COST STSM Reference Number: COST-STSM-CM0601-6261
STSM Applicant: Dr Sylwia Ptasinska,The Open University, Milton Keynes (UK) , s.ptasinska@open.ac.uk
Period: 01/05/2010 to 30/05/2010
Host: Paul Scheier,Institut für Ionenphysik und Angewandte Physik,Innsbruck (AT), paul.scheier@uibk.ac.at
STSM Topic: Molecular synthesis induced by low energy electrons in low temperature regime

SCIENTIFIC REPORT

1. Purpose of the visit:

The main aim of my STSM to Nano-Bio-Physics Group lead by Prof. P. Scheier in Innsbruck was to study chemical reactions in a ultra low temperature regime, that is in superfluid He droplets, which provide a temperature of 0.37 K. In spite of a number of publications, which report the formation of new complex compounds from a mixture of molecules in the condensed phase. However, similar experiments in He droplets have not been previously carried out.

Two objectives were proposed for this one month mission; the formation of an ozone molecule which is considered to be one of the biomarkers in the interstellar medium and the simulation of Titan's atmosphere. Both projects were successfully performed and the main results obtained are presented below.

2. Description of the work carried out during the visit:

In the present studies pure O_2 or CO_2 gases, the binary mixture of N_2 and CH_4 gases and O_2/CO_2 with C_{60} fullerenes were embedded in superfluid He droplets and then ionized by electrons with energies of 70 eV. The helium cluster source was used to form droplets (with mean size from 10^3 to 10^6 depending on temperature and pressure in the cluster source) in a supersonic expansion through the nozzle. The products of electron ionization were analyzed by means of Time-of-Flight mass spectrometer (TOF-MS) able to detect the mass up to 20000 thomson with a mass resolution ($m/\Delta m$) of about 5000.

For the gas mixture experiments, the gas inlet unit of the apparatus was modified which allowed preparing a well defined gas composition. The total pressure of the mixture was measured by barotron and was set at the pressure of 1 bar. After installation of the gas mixture chamber the experiments for different ratios of two gases were carried out. The positive mass spectra for pure as well as for gaseous mixtures were collected and analysed with a particular focus on new products formed.

3. Description of the main results obtained:

A. The formation of ozone and oxygen clusters

a) from pure O_2 or CO_2

Among many biomarkers such as water, oxygen and carbon dioxide, ozone is believed to be an essential component of any planetary atmosphere capable of sustaining life. A high concentration of molecular oxygen in the atmosphere allows for the formation of ozone via Chapman reactions initiated by UV radiation (below 240 nm) which lead to dissociation of oxygen molecules. The formed atomic oxygen combines very rapidly with other oxygen molecule to form ozone via a three-body collision.

The similar two-step reaction process can be attributed to the ozone formation in He droplets induced by electron impact as follows:

$$O_2 + e^- \rightarrow O^+ + O$$

$$O^+ + O_2 \rightarrow O_3^+$$

Mass spectra of clusters formed from O_2 and CO_2 obtained at the same cluster source conditions (i.e. 10 K) are presented in Fig. 1 and 2, respectively. The recorded spectra show also heterogeneous clusters due to some contaminations in the ion source.

