# Photochemical studies in low Earth orbit for organic compounds related to small bodies, Titan and Mars. Current and future facilities.

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**Abstract:** The study of the evolution of organic matter subjected to space conditions, and more specifically to solar photons in the vacuum ultraviolet range (120-200 nm) has been undertaken in low Earth Orbit since the 90's, and implemented on various space platforms. The most recent exposure facilities are BIOPAN outside the Russian automatic capsules FOTON, and EXPOSE-E & -R (1&2) outside the International Space Station. They allow the photolysis of many different samples simultaneously, and provide us with valuable data about the formation and evolution of organic matter in the Solar System (meteorites, comets, Titan's atmosphere, the Martian surface...) and in the Interstellar Medium. They have been used by European teams in the recent past

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(ORGANIC on BIOPAN V-FOTON M2 and UVolution on BIOPAN VI-FOTON M3, PROCESS on EXPOSE-E, AMINO and ORGANICS on EXPOSE-R), and a new EXPOSE set is currently exposed outside the ISS (PSS on EXPOSE-R2). These existing tools are very valuable; however, they have significant limitations that limit their capabilities and scientific return. One of the most critical issues for current studies is the lack of any in-situ analysis of the evolution of the samples as a function of time. Only two measurements are available for the experiment: one before and one after the exposure. A significant step forward has been achieved with the O/OREOS NASA nanosatellite and the OREOcube ESA project with onboard UV-visible measurements. However, for organic samples, following the evolution of the samples would be more informative and provide greater insight with infrared measurements, which display specific patterns characteristic of major organic functionalities in the mid-infrared range (4000-1000 cm<sup>-1</sup>).

## **1** Introduction

Organic matter thought to be the starting material for prebiotic chemistry could have partly had an extraterrestrial origin (Chyba & Sagan 1992). This addition could have been performed by an intense phase of bombardment by comets (Oro & Cosmovici 1997), meteorites (Sephton 2002) and micrometeorites (Dobrica et al. 2011), which contain organic molecules. The extent to which such extraterrestrial contribution may have had a significant contribution depends both on the intensity of the extraterrestrial bombardment on early Earth (Nice model and Late Heavy Bombardment and other scenarii, Morbidelli 2010) and the stability of the imported space organic material versus solar radiation, especially if they are not efficiently protected by the mineral component of the extraterrestrial objects. In order to test this hypothesis, it is necessary to study the conditions in which these molecules could have been imported to a primitive atmosphere, and their stability in space.

Photochemistry is one of the main factors of chemical evolution of organic matter in the Solar System, in particular in the vacuum UV (100-200 nm). Under this radiation, molecules can be photolysed and, in the long term, organic matter can be transformed or destroyed. For instance, organic matter contained in micrometeorites could be destroyed by solar radiation before reaching the atmosphere of a planet. Solar radiation may also affect organic chemistry in planetary environments, such as the atmosphere of Titan where complex chemistry occurs (Waite et al. 2007) and turns light gaseous organic compounds such as methane, into heavy and solid organic aerosols. It can also erase the organic traces of past life at the surface of planets, such as Mars (Oro & Holzer 1979; Stalport et al. 2010a).

This review paper provides an outlook about our main recent implementations of exposure experiments in low Earth orbit, a description of the hardware used, as well as some possible evolution of such experiments in the future.

### 2 Ground laboratory experiments and space exposure

Numerous experimental programs are conducted to study the photostability of solid and gaseous organic compounds in the laboratory. However, this kind of experiments is facing problems: for example, it is extremely difficult to simulate the whole spectrum of wavelength corresponding to the most energetic part of solar radiation (Figure 1). This results in important difference between kinetics measurements related to photochemistry measured directly in space and similar experiment conducted in "classical" ground laboratories and then extrapolated to space conditions (Figure 2)(Guan et al. 2010). Moreover, these simulations do not take into account simultaneously UV rays, the variation of temperature, the solar wind and the cosmic rays. The laboratory experimental simulations are then advantageously complemented with in situ experiments in order to evaluate to which extent

they reflect the reality of spatial environment. In the last decade, six experiments in low Earth orbit have been implemented: ORGANICS (Ehrenfreund et al. 2007), UVolution (Cottin et al. 2008; Stalport et al. 2010a,b; Guan et al. 2010), PROCESS (Bertrand et al. 2012; Cottin et al. 2012; Noblet et al. 2012), ORGANIC (Bryson et al. 2015), AMINO (Bertrand et al. 2015; Carrasco et al. 2015; Cottin et al. 2015; Vergne et al. 2015) and PSS. Most of these experiments (Figure 3) are held outside the International Space Station (ISS) in the EXPOSE facilities (Figure 4).

