FROM ASTROPHYSICS TO ASTROCHEMISTRY TOWARDS ASTROBIOLOGY

IV Workshop della Societa' Italiana di Astrobiologia

Dipartimento di Chimica, Università degli Studi di Perugia
September 19-21, 2012

BOOK OF ABSTRACTS

Edited by Nadia Balucani

Virt&l-Comm Special Issue (2012). Published by: MASTER-UP S.R.L. ISSN: 2279-8773
Virt&l-Comm is a new international online electronic scientific magazine offering a forum for presenting the work carried out by Virtual Innovation, Research, Teaching & Learning Communities. This magazine is the result of a joint endeavour of the COMPCHEM Virtual Organization (VO), of the European Chemistry Thematic Network (ECTN) Association and of the University of Perugia spinoff Master-Up.

Virt&l-Comm is a scholarly open access online Magazine requiring no payment neither from the authors nor from the readers.

Virt&l-Comm publishes at present two issues per year to promote Molecular and Materials Science, Teaching and Learning, Computer Science research. The magazine is also specialized in education and innovation and focuses on Service Oriented approaches. Therefore, in addition to articles, news, projects, reports of (successful or failed) attempts to build services relevant to the field of interest, lists of best practices, products used, the advantages and disadvantages of the solutions adopted will be considered for publication. In particular, all the information useful to build the puzzle of innovative complex applications in education (EDU), information and communication technology (ICT) and research and development (R&D) in Molecular and Materials science are welcome.

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The cover picture has been shot by Nadia Balucani (with the help of Arianna and Dimitris Skouteris) at Sarakiniko (Milos, Cyclades Islands).
It could represent one of the “warm little ponds” - far from the ocean currents - where the very first forms of life have originated, as suggested by Darwin.
IV Workshop Italian Astrobiology Society
“From Astrophysics to Astrochemistry towards Astrobiology”

PROGRAMME

Wednesday, September 19

8.30 – 9.30
Registration

9.30
Welcome and opening remarks
(Prof. Fausto Elisei, Preside della Facoltà di Scienze MM FF NN; Prof. Antonio Laganà, Direttore del Dipartimento di Chimica; Dr. John R. Brucato, Presidente della Società Italiana di Astrobiologia)

10.00-10.45
Cecilia Ceccarelli (Institute de Planétologie et d'Astrophysique de Grenoble) Solicited Our Chemical Origins

10.45-11.30
Raul Baragiola (Univ. of Virginia)
UV-induced Molecular Synthesis below the Surface of Icy Satellites: Implications for Extraterrestrial Ice

11.30-12.00 Coffee Break

12.00-12.20
Angela Occhiogrosso (University College London)
Modelling of Methyl Formate Formation Towards Various Astronomical Environments

12.20-12.40
Savino Longo (Univ. Bari)
Simple models of meteor entry in planetary atmospheres

12.40-13.00
Tommaso Grassi (Univ. Roma “La Sapienza”)
Studying the Chemical Evolution of ISM Regions Via Numerical Methods

13.00-15.00 Lunch Break

15.00-15.45
Wolf D. Geppert (Stockholm Univ.) Solicited Formation of Biomolecule Precursors in Space

15.45-16.05
Cristina Puzzarini (Univ. Bologna)
Astrophysical Investigations: the Role Of Rotational Spectroscopy
Sonia Melandri (Univ. Bologna)
*Flexibility in Complex Organic Molecules: a Challenge for Spectroscopy and Computational Methods*

16.25-17.00 Coffee Break

17.00-17.20
John R. Brucato (INAF-Obs. Arcetri)
*MarcoPolo-R: Asteroid Sample Return Mission*

17.20-17.50
Renè Demets (ESTEC-Noordwijk)
*ESA Astrobiology – an Overview*

17.50-18.10
Gian Paolo Tozzi (INAF-Obs. Arcetri)
*Organic Ice in Comet 103P/Hartley 2 at the Time of the EPOXI Mission Fly-By*

18.10-18.30
Franco Cataldo (INAF-Obs. Catania)
*Solid State Radiolysis of Non-Proteinaceous Amino Acids: Astrobiological Implications*

18.30-18.50
Nadia Balucani (Univ. Perugia)
*The Reactions of Atomic Oxygen with Unsaturated Hydrocarbons in Extraterrestrial Environments*

Thursday, September 20

9.00-9.45
Piero Ugliengo (Univ. Torino) *Solicited*
*Interstellar Prebiotic Formation of Glycine, Delivery to Earth and Polymerization on Feldspars*

9.45-10.05
Franco A. Gianturco (Univ. Roma “La Sapienza”)
*Metastable Anions of C-rich Molecules: Dynamics and Role in Planetary Atmospheres and the ISM of Polyynes and PAHs*

10.05-10.25
Silvano Onofri (Univ. Tuscia)
*Safe Travelling Of Microbes Through Outer Space Within Rocks*

10.25-10.45
Giovanni Strazzulla (INAF-Obs. Catania)
*Energetic Processing of Ices and the Search for Life on Enceladus*
10.45-11.05
Oscar Trippella (Univ. Perugia)
*Stellar Origin of Early Solar System Short-Lived Radioactivities and Their Role in Melting and Differentiating Solid Bodies*

**11.05-11.30 Coffee Break**

11.30-12.15
Manuela Coci (Univ. Catania) *Solicited*
*Lithotrophic Bacteria and Archaea in Aquatic Environments*

12.15-12.35
Marco Casarosa (Univ. Firenze)
*Evidence of DNA Primary Damage in Space Environment*

12.35-12.55
Teresa Fornaro (INAF-Obs. Arcetri)
*Adsorption of Nucleic Acid Bases on Magnesium Oxide (MgO): Hints of Life Detection on Mars*

**13.00-15.00 Lunch Break**

15.00-15.45
Giacomo Certini (Univ. Firenze) *Solicited*
*Do Extraterrestrial Soils Exist?*

15.45-16.05
Giovanni Vladilo (INAF – Trieste)
*Studies of Planetary Habitability Performed with Energy Balance Climate Models*

16.05-16.25
Eugenio Simoncini (INTA-CSIC, Madrid)
*Thermodynamics Disequilibrium as a Parameter to Redefine Habitability*

16.25-16.45
Guido Barone (Univ. Napoli “Federico II”)
*The Possible Role of Clathrate Hydrates as Storage and Sink for Prebiotic Molecules in Extreme Conditions*

**16.45-17.15 Coffee Break**

17.30-19.00
*RUND TABLE* “Da Armstrong a Curiosity, da Marte alle galassie. Biomedicina spaziale e ricerca di vita aliena' presso la sala del 100dieci (Via Pascoli)
Cecilia Ceccarelli (Institut de Planétologie et d'Astrophysique de Grenoble); Mariano Bizzarri (Presidente del Consiglio Scientifico dell’Agenzia Spaziale Italiana, Università di Roma “La Sapienza”); Rene Demets (ESA-ESTEC); Valfredo Zolesi (Kayser Italia)
**Moderatore:** Fabio Pagan (Biologo, giornalista e divulgatore scientifico)

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Surface-Enhanced Raman Scattering Investigation of Nucleobases Adsorbed on a Martian Meteorite and Samples of Martian Analogue Material

9.20-9.40  
Stefano Stranges (Univ. Roma “La Sapienza”)  
Interaction of Chiral Molecules with Synchrotron Radiation: Enantioselective Study of Oxirane Derivatives

9.40-10.00  
Alessandro Donati (Kayser Italia)  
FEBO: an ASI Facility for Astro- and Exo- Biology Observations

10.00-10.20  
Daniela Billi (Univ. Roma “Tor Vergata”)  
Desert Cyanobacteria Go to ISS: Ground-based Simulations in Preparation of the EXPOSE-R2 Mission

10.20-10.40  
Daniela Ascenzi (Univ. Trento)  
Growth of Organic Molecules in Planetary Atmospheres Via Ion-Molecule Reactions

10.40-11.00  
Domenico Stranges (Univ. Roma “La Sapienza”)  
Ultraviolet Photodissociation of Hydrocarbon Radicals

11.00-11.30 Coffee Break

11.30-11.50  
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N+O Associative Ionization with Formation of NO+: a Viable Route in the Interstellar Medium?

