in the context of the hypothesis that protonated polycyclic aromatic molecules (PAHs) might contribute to the astronomically observed Unidentified Infrared Emission (UIR) Bands.

MO 14.4 Mo 17:15 6D

Orbital-Dependent Stabilization in the Ionization of CS_2 Cluster — •Jürgen Plenge[1], Takaki Hatsui[2], Nobuhiro Kosugi[2], and Eckart Rühl[1] — [1]Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — [2]Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

Molecular van der Waals clusters offer the opportunity to study the gap between the isolated molecule and condensed matter. It is known that the formation of clusters leads to a decrease in the ionization energy with respect to the molecule, which is commonly interpreted in terms of final state polarization due to the created hole. In the case of valence ionization of molecular clusters, the created holes are generally delocalized within the molecule, where the shape of the hole is characteristic for the molecular valence orbital.

We present results on molecular orbital dependent stabilization of valence-ionized states in CS_2 clusters. Valence photoelectron spectra of isolated CS_2 molecules and CS_2 clusters are measured using synchrotron radiation (UVSOR-II, beamline BL3U) and a He-I discharge lamp. The experimental spectra indicate a shift of the molecular photoelectron bands in the cluster between 0.55 eV (ground state) and 0.70 eV (C state) to lower binding energy. These results are compared to results on CO_2 clusters and they are discussed in terms of a molecular orbital dependent stabilization of the final ionic states in molecular clusters, where ionized states with the lower binding energies are found to show a smaller stabilization effect.

MO 14.5 Mo 17:30 6D

Laserspektroskopie massenselektierter Ion-Molekülcluster: Chlorid-Anionen in Ammoniak — •Martin Tschurl und Ulrich Boesl — TU München, Department Chemie, Physikalische Chemie 1, Lichtenbergstraße 4, D-85748 Garching

Die Solvatation von Ionen spielt eine zentrale Rolle in verschiedensten Gebieten der Chemie und Physik. Durch das Studium kleiner Komplexe erhofft man sich, theoretische Modelle verfeinern und schlussendlich Effekte in Lösung besser erklären zu können.

Die Anionen-Photoelektronenspektroskopie (PES), die Photodetachmentspektroskopie (PDS) und die IR-Dissoziationsspektroskopie (IR-DS) zählen hierbei zu den leistungsstärksten Methoden bei der Untersuchung solcher Komplexe. Unsere Apparatur erlaubt nun erstmals die Kombination dieser drei Methoden. So ist gewährleistet, dass die Komplexe bei denselben Bildungsbedingungen studiert werden.

Anhand des kleinsten Chlorid-Ammoniak Komplexes soll exemplarisch das Zusammenspiel von PDS und IR-DS gezeigt werden. Beide Methoden liefern neue Erkenntnisse über diesen Komplex. Da keine Spektren von Chlorid Komplexen mit mehreren Ammoniakmolekülen in der Literatur vertreten sind, wurden diese mittels IR-DS untersucht. So konnten Informationen von Komplexen bis zu einer Größe von vier Ammoniakmolekülen pro Chloridion erhalten werden, die Aussagen über die involvierten Komplexgeometrien liefern.

MO 14.6 Mo 17:45 6D

Photoelectron spectroscopy of molecular diamonds — •Kathrin Klünder[1], Christoph Bostedt[1], Tobias Richter[1], Lasse Landt[1], Peter Zimmermann[1], Thomas Möller[1], Trevor Willey[2], Tony van Buuren[2], Jeremy Dahl[3], SG Liu[3], and Robert Carlson[3] — [1]TU Berlin, Germany — [2]LLNL, Livermore CA, USA — [3]MolecularDiamond Technologies, Richmond CA, USA

Diamondoids are ideal molecular diamond clusters. They are perfectly size- and isomer-selected, neutral and hydrogen-terminated clusters in the diamond bulk lattice configuration. Diamondoids are a perfect system for investigating the electronic properties of semiconductor nanostructures in the molecular limit.

First x-ray absorption experiments of diamondoids showed no particle size dependence of the lowest unoccupied states which has been confirmed by quantum monte carlo simulations. In contrast to the unoccupied states, however, the calculations predict strong quantum size effects in the occupied states.

We have studied the highest molecular orbitals and core levels of a series of diamondoids by means of photoelectron spectroscopy. The experiments were performed at the beamline UE56/2 of the Bessy synchrotron source with a Scienta hemispherical photoelectron analyser. The valence band photoelectron spectra show a clear energy shift of the highest molecular orbitals to lower binding energies for increasing particle size. The results will be discussed and compared to recent theory.