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Roadmap

Roadmap on carbon molecular nanostructures in space

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Abstract In this roadmap article, we consider the main challenges and recent breakthroughs in understanding the role of carbon molecular nanostructures in space and propose future avenues of research. The focus lies on small carbon-containing molecules up to fullerenes, extending to even larger, more complex organic species. The roadmap contains forty contributions from scientists with leading expertise in observational astronomy, laboratory astrophysics/chemistry, astrobiology, theoretical chemistry, synthetic chemistry, molecular reaction dynamics, material science, spectroscopy, graph theory, and data science. The concerted interdisciplinary combination of the state-of-the-art of these astronomical, laboratory, and theoretical studies opens up new ways to advance the fundamental understanding of the physics and chemistry of cosmic carbon molecular nanostructures and touches on their wider relevance and impact in nanotechnology and catalysis.

1 Introduction

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Carbon is ubiquitous in space; the fourth most abundant chemical element in the observable Universe is present in the form of small carbon and hydrocarbon molecules up to fullerenes and large but currently unidentified polycyclic aromatic hydrocarbons (PAHs), carbonaceous dust particles and, ultimately, life. The clear identification of the fullerene C_{60} in the interstellar medium (ISM) and around old dying stars in planetary nebulae has provided us with a tangible key to unlock the mysteries and complexities of cosmic carbon. This opportunity is being exploited through a synergistic combination of expertize from observational astronomy, laboratory astrophysics/chemistry, spectroscopy, molecular reaction dynamics, theoretical chemistry, data science, synthetic chemistry, material science and astrobiology. State-of-the-art astronomical infrastructures and large-scale user facilities are being employed to understand the formation and astrochemical consequences of complex cosmic carbon nanostructures, with implications also for their applications in nanotechnology and catalysis. In this roadmap article, we present forty contributions where both early career and more senior researchers from a wide range of disciplines share their views on the challenges, recent breakthroughs, and future avenues of research within their areas of expertize.

Kwok opens up the roadmap describing the main unexplained spectral phenomena in the ISM and their possible organic carriers. In order to solve these long-standing astronomical spectral mysteries, at least a two-pronged approach is needed, involving laboratory synthesis and characterization of complex carbon materials and powerful quantum chemistry simulations.

Peeters and Cami review the aromatic infrared bands, a central unexplained spectral phenomenon in space, and the PAHs as their likely carriers. They summarize our current knowledge and the main challenges about interstellar PAHs and they point out progress in IR astronomical facilities, advances in laboratory astrophysics mimicking interstellar conditions, machine learning and high-performance computing as key aspects for the identification of specific PAH species in space.

Cami et al. show how the identification of fullerenes in space and the recent interdisciplinary work on these key species is offering a clear path forward to the understanding of carbon molecular complexity in space. A concerted effort of new observational studies (e.g., using the James Webb Space Telescope), sophisticated laboratory experiments, and chemical computations are needed to meet the challenges.

Cami et al. also describe the long-standing astronomical mystery of the diffuse interstellar bands (DIBs), the oldest (a century-old) unexplained spectral phenomenon in the ISM. Multidisciplinary approaches and the integration of cutting-edge technologies are required to address the challenges posed by the DIBs astronomical problem.

Jacovella and E.K. Campbell describe advances in laboratory methods for recording electronic transitions and spectra of large mass- and isomer-selected ions to temperatures below 10 K, key information to elucidate the DIBs enigma. A new approach that holds promise is the combination of cavity ring-down spectroscopy (CRDS) with ion trapping, and mass- and isomer-selection.

Gómez-Muñoz et al. show that hydrogenated amorphous carbon (HAC) grains can explain other unexplained spectral phenomena observed in evolved stars like a broad 12 μm plateau emission feature and peculiar UV extinction. Future challenges involve, e.g., the development of more laboratory experiments to obtain the optical constants of HAC-like dust grains with several structures and composition at different physical conditions. Such future collaborative interdisciplinary work has also the potential to unveil the formation of fullerenes in astrophysical environments.

Mohan, Bartkowski, and Giordani focus on carbon nano-onions (CNOs) as carriers of the UV bump at 217 nm widely observed in the ISM. Here, key challenges are the simulation of CNOs at the quantum chemistry level of theory as well as the synthesis of uniform CNOs in the laboratory.

Hou discusses metallofullerenes as obvious possible carriers of both unidentified infrared (IR) emission bands and DIBs. Future challenges involve, e.g., use of cryogenic ion trap technology to measure high-quality optical or IR spectra of specific gas phase metallofullerene species and the extension to other more complex fullerene derivatives (e.g., those including hydrocarbons).

Huertas-Roldán et al. show the power of sensitive astronomical observations in the radio domain to detect big molecules (20–60 atoms, i.e., from small hydrocarbons to big fullerenes). Such challenges will only be possible to meet if there is a complete database of experimental measurements and theoretical predictions on their rotational transitions.

Došlić and Došlić review the utility of graph theory to study and predict properties of organic compounds, e.g., from benzenoids to fullerenes. Here, a key challenge is to understand why graph theory seems to work as a stability indicator for hydrogenated fullerenes but not in other fullerene species. New easy-to-compute graph-theoretical invariants showing a good correlation with isomeric energies are to be found.

Catalano generally describes the quantum chemistry studies and spectral models needed for decoding unknown spectral signatures of carbon species in space with a focus on exoplanetary atmospheres. A multidisciplinary effort is needed to produce more molecular spectroscopic data (line lists) that would permit new molecular detections in exoplanetary atmospheres.

Yesiltas discusses some of the main challenges in the identification and characterization of carbon species in extraterrestrial materials. The development of new novel high-resolution (at the nanoscale) spectroscopic and microscopic methods are keys to identify and characterize primordial (in)soluble organic matter in extraterrestrial samples such as those from returned asteroid samples and meteorites.

Ferrari et al. highlight new unique laboratory techniques at FELIX Laboratory, combining mass spectrometry and IR spectroscopy (either in ion traps or molecular beams) that permit the collection of reference laboratory spectra (from the mid- to the far-IR) for a variety of carbon-bearing species under space conditions.

Pitanti et al. describe how new kinds of (sub-)THz detectors exploiting bolometric effects, are gaining attraction as novel emergent technologies for the development of uncooled thermomechanical bolometers, e.g., efficient space detectors operating in the far-IR range, where most carbon compounds display clear spectroscopic signatures. Future challenges involve, e.g., the introduction of device arrays and finding materials with a wide far-IR absorption band.

Hochlaf et al. describe present theoretical limitations for the characterization of carbon chains due to their complex electronic structure and the subsequent generation of their complex multi-dimensional potential energy surfaces (mD-PESs). New methods based on machine learning (ML) approaches are key for an effective description of the mD-PESs of such C-bearing species.

Potapov, Gezer, and Erbahar highlight the need for collaborations between astronomical observations, theoretical simulations, and laboratory experiments, providing some recent examples of successful studies like the formation of CO_2 on water-containing carbon grains or fullerenes' catalytic effects. Such interdisciplinary collaborations are keys to understand the astrochemical origins of the majority of detected organic species in diverse astrophysical environments.

Hansen, Zettergren, and Schmidt present thermal photon emission studies of pure carbon clusters or carbon-based species (both cations and anions) as measured in storage rings. Particular emphasis is given to recurrent fluorescence (RF) and its hitherto overlooked consequences for both the survival of highly excited molecules in space and for its contribution to the Extended Red Emission. The experimental and theoretical challenges needed for the characterization of molecular ions in storage rings are mentioned.

Stockett, Ashworth, and Bull present the importance of RF in the radiative cooling of PAH ions. More efficient fluorescent photon collection instrumentation and storage of ions over sufficiently long timescales are keys to understand the detailed cooling dynamics of PAHs.

Fárník focuses on two types of novel molecular beam (MB) experiments on large PAHn clusters and PAHs adsorbed in ice nanoparticles. They outline the issues and challenges required to advance the field. For example, systematic theoretical studies on the binding energies would be desirable for the PAHn clusters and several molecules in order to complement the MB experiments.

Wakabayashi describes the most recent measurements of the IR spectrum of fullerene (C_{60}) molecules in the laboratory. The IR emission spectroscopy of fullerenes (and other related molecules such as PAHs) at elevated temperatures in the laboratory seems promising for understanding the excitation mechanism of IR emission in space. This is particularly interesting for fullerenes; a key actual challenge.

Ganner, Kappe, and Gruber briefly review the messenger spectroscopy of cold molecular ions and present new methods using superfluid helium nanodroplets (HNDs), developed at the University of Innsbruck, to produce He-tagged molecular ions. Such novel laboratory methods hold promise for providing the electronic spectra of a variety of complex molecular ions (e.g., fullerene-based species) for a simplified comparison with astronomical observational data with a significant potential to reveal new DIB carriers.

Pardanaud, Dezalay, and Noble describe the state-of-the-art of electronic spectroscopy in a cryogenic ion trap and Raman microspectroscopy as probes of carbonaceous molecules and solids, respectively. Future challenges involve, e.g., understanding how the presence of heteroatoms like N and O affects the spectroscopic and photophysical properties of PAHs and hydrogenated amorphous carbon (HAC). The authors list three different but complementary laboratory strategies that could be undertaken to meet the challenges.

Tőkési et al. show the efficiency of their new method to extract the optical constants for solid materials from experimentally measured reflection electron energy loss spectroscopy (REELS) spectra. As an example, they present results for iron but the method could be applicable to carbonaceous solid materials, and the corresponding optical constants (n and k indices) could be used to model astronomical spectra.

Yang et al. describe how IR laser-induced breakdown spectroscopy (LIBS) has emerged as a powerful tool to study carbon nanostructures and discuss the particular case of anthracene as a PAH model compound. Here, extensive IR signature databases of carbon nanostructures in high-temperature environments are needed to understand the chemical processes happening in laser-induced plasmas and their potential applications in very different fields.

Zettergren and Schmidt describe the importance of mutual neutralization (MN) in collisions between cations and anions in some space environments such as dark interstellar clouds as well as recent laboratory advances. They point out the major challenges in future studies of MN reactions involving molecular and cluster ions and recent efforts at European level.

Shmavonyan, Misakyan, and Shmavonyan generally describe nanostructured materials and the recently developed substrate rubbing technology (SRT) for the production of nanostructured materials with nanostriped surfaces. The speculation of such materials having the potential to bridge the gap between Earth and Space is offered.

Sciriha provides a reflection about ballistic conduction of carbon molecules and how a full use of the mathematical, scientific and technological expertize can lead to significant progress.

Gezer and Erbahar focus on the catalytic properties of fullerenes in non-terrestrial environments, with a particular emphasis to life-related molecules. Future challenges involve, e.g., understanding the chemical reactivity of fullerenes and photocatalytic properties, among others.

Suriyaprasanth and Gupta present a method to predict the electron impact partial ionization cross section (PICS) of biomolecules and that can be extended to complex carbon species. Here, independently from parallel theoretical advances and the exploration of ML methods, they stress the main need of getting PICS laboratory measurements.

Kalchevski et al. present an ab initio study of carbon clusters involving metadynamics. They start from 25 randomly positioned carbon atoms and they find quasi-spherical nanoparticles as resulting structures. They speculate that previous astronomical IR emission detections attributed to pure fullerenes (C_{60} and C_{70}) could be due to such defective fullerene-like nanoparticles.

Caro briefly reviews the new emerging field of atomistic ML for the structural simulation of disordered hydrogenated carbon materials that is revolutionizing the field of atomistic materials modeling with a potential impact on our understanding of the reaction pathways under which complex hydrocarbons form in the ISM. Here, challenges and future prospects aim to develop accurate ML interatomic potentials of doped amorphous carbon materials (a-C:X; with X=H, O, and N).

Jacovella focuses on the vacuum ultraviolet photoprocessing of PAHs and its importance to understand the physics and chemistry of the photodissociation regions (PDRs) associated with star-forming regions. Key challenges are the synthesis of gas phase PAHs with distinctive structures (including defects) at astrophysical conditions and the extension to the less studied cationic PAHs, for which an experimental set-up is proposed.

Sadjadi and Parker present theoretical calculations on the ionization tolerance of cosmic fullerenes and present theoretical and experimental limitations like the extensive computational power and time and the scarcity of experimental data, respectively. Advances in artificial intelligence (e.g., to tackle the fullerenes' structural isomerism) and laboratory techniques (e.g., based on attosecond phenomena) are needed to open up new avenues in the study of the ionization of a molecule or ion-molecule processes.

Lombardi and E.E.B. Campbell describe the potential of endohedral fullerenes as reaction sites for the complex chemistry taking place in space. Future challenges to unveil the role of endohedral fullerene reactions for molecular formation in space involve both theoretical and experimental advances as well as the selection of the best prototypical systems to begin with.

Potapov and McCoustra highlight the role of cosmic dust grains and the physical and chemical processes on their surfaces like the catalytic formation of prebiotic molecules. Future challenges and prospects aim at the in situ detection of species formed in surface reactions, using complementary techniques not commonly adopted in laboratory astrochemistry like matrix-assisted laser desorption ionization (MALDI), among others.

Koch et al. discuss how chemistry on dust grain surfaces triggered by high-energy cosmic rays has been an uncharted territory until now. They present ongoing laboratory work to investigate the chemical processes (e.g., formation of complex organic and prebiotic molecules) in cold, dense astrophysical environments by studying energetic-ion triggered chemistry in mixtures of cosmic dust grain analogues with ices at low temperatures.

Kerkeni et al. focus on quantum chemistry studies of glycine, a basic prebiotic molecule, on interstellar ices. They report new accurate binding energy calculations for two glycine conformers, COOH, and NH_2 CH_2 that could have consequences for the formation of glycine. Such computational studies could be extended to other prebiotic molecules on interstellar ices.

Chuang, Jäger, and Chen briefly review our present understanding of surface interactions between ice and dust in planet-forming regions, as seen in the laboratory. The most recent experiments support the direct release of CO_2 molecules by the double oxygenation of carbon atoms bound to dust surfaces. Future work should concentrate in exploring if other molecules could also induce carbon erosion and how carbonaceous dust is destroyed by the harsh irradiation in the inner protoplanetary disks.

Manchado et al. briefly review the present understanding of the formation of amino acids in space. Yet, a main challenge is to find credible chemical routes from the simplest abundant molecules (H_2O, NH_3, CO, etc.) to more complex species at sufficiently fast rates to be relevant in space. Extensive computational chemistry studies (e.g., energetically favorable reaction pathways, dust particles compositions, and reaction mechanisms), not yet available in the literature, would be needed to meet the challenge.

It is, unfortunately, not possible to cover all the fascinating research activities dealing with carbon molecular nanostructures in space within this roadmap. However, the compilation presented here shows a rapidly advancing, highly interdisciplinary field where new observational, experimental and theoretical techniques and methods are continuously under development, and where future directions share common challenges. The interdisciplinary combination of new and improved ground- and space-based facilities in astronomy, laboratory techniques and theoretical methods, promoted by the NanoSpace COST Action CA21126 (https://research.iac.es/proyecto/nanospace), is essential to advance the understanding of the role of carbon molecular nanostructures in space and of their terrestrial relevance within nanoscience and catalysis. Such an interdisciplinary platform is essential to tackle the current and future challenges outlined in this roadmap. The article is based upon work from COST Action CA21126-Carbon molecular nanostructures in space (NanoSpace), supported by COST (European Cooperation in Science and Technology). That can be found in the Publications section of the NanoSpace website (https://research.iac.es/proyecto/nanospace/pages/publications.php), which also lists all publications from Action members.

2 Complex organics as possible carriers of unexplained spectral phenomena in the interstellar medium

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Status

Currently there are a number of astronomical spectral phenomena that have remained unidentified in spite of decades of extensive observations. The diffuse interstellar bands (DIBs), the 220 nm feature, unidentified infrared emission (UIE) bands, extended red emissions (ERE), and 21 and 30 μm emission features are seen in a wide variety of astrophysical environments. While the DIBs are probably the result of electronic transitions of molecules, the remaining others are likely manifestations of complex organic compounds. However, the exact chemical compositions of the carriers are still uncertain.

These unexplained spectral phenomena are observed throughout the Universe. The 220 nm feature has been detected in interplanetary dust particles in the Solar System as well as in distant galaxies with redshift > 2. A survey of 150 galaxies by the AKARI satellite found that $\sim 0.1\%$ of the total energy of the parent galaxies is emitted through the 3.3 μm UIE band. The Spitzer satellite has found that up to 20% of the total luminosity of some active galaxies is emitted in the UIE bands. The 3.3 μm UIE band is detected by James Webb Space Telescope (JWST) in a galaxy of redshift 4.2, suggesting that organic compounds were synthesized as early as 1.5 billion years after the Big Bang [1].

Unidentified infrared emission bands

The UIE bands consist of major bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm, minor emission features at 3.4, 12.1, 12.4, 12.7, 13.3, 15.8, 16.4, 17.4, 17.8, and 18.9 μm, and strong, broad emission plateaus features at 6–9, 10–15, and 15–20 μm.

The UIE bands are observed in emission above a broad continuum commonly attributed to thermal emission from solid-state particles. The UIE bands have been observed in planetary nebulae, reflection nebulae, Hii regions, novae, in the diffuse interstellar medium in the Milky Way Galaxy and in external galaxies (Fig. 1).

The UIE bands usually appear together as a family, with minor variations in peak wavelengths and profiles depending on the astronomical sources from which they appear [3].

The 220 nm feature

The 220 nm ultraviolet feature is seen in absorption along the line of sight of many stars. It has a characteristically consistent profile and a peak wavelength of 217.5 nm. The feature is likely to originate from the bandgap (5.7 eV) in the material of the carrier.

Extended red emissions

The extended red emission (ERE) is a broad ($\Delta\lambda \sim 80$ nm) emission band peaking between 650 and 800 nm. ERE has been detected in reflection nebulae, dark nebulae, cirrus clouds, planetary nebulae, HII regions, diffuse interstellar medium, and haloes of galaxies. It is commonly attributed to photoluminescence of a carbonaceous compound after absorption of far UV photons. It is estimated that $\sim 4\%$ of the energy absorbed by interstellar dust at $\lambda < 0.55\mu$m is emitted in the form of the ERE [4].

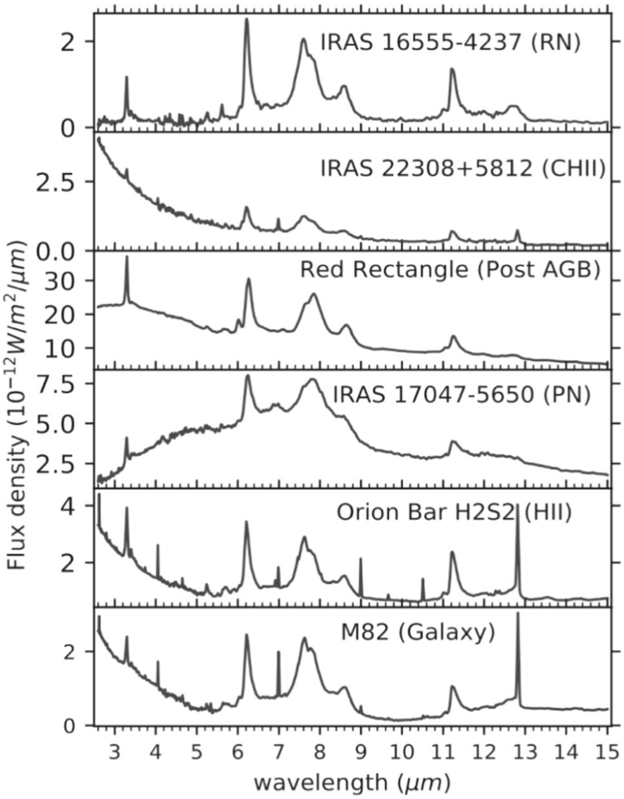

Fig. 1 The UIE bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm are observed in different astronomical environments. The narrow features are atomic lines. Figure reproduced from reference [2]

21 and 30 μm bands

The 21 and 30 μm are strong and broad emission features first observed in evolved stars. The 21 μm feature has an asymmetric profile and a peak wavelength of 20.1 μm. The 21 and 30 μm features can carry, respectively, up to 8 and 20% of the total energy output of the objects [5].

Chemical nature of the carriers

Because of the strengths and ubiquitous nature of these unexplained spectral phenomena, the carrier must be made of common, abundant elements. The carrier of the 220 nm feature is likely to be a carbonaceous solid such as amorphous carbon, carbon onions, hydrogenated fullerenes, or polycrystalline graphite. Hydrogenated amorphous carbon (HAC), PAHs, quenched carbonaceous composite particles (QCC), fullerenes, and nanodiamonds have been suggested as carriers of ERE. The 30 μm feature is generally taken to be due to MgS, possibly in combination with other sulfides [6].

The UIE bands are generally attributed to vibrational bands of carbonaceous compounds [7,8]. Proposed carriers of the UIE bands include polycyclic aromatic hydrocarbon (PAH) molecules [9–11], small carbonaceous molecules, HAC, soot and carbon nanoparticles, QCC, coal and kerogen, petroleum fractions, and mixed aromatic/aliphatic organic nanoparticles (MAON) [12] (Fig. 2). The PAH hypothesis is currently the most popular model in the astronomical community.

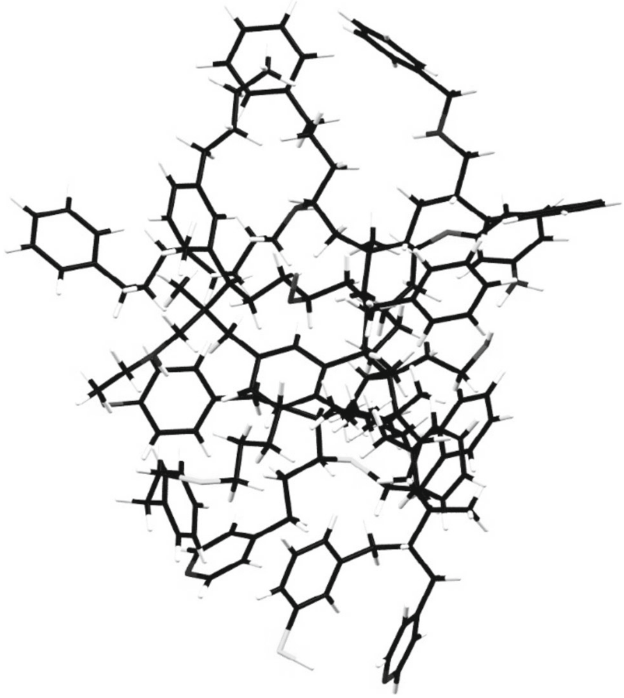

Fig. 2 An example of a MAON molecule with 169 C atoms (in black) and 225 H atoms (in white), 4 O atoms (in red), 7 N atoms (in blue), and 3 S atoms (in yellow). It is characterized by a highly disorganized arrangement of small units of aromatic rings linked by aliphatic chains. Figure adapted from [13]

Current and future challenges

Since the UIE phenomenon is seen throughout the Universe, a correct identification of the carrier is of great importance. The strengths of the UIE bands suggest that the carrier must be a major reservoir of carbon. Many current models of the interstellar medium are based on the premise that PAH molecules are the dominant factors in photoelectric heating of interstellar gas and in the ionization balance inside molecular clouds. Since the UIE bands are widely used as diagnostic of the galactic environment, a correct identification of the carrier of the UIE bands will have significant implications on our understanding of cosmic chemical synthesis, energy exchange between stars and the interstellar medium, and galactic chemical enrichment.

Advances in science and technology to meet challenges

Amorphous organic solids are often the natural results of combustion. When a mixture of hydrocarbon gases is subjected to energy injection (UV, electric discharge, laser ablation, or flame combustion) and the evaporated condensates are collected on cooled substrates, the resulting substances are often amorphous carbonaceous compounds. A recent experiment designed to simulate molecular and solid synthesis in circumstellar low-temperature and low-density conditions has yielded simple molecules such as acetylene and ethylene, as well as carbonaceous solids such as amorphous carbon nanograins and aliphatic carbon clusters [14].

Advances in computing capabilities have allowed vibrational spectra of complex molecules to be calculated. To solve these long-standing spectral mysteries, we need a two-prone approach: laboratory synthesis of artificial carbonaceous compounds and measurements of their spectral properties; and theoretical quantum chemistry calculations on large organic molecules.

Concluding remarks

Although the Universe was once considered as composed of stars and interstellar atomic gases, we have now come to the realization that interstellar space is filled with complex organic molecules and solids [15,16]. The resolution of the unidentified spectral mysteries will gain us an improved understanding of the complexity of the Universe.

Acknowledgments

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3 The aromatic infrared bands

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Status

Since the 1970 s, a series of prominent infrared (IR) emission features between 3 and 20 μm have been observed ubiquitously in the Universe. These features, originally referred to as the Unidentified Infrared Bands (UIBs) and now collectively known as the Aromatic Infrared Bands (AIBs), appear in a wide range of environments, including photodissociation regions (PDRs), proto-planetary disks, circumstellar shells, the interstellar medium (ISM), and galaxies (up to $z \sim 4.2$). Despite their ubiquity, their origin remained a mystery for a decade.

The AIBs consist of a series of main bands centered at 3.3, 6.2, 7.7, 8.7, 11.2, and 12.7 μm and a plethora of weaker bands (Fig. 3).

Substructure is also seen in several AIBs. A detailed spectroscopic inventory based on JWST observations of the Orion Bar is given by Chown et al. [17]. The AIBs are perched on top of continuum emission generally attributed to stochastically heated Very Small Grains (VSGs). The spectral decomposition of the AIBs and the continuum emission is uncertain and several methods are in use (for details see, e.g., [19]).

While the AIB emission spectrum is, to zeroth order, rather generic (i.e., similar for most sight lines), the AIBs display (sometimes) subtle, yet significant spectroscopic variability in terms of absolute total luminosity, relative band strengths, peak position and band profile (e.g., [17,20–23]). These spectroscopic variations reflect that the carriers of the AIBs are not static, but undergo processing that alters the characteristics of the species and thus, the chemical make up and/or molecular structure of the population of AIB carriers.

The following key pieces of evidence have led to the conclusion that the AIBs are due to free-flying carbonaceous molecules that are largely aromatic in nature: polycyclic aromatic hydrocarbons (PAHs) and related compounds:

- **Spectral Characteristics:** The observed emission features correspond closely to vibrational modes of aromatic hydrocarbons, specifically C-H and C-C stretching and bending modes in aromatic ring structures ([8,10,11]).
- **Excitation Mechanism:** The intensity and profiles of these features (including emission at NIR wavelengths) are consistent with a mechanism where large molecules are stochastically heated by ultraviolet (UV) photons, a behavior characteristic of small, free-flying particles like PAHs ([9–11]).
- **Laboratory and Theoretical Studies:** Laboratory and theoretically calculated spectra of neutral, ionized, and substituted PAHs reproduce the observed IR features remarkably well, providing direct support for this identification (e.g., [24]).
- **Correlations with UV Radiation:** The strength of the AIBs correlates strongly with regions of active UV processing, such as star-forming regions and PDRs, consistent with PAHs being photo-excited.
- **Carbon Abundance:** The inferred abundance of PAHs matches the expected fraction of interstellar

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Other, less common, nomenclatures are: unidentified IR emission (UIE) bands, IR emission features/bands (IEFs/IEBs), aromatic IR features (AIFs), aromatic feature emission (AFEs), ...

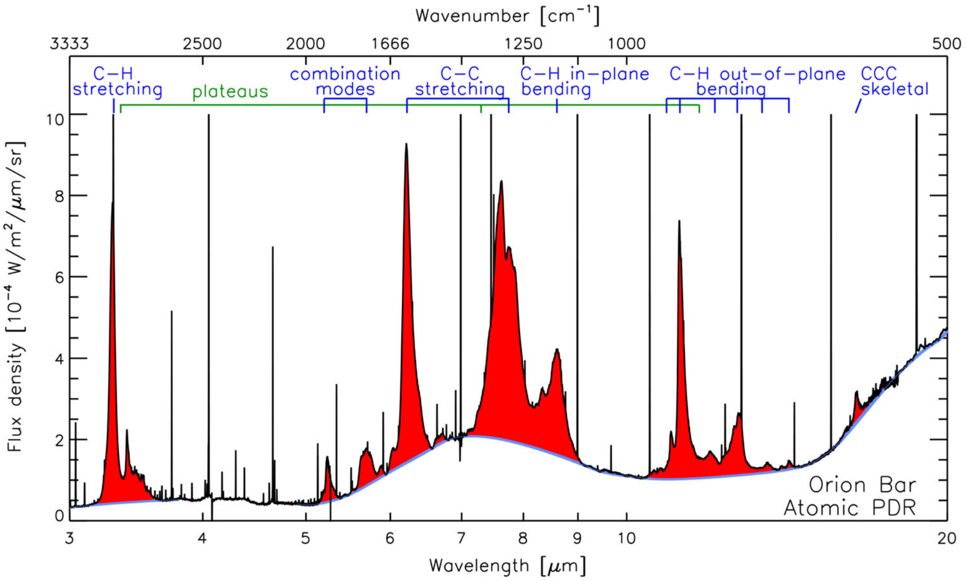

Fig. 3 AIB emission (highlighted in red) toward the atomic zone of the Orion Bar photodissociation region (PDR). Spectroscopic assignments for the main bands are given at the top. Figure adapted from [17,18]

carbon that would reside in such large, aromatic molecules [19].

