Scientific report

EIPAM Exchange Grant Number 1773

Title: Dissociative electron attachment to complex molecules in the gas phase and in clusters

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The aim of the visit was to support the design and construction of a new experiment for measurements of dissociative electron attachment (DEA) to single molecules and clusters of non-volatile molecules. A very broad and new scope of experiments on DEA can be conducted with such an instrument that will contribute to establish new directions in research within the EIPAM program. The apparatus is built from scratch and since different functionalities are combined in one instrument certain design issues turned out to be very complex.

The apparatus consists of an expansion chamber and a reaction chamber that is connected to a Reflectron Time-of-Flight (TOF) mass spectrometer. The reaction chamber is housing a trochoidal electron monochromator and an ion lens system that accelerates the generated anions into the mass spectrometer. A cluster beam is generated by supersonic expansion through a pulsed valve into the expansion chamber and the sample molecules are seeded into the cluster beam. The clusters enter the collision chamber through a skimmer and are ionised by collisions with low-energy electrons.

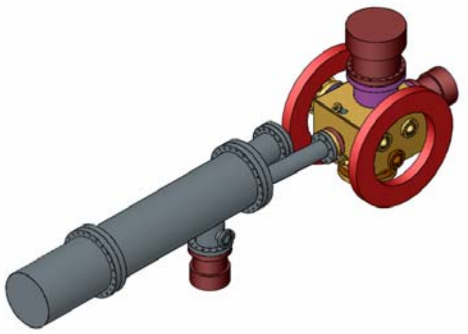
The molecules of particular interest are non-volatile and fragile, e.g. biomolecules. Laser desorption is used to yield gas phase, neutral and intact molecules.

The overall design was discussed and it was decided that a trochoidal electron monochromator will be built in favour of a hemispherical electron monochromator.

The final design of the apparatus is shown in figure 1 which is basically the outcome of the last six-month design work that was done with Elias Bjarnasson. A large part of his Ph. D work is concerned with the design and construction of this new instrument.

The instrument consist of three differentially pumped chambers; the expansion chamber, the interaction chamber and the detection chamber. The expansion chamber contains the reaction chamber and both are connected by a skimmer as can be seen on the right side of figure 1.

The outer chamber is pumped by a 500 Ls^{-1} turbomolecular pump and the inner chamber is pumped by a 200 Ls^{-1} turbomolecular pump. The particular arrangement of both chambers significantly reduces the conductance of the chamber. Hence a careful design was necessary to be able to maintain a pressure of approximately 10^{-6} - 10^{-5} mbar with a 500 Ls^{-1} pump during the operation of the pulsed valve for cluster beam generation. The trochoidal monochromator is situated in the inner chamber and is constructed of square electrodes made out of molybdenum. Figure 2 shows the arrangement of electrodes in the monochromator along with the ion optics. Electrons are generated by a Bariumoxide disc filament and guided by three electrodes into the dispersion region. The monochromatic electrons are accelerated/decelerated by three more electrodes after the dispersion region and before they enter the reaction volume where they interact with sample molecules. Behind the interaction region the electrons are again dispersed to prevent backscattering of electrons and are finally collected by a faraday cup. The voltage of the third lens after the filament is pulsed in order to create a pulsed electron beam. To prevent disturbing electric fields the pulsed electrode is shielded. A pulsed electron beam is necessary to establish pulsed ion extraction into the TOF mass spectrometer. The pulsing mode and electrical connections were argued in detail, since it should be prevented to put either the mass spectrometer or the monochromator on high-voltage potential. Therefore it was decided to provide only the ion extraction optics with high-voltage pulses. The extracted ions are then focused by a deflector before entering the field-free drift tube. A reflectron establishes improved mass resolution and provides the possibility to measure metastable ion fragmentation for the case that a parent ion was selected previously at a gate or at the deflector, respectively. After a second field-free drift tube the ions are detected by a micro-channel plate detector. The mass spectrometer is modified to measure the autodetachment and dissociation lifetime of molecular ions by introduction of a moveable electrode into the first drift tube.



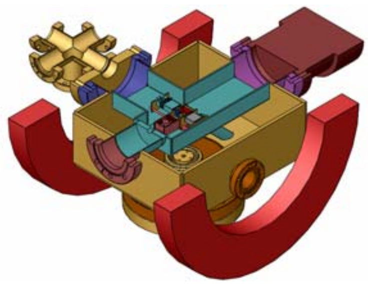


Figure 1: Overview of the experimental setup showing the expansion chamber connected to the reflectron TOF MS (left), and a more detailed cross section of the expansion chamber that is housing the reaction chamber (right).

The measurement of electron attachment to complex molecules and clusters raises the question of a clear identification of target species present in the reaction volume. To improve the availability of information on the target molecules another analytical tool apart from electron impact ionization will be introduced, that is photoionization. For this, two viewports connected by tubes are located on the expansion chamber in order to access the reaction zone by an excimer laser. A Lumonics 500 excimer laser that was no more in use in our laboratory was repaired and recovered within the last months. It was cleaned, leaks in the gas inlet system have been removed and windows exchanged. It can be operated either with XeCl or KrF and is now ready to use for photoionization studies in the new instrument. With this setup we can also detect neutral products that are generated *via* dissociative electron attachment.

