Scientific report on my STSM visit (COST-STSM-P9-00264) at the University of Innsbruck

by Dagmar Mayr

1. Purpose of visit

Water is a dominant component in any biological cell. Electron interactions with a water molecule are fundamental processes in the radiation action on biological matter. The values for dissociative electron attachment (DEA) to water are more than 30 years old when good discrimination was difficult to achieve. Therefore we wanted to re-measure them with a crossed electron/molecular beams apparatus available in T.D. Maerk's group at the Institute for Ion physics at the University of Innsbruck. Furthermore we planned to measure the electron attachment (EA) to the biomolecule 5-Bromouridine, which consists of a nucleotide and a sugar in order to get more information about its radiosensitive properties.

2. Description of the work carried out during the visit

DEA to Water

We have performed an experimental study of DEA to water using a crossed electron/molecular beams apparatus (Fig. 1, image from the website of the Institute for Ion Physics). The beam of e- with well characterized energy distribution enters the interaction region where it is crossed with a beam of neutral water molecules. The negative ions produced are extracted from the interaction region by a weak electrostatic field and focussed into the entrance aperture of a quadrupol mass spectrometer. The ions are detected in a channeltron multiplier. This study was performed in the electron energy range of about 0- 15eV.

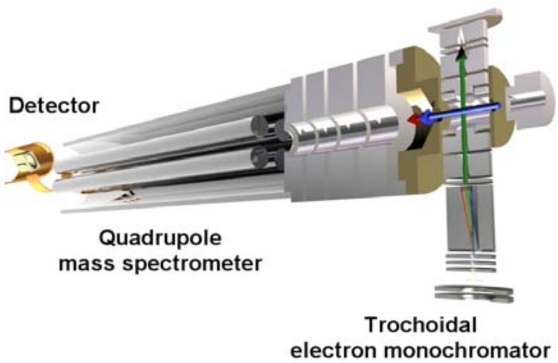
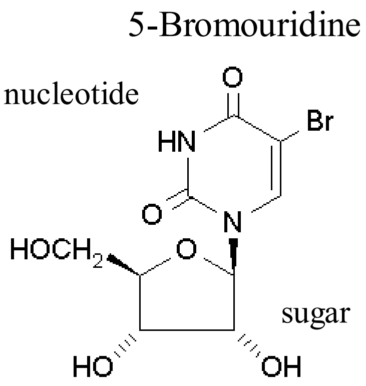


Fig. 1: Crossed electron/molecular beams apparatus used for studying DEA to water.

EA to 5-Bromouridine

We studied EA to 5-Bromouridine (structure shown in Fig. 2) by a crossed electron/molecular beams apparatus (Fig. 3, image from the website of the Institute for Ion Physics). The 5-Bromouridine is in powder form and thus heated in an oven to become gaseous and be injected into the apparatus. We measured positive ions using electron energies of 70 eV at different temperatures in order to find the temperature where decomposition of the biomolecule in the oven occurs. The compound started to break up at a temperature of T_d~145°C (identified by a strong increase of fragments in the mass spectra). We then performed the measurements at 130°C to be well below

T_d. We measured the appearance energies of the positive ions and the electron attachment cross sections.



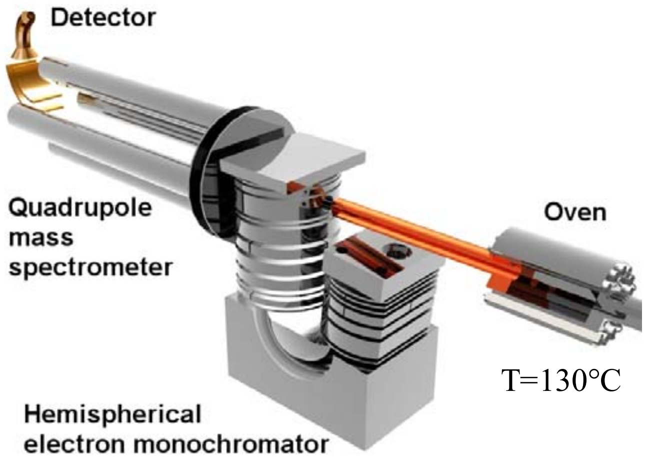


Fig. 2: Structure of 5-Bromouridine

Fig. 3: Crossed electron/molecular beams apparatus used for EA studies to 5-Bromouridine

3. Description of the main results obtained

DEA to Water

We compared our data with data from other groups (Melton and Jungen, see Fig. 4). Melton's values are the recommended ones.