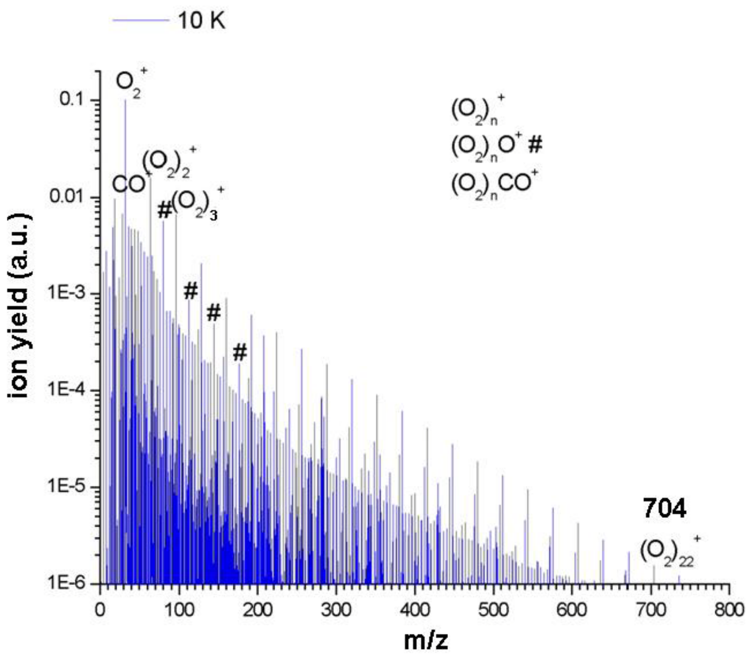

Fig. 1. The mass spectrum obtained from pure O_2 molecules picked up by He droplets.

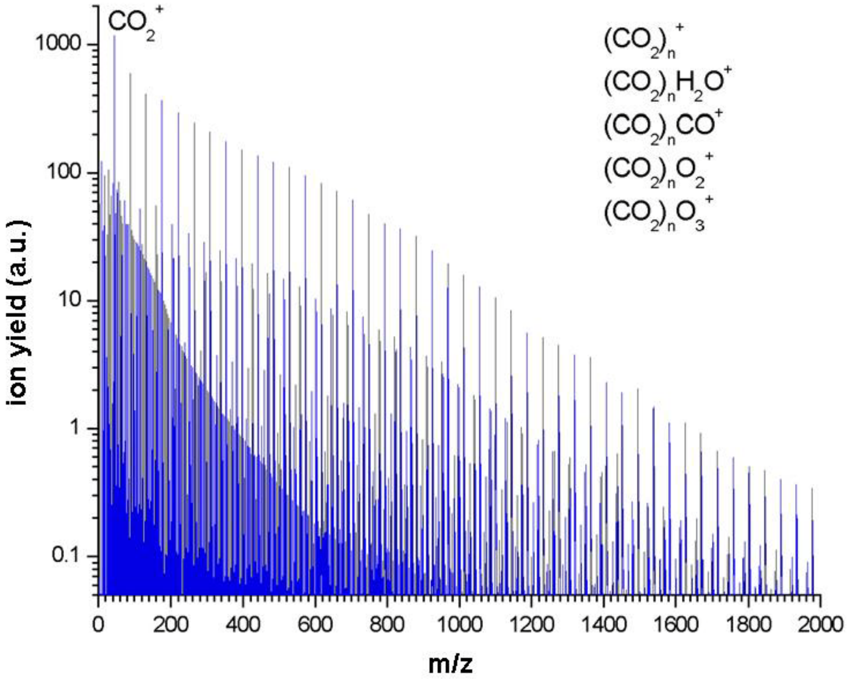

Fig. 2. The mass spectrum obtained from pure CO_2 molecules picked up by He droplets.

Fig. 3 exhibits two series of oxygen cluster ions. The intensity of clusters which contain an even number of oxygen atoms ($(O_2)_n^+$) is much higher than those with an odd number ($(O_2)O_n^+$). The highest intensity of odd numbered oxygen clusters is at the mass of 48 Th. This mass can be attributed to the formation of either O_3^+ or $(O_2)O^+$ (Fig. 4). The stability of such clusters formed in the supersonic expansion of molecular oxygen were measured in previous studies by Walder et al. (J. Chem. Soc. Faraday Trans. 86 (1990) 2395) which revealed that 0.5% of a total number of ions decay into $O_2^+$and O. Also clusters with higher odd numbers of oxygen atoms can contain the ozone molecule in their complex structure.