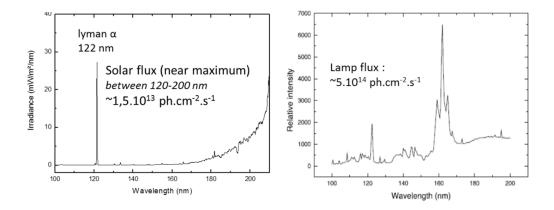


Figure 1: Comparison between the solar spectrum between 100 and 200 nm (Thuillier et al. 2004) (left) and a typical laboratory UV lamps (H2) (Cottin et al. 2003) (right). To date, no laboratory lamp is able to accurately simulate the solar spectrum in the VUV.

These astrochemistry experiments have been selected by ESA (European Space Agency). These projects mostly study molecules of cometary interest (in order to understand the results of the ROSETTA mission), the chemistry of Titan (mission Cassini-Huygens), or the organic chemistry of the Martian environment (Curiosity, ExoMars project). The main results of these experiments are summarized below.

- The ORGANICS experiment was flown on BIOPAN-5 in 2005 (Ehrenfreund et al. 2007). The small fluence that was collected during the FOTON capsule flight was not sufficient to measure any photo-destruction. However, the results confirmed that PAH molecules are very stable compounds in space.
- The UVolution experiment on BIOPAN-6 in 2007 (14 days in orbit, and about 30 hours of direct sun exposure) successfully tested the exposure of gas mixtures in space in sealed cells and compared the kinetics of photolysis in space and in the laboratory for solid state samples related to comets and Mars. The results have shown that current extrapolation procedures of laboratory simulations to space conditions (typically by taking into account only the influence of the Lyman  $\lambda$  line at 122 nm) are extremely hazardous and can lead to errors of a factor 100 on the kinetics for some molecules (Guan et al. 2010). The case of Martian simulations is more favorable, showing that the lamps simulating the UV flux reaching the surface of Mars ( $\lambda > 190$  nm) are more acceptable than in the case of unfiltered flux. However, there still remains a factor of 2 to 13 between space and lab results depending on the molecule (Stalport et al. 2010a). Interestingly, UVolution results have shown that the photolysis of organic molecules is activated by the presence of a mineral analogue of Martian soil. Stability of carbonates have also been studied, but the duration of the exposure was too low to be significant (Stalport et al. 2010b).
- PROCESS was part of the payload of EXPOSE-E on the EUTEF facility from February 2008 until September 2009 after 1.5 year in space ( $\sim$  1500 hours of direct Sun exposure). Samples

Molecule	J measured in space (s-1)	J' measured in the lab. (s-1)	J' extrapolated at 1 AU (s-1) (lyman α)	Ratio (space/lab.) (lyman α)	J' extrapolated at 1 AU (s-1) (115-200 nm)	Ratio (space/lab.) (115-200 nm)
glycine	1,0E-06	8,6 10 <sup>-6</sup>	6E-09	167	1E-07	10
adenine	< 1,9E-7	2,7 10-7	8E-10	< 238	1,5E-08	< 13
guanine	< 1,9E-7	< 2,7 10 <sup>-7</sup>	< 8,2 10 <sup>-10</sup>		< 8,2 10 <sup>-10</sup>	
xanthine	5,0E-07	1,3 10 <sup>-6</sup>	4E-09	125	7E-08	7
hypoxanthine	< 1,9E-7	3,7 10 <sup>-6</sup>	1,1E-08	< 17	2E-07	< 1
urea	< 1,9E-7	< 2,7 10 <sup>-7</sup>	< 8,2 10 <sup>-10</sup>		< 8,2 10 <sup>-10</sup>	
C3O2 polymer(*)	1,3E-06	1,3 10 <sup>-5</sup>	1,1E-08	118	2E-07	6,5
polyHCN	8,0E-07	2,0 10 <sup>-6</sup>	2E-09	400	3,5E-08	23

(\*) CN band

Figure 2: Comparisons between kinetics photolysis constant J measured in space and in the laboratory. The first two columns are results from measurements (1) in space and (2) in the laboratory, the 3rd column gives values of J measured in the laboratory extrapolated to space conditions assuming the whole photolysis occurs at Lyman  $\alpha$  only, and the next column is the ratio between J measured in space and J measured in the laboratory and extrapolated to space calculated for this first hypothesis. The 5th column gives values of J measured in the laboratory extrapolated to space conditions assuming photolysis occurs up to 200 nm. The last column is the ratio calculated for this second hypothesis.

