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Feasibility analysis of an astrochemistry payload for CubeSat

Tesi di Laurea Magistrale in
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Abstract

Astrobiology is an inter-disciplinary science aiming to study the origins of life in the universe. In particular, the sub-field of *astrochemistry* deals with the distribution of molecules in the universe and how they behave in the different environments. This master thesis is dealing with the understanding of photochemical degradation processes and the stability of relevant organic molecules, when they are exposed to radiations and solar rays in deep space. These molecules are selected among interesting ones recently detected in deep space or molecules involved in biological and structural pathways. In order to better model their degradation processes, the feasibility of a *in-situ* analysis platform mounted on a miniature CubeSat payload is studied. The high level and functional requirements which arise from such objective are formulated and an high-inclination LEO orbit is chosen to satisfy both accessibility and a significant irradiation intensity. The molecules' stability can be studied *in-situ* through different innovative spectroscopy techniques, which are compared to suit the different requirements at best. Regarding their precision and miniaturisation, two techniques are used on-board. First Fourier-transform infrared spectroscopy provides insight on the molecules' structures while using the Sun as a light source. Then, the evolution of the molecular concentration and the kinetics of the photochemical degradation reactions can be assessed by fluorescence spectroscopy induced by LEDs in the UV range. The instruments to perform such methods are set up in order to suit the payload's size and configuration. Indeed, to carry out spectroscopy on all the samples, this thesis proposed a design including cylindrical sample cells fixed in a rotating ring. The rotation of the ring allow the samples to regularly change configuration and be analyzed *in-situ* throughout the whole mission, thanks to both infrared and fluorescence spectrometer. To this experiment are added sensors to assess the encountered environment, in terms of radiations levels, sunlight intensity and temperature.

Keywords: Astrochemistry, Photostability, CubeSat, *In-situ*, Organic molecule, Spectroscopy

Abstract in lingua italiana

L'astrobiologia è una scienza interdisciplinare che mira a studiare le origini della vita nell'universo. In particolare si occupa della distribuzione delle molecole nell'universo e del loro comportamento in diversi ambienti. Questa tesi di laurea magistrale si occupa della comprensione dei processi di degradazione fotochimica e della stabilità di molecole organiche rilevanti quando esposte a radiazioni e raggi solari nello spazio profondo. Le molecole sono selezionate fra le più interessanti tra quelle osservate di recente nello spazio profondo o tra quelle coinvolte in percorsi biologici e strutturali. Al fine di modellare al meglio i loro processi di degradazione viene effettuato uno studio di fattibilità di una piattaforma di analisi in situ montata su un payload miniaturizzato. In base a tale obiettivo vengono formulati i requisiti funzionali e di alto livello e viene scelta un'orbita LEO ad alta inclinazione in modo da soddisfare sia l'accessibilità sia una significativa intensità di irradiazione. La stabilità delle molecole può essere studiata ´in-situ´ attraverso diverse tecniche innovative di spettroscopia che vengono confrontate per soddisfare al meglio i diversi requisiti. Per quanto riguarda la precisione e la miniaturizzazione vengono utilizzate due tecniche a bordo: la spettroscopia infrarossa a trasformata di Fourier fornisce informazioni sulla struttura delle molecole utilizzando il Sole come fonte di luce, mentre l'evoluzione della concentrazione molecolare e la cinetica delle reazioni di degradazione fotochimica possono essere valutate mediante la spettroscopia di fluorescenza indotta da LED nella gamma UV. Gli strumenti per l'esecuzione di tali metodi sono impostati in modo da adattarsi alle dimensioni e alla configurazione del payload. Infatti, per effettuare la spettroscopia su tutti i campioni, questa tesi propone un progetto che include cellule campione cilindriche fissati su un anello rotante. La rotazione dell'anello consente ai campioni di cambiare regolarmente configurazione e di essere analizzati in situ durante l'intera missione, grazie a uno spettrometro a infrarossi e a uno a fluorescenza. A questo esperimento si aggiungono sensori per valutare l'ambiente circostante in termini di livelli di radiazione, intensità della luce solare e temperatura.

Parole chiave: Astrochimica, Foto stabilità, CubeSat, *In-situ*, Molecole organiche, Spettroscopia

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Contents

1 | A brief introduction to astrobiology

1.1. Introduction

Astrobiology is an inter-disciplinary scientific field that aims to study the origins of life on Earth and its distribution in the universe. It gathers biology, astrophysics, chemistry, geology and other disciplines [1].

The increasing knowledge about the universe and more specifically the solar system enables scientists to better model the formation of the Earth and other bodies of the solar system. Moreover, historical space missions such as *Hubble* telescope, *Galileo* and *Huygens* probes, opened new perspectives for astrobiology through the discovery of Europa's (Jupiter's moon) and Titan's (Saturn's moon) characteristics for instance. New data available describing atmospheres, soils and interstellar medium compositions reinforces the interest towards known organic molecules behaviour in deep space and their degradation pathways. From such breakthrough is born *astrochemistry*.

Astrochemistry is a sub-field of astrobiology, which focuses on the distribution and behaviour of molecules in the universe, as well as in the interstellar medium (ISM) as in the solar system [2]. Astronomical observations carried out during the last decade, illustrated an ubiquitous presence of carbon in the universe, in solid and gaseous form. Majority of carbon is traced under the form of aromatic molecules (50 % of carbon in the ISM) and more specifically polycyclic aromatic hydrocarbon (PAH). Moreover other molecules can be detected in small fractions such as ones involved in biological processes and fullerenes ions (C_{60}^{+}). This abundance of complex organic molecules in the ISM, suggests that some regions such as interstellar clouds, could be at the basis of the synthesis of more complex molecules found on Earth and in the solar system, and thus reinforce the need to study the link between the ISM and the formation of the solar system [3].

Furthermore, a significant number of molecules that are entailed in biological processes (amino acids, purines, fatty acids...) can be found in the ISM, on planets, asteroids,

comets... To answer the questions raised by the little known origin of life in the universe, it is fundamental to understand the chemical evolution of such molecules in deep space environment. The study of their stability, reactions and survival could enrich knowledge on how the "prebiotic organic reservoir" [4] reached the Earth.

This scientific problem is partially addressed by chemistry experiment, oriented towards astrobiology. Their objective is to expose molecules to deep space radiations and consider their photo-stability and the eventual products if they react. The aim is to answer the question approached in [5] : *"How was chemistry leading to the origin of life on Earth, influenced by processes in space ?"*

Although it is possible to perform such experiment in laboratories on Earth, the ability to recreate deep space environment is restricted. Indeed, it is difficult to fully reproduce the Sun's UV spectrum and its variations. Thus, the best way to carry out more accurate experiments, is to do them in space. Despite the significant astrochemistry experiment conducted on board of the ISS and simulators, innovation is now focused on *in situ* analytic techniques. These methods allow the description of whole reaction processes. Moreover, thanks to the democratization of miniature satellites (CubeSats and nanosats), spacecraft can be sent to higher altitude and at a lower cost.

The feasibility of this approach serves as the research problem of this thesis. Specifically, this paper will focus on the analysis of the photo-stability of relevant organic molecules, using non-destructive *in-situ* spectroscopy methods on a CubeSat. From the review of past missions and their results, this paper aims to introduce a mission proposal and the corresponding functional requirements. Following a trade-off analysis regarding the possible analytic techniques, the study will be focused on fluorescence and infrared spectroscopy. The Earth orbits environment will as well be studied, to give insight on the radiation levels encountered and propose the most suitable orbit. Then a preliminary design of a scientific payload hosting a astrochemistry experiment will be described, especially the experiment configuration, the thermal control system and the mass and power budgets.

1.2. Previous missions

Astrobiology is a topic frequently addressed by space agencies since the beginning of space exploration. Indeed a significant number of payload have been dedicated to biology and chemistry since 1966.

Firstly, exposure facilities were mounted outside *Gemini* 9 and 12 [6] and *Apollo* 16 modules [7], to expose microorganisms to space environment for a short period of time.

Since then, spacecraft entirely dedicated to astrobiology experiment were designed. The NASA *Long duration exposure facility* (LDEF), which was launched in 1984 by the Space shuttle (STS-41-C) was a 10 tons cylindrical spacecraft hosting organisms such as tomato seeds or spores. It stayed in space for more than 2000 days (the longest space exposure duration) and was then retrieved by STS-32 [5]. Moreover, *EURECA* (EUropean REtrievable CArrier), a satellite designed by Europe and launched from the space shuttle (STS-46) in 1992, hosted a payload called *ERA* (Exobilogy and radiation assembly) aiming to study the survival and evolution of bacteria to space radiations during a few months. Also, complex organic residues produced in laboratory were exposed to the whole UV spectrum of the sun and in vacuum, with the aim to better understand chemical evolution of interstellar grains [8]. The russian *Foton* capsule, has also hosted between 1992 and 2007 a payload dedicated to astrobiology: *BIOPAN*, whose purpose was to study astrobiology, chemical evolution, radiation biology and radiation dosimetry. The particularities of this experiment are that the satellite was orbiting in an high inclination low earth orbit (LEO), it contained two batches of samples, one exposed to the UV and one protected from them, a wide variety of sensors to assess the environment and it was recovered on Earth after re-entry. Moreover the payload was equipped with a thermal control system to regulate the temperature within the samples. It is represented in fig. 1.1. These three payloads were mounted on so-called "free-flying" satellites and were designed to be recovered. The data would therefore be studied after retrieval [5].

Furthermore, exposure facilities dedicated to astrobiology were designed to be mounted outside the international space station (ISS), with the heritage of the *ERA* platform. One of them, *EXPOSE* whose aim is to provide a long term exposure to solar UV and radiations in LEO, either in space vacuum or a specific atmosphere, initiated experiments in 2009. Its first version : *EXPOSE-R*, hosted for instance the *ORGANIC* experiment, which exposed for 682 days PAHs and fullerenes to a constant flow of deep space radiations and 2900 hours of sunlight. The organic molecules were deposited via vacuum-sublimation on MgF_2 windows, which are transparent to UV light. The stability of these molecules was analyzed at the end of the experiment, after retrieval. Brought back to ground stations,

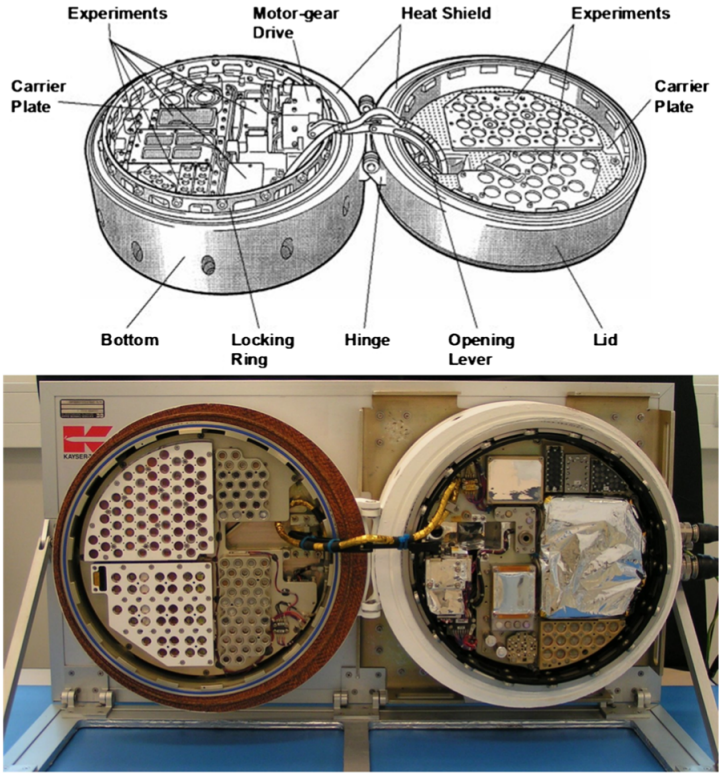


Figure 1.1: Representation and picture of the *BIOPAN* facility [5]

they were compared to witness samples using UV-Vis spectroscopy [9]. In 2015, the *EXPOSE-R2* (fig. 1.2) has been installed outside the ISS, carrying multiple experiments, some of them re-creating Mars conditions, on both biological and molecular samples. The duration of the exposure was 531 days, during which environmental data were also collected [10]. The *EXPOSE* facility, allowed scientists to perform a wide diversity of experiments on a significant number of samples during the last decade.

Finally, thanks to instruments miniaturization, innovative missions are heading towards CubeSats orbiting in low earth orbit, allowing the in-situ recording of the exposure of biological and chemical samples have been designed. The *O/OREOS* (Organism/Organic Exposure to Orbital Stresses) mission from NASA, is a 3U CubeSat which has been launched in November 2010 (fig. 1.3). The innovative character of this mission is characterized by choice of a highly inclined (72°) LEO orbit and an *in-situ* analysis of the samples thanks to autonomous instruments and sensors. The spacecraft contained two 1U payloads : *SEVO* (Space Environment Viability of Organics) and *SESLO* (Space Environment Survivability of Living Organisms). The aim of this mission was to expose samples to higher radiations doses than on the ISS orbit, and record the whole evolution of both biological and organic samples, whereas they were only analyzed before and after

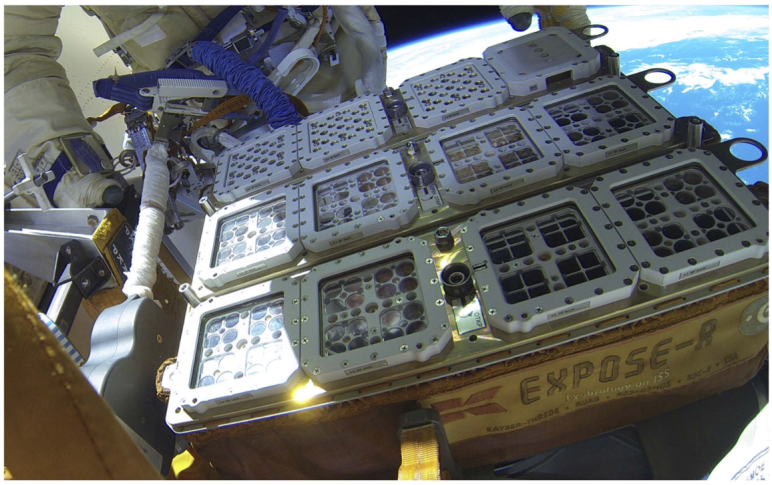


Figure 1.2: *EXPOSE-R2* facility, outside the ISS [10]

exposure during past missions. The exposure time was 6 months, and the daily data collected by the UV-Vis-NIR spectrometer were directly downlinked to the Earth [11]. This mission was a pioneer for *in-situ* analysis in space, and inspired projects such as *Spectrocube* and *Spectromodule*.

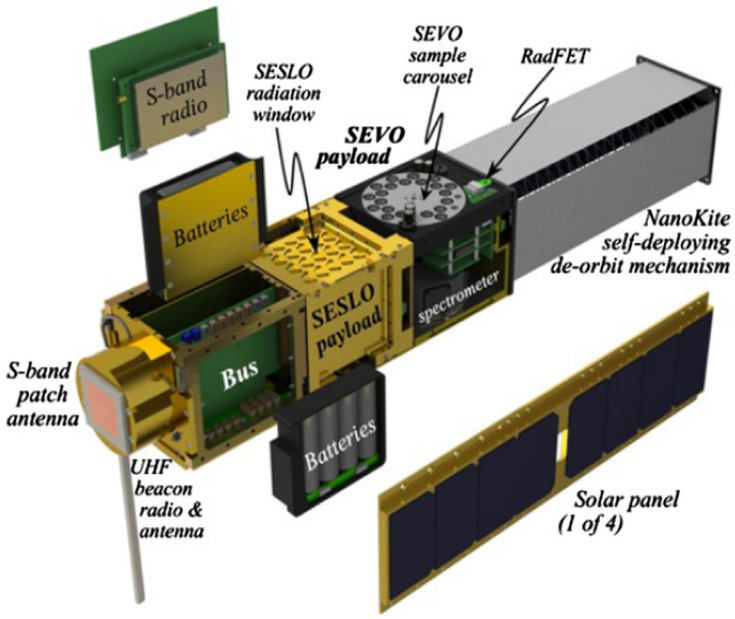


Figure 1.3: *O/OREOS* CubeSat [11]

Spectrocube is 6U nanosatellite European project, recording *in-situ* the photochemical changes within organic molecules, when exposed to space environment, using a IR spectrometer. Likewise *O/OREOS*, *Spectrocube* would be placed on a highly elliptical orbit (Molniya orbit), thus providing a greater exposure to UV and radiations than LEO.

