



Laboratory Astrochemistry

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Received: 14 May 2024; Accepted: 28 May 2024

Abstract. Recent advances in astronomy showed that a variety of simple and complex organic molecules are abundantly observed in the interstellar medium. Astrochemical models confirmed that the physical and chemical conditions in regions where stars and planets are born affect the formation and destruction of life-related molecules in space. However, the exact formation mechanisms of those species, their ability to survive under harsh conditions in space, and their inclusion in planets are still largely unknown. Laboratory work can aid a better understanding of whether prebiotic species found on Earth have a ubiquitous extra-terrestrial heritage. Here, we review a selection of contributions presented at the second Italian National Congress on (Proto-)Planetary Astrochemistry hosted by the University of Trieste on 11-14 September 2023 showcasing some of the worldwide cutting-edge work currently done in the field of laboratory astrochemistry.

Key words. Astrochemistry – Methods: laboratory - Molecular processes

1. Introduction

In recent years, ground-based (e.g., Atacama Large Millimeter/submillimeter Array - ALMA) and spaceborne telescopes (*Spitzer* and Hubble Space Telescopes) have revolutionized our understanding of our Molecular Universe, with more than 300 gas-phase species now observed in the interstellar medium (ISM) and circumstellar shells (see <https://cdms.astro.uni-koeln.de/classic/molecules>). Species containing

elements such as carbon, hydrogen, oxygen, nitrogen, and sulphur (CHONS) are important ingredients of planetary atmospheres and contribute to the organic content observed on interstellar dust grains as well as in meteorites and comets in the Solar System. The James Webb Space Telescope (JWST) has recently allowed the first direct detection of interstellar complex organic molecules (iCOMs) in ice grains and it has traced ice molecules from the darkest and densest regions ever observed

to the photo-dominated regions (PDRs) of the ISM, where the onset of surface chemistry occurs (Berné et al., 2022; McClure et al., 2023; Rocha et al., 2024).

The physicochemical interplay between gas-phase species and ice covered (or bare) grains is key to unraveling the origin of molecular complexity in space and its delivery to planets like Earth (Herbst & van Dishoeck, 2009). Considerable progress has been made in recent years toward a better understanding of the composition and evolution of the gas, dust, and ice in the ISM (Cuppen et al., 2024). Laboratory investigations of gas-phase reactions, dust analogs, and simulations of interstellar ice grain processing have made this possible. However, to date, it is not fully understood whether ice grains are the place where all iCOMs form and are stored before inclusion into planets in Solar-like systems, or whether interstellar ices simply feed the gas with the precursors of iCOMs that are then formed through gas-phase reactions. Further laboratory work that applies new techniques and methodologies is needed to aid a correct interpretation of current observations.

This work is based on a selection of contributions presented at the second Italian National Congress on (Proto-)Planetary Astrochemistry hosted by the University of Trieste on 11-14 September 2023 and it reviews some of the laboratory work that is currently performed worldwide to aid a better understanding of chemistry and physics of star-forming regions. The topics discussed in this article are organized in the next section as following: gas-phase reactions (subsection 2.1), spectroscopic characterization of unstable molecules (subsection 2.2), photostability of larger complex molecules (subsection 2.3), evolution of organics in the ISM (subsection 2.4), energetic processing (subsection 2.5), and an overview of a few larger scale facilities (subsection 2.6).

2. Laboratory Astrochemistry Topics

2.1. Low temperature and collision-free experiments for gas-phase reactions

A thorough characterization of gas-phase elementary reactions relies on complementary approaches because, in most cases, the experimental techniques that can reproduce low-temperature (T) conditions of interstellar clouds are not able to reproduce the low-pressure (P) conditions. In general, low T conditions are reproduced by methods such as the reaction kinetics in uniform supersonic flow technique (French: Cinétique de Réaction en Ecoulement Supersonique Uniforme, CRESU; Smith & Rowe, 2000) and low P conditions are usually studied in collision-free experiments (Casavecchia et al., 2015). In this way, while the CRESU or other flow kinetics techniques can provide the decay rate of the reactants also at temperatures as low as 10 K, collision-free experiments allow us to identify the nature of the primary reaction products (that are often very reactive radicals) and their branching fractions by avoiding the effects of wall collisions or secondary collisions. We will now describe some recent examples to illustrate the capabilities of those methods.

