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Electron driven reactions in clusters of biomolecules embedded inside superfluid helium droplets.

Purpose of the visit:

Recent work of the Gdańsk Electron Spectroscopy Group focused on interactions of low energy electrons ($E < 20\text{eV}$) with biological molecules analogues in a gas phase [1,2]. In recent years it has been shown that electrons with sub-excitation energies can cause single and double strand breaks in the DNA [3,4]. The most important mechanism which could cause damage is dissociate electron attachment proceeding via negative ion resonances. Since low energy electrons are produced in biological environment in large quantities ($\sim 10^5/\text{MeV}$) by high energy particles and radiation, obtaining a full description of these electron - induced processes is important goal of radiobiology. Gas phase experiments with isolated molecules do not bring any information about influence of the environment (other molecules or water) on electron-induced processes. Performing such measurements is also challenging because biological compounds have low vapour pressure. To achieve desired pressures they must be heated, which may lead to thermal excitation and decomposition, complicating the obtained results.

Superfluid helium droplets turned to be a powerful technique in spectroscopy of large molecules in a condensed phase [5]. The way to obtain complex biological molecules is to evaporate their constituents and then condense them inside the helium droplet where they can create electrostatic or van der Waals bonds.

The aim of the visit is to gain practical knowledge and use this experimental approach to extend our gas phase studies on biological molecules into the measurements of molecules and clusters embedded in superfluid helium droplets.

Description of the work carried out during the visit:

Experimental setup consisted of cluster source and mass spectrometer [6,7]. The high-pressure (22 bar), high purity (>99.9999%) helium undergoes supersonic expansion into the vacuum. Generated helium droplets beam is skimmed before entering the pick-up region. Measurements of acetic acid and sulfur hexafluoride were performed. The acetic acid liquid was contained in stainless steel tube. Its vapors entered the pick-up region through the needle valve. Sulfur hexafluoride was introduced from cylinder through the needle valve. After the pick-up beam was skimmed before entering the interaction region, where it was crossed with electron beam (energy resolution ≈ 1 eV). Resulting ions are extracted by system of lenses and analyzed by modified 2 sector field Varian-MAT CH5 mass spectrometer. Both positive and negative ion mass spectra were collected as well as energy dependence spectra.

Description of the main results obtained:

Acetic acid is after a formic acid simplest of organic acid. Investigating its interactions with low energy electrons in cold environment of helium droplet may give some information on generation of a complex biomolecules in the interstellar medium. Negative ion mass spectra indicate presence of stable dimer and dimer-H anion. Dimer- H_2O is also present. Because loss of water may be associated with bound formation, measurements were repeated for deuterated acetic acid. Stable trimer and trimer- D_2O were observed. This suggest electron induced chemistry resulting in acetic anhydrate production.

Sulfur hexafluoride is important for electron attachment investigations since it is commonly used as calibrant [8]. First the positive ions were examined to probe the cluster size distribution. Positive ion mass spectra is presented in Fig.1. $(\text{SF}_6)_n\text{SF}_3^+$, $(\text{SF}_6)_n\text{SF}_5^+$ and $(\text{H}_2\text{O})_m(\text{SF}_6)_n\text{SF}_5^+$ are clearly visible above the He_n^+ series. Inset presents the results of high resolution, low mass measurements, performed to identify the He_nF^+ , He_nSF^+ , He_nSF_2^+ and He_nSF_5^+ series.

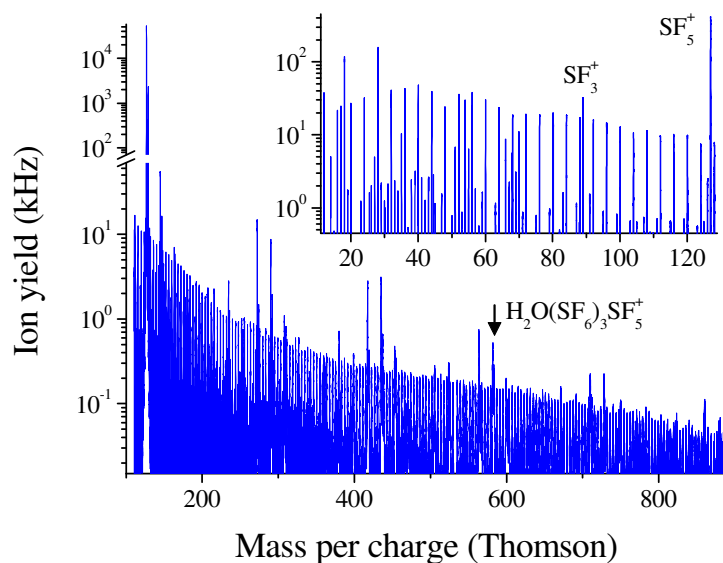


Fig.1 Positive ion mass spectra of He droplets doped with SF_6

Negative ion mass measurements revealed the parent, dimer and fragment ions, namely: F^- , F_2^- , SF_2^- , SF_3^- , SF_4^- , SF_5^- , some of them strongly bounding helium, giving rise to He_nX^- series with n values up to n=47. These experimental results will serve as a base for theoretical studies of helium affinity to ionized species embedded in helium droplets. Energy dependence for the anions formation were measured, as well as the temperature dependence of parent anion formation. The temperature of the cryostat was varied from 9.5 to 15 K.

Literature:

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- [8] L. G. Christophorou, J. K. Olthoff, Int. J. Mass. Spec. **205** (2001) 27

Future collaboration with host institution:

Performed measurements were limited by poor energy resolution of electron gun. Second cluster source, incorporating hemispherical electron monochromator will be developed in Innsbruck laboratory. Its superior resolution will enable to resolve broad structures in energy dependence spectra of ion formation. This measurements would extend my knowledge about embedding molecules in superfluid helium droplets.

Projected publications/articles resulting or to result from grant:

“Electron impact ionization to CCl_4 and SF_6 embedded in helium superfluid helium droplets” have been already submitted to International Journal of Mass Spectrometry. Other articles are also in future plans.