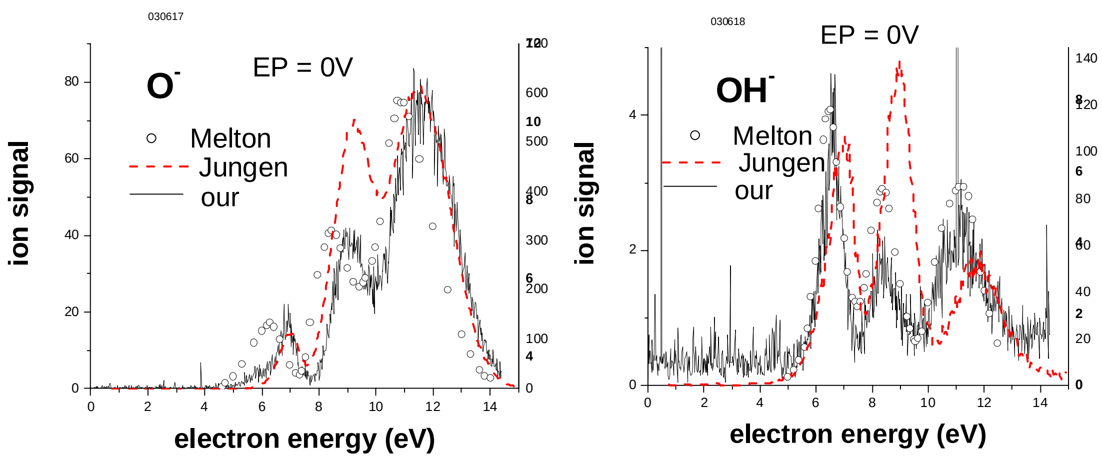


Fig. 4: Comparison of DEA data from different groups

Comparison of the results:

For O⁻ :

- Energy shift of Melton's data compared to ours and Jungen's data
- Christophorou (data not shown in Fig. 4): peak positions agree with ours and Jungen's
  - ➡ Melton's data must be in doubt

Why do Melton's peaks have a shift in energy?

- Melton used calibration with appearance energy of O-/CO and O-/O2 and did not have very good resolution
- all other works used CCL4 or SF6

Intensity of peaks:

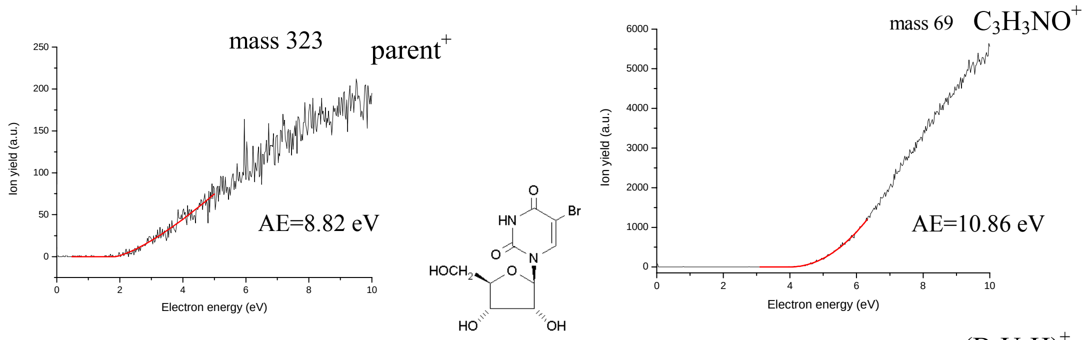
- Melton's, Christophorou's and ours agree (all measured by minimizing the discrimination of ions)
- Jungen's data differ – Discrimination?