Until recently, the application of the CRESU technique has been limited to the case of reactions with room temperature rate coefficients of at least $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ because of sensitivity problems. In recent years, however, the CRESU technique has been applied to a class of reactions involving the OH radical and oxygenated organic compounds for which the room temperature rate coefficients are just at the limit of $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ or even slightly below (Heard, 2018). These reactions are known to have an experimental activation energy and are characterized by an entrance barrier in the range of 10 kJ mol^{-1} . Despite that, below 200 K the rate coefficients for these reactions change their slope with the temperature and start increasing with decreasing temperature. This unexpected behavior was explained by invoking the role of a pre-reactive complex and tunneling through the entrance barrier. In

other words, those experiments posed a serious caveat against the extrapolation of rate coefficients outside the investigated range of temperatures (Heard, 2018).

Kinetics experiments are rarely able to determine the nature of the primary products. Free-collision experiments, instead, allow the identification of the reaction mechanism and, if empowered by versatile detection techniques like mass spectrometry, the determination of product branching fractions (Casavecchia et al., 2015). This is important for accurate modeling of interstellar chemistry since the products of one reaction become the reactants of a subsequent one in the intricate network of chemical reactions typical of those models. When the products are unknown, they are usually guessed by analogy with similar systems. However, this can lead to serious mistakes. For instance, in the reactions between atomic oxygen and small aromatics (benzene, pyridine, and toluene) a notable difference in the product branching fractions was noted, even though benzene and pyridine are isoelectronic and benzene and toluene have a very similar structure differing only by a methyl substitution. In particular, the CO formation channel (accompanied by the formation of cyclopentadiene, pyrrole, and methylcyclopentadiene, respectively) accounts for ca. 30% in the case of benzene, 98% for pyridine, and only 10% in the case of toluene (Vanuzzo et al., 2021; Recio et al., 2022; Balucani et al., 2024).

2.2. Laboratory studies of unsaturated carbon chains produced by pyrolysis

In the increasingly large sample of molecules detected in space, the class of unsaturated carbon chains is highly represented (e.g., see Thaddeus & McCarthy, 2001). These are usually highly reactive species that are unstable under terrestrial conditions thus, for most of them, the spectroscopic characterization remains a challenging task. In fact, for short-lived molecules, the conventional approaches based on chemical synthesis, purification, and isolation are usually not viable. For generat-

ing such compounds, flash vacuum pyrolysis has proven to be a reliable methodology (for a review, see Bizzocchi & Degli Esposti, 2008), and has been recently employed to investigate several astrophysically important molecules, such as imines (e.g., Bizzocchi et al., 2020).

As an example, the astrophysically relevant propadienone, cyanovinylacetylene, and allenylacetylene were recently generated and studied in the gas phase using a frequency modulation millimeter-wave spectrometer equipped with a flow-pyrolysis system described in Puzzarini et al. (2023). Three different stable precursors were employed: acrylic anhydride, 2,3-pyridinedicarboxylic anhydride, and dipropargylamine. Although the rotational spectra of the target molecules have been already experimentally investigated in the low-frequency regime (for a comprehensive list of references, see Melli et al., 2022), to date, their complete characterization is not available and crucial spectroscopic parameters are missing. For instance, the incomplete modeling of the centrifugal distortion effects leads to poor extrapolation of the rest-frequency at higher frequency regimes, where sextic terms (i.e. depending on J^6) produce important changes in the appearance of the spectral patterns. For this reason, to support the analysis of the experimental data and to improve the final spectral calculation, state-of-the-art quantum-chemical computations were also recently carried-out (Melli et al., 2022).

About 2000 new rotational transitions were recorded in the 80–400 GHz frequency interval. Allenylacetylene and both (*E,Z*) isomers of cyanovinylacetylene are found to behave as semirigid molecules, hence their rotational spectra can be accurately computed over an extensive frequency range. Conversely, the rotational spectrum of propadienone is complicated by a large amplitude motion that switch the molecule between two equivalent structural configurations. Tunneling doublets thus appear in correspondence of almost any predicted line positions. The two components were then modeled separately, each one with a conventional Watson-type Hamiltonian, together with a set of suitable interaction parameters. Though not exempt from caveats and

limitation, this approach is accurate enough to reproduce almost all the recorded lines within experimental accuracy, and to generate a catalog of reliable rest frequencies to support astrophysical studies.

2.3. Photofragmentation of Buckybowls - Corannulene ($C_{20}H_{10}$) and Sumanene ($C_{21}H_{12}$) cations - and its Astrophysical Implications

Polycyclic aromatic hydrocarbons (PAHs) have become a prime focus in astrochemistry ever since the Unidentified Infrared (UIR) bands were postulated to arise from aromatic molecules (Tielens, 2005). PAHs in space can exist in either neutral or ionic forms, absorbing UV photons and undergoing fragmentation, which produces a rich source of smaller hydrocarbons (Peeters et al., 2021). This top-down mechanism of larger PAHs fragmenting into smaller species is of utmost importance in PDRs in space.