- Detection of small gas-phase PAH molecules: pure PAHs (i.e., consisting of only hydrogen and carbon atoms) generally do not exhibit allowed rotational transitions (as they lack a dipole moment), hampering their detection and identification at radio wavelengths. Nevertheless, rotational emission from a few, small gas-phase polycyclic hydrocarbon molecules has been detected in the cold molecular cloud OMC-1 (e.g., [25–27]).

Why is this research field so important? Understanding PAHs enhances our comprehension of how organic matter evolves across cosmic environments and informs theories of life's origins. PAHs are intermediates in the formation of complex organic molecules, potentially contributing to prebiotic chemistry. Moreover, PAHs play a key role in several physical and chemical processes and thus influence star and planet formation and galaxy evolution. For example, they dominate the heating of the neutral ISM through the photo-electric effect [28] and thus set the temperature in the neutral ISM, including surfaces of proto-planetary disks. Likewise, PAHs control the charge balance in diffuse and dense clouds [29]. As interstellar gas phase chemistry is dominated by ion-molecule reactions, PAHs play a central role in setting molecular abundances in these clouds [30]. Due to their omnipresence, AIBs are used as a vital tracer for UV photochemistry and star-formation across the Universe (e.g., [17,31,32]).

What will be gained with further advances? Improved characterization of the spectroscopic signatures of AIBs and their dependence on the local environment in which they reside, combined with refined astronomical modeling of the PAH population and improved and extended instrisic PAH spectra based on laboratory and theoretical advances, will enhance our understanding of the formation, evolution, and destruction of the PAH population. Improved characterization of the PAH population will refine our models of cosmic carbon chemistry and PDRs (PAHs are most prominent in PDRs) and provide better interpretations of astronomical spectra and phenomena. Furthermore, a deeper understanding of PAHs-along with their formation, processing, and destruction-will provide crucial insights into their role in the broader life cycle of cosmic carbon, linking them to other important species such as the Diffuse Interstellar Bands (DIBs), fullerenes, and VSGs. Advances could shed light on the pathways leading from simple molecules to biologically relevant compounds, bridging gaps in our understanding of life's building blocks.

Current and future challenges

The key challenge is that we don't know what specific species are responsible for the AIBs. While rotational emission of individual small PAHs has been detected in a cold molecular cloud, AIBs are observed in warmer photodiscocciation regions where they can be excited by UV or visual photons and the connection between the PAHs in both environments is yet to be revealed. An additional major challenge lies in disentangling the complex spectra of PAHs from other molecular and dust contributions in astronomical observations as well as disentangling the subcomponents, and thus PAH subpopulations (in terms of size, charge, molecular structure, excitation), of individual AIBs. Combined, these challenges also hamper the spectroscopic assignment of the AIBs and their sub-structure and thus our understanding of the photochemical processing of the PAH population. Additionally, the role of PAHs in environments with extreme UV radiation and AGNs (active galactic nuclei), shocks, or low temperatures requires further exploration.

Recent advances have enabled anharmonic calculations of intrinsic spectra for a few small PAHs, improving upon traditional harmonic methods (e.g., [33]). However, applying these anharmonic calculations to larger species responsible for AIBs, as well as to a broader sample of PAHs for systematic characterization, presents significant computational challenges. The development of innovative algorithms may help mitigate (some of) these computational difficulties. Ideally, general rules should be developed to correct harmonically calculated spectra for anharmonicity effects. These rules can then be applied to existing harmonic PAH databases, leveraging these extensive data sets and reducing the need for costly anharmonic calculations.

Interpretation of the observations furthermore requires astronomical modeling of the PAH population. These models need refinement to predict PAH behavior and AIB characteristics in diverse environments and link them to observational data. However, astronomical modeling of the PAH population relies on fundamental parameters that are often only experimentally measured for a handful of very small PAHs. Experimental challenges include replicating interstellar conditions in the lab to study gas-phase PAHs of typical sizes expected in space (e.g., Joblin et al., 2020). Additional fundamental parameters required for PAH modeling include UV absorption cross sections, ionization cross sections and potentials, electron recombination rates, dissociation energies (and channels), isomerization energies, relaxation rates, reaction rates (e.g., with C^+) for PAHs, super- and de-hydrogenated PAHs, fullerenes, cages, PAH clusters and VSGs.

Advances in science and technology to meet challenges

Progress in infrared astronomy, exemplified by instruments like the James Webb Space Telescope (JWST), offers unprecedented spatial and spectral resolution combined with high sensitivity to isolate PAH features and study the changes in the full 3–20 μm AIB emission on physical scales on which the photochemical evolution of the PAH population occurs. Advances in laboratory astrophysics enable controlled studies of the formation, excitation and destruction of large carbonaceous species under interstellar conditions. Machine learning and high-performance computing are revolutionizing spectral analysis, allowing the identification of specific PAH species in complex datasets and allow for more advanced computationally heavy theoretical calculations (such as anharmonic intrinsic PAH spectra). Developing a more comprehensive database of PAH spectra will aid in comparing observational, theoretical, and experimental results.

Concluding remarks

PAHs remain central to understanding the organic chemistry of the Universe. Addressing current challenges through technological and theoretical innovations will deepen our knowledge of their roles in cosmic evolution and their implications for the origins of life.

4 Cosmic Fullerenes

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Status

Ever since the buckminsterfullerene C_{60} was discovered on Earth in experiments simulating the carbon-rich circumstellar environments of evolved stars, they were predicted to be widespread and abundant in the Universe [34]. Almost forty years later, C_{60} and C_{60}^+ have been reliably detected and identified in space [35,36] (see also Fig. 4).

Especially the infrared features of C_{60} have been seen in diverse astrophysical environments - from the surroundings of various types of evolved stars to interstellar clouds and to the planet-forming disks around young stars. Fullerenes are not frequently detected however; for example, only a few percent of the C-rich planetary nebulae that have been observed with the Spitzer-IRS spectrograph show the characteristic C_{60} features. When they are seen, their estimated abundance is rather high for a single molecular species - ranging from 10^{-4} to 3% of the available carbon (see , e.g., [38], for an overview). Thus, C_{60} is certainly widespread in space, and when it is seen, it is also abundant. There appears to be only one clear case for the presence of C_{70} thus far [37]. Searches for C_{60}^-, for smaller or larger fullerene cages, as well as searches for protonated or metal-complexed C_{60} compounds have been inconclusive [39–43].

Despite much research since the initial discovery, the inter- and circumstellar fullerene field is still in its

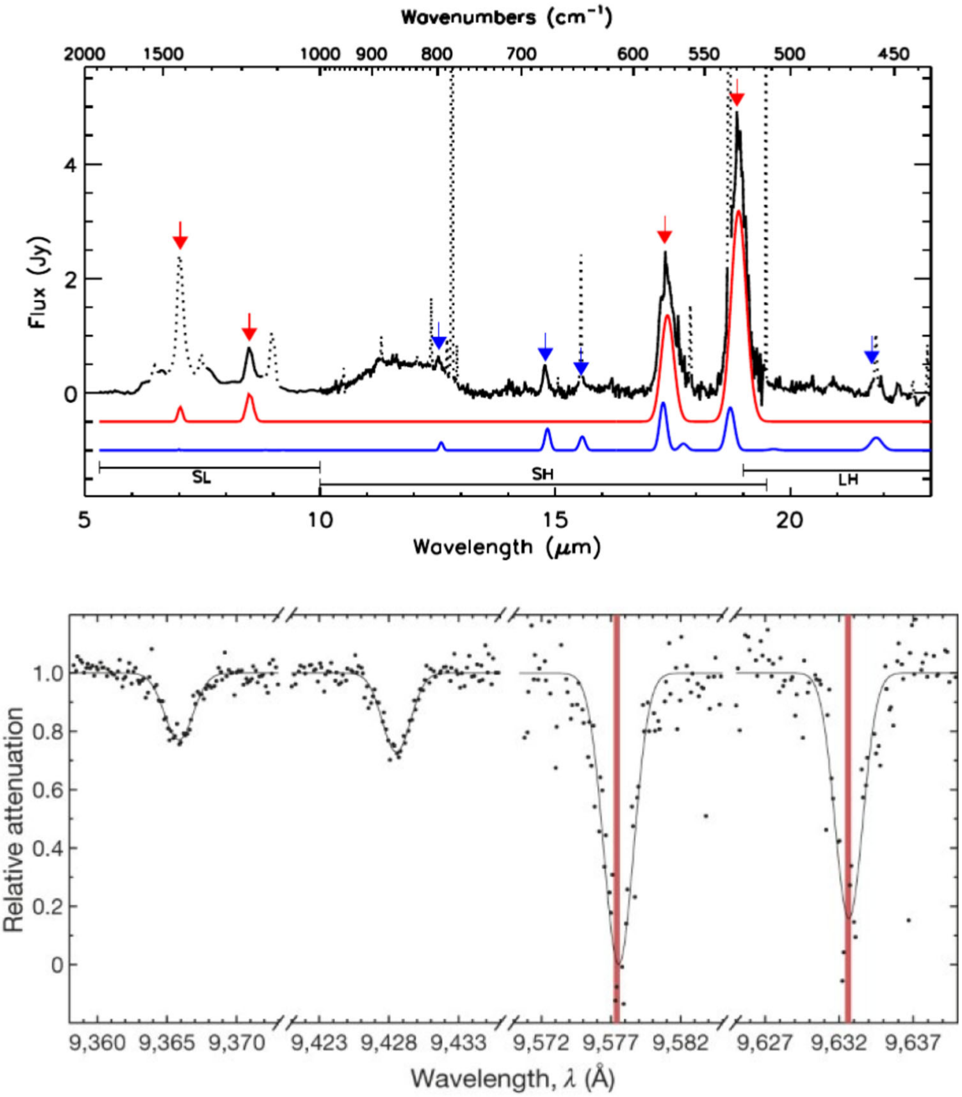

Fig. 4 (Top) The continuum-subtracted Spitzer-IRS spectrum of the planetary nebula Tc 1 (black) compared to (thermal) models for C_{60} (red) and C_{70} (blue). Figure taken from Ref. [37]. (bottom) Laboratory spectrum of showing clear absorption bands at the wavelengths of the observed DIBs at 9577 and 9632 Å. Figure reproduced from Ref. [36]

infancy, and the full extent of the role and implications of cosmic fullerenes remains a tantalizing mystery.

Why is this research field so important? In recent years astronomical surveys have resulted in the detection of larger and larger species, underlining that we live in a molecular Universe, capable of species as complex as C_{60}. This fullerene is also the only identified large aromatic species that has been seen in a variety of objects across the stellar lifecycle. The molecular physics of fullerenes is expected to be similar (albeit with perhaps slightly different parameters) to that of polycyclic aromatic hydrocarbon (PAH) molecules that represent a much larger fraction of the cosmic carbon, and whose IR glow pervades the local and distant Universe. However, progress here has been hampered by the fact that the PAH emission represents the combined emission of an entire family of molecular species whose response to the local conditions depends on molecular size, charge state, geometry and precise chemical makeup. This makes it very hard - if not impossible - to critically test theoretical models for the evolution and excitation of large molecules in space. Just like PAHs, C_{60} emission is seen in photo-dissociations regions (PDRs), but in contrast to PAHs, they have clearly distinct spectral features. Detailed studies of C_{60} may thus offer the most critical test possible of our models for the formation, excitation and evolution of large carbonaceous molecules.

What will be gained with further advances? Further advances in the field, aimed to understand the formation mechanisms, distribution, excitation and abundance of fullerene compounds in space will allow us to build a solid foundation to describe the molecular physics and the detailed chemistry that governs these species in various environments. Fullerene studies will pave the way for a more general description of how carbonaceous molecules interact with their environment, and how the environment affects their chemistry. Such a description will be crucial to update our models for the large-scale processes that are driven by these species, such as star and planet formation, and galactic evolution.

Current and future challenges

Despite the progress made in identifying cosmic fullerenes, we face several hurdles in our efforts to reach a complete picture. A first one is that we do not have a full inventory yet of the fullerene compounds that are present in space. While C_{60} can have strong emission bands (since it only has 4 IR active modes), other fullerene compounds (with a lower level of molecular symmetry) may be much weaker and thus much harder to detect. Another key problem is that current models for the excitation and charge state of fullerenes do not accurately predict the observed IR spectra [44], indicating that something is missing from our models. Chemical pathways may change pure C_{60} into other compounds including structural variants, as well as hydrogenated or otherwise functionalized species. Subtle molecular physics processes, including complex electronic excited state dynamics, may become important under certain conditions. Finally, a coherent picture of the formation and evolution of fullerenes is sorely missing. Theoretical calculations [44] and laboratory experiments [45] have suggested that C_{60} can form from dehydrogenation of large PAHs, but it is not clear how this process can explain the appearance of C_{60} in young, low-excitation planetary nebulae while they are absent in their more mature counterparts that sometimes show copious PAH emission. In addition, other fullerene formation processes include the photochemical processing of hydrogenated amorphous carbon grains (HACs) [46] and the shock-heating and ion bombardment induced processing of SiC grains [47]. There are likely multiple formation pathways that are relevant for different environments. Finally, there is a clear relation to the problem of the diffuse interstellar bands (DIBs), since currently the only identified DIBs are due to C_{60}^+. This begs the question what other DIBs could be related to other fullerene compounds.

Advances in science and technology to meet challenges

To meet the challenges, we need a concerted effort of observational studies, targeted laboratory experiments, theoretical calculations and computational chemistry. Much progress can be expected from detailed studies of C_{60} in different environments with the JWST, and from follow-up studies (e.g., correlation studies, line profile analysis) involving the C_{60}^+-DIBs. Laboratory experiments will not only provide us with state-of-the-art spectra of different fullerene compounds for comparison to optical and IR observations, they are also crucial to measure the reaction rates for various physical processes and chemical reactions. Those are indispensable to update our models. Laboratory experiments simulating astrophysical conditions can aid in understanding the formation mechanisms and stability of fullerene compounds in space. Computational models of astrochemistry will play a pivotal role in simulating the complex interactions of carbon-bearing molecules in various astrophysical environments, guiding observational and experimental efforts and interpreting data.

Concluding remarks

The exploration of cosmic fullerenes stands at the forefront of modern astrophysics, offering a unique gateway to understanding the cosmic carbon cycle and the complexity of interstellar chemistry. As we navigate the cosmos with cosmic fullerenes as our guide, collaboration between astronomers, chemists, and physicists becomes paramount. The integration of observational, laboratory, and theoretical efforts will unlock the mysteries encoded in these carbon structures, reshaping our comprehension of the dynamic and ever-evolving Universe.

During the preparation of this manuscript we were informed of the death of Harold Linnartz, whose life was cut tragically short. His contribution to the field was significant and he leaves behind a wealth of results future generations can build on.

5 The diffuse interstellar bands

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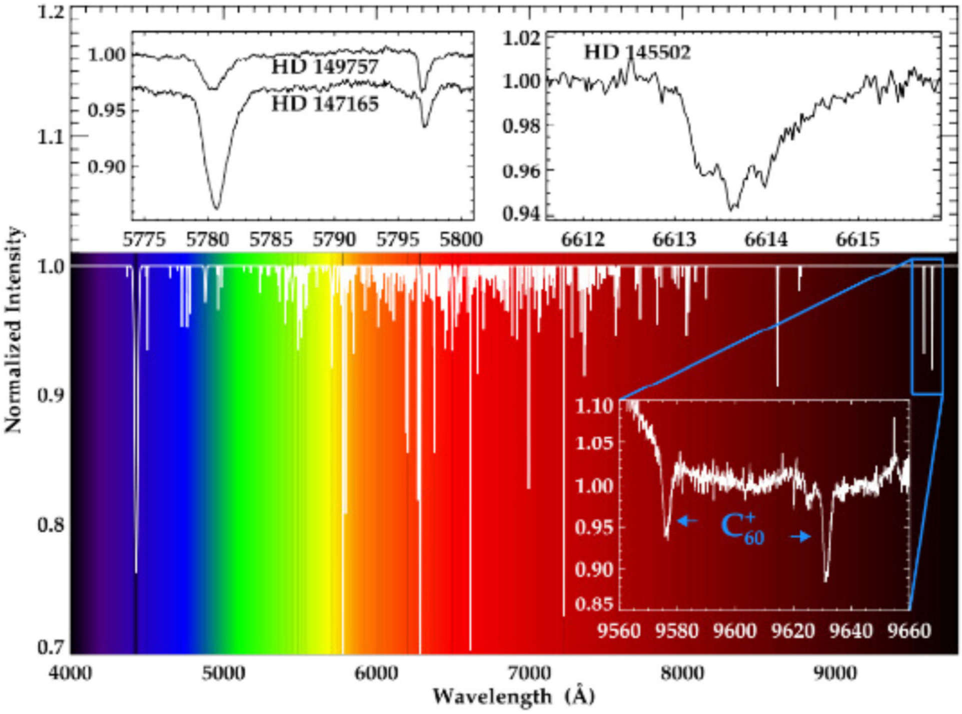

Fig. 5 Synthetic DIB spectrum as observed toward HD 183143 [54]. The inset in the main figure shows the two strong DIBs at 9577 Å and 9632 Å

Status

The diffuse interstellar bands (DIBs) are a set of more than 600 absorption bands that are detected in the light of reddened stars crossing diffuse and translucent interstellar clouds. DIBs are omnipresent and have been observed even toward other Galaxies. The first DIBs were detected in 1919 (but reported only a few years later; [48]), and for over a century, they have intrigued astronomers. To date, 559 DIBs have been catalogued in the visual range [49]; another 63 at near-infrared wavelengths [50, 51].

The DIBs show a good, though not perfect, correlation with interstellar extinction [52] and show clear variations in their relative strengths in different environments (e.g., [53]). They are likely stemming from large molecules in the gaseous state within the diffuse interstellar medium (ISM) (Fig. 5).

The key problem is that the precise identity of the species responsible for the DIBs is still a mystery - with the notable exception of two strong and three weak DIBs that have been identified as due to electronic transitions in the buckminsterfullerene cation [36], see also [55].

Over the past 30 years, numerous studies have expanded our DIB catalogues, have refined the band profile parameters, and have investigated relations between the DIBs mutually and with other line-of-sight parameters. However, the precise origins and nature of the DIBs remain largely enigmatic. Research into DIBs is pivotal, not just for decoding the composition of the ISM, but also for understanding the physical and chemical processes shaping interstellar and circumstellar environments - in our Milky Way as well as in other galaxies.

Why is this research field so important? The significance of studying DIBs (that lock up ~0.5% of the cosmic carbon) poses fundamental questions about the composition and evolution of the ISM. The ubiquitous nature of the DIBs makes them direct evidence of the presence, and survival, of a large inventory of complex, probably organic molecules even in the diffuse interstellar medium, where matter is mostly atomic. They therefore provide a direct probe into its elusive chemistry.

The DIBs are uniquely associated with the complexity of the diffuse ISM, composed of multiphase and turbulent environments. Furthermore, they act as distinctive tracers of the ISM's physical conditions, thus offering a powerful diagnostic tool to increase our knowledge of the interplay between gas, dust, and radiation, and for studying this complexity in relation to the thermal and turbulent properties of the diffuse ISM.

In addition, DIBs may link the chemical debris from dying stars to the birth of new stars and planets. Deciphering the DIB enigma is thus essential for understanding the matter cycle within the cosmos. Pushing the frontiers of astronomical research, DIBs offer a unique opportunity to explore the cosmos at both macro and micro-scales.

What will be gained with further advances? The DIBs have an enormous diagnostic potential. Progress in understanding the DIBs could reveal the carrier molecules responsible for these absorption features and provide detailed insights into the complex chemistry and physical conditions in the space between stars, in addition to a better understanding of molecular stability in harsh environments. This knowledge is not only essential for advancing our understanding of astrophysics and astrochemistry but also has implications for astrobiology, as the organic molecules associated with DIBs, ultimately, may survive in the formation of planetary systems and play a role in the emergence of life.

Current and future challenges

Despite a century of research, the DIBs still present formidable challenges that demand innovative solutions. One of the primary challenges is the identification of the specific molecules responsible for individual DIBs, especially when considering the enormous number of possible carrier molecules to test.

Another challenge lies in deciphering the spatial and temporal variations of DIBs across different astronomical environments and linking them to the chemical, physical and dynamical complexity of the diffuse ISM. Understanding the factors that influence the strength and profile of DIBs is crucial for interpreting the observations and extracting meaningful information about the interstellar medium.

Advances in science and technology to meet challenges

Addressing the challenges posed by DIB research requires a multidisciplinary approach and the integration of cutting-edge technologies. Laboratory astrophysics, computational chemistry, magnetohydrodynamic simulations, and innovative observational techniques are at the forefront of this pursuit. An identification requires an irrefutable match between cold, gas phase experimental spectra and high-resolution observations at a high signal-to-noise ratio. Observational and computational studies will guide the laboratory efforts and narrow down the potential DIB carrier molecules. High-resolution spectroscopy and modern telescopes (including Extremely Large Telescopes) with advanced detectors from the UV to the infrared will enhance the precision of DIB observations, unraveling their intricate profiles. The technological challenge posed by DIBs is peculiar in astronomy, in that it requires pushing high resolution spectroscopy of relatively bright objects to extreme signal-to-noise ratios, over broad spectral ranges. Moreover, advancements in computational modeling will play a crucial role in simulating the multi-phase, turbulent interstellar environments and predicting the expected DIB patterns under various physical and chemical conditions.

Access to highly specialized observatories, like the ground-based VLT-UVES and VLT-CRIRES+ or Hubble, James Webb and Gaia space missions as well as continuously improving laboratory and computational methods, including machine learning techniques, will make it possible to progress in the identification and use of DIBs as diagnostics of the environment they reside in.

Concluding remarks

The exploration of Diffuse Interstellar Bands stands at a crucial juncture, with the promise of delivering profound insights into the composition and dynamics of the interstellar medium. Success hinges on collaboration across astronomy, chemistry, and physics, integrating theoretical models, laboratory experiments, and precise observations. This concerted effort is key to advancing DIB research and potentially resolving a century-old cosmic mystery.

During the preparation of this manuscript we were informed of the death of Harold Linnartz, whose life was cut tragically short. His contribution to the field was significant and he leaves behind a wealth of results future generations can build on.

6 Perspective on laboratory electronic spectroscopy for comparison with diffuse interstellar bands

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Status

Absorptions in the visible to near-IR range of the electromagnetic spectrum ($\lambda = 400$-1500 nm), known as the diffuse interstellar bands (DIBs), have been observed for over a century on the interstellar extinction curve of various lines-of-sight in the Universe [56]. The only identified carrier of DIBs is C_{60} in its cationic form (C_{60}^+). This assignment supports the widely accepted hypothesis that DIBs carriers are mainly large carbonaceous molecules. C_{60}^+ is responsible for just a handful [57] out of more than 600 catalogued DIBs while the identity of the molecules responsible for the remaining interstellar absorptions is an outstanding problem. Due to the lack of perfect correlation among nearly all strong DIBs [58], the inventory of molecules giving rise to them is anticipated to represent a significant, unexplored reservoir of chemical complexity in space.

Unequivocal insights will only follow from the acquisition of the electronic spectra of large, gas phase molecules and ions under appropriate laboratory conditions such that they are directly comparable with astronomical observations. This is a major challenge for laboratory astrophysics, and one that must be met to

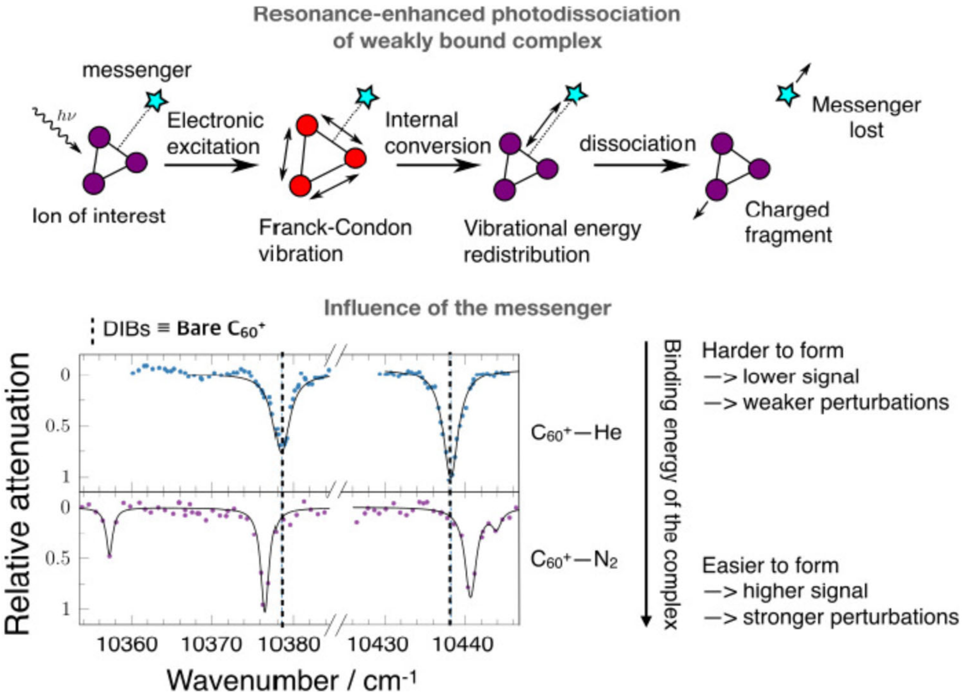

Fig. 6 Messenger spectroscopy of molecular ions. The bottom left is adapted from Ref. [59]

interpret the DIB enigma and decipher the chemical complexity of the ISM. In the following, we focus on current and future laboratory methods to record the spectra of gas phase molecular ions to tackle the DIB problem.

Current and future challenges

Ions are commonly studied using action spectroscopy, which exploits mass spectrometry to detect the outcome of photo-induced processes. These approaches offer higher sensitivity than conventional, direct absorption spectroscopy and are frequently applied in combination with cryogenically-cooled ion traps. Such instrumentation and methodologies have enabled access to the spectra of large, complex ions by reducing quantum state spread through buffer gas cooling.

A widely-used method involves photodissociation with a messenger atom or molecule such as He or N_2 weakly bound to the ion of interest; resonance-enhanced photodissociation (REPD, Fig. 6).

Spectra can be obtained by monitoring the loss of the messenger as a function of excitation wavelength. A powerful feature of this approach is the fact that electronic excitation in the visible to near-IR often results in dissociation in a single photon process, enabling experiments to be carried out with a single laser. For example, because the binding energy of He to C_{60}^+ is around 100 cm^{-1}, electronic excitation with photon energies > 10000 cm^{-1} followed by internal conversion easily leads to He loss. This approach is particularly useful in the case of very stable cage structures like C_{60}^+ where tens of eV of energy would be required to observe fragmentation of the bare ion on the experimental timescale. Messenger spectroscopy has proved successful for obtaining spectroscopic information on large, internally cold molecular ions, but care must be taken inferring band profiles, central wavelengths and intensities of the bare ion based on such data. Helium has been frequently adopted as the messenger of choice for such studies as the perturbation to the bare ion spectrum is weaker than in the case of other atomic/molecular messengers.

An alternative to ion trapping approaches is through the use of helium nanodroplets. This method involves monitoring the ejection of the ion of interest from a He nanodroplet as a function of the excitation wavelength. Lately, a major breakthrough came from using He nanodroplets to efficiently produce helium-tagged ions. The ejection of ions from He nanodroplet usually generate spectra that are too broadened and perturbed (relative to the spectrum of the bare ion) to be used for comparison with astronomical observations. However, the He-droplet methodology pioneered by P. Scheier's group (Innsbruck) to generate small size He-tagged species has now been applied to look for potential DIB carriers [60]. This approach can significantly enhance the repetition rate of experiments compared to He tagging within a cryogenic ion trap.

Resonance-enhanced photodissociation can also be applied without a messenger atom or molecule by fragmentation of the bare ion structure. This has been utilized in both trapping and molecular beam instruments. For many molecular ions, however, the probed excited states (vibrational or electronic) lie below the first dissociation limit, thus these states cannot be observed using single-photon REPD spectroscopy. A remedy is the use of multi-photon processes to overcome the energy required for fragmentation. However, the REPD technique has the disadvantage of convolving the absorption spectrum by the dissociation efficiency, leading to the potential loss of spectral information, in particular on the relative intensities and spectral profiles of the observed transitions. Several more action spectroscopy approaches have been developed and employed using traps, including laser induced inhibition of complex growth [61], leak out spectroscopy [62], and laser induced reactions [63], however, as of yet none have been routinely applied to electronic transitions of large molecular ions.