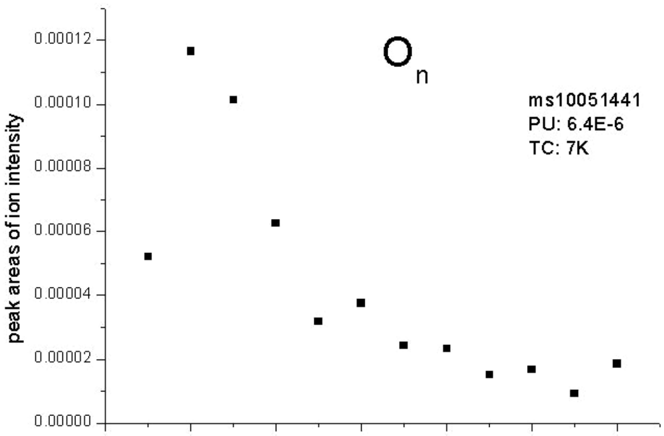

Fig. 3. The oxygen cluster distribution formed from oxygen cluster in He droplets.

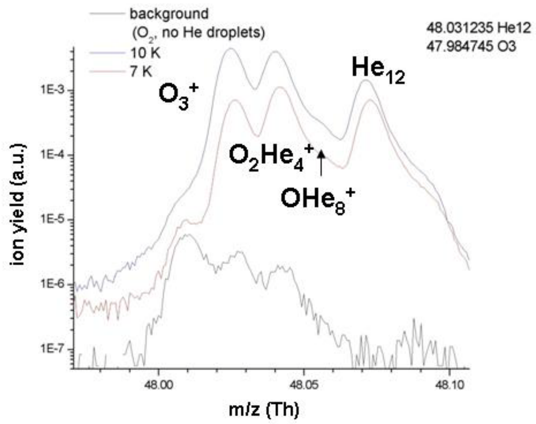

Fig. 4. The high mass resolution spectra for the mass region corresponding to mass 48 Th. The spectra were obtained at He cluster source temperatures of 7 and 10 K. The background spectrum for O_2 without He droplets is also presented.

For example, Fig. 5 presents the high resolution mass spectrum for the mass region of 80 Th which corresponds to O_5^+. Previous studies by Parajuli et al. (Int. J. Mass Spec. 220 (2002) 221) on the production and stability of O_5 ions in the supersonic beam showed that the parent ion O_5^+ decays exclusively into O_2^+. The other product(s) can be three neutral oxygen atoms, an O_2 molecule and a single oxygen atom or an intact ozone molecule.

It would be interesting to investigate the life time of these ions and if their decays are also observed in He droplets. However, these studies are not able to be performed at the present set-up and they are planed for further collaborative work.

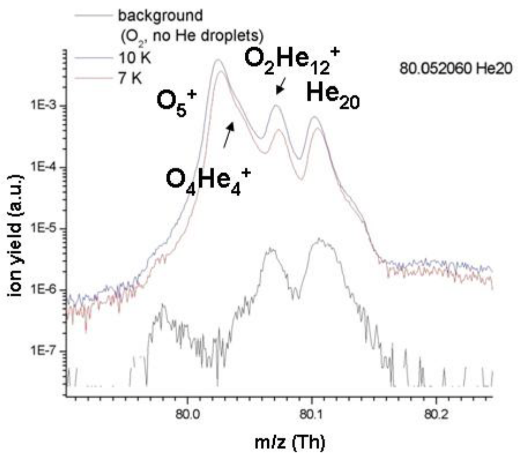

Fig. 5. The high mass resolution spectrum for the mass region corresponding to mass 80 Th. The spectra were obtained at He cluster source temperatures of 7 and 10 K. The background spectrum for O_2 without He droplets is also presented.

In the case of experiments, where pick up of CO_2 by He droplets was performed no formation of ozone has been observed. However, it is possible that ozone can be attached to CO_2 or its clusters as is presented in Fig. 6.