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Marzio Rosi (Univ. Perugia)  
Dimerization of Methanimine and Implications for the Atmosphere of Titan

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Stefano Falcinelli (Univ. Perugia)  
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Michela Delfino (Univ. Tuscia)
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Marco Moracci (CNR – Napoli)
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CONTRIBUTIONS

(in alphabetical order by the name of presenting attendants)
Growth of organic molecules in planetary atmospheres via ion-molecule reactions

Daniela Ascenzi, Paolo Tosi

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Unraveling the growth mechanisms of hydrocarbons (mainly aromatic and polyaromatic) is a challenging topic for understanding the chemical evolution of planetary atmospheres and the interstellar medium, where large molecules, mostly of organic nature, have been observed. Great effort is currently devoted to the modelling of the atmosphere of Titan, Saturn’s largest moon, where numerous heavy hydrocarbons and N-bearing species have been observed during the Cassini-Huygens mission [1]. PAH, nitrile aromatic polymers, fullerenes and polyphenyls have been proposed as potential candidates for the large mass cations and anions detected at ionospheric altitudes. An important role in the growth of large organic molecules is played by ion-molecule association reactions in particular those involving two medium sized pre-formed building blocks. Such type of processes have the advantage – over alternative mechanisms requiring sequential additions of small species - of attaining substantial growth in molecular size within a single reactive encounter.

To shed light on such mechanisms, we are investigating association processes affording covalently bound species, in particular C-C coupling reactions involving phenyl [2], ethyl [3], naphthyl [4] and biphenyl [5] cations with neutral arenes. Ion-molecule reactivity is investigated using tandem mass spectrometric techniques, which allow mass selection and manipulation of both reactant and product ions. The ion under study is generated by dissociative ionization of an adequate precursor, either in an electron impact ion source or in an atmospheric pressure chemical ionization APCI source. The latter source allows the generation of molecular ions with a lower degree of internal excitation than the former. We can estimate branching ratios of ionic products and absolute values of reactive cross sections as a function of the collision energy. A complementary experimental and theoretical approach is necessary to obtain reliable information on reaction mechanisms on systems with a large number of degrees of freedom. We use DFT methods to calculate energy and structures of the most relevant points on the reactive potential hypersurface.

The reactions of atomic oxygen with unsaturated hydrocarbons in extraterrestrial environments

Nadia Balucani, Francesca Leonori, Angela Occhiogrosso, Luca Angelucci, Stefano Falcinelli, Domenico Stranges, Piergiorgio Casavecchia

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The observation in hydrocarbon-rich planetary atmospheres and interstellar clouds of highly unsaturated organic molecules (such as acetylene) poses the question of how these molecules can survive in the upper atmospheres where atomic and radical species are relatively abundant. From a chemical point of view, indeed, each unsaturated C-C bond is a potential site for addition reactions especially when radicals are involved. Part of this puzzle is actually explained by the fact that the reactions of small alkynes, alkenes and dienes with several atomic and radical species (such as atomic carbon or CH, C₂H, C₂ and CN radicals) do not destroy the C-atom skeleton of unsaturated species, but rather elongate it. Notable examples are the reactions between C, C₂, C₂H, CH, CN with acetylene (HCCH) and diacetylene (HCCCCH) which, in laboratory experiments, have been verified to generate the products C₃, C₄H, C₅H₂, C₆H, C₇H, C₈H₂, HC₃N and HC₅N [1]. Some of these species have been identified in hydrocarbon-rich atmospheres, including the atmosphere of Titan or several interstellar objects. Quite interestingly, analogous oxygen-containing highly unsaturated species have not been identified and oxygen is mostly locked in CO₂, H₂CO and CO.

In our laboratory we have started a systematic investigation of several reactions involving atomic oxygen and unsaturated hydrocarbons (C₂H₂, C₃H₄, CH₂CCH, CH₂=C=CH₂) by means of the crossed molecular beam technique with mass spectrometric detection and time-of-flight analysis [2-5]. Quite interestingly, we have observed that C-C bond fission channels are always relevant or dominant reaction pathways. The most illustrative case is the reaction between O and allene (CH₂=C=CH₂) where ~ 90% of the reaction leads directly to the stable products CO+C₂H₄ [5], but also significant fractions of the reactions O+C₂H₂ and O+C₂H₄ lead to the products CO+CH₂ and HCO+CH₃, respectively [2,3]. In other words, the reactions of unsaturated hydrocarbons with atomic oxygen are not only terminating the hydrocarbon growth in oxygen-rich environments, but are also able to convert relatively abundant and widely spread small unsaturated hydrocarbons directly into CO or its precursor HCO. Implications for the chemistry of the planetary atmospheres and interstellar medium will be noted.

UV-induced molecular synthesis below the surface of icy satellites: Implications for extraterrestrial ice

Raúl Baragiola, Jianming Shi, Ujjwal Raut, Jung-Hwan Kim
University of Virginia, Charlottesville, VA, USA.

Mark Loeffler
NASA Goddard Space Flight Center, Greenbelt, MD, USA.

The mass uptake of ambient oxygen in porous ice is enhanced by irradiation with 193 nm photons, due to conversion of O$_2$ into H$_2$O$_2$ and O$_3$. In the presence of carbon, CO$_2$ molecules are also formed. These findings show a new way to synthesize molecules on icy surfaces in the outer solar system at depths much larger than are accessible by typical ionizing radiation, with possible astrobiological implications.
The Possible Role of Clathrate Hydrates as Storage and Sink for Prebiotic Molecules in Extreme Conditions

Guido Barone,1 Elena Chianese2

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2Dipartimento di Scienze Applicate – Università di Napoli “Parthenope”

The syntheses of gas clathrates hydrates was well known from 1810 [1]. Up to the half last century these compounds remain confined as scientific curiosities. From the middle of ‘30 years, the engineers, managing petroleum pipelines in the cold regions (Siberia, Canada and Alaska), discovered the formation of some dirty crystals incrusting the pipes and often blocking the transmission of oil at temperatures near 0 °C or below [2-4].

Today the technological interest is devoted to ascertain the consistency and to study the possibility of exploiting the enormous reservoirs of natural gas clathrates present under the permafrost of circumarctica territories and under the soundings of continental escarpments and oceans. In the following years the existence of large fields of methane and low hydrocarbon hydrates was ascertained in several places, especially under the sedimentary planes, the continental marine shelves and the off shore submarine rifts. Then high attention and economic and technological efforts were directed to the physical-chemical characterization of the hydrocarbon clathrate hydrates and to the exploration and exploitation of these new promising sources of energy [5-7].

In spite of the very large number of papers concerning the natural gas hosted in water clathrates, only few works treated the properties of clathrate hydrates of polar organic molecule [7-12]

Here we would like to summarize the known crystal structures of this kind of inclusion compounds and other physical chemical properties. On this basis we would discuss the possibility that solid cages of water molecules can include, store and protect prebiotic molecules or their precursors (in the extreme conditions of the solar system, as ice powders, inorganic dusts, solid surfaces and micropores), so acting as sinks and sources for more complex processes.

Desert cyanobacteria go to ISS: ground-based simulations in preparation of the EXPOSE-R2 mission

Daniela Billi¹, Mickael Baqué¹, Jean-Pierre Paul de Vera², Petra Rettberg³

¹ University of Rome “Tor Vergata”, Department of Biology, Rome, Italy
² DLR Institute of Aerospace Medicine, Radiation Biology Department, Köln, Germany
³ DLR Institute of Planetary Research, Berlin, Germany

The Low Earth Orbit experiments BOSS (Biofilm Organisms Surfing Space) and BIOMEX (BIOlogy and Mars Experiment) are two interdisciplinary and international space research projects selected by ESA. The experiments will be accommodated on the space exposure facility EXPOSE-R2 on the International Space Station (ISS) and are foreseen to be launched in 2013. These two projects by focusing on extreme tolerant organisms and their cellular components, represent a follow up of previous astrobiology missions on platforms like EXPOSE and BIOPAN and of ground-based experiments, but also involve the exposure of new organisms and the use of novel approaches in astrobiology [1, 2].

BOSS aims to investigate the resistance of microbial biofilms compared to planctonic cultures. Biofilms are among the oldest clear signs of life on Earth and these might also be the first forms of life to be detected on other planets and moons of our solar system. BIOMEX investigates extreme tolerant organisms and their constituents (pigments and cell wall components) embedded within lunar and Mars regolith analogues. Such an approach will provide further understanding of the space resistance of life as we know it in the context of (litho-) panspermia and will contribute to realize a biosignature database for the search of life beyond Earth.

BOSS and BIOMEX experiments will include strains of the desert cyanobacterium *Chroococcidiopsis*; this cyanobacterium is a photosynthetic desiccation-, radiation-tolerant prokaryotes, that thrives in different deserts on Earth including the most extreme ones, like the Atacama Desert, Chile and Dry Valleys, Antarctica [3–5]. It has been selected for the next EXPOSE-R2 mission also because of its resistance to some space constraints tested on the previous space mission EXPOSE-E and ground simulations [6, 7]. Results on its survival and subcellular integrities after exposure to the newly performed ground simulations in preparation for the EXPOSE-R2 mission will be presented.

ILSRA-AO2009 projects BOSS-Cyano and BIOMEX-Cyano have been selected for funding by the Italian Space Agency.