All action spectroscopy methods face challenges with respect to inferring or acquiring unperturbed spectral data. In contrast, direct spectroscopy, by monitoring the attenuation of light, offers access to absolute wavelengths, profiles and intensities of transitions but lacks sensitivity due to low ion densities. Cavity ring-down spectroscopy (CRDS) overcomes sensitivity limitations through the use of kilometric absorption lengths. It is based on the coupling of a small fraction of a tunable laser radiation in a high finesse optical cavity consisting of two mirrors with a very high reflectivity ($R > 99.99\%$). The rate of photons escaping from the cavity is described by an exponential decay and the lifetime of the photons in the cavity reflects the absorption cross section of the absorber. Electronic spectra of molecular ions have been successfully obtained using CRDS in a supersonic expansion coupled with electric discharges. However, identifying different species becomes challenging because there is no mass selection, and the plasma source simultaneously generates multiple molecules, complicating the measured spectra. Moreover, vibrational relaxation of molecules as large as C_{60} is inefficient in expansions and requires buffer gas cooling approaches.

In addition to the requirement for sensitive methods for the acquisition of spectra, many molecular structures of astrochemical interest have not been produced in macroscopic quantities and lack a traditional organic chemistry synthesis route. One method used to overcome this is through laser ablation of a solid target to generate gas phase molecular ions. This has been applied in combination with cryogenic traps to gain access to molecular ions of various sizes composed solely of carbon atoms [64]. Recently, ion mobility has been used in combination with laser ablation and cryogenic trapping to enable isomers possessing different shapes of a given m/z to be separated prior to spectroscopic probing [65]. This is particularly useful in cases where more than two isomers exist, and obviates the need for 2-color hole burning experiments to obtain isomer specific spectra.

Advances in science and technology to meet challenges

To circumvent issues associated with action spectroscopy, CRDS could be carried out in an ion trap once the molecular targets have been sorted out with respect to both their shape and mass-to-charge ratio. For example, ions generated by laser ablation, or other ion source technology, can be mass-selected prior to injection into an ion mobility module. Following this, isomers of a given m/z can be isolated based on differences in collisional cross sections with He and accumulated in a cryogenic trap. In the trap, the ions can undergo millions of collisions with buffer gas to ensure vibrational modes are cooled to their ground state. An optical cavity enclosing the ion trap can be formed using high reflectivity mirrors to enable direct absorption spectra to be acquired through CRDS. To date, the only successful attempt at recording the spectrum of a charged polyatomic species using an optical cavity and ion trap was reported by the group of A.Terasaki. CRDS measurements of Ag_9^+ with photon energies between 3.92 and 4.12 eV were reported in an apparatus that utilizes a 40 cm long octupole ion trap cooled to 10 K [66].

Concluding remarks

Advances in laboratory methods for recording electronic transitions have provided access to the spectra of large, mass- and isomer-selected ions, buffer gas cooled to temperatures below 10 K. A variety of action spectroscopy methods have been used to-date, each with their own advantages and disadvantages. In some cases, where lifetimes of excited states are in the order of picoseconds, indirect, action spectra can provide the requisite spectroscopic data for comparison with observations. However, the ultimate goal is direct absorption spectroscopy; one approach that holds promise is the combination of CRDS with ion trapping, and mass- and isomer-selection. Spectra obtained using this methodology would pave the way to temperature dependent studies through which one could gain insight not only into the inventory of large molecules in interstellar clouds, but conceivably also the physical conditions in different astrochemical environments.

Acknowledgments

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7 Hydrogenated amorphous carbon grains as possible carriers of unexplained spectral phenomena in evolved stars

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Status

Evolved stars of low- and intermediate-mass (LIM; ∼0.8−8.0 $M_\odot$) play a crucial role in the production of cosmic dust. As LIM stars evolve toward the planetary nebula (PN) phase, they undergo a strong mass loss during the preceding asymptotic giant branch (AGB) phase. The mass loss significantly enriches the surrounding circumstellar and interstellar medium (ISM) with dust grains and molecules that are commonly observed throughout the Universe.

Thanks to astronomical observations made with infrared (IR) telescopes, such as the IR Space Observatory (ISO) and Spitzer, aromatic IR emission bands (AIBs, e.g., those at 3.3, 6.2, 7.7, 8.6, and 11.3 μm) have been detected in evolved stars like C-rich PNe. These AIBs are believed to be originated by various stretching and bending modes of aromatic hydrocarbon compounds and are usually associated with PAHs ([11], but see [67] and cf for instance Sect. 3 for a recent review). Interestingly, these AIBs are often accompanied by discrete aliphatic features as well as strong and still unidentified IR (UIR) broad emission plateau features at 6–9 (hereafter 7μm), 9–13 (hereafter 12μm), 15–20, and 25–35μm (see Fig. 7, [13] for a review).

In particular, the very broad 7 and 12μm UIR plateau features have been suggested to emerge from hydrogenated amorphous carbon (HAC) dust grains [2] or similar mixed aromatic-aliphatic organic nanoparticles [13]; HAC-like hereafter.

Similarly, the ISM extinction curves also contain crucial information about the composition and size distribution of the dust grains, particularly the so-called ultraviolet (UV) bump (∼ 2175 Å) and the far-UV rise (≤ 2000 Å) absorption features. Many efforts have been done to identify the possible carriers of these absorption features, including graphite [69] and more disordered species such as HACs, soot particles, and other carbonaceous materials, e.g., [70]. The longstanding challenge of identifying the carriers responsible for the UIR plateau features and ISM or circumstellar extinction observed toward diverse astrophysical objects has recently seen significant progress. The use of the laboratory optical constants of specific (in terms of structure/composition) HAC-like grains, in conjunction with radiative transfer models, have demonstrated that HAC-like dust grains can convincingly reproduce the 12 μm plateau emission feature observed in the C- and fullerene-rich PN Tc 1 (Fig. 7; [68]). In addition, they are capable of reproducing the far-UV rise circumstellar extinction observed in two C-rich PNe (Fig. 8) [71].

Furthermore, the HAC-like dust grains have attracted a lot of attention since the discovery of fullerenes (like C_{60} and C_{70}; Figure 7) in the C-rich PN Tc 1 [37]; this is because the formation of fullerenes could be related to the processing and/or destruction of HAC-like dust grains [72].

Current and future challenges

For the first time, HAC-like grains convincingly reproduce the 12 μm plateau emission feature seen in the prototypical fullerene-rich PN Tc 1, posing serious doubts on the generally accepted SiC identification in the literature as the main carrier of this feature. Remarkably, the HAC-like grains naturally provide an important fraction of the IR dust continuum emission and are still consistent with the other UIR features observed such as the 7 μm plateau feature (Fig. 7) [68]. However, the understanding of the precise chemical structure/composition of such HAC-like dust grains as carriers of the 12 μm plateau emission feature remains incomplete. Equally challenging is the origin of the other broad IR plateau emission features seen in C-rich PNe like the broad 7, 15–20, and 25–35 μm features.

In the same context, the possible presence of HAC-like grains affecting circumstellar extinction has been found only in two C-rich PNe (Tc 1 and Hen 2–5; [71]). Although the presence of mixed aromatic-aliphatic hydrocarbon material, like HACs, in the circumstellar matter may be a consistent picture for these C-rich PNe, we still cannot completely discard that their anomalous extinction is just peculiar foreground extinction, toward those sources, due to the arbitrary variation of extinction curves in the Galaxy.

Another big challenge in the study of the UIR plateau emission and UV absorption features is the availability of laboratory optical constants (the complex refractive index or the complex dielectric function) of HACs. Such optical constants are mainly used to calculate opacities from different grain size distributions, which are needed to simulate the UV-IR spectra of astronomical sources using spectral synthesis and radiative transfer codes (e.g., CLOUDY and DUSTY). Unfortunately, the only available laboratory optical constants, covering the appropriate wavelength range (0.1–17 μm), for such studies are for two HAC films with a specific struc-

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https://gitlab.nublado.org/cloudy/cloudy/-/wikis/home.
https://github.com/ivezic/dusty.

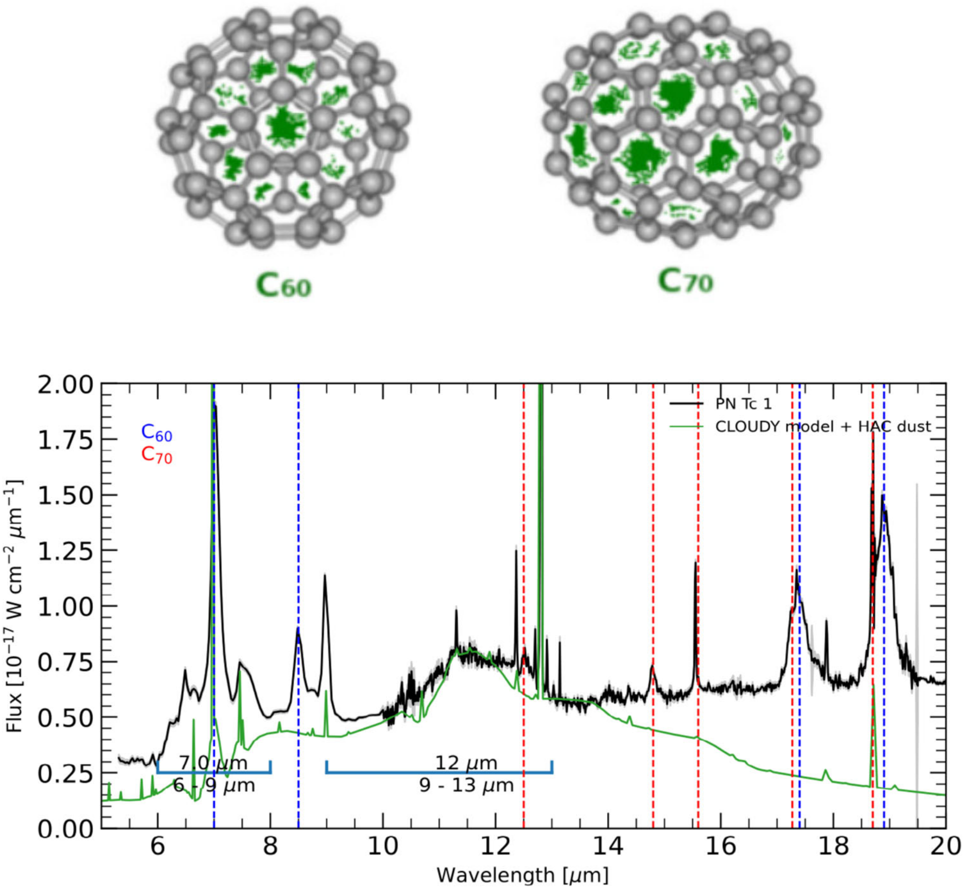

Fig. 7 Top-panel: The C_{60} and C_{70} fullerenes sketch. Bottom-panel: Spitzer IR spectrum of the PN Tc 1 (black) compared with a photoionization model including the HAC dust grains (green). The C_{60} (blue) and C_{70} (red) emission bands and broad UIR emissions are indicated. Figure adapted from Ref. [68]

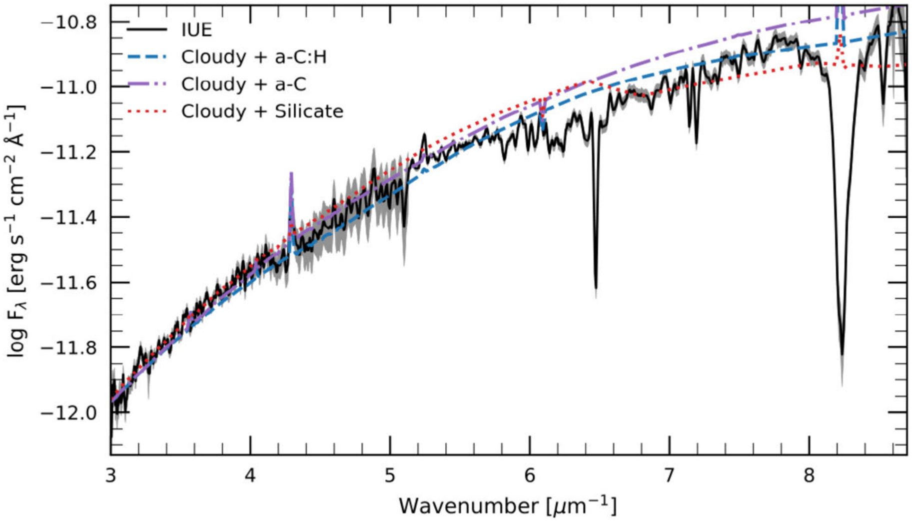

Fig. 8 CLOUDY models of Tc 1 fitted to the UV observed spectrum with HAC (dashed line), amorphous carbon (a-C; dashed-dotted), and silicates (dotted line). A very small grains law was used in all models. Figure adapted from [71]

ture/composition (e.g., hydrogen concentration and/or deposition temperature of 77 and 300 K; W. Duley, priv. comm.; see [73]), strongly limiting the extension of previous work on PN Tc 1 to more PNe or even other astrophysical objects.

Advances in science and technology to meet challenges

As we mentioned above, the exact nature of the carriers of the broad UIR plateau emission features observed in C-rich PNe, among other astrophysical sources, like those at 7, 12, 15–20, and 25–35 μm, is not well understood yet. However, the James Webb Space Telescope (JWST) presents a unique opportunity to study these features with significantly higher sensitivity compared to the previous ISO and Spitzer space telescopes. By observing variations in their positions and shapes, the JWST can provide valuable constraints for future modeling studies; potentially even resolving possible substructures within these intriguing emission features. Such spectroscopic observations may also reveal the presence of new IR emission features potentially due to fullerene-related species, such as fullerene-adducts, metallofullerenes, etc. (e.g., [41]).

In the same way, UV observations using the Hubble Space telescope (HST) offer another great opportunity to investigate the extinction in the line-of-sight of C-rich PNe. Such spatially resolved long-slit spectroscopic observations would provide sufficient information to precisely study the extinction variation toward C-rich PNe, providing new additional constraints for future modeling studies.

There is no doubt that nano- and micro-sized particles in the ISM and circumstellar matter play an important role in astrophysical processes that lead to the formation of such exotic UIR emissions seen in the spectra of C-rich PNe and other astrophysical objects. The optical constants of different materials (e.g., graphite, SiC, HAC, and MgS) are commonly used, in conjunction with radiative transfer codes, to explain the origin of the IR emission in astronomical spectra, e.g., [68, 71]. However, more laboratory efforts are needed in order to definitively reveal the carriers of the UIR emission in C-rich PNe. In particular, the laboratory optical constants of HAC-like particles of different chemical composition and deposition temperatures (e.g., by transmission spectroscopy measurements [74]), covering sufficient wavelength range (0.01-40 μm) are needed to extend the model studies to other evolved stars or astrophysical objects. Such models can be obtained by means of spectral synthesis and radiative transfer codes by including the opacities as a product of the laboratory optical constants of HACs.

Concluding remarks

The mid-IR spectra of C-rich PNe are dominated by aliphatic hydrocarbon-rich dust showing different UIR emission features. Remarkably, HAC-like dust grains are, for the first time, a convincing alternative explanation (i.e., different from the often assumed SiC) for the broad 12 μm plateau emission feature. Such HAC-like grains may also explain the FUV rise seen in extinction curves toward the same sources. This strongly encourages more laboratory experiments to obtain the refractive indices n and k (from the UV to the far-IR) of HAC-like dust grains with several structures/composition as well as at different physical conditions. Such collaborative interdisciplinary work for future modeling studies has the potential to clearly identify HAC-like dust grains as carriers of some unexplained spectral phenomena like the UIR bands and UV extinction as well as its possible role in the formation of fullerenes in astrophysical environments. In particular, more sophisticated laboratory experiments on the structural transformation of HAC-like grains at circumstellar conditions would be needed to unveil the details of fullerene formation via chemical reaction routes. Such cutting-edge laboratory experiments could be carried out by the novel StarDust machine [75]; a leading instrument in lab-based carbon studies for astrochemistry and astrophysics.

Acknowledgments

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8 Are carbon nano-onions (CNOs) Carriers of the 217.5 nm interstellar UV bump?

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Status: description of the state of the art

The UV "bump" at 2175 Å (4.6 μ m^{-1}, 5.7 eV) in the extinction spectra of interstellar dust (Fig. 9) has remained a mystery for decades and has not been comprehensively explained by lab models [76]. While many carbon nanomaterials-such as graphite, graphene, hydrogenated amorphous carbon, and polycyclic aromatic hydrocarbons (PAHs)-display absorbance at the specified wavelength, these models fail to account for the up to 30% variation in width between different lines of sight. Theodore Stecher first observed this feature in 1965 and attributed it to the π-plasmons in small graphite particles [77]. Further investigations over mul-

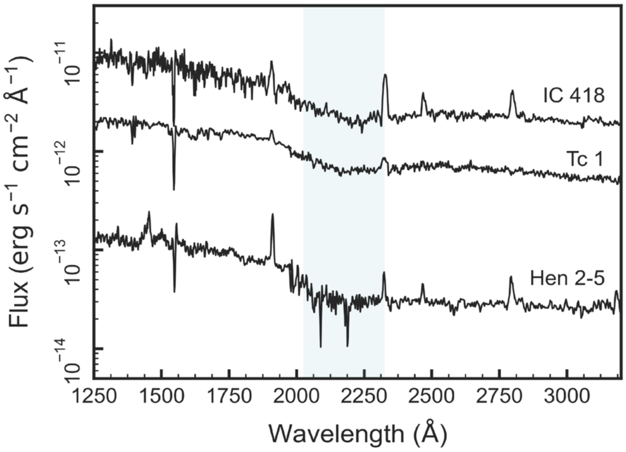

Fig. 9 Far-UV spectra of a selection of planetary nebulae, highlighting the "bump" at 2175 Å. Based on INES data from the IUE satellite

tiple galactic lines of sight proved the variability of peak widths of the UV bump. Other experimental and theoretical models have not comprehensively explained the variation.

Carbon nano-onions (CNOs) have been proposed as carriers of the UV bump. These spherical carbon nanoparticles consist of multiple fullerene-like layers and range in size from 1.4 to 50 nm, depending on the production method. While typically consisting of sp^2 carbon atoms, sp^3 defects are present in many samples; CNOs can also contain heteroatom dopants such as boron and nitrogen [78]. Nanodiamonds (NDs), a precursor material to CNOs, can be found in interstellar space, formed from methane and other carbon-rich sources [79]. Thermal annealing at around 1700 °C is the typical laboratory preparation method, but this temperature is not typically encountered in space. Instead, CNOs are likely formed by the bombardment of NDs with high-energy particles.

In 2004, Tomita et al. proposed a defective CNO model that replicated the absorbance properties of interstellar dust [80]. The complexity of these nanostructures yields to the presence of an array of defects as have been observed in laboratory-prepared samples through various physico-chemical characterization techniques. However, it is important to note that CNOs produced in laboratories form aggregates-they are not singular particles like their interstellar counterparts; this can be seen in the 260 nm peak in their absorbance spectra. The dielectric model proposed by Tomita et al. consisted of a core of radius r and defective graphite shells of radius R arranged in a spherical method. When the calculated absorption spectrum of an isolated CNO was compared to an extinction curve of interstellar dust, the defective CNO model produced a much better fit than the pristine CNO model. Initially, changing the r/R value from 0.14 to 0.5 resulted in a $> 30\%$ decrease in peak width and an 8% shift in peak maximum, which was larger than that observed experimentally. The observed data also displayed remarkable consistency regarding the peak position, which was not seen in the simulation. This was fixed by adjusting the dielectric constants chosen.

Ruiz et al. took the simulation of CNO electronic spectra a step further with a random phase approximation (RPA) analysis [81]. This approach bridges classical and quantum simulations and approximates microscopic quantum mechanical interactions in matter through a one-electron description. It leverages a Hückel model for the valence π and σ structure of fullerene shells, revealing that in CNOs with six or more layers, the $\pi - \sigma$ electron coupling vanishes. This simplifies RPA simulations for larger CNOs to consider only π-electrons for the significant π-plasmon feature in interstellar absorbance bands. This model agrees excellently with laboratory absorbance measurements of CNO films performed by Chhowalla et al. [82]. These measurements match the interstellar spectrum both position and width-wise. Overall, this study strongly supports CNOs as the cause of the interstellar absorption band.

Observational studies also suggest that CNOs could be carriers of the very broad 4428 Å diffuse interstellar band (DIB) observed in the optical spectra of the fullerene-rich planetary nebulae (PNe) Tc 1, M1-20, and IC 418 [83]. C_{60}^+ is the only DIB carrier identified so far. Studies by García-Hernández et al. also suggest that CNOs could be carriers of the 4428, 6309, and 6525 Å diffuse interstellar bands (DIBs) observed in the optical spectra of Tc 1, M1-20, and IC 418 planetary nebulae [71,84]. C_{60}^+ is the only DIB carrier identified so far.

Challenges and future directions

The main challenge in studying the formation, spectroscopy, and characteristics of interstellar CNOs is simulating the carbon nanoforms at the quantum mechanical level of theory. The large size and mass of CNOs compared to other carbon nanomaterials, such as carbon dots, C_{60} fullerenes, nanographene flakes, and nano-horns, increase the complexity and resource cost of developing a model at the quantum mechanical level.

The diversity of these multi-layered fullerenes is also an important facet of discussion. Many synthesis methods exist for CNOs, producing particles of varying sizes and distributions. The stress and strain on each onion layer vary, increasing in inner layers proportionally to their increased curvature. CNOs' core composition must also be accounted for; heating NDs to temperatures under $\sim$ 1700 °C will result in an sp^3 diamond core surrounded by sp^2 carbon layers, affecting CNOs' spectroscopic properties. As highlighted by Tomita et al. [80], defects in the CNO structure can affect the electronic properties of the particles. These sp^3 defects arise from oxidation, mechanical stress, or the presence of dopants such as nitrogen, boron, and phosphorus.

Until recently, the best simulations of CNOs have been limited molecular dynamics and electronic simulations of pristine 3-layer CNOs. Černevičs et al. recently published a study investigating the metallic-like behavior of "real" disordered CNOs using the bond order potential and charge self-consistent density functional tight-binding (SCC-DFTB) level of theory [85]. A Morse potential term was used to simulate the non-bonding interactions between layers, and van der Waals forces were incorporated by the internal DFTB+ implementation of Grimme's DFT-D3 dispersion correction. The conditions of interstellar CNOs lend themselves well to computational simulations, as they exist in a vacuum at very low temperatures, likely as singular particles; this reduces the computational resources required to simulate their environment. Even so, using a perfect fullerene-like model, Černevičs et al. could only simulate CNOs of up to 7 shells and $> 13,000$ carbon atoms. Models of more "realistic" nano-onions with broken shells and sp^3 defects in the form of curved, multi-layer graphene flakes were also investigated.

It was found that more simple descriptions of CNOs with perfect fullerene layers yield semiconducting properties, while breaking of the layers gives metallic properties to the simulated CNOs. The metallic material agrees with experimental observations more closely; "real" CNOs likely exist between both models, with perfect fullerene inner layers and more defective outer layers. Unfortunately, the spectroscopic properties of these onions have not been simulated, and more work is needed to describe the UV and IR absorption properties of interstellar CNOs.

With the increasing power of computational analysis in the coming years, the simulation of complete, "real" CNOs with their range of defects may be possible. This would lead to more accurate simulations of spectroscopic properties and their formation in space.

Challenges in synthesizing uniform CNOs in the lab also need to be addressed. Current methods produce a wide distribution of CNO sizes, level of defects, and presence of dopants such as nitrogen and oxygen.

Conclusions

CNOs are possible carriers of the 217.5 nm UV bump observed in interstellar dust across multiple lines of sight. They are also possible carriers of the unusually strong and broad 4428 Å DIB observed in the fullerene-rich PNe Tc 1, M1-20, and IC 418. Experimental observations of lab-made onions agree with interstellar observations; however, the best simulations of CNO electronic spectra have only been completed at classical and semi-classical levels. More work needs to be done to simulate the spectra of these particles at the quantum mechanical level to confirm if they are carriers of these spectroscopic features. Another challenge is the laboratory synthesis of CNOs, which produces monodisperse particles with similar levels and types of defects, which proves challenging and needs more work.

Acknowledgements

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9 Fullerene derivatives: carriers of the mysterious astronomical spectroscopic features?

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Status

There exist two sets of astronomical spectroscopic features, whose carriers have been puzzling astronomers and astrophysicists for many decades. One set of these features are the absorption features occurring mainly at optical and near infrared wavelengths that are observed in the astronomical spectra of objects in Milky Way and extragalactic galaxies. These are the so-called diffuse interstellar bands (DIBs), which were discovered by Heger in 1919 [52]. To date, among over 600 DIBs, only five at 9632, 9577, 9428, 9365, and 9348 Å are identified to be due to the ionized buckminsterfullerene, C_{60}^+ [36, 86].

The other set of astronomical features are the infrared emission bands lying in the far- to mid-infrared wavelength range of 3–20 μm, which were discovered by Russell et al. in the 1970 s firstly in a young carbon-rich planetary nebula (PN) NGC7027 [87]. These features have been observed in a variety of astrophysical environments, such as protoplanetary nebula, reflection nebula, interstellar medium, star-forming regions, and extragalactic objects, and are commonly termed as unidentified infrared emission (UIE) bands [88]. The carriers of these UIE bands are generally attributed to organic compounds that are widely spread in cosmic environments, but their accurate composition is largely unknown. The identification of UIE carriers has been a long-standing open question. In 2010, Cami et al. confirmed neutral C_{60} to be responsible for the four infrared spectral signatures at 7.0, 8.5, 17.4, and 18.9 μm observed in young PN Tc 1 [37]. Ever since, the four C_{60} features have been observed in many other objects [89], but not any other specific molecules, except for C_{60}^+ and C_{70}, have been confirmed to be the UIE carriers.

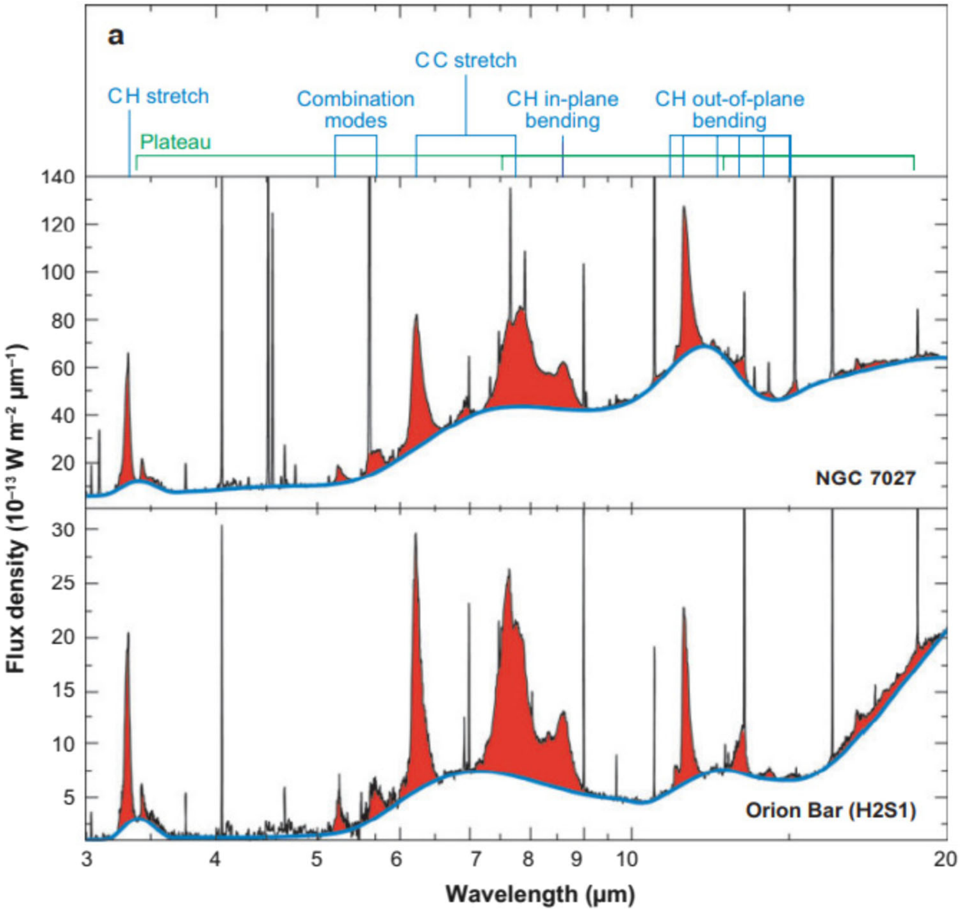

Fig. 10 The mid-infrared spectra of the photodissociation region in the planetary nebulae NGC 7027 and Orion Bar. Figure adapted from Ref [88]. ©2013 American Physical Society

Current and future challenges

Both DIBs and UIE bands contain a wealth of information about the physical and chemical conditions of astrophysical objects, of vital importance for understanding the cosmic star formation history, interstellar chemistry, galaxy evolution, and the origin of life in the Universe [88,90]. However, understanding their carriers presents unexpected challenge as demonstrated above (Fig. 10).