EXPERIMEN T	SUPPORT	LAUNCH/RETURN	DURATION IN ORBIT	INTEREST FOR
ORGANICS	BIOPAN 5 (FOTON capsule)	May 31 <sup>st</sup> 2005 - June 16 <sup>th</sup> 2005	15,8 days	Interstellar medium
UVolution	BIOPAN 6 (FOTON capsule)	September 14 <sup>th</sup> 2007 – September 26 <sup>th</sup> 2007	11,8 days	Comets, Titan, Mars
PROCESS	EXPOSE-E on the ISS	February 2008 - August 2009	18 months	Comets, Titan, Mars, meteorites
AMINO	EXPOSE-R on the ISS	March 2009 - March 2011	24 months	Comets, Titan, meteorites
ORGANIC	EXPOSE-R on the ISS	March 2009 – March 2011	24 months	Interstellar medium
PSS	EXPOSE- R2 on the ISS	24/07/2014 – end of 2015/early 2016	In progress (12 to 18 months)	Comets, Titan, Mars, meteorites, interstellar medium, biochips

Figure 3: Recent astrochemistry experiments conducted in low Earth orbit.



Figure 4: The EXPOSE-R ESA facility outside the Russian Zvezda module of the Interstellar Space Station (Picture credit: STS-129 Crew, NASA).

exposed in PROCESS were in the solid or in the gaseous phase. Open and closed cells were used. A total of 40 samples were exposed to space in PROCESS. Measurements regarding the photostability of amino and carboxylic acids were conducted, and lifetimes calculated (Bertrand et al. 2012; Cottin et al. 2012; Noblet et al. 2012). The exposure cells designed for gaseous samples were not tight enough to ensure that the mixtures did not leak into space (Cottin et al. 2012). This aspect was significantly improved for the AMINO experiment.

- The ORGANIC experiment (Bryson et al. 2015) was one of 10 experiments integrated into the EXPOSE-R multi-user facility mounted on an external platform of the Service Module Zvezda, part of the Russian Segment of the ISS. The ORGANIC experiment exposed thin films (typically 100 300 nm) of selected Polycyclic Aromatic Hydrocarbons (PAHs) and fullerene-type molecules to an interplanetary environment. ORGANICS spent 682 days outside the ISS from 2009 to 2011, providing continuous exposure to the cosmic-, solar-, and trapped-particle radiation background and >2500 h of unshadowed solar illumination
- The AMINO experiment was also part of the payload of EXPOSE-R. As in the ORGANICS experiment, 30 samples were exposed to space. Open and closed cells were used (Cottin et al. 2015). Samples were made of new amino acids mixtures (Bertrand et al. 2015), and gaseous samples in new extremely tight cells that have proven to be sufficiently tight. Photochemistry of methane has been for the first time studied in space in a quantitative manner (Carrasco et al. 2015). However, the VUV transmission of the closed cells MgF<sub>2</sub> windows was degraded during the industrial process for their production. We have addressed this issue for the new PSS experiment. The entire EXPOSE-R facility was however subjected to an important contamination most probably originating from the facility itself (Demets et al. 2015). This has jeopardized

the analysis of the results of some of our samples.

• PSS is part of the EXPOSE-R2 facility. This is a new use of the EXPOSE-R facility, for which we hope a contamination event similar to the one that occurred in EXPOSE-R won't happen again. Hardware has been optimized in order to accommodate more samples (75 exposed samples) and new kind of samples still mostly related to meteorites, comets, Mars, Titan, with addition of new subjects such as interstellar medium and biochips (Vigier et al. 2013).

## 3 Current facilities

### 3.1 EXPOSE, open and closed cells

The EXPOSE facility is shown in Figures 5 and 6. Three experiment trays are equipped with four squared sample carriers. Sample carriers for experiments related to astrochemistry can contain up to 25 sample cells with  $MgF_2$  windows allowing the transmission of UV photons down to 110 nm. ESA usually provides selected experiments with sample cells that are open (or vented), towards open space, or semi-tight (called here RUAG closed cells). This results in the loss of gaseous compounds produced by the degradation of the exposed refractory molecules. It also makes the irradiation of gaseous mixtures impossible. Since one of our goals is also to analyze gaseous compounds, the scientific team at LISA, and CNES, has been working on the development of closed cells (called here CNES closed cells) which have been used since 2007 and continuously improved since then.

