

MO 4: Spectroscopy in He droplets

Time: Monday 16:30–17:45

Location: F 142

Invited Talk

MO 4.1 Mo 16:30 F 142

Rock and Roll in He Nanodroplets: Aggregation at Ultracold Conditions — ●GERHARD SCHWAAB¹, ELSA SANCHEZ-GARCIA², ANJA METZELTHIN³, WOLFRAM SANDER⁴, and MARTINA HAVENITH¹ — ¹Physical Chemistry II, Ruhr-University Bochum, D-44780 Bochum, Germany — ²MPI für Kohlenforschung — ³DPG Bad Honnef — ⁴Organic Chemistry II, Ruhr-University Bochum

Helium nanodroplets provide a unique environment to study intermolecular interactions. Their large pickup cross section allows the embedding of low vapor pressure compounds in the 10^{-7} to 10^{-4} mbar range. Evaporation of He atoms cools droplet and dopant molecules to 0.37 K typically within 1 ns. The superfluid He acts as 'soft' matrix that shifts energy levels only slightly compared to gas phase values.

Aggregation of molecules with large dipole moments in a typical droplet with radius of 5 nm is dominated by long range electrostatic interactions, e.g dipole-dipole interactions. Famous examples are HCN aggregates with up to 12 monomers or formic acid dimer where the formation of a polar acyclic structure was observed.

In contrast, the interaction energy governing the step by step aggregation of molecules with small or vanishing dipole moment in helium nanodroplets is small even compared to the thermal energy at 0.37 K. In these cases short range interactions and rotation will stabilize certain conformers while at the same time preventing the formation of others. Examples for both aggregation processes obtained from high resolution infrared spectroscopy in combination with extensive calculations on different levels of theory will be presented.

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Spectroscopy of PTCDA oligomers in helium nanodroplets — ●JAN RODEN and ALEXANDER EISFELD — MPIPCKS, Dresden, Germany

During the past few decades there has been intensive experimental and theoretical research into energy transfer [1] and optical properties [2] of molecular aggregates (molecules interact via dipole-dipole interaction), where coupling to vibrations often plays an important role. This research addresses e.g. the prominent light absorption of J- and H-aggregates or the transfer of electronic excitation energy in photosynthetic units and organic solar cells.

The helium nanodroplet isolation (HENDI) spectroscopy enables measuring fully vibrational resolved spectra of single molecules and aggregates with varying number N of molecules at temperatures below 1 K [3].

Including vibrational modes of the molecules, we calculate N -dependent oligomer spectra of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA). Comparison of the calculated spectra with experimental results shows good agreement.

[1] J. Roden, G. Schulz, A. Eisfeld, J. Briggs, *J. Chem. Phys.* 131(2009) 044909

[2] J. Roden, A. Eisfeld, W. Wolff, W. Strunz, *PRL* 103 (2009) 058301

[3] M. Wewer, F. Stienkemeier, *Phys. Rev. B* 67 (2003) 125201

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Electronic Spectroscopy of Anthracenes in superfluid helium droplets I: finestructure — ●DOMINIK PENTLEHNER and ALKWIN SLENCZKA — Universität Regensburg, Institut für Physikalische und Theoretische Chemie, 93053 Regensburg, Germany

In the last decade, Helium nanodroplets became a popular matrix for the spectroscopy of single atoms, molecules and clusters.[1] Compared to the corresponding spectra in a supersonic beam, electronic spectra of molecules exhibit a solvens shift, phonon wings (PWs) and in various cases a splitting, missing or broadening of the zero phonon line (ZPL) of vibronic transitions.

We have investigated the electronic spectra of anthracene and some substituted anthracenes in helium droplets. A splitting of the ZPLs could only be found for the unsubstituted anthracene. The transitions of all other compounds are dominated by a single ZPL accompanied by a PW exhibiting a finestructure which is similar for different anthracene compounds. PWs represent the excitation spectrum of the helium environment. The occurrence of PWs in electronic spectra of molecules in helium droplets will be discussed on the basis of an empirical model in analogy to the Franck-Condon principle for molecular vibrations. The finestructure of the anthracene molecules will be compared to those of Phthalocyanine and Fluorazene representing different cases of the model.

[1] Stienkemeier, F. and Lehmann, K. K.; *J. Phys. B: At. Mol. Opt. Phys.* 39 (2006) R127-R166

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Electronic Spectroscopy of Anthracenes in superfluid helium droplets II: broadening of spectra — ●DOMINIK PENTLEHNER, CHRISTIAN GREIL, BERNHARD DICK, and ALKWIN SLENCZKA — Universität Regensburg, Institut für Physikalische und Theoretische Chemie, 93053 Regensburg, Germany

Superfluid helium droplets are a favored cryogenic matrix due to a low temperature of only 0.37 K and its gentle interaction with dopants. Under these conditions, electronic spectra of rigid molecules like planar aromatic molecules use to show very sharp transitions. Though, electronic spectra of some organic molecules exhibit a broadening of zero phonon lines compared to the corresponding gas phase spectra.

The electronic spectra of anthracenes with a methyl or phenyl substituent will be discussed with particular emphasis on low frequency vibrational modes (torsions). In the case of extended Franck-Condon progressions in these modes, which indicate that a conformational change is induced by the electronic excitation, extensive line broadening appeared. For short Franck-Condon progressions the transitions remain sharp. We propose a model to explain the broadening by an enhanced dissipation of vibrational energy into the droplet leading to a homogeneous broadening of transitions. From the linewidth we estimate the time constant for the energy dissipation to be about 0.2 ps in the case of 9-Phenylanthracene and 0.5 ps for 2-Methylanthracene.