The major challenges to identify the carries of DIBs and UIE bands lie in several folds. Observationally, over 600 DIBs have been identified in the optical region and more than 30 distinct infrared features have been identified in the spectral range of 3–20 μm [90].

The possible identification of a particular species to be the carriers of either DIBs or UIE bands first requires at least laboratory data that can match with astronomical observations. However, such laboratory effort has been proven to be of tremendous challenge, as exemplified by verifying the C_{60}^+ as a DIBs carrier, which takes over 20 years since Foing and Ehrenfreund made the first proposal in 1994 [91]. In general, organic species containing 30–100 carbon atoms, in particular PAHs and fullerenes, have been thought to be the potential candidate carriers of DIBs or UIE bands, however, it is still blind for laboratory spectroscopists which particular molecule to choose from a large body of organic inventory. Also, measuring the high-quality optical spectra or infrared spectra of a gas phase species, especially, in a one photon absorption regime, thus the obtained spectral intensity follows a linear relationship, is not trivial. Sophisticated experimental technique, in particular, cryogenic ion trap technology, is required.

Advances in science and technology to meet challenges

In 2015, with the newly developed cryogenic 22-pole radio-frequency ion trap and He-tagging action spectroscopy technique in the near-infrared spectral region, Campbell et al. measured the electronic absorption spectrum of gas phase C_{60}^+ [36]. They found that the measured absorption features of C_{60}^+ at 9577 and 9632 Å are within 0.1% of the astronomically observed DIBs in this region. They also found three other weaker features at 9428, 9365, and 9348 Å in their measurement, which were confirmed later by Hubble Space Telescope [86].

Apart from DIBs, the carriers of UIE are also in long sought of astronomers and spectroscopists [88–90]. Recently, we developed an experimental protocol to synthesize and measure the laboratory infrared spectroscopy of gas phase fullerene-metal cationic complexes via dual laser ablation and messenger-tagged infrared multiple photon dissociation (IRMPD) spectroscopy [92]. We found that well-selected density functional theory calculations can reliably predict the infrared spectra of C_{60} complexes with cosmically abundant metals, such as Li, Na, K, Mg, Ca, Fe, and Al. Calculations show that all these fullerene-metal complexes have similar infrared spectral patterns as that of $C_{60}Fe^+$, and detailed vibrational analysis suggests that most of the infrared features come from the motions of the C_{60} cage perturbed by the attaching metal atoms.

We compared the laboratory spectrum of the $C_{60}Fe^+$ complex with the Spitzer spectra of several fullerene-rich planetary nebulae and found a strong positive linear cross-correlation. The co-existence of different $[C_{60}\text{-Metal}]^+$ complexes in the same object could slightly modify the band positions and intensities, which may explain the shoulders and asymmetric band profiles observed in the 17-20 μm region, and regulate the ratios of the four C_{60} bands by the varied spectral intensities for different metals, thus potentially resolve the long-standing issue about the wide-spread observational intensity ratios of the four C_{60} bands. In addition, we found that the infrared spectra of fullerene-metal complexes may also explain several other yet unidentified features.

Figure 11 shows the temperature and abundance required for each species to replicate the observed emission spectra of the four fullerene-rich PNe, based on thermal emission models that treat the fullerene-metal complexes as a microcanonical ensemble. We found that about $2.6 - 7.7 \times 10^{-8}$ solar mass ($M_\odot$) of pure C_{60} is required to reproduce the four main emission bands. While for $C_{60}Fe^+$, about $\sim 0.69 - 2.1 \times 10^{-7} M_\odot$ of $C_{60}Fe^+$ or $\sim 1.9 - 6.1\%$ of the available carbon with excitation temperatures above $\sim$ 400 K can give an equally good fit, in addition to the fact that they could also account for some additional emission features. Since both C_{60} and $C_{60}Fe$ have low ionization potentials, their ionized form could be favored, although it would be challenging to accurately estimate the fractions considering the complicated charge balance, i.e., competition among ionization, electron attachment, and recombination events as well as the lack of parameters associated with those processes.

Based on the high cross-correlation coefficients and good fits of the thermal emission model, we proposed that gaseous ionized fullerene-metal complexes are potentially promising candidates for explaining the infrared emission spectra of the fullerene-rich PNe in addition to neutral C_{60}. Moreover, the complexation of metals with fullerenes could lead to a far richer spectrum in the visible and near-infrared spectral range than fullerenes themselves, due to the charge transfer from metal to carbon cage, thus being potential candidates for DIBs. Metals are widely known to be active catalysts for the synthetic production of various carbon nanostructures, including carbon cages under oxygen- and hydrogen-rich conditions, and might play a catalytic role in fullerene formation in space. Considering the role of metals in cosmic chemical transformations could lead to a breakthrough in our understanding of cosmic carbon chemistry.

Concluding remarks

Looking at the sky, where are we from and what's the origin of life? Those philosophical questions keep inspiring human beings. Our proposal on the potential existence of fullerene-metal complexes in space opens the door for a real consideration of Kroto's hypothesis and will stimulate astronomers and spectroscopists to search for them in space and to obtain more laboratory evidence to prove or refute it, since the presence of fullerene-metal complexes can potentially link the chemical pathways and mechanisms of the formation and evolution of various carbonaceous species and thus carbon chemistry in space. On one hand, measuring the absorption spectra of fullerene-metal clusters in the ultraviolet–visible and near infrared spectral range is expected to attract great attention since that may link to the century mystery about the carriers of DIBs. On the other hand, study the potential relevance of fullerene-organic molecular clusters, in particular those with aromatic hydrocarbons, deserves investigation since both fullerene and aromatic hydrocarbons have been found in the same astrophysical conditions and their cycloaddition reactions are facile.

Acknowledgments

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10 Toward an unambiguous identification of complex nanocarbons in the radio domain

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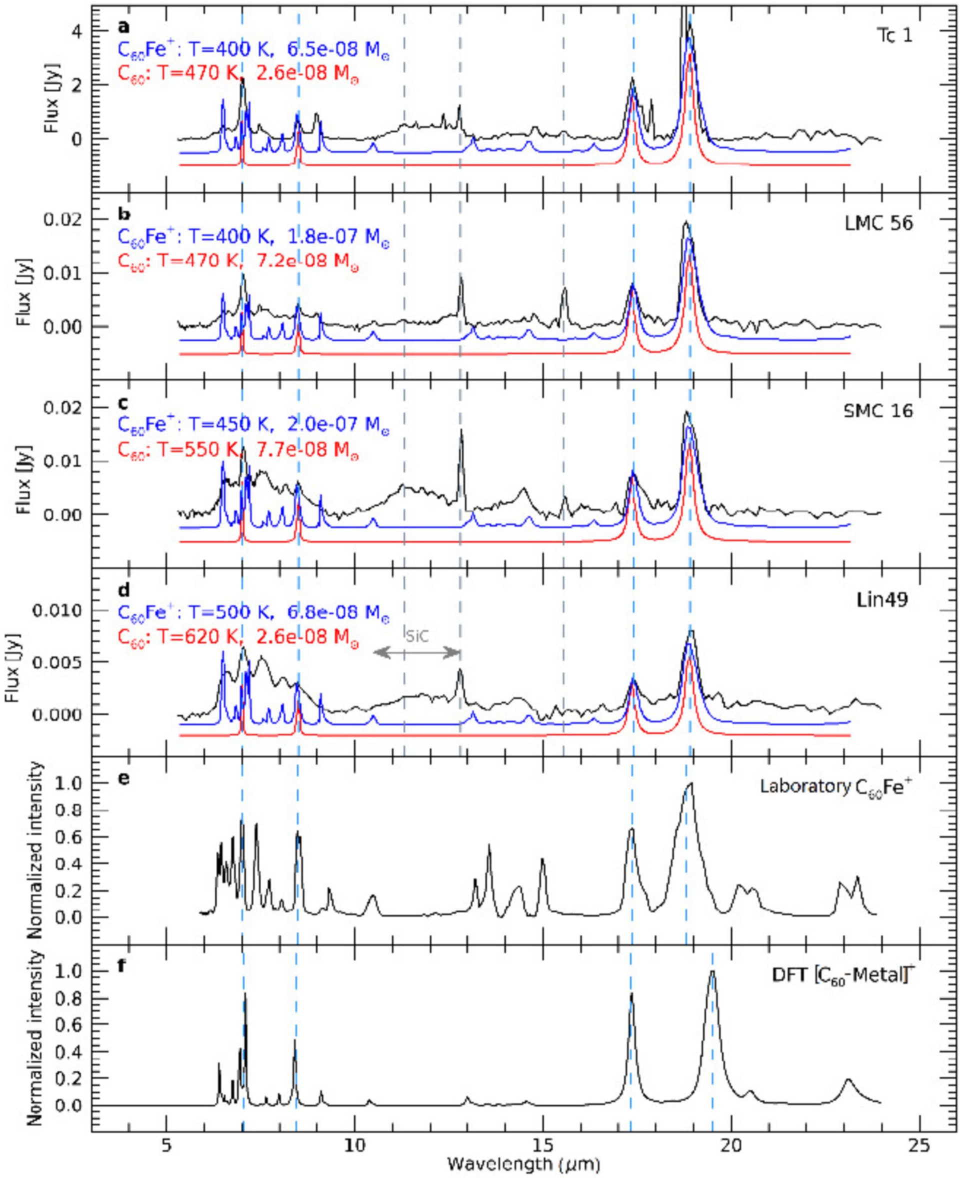

Fig. 11 Comparison between the Spitzer infrared spectra of four fullerene-rich PNe (black) and the thermal emission model for C_{60} (red) and $C_{60}Fe^+$ (blue). **a** Tc 1, **b** LMC 56, **c** SMC 16, **d** Lin49, **e** Laboratory infrared spectrum of $C_{60}Fe^+$, and **f** Summed theoretical spectrum of $[C_{60}\text{-Metal}]^+$. Figure reproduced from Ref [92]

Status

Radio telescopes all around the world, both single dish antennas and interferometers, collect data from very different space environments like molecular clouds, circumstellar envelopes of evolved stars and galaxies, among others. The radio data, available at a wide frequency range, provide very useful information, which is complementary to the astronomical data at other wavelengths (e.g., from the ultraviolet to the far infrared). All these astronomical data let us to move forward for a better comprehension of the organic molecular complexity in space.

Since radio astronomy is mainly sensitive to the spectral lines produced by the rotational transitions of molecules, it makes possible to unambiguously identify organic molecules with dipolar moment. The first molecule detected was CH in 1937 and since then, the list of molecular species detected in space has grown up to ∼240 (e.g., [93]). The variety of detected species in the radio domain goes from the simplest organic molecules, such as CH or CO, to complex polycyclic aromatic hydrocarbons (PAHs) like 1/2-cyanonaphtalenes (1/2-$C_{10}H_7CN$) and indene (C_9H_8), and more recently two cyano derivatives of the PAH acenaphthylene ($C_{12}H_8$) (e.g., [26,94]; but see also [93] for a recent review). The most complex organic species

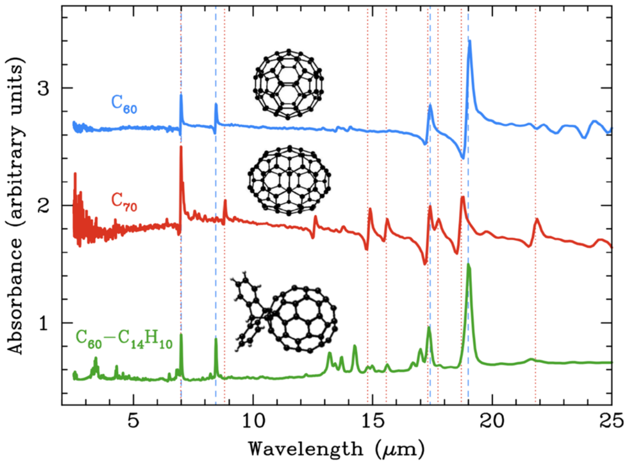

Fig. 12 Examples of the laboratory IR spectra of three different fullerene species (C_{60}, C_{70} and the C_{60}-PAH adduct C_{60}-$C_{14}H_{10}$). All fullerene species show their strongest emission features at similar wavelengths (i.e., at ∼7.0, 8.5, 17.4 and 18.9 μm). This fact makes very difficult to unambiguously identify which species has been detected in IR astronomical spectra (usually at much lower sensitivities than in laboratory)

detected in space are the C_{60} and C_{70} fullerenes (e.g., [37, 72]), which have been detected in the infrared (IR) spectral range. However, the unambiguous distinction of specific PAHs or fullerene-related species is challenging in the IR domain (see Fig.12.

Specific PAHs like those mentioned above have only been very recently detected via their rotational transitions in the radio domain. In addition, fullerene-based species like metallofullerenes and fullerene-PAHs adducts, among others, mainly emit through the same IR vibrational frequencies as isolated C_{60} (e.g., [41, 92]) but they exhibit significantly higher dipole moments; then they should, in principle, be detectable in the radio range.

In short, even though the current list of organic species detected in space is quite large, the exact chemical pathways necessary to produce each species remain unclear. More molecular species (e.g., key molecular by-products or precursors; especially in the actual gap between small PAHs and fullerenes) need to be detected in order to drive the field forward and to have an inventory of complex nanocarbons in space as complete as possible. Such key possible molecular species have remained undetected because of their weak rotational transitions, e.g., likely caused by their low abundances and/or low dipolar moment values.

Current and future challenges

The detection of more complex nanocarbons in space is still challenging despite the great recent technological improvements that have significantly increased the sensitivity of radio telescopes and their receivers. Also, a higher number of atoms translates into larger partition functions, and the corresponding weakening of the molecular lines. This makes very difficult to detect the radio lines of big organic species, especially when short integration times are used.

Weak radio molecular lines are visible only when the noise level is low enough to let them appear. These kind of weak emission lines have remained hidden for years, but nowadays better radio receiver sensitivities together with the use of larger single dishes and longer exposure times (so-called "deep radio observations") are unveiling a plethora of new unidentified molecular lines never observed before (see Fig. 13).

Very recent deep radio observations programs toward the molecular cloud TMC-1, such as GOTHAM (Green Bank Telescope; [96]) and QUIJOTE (Yebes-40 m; see [94] and references therein), are revolutionizing our understanding of the organic molecular inventory in astrophysical environments.

Theoretical and/or laboratory spectral data from rotational transitions for molecules with 2 to 19 atoms is available in public catalogues like CDMS (https://cdms.astro.uni-koeln.de/) or JPL (https://spec.jpl.nasa.gov/) but there is completely missing data, e.g., in the range ∼ 20–60 atoms (i.e., from small PAHs to big fullerenes). Thus, the astronomers face now the challenging problem of identifying the numerous unidentified molecular lines detected in very different astronomical sources. The unidentified features (UF) could arise from very abundant nanocarbon species having low dipole moment and/or very large partition functions or from less abundant species with large dipole moment. The best way to solve this problem in astrochemistry is via a multidisciplinary collaboration between astronomers, laboratory spectroscopists and theoretical chemists.

An additional challenge is to carry out such multidisciplinary studies for nanocarbon species of increasing size (>15-20 atoms). The complexity of laboratory measurements and theoretical chemistry simulations exponentially grows with the number of atoms of the molecule. Deep radio observations along with sophisticated laboratory experiments and theoretical predictions on rotational transitions of big molecules would allow to unambiguously detect more complex nanocarbons and their derivatives in space. Nevertheless, in order to carry out such multidisciplinary molecule identification process a main challenge is the description of the mathematical framework to reliably connect the observational, experimental and theoretical strength (intensity) of the rotational transitions.

Advances in science and technology to meet challenges

The unambiguous radio detection of new complex nanocarbon molecules in space is only possible if there is a complete database of experimental measurements

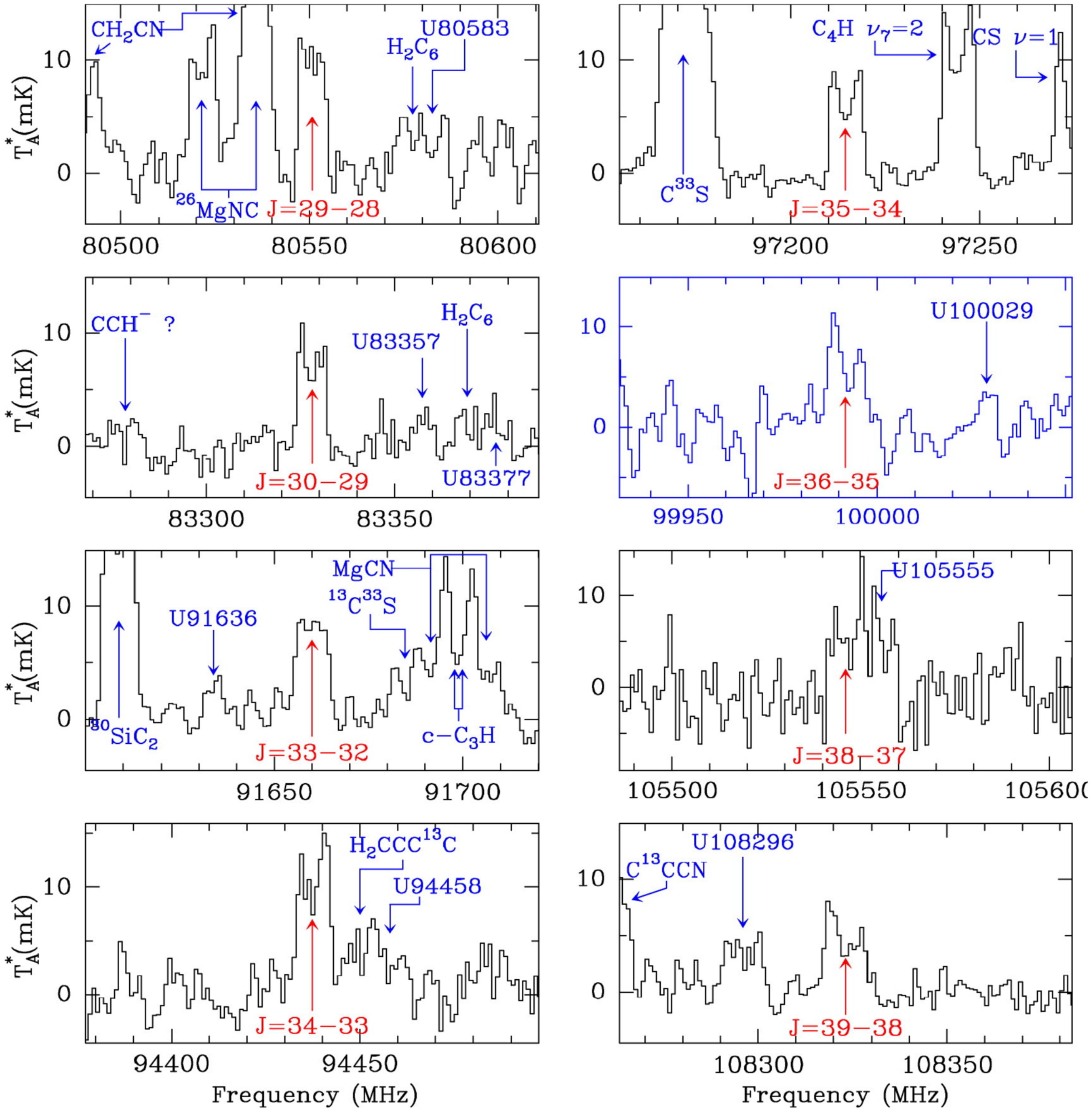

Fig. 13 Examples of weak unidentified features (UF) in deep radio spectra (from 80 to 108 GHz) of the evolved star IRC+10216. Figure adapted from [95] ©AAS. Reproduced with permission

and theoretical predictions on their rotational transitions.

The wavelengths of the rotational transitions can be theoretically predicted well by semi-classical approximations using available software's for rotational, vibrational and electronic molecular spectra like the PGOPHER code (https://pgopher.chm.bris.ac.uk/). In contrast, the corresponding intensity of the rotational transitions remains as the fundamental backward since large errors can be obtained for big molecules. A specific mathematical approach needs to be developed to reliably simulate the rotational transitions intensity for big organic species.

Laboratory experiments done with spectrometers like the chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer (see the description in [97] and an example of use in [98]), the cavity-enhanced Fourier transform microwave spectrometer (see e.g., [99]) or a frequency modulation millimeter/submillimeter-wave spectrometer (see , e.g., [100]), have allowed astronomers to confirm the detection of many small molecules in space by obtaining the frequencies at which rotational transitions take place. However, there are still some issues that complicate getting correct experimental results.

On the one hand, molecular samples could be contaminated and the impurities appear on the spectrum as undesired contributions. One can remove all these contributions by comparing the experimental spectrum with the theoretically simulated spectrum, which has been calculated for a pure sample of the molecule. Moreover, by increasing the size of the molecule of study, its synthesis and isolation becomes more complicated. Experiments with big molecules are done with solid samples that have to be sublimated. It is in this process of sublimation where the chemical structure of the molecules could change. If this happens, the gaseous final state is made of different chemical compounds, i.e., different from the initial solid state, and the final spectrum would not correspond to the one of the molecular type under study.

On the other hand, an improvement on experimental devices is needed. Finding more efficient processes to synthesize (and isolate) pure chemical samples or making even more sensitive and precise spectrometers would allow to obtain high precision and reliable molecular spectra. A recent promising example is the use of tailored supramolecular masks as a synthetic strategy to produce fullerene-related species (and specific isomers) such fullerene-PAH adducts (e.g., [101]).

Concluding Remarks

The presence of relatively small (<20 atoms) C-based molecules in space is well confirmed by radio astronomical observations. However, the detection of more complex organic molecules (i.e., from small PAHs to big fullerenes) is still challenging. On the one hand, high sensitivity radio spectra are needed to find weak UFs corresponding to new species. On the other hand, the association of UFs with specific species is only possible if there is a complete (and reliably) database of experimental measurements and theoretical predictions on their rotational transitions. The only way to address this problem in astrochemistry is through the collaboration of astronomers, laboratory spectroscopists and theoretical chemists. Such multidisciplinary effort would permit the unambiguous detection of more complex nanocarbons and their derivatives in space.

Acknowledgments

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11 Stability indicators for hydrogenated fullerenes

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Status

The use of graphs in the study of chemical components goes all the way to the 19th century. Particularly fruitful are the numerous applications of graph theory in organic chemistry, where the unusual versatility of carbon atoms in creating different patterns of connectivity results in a wealth of existing and potential structures that can be investigated by studying the corresponding graphs. Fullerenes fit this pattern perfectly - the most common isomer of C_{60} was predicted on purely theoretical grounds by Eiji Osawa 15 years before it was discovered [102], and its fully hydrogenated derivative, the icosahedral $C_{60}H_{60}$, was postulated even earlier. Crucial for the prediction was the observation that corannulene appears as a subgraph of the graph representing the truncated icosahedron, one of the Archimedean solids, and, incidentally, the Telstar soccer ball, the official FIFA ball of the 1970 Mexico World Cup. It remains unknown whether Osawa's prediction was in any way inspired or affected by the World Cup.

As soon as the fullerenes were first observed, and then also experimentally verified, it became clear that there are many more potential structures than the observed ones. In fact, only a handful of fullerene isomers have been synthesized or observed so far, a negligible fraction of the vast number of possible structures. A good part of all research on fullerenes over the last three and a half decades has been driven by desire to find some structural characteristic that could select potentially stable isomers out of myriads of possible ones. The Isolated Pentagon Rule has been quickly established and subsequently verified, but it is not sufficient, since the number of structures satisfying it grows very fast with the number of atoms. Hence, a number of other graph-theoretic invariants have been investigated and tested over the years, none of them with fully satisfactory results.

Polyhedral structure and local uniformity make fullerene molecules well suited for representation by graphs. Fullerene graphs are planar, cubic and 3-connected graphs with only pentagonal and hexagonal faces. Such graphs exist for any even number of vertices n greater than 22 and also for $n = 20$ [103]. Hence, there could be, in principle, fullerene molecules with any number of $n \geq 20$ atoms with sole exception of $n = 22$. It follows easily from the Euler formula that the number of pentagons is always 12, regardless of the number of atoms, and the number of hexagons is $n/2 - 10$. Among many other interesting properties, it can be shown that all fullerene graphs have perfect matchings, mathematical representations of resonant patterns known in chemistry as Kekulé structures.

It has been known for almost a century that the number of Kekulé structures is crucial for the stability of benzenoid compounds. Benzenoid hydrocarbons are represented by the corresponding graphs and Kekulé structures are represented by perfect matchings in those graphs. There are many similarities between fullerene and benzenoid graphs - far from pentagons, portions of large fullerenes look locally as benzenoids. There are also many differences, and one of the more important seems to be the fact that fullerene graphs are not bipartite. This is due to the presence of pentagons and other odd cycles.

Current and future challenges

It became clear very early that the number of perfect matchings/resonant patterns in fullerenes does not affect their stability in the same way as in benzenoids: The most stable (in fact, the only stable) isomer of C_{60}, the icosahedral buckyball, with its 12500 perfect matchings, is only 20-th richest among all 1812 possible isomers [104]. Even worse, the largest number of perfect matchings, 16501 of them, is found in the narrow nanotube with two hemi-dodecahedral caps, that seems to be the least stable isomer of C_{60}. Hence, the number of perfect matchings itself is not very useful as a predictor or selector of potentially stable isomers. The reason must be, obviously, in the presence of pentagons and in the interplay of topological and metrical aspects of their positions. Similar conclusions were drawn by studies of other fullerene isomers.

While the number of perfect matchings itself is clearly not suitable as a stability predictor, there are still ways it can play a significant enough role. One way is to combine it with some other invariant, that may be more sensitive to various local connectivity patterns. Another way could be to look at the number of perfect matchings in fullerene cages whose structure has been altered by introducing various defects into their connectivity patterns [105]. The defects could be of several types - deletions, substitutions and/or additions.

In this work we plan to follow both lines of research. We start by examining the number (and the existence) of Kekulé structures in the icosahedral C_{60} isomer after addition of a small even number of hydrogen atoms. This is mathematically described as deletion of vertices in the corresponding graph. On the other hand, the problem of assessing the stability of a large number of hydrogenated fullerene isomers is best addressed by using electronic structure methods. For the 23 possible isomers of $C_{60}H_2$, geometry optimizations have been performed with semi-empirical methods as well as with density functional theory (DFT) methods using the PBE0 and M062X functionals [106]. Figure 14 shows the dependence of the relative energy of the 23 isomers of $C_{60}H_2$ as obtained with M062X/SVP. A clear pattern of negative correlation between the number of perfect matchings in the remaining graph and the energies of the corresponding structures computed with electronic structure methods is visible. In the most stable hydrogenated isomer, shown in the inset of Fig. 14, two hydrogen atoms are added to a double bond shared by two hexagons. This result is reproduced by using different DFT functionals and basis sets.

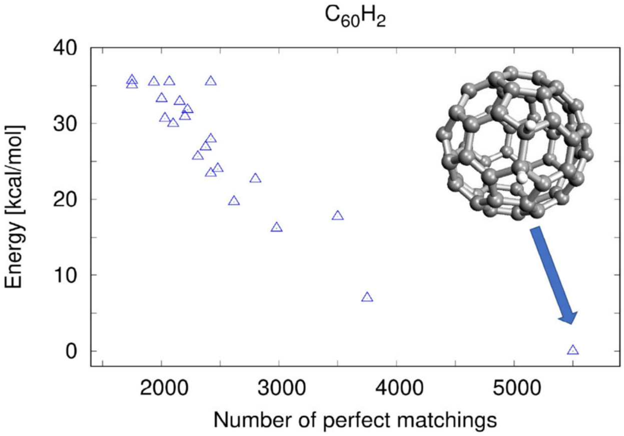

Fig. 14 The dependence of the relative energies of 23 isomers of $C_{60}H_2$ on the number of perfect matchings

It appears that the most energetically favorable configurations are obtained by adding hydrogens as dimers, to adjacent carbon atoms. This is clearly visible in Fig. 15 where the PM3 relative energies (red) of the 4190 isomers of $C_{60}H_4$ are shown.

Blue dots indicate the energies of so-called dimeric structures, that is of hydrogenated fullerenes in which H_2 addition has taken place on adjacent carbon atoms. One can see that some dimeric structures are among the most stable isomers of $C_{60}H_4$. We reoptimized the most stable PM3 structures of $C_{60}H_4$ with PBE0/SVP [107] level and found that the 6 most stable $C_{60}H_4$ isomers correspond to dimeric structures. Again, the most stable isomer of $C_{60}H_4$ has the largest number of perfect matchings.

These findings are somewhat surprising, since the number of perfect matchings is not a good indicator of fullerene stability [104,108]. Why then the number of perfect matchings correlates well with the stability of lightly hydrogenated fullerenes? Does the pattern break for more heavily hydrogenated fullerenes, and if, then when? And what other invariant(s) could serve as useful co-indicator(s)?