For OH⁻ :

- Melton's, Christophorou's and our data agree
- Jungen's data relative heights different - Discrimination?

EA to 5-Bromouridine

We determined the appearance energies (AE) of the obtained ions (Fig. 5). Krypton (Kr) was used as a calibration gas. The fragment ions have a higher AE than the parent ion, which indicates that there was no decomposition in the oven (more energy is needed for ionisation plus fragmentation as for ionisation only).



Mass	AE (eV)	Real AE (eV)	Shift	
Kr	7.117	14	6.883	
28	7.012	13.895		CO
18	5.607	12.49		H2O
28	4.463	11.346		CO
69	3.977	10.86		C3H3NO
147	3.799	10.682		?
190	2.553	9.436		Br-Uracil -H
112	2.552	9.435		Ribose -H
323	1.855	8.822		Parent

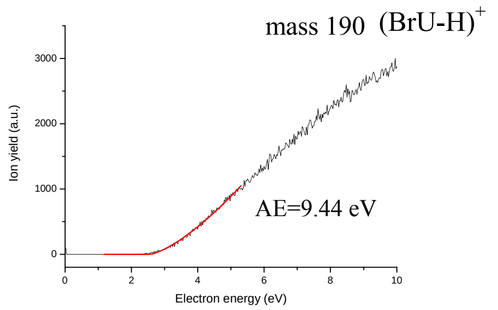


Fig. 5: Measured appearance energies (AE)

We measured and determined the cross sections for the formation of the parent ion Bromouridine⁻ , the main fragment ion Brom⁻ (see Fig. 6) and some other fragments from EA to 5-Bromouridine. We used Cl⁻ from EA to CCl_4, which has a resonance at 0.8 eV with a well known cross section to calibrate the cross sections.

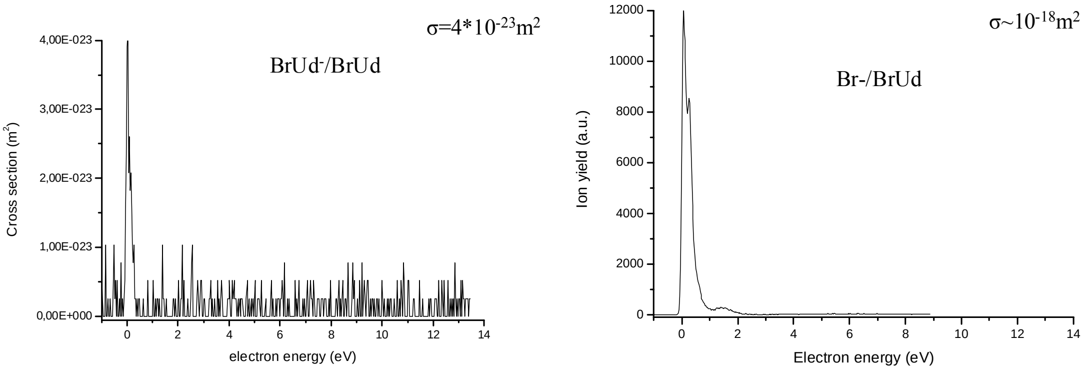


Fig. 6: Electron attachment cross sections for the parent ion $BrUd^-$ and the main fragment Br^-

4. Future collaboration with the group in Innsbruck

We obtained very interesting results and would like to extend both studies:

DEA to Water

- measure H^- from DEA to water
- Vary the extraction potential to get information about the kinetic energies
- Study isotope effects (H_2O vs D_2O)

EA to biomolecules

- EA to 5-bromodeoxyuridine and comparison with 5-bromouridine to see whether treatment is more selective towards deoxynucleoside
- 4-Thio-5-bromo-2’-deoxyuridine – to see if it is more radiosensitive

5. Projected publications/articles resulting or to result from the STSM

It is planned to publish the results of the water and the Bromouridine study, respectively, as soon as the data analysis and comparison with other data has been finished. However, some results of the planned experiments described in “Future collaboration” might be needed to publish the work.