

Vibrational Spectroscopy and Intermolecular Interactions

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There is still a wide size gap between molecules which are accessible to accurate quantum mechanical treatment and functional polymer systems which are of relevance in the materials and life sciences. The interaction between molecular segments and molecules is of particular relevance for the properties of such synthetic and bio-polymers. This calls for the spectroscopic study of small molecular clusters which contain essential interactions and allow for an accurate assessment of the performance of theoretical models. We specialize on unique cluster spectrometers based on direct absorption infrared spectroscopy and spontaneous Raman scattering of aggregating molecules in supersonic expansions. Hydrogen-bonded clusters are generated under well-defined conditions and their spectra can be directly related to quantum-chemical predictions. Chemical aggregation processes leading to aerosols and other nanoparticles are also of interest.

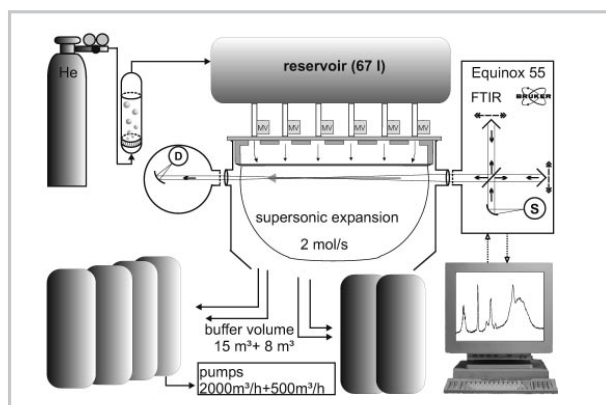


Fig. 1: Schematic drawing of a pulsed slit jet cluster FTIR spectrometer involving a high temporary gas flow of 2 mol/s which is synchronized to rapid scan interferometry [2].

The assembly of molecules to functional supramolecular units is a central theme in many areas of the natural sciences and in applications, reaching far beyond chemistry. It is governed by intermolecular forces such as electrostatic interactions, induction and van der Waals forces on one side and Pauli repulsion on the other. Hydrogen bonds are a particularly important class of interactions in nature, which involves all four ingredients to a varying extent. The fundamental laws are well known, and so is the machinery to calculate them accurately. However, these highly accurate quantum-chemical methods scale unfavourably with system size and by the time one reaches supramolecular systems of interest like enzyme-substrate complexes or functional

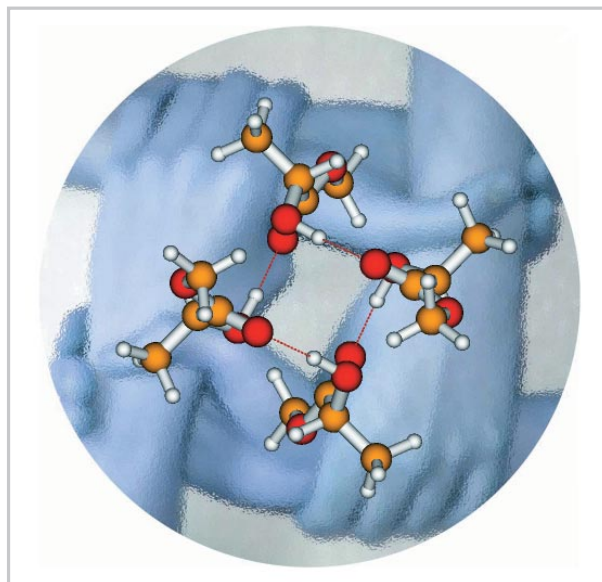


Fig. 2: A complex example of chirality recognition in the gas phase: Only alternating left- and right-handed methyl lactate molecules fit together in this arrangement with isolated hydrogen bonds [2].

polymers, one has long run out of computer power. Of course, clever and highly successful approximate workarounds have been developed, culminating in impressive classical molecular dynamics calculations of systems involving millions of atoms. They rely on empirical, semi-empirical or approximate quantum chemical input and, if applied wisely, they have enormous applications in reproducing and understanding the essence of biophysical processes and polymer dynamics. However, there are always limits for such approximate models and one can rarely be sure whether one is stretching these limits too much in a particular application. This is the price of complexity.

We see our main mission in providing accurate experimental benchmark data for the simplest systems of a given kind of intermolecular interactions. For this purpose, we use vibrational spectroscopy on well-defined assemblies of simple molecules with functional groups relevant for supramolecular interactions. We generate them in the vacuum at very low temperatures in so called supersonic jets, to establish the closest-possible connection to rigorous quantum chemical predictions. Although these are not the typical conditions under which life happens and materials are used, these vacuum-isolated assemblies provide essential and quantitative information on how well approximate methods work and how much they rely on error compensation, which makes it a lot harder to extrapolate them.