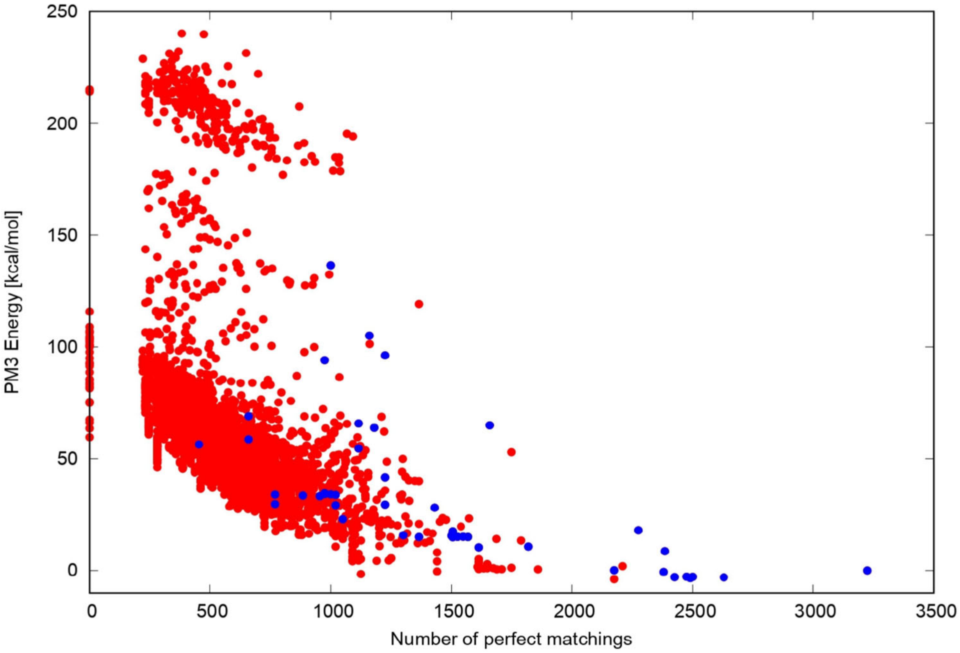

Fig. 15 The dependence of the relative energies of 4190 isomers of $C_{60}H_4$ on the number of perfect matchings. Blue dots indicate dimeric structures

Concluding remarks

The problem of predicting stability of fullerenes and their hydrogenated derivatives is still far from being solved. We hope to be able to find some easy-to-compute graph-theoretical invariants which will yield good correlation with energies of the corresponding isomers computed with high-level electronic structure methods.

Acknowledgments

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12 Quantum chemistry and spectra models for decoding unknown spectral signatures of nanocarbons (nC) in space

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Status

The vastness of the Universe serves as a colossal library for searching biosignatures based on carbon, teeming with information carried by the electromagnetic spectrum it radiates. Spectroscopy is a vital key that unlocks the coded information contained within these fields. In recent times, the evolution of quantum modeling has provided us with enhanced tools to delve more deeply and precisely into these spectra. Particularly, it has proved invaluable for discerning and identifying the isotope variations of carbon-based molecules. The ramifications of these advancements are not only multifaceted but also revolutionary in nature. This can offer a comprehensive exploration of these groundbreaking techniques, highlighting their transformative impact on our comprehension of astrophysical electromagnetic spectra [109]. The quest to discover nanocarbons (nC) in the cosmos is a monumental venture that necessitates the synergistic efforts of multiple scientific domains. This necessitates a systematic guide to predicting, pinpointing, and comprehending the presence and distribution of these enigmatic particles amidst the infinite cosmic tapestry. To truly grasp the distinct spectral characteristics of nC, it is imperative to build theories grounded in contemporary chemical wisdom and to forge models capable of forecasting the spectral traits of nC across the UV-radio spectral continuum [110]. This not only aids in the prediction but also ensures accurate interpretation of raw observational data emanating from the vast expanse. From experimental point of view, laboratory spectroscopy strategies can be used such as key experimental frameworks that consists in designing and initiating laboratory experiment programs with a focus on validating the theoretical forecasts related to spectral characteristics. Furnishing experimental spectral information for both neutral and ionized nC forms can be possible through advancements in quantum chemistry such as an endeavor to predict spectral imprints. This fundamental for guaranteeing that the spectral information conforms to the necessary resolution standards, ensuring its compatibility with the data obtained from space observations [111].

Current and future challenges

Quantum chemistry is a field of chemistry that uses quantum mechanics to study the behavior of molecules, especially their electronic structure. One of the most prominent applications of quantum chemistry is in the calculation and prediction of molecular spectra. These spectra arise from the transitions between different electronic, vibrational, and rotational states of a molecule and it can be applied to discover nC species [109].

When examining nanocarbon forms like fullerenes, carbon complex chemical structures, and graphene in space, their distinctive electronic and vibrational signatures act as identifiers. These unique signatures emerge from the special quantum behaviors and electronic make-up of such carbon forms.

Key points on detecting nanocarbon in space:

1. It has immense relevance in astrochemistry. Its core data plays a pivotal role in studying rich spectral regions, underlining detection uncertainties, and guiding subsequent space studies to clearer spectral regions.
2. Comparing different spectra can provide insights for prioritizing tests and advanced quantum chemical calculations for various molecules. This helps in identifying molecules when complete spectral lists aren't available.
3. Fullerenes: Certain fullerenes, like C_{60} and C_{70}, have been identified in space due to their distinct electronic absorption patterns in the visible to near-infrared range. They also possess infrared bands helpful for pinpointing them.
4. Recent observations from the James Webb Space Telescope (JWST) have shed light on the molecular components of exoplanetary atmospheres. Notably, the latest infrared spectrum data indicates clear signs of atmospheric CO_2 and light-induced carbon species on exoplanets [111].

The recognition of such molecules is enabled by the availability of comprehensive molecular spectral data, mainly line lists. These lists contain exhaustive data on energy levels and transition intensities. The successful identification hinges on the synergy between precise experimental results and advanced quantum chemical evaluations. Important databases like HITRAN/HITEMP, ExoMol, and MoLLIST can be pivotal in providing necessary data for matching observations in various cosmic bodies [112].

However, curating this comprehensive spectral information is time-consuming and intricate. This is showcased by the mere 100 or so molecules with existing line lists, restricting possible new molecular discoveries. A case in point is an unidentified spectrum; no present molecular line list can determine its precise wavelength or bandwidth.

Due to the complexity in generating detailed spectral data and the current constraints, a new extensive data method has been proposed. This method acknowledges that an infrared spectrum of a molecule is mainly defined by its functional group vibrations. It rapidly gives an initial spectrum estimate for each molecule, indicating relative transition intensities for associated bands.

Advances in science and technology to meet challenges

Emerging quantum techniques for modeling carbon spectra have broad applications, especially for identifying isotope variants of carbon-based entities. This offers a fresh perspective on evaluating astrophysical electromagnetic field spectra. It overlooks the impact of the surrounding chemical environment on predicted wave frequencies and doesn't evaluate frequencies in the specific spectral region primarily associated with overall vibrations. For molecules sharing similar structures, these limitations imply that their spectra might closely resemble each other. This resemblance could result in mistakes and confusions, hence limiting its general applicability.

Detecting such nanostructures in the cosmos comes with challenges. In the case of graphene's electronic configuration results in unique absorption and emission patterns in the ultraviolet (UV) and visible parts of the spectrum and it can be affected by:

- Dilution: Their presence in space is minuscule, making their spectral signs faint.
- Interference: Other existing molecules and cosmic dust can overshadow the spectral characteristics of nanocarbon entities.

Carbon molecules have distinct electronic and vibrational attributes. Their electronic patterns are determined by their twist and width. Their radial breathing mode (RBM) in the infrared section stands as a distinguishing vibrational hallmark [113]. Recognizing the value of this expansive preliminary spectral data for identifying molecules in exoplanet atmospheres, we propose a novel approach employing conventional quantum computational techniques.

In this regard there are several challenges and limitations associated with quantum chemistry models, particularly when applied to decoding unknown spectral signatures of nanocarbons (nC) in space. Challenges are related to computational complexity given that quantum chemistry calculations often involve significant computational resources due to the complexity of electronic interactions within molecules. A possible solution approach to this challenge consists in the application of methods such as Cholesky decomposition which can reduce computation time [114], but they may introduce systematic errors that must be carefully controlled.

Additionally, only a limited number of molecules have high-resolution spectroscopic data available, which restricts the ability to identify new molecular candidates in exoplanetary atmospheres. In addition, nanocarbons in space display weak faint spectral signs due to dilution and interference from other molecules or cosmic dust. This complicates their detection and characterization. Similarity in spectral characteristics favor molecules with similar structures may exhibit closely resembling spectra, leading to potential misidentifications. Although high-throughput quantum chemistry approaches can rapidly generate vibrational spectral data for a wide array of molecules, these approximations often lack the accuracy needed for definitive molecular identifications. A possible solution to address this challenge is based on automated high-capacity systems that leverages a largely automated system to rapidly approximate vibrational spectral data, enabling the analysis of multiple molecules crucial for nanocarbon detection. Additional solutions are based on functional group vibrations. The approach provides initial spectrum estimates with relative transition intensities, offering a streamlined path to identify molecules. The most pragmatic solution is the integration with laboratory and space observations: combining quantum chemistry predictions with laboratory spectroscopy and space-based microscope data ensures the approach aligns theoretical forecasts with empirical findings and addressing these challenges is essential for enhancing the reliability and accuracy of such approaches.

Concluding remarks

Spectral chemistry findings of nanocarbon molecules aren't precise enough to decisively pinpoint molecules in exoplanetary atmospheres to be detected, they do allow for the identification of possible molecular contenders for unidentified spectral signals. The physical conditions in space (like UV radiation, cosmic rays, and temperatures) can alter the structure and hence the spectra of these nanostructures [115]. Finally, for successful detection, space-based telescopes equipped with spectrometers capable of resolving these features are necessary.

In addition to telescopic observations, laboratory experiments on Earth that simulate space conditions and study the spectral features of nanocarbon under these conditions are vital. By combining quantum chemistry predictions, laboratory experiments, and astrophysical observations, one can hope to detect and understand the presence and role of nanocarbon in the vast expanse of space. The launch of the James Webb Space Telescope (JWST) has unlocked a new and stimulating avenue to survey exoplanetary atmospheres. Molecular spectroscopic data are crucial to maximizing the gains in our understanding of the molecular composition of exoplanetary atmospheres, providing insights into the planets' physical, chemical, and even potential biological processes [116]. High-resolution, high-completeness spectroscopic data in the form of line lists are rapidly being produced to allow these detections but is still only available for a relatively small number of species, limiting the scope of new molecular detections in exoplanetary atmospheres. The dance of carbon-based molecules, illuminated through the prism of electromagnetic spectra, carries with stellar lives, and the very nature of based molecules which gave rise to carbon chemistry. By marrying the principles of quantum mechanics with the study of these spectra, it's possible to gain a clearer view of these stories but are also venturing into uncharted territories of knowledge. The spectral view of nC, with all its mysteries, beckons, and quantum modeling might just be the key to unlocking some of its secrets.

13 Carbon in the extraterrestrial materials: identification and characterization

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Status

Carbon is a key element for life. Extraterrestrial carbon plays an important role in the formation of complex organic molecules that are of astrobiological importance. A variety of carbon-based organic species has been identified in many astronomical regions and objects, such as star-forming regions, disks surrounding young stars, the interstellar medium, molecular clouds, protoplanetary disks, comets, and asteroids [117–120].

Comets contain the most primitive materials in our Solar System. Carbon-rich asteroids are also a major source of such materials. Together, they delivered large amounts of exogenous carbon to early Earth during the late heavy bombardment period, enabling the prebiotic synthesis of biochemical materials that are needed for life. Small amounts of carbon still arrive even today through falling meteorites and cosmic dust.

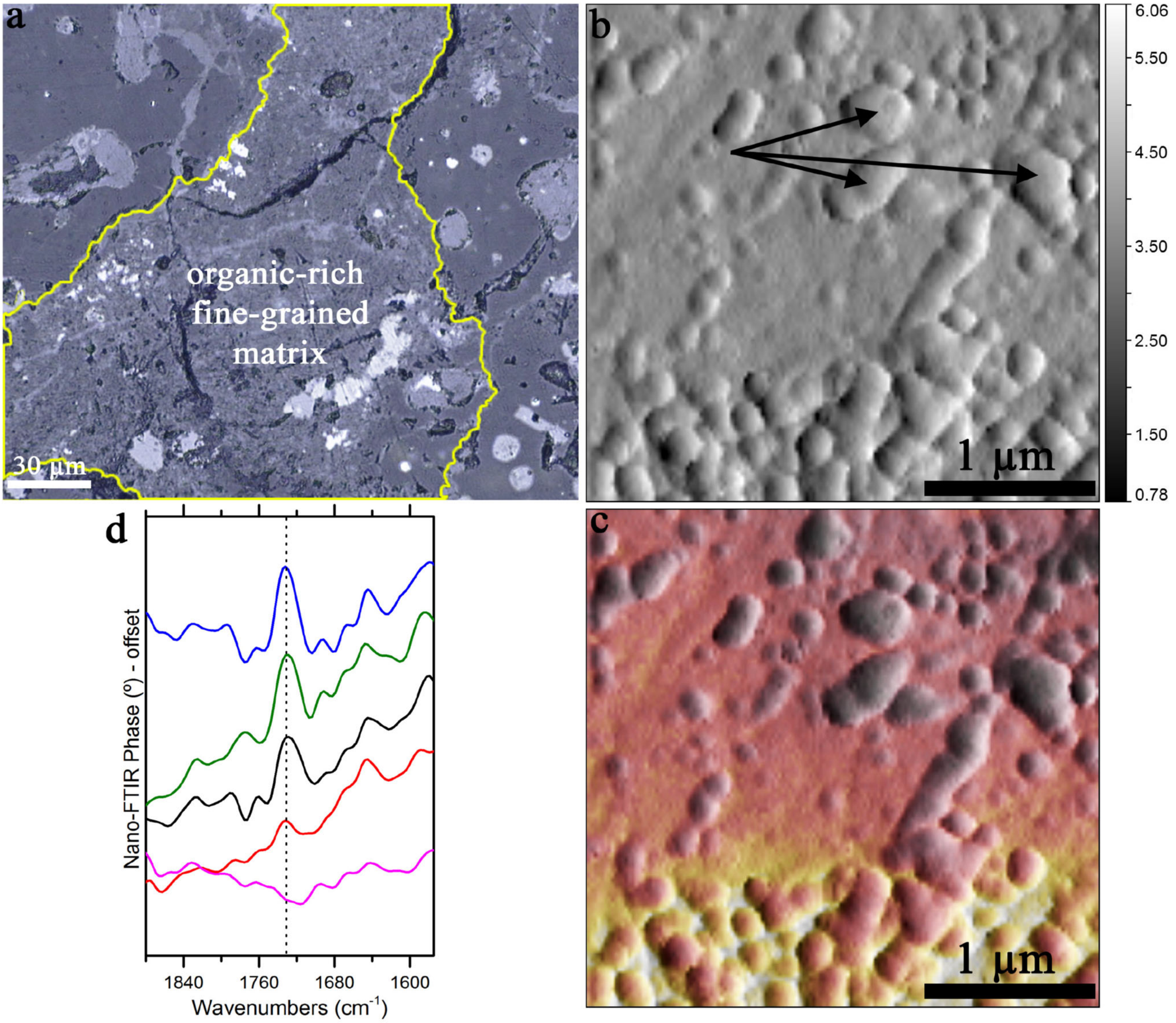

Fig. 16 Nanoscale infrared investigation of prebiotic organic matter in the DOM 08006 carbonaceous chondrite. **a** Optical micrograph of the meteorite. Yellow line outlines the organic-rich region. **b** Mechanical amplitude image. Black arrows indicate carbonyl nanoglobules. **c** Optical amplitude image (integrated spectral signal representing the broadband reflectivity). **d** Nano-infrared spectra of the carbonyl nanoglobules with characteristic peak at 1730 cm^{-1} due to C=O stretching vibrational modes. Pink curve is the spectrum of the middle of the measured matrix area where there is no nanoglobules present. Spatial resolution is $\sim$ 20 nm. Figure adapted from [123]

Asteroids, leftover material from the formation of the Solar System, did not experience the harsh planetary accretion processes. Therefore, they still retain the primordial compounds, including organic matter, that could provide information on the formation and evolution of our Solar System as well as the processes that took place during the early period and shaped the Solar System and our planet. Figure 16 shows prebiotic carbonyl nanoglobules present in the DOM 08006 carbonaceous chondrite. In order to access and investigate those pristine solar system materials, missions were organized to bring asteroid samples and cometary dust to Earth for detailed laboratory investigations [121, 122].

Meteorites are mostly pieces of asteroids. Currently, there are 72,899 known official meteorites in the world's collection, of which 3078 are carbonaceous chondrites. Carbonaceous chondrites contain up to several wt.% carbon in their composition, most of which is in the organic content. Some meteorites also contain dusts containing diamonds, silicon carbide and graphite that originate from stars other than ours. As such, carbon in extraterrestrial materials provides a unique window into the solar system as well as the nebular materials and conditions.

Cosmic dust samples include cometary dust (returned by the Stardust mission from comet Wild-2), interplanetary dust particles (collected in the Earth's stratosphere), and micrometeorites. They are primarily composed of minerals and organic matter.

As new meteorites and returned samples are collected and studied using newly developed high-resolution techniques, the role of carbon in space and in the origin of life on Earth will be better understood and constrained.

Current and future challenges

The current challenges in identification and characterization of carbon in extraterrestrial materials are many folds. Here, only some of the challenges are discussed.

Sample contamination: Meteorites have long been the only source of primordial material available for study. Upon landing on the ground, they weather and decay rapidly, and face the risk of being contaminated by terrestrial molecules including terrestrial organic matter, making it a challenge to identify and characterize the primary carbon phases and organic matter. In addition, terrestrial sulfates can gradually form in meteorites due to the interaction of the sample with Earth's atmosphere.

Heterogeneity of carbon: Organic molecules in meteorites quite often exhibit diverse composition. They are also usually fine-grained, amorphous, and dispersed randomly in the samples. Identification of organic matter in cometary and interplanetary dust particles is even more challenging as the samples themselves are extremely small (a few microns to a few tens of microns) [124].

Available techniques: The study of carbon-rich phases and organic matter in extraterrestrial materials is an inherently difficult task. Part of the reason is their small size. Organic matter in extraterrestrial samples is either soluble or insoluble, and together they constitute approximately 1–25% and 75–99%, respectively. The former varies between ppb to ppm, whereas the latter is *sim* 5 wt.%. The size of both types of organic molecules is predominantly submicron in size (mostly nanoscale, e.g., nanoglobular organic matter in meteorites). Many of the analytical techniques are not capable of detecting such small carbon-rich molecules in situ. In that case, the insoluble components are extracted and isolated by either solvents or acids for analyses, which unfortunately removes the spatial context of the chemical components in the samples. It is evident that high-resolution non-destructive methods and techniques are needed to identify and characterize indigenous organic matter and carbon-rich phases in extraterrestrial materials. Some extraterrestrial samples also contain presolar grains and organics. On the other hand, the study of carbon-rich molecules in distant objects and regions relies on telescopic observations. Ground-based telescopic observations are often overwhelmed by atmospheric water vapor. Space-based telescopes require high resolving power and sensitivity.

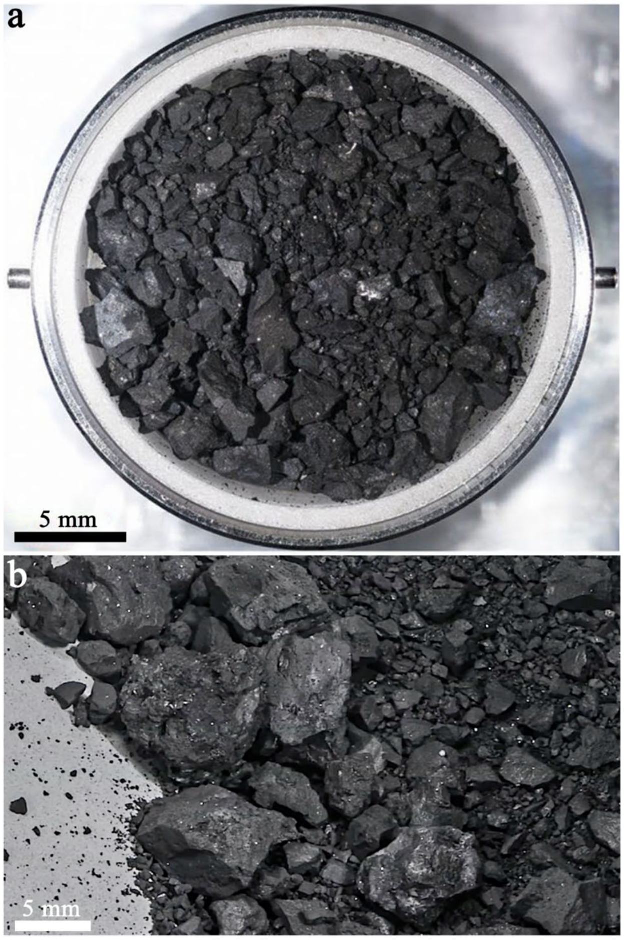

Fig. 17 Carbonaceous asteroid samples that have been returned from the regolith of **a** Ryugu (adapted from [93]) and **b** Bennu (credit: NASA) by the Hayabusa2 and OSIRIS-REx missions, respectively. These samples contain abundant primordial organic matter and water, which are key molecules for life. Figure adapted from [125] and public NASA material, ©NASA

Advances in science and technology to meet challenges

Sample return missions provide the most pristine and uncontaminated samples of solar system bodies. Cometary samples were collected from comet Wild 2 and returned to Earth in 2006 by the Stardust spacecraft (NASA). Recently, samples of carbon-rich asteroids Ryugu and Bennu have been returned to Earth through Hayabusa2 (JAXA) and OSIRIS-REx (NASA) sample-return missions, respectively. Figure 17 showcases some of the returned carbonaceous asteroid samples. Returned cometary dust and asteroid samples allow scientists to access primordial prebiotic organic molecules that are otherwise currently not possible in space or inaccessible in most meteorites.

Although laboratory investigation of extraterrestrial organic matter offers many advantages, scientific advances are restricted to available analytical laboratory instruments. It is evident that advanced analytical techniques are necessary to study extraterrestrial organic matter and carbon phases. For instance, novel high-resolution (i.e., nanoscale) spectroscopic and microscopic methods are needed to identify and characterize primordial insoluble organic matter in extraterrestrial samples, such as meteorites and returned asteroid samples [123,126,127]. In the case of soluble organic matter (such as amino acids and nucleobases), parts per billion (ppb) to parts per trillion (ppt) level sensitivity is needed for small-scale detection [128].

Recent advances in experimental analysis methods have significantly enhanced our ability to investigate carbonaceous materials in extraterrestrial materials. Pioneering techniques such as synchrotron-based nanoscale X-ray investigations, nano-FTIR, and atom probe microscopy have become invaluable for not only detecting and characterizing organic compounds but also providing unprecedented insights into the composition and structure of extraterrestrial carbon at spatial scales that are ideally suited for carbon-rich compounds. Ongoing advancements in analytical tools and correlative investigations are therefore crucial for understanding the formation, evolution, and potential origins of organic matter in materials from celestial bodies.

Concluding remarks

Despite decades of research, the formation mechanisms of organic matter in space is still not fully understood. Identification of extraterrestrial organic matter in different locations and objects can have implications for better constraining the formation mechanisms and evolution of extraterrestrial organic matter. This task clearly presents a number of challenges. Astronomical observations of distant objects and laboratory experiments are key parts of the exploration of carbon in space. Development of advanced high-resolution non-destructive instruments and multi-modal approaches will surely serve to the better detection and characterization of carbon and organic matter both in space and in the laboratory.

Acknowledgments

NASA-Johnson Space Center is acknowledged for providing the DOM 08006 meteorite sample.

14 The use of (far)-infrared spectroscopy to probe interstellar carbon-bearing molecules

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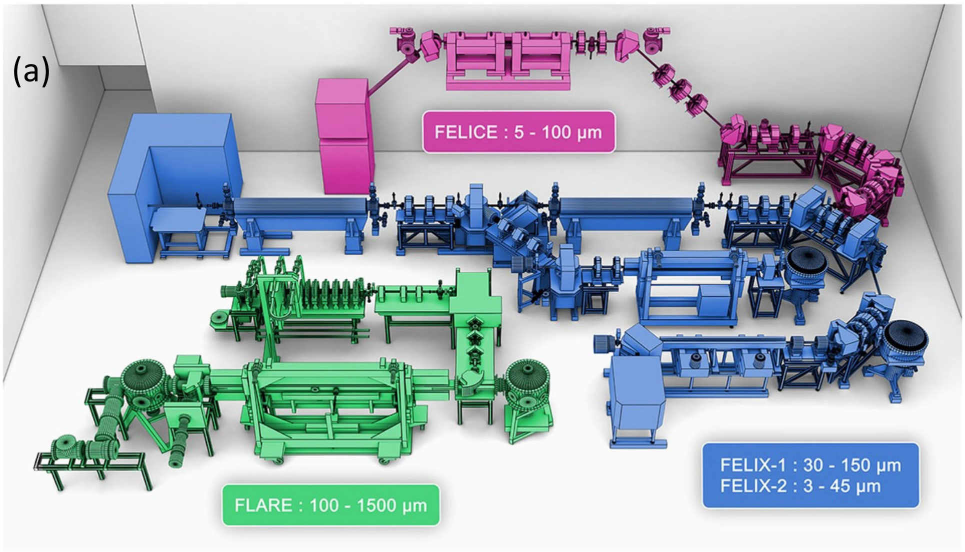
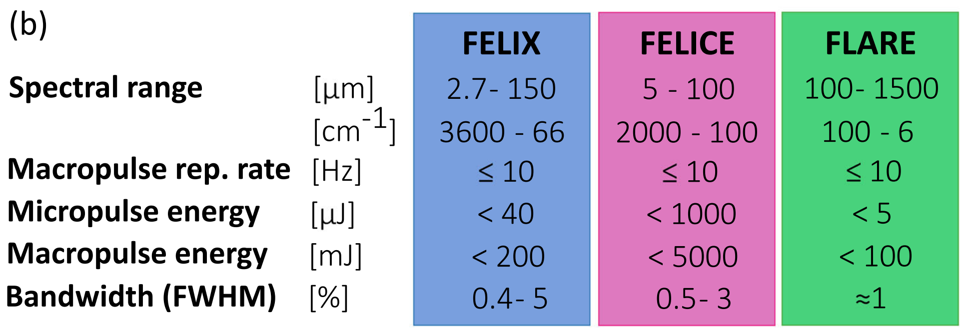
Status

Carbon is ubiquitous in space, being the fourth most abundant element in the Universe. Due to its rich chemistry, with the ability of forming single, double and triple bonds, carbon is found in a variety of allotropic forms and in diverse molecular species. As of today, more than 300 molecules have been identified in space, most of which involve carbon atoms, either in all-carbon form or as part of carbon-bearing species [129]. Famous examples include C_{60} [37], small polycyclic aromatics like cyanonaphthalene ($C_{10}H_7CN$) [25], and polycyclic aromatic hydrocarbons (PAHs).

Most of the currently identified molecules have been discovered by a combination of radio astronomy observations and laboratory microwave spectroscopy, addressing rotational transitions [129]. The latter technique is highly sensitive and molecule-specific, but is only applicable to species of limited size and with a permanent electric dipole moment. Hence, apolar molecules are invisible in this wavelength range. Infrared spectroscopy provides a powerful alternative to explore the complex carbon chemistry in space, by allowing the precise characterization of the vibrational modes of carbon-bearing molecules. Laboratory IR spectra can also be compared with observations, particularly after the launch of the James Webb Space Telescope (JWST) operating in the infrared spectral region.

The FELIX Laboratory provides unique possibilities for recording reference infrared spectra of carbon-bearing molecules in the laboratory under astronomically relevant conditions. The laboratory operates four free electron lasers (FELs), FELIX 1 and 2, FELICE and FLARE, depicted in Fig. 18a. As summarized in Fig. 18b, together they deliver intense and tunable laser light over a wide spectral range, covering mid- and far-infrared wavelengths. Connected to the FELs, different end stations employ a variety of complementary gas phase action spectroscopic techniques to record infrared spectra of neutral and ionic molecules. FELIX operates as a user facility, hosting scientific campaigns of national and international researchers, in addition to a strong in-house research program in the field of laboratory astrochemistry.




(b)

		FELIX	FELICE	FLARE
Spectral range	[µm]	2.7- 150	5 - 100	100- 1500
	[cm^{-1}]	3600 - 66	2000 - 100	100 - 6
Macropulse rep. rate	[Hz]	≤ 10	≤ 10	≤ 10
Micropulse energy	[µJ]	< 40	< 1000	< 5
Macropulse energy	[mJ]	< 200	< 5000	< 100
Bandwidth (FWHM)	[%]	0.4- 5	0.5- 3	≈1

Fig. 18 **a** Overview of the four free electron lasers at FELIX in Nijmegen, The Netherlands, with a summary of their main characteristics in panel **b**

Current and future challenges

The use of the facilities at FELIX to uncover carbon networks in space is illustrated by examples highlighting the diversity of species that can be investigated, while also pointing to future challenges. Figure 19a presents the IR spectrum of gaseous $C_{60}H^+$, measured in a room temperature quadrupole ion trap (Bruker AmaZon) [40], recorded via infrared multiple-photon dissociation (IRMPD) spectroscopy.