MarcoPolo-R: Asteroid Sample Return Mission


¹INAF-Obs. of Arcetri, I, ²LESIA-Observatoire de Paris, F, ³Univ. Nice, CNRS, OCA, F, ⁴JHU-APL, Maryland, USA, ⁵MPS, Katlenburg-Lindau, D, ⁶INAF-Obs. of Roma, I, ⁷Univ. of Leiden, NL, ⁸Open Univ., Milton Keynes, UK, ⁹Open Univ., Milton Keynes, UK, ¹⁰IAA-CSIC, Granada, E, ¹¹CRPG, Nancy, F, ¹²ESTEC, ESA, NL

MarcoPolo-R is a sample return mission to a primitive Near-Earth Asteroid (NEA) selected for the assessment study in the framework of ESA Cosmic Vision 2015-25 program. MarcoPolo-R is an European-led mission with a proposed NASA contribution. MarcoPolo-R will rendezvous with a primitive carbon-rich NEA, scientifically characterize it at multiple scales, and return a unique sample to Earth unaltered by the atmospheric entry process or terrestrial weathering.

The baseline target is a binary asteroid (175706) 1996 FG3, which offers a very efficient operational and technical mission profile. A binary target also provides enhanced science return. The choice of this target will allow new investigations to be performed more easily than at a single object, and also enables investigations of the fascinating geology and geophysics of asteroids that are impossible at a single object. Several launch windows have been identified in the time-span 2020-2024. The baseline mission scenario of MarcoPolo-R to 1996 FG3 foresees a single primary spacecraft, carrying the Earth re-entry capsule and sample acquisition and transfer system, launched by a Soyuz-Fregat rocket from Kourou.

The scientific payload includes state-of-the-art instruments, e.g. a camera system for high resolution imaging from orbit and on the surface, spectrometers covering visible, near-infrared and mid-infrared wavelengths, a neutral-particle analyser, a radio science experiment and optional laser altimeter. If resources are available, an optional Lander will be added to perform in-situ characterization close to the sampling site, and internal structure investigations.

MarcoPolo-R will allow us to study the most primitive materials available to investigate early solar system formation processes. The main goal of the MarcoPolo-R mission is to return unaltered NEA material for detailed analysis in ground-based laboratories. Only in the laboratory can instruments with the necessary precision and sensitivity be applied to individual components of the complex mixture of materials that forms an asteroid regolith, in orer to determine their precise chemical, mineralogical and isotopic composition. Such measurements are vital for revealing the evidence of stellar, interstellar medium, pre-solar nebula and parent body processes that are retained in primitive asteroidal material.

In addition to addressing the exciting science goals, the MarcoPolo-R mission also involves technologies for which technical development programmes are well under way. It is the ideal platform to (i) demonstrate innovative capabilities such as: accurate planetary navigation and landing, sample return operational chain; (ii) prepare the next generation of curation facilities for extra-terrestrial sample storage and analysis; (iii) develop high speed re-entry capsule; (iv) pave the way as a pathfinder mission for future sample returns from bodies with high surface gravity.
Evidence of DNA primary damage in space environment

Casarosa M.\textsuperscript{1,2}, De Sio A.\textsuperscript{1}, Pace E.\textsuperscript{1}, Tozzetti L.\textsuperscript{1}, and Gallori E.\textsuperscript{1}

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The study of the interaction between radiation and complex organic biomolecules (nucleic acids, proteins) is one of the most important topics in Astrobiology, Astronautics, and Space Medicine. It is known that cosmic rays (CR), and SCR (secondary CR) are important factors of instability \cite{1} for both the research of exogenous origin of life and for the security of astronauts during the space missions.

Many studies have been done concerning the behaviour of organisms and cells in space environment. However, results so far obtained are not sufficient to have a complete picture of this matter, in particular as for as is concerned the direct interaction between particle radiation present in space and genetic material.

The aim of this work was to characterize the typology of damages occurred on "naked" DNA after its exposition to the International Space Station (ISS) environment. To this aim, DNA samples were sent on the ISS with the STS 134 mission. During the flight (16/05/2011-30/05/2011), the genetic material was exposed to the same CR and SCR of the space crew. Subsequently, samples returned to the Earth were analyzed by gel-electrophoresis \cite{2}, to assess the presence and the nature of damages.

Results we have obtained, indicated that CR and SCR induced both single and double strand breaks on DNA. Moreover, it can be hypothesize the induction of substitutions, modifications and abasic sites on DNA sequence. These could be ascertained, in future experiments, by using specific restriction enzymes which recognize these kinds of damages.

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Solid state radiolysis of non-proteinaceous amino acids: astrobiological implications

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The analysis of the amino acids present in Murchison meteorite and in other carbonaceous chondrites has revealed the presence of 66 different types of amino acids. Only 8 of these 66 amino acids are proteinaceous amino acids used by the present terrestrial biochemistry in protein synthesis, the other 58 amino acids are somewhat “rare” or unusual or even “unknown” for the current terrestrial biochemistry. For this reason in the present work a series of “uncommon” non-proteinaceous amino acids, namely, L-2-amino-3-butyric acid, R(-)-2-amino-3-butyric acid, 2-amino-3-isobutyric acid (or α-amino-3-isobutyric acid), L-norleucine, L-norvaline, L-β-leucine, L-β-homoalanine, L-β-homoglutamic acid, S(-)-β-methylvaline and DL-3-aminoisobutyric acid were radiolyzed in vacuum at 3.2 MGy a dose equivalent to that emitted in 1.05x10^9 years from the radionuclide decay in the bulk of asteroids or comets. The residual amount of each amino acid under study remained after radiolysis was determined by differential scanning calorimetry (DSC) in comparison to pristine samples. For optically active amino acids, the residual amount of each amino acid remained after radiolysis was also determined by optical rotatory dispersion spectroscopy (ORD) and by polarimetry. With these analytical techniques it was possible to measure also the degree of racemization undergone by each amino acid after radiolysis. It was found that the non-proteinaceous amino acids in general do not show a higher radiation and racemization resistance in comparison to the common 20 proteinaceous amino acids studied previously. The unique exception is represented by α-amino-3-isobutyric acid which shows an extraordinary resistance to radiolysis since 96.6% is recovered unchanged after 3.2 MGy. Curiously α-amino-3-isobutyric acid is the most abundant amino acid found in carbonaceous chondrites. In Murchison meteorite α-amino-3-isobutyric acid represents more than 20% of the total 66 amino acids found in this meteorite.

Our Chemical Origins

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The Solar System was born about 4.5 billions years ago from a condensation inside a cold (~10K) molecular cloud. What happened to that initial condensation and how did it evolved up to form the Earth and its environment that permitted life to thrive?

To answer these questions, we need to assemble many pieces of a giant puzzle that covers different fields. The chemical composition of comets and some parts of meteorites provide us with some precious pieces when it is compared to that in sources which will eventually become other Suns and planetary systems. For example, it tell us that Earth inherited water from cold iced bodies, that comets conserved only in part the imprint of interstellar chemistry while some pieces of meteorites have imprinted it forever, that nitrogen in comets is an heritage from different interstellar molecules, that deuterium in meteorites spots is inherited from the material of the primordial condensation. And all this tells us the story of how and from what the Earth and the Solar System bodies formed.

In this presentation, I will give an overview of the link between the interstellar chemistry and the Solar System origin.
Do extraterrestrial soils exist?

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Soil lacks a universally accepted definition, partly because of its multifunctionality. One of the consequences is the ongoing debate on the possible occurrence of soils outside Earth. Space scientists often use the term regolith to refer to any loose extraterrestrial surface, but it is a too vague term, indicating any type of heterogeneous material covering solid rock. On our planet, soil form thanks to the combined action of at least five factors: parent rock, time, climate, topography, and biota. However, the necessity of biota is debated. In fact, important parts of Earth, such as the hyperarid Atacama Desert of Chile and the Dry Valleys of Antarctica, host virtually life-free soils with advanced horizonation, which is often considered a crucial feature of soil. Actually, although most people invokes the ability to support plant growth as sine qua non of soil, a scientific definition considers soil to be any in situ weathered veneer of a planetary surface that retains information on its climatic and geochemical history. For the author, a current or past chemical weathering is the pivotal requisite for soil.

What soil genesis cannot prescind from is a rocky parent material, which in the Solar System occurs in the four inner planets, a few moons, and the asteroids. On Earth, weathering is chiefly promoted by liquid water, which is the solvent where most of reactions happen and a carrier of matter and energy. Oxygen or, in anaerobic environments, weaker electron acceptor such as nitrates, sulphates and ferric iron allow the altering action of proton donors. Several sources of energy are finally the motor of pedogenesis. In extraterrestrial landmasses, most water probably occurs as ice, but weathering might be caused by thin layers of liquid water at the rock-ice interface, as documented to happen in frozen soils on Earth. Furthermore, there are several polar solvents able to replace liquid water, such as strong acids, ammonia, methanol and hydrazine. Finally, a variety of energy sources can drive chemical reactions in space: thermal, osmotic and ionic gradients, meteorite bombardment, solar wind and cosmic rays, magnetism and radioactivity are the most important ones.

