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Analytical performances of the LAB-CosmOrbitrap mass spectrometer for astrobiology

L. Selliez¹ (corresponding author), C. Briois¹, N. Carrasco², L. Thirkell¹, B. Gaubicher¹, J.-P. Lebreton¹,
F. Colin¹

1-LPC2E, UMR CNRS 7328, Université d'Orléans, Cedex 2, France

2-Université Paris-Saclay, UVSQ, CNRS, LATMOS, 78280, Guyancourt, France

ABSTRACT:

A new generation of High Resolution Mass Spectrometers (HRMS) for space exploration is being developed for several years to augment significantly the analytical performances of these instruments in extraterrestrial environments. To this day, in-flight instruments have shown mass resolving powers up to 9,000 at Full Width at Half Maximum (FWHM) (Balsiger et al., 2007). Future instruments aim at reaching mass resolutions of a few tens of thousands to more than one hundred thousand in a mass range of a few thousands. In this frame, this paper presents results of the LAB-CosmOrbitrap, a high resolution mass spectrometer challenging to couple a laser ionization system with an OrbitrapTM cell. The mass analyzer called CosmOrbitrap is involved in a Technology Readiness Level (TRL) development. Tests have been conducted on three organic compounds to prove the relevance of this simple instrument configuration for astrobiology through a successful repeatability study in which a few tens to hundreds mass spectra have been analyzed. Mass resolving powers from 60,000 to more than 100,000 have been obtained in the mass range 136 to 431 u. The best result obtained shows a mass resolving power of 380,000 at m/z 136 (adenine) with a longer acquisition

time of the transient signal and a larger number of points for the Fast Fourier Transform (FFT) operation. Mass accuracies of -3 ppm with a target material mass calibration and -1 ppm with an internal mass calibration has been evidenced. Perspectives are opened thanks to the preliminary results obtained on the isotope abundances with errors calculated at 1.64% and -2.88% for respectively a $^{13}\text{C}/^{12}\text{C}$ replacement and a $^{15}\text{N}/^{14}\text{N}$ replacement at m/z 137 for a transient length of 350 ms and 2.7% calculated for a $^{34}\text{S}/^{32}\text{S}$ replacement at m/z 433 with a transient length of 500 ms. These results support some guidelines for the TRL development of the CosmOrbitrap and the design of a future space laser ablation/desorption mass spectrometer based on it.

I) Introduction

Astrobiology is a multidisciplinary science involving chemistry, biology, geology, physics and astronomy, among others. This field aims at understanding the emergence of life on Earth (ingredients, conditions, time scale) and its search beyond Earth, in the Solar System and further in the Universe. From a chemical point of view, these investigations are based on the study of the complex organic matter. Building blocks of life are composed by simple chemical elements such as Carbon, Hydrogen, Oxygen, Nitrogen, Phosphorous and Sulphur - so-called "CHNOPS" – which represent up to 97% of the mass in living cells (Wackett et al., 2004). These simple elements form prebiotic compounds such as the amino acids constituting proteins and the nucleobases composing nucleic acids of DNA. Under certain conditions of temperature, availability of liquid water, organic compounds, energy source(s) and time, life is expected to appear. In the first stages of the emergence of life, we know that the simplest organic compounds come from inorganic matter and grow into complex organic blocks. These complex organic molecules are thus able to interact with each other and to initiate reaction chains. Some of these pathways are still not well understood. But building blocks of life such as CHNOPS molecules and prebiotic compounds are actively searched on other celestial bodies of the Solar System as a proof of a presence of life, past or emerging.

Several Solar System bodies are particularly targeted in the search of complex organic matter: Mars for the possible emergence of life during its early times; icy moons such as Jupiter's Europa and Saturn's Enceladus, based on the existence of subsurface oceans under their icy crusts; Titan, the biggest moon of Saturn, for the extremely rich organic chemistry detected from the surface to the ionosphere; and small bodies such as comets and asteroids, assumed to be sources of water and organic matter on Earth.

A large variety of analytical tools was used for decades to characterize extraterrestrial environments, to detect relevant compounds and to analyze chemical pathways leading to the growth of organic molecules involved in life. A powerful analytical tool used in space instrumentation for the study of

chemical compounds is mass spectrometry. The identification of organic molecules leads to a good understanding of extraterrestrial environments and chemical pathways occurring at the surface or in the atmosphere. A reliable interpretation of the data obtained depends on the instrument performances.

A wide range of space mass spectrometers (MS) have been developed in the last 50 years. MS instruments have been flown since the beginning of space exploration (on Apollo 15, 16, 17 ; Hodges et al., 1974) and later onboard the Mars Viking probes in 1976 (Nier et al., 1976; Owen T. and Biemann K., 1976).

Both the INMS (Ion and Neutral Mass Spectrometer) instrument and GCMS (Gas Chromatography Mass Spectrometer) on the Cassini-Huygens mission has allowed identifications of many heavy organic compounds and showed the polymeric growth occurring in Titan upper atmosphere (Vuitton et al., 2007; Westlake et al., 2014). Our knowledge about the organic chemistry on Titan has been immensely improved with all the data recorded thanks to this space mission. However, it has also opened new scientific questions that can only be addressed by instruments with better (factor of 10 to 100) analytical performances. The INMS mass resolving power was 100 in the [1-100] m/z range allowing to distinguish chemical species with different nominal masses (but not isobars, for instance).

The most powerful MS to date that has flown on a space mission is the DFMS-ROSINA (Double Focusing Magnetic Mass Spectrometer-Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) experiment on the Rosetta mission, with a mass resolving power of 9,000 at FWHM at m/z 28 (Balsiger et al., 2007). N_2 and O_2 have been detected in the environment of comet 67P/Churyumov-Gerasimenko and the glycine amino acid has been evidenced *in situ* for the first time in the coma of the comet (Altwegg Kathrin et al., 2016.; Bieler et al., 2015; Rubin M. et al., 2015). The available mass range, up to 150 mass units, limited the studies to low mass organic compounds.

The next generation of mass spectrometers for the future space missions need a mass resolution above 10,000 to make a difference, particularly in life detection. Indeed, such mass resolutions allow

the unambiguous identification of the building blocks of life – the nucleobases of DNA but also proteins, peptides (among others heavy and complex organic compounds) and the understanding of their possible interactions with the non-organic matter. The complex matrix composed by organic compounds and mineral matter can be deciphered using High Resolution Mass Spectrometers (HRMS).

The development of the specific technologies required for the development of space instruments may take many years to reach a Technology Readiness Level (TRL) sufficient to be considered for selection by Space Agencies. A new generation of HRMS instruments based on different techniques is being developed: multi-bounce time of flight (MBTOF) for instance the MASPEX (MAss Spectrometer for Planetary Exploration) instrument (T. G. Brockwell et al., 2016) developed for the NASA Europa Clipper mission planned for launch in 2024; or the MULTi-Turn time-of-flight Mass spectrometer – MULTUM – instrument (Shimma et al., 2010) proposed for the OKEANOS (Oversize Kite-craft for Exploration and AstroNautics in the Outer Solar system) mission led by JAXA, planned for launch in 2030s and rendezvous with a Jupiter Trojan asteroid in 2040s (ITO et al., 2021).