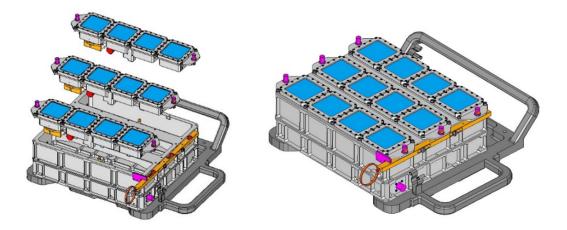


Figure 5: The EXPOSE facility (480 x 520 x 327,5 mm) is made of three experiment trays into which four square sample carriers (77 x 77 x 26 mm) are fitted. Pictures courtesy of RUAG/Kayser-Threde GmbH.

#### 3.1.1 Open cells.

Open cells used in the PSS experiment on EXPOSE-R2 are shown in Figure 7. Both configurations can be used for P.S.S. Samples are deposited on the inner side of the window (MgF<sub>2</sub>). Such cells are used for pure kinetics studies of solid organic compounds. Gaseous photoproducts cannot be analysed because they are vented to space. This effect is beneficial for accurate kinetic measurements because the gases cannot interact with the sample as it would be the case in a closed cell.

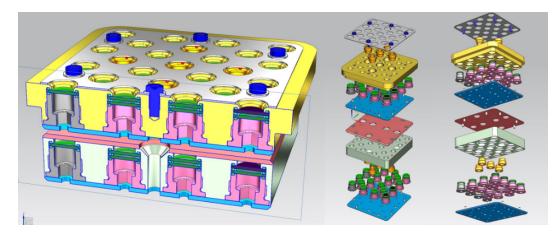


Figure 6: Sample carrier for PSS was designed to receive up to 25 exposure cells. They can accommodate open cells (grey) RUAG closed cells (purple) or CNES closed cells (yellow, more easy to see on the right panel). Two layers of samples are flown at the same time: one layer exposed to space, and one layer right below acting as a flight control layer. Pictures courtesy of RUAG/Kayser-Threde GmbH.

#### 3.1.2 RUAG closed cells.

For some samples, a slightly different configuration is used, called RUAG closed cells (Figure 8). Two discs separated by a spacer are accommodated inside the sample carrier and locked with a bushing. This configuration can be used for semi-volatile samples to prevent their passive pumping towards space. Those cells however are not tight enough to be used for gaseous samples, or if one wish to keep the gaseous photoproducts of solid samples. Incidentally this configuration is protecting samples in case of contamination event from the inside of the facility. RUAG closed cells are also used for radiation measurements conducted on graphite disks samples, for safety reason since those samples are extremely fragile.

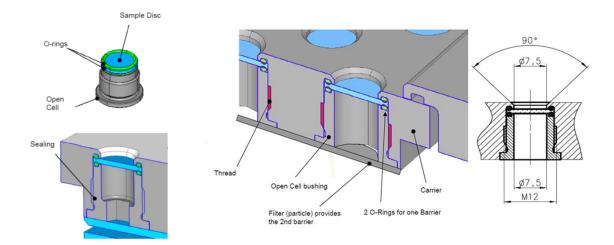


Figure 7: When open cells are used, samples are deposited on a  $MgF_2$  disc which is accommodated in a sample carrier and held by a bushing screwed from below. The organic sample is deposited onto the inside face of the window. Picture courtesy of Kayser-Threde GmbH/RUAG.

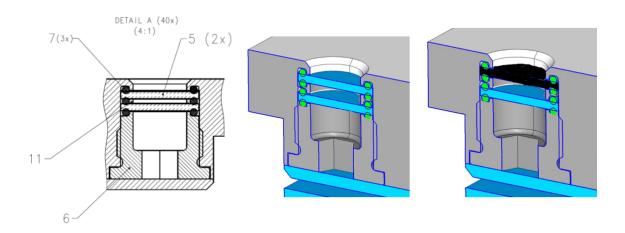


Figure 8: RUAG closed cells are made of two discs accommodated in a sample carrier with a bushing. The organic sample is deposited onto the inside face of the upper window. This upper window can be replaced by a graphite disk. Picture courtesy of Kayser-Threde GmbH/RUAG.

