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Laboratory studies of organics with Cosmorbitrap, a new HRMS analyser, in the framework of future missions to Titan and other organic worlds

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Abstract

In space exploration, searching for organic molecules is strongly related to astrobiology. Their presence and complexity enlighten us about how abiotic processes can sustain prebiotic chemistry and the emergence of life. Mass spectrometry is among the best instrument to detect and to study organic matter and organic-rich environments. We will present a space mass analyzer called Cosmorbitrap, based on the Orbitrap™ technology. This new kind of instrumentation reaches the performances of existing space mass spectrometers and will answer to the challenges raised by the Cassini-Huygens space mission on Titan's organic world.

1. Introduction

The Cassini-Huygens mission has highlighted, among many discoveries, the chemistry occurring in Titan atmosphere detecting positive and negative ions at very high masses [1]. This surprising detection was allowed by the mass spectrometers on board the spacecraft and data collected have increased our knowledge about this moon. The resolution of these same instruments limits the identification of the molecules detected.

1.1 Orbitrap™ technology and Cosmorbitrap

A new generation of mass analyzer is extensively used in laboratory: the Orbitrap™ technology. Based on the use of the electric field, a Fast Fourier Transform (FFT) is applied in order to convert the signal recorded (oscillation frequencies of ions present inside the cell). The commercial instrument enables to reach a mass resolution of 10^6 at m/z=200 ([2], [3]). In collaboration with Alexander Makarov, the inventor of this technology, our consortium of five French CNRS laboratories (LPC2E, LATMOS, LISA, IPAG, CSNSM) is developing a space version of this new generation mass analyzer. This sub system comprises 4 main elements: the Orbitrap™ cell adapted for space, the high stability voltage pulsed power supply, the highly sensitive current pre-amplifier, and the digital electronics for control, data acquisition and FFT processing. This development is called Cosmorbitrap.

1.2 Laboratory prototype

In laboratory, to perform our tests we have coupled the Cosmorbitrap with a Nd-Yag laser at 266 nm (figure 1).

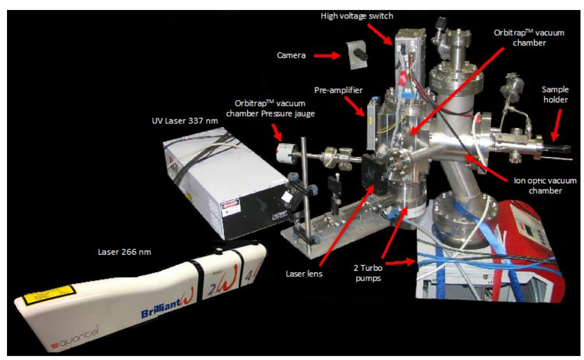

Figure 1: Laboratory prototype at LPC2E.

Results on metals have been reported in Briois et al, 2016 [4]. In this work, the goal is to present results obtained on organics, relevant in the framework of a future space exploration of an organic world like Titan environment.

2. Blind test: identification of unknown organic molecules

During a space mission, we do not know which molecules are going to be detected. For this reason, and to test the capabilities of our instrument, we performed a blind test on unknown complex organic molecules. A JAXA team sent us two samples to be identified with the Cosmorbitrap. All tests were performed with the Cosmorbitrap. The mass accuracy was a very important parameter to detect the parent peak but also the mass gaps between fragments. Data treatment was done with Attributor, software dedicated to HRMS (developed at IPAG, France). We used different complementary information like the Mass Defect vs Exact Mass diagram (figure 2).

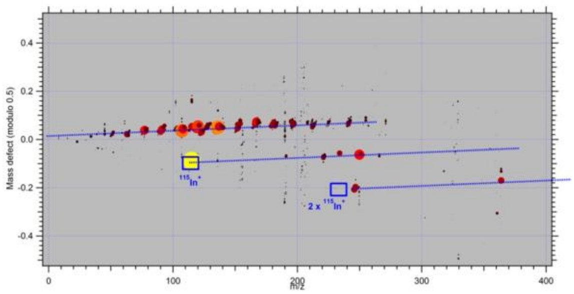

Figure 2: MDVM diagram of sample "A".

The inferred structures were confirmed using the fragmentation patterns compared with the NIST database. We identified the first molecule as HOBt, at m/z 136u and the second as BBOT with m/z 431u. The JAXA team confirmed our results, validating the ability of Cosmorbitrap to identify complex organic molecules.

3. Evolution of the mass resolving power with the background pressure

Pressure is a key parameter in mass spectrometry. A low vacuum pressure is indeed required in the chamber of the analyzer and it determines the performances of the instrument. However pressure depends of the object selected for a future space mission. When the background pressure is as high as in Titan's atmosphere, it is a challenge to deal with a reasonably small vacuum pumping system and a satisfying performance of the instrument to answer the scientific questions raised.

In the context of Titan environment, we characterized the decrease of the Cosmorbitrap optimal performances when increasing the pressure in the trap. We performed this test using 3 different organics. The lowest pressure recorded in the Orbitrap™ chamber is about 10^{-10} mbar. We increased this pressure until 5.10^{-7} mbar. Spectra were recorded at these two pressures and at several intermediate pressures. With these data, we were able to quantify the evolution of the mass resolving power for various organic molecules.

4. Summary and future work

In the context of exploring Titan environment with a future space mission, we have addressed two important questions using Cosmorbitrap. In a first project, we have shown that the instrument was able to identify the structure of complex organic molecules through a blind test jointly organized with JAXA. And in a second project we have characterized the evolution of the instrument performances when increasing the background pressure as it can be critical when exploring Titan's dense atmosphere. A repeatability study is in progress to finalize these projects.

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References

[1] Waite et al, (2007): "The process of tholins formation in Titan's upper atmosphere". Science, 316, 870-875

[2] Makarov, (2000): "Electrostatic axially harmonic orbital trapping: A high-performance technique of mass analysis". Analytical Chemistry, 72, 1156-1162

[3] Denisov et al, (2012): "Orbitrap mass spectrometry with resolving powers above 1,000,000". International Journal of Mass Spectrometry, 325-327, 80-85

[4] Briois et al, (2016): "Orbitrap mass analyzer for in situ characterization of planetary environments: performance evaluation of a laboratory prototype". Planetary and Space Science, vol. 131, 33-45