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Beneficiary: Pr Oddur Ingolfsson, University of Iceland
Host: Eugen Illenberger, Freie Universitaet Berlin
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SCIENTIFIC REPORT

PURPOSE OF THE VISIT

The main purpose of this STSM was to work on a method to transfer larger *neutral* molecules *intact* into the gas phase. This method (LIAD, laser induced acoustic desorption)[1] represents a flexible alternative to MALDI (matrix assisted laser desorption). In the Berlin LIAD experiment the second harmonic of a Nd:YAG laser (532 nm) is transferred into the chamber by an optical fibre and focused on the backside of a thin (12.7µm) Ti foil. The high power during the short (3-5 ns) laser pulse generates an acoustic wave which results in desorption of the material at the front side of the foil. The mechanical energy provided by the acoustic wave couples into the desorption stage, but is insufficient to ionise unless the analyte material is pre-charged in the deposit. This method enables the soft desorption of large molecules without increasing their internal energy, i.e., heating them up. LIAD should therefore be ideal for gas phase experiments on relatively large molecules and should enable us to extend our work on low energy electron interaction with biologically relevant molecules to larger molecules such as oligonucleotides and peptides.

UHV method development and instrumentation requires repeated venting and evacuation of the apparatus. Therefore we used the time to do parallel electron attachment experiments on selected model compounds. The model compounds we chose were alanine and trifluoro alanine, hexafluoroacetone azine and proponyl chloride.

DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT

Thje following work was carried out during the visit:

Characterization and optimization of the desorption process for the laser induced acoustic desorption experiment by using C_{60} and Rhodamine 6G.

Optimation of the ionisation and detection process through low electron attachment to well characterized gas phase electron scavengers such as CCl_4 and SF_6.

Initial attempts to combine LIAD with low energy electron attachment using the well characterized solid state scavenger C_{60} as model compound.

Electron attachment experiments on the compounds alnine, trifluoro alanine, hexafluoroacetone azine and proponyl chloride were conducted in the gaseous phase.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The STSM was very successful with regard to the LIAD experiment. First time desorption was obtained with a Minilite 1; Nd-YAG at 532 nm. The desorption characteristics were explored with regard to the power density, qualitative estimates of the attained desorption distance, i.e., the length of travel of the expanding plume were made and the influence of the thickness of the analyte layer was examined. A minimum power density of about 10 mJ/mm^2 was determined for the desorption process and a close to linear power dependency of the desorption rate.

Exact thickness of the prepared films were not determine, but no clear dependency of the desorption rate was observed in the range tested. The travel length was estimated visually by observation of the scatter light of a HeNe LASER perpendicular to the direction of desorption. The length of travel was found to exceed 5 mm.

Electron current and energy as well as the ion optics were optimized by using the Cl^- signal from CCl_4

By using the parameter acquired above the focal length and the ion optics were optimized to allow desorption and detection of C_{60} after mass analyses. The attempt to detect mass selected C_{60} was unsuccessfully as the mass spectrometer was not working properly and could not be repaired in the short time frame of the visit. .

Next steps in the optimization of the LIAD experiment after obtaining mass selected C_{60} signal is the optimization of the electron and ion optics and the detection and recording electronics. For the optimization of the electron and ion optics SIMION simulation are in preparation.

Electron attachment experiments on the model compounds alnine, trifluoro alanine, hexafluoroacetone azine and propionyl chloride were conducted in the gaseous phase.

The energy dependency of the dissociative electron attachment process was determined for trifluoro alanine, and proponyl chloride for comparison with their none halogenated analogs, i.e., alanine and propanoic acid. As an initial step in an systematic approach to map the influence of individual functional groups we also chose to measure the electron attachment profiles of hexafluoroacetone azine. There are still ambiguities in the intepitation of some mass to charge ration observed from trifluoro alanine that are in the process of being clear. Different to propanoic acid, proponyl chloride forms a stable molecular anion close to 0 eV, though the molecular ion is formed with rather low intensities. The most pronounced channel is the Cl^- formation which appears with comparable intensities through a relative narrow feature close to 0 eV and another broader one around 1.5 eV. Other fragments observed through DEA to proponyl chloride are $HCOCl^-$ and CH_2COCl^- which are the analogues of the fragments HCOO- and CH_2COO-propanoic acid and show remarkably similar resonance profiles.

Electron attachment to hexafluoroacetone azine $(CF_3)_2C=N-N=C(CF_3)_2$ in the range from few meV to 10 eV leads to the formation of fragments with the mass to charge ratio (m/Z): 164, 69, 26 and 19. We attribute these to the fragments $(M/2)^-$, i.e., $[(CF_3)_2C=N]^-$, CF_3^-, CN^- and F^-. The most pronounced are $[(CF_3)_2C=N]^-$ and CF_3^-. $[(CF_3)_2C=N]^-$ appears through two structured contributions, one centered around 0.3 eV and a broad higher energy feature centered at 2.3 eV, CF3- through appears through a fairly broad peak with an onset close to 2 eV and a maximum at about 4 eV.

FUTURE COLLABORATION WITH HOST INSTITUTIONS

Future collaboration with the host institute was established on two projects:

One is on desorbed bimolecules, where UI will conduct fragmentation studies on large desorbed biomolecules after protonation and deprotonatin in a conventional MALDI instrument to compare with DEA experiments with the LIAD setup in Berlin. Further extention of this collaboration includes experiments on a laser desorption electron attachment instrument which is under construction at UI.

The second collaboration is on fragmentation studies on ribose, deoxyribose and analoge polysccarides. To realize this project Ilko Bald will be visiting UI to do experiments on metastable fragmentation of sugars after deprotonation and after protonation. These experiments will be an extension to the part of his PhD. work concerned with DEA to ribose and deoxyribose.

PROJECTED PUBLICATIONS/ARTICLES RESULTING OR TO RESULT FROM THE STMS

The STSM with regard to the LIAD experiment was a valuable contribution to the construction of the experiment, but nonetheless it was only one step of many in that process. The projected number and significance of publications from the LIAD project are considerable but they can not be seen as a direct result of this STMS.

One paper on the electron attachment experiments has been submitted as a poster to EIPAM 06, further conference contributions will result from this visit and at least two research articles will be submitted to pier reviewed journals.