#### 3.1.3 CNES closed cells

CNES closed cells can be used either to study the photolysis of a gaseous mixture (simulation of an atmosphere), the photolysis of a solid molecule in interaction with a simulated atmosphere (for example a molecule at the surface of Mars), or to collect the photodissociation products of a solid molecule, in addition to results derived from exposition in open cells. CNES closed cells have been used in UVolution, PROCESS, AMINO and PSS (Figure 9). Although the concept is the same since 2007, the manufacturing process has drastically changed since their first use in UVolution and PROCESS. The first generation of closed cells was made of two aluminium cylinders which where screwed one into the other. A MgF<sub>2</sub> window was glued at each end of the cell. Tightness was ensured by a Viton O-ring between the two parts. It has been shown that, although the level of vacuum-tightness is sufficient for short duration experiments like UVolution (14 days in space, and roughly one month between the preparation of the samples, and their analysis after return), it is not enough for long duration experiments such as the ones conducted outside of the space station. Some of the PROCESS CNES closed cells were empty when they returned to Earth. A new generation of closed cells has been manufactured for AMINO, under the supervision Air Liquide (DTA Grenoble, France). This time, the body of the cell is made of stainless steel, the windows are brazed and the vacuum-tightness between the two parts of the cells is ensured by laser soldering. This results in a leak level below  $10^{-10}$  mb L s-1, compatible with long duration experiments in orbit (loss < 10% for 2 years in space). Unfortunately, we have shown that the manufacturing of these new cells results in an uncontrolled degradation of the optical properties of the windows in the VUV during the brazing process. Further R&D work has been conducted to optimize the process and closed cells available for PSS. have good VUV transmission properties.

A new significant improvement of the CNES closed cells is the possibility to include specific filters (Figure 10), for instance to turn the CNES closed cell into a Martian simulator if the samples are deposited below a KBr disk (Figure 11b). The outside of the cell remains the same and does not have to get through a series of space qualification process each time we chose a new filter. Such a configuration is used in the PSS experiment. This will allow also conducting specific studies as a function of the wavelength in the future (Figure 11c).

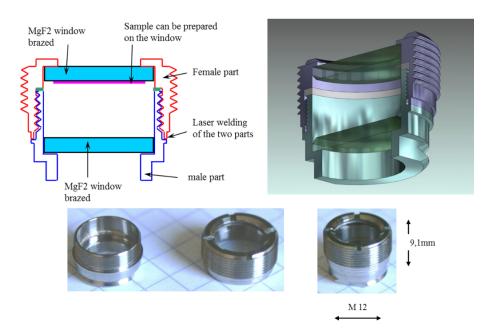


Figure 9: CNES closed cells. For the first generation of CNES closed cells, two aluminum cylinders are screwed into each other. Two  $MgF_2$  were glued at both ends to allow the analysis of molecules inside the cell by spectroscopy. Sealing (relative to lab atmosphere or vacuum in space) was ensured by a Viton O-ring. For the new generation of closed cells used since the AMINO experiment, the body is made of inox, windows are brazed, and sealing is ensured thanks to laser soldering.

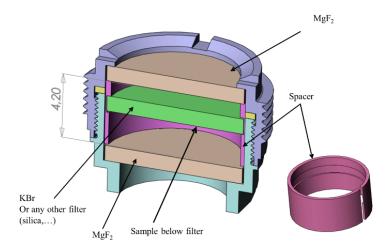


Figure 10: CNES closed cell use in a configuration with a specific filter. VUV photons down to 115 nm are transmitted through the upper  $MgF_2$  window and then filtered by an appropriate material onto which the sample is deposited. In the case of a Martian simulation, the filter is KBr.

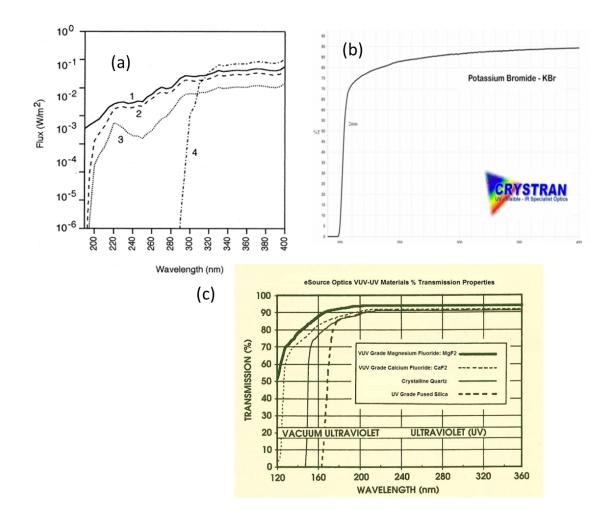


Figure 11: (a) Estimated irradiance curve in the UV: 1. at the top of the Martian atmosphere, 2 & 3. at the surface of Mars for various inclination and seasons, 4 at the surface of the Earth (from Cockell 1999). (b) Transmission spectrum of a 2 mm thick KBr window, to be compared with curve (a)-2. (c) Various filters that could be used for wavelength sensitivity studies in future experiments. CaF<sub>2</sub> could be used to get rid of the Lyman  $\alpha$  line, as well as different kind of quartz and silica (source: eSource Optics / Whitinsville, MA USA).