We specialize on experimental methods which can be applied to all kinds of model systems for molecular interactions, independent on the existence of a suitable electronically excited state or a net charge. Every molecule has a Raman vibrational spectrum and most of them absorb infrared radiation. Some of these vibrations react very sensitively to clustering. They serve as our probes, because such effects are also easily computed. The jet-spectrometers we have developed are uniquely sensitive – they involve the most powerful continuous lasers, the largest expansion nozzles, vacuum chambers up to 23 m³ in size and highly sensitive photon detectors. We give them colloquial acronyms such as “ragout”, “filet”, “curry”, “popcorn”, or “muesli” which have multiple meanings – too many to be explained here. We complement these vibrational techniques by mass spectrometry, nanoparticle metrology, and computational methods.

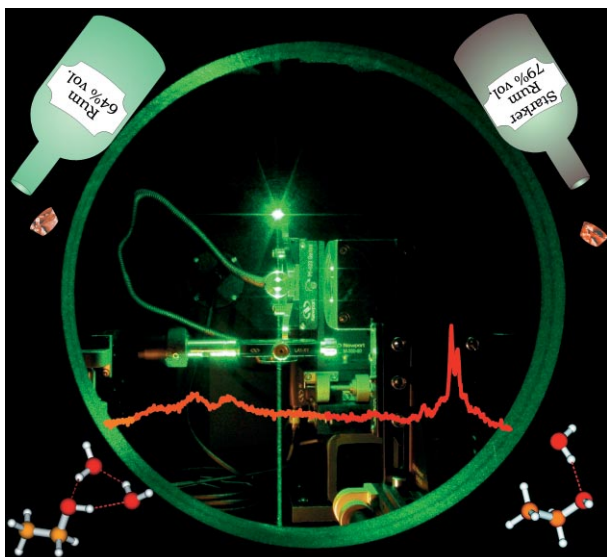


Fig. 3: Raman setup used to study the vibrational spectra (red trace) of the smallest liquor clusters, corresponding to 64 and 79% Vol. alcohol [1].

A few examples of prototype systems which we have recently characterized for the first time in vacuum isolation may be mentioned: A trimer involving two water molecules and one ethanol molecule – the smallest building unit of liquors, 64 vol% in this case [1]. A racemic tetramer of the methyl ester of lactic acid – probably the most complex cluster involving strong chirality recognition in the gas phase which has been structurally characterized so far [2]. Hydrogen-bonded dimers of formamide, acetamide and their derivatives – the simplest models for peptide aggregation [3]. Furthermore, we have recently probed the stiffness of the most elementary double hydrogen bond in formic acid dimer and of cooperative hydrogen bonds in methanol, the subtle influence of fluorine on hydrogen bond interactions, the solvation of electrons in sodium-alcohol clusters [4], the onset of electrolytic dissociation of HCl as a function of water molecules, the slow-down of



Fig. 4: A molecular sociology view of supersonic jet expansions. See www.molekularsoziologie.de for more.

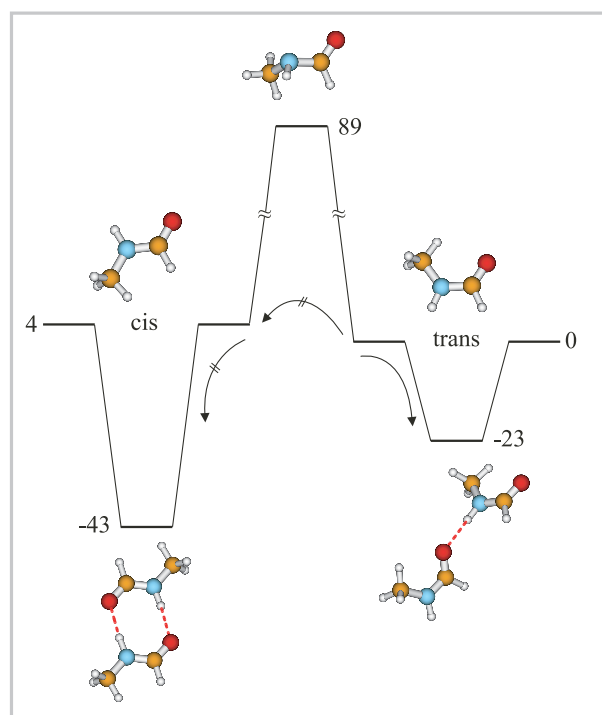


Fig. 5: Which way does N-methylformamide, a peptide bond model, aggregate? Kinetic control leads to an unfavorable structure with only one hydrogen bond [3].

tunneling protons in malonaldehyde, the conversion between almost degenerate molecular conformations, the synchronization of chirality in alcohol clusters, the nano-coating of molecules by rare gas atoms, the suppression of ozone-induced aerosol formation, and the ultrafast energy flow in strongly hydrogen-bonded systems. For more details on this and other research, see the list of publications on our web-site www-suhm.uni-pc.gwdg.de. We also try to draw analogies between the molecular behaviour we observe and human social behavior, tongue-in-cheek of course, see www.molekularsoziologie.de.

