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Monday 4:00 pm

Physikalische Institute Köln

Lecture Hall III

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Linear Vibrational Spectroscopy of Supersonically Cooled Molecules and their Aggregation

Our molecular picture of the interstellar space is somewhat biased due to the high visibility of strongly polar molecules in rotational spectroscopy. This talk will address a few molecules and molecular dimers with partially low or vanishing dipole moments, which we have studied in the laboratory in vacuum isolation at low temperature. The experimental tools are spontaneous Raman scattering and FTIR spectroscopy in supersonic jets [1]. In the main part, it will be shown how isolated linear alkanes fold under the influence of London dispersion forces, overcoming conformational barriers. Depending on how well a theoretical model describes van der Waals attraction between the chain ends and the conformational landscape, it will predict this to happen at a different chain length. Experiment now says it will happen beyond 17 or 18 carbon atoms [2]. Time permitting, one or more examples from the series $\text{HO}-(\text{CH}_2)_n-\text{CH}=\text{O}$ with $n=0,1,2$ will be discussed. Formic acid ($n=0$) is itself polar, but it forms a non-polar dimer, for which we were recently able to establish the experimental binding energy within 1% [3]. Glycolaldehyde ($n=1$) was the first "sugar" molecule detected in space. Its dimers show a wide range of polarities and we could show that the global minimum structure is rather polar, offering at least a remote possibility to detect it in interstellar space [4]. Malonaldehyde ($n=2$) shows little tendency to dimerize, but a well-known THz tunneling splitting due to proton transfer in a symmetric double well. We were able to measure this tunneling splitting in more than a dozen vibrationally excited states, showing wide variations with the character of the normal mode [5].

[1] M. A. Suhm, F. Kollipost; Femtosecond single-mole infrared spectroscopy of molecular clusters, *Phys. Chem. Chem. Phys.* 15 (2013) 10702-10721

[2] Nils O. B. Lüttschwager, Tobias N. Wassermann, Ricardo A. Mata, and Martin A. Suhm; The Last Globally Stable Extended Alkane, *Angew. Chem. Int. Ed.* 52 (2013) 463-466

[3] F. Kollipost, R. Wugt Larsen, A. V. Domanskaya, M. Nörenberg, and M. A. Suhm; Communication: The highest frequency hydrogen bond vibration and an experimental value for the dissociation energy of formic acid dimer, *J. Chem. Phys.* 136 (2012) 151101

[4] Jonas Altnöder, Juhyon J. Lee, Katharina E. Otto, Martin A. Suhm; Molecular Recognition in Glycolaldehyde, the Simplest Sugar: Two Isolated Hydrogen Bonds Win Over One Cooperative Pair, *ChemistryOpen* 1 (2012) 269-275

[5] Nils O. B. Lüttschwager, Tobias N. Wassermann, Stéphane Coussan, and Martin A. Suhm; Vibrational Tuning of the Hydrogen Transfer in Malonaldehyde – A combined FTIR and Raman Jet Study, *Mol. Phys.* (2013) in press