This work presents the performances reached with a Laser ionization (Laser Ablation and Laser Desorption Ionization) Mass Spectrometer (LA/LDI-MS) based on the Orbitrap™ technology (Makarov, 2000), an ion trap using a quadro-logarithmic electrostatic field for trapping the ions. The ionization source uses a 266 nm laser operating in a transitional regime between ablation and desorption ionization. The ability of this set-up to identify organic compounds has been demonstrated through a previous blind test (Selliez et al., 2019). Experiments conducted on metals (Briois et al., 2016), aerosol analogs of Titan (Selliez et al., 2020) and prebiotic compounds (Arevalo Jr et al., 2018) have shown a mass resolving power up to 120,000 at m/z 136 and mass accuracies better than 3 ppm on this wide variety of samples. To go further, this paper addresses the reproducibility of the analytical performances obtained on organics samples, through the acquisition

of a high number of mass spectra on organic compounds, and a preliminary study on the isotopic abundances.

II) Methodology

a) Instrument configuration

The laboratory device, LAB-CosmOrbitrap, used for the experiments has been fully described in previous papers (Briois et al., 2016; Arevalo Jr et al., 2018; Selliez et al., 2019). It is composed of the CosmOrbitrap mass analyzer (Briois et al., 2016) directly coupled with a laser ionization system. The different elements are shown in Figure 1 (left).

Samples are ionized in a first vacuum chamber (10^{-7} mbar). Ionization is made using a Nd-YAG laser emitting at 266 nm. This wavelength is optimal for organic compounds (Goesmann et al., 2017) and a Technology Readiness Level (TRL) development has already been conducted for the MOMA (Mars Organics Molecule Analyzer) instrument (W. B. Brinckerhoff et al., 2013) and currently in progress for the CORALS (Characterization of Ocean Residues And Life Signatures) instrument (M. Fahey et al., 2020, Figure 1 (right)) for future planetary missions dedicated, for instance, to the Europa exploration. This shows the relevance of the use of this wavelength for future spaceflight applications. In our set-up, fluence on the sample ranges from 2.9 to 12 J/cm^2 . We thus observe a transitional laser regime between pure ablation ($> 10 \text{ J/cm}^2$) and laser desorption ($< 1 \text{ J/cm}^2$) leading to the formation and detection of different kind of ions including thermo-desorbed and fragment ions (detailed in the result sections). Polymeric patterns specific to the aerosol analogs of Titan have demonstrated that ions extracted are representative of the sample (Selliez et al., 2020).

Ions produced are injected, through a specifically-designed ion optics, into the OrbitrapTM analytical cell placed in a second vacuum chamber (10^{-9} mbar). In this simple instrument configuration, all ions produced which enter the cell can be analyzed and there is neither C-trap nor ion selection. In the commercial instrument, ions selection and accumulation are made using a C-trap and stored ions enter the OrbitrapTM cell into very short pulsed packets (Scigelova and Makarov, 2006).

The High Voltage (HV) applied on the OrbitrapTM mass analyzer has two essential functions: to optimize the trapping of the injected ions and to maintain a stable oscillation frequency of these

same ions. The trapping is coupled to the duration of the voltage switching at the time of ion injection. The stabilization of the oscillation frequency is proportional to the relative stability of the HV level applied during the measurement of the image current induced by the ions on the detection electrodes.

The Orbitrap™ cell has been modified to meet mechanical constraints as required for a space mission. Its current length is 81 mm for a diameter of 40 mm.

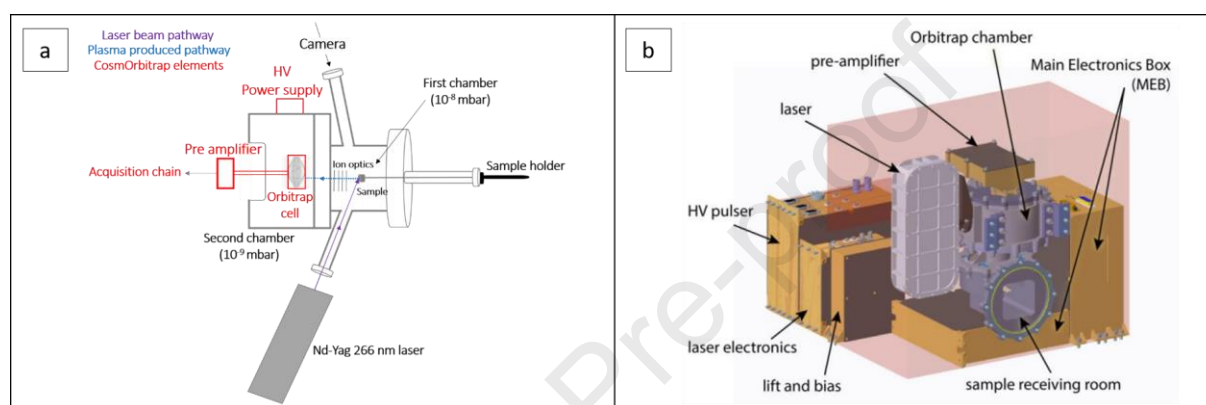


Figure 1 : (a) Schema of the LAb-CosmOrbitrap from Selliez et al., 2019 with the CosmOrbitrap mass analyzer currently under TRL development in red and (b) solid model of the CORALS instrument as described in the Europa Lander PIP document, from Willhite et al., 2021.

b) Samples

Three organic samples have been studied in this work. They are all nitrogenous and/or sulfurous compounds, covering masses from m/z 136 to m/z 431. One of them is the well-known adenine, nucleobase involved in DNA and thus, of primary interest to astrobiology. This compound has also been detected in Titan' aerosols analogues (Hörst et al., 2012). Its chemical formula is $C_5H_5N_5$, detected in this study under its positive ion and protonated form: $C_5H_5N_5+H^+$, at a theoretical m/z 136.0618. The two other compounds are named HOBt and BBOT standing for 1H-Benzotriazole,1-hydroxy- and 2,5-Bis(5-tert-butyl-2-benzoxazolyl)thiophene. They have been identified through a blind test with the LAb-CosmOrbitrap (Selliez et al., 2019). These two compounds are good isotopic

and elemental SIMS (Secondary Ion Mass Spectrometry) standards, mainly in meteorites analyses, and more specifically BBOT, an isotopic standard for NanoSIMS in cosmochemistry (Ito et al., 2014). Detected with the LAb-CosmOrbitrap under their positive ion and protonated form, molecular formulae are $C_6H_5N_3O+H^+$ (HOBt) and $C_{26}H_{26}N_2O_2S+H^+$ (BBOT) at, respectively m/z 136.0505 and m/z 431.1782. In the present study, they become relevant standard organic compounds for testing the capabilities of the LAb-CosmOrbitrap.

The methodology of the sample preparation has been previously described in Selliez et al., 2019. Shortly, solid powder of each sample is pressed onto a metallic sample holder (indium). The malleability of indium allows the sample to be embedded in the sample holder. This technique leads to the formation of indium clusters such as $[In+In]^+$ and/or $[In+organic]^+$ observed in the mass spectra, and will be developed in the results section as clusters play a crucial role for the mass calibration. These experiments aim at studying the reproducibility of the results obtained on organic species with criteria defined in the next section. To this end, 92 mass spectra have been recorded on Adenine, 166 on HOBt and 271 on BBOT. The number of mass spectra recorded ensures good quantification of the performances of the LAb-CosmOrbitrap, despite the variability observed in the mass spectra.

c) Analytical criteria

Three main analytical criteria are considered here: (1) mass resolving power (MRP), (2) mass accuracy related to the mass calibration accuracy effect and (3) isotope abundance as a preliminary study. Formulae used and definition of each analytical criterion are detailed below. These three criteria have been chosen as they are critical for providing significant performance improvements from previous space instruments in order to be eligible for selection by Space Agencies.

