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The Astrochemical Observatory: Molecules in the Laboratory and in the Cosmos

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Astrochemistry is a discipline consolidated recently, although its roots extend back to the dawn of early civilization with the observation and mapping of the sky. The way to the understanding of the common natural laws on earth and in space paved by Galilei's observations by the telescope, has been extended in the last decades, by new technologies such as radioastronomy and space missions. Plenty of new chemistry was surprisingly discovered. Extreme rich information on the chemical "composition" of the universe is being obtained, either from the other planets and satellites in the Solar System, from meteorites and comets, or from the interstellar space. In this article we will present selected topics regarding the chemical structures and reactions being discovered. Particular attention will be devoted to aspects considered as relevant for the prebiotic processes on earth, such as those involving chirality and its role played in the origin and evolution of life.

Keywords: Chirality; Evolution biochemistry.

INTRODUCTION

Exactly four centuries ago Galileo Galilei started to point his just invented telescope to the sky, guided by the profound conviction that science had to be founded on experiments, and natural laws should been investigated both in laboratories on earth and by observations of the cosmos. The chemical nature of the universe is the focus of this article and we like to think that Galileo would have been pleasantly surprised to know about the recently disclosed chemistry in the planets of the solar system, in the stars and in the interstellar medium: information is becoming available on the abundance of the elements and their isotopic distribution, on the chemical composition of the universe, on the reactions of atoms and molecules and on their interactions with ultraviolet radiation and cosmic rays. In the last decades these discoveries have become an area of research, spanning the traditional scientific disciplines, from physics to biology, through chemistry acting as a bridge. It is common nowadays to refer to this field of investigations as "astrochemistry".[1]

These tremendous advancements have been fostered particularly by radio-astronomical observations and also, more recently, by extension of spectroscopic measurements to other wavebands (see ref. 2). Comparison of astronomical observations with laboratory experiments and theoretical modellings has allowed the identification of hundreds of molecules in space, including also complex organic molecules. Direct space exploration and sampling have further enlarged the perspectives of our understanding of the chemical evolution of the universe. The discovery of amino-acids and other protobiological molecules in meteorites,[3] and possibly in other space environments, has opened the debate on the origin of the building blocks of life in the universe.

An intriguing aspect connected to the origin of life is the role played by molecular chirality (see ref. 4). Most of the molecules implied in biological systems have a specific chirality: every student is told that only dextrorotatory sugars and levorotatory aminoacids participate in the processes of life. Mechanisms proposed for tackling the very basic problem of the origin of the striking manifestations of a chiral selectivity in the molecules associated with life invoke either the weak forces of beta-decay or the action of polarized light. In this report we focus on orientational effects in aligned molecular, exploiting recent progress coming from extensive molecular beam scattering experiments on intermolecular collisions and interactions.[5,6] Alignment in gaseous streams propitiates chiral effects in the differential scattering of oriented molecules (see ref. 7, 8) and references therein). We point out that it may be of pre-biotical interest to focus on mechanisms for chiral bio-stereochemistry of oriented reactants, when flowing in atmospheres of rotating bodies, such as the planet Earth, as well as in vortex motions of celestial objects.

The article is organized as follows: in Section 2 we introduce the astrochemistry as a bridge between physics and

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biology; in Section 3 some examples of reactions of importance in astrochemistry; in Section 4 we deal with chirality issues; conclusions and perspectives follow in Section 5.

ASTROCHEMISTRY: A BRIDGE BETWEEN PHYSICS AND BIOLOGY
Molecular physics and quantum chemistry

Astrochemical investigations have to be assisted by quantum-chemical calculations of molecular properties, (such as structures, transition frequencies, etc.) to drive and interpret observations, line assignment and data analysis in the most complicated and new cases. A paradigmatic example is that of spectroscopic techniques, which are widely used to infer information on molecular structure and dynamics and are therefore playing a crucial role in the investigation of atmospheric chemistry and interstellar medium,[9] since the last decades. The primary target is the identification of chemical compounds in space as well as in planetary atmospheres.[10,11] The formation of complex molecules involves reactions occurring in gas-phase and at the surface of either icy particles or minerals, these latter acting as effective catalysts involving proton/electron transfer, nucleophilic/electrophilic attacks, etc.. These processes challenge theory requiring approaches based on more refined representations of the wave function such as Moeller-Plesset (MP2) and coupled cluster methods, which are adopted when high accuracy is needed (see ref. 12 and references therein). Applicability of these methods depends on the size of the system to model. Approaches based on electron density (DFT) rather than on the wave function have became computationally convenient alternatives to MP2 and CCSD(T), while achieving acceptable accuracy by means of well designed electron density functionals.