With a payload similar to the *SEVO* one, the analysis would be performed by a Fourier transform infrared spectrometer (FTIR) [12]. *Spectromodule* is a similar *in-situ* study platform, which would be placed on the ISS. It would host multiple experiments, to study organisms and organic molecules, using different analysis techniques : fluorescence measurement, UV-Vis and IR spectroscopy. The recording of solar spectrum and a variety of other sensors would allow to assess the environment and help to build correlations with the obtained *in-situ* spectrum [13].

1.3. Innovation perspectives

As described in the previous section, despite the high number of astrobiology experiments performed during the last decade, there is still room for innovation and improvement. Indeed, most of the astrobiology experiment have been conducted on LEO orbit, at a low inclination and altitude. This orbit, due to the shielding of the Earth's magnetosphere, does not provide a significant exposure to galactic cosmic rays (GCR), which are highly energetic and whose effects are relevant to study. Moreover the environment surrounding the ISS is a rather polluted one, due to the continuous out-gassing of the ISS, the docking/undocking manoeuvres and the presence of debris. This pollution can either interfere with measurement, chemically speaking, or even damage the facilities. Consequently, the use of orbits at higher altitude or inclination (to benefit from the higher radiations rates near the poles), would provide new results of better quality [5].

Moreover, *in-situ* analysis of the samples, which has been developed in the past decade, provide a better insight of the photochemical evolution of the molecules or the whole behaviour of the organisms, than a simple before/after analysis. Indeed the results brought from experiments performed without *in-situ* techniques, must rely on assumptions concerning what happened throughout the experiment. The analysis methods used in payloads could also be diversified. Indeed, the use of IR spectroscopy in the MIR range provides better insight into the vibrational modes of organic molecules, and thus their structures than NIR spectroscopy. Also, fluorescence spectroscopy in the UV-Vis range is an innovative technique, that could provide details on the evolution of molecules [5].

Finally, most of past experiments were performed without the use of temperature control system inside the samples facility. The high variation of temperature in space (-20°C to 40°C on *EXPOSE*), can sharpen the panel of studyable molecules and organisms and damage samples [5].

2 | Mission proposal description

2.1. Mission objectives and high level requirements

Taking into consideration the past missions and the innovations possibilities described in chapter 1, we can set the mission objectives and high level requirement, which feasibility will studied in this paper.

This mission aims to focus on the study of organic molecules, relevant to the current astrochemistry questioning, and answer the problem presented in chapter 1 :

How was chemistry leading to the origin of life on Earth, influenced by processes in space ?

The mission seeks to improve knowledge about organic molecules' photostability in space, both on the molecules' evolution and its link with the environment encountered. Photostability may be defined as the response of a molecule to the exposure of UV-Vis light. The absorption of UV-Vis light can lead to a chemical change through a photochemical degradation process, which can be observed by spectroscopy techniques [14] [15].

As a consequence, the mission objectives are set as :

- Study of the photostability of the chosen organic molecules
- Recording of their photochemical degradation processes (products and kinetics)
- Assessment of the environment to which molecules are exposed

These objectives are further declined into high level requirements reported in table 2.1.

ID	Requirement
M-HLR-01	The payload shall host scientifically relevant organic molecules
M-HLR-02	The payload shall record *in-situ* the organic molecules' stability in space environment
M-HLR-03	The payload shall record *in-situ* the photochemical degradation of organic molecules
M-HLR-04	The payload shall record photochemical reactions' kinetics
M-HLR-05	The payload shall record outer space environment characteristics (UV, radiations...)

Table 2.1: High level requirements

2.2. Candidate analysis approaches : trade-off

In order to fulfill the high level requirements derived from the mission's objectives, the different analysis approaches must be compared to find the most suitable one. The trade-off analysis is based on multiple criterion :

- The technique shall be a non-destructive one. Indeed, as the molecules shall be "damaged" by space environment only, it is mandatory to perform the *in-situ* analysis using a non-destructive technique.
- The technique shall give insight on the molecular concentration and be as much precise as possible to detect photochemical degradation reactions.
- The technique shall give insight on the molecular structure, to detect the structural modifications induced by the photochemical degradation reactions.
- The instruments to perform such analysis technique shall be available at a small size and requiring a low power.
- The analysis technique should have a low detection limit and high precision, to cope with the limited amount of samples carried on-board.
- The analysis technique should be performable on organic films (chapter 4).

In the following table (table 2.2, table 2.3) are reported some of the most commonly used molecular characterisation techniques, and how they meet the trade-off analysis criterion [16].

Criteria / **Analysis technique**	Characteristic property	Application	Non-destructive	Molecular concentration
X-ray spectroscopy	Inner electron ionization	Elemental analysis	Yes	No
UV-Vis spectroscopy	Outer electron excitation	Reactivity analysis	Yes	Yes
IR spectroscopy	Molecular vibration	Chemical bond type analysis	Yes	No
Mass spectroscopy	Mass to charge ratio	General molecular analysis	No	Yes
NMR spectroscopy	Absorption of radiations	Molecular connectivity	Yes	No
Chromatography	Molecule-solvent affinity	Molecular detection	No	Yes
Raman spectroscopy	Scattering of radiations	Molecular orientation	Yes	No
Fluorescence spectroscopy	Emission of radiations	Reactivity analysis	Yes	Yes

Table 2.2: Trade-off analysis table part 1

Criteria / **Analysis technique**	Molecular structure	Miniature instrument	Low detection limit	High precision	Molecular state
X-ray spectroscopy	No	No	Yes	Yes	Cristals
UV-Vis spectroscopy	No	Yes	No	Yes	Liquid, films
IR spectroscopy	Yes	Yes	Yes	Yes	All
Mass spectroscopy	Yes	Yes	Yes	Yes	Gas
NMR spectroscopy	Yes	No	No	Yes	All
Chromatography	No	No	Yes	Yes	All
Raman spectroscopy	Yes	Yes	Yes	Yes	All
Fluorescence spectroscopy	No	Yes	Yes	Yes	All

Table 2.3: Trade-off analysis table part 2

From table 2.2 and table 2.3, is is possible to select four analysis techniques that match the trade-off criterion : UV-Vis spectroscopy, IR spectroscopy, Raman spectroscopy and Fluorescence spectroscopy. These methods belong to the absorption (UV-Vis, IR and Raman) and emission (Fluorescence) spectroscopy categories. When molecules absorb light, exploiting the electronic transitions inside the molecules or their vibrations, it is possible to derive data about their concentration or their structures. According to the wavelength range studied, the molecular phenomenon which is exploited differs, as well as the resulting data.

2.3. Absorption spectroscopy

2.3.1. Absorption in the UV-Vis range

Absorption spectroscopy in the UV-Vis range simply uses the absorption of an electromagnetic wave (or photon) by a molecule. This absorption can be followed by an excited state emitting a photon of a lower energy than it absorbed : this phenomenon is called fluorescence. For the electronic transition to happen within the energy bands of the molecule, the energy of the photon has to match an energy gap between two electronic bands. A simplified scheme of this phenomenon is displayed in fig. 2.1. The structure and energy levels of the energetic bands within a molecule, are determined by how atoms are sharing electrons together, and thus by the type of bonds (simple, double...) they form. Indeed, each molecule has a specific absorption spectrum and a wavelength which is more strongly absorbed, called λ_{max} [17].

As a consequence, the absorption or fluorescence spectrum of a molecule acts as a molecular ID, giving insights, when the molecule's λ_{max} is known, on its presence and concentration.

But what is the difference between the study of the absorbance spectroscopy and fluorescence spectroscopy in the UV-Vis range? Even though these two type of spectroscopy bring the user to the same result, the sensitivity of fluorescence spectroscopy is assessed to be 1000 times higher than UV-Vis spectroscopy. Indeed, spectrofluorometer have a very low detection limit, and don't need as much sample material as UV-Vis spectrometers. However, not all molecules produce fluorescence in the UV-Vis range, which restrict the application field of fluorescence spectrometry, whereas most molecules will absorb light in the UV-Vis range [19].

According to the mission objectives, which must be achieved with the use of a CubeSat, the high sensibility of the spectrofluorometer would be suitable to the small size of the satellite

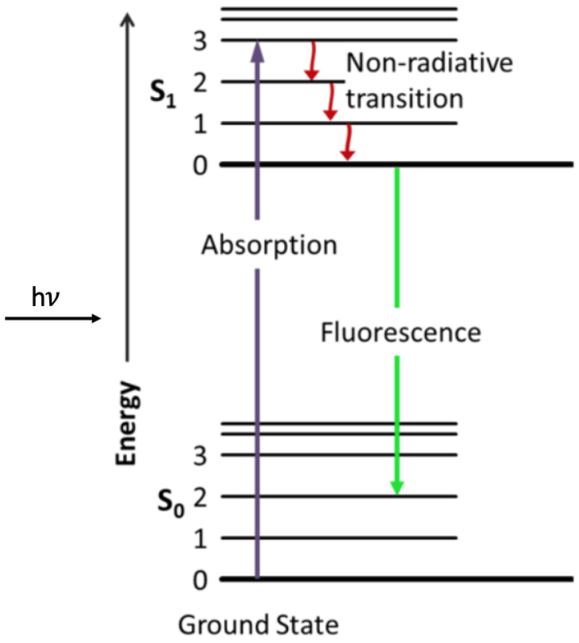


Figure 2.1: Absorption and fluorescence induced by a photon [18]

and thus the limited quantity of sample material. Nevertheless, this choice of analysis technique imposes contraints on the molecules choice, which will be further discussed in chapter 4.

2.3.2. Absorption in the IR range

As shown in table 2.3, both IR and Raman spectroscopy provide information on the structure of the molecules and the nature of their chemical bonds. Raman spectroscopy is a technique relying on molecular vibration induced by Raman scattering, changing the polarizability of the molecule. More precisely, Raman spectroscopy gives insight on the *fingerprint* region located between 500 and 1000 cm^{-1}, which will be further detailed in chapter 4. Hence, as IR spectroscopy's range is much larger (30-12800 cm^{-1}), it will be preferred over Raman spectroscopy [16].

The structure of an organic molecule can be assessed thanks to IR spectroscopy techniques. The latter can be defined through the identification of different peaks in the absorption spectrum obtained by the spectrometer, then relating these peaks to a specific molecule. The relation between a molecule and its characteristic absorption band can be explained by analytical chemistry theory. Indeed a complex molecule is composed of covalent bonds connecting atoms together. A covalent bond is a sharing of electrons (which can be at different level of energy) between two atoms. These particular energy state configurations

induces vibrations and rotations modes specific to each type of bond.

Moreover, in the case of organic molecules, some carbon-atoms bonds configurations present functional groups, also having peculiar vibrations modes. As a result, when a whole molecule encounters an electromagnetic wave, it absorbs the different wavelengths corresponding to the vibrations modes frequencies of its bonds and eventual functional groups. An example of the IR transmission spectrum of a few PAHs are shown in fig. 2.2. On this type of spectrum, specific patterns are observable for each molecule type. This allows to assess the structure of a molecule from an IR absorption/transmission spectrum.

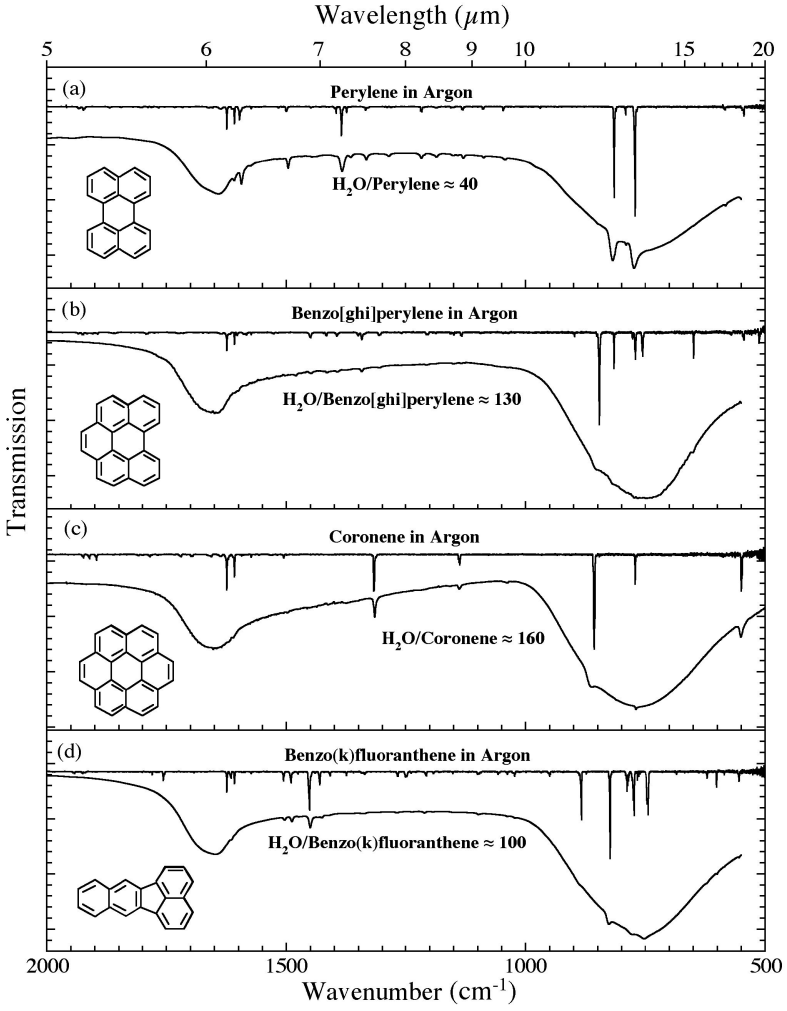


Figure 2.2: IR transmission spectrum of four PAHs [20][21]

IR spectrometer can be declined in different configurations, which two of them will be compared.

A *classic* IR spectrometer measures the absorption of an IR monochromatic beam of light passing through a sample. They are often called *dispersive* spectrometer. On the other

hand, a Fourier Transform Infrared Spectrometer (FTIR), is an instruments which uses interferometry and more specifically a Michelson interferometer. Indeed, instead of using a single beam of light, the FTIR can be illuminated by a broadband light source. This light source, passing through the Michelson interferometer, will result with a polychromatic beam of light illuminating the sample. Then the position of the mirrors in the interferometer can be modified, to produce a different beam of light. The final interferogram is then post-processed using the Fourier transform in an transmission or absorption spectrum. As a result, wavelengths can be collected simultaneously, which induces a better signal-to-noise ratio and rapidity. Although FTIR are faster and more precise than dispersive techniques, they bring mechanical constraints due to the Michelson interferometer's mirrors and complexity [22]. Nevertheless miniature models are being developed [23].

As a consequence, a FTIR would be suitable according to the mission objectives.

Finally, we have seen that both UV-Vis fluorescence spectroscopy and IR spectroscopy bring complementary results to study molecules' photostability and evolution. Indeed, UV-Vis fluorescence spectroscopy allow us to follow molecules' concentration and presence, while IR spectroscopy describes their structure.

2.4. Functional analysis

Once a general approach to the problem has been defined, it is possible to proceed with the preliminary design of the experiment compartment, capable of satisfying the mission objective. First of all, functional decomposition must be developed for then proceeding with a preliminary architecture definition. In table 2.5 all the payload functionalities are reported, highlighting the subsystem to which their are related.