#### 3.2 Sample preparation

Solid samples can be prepared in a vacuum sublimation system, similar to the one described in Ten Kate et al. (2005) and Guan et al. (2010). Such systems are available at LISA, LEIDEN observatory and NASA AMES. The thickness of the deposit can be monitored by interferometry in order to ensure that the sample will be homogeneously photolysed in space. Solid samples that cannot be sublimated prior to being degraded are deposited using an evaporative method. This involves firstly dispersing the molecule as a powder throughout a solvent to prepare a suspension by mechanical agitation and then depositing this solution in the cell. Finally, the sample is obtained after the total evaporation (vacuum evaporation) of the solvent. This method is described in Boillot et al. (2002). Additionally, some organic solids samples have been prepared at INAF-OACt by 200 keV He<sup>+</sup> irradiation of frozen icy mixtures, directly on the MgF<sub>2</sub> windows meant to be included in the open cells (Baratta et al. 2014). These residues simulates organic material in some astrophysical environments as comets.

Gaseous samples are prepared in an "analytical cell" such as the one shown in Figure 12. Although called "analytical", it is used for both filling and sampling the sealed cells with gas, and for infrared analysis of the gaseous content of the sealed cells. It consists of two main stainless steel parts on the

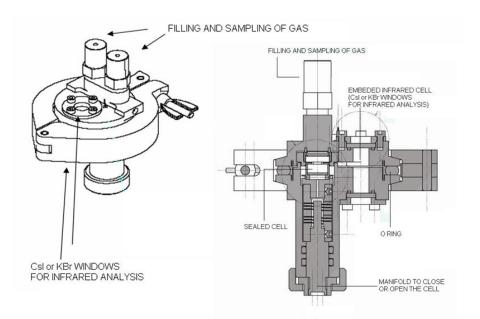


Figure 12: Design of the analytical cell. It allows the filling or sampling of gases inside a sealed cell, which can be fitted inside the holder. An embedded infrared cell can be used for the analysis of gases in the infrared range. Picture courtesy of COMAT aerospace.

inside of which both parts of a CNES closed cell are separately fitted. The two analytical cell parts are adjusted one opposite the other. The gaseous component of the experiment can then be introduced inside the analytical cell before screwing the two parts of the closed cell one into the other, using a screw connecting one part of the sealed cell to the outside of the analytical cell, thus enclosing the gases inside the sealed cell. The closed cell can then be removed from the analytical cell, soldered by laser, and placed onto a sample holder for the experiment in space.

### 3.3 Sample exposure principle

For each kind of sample (pure molecule, mixture...), the following pattern is applied: two cells are exposed (first layer on the left of Figure 11, exposed to the influence of UV, cosmic rays, temperature, vacuum), two cells act as flight dark control (second layer in the right of Figure 13, exposed to the influence of transmitted cosmic rays, temperature, vacuum). On the ground at DLR Cologne (Germany), sample cells are stored in a vacuum facility, either photolyzed by a ground solar simulator  $\lambda > 190$  nm only) or in the dark, and have a temperature history similar to the samples in space (transmitted via telemetry for study of the influence of temperature and vacuum), and a last set of two cells are stored in a vacuum facility at 5°C (to study the influence of vacuum).

### 3.4 Sample analysis

Samples can be measured by VUV, UV-Vis, Raman and IR spectroscopy before launch and after retrieval. From the results, constraints on the photochemical reactivity of these compounds can be derived and the kinetic details of photochemical degradation characterized. Additionally gas chromatography-mass spectroscopy (GC-MS) analysis of all the samples after retrieval can be conducted, comparing the UV-exposed and ground control samples in order to identify photo-products and fragments that cannot be unambiguously determined via optical spectroscopy. Additional laboratory experiments include ground control sample exposure to a UV  $H_2$ -discharge lamp illumination

