

**JET-COOLED HIGH RESOLUTION INFRARED SPECTROSCOPY OF MOLECULAR COMPLEXES**

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For several decades, the implementation of the supersonic jet technique in the field of high resolution spectroscopy has opened the way to various experiments, in particular infrared absorption with Fourier Transform Spectroscopy (FTS) and lasers. These studies enabled to characterize the intra- and intermolecular properties of non covalent systems, based on the many advantages provided by the supersonic expansion such as spectral simplification, sub-Doppler resolution and production of molecular sized clusters. A deeper knowledge of intermolecular interactions between several subunits, as for example within small HF clusters or weakly bound complexes involving water, would require to collect more accurate structural and vibrational dynamics data by probing intermolecular modes and intramolecular proton donor bonded vibrations in the far- and mid-IR ranges, respectively [1].

In this context, we are currently developing two sensitive infrared probes for direct absorption: (i) the Jet-AILES set-up, a supersonic free jet with high molar gas flows up to 100 mol/h coupled to a high resolution FTS equipping the AILES beamline of the synchrotron light source SOLEIL, (ii) the SPIRALES set-up, a pulsed supersonic jet coupled to a tunable mid-IR external cavity quantum cascade laser (EC-QCL).

Experimental details for both set-ups will be presented. The complementarity between FT broadband and laser narrowband spectroscopies will be discussed regarding to their respective performances in sensitivity and resolution, and to what bond strength and size of molecular systems can be dedicated this hydrogen bonded cluster research.

Recent results obtained with Jet-AILES in the far-IR range about cyclic (HF)<sub>3</sub> and (HF)<sub>4</sub> clusters will be presented to highlight the interest of this alternative approach, in the case where microwave and mid-IR spectroscopies failed to bring rovibrational information [2]. Preliminary high resolution studies of complexes produced in pulsed supersonic expansions with an EC-QCL will be also described.

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**VIBRATIONAL SPECTRA AND STRUCTURES OF SILICON HYDRIDE  
CLUSTER CATIONS**Martin Andreas Robert George, Marco Savoca, Judith Langer, Truong Nguyen, Otto Dopfer

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Silanes and their derivatives and ions are fundamental species in a variety of chemical disciplines. IR spectra of silicon hydride cluster cations  $\text{Si}_x\text{H}_y^+$  produced in a supersonic plasma molecular beam expansion of  $\text{SiH}_4$ , He, and Ar are inferred from photodissociation of cold  $\text{Si}_x\text{H}_y^+$ -Ar/Ne complexes obtained in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source and an octopole ion trap. In addition, the clusters are characterized in their ground electronic states by quantum chemical calculations to investigate the effects of ionization and Ar/Ne complexation on their geometric, vibrational, and electronic structure. We present initial results for  $\text{Si}_2\text{H}_6^+$  [1],  $\text{Si}_2\text{H}_7^+$  [2] and  $\text{Si}_3\text{H}_8^+$  [3], which have complex potential energy surfaces, with low-energy isomers featuring unusual three-center two-electron (3c-2e) bonding. The IR spectrum of disilanium,  $\text{Si}_2\text{H}_7^+$ , a fully H-passivated  $\text{Si}_2$  core with a Si-H-Si bridge is described by a 3c-2e bond. The excess proton in the Si-H-Si bridge generates three additional fundamentals, which provide the fingerprint of the 3c-2e bond. First results on protonated silanols will be presented.

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## TRANSITION STATE SPECTROSCOPY OF THE [H,C,N] MOLECULAR SYSTEM

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The central paradigm of transition state theory is based on the highest point along the lowest energy path of the chemical reaction. In this work we demonstrate how we can extract chemically relevant *saddle point* energies from spectroscopically measured quantities: a simple vibrational effective frequency analysis [1] allows the determination of the energy and shape of the isomerization barrier and of the two minima of the isomers. This is the first time the concept of the transition state is accessible through vibrational spectroscopy.