In 2021, a spectral line survey by Green Bank Observatory of the TMC-1 molecular cloud exposed the presence of the small PAH, Indene (C_9H_8), a fused hexagon and pentagon ring (Burkhardt et al., 2021). This discovery emphasized the importance of pentagons in PAHs – a class of species previously ignored in PAH studies. With the high-sensitivity infrared data received from JWST (Chown et al., 2024), laboratory experiments producing spectroscopic data of specific organic molecules are key to compare with the observations to identify more PAHs with pentagon rings. Such PAHs are considered as the building blocks of fullerene, which is a known compound of the ISM (Campbell, 2020). Observations have revealed that the abundance of C_{60} increases rapidly close to stars while the abundance of PAHs decreases, likely reflecting photochemical fragmentation and isomerization processes under the influence of the strong radiation fields (Tielens, 2021). The photochemical relationship between PAHs and C_{60} carries direct hints on the processes that are dominant in the evolution of interstellar PAHs. The pentagon rings leads to the curvature of a planar PAH

structure closing upon itself (Chen & Wang, 2020). Pentagon formation is thus a prerequisite for the photochemical transformation of PAHs into fullerenes.

Recently, the photo-fragmentation pathways of two astronomically significant PAH cations and dications, corannulene ($C_{20}H_{10}$) and sumanene ($C_{21}H_{12}$), were investigated by using a Dye laser integrated to the i-PoP setup (Zhen et al., 2014) to understand their sequential fragmentation pathways. In brief, the buckybowls are brought to the gas phase by heating under vacuum, and they are ionized by an electron gun to make cations. These cations are directed to a quadrupole ion trap through standard gating procedures using Einzel lens system, i.e., by applying DC voltages to inlet or stop the ion flow into the trap. These cations are then stabilized using a Helium buffer gas and subject to photolysis by a Dye laser (620-630 nm). Consequently, the photofragments are directed to a reflectron time-of-flight chamber for mass analysis. The photofragmentation experiments with these bowl-shaped PAHs exhibit hydrogen loss channels that are much different from other planar PAHs. The breakdown of carbon skeleton is found to have different pathways for $C_{20}H_{10}$ and $C_{21}H_{12}$ because of the number and positioning of pentagon rings, yet the most abundant low mass cations produced by these two species are found to be similar. These low mass cations identified in our experiments could be of utmost interest for their ISM observation.

2.4. Evolution of organics in the interstellar medium

The nature and the chemical composition of dust in diffuse and dense regions of the ISM clearly exhibits dichotomy. Regarding the organic matter, this is one of the notable variances. An aliphatic organic component is a widespread constituent of diffuse dust. The $3.4 \mu\text{m}$ absorption band, with sub features at 3.38 , 3.42 , and $3.48 \mu\text{m}$ because of the C-H stretching modes in the methyl (CH_3) and methylene groups (CH_2), indicates its presence in the diffuse clouds of the ISM (Pendleton et al., 1994). Dense cloud dust lacks the aliphatic compo-

nent; yet, the spectrum of young star objects immersed in molecular clouds is characterized by a band at $3.47\ \mu\text{m}$ (Allamandola et al., 1993; Brook et al., 1999). The discrepancy in the C-H stretching spectral region between diffuse and dense clouds has posed a longstanding puzzle. Given the rapid exchange of materials between these environments, one would expect similar grain properties. However, any explanation for the formation and evolution of interstellar organic matter is severely constrained by the absence of aliphatic C-H bonds in dense clouds.

Laboratory simulations of interstellar processing under simulated diffuse and dense medium conditions clearly show that UV photons and ions may easily break C-H bonds in the aliphatic CH_2 and CH_3 groups (e.g., Mennella et al., 2001). Based on the experimental destruction cross sections of these processes, we can conclude that C-H bonds should be destroyed in diffuse clouds within 10^4 years, and that the aliphatic bands should not be visible in the diffuse region's spectra. Their detection points to the existence of an ongoing process that is capable of forming C-H bonds and preventing their dissolution. The process was identified with the interaction of carbon grains with hydrogen atoms. The presence of aliphatic organics in the diffuse ISM arises from the competition between the production and destruction of C-H bonds that leads to an equilibrium value for grain hydrogenation. This is demonstrated by the formation cross section estimated from experiments of carbon grains exposed to H atoms (Mennella et al., 2002). Moreover, as indicated by experiments of H atom irradiation under simulated dense medium regions, unlike the aliphatic CH bonds, those responsible for the $3.47\ \mu\text{m}$ band are activated by H atoms that counteract their destruction by cosmic rays and UV photons (for more details, see Mennella, 2010).

