Symposium High resolution spectroscopy – modern trends and new techniques (SYHR)

veranstaltet vom
Fachverband Molekülphysik (MO)

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Übersicht der Hauptvorträge und Fachsitzungen

(Hörsaal VMP 8 R05)

Hauptvorträge

SYHR 1.1	Do	10:30–11:10	VMP 8 R05	**High-Resolution Rotational Spectroscopy: New Waves** — •Jens-Uwe Grabow
SYHR 1.2	Do	11:10–11:50	VMP 8 R05	**Some like it cold – aggregation and dissociation of HCl and water in helium nanodroplets** — Gerhard Schwaab, •Ozgur Birer, Anna Gutberleth, Martina Havenith
SYHR 1.3	Do	11:50–12:30	VMP 8 R05	**High resolution electronic spectroscopy of anisole dimer** — •Giangaetano Pietraperzia, Massimiliano Pasquini, Nicola Schiccheri, Giovanni Piani, Maurizio Becucci
SYHR 2.1	Do	14:00–14:40	VMP 8 R05	**Microwave Spectroscopy of Weakly Bound Systems and Floppy Molecules** — •Wolfgang Stahl
SYHR 2.2	Do	14:40–15:20	VMP 8 R05	**Rovibrational spectroscopy on cold trapped molecular ions below 0.1 K** — •Bernhard Roth
SYHR 2.3	Do	15:20–16:00	VMP 8 R05	**Eigenstate-resolved electronic spectroscopy of large molecules in the gas phase.** — •David W. Pratt
SYHR 3.1	Do	16:30–17:10	VMP 8 R05	**Automated fitting of High Resolution spectra from the MW to the UV** — •W. Leo Meerts
SYHR 3.2	Do	17:10–17:50	VMP 8 R05	**High resolution spectroscopy using supersonic planar plasma expansions** — •Harold Linnartz
SYHR 3.3	Do	17:50–18:30	VMP 8 R05	**Discussion of the Results of the Symposium** — •David Pratt, Harold Linnartz, Wolfgang Stahl, Gerhard Schwaab, Jens-Uwe Grabow, Bernhard Roth, Giangaetano Pietraperzia, W. Leo Meerts

Fachsitzungen

SYHR 1.1–1.3	Do	10:30–12:30	VMP 8 R05	**High resolution spectroscopy - modern trends and new techniques I**
SYHR 2.1–2.3	Do	14:00–16:00	VMP 8 R05	**High resolution spectroscopy - modern trends and new techniques II**
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SYHR 1: High resolution spectroscopy - modern trends and new techniques I

Zeit: Donnerstag 10:30–12:30 Raum: VMP 8 R05

Hauptvortrag SYHR 1.1 Do 10:30 VMP 8 R05
High-Resolution Rotational Spectroscopy: New Waves — •Jens-Uwe Grabow — Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie & Elektrochemie, Lehrgebiet A, Callinstrasse 3A, 30167 Hannover

Small particles, larger molecules and clusters are of increasing technological importance with numerous fundamental questions on their structure and dynamical behavior waiting to be answered. Targeted by high resolution spectroscopy they impose a number of challenges, theoretically and experimentally.

From the theoretical point of view, e.g., internal large amplitude motions result in complicated energy level schemes. For larger species exhibiting multiple internal motions at low barriers, the resulting spectra will be rather difficult to predict. From an experimental point of view, dense spectra at the presence of wide splitting patterns are difficult to assign. With narrow-banded techniques, even though very sensitive, identification of the spectral features becomes a paramount task.

Quantitative information on the structure, charge distribution, characterization of the chemical bond, details on internal dynamics, etc. - at the highest precision available to date - are encoded in pure rotational spectra obtained by microwave spectroscopy. Right now - about a quarter century after the introduction of supersonic-jet resonator Fourier-transform microwave spectroscopy - new exciting technical developments aiming to overcome still existing limitations are expected to pave the way for a promising future of rotational spectroscopy.

Hauptvortrag SYHR 1.2 Do 11:10 VMP 8 R05
Some like it cold – aggregation and dissociation of HCl and water in helium nanodroplets — Gerhard Schwaab[1], •Ozgur Birer[2], Anna Gutberleth[1], and Martina Havenith[1] — [1]Physical Chemistry II, Ruhr University Bochum, D-44780 Bochum, Germany — [2]Chemistry Department, Koc University, Rumelifeneri Yolu, Sariyer 34450 Istanbul, Turkey

Helium nanodroplets provide a gentle, ultracold matrix for studies of agglomeration processes. Due to the superfluidity of He at 0.37 K a combination with high-resolution infrared spectroscopy provides an ideal tool to separate local and global minimum structures of aggregates.