Clearly, the spectrum of $C_{60}H^+$ is richer than that of C_{60}, due to symmetry breaking caused by the added proton. Harmonic vibrational frequencies computed by density functional theory (DFT) reveal a good match with the experiment. Importantly, a comparison with emission spectra observed from the planetary nebulae LMC56 and SMC16 suggests $C_{60}H^+$ as a contributor to several unexplained astronomical IR features. Still, $C_{60}H^+$ alone cannot explain the entire emission spectra, emphasizing the need for further studies of analogous species [130].

One of such alternatives is the complexation of C_{60} with metal atoms. This was explored in experiments within the FELICE free-electron laser cavity, giving access to higher laser powers and/or larger interaction volumes. Here, infrared spectra of $C_{60}Fe^+$ and $C_{60}V^+$, synthesized in a molecular beam environment, were recorded in the 5 - 25 μm spectral region, as depicted in Fig. 19b [92]. Notably, several unexplained features of planetary nebula coincide with IR bands of these complexes. While the match of emission spectra and the IR spectrum of each individual complex is not perfect, the analysis reveals that C_{60}-metal complexes can be potential carriers of astronomical bands (more details are discussed in section 9). Key reaction intermediates for forming quinolizinium ($C_9H_8N^+$) from cationic pyridine ($C_5H_5N^+$) and neutral acetylene (C_2H_2) were revealed by an experimental approach combining kinetic and infrared spectroscopy measurements [131]. Using a cryogenic 22-pole ion trap, $C_5H_5N^+$ ions were isolated and cooled to 150 K, after which they interacted with gaseous C_2H_2 for varying storage times. An example of such kinetic data is presented in Fig. 19c-left, showing a decrease in pyridine$^+$ (m/z 79) intensity, along with increases of the m/z 104 and 105 reaction intermediates. At longer storage times, a product with m/z 130 was formed. These reaction products are spectroscopically investigated with FELIX, confirming the identity of the m/z 130 ion as quinolizinium, an endoskeletal N-PAH, and

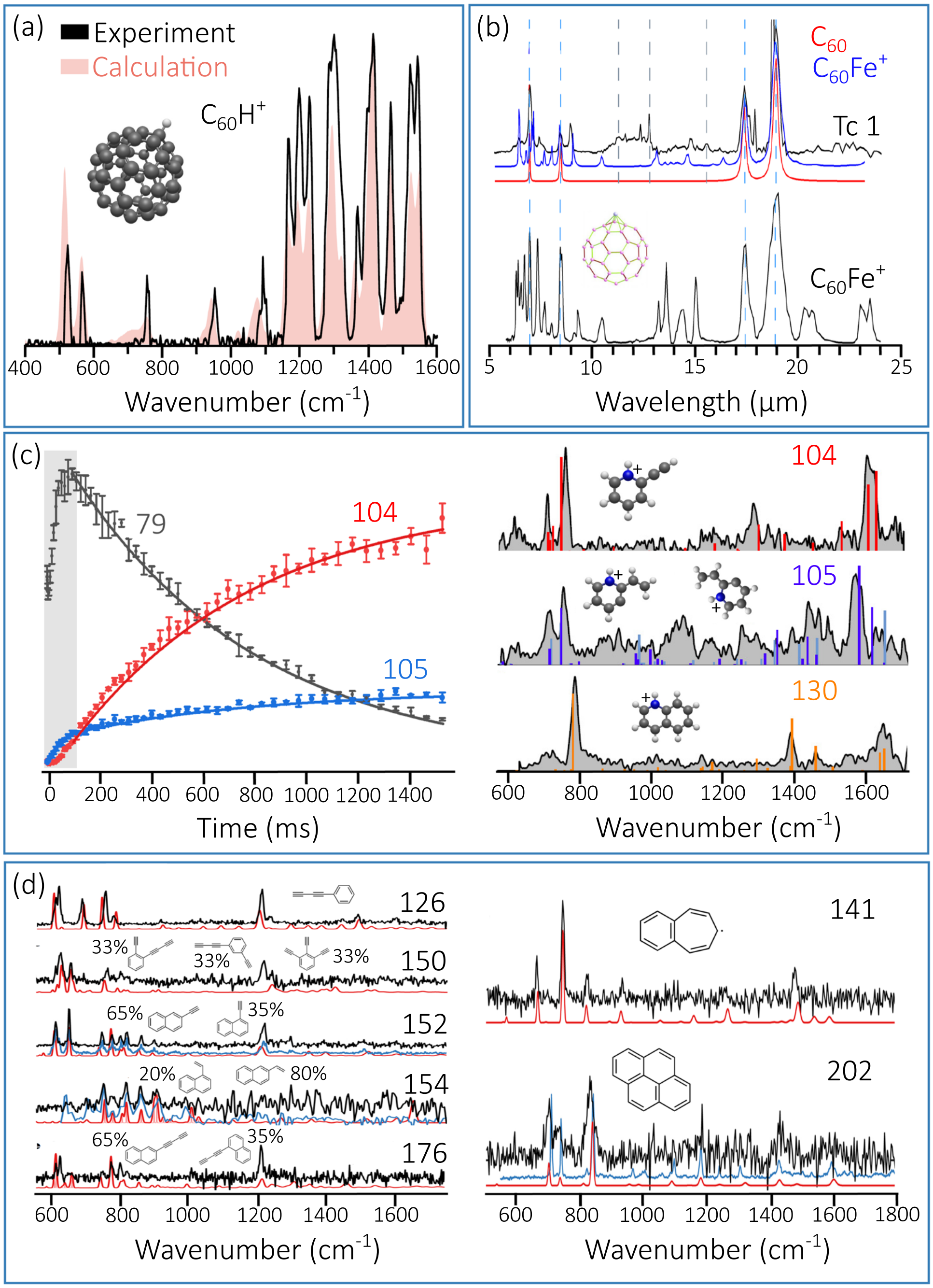


Fig. 19 **a** IR spectrum of $C_{60}H^+$ compared with DFT calculations [40]. **b** Comparison of the Spitzer IR spectrum of the planetary nebula Tc 1 with data recorded for Ar-tagged $C_{60}Fe^+$. The color curves are thermal emission models for $C_{60}Fe^+$ and C_{60} [130]. (c) Left: Kinetic profiles of the formation of m/z channels 104 and 105, from the precursors pyridine (m/z 79) and acetylene. Right: Infrared spectra of reaction intermediates with m/z 104 and 105, as well as the final product quinolizinium (m/z 130) [131]. **c** Infrared spectra of neutral products formed in a discharge of naphthalene ($C_{10}H_8$) in a cold molecular beam. The measured spectra are compared with DFT calculations of different isomers. Figure adapted from [40, 130–132]

the m/z 104 and 105 ions as intermediates. Accompanying quantum-chemical calculations suggest two formation pathways, involving either the addition of acetylene to the N site of pyridine$^+$, or to one of its C atoms. The geometries assigned by spectroscopy to the intermediates reveal that both reaction pathways are followed, although the latter was predicted to be endothermic and thus not considered in astrochemical networks.

In the previous examples, charged species were studied, although neutral molecules are abundant in space [129]. Neutral species have also been investigated at FELIX, in a molecular beam experiment where cold samples of neutral species are resonantly ionized allowing to record infrared spectra via ion-dip spectroscopy. Utilizing an electrical discharge source, the formation and degradation pathways of PAHs starting from neutral naphthalene ($C_{10}H_8$) were investigated [132]. This is detailed in Fig. 19d, where several smaller discharge products are identified. Moreover, the formation of larger PAHs, such as phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$), is observed. Hence, this type of studies provides key insights into the complex network of neutral PAHs that emerge in energetic interstellar environments.

Advances in science and technology to meet challenges

The studies showcased here address the diversity of carbon-bearing molecules likely occurring in the interstellar medium (ISM), possessing unique spectroscopic signatures. Clearly, it is of paramount importance to study these species in the laboratory, under relevant astrochemical conditions. Despite the progress made, several open questions remain. An important technical step forward was recently undertaken at FELIX, by installing a new undulator for the FELIX 2 laser. This allowed for an extension of the wavelength range down to 2.7 μm with high power, which is very important for identifying high-binding energy molecules in the ISM. The examples discussed here also emphasize the importance of complementing experiments with quantum-chemical calculations, in order to address the precise molecular structure of the studied species, as well as predicting relevant properties such as vibrational normal modes, dissociation energies, reactivities and potential energy surfaces. It was shown that advanced computational modeling is required to fully capture the complex nature of carbon-bearing molecules, even for species composed of only a handful of atoms. For instance, a careful treatment of anharmonicities is a necessity. Still, anharmonic calculations are computationally expensive, and most quantum-chemistry software is restricted to two quanta modes. In some cases, however, cubic and quartic force fields are needed for obtaining a good agreement with experiments [133]. Along the same lines, the effect of temperature and the possibility of having weakly bound species, such as clusters of PAHs, microsolvation or species with proton transfer, should be investigated carefully, given the shallow potential energy surfaces of these complexes. Manifestations of these effects are reflected in the IR spectra, for instance as broadening of adsorption features [134]. These can also be relevant when comparing with astronomical observations. In the harsh conditions of the ISM, UV irradiation can trigger a plethora of physicochemical processes. For example, triplet electronic states can be excited, which may be sufficiently long-lived, creating an appreciable fraction of excited molecules in the ISM population. Moreover, species can have high spin multiplicity in their ground states. Thus, investigating carbon-bearing species in excited electronic and high multiplicity states is a key step. Overall, strong collaborations between computational and experimental groups, together with astronomers in the field of observational astrochemistry, should be built to address the many questions involving carbon in space. Such an interdisciplinary network of researchers was recently launched as part of the Dutch Astrochemistry Network (DAN), within the project "Dutch Astrochemistry in the era of JWST".

Concluding remarks

The experimental facilities at the FELIX laboratory have been discussed in the context of identifying the spectroscopic signatures of a wide diversity of carbon-bearing molecules present in the ISM. The key essence of the studies highlighted here is the combination of mass spectrometry and infrared spectroscopy, using the unique capabilities of FELIX. This enables, either in ion traps or molecular beams, the characterization of the spectroscopic signatures of carbon-bearing molecules in the far- and mid-infrared spectral range, where JWST is most sensitive. While much insight has been obtained, further exploration is warranted, combining novel experimental schemes, accurate quantum chemical calculations, and close collaborations with astronomers.

Acknowledgments

We gratefully acknowledge the support of Radboud University and of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) for supporting the operation of the FELIX Laboratory, through the research program "National Roadmap Grootschalige Wetenschappelijke Infastructuur" 184.034.022. FELIX could not operate without the constant support from the in-house technical team, of which we are thankful. Moreover, we acknowledge the hard work of many generations of Master and PhD students, as well as Postdocs and senior researchers. Finally, we thank the external users that regularly visit our laboratory.

15 Uncooled thermomechanical bolometers as far-infrared radiation detectors

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Status

Some of the most recent challenges of astrophysical research consist in identification and investigation of molecular compounds in space, giving precious hints in star formation processes [135] or abiogenetic theory of life, as pushed by the discovery of interstellar glycine by the Rosetta mission [119]. Efficient astrochemistry investigation relies on the possibility of realizing small-footprint and efficient detectors operating in the far-infrared range, where the most interesting compounds show a clear spectroscopic signature. Terahertz and mid-infrared ranges are critical for detecting carbon-based organic compounds in space due to their characteristic absorption and emission lines, including those of PAHs; large organic molecules believed abundant in interstellar space ([136], cf for instance section 16 PeetersCami). In this context, novel kinds of THz and sub-THz detectors based on micro-electro-mechanical systems (MEMS) [137,138] and exploiting bolometric effects, are gaining attraction as versatile systems offering uncooled operation and possibility for creating large focal plane imaging arrays. Detector geometries based on trampoline membranes are particularly appealing [138]; being constituted by a wide plate - with an area on the order of the wavelength square - suspended through narrow tethers connected to a substrate which acts as a thermal sink, they offer engineerable thermal conduction as well as a wide absorbing area, giving an overall efficient interaction with the radiation at video rate operational speed. The further possibility to reach ultra-high-quality factors for the mechanical modes (mainly limited by the pressure of the operating environment and therefore favored for in-space operation) boosts the device sensitivity to extremely high values, in a radiation bandwidth limited by the choice of a proper absorbing layer to be embedded within the device.

The working principle of thermomechanical bolometers (TMB) is depicted in Fig. 20a and b.

The device fundamental mode of oscillation has a specific frequency which, in our mm and sub-mm sized devices, ranges from tens of kHz to tens of MHz. When electromagnetic radiation illuminates the device, it heats up due to direct radiation absorption which in turns modifies the eigenmode frequency: detecting the frequency shift allows one to infer the power of illuminating radiation. Promising results have been shown in prototype devices characterized at room-temperature in a wide spectral range roughly from 140 GHz to 550 THz. Here the mechanical frequencies were monitored by optical interferometry, showing video rate operation and a noise-equivalent power (NEP) less than 100 $\mathrm{pW}/\sqrt{\mathrm{Hz}}$ in 1 mm-framed trampoline resonators [138].

Current and future challenges

The basic device architecture showed a great potential for far-infrared detection, which would be fully enabled by addressing specific characteristics which need to be targeted in order to validate the technology in real-world applications.

Granting all-electrical control of the TMBs is pivotal to device integration and parallelization in large-scale arrays for scan-less imaging. Adding simple permanent magnets on the chip side (which generate a planar, homogeneous magnetic field of about 250 mT) allows the exploitation of the electromotive voltage for electrical probing and Lorentz's force for electrical actuation [139]. The former effect is essentially given by the Faraday's and Lenz's laws, which give a electromotive voltage generated on a conductor moving perpendicularly to a magnetic field. The latter instead describes the force acting on a current-carrying conductor in a magnetic field. Both phenomena can be enabled by adding conducting wires crossing the TMBs through the tethers. In this configuration, we can model the electromotive voltage considering an arm of the TMB as a string of length L oscillating with vertical displacement amplitude u. The electromotive voltage is then simply given by:

$$V = -\mathbf{B} \cdot L_{\mathrm{eff}} \frac{\mathrm{d}u}{\mathrm{d}t}, \tag{1}$$

where $\mathbf{B}$ is a static magnetic field oriented perpendicularly to the string velocity. $\mathrm{d}u/\mathrm{d}L_{\mathrm{eff}}$ is the string effective length which, for its fundamental mode of oscillation, is given by $L_{\mathrm{eff}} = 2L/\pi$. Using typical device parameters, we expect read-out voltages of the order of tens of μV, which are well verified in the experiments, as the one reported in Fig. 20c. Here the device was actuated using a piezoelectric ceramic stack holding the whole chip, but we also verified the possibility of Lorentz-based forcing, as given by the force density $\delta\overrightarrow{\rho} \times \overrightarrow{B}$, where $\overrightarrow{\rho}$ is the linear current density along the wire.

Device characterization shows a minimal impact of the addition of metallic contacts on the device performance, as shown in the beam-profiling of a continuous wave (CW), 10 mW integrated power, 140 GHz source, where the single TMB has been shifted pixel-by-pixel to produce the experimental map (see Fig. 20d).

Further challenges require the introduction of device arrays, which can all be interrogated in series employing a single wiring contact.

While the TMBs input–output technology could be used to simplify device integration within our system, a separate optimization is focused on the performance

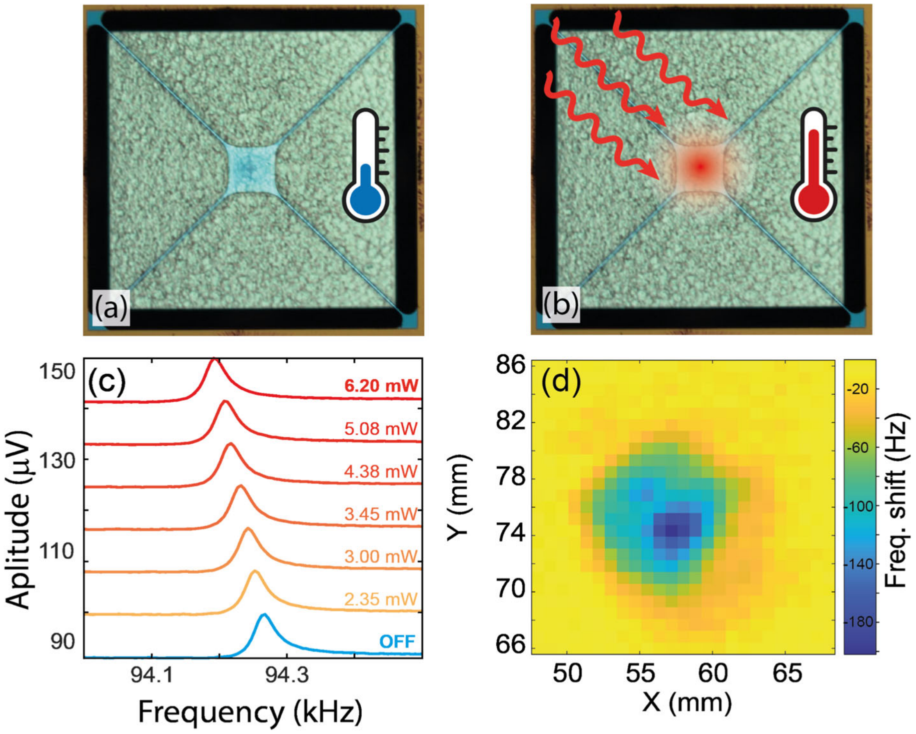

Fig. 20 Working principle of TMBs. A resonator at a certain temperature (**a**) has a specific resonant frequency of its mechanical modes (c - fundamental mode, OFF). Radiation absorbed by the device raises its temperature (**b**), simultaneously shifting its resonance frequency (c - increasing power). **c**—Typical mechanical resonator shift as a function of a 550 THz laser impinging power. **d**—Beam profiling of the 140 GHz source taken by scanning the position of a single TMB

itself, which can be largely improved by operating on the absorbing layer, for maximized and broadband operation. In fact, the prototype device was completely coated with ~50 nm of Cr/Au which prevent electrical probing and giving only a small absorption enhancement (~ 3% at 140 GHz) over the essentially transparent Si_3N_4 layer constituting the main TMB body. Finding light and stiff materials with a wide absorption band in the far-infrared range is a interesting challenge which would produce extremely relevant improvements on the TMB performances (Fig. 21).

Advances in science and technology to meet challenges

Further advances in the detector performance are related to its efficiency in converting the radiation energy into heat. As the Si_3N_4 membrane constituting the main TMB body is transparent in the THz frequency range it is essential to add an absorbing layer to ensure temperature increase as a response to the radiation. Depending on the targeted application of the single-pixel or array detector, the absorption in a broad or narrow frequency range is needed. This functionality can be realized via the structure and composition of this layer.

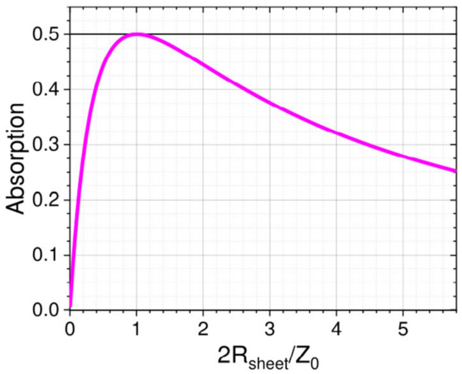

Fig. 21 Calculated absorption of a thin conductive film as a function of its sheet resistance

Thin uniform conductive layer allows for broadband absorption. Considering propagation of an electromagnetic wave normally incident onto a thin conductive film, it can be shown that the peak absorption, equal to 50%, is reached when sheet resistance of film $\mathbf{R}_{\mathrm{SH}} = \rho/\mathbf{d}$ is equal to half of the vacuum impedance which is defined as $\mathbf{Z}_0 = \sqrt{\mu_0/\epsilon_0} = 377\Omega$ [140]. Here ρ is the material resistivity and $\mathbf{d}$ is the thickness of the film. Such absorption in a broad spectral range can be obtained if the film thickness is much smaller than the skin depth, which is determined by frequency dependent dynamic conductivity and must satisfy the "metallicity" criterion:

$$\sigma(\omega) > \epsilon_0 \omega, \tag{2}$$

where $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m and ω is the characteristic cycle frequency. Fabrication of metallic coating with a sheet resistance of $\sim 200\Omega$/sq. is challenging since the corresponding thickness is less than 10 nm. In this case, the relative thickness uniformity is poor and most metals tend to oxidize and otherwise degrade if exposed to ambient air. Therefore, it is advantageous to use conductive graphitic films [141] as an absorptive layer. One of the best choices is the pyrolyzed carbon film (PyC) film that is formed on any solid surface due to carbon precipitation from a methane-hydrogen mixture at a temperature of about 1000 °C. This material has a conductivity of about 10^5 S/m which is two orders of magnitude smaller than that of gold. Importantly, the PyC conductivity can be tuned by the synthesis conditions (synthesis temperature, ratio methane to hydrogen flow ratio). A PyC film with a sheet resistance of 200 Ω/Sq. has a thickness of about 50 nm and does not add more than 20% to the mass of the trampoline. In fact, our recent results show that PyC film with a thickness of just 20 nm allows for as much as 40% of THz radiation absorption in the frequency range from 0.3 to 10 THz [142]. We thus expect that the sensitivity of the bolometric detectors described in the previous subsection can be increased at by least 10 times due to the addition of a PyC layer onto the Si_3N_4 membrane. To further improve the absorption performance of the nanocarbon enhanced membranes, a metamaterial type structure could be applied. One of the best for electromagnetic performance solution could be graphene made regular hemispheres array, extremely robust to the various graphene nano- and even microscopic defects, see [143]. Moreover, graphene imperfectness which could easily happen in space conditions is the source and physical origin of extremely broadband (1–10 THz) almost perfect absorption performance of these graphene hemispheres [144]. What is also good about graphene-based THz detectors for space applications, is that they are ionizing radiation tolerant, at least for most of the substrates used in space conditions [145].

Concluding remarks

Terahertz range spans over two decades in frequency and the THz radiation carriers a lot of valuable information about the space objects from solar system to remote galaxies. The technology described here allows for the creation of supersensitive THz vision systems for space science applications. The advantages of our approach include but are not limited to high sensitivity, energy efficiency, ionizing radiation rigidity, and chemical stability.

Acknowledgments

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16 Advanced ab initio methodologies for the detection of small carbon chains and related species in astrophysical media

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Status

To-date, several gas phase small and medium-sized carbon clusters (C_n) and their related species (C_nX (X=H, O, N, S) or PAHs) are detected in astrophysical media and in laboratory (cf. for instance Sections 8, 10, 14, 17, 18). Also, some of their positively and negatively charged ions are identified there, while the number of the later are distinctly smaller because of the less available data in laboratory motivating their search. Indeed, experimental studies to characterize C_n bearing molecular ions are still challenging [146] (cf for instance section 18). Theoretical investigations of C_n's and related species represent good alternatives since the achieved accuracy of the computed data using advanced *ab initio* methodologies is enough to guide assigning state-of-the-art experimental spectra; the achieved accuracy using advanced *ab initio* methodologies is competitive with the state-of-the-art experimental techniques.

Spectroscopy and dynamics of these molecular species require their good description either isolated or interacting with the most abundant species in astrophysical media (i.e., H, He and H_2). The former allows the determination of the rotational or rovibrational or electronic bands and their assignments for the identification of these species in the surveys (see for instance section 12). The latter are needed to estimate their collision rates and thus their abundances, for instance, in interstellar medium, questioning the local thermodynamic equilibrium (LTE) approximation and to propose physical chemical models for their formation [147]. For those purposes, one needs the generation of their precise multi-dimensional potential energy surfaces (mD-PESs) followed by nuclear motions treatments on these potentials using quantum approaches. For polyatomic C_n bearing molecules, these mD-PES are complex exhibiting several potential minima separated by low potential energy barriers favoring their interconversion

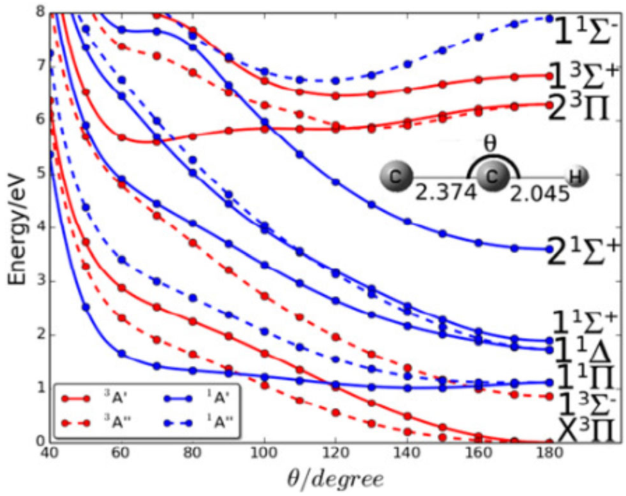

Fig. 22 One-dimensional cuts of the 3D-PESs of the electronic states of C_2H^+ vs. the in-plane bending angle θ, as computed at the MRCI/aug-cc-pV5Z level of theory. Figure reproduced from Ref. [150]. Copyright owned by Royal Society of Chemistry

via the respective transition states. Also, it is common that several minima have close energies, making the determination of the most stable form a difficult task. This is the case, for instance, of linear and cyclic C_4 or C_4^+ tetratomics, where the relative energies between both isomers vary between −0.1 and +0.2 eV, depending on the *ab initio* method used for computations [148]. Note that experiments cannot solve such problem.

For electronic structure computations, we established an accurate enough first principles methodology to map these mD-PESs in their electronic ground states with relatively low computational costs. Indeed, we showed that the use of explicitly correlated methods (e.g., CCSD(T)-F12) in conjunction with appropriate atomic basis sets are efficient and accurate enough [149]. Such methodologies are nowadays used routinely by several groups over the world. Nevertheless, the patterns of the electronic excited states may be extremely complex and a high density of states is found, as illustrated in Fig. 22 for CCH^+ [150].

This favors their mutual interactions via vibronic and/or spin-orbit couplings and the subsequent mixing of their electronic wavefunctions. For such molecular systems, the computationally costly multi-configuration methods (e.g., the complete active space self-consistent field (CASSCF) approach, followed by the internally contracted multi-reference configuration interaction (MRCI) method or its explicitly correlated version (MRCI-F12)) should be used [151]. Such methods are implemented in several homemade or commercial quantum chemistry packages.

For nuclear motions treatments, fully quantum methodologies should be used. In particular, one needs the full description of all internal motions and their interactions with the H, He and H_2. These techniques include variational approaches, time dependent and independents techniques, whereas perturbation theory (PT), as implemented in commercial codes, is usually useless. Indeed, the mD-PESs of C_n bearing species are shallow close to minima exhibiting thus strong anharmonic effects, which cannot be accounted for by the use of the derivatives of the PESs at this minimal structures and PT. As can be seen in Fig. 23, the C_3^+ ground state potential extends over a wide range of CCC in-plane angles (from 60° to 180°) where linear and triangular C_3^+ forms can be found. A small potential barrier (< 0.2 eV) separates both minima. This confers a quasilinear character for this ion. For the neutral C_3, such quasi-linear character complicates the pattern of its ro-vibronic levels, making the assignment of the corresponding experimental spectra a challenging task. Again, predicting CCH^+ spin-rovibronic spectra to allow its detection is notoriously a challenging task, because of various couplings to be considered such as vibronic, Renner-Teller and spin-orbit.

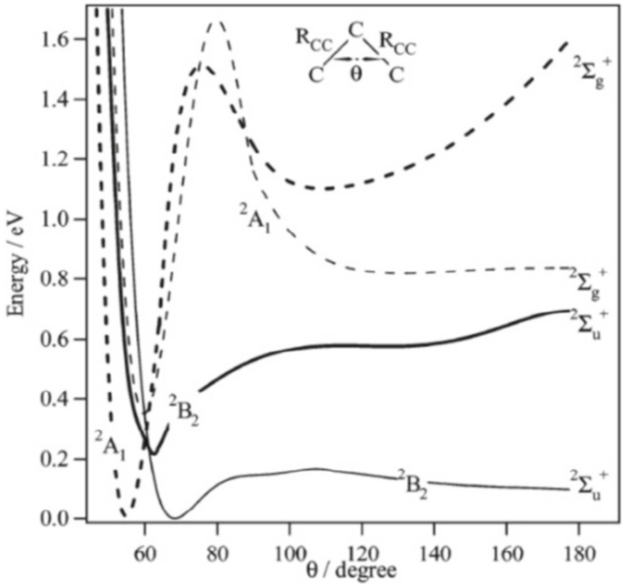

Fig. 23 One-dimensional cuts of the 3D-PES of the ground electronic state of C_3^+ vs. the in-plane bending angle θ, as computed at the MRCI/spdf cc-pVQZ level of theory. Solid (dashed) lines are for CC distances equal to 2.65 (2.45) Bohr. Figure reproduced from Ref. [146]. Copyright owned by ACS

For the computations of collision rates, the most commonly used approaches consist on considering the C_n bearing species as rigid rotor. Although this approximation is valid for rotational (de-)excitation rates for a wide range of molecular species colliding with H, He or H_2, this is not the case for C_n bearing molecules because of their floppy behavior, in particular along the bending coordinates [148]. In the case of C_3 colliding with He, one needs indeed to consider the bending for accurate predictions [151]. But this remains challenging for larger C_n species. Also, Renner-Teller systems (e.g., C_4H) colliding with H, He or H_2 are extremely complex to treat without new methodological developments.