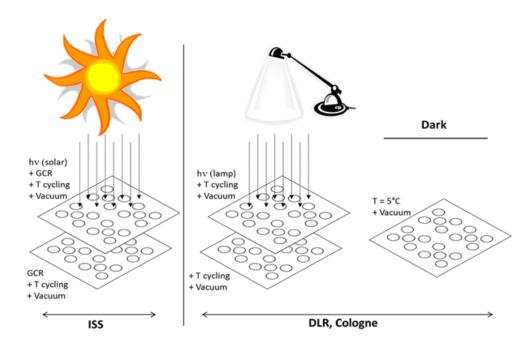


Figure 13: Scheme showing the experimental breakdown of samples between the ISS and DLR Cologne, and the environmental conditions to which they are exposed. In the recent case of the PSS experiment a total of 75 samples can be exposed directly in LEO, with 75 dark controls directly below them (A). The same disposition is reproduced in an irradiation chamber at DLR Cologne (B), with an additional series of samples that will be kept in vacuum, in the dark, at  $5^{\circ}C(C)$ . (only one sample carrier position shown in the figure).

to provide short-wavelength, high-energy UV radiation that simulates interplanetary and interstellar conditions, respectively. After processing of the measurements, it is possible to calculate the photochemical lifetime of the molecule at 1 AU, which can subsequently be extrapolated at other heliocentric distances and other astrophysical environments (diffuse interstellar medium, dark clouds).

## 4 Limits and way towards future facilities

With the current space exposure facilities such as BIOPAN (Demets et al. 2005) and EXPOSE (Rabbow et al. 2012), only passive exposure facilities are available, with only two measurements points to derive the kinetics: one before flight and one after. Recently, the NASA O/OREO nanosatellite has offered the possibility to measure the evolution of organic sample with an onboard UV-Vis spectrometer (Mattioda et al. 2012). The follow up of this project is currently under development by ESA and is called OREOCUBE (Elsaesser et al. 2014). OREOCUBE was selected in the pool of the ILSRA 2009 projects. It is an implementation of the O/OREO NASA nanosat payload instrument for ISS. The facility is made of an identical pair of 10-cm cube instruments, each weighing < 2 kg and containing a UV-visible-NIR spectrometer, a 24-sample carousel, and optics enabling the use of the Sun as light source for spectroscopy along with the electronics, microcontroller, and data storage to make each cube an autonomous stand-alone instrument requiring only a standard power-and-data interface.

A next step would be to implement a mid-infrared in-situ diagnostic to follow the evolution of the samples during exposure as a function of time. Infrared spectrometry would have the advantage over UV that it would allow a careful monitoring of the sharp infrared features of organic molecules between 4000 and 1000 cm<sup>-1</sup>, and identify new molecules produced during the photolysis. A concept diagram of the instrument is shown in Figure 14. Such a concept is currently under study with CNES

support. A compact design inspired by cubesat technology would enable the use of this tool either outside the International Space Station or within cubesats or as a "hitch-hiker" on planetary missions. This could therefore be used much beyond the current expected lifetime of the International Space Station.

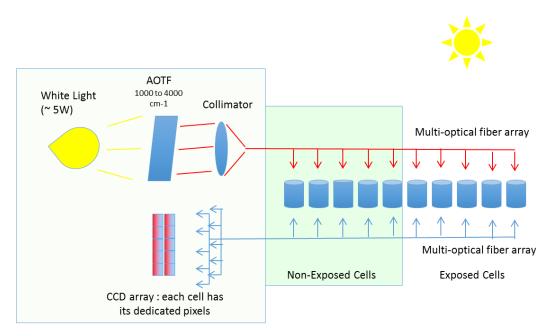


Figure 14: Concept diagram of an exposure platform with an infrared spectrometer for in situ diagnostic of the evolution of the exposed samples. Cells would have the same geometry than the ones used in EXPOSE.

## 5 Conclusions

Hardware developments in the last ten years have substantially broadened the range of astrochemical and exobiological experiments conducted in Earth Orbit. Since the first experiments lead by A. Brack and B. Barbier at Centre de Biophysique Moléculaire (CNRS, Orléans, France) (Barbier et al. 1998), the possibilities to expose a large variety of organic samples, with the intent to measure quantitative kinetics data about the photostability of organic molecules have been enhanced. Now, thin homogeneous organic film can be prepared and exposed, as well as gaseous mixtures.