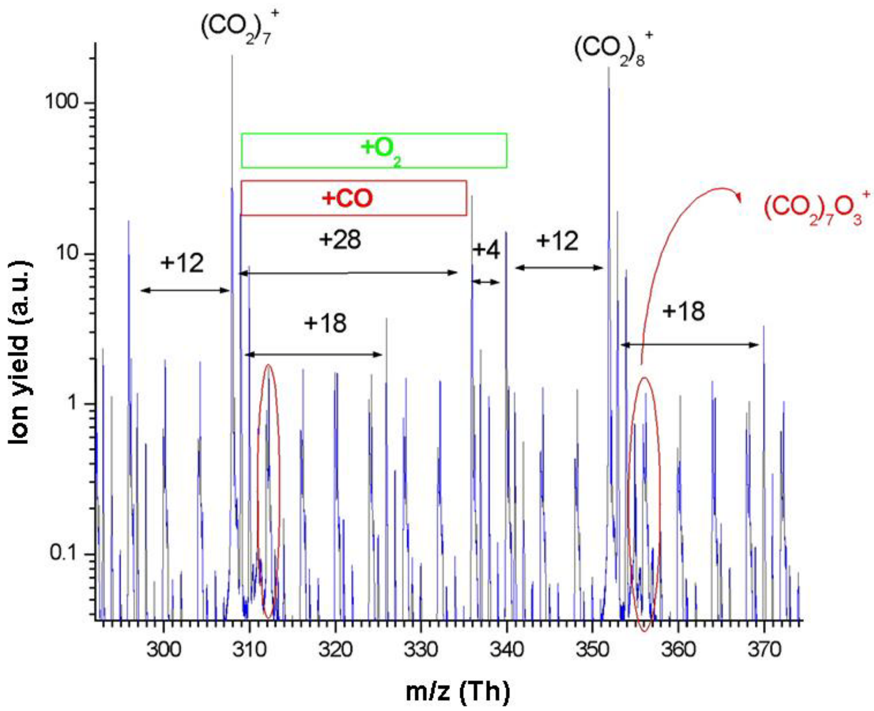

Fig. 6. The mass spectrum for the range of 290 – 380 Th obtained from pure CO_2 molecules picked up by He droplets. The peaks corresponding to CO_2 clusters with attached ozone molecules are circled.

b) from pure O_2 or CO_2 with C_{60} fullerenes

In the present experiment many mass spectra were obtained by electron ionization of O_2 or CO_2 with C_{60} embedded in He droplets. Fullerenes were chosen to serve as a model of carbon based nanosurfaces. Such nanoparticles covered by icy layers of molecules if irradiated by high energy particles can be considered as a catalyst for the formation of a new compound. The intensity of pure oxygen clusters and these clusters in the complex with C_{60} as a function of oxygen atom number are presented in Fig. 7 and 8, respectively. For both cases the formation of even numbered clusters is more favourable than clusters with an odd number of oxygen atoms. This is more visible for oxygen clusters on the fullerenes. In this case also the positive charge is accumulated on the fullerene site, while attached oxygen clusters are neutrals. Theoretical studies (Sabirov et al., Fullerenes, Nanotubes and Carbon Nanostructures 16 (2008) 534) showed that the ozone attack on the C_{60} fullerenes is exothermic reactions without an activation barrier due to the orbital structure of reactants (a high overlapping of HOMO- C_{60} and LUMO- O_3).