In order to address the question of the possible destruction of C_n bearing species by ionizing light (VUV or X Rays, cosmic radiations) or energetic particles impact (e^-, H^+, ...) in astrophysical media, one needs their ionization energies. Efficient composite schemes are benchmarked, where core-valence, relativistic and zero-point vibrational energy effects are considered on top of full geometry optimizations using either the post-Hartree-Fock methods cited above or the less expensive DFTs as described in Ref. [149].

Current and future challenges

Small sized C_n bearing compounds are still challenging up-to-date theoretical methodologies for their full treatment because of their complex electronic structure and the subsequent complex mD-PESs and couplings. Although accurate approaches are available for di- tri and teratomic species, the extension to larger C_n bearing systems remain an open question. Indeed, either the computations are out of capacities of available resources or that the methodologies are not implemented. Recent benchmarks showed that we can use models for that. For instance, mD-PESs based on SAPT approximations are viewed to be good alternatives [152]. For ionization energies predictions, we showed recently that coronene derivatives may be used to model ionization energies of larger PAHs targeting graphene 2D material [153].

Advances in science and technology to meet challenges

Among the up-to-date methodological developments to meet the challenges we can refer to those using graph theory (cf. section 11), machine learning techniques (cf. section 31). In particular, some machine learning-based algorithms are proven to be effective in describing mD-PESs for incorporation into quantum nuclear motion treatments for spectroscopy or dynamics of astrochemical molecular systems. For example, the application of neural networks to reactive cross-section calculations [154] was viewed to be very promising. Finally, the recent and huge developments and implementations will be efficient enough to help overcoming, at least partially, the challenges described above.

Concluding remarks

For the detection of molecules in astrophysical media, accurate energetics and structural properties and accurate electronic, rotational and rovibrational spectra of several isomers of C_n containing species are required. To-date, mostly pure C_n or C_nX linear chains, either neutral or ionized, are detected, for instance, in interstellar medium in spite that some of the corresponding nonlinear isomers are distinctly more thermodynamically stable than the linear ones. This is a signature of specific chemistry in action there. Nevertheless, the up to-date astrochemical models are not sufficiently advanced to propose any convincing explanation. This is due to the complex chemical networks that should be implemented and the need of the knowledge and the characterization of all reactions considered in these networks. This program is far from realistic to implement. Instead, global chemical models with some selection rules should be elaborated. Such simple models were proposed for the reactivity of CnX anions in interstellar media and on their possible detectability there [155]. Dedicated global chemical models should be developed in order to simulate and understand their chemistry, both in the gas and condensed phase. Besides, our work showed that we should implement theoretical approaches that go beyond the standard Born-Oppenheimer approximation to assign the astrophysical surveys.

Acknowledgements

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17 Experiments and models seek observations

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Status

For now, more than 300 molecular species have been detected in interstellar and circumstellar environments and atmospheres of (exo)planets, from simple two-atomic species to complex organic molecules consisting of more than 10 atoms, polycyclic aromatic hydrocarbons (PAHs), and fullerenes [129]. Laboratory experiments and astrochemical models reveal (or pursue to reveal) physico-chemical processes in astrophysical environments, provide necessary data for the identification of detected species, and demonstrate possible pathways to simple and complex molecules. Many examples can be provided in this context, in the following we focus on a few most interesting for our research.

Several complex organic molecules (COMs) have been detected in diffuse and translucent interstellar clouds [156,157]. The formation of COMs was always linked to complex ice chemistry in dense interstellar

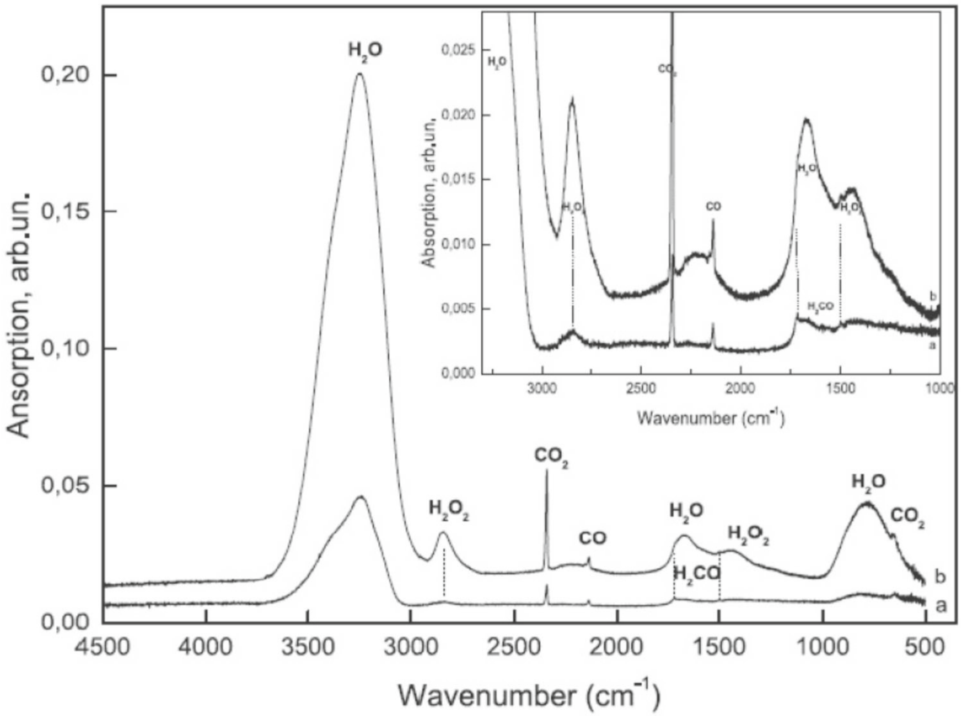

Fig. 24 Difference spectra before and after O/H bombardment of carbon grains: **a** $[O_2]/[H_2] = 1/60$, **b** $[O_2]/[H_2] = 10/70$. Inset: zoom-in of the 3300–1000 cm^{-1} spectral range. Figure reproduced from [158]. ©AAS, reproduced with permission

clouds and not really expected for regions, where dust grains have no or minor ice coating. Laboratory results on the formation of H_2CO on bare carbon grains by H/O atom addition [158] can explain the synthesis of COMs. Figure 24 shows the difference in IR spectra before and after O/H bombardment of carbon grains, where the reader can observe two bands related to H_2CO.

A direct evidence of the efficient formation of CO_2 on carbon surfaces covered by water ice at high temperatures (up to 150 K) was recently presented [159], justifying that the known low-temperature formation route of CO_2, C-grains + H_2O-ice + UV photons, remains valid at high temperatures as long as H_2O is present on carbon grains. This provides an alternative explanation for the loss of solid carbon in inner regions of planet-forming disks that could result in the formation of carbon-poor Earth and other terrestrial planets in the Solar System.

On the modeling side, density functional theory (DFT) calculations combined with spectroscopic techniques (NEXAFS, XPS) revealed that water adsorption on C_{60} and $C_{59}N$ might have implications for astrobiology even under ultra-high vacuum conditions [160]. Furthermore, C_{60} might come as a catalyst in PAH formation [161]. Atomistic simulations investigated organic molecule adsorption on carbon nanoparticles. Aromatic organic molecules were found to prefer adsorption over aliphatic ones. This study proposed a pathway for the formation of PAHs.

The effort in this domain is thriving however, in spite of all the studies, understanding of the astrochemical origins of the majority of detected species remains as a major challenge.

Current and future challenges

Observational studies provide new inputs for laboratory experiments and chemical models and proof of reaction products of experimentally and theoretically investigated chemical reactions. Laboratory experiments and chemical models provide data for analysis of observations and for understanding the origin of detected species. Laboratory experiments support chemical modeling by providing new inputs for chemical models and proof of theoretical reaction pathways. Chemical modeling, in turn, provide understanding of experimental chemical networks and predictions of which reaction pathways may dominate under astrophysical conditions.

Thus, it's clear that astrochemical observations, astrochemical modeling, and laboratory experiments should go hand in hand providing a full circle astrochemistry research. However, the main challenge is to convince scientists working in these fields to collaborate. From our experience, a necessity of laboratory data (except the simplest case of spectral and mass signatures of species) is not clear for many observers. However, the origin of detected species can be revealed only

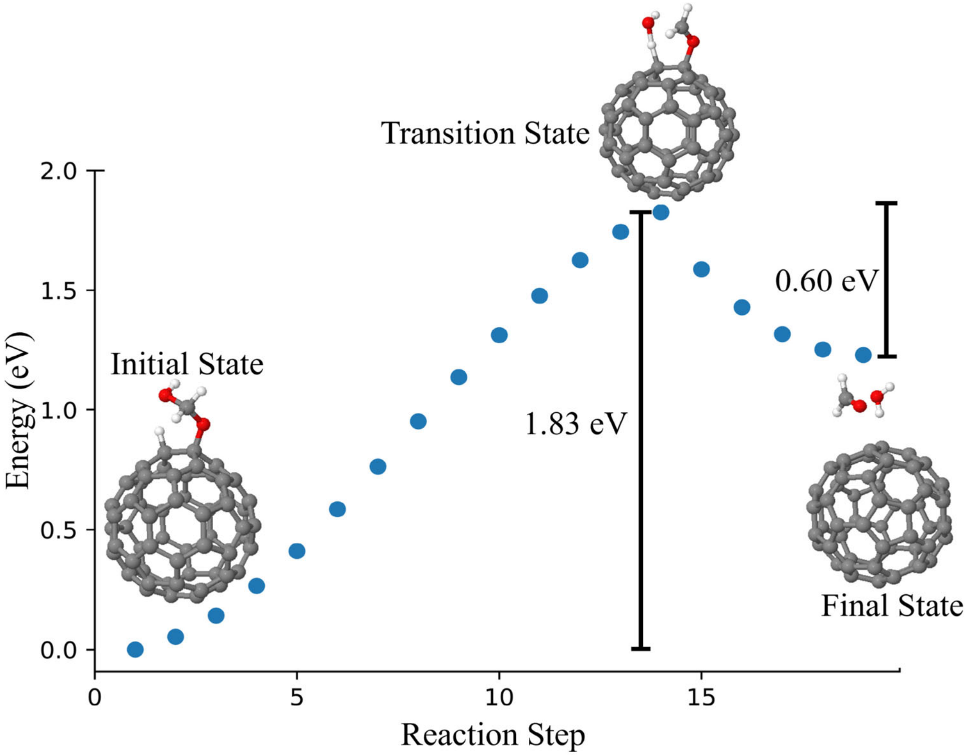

Fig. 25 Theoretical calculation of the reaction barrier of methanediol decomposition into formaldehyde and water. The barrier without the existence of fullerene is also calculated as 2.32 eV and 1.40 eV from left and right sides, respectively (unpublished own work)

with support of laboratory experiments. Vice versa, a necessity of astronomical observations is not clear for many laboratory people providing impressive results on, e.g., formation of new complex species. However, detection of those species is the only proof for the relevance of laboratory processes to real processes taking place in astrophysical environments.

Advances in science and technology to meet challenges

Now, in the era of powerful astronomical instruments, such as the Atacama Large Millimeter/submillimeter Array (ALMA) and the James Webb Space Telescope (JWST), and a few new instruments on horizon (e.g., EELT, Ariel, SKA, Origins), a lot of possibilities for the realization of observational ideas are and will be open. On the other hand, a good support for space research in provided on Earth by well-developed astrochemical networks containing thousands of reactions, e.g., NIST and KIDA, new simulation tools, e.g., TRICKS (copyright R.T. Garrod, 2022) and new laboratory techniques, e.g., high-resolution spectroscopy of molecules desorbed from surfaces [8,9] allowing for previously not available measurements of spectra of complex organic molecules formed in surface reactions and their subsequent detection in space.

Theoretical studies involving quantum mechanical simulations, molecular dynamics calculations and emerging field of machine learning techniques has gained importance in interpreting the experimental and observational results if not simply guiding their direction. Figure 25 represents one such result from our studies where fullerene existence has been shown to reduce the reaction barrier hence pointing out a catalytic effect on one of the key reactions in Miller-Urey experiment.

The integration of quantum mechanical simulations [162] and machine learning techniques has opened new possibilities in recent years especially in the field of theoretical condensed matter physics. The quantum mechanical simulations have provided valuable insights into the electronic structure, catalytic behavior, etc. properties of materials in the atomic scale. This advancement has facilitated the design and interpretation of experimental approaches.

From our point of view, the main advance in modern science to meet challenges, except the aforementioned instruments and tools is a possibility of (broad) synergy collaborations between experts in the fields of astronomical observations, astrochemical modeling, and laboratory experiments. The focus of future research should be done on such collaborations and only together we will be able to answer big scientific questions, such as discussed in the previous section.

Concluding remarks

Astrochemical observations, astrochemical modeling, and laboratory experiments should go hand in hand to provide a comprehensive picture of physico-chemical processes in astrophysical environments. With this short letter we aim at adding one more brick into the foundation of future collaborations between experimentalists, theoreticians, and observers. As the title of the letter states: experiments and models seek observations; and we will be happy to provide more information and to establish new contacts and collaborations with experts in observational astronomy.

Acknowledgments

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18 Thermal photon emission of carbon-based species measured in storage rings

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Status

Radiative cooling of excited molecules and clusters plays an important role for stabilizing them in the virtually collision-free environment in interstellar space. In laboratory studies of unimolecular decays of highly excited molecular species, radiation is commonly detected as a channel competing with the better known channels of unimolecular loss of atoms or molecules and thermal electron detachment (thermionic emission). With parallel decays radiation is manifested in a suppression of the unimolecular decay rate [163]. The alternative of measuring emitted photons directly is rarely feasible because of the usually low molecular beam densities and low photon detection efficiencies. That has therefore only been accomplished in a cases so far [164,165].

The main part of radiative cooling studies have been performed in storage rings and linear traps. These devices typically cover time scales ranging from several tens of microseconds to seconds or, for the cryogenic varieties, to several thousand seconds [166–168]. However, it is now clear that some systems, mainly metallic or semiconductor clusters, radiate efficiently on very short time scales, better covered by time-of-flight mass spectrometers [163,169,170]. Notably, these emission rates are often orders of magnitude larger than typical IR emission rates.

An essential feature in these experiments, whether of storage ring or single pass type, is that unimolecular decays occur with a power law rate, with the power close to -1 [171]. This special form for the decay rate arises from the broad excitation energy distributions generated in the cluster and molecular ion sources that are commonly used to produce intense ion beams in the experiments. The thermal photon emission suppression of the unimolecular decay manifests itself as an exponential decay of this power law decay, in its simplest form as $\exp(-k_\mathrm{p}t)/t$, where k_p is the photon emission rate constant [172,173].

At present, a range of molecular ions and clusters, both anions and cations, have been studied with this method. The results show a remarkable degree of variety across the size and composition space. The values of k_p frequently vary by orders of magnitude, even between species in homologous series. Pure carbon clusters and carbon-based species are both prime examples of this and of prime importance in astrophysical contexts. The cooling timescales for C_5^- and C_7^- are both on the order of ten ms, whereas C_4^- and C_6^- radiate on three orders of magnitude shorter timescales [172].

Whereas the ms radiative cooling rates for the odd-numbered carbon anion clusters conform to expectations for infrared, vibrational transitions, the very high emission rates for even-numbered clusters can only be understood as emission from thermally excited low-energy optically active electronic states [173]. Another example of particular interest for astrophysics is the decay of the doubly charged anion C_7^{2-} for which lifetimes exceed previously measured values by a large factor, with concomitant consequences for their survival [174].

Current and future challenges

The emitted thermal radiation has two important consequences, and an important task will be to map the radiative behavior of astrophysically relevant molecules and clusters. One aspect of the radiation is molecular survival rates, i.e., how efficient radiation quenches unimolecular decay. For this aspect the radiation from thermally populated electronically excited states, denoted recurrent fluorescence (RF, see section 19 and, for example, refs. [164,175]), is of particular importance. This type of energy dissipation will be significantly more efficient in stabilizing the molecules compared to the much slower vibrational and rotational radiative transitions. Figure 26 shows the example for C_4^-.

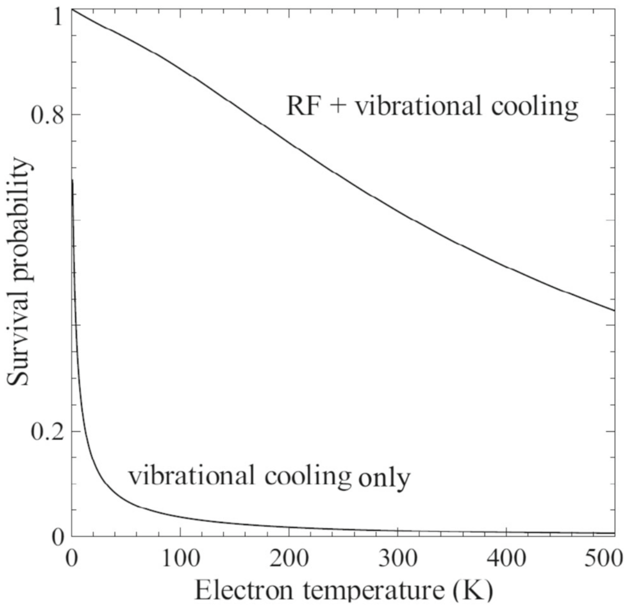

Fig. 26 The survival probability for the C_4 anion against electron detachment at asymptotically long times after anion formation by attachment to the vibrational ground state by an electron from a thermal distribution with the temperature given on the abscissa. The curves are calculated with data from Ref. [172]

There will be a strong size dependence of the stabilizing effect of thermal radiation, cf. the size dependence of radiation time constants for small carbon clusters, both anionic and cationic [164,172,175]. Importantly, the difference is expected to be independent of the mode of excitation, whether it occurs by photon absorption or by collisional attachment/fusion of molecules. The only requirement is that these production processes lead to statistical mixing. Experimentally, this mixing seems to hold very well.

The other consequence of radiation is the contribution to observed optical spectra. This aspect has so far only been explored marginally for the RF, whereas the vibrational sector is far better known, at least for stable molecules. Also here have carbon clusters provided some interesting results. Carbon cationic clusters up to sizes beyond N=20 radiate by RF and given their high stability against unimolecular decays, the stability limit will for some sizes exceed an excitation energy of 1 Ry [175]. Although the emission spectra of these clusters have not yet been measured, they will most likely be strongly red-shifted and, by the nature of the RF mechanism, with a concomitant photon emission quantum efficiency above unity, both features which are consistent with the characteristics of the Extended Red Emission [176], also discussed in section 2.

Advances in science and technology to meet challenges

The challenges for the characterization of the RF radiation are both theoretical and experimental. The experimental part of the enterprise is basically a laboratory astrophysics project and the difficulties will be addressed with the development of ion traps and storage rings with detection ability for photons emitted under a large solid angle. A good time resolution is also desirably in order to detect the emission time-resolved after photo-excitation. Also the detection of single low energy photons, from the NIR and toward the red, is a very desirable goal. While the decisive role of RF is evident [163,177], discussions of the detailed interpretations of already feasible experiments, such as [178] are ongoing [179,180].

The theoretical challenges are associated with the description of the properties of highly excited molecules and clusters. For the purpose of explaining or predicting their emission spectra it is necessary to go beyond ground state geometries and the Franck-Condon principle. At the relevant high excitation energies one must expect melting, or the finite size equivalent to melting, to be present, for example. Curve crossing and thermal electronic excitation requires tools to incorporate non-Born-Oppenheimer dynamics. The exploration of the quantum state structure in such systems is a formidable task, but one that promises to allow to nail down the origin of observed diffuse and broad spectral features.

Some first theoretical results have, however, already been obtained for small boron clusters [181].

They indicate a significant broadening of the spectra compared to those calculated from frozen ground state structures. Both visible and NIR spectra will show large deviations from the simple ground state, easily computationally spectra of sharp lines of well-defined positions, similar to the effects seen the spectrum in Fig. 27, which was limited to computational times of less than a picosecond due to the extremely high computational demand of the calculation. Also the photon emission rate constants will be modified. For the simulations on boron clusters the increase was up to two orders of magnitude for some cluster sizes.

Concluding remarks

The presence of thermal radiation, in particular of the recurrent fluorescence type, plays a potentially very important role in the life cycle of the interstellar molecular species, including those that are relevant for the formation of molecules of biological nature. Revealing the full picture requires a concerted effort of laboratory experiments, quantum theory and observational astronomy.

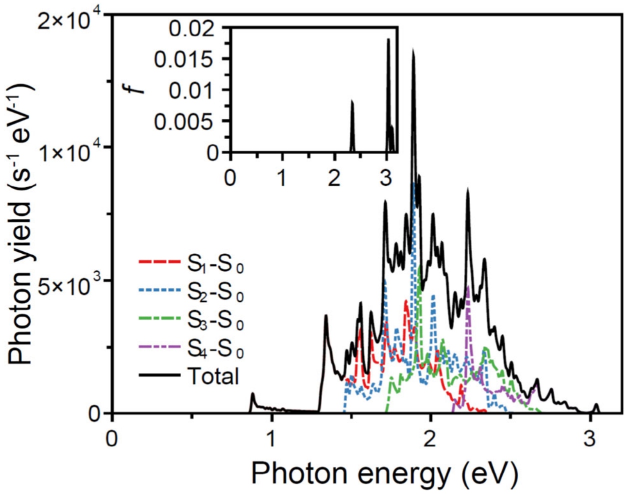

Fig. 27 The calculated emission spectrum of B_{13}^{+} at the energy defined by the limit of stability vs. fragmentation. The inset shows the ground state absorption spectrum. The colored curves give the transition from the four lowest excited states and the black curve their sum. The calculation is based on a molecular dynamics simulation with a high level quantum mechanical treatment of the electrons. The computer-intense calculations limit the simulated time to 850 fs (See Ref. [181] for more details). Longer simulation times must be expected to show even stronger spectra broadening. The figure is adapted from [181]

Acknowledgments

H.Z. and H.T.S. thank the Swedish Research Council for individual project grants (with contract Nos. 2020-03437 and 2022-02822), and acknowledge the project grant ”Probing charge- and mass-transfer reactions on the atomic level” (2018.0028) from the Knut and Alice Wallenberg Foundation.

19 Recurrent fluorescence in the radiative cooling of PAH cations

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Status

Polycyclic aromatic hydrocarbons (PAHs) have long been thought to be ubiquitous in the ISM, based on the infrared emission bands observed by astronomers at wavelengths coincident with their vibrational transition energies. However, these so-called aromatic infrared bands (AIBs) are common to all PAHs and cannot be used to identify specific molecular species. Over the last few years, radio telescope observations of the interstellar cloud TMC-1 have identified two isomers of cyanonaphthalene [25], indene [99], and 2-cyanoindene [182] by their rotational emission lines. Intriguingly, all four PAHs were observed in substantially higher abundances (by several orders of magnitude) than astrochemical models predicted, indicating that the models either overestimated destruction and/or underestimated formation mechanisms. Holistically, the survival of PAHs in environments such as TMC-1 is defined by the balance between formation, destruction (dissociation), and resilience (radiative cooling) mechanisms (Fig. 28).

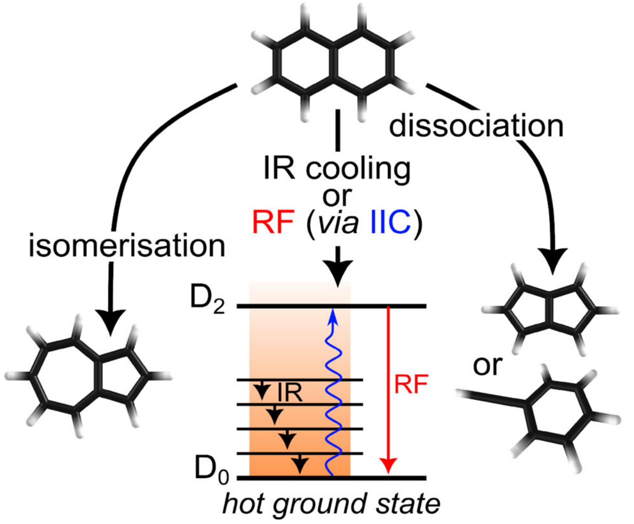

Fig. 28 Possible relaxation pathways for an energized PAH (naphthalene) cations. Reversible isomerization to azulene, dissociation to one of two possible products, IR cooling of the hot ground state, or inverse internal conversion (IIC) to an excited state that may relax through emission of a recurrent fluorescence (RF) photon. Reactive pathways are not considered for molecules in isolation

These processes can be understood using controlled laboratory experiments with which to calibrate astrochemical models. While the PAHs observed in space to date are neutral, in the laboratory environment, it is not possible to generate, isolate, and probe neutrals over astrochemically-relevant timescales. Instead, the focus is on studying ions, as they can be stored in electrostatic storage devices offering conditions that mimic cold molecular clouds.

While IR emission is well observed, and its importance is highlighted by the recent deployment of the James Webb Space Telescope, another radiative emission process, recurrent fluorescence (RF, Fig. 28) [183], is proving to play a critical role (and even dominate) radiative cooling of energized PAHs. To date, experimental studies on RF and the competition with other relaxation pathways have been limited. RF is a radiative stabilization process that is neglected in astrochemical models, whereby UV/vis photons are emitted from thermally excited electronic states. This process may only occur in ultrahigh vacuum environments due to the absence of collisional energy quenching (Fig. 29).

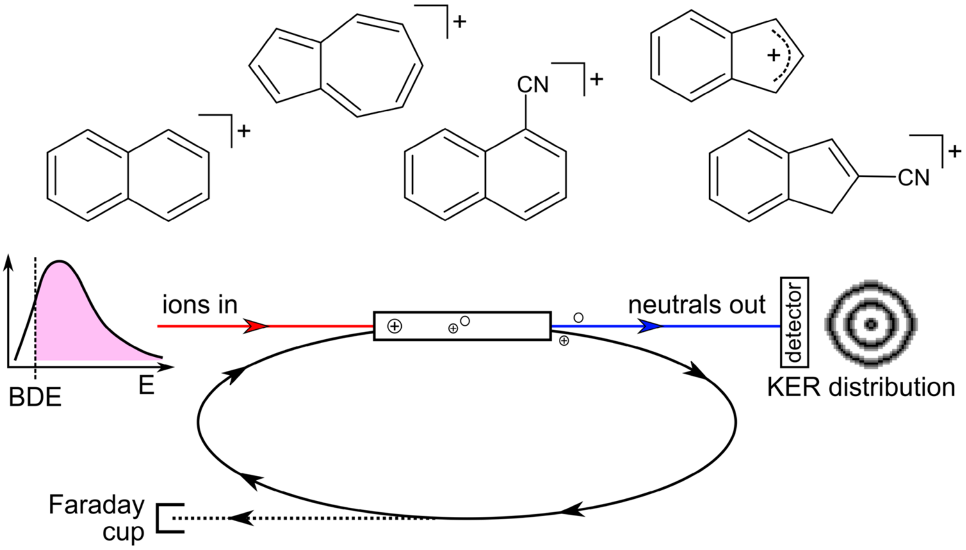

Fig. 29 Structures of several cationic PAHs studied at DESIREE (Double ElectroStatic Ion Ring ExpEriment) [166]. The schematic of one of the DESIREE storage rings illustrates spontaneous neutralization measurements performed on a hot ensemble of cations (formed in an electron cyclotron resonance ion source). BDE is bond dissociation energy and KER is kinetic energy release. Ions are stored in the 8.6 m circumference storage ring, which has a residual pressure $\approx 10^{-14}$ mbar and is cooled to $T \approx 13$ K. These conditions emulate those in cold, dark molecular clouds (e.g., TMC-1). In an experiment, energized ions stored in the ring and neutral dissociation products are detected

Current and future challenges

Direct observation of RF is challenging, requiring purpose-built instrumentation, as demonstrated recently for the naphthalene cation (Np^+) [165].