Protobiological Issues

The exploration of the space has opened a new way to the study of the synthesis of prebiotic molecules in a planetary-scale laboratory, somehow extending the Miller's experiment. This perspective raises the question whether the simple organic molecules are the link between matter in the universe and matter in living entities: additionally how were they formed to begin with? A partial response comes from the recent discovery that most of the molecules and ions composing the interstellar and circumstellar medium, comets and meteorites are rich in carbon atoms.

The recent detection of molecules containing carbon having a prebiotic nature has further stimulated 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,[13] and possibly in other space environments. Then many efforts are being focused on the physical, chemical and astrophysical processes by which prebiotic molecules, typically chiral, can be produced in interstellar dust and spread out all over, to the earth or other planets.

The role that the chirality plays in the origin of life is in connection with the origin of homochirality in biology. Many advanced hypotheses are under scrutiny and none has yet received a global consensus (see ref. 4 and references therein). The latter topic will be discussed further in Section 5.

Dynamics of Elementary Processes

To understand how the molecules in the universe can be generated, one has to look at the chemical processes taking place in space, then chemical reaction systems have to be considered as complementary to the usual physical models for objects in space.

Such reactions occur in a number of environments, as astrophysical plasmas, atmosphere of stars, interstellar medium and so on, and the knowledge of their cross sections and rate constants is crucial in the modelization of these mediums.

The many kinds of molecular processes involve gas-phase chemistry, surface chemistry, low and ultralow temperature chemistry as well as high temperatures, suprathermal atoms and molecules.[14] The theoretical treatments need to be developed by using *ab initio* molecular calculations, and classical, semi-classical[15,16] and quantum dynamics[17] approaches. (See also refs. 18-41 for what concerns three-body systems, refs. 42-47 for the four-body systems, and refs. 48-59 for polyatomic systems and clusters). Two main classes of treatments can be distinguished: the methods of chemical kinetics and those involving dynamics, aimed at the detailed study of the reactive encounters collision and reaction at a state-to-state level.[60-64] The most complete knowledge of the complex chemical environment can only be reached by combining these two approaches to obtain state-to-state kinetic models and to produce the corresponding databases.[65]

An important tool for the study of dynamics of chemical reactions is that of molecular crossed beams. It permits to study processes of astrophysical relevance. In our laboratories many of these reactions have been investigated (for theoretical and experimental studies, see refs. 66-71 and references therein). Among these reaction, those involving

CH_4 and $N(^2D)$ are particularly important (see ref. 72). The first one initiates the processes leading to the higher hydrocarbons, while the second one initiates nitril formation processes.

## REACTIONS OF INTEREST IN ASTRO-CHEMISTRY

In this section we report some reactions and aspects of science of current interest in astrochemistry.

$N(^2D)$ in the atmosphere of Titan

The generation of atomic nitrogen in the first electronically excited state, ^2D, is extremely relevant in assessing the role of neutral nitrogen chemistry in the atmosphere of titan. The radiative lifetimes of the metastable states $^2D_{3/2}$ and $^2D_{5/2}$ are quite long (12.3 and 48 hours, $\Delta E(^2D-^4S)$ = 230.5 kJ/mol) because the transition from a doublet to a quartet state is strongly forbidden. In addition, collisional deactivation of $N(^2D)$ by N_2 is a slow process and therefore the main fate of $N(^2D)$ above 700 km is chemical reaction with other constituents of Titan's atmosphere. The production of N atoms in the ^2D state is important, because $N(^4S)$ atoms exhibit very low reactivity with closed-shell molecules and the probability of collision with an open-shell radical is small. On the contrary the reactions of $N(^2D)$ with several molecules identified in the atmosphere of Titan (including CH_4, C_2H_2, C_2H_4, C_2H_6) can give an important contribution to the chemical evolution of the atmosphere and lead to the formation of molecules containing a C-N bond.[72]

Methanimine, a precursor of glycine

Methanimine $H_2C=NH$ is a precursor of glycine, it absorbs in the UV region and can photodissociate directly (or in two steps) to HCN (another prebiotic species). A new efficient route towards the formation of HCN on Titan:

$$N(^2D) + CH_4 \rightarrow CH_2NH + H$$
$$CH_2NH + h\nu \rightarrow HCN(HNC) + H_2/2H$$
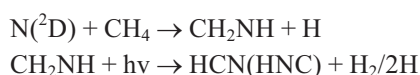
CH_2NH has a double bond and can polymerize or co-polymerize with other unsaturated imines/nitriles or unsaturated hydrocarbons or radicals. Methanimine might be responsible for the formation of the observed N-rich aerosols of Titan.[73]