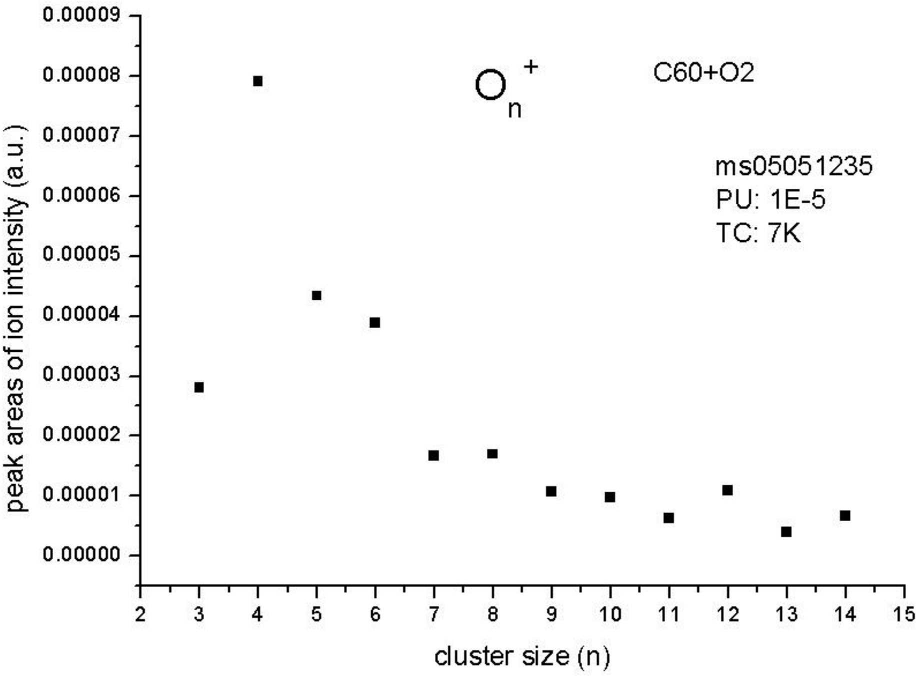

Fig. 7. The oxygen cluster distribution formed from O_2/C_{60} complexes in He droplets.

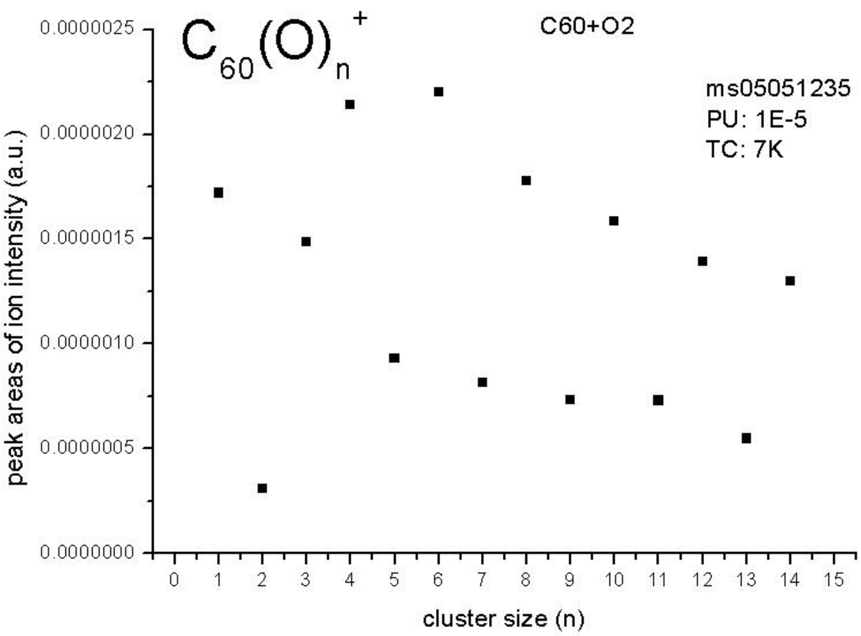

Fig. 8. The distribution of oxygen clusters attached to the C_{60} fullerene formed from O_2/C_{60} complexes in He droplets.