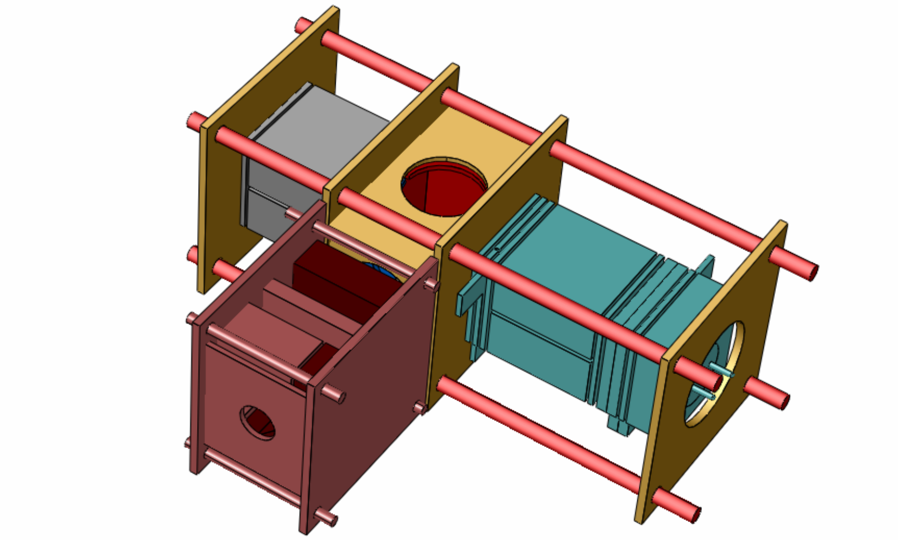


Figure 2: Scheme of the trochoidal electron monochromator (green), the collision chamber (bright red), the electron collector (grey) and the ion extraction optics (dark red). The filament is situated on the right-hand side of the figure.

Laser desorption of large molecules is established by two different means, either by direct laser irradiation of sample molecules (possibly cocrystallized with matrix molecules (MALDI)) placed on a rod using an N_2 laser or the higher harmonics of a Nd:YAG laser. Alternatively molecules can be desorbed from a thin metal foil by laser irradiation of the backside of the foil (laser-induced acoustic desorption, LIAD). The main challenge is that both laser desorption methods require a different laser beam pathway and application of both methods make the experimental setup more complex. Therefore a sample holder was designed that provides both methods by a simple changing of the sample probe. In either case the desorbed molecules are picked up by a stream of rare gas atoms that enter the expansion chamber through the pulsed valve. To date the study of electron-molecule interactions was limited to thermally stable molecules that are easy to evaporate. With the present setup we are able to study larger, more complex and fragile molecules. Both MALDI and LIAD will be applied and compared.

In addition to working on designing and constructing the new electron attachment instrument and ordering materials additional measurements on the running MALDI instrument have been performed and previously acquired data that are also within the scope of EIPAM have been published.

In summary three publications resulted from the stay in Iceland and three more publications are in preparation. More precisely, these are:

A review article on electron-molecule interaction has been written and was published this month in the International Journal of Mass Spectrometry (*Int. J. Mass Spectr.* **2008**, *277*, 4-25.).

A manuscript about fragmentation of negatively charged sugars in a MALDI instrument was composed and submitted to the International Journal of Mass Spectrometry. Additional measurements on metastable and fast fragmentation of deprotonated D-fructose and its isotope labelled analogues have been performed during the present stay and a manuscript is now in preparation.

Previously we performed measurements on DEA to different fluorinated benzene derivatives, i.e. perfluorophenylisocyanate (C_6F_5NCO) and perfluorophenyloacetonitrile ($C_6F_5CH_2CN$). These molecules are good examples to demonstrate how formation of different π^* and σ^* resonances lead to specific dissociation reactions. Furthermore the formation of neutral HF was observed to be a remarkably efficient process. The respective manuscript is in the final stage and will be submitted in October or November.

Furthermore experiments have been conducted within the exchange visit, which demonstrate that electron induced processes are also relevant for the ionization mechanisms in MALDI. Free electrons with very low energy are created by laser irradiation of the MALDI target and subsequent electron attachment reactions have an influence on the final ion distribution observed in the mass spectrometer. The role of electrons in the MALDI process was investigated by means of measurements at different wavelengths (UV and visible range) of the desorbing laser. A dye laser was used for this purpose and different model substances were investigated. The presence of free photoelectrons at small wavelengths was observed by means of SF_6^- formation formed by electron attachment to SF_6 gas introduced into the ion source. Furthermore ion formation from C_{60} fullerenes was investigated at different wavelengths giving valuable information about the primary ionization mechanisms in MALDI. These results will be presented in a talk and a poster presentation at the ESF conference "Chemical Control with electrons and Photons" in Obergurgl. One manuscript is in preparation that discusses the formation mechanisms of C_{60}^- in MALDI at different laser wavelengths and pulse energies. Another manuscript will be published on specific wavelength dependent phenomena in MALDI, which can be explained by generation of low-energy photoelectrons and subsequent formation of transient negative ions of matrix or analyte molecules.

Finally I want to thank EIPAM for generously supplying the exchange grant. In the meantime I got a postdoctoral position at the University of Iceland for at least six more months to continue the work on construction of the new experiment. This gives enough time to start first measurements and will hopefully lead to publishable results.