Hydrogen peroxides and related compounds in interstellar space

Detection of hydrogen peroxide for the first time in interstellar space[74] is very recent: it gives a boost to a current topic regarding water, the most important molecule for life, and its formation in interstellar space. Disproportionation of H_2O_2 is also related to the presence of O_2 at the surface of earth before the origin of photosynthesis. This made possible the aerobic respiration, although the presence of oxygen were very low. O_2 might have been brought to the surface, by transportation from the equatorial stratosphere to the polar region and consequently downward transported in the polar vortex.[75] Gas-phase hydrogen peroxide has been observed in the Martian atmosphere (see ref. 74) and references therein). We made extensive studies on peroxides (and persulphydes), which are the simplest chiral molecules, the two enantiomeric forms correspond to the minima, which interconvert by torsion motion around the O-O (or the S-S) bond.[69,76-85] For chirality changing mechanisms see also Elango *et al.*[86-87]

Radiative association

This class of reactions is of importance for the early universe chemistry, concerning the formation of simple diatomic molecules as H_2, HD or LiH, and the reaction He + H_2^+ [28,32,88] assumed to be crucial in the description of the spherical collapse of primordial gas clouds. Related processes have also been proposed for the formation of H_2O from atomic oxygen and H_2 in the high atmosphere of stars in the 1500-3000 K temperature region. (See also ref. 11)

Charge transfer processes

Another important class of processes is that of charge transfer between multiply charged ions and neutral targets (for example $C^+(^2P) + S(^3P)$). This is a relevant process for the description of the interstellar medium which drives the ionization balance of charged species. the charge transfer which is a fundamental reaction of the interstellar medium, driving the ionization balance of carbon and sulfur.

CHIRALITY

Chirality in nature

The mirror symmetry is common in nature and involves many areas such as chemistry, biology and astrophysics. It might provide responses to the key questions that modern science poses about the origin and evolution of life in our planet. The hands are the most common example of this effect, defined "chirality" (from the Greek "cheir", hand) by Lord Kelvin is well studied from a molecular point of view, so that molecules, like hands, are conventionally defined as left-handed and right-handed. They are identical in all their properties and a double reflection would perfectly match them. It is surprising that in bio-

chemistry most of the molecules found in living organisms have a well defined chirality, so that all aminoacids are left-handed, while sugars are right-handed. This phenomenon is called homochirality. Although many hypotheses have been proposed to explain it, as was anticipated in Section 3, no one has received a general consensus. For example, evidence of the role of circularly polarized light and in general of magnetic and electric fields, although experimentally demonstrated, appears circumstantial, because intensity of such fields has not been proved to be sufficient to induce substantial effects in the production of a specific enantiomer of a chiral species.[89-90] The latest experimental observations of dichroic effects in photoionization (see ref. 91), which required very intense circularly polarized synchrotron radiation, probably not available in nature.

A possible explanation would be indeed extremely important regarding the origin of life. For instance, the recent discover that in certain meteorites found in Antarctica an excess of right-handed aminoacids has been found, supports the hypothesis of the existence of extraterrestrial life or even that of the extraterrestrial origin of life. However, it is not possible to exclude that such homochirality derives from previous contaminations of the meteorites by agents of the terrestrial biosystem.

Alignment and orientation

Alignment and orientation are commonly used to control the spatial arrangement of molecules in order to understand the basic collisional mechanisms (other uses of oriented molecules will be discussed in the next paragraph). (See ref. 92 for a definition of alignment and orientation). Experiments on the expansion of the supersonic seeded beams of benzene molecule demonstrated that the anisotropy of intermolecular forces is a characteristic feature for alignment.[93-94] We call "natural" the molecular alignment which can be generated by collisions in gaseous streams.[5,95-114] Other techniques consist in applying external fields. In such a case it is possible to obtain also molecular orientation (see ref. 115-116).

Stereodynamics of chirality

Nowadays, progress in stereodynamics is being shown to be relevant also for those mechanisms of induction of chirality in processes where oriented molecules are involved, (see refs. 7 and 117 and references therein).

Recent investigations on the origin of asymmetry based on quantum chemical calculations have shown that parity violation due to weak forces leads to extremely small energy difference for enantiomers.[118,119] Ray et al.[120] have

shown that when chiral molecules are given a specific orientation in a film, asymmetry results for the scattering by polarized electrons. More recently Kim et al.[121] studied photoemission by absorbed chiral molecules. Gerbi et al.[122-123] demonstrated stereodynamic effects in scattering from surface of aligned molecules.