Clear evidences of chemical weathering were found in the investigated surfaces of Mars, our moon, and the little asteroid Itokawa, which hence deserve the rank of soils.

A definition of soil that may represent a simple reliable point of reference for any terrigenous Outer Space landmass is provided.
Lithotrophic Bacteria and Archaea in aquatic environments

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Over 8,000 species and nearly 1,550 genera of prokaryotes were tabulated as of 2007 (Taxonomic Outline of \textit{Bacteria} and \textit{Archaea} (TOBA 7.7, 2007) representing only the “tip of the iceberg” of the enormous diversity based on 16S ribosomal DNA in natural populations (Hugenholtz et al., 1998). Even though few, cultivated chemolithotrophic Bacteria and Archaea exhibit extraordinary diversity of substrates, physiology, modes of carbon nutrition, morphology and habitat, making artificial the grouping of chemolithotrophs into some kind of homogeneous taxonomic unit. To make it more complex is that microorganisms proved to be facultatively chemolithoautotrophs, mixotrophic or chemolithotrophic heterotrophs. The concepts of autotrophy (the assimilation of carbon dioxide as the major or sole source of biosynthetic carbon) and chemolithotrophy (growth with inorganic energy sources) thus were accepted as separate processes obligatorily linked in some specialized types of organisms. Reactions unequivocally established as sources of chemolithothrophic energy are the oxidation of hydrogen, ammonia, nitrite, sulfur and its reduced compounds, ferrous iron, and possibly cuprous copper, antimony, and uranium (IV). In particular reduction-oxidation reactions of nitrogen compounds offer a great potential of energy-generation by microorganisms. Surprisingly the discovery of new processes and players in the nitrogen cycle are quite recent: as for example, the discovery of anaerobic ammonia oxidation (anammox) in the early 1990’s and the cultivation of chemoaotrophic Archaea nitrifiers in 2005 meaning that among known bacteria there is a great potential for chemolithotrophy and proving that a lot need still to be discovered. In addition, aquatic, that is marine, estuarine and freshwater and terrestrial environments are differently investigated and known with respect to the nitrogen cycle. Finally, chemiolithotrophic metabolisms lead to discussion relevant to the origin of life as well as to extraterrestrial systems.
Role of Iron Meteorites in the Prebiotic Chemistry of Formamide

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A variety of non-terrestrial amino acids similar to those found in life on Earth have been detected in meteorites. In addition to amino acids, sugar-like molecules, activated phosphates, and nucleobases have also been determined to be indigenous to numerous meteorites. Because these molecules are essential for life as we know it, it is plausible that the origin(s) of life on Earth was(ere) aided by extraterrestrially-synthesized molecules. Understanding the role of meteorite in the prebiotic synthesis of biomolecules help to answer the question of whether biology is unique to Earth. [1]

Recently, during our studies on the prebiotic chemistry of formamide [2] we reported the efficient synthesis of nucleic acid derivatives in the presence of dust from the Murchison meteorite [3]. As a continuation of these studies here we describe the results of thermal condensation of formamide in the presence of various iron meteorites, including Campo del Cielo e Sikkolite. Simple heating the system to 60 °C in the presence of a catalytic amount of minerals afforded nucleic acids derivatives, amino acids, carboxylic acids and their derivatives (such as esters and amides) in high yield. Among the amino acids, the presence of unnatural derivatives, normally observed in non-terrestrial bodies, emphasizes the role played by the formamide as chemical probes for prebiotic processes in non-terrestrial environment. A comparison between the catalytic role of iron meteorites and Murchison and Orgueil carbonaceous chondrites will be also discussed.

ESA Astrobiology – an overview

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History:
Between 1992 and 2012 eight sets of astrobiological experiments from the European Space Agency (ESA) were flown in low-Earth orbit to expose biological and biochemical test samples to the harsh space environment. The flight duration varied from 12 days to 22 months. The total number of experiments was 60. The samples were analysed on ground after the flight, there was no monitoring in space.

Flight equipment:
Four different exposure facilities were used: ERA, BIOPAN, EXPOSE and STONE. The first three were aimed to investigate the effects of vacuum, full-spectrum solar light, freeze/thaw cycles, cosmic radiation and microgravity. STONE was conceived to test the effects of atmospheric entry.

Some results:
- Survival of particular terrestrial organisms was demonstrated after up to 22 months of space exposure;
- Among the survivors were macroscopic eukaryotic organisms like lichens and plant seeds;
- The most lethal space factor was solar UV. Protected against UV even more organisms were able to survive;
- Survival is restricted to organisms able to enter into dormancy;
- Space exposure had no effect on the chirality of organic molecules;
- Sedimentary rocks remained intact during atmospheric entry.

The new results from the 18-month EXPOSE-E mission have just been published [1].

Prospects for the future:
EXPOSE is planned for a new flight in 2013-2015 on the ISS, loaded with four experiments. A new development is OREOCUBE, also on the ISS, designed to monitor UV processing of organic molecules during flight. The European EXOMARS rover is slated for launch by the end of this decade. Equipped with a drill, EXOMARS can collect and analyse Martian soil samples from 2 meters depth.

FEBO: an ASI Facility for Astro- and Exo- Biology Observations

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Space biology with the disciplines of astrobiology, exobiology and radiation biology requires experiments directly exposed to space environment for short, medium and long periods of time. These experiments can require direct exposure to space environment for studies on UV and solar radiation, on cosmic radiation and on particles at high altitudes. The FEBO program of the Italian Space Agency (ASI), that has recently concluded successfully its Phase B, can provide the suitable environment and resources necessary to accommodate most of the above mentioned disciplines outside the International Space Station (ISS). The status of the program, together with the wide application capabilities of the FEBO platform and the already identified candidate experiments are described. Finally, the new payload upload and download scenarios after the retirement of the Space Shuttle has been assessed, confirming the full possibility to bring to completion the program.
Dissociation of the CO$_2$ dications in the upper atmospheres of planets - a new route of CO$^+$ and O$^+$ formation

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The first observation of the CO$_2^{2+}$ dication formed by electron impact ionization of carbon dioxide was reported in 1961 [1]. Since that experiment, the double ionization of CO$_2$ has been studied in several laboratories [2–5]. These kinds of processes are of great interest because of the involvement of CO$_2$ in several atmospheric phenomena of the Earth and of other planets and in plasma environments. In Mars’ atmosphere, where CO$_2$ is the main component, the importance of the CO$_2^{2+}$ dication and its dissociation has been recently demonstrated [6]. In this contribution we present a double photoionization of CO$_2$ molecules studied in the 34-50 eV photon energy range, by the use of synchrotron radiation and detecting electron-ion and electron-ion-ion coincidences. The experiment has been carried out at the synchrotron light laboratory ELETTRA (Trieste, Italy) by the use of the ARPES end station of the Gas Phase Beamline [7,8]. The CO$_2$ molecular beam and the vuv light beam cross at right angles, with the light polarization vector being parallel to the synchrotron ring plane and perpendicular to the time-of-flight direction of detected ions. Three processes have been observed: (i) the formation of the CO$_2^{2+}$ molecular dication, (ii) the production of a metastable (CO$_2^{2+}$)* that dissociates, with an apparent lifetime of 3.1 μs, giving rise to CO$^+$ and O$^+$ ions, and (iii) the dissociation leading to the same products, but occurring with a lifetime shorter than 0.05 μs. In the photon energy range investigated, the double dissociative photoionization reaction of CO$_2$ leads to an isotropic distribution of CO$^+$ and O$^+$ product ions with respect to the polarization vector of the light. When the photon energy increases, the distribution of products becomes anisotropic, with the two ions preferentially emitted along the direction of the light polarization vector. This implies that the molecule photoionizes when oriented parallel to that direction and also that the CO$_2^{2+}$ dication just formed dissociates in a time shorter than its typical rotational period. At low photon energy, the CO$^+$ and O$^+$ product ions separate predominantly with a total kinetic energy between 3 and 4 eV. This mechanism becomes gradually less important when the photon energy increases and, at 49 eV, a process where the two products separate with a kinetic energy between 5 and 6 eV is dominant.

Glycosylation in the crenarchaeon Sulfolobus solfataricus

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Glycosylation, once believed to be restricted to Eukarya, is one of the most prevalent posttranslational modifications in organisms of all domain of life, expanding the diversity of the proteome by the addition of different glycan moieties. The first example of prokaryotic Nglycosylated protein was reported in the haloarchaeon Halobacterium salinarum [1], and from this discovering, it is now clear that the prevalence and the structural variety of the N-glycosylated proteins are more prominent in Archaea than in Bacteria. In the N-glycosylation pathway, Archaea combines particular aspects of the bacterial and eukaryal pathways, such as monomeric oligosyltransferases and dolichol phosphate carrier respectively, along with traits unique to this life form [2]. The majority of the data available concerns euryarchaeal model species [3]. Preliminary studies on Crenarchaea, a phylum evolutionarily distant from Euryarchaeaa, indicate that glycosylation is indispensable for cell survival [4] and even more widespread than in Euryarchaeaa [5]. Nevertheless, little is known about the nature of the glycosylated proteins and the machinery involved in the crenarchaeal glycosylation.