We use, for the analysis the [H,C,N] level set [3-4], the most extensive and complete rovibrational level set determined for any polyatomic molecule. As the experimental results reach only up to  $v_2=15$  of the bending excitation, we combine the experimental results with calculated ab initio rovibrational eigenenergies. The existence of an ab initio eigenenergy spectrum seems not to be helpful at first sight: the eigenenergies, labelled only by the rigorously good quantum numbers (J and parity), do not permit direct extraction of any physical insight from these data. To search for new classes of patterns in the spectra of vibrationally highly excited small polyatomic molecules and to investigate the validity of the vibrational model (the organization of rotational levels into vibrational levels) used at low internal excitation, the ab initio eigenenergy spectrum must be analyzed in a way similar to how high resolution spectra are assigned and modelled. In this work we report the *complete* assignment of all 168110 ab initio rotation-vibration eigenenergies up to  $18000\text{ cm}^{-1}$  above the minimum of the potential energy surface calculated by the Tennyson group [5]. *This is the first time that such a complete analysis of the rovibrational spectrum of a polyatomic molecule has been achieved*, including all rovibrational states below and  $1500\text{ cm}^{-1}$  above the isomerization barrier. In a preliminary result of this ab initio analysis, it was possible to show [2] for the first time the vibrational angular momentum dependent Dixon-dip like trend of the vibrational energies as the vibrational excitation approaches the energy of the saddle point. In this work we use the newly assigned vibrational frequencies at the saddle point for 9 HCN/HNC pure bending and combination bands to demonstrate that, using a very simple effective frequency analysis [1], it is possible to obtain up to 1% accurate saddle point energies using hot band spectroscopy. The method demonstrated in this work opens the possibility to use the hot gas molecular emission experiments in Giessen to access directly the transition states of some fundamental chemical reactions.

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## HYDRATION STATE AND NUMBERS OF HIGHLY POLAR COMPOUNDS IN AQUEOUS SOLUTION

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The hydration numbers ( $n_H$ ) of typical polar substances bearing dipole moments larger than 3 D, such as nitro compounds and nitriles, were precisely determined in aqueous solution using high frequency dielectric relaxation techniques up to a frequency of 50 GHz at 25 °C. Since the relaxation strength of free water molecules in aqueous solutions is exactly evaluable in a frequency range higher than 20 GHz at 25 °C, the amount of water molecules hydrated to solute molecules was precisely determined. Differences between free and interacting water molecules to the highly polar solutes were also investigated using near infrared (NIR) absorption spectroscopic techniques. The first overtone spectra of OH stretching bands of water molecules markedly altered depending on the strength of interaction to the polar solutes. The hydration number,  $n_H$ , is one of the most quantitative parameters for determining the hydrophilicity of a compound. The  $n_H$  value of various nitriles, such as acetonitrile, propionitrile and *n*-butyronitrile bearing cyano groups, were determined to be ca. 0, irrespective of the species of molecule. Moreover, the  $n_H$  values of some nitro compounds like nitromethane, nitroethane and 1-nitropropane were also evaluated to be ca. 0. These findings reveal that neither cyano nor nitro groups form strong hydrogen bonds to water molecules. Then, neither nitro compounds nor nitriles are hydrophilic, despite their large dipole moments. Consequently, these compounds are “hydroneutral,” with hydrophilicities intermediate between hydrophilic and hydrophobic molecules. Frequency ( $\omega$ ) dependencies of the real and imaginary parts of the electric permittivity ( $\epsilon'$  and  $\epsilon''$ ) for an aqueous nitromethane (NO<sub>2</sub>M) solution at a concentration of  $c = 0.78$  M and 25 °C are shown in Fig. 1 as a typical example. The dashed lines represent constituent two Debye-type relaxation functions ( $\epsilon_1'$  and  $\epsilon_1''$ , and  $\epsilon_2'$  and  $\epsilon_2''$ ) and high frequency limiting electric permittivity ( $\epsilon_\infty$ ) to reproduce the  $\epsilon'$  and  $\epsilon''$  data as shown by solid lines: a fast mode with relaxation strength ( $\epsilon_1$ ) and time ( $\tau_1$ ) corresponding to the rotational relaxation of free water molecules and a slow mode with  $\epsilon_1$  and  $\tau_2$  caused by the presence of NO<sub>2</sub>M molecules. The agreement between  $\epsilon' - \epsilon_1' - \epsilon_\infty$  (closed circles) and  $\epsilon_2'$ , and  $\epsilon'' - \epsilon_1''$  (closed squares) and  $\epsilon_2''$  in Fig.1 strongly manifests the presence of two relaxation modes in the solution. The motions of the polar solutes in aqueous solution were well described with single Debye-type relaxation mode as the mode 2 with little interaction between the solute and water molecules, but with relatively strong interactions between the solute molecules because of the Kirkwood factor ( $g_K < 1$ ). The small  $g_K$  values indicated that both nitro and cyano groups have a tendency to align in an anti-parallel configuration caused by strong dipole-dipole interactions due to large dipole moments. NIR spectra of water OH stretching bands found around 7000 cm<sup>-1</sup> in aqueous solutions of the polar molecules clearly showed an increase in the number of dangling OH without hydrogen bond formation to the polar solutes with increasing concentrations.