The MRP is defined as the capability of separating two close peaks. Named $m/\Delta m$ and calculated at FWHM (or 50%), this value with the OrbitrapTM cell highest for the lowest m/z range is decreasing as a function of the mass on charge ratio (m/z) of the compound. Due to the physics inside the cell, the

mass resolution is decreasing with the square root of the m/z ratio. The following equation (Eq 1) defines the mass resolution power law of this device (Makarov, 2000):

$$\left(\frac{m}{\Delta m}\right)_{50\%} = k * \left(\frac{m}{z}\right)^{-1/2} \quad (\text{Eq 1})$$

Briois et al., 2016 have previously shown that metallic species from $^9\text{Be}^+$ to $^{206,207,208}\text{Pb}^+$ follow this power law. In this work, we first validate the trend of organic ions as a function of this power law, by comparison to the metallic ions, then we have studied the effect of the acquisition time and the number of points included into the Fast Fourier Transform (FFT) algorithm.

The second analytical criterion studied is the mass accuracy. This parameter is the mass difference between the observed m/z ratio of a compound and its theoretical value:

$$\Delta_{\text{mass}} = \left(\frac{\text{observed} \frac{m}{z} - \text{theoretical} \frac{m}{z}}{\text{theoretical} \frac{m}{z}} \right) * 10^6 \quad (\text{Eq 2})$$

This parameter (expressed in ppm) described any instrument bias and is improved by mass calibration. In this study, different kinds of mass calibration (single, double, on a target material species and on the organic studied) have been done and compared to each other, as described in the next section.

The third criterion considered here addresses the quantification of isotopic abundances in the studied sample. We calculate the error (%) on the observed abundances depending on the isotope considered from its natural value:

First, we calculate the intensity ratio between the parent ion and the isotopologue using the following formula:

$$\text{Observed ratio} = \left(\frac{\text{Isotopologue intensity}}{\text{Parent intensity}} \right) * 100 \quad (\text{Eq 3})$$

Then the error called $\Delta_{\text{isotopic error}}$ and expressed in %:

$$\Delta_{isotopic\ error} = \left(\frac{theoretical\ ratio - observed\ ratio}{theoretical\ ratio} \right) * 100 \text{ (Eq 4)}$$

Table SI-3 summarizes the theoretical data and expected intensities of the isotopes studied with HOBt and BBOT.

d) Experimental parameters and data treatment

Software - For these experiments, the data acquisition was performed by the Alyxan software (data acquisition board Acquitek CH-3160, 12-bit with different input gains). The maximum number of data points recorded is 4,194,304. In the standard operating mode, it corresponds to a transient duration of 838 milliseconds (ms) at a sampling frequency of 5 MHz. Other sampling frequencies (10 MHz, 20 MHz) lead to shorter transient durations (around respectively 400 and 200 ms).

The FFT algorithm is used to convert the time transient (the sum of sinusoid signals generated by each oscillating ions) into a frequency spectrum. Then, after a calibration, the frequency spectrum is converted into a mass spectrum. The FFT can be applied on the whole signal or on slices of it but we systematically remove the six first milliseconds, which are spoiled due to HV switching. This leads to a maximal transient duration of 832 ms and a FFT using at the most 4,164,305 points.

Data processing - A Hann window is applied on the data. Triple zero filling is used in order to increase the number of data points (three times in this case) in the frequency spectrum, hence in the mass spectrum, which allows to better define the peak shape because of a higher number of points. This technique aims at improving the mass accuracy. A single and a double method of mass calibration have been performed in this study. The single mass calibration method is the simplest acquisition that could be done in an extraterrestrial environment, if data processing would be done on board. In that mode, one calibration is done on the metallic species composing the sample-holder and another one on the parent protonated ion of our studied compound. The double mass calibration method on

the ions (and also clusters of them) extracted from the metallic sample-holder has been tested to improve the mass accuracy at higher masses. There is no peak-fitting applied to compute the peak parameters (measured mass, mass resolution...) on top of zero-filling.

In order to quantify the improvement of the MRP with increasing the number of points used for the FFT algorithm (second results section), we have increased the acquisition time of a series of experiments performed on adenine. The data have been recorded with an analog/digital converter called Picoscope®. The longest transient duration was recorded during 3,352 ms with 16,777,216 points.

III) Results

1) Validation of the CosmOrbitrap performances with organic material

The CosmOrbitrap time transient recorded represents the image current induced by the oscillations of the ion along the spindle-like central electrode of the Orbitrap™ cell. The mass resolution is a function of the transient duration (and number of oscillations recorded during this time) and data interpretation is depending on the MRP. As a $m/\Delta m$ calculated at FWHM higher than 1,000 is sufficient to allow the separation of two nominal masses (m/z 136 and m/z 137 for instance), a value higher than 100,000 leads to the identification of isobaric species (at the same nominal mass).

In the transitional laser regime observed in our set-up - between laser ablation and laser desorption – different kind of ions are produced in the first vacuum chamber, at the laser beam- sample interface, before injection into the second vacuum chamber and then into the Orbitrap™ cell. The laser ablation regime, a hard ionization process, produces many fragment ions. The laser desorption regime, softer ionization process, allows (among other) the detection of the protonated and cluster ions. We first confirm that mass resolution calculated on the various organic ions detected are still

aligned on the theoretical power law (described in the previous section, Eq 1). Figure 2 shows this comparison, using a transient duration of 832 ms. Data obtained in Briois et al., 2016 with metals have been added (red dots). Various organic ions resulting from the ionization of adenine, HOBt and BBOT are detected: molecular ions and fragment ions such as CNH_2^+ at m/z 28.0182, $\text{C}_6\text{H}_5\text{N}_3^+$ at m/z 119.0478, $\text{C}_{15}\text{H}_{11}\text{N}_2\text{OS}^+$ at m/z 267.0585 and $\text{C}_9\text{H}_9\text{O}^+$ at m/z 133.0646. The mass resolving power of each organic compound is indicated as a function of the m/z ratio with the blue triangles.