B. Titan's atmosphere

The atmosphere of Titan is a unique chemical mixture of nitrogen (94%) with remaining 6% of the atmosphere containing of the hydrocarbon gases: methane, acetylene, ethylene and ethane. All processes occur by both heterogeneous reactions and homogeneous gas phase reactions involving both ion and neutral chemistry. The neutrals and ion present in Titan's ionosphere are sampled by a quadrupole mass spectrometer on the Cassini spacecraft. Therefore it is important to understand the chemistry that might occur in such an environment (Anicich et al. Icarus 1999).
In the present experiment the mixture of nitrogen and methane gases were prepared with the total pressure of 1 bar but with different N_2:CH_4 ratios: 99:1, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50. All mass spectra were recorded at the temperature of the He source of 9 K and ionized by 70 eV electrons. Although molecular nitrogen is unreactive, N^+ and N_2^+ ions can undergo a range of reactions with methane. Such ion-neutral reactions produce nitrile ions which then may form larger nitriles in the further reactions. Fig. 9 shows mass spectra obtained from pure N_2, CH_4 and the mixture of both gases with the N_2:CH_4 ratio of 9:1. The mass spectrum of the mixture exhibits a range of new products which have not been observed for pure gases. The new peaks with the highest intensity appeared at the masses of 43, 44, 73, 101 Th and a plenty of peaks at higher masses but with lower intensities. Also by means of isotopically labelled molecules, e.g., $^{13}CH_4$ we could identify molecular formulas of new compounds.

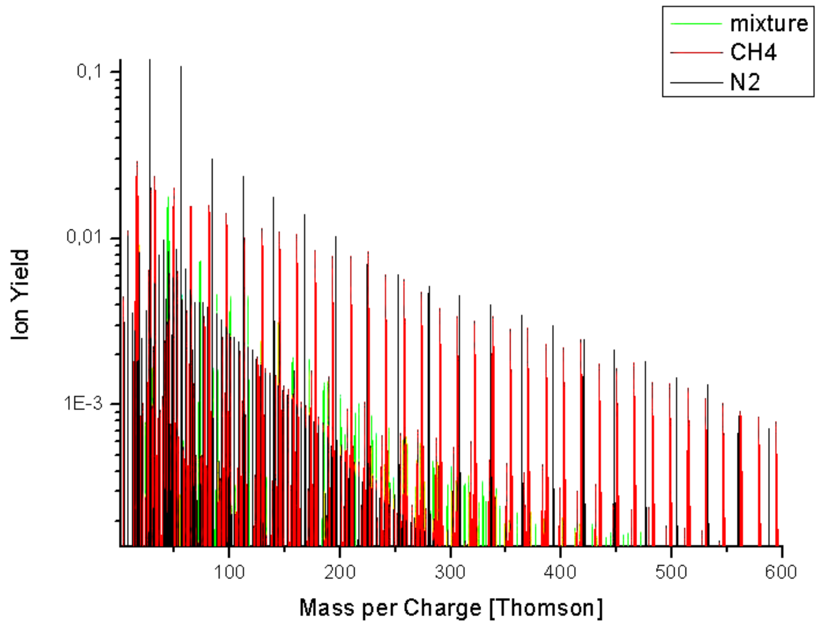

Fig. 9. Mass spectra obtained from pure N_2 (black), CH_4 (red) and the mixture of both gases with the N_2:CH_4 ratio of 9:1 (green).

The peak at the mass around 43 Th defined as C_2H_5N can be attributed to acetaldimine, ethylenimine and ethenamine. All molecules have the same molecular formula but a different structure (Fig. 10). Fig. 11 shows peaks in the mass range at around 44 Th, where the new peak can be exclusively assigned as CH_4N_2 (methyl diazene). Other peaks at 45 and 73 Th have a molecular formula of C_2H_7N (N-methylmethanamine or ethylamine) and $C_2H_7N_3$ (N-methylguanidine) or $C_4H_{11}N$ (1-butanamine, N-ethyl-ethanamine, 2-butanamine, N-methyl-2-propanamine, N,N-dimethyl-ethanamine, N-methyl-n-propylamin, 2-methyl-2-propanamine, 2-methyl-1-propanamine). Moreover, the different N_2:CH_4 ratios showed the formation of other compounds depending on the amount of these two gases.