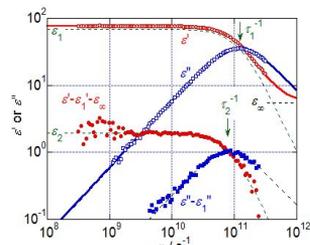


Fig. 1 Dependencies of  $\epsilon'$  and  $\epsilon''$  on  $\omega$  for an aqueous NO<sub>2</sub>M solution at  $c = 0.78$  M and 25 °C.

**HIGH-RESOLUTION INFRARED SPECTROSCOPIC INVESTIGATION OF  
AMMONIA-CONTAINING MOLECULAR COMPLEXES AROUND 1.5 MICRON**

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The FANTASIO experimental set-up coupling a supersonic expansion with a cavity ring down spectrometer (CRDS) has been used in the past to investigate molecular complexes containing acetylene [1] and/or water [2]. We recently recorded spectra of ammonia-containing complexes in the NIR spectral range (around 1.5  $\mu\text{m}$ ) [3]. We report on the observation and assignment of two bands of Ar-NH<sub>3</sub> and one of Kr-NH<sub>3</sub>, probing the 2 NH stretching state. This leads to the determination of rotational constants for the excited states of the transitions. Several further analyses were performed, such as predissociation lifetimes, rotational temperature of the expansions, and Coriolis perturbations. We have also observed resolved structures of larger multimers and the latest results will be presented. (T. Vanfleteren is “Boursier FRIA”)

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**EXPERIMENTAL STUDY OF PHASE TRANSFORMATIONS IN METHANOL**

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This work is devoted to the investigations of phase transitions in methanol. The experimentally obtained FTIR spectra of methanol trapped in argon and nitrogen matrices are presented. The methods of cluster isolation in inert gases matrices [1] provide the possibility to study individual clusters of different sizes. The transformation of the FTIR bands of free O–H groups ( $3600 - 3800 \text{ cm}^{-1}$ ) into diffuse bands ( $3000 - 3600 \text{ cm}^{-1}$ ), which were assigned to the stretching vibrations of the H-bonded O–H groups in various clusters [2], was monitored in its initial stage during softening the matrices by heating from 20 K to 50 K. The analysis of the temperature evolution of the registered spectra allowed us to trace the changes of structure transformations in methanol from individual molecules to hydrogen-bonded clusters and to consider such experiments as an experimental model of the phase transition from gas to liquid.

FTIR spectra of methanol in the condensed state were registered in a wide temperature range. In order to explain the structure transformations in methanol at the phase transition liquid – solid quantum-chemical calculations were carried out. The calculations for different cluster types were made using the program set Gaussian 03 by DFT method in B3LYP approximation with 6-31G(d,p) and 6-311G basis sets.

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**IR SPECTROSCOPY OF LIMONENE AND ITS OXYDATION PRODUCTS  
COMPLEMENTED BY QUANTUM CHEMICAL CALCULATIONS**

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Large quantities of monoterpenes are emitted by a variety of plants and coniferous forests. These molecules and their oxydation and degradation products with OH, O<sub>3</sub>, NO<sub>x</sub>, etc. play a major role in atmospheric chemistry. We have studied the gas phase spectroscopy of limonene (C<sub>10</sub>H<sub>16</sub>), as well as three oxydation products: perillaldehyde, carvone (C<sub>10</sub>H<sub>14</sub>O) and limonene oxide (C<sub>10</sub>H<sub>16</sub>O). In the first step of this work, quantum chemical calculations and microwave spectroscopy were used in order to evidence the most stable conformers and their relative energies, using a well-established methodology [1-3]. In a second step infrared spectra have been recorded on the FTIR spectrometer of the AILES beamline at synchrotron SOLEIL, using a long path cell. Special attention was paid to the 700–1300 cm<sup>-1</sup> atmospheric window, to the CH vibration region, and to the fingerprint FIR region. Quantum chemical calculations have been performed at different levels of theory (DFT, ab initio). In particular anharmonic force fields were obtained in order to model the vibrational structures. The preliminary IR results will be presented.

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