The same carbon grain population can absorb at the two wavelengths as a consequence of evolutionary transformations caused by processing. The transformations are compatible with the time-scale required by fast cycling of materials between dense and diffuse regions of the ISM. Furthermore, the laboratory results suggest an evolutionary connection between

the interstellar carbon dust and the aliphatic organics observed in the solar system materials (Mennella, 2010). This is fully consistent with the detection in situ of aliphatic organics in the comet 67P/CG. (Raponi et al., 2020).

2.5. Energetic processing of ices, dust, and ices/dust complexes of astrophysical interest

In the ISM, ices and dust are continuously exposed to energetic processing due to energetic ions and photons coming from different astrophysical sources. Energetic ions passing through a material lose energy through (in)elastic collisions with nuclei and electrons of the species constituting the target. These interactions produce several effects inside the target, such as ion, atom, molecule, and cluster sputtering, structural and morphological modifications, ionization, and breaking of the constituting species, which in turn may initiate chemical reactions and the formation of new species originally not present (Strazzulla et al., 2001; Palumbo et al., 2004; Fulvio et al., 2016; Schaible et al., 2017; Laczniak et al., 2024).

Additional interesting results have been seen when considering ion irradiation of ices/dust complexes or, in other words, icy films deposited on top of analogues of the carbonaceous or siliceous cosmic dust component. As an example, ion irradiation of various carbonaceous samples covered with a water ice film results in the synthesis of CO_2 and CO, implying that the projectile ions can provoke erosion of the C atoms bonded in the substrate and formation of these molecules at the expenses of the dust grains (Mennella et al., 2004; Gomis & Strazzulla, 2005; Raut et al., 2012; Sabri et al., 2015). Such a formation mechanism results extremely interesting when trying to interpret the low abundance of CO_2 in the gas phase in star-forming regions and quiescent clouds together with its relatively high abundance observed in the solid phase within ices covering cosmic dust grains. Experiments suggest that part of this CO_2 could be synthesized by energetic processing directly within the ices and/or at the inter-

face ice/dust. Energetic photons may also initiate chemical reactions (e.g., Gerakines et al., 2001; Meinert et al., 2016; Baratta et al., 2019; Chuang et al., 2022). Somehow similar to the results of the ion bombardment experiments, UV processing experiments of water ice deposited on top of carbonaceous samples confirm the synthesis of CO and CO₂ molecules (Mennella et al., 2006; Shi et al., 2015). It is interesting to note that the photosynthesis of CO₂ was also observed in UV irradiation experiments where the carbonaceous sample was covered with icy oxygen O₂ (Fulvio et al., 2012) and where silicate samples were covered with methanol ice (Ciaravella et al., 2018).

Finally, an innovative recent direction focuses on laboratory experiments with samples which are intimate mixtures of dust grains and ices rather than ices/dust complexes (Potapov et al., 2021). This novel experimental approach shows a huge potential for the production of new laboratory data representing the structure and relationship among ices and dust grains in space in a more realistic way. As an example, UV processing of mixtures made of carbon grains and icy water have shown not only CO₂ formation but also its partial trapping and survival into the mixture up to temperatures much higher than the desorption temperature of the pure species, i.e. about 150 K rather than 80-90 K (Potapov et al., 2023). This and similar results open new scenarios for the possible presence of icy species in astronomical environments where they would not be expected, with strong implications for the interpretation of the future astronomical observations and astrochemical models.

2.6. Laboratory Astrochemistry at Large Scale Facilities

In recent years, Europe has built a world-class infrastructure of facilities accessible to a variety of different scientific communities, including nuclear physics, astrochemistry, planetary science, astrobiology, and, more broadly, space science, through several Research Infrastructures (RIs) such as Europlanet 2024 RI, ChETEC-INFRA, and NFFA-Europe, and many topic-focused COST

actions to foster innovation and collaboration across different fields and sectors. Transnational access to European facilities has allowed space scientists to validate space instrument design and performance, study astrophysical, astrochemical, and geological processes that form specific (exo)planetary environments, and evaluate biogeochemical processes that control whether life can evolve and/or survive. Several of the user stations at the large-scale facilities that are mentioned below are designed to study the properties of planetary and interstellar ices embedded in high radiation environments associated with missions including ESA's JUICE and NASA's Europa Clipper as well as potential missions to Uranus and Neptune, and missions to asteroid and cometary bodies.