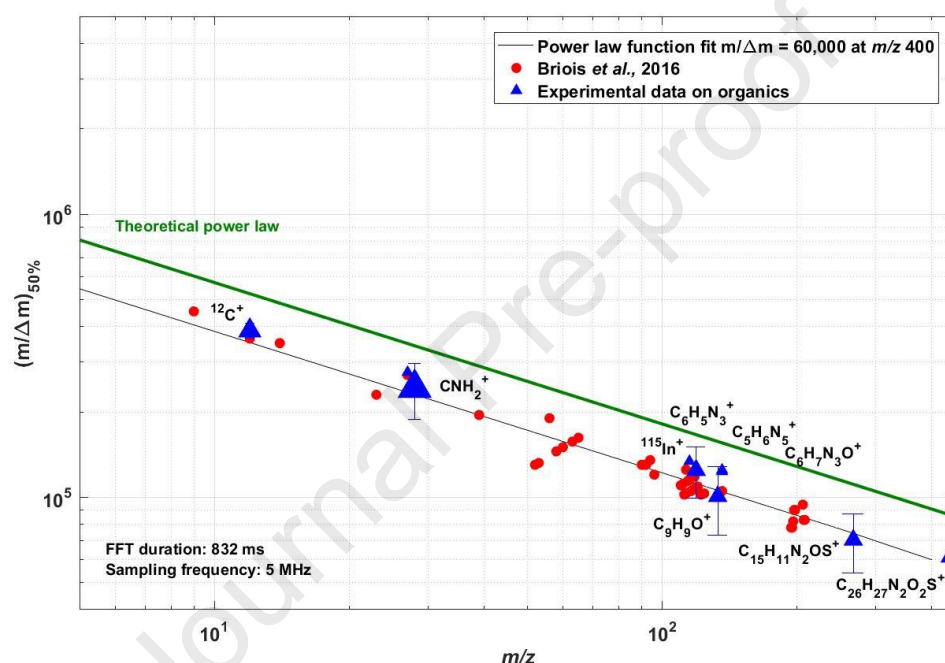


Figure 2 : The figure shows the MRP calculated at FWHM (Full Width at Half Maximum) as a function of the m/z of compounds studied. The red dots represent results on metals reported in Briois et al., 2016. Only one red dot is about an organic molecule: adenine at the nominal m/z 136. The blue triangles are protonated and fragments ions from organic compounds: HOBt+H (nominal m/z 136), adenine+H (nominal m/z 136) and BBOT+H (nominal m/z 431) and the main isotope ion of indium (nominal m/z 115) from the sample-holder. All these points are aligned on the power law fit function (black line). The theoretical power law specific to the OrbitrapTM cell is drawn as a green line, reduces by a factor 2 in order to simulate the application of a Hann window. A Hann window has been applied for each mass spectrum analyzed, from a time transient of 832 ms.

All experimental data on organics and metals are aligned on the power law fit function. Each red dot represents the analysis of only one mass spectrum. The size of the blue triangles is proportional to the number of mass spectra analyzed for the same compound (usually tens of mass spectra). Both organic and metallic compounds have a mass resolution consistent with the power law of the Orbitrap™, as both lines (fit function and theoretical power law) are parallel.

With a similar transient duration and the same FFT parameters as those used with metals in Briois et al., 2016, we observe a mass resolving power around 60,000 at $m/z > 400$. A mass resolution higher than 100,000 is obtained at a $m/z > 100$. These performances allow to distinguish two compounds or isotopologues at the same nominal mass. For instance, the HOBt compounds generates two isotopologues at the same nominal m/z 137: one with an isotopic replacement of one carbon atom (^{12}C replaced by ^{13}C) and another with one nitrogen atom (^{14}N replaced by ^{15}N). They are respectively observed at m/z 137.0539 and m/z 137.0476. The mass difference of 0.0064 mass units ($m/\Delta m$ 21 400) is well-separated thanks to the MRP of 110,000.

With the Fourier Transform mass spectrometers, such as the Orbitrap™ instruments, the mass resolution can be also degraded with the amount of ions inside the trap. In the case of our laboratory device, all the ions produced are directly injected inside the cell, with no accumulation and no selection of such m/z ranges. If the sample analyzed is easily ionized with the 266 nm wavelength used, the number of ions produced and injected inside the Orbitrap™ cell will depends on the energy applied for the ionization. The sampling of complex mixtures is thus possible, as any saturation observed on the signal recorded can be adjusted with the energy applied (from 50 to 500 μJ).

This first result shows the capability of the LAb-CosmOrbitrap to obtain similar mass resolution performances with organic molecules to those obtained with metals despite the fragmentation and the sample consumption due to the laser ablation ionization process. Metals present a homogeneous surface on the sample-holder, whereas organic samples are powders pressed onto a malleable

metallic surface and consumed by the successive laser shots. This may induce a change of the surface conditions and thus a higher variability on the performances for organic samples (depending on the predominance of a signal coming from the metallic sample-holder ion for example).

In the context of an *in situ* space experiment, the sample collection will depend on the target studied and the mission architecture (lander, orbiter operating fly by...). A sample collection similar to the one used in our study (onto a metallic plate) can be foreseen. With the heritage of the COSIMA (Cometary Secondary Ion Mass Analyzer) instrument (Kissel et al., 2007) on the Rosetta space mission, one can imagine that a robotic arm (called TMU standing for Target Manipulator Unit, on the COSIMA instrument) would expose the metallic plate to a specific environment then to the mass spectrometer for the experiment.

An instrumental improvement in our case could be provided by the visualization of the sample-holder through a camera such as the optical microscope COSISCOPE (Langevin et al., 2016) still from the COSIMA mass spectrometer. This would help to focus the laser shots on the sample and to move on the sample-holder when the sample is totally consumed. It would also give important information about the sample typology, optical properties and laser shots characterization (spot size leading to the fluence calculations).

2) Effect of the FFT duration on the mass resolving power

The digital Picoscope® described in the methodology section is able to record signals of duration up to a few seconds. Our goal is to record transients longer than our reference duration (838 ms) to record more oscillations and with a higher number of points. Three sampling frequencies are used: 5.2, 10.4 and 20.8 MHz. For each experiment, 5 mass spectra are recorded. The results of the analysis

of the longest signal recorded is shown in Figure 3. It corresponds to a sampling frequency of 5.2 MHz; 16,777,216 points and a transient duration of 3,352 ms.

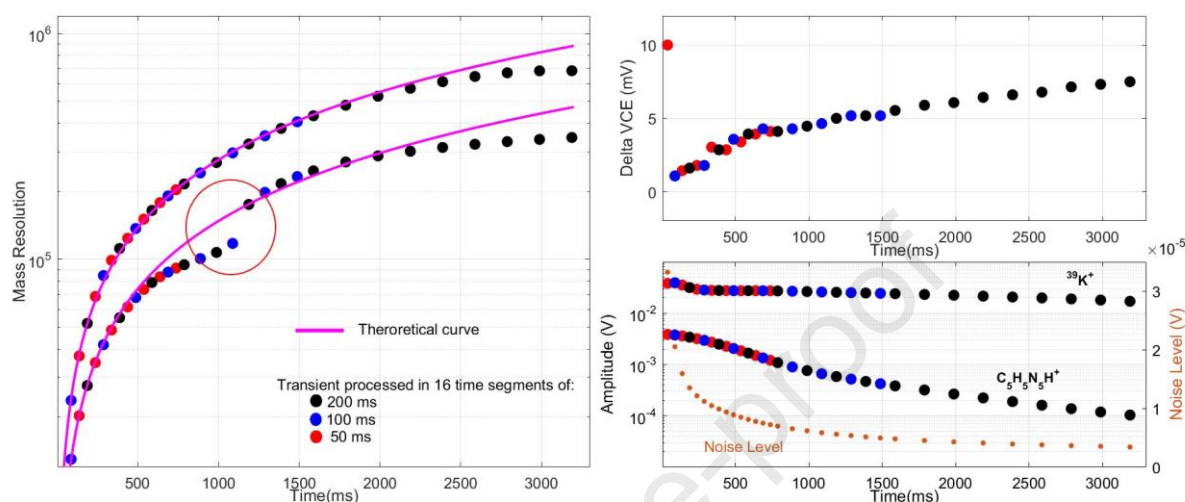


Figure 3 : The left window shows the MRP (FWHM) of the organic sample adenine $\text{C}_5\text{H}_5\text{N}_5\text{H}^+$ and potassium element K^+ depending on the FFT duration (until 3,352 ms). The transient has been processed in 16 time segments of 200 (black dots), 100 (blue dots) and 50 (red dots) from the beginning of the whole transient. The theoretical curves are drawn in violet. The top-right window shows the image of the VCE (Voltage Central Electrode) set to 3,500 V. The bottom-right window presents the peak amplitude of both species studied and the noise level (in brown). The sampling frequency is 5.2 MHz, with a record of 16,777,216 points during 3,352 ms.