Considering events in chiral physical fields, circularly polarized photons, and the magnetochiral effect induced by the magnetic field and unpolarized light, are well known to be enantioselective in photochemical reactions. Interestingly, also general translation-rotation motion are "true" chiral force fields: recently, liquid vortex motions have been shown to induce chiral discrimination in the formation of mesophase aggregates of achiral porphyrins,[124] although some controversy was also generated.[125]

Some theoretical evidence was provided[7] that in collisions between unpolarized projectiles and chiral molecules, the differential cross sections for a molecule and its enantiomer differ if the molecules are oriented.[7] Also, left- and right-handed molecules can scatter unpolarized electrons differently in a chiral framework which must be provided by at least three non-coplanar polar vectors defined in the collision processes. Note that no experimental verifications of these predictions appear to be so far available. Very recently, molecular collisions have been proposed as a possible mechanism for chiral discrimination,[117,126-127] while H. N. Lee et al.[128] have given a direct experimental proof of discrimination between optical rotamers of simple organic molecules induced by macroscopic translation-rotational motions.

Molecular orientation, as described above in Sec. 4.2 in reference to molecular beam experiments in the laboratory, can be presumably also generated by molecular gaseous streams on the earth and in the universe. On the earth, vortices of liquid and gaseous matter (tornado), and collisions of surfaces can generate chirality by collision. Even in the interstellar clouds, collisions of molecules in gaseous streams, for example with surfaces, or in vortices of such clouds could provide a mechanism for the origin of the homochirality. Figure 1 shows a schematic view of the separation of the enantiomers in a supersonic seeded beam of an oriented hydrogen peroxide by collision and in a vortex.

CONCLUSIONS AND PERSPECTIVES

This article provides a perspective on the state-of-the-art of astrochemistry. Significant advances made by combined technological advances, in the laboratory and in
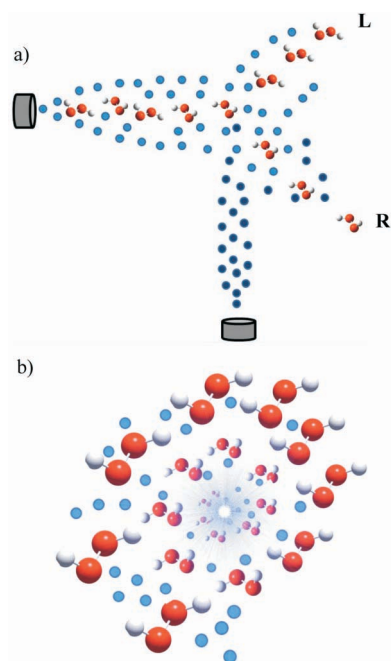
Fig. 1. The figure shows two stereodynamics mechanisms of chiral discriminations. In Figure a) we report a schematic view of the scattering between an oriented chiral molecule supersonic seeded beam (hydrogen peroxide) and a generic closed-shell atom. It has been proved theoretically[7] that in collisions between unpolarized projectiles and chiral molecules, the enantiomers can give distinct differential cross sections. Such chiral separation is ensured if a chiral framework is provided by at least three non-coplanar polar vectors defined in the collision processes: in the figure the three required vectors are the velocity of the molecule before and after the collision and the molecular axis.[7] The latter vector is provided by the molecular orientation. In Figure b) a schematic view of a hydrogen peroxide supersonic seeded beam within a tornado-like vortex is illustrated. The roto-translational motion is a "true" chiral force which can produce enantiomeric separation.

the observation of the cosmos, also accompanied by the development of new computational methods allows us to acquire a set of information that goes far beyond simple images obtained by a telescope. Thus, one of the first goal followed by astrochemists, more precisely theoretical and computational chemists, is the handling of the vast amount of data sent by probes exploring the solar system on the processes taking place in the atmospheres of planets and satellites, and the exploit of the information coming from largely unexpected radio-astronomic and spectroscopic discovery of numerous molecules of increasing complexity in interstellar space.

Nowadays, astrochemical investigations include the chemical processes of the early universe (hydrogen and deuterium plasmas, helium and lithium[129-133]) and the present universe; role of dust grains in the formation of early cosmic structures; molecules in the interstellar medium. In this regard, the discovery of hydrogen peroxide[74] has raised great interest giving a twist to the formation of water in these regions of the universe. Space missions that have taken place in the last decades have allowed astrochemists to investigate the composition and processes of the planets of the Solar System and their atmosphere. The number of discovered molecules, especially the organic ones, is continuously growing, among them the dynamics of carbon-chain-anions and formation of polycyclic aromatic hydrocarbons (also known with the acronym oh PAHs),[134] which are assumed to compose the primordial soup of the Earth, playing an important role in the origin of life. Astrochemists are also involved in the study of chemistry under extreme conditions, such as low and ultralow temperatures, high temperatures, suprathermal particles, and chemical mechanisms related to the origin of homochirality in the biosphere.

As evidence of the preeminence of the areas of investigations of astrochemistry, we conclude quoting an article by Philip Ball[135] that on the occasion of the International Year of Chemistry, celebrated in 2011, provides a list of ten unsolved "mysteries" of chemistry. Question number 1 is "how did life begin"; question number 2 is "how do molecules form".

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