ID	Functionality	Rational	Subsystem
M-FR-00	The payload shall host PAHs, fullerenes, purines, pyrimidines, fatty acids and amino acids	M-HLR-01	P/L
M-FR-01.1	UV-Vis spectrofluorometer shall record *in-situ* the UV-Vis fluorescence of the molecules	M-HRL-04	Optics

M-FR-01.2	IR spectrometer shall record *in-situ* the IR absorption spectrum of the molecules	M-HLR-02 M-HLR-03	Optics
M-FR-01.3	UV-Vis spectrofluorometer light sources shall be specific to each molecule's excitation wavelength	M-HLR-04	Optics
M-FR-01.4	Molecules studied through UV-Vis fluorescence spectroscopy shall not receive other wavelengths than the one from the excitation light source	M-HLR-04	Optics
M-FR-01.5	Molecules studied through IR spectroscopy shall receive light from the mid-infrared range	M-HLR-02 M-HLR-03	Optics
M-FR-02.1	A sensor suite shall record *in-situ* the radiations intensity to which molecules are exposed	M-HLR-05	Optics
M-FR-02.2	A sensor suite shall record *in-situ* the sun rays intensity to which molecules are exposed	M-HLR-05	Optics
M-FR-02.3	A sensor suite shall record *in-situ* the temperature inside molecules containers	M-HLR-02 M-HLR-03	Optics
M-FR-02.4	A sensor suite shall record *in-situ* the temperature of electronic components	M-HLR-02 M-HLR-03	Optics
M-FR-03	The payload shall host each type of molecule in separate and suitable container	M-HLR-01	Structure
M-FR-03.1	The payload's structure shall protect the molecules from launch vibrations	M-HLR-01 M-HLR-02 M-HLR-03	Structure
M-FR-03.2	The payload's structure shall protect the instruments from launch vibrations	M-HLR-01 M-HLR-02 M-HLR-03	Structure

M-FR-03.3	The payload's structure shall protect the molecules from radiations (trapped particles, GCR) before the start of the experiment	M-HLR-02 M-HLR-03 M-HLR-05	Structure
M-FR-03.4	The payload's structure shall protect the molecules from solar radiations before the start of the experiment	M-HLR-02 M-HLR-03 M-HLR-05	Structure
M-FR-03.5	The payload's structure shall allow the exposure of molecules to UV solar rays	M-HLR-02 M-HLR-03 M-HLR-04	Structure
M-FR-03.6	The payload's structure shall allow the exposure of molecules to radiations (trapped particles, GCR)	M-HLR-02 M-HLR-03 M-HLR-04	Structure
M-FR-03.7	The payload's structure shall allow the positioning of samples in all analysis modes	M-HLR-02 M-HLR-03 M-HLR-04	Structure
M-FR-04	Temperature inside containers shall be in [10-25]°C range	M-HLR-02 M-HLR-03 M-HLR-04	TCS
M-FR-05.1	IR spectrum shall be acquired every day for the first week	M-HLR-02 M-HLR-03 M-HLR-04	OBDH
M-FR-05.2	Fluorescence spectrum shall be acquired every day for the first week	M-HLR-02 M-HLR-03 M-HLR-05	OBDH
M-FR-05.3	The sampling frequency shall progressively decrease after the first week of mission	M-HLR-02 M-HLR-03 M-HLR-05	OBDH
M-FR-06	The payload shall transmit data to the Earth		Spacecraft

Table 2.5: Functional requirements

2.5. Payload architecture

Once described the functional requirements related to the overall mission, it is possible to proceed with the definition of a preliminary architecture for the instrument. A general architecture for the spacecraft is provided in fig. 2.3, while a detail of the experiment architecture is reported in fig. 2.4. All the subsystems characterizing the instrument are highlighted with their interconnections.

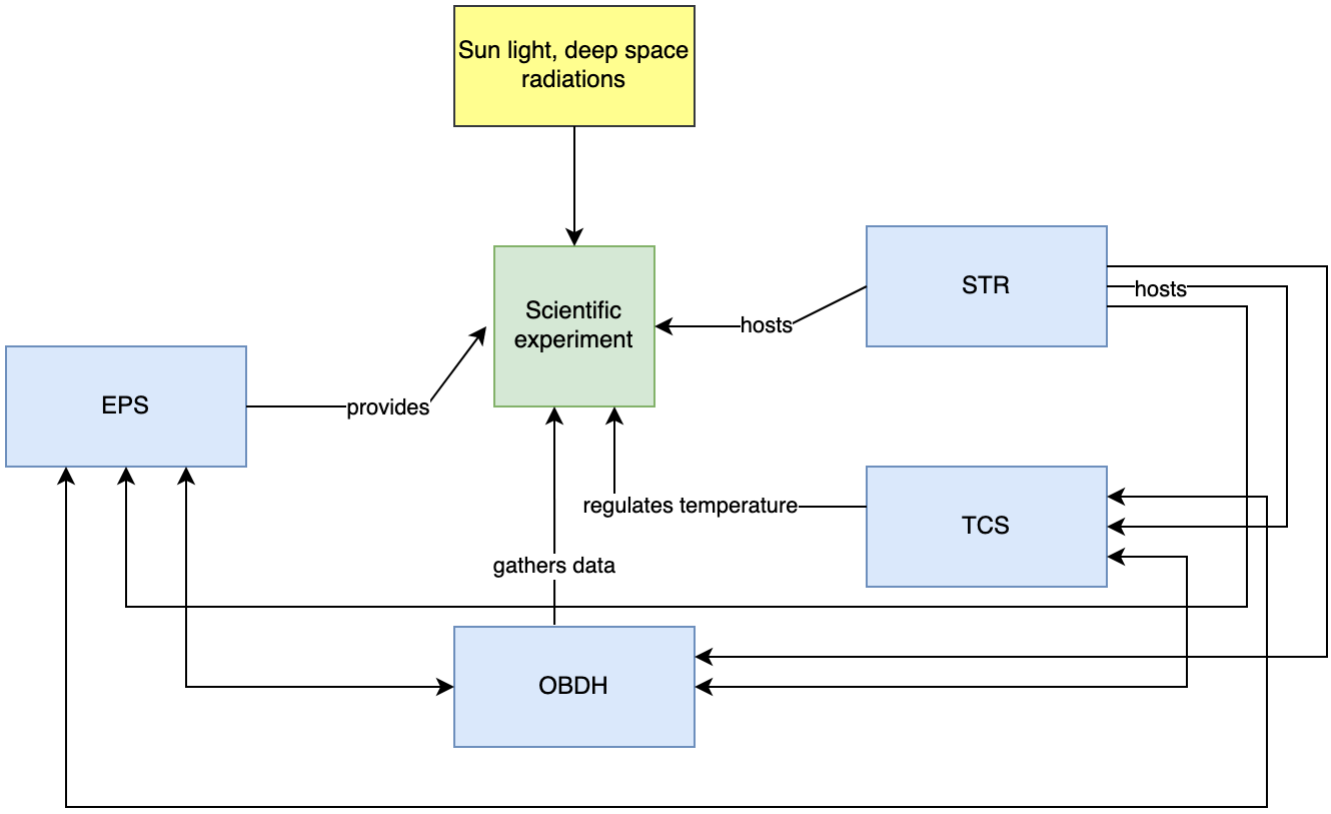


Figure 2.3: Spacecraft architecture

In particular, in fig. 2.4 are shown the components of the spetrofluorometer and the FTIR, which will be further described.

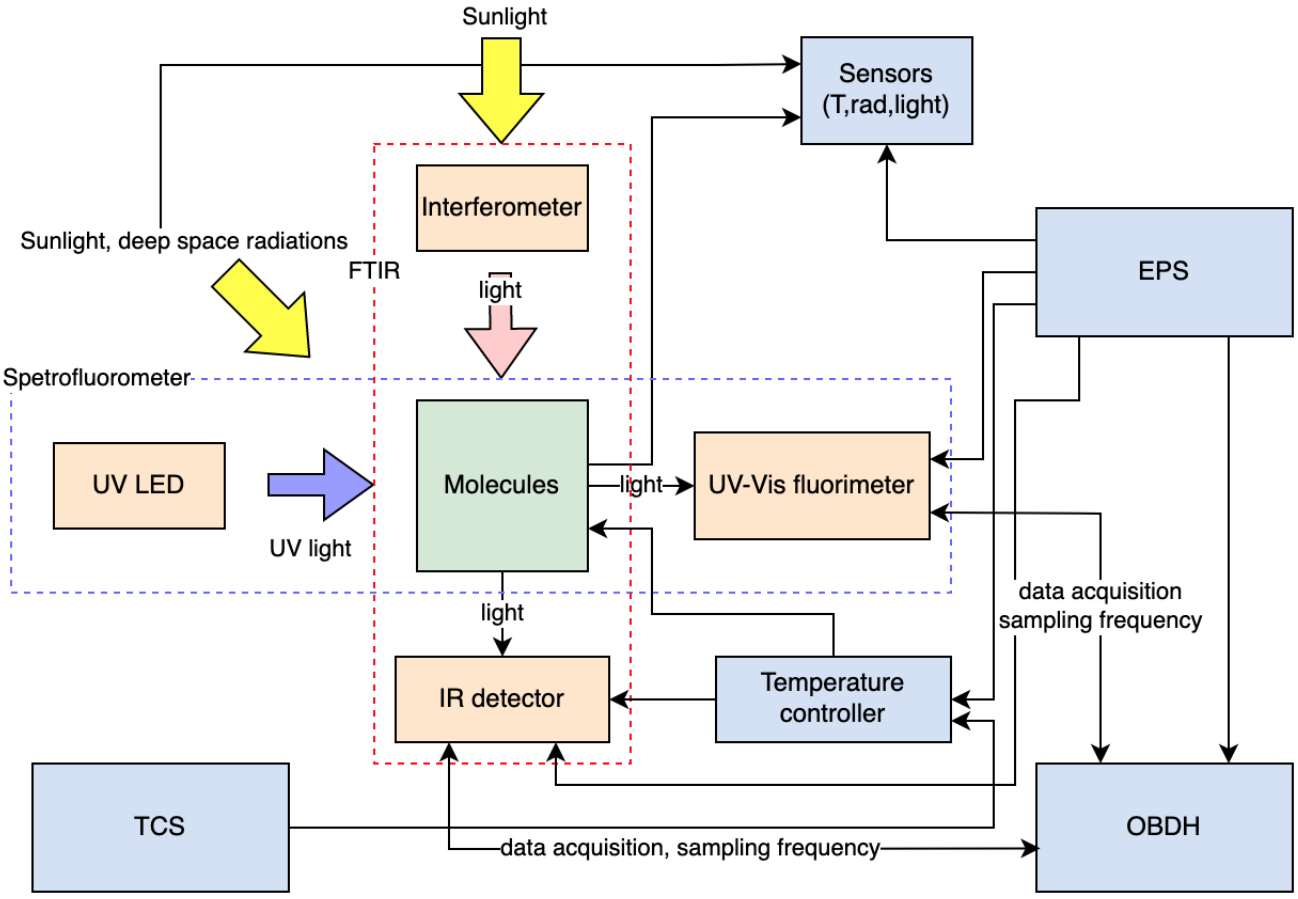


Figure 2.4: Experiment architecture

3 | Mission and environmental analysis

3.1. About sun rays and radiations

Energetic particles in the solar system are from solar and galactic origin (fig. 3.1)

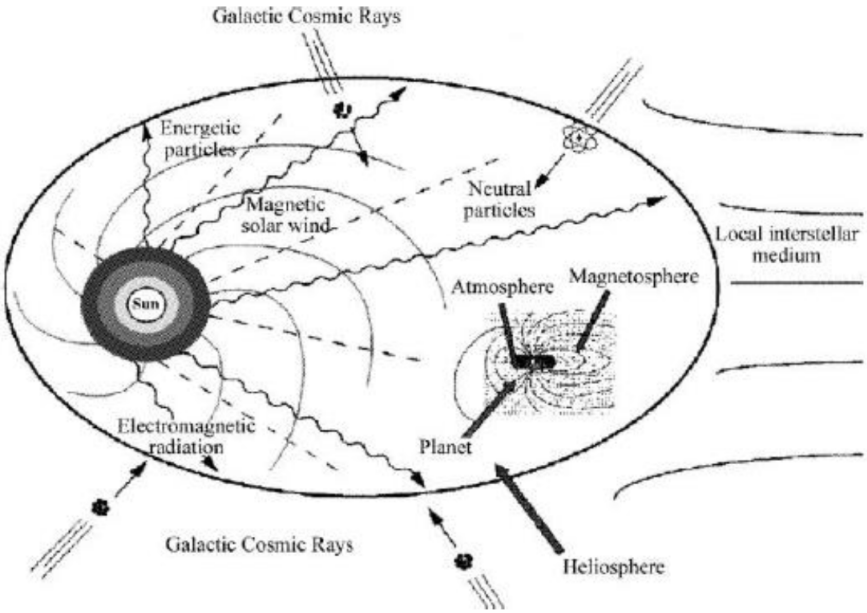


Figure 3.1: Radiation origins in the solar system [24]

3.1.1. Solar radiations

The Sun, which could be compared to a an enormous thermonuclear reactor, constantly releases energy into the solar system as well as particles. The electromagnetic radiations emitted by the sun range from gamma rays to radio waves. The distribution of these radiations and their intensity, depend on the activity of the Sun. Due to the deformation of its own magnetic field, events such as sunspots, flares or coronal mass ejections can induce radiations and particles emissions peaks. These peaks are characterised as *Solar*

Particle Events (SPE). Although these intensity variations are not uniform within the whole electromagnetic spectrum, they are particularly significant in the VUV region (120-200nm), around Lyman-α line for instance [5]. In addition to electromagnetic radiations, particles are released by the sun at a rate of $8 * 10^8 kg/s$. 95% of them are electrons and protons and the rest heavy ions ; they are called solar energetic particles (SEP) [25]. The combination of both these radiations sources form the *Solar Cosmic Radiations* (SCR), carried out by the solar wind through the solar system [24].

3.1.2. Galactic cosmic rays

Galactic cosmic rays, which have been discovered in 1912, are highly energetic ionizing particles constantly bombarding the solar system. Most of their flux is independent from the solar activity, which suggests an extra-solar origin, probably from supernovae remnants. Their energy level vary from 10^9 to 10^{18} eV. They are mainly composed by protons (95%) and helium (4%), and 1% of heavy nuclei, electrons and positrons [5][24].

3.2. Orbit selection

As stated in chapter 1, the choice of the orbit is decisive of the level of radiations the molecules will be exposed to. Indeed, the Earth is protected from the energetic particles emitted by the sun and deep space by the magnetosphere. The magnetosphere, whose shape is represented in fig. 3.2, is a region formed by the Earth's magnetic field. However the magnetospheric shielding is not uniform around the globe. Indeed, there are zones where energetic particles are concentrated : *Van Allen* radiations belts, resulting from the interaction between of GCR and SCR with the Earth's magnetic field. Moreover polar regions are also less protected, due to the structure of the magnetosphere.