Here, we report the identification and biochemical characterization of a novel β-glucosidase/β-N-acetylglucosaminidase in Sulfolobus solfataricus P2. The enzyme is encoded by the ORF SSO3039, and represents the first member of the family GH116 (http://www.cazy.org) able to hydrolyze N-acetyl-β-D-glucosaminides. In addition, by using a glycoproteomic approach, we analyzed the sugar composition and structure of the glycoproteins from S. solfataricus.

A better understanding of crenarchaeal glycosylation will provide new insights into this posttranslational modification across evolution as well as adaptation to extreme conditions.

Adsorption of Nucleic Acid Bases on Magnesium Oxide (MgO): hints of life detection on Mars

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The adsorption of organic molecules on mineral matrices might have played a fundamental role in processes that led to the emergence of life. We investigated the adsorption properties of the nucleobases adenine, cytosine, uracil and hypoxanthine on magnesium oxide (MgO), determining the single solute batch equilibrium adsorption isotherms. Langmuir-type isotherms were fitted to data, assuming a rapid reversible equilibration of adsorption, demonstrated effectively through desorption experiments. The Langmuir equilibrium adsorption constant $K$ and the amount of the solute per unit of adsorbent mass necessary to complete the monolayer $b$ were calculated. The results indicate that magnesium oxide is a good adsorbent for nucleobases (adenine $>$ uracil $>$ hypoxanthine $>$ cytosine), suggesting a role of metal oxides in concentrating biomolecules in prebiotic conditions that might have favored the passage from geochemistry to biochemistry.
Formation of biomolecule precursors in space

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The possibility of an extraterrestrial origin of biomolecule building blocks has been a subject of intense discussions for many years. The detection of amino acids in meteorites opens the possibility of a delivery of biomolecules synthesized in the interstellar medium or star-forming regions to the primeval Earth. Whereas it can be doubted if more complex species like amino acids and carbohydrates can survive the strong UV radiation in the early Solar System, this does not necessarily hold for more primitive precursor molecules like alcohols and nitriles. [1]

If these compounds can be synthesized in the interstellar medium, the question of their formation sites and pathway arises. It has been a long-standing issue to what extent comparatively complex carbon-containing interstellar molecules like methanol, ethanol, dimethyl ether and formic acid are produced in the gas-phase or on grain surfaces. I will discuss possibilities to solve these questions through experimental, computational and observational studies.

Nitriles can serve as amino acid and nucleobase precursors and can also be synthesized very efficiently in methane-nitrogen dominated atmospheres like the one present on Titan and, possibly, the early ages of Earth. Therefore I will also discuss the formation and degradation processes of nitriles in Titan's atmosphere and on their possible role in the generation of biomolecules.

Metastable anions of C-rich molecules: Dynamics and role in planetary atmospheres and the ISM of polyynes and PAHs

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The recent discoveries of the C$_3$N and C$_5$N radicals [1] and of the confirmed presence of the C$_3$N$^-$ and C$_5$N$^-$ anions in circumstellar envelopes [2,3] have triggered a great deal of interest on the characterization of the specific properties of the linear carbon chains of the type C$_{2n+1}$N. In particular, the C$_3$N and the C$_5$N radicals and their anionic counterparts were discovered in the expanding circumstellar envelope of the carbon star IRC+10216 and in the dark cloud TMC1, using radiotelescopes: they are key cyanopolyacetylides and constitute important drivers of interstellar chemistry as are seen as potentially significant constituents of Titan’s atmosphere[4]. It is therefore of current interest to revisit the formation processes of the observed linear anions (for example, C$_3$N$^-$ and C$_5$N$^-$) by considering the dynamics, at the molecular level, of the environmental electrons which can undergo scattering from closed shell species which could thus provide the precursors species in the planetary atmospheres: examples are given by the HC$_3$N and HC$_5$N neutral polar partners but other, similar processes also involve nonpolar species like HC$_2$H, HC$_4$H or NC$_2$N and NC$_4$N. We wish to study here the structures and localizations of possible resonances (metastable compound states) which can originate from the quantum interaction between the above molecules and the “hot” electrons expected to be present in the planetary and protoplanetary atmospheres mentioned at the beginning, in order to link to each of such resonances a specific stabilization path which could lead to the formation of the observed anions of the C$_{2n+1}$N$^-$ type, or of the HC$_n^-$ and C$_n^-$ types as detected in the interstellar medium (ISM) as smaller fragments of the C$_n$H variety after dissociative electron attachment in multidimensional molecular space. In the previous studies on the formation rates and mechanisms for C$_n$H anions in interstellar and circumstellar media it was pointed out that, since the binding energy of an electron to a neutral species (i.e. its electron affinity, EA) is typically smaller in energy than the average chemical bond (which is usually around 4 eV), then the dissociative attachment process is normally an endothermic one: 

\[ \text{M}^- + \text{H} + e^- \rightarrow [\text{MH}]^* \rightarrow \text{M}^- + \text{H} \]

Therefore, in order for the DEA process to take place at low temperatures and for low-energy electrons (that is in order to be an exothermic event) there must be a weakening of one or more of the relevant bonds during the formation of a metastable precursor state, [MH]$^*$, in reaction above. The present analysis of such "weakening" events in the broad variety of linear molecules we are considering is therefore based on: (i) the formation of a metastable anion in the continuum for lifetimes at least comparable with that of a vibrational mode; (ii) the existence of additional antibonding features along a specific bond (the "weakening effect") caused by the newly attached electron; (iii) the partial or total redistribution of the excess electron energy within the internal molecular bonds (intramolecular vibrational redistribution, IVR) and (iv) possible radiative stabilization of an anionic fragment corresponding to one of the species experimentally observed.

In the analysis of the quantum dynamics which we shall be presenting at the talk we shall therefore focus on the features of the resonant, intermediate complexes, i.e. of the possible metastable anionic states formed by electron attachment in neutral, closed-shell linear molecules which are expected to act as "doorway" states to the ensuing formation of stable negative ions after fragmentation. We shall be able to
provide evidence that only those metastable states which correspond to long-lived electron attachment states, and which occur for near-threshold electron projectiles, have a realistic chance of competing successfully with the autodetachment channels and therefore manage to stabilize anionic species. The latter shall be either of the unfragmented molecule or shall identify specific fragments of the latter, depending on the bond weakening effects caused by the metastable excess electrons. Examples of the various options in anionic stabilization paths will be given during the present talk.

Studying the chemical evolution of ISM regions via numerical methods

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Chemistry is one of the most important ingredients in many astrophysical simulations. Unfortunately chemical processes consist of a large ensemble of reactions that are computationally expensive when embedded into more complex and realistic ISM simulations.

Moreover, there are large uncertainties related to the rate coefficients that in turn determine equally large uncertainties in the ISM model evolutions. In this framework we present and discuss a novel network-reducing technique which allows marked reductions of the computational times and we shall illustrate the influence of some ab initio calculations of reaction rates involving PAHs on the overall chemical evolutions in dark molecular clouds.
Pyrolysis of chiral alcohols in the presence of catalysts of interstellar interest

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The study of chiral molecules is important to find the source of homochirality in biology which is an essential step to understand the origin of life on the earth [1,2]. The thermal stability of chiral molecules will give insight on their decomposition and survivability. A consequence of the high temperature is the loss of optical activity of the chiral molecules by racemization [3]. In this study, the pyrolysis mechanism of 1-phenylethanol and its racemization has been studied by online pyrolysis gas chromatography–mass spectrometry, in the presence of different catalysts inserted directly in the pyrolyzer furnace without further complications. The use of the chiral column allows one to discriminate between enantiomers and evaluates the extent of the racemization at different temperatures. Using the trend of the enantiomeric excess in function of the temperature, a new approach to calculate the rate of racemization is proposed.

References
Simple models of meteor entry in planetary atmospheres

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The determination of physical conditions experienced by meteors in crossing planetary atmospheres is important to connect the entry conditions to surface alteration of meteorite samples, to study the influence of meteors on atmospheric chemistry, and in the context of this workshop to better evaluate the possibility of organic matter delivery to planet surfaces via meteorites. Models for the physical conditions and phenomena in meteor entry can be based on dynamic and conservation equations. These models include drag, ablation, radiation and can relate the entry conditions to the mass loss and final speed, basically still following the chemical/physical analysis of the problem in the pioneering work by EJ Opik, while of course taking into account the huge subsequent literature and the availability of powerful computational tools. A possibility to validate simple modes is to apply them to entry conditions of space vehicles for which on-flight measurements are available. In the laboratory, the predicted conditions can be reproduced on real meteor samples or analogous materials by using arc plasma methods already developed for the aerospace industry or focusing a laser radiation on the sample.
Is it possible to detect homodimers of organic acids in the interstellar medium or circumstellar shells?