The MRP of the potassium ion K^+ and protonated ion of adenine $\text{C}_5\text{H}_5\text{N}_5\text{H}^+$ are represented as a function of the acquisition time on which the FFT operation has been applied. The violet line is the theoretical curve with a Hann window.

Results show that the increase of the length of the time transient hence the increase of the FFT frequency resolution improves the mass resolving power up to a certain point. The signal attenuation (low SNR) is, at such point, catching up and affects the performances. For the usual sampling frequency of 5 MHz coupled with the increased acquisition time from 838 to 3,352 ms, the MRP

increases significantly from 110,000 to 380,000 for the same compound, in agreement with the FFT theory. Indeed, according to the formula, one would expect an increase by a factor of 4.

However, from 2,400 ms FFT to 3,300 ms, this improvement is reduced. An attenuation of the sinusoidal signal (generated by each oscillating ion) as a function of time was expected. It is due to the limited lifetime of ions and their free mean path depending on the pressure inside the cell. The induced signal on the electrodes also acts as a resistive load on the ion motion, damping them. An apparent drift of the reconstructed profile of the HV applied on the central electrode (VCE) seems also to accentuate the deviation of the MRP from the theoretical curve (as seen in the top-right window of Figure 3). HV are set for the usual maximal duration of 838 ms, our reference acquisition time. With longer acquisition time and greater number of points for the FFT, the HV parameters are less optimized. A variation of the HV induces a frequency deviation which will impact the MRP. One can note that there are several parameters playing a role on the analytical performances, not only the HV. The central electrode inside the OrbitrapTM cell can be responsible for instability of the ions in the trap at long durations. Due to the presence of the central electrode (and depending on the number of ions introduced into the cell, the electric trapping and the pressure) ions cannot stay long stable in the cell. The shift of the MRP values from the theoretical curve (observed from 2s transient on the left window) can also be correlated with the decrease of the peak amplitude, as shown on the bottom-right window.

On the left window, a shift of the MRP values of adenine from the theoretical curve is observed around 1,000 ms (red circle). These anomalies are due to the presence of double peaks not properly discriminated.

This experiment confirms the importance of the acquisition time and the number of points included into the FFT algorithm. Frequency resolution is proportional to the time transient duration, impacting the MRP. We show here the possibility to obtain a mass resolving power of 380,000 at a nominal m/z 136, on an organic ion, with a data acquisition about 3.3 s. The asymptotic trend of this improvement

suggests that a limit exists mainly based on the ion stability inside the cell. With the HV sets in this study, a transient duration of 2.5 s is long-enough. This result has a crucial interest for a space mission as it shows the connection between experimental parameters, such as the HV and the acquisition time, and the analytical performances, like the MRP. Commercial instruments have reached MRP of 1,000,000 on the m/z range 300-400 with 3 seconds transient and specific tunings (Denisov et al., 2012). For *in situ* astrobiology studies, this is relevant as some heavy organic ions are suspected and searched. One can note the positive and negative ions up to (respectively) a few hundreds and a few hundreds of thousands of mass units (Waite et al., 2007) in Titan's atmosphere by the CAPS (Cassini Plasma Spectrometer) instrument or the organic ions up to m/z 200 detected in the Enceladus plumes (Waite Jr et al., 2009; Postberg et al., 2018) by the CDA (Cosmic Dust Analyzer) instrument. To increase the MRP can be particularly interesting in this case, as it decreases with the m/z . A mode with specific HV parameters coupled with a longer acquisition time would lead to deeper analyses of heavy organic ions and their isotopologues, at ultra-high mass resolution.

3) Mass accuracy improved with mass calibration

The previous section points out the importance of the MRP in the distinction of peaks with close masses on the mass spectrum. In addition, the mass calibration needs to be accurate in the m/z range studied at a level commensurate with the mass resolution.

We first simulate the case in which we don't know the compounds analyzed, like during an *in situ* space experiment. The mass calibration is made with the ions from the metallic target: Indium $^{115}\text{In}^+$ in our case. This species is the only one to be known in the mass spectrum as it composes the surface of the sample-holder.

This experiment demonstrates the importance of a known species (for example, the target material) for use as a calibrant. It allows to start the analysis with a relevant mass calibration to identify the main organic species composing the sample. In our study, this known species is present by design as

it is a fundamental part of the experimental configuration: the metallic sample-holder. From this point of view, this species is not considered as a contamination but as the mass calibrant of the mass spectrum obtained.

Mass calibration on ^{115}In is done on the 150 mass spectra (as a reminder 75 on the HOBt analysis and 75 on BBOT). We note that the $\Delta_{m/z}$ of HOBt with the indium ion is significantly smaller than the $\Delta_{m/z}$ of BBOT with the indium ion: 21 mass units between indium and HOBt ions and 316 mass units between indium and BBOT ions.

About HOBt, the median of the mass accuracies is close to -3 ppm. About BBOT, this result is about -7 ppm. The mass difference between HOBt and BBOT with the indium ion clearly affects the mass accuracies calculated. The closer in mass with the calibrant, the better is the mass accuracy (the Figure SI-1 illustrates these results obtained using box plots).

To solve this deviation at higher masses, we look for a calibrant with a closer m/z from the BBOT m/z value in order to quantify the impact on the mass accuracy. Results are presented in the Figure 4. Mass calibration is done both (1) on the main ion of indium at the nominal m/z 115 (exact m/z 114.9033; lower part of the figure, blue) and (2) on the cluster of two indium ions at the nominal m/z 230 (exact m/z 229.8067; upper part of the figure, red). Indium clusters have indeed already been observed in previous CosmOrbitrap studies. They proved to be extremely useful, as they were shown to help for the identification of some unknown compounds when the cluster is composed by one indium element added to an organic species (Arevalo Jr et al., 2018; Selliez et al., 2019). The cluster can be also composed by two or more indium elements. In some other cases, they lead to the detection of very low masses organic species involved in Titan-like chemical pathways (Selliez et al., 2020).