Hence, according to the mission objectives, which is to study the effects of radiations on organic molecules, the aim is to choose an orbit maximizing the exposure to radiations. There are two possibilities : either increase the altitude of the orbit (to escape the magnetospheric shielding) or exploit the presence of trapped radiation and the magnetosphere's shape with a high-inclination (i>65°) orbit. With *SPENVIS* software, it is possible to compute the absorbed radiation dose in carbon (graphite), as a function of aluminium shielding thickness. This indicator is often used to assess the level of radiation exposure on a orbit, and can be used to compare different type of orbits. In table 3.1, inspired from [5], are displayed different orbit type and their characteristics. In addition, the graphs representing the ionizing dose as a function of shielding thickness for each orbit type are displayed in fig. 3.3. We can observe on both this table and graphs, that orbits within

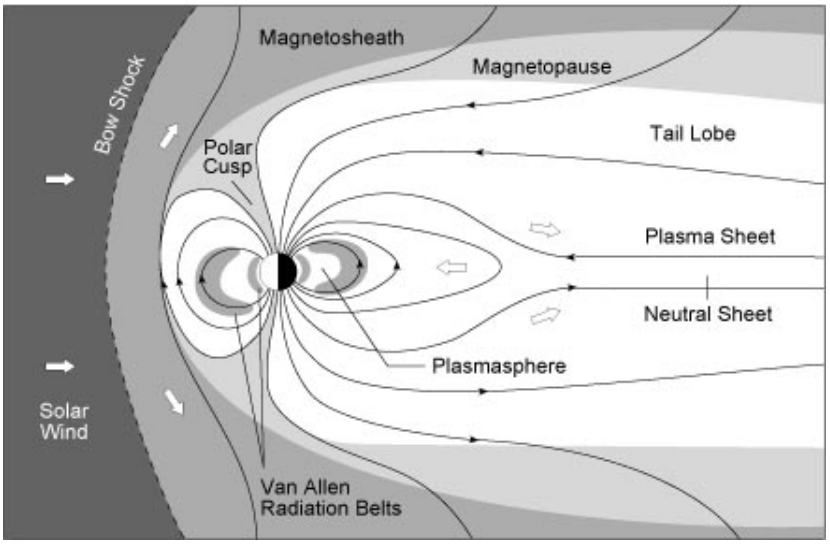
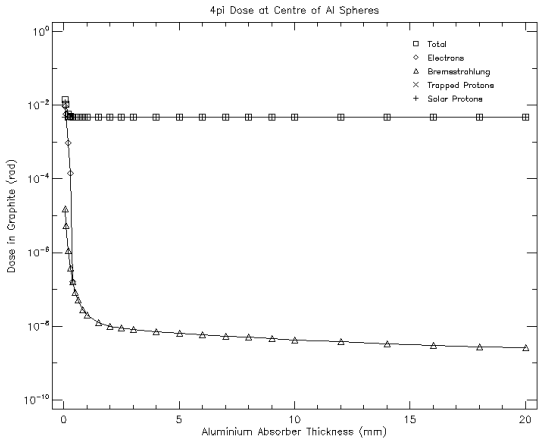


Figure 3.2: Earth's magnetosphere, credits : NASA

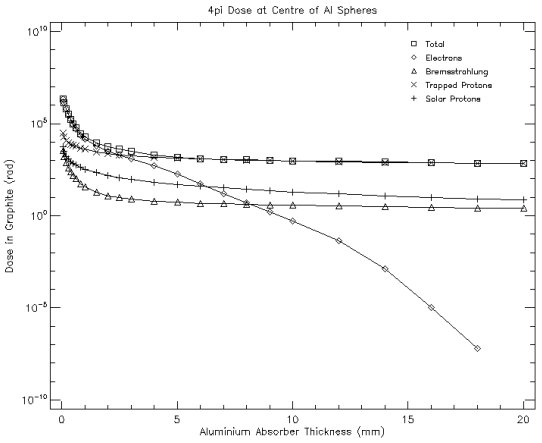
the magnetosphere, still provide a significant exposure to radiations, due to the presence of Van-Allen belts and the magnetosphere structure.

Orbit type	**Altitude [km]**	**Inclination [deg]**	**Period around Earth**	**Main radiation source**	**Radiation dose with 1mm aluminium shielding for 1 month [krad]**
ISS LEO	330-435	51.6	91-93min	electrons, protons	10^{-5}
High inclination LEO	400-2000	65-115	92-127min	electrons, protons, GCRs, SEPs	10
MEO	2000-35750	Various	2-23.9h	trapped electrons and protons,	1000
GEO	35786	0	23.93h	trapped electrons	100
Interplanetary	>100000	/	/	GCRs, SEPs	1

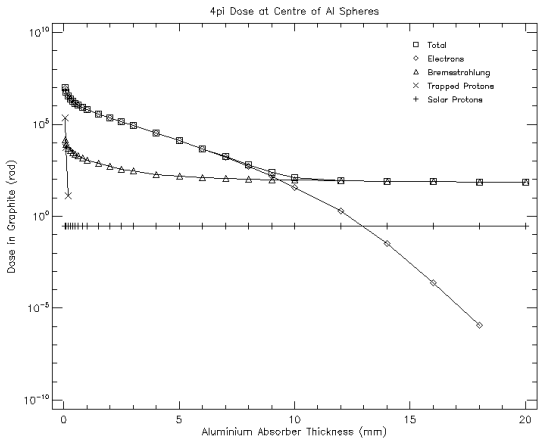
Table 3.1: Different orbits and their characteristics



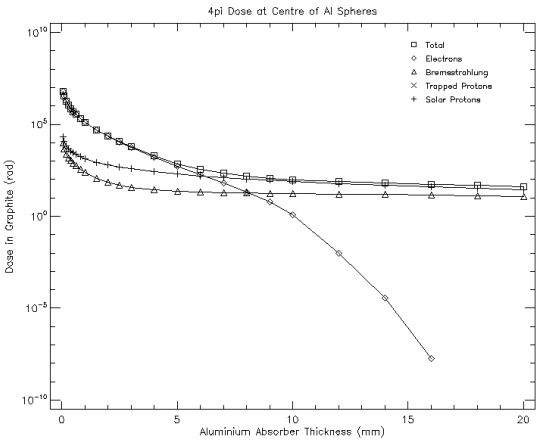
(a) Ionizing dose on LEO (ISS)



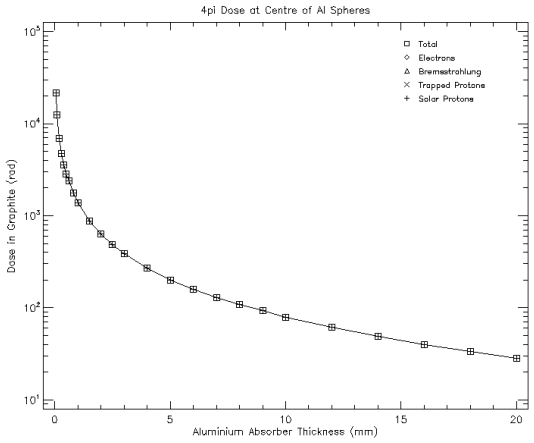
(b) Ionizing dose on high inclination LEO (1000 km altitude)



(c) Ionizing dose on MEO (20000 km altitude)



(d) Ionizing dose on GEO



(e) Ionizing dose on interplanetary orbit (1.01 AU distance from the Sun)

Figure 3.3: Ionizing dose in graphite as a function of aluminium shielding, 1 month exposure

From table 3.1 and past mission review, a suitable orbit to fulfill mission objectives is a high-inclination LEO orbit. Indeed, the inclination of such an orbit provides a path through less protected areas and thus high radiation rates, without the necessity of a high altitude (and thus bigger launcher). Nevertheless, as stated in 1, LEO orbits can be defined as *hostile* from the environmental point of view due to pollution. The radiations levels and the accessibility of high inclination LEO still make this orbit a suitable choice though. Moreover, this orbit type provides a suitable communication with ground stations, which is necessary for *in-situ* analysis.

As a consequence, the orbital parameters and the representation of a potential suitable orbit for the mission, are reported in table 3.2 and fig. 3.4.

Orbit type	**Altitude [km]**	**Inclination [deg]**	**Period around Earth**
High-inclination LEO orbit	650	72	97min

Table 3.2: Possible orbit characteristics

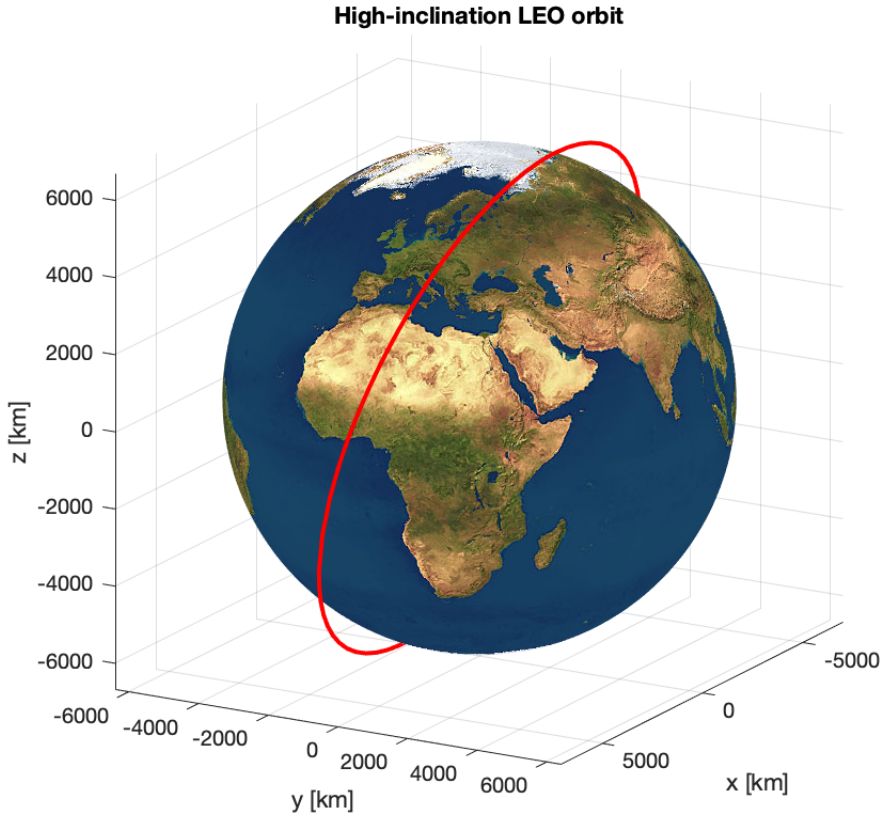


Figure 3.4: Mission's orbit

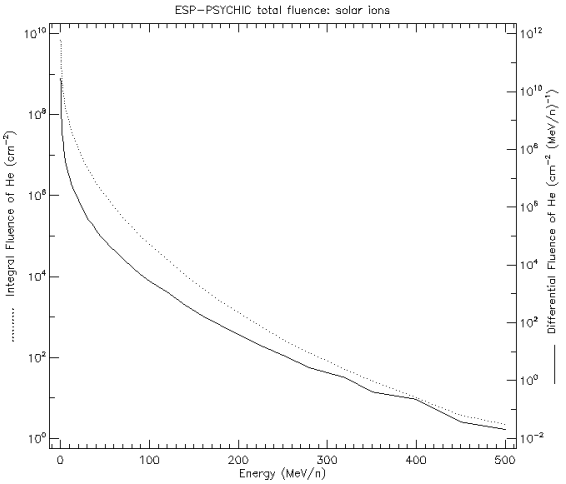
3.3. Environmental analysis

From the orbit previously described, it is possible to decline an analysis of the environment encountered by the spacecraft and thus the organic samples.

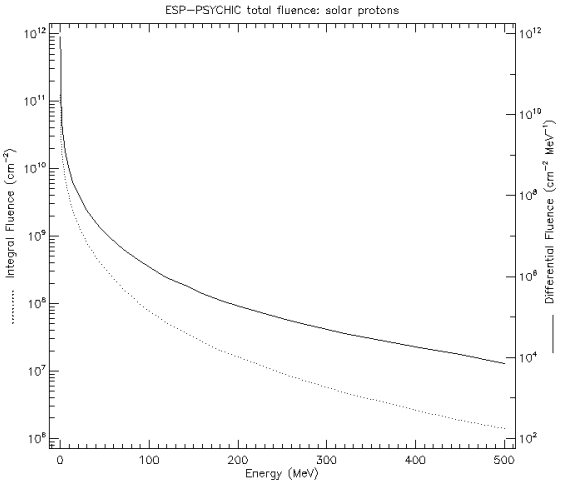
The main hazard faced by spacecraft in high inclination LEO orbit is the interaction with particles, either from the ionosphere, the sun or galactic cosmic rays. As previously mentioned, this orbit type is affected by GCRs, SEPs, electrons and protons, which can jeopardize the functioning of electronics for instance. Moreover, the ionosphere and especially atomic oxygen can interact with the spacecraft structure causing erosion and recombination of oxygen atoms [25]. Nevertheless it is not mentioned so far in literature to interact with organic molecules. Temperature variation is a pertinent hazard as well, due to his potential impact on molecules stability.

By means of *SPENVIS* software, the radiations fluxes encountered on the orbit during 6 months have been simulated. Their intensities are plotted in fig. 3.5.

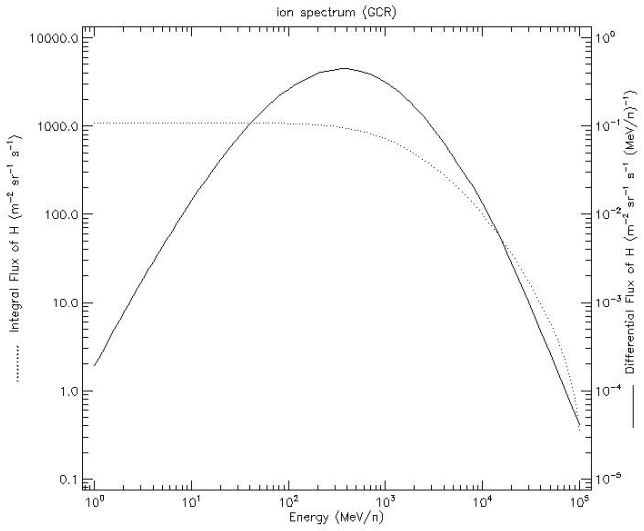
For such simulation, it is possible to plot in fig. 3.6 the ionizing dose in carbon (graphite) as a function of aluminium shielding thickness. Carbon aiming to partially represent organic molecules, this graph gives an idea of the radiation dose level absorbed by the organic samples, which are, on purpose, not shielded from radiations. Consequently we can assume that organic samples would be exposed to an ionizing dose of 100 krad during the whole mission (6 months). For comparison, the annual dose on Earth is on average of 0.3 rad.