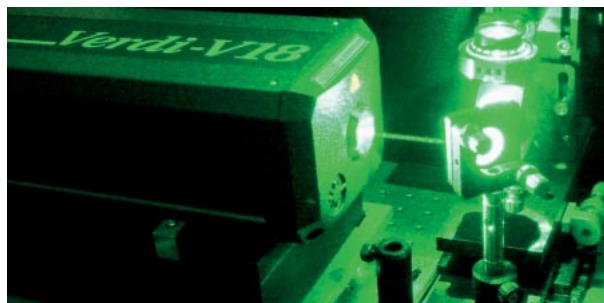


Fig. 6: Using the power of more than 20 000 green laser pointers, we detect down to one photon per hour per CCD pixel of Raman scattered light [1]. This is all we need to obtain nice hydrogen-bonded cluster spectra.

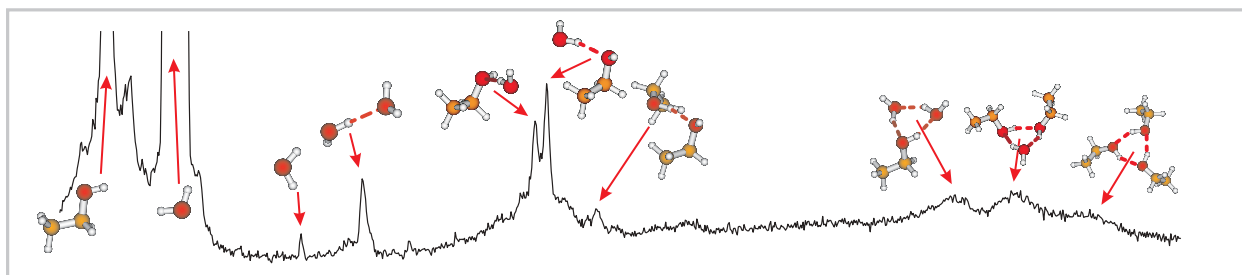


Fig. 7: Jet Raman spectrum of ethanol-water expansions, featuring different molecular and cluster signals.



Selected publications

- [1] Marija Nedić, Tobias N. Wassermann, Zhifeng Xue, Philipp Zielke, and Martin A. Suhm, Raman spectroscopic evidence for the most stable water/ethanol dimer and for the negative mixing energy in cold water/ethanol trimers *Phys. Chem. Chem. Phys.* 10 (2008) 5953-5956
- [2] Anne Zehnacker and Martin A. Suhm, Chirality Recognition between Neutral Molecules in the Gas Phase *Angew. Chem. Int. Ed.* 47 (2008) 6970-6992
- [3] Merwe Albrecht, Corey A. Rice and Martin A. Suhm, Elementary Peptide Motifs in the Gas Phase: An FTIR Aggregation Study of Formamide, Acetamide, N-Methylformamide, and N-Methylacetamide *J. Phys. Chem. A* 112 (2008) 7530-7542
- [4] Ingo Dauster, Martin A. Suhm, Udo Buck and Thomas Zeuch, Experimental and theoretical study of the microsolvation of sodium atoms in methanol clusters: differences and similarities to sodium-water and sodium-ammonia *Phys. Chem. Chem. Phys.* 10 (2008) 83-95



Martin Suhm was born in 1962 and got his chemistry diploma at the University of Karlsruhe (TH) in 1985. A pre-doctoral year at ANU in Canberra was followed by a PhD thesis at ETH Zürich on HF dimer under the supervision of Martin Quack. In 1990, he joined David Nesbitt for a postdoctoral stay at JILA/Colorado and came back to ETH for his habilitation. In 1997, he became professor of Physical Chemistry at the University of Göttingen. He was the first Dean of Studies at the Chemistry Department (2003-5) and is coordinates a DFG research training group (2002-11, see www.pcg.de).

Awards include the medal of the ETH, the Latsis prize, the ADUC prize as well as an FCI lecturer scholarship. Currently, he is Deputy Chair of the Editorial Board of *Physical Chemistry Chemical Physics*. His research interests focus on intermolecular interactions, in particular hydrogen bond dynamics, as probed by vibrational spectroscopy.