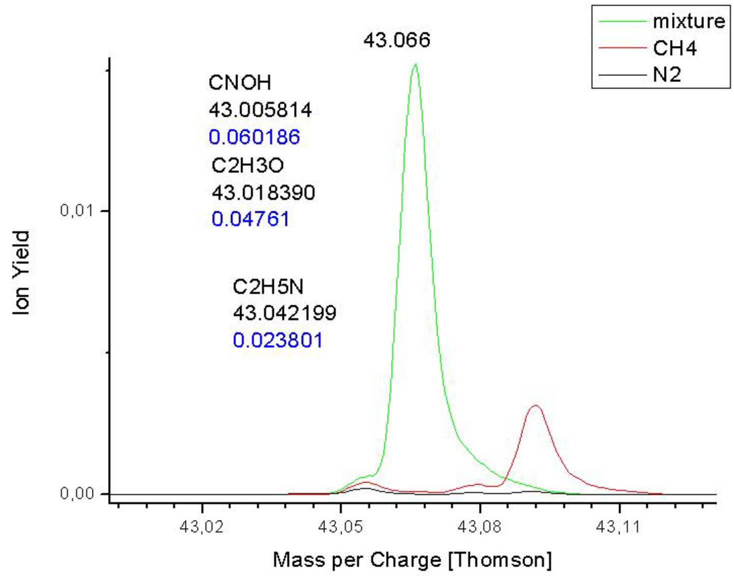

Fig. 10. The high mass resolution spectrum for the mass region corresponding to mass 43 Th. The spectra were obtained from pure N_2 (black), CH_4 (red) and the mixture of both gases with the N_2:CH_4 ratio of 9:1 (green).

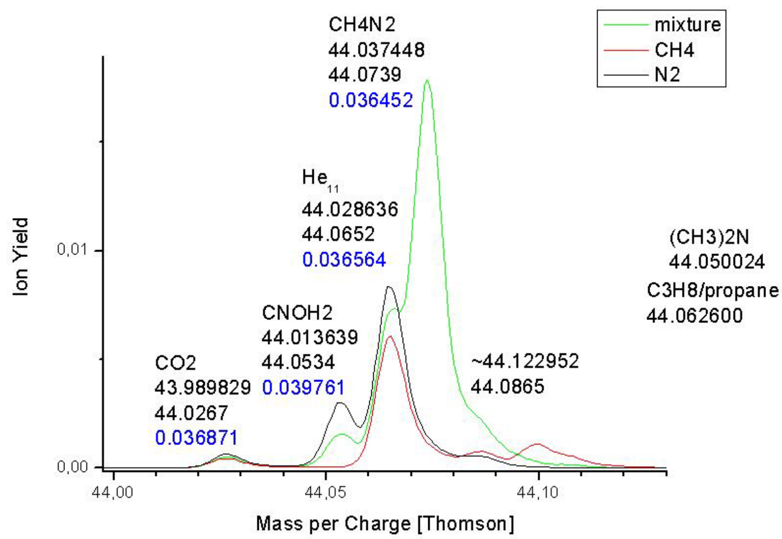

Fig. 11. The high mass resolution spectrum for the mass region corresponding to mass 44 Th. The spectra were obtained from pure N_2 (black), CH_4 (red) and the mixture of both gases with the N_2:CH_4 ratio of 9:1 (green).

4. Future collaboration with host institution:

The further collaboration between the applicant and the host institution is planned to continue the studies on the stability of O_3 ions in He droplets in order to deduce the molecular structure of this ion.

5. Projected publications/articles resulting from the STSM:

Presented results in this report are going to be published after more detailed analysis of all experimental data.