(a) Solar ions total fluences



(b) Solar protons total fluences



(c) GCR ion spectrum

Figure 3.5: Ions and protons fluences during 6 months mission

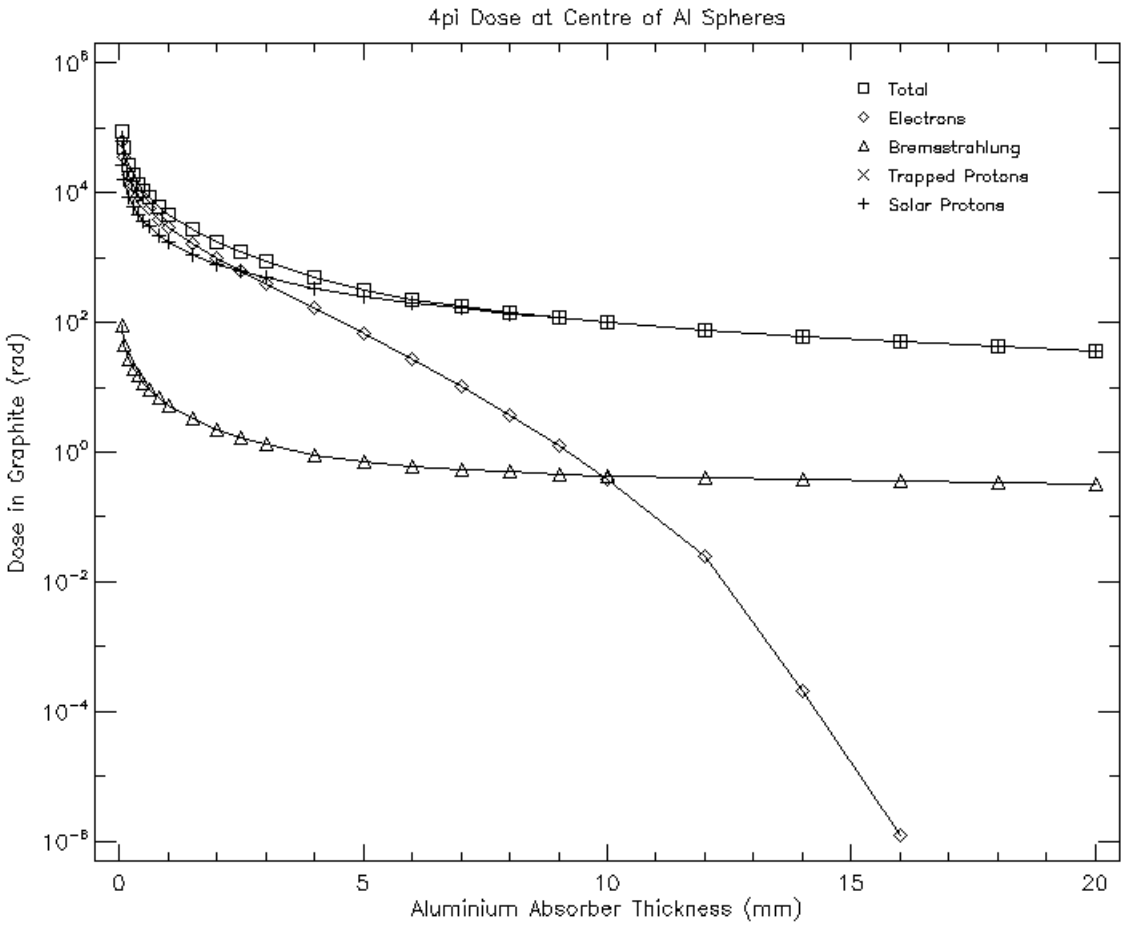
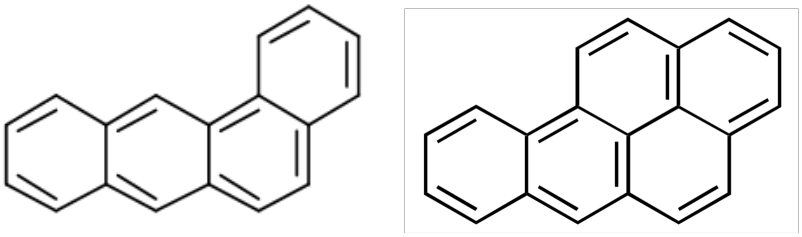


Figure 3.6: Ionizing dose in carbon as a function of shielding thickness

4 | Experiment design

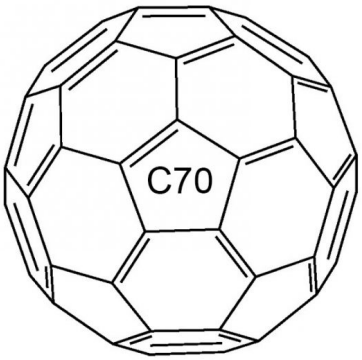
4.1. Molecules selection

The selection of the organic molecules to be studied is based on their relevance to astrochemistry questionings. As mentioned in chapter 1, observations and samples obtained from the solar system highlighted the potential of PAHs and fullerenes (represented in fig. 4.1), which are organic molecules potentially playing a essential role in the carbon production in the universe.



(a) Benza(a)nthracene (PAH)

(b) Benzo(a)pyrene (PAH)



(c) Fullerene C_{70}

Figure 4.1: Exemple of PAHs and fullerene

Moreover, molecules involved in biological processes have also been detected in space [3],

and are thus relevant to study. As suggested in *OREOcube* project, amino acids, fatty acids, purines and pyrimidines are one of these molecules [26].

An amino acid is a type of molecule made of a carboxylic acid ($-COOH$) and an amine ($-NH-$ or $-NH_2$). There are more than 500 amino acids in the living world. Amino acids are notably implied in the constitution of proteins. They are essential to life. An example of an amino acid's structure is shown in fig. 4.2.

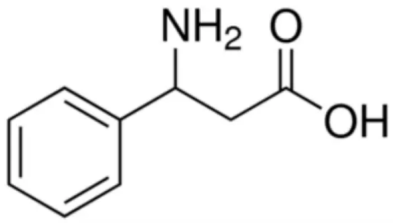
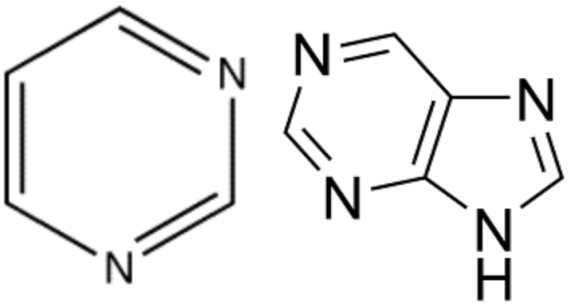


Figure 4.2: Amino acid example : phenylalaline

Pyrimidines and purines are aromatic heterocyclic organic compounds, which means they are composed of a carbon cycle containing an nitrogen atom (fig. 4.3a, fig. 4.3b). Purine is a derivative of pyrimidine and composes two of the of the nucleobases (Adenine and Guanine), while the three others (Thymine, Cytosine and Uracile) are pyrimidine derivatives. Nucleobases are the molecules involved in the structure of DNA and RNA, the supports of genetic information on Earth. Four of them are represented in fig. 4.4.



(a) Pyrimidine (b) Purine

Figure 4.3: Pyrimidine and purine

Finally, it is pertinent to study the stability of molecules essential to the production of energy in living organisms, such as fatty acids. Fatty acids are carboxylic acids with a aliphatic chain (organic chain) (fig. 4.5), they are involved in energy production but also cellular structure. They have been selected as samples during past astrobiology missions, especially ω_3 or ω_6 due to their relevance in biology [27].

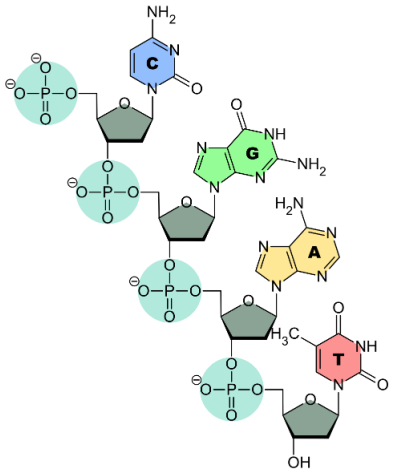


Figure 4.4: Nucleobases on a single strand

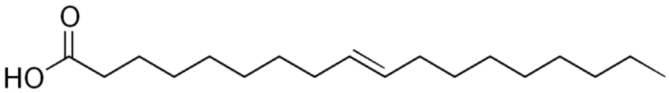


Figure 4.5: Fatty acid example : trans-Oleic acid

In addition to their scientific interest, organic samples shall be chosen according to the instruments constraints. While IR spectroscopy can be applied to all organic molecules, as mentioned in section 2.2, the selection of the fluorescence spectroscopy techniques restrict the panel of molecules to be studied since not all molecules emit fluorescence in the UV-Vis range. Hence, the potential to emit fluorescence of the organic molecules earlier presented has been studied :

- PAHs : PAHs are molecules which emit fluorescence is the UV-Vis range. Fluorescence spectroscopy is recognized to be an efficient method to measure their concentration, especially in the petroleum combustion field [28].
- Fullerenes : Fullerenes are complex organic molecules whose high number of bonds and shared electrons provide a weak fluorescence in the UV-Vis region [29].
- Purine, pyrimidine : Purines and pyrimidines also emit appreciable fluorescence which can be exploited for spectroscopy [30].
- Amino acids : According to Hilaire et al (2017) [31], the fluorescence of amino acids is widely used for biology purposes. Amino acids such as tyrosine, thryptophan and phenylalanine can be studied through fluorescence spectroscopy.
- Fatty acid : Fatty acids in general can also be detected using fluorescence spec-

troscopy, with an efficiency depending on the molecule type. This method is espacially used in the agri-food field [32].

As a consequence, the following organic molecules to be studied are chosen :

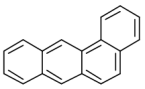
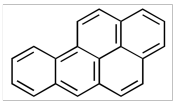
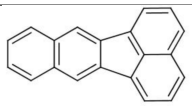
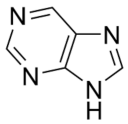
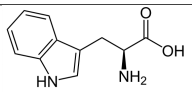
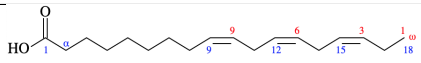
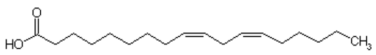
Molecule type	Molecule name	Formula	Skeletal formula
PAH	benz[a]anthracene	$C_{18}H_{12}$	
PAH	benzo[a]pyrene	$C_{20}H_{12}$	
PAH	benzo[b]fluoranthene	$C_{20}H_{12}$	
Fullerene	fullerene C_{70}	C_{70}	
Pyrimidine	1,3-diazabenzene	$C_4H_4N_2$	
Purine	9H-purine	$C_5H_4N_4$	
Amino-acid	tryptophan	$C_{11}H_{12}N_2O_2$	
ω_3 Fatty acid	α-linolenic acid	$C_{18}H_{30}O_2$	
ω_6 Fatty acid	linoleic acid	$C_{18}H_{32}O_2$	

Table 4.1: Molecule selected for the experiment

4.2. Fluorescence spectroscopy

4.2.1. Spectrofluorometer design

Fluorescence spectroscopy is performed using a spectrofluorometer. The light source is usually provided by a gas lamp such as Xenon lamps. In order to restrict the wavelength range to select the excitation wavelengths, monochromators such as mirrors and gratings series are often used. Then, the emission spectrum emitted by the sample fluorescence is

as well filtered and then collected by a sensor [33]. A simple scheme of such a mechanism is displayed in fig. 4.6.

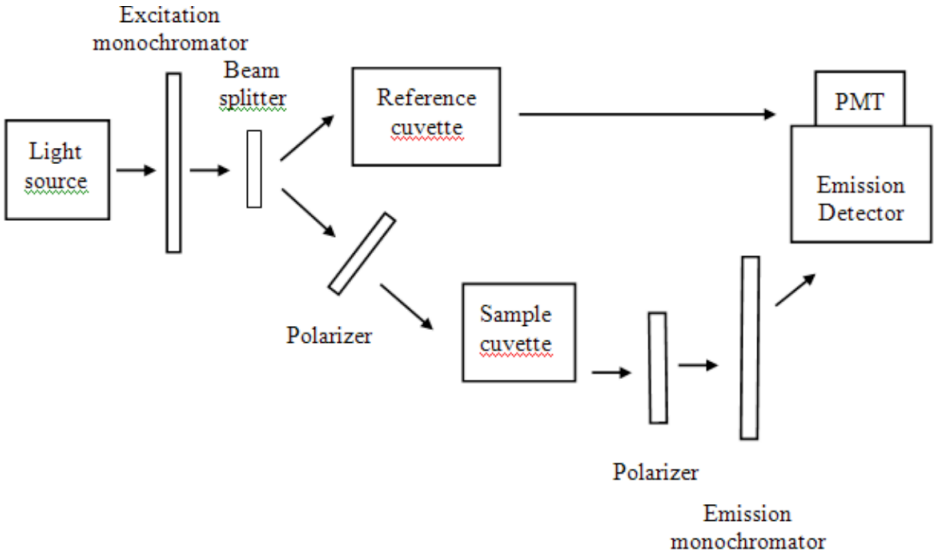


Figure 4.6: Spectrofluorometer reference scheme [33]

Another type of spectrofluorometer are laser induced fluorometer (LIF). Thanks to the narrow wavelength range and power provided by lasers, LIF is a efficient spectrometry method for molecules detection [34], mentioned as a promising analysis technique in Cottin et al (2017) [5].

Likewise, LED-induced fluorescence is a technique exploited in biology for instance. LEDs are an efficient alternative to the high cost and power of lasers and the complexity of broadband light source's utilization [35].

In order to choose the most suitable configuration, excitation and emission wavelengths shall be compared to assess the possibility to use the Sun as a light source and monochromators. The excitation and emission wavelengths associated to the chosen samples are shown in table 4.2. The excitation wavelengths of purines and pyrimidines have not been found in literature, hence their excitation range shall be studied in laboratory prior to the final design of the payload.

It is visible in table 4.2, that the excitation range for all the samples is too wide (192 nm) to be filtered by a unique monochromator. Hence, the most suitable configuration to minimize the instrument size and complexity is a LIF or LED-IF one. Although lasers are powerful and precise instruments, they are not always suitable to CubeSats, espacially due to their power consumption. Thus, as suggested in the *Spectromodule* project, fluorescence measurements can be performed using UV LED as light sources [13].

Molecule name	$\lambda_{excitation}$ [nm]	$\lambda_{emission}$ [nm]
benz[a]anthracene	288	387
benzo[a]pyrene	297	405
benzo[b]fluoranthene	307	403
fullerene C_{70}	470	740
Pyrimidine	?	~ 580
Purine	?	~ 580
tryptophan	280	350
α-linolenic acid	360	460
linoleic acid	350	~ 460

Table 4.2: Molecular samples excitation and emission wavelengths [36][37][32][38]

To perform LED induced fluorescence, the constraints lie on the LEDs' power and range precision. Companies provide commercial–off-the-shelf (COTS) UV LEDs in the different UV domains (B, C), which can be suitable for space application. For instance *Laser Components* supply LEDs with a narrow $\Delta\lambda$ ($\sim$ 10 nm) [39][40].

As a suggestion, the LEDs presented in table 4.3 could be chosen within COTS components for such a fluorescence analysis. A wide range of power is accessible, from very low power LEDs (2mW) to high power ones (110 mW). Although high power LEDs provide a better SNR [35], available power depends on the spacecraft's electric power system. In this case, the highest power available will be suggested, for an optimal excitation of the molecules.

Molecule name	$\lambda_{excitation}$ [nm]	LED λ_{peak} [nm]	$\Delta\lambda$	**Optical power** [mW]
benz[a]anthracene	288	295	12	110
benzo[a]pyrene	297	295	12	110
benzo[b]fluoranthene	307	308	15	110
fullerene C_{70}	470	470	10	170
tryptophan	280	275	10	110
α-linolenic acid	360	360	15	100
linoleic acid	350	340	20	0.33

Table 4.3: Suggestion of LEDs selection for each sample [39][40][41][42][43]

The detector to record molecules' fluorescence shall be chosen according to the wavelength range to be studied. A suitable detector choice for the UV-Vis range are silicon-based detectors such as CCD arrays, exploiting the photovoltaic effect of silicon [44]. A suitable sizing of the CCD array (table 4.4) can be inspired by the space-proven UV-Vis spectrometer from the NASA *LCROSS* mission. Such CCD silicon array is manufactured

by *Hamamatsu* for instance and is suitable for fluorescence detection [45]. As done on *LCROSS*, some pixels can be allocated outside the light slit and provide a dark reference [46].

Detector material	Silicon (Si)
Detector size [mm]	12.7x1.5
Number of pixels	532x64
Pixel size [μm]	24

Table 4.4: CCD array sizing suggestion

Finally, as suggested in fig. 4.6 and despite the narrow range of the LEDs, it is necessary to add two bandpass filter, one playing the role of the excitation filter and the other one of the emission filter. As suggested in D.C. Mukunda et al (2022) [35], miniature optical bandpass filters of a few centimeters size can be used. For instance, *Omega optical* provide small emission and excitation filters for such applications [47].

4.2.2. Data post-processing

In this experiment, the purpose of performing fluorescence spectroscopy is to assess the photodegradation process happening within molecular samples. More specifically, the molecular concentrations and the reactions' kinetics need to be studied.