Commissioned in 2022 as part of a Europlanet 2024 RI initiative (<https://europlanet.atomki.hu/>), the Ice Chamber for Astrophysics/Astrochemistry (ICA) and the Queens University Ice chamber for Laboratory Astrochemistry (AQUILA) user stations are respectively located at the ATOMKI Tandetron laboratory and the ATOMKI ECRIS laboratory in Hungary. The two ultrahigh vacuum (UHV) setups have several common features in their design to systematically study space-relevant ices under different ion impact conditions (e.g., energy, fluxes, type of projectile) so as to better understand the origin and evolution of the building blocks of life. Both chambers are equipped with different target deposition methods (i.e., evaporation, background and direct deposition) to investigate astronomically relevant ices in the range 20-300 K by means of Fourier transform infrared (FTIR) transmission-absorption spectroscopy and mass spectrometry. As opposed to AQUILA that has a single window holder, ICA mounts a four windows holder and a 2 keV electron gun to compare ion vs electron irradiation effects on ices. The Atomki 2 MV Tandetron source connected to ICA can deliver projectile ions (H to Au) with singly or doubly charge state and energies in the range 200 keV to 10 MeV simulating high-energy galactic cosmic rays. The Atomki electron cyclotron resonance (ECR) ion source makes AQUILA

a complementary setup compared to ICA because it delivers ions with singly to multiply charge state and energies in the range 50 eV to 900 keV. The ECR can produce both positively and negatively charged ions making it an ideal source to simulate lower energy stellar winds and giant planetary magnetospheric plasmas (e.g., Herczku et al., 2021; Mifsud et al., 2021; Ivlev et al., 2023; Rácz et al., 2024).

Among the facilities devoted to astrochemistry, *Stardust machine* is an experimental station housed at the Instituto de Ciencia de Materiales de Madrid (Spain), fully operational since 2019. It has been designed to mimic in the laboratory both the complex conditions of cosmic dust formation around evolved stars and the processing suffered by the dust in different astrophysical environments. The whole setup comprises six interconnected UHV modules, offering a high level of control over fabrication, processing, and in-situ characterization of cosmic dust analogues (e.g., Martínez et al., 2018; Santoro et al., 2020a). In *Stardust machine*, the chemistry proceeds via atom aggregation under conditions in which most of the reactions that occur are neutral-neutral, closely resembling what happens in the circumstellar envelopes of asymptotic giant branch (AGB) stars. Martínez et al. (2020) investigated the synthesis of carbonaceous grains from the interaction between atomic carbon and molecular hydrogen under physical conditions mimicking those in the atmosphere of evolved stars. They experimentally demonstrated that the aromatic component has not formed effectively in the atmospheres of evolved stars, as commonly believed over the last 30 years. In Santoro et al. (2020b), the complex chemistry occurring when atomic carbon interacts with acetylene (C_2H_2 , the most abundant hydrocarbon in the atmospheres of evolved stars) was studied. They found that the synthesis of aggregates (clusters) of pure and hydrogenated carbon consisted of a complex mixture of sp , sp^2 , and sp^3 hydrocarbons. In Accolla et al. (2021), the chemistry between atomic silicon and hydrogen was studied, finding the efficient synthesis of silane (SiH_4), disilane (Si_2H_6), and amorphous hydrogenated silicon grains.

In conclusion, the *Stardust machine* is particularly suited to understand the formation of silicates (olivines and pyroxenes) in the atmospheres of AGB stars, synthesizing and characterizing the nanoparticles formed from the gas-phase reactions between atomic Si, Mg, and Fe under a controlled oxygen-rich atmosphere.

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Acknowledgements. S.I. acknowledges support from the Danish National Research Foundation through the Centre of Excellence ‘InterCat’ (grant no. DNRF150). M.A. and D.F. acknowledge support from the Istituto Nazionale di Astrofisica (Bando Ricerca Fondamentale 2022 - MINI-GRANTS RSN3). N.B. acknowledges support from the Italian Space Agency (Bando ASI Prot. n. DC-DSR-UVS-2022-231, Grant no. 2023-10-U.0 “Modeling Chemical Complexity: all’Origine di questa e di altre Vite per una visione aggiornata delle missioni spaziali (MIGLIORA)”). P.S. acknowledges the European Union and Horizon 2020 Postdoctoral funding awarded under the Marie Skłodowska-Curie action (grant no. 101062984).

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