However, there are limitations to the current facilities. Passive exposure platform like EXPOSE do not allow direct in situ measurements of the evolution of the samples. New generation platforms such as the O/OREOS NASA nanosat (Mattioda et al. 2012; Ehrenfreund et al. 2014) and the forthcoming Oreocube platform outside the ISS (Elsaesser et al. 2014) allow in situ measurement in the UV-Vis domain. Beyond these recent platforms, the next generation of exposure facilities should enable a mid-infrared diagnostic for a greater science return. This would be the next step to achieve a significant improvement in exposure facilities. One step beyond, for the study of the organic chemistry of the outer solar system (icy satellites, comets), and dense molecular clouds, which occurs at low temperature, enabling the exposure of samples as ice mixtures would also be another major feature to be implemented in space.

The environmental conditions of the exposure platforms are a last issue to address. Experiments conducted in low Earth orbit are efficiently protected by the Earth radiation belt from most of the high energy particles (galactic cosmic rays and solar wind radiations). New space exposure studies

should be implemented in other environments than the low Earth orbit, either with higher inclination regarding the Earth plane (polar orbit) or higher altitude (geocentric transfer orbit). Great challenges are still ahead to develop the most suitable exposure platforms, but we are confident that the science return of these new and ambitious programs will be significant.

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## References

Baratta, G.A. et al. 2014, in European Planetary Science Congress (EPSC), EPSC2014-49, vol. 9 Barbier, B. et al. 1998, Planetary and Space Science, 46(4), 391-398 Bertrand, M. et al. 2012, Astrobiology, 12(5), 426-435 Bertrand, M. et al. 2015, International Journal of Astrobiology, in press, DOI: 10.1017/S1473550414000354 Boillot, F. et al. 2002, Origins of Life and Evolution of the Biosphere, 32, 359-385 Bryson, K.L. et al. 2015, International Journal of Astrobiology, in press, DOI: 10.1017/S1473550414000597 Carrasco, N. et al. 2015, International Journal of Astrobiology, in press, DOI : 10.1017/S1473550414000238 Chyba, C. & Sagan C. 1992, Nature, 1992, 355, 125-32 Cottin, H., M.H. Moore, & Y. Bénilan, 2003, The Astrophysical Journal, 590, 874-881 Cottin, H. et al., 2008, Advances in Space Research, 42(12), 2019-2035 Cottin, H. et al. 2012, Astrobiology, 12(5), 412-425 Cottin, H., et al. 2015, International Journal of Astrobiology, in press, DOI: 10.1017/S1473550414000500 Demets, R., W. Schulte, & P. Baglioni 2005, Advances in Space Research, 36, 311-316 Demets, R. et al. 2015, International Journal of Astrobiology, in press, DOI: 10.1017/S1473550414000536 Dobrica, E. et al. 2011, Meteoritics & Planetary Science, 2011, 46(9), 1363-1375 Ehrenfreund, P. et al. 2007, Planetary and Space Science, 55(4), 383-400 Ehrenfreund, P. et al. 2014, Acta Astronautica, 93, 501-508 Elsaesser, A. et al., Organics Exposure in Orbit (OREOcube): A Next-Generation Space Exposure Platform. Langmuir, 2014 Guan, Y.Y. et al. 2010, Planetary and Space Science, 58, 1327-1346 Mattioda, A. et al. 2012, Astrobiology, 12(9), 841-853 Morbidelli, A. 2010, Comptes Rendus Physique, 11 Noblet, A. et al. 2012, Astrobiology, 12(5), 436-444 Oro, J. and Holzer, G. 1979, 14(1-3), 153-160 Oro, J. & Cosmovici C.B., 1997, in Proceedings of the 5th International Conference on Bioastronomy; Editrice Compositori: Bologna, Italy., eds C.B. Cosmovici, S. Bowyer, and D. Werthimer, 97-120 Rabbow, E. et al. 2012, Astrobiology, 12(5), 374-386 Sephton, M.A., 2002, Natural Product Reports, 19(3), 292-311 Stalport, F. et al. 2010a, Astrobiology, 10(4), 449-461 Stalport, F. et al., 2010b, Planetary and Space Science, 58, 1617-1624 Ten Kate, I.L. et al. 2005, Meteoritics and Planetary Science, 40, 1185 Thuillier, G. et al. 2004, in Proceedings of the American Geophysical Union: Washington, DC, eds J.M. Pap and P. Fox, 171-194 Vergne, J. et al. 2015, International Journal of Astrobiology, in press, DOI: 10.1017/S147355041400024X Vigier, F. et al. 2013, Advances in Space Research, 52(12), 21682179 Waite, J.H., et al. 2007, 2007, 316, 870-875