As stated in section 2.2, the molecular concentration is correlated to the absorption intensity. The absorbance is inferred from the intensity of the light which passed through the sample and the reference intensity (eq. (4.1)).

$$A = \log_{10}(\frac{I}{I_0}) \tag{4.1}$$

Where, I_0 is the reference intensity and I is the transmitted one.

Then *Beer-Lambert* law (eq. (4.2)) is a quantitative law used to determine the concentration of an absorbing specie.

$$A = \epsilon l c \tag{4.2}$$

Where A is the absorbance, ϵ the absorptivity, l the optical length in cm and c the concentration.

Moreover, the quantum efficiency of the fluorescence can be expressed such as in eq. (4.3).

$$\Phi_f = \frac{I_f}{I_A} \text{ with } I_A = I_0 - I \tag{4.3}$$

Where I_f is the fluorescence intensity, I_A the absorbed intensity.

Hence, it is possible to express the fluorescence intensity as a function of the concentration, as shown in eq. (4.4).

$$\begin{aligned}\Phi_f &= \frac{I_f}{I_A} \\ &= \frac{I_f}{I_0 - I} \\ &= \frac{I_f}{I_0(1 - 10^{-A})} \text{ using } eq.\ (4.1)\end{aligned}$$

Then, if $A < 0.05$, the approximation $10^{-A} \approx 1 - 2.3A$ can be used. Finally, replacing A with eq. (4.2), we obtain :

$$\boxed{I_f \approx 2.3\Phi_f I_0 \epsilon l c} \tag{4.4}$$

In the practical case, Φ_f is known and depends on the molecule itself. If $A > 0.05$, the relation between I_f and c is no more linear. Moreover, correction can be added to these expression to take into account perturbations such as scattering, variations of light intensity...

Once the concentration of the molecule of interest is known, it is possible to assess the kinetics of the photodegradation process. Indeed, the kinetics of a reaction describes how fast the reactant concentration decreases. The kinetics can be of first or second order. To spot a first order reaction, $ln(\frac{[mol]}{[mol]_0})$ is plotted as a function of time, where [mol] is the concentration of the molecule. If it is a first order reaction, the relation can be approximated as linear and the R^2 value of the linear regression shall be superior to 0.8. For a second order, $\frac{1}{[mol]}$ is plotted as a function of time. Similarly, if it is a second order reaction, the slope shall be approximated as linear with an adequate R^2 value. .

4.3. Infrared spectroscopy

4.3.1. FT-MIR spectrometer design

In this experiment, infrared spectroscopy is performed using an FTIR. Indeed, as concluded in the trade-off analysis, FTIR provide a better precision and rapidity with respect to IR dispersive spectroscopy. As shown in table 4.5, molecules of interest have their characteristic vibrational bands in the MIR region, and some of them in the so called

fingerprint region which is between 500 and 1500 cm^{-1}. Studying the absorption spectra in the fingerprint region, provides precise information about molecules' structure and can allow the user to distinguish two similar molecules.

Molecule name	**σ range of study** $[cm^{-1}]$	**IR range**
benz[a]anthracene	$3500 - 800$	MIR
benzo[a]pyrene	$4000 - 700$	MIR
benzo[b]fluoranthène	$3300 - 700$	MIR
fullerene C_{70}	$2000 - 500$	MIR
Pyrimidine	$4000 - 650$	MIR
Purine	$4000 - 800$	MIR
tryptophan	$4000 - 700$	MIR
α-linolenic acid	$4000 - 840$	MIR
linoleic acid	$4000 - 600$	MIR

Table 4.5: Molecular samples IR range of interest [48][49]

As stated in section 2.2, the particularity of a FTIR is that the incoming beam of light is passing through an interferometer, usually a Michelson one, to illuminate the sample with a polychromatic beam of light. Although miniature FTIR spectrometer are usually developed in the NIR region with a good resolution, FT-MIR spectrometer are more and more used and compact ones under development. Indeed the positioning and movements of the mirrors constrain the resolution of the spectrometer as the studied wavelengths increase [23]. Moreover, the highest sensitivity in the MIR range is achieved with narrow-band detectors, restricting the spectral range to $750cm^{-1}$ [50]. However, compact COTS FT-MIR spectrometer are available and can be customized to suit partially the experiment constraints. Indeed, *ARCOPTIX* provided a customized FTIR spectrometer for the *Spectrocube* payload [12].

In the case of this paper, a few parameters differ from past astrobiology missions such as the light source and the IR field of study, which are here the Sun and the MIR region respectively. Indeed both of these parameters raise constraints. For instance, the sun as light source restrict the choice of window and half mirror material which must not filter the MIR wavelengths ; the detector's material choice is critical as well for the same reasons. Hence, there are two possibilities to design the MIR spectrometer according to the extent of the MIR range of study.

If the analysis aims to take into account the information from the fingerprint region, the spectrometer shall detect wavelength until 500 cm^{-1} or $20\mu m$. Consequently, the detector shall be made of **Lithium tantalate** ($LiTaO_3$) which is efficient from 10000 to $400cm^{-1}$

and operating at room temperature. Its resolution shall be a high enough ($<8\ cm^{-1}$) as it is necessary to differentiate the close molecular patterns [23] (fig. 4.7). Nevertheless, miniature FTIR spectrometer providing data in such a range are not frequently mentioned in literature and do not seem to be widely used for analytic chemistry purposes.

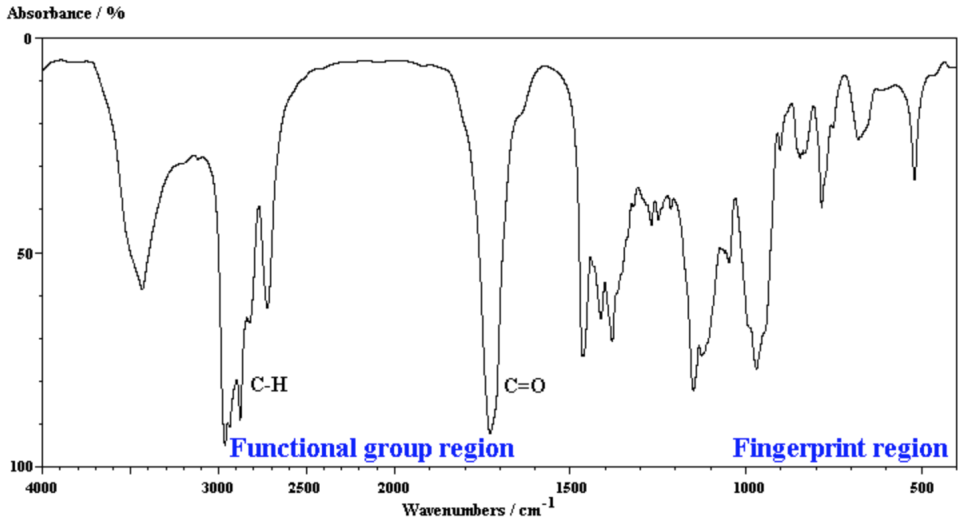


Figure 4.7: Example of the fingerprint region in an IR spectrum [51]

On the other hand, it is possible to restrict the range of study to $[5000\text{-}800]cm^{-1}$. Indeed, as specified in [52], double bonds patterns (C=O, C=C) are visible between 1950 and 1550 cm^{-1} and single bonds patterns (C-O, C-N, C-C) between 1300 and 800 cm^{-1}. Such bonds are those pertinent to study in this experiment, as it can be seen on the skeletal formulas shown in table 4.1. The range between 800 and 500 cm^{-1} is typically dedicated to absorption bands of halogen compounds [53], which are not relevant in this study.

As a consequence, the choice of detector and interferometer can be made among COTS devices. For instance *Arcoptix* or *Agilent* companies, provide low weight and compact FT-MIR spectrometer in the $[5000\text{-}800]cm^{-1}$ range. The *Rocket* FTIR interferometer from *Arcoptix* is represented in fig. 4.8. Such interferometer is a *dual corner cube* one, in which the two mirrors are fixed in a common swigging arm. Just as in an Michelson interferometer, the arm can move to modify one of the mirror's position and thus create an optical path difference. The benefit of such configuration is the stability of the mirrors, which do not have to be re-aligned. This characteristic is very interesting for space applications as the mirrors alignment is resistant to vibrations and temperature change, which are major constraints on a spacecraft.

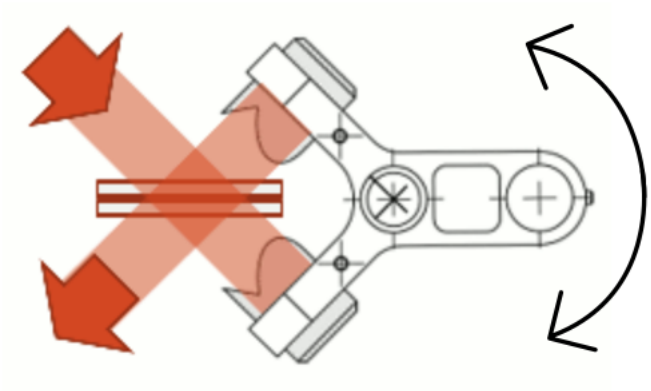


Figure 4.8: Arcoptix *Rocket* FTIR interferometer. The arm on which are fixed the two mirrors can rotate to modify the optical path [54]

The light after being reflected by the two mirrors and the beam-splitter, is transmitted towards the sample for absorption. The beam-splitter, as well as the sample cell's window, must be chosen according to the spectral range of interest, to not filter out the interesting wavelengths. Then the partially absorbed beam of light is directed towards the detector through an optical fiber, whose type also depends on the studied spectral range. In this range, detectors are traditionally made of **Mercury-cadmium-telluride** (MCT), a photo-conductive material [55] and need to be cooled.

The resolution achievable by this FTIR device is $4cm^{-1}$, which is a suitable one for IR spectrum study. It varies depending on the detected wavelength, as shown in fig. 4.9.

The technical characteristics of the COTS Arcoptix *Rocket* FTIR are summed up in table 4.6.

σ range of study $[cm^{-1}]$	5000-830
λ range of study $[\mu m]$	2-12
Beam-splitter material	ZnSe
Detector type	MCT cooled
Resolution $[cm^{-1}]$	4
Fiber	polycristalline fiber
Scan frequency	1 spectrum / second
A/D converter	24 bit
Operating temperature [°C]	10-40
Power requirement [W]	10
Dimensions [mm]	180x160x80
Weight [g]	1800

Table 4.6: technical characteristics of the COTS Arcoptix *Rocket* FTIR [54]

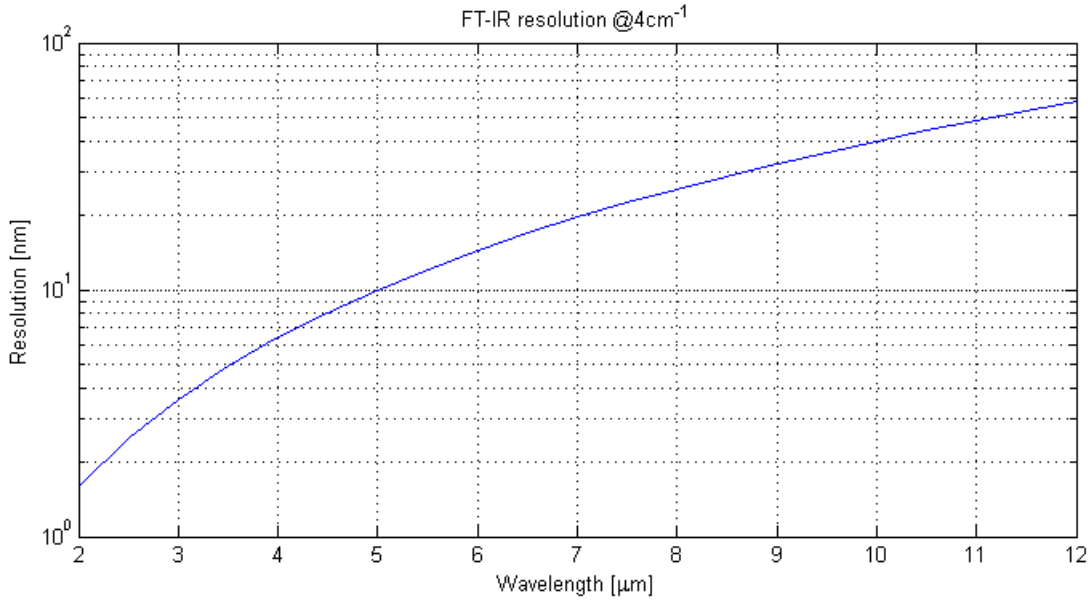


Figure 4.9: FTIR spectral resolution conversion in wavelength [54]

4.3.2. Post-processing of the data

The post-processing of the IR spectrum obtained thanks to the FTIR spectrometer, lies on the recognition of molecular patterns. Indeed, as explained in section 2.2, the study of the position and the shape of absorption bands give insight on molecular structures. Concerning this experiment, the aim is to assess the photodegradation of the molecule. Hence, the analysis of IR spectrum through time, allow the user to observe the modification occurring within the molecules. Depending on the precision of the spectrum, it is either possible to conclude the disappearance or modification of a functional group for instance, or even guess the new structure of the molecule.

Thus, thanks to the *in-situ* spectral acquisition, the user have access to the whole structural evolution of the molecular samples, studying the variations of the IR absorption spectrum.

4.4. *In-situ* spectral acquisition

The *in-situ* spectral analysis in this experiment is characterized by the ability of the CubeSat to acquire IR and fluorescence spectrum automatically throughout the whole mission and store or transfer spectrum to ground.

The acquisition frequency should not necessarily be fixed during the whole mission. Indeed, as explained in [56], the acquisition frequency shall be the highest during the first

mission days at the beginning of the exposition, when molecules will undergo most modifications. Hence the acquisition frequency can be set to one per day during the first weeks of the mission and then progressively decrease to reach a biweekly acquisition, as done on *O/OREOS*.

Moreover, as the experiment compartment host multiple samples, one acquisition process represents actually the recording of both the UV florescence and IR spectra of all different molecular samples ; hence the acquisition of 19 spectrum.

4.5. Sample cell configuration

The sample cell is the payload's component which aims to host and protect the molecular samples and to expose them to sunlight as well. As done in multiple experiment [5], an efficient way to expose organic samples to sun rays and radiations is to deposit them on a window via vacuum-sublimation, under the form of an organic film. Such structure is a commonly used one during space mission, and thus space-proven.

However, the choice of the windows' material depends on the mission objectives. Indeed, the first windows serves as a support for the organic sample, as well as a filter. Yet the different materials do not filter the same wavelength. For instance, a few materials proprieties are displayed in table 4.7. It can be seen that there is no material transmitting a wide range of both UV and IR rays. Therefore the choice of such a window material leads to compromise.

Material name	**Transmission range** [nm]
MgF_2	$120 - 7000$
Quartz	$250 - 3500$
KBr	$250 - 26000$

Table 4.7: Different materials transmission range

As previously stated, the sun acts as the light source in the IR spectrometry analysis in which the IR range of interest in this experiment is the MIR one, especially between $[5 - 12]$ μm. On the other hand, the mission objectives impose the constraints that samples must be exposed to the hazards of UV rays from the Sun. As described in chapter 3, the distribution of the intensity of electromagnetic radiations emitted by the Sun is not uniform, and depends on the wavelength range. In particular, we can observe on fig. 4.10, that the intensity of electromagnetic radiations increases till 500nm. Thus, an irradiation including only UV rays after 250nm is still intense. Moreover, the radiations in the VUV domain, are very irregular ones and are difficult to model. Hence, these

irregularities could add uncertainties into the interpretation of data. Finally, it is relevant to notice that all the molecular excitation wavelengths (table 4.2), are above 250nm.