We used Helium nanodroplets in combination with a cw OPO and a mass spectrometer as detector unit to study the aggregation and solvation of HCl in water. Besides signals of pure HCl, undissociated HCl-H_2O, and rotationally resolved HCl dimer, broadened peaks around 2670 cm^{-1} were found. Optically selective mass spectroscopy (OSMS) allowed unambiguous assignment of the according parent species as solvent separated ion pair $H_3O^+(H_2O)_3Cl^-$. A replacement of HCl by DCl produced a slight spectral shift and a further splitting. This is in excellent agreement with theoretical calculations.

The observation of, what we believe is the "smallest droplet of an acid", opens the way for spectroscopic investigation of microsolvation processes at ultracold temperatures such as zwitterion formation of amino acids.

Hauptvortrag SYHR 1.3 Do 11:50 VMP 8 R05
High resolution electronic spectroscopy of anisole dimer — •Giangaetano Pietraperzia[1], Massimiliano Pasquini[1], Nicola Schiccheri[2], Giovanni Piani[2], and Maurizio Becucci[1] — [1]LENS and Dipartimento di Chimica, Polo Scientifico e Tecnologico Università di Firenze, Via Nello Carrara 1, I-50019 Sesto Fiorentino (FI), Italy — [2]LENS Polo Scientifico e Tecnologico Università di Firenze, Via Nello Carrara 1, I-50019 Sesto Fiorentino (FI), Italy

We report the results of an experimental study of the anisole dimer, formed in a molecular beam apparatus. The dimer was studied by the resonance enhanced multiphoton ionization (REMPI) and by high resolution laser induced fluorescence (HR-LIF)techniques. From a complete assignment of the rotational structure of the band it was possible to obtain important structural information. From a comparison with the results of high level quantum calculations it was possible to infer the equilibrium structure of the complex experimentally studied. The study presented here reports on the first results of a characterization of a complex stabilized mainly by the stacking interaction, investigated at complete rotational resolution.

SYHR 2: High resolution spectroscopy - modern trends and new techniques II

Zeit: Donnerstag 14:00–16:00 Raum: VMP 8 R05

Hauptvortrag SYHR 2.1 Do 14:00 VMP 8 R05
Microwave Spectroscopy of Weakly Bound Systems and Floppy Molecules — •Wolfgang Stahl — Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany

FT microwave spectroscopy using molecular beams is an excellent tool to study weakly bound systems like rare gas clusters and hydrogen bonded systems. Here the molecular beam conditions are necessary to form these species and the inherently high resolution of FT microwave spectroscopy allows to accurately determine their structure and dynamics. However, experimental and also theoretical limitations exist. Experimentally, the rather low sensitivity of FT microwave spectroscopy compared to other methods is probably a bigger problem than resolution. The biggest theoretical limitation is currently the proper treatment of large amplitude motions which are almost always present in weakly bound systems but also in stable molecules. Here in recent years some progress has been made, however, due to the multidimensional potentials found in many weakly bound systems assignment of the spectra is difficult and sometimes impossible. In many cases only fundamental states have been analyzed but also many observed transitions remain unassigned. Including these lines which often are due to higher tunneling states would provide a source for parameters describing the potential surface.

Some examples for solved and yet unsolved problems with weakly bound systems and floppy molecules will be discussed.

Hauptvortrag SYHR 2.2 Do 14:40 VMP 8 R05
Rovibrational spectroscopy on cold trapped molecular ions below 0.1 K — •Bernhard Roth — Institut für Experimentalphysik, Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf

Molecular hydrogen ions (H_2^+, HD^+, ...), the simplest molecules in nature, are interesting systems for fundamental tests of physics and for methodological quantum-optical studies. Their three-body nature also makes them benchmark systems for quantum theoretical calculations.

One interesting aspect is the dependence of vibrational and rotational energies in molecular hydrogen ions on certain fundamental constants, e.g. m_e/m_p, m_p/m_d, or m_p/m_t. Significant theoretical advances now permit to calculate these energies ab-initio with an inacccuracy below 1 part in 10^9, including important contributions from relativistic and QED corrections. High-resolution spectroscopic measurements of energy differences between those levels can be combined with precise theoretical calculations to obtain improved values for m_e/m_p and m_p/m_d, for example. The dependence of the transition energies on the particle mass ratios makes these molecules also interesting candidates for a laboratory search for a possible time-variation of these constants.

