REFERENCE: Short Term Scientific Mission, COST P9

Beneficiary: Dr Janina Kopyra, University of Podlasie

Host: Prof. Dr. Eugen Illenberger, Freie Universität Berlin

Period: from 5/11/2006 to 5/12/2006 Place: Berlin (DE)

Reference code: COST-STSM-P9-02358

SCIENTIFIC REPORT

Title: Investigation of the low energy electron interactions with molecular constituents of DNA.

Purpose of the visit

The purpose of the visit was to investigate interactions of the low energy electrons with biomolecules in the gas phase. The study is a part of the effort to understand radiation damage of DNA basic subunits. Recently, the gas phase dissociative electron attachment experiments have been performed for the pure sugars, 2-deoxyribose and ribose. From these studies it is known that the sugars demonstrate a pronounced sensitivity towards low energy electrons. However, 2-deoxyribose and ribose in DNA/RNA do not possess OH groups and therefore the relevance of using free sugars as model for the response of the sugar unit in DNA/RNA is limited. For this reason the sugar ester 1,2,3,5-tetra-O-acetyl-β-D-ribofuranose (tetraacetylribose, (TAR)) was chosen as a subject of the experiment to complete the earlier findings for pure sugar molecules.

Description of the work carried out

The experiments were performed with a crossed electron-molecular beam apparatus. The apparatus consists of an electron source, an oven, a quadrupole mass analyzer and a detection system. An electron beam of the defined energy generated from a trochoidal electron monochromator (resolution 100 meV FWHM) crossed perpendicularly with a molecular beam consisting of TAR. To obtain a sufficiently high pressure of intact molecules a temperature of about 340-350 K (measured by a platinum resistance) was used during the experiments. The generated negative ions are extracted by an electric field and accelerated by a series of parallel electrodes onto the entrance hole

of quadrupole mass analyzer and detected by a single pulse counting technique as a function of incident electron energy. The energy scale was calibrated by measuring the formation of SF_6^- ions, which exhibits a sharp peak of known cross section located near 0 eV.

Description of the main results obtained

Tetraacetylribose (TAR) as a sugar ester with acetyl groups coupled at the relevant positions to the five membered ribose ring may serve as an appropriate model compound to simulate the behaviour of the sugar unit in DNA/RNA.

Tetraacetylribose possesses an appreciable sensitivity towards low energy electrons. The interaction of low energy electrons with TAR leads to dissociation into various fragments, however, without stable parent negative ion. The major anionic dissociation products are caused by following reaction pathways:

$TAR + e^- \rightarrow TAR^{\#-}$	$\rightarrow C_9H_{11}O_6^-$ + fragments	215 amu
	$\rightarrow C_6H_9O_5^-$ + fragments	161 amu
	$\rightarrow C_7H_6O_4^-$ + fragments	154 amu
	$\rightarrow C_4H_7O_4^-$ + fragments	119 amu
	$\rightarrow C_5H_5O_3^-$ + fragments	113 amu
	$\rightarrow C_4H_4O_3^-/ C_5H_8O_2^-$ + fragments	100 amu
	$\rightarrow C_4H_4O_2^-/ C_5H_8O^-$ + fragments	84 amu
	$\rightarrow C_4H_6O^-$ + fragments	70 amu
	$\rightarrow C_2H_3O_2^-$ + fragments	59 amu

The general features of the ion yield curves allow the anionic products to be categorised as follows:

1) The dominant signal observed at 59 amu, the only ionic product which is generated from all the different resonant features present in the target compound, at very low energy (close to zero eV), in the energy domain 1-3 eV and in the region 7-11 eV (Figure 1). This fragment ion can unambiguously be assigned to

CH_3COO^-, i.e. the closed shell acetate anion. The most direct pathway for its formation is rapture of one of the C-O bonds at the C1, C2, C3 or C5 position.

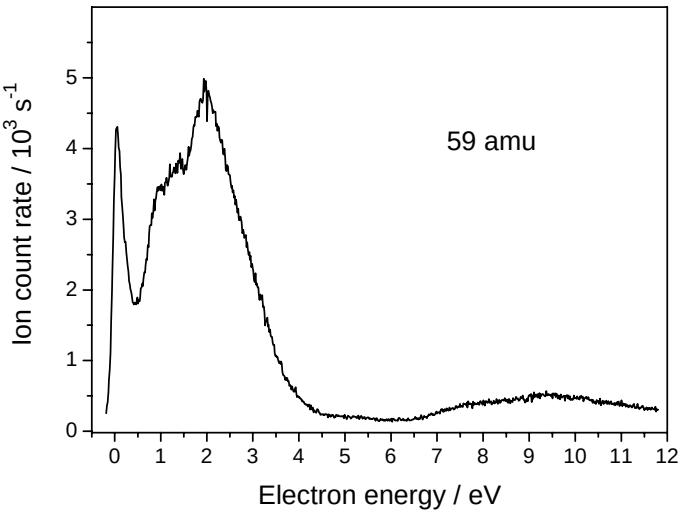

Figure 1. Ion yield of the dominant signal observed at 59 amu.