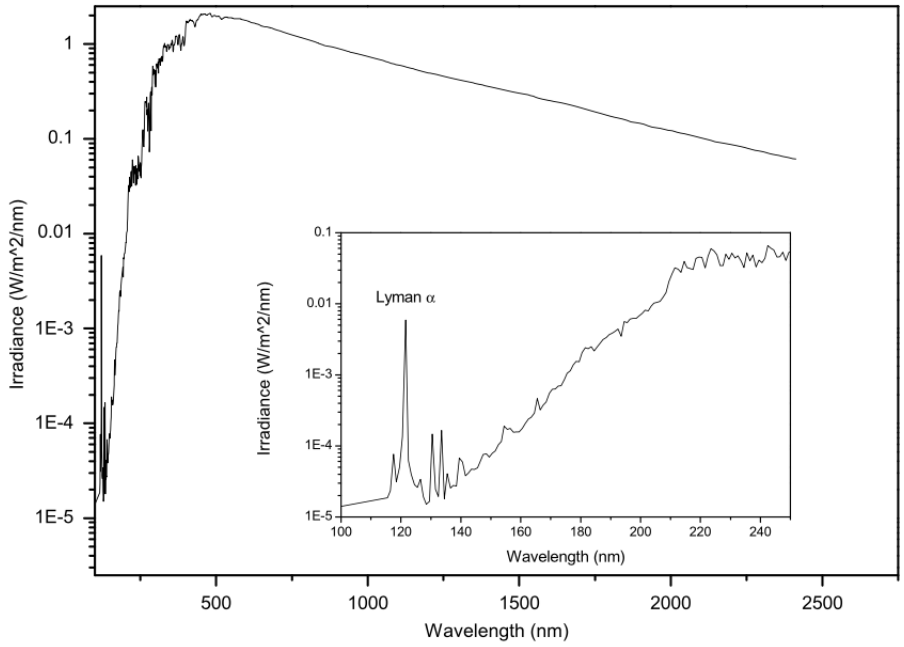
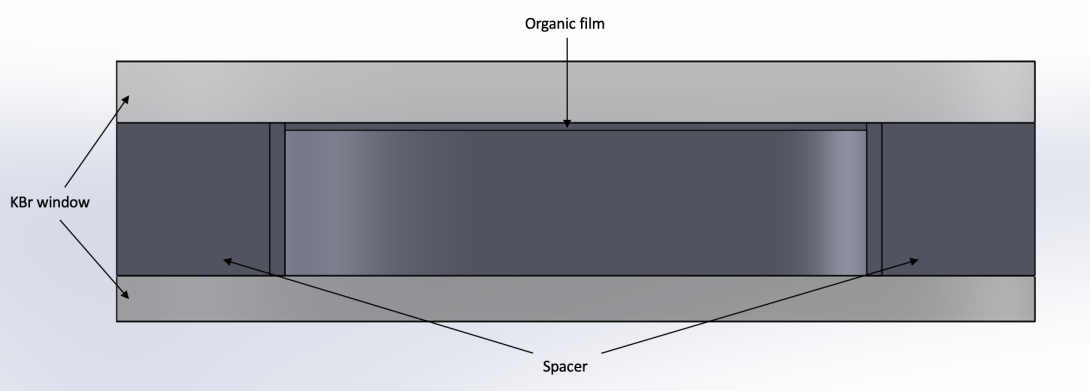


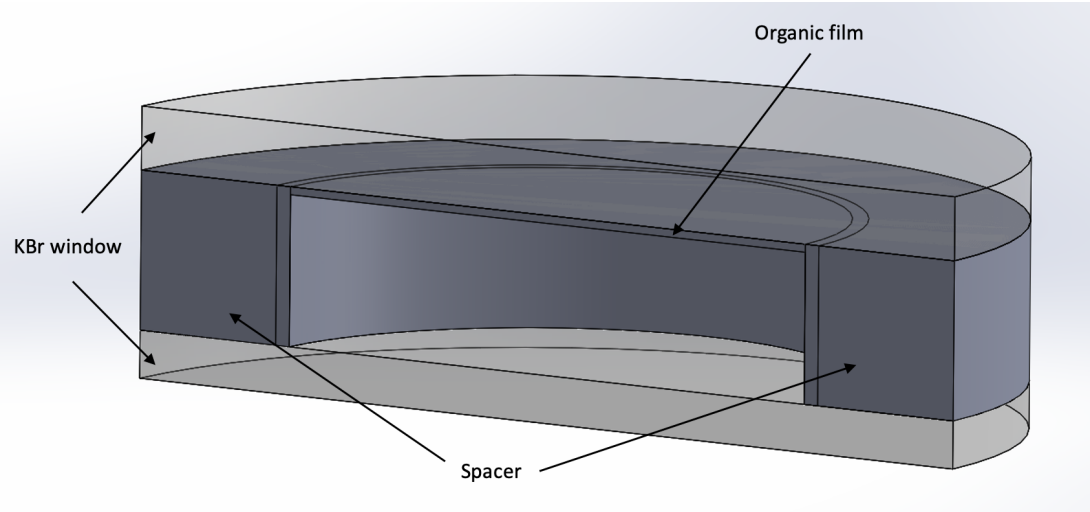
Figure 4.10: Distribution of UV irradiance intensity from 100 to 2500 nm [5]

As a consequence, following the mission objectives and the interpretation of fig. 4.10, a **KBr** window is chosen, prioritizing the transmission in the MIR domain over the UV one, under the assumption that molecules will be sufficiently irradiated, even after 250nm.

One sample cell has been modeled using *SOLIDWORKS* software. The design is displayed in fig. 4.11.



(a) Sectional front view of the sample cell



(b) Sectional side view of the sample cell

Figure 4.11: 3D sample cell design

4.6. Sensors

A sensor suite shall be embedded on board of the payload for both experimental data assessment and *housekeeping*. The sensors required for the experiment are :

- Temperature sensor : to assess the temperature both within the sample cells and at the detectors surface. Indeed, functional requirements impose a control of the temperature at which samples are exposed, to avoid thermal degradation. Then, the MCT detector needs a thermal control to operate properly. For instance, the *LCT2996* temperature sensor from *Linear Technology* could be a suitable choice [57].
- Radiation dosimeter : to assess the ionizing dose received by the samples. In order to link photostability and space environment, it is necessary to record the level of radiations encountered during the whole mission. Moreover, such sensors are as well useful to check the functioning of electronic devices, which are sensitive to radiations. *RadFETS* (radiation-sensitive-field-effect-transistor) which are commonly used sensors in the space-field can be chosen for such measurements [11]. More complex instruments such as Geiger counter can also be used to focus on gamma ray radiations background. For instance a suitable choice could be the *SkyFox Labs piDOSE-DCD*, a TRL 9 space-proven device [58].
- Solar intensity sensors : to monitor when the solar intensity is sufficient for IR spectrum acquisition and measure the UV-light intensity.

4.7. Global configuration

As a conclusion of this chapter, the global configuration of the experiment aims to perform *in-situ* both fluorescence and IR spectroscopy as well as the recording of the environment characteristics.

table 4.9 summarizes the functional requirements driving the whole design of the experiment compartment.

ID	Functionality	Rational	Subsystem
M-FR-01.1	UV-Vis spectrofluorometer shall record *in-situ* the UV-Vis fluorescence of the molecules	M-HRL-04	Optics

M-FR-01.2	IR spectrometer shall record *in-situ* the IR absorption spectrum of the molecules	M-HLR-02 M-HLR-03	Optics
M-FR-01.3	UV-Vis spectrofluorometer light sources shall be specific to each molecule's excitation wavelength	M-HLR-04	Optics
M-FR-01.4	Molecules studied through UV-Vis fluorescence spectroscopy shall not receive other wavelengths than the one from the excitation light source	M-HLR-04	Optics
M-FR-01.5	Molecules studied through IR spectroscopy shall receive light from the mid-infrared range	M-HLR-02 M-HLR-03	Optics
M-FR-02.1	A sensor suite shall record *in-situ* the radiations intensity to which molecules are exposed	M-HLR-05	Optics
M-FR-02.2	A sensor suite shall record *in-situ* the sun rays intensity to which molecules are exposed	M-HLR-05	Optics
M-FR-02.3	A sensor suite shall record *in-situ* the temperature inside molecules containers	M-HLR-02 M-HLR-03	Optics
M-FR-02.4	A sensor suite shall record *in-situ* the temperature of electronic components	M-HLR-02 M-HLR-03	Optics
M-FR-03	The payload shall host each type of molecule in separate and suitable container	M-HLR-01	Structure
M-FR-03.1	The payload's structure shall protect the molecules from launch vibrations	M-HLR-01 M-HLR-02 M-HLR-03	Structure
M-FR-03.2	The payload's structure shall protect the instruments from launch vibrations	M-HLR-01 M-HLR-02 M-HLR-03	Structure

M-FR-03.3	The payload's structure shall protect the molecules from radiations (trapped particles, GCR) before the start of the experiment	M-HLR-02 M-HLR-03 M-HLR-05	Structure
M-FR-03.4	The payload's structure shall protect the molecules from solar radiations before the start of the experiment	M-HLR-02 M-HLR-03 M-HLR-05	Structure
M-FR-03.5	The payload's structure shall allow the exposure of molecules to UV solar rays	M-HLR-02 M-HLR-03 M-HLR-04	Structure
M-FR-03.6	The payload's structure shall allow the exposure of molecules to radiations (trapped particles, GCR)	M-HLR-02 M-HLR-03 M-HLR-04	Structure
M-FR-03.7	The payload's structure shall allow the positioning of samples in all analysis modes	M-HLR-02 M-HLR-03 M-HLR-04	Structure

Table 4.9: Functional requirements driving the experiment design

To fulfill the mission requirements, the samples shall be exposed to three different light source in total : sunlight, UV light at the excitation wavelength from the LEDs and IR light coming from the interferometer.

An efficient way to cope with this constraint is to create a rotation ring to host the samples. Such ring is represented in fig. 4.15, fig. 4.14, fig. 4.12 and fig. 4.13. The ring would be composed of 9 samples cells (in cyan) and 10 empty cells (in gray). The rotation of the ring could allow the samples to switch configuration :

- Exposure configuration : the organic samples are exposed to sunlight and radiations thanks to the KBr window. During this configuration, no analysis is performed and the empty cells remain in the other configurations.
- Fluorescence spectroscopy : LED-induced fluorescence implies that the molecules shall be excited by a precise wavelength range which is provided by specific UV-LED. Hence, the molecules shall not be exposed to other light than the one from the LED. As a consequence, in such configuration, the cell is covered by a lid on which is fixed the circuit (in brown) hosting the LED underneath, illuminating the sample. The lid itself is not attached to the ring, but to an external structure,

allowing the cells to freely change configuration. As each molecular sample has a specific excitation wavelength, there are as much lids as samples. When the fluorescence spectroscopy is performed, the ring rotates to set the nine samples in this configuration where each sample is illuminated by the proper LED.

- FTIR spectroscopy : To study the IR absorption spectrum of the molecules, the sunlight must be filtered by the Michelson interferometer (in light gray). Hence, there is a slit in the interferometer compartment, to which can be added baffles to reject parasite light. Due to the weight and size of the FTIR spectrometer, one cell is allocated to this analysis configuration and one sample at the time is analyzed.
- Witnesses : As in every chemistry or biology experiment, sample cells must remain empty to be witnesses of the experiment. In this case, the empty cells will allow the user to obtain the solar IR spectrum as well as the different LED emission spectra. The resulting spectra will serve as reference for the interpretation of data, as well as to highlight eventual contamination or technical issues and assess the quality of incoming spectra.