In this talk I will describe the status of the Düsseldorf experiment on precision laser spectroscopy of sympathetically cooled HD^+ ions, including the most recent developments towards enhanced precision.

Hauptvortrag SYHR 2.3 Do 15:20 VMP 8 R05
Eigenstate-resolved electronic spectroscopy of large molecules in the gas phase. — •David W. Pratt — University of Pittsburgh, Pittsburgh PA USA

Remarkable progress has been made in the last few years in determining both the structural and dynamical properties of large polyatomic molecules and their clusters in the gas phase, and how these change when the photon is absorbed, using high resolution CW lasers operating in the UV, molecular beam machines, and rapid data analysis methods. Following a brief description of these methods, this talk

will describe recent applications of this technique to several systems in which significant charge redistribution accompanies the excitation process, including hydrogen-bonded water complexes, base pairs and their mimics, and other molecules of importance to biology. These applications include studies of such spectra in the presence of applied electric fields, yielding conformer-specific values of the electric dipole moments in both electronic states.

This work has been supported by the U. S. National Science Foundation (CHE-0615755).

SYHR 3: High resolution spectroscopy - modern trends and new techniques III

Zeit: Donnerstag 16:30–18:30 Raum: VMP 8 R05

Hauptvortrag SYHR 3.1 Do 16:30 VMP 8 R05

Automated fitting of High Resolution spectra from the MW to the UV — •W. Leo Meerts — Molecular- and Biophysics Group, Radboud University Nijmegen, NL 6500 Nijmegen

The usefulness of an evolutionary algorithm (EA) based approach to the automated evaluation of molecular parameters from various kind of spectra is shown. The applicability of the method ranges from rotationally resolved electronic spectroscopy of large molecules to nuclear magnetic resonance (NMR) spectroscopy of molecules, which are partially oriented in an anisotropic liquid-crystalline environment.

The application of both the genetic algorithm (GA) and the evolutionary strategy algorithm (ES) approaches for the assignment of complex spectra and the necessity of fitting meta para- meters, which are not related to the parameters of the model describing the spectra are discussed. Examples for the possible applications will be discussed.

Hauptvortrag SYHR 3.2 Do 17:10 VMP 8 R05

High resolution spectroscopy using supersonic planar plasma expansions — •Harold Linnartz — Laboratory for Astrophysics, Leiden Observatory, University of Leiden, Leiden, the Netherlands

Transient molecules - typically radicals, ions and ionic complexes - belong to the chemically most reactive species. They are considered to be important intermediates in processes ranging from combustion to interstellar chemistry. The high reactivity, however, also complicates systematic spectroscopic gas phase studies.

In this talk the use of planar plasma sources [1] is reviewed, capable of producing molecular transients with high densities at low rotational temperatures in a Doppler free environment. Fully rotationally resolved spectra of rovibronic and rovibrational transitions are presented for exotic and highly unstable molecules. It is demonstrated how sensitive detection techniques, such as cavity ring down spectroscopy and plasma modulation techniques, can be used to record fully resolved spectra in direct absorption.

[1] H. Linnartz, 'Cavity ring down spectroscopy of molecular transients of astrophysical interest' in Cavity Ring-down Spectroscopy: Techniques and Applications, Eds. G. Berden and R. Engeln, Publisher: John Wiley & Sons, Ltd. (2009).

Hauptvortrag SYHR 3.3 Do 17:50 VMP 8 R05

Discussion of the Results of the Symposium — •David Pratt[1], Harold Linnartz[2], Wolfgang Stahl[3], Gerhard Schwaab[4], Jens-Uwe Grabow[5], Bernhard Roth[6], Giangaetano Pietraperzia[7], and W. Leo Meerts[8] — [1]University of Pittsburgh — [2]University of Leiden — [3]RWTH Aachen — [4]Ruhr University Bochum — [5]Gottfried-Wilhelm-Leibniz-Universität Hannover — [6]Heinrich-Heine-Universität Düsseldorf — [7]Universita di Firenze — [8]Radboud University Nijmegen

The possibilities and limits of new techniques and current trends in high resolution molecular spectroscopy will be discussed by the contributors to the Symposium. Discussion contributions from the audience are highly welcome.