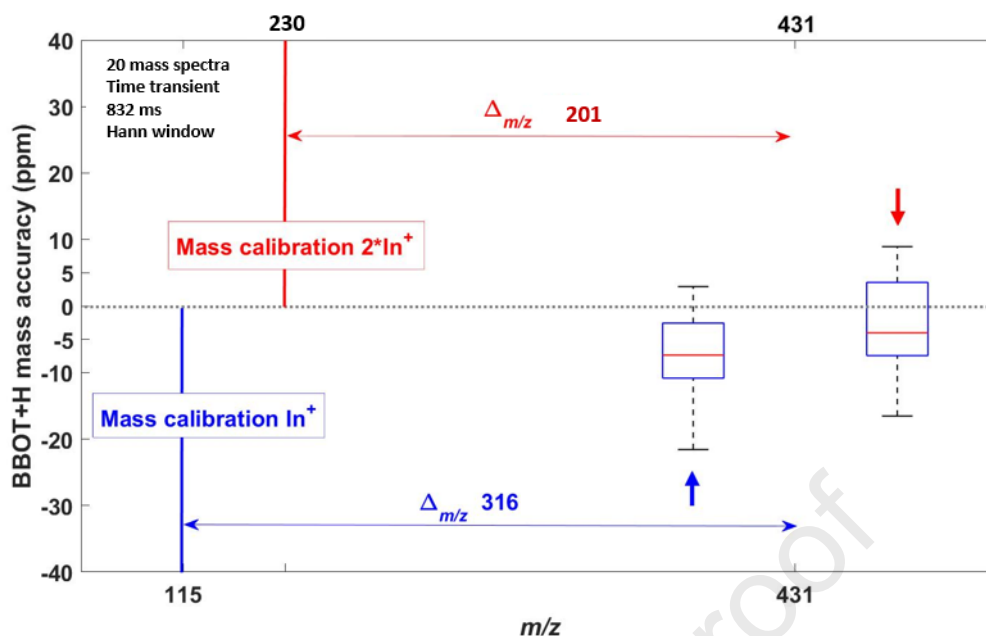


Figure 4 : Box plots showing the mass accuracy of the protonated ion of BBOT at m/z 431. Mass accuracies have been calculated (1) with a mass calibration of the mass spectra on the main isotope of indium at nominal m/z 115 (vertical line, bottom of the figure, in blue), meaning with a $\Delta m/z$ of 316 (exact $\Delta m/z$ 316.2749) between the indium and the BBOT ions (boxplot to the left, indicated by the blue arrow) and (2) with a mass calibration of the mass spectra on the indium cluster ion ($\text{In}+\text{In}^+$) at nominal m/z 230 (vertical line, top of the figure, in red), presenting a $\Delta m/z$ of 201 (exact $\Delta m/z$ 201.3715) between the cluster and the BBOT ions (boxplot to the right, indicated by a red arrow). The mass calibration on the cluster ion of indium allows a mass calibration closer to the BBOT ion m/z than the indium ion. The effect is visible, as the right boxplot shows better mass accuracies, closer to 0 ppm. This comparison have been made on 20 mass spectra, selected to present both indium ion and cluster ion of indium.

Moving the mass calibration from m/z 115 to m/z 230, we reduce by 115 mass units the mass difference between the calibration point and the mass of the organic species. The impact on the mass accuracy calculated is shown on Figure 4. We observe a shift of the median mass accuracy from -7 ppm (mass calibration on In^+) to -4 ppm (mass calibration on $2*\text{In}^+$).

We then consider we know the analyzed sample. Using well-known specific peaks such as molecular, protonated and/or fragment ions, we are able to calibrate the whole mass spectrum in order to study, for instance, isotopic patterns and isotopologues. By definition, the observed m/z are equal to the theoretical m/z for the calibration peaks.

Once the protonated ion of BBOT (m/z_{th} 431.1782) has been well-identified thanks to the previous calibration step, we use this peak as a specific calibration point for the identification of BBOT isotopologues (first isotopologue at the nominal m/z 432, $^{12}C_{25}^{13}C_1H_{26}N_2O_2S+H^+$, identifying the replacement of a carbon-12 atom by a carbon-13 atom). The mass difference between the protonated ion and its isotopologue is 1.0034 mass units. 88 mass spectra have been studied to show the relevance and reproducibility of results. The median of the mass accuracies obtained is comprised between 1 and 0 ppm. 50% of mass accuracies calculated are included between +2 and -1 ppm. Four outliers are observed on the 88 studied. This could be explained by an asymmetry of the protonated ion or an absence of the peak in the case the sample was totally consumed leading to a shift in the mass calibration. Results on the 88 mass spectra obtained with BBOT show the reproducibility of the mass accuracy on a high-mass organic species for a known-compound (the Figure SI-2 illustrates these results).

To conclude on the calibration methodology, a mass calibration on the metallic species composing the sample-holder, here ^{115}In , appears to be a relevant first step in the study of unknown compounds and/or mixtures. The capacity of indium to form clusters with itself allows mass calibrations at higher masses if the species of interest seems to be located at a few hundred mass units in the mass spectrum. Once the species to analyze are identified, another mass calibration on the parent ion leads to a thorough chemical analysis of the isotopologues and the isotopic patterns. In all cases, mass accuracies of a few ppm are obtained: -3 and -4 ppm with a target material mass calibration, +2 and -1 ppm with a specific mass calibration on organics. Reproducibility is demonstrated, as these results have been obtained with tens of mass spectra. This result highlights the interest of a mass calibration on the metallic sample-holder species. This is particularly relevant in the case of a space mission and an *in situ* experiment. First, this demonstrates which methodology can be applied to optimize the mass calibration of the mass spectra.

In addition, it supports the simple sample preparation (described previously) as it allows the detection of cluster ions and some mixing of the organic studied and the metallic species used for the sample-holder. The choice of the metal composing the sample-holder depending on some physical properties will be evaluating in further studies.

5) Preliminary results on the isotope abundances

The aim of this preliminary study is to address if isotope abundances can be inferred from the CosmOrbitrap measurements. For this quantitative aspect, experiments have been conducted on the HOBt organic sample and calculations have been made on one typical mass spectrum in order to identify a trend. Composed by 6 carbon atoms and 3 nitrogen elements, the HOBt compound contains an isotopic doublet on its first isotopologue at the nominal m/z 137. We recall these two isotopologues ($\text{C}_6\text{H}_5^{14}\text{N}_2^{15}\text{N}_1\text{O}+\text{H}^+$ at m/z 137.0476 and $^{12}\text{C}_5^{13}\text{C}_1\text{H}_5\text{N}_3\text{O}+\text{H}^+$ at m/z 137.0539) are separated from each other by 0.0064 mass unit.

The isotopologue corresponding to the carbon isotopic replacement should be observed, in terms of intensity, at 6.6% of the protonated (parent) ion. The other isotopologue of this doublet, corresponding to the nitrogen isotopic replacement, should have an intensity of 1.11%. All natural abundances and expected intensities depending on the molecule studied have been reminded in the Table SI-3.

First, as the two isotopologues composing the doublet at m/z 137 are very close, the MRP has to be high-enough in order to separate both of them. Figure 5 is part of a mass spectrum focused on the mass window m/z 137.042 to 137.067 in which both isotopologues can be observed. It shows the effect of the segment duration on which the FFT is applied on the isotopologues separation. The black line represents the longest one of 832 ms. Other color lines, from blue to red, show the decrease to the lowest one of 100 ms (red line). With this shortest segment duration, the first

isotopologue cannot be readily detected but it visibly creates a clear asymmetry in the peak. For the second one (carbon replacement), a very large peak is detected. With 200 ms transient duration (brown line), the first isotopologue is still not observed but the second one is thinner. The yellow line shows the shortest time length (300 ms) allowing the distinction of these two isotopologues.