2) A series of fragment ions (at 100, 84 and 74 amu) observed from resonant feature close to 0 eV and with an additional weaker and broader contribution in the energy range about 7-11 eV (Figure 2). Possible stoichiometric assignments for this group of fragments, proposed above, could represent five membered ring radical anions.

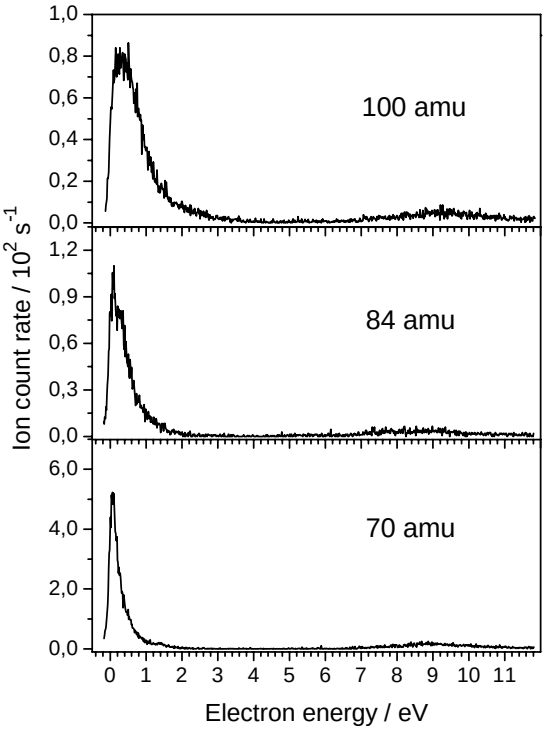

Figure 2. Ion yields of the fragments with an appearance energy near zero eV and an additional weak contribution in the energy range 7-11 eV.

3) A series of fragment ions (at 215, 161, 154, 119 and 113 amu) appear within a resonance having a maximum in the energy range 1.6-1.8 eV. Figure 3 presents the ion efficiency curves of $C_6H_9O_5^-$, $C_7H_6O_4^-$, $C_4H_7O_4^-$ and $C_5H_5O_3^-$. An ion of 215 amu is not included in this figure since the signal was barely above the detection limit but its maximum could be localised near 1.8 eV.

   The further observations is that all fragments of this group do not appear from the high energy resonant feature (7-11 eV).

   Based on the calculations on transient anions, adopting the stabilization method, this features is assigned to a series of closely spaced shape resonances of π^* character with the extra electron localised on the acetyl groups outside the ribose ring system.

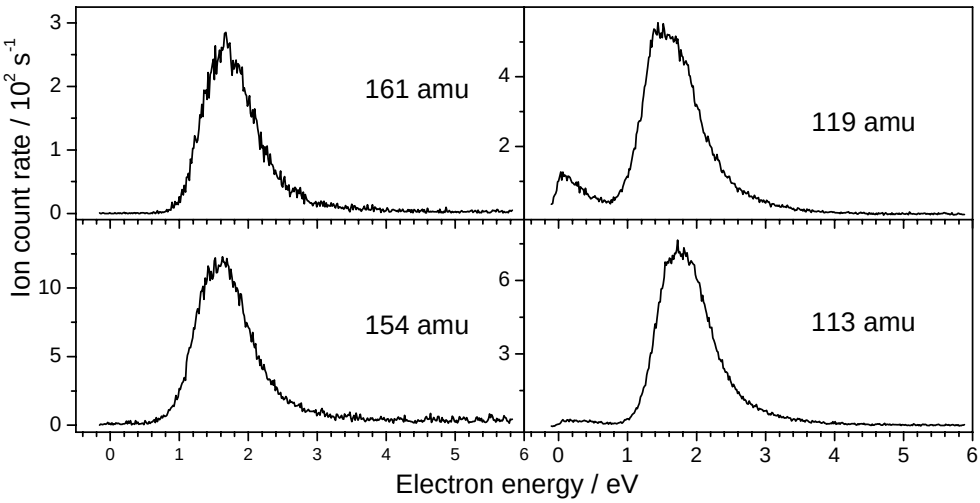

Figure 3. Ion yields of the fragments with a maximum in the energy range 1.6-1.8 eV. These ions arise from a π* shape resonance located at the acetyl groups.

Future collaboration with host institution

It is expected to continue the collaboration in the area of electron interaction with molecules of biological interest.

Projected publications resulting from the grant

The publication of presented results was submitted (November 2006), Title: *Low Energy Electron-Induced Reactions in Gas Phase 1,2,3,5-tetra-0-acetyl-ß-D-ribofuranose: A Model System for the Behaviour of Sugar in DNA.*

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Host Confirmation

I herewith declare that Dr. Janina Kopyra visited the Berlin laboratory in the period between 05 November 2006 and 05 December 2006 to study electron induced reactions in sugar derivates. A publication emerging from this collaboration is submitted.

Dr. Eugen Illenberger
Professor of Physical Chemistry