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Scientific Report

Purpose of visit

The purpose of this visit was to measure the dissociative electron attachment to Iodo-Uridine monophosphate using Laser Induced Acoustic Desorption (LIAD) technology to desorb the neutral molecules intact into gas phase without heating. This has shown to be an effective method to introduce intact molecules into gas phase, making it possible to measure DEA on larger biomolecular systems than with the methods commonly used.

In this instrument the sample molecules are deposited as a thin layer on a titanium foil with a 12.7 microns thickness. A pulsed Nd:YAG laser irradiates the foil from the backside and creates shock waves that lead to desorption of the molecules at the opposite side. The desorbed neutral and intact molecules interact with a low energy electron beam (0-20 eV) and the generated anions are mass selected and detected with a quadrupole mass spectrometer in dependency of the incident electron energy.

Work carried out

During the short term scientific mission (STSM) work was carried out on a gas phase electron attachment instrument with a trochoidal electron monochromator and a quadrupole mass spectrometer. We measured three different molecules in gas phase, the isotope labelled fructose in first position; D-fructose 1-C13 (Figure 1), and two halogenated bi and tri aromatic compounds; 9-chloromethyl-anthracene (Figure 2) and 7-hydroxyl-4(trifluoromethyl)coumarin (Figure 3).

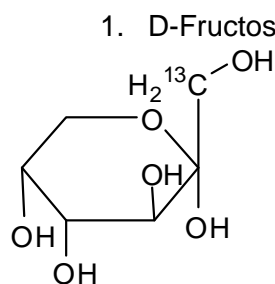


Figure 1.
D-Fructose 1-C13

Dissociative electron attachment to D-fructose has already been measured by Sulzer et al ¹ showing several different fragments formed at 0 eV. These fragments are characterized by their neutral leaving groups, i.e. different combinations of water and formaldehyde are lost in order to form the fragments observed. In order to recognise from where the neutral formaldehyde leaving groups leave and if there is site selectivity in the process we have now measured this isotope labelled fructose. Bald et al ² did a detailed study on the site selectivity of D-ribose showing quite extraordinary selectivity for the site of removal of formaldehyde neutrals. We now continued this study, for further details of the fragmentation of fructose.

2. 9-chloromethyl anthracene

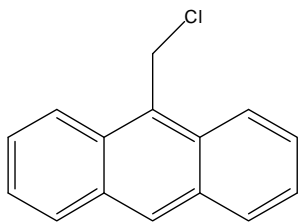


Figure 2. 9-chloromethyl anthracene

Dissociative electron attachment to 9-chloromethyl anthracene shows four resonances at ~ 0 eV, 1.1 eV, 3.0 eV and 5.1 eV these resonances result in only two fragment anions with m/Z ratios 191 amu and 35/37 amu associated with the fragments $[M-Cl]^-$ and Cl^- respectively, where the chloride anion is only formed at the lower energy resonances (~ 0 eV and 1.1 eV) and the $[M-Cl]^-$ anion is only formed at the higher resonances.

3. 7-hydroxy-4(trifluoromethyl)coumarin

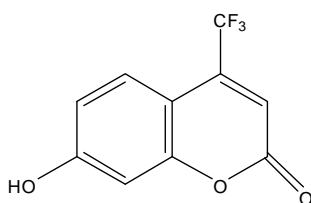


Figure 3.
7-hydroxy-4-
(trifluoromethyl)coumarin

There are resonances for low energy electrons at ~ 0 eV, 1.1 eV, 3 eV and 9 eV. Forming eight different anions, seven of those have m/Z ratios 230, 210, 190, 184, 163, 134, and 19 amu assigned to M^- , $[M-HF]^-$, $[M-2HF]^-$, $[M-HCOOH]^-$, $C_6H_2F_3O_2^-$, $C_8H_5O_2^-$ and F^- . The most pronounced ion is the parent ion, only at 0 eV. In addition we observed one fragment at mass 226. This mass can only be assigned to the fragment $[M-2H_2]^-$, which can only be formed when the electron affinity of the molecule is very high and thus not probable. Ab initio calculations will be done to clarify the formation of this fragment.

Collaborations and Publications

The results on the isotope labelled D-fructose are being prepared for publication. The D-fructose 2-C13 and D-fructose 6-C13 will also be measured in the gas phase machine in Berlin. Ilko Bald and Helga Dögg Flosadóttir have measured these samples in Matrix Assisted Laser Desorption Ionisation time of flight Mass Spectrometer (MALDI tof MS) in order to observe the similarities and differences between these two methods of ionisation. Results on 9-chloromethyl anthracene and 7-hydroxy-4-(trifluoromethyl)coumarin will be compared with in source and metastable fragmentation in MALDI before publishing.

Citation

1. P. Sulzer, S. Ptasinska, F. Zappa, B. Mielewska, A. R. Milosavljevic, P. Scheier, T. D. Mark, I. Bald, S. Gohlke, M. A. Huels and E. Illenberger, *Journal of Chemical Physics* **125** (4) (2006).
2. I. Bald, J. Kopyra and E. Illenberger, *Angewandte Chemie-International Edition* **45** (29), 4851-4855 (2006).