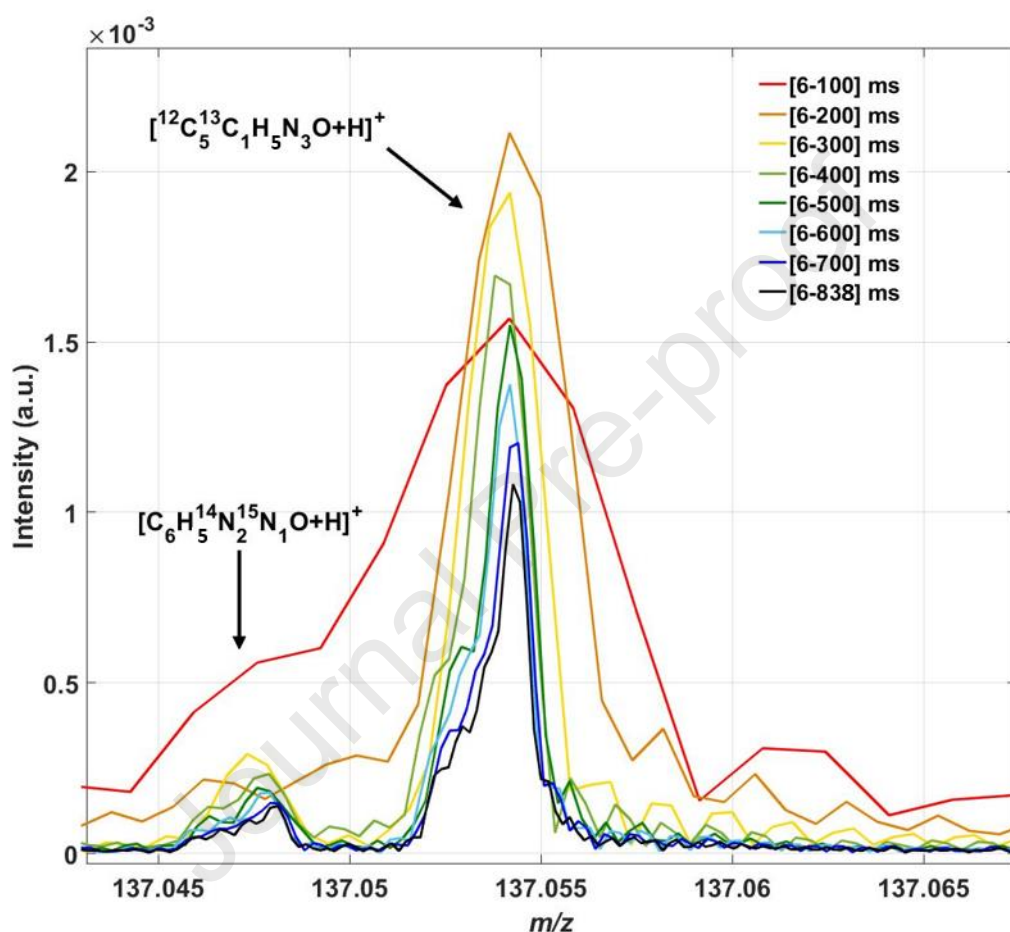


Figure 5 : Mass spectrum showing the two first isotopologues of HOBt at the nominal m/z 137. Molecular formulae of the two ions are indicated. The color scale shows the mass spectrum obtained with different time transients, from 94 ms (FFT with 470,000 points) in red to 832 ms (FFT with 4,160,000 points) in black. The effect of the acquisition time on the mass resolving power is apparent. Shorter time transients until 200 ms are no long-enough to allow the distinction of the two isotopologues. The minimum required here is 300 ms (yellow curve) to observe both peaks.

For the study of isotopic abundances, we have changed the number of points involved in the FFT operation based on a time transient of 832 ms to get high-enough mass resolution and to derive quantitative data as illustrated in the Figure 6. The figure shows the error on the isotopic abundances

expected as a function of the time transient. This error is calculated using the formula described in the methodology section.

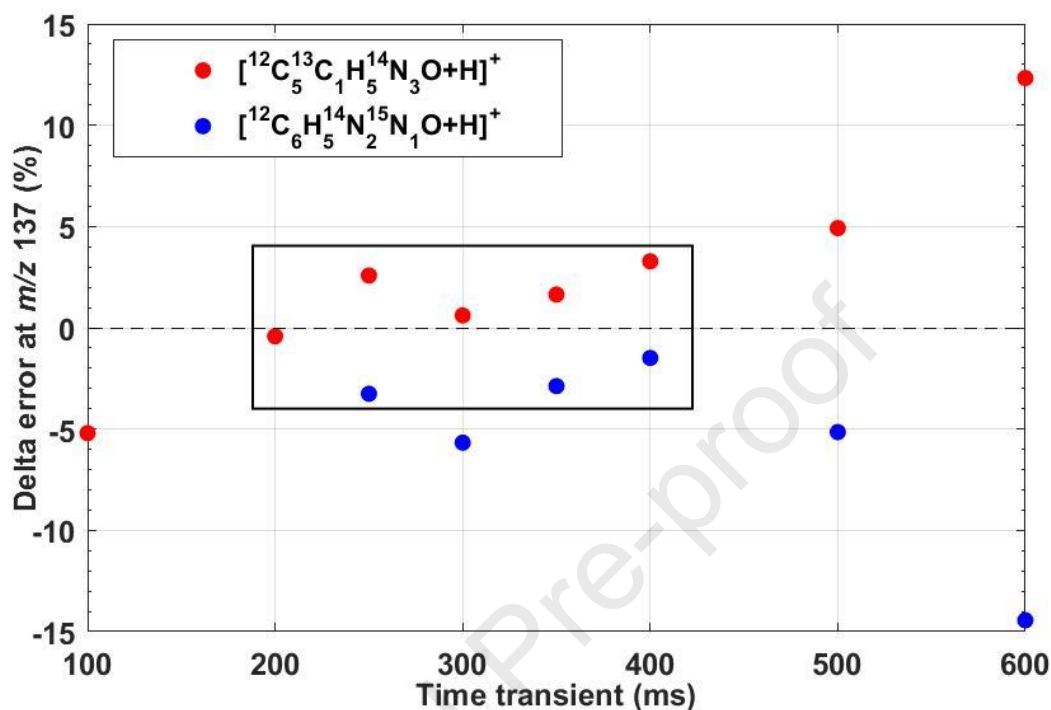


Figure 6 : Isotope abundances corresponding to the replacement of ^{12}C by ^{13}C and ^{14}N by ^{15}N in the HOBt molecule, at m/z 137.0539 and 137.0476 as a function of the transient duration (from 100 to 600 ms) on a typical mass spectrum. The black rectangle shows that the shorter time transients (between 250 to 400 ms) minimize the error on the isotopic abundance (errors comprised between 4 and -4%).

Red dots are the errors calculated on the isotopologue with a carbon replacement. Blue dots are the errors on the other isotopologue (nitrogen replacement). On the one hand, the shortest transient durations (from 100 to 200 ms) don't show results on the nitrogen replacement. The peak is not defined enough due to a low mass resolving power as shown in the Figure 5. On the other hand, with acquisition times longer than 300 ms, errors increased. The interesting window is therefore centered on 300 ms: errors calculated are more reproducible and closer to 0% between 250 to 400 ms (from -0.42 to 3.28% for the errors on the carbon replacement and from -1.49 to -5.67% for the errors about the nitrogen replacement). All results are reported in Table SI-3.

Calculations have been made on the BBOT isotopologues as well. This time, there is no doublet at a same nominal m/z but two different isotopologues at two nominal m/z ratios: a carbon replacement at m/z 432.1821 and a sulfur replacement at m/z 433.1746. We observe here a high number of carbon atoms in the molecule (26 times) unlike sulfur atoms (only one). The strong difference of expected intensities leads us to consider two acquisition times because these two peaks don't need the same duration to reach a sufficient mass resolving power. On the same mass spectrum, we obtain errors at 3% with 100 ms on $^{12}\text{C}_{25}^{13}\text{C}_1\text{H}_{26}\text{N}_2\text{O}_2\text{S}+\text{H}^+$ and -2.7% with 500 ms on $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_2^{34}\text{S}+\text{H}^+$.