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The two smallest organic acids have been already detected in the interstellar medium or circumstellar shells, they are the formic acid (H-COOH) [1] and the acetic acid (CH₃-COOH) [2]. On the other hand, two substituted propenes, such as acrylonitrile (CH₂=CH-CN) [3] and acrolein (CH₂=CH-CHO) [4], have been observed. It seems then reasonable to assume the presence of the unsaturated acrylic acid (CH₂=CH-COOH).

So far no weakly bound molecular complexes have been detected in the interstellar medium or circumstellar shells. However, pairs of carboxyl groups bind strongly (about 60 kJ/mol), given that both groups act as proton donor and acceptor forming a ring containing two hydrogen bonds, so the dimers of organic acids could be the most reasonable candidates for this kind of research.

Rotational spectroscopy is a powerful tool to identify molecules in gas phase. When coupled with supersonic expansion of the sample, it allows: (i) to reach very low rotational temperatures (few kelvins) obtaining simplified spectra and (ii) to stop the collisions within molecules, making it possible the investigation of usually unstable species like radicals, ions and weakly bond molecular complexes.

In order to show a rotational spectrum, a species must have a permanent electric dipole moment (μ), so the homodimers of formic and acetic acid are not visible, because the dipole moments of the units are antiparallel and their sum is zero. The case of acrylic acid is different because, depending on the cis or trans orientation of the double bonds, it has two almost isoenergetic possible conformations (E_trans−E_cis=58±20 cm⁻¹ [5]): when two cis or two trans conformers form a dimer μ=0, but when a cis unit binds a trans one μ≠0 and the dimer can be studied by rotational spectroscopy.

We observed the pulsed jet Fourier transform microwave spectrum of the cis-trans dimer of acrylic acid and its hydroxyl deuterated isotopologues. For each species we observed two series of lines due to the concerted double transfer of the hydroxyl protons between the monomers. Based on the experimental and quantum chemical calculated data, a flexible model [6] was applied to characterize the double minimum potential energy surface that generate the tunneling doubling.

The detection of molecules in space, is based on their spectroscopic features and high resolution spectral data is needed to allow an unambiguous identification of them. Many of the molecules detected in space are complex organic molecules containing chains of carbon atoms and which therefore show a high degree of molecular flexibility. The high number of low energy conformations and the presence of large amplitude motions on shallow potential energy surfaces are peculiar to this kind of systems. The presence of a high number of stable conformers - often interconverting through small energy barriers - usually gives rise to very complex spectra, which represent a challenge for spectroscopic and computational methods.

We will give examples of rotational spectroscopy of highly flexible organic molecules and biological building blocks of astrophysical interest studied in the isolated conditions of a free jet expansion in the 60-78 GHz region. The interpretation of their rotational spectra with appropriate models is essential to correctly predict their spectral features at higher frequencies.
Interrupted genes in early organisms

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Translational recoding includes a group of events occurring during gene translation, named programmed -/+1 frameshifting, ribosome hopping, and codon reassignment, that have been found in organisms from all domains of life [1]. This mechanism of translational regulation represents a relatively less known exception to the traditional central 'dogma' of biology that information flows as DNA→RNA→protein and that it is stored in a colinear way between the 5'→3' of nucleic acids and N→C-terminal of polypeptides. In Archaea, the living organisms that are considered among the closer to the Last Universal Common Ancestor, since recently, the only known recoding events were termination codon readthrough leading to the decoding of the 21st and 22nd aminoacids selenocysteine and pyrrolysine, respectively [2]. However, we demonstrated in the archaeon Sulfolobus solfataricus that two ORFs, SSO11867 and SSO3060, encode for a α-L-fucosidase expressed by programmed -1 frameshifting [3]. In addition, more recently, we demonstrated by functional highthroughput proteomic approaches, that disrupted genes leading to functional products can be frequently found in archeal genomes and possible novel examples of genes expressed by recoding events have been proposed [4]. These results will be described here and discussed with particular focus on the functional meaning of interrupted genes and their mechanisms of expression. In fact, disrupted genes and translational recoding are relevant for origin of the genetic code and the organization of the genome in early organisms.

This work was supported by the project MoMa n. 1/014/06/0 of the Agenzia Spaziale Italiana.

Metagenomic analysis of an extreme biotope

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The Pisciarelli solfatara, located in Agnano (Naples, Italy) in the Phelgrean Fields, although not extended in size (800 m²), is characterized by a remarkable diversity in terms of temperature and pHs of the different mud pools and solfataric vents [1]. In addition, in this site several thermoacidophilic species, such as Sulfolobus, Acidianus, Pyrobaculum, Archaeoglobus spp and several viruses have been isolated in the past [1]. In order to map the composition of this biotope in terms of number and abundance of the different species, we decided to embark in a metagenomic deep sequencing project of soil and water/mud pools of Pisciarelli solfatara. Here we will show our preliminary results of the metagenomic analysis performed on samples from the main water pool. Water samples were centrifugated and total DNA was extracted from the pellets. We performed the de novo assembly of the sample metagenomic using Illumina paired-end sequencing technology. In a single run, we produced ~3.0 Gb total nucleotides. These reads were assembled into 1,543 contigs with an N50 of 15863 bp, and a total of 17,652 Open Reading Frames (ORFs) were identified. These ORFs were subjected to BLAST similarity searches and annotated with KEGG, eggNOG and NR database respectively. The clean reads rate was 99.7% and a total of 17,652 Open Reading Frames (ORFs) were identified. Phylogenetic analysis revealed that the majority (77%) of the species found belonged to the Crenarchaeota phylum, which branches deeply in the phylogenetic tree of life, followed by Proteobacteria (22%), and, in much lesser amounts, Euryarchaeota, Actinobacteria, and others. The number of species identified is much higher than those found by a conventional PCR-based approach [2]. In addition, metabolic profiles inferred from this analysis allowed the identification of a considerable number of ORF involved in the carbohydrate metabolism. Details on the microbiome composition and on the relative abundance of metabolic pathways and/or specific ORFs will be described as well as the importance, in an astrobiological perspective, of metagenomic studies in mapping extreme biotopes will be discussed.

This work was supported by the project MoMa n. 1/014/06/0 of the Agenzia Spaziale Italiana, and by the project PON01_01966 “ENERBIOCHEM - Filiere agro-industriali integrate ad elevata efficienza energetica per la messa a punto di processi di Produzione Eco-compatibili di Energia e Bio-chemicals da fonte rinnovabile e per la valorizzazione del territorio” of the Programma Operativo Nazionale Ricerca e Competitività 2007-2013 -MIUR-Italy.

Modelling of Methyl formate formation towards various astronomical environments

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Methyl formate is an important organic complex molecule since it leads to the synthesis of biopolymers. Methyl formate has been detected towards several hot cores and hot corinos, two different regions in the interstellar medium. Chemical models based only on gas-phase reactions are unable to account for its observed abundances, then gas-grain chemical model are needed.

In the present study, we update the gas-grain UCL CHEM chemical model (Viti et al. 2004) to include recent experimental results (Modica & Palumbo 2010) involving methyl formate and we qualitatively model its potential astronomical sources in order to compare our theoretical column densities with those from the observations (Occhiogrosso et al. 2011).

Acknowledgments
The research leading to these results has received funding from the [European Community’s] Seventh Framework Programme [FP7/2007-2013] under grant agreement n° 238258.

Chiral recognition in diastereomeric adducts of organofluorines

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It is wholly accepted that aggregation and self-recognition played an important role in prebiotic earth. Over the several hundred million years of chemical evolution that brought to the first living organisms, simple molecules evolved into larger and more complex systems, often through processes mediated by supramolecular interactions. Chirality is an important element of terrestrial life either at molecular and supramolecular level and various hypotheses have been proposed to explain its abiotic origin [1]. However, several evolutionary steps were required to produce, implement, and maintain chirality in the terrestrial type of life. The specific chemical mechanisms that lead to the first replicable homochiral substance still remain unknown, though it is certain that chiral recognition through supramolecular interactions played a major role in prebiotic earth and in the evolution of life. The in-depth comprehension of stereospecific, non-covalent interactions is a major issue to understand the origin of life and all processes that occur in living organisms.

Information on molecular structure, dynamics, reactivity, energetics of diastereomeric complexes can be achieved by spectroscopic techniques. Though it can be argued that the properties of isolated complexes cannot be directly extended to the condensed phase, gas phase studies have the advantage that tailor-made diastereomeric clusters can be investigated at the molecular level and are appropriate for an accurate understanding of the forces at play in chiral recognition. The results of gas-phase experiments can be used by theoretical chemists as benchmark for the validation of different approximations for ab-initio calculations in chiral systems. Resonant Two Photon Ionization (R2PI) spectroscopy, coupled with time of flight mass spectrometry, is a powerful tool for studying non-covalent molecular interactions involved in chiral recognition [2], allowing to evaluate the gas-phase structure and the energetics of diastereomeric complexes.

Recently, we have applied these studies to adducts of fluorinated chiral aromatic alcohols and a variety of chiral solvent molecules [3], with the aim of determining the effect of fluorine substitution on the structure and reactivity properties of their complexes and to verify the role of the fluorine substitution on the chiral recognition process. Here we report on the application of R2PI spectroscopy to gas-phase complexes of chiral fluoroophenylethanol chromophores with chiral and achiral solvents. The results have been interpreted with the aid of theoretical predictions.

Chiral effects in oriented molecules collisions: investigating the origin of the building blocks of life

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The exploration of the space provides a new perspective in the study of the synthesis of prebiotic molecules: the Miller’s experiment is extended to a planetary-scale laboratory raising the questions whether the simple organic molecules are the link between matter in the Universe and matter in living entities, and way on how they were formed to begin with. [1,2] The recent discovery that most of the molecules and ions composing the interstellar and circumstellar medium, comets and meteorites are rich in carbon atoms added up to the detection of molecules containing carbon having a prebiotic nature gave us a first response and opened the debate on the origin of the building blocks of the life in the universe opened by the discovery of amino acids and other protobiological molecules in meteorites, and possibly in other space environments. [3]

Special attention is being devoted on those processes by which prebiotic molecules, most of them chiral, can be produced in interstellar dust and spread out all over, to the earth or other planets. The role played by chirality on the evolution of life is a key to understand the not yet solved problem of the origin of homochirality. [4-6]

Chiral discriminations have been revealed in the observables obtained by molecular collisions involving chiral molecules characterized by rotatory or whirling motions. Molecular alignment and orientation, obtained for example by seeding effects in supersonic beams and by applying electric fields, are prerequisite for the manifestation of effects of chirality. (See [7,8] and references therein).

Surface-Enhanced Raman Scattering Investigation of Nucleobases Adsorbed on a Martian Meteorite and Samples of Martian Analogue Material

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Surface Enhanced Raman Scattering (SERS) is a powerful technique for the chemical and structural analysis of minerals and organic molecules. This technique provides an huge enhancement of the Raman signal by means of the interaction with silver, gold or copper nanoparticles [1]. In recent years this technique has gained a increased attention especially for the study of trace biological molecules, owing to its high sensitivity, without sample preparation or manipulation. The possibility to employ “in situ” this technique, as well as the feasibility of instrumental miniaturization, makes it potentially suitable in the extraterrestrial exploration [2, 3].

Since microbial life, if extinct or extant on Mars, would give rise to the formation of biomolecules that could be adsorbed on rocks and sediments, the SERS investigation of nucleic acids is important to understand if and how primitive life originated in extraterrestrial environments. Two main limitations usually impair the employment of the conventional Raman technique for this purpose, the low sensitivity and the occurrence of fluorescence, which could interfere with the observation of vibrational bands. The SERS spectroscopy allows overcoming these issues, by detecting absorbed molecules up to subpicogram level [3].

Therefore, we tested the SERS response of biological molecules on the Martian meteorite Dar al Gani (DaG) 670 [4] and on polished samples of terrestrial calcite, dolomite, magnesite, siderite, anhydrite, and gypsum [5] (minerals contained in Martian regolith); all the analyzed samples belong to the collection of the Museo di Scienze Planetarie in Prato (Italy).

In particular, the Martian meteorite sample was treated only with adenine whereas both adenine and hypoxanthine – nucleobases detected in several meteorites [7] – have been deposited as dilute solution on the Martian analogue materials. The Raman bands of these nucleobases were enhanced by SERS effect, allowing their identification as small traces (about $10^{-12}$ to $10^{-13}$ g).

The results displayed here suggest the adoption of SERS as analytical procedures for in situ investigation on Mars. This only requires that the Raman spectrometer adopted for the ESA ExoMars mission have the most appropriated wavelength laser source and an automatic Ag hydrosol sprayer.

Astrophysical investigations: the role of rotational spectroscopy

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The knowledge of very accurate rest frequencies is important for astrophysical purposes: precise transition frequencies are essential, for instance, in studies of molecular excitation, radiative transfer, systematic velocity gradients, ambipolar diffusion in star-forming regions, and also for the identification of new species. On a general ground, the investigation of the phenomena that allow to understand the chemistry of the interstellar medium requires laboratory investigations, as astronomical observations require the knowledge of either the spectroscopic parameters or the transition frequencies involved.

Rotational spectroscopy, thanks to its intrinsic high resolution, is a powerful tool for providing most of the information mentioned above: accurate or even very accurate rotational transition frequencies, accurate spectroscopic as well as hyperfine parameters, accurate pressure-broadening coefficients and their temperature dependence. For instance, by exploiting the Lamb-dip technique it is possible to further increase the high resolution power of rotational spectroscopy and then resolve hyperfine structures and/or measure very accurate rest frequencies [1,2]. With respect to collisional phenomena and line shape analysis studies, by applying the source frequency modulation technique it has been found that rotational spectroscopy may provide very good results: not only this technique does not produce uncontrollable instrumental distortions or broadenings, but also, having a high sensitivity, it is particularly suitable for this kind of investigations [3,4].

A number of examples will be presented to illustrate the role of rotational spectroscopy in the field of astrophysical investigations with particular emphasis on the work carried out at the Laboratory of Millimeter-wave Spectroscopy of Bologna. The fruitful support by quantum-chemical calculations will be also pointed out [2,5].

Dimerization of methanimine and implications for the aerosols formation in the upper atmosphere of Titan

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Methanimine is a molecule of interest in astrobiology [1,2], as it can be a precursor of the simplest aminoacid glycine. It has been observed in the interstellar medium and in the upper atmosphere of Titan. In particular, it has been speculated that its polymerization can contribute to the formation of the haze aerosols that surround the massive moon of Saturn [3]. Unfortunately, such a suggestion has not been proved by laboratory experiments. As a matter of fact, methanime is difficult to investigate in laboratory experiments because it is a transient species that must be produced in situ because of its high instability.

To assess its potential role in the formation of Titan’s aerosol, we have started a theoretical investigation of its dimerization. The aim of this study is to understand whether this (and, eventually, polymerization) process is possible under the condition of the atmosphere of Titan. Electronic structure calculations of the stationary points along the minimum energy part will be presented.

Thermodynamics disequilibrium as a parameter to redefine habitability

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Thermodynamics of non-equilibrium has been used to study the effect of life emergence on Earth’s evolution. Clear evidences of this effect are seen in atmospheric and crust composition and biogeochemical cycles characteristics. More specifically, atmospheric disequilibrium has been proposed as a sign of habitability of Earth and, in general, of a planet [1, 2].

We have developed a new formulation to account for the thermodynamic conditions of a wide range of planetary atmospheres, from terrestrial planets, and icy satellites to hot exoplanets. Using this new formulation, we estimate the departure of different planetary atmospheres from their equilibrium conditions, computing the dissipation of free energy due to all chemical processes [3,4].

Here we present a first comparison of the thermodynamics disequilibrium in Earth’s and Mars’ atmospheres. Our results have an impact in the definition of Habitable Zone.

N+O associative ionization with formation of NO$^+$: a viable route in the interstellar medium?

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Atomic nitrogen and oxygen, as well as the NO$^+$ ion, are important species of upper planetary atmospheres and interstellar clouds. The dissociative recombination of the NO$^+$ ion has been extensively studied, while much less is known on the reverse process $N + O \rightarrow$NO$^+$ + e$^-$. Its potential role in the ionospheres of planets or interstellar clouds has still to be assessed. To characterize associative ionization of N+O, we have used a time-dependent quantum wavepacket method. This study furnishes also complementary information on the dissociative ionization of NO$^+$. Boltzmann averaging enables us to derive thermal rate constants for the process which will allow assessing the possible relevance of this process in planetary atmospheres rich of nitrogen and oxygen species.
Ultraviolet Photodissociation of Hydrocarbon Radicals

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In hydrocarbon-rich planetary atmospheres, an important role to initiate chemical evolution is played by UV photodissociation. The photodissociation products of abundant hydrocarbons, indeed, are reactive radicals that undergo subsequent elementary reactions. Those hydrocarbon radicals, however, can also undergo further UV photodissociation, especially in the more rarefied regions of the upper atmospheres.

In this talk, results on the UV photodissociation dynamics of allyl, CH$_2$CHCH$_2$-, and isopropyl, (CH$_3$)$_2$CH, radicals will be presented and discussed. Allyl radicals can be formed by photodissociation of propene and isopropyl radicals by photodissociation of propane. Both propane and propene have been detected in the atmosphere of Titan and, therefore, allyl and isopropyl radicals are expected to be present in the upper atmosphere of this massive moon of Titan. To be noted that hydrocarbon radicals adsorb at larger wavelengths (where the solar photon flux is higher) with respect to their parent molecules. In our laboratory we gave characterized the photodissociation dynamics of allyl and propyl radicals by using the method of molecular beam Photofragment Translational Spectroscopy (PTS) following excitation by 248 nm photons. The spectroscopy of allyl radical has been detailed by several studies, and its photodissociation has been examined both by sophisticated laser techniques [1] and by molecular beam methods [2,3]. Following excitation to the C(2^2B_1) electronic state, fast internal conversion takes place and is followed by dissociation on the ground electronic surface to give principally hydrogen atom loss. A second channel, observed in earlier molecular beam measurements [2], leads to methyl radicals plus acetylene. We have studied the photodissociation of 2-`d-allyl radical in order to elucidate the mechanisms involved for the latter channel. The experimental results demonstrate that there are at least two different mechanisms leading to the formation of methyl radicals plus acetylene [3]. All the isomerization and dissociation processes involved will be discussed from a statistical point of view, by microcanonical RRKM calculations, and by quasiclassical trajectory calculations [4,5]. Very recently, we have undertaken the study on the photodissociation of the isopropyl radical at 248 nm. Preliminary results show the presence of at least two primary dissociation channels: H + CH$_3$-CH=CH$_2$ and H$_2$ + C$_3$H$_5$. The analysis of the experimental data has been complicated by the absorption of a second photon from internally “hot” propene, which cannot be avoided.

Interaction of chiral molecules with synchrotron radiation: enantioselective study of oxirane derivatives

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Molecular dissymmetry plays a role of paramount importance in life science on both macroscopic and microscopic scale. The unknown origin of the homochirality in terrestrial life and the high enantio-selectivity in processes involving biologically important chiral molecules are among the most intriguing aspects to study in natural phenomena and related technologies. Investigating of enantiomeric nature of molecular systems has therefore a strong impact in chemistry in various areas, such as heterogeneous enantioselective catalysis, photochemical asymmetric synthesis, drug activity, enzymatic catalysis, and chiral surface science involving supramolecular assemblies. The interaction of circularly polarized light with chiral systems has been extensively studied since Paster’s pioneering experiments on optical activity leading to the enantiomer recognition. Although measuring optical rotation and circular dichroism (CD) by absorption of visible/UV light is a routinely analytical method, extension of studying chiroptical properties to the ionization regime is still a not fully exploited research area. Since the first experimental measurement of CD in photoionization processes from free enantiomers [1], relatively few investigations using energetic photons have been accomplished to investigate chiral systems to date. Development of third generation synchrotron radiation facilities has allowed intense radiation with high degree of circular polarization to be used in experiments. Such sources can reveal Circular Dichroism in randomly oriented chiral molecules by photoabsorption and angle-resolved photoelectron spectroscopy (ARPES) by exciting valence or inner-shell electrons. Results obtained by ARPES studying enantiomers of oxirane derivatives [2-5], as model chiral systems, will be described, as well as the most recent developments and perspectives of an ongoing research activity in this field will be discussed.

Energetic processing of ices and the search for life on Enceladus

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The discovery of water vapor plumes ejected from the south pole of Enceladus offers the opportunity to study the possible presence of extant life in the Solar System. Indeed that moon has a noteworthy geothermal energy and the large temperature gradient between the material in the plumes and the surrounding environment, allows the weathering of rocks by liquid water at the rock/liquid interface. Such a weathering and any concomitant radioactive emissions are possible incipient conditions for life [1] particularly if CO, CO$_2$ and NH$_3$ are present as gas phase species in the plumes. If this is the case it would support the hypothesis of a complex chemistry, induced by radioactive decay, at the rock/liquid or rock/ice interface of Enceladus.

Experimental studies of the chemistry induced by energetic processing at the interface between icy species and carbon and sulfur rich solids have been conducted in some laboratories among which the one in Catania (for a review see [2]). Here I will discuss some of the results obtained so far as e.g. (1) low-temperature ion bombardment of water ice deposited on asphaltite [3], and (2) solid acetylene irradiated with ions [4] and UV-photons (Cuylle, Linnartz, Strazzulla et al., work in progress) that showed evidence of carbon-chain extension.

The experimental results will be discussed in the light of the relevance they could have to support the presence of bio-chemical activity on Enceladus.

Organic ice in comet 103P/Hartley 2 at the time of the EPOXI mission fly-by

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Comet 103P/Hartley 2 was observed on Nov. 16, 2010, coinciding with the fly-by of the space probe EPOXI. The goal was to connect the large scale phenomena observed from the ground, with those at small scale observed from the spacecraft. The comet showed strong activity correlated with the rotation of its nucleus, also observed by the spacecraft. We report here the characterization of the solid component produced by this activity, via observations of the emission in two spectral regions where only grain scattering of the solar radiation is present. We show that the grains produced by this activity had a lifetime of the order of 5 hours, compatible with the spacecraft observations of the large icy chunks. Moreover, the grains produced by one of the active regions have a very red color. This suggests an organic component mixed with the ice in the grains.
I review the status of knowledge on the stellar origin of short-lived (tau < 10Myr) radioactive nuclei that were found to be alive in early solid condensates of the Solar System. In particular, I underline the present uncertainties related to their origin in a nearby supernova or a dying red giant star. I also comment on the enormous abundances that some of these nuclei had in the Early Solar System, especially for 26Al, and how this peculiarity played a crucial role in melting and differentiating solid bodies that subsequently formed the terrestrial planets. Taking this constraint into account is crucial for any attempt at finding Earth-like bodies outside the Solar System.
Interstellar prebiotic formation of glycine, delivery to Earth and polymerization on feldspars

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Reactions of simple molecules (H$_2$CO, NH$_3$, HC≡N) occurring at the surface of interstellar icy-based particles to give glycine, its capture on defects at a silica matrix simulating a meteoritic grain and its delivery to primordial Earth and, finally, its polymerization catalyzed by feldspar surfaces have been dealt with by molecular modeling approach based on density functional theory in a cluster approach. Two reaction channels were studied for the glycine formation in the interstellar medium: i) a Strecker-like mechanism involving H$_2$CO, NH$_3$ and HC≡N molecules catalyzed by neutral icy particles; ii) a mechanism involving CO and H$_2$CNH catalyzed by radical neutral/cation icy particles. Whereas channel i) was found to be hindered by too high kinetic barriers for the conditions found in the interstellar medium[1], channel ii) provided much easier paths towards glycine formation [2]. The delivery of glycine to primordial Earth was then studied by its reaction with defects at the silica grains, modeling the surface of meteoritic/cometary particles. When the grain finally reached a warm water-rich pool present on the primordial Earth, glycine is easily released[3] and becomes available for polymerization. This last step was found to be catalyzed when glycine is adsorbed on the surfaces of common feldspars, particularly abundant on the early Earth, showing that the interplay between a surface Brönsted acidic site and a nearby Lewis one was essential to activate the peptide bond formation[4, 5].

The study of the habitability and potential for life formation of extrasolar planets is hampered by the limited amount of observational constraints typical of this type of research. Also in the case of our own planet the paucity of experimental Archean data severely limits the study of the physical conditions present on the Earth at the epoch of the origin of life. Given this shortage of experimental data the study of the habitability of terrestrial planets requires a significant effort of modelization.

Here we focus on the modelization of the surface planetary temperature, a physical quantity used to define the habitability via the liquid water criterion. Energy Balance Models (EBM) of planetary climate provide a simple way to calculate the temperature-latitude profile of terrestrial planets with a small amount of computing resources. In the framework of astrobiology studies carried out by our group we have implemented a climate EBM to be applied in studies of the habitability of terrestrial planets.

After testing our code against results obtained in previous work [1,2], we have introduced a novel parametrization of the latitudinal heat transport and planetary albedo. Our model successfully reproduces the main features of the present-day Earth climate and can be applied to probing variations of astronomical and geophysical parameters, such as stellar luminosity, orbital semi-major axis and eccentricity, obliquity of the planetary axis, planet rotational velocity, land/ocean area ratio, and latitudinal heat diffusion.

We present specific examples of application of our EBMs to studies of habitability of terrestrial planets. In the first part we focus on the primitive Earth, taking into account the effects of the higher speed of Earth rotation and reduced solar luminosity at the epoch of life formation. In the second part we provide examples of habitability studies of planetary systems discovered in surveys of exoplanets. These examples allow us to critically discuss the concept of circumstellar habitable zone.

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