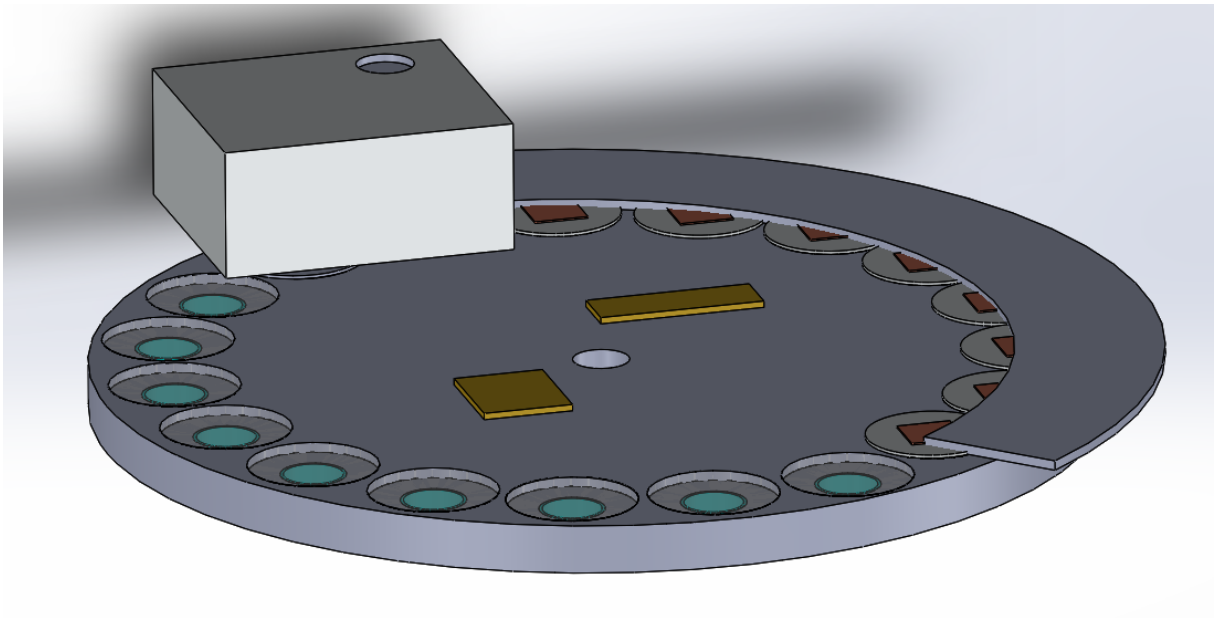


Figure 4.12: 3D view of the experiment ring

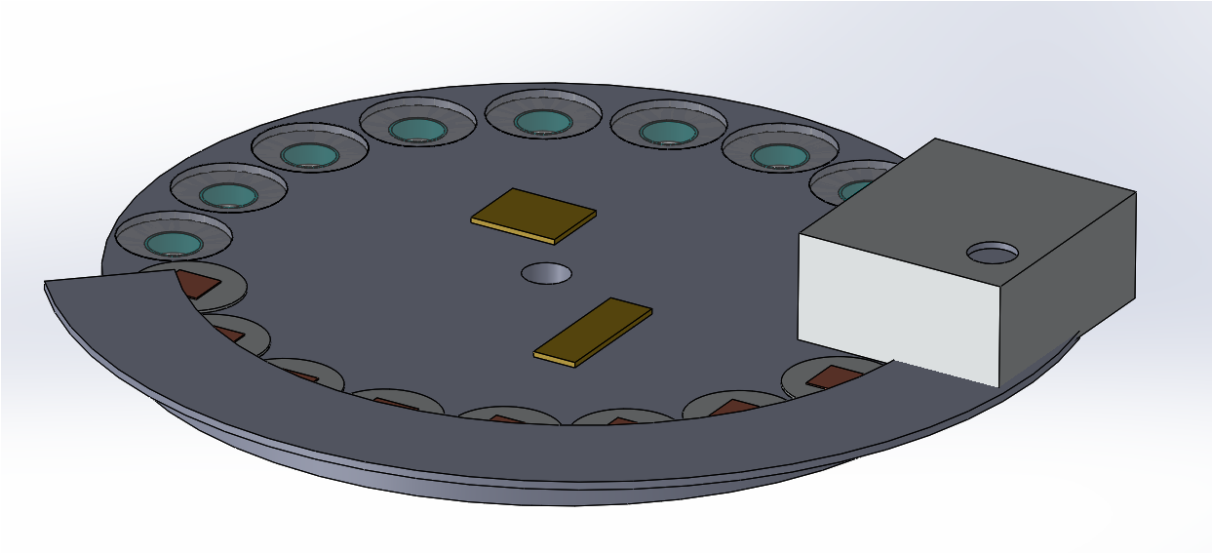


Figure 4.13: Second 3D view of the experiment ring

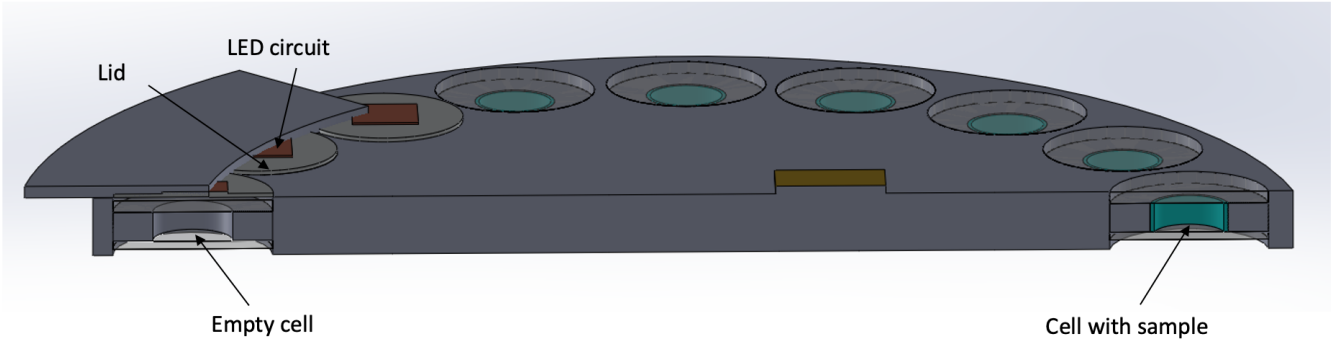


Figure 4.14: Sectional view of the experiment ring

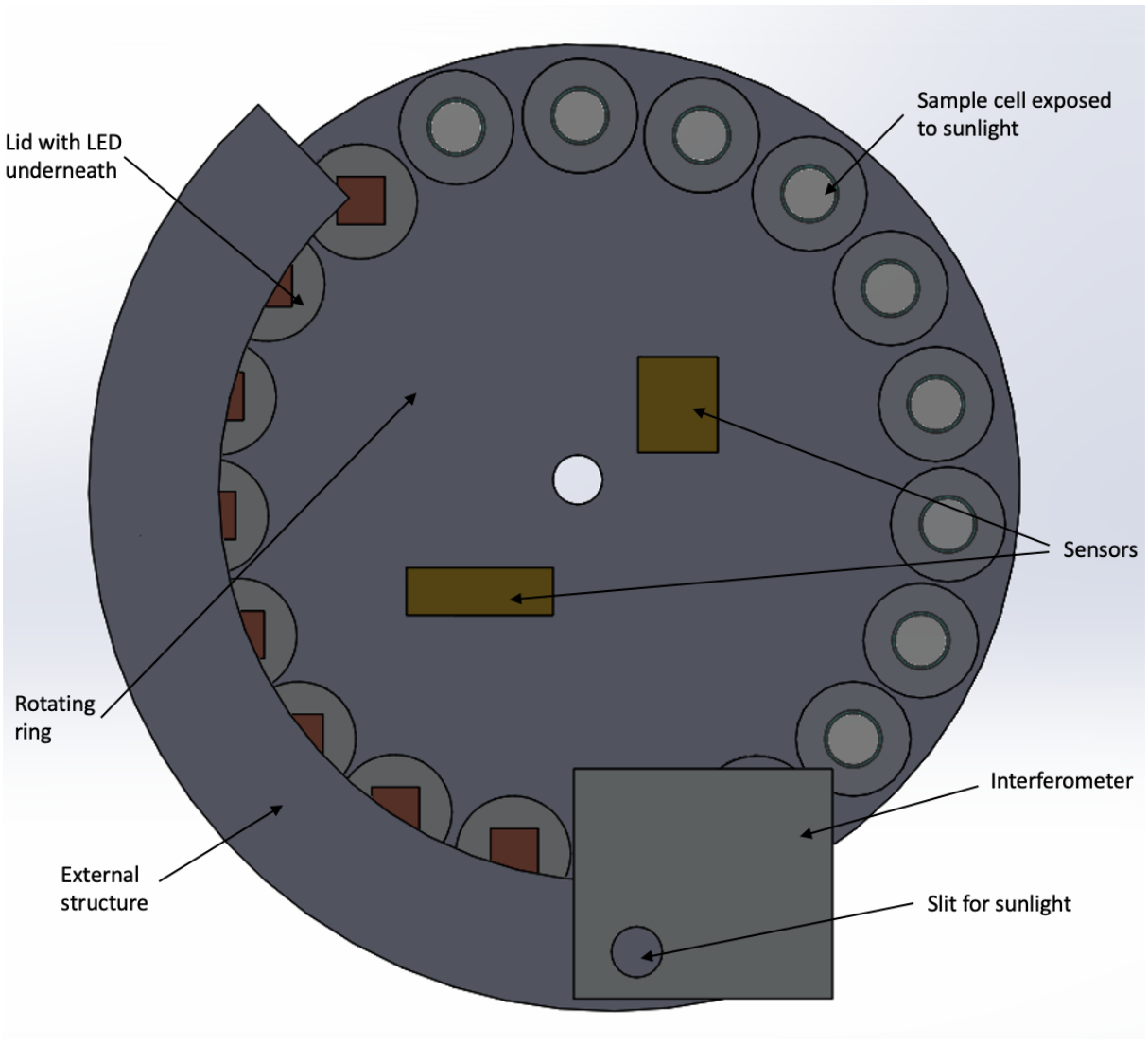


Figure 4.15: Upper view of the experiment ring

5 | Subsystems

5.1. Thermal control system

The thermal control system of the spacecraft aims to control the temperature within the experiment compartment, for both samples and detectors.

As mentioned in chapter 1, one of the innovation perspectives for astrobiology experiment, is the control of the temperature to which samples are exposed. Indeed, controlling the samples' temperature, allows to restrict the molecular degradation to the one due to radiations and UV-rays. As done during the *BIOPAN* mission, a suitable temperature range for experiments would be of $[10 - 20]$°C [5].

Moreover, the operation temperature range of electronic devices used on-board of the payload are reported in table 5.1.

Device	**Operating temperature range** [°C]
UV LEDs (average)	$-30 - +50$
CCD arrays	$-50 - +50$
FTIR	$+10 - +40$
MCT detector	-75

Table 5.1: Operating temperature ranges

In a Cubesat, temperature can be controlled using different technologies, passive or active.

Passive technologies such as coating, radiators, thermal fillers, multi layers insulators, are suitable when the operating temperature range is sufficiently wide. In this case, the temperature control of the LEDs, the CCD arrays and the FTIR could be performed by a passive technology.

On the other hand, the temperature within the MCT detector and the sample cells should be controlled by an active device, such as electric heater/cooler [59]. For instance, MCT detectors are usually cooled using Peltier thermoelectric coolers. As done on board of the *FOTON* capsule, a stable temperature between $[10 - 20]$°C can be reached with electric heaters [5].

5.2. Power budget

This section aims to propose a succinct power budget for the experiment compartment components. According to the margin philosophy of ESA [60], their respective power has been associated with proper margin regarding the TRL at hand. Already space-proven components have been allocated a margin of 5%, while COTS components requiring minor modification to suit the spatial environment constraints lead to a margin of 10%. Overall, a 20% margin at subsystem level is justified by the use of customized technologies and configurations related to the mission goal.

Device	**Power** [W]	**Margin** [%]	**Power with margins** [W]
UV LED 295nm (x2)	6	10	6.6
UV LED 308nm	3	10	3.3
UV LED 470nm	1.12	10	1.23
UV LED 275nm	3	10	3.3
UV LED 360nm	0.07	10	0.077
UV LED 340nm	0.11	10	0.12
CCD arrays	0.0013	5	0.0014
FTIR (with MCT detector)	10	10	11
Sensor suite	0.1	5	0.105
Total	23.4	20	28.08

Table 5.2: Power budget

5.3. Mass budget

The mass budget of the experiment compartment has as well been evaluated. In particular, the mass of the sample cells and the rotating ring have been computed under the assumption that :

- These metallic components are made of aluminum.
- The sample cell diameter is about 30 mm.
- The diameter of the organic film is about 20mm.
- The rotating ring diameter is about 20 cm.
- The height of both the sample cell and rotating ring is evaluated at 15mm.

Then, the mass of all the sample cells have been removed form the rotating ring's, as they are inserted inside it. Moreover, the computation the sample cells' mass takes into

account the windows' masses ($\sim$ 30 g) [61].

As well as for the power budget, margins have been applied following the ESA recommendation for dry-mass margins : 5% for COTS space-proven components, 10% for COTS components with minor modifications and 20% for new designed items.

Device	**Mass** [kg]	**Margin** [%]	**Mass with margins** [kg]
UV LED 295nm (x2)	0.02	10	0.0202
UV LED 308nm	0.01	10	0.0101
UV LED 470nm	0.01	10	0.0101
UV LED 275nm	0.01	10	0.0101
UV LED 360nm	0.01	10	0.0101
UV LED 340nm	0.01	10	0.0101
Sensor suite	0.05	5	0.0502
CCD arrays	0.1	5	0.105
FTIR (with MCT detector)	1.8	10	1.98
Sample cell (x19)	1.062	20	1.274
Rotating ring	4.018	20	4.821
Total	7.1	20	8.52

Table 5.3: Mass budget

6 | Discussion

The payload's characteristics such as the mission goal, the requirements and the components and configuration's choices can be discussed.

First of all, it is relevant to remind that the goal of this paper is to study the feasibility of an innovative way to study *in-situ* the photostability of organic molecule in space environment. From the literature review, it can be seen that most of the autonomous spacecraft flying with instruments performing on-board spectroscopy, are studying samples absorption in the UV-Vis and NIR ranges. As stated in chapter 4, the decision to study the feasibility of performing fluorescence spectroscopy and IR spectroscopy in the MIR range, brought difficulties and constraints for the light source selection, detector's choice etc. However, the aim was to explore more complex solutions.

Concerning the molecules' choice, the selection of the molecular type to be studied has been made based on literature review. Indeed, the abundance of PAHs and fullerene in the universe [3] reinforces the interest towards these molecules' photostability. Then the study of molecular elements implied in the structure of molecules essential to life (genetic information, proteins, transport of energy) is also relevant according to the questions raised by astrochemistry in general and the origin of life in the universe. Nevertheless the selection of the molecule itself can be discussed. Indeed, this analysis did not take into account the constraints linked to toxicity or caution while the depositing of the samples on the windows. Moreover, there may be additional arguments related to specific chemistry aspects to drive the molecules' choice that were not considered, as this paper being focused on payload design from the engineering point of view. Furthermore, recent studies have also highlighted the significance of astrophysical ices and their role into the formation of complex organic molecules [62]. For instance analysis through IR and mass spectroscopy of organic molecules kept at a very low temperature (35K) in a solid film and exposed to UV, have shown formation of more organic products [63]. As emphasized in Cottin et al (21017) [5], the study of molecules in icy environment is a relevant research question as well, which can be possible by means of thermal control on board of the spacecraft.

As it has been discussed in chapter 3, the choice of the orbit for such experiment is a crucial

one, as it will further affect the intensity of radiations received by the molecules. In this analysis, the choice of a highly-inclined LEO orbit was made, embracing the acceptable radiations intensity level and its easy accessibility. However as previously mentioned, a higher altitude orbit would be optimal for such study, although it raises budget and launcher constraints.

Finally the last discussion part lies on the selection of the instruments and experiment compartment components. While most of them were chosen based on the review of past astrobiology missions, some components were selected from COTS technologies, such as LEDs and filters. These technologies, which are widely used in the field of chemistry and biology, are not necessarily space proven. Hence if this project led to an advanced design phase, additional test shall be run on such components to verify their ability to operate in space. Then, the design of the experiment compartment which was proposed, involves a rotation ring to allow the nine samples to be studied by both of the instruments and acquire witness spectrum. Despite rotating rings were also used in the *SEVO* payload of *O/OREOS* mission [4], such mechanism brings out constraints on the spacecraft to ensure its protection.

7 | Conclusions and future developments

As a pursuit of past missions dedicated to astrochemistry experiments, this thesis partially depicts the phase A design of an miniature astrochemistry payload aiming to perform *in-situ* analysis of organic molecules' photostability. The comprehension of how *bricks* of life were brought from the interstellar medium to Earth and the solar system system, is still an unsolved research question, and experiments addressing such topic are needed.

As previously discussed, the most suitable analysis techniques were chosen to reach both an innovative nature and the missions objectives. Exploiting the knowledge and results of past missions, the methods of fluorescence and FTIR spectroscopy have been chosen regarding their precision, low detection limit and reliability.

However one critical choice for such experiment is the orbit selection as it drives the intensity of radiations the samples will encountered. Although a high-inclination LEO orbit was chosen, future space missions such as *Artemis* open new perspectives. Indeed, *Artemis* missions plan to launch spacecraft to the Moon and build a lunar space station : the Lunar Gateway [64]. Such journey and infrastructure could allow the development of similar astrobiology and astrochemistry experiment in the vicinity of the Moon, as a continuity of the exposure facilities on the ISS. Moreover, out of the magnetospheric protection of the Earth, samples would be exposed to a significant level of radiations and UV (chapter 3). However the ability to perform *in-situ* analysis imposes either to carry on-board a sufficient memory or the ability to regularly send data to ground stations. This last constraint can be problematic on such orbit due to its distance for earth for instance [65].

Such phase A analysis, focused on the study of organic molecules, relies on the use of miniature components for CubeSats, to minimize the cost and weight of the payload. Nevertheless, miniaturisation is restraining the performance capacity of some instruments as well as the samples quantity to be carried on-board. While technological development is more and more expanding, one can expect that future developments will allow

to perform more complex and advanced experiments on CubeSats. In particular, miniature FTIR spectrometers operating in at bigger IR wavelengths are under development [23]. Such instrument could provide data deeper into the fingerprint region and thereby precise information on molecular structures. The development of miniature lasers is also meaningful to perform laser-induced-fluorescence on board of CubeSats.

To conclude, the field of astrochemistry experiments in space has still room for innovation and new discoveries to be made. Although space exploration is a thrilling scientific topic, one must not forget that the struggle scientists express to explain how life was brought to Earth, shall remind us of the scarcity of our living world. The preservation of our biodiversity, which is the consequence of such a barely explicable chance, can only be possible by maintaining the exploration of space for scientific purposes.

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List of abbreviations and symbols

Name	Description
ISM	interstellar medium
PAH	polycyclic aromatic hydrocarbon
LEO	low earth orbit
MEO	mid-earth orbit
GEO	geo-synchronous earth orbit
ISS	international space station
UV-Vis	ultra-violet-visible
IR	infrared
NIR	near infrared
MIR	mid infrared
NMR	nuclear magnetic resonance
FTIR	fourier transform infrared spectrometer
GCR	galactic cosmis rays
SEP	solar energetic particles
P/L	payload
EPS	electronic power system
TCS	thermal control system
OBDH	on-board data handling
STR	structure
LIF	laser induced fluorometer
COTS	commercial off-the-shelf
MCT	mercure cadnium telluride
TRL	technology readiness level

Table 7.1: Abbreviations

Variable	Description	SI unit
$\lambda_{excitation}$	Excitation wavelength	m
$\lambda_{emission}$	Fluorescent emission wavelength	m
σ	Wavenumber	cm^{-1}
A	Absorbance	/
I	Transmitted intensity	cd
I_0	Reference intensity	cd
I_f	Fluorescence intensity	cd
I_A	Absorbed intensity	cd
ϵ	Absorptivity/molar exctinction coefficient	$l * mol^{-1}$
l	Optical length	cm
Φ_f	Fluorescence quantum efficiency	/
R^2	Coefficient of determination	/

Table 7.2: Symbols