Considering a short acquisition time of 300 ms, an error of 0.61% about the carbon isotopic abundance at the nominal m/z 137 is a very encouraging result. More studies are needed to improve this last analytical criterion with an optimization of the HV applied (regarding the first hundreds ms of the signal) and the record of many mass spectra to improve statistics and compensate the variability coming from the laser ionization. The high MRP and mass accuracies coupled with consistent isotopic abundances would give to this set-up a strong analytical power, particularly for the characterization of extraterrestrial environment. The improvement of results about isotope abundances will be thus thorough in the next studies.

IV) From laboratory to spaceflight applications

Two laser-CosmOrbitrap based instruments are currently in development for future spaceflight applications. One of them, the CORALS instrument (Figure 1, right), is operating at 266 nm like the laboratory device LAb-CosmOrbitrap. The whole instrument (laser source, ion transfer optics and CosmOrbitrap mass analyzer) aims at being a versatile and low size (11,000 cm²), weight (8 kg) and power (41 W peak) mass spectrometer (L. Willhite et al., 2021). Heritage of the MOMA laser, the CORALS laser provides three times more output energy than the latter with 450 μJ at 266 nm and a fluence about 20 J/cm² (M. Fahey et al., 2020). As shown on the Figure 1 (right), despite a different design the elements composing the LAb-CosmOrbitrap device and the CORALS prototype are similar

as well as their working principle. The energy output and fluence of both configurations lead to the detection of the same kind of species, previously described. The similarities, in terms of constituents and working, allow us to compare and to extrapolate the results obtained with the LAb-CosmOrbitrap device with those expected with a laser-CosmOrbitrap based instrument such as the CORALS one. Another configuration named CRATER (Characterization of Regolith and Trace Economic Resources) and working at the 213 nm wavelength is currently in development as well.

V) Conclusion and perspectives

Results presented in this paper have been obtained through a repeatability study to show the relevance of the analytical performances of the LAb-CosmOrbitrap (CosmOrbitrap elements coupled with a laser ionization system at 266 nm). Tests have been performed on three organic molecules, as we aim to show the relevance of this simple instrument for astrobiology studies and future space missions (with the CORALS instrument for example). 92 mass spectra have been recorded on Adenine, 166 on HOBt and 271 on BBOT, three nitrogenous and sulfurous organic compounds covering a mass range from 136 to 431 mass units. Three analytical criteria have been studied: (i) the mass resolving power, (ii) the mass accuracy with a focus on the importance of the mass calibration and (iii) the isotopic abundances. The last one was not included in the repeatability study but is shown as a preliminary work opening new perspectives.

(i) Above m/z 100, mass resolving power higher than 100,000 have been obtained. Above m/z 400, mass resolving power is around 60,000. With an increase of the acquisition time, mass resolving power up to 380,000 have been shown on Adenine.

Adjustment of the HV with the acquisition time has shown that 2 seconds transients even allow to increase significantly the mass resolving power which could occasionally help on the study of heavy masses.

(ii) Among the several mass calibrations tested, we highlight the use of the metallic sample holder with a target material mass calibration on the indium ion 115^+ and on clusters of indium to obtain accurate measurements at higher masses. With these calibrations, mass accuracies between -3 and -4 ppm have been obtained. With an internal mass calibration on the organic species of interest, we have shown mass accuracies comprised between +2 and -1 ppm on the isotopologues.

We conclude that the sample-holder metallic species provides a good known mass calibration allowing the identification of the main chemical species in the sample. A second mass calibration, on the compound of interest leads then to a deep chemical analysis of the isotopologues.

For these two first analytical criteria, the repeatability study has been successful despite the change of the surfaces conditions and sample consumption following a large number of laser shots. Some guidelines for the TRL development of CosmOrbitrap have also been evidenced. For example, a camera coupled to the sample-holder would be needed first to position efficiently the laser beam on the sample and then to derive some optical properties (before the ionization) and fluence calculations (after the ionization).

(iii) Finally, preliminary tests on isotopic abundances have demonstrated encouraging results on the FFT range 250 to 500 ms with errors calculated between -0.42 and 3.28% on carbon replacement and between -1.49 and -5.67% on nitrogen replacement, for the HOBt molecule. A consistent result has been obtained on the BBOT molecule, for the carbon replacement, with an error at 3% calculated with 100 ms FFT. On this compound, we also calculate an error at -2.7% on the sulfur replacement.

Consistent results on this last analytical criterion have been thus obtained on different isotopes (carbon, nitrogen and sulfur) for time transients comprises between 100 to 500 ms. This work has to be pursued, with an optimization of the HV on short acquisition time and with the record of more mass spectra, as it would lead to a deep chemical study of organic samples of a primary interest for astrobiology.

This study supports the interest of using an Orbitrap™ cell, a powerful analytical mass analyzer with mass resolving powers never achieved in space mission to this day, inside a very simple instrument concept with a direct ionization and ions injection leading to relevant analyses of heavy nitrogenous and sulfurous organic compounds, which are representative of molecules possibly involved in the life emergence. Heavy and complex organic compounds have been evidenced for instance on the Enceladus plumes thanks to the Cassini-Huygens mission (Postberg et al., 2018; Waite Jr et al., 2009) with compounds at m/z higher than 200. Ocean worlds such as Enceladus or Europa, among other, are suspected to host building blocks of life evolving in a liquid water environment and this subsurface material may be ejected by plumes. Univocal identification of heavy organic compounds, organics mixed with ices, salts and minerals would be needed for the future exploration of these bodies as well as isotopic studies to characterize the primitive and prebiotic material detected on the surface of small bodies such as comets or asteroids in order to constrain their origin on Earth and giving clues about the Solar System formation.

The consistent characterization of organic samples would be provided by the new High Resolution Mass Spectrometers generation. These instruments will help to determine the chemical nature of these compounds and their biotic (or abiotic) source. Many mission projects are defined in the frame of the new programs and calls from Space Agencies. We cited the JAXA OKEANOS mission including the MULTUM instrument, with a mass resolving power of 30,000 at m/z 20 (ITO et al., 2021), and the NASA Europa Clipper mission with the mass spectrometer MASPEX which will reach a mass resolving power of 50,000 (FWHM) (T. G. Brockwell et al., 2016). Many missions concepts have been proposed for the ESA call for the future M7 mission (such as the *Castalia* mission (Snodgrass et al., 2018) aiming at studying the MBC (Main Belt Comet) 133P/Elst-Pizarro). Enceladus is also supported by many mission concepts for several years (Cable et al., 2021; Mitri et al., 2021, 2018; Reh et al., 2016)). In the frame of the future space exploration of complex organic samples, the analytical performances of a simple and compact laser-CosmOrbitrap instrument for a spaceflight application

appears as highly competitive and would bring a significant improvement for the *in situ* study of the bodies listed above and would help to answer key questions in astrobiology.

Journal Pre-proof

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Highlights:

- Successful repeatability study on three organic samples of a primary interest for astrobiology
- Highest mass resolving power obtained with the CosmOrbitrap mass analyser at m/z 136
- First promising results on the isotopic abundances with the Laser-CosmOrbitrap
- Relevance of this simple and compact mass spectrometer for space exploration of icy moons and ocean worlds

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: