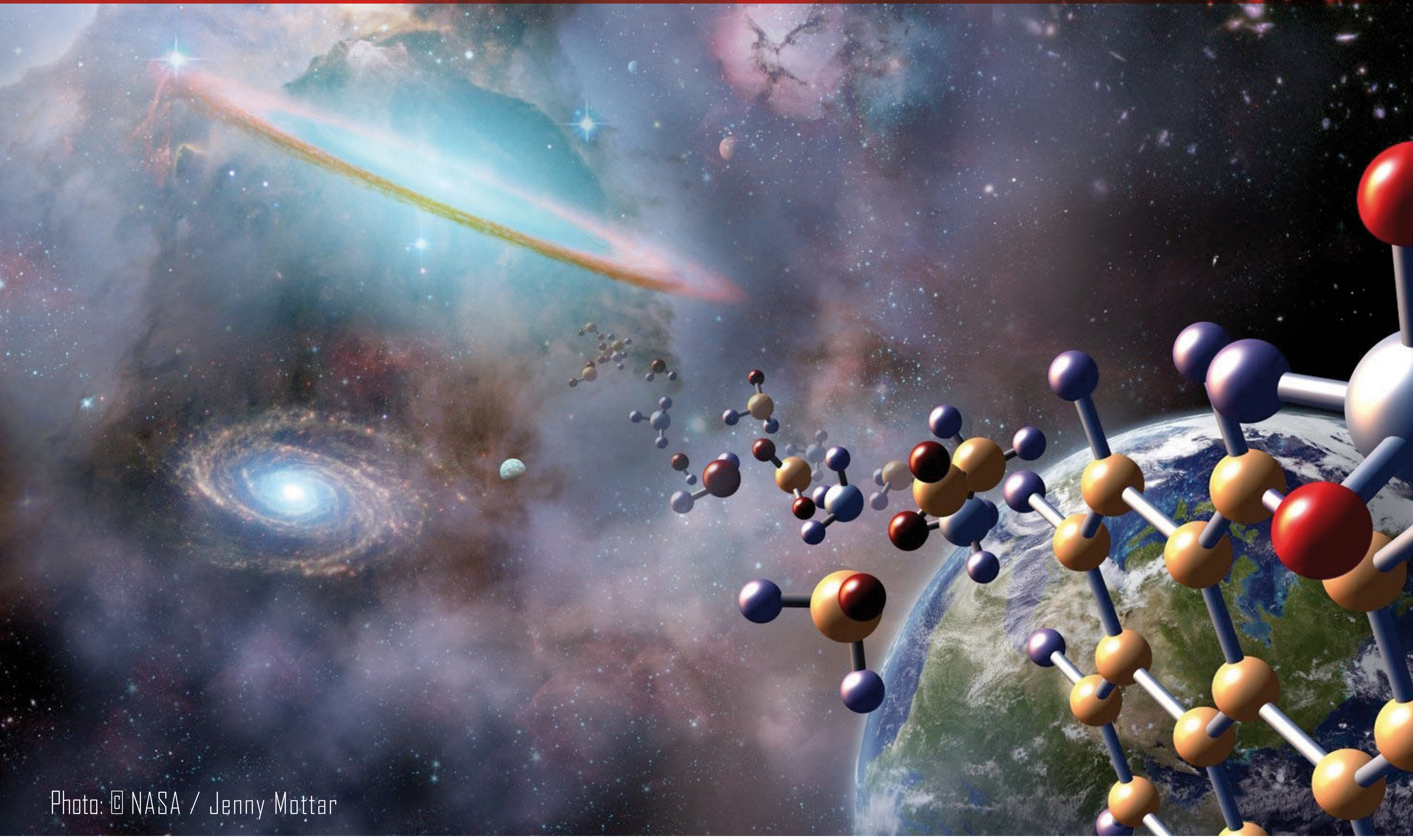
1ST ITALIAN WORKSHOP ON ASTROCHEMISTRY



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10-11 MARCH
2016

Sala Altana
Palazzo Strozzi
Piazza Strozzi
Firenze

ASTRONOMICAL COMPLEX ORGANIC MOLECULES IN DIFFERENT ENVIRONMENTS

BOOK OF ABSTRACTS

Elaborazione a cura del Servizio Comunicazione e Relazioni Esterne | SNS

SCUOLA
NORMALE
SUPERIORE

DREAMS

INAF
ISTITUTO NAZIONALE
DI ASTROFISICA
NATIONAL INSTITUTE
FOR ASTROPHYSICS

iALMA

RATIONALE

In order to understand the cosmic origins of life it is necessary to follow step-by-step the transition from the simplicity of the first atoms to the complexity of prebiotic molecules. Recent advances in sub-millimetre (ALMA, NOEMA) and IR (Spitzer, Herschel, SOFIA) observational facilities allow us to obtain a census of the chemical complexity in space. Astronomical Complex Organic Molecules (ACOMs) have been observed in nearby forming stars at all evolutionary stages (from pre-stellar cores to proto-stars and proto-planetary disks) as well as in nearby and high-z galaxies. The comprehension of the gas and dust chemical evolution in space requires a strong synergy between astrophysicists and chemists, flowing into the field of astrochemistry. Thanks to the great advances in the modelling of gas-phase and surface chemistry through laboratory works as well as quantum chemistry calculations, we now have the tools to investigate the formation routes of ACOMs in space, building blocks of pre-biotic molecules such as amino-acids and sugars.

The main goal of the 1st Italian Workshop on Astrochemistry is to bring together astrophysicists and chemists working on observations, theoretical models, and laboratory experiments to present their recent advances, to discuss about the open questions, and to plan future collaborations. In particular, the workshop will be focussed on four topics:

- **Observations of (complex) molecules in space**
- **Kinetics and molecular spectroscopy**
- **Modelling and experiments of complex organic molecules formation**
- **Prebiotic chemistry**

Interaction between the different communities will be encouraged through long discussions at the end of each session.

PROGRAMME

Thursday March 10, 2016

Morning Session

OBSERVATIONS OF (COMPLEX) MOLECULES IN SPACE

09.00 - 09.30	**Chiara Feruglio [I]** *Searching for molecular complexity in the distant universe*
09.30 - 09.50	**Francesco Costagliola [C]** *Exploring the molecular chemistry and excitation in obscured luminous infrared galaxies*
09.50 - 10.10	**Jose' Cernicharo [C]** *The MADEX code and the quest for new molecular species*
10.10 - 10.40	Coffee break
10.40 - 11.10	**Paola Caselli [I]** *The deuteration of interstellar molecules and links to our Solar System*
11.10 - 11.30	**Claudio Codella [C]** *Pristine protostellar jet-disk systems: from darkness to the cradle of life*
11.30 - 11.50	**Victor M. Rivilla [C]** *Understanding the formation of astrobiological molecules in star-forming regions*
11.50-12.40	**Discussion (Chair: Simona Gallerani & Linda Podio)**
12.40-14.10	Lunch break

PROGRAMME

Thursday March 10, 2016

Afternoon Session

KINETICS AND MOLECULAR SPECTROSCOPY

14.10 - 14.40	**Cristina Puzzarini [I]** *Astronomical complex organic molecules in space: the crucial frequency information from rotational spectroscopy*
14.40 - 15.00	**Francesco Fontani [C]** *Deuterium fractionation as a tool to investigate gas-phase versus surface chemistry*
15.00 - 15.20	**Sergio Rampino [C]** *On the temperature dependence of the rate coefficient of formation of C_2^+ from $C + CH^+$*
15.20 - 15.50	Coffee break
15.50 - 16.20	**Nadia Balucani [I]** *Gas-phase formation routes of complex organic molecules in the interstellar medium*
16.20 - 16.40	**Daniela Ascenzi [C]** *Growth of complex organic molecules via ion-molecule reactions*
16.40 - 17.00	**Stefano Falcinelli [C]** *Molecular dications in planetary ionospheres*
17.00 - 17.50	**Discussion (Chair: Cristina Puzzarini)**

Evening

18.00 - 20.00	Aperitif

Friday March 11, 2016

Morning Session

MODELS AND EXPERIMENTS OF COMPLEX ORGANIC MOLECULES FORMATION

09.00 - 09.30	**Serena Viti [I]** *Complex molecules formation in galactic and extragalactic environments*
09.30 - 09.50	**Cecilia Ceccarelli [C]** *Dimethyl ether and methyl formate, inseparable friends*
09.50 - 10.10	**Francesco Gianturco [C]** *Forming PAHs in diffuse and dark Interstellar clouds: a quantum modelling from electron-mediated dynamics*
10.10 - 10.40	Coffee break
10.40 - 11.10	**Elisabetta Palumbo [I]** *Formation of complex molecules after cosmic ion bombardment and UV photolysis of interstellar ice analogues*
11.10 - 11.30	**Fabrizio Capaccioni [C]** *67P/Churyumov-Gerasimenko: a portrait of a primitive Solar System body*
11.30 - 11.50	**Maria Cristina De Sanctis [C]** *The complex chemistry of the dwarf planet Ceres*
11.50-12.40	**Discussion (Chair: Cecilia Ceccarelli)**
12.40-14.10	Lunch break

Friday March 11, 2016

Afternoon Session
PREBIOTIC CHEMISTRY

14.10 - 14.40	**Piero Ugliengo [I]** *The role of surfaces in prebiotic chemistry*
14.40 - 15.00	**M. Merced Montero-Campillo [C]** *Identifying Substituted Cyanobutadiynes By Gas-Phase Infrared Spectroscopy: Theory & Experiments*
15.00 - 15.20	**Fanny Vazart [C]** *Feasible reaction mechanism for formamide formation in cold interstellar clouds*
15.20 - 15.50	Coffee break
15.50 - 16.20	**Raffaele Saladino [I]** *Chemical gardens: the first evidence of a spontaneous catalytic compartmentalization process in prebiotic chemistry*
16.20 - 16.40	**Savino Longo [C]** *Complex organic matter delivery by carbonate-rich meteorites: kinetic models*
16.40 - 17.00	**Teresa Fornaro [C]** *Inspecting the role of minerals in prebiotic processes and space-like conditions*
17.00 - 17.50	**Discussion (Chair: Dimitrios Skouteris)**

Evening

18.00 - 19.30	**Public Lectures**
18.00 - 18.45	**Andrea Ferrara** *C'è qualcuno lì fuori ?*
18.45 - 19.00	**Leonardo Testi** *La chimica dell'Universo: alla ricerca delle nostre origini cosmiche con ALMA*

Searching for molecular complexity in the distant universe

Chiara Feruglio
Scuola Normale Superiore, Pisa, Italy

The study of complex molecules in the Milky Ways interstellar medium provides information on its physical properties (temperature, density), as well as heating and cooling mechanisms. These information are crucial to understand the processes of gas collapse and formation of new stars as a function of the environment. Extending the study of complex molecules to extragalactic environments, and in particular in star-forming galaxies at (a) the peak epoch of galaxy assembly, z=1-3, and (b) the epoch of the formation of the first galaxies, $z > 5 - 6$ is today possible thanks to the improvements in previous generation mm interferometers, such as SMA and NOEMA, and the advent of ALMA. This opens the way to unveil gas collapse and star formation in environments different from those usually found in the MW and in the local group. High redshift star-forming galaxies are in fact characterised by different metallicity, compact star-forming regions, high molecular cloud filling factor, high SN rates, and often an active nucleus. I will review the current knowledge and future perspectives of the use of complex molecules to study the distant universe.

Exploring the molecular chemistry and excitation in obscured luminous infrared galaxies

Francesco Costagliola
Chalmers University of Technology, Gothenburg, Sweden - Italian ARC, Italy

Until recently, the study of the molecular interstellar medium of galaxies has been mostly focused on a few, relatively abundant, molecular species. Recent attempts at modelling the molecular emission of active galaxies have shown that standard high-density tracers do not provide univocal results and are not able to discriminate between different relevant environments (e.g., star-formation vs AGN). Spectral lines surveys allow us to explore the richness of the molecular spectrum of galaxies, provide tighter constrains to astrochemical models, and find new more sensitive tracers of specific gas properties. What started as a time-consuming pioneering work has become now routinely accessible with the advent of ALMA. Here I will report the results of the first ALMA spectral scan of an obscured luminous infrared galaxy (LIRG).

The MADEX code and the quest for new molecular species

José Cernicharo
CSIC, Madrid, Spain

The search for new molecular species requires a good understanding of the spectroscopy of the most abundant species, its isotopologues and vibrationally excited states, in order to identify these obvious spectroscopic features in any spectra obtained with sensitive radio telescopes and/or interferometers. Once all “seeds” have been identified we can start the search for new molecular species. Ten years ago we started a line survey of the Orion hot-core in which we detected more than 16000 features of which 8000 were unknown. The number of U-features has been reduced to less than 4000 thanks to a close collaboration with several spectroscopic laboratories and the MADEX code, a spectroscopic data base that permits to generate synthetic spectra and to compare with the astronomical data. I am going to show the results we have obtained in Orion and discuss the possible candidates for the remaining U-lines.

MADEX contains all collisional rates published so far for molecules of astrophysical interest and spectroscopy for 5300 molecular species. I have developed it during the last 30 years. Inside MADEX there is a LVG code, a multi-shell LVG code adapted to the spectroscopy of AGB stars, a 3D LVG utility and the rotational constants for the 5300 species. MADEX uses a large set of Hamiltonians to compute the spectra of the included molecular species. Hence, it does not stock the frequency, energy and intensity of the lines, but computes these parameters each time a molecule is selected.

The rotational constants are obtained from a fit to the published data using a set of programs I have written and that provide fortran routines that are incorporated into MADEX.

The deuteration of interstellar molecules and links to our Solar System

Paola Caselli
Max-Planck-Institut für extraterrestrische Physik, Garching, Germany

Before the formation of Sun-like stars, molecular clouds in our Galaxy fragment and produce dense regions called pre-stellar cores. These objects represent the initial conditions in the process of star and planet formation. They are cold (kinetic temperature < 10 K), dense (number density of H2 molecules > 10^5 cm^{-3}, at least ten times higher than the surrounding parent cloud), and quiescent (line broadening is dominated by thermal motions). Dust grains are covered with thick icy mantles and the first steps toward Deuterium enrichments, also measured in comets, meteorites and on Earth, proceed at these early stages. Here, I shall discuss our understanding of the chemical structure of pre-stellar and protostellar cores, protoplanetary disks as well as recent theoretical predictions about protoplanetary disks in their earliest phases of evolution. Links to our own Solar System will be highlighted.

Pristine protostellar jet-disk systems: from darkness to the cradle of life

Claudio Codella
INAF - Osservatorio Astrofisico di Arcetri, Italy

What is the role of the pre-solar chemistry in the chemical composition of the Solar System bodies? The molecular complexity builds up at each step of the forming process, ending up in Complex Organic Molecules (COMs). It is essential to have reliable information on the COMs spatial distribution to study their association with different ingredients of the star formation recipe (e.g. accretion disks, shocks). Thanks to the advent of new telescopes such as ALMA and NOEMA, it is now possible to verify whether the regions precursor of planetary systems are already rich in pre-biotic molecules.
What are the conditions for the emergence of life? What are the basic chemical mechanisms that led atoms to molecules and then to life? What is the role of the pre-solar chemistry in the present chemical composition of the Solar System? The molecular complexity builds up at each step of the process leading to star formation, starting from simple molecules and ending up in Complex Organic Molecules (COMs). The detection of COMs is thus key to understanding the formation of pre-biotic molecules in the interstellar medium.

However, observations of COMs have been and still are instrumental in making progress; it is of paramount importance to have reliable information on the spatial distribution of COMs in order to investigate their association with different ingredients of the star formation recipe (warm envelopes and cavities opened from hot jets, accretion disks and shocks), which requires spatial resolutions less than 100 AU. Thanks to the combination of the high-sensitivities and high-angular resolutions provided by the advent of new telescopes such as ALMA and NOEMA, it is now possible to image in details the earliest stages of a Sun-like star formation. In particular, we will discuss the results obtained in the framework of Large Programs at mm and sub-mm wavelengths (such as ASAI, CALYPSO, and SOLIS), showing how to verify whether the regions precursor of planetary systems are already rich in pre-biotic molecules.

Understanding the formation of astrobiological molecules in star-forming regions

Victor M. Rivilla
INAF - Osservatorio Astrofisico di Arcetri, Italy

The increasing number of detections of complex organic molecules around young stellar objects strongly suggests that they are part of the material of which planetary systems are made of. These molecules play a central role in interstellar prebiotic chemistry and may be directly linked to the origin of life. Since the hot and dense molecular cores surrounding massive stars harbour the richest chemistry in the interstellar medium, they are the best natural laboratories to study the formation of these complex molecules. In my talk I will present our results from observations towards the hot molecular cores G31.41+0.31 and W51e2, where we have detected members of three families of prebiotic molecules: aldoses, polyols and esters. I will discuss how these findings can help us to understand the formation of these building blocks of life in the interstellar medium, with the help of chemical models and laboratory works.

Astronomical complex organic molecules in space: the crucial frequency information from rotational spectroscopy

Cristina Puzzarini
Dipartimento di Chimica "Giacomo Ciamician", Bologna, Italy

Understanding the chemical evolution of interstellar clouds and star-forming regions is a central problem in astrophysics and astrochemistry. The starting point is the identification of the chemical species through their spectroscopic signatures: the frequency information in fact provides the unequivocal proof of the presence of a chemical species. Such identification requires the direct comparison of the frequencies retrieved from the astronomical observations with those obtained in the laboratory, with gas-phase species being mostly discovered via their rotational signatures (with frequencies going from the millimetre-wave region to far-infrared).

The systematic observation of a given astronomical source at all wavelengths leads to line surveys that in principle provide a complete census of the molecular content. The assignment of these line surveys allows for an unbiased picture of the chemical composition that in turn can also be used to infer information on physical conditions (such as temperature and density). The new powerful astronomical facilities (like ALMA, Herschel and SOFIA, just to mention a few examples) opened up to unprecedented resolution and sensitivity as well as frequency coverage, thus offering unique opportunities to extend the chemical inventory, in particular to organic species of increasing complexity (the so-called astronomical complex organic molecules). On the other hand, sensitivity and resolution increase the line confusion in spectral observations, thus requiring a large effort to be taken in laboratory measurements (from both an experimental and computational point of view) to help in unravelling it.

Furthermore, to interpret and analyse the astronomical observations, an important piece of information is provided by the collisional excitation rates of the molecules with the predominant collision partners (like H_2 and He); these rates can be calculated using quantum-chemical methods or measured in the laboratory.

In this contribution, the role played by laboratory (experimental and computational) rotational spectroscopy in the field of astronomical observations and in the investigation of astronomical complex organic molecules will be illustrated through a number of examples and case studies.

Deuterium fractionation as a tool to investigate gas-phase versus surface chemistry

Francesco Fontani
INAF - Osservatorio Astrofisico di Arcetri, Italy

The process of deuterium enrichment in molecules from the main reservoir HD is initiated in molecular clouds by exothermic gas-phase reactions, which boost the formation of deuterated species in cold ($T < 20$ K) gas, and inhibit it in warmer environments. For this reason, in the star formation process, the fraction of deuterated molecules is thought to increase during the cold pre-stellar phase and then it is expected to drop after protostellar birth. Although this general framework remains true, growing observational evidence is showing that the story is not so simple. In fact, important molecules like NH_3, H_2O, and their deuterated forms, as well as relevant complex organic molecules like CH_3OH, can be formed also on the icy mantles of dust grains during the early cold phase, and then released into the gas due to evaporation/erosion of these mantles at later stages. This contribution from surface chemistry can hence make significant differences in the dependence with time of the observed deuterated fraction for molecules formed uniquely in the gas phase and those formed also on dust grains. Based on these theoretical expectations, I will discuss the main results obtained from observations of single-dish telescopes (IRAM-30m, Nobeyama-45m, GBT-100m), and interferometers (PdBI) with which we have surveyed several deuterated molecules formed both in gas and on grain surfaces in different kind of star forming cores.

On the temperature dependence of the rate coefficient of formation of C_2^+ from C + CH^+

Sergio Rampino
Consiglio Nazionale delle Ricerche, Italy

We carried out quasi-classical trajectory calculations for the C + CH^+ —> C_2^+ + H reaction on an ad hoc computed high-level ab initio potential energy surface (Rampino et al, MNRAS, submitted; Pacifici et al, JPCA, submitted) obtained through an optimal bond-order based configuration-space sampling (Rampino, JPCA 2015, DOI: 10.1021/acs.jpca.5b10018). Thermal rate coefficients at the temperatures of relevance in cold interstellar clouds were derived and compared with the assumed, temperature-independent (Langevin model) estimates publicly available in kinetic databases KIDA and UDfA. For a temperature of 10 K the database value overestimates by a factor of two the one obtained by us (thus improperly enhancing the destruction route of CH^+ in astrochemical kinetic models) which is seen to double in the temperature range 5-300 K with a sharp increase in the first 50 K. The computed values were fitted via the popular Arrhenius formula and best-fitting parameters to be included in the online mentioned databases are provided. Further investigation shows that the temperature dependence of the thermal rate coefficient better conforms to the recently proposed so-called "deformed Arrhenius" (Aquilanti et al, CPL 2010, 498, 209; Aquilanti et al, CP 2012, 398, 186).

Gas-phase formation routes of complex organic molecules in the interstellar medium

Nadia Balucani
Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Italy

Relatively complex organic molecules (COMs), such as formamide or cyanomethanimine, have been detected in the gas-phase of various regions of the interstellar medium. Some difficulties in assessing their formation routes under the harsh conditions of interstellar objects have progressively brought the current astrochemical models to privilege grain-surface over gas-phase chemistry to explain their formation. In this scenario, grain-surface chemistry is not only responsible for the hydrogenated molecules of the pre-collapse phase, but also for the whole set of the observed COMs (see, for instance, Garrod & Herbst 2006).

Nevertheless, as recently pointed out by a theoretical investigation of two gas-phase reactions leading to formamide and cyanomethanimine (Vazart et al. 2015, Barone et al. 2015), many gas-phase routes have actually been overlooked and not considered in the astrochemical models, while their inclusion with the parameters determined in laboratory experiments or via accurate theoretical calculations could be decisive in reproducing the observed abundances.

In this contribution, we report on recent effort in searching for new formation routes of COMs in the gas-phase by: 1) extensive literature search of previously overlooked bimolecular reactions; 2) testing the new formation routes in astrochemical models. The approach is the same recently used to address the formation of methylformate starting from the parent molecule dimethylether via a set of bimolecular reactions which were studied in laboratory experiments in the 80's but completely ignored in previous astrochemical models (Balucani et al. 2015).

The input of state-of-the-art experimental techniques (CRESU, Crossed Molecular Beam method) will also be noted (Jiménez et al. 2015, Casavecchia et al. 2015).

N. Balucani, C. Ceccarelli and V. Taquet, 2015, MNRAS 449, L16–L20
V. Barone, C. Latouche, D. Skouteris, F. Vazart, N. Balucani, B. Lefloch, C. Ceccarelli, 2015, MNRAS 453, L31-L35
R.T. Garrod and E. Herbst, 2006, A&A, 457, 927
E. Jiménez, M. Antiñolo, B. Ballesteros, A. Canosac, J. Albaladejo, 2016, PCCP 18, 2183
F. Vazart, C. Latouche, D. Skouteris, N. Balucani, V. Barone, 2015, ApJ 810, 111.

Growth of complex organic molecules via ion-molecule reactions

Daniela Ascenzi
Dipartimento di Fisica, Università di Torino, Italy

Due to the long range attraction forces between a charged and a neutral species ion-molecule reactions are usually barrier-less and spontaneous in the gas phase, hence they can play an important role in the formation of molecules in various astronomical environments. In addition to the heterogeneous chemistry occurring on the surface of ice grains in molecular clouds, it has been proposed that ion-molecule reactions may contribute to the growth of complex organic species by post-processing the organic material liberated from the grains. A special attention is devoted to reactions involving two medium sized pre-formed building blocks, because 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. Our contribution is in the laboratory measurements of kinetic parameters (i.e. cross sections and branching ratios as a function of the collision energy) for the reaction of charged molecules with neutrals, using tandem mass spectrometric techniques and RF octupolar trapping of charged species. In the talk I will focus on some recent results that are of particular relevance for understanding the chemical evolution of Titans atmosphere: the reactivity of methyl cations with methyl substituted acetylenes and of CH_2CN^+ cations with C_2H_2 and CH_4, as well as isomer-selective reactivity of CH_3CN^+/CH_2CNH^+ radical cations with C_2H_4.

Molecular dications in planetary ionospheres

Stefano Falcinelli
Dipartimento di Ingegneria Civile e dell'Ambiente, Università di Perugia, Italy

In the chemistry of planetary ionospheres molecules can interact with electromagnetic waves: γ, X rays and ultraviolet (UV) light. The dissociative double photoionisation processes induced by VUV and EUV photons leading to fragment ions formation with a high kinetic energy content could give an important contribution to the ions escape from the atmosphere of some planets of the Solar System, like Venus, Mars and Titan. These processes occur via formation of intermediate molecular dications that can dissociate by Coulomb explosion towards the formations of two ion fragments having a kinetic energy released (KER) of several eV, and therefore much larger than the limiting thermal escape velocity. When CO_2, C_2H_2 and N_2O molecules are ionised using photons with an energy in the range of 30 to 65 eV, molecular fragmentation can be induced. These ionic species (CO^+, O^+, N_2^+, N^+, NO^+, H^+, C^+, CH^+, CH_2^+ and C_2H^+) are characterised by a translational energy ranging between 1.0 and 5.5 eV, which is large enough to allow some of them to escape from the atmospheres of Mars and Titan. In the case of O^+, we can conclude that the dissociative double photoionisation of CO_2 in the ionosphere of Mars can contribute to explain the observed behaviour of the O^+ ion density profile measured by the Viking 1 lander. Finally, the angular distributions of product ions with respect to the light polarisation vector direction are discussed.

Complex molecules formation in galactic and extragalactic environments

Serena Viti
University College London, UK

Complex Organic Molecules (COMs) are now routinely observed in the Interstellar Medium. In this talk I will give an overview of the chemical complexity observed in space with particular emphasis on their different "signature" across environments, from galactic star forming regions to extragalactic environments such as starburst and ultra luminous infrared galaxies. COMs can be divided in subgroups, depending on their interrelationship during formation and destruction: ratios of COMs are time dependent, and strongly vary with the physical conditions of the gas as well as its energetics. I will discuss the possible formation routes of COMs and highlights the needs astronomers have of experimental data including accurate rest frequencies, temperature dependent intensities, as well as rate coefficients for all their gas and solid phase formation routes.

Dimethyl ether and methyl formate, inseparable friends

Cecilia Ceccarelli
IPAG, Grenoble, France

Dimethyl ether (DME) and methyl formate (MF) are two astronomical complex organic molecules (ACOMs) which have been detected in several star forming regions and even in cold molecular clouds. Despite they have been detected for more than four decades, we still do not know how they are formed. Two basic mechanisms are evoked in the literature: grain-surface or gas phase chemistry. In this contribution, I will briefly review the observational framework and show that the ratio of the measured DME and MF abundances is of the order of unity in all observed sources. I will then discuss how this is in favour of a gas-phase formation route for these species.

Forming PAHs in diffuse and dark Interstellar clouds: a quantum modelling from electron-mediated dynamics

Francesco Gianturco
University of Innsbruck, Austria

The formation of very complex and large Carbon-bearing systems has been suggested, and recently observed through C60+ detection, for a long time in the prestellar aggregates and in the molecule-rich interstellar regions. In my talk I shall show examples of quantum modelling of their formation through electron-soaking quantum dynamics that can also occur on the outer regions of the PDRs. The processes considered will report the metastable attachment of free electrons to large systems (e.g. coronene and others) and indicate the path for further ionic chemical reactions for the growth of the initial anionic metastable species into larger PAHs.

Formation of complex molecules after cosmic ion bombardment and UV photolysis of interstellar ice analogues

M. Elisabetta Palumbo
INAF – Osservatorio Astrofisico di Catania, Italy

Energetic ions (keV-MeV) passing through molecular solids (such as interstellar ice analogues) release energy to the target along the ion track. As a consequence molecular bonds are broken and in a very short time (one picosecond or less), radicals and molecular fragments recombine giving rise to molecular species not present in the original sample, furthermore the structure of the target is modified. In the case of UV photolysis the energy is released to the target material through single photo-dissociation or ionisation events per incoming photon. Thus after ion bombardment and UV photolysis the chemical composition and the structure of the sample is modified. Infrared and Raman spectroscopy are two powerful and complementary techniques to study the physical and chemical properties of icy samples. In particular, it is possible to identify molecular groups and specific molecules by IR spectroscopy. Raman spectroscopy gives further information on the presence of IR inactive vibrational modes and on the structural properties of the sample.

Here I will present some recent laboratory experiments which show the formation of (complex) molecular species after ion bombardment and UV photolysis of simple ices. In particular I will focus on experimental results which show the formation of methyl formate, formamide, polynes, ammonium carbamate and ammonium formate after ion bombardment of simple ices.

67P/Churyumov-Gerasimenko: a portrait of a primitive Solar System body

Fabrizio Capaccioni
IAPS-INAF, Rome, Italy

Comets harbour the most pristine material in our solar system in the form of ice, dust, silicates, and refractory organic material with interstellar heritage. The observations of the VIRTIS imaging spectrometer [1] onboard the Rosetta orbiter, have revealed a very complex surface showing varied morphologies related to active processes. The reflectance spectra collected across the surface display a low reflectance factor over the whole spectral range [2], two spectral slopes in the visible and near-infrared ranges and a broad absorption band centred at 3.2 μm. These spectral features describe a largely dehydrated surface, rich in organic compounds and opaque minerals [3]. The low albedo of comet 67P/CG is described by a dark refractory polyaromatic carbonaceous component mixed with opaque minerals. A semi-volatile component, consisting of a complex mix of low weight molecular species not volatilised at T~220 K, is likely a major carrier of the 3.2 μm band.

COOH in carboxylic acids is the only chemical group that encompasses the broad width of this feature. It appears as a highly plausible candidate along with the NH_4^+ ion. Photolytic/thermal residues, produced in the laboratory from interstellar ice analogs, are potentially good spectral analogs [4].

[1] Coradini et al., SSRev, 128, 2007;
[2] Ciarniello et al, A&A, 583, 2015;
[3] Capaccioni et al., Science, 347, 2015;
[4] Quirico et al., Icarus, in press

The complex chemistry of the dwarf planet Ceres

Maria Cristina De Sanctis
IAPS-INAF, Rome, Italy

The Dawn NASA mission is observing Ceres surface with its suite of instruments [1] including a Visible and InfraRed Mapping Spectrometer [2]. Since the first data, near-infrared spectra revealed a dark surface with strong and complex absorption bands in the spectral region around 3μm [3]. These features are distinctive for OH-bearing minerals, like some phyllosilicates. We find here that the surface contains ammoniated phyllosilicate added to a dark material (likely magnetite), Mg-phyllosilicates and carbonate [3]. Particularly interesting are the bright materials present in some craters that show different proportions of the components of the mixture. The retrieved mineralogy and composition indicates pervasive aqueous alteration of the surface, processes that are expected to be favoured on large bodies like Ceres . Furthermore, Ceres low density and the presence of OH-bearing minerals, suggests a high content of water inside the body, consistent with extensive differentiation and hydrothermal activity, and possibly even a present-day liquid subsurface layer [4]. The presence of ammoniated clays together with the low density, may indicate that Ceres retained more volatiles than objects represented in the meteorite collection, or that it accreted from more volatile-rich material typical of the outer solar system [3].

[1] Russell et al., Science, 336, 684, 2012;
[2] De Sanctis et al., SSR, 2010;
[3] De Sanctis et al., Nature, 2015;
[4] Neveu & Deush, GRL, 2015.

The role of surfaces in prebiotic chemistry

P. Ugliengo[1], M. Sodupe[2], J. Navarro-Ruiz[2] and A. Rimola[2]
[1]Dip. Di Chimica - Università di Torino, Italy
[2]Dep. de Química, Universitat Autonòma de Barcelona, Spain

The usual interpretation of the complex scenario of molecular reactions occurring in the interstellar medium is through a cascade of gas-phase reactions [1]. Ab initio quantum mechanical methods of very high quality and computational cost helps in elucidate paths along the reactive potential energy surface. Alternatives are sophisticated gas-phase model experiments in terrestrial labs, mimicking the harsh conditions of the interstellar medium. Nevertheless, it has since long recognised [2], with kinetic models, that gas-phase process alone cannot justify the abundance in the universe of even the simplest molecule, H_2. Resort to reactions occurring on interstellar grains, present in interstellar clouds, is mandatory to reconcile prediction with observation [3]. The core of the dust grains is mainly due to silicates (of the olivine family) while the kind and thickness of the mantle depends on the kind of clouds, either diffuse or dense. In diffuse clouds, the core grain dominates the adsorption process, while in dense clouds it occurs mainly at the icy surface of the external mantle. While quantum mechanical simulation of purely gas-phase processes is well established, far less developed methods are at hand for reactions occurring at the surfaces of grains. The difficulty is on modelling the grain structure (from both chemical composition and aggregation state) to be close enough to that present in the interstellar clouds. Also, it is challenging to accurately model reactions at extended surfaces as the methods are less developed than for molecular processes. In the talk, we discuss few examples from our own work for simulating H_2 formation on silicate grains as well as reaction of simple molecules on models of icy grains. We will discuss both strength and weakness of different approaches in a perspective also addressing the formation of biopolymers on mineral surfaces.

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Identifying Substituted Cyanobutadiynes By Gas-Phase Infrared Spectroscopy: Theory & Experiment

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Cyanobutadiyne was detected in interstellar medium in 1976, whereas MeC5N (2,4-hexadiynenitrile), its methyl derivative, was observed 30 years later. We recently reported the synthesis of compounds MeC5N and 5-bromo-2,4-pentadiynenitrile (BrC5N), the later being a potential precursor to access to higher homologues such as HC7N and its methyl derivative MeC7N. The IR spectra of BrC5N and MeC5N have been recorded within the 4000-500 cm^{-1} spectral region and calculated by means of high-level ab initio and density functional theory calculations. Although their structures are very similar, there are subtle differences arising from the strength of the triple C-C bond not directly bound to the substituent. As revealed by both experiment and theoretical evidences, this fact would allow to correctly differentiate them and explains the role of the substituents. Moreover, the IR spectrum of MeC5N gives a tool for its detection and quantification in comets or planetary atmospheres, if present in these media.

Feasible reaction mechanism for formamide formation in cold interstellar clouds

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In prebiotic chemistry, formamide is a crucial compound to connect metabolism (conversion of energy), which is ruled by proteins, and genetics (passage of information), ruled by RNA and DNA. Moreover, its key role in the interstellar medium appears to be also remarkable since it has been detected in the galactic center sources Sgr A and Sgr B2 [1], in the Orion-KL region (an active site of high-mass star formation embedded in OMC-1) [2] and more recently in a solar-type protostar [3].

Several reaction channels leading to the formation of formamide have therefore been investigated by a computational strategy integrating state-of-the-art electronic structure calculations and kinetic calculations. Our results indicate that formation of formamide starting from OH radical and methanimine as reactants is barrierless and can, therefore, occur under the low temperature conditions of interstellar objects.

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Chemical gardens: the first evidence of a spontaneous catalytic compartmentalisation process in prebiotic chemistry

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The pathway from simple abiotically made organic compounds to the molecular bricks of life as we know it is unknown. The most efficient geological abiotic route to organic compounds results from the aqueous dissolution of olivine, a reaction known as serpentinization [1]. In addition to H_2 and a reducing environment, the serpentinization reactions lead to high-pH alkaline brines that can become easily enriched in silica. Under these chemical conditions the formation of self-assembled nanocrystalline mineral composites, namely metal silicate hydrate (MSH) tubular membranes (chemical gardens) and/or silica/carbonate biomorphs, is unavoidable [2]. These structures have remarkable catalytic properties. Among one-carbon compounds, formamide (NH_2CHO) has been shown to trigger the formation of complex prebiotic molecules under mineral-driven catalytic conditions [3], proton irradiation [4], and laser-induced dielectric breakdown [5]. Here we show that chemical gardens act as heterogeneous catalysts for the thermal condensation of NH_2CHO, yielding biologically relevant compounds, including nucleobases, carboxylic acids, and amino acids. The collections of compounds forming inside and outside the tubular membranes are clearly specific, demonstrating that the mineral self-assembled membranes at the same time create space compartmentalisation and selective catalysis of the synthesis of relevant compounds. Rather than requiring odd local conditions, the prebiotic organic chemistry scenario for the origin of life appears to be common at a universal scale and, most probably, earlier than ever thought for our planet.

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Complex organic matter delivery by carbonate-rich meteorites: kinetic models

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The author reports on work in progress to evaluate the capability of carbonate-rich meteors, or grains, entering a planetary atmosphere, to deliver complex organic molecules. An atmosphere entry model is used to discuss the scenario. The analysis of the composition data of the most promising meteorite minerals leads to suggest magnesite as a suitable test case for simplified estimates. This mineral is much more thermolabile than most meteorite constituents and undergoes facile endothermic degassing. Using kinetic theory and thermochemical considerations, the decomposition rate is estimated for several scenario. Promisingly, it is found that magnesium-rich materials, actually similar to those found in meteorite carbonate globules, may offer much better protection to complex organic matter than silicates and still significant better than limestone. Furthermore, the degassing of carbon dioxide provides additional radiative energy dissipation in the vapour cap thereby reducing the thermal load. The limits of the present quantitative approach are discussed, in particular the incertitude related to diffusion processes in the solid and the importance of a better state-to-state kinetics of carbon dioxide.

Inspecting the role of minerals in prebiotic processes and space-like conditions

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The passage from geochemistry to biochemistry probably resulted from the combination of multiple complex phenomena between organic and inorganic systems, and studying how organic molecules interact with minerals may be a step forward in resolving unsolved questions about the origin of life. Investigations on the binding mechanism of building blocks of life such as nucleic acid components to mineral surfaces, the stability and reactivity of molecule-mineral complexes under plausible prebiotic and space-like conditions, would give key inputs to figure out the physico-chemical phenomena that led to the emergence of life on Earth as well as the molecular chemical evolution in space. The high complexity underlying such processes has been faced both experimentally by investigation of the thermodynamics of the adsorption process, characterisation of the nature of molecule-mineral interactions through infrared spectroscopy measurements, study of the photostability of molecule-mineral complexes through UV irradiation experiments, and theoretically through computational spectroscopy, surface complexation studies and molecular modelling of mineral-molecule interactions. Such results contribute to unravel the role of minerals in the transformation/preservation of biomolecules in abiotic environments, shedding light on the intricate prebiotic geochemical processes on the early Earth and on the chemical evolution of complex molecular systems in space.

Molecular Spectroscopies of Polycyclic Aromatic Hydrocarbons with a twist: the Helicenes

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Helicenes are molecules made of sequentially ordered fused benzene rings, and are characterised by two apparently conflicting properties, namely conjugation and non-flat structure. These properties make them prototypic molecules for chiral organisation with large higher order susceptibility. Simple helicenes exhibit large optical rotation (OR) and circular dichroism (CD) spectra. Not long ago we were able to record chiroptical spectra in the infrared range and associated with Raman activity, i.e. associated to vibrational activity, called VCD and ROA spectra, respectively [1,2]. IR spectroscopy of helicenes shows very specific fingerprints of the hydrogenated molecular edge, similarly to other members of the wide family of PAHs [3]. These techniques appear more useful than UV-CD to chase these molecules in dark stellar sooths. We also recorded chiral luminescence phenomena (CPL) and obtained quite useful information on electronic excited states [4]. The role of hetero-atoms in quenching OR and in enhancing CPL will be pointed out [5].

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The first hot corino in a Class I object in Perseus as observed by ASAI

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Complex organic molecules (COMs) have been detected towards the early stages (prestellar cores, Class 0) and the Solar System, demonstrating the existence of efficient pathways to chemical complexity. However the COMs observations in the intermediate stages (Class I / Class II) are still missing.
We report here the results of the ASAI large program, aimed to observe with the IRAM 30-m antenna several targets sampling different stages of the Sun-like star formation.

We report the first detection of a hot corino around a Class I object, SVS 13A. The source, driving a large scale outflow, is a member of the NGC1333 cluster in Perseus. On the other hand, no evidence of a rich chemistry is observed towards the younger object (Class 0) SVS 13B, which is driving a collimated jet.

We detect towards SVS13A a large number (more than 100) of emission lines due to COMs such as acetaldehyde, methyl formate (MF) and dimethyl ether (DME), in addition to other less complex organics like methanol and formaldehyde. The identified lines cover high-excitation energies, up to ~ 200 K, implying T_{rot} close to 100 K. As in previously observed Class 0 hot corinos, methoxy (CH_3O) is not detected, questioning the current models that consider CH_3O as a precursor of DME and MF. The COMs column density ratios will be analysed to discuss possible evolutionary effects of the chemistry associated with Class 0 and Class I hot corinos.

The reactions of atomic oxygen with unsaturated hydrocarbons and interstellar hydrocarbon growth

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The observation of highly unsaturated organic molecules (e.g. polyynes, and cyanopolyynes) in the interstellar medium (and in other extraterrestrial environments such the atmosphere of Saturn's moon Titan) poses the question of how these molecules can survive in media rich in molecular and atomic hydrogen as well as other atomic and radical species. From a chemical point of view, indeed, each unsaturated C-C bond is a potential site for addition reactions, especially if one considers the electrophilic nature of the atomic and molecular radicals abundant in the interstellar medium. Part of this puzzle is actually explained by the fact that the reactions of polyynes and other unsaturated hydrocarbons (alkenes, dienes) with several atomic and radical species (such as atomic carbon or CH, C_2H, C_2 and CN radicals) do not destroy the C-atom skeleton of unsaturated species, but rather elongate it. Oxygen-containing highly unsaturated species have not been identified so far in interstellar objects, with the only exceptions being HCCO, ketene ($CH_2=C=O$), vinyl alcohol ($CH_2=CHOH$) and propynal ($HC\equiv CCHO$). Oxygen in C-rich environments appears, instead, to be mostly locked in CO, H_2CO and H_2O species (Agundez et al. 2010 and references therein).

In our laboratory we have started a systematic investigation of several reactions involving atomic oxygen and unsaturated hydrocarbons (C_2H_2, C_2H_4, CH_3CCH, $CH_2=C=CH_2$, $CH_3CH=CH_2$, $C_2H_5CH=CH_2$) by means of the crossed molecular beam technique with mass spectrometric detection and time-of-flight analysis (see Casavecchia et al. 2015 and references therein). 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 ($CH_2=C=CH_2$) where ~ 90% of the reaction leads to the products $CO+C_2H_4$(Leonori et al. 2012), but also significant fractions of the reactions $O+C_2H_2$, $O+C_2H_4$, and $O+CH_3CH=CH_2$lead to the products $CO+CH_2$, HCO $+CH_3$, and $HCO+C_2H_5$respectively (Leonori et al. 2014, Balucani et al. 2015, Leonori et al. 2015). 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 C-rich and O-rich interstellar objects will be noted.

Glycolaldehyde in Perseus young Solar analogs

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Glycolaldehyde ($HCOCH_2OH$) is the simplest of the monosaccharide sugars and it is expected to be a precursor of ribose, an RNA component; it is playing a major role in the prebiotic chemistry in low-mass star forming regions from the astro-biological perspective. As part of the CALYPSO (http://irfu.cea.fr/Projects/Calypso) survey with the IRAM PdBI interferometer, we have obtained high angular resolution (< 1”) spectral maps at 1.3 mm and 1.4 mm of 12 Solar-mass Class 0 protostellar systems in L1448 and NGC-1333 regions in Perseus. This deep survey led to the detection of a large number of lines emitted by complex organic molecules in several sources: our analysis was based on the searching of Glycolaldehyde emission. Preliminary results: (i) 4 (33%) of 12 individual sources suggest $HCOCH_2OH$ emission; (ii) detection of several lines covering a large spread in excitation (30 to 370 K); (iii) The line intensities seem to be consistent with a single temperature LTE emission (~100-180 K). Our results suggest that the Glycolaldehyde emission is confined to a limited region of the inner envelope where the gas temperature is sufficiently high to evaporate the ice mantles. Our preliminary analysis shows that the Glycolaldehyde gas phase abundance relative to molecular hydrogen has a spread of a factor of ~10 among the detected sources.

Water in comets: First near-IR spectral survey of H_2O in comet C/2014 Q2 Lovejoy with TNG/GIANO

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Comets are the most pristine bodies of Solar System and water is the most abundant constituent of cometary ice. Its production rate is used to quantify cometary activity and the measurements of ortho-para ratio can clarify the nature and meaning of the spin temperature in the cosmic context. In February 2015, we acquired the first comprehensive high resolution spectral survey of comet C/2014 Q2 Lovejoy in the 0.9-2.5 μm range, by observing with GIANO at TNG (La Palma, Canary Islands, ES). We detected emissions of radical CN, water (H_2O), and many unidentified emission features. We quantified the water production rate by comparing the calibrated line fluxes with the NASA Goddard full non resonance fluorescence cascade model for H_2O. The production rate of ortho and para water provide an estimation of ortho to para ratio consistent with statistical equilibrium (3.0), but the confidence limits are not small enough to enable a critical test of the nuclear spin temperature in this comet. Until now, high-resolution spectroscopy in the infrared (2.7 - 5 μm) has been a powerful tool to quantify molecular abundances in cometary comae. Today the expansion to the near-IR region (0.9-2.5 μm) will extend this capability to new band systems. Our observations open a new pathway for cometary science in the near-IR and establish the feasibility of astrobiology-related scientific investigations with future high resolution IR spectrographs on 30-m class telescopes, e.g., the HIRES on E-ELT.

Dimerization of methanimine and its charged species in the atmosphere of Titan and interstellar/cometary ice analogs

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Methanimine is an important molecule in prebiotic chemistry since it is considered a possible precursor of the simplest amino acid, glycine, via its reactions with HCN (and then H_2O) or with formic acid (HCOOH). According to this suggestion, the simplest amino acid can be formed 'abiotically' starting from simple molecules relatively abundant in extraterrestrial environments and primitive Earth. Interestingly, methanimine has been observed in the upper atmosphere of Titan, which is believed to be somewhat reminiscent of the primeval atmosphere of Earth. Methanimine can be produced in the atmosphere of Titan by the reactions of $N(^2D)$ with both methane and ethane, or by other simple processes, including the reaction between NH and CH_3 or reactions involving ionic species [1]. Recent models derived a larger quantity of methanimine than that inferred by the analysis of the ion spectra recorded by Cassini Ion Neutral Mass Spectrometer. Growing evidence suggests that nitrogen chemistry contributes to the formation of the haze aerosols in the Titan upper atmosphere. In this respect, since imines are well-known for their capability of polymerizing, CH_2NH is an excellent candidate to account for the nitrogen-rich aerosols of Titan through polymerization and copolymerization with other unsaturated nitriles or unsaturated hydrocarbons. Polymerization of methanimine provides an important contribution to the formation of the nitrogen-rich aerosols, but a quantitative inclusion of this process in the model could not be obtained as there is no information on methanimine polymerization. Since the first step of polymerization is dimerization, in this contribution we report on a theoretical characterization of methanimine dimerization. Electronic structure calculations of the potential energy surfaces representing the reactions of electronically excited atomic nitrogen, $N(^2D)$, with methane and ethane are also presented, as they are possible formation routes of methanimine under the conditions of the upper atmosphere of Titan [2].

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ALMA/VLA observations of the dust properties across the CO snowline in the HD163296 disk

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Recent interferometric observations with ALMA allowed to resolve the CO snowline in the midplane of the disk around HD163296.

From the comparison between images at different wavelengths (ALMA Band 6 and 7, VLA Ka Band) it was possible to infer the size of the grains as a function of the radius, through the measurement of the opacity spectral index. This analysis suggests the presence of larger grains (millimeter to centimeter sized) in the inner regions inside the CO snowline, and smaller grains (less than millimeter sized) in the outer regions. The results are consistent with the hypothesis that grain have been processed in this disk and have experienced inward migration. Re-analysing ALMA Band 7 Science Verification data we found a (radially) unresolved excess in the continuum emission centered near the location of the CO snowline at ~90 AU, that could be due to a change in the dust properties near the CO condensation front. Further observations are needed to investigate the origin of this feature.

ASAI: Astrochemical Surveys at IRAM The astrochemical evolution from interstellar clouds to young stellar objects

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The ASAI project addresses the question of our “chemical origins”. Based on observations with the IRAM 30-m radiotelescope in Pico Veleta (Spain), it joins the efforts of specialists in Astrochemistry to a complete census of the gas chemical composition, including pre-biotic molecules, and its evolution along the main stages of the star formation process, from prestellar cores and protostars to protoplanetary disks. The resulting data set will remain as a reference database for astrochemists (astronomers, chemists, and theoreticians), while triggering many followup studies. It constitutes a big step forward in the understanding of molecular complexity of the infancy of our own solar system.

The project consists of high-sensitivity systematic spectral line surveys (in the wavelength ranges around 1, 2, and 3 mm) of 10 targets at different stages of the early protostellar evolution. In order to determine the chemical abundances and the physical and dynamical conditions of the sources, the observations are complemented with radiative transfer and chemical modelling.

Methanol in the inner 100 AU of the pristine jet/disk HH 212 protostellar system

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The birth of a Sun-like star is a complex game played by several participants (hot corino, circumstellar disk, ejected material) whose respective roles are not yet entirely clear. In particular, the nature of the warm (~100 K) gas surrounding low-mass protostars and enriched by complex molecules is still not properly understood. Indeed, we still do not know whether hot corinos trace only the thermal evaporation of icy grain mantles or whether non-thermal ice desorption processes also contribute (sputtering in shocks, photodesorption along cavity walls).

In this contribution, I will present ALMA observations of HH 212, a Sun-like class 0 protostar driving a spectacular bipolar H_2/SiO collimated jet. The data trace with unprecedented detail all crucial ingredients involved in the star-disk formation recipe, namely: (i) the dusty flattened envelope/disk (possibly in Keplerian rotation with radius 0.2"); (ii) the axial jet launched by it; (iii) the biconical outflow cavities; (iv) the parent infalling envelope; (v) the hot corino, the first ever detected in Orion on such spatial scales.

In particular, I will focus on the properties of methanol, a key ingredient for the formation of complex molecules, here observed at scales less than 100 AU. At least seven lines are detected with upper energies up to ~300 K implying a rotational temperature of ~100 K. The CH_3OH kinematics and abundance will be compared with that of HDO as well as of another complex molecule such as CH_3CHO.

Vibrational Spectroscopies for large Quantum Number Transitions: NIR, NIR-VCD and Raman

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Near Infrared (NIR) spectroscopy is often overlooked from a fundamental point of view, even though it is widely employed in industry and in medicine, with a quite empirical approach: indeed, all the apparently silent NIR regions contain the overtones of CH/OH/NH etc. stretching vibrational modes. Lot of interest was raised some time ago by a quite attractive interpretive model, the local mode model, which allowed to easily make use of NIR absorption spectra of several organic molecules. Based on this, Kjaergaard intensively studied the content of water or pollutants in higher atmosphere. We used extensively the local mode model to study NIR intensities [1]. We also applied for the first time chiroptical spectroscopies (NIR-VCD) to characterise alcohols and particularly internal hydrogen bonds as well as CH-stretching vibrational overtones of chiral molecules [2,3]. We are presently carrying on Raman spectra for higher CH-stretching overtones, a technique which had shown limited success in the past. We expect that these studies might be relevant for studying planet atmospheres in the astrochemistry field.

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Molecular Evolution described by Lognormal Stochastic Processes

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In a series of mathematical papers published over the last five years, this author developed a mathematical model of Evolution and SETI called "Evo-SETI".
Evolution of life on earth over the last 3.5 billion years is defined as one particular realization of a lognormal stochastic process whose mean value is known and it could be either an exponential (Geometric Brownian Motion (GBM)) or a polynomial in the time, or any other continuous time function.
This model might be applied to Molecular Evolution if the scientists working in this field would provide the relevant molecular data to this author.
The MOLECULAR COMPLEXITY increasing in time is measured by the Shannon ENTROPY of Information Theory, and thus it is measured in bits/molecule.
In this presentation we will outline just the inputs and the outputs of our Evo-SETI model, without indulging in any mathematical demonstration of the models lognormal stochastic properties, since any mathematical demonstration would require too much time.

Detection of hydrocarbons in Mighei carbonaceous chondrite by the SPectral IMager (SPIM)

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Hydrocarbons content in pristine chondrites is very important since they could have had prebiotic implications on the origin of life [1]. We report the preliminary results of micro-scale reflectance spectroscopy investigations on Mighei CM2 chondrite. Data were collected by means of Spectral Imager SPIM facility [2]. SPIM is a replica of the Visible InfraRed imaging spectrometer (VIR) [3], onboard the DAWN spacecraft. The spectrometer covers the 0.25-5.05 µm spectral range. Seen through SPIM Mighei powders show several absorption features that are related to different minerals [4]. Moreover in most of the pixel spectra different band absorptions were found in the range between 3.1-3.6 µm. Absorption features in this range are related to C-H compounds. Mighei grains show broad 3 µm band due to O-H, a weak 3.27 µm band due to aromatic C-H, an intense band from 3.38 µm to 3.41 µm due to aliphatic C-H stretching. These spectral features are in good agreement with those detected in organic matter of Murchison CM2 chondrite [5].

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Protostars: forge of cosmic rays?

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Galactic cosmic rays are particles presumably accelerated in supernova remnant shocks that propagate in the interstellar medium up to the densest parts of molecular clouds, losing energy as well as their ionisation efficiency because of the presence of magnetic fields and collisions with molecular hydrogen.

Recent observations hint to high levels of ionisation and to the presence of synchrotron emission in protostellar systems, therefore leading to an apparent contradiction.

We suggest a mechanism able to accelerate both cosmic-ray protons and electrons up to relativistic energies through the diffusive shock acceleration. We find that jet shocks can be efficient accelerators of cosmic rays, which can be boosted up to relativistic energies. Another promising acceleration site is represented by protostellar surfaces, where shocks caused by impacting material during the collapse phase are strong enough to accelerate cosmic rays.

The existence of an internal source of energetic particles can have a strong and unforeseen impact on the ionisation of a protostellar disc, on the star and planet formation process as well as on the formation of pre-biotic molecules.

Polyatomic molecules of Li-Be-B: relevance for the astrochemistry of the early to late universe

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The big bang nucleosynthesis (BBN) model predicts that three elements were synthesized in the early universe: H/D, helium (^{3}He, ^{4}He) and lithium [1]. Thus, a number of small diatomic molecules or ions such as, for example, HeH^+ and LiH^+ were likely formed only a few minutes after the BBN. On the other hand, elements heavier than Li were produced in a second stage both inside the cores of newly formed stars and following the explosions of supernovae. While a large number of carbon-based (organic) interstellar molecules are known to date, less information is available about the stability of polyatomic molecules containing different combinations of the first three elements of the second period, namely lithium, beryllium, and boron. We have therefore started a systematic study of the geometries and electronic structures of these molecules and molecular ions with the aid of modern quantum chemistry methods. The chemical bonding in the studied molecules is analysed with the quantum theory of atoms in molecules (QTAIM). It is hoped that the results of this study will shed some light on the astrochemistry that characterised the transition from the early to late universe.

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Computational study of reaction between prebiotic molecule C_2N and CO on carbon surface

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The study of chemical reactions occurring in the outer space is made difficult by the complications in reproducing in laboratory the extraterrestrial conditions. Computational chemistry is surely a helpful tool for such kind of investigations.

Aim of the work is the computational modelling of the reaction between carbon monoxide and the prebiotic species CnN (with n = 1, 2, 3) in a carbon-rich dense molecular cloud which produces molecules that have all the elements of the amino acids backbone.

The mentioned reactions have been investigated on two carbon surfaces: graphene, as a model of an interstellar grain covered by carbonaceous materials, and a polycyclic aromatic hydrocarbon, abundantly present in dense molecular clouds.

Among all the reactions investigated, the one leading to the C_3NO formation is by far the most exoergic, therefore it was extensively studied and two reaction mechanisms have been suggested. The first one is a Langmuir-Hinshelwood-type, investigated by means of DFT calculations. The second one is an Eley-Rideal-type, studied by ab initio molecular dynamics, performed at the DFT level according to the SIESTA method. The energetic aspects of the Eley-Rideal mechanism are detailed through a velocity distribution function analysis.

Synthesis of formamide and isocyanic acid after ion irradiation of frozen gas mixtures

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Among the complex organic molecules observed in the gas phase of pre- and protostellar objects and in cometary comae, formamide and isocyanic acid are particularly intriguing because of their possible role in prebiotic chemistry. An open debate concerns their formation route and, in particular, if they are formed by chemical reactions in the gas phase and/or on the grains surface. In the latter case it is important to understand the role of energetic processing in forming them from simpler frozen molecular species.

Here we present new laboratory experiments showing that the formation of both formamide and isocyanic acid can be induced by energetic processing of astrophysical ice analogues.

Ice mixtures (H_2O:CH_4:N_2, H_2O:CH_4:NH_3 and CH_3OH:N_2) have been processed by energetic (30-200 keV) ions (H^+ or He^+) and FTIR spectroscopy allowed a quantitative measure of the amount of HNCO and NH_2HCO produced.

The experimental results show that energetic processing can quantitatively reproduce the amount of formamide observed in cometary comae and in many circumstellar regions. Even HNCO is formed, but additional formation mechanisms have to be taken into account to explain the abundances obtained from astronomical observations.

We suggest that energetic processing of ices is the main mechanism to produce formamide. Once formed, this molecule is injected in the gas phase after grain mantles desorption.

Radioresistance of adenine to cosmic rays

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Adenine, $C_5H_5N_5$, is the simplest purine nucleobase. It is an integral part of biomolecules of unique importance such as DNA, RNA and FAD. Several theories claim that adenine or its precursors may possibly have reached the early Earth via comets and meteorites and possibly contributed to the emergence of life. In this work, we focus on the effects on adenine from exposure to galactic cosmic rays analogues. We studied the adenine radioresistance in solid phase at low temperature under bombardment of heavy ions. The experiments were performed in a high vacuum chamber at GANIL (Caen, FR) and GSI (Darmstadt, DE). Adenine films were irradiated by 820 MeV Kr^{33+}, 190 MeV Ca^{10+}, 92 MeV Xe^{23+} and 12 MeV C^{4+} ion beams. The evolution of adenine molecules under heavy ion irradiation was studied by infrared absorption spectroscopy as a function of projectile fluence. New infrared absorption bands arise under adenine irradiation and can be attributed to HCN, CN^-, $C_2H_4N_4$, CH_3CN and $(CH_3)_3CNC$. By using different swift heavy ions, we have determined the destruction cross section (σ) of adenine as a function of the electronic stopping power (Se) in the form: σ = A Se^n, where n = (1.175006). Our results show that destruction of adenine exposed to cosmic rays is dominated by iron and hydrogen ions. Moreover, the half lifetime of adenine exposed to cosmic rays in the interstellar medium was estimated as (1.058) x 10^6 years.

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