To date, RF direct-detection experiments have used electrostatic ion beam storage devices to achieve the required isolation times [165]. A more common approach involves the indirect inference of RF time-resolved measurements of dissociation or other destruction channels for isolated ion ensembles with broad internal energy distributions (Fig. 30). Radiative cooling introduces a lower bound on the measured destruction rate coefficient, as ions with lower energies, and thus destruction rate coefficients lower than this critical value, will be radiatively stabilized rather than destroyed. In this approach, RF is invoked when the measured critical rate coefficient is too high to be explained by sequential emission of IR photons (Fig. 30a)

Indirect determinations of RF rates are sensitive to the absolute rate coefficient of the monitored destruction channel, which is either calculated using simple statistical models (Fig. 30b) and/or determined through separate mass spectrometry experiments. A series of measurements at DESIREE have found similar RF cooling dynamics for a range of small PAH cations (Fig. 29), suggesting a universal mechanism [178].

Experimentally, we require direct and indirect measurements of RF dynamics across a series of small (few rings), medium, and large ($\geq$ 10 rings) PAHs and to develop rules-of-thumb for robust, predictive models on the importance of RF and associated time-resolved dynamics. These data will ultimately guide astrochemical models.

While RF is clearly an essential relaxation process, important aspects remain unclear. For example, measured dissociation rates for PAH cations frequently exhibit non-exponential cutoffs after radiative cooling becomes competitive. This behavior is not reproduced by state-of-the-art master equation simulations. Multiple hypotheses have been put forward, including sequential fragmentation processes [185] and temperature-dependent oscillator strengths. The development of a common, generally applicable framework for interpreting such results is needed to gain new insight into the detailed cooling dynamics of PAHs.

Advances in science and technology to meet challenges

The principal advancements in science and technology required to address the current deficiencies involves new instruments able to reliably probe RF for astrochemically relevant ions. For electrostatic storage devices, such as DESIREE, the main challenge is that the ion beams are physically extended, making efficient photon collection difficult, resulting in extremely low count rates. Purpose-built instrumentation with improved optical access to the stored ions is thus desired.

Even using today's most powerful telescopes, identifying PAHs in interstellar environments is a laborious task. Narrowing down the search list of candidates could accelerate efforts to complete the interstellar organic inventory. While RF has been iden-

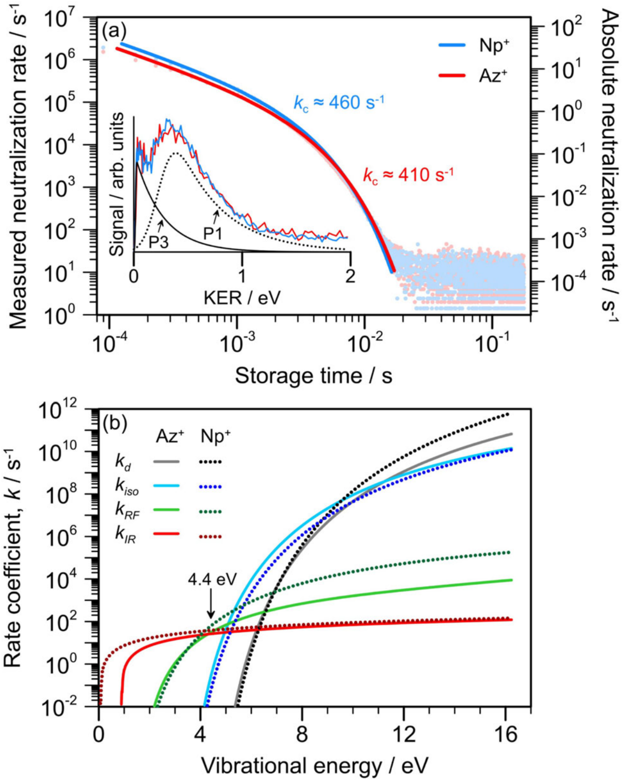

Fig. 30 Spontaneous neutralization of energized cationic naphthalene (Np^+) and azulene (Az^+) recorded at DESIREE [184]. **a** Measured and fit neutralization rate with ion storage time (inset: single-pass KER distributions). The decay curves are well-described by a power-law fit [171] returning $k_c > 400$ s^{-1}, indicating that cooling is faster than can be described by IR emission alone. **b** Modeled rate coefficients for C_2H_2-elimination (k_d), isomerization (k_{iso}), recurrent fluorescence (k_{RF}), and infrared cooling (k_{IR}). The model uses a coupled Master equation combining RRKM rates with coupled-cluster quality potential energy surfaces, and models for IR and RF emission. Figure adapted from Ref. [184]

tified as an important radiative stabilization process in many PAHs, a scalable computational predictive pipeline is needed for quantitative insights from multifaceted laboratory studies of key molecules identified (or suspected of being present) in space. Such a pipeline could be based on state-of-the-art quantum chemical calculations, providing electronic transition probabilities, including Herzberg-Teller vibronic coupling, with input from next-generation direct RF detection experiments. Improved models of destruction and stabilization rate coefficients, incorporating anharmonic effects, could be benchmarked against experiments from electrostatic ion beam storage devices. The resulting energy-dependent survival probabilities could be folded with important excitation mechanisms in various interstellar regions to determine if a given candidate molecule could plausibly survive there.

Concluding remarks

State-of-the-art experiments indicate that RF plays a key role in the radiative cooling and lifecycle of PAHs in space, and RF is important for defining the abundances of these species. Yet, to date, studies on RF are sparse due to challenges associated with storage of ions over sufficiently long timescales, and difficulties in the detection of the fluorescence photons.

20 Molecular beam experiments with PAH molecules and nanoparticles

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Status

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are omnipresent in the interstellar medium (ISM). They can form clusters and nanoparticles, which are part of the life-cycle of the large carbonaceous molecules. On the other hand, the PAH molecules can be removed from the gas phase by their deposition onto the ice/dust grains in the ISM, where they can undergo further chemistry, e.g., triggered by cosmic radiation. Thus, the PAH molecules either within the PAH clusters or deposited on/in the ice mantels of the dust particles can be involved in the synthesis of the complex molecules in the ISM playing an important role in the astrochemical evolution [186].

Laboratory molecular beam (MB) techniques are an ideal tool to provide a detailed molecular-level insight into the elementary processes in free clusters and nanoparticles [187,188]. Clusters in MBs fly isolated in vacuum and can be probed by a variety of spectroscopic and mass spectrometric techniques. The clusters can pick up different molecules and their chemistry triggered by photons, electrons or ions of different energies can be studied in detail. Therefore, the laboratory MB experiments with clusters can provide unprecedented insight into the elementary processes involving PAH molecules in cluster environments.

The clusters of PAH molecules and mixed clusters of PAHs with other astrochemically relevant molecules such as water were studied in MBs by different techniques, e.g., IR and UV spectroscopy, mass spectrometry, photoelectron spectroscopy etc. [189,190]. However, most of the studies up to date concerned relatively small clusters composed of a few molecules. The MB investigations of large clusters composed of hundred(s) of the PAH molecules, i.e., nanometer-size particles - are relatively scarce [191,192].

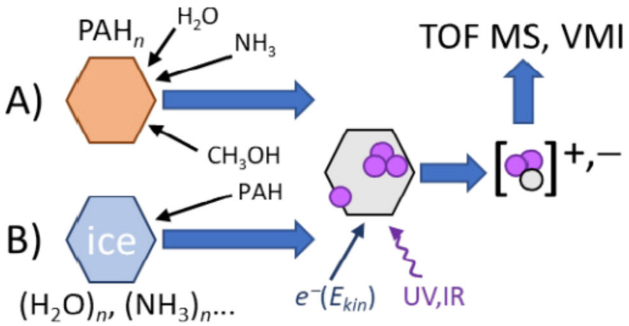

Fig. 31 A schematic representation of the MB experiments with PAH and ice nanoparticles on CLUB

Current and future challenges

Here, we focus on two kinds of MB experiments relevant to the role of PAHs in ISM, Fig. 31:
A) large PAH$_n$ clusters; B) PAH molecules on ice nanoparticles.

A) We have recently generated large PAH$_n$ clusters in MB composed of hundred(s) of the PAH molecules and explored the uptake of different molecules by these nanoparticles [191,192]. Investigating the uptake and accommodation of molecules on PAH nanoparticles is desirable for a molecular-level understanding of the chemistry of PAH grains in the interstellar space, where they can interact with different molecules. First, we have established our pick-up method with the benzene clusters Bz$_n$ of the mean size $n \approx 300$ molecules, investigating the uptake of the hydrogen bonding molecules: water, methanol and ethanol [191]. The neutral cluster size of Bz$_n$ could be characterized from the Poisson distribution of the number of picked up molecules, which corresponded to the geometrical cross section of the cluster with the mean radius of about $R \approx 2.2$ nm, i.e., the nanoparticles larger than 4 nm. We have quantified the uptake of different molecules defining the relative uptake ratio. For water it was by about 30% lower than for methanol and ethanol, which were approximately the same. This can be relevant when considering the interaction of water and methanol with the PAH nanoparticles in the ISM.

Subsequently, we have extended our investigations from benzene nanoparticles to more complex PAH$_n$ of naphthalene, anthracene, phenanthrene, and pyrene, including also the five-membered ring containing PAHs indene and fluoranthene. In addition to water, methanol and ethanol, the uptake of ammonia, methane, oxygen, and carbon dioxide was studied. We have determined the relative uptake ratios for different molecules on the different PAH nanoparticles, and discussed the mobility and coagulation of these molecules on the nanoparticles.

Thus, these experiments provided a detailed insight into the uptake of molecules on PAH nanoparticles, nevertheless, they also pointed to some issues and challenges of such MB experiments. First important question is the PAH$_n$ size. The uptake depends on the size, however, the determination of the neutral cluster size in MB is challenging. Mass spectrometry is not a reliable method due to the strong cluster fragmentation and size dependent detection sensitivity. The method of Poisson distribution implemented in our studies is only applicable under some non-trivial assumptions and cannot be used for the nanoparticles and molecules, where the uptake and the coagulation of the molecules on the nanoparticle are inefficient. Second crucial issue represents the nanoparticle temperature, which is very difficult to determine and control experimentally. In MB experiments in vacuum the cluster temperatures can vary largely between less than 10 K to several 100 K. Thus, the uptake and evaporation of molecules can vary severely with the cluster temperature. Further issues requiring significant attention in future studies represent the binding energies of the molecules to PAH nanoparticles and the ion-molecule reactions after the nanoparticle ionization for the fragment detection.

B) Using MB techniques, the PAH molecules can be adsorbed on/in other clusters mimicking the interstellar ice/dust particles. From such experiments, an insight into the uptake of PAH molecules by the interstellar ice/dust particles can be gained. The ice nanoparticles with the adsorbed PAH molecules can be further interrogated by radiation (photons, electrons or ions of different energies) to reveal the chemistry relevant to PAH in ice mantles of the dust particles in the ISM.

The PAH molecules can be picked up by large nanometer-size water clusters (ice nanoparticles) - alternatively, large ammonia or other clusters can be implemented to reveal some amine chemistry. To the best of our knowledge, such experiments have not been done in MBs. Indeed, adsorption and reactions of PAH on bulk ice surfaces have been investigated, however, the isolated clusters in vacuum can provide more detailed insight into the primary processes, since the reaction products can escape the finite-size cluster, which is often decaying, and can be detected directly without undergoing secondary and further processes. Besides, the reactions on a curved nanoparticle surface can proceed differently from the infinite flat bulk surface. On the other hand, small clusters consisting of a PAH molecule with a few water, methanol, ammonia or other molecules attached were investigated too as analogues to the interstellar ices [189]. However, the large nanoparticles have not been used to pick up the PAH molecules yet. In our laboratory, uptake of molecules by ice nanoparticles and large ammonia clusters in MB has been investigated [187,188]. Thus, we plan to explore the uptake of PAHs and their reactions on/in the ice nanoparticles.

Advances in science and technology to meet challenges

For the above described experiments with clusters in MB and pickup of molecules, our cluster beam apparatus (CLUB) in Prague [187,188] represents a suitable tool. It is a very versatile device, which allows for different experiments with clusters: the pickup of molecules, determination of pickup cross-sections, mass spectrometry of positive and negative ions, electron ionization, photoionization, electron attachment, photodissociation with velocity map imaging of photofragments, etc. However, the above outlined issues and challenges require some advances in the methodologies discussed below.

Among the issues raised above is the size and temperature of the nanoparticles. This is difficult to resolve for the PAH nanoparticles formed in supersonic expansions. An option can be generating the PAH_n clusters in He-nanodroplets (HND) in MB. The HND are large He clusters of $10^3 - 10^9$ He atoms of a well-established temperature of 0.4 K. These species are superfluid, pick up very efficiently most molecules (e.g., PAH), which then coagulate to clusters in HND and the evaporation of He atoms cools them to the HND temperature of 0.4 K. This method is used, e.g., in the group of P. Scheier and E. Gruber [193].

On the other hand, the cluster sizes and temperatures of water clusters (and, e.g., ammonia and methanol) were investigated experimentally and theoretically in details. They turned out to be determined by the expansion conditions. Thus, the size and temperature in the experiments with the ice nanoparticles can be relatively well established and controlled by the expansion.

Further above-mentioned issues requiring attention in the future studies are the binding energies of the molecules to the PAH nanoparticles. Indeed, many individual - namely theoretical - studies exist for selected molecule-PAH pairs and for small clusters, but systematic theoretical studies are desirable for the PAH_n clusters and various molecules complementing the experiments.

In the evaluation of the uptake experiments, also the ion-molecule reactions have to be considered, which take place after the nanoparticle ionization necessary for the fragment detection. The mass spectra used to obtain the uptake ratios [191,192] can be analyzed in more details in terms of the ionization mechanism and possible ion-molecule reactions. In addition, different ionization can be implemented to disentangle the reaction and fragmentation pattern. Our CLUB apparatus offers different ionization methods, e.g., the electron ionization, electron attachment, photoionization (UV resonant and non-resonant multiphoton techniques), by which the MB can be interrogated in the same place. Thus, the different mass spectra correspond to different fingerprints of the same neutral species. In addition, the understanding of the ionization and ion-molecule processes has to be assisted by theoretical calculations. The electron attachment experiments can also reveal the structure and stability of the anions [194].

Concluding remarks

We have discussed the recent experiments with clusters and nanometer-sized particles in MBs. Two research lines have been proposed for the future MB investigations: A) large PAH_n clusters, and B) PAH molecules on/in ice nanoparticles. The different experiments with such clusters performed with our versatile CLUB apparatus in Prague can be complemented by experiments in other groups, e.g., HND research in Innsbruck [193] (see section 22), and the PAH cluster collisions with fast ion beams at GANIL in Caen [195], and also by the corresponding theoretical investigations. The joint effort can offer a detailed molecular-level insight into the various processes, thus elucidating the life-cycle of the carbonaceous molecules in the ISM.

Acknowledgments

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21 Laboratory studies on the infrared emission of fullerene C_{60} and related molecules

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Status

Since the first report of evidence for cosmic fullerene C_{60} and C_{70} by their infrared (IR) emission bands in the planetary nebula, Tc1, in 2010 [37], the same emission bands of molecular vibrational transitions of C_{60} have been confirmed by using the same satellite observatory, Spitzer/IRS, in many objects in late stages of the stellar evolution, such as post asymptotic giant branch (post-AGB) stars, protoplanetary nebulae (PPNe), planetary nebulae (PNe), reflection nebulae, and young stellar objects (YSOs) [72,196–198]. Key questions arisen for cosmic fullerenes are the formation mechanism and the excitation mechanism [198]. Shock heating and UV irradiation of carbonaceous dusts and hydrocarbon molecules are suggested for the former, while the thermal emission [37] and fluorescent IR emission [196] are still under debate for the latter [198]. It is natural to consider that relative IR-emission band intensity between the modes of different vibrational frequencies changes by vibrational temperature and is used as a probe for physical and chemical conditions as well as the abundance of the molecule in space. However, there have only a few reports on the IR emission spectra of C_{60} in the laboratory [199,200]. In order to establish a protocol which connects between spectral intensity and physical parameters, experimental studies are needed for quantitative analyses of molecular spectra, for the IR emission in particular, thereby solv-

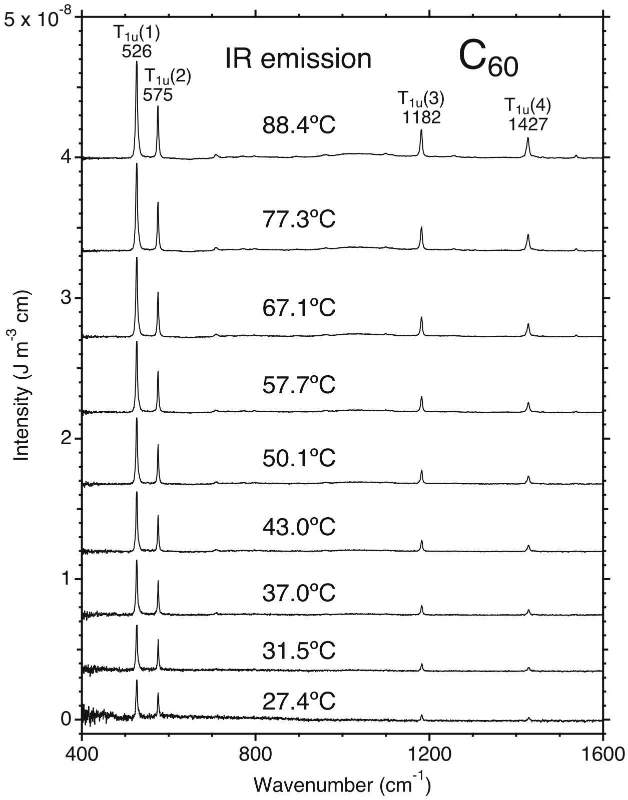

Fig. 32 Infrared emission spectra of a thin film of fullerene C_{60} deposited on a KBr disk. Upon increasing temperature, bands of four vibrational T_{1u} modes of C_{60} intensify and the relative intensity changes. Figure reproduced from [201]. ©2024 American Physical Society

ing the question of which mechanism is more important for the excitation of fullerene C_{60} in space.

Current and future challenges

Recently, we have launched a project for the measurement of IR emission spectra of C_{60} molecules deposited on a KBr slab. For this purpose, a commercially available Fourier transform IR (FTIR) spectrometer was modified and the power spectrum of thermal emission of radiation was measured for the sample as an external light source [201]. Figure 32 shows a series of IR emission spectra of C_{60} recorded at elevated temperatures within a range of 300–400 K. For each spectrum, four bands of the IR-active vibrational T_{1u} modes of the C_{60} molecule are conspicuous. All these bands intensify with increasing temperature, and the increase in emission intensity is more pronounced for higher frequency modes of $T_{1u}(3)$ and $T_{1u}(4)$ compared to the increase for lower frequency modes of $T_{1u}(1)$ and $T_{1u}(2)$. The increasing intensity at higher temperature is rationalized simply by increasing population of the molecules in vibrationally excited states from which the IR photon can be emitted.

It is natural to consider that the relative intensity between the four T_{1u} modes of C_{60} is exploited as a promising probe for vibrational temperature of an ensemble of C_{60} molecules in space. However, debates are continued around two mechanisms for the molecular IR emission, i.e., thermal emission [37] and UV-induced IR fluorescence [196]. The discussion is still far from conclusiveness. We have thought that a quantitative experimental work and a fundamental theoretical work may help the discussion to proceed further.

For interpretation of the temperature dependence of the IR emission band intensity of C_{60} in Fig. 32, we have developed a theoretical model based on spontaneous emission of radiation from vibrationally excited states in Boltzmann distributions, by taking 46 fundamental normal modes of vibration for icosahedral C_{60} and their overtones and combinations into considerations. Using vibrational excitation up to seven vibrational quanta, we made a list of more than 1.2×10^{12} states including degeneracy for 1.5×10^{8} vibrationally excited levels to simulate the temperature dependence of the IR emission intensity for the T_{1u} modes of C_{60}. Figure 33 depicts the simulated IR intensity for the four bands of the IR-active T_{1u} modes of C_{60} [201]. The molecule is essentially IR silent in emission below 100 K, where the molecule populates mostly at its vibrational ground level. The low frequency T_{1u} modes, namely $T_{1u}(1)$ and $T_{1u}(2)$, predominates in IR emission spectra between 100–200 K, where the molecules in population of fundamental $v = 1$ levels of T_{1u} modes are responsible for the emission bands. Bands of higher frequency modes, namely $T_{1u}(3)$ and $T_{1u}(4)$, appear above 200 K, and increase in intensity constantly in between 300–400 K, where the population of molecules shifts mostly to vibrationally excited levels of overtones and combinations. It is apparent that considerations on transitions between vibrationally excited levels, namely hot bands, are crucial for conditions of the IR emission spectra at elevated temperatures.

Challenges planned for the future are to extend the measurement to a wider range of temperatures and to various materials to be explored. Thereby, comparison with spectra obtained by using the satellite observatory, James Webb space telescope (JWST), will provide us with better understanding of the molecular IR emission features. Laboratory experiments for the IR emission spectra of molecular species related to interstellar molecules, such as polycyclic aromatic hydrocarbons (PAHs), are intriguing also for relevance to cosmic fullerenes and related phenomena.

Advances in science and technology to meet challenges

The laboratory measurement of the IR emission spectra of fullerene C_{60} has been limited to two experiments in the gas phase at high temperatures [199,200]. Our method using solid samples deposited on a KBr slab

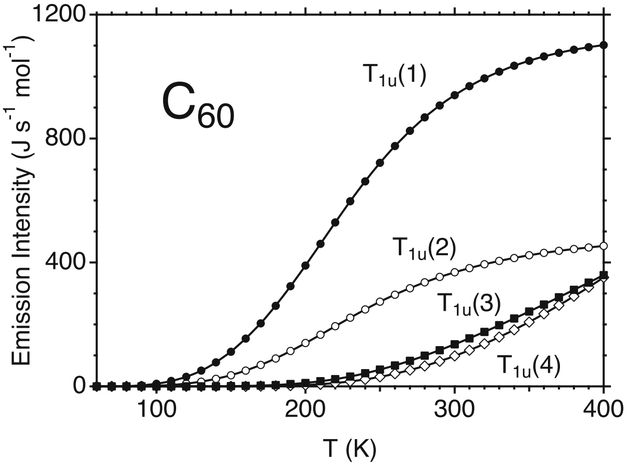

Fig. 33 Simulated temperature dependence of the IR emission band intensity for four IR-active T_{1u} modes of fullerene C_{60}. Figure reproduced from [201]. ©American Physical Society

enables measurements in a wider temperature range and is applicable to various molecular species including fullerenes, PAHs, and other hydrocarbons. This will lead to detailed understanding of physical conditions and behaviors concerning the molecular IR emission.

Theoretical descriptions are crucial for understanding of the mechanism of the molecular IR emission. They are compared with data not only from the laboratory experiments but also from the astronomical observations. From the relative intensity for multiple bands of a single molecular species, vibrational temperature can be deduced for the molecule thus for the physical condition of interstellar objects such as PNe, PPNe, and post-AGB stars. The experimental approach in a close contact with the theoretical simulation can settle the problem whether the thermal emission model or the UV-induced fluorescent model is responsible for the interstellar IR emission bands of fullerene C_{60} and C_{70} molecules. This will influence on the interpretation on the IR emission of the other molecules such as PAHs. In this sense, the experimental IR emission studies on PAHs are thought to be more important challenges along this project on fullerenes.

Concluding remarks

In contrast to IR-absorption spectroscopy as one of the conventional analytical tools in chemistry, IR-emission spectroscopy is a relatively new method as a chemical probe. It makes a bridge for direct links to the astronomical observations using the space telescopes, namely Spitzer/IRS and JWST. In connection with the high-resolution vibrational spectroscopy of C_{60} molecules isolated in solid parahydrogen at cryogenic temperature, providing detailed information on the fundamental transitions of the IR-active T_{1u} modes and some combination bands [202], the IR emission spectroscopy at elevated temperatures in the laboratory is promising for understanding of the mechanism of IR emission in space.

Acknowledgments

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22 Messenger spectroscopy of cold molecular ions using helium nanodroplets

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Status

One of the most crucial methods for identifying nanocarbon (nC) species in space is gas phase spectroscopy in the laboratory providing absorption spectra that serve as references for astronomical observations. Generally, the density of gas phase molecular beams is insufficient for recording spectra using traditional absorption spectroscopy techniques. An alternative approach for recording the absorption spectrum is action spectroscopy, i.e., detecting a reaction resulting from photon absorption. An example of this is messenger spectroscopy. Messenger spectroscopy involves tagging the molecules/ions of interest with a weakly bound atom or molecule. Photon absorption by the tagged molecules/ions leads to the evaporation of the attached tag and the formation of the bare molecules/ions as photofragments. The detection of either the photofragment signal or the depletion of the tagged precursor as a function of the photon energy yields the absorption spectrum.

Helium atoms represent excellent tags for messenger spectroscopy due to their minimal binding energy to the molecule or ion of interest, ensuring that the matrix shift in the absorption spectrum is small. For instance, Campbell et al. utilized messenger spectroscopy with helium in 2015 to identify C_{60}^+ as a carrier of several diffuse interstellar bands (DIBs) [36]. The internal cooling and helium-tagging in this case were accomplished by using a cryogenic ion trap [36].

At the University of Innsbruck, we employ a different method to create helium-tagged ions which is by using superfluid helium nanodroplets (HNDs), as illustrated in Fig. 34. Droplets of superfluid helium with an equilibrium temperature of 0.37 kelvin are produced in the supersonic expansion of precooled and pressurized helium gas (20–30 bar, ca. 8 kelvin) into vacuum. Subsequent electron ionization results in the formation of multiply charged HNDs. Depending on the electron energy, anionic or cationic HNDs can be formed. The charged HNDs are then doped with the gas phase molecules of interest, which subsequently become ionized through charge transfer or Penning ionization inside the HNDs [193].

To efficiently extract ions that are tagged with only a few helium atoms from the HNDs, two methods have been established. One method to obtain He-tagged ions involves splashing the doped HNDs onto a surface [203]. More recently, a novel setup has been established in which the doped HNDs collide with room-temperature helium gas atoms [60]. This leads to the shrinking of the droplet and the extraction of helium-tagged ions from the HND due to Coulomb repulsion [60].

These helium-tagged ions are now well-suited for messenger spectroscopy. Accordingly, they are merged with the beam of a wavelength-tunable laser. The resulting ions, including photofragments and precursors, are recorded using a time-of-flight mass spectrometer. The novel setup is additionally equipped with a quadrupole mass filter which enables the selection of a specific precursor ion species by its mass-to-charge ratio before the laser irradiation, as illustrated in Fig. 34 [60]. The quadrupole mass filter allows us to measure the absorption spectrum by recording both the photofragment signal and the depletion of the precursor ion yield. This method provides spectra with a superior signal-to-noise ratio because the photofragments emerge from almost zero background.

In contrast to the cryogenic ion trap method, utilizing HNDs offers the advantage that multiple helium atoms can be easily attached to the ions. By measuring the absorption spectrum of the ion with various numbers of attached helium atoms, we can estimate the matrix shift resulting from the helium tagging. Consequently, this often enables the estimation of the absorption band positions of the bare ion through extrapolation, simplifying the comparison with astronomical observational data.

Figure 35 displays the absorption spectrum of $C_{60}He_2^+$ (depicted in red) obtained by using the novel setup [60]. For reference, the lower graph in Fig. 35 shows the absorption spectrum of C_{60}^+ as reported by Campbell et al., which led to the identification of C_{60}^+ as a carrier of the DIBs in 2015 [36]. This spectrum was recorded by measuring the depletion of $C_{60}He^+$ upon photon absorption in a cryogenic ion trap.

Current and future challenges

Despite significant efforts to identify the carriers of the nearly 600 DIBs, only C_{60}^+ has been unequivocally identified so far. Other promising candidates are C_{60} analogues, such as $C_{60}H^+$ and endohedral (see section 35) as well as exohedral complexes between C_{60}^+ and other elements which are abundant in space like Na, K, Ca, Fe, Mg, etc. Metallofullerenes are of particular interest due to their catalytic role in the nucleation and growth of nC species, including carbon nanotubes (CNTs) and carbon cages. The presence of metallofullerenes could be critical to understanding the chemical pathways involved in the formation and evolution of various carbonaceous species, thus influencing carbon chemistry in space (see contribution 9).

Other research groups have recently started to spectroscopically investigate some of the above-mentioned C_{60} analogues isolated in the gas phase [40,92] but the data are limited to the IR wavelength range so far (see contribution 14). Nevertheless, their findings are promising, as no contradictions to astronomical observations were found [40,92]. Additionally, time-dependent density functional theory calculations predicted that $[C_{60}\text{-metal}]^+$ ions exhibit numerous electronic transition bands in the ultraviolet (UV) to near-infrared (NIR) spectral range, supporting the idea that they are potential DIB carriers [92]. However, laboratory electronic spectra of these ions, which are necessary for unambiguous identification, are still lacking. New developments in messenger spectroscopy, as previously described, hold promise for providing this data, potentially revealing new DIB carriers.

Other noteworthy candidates for DIBs include fullerene anions and multiply charged fullerenes (see contribution 34), which can be formed through stepwise ionization by UV and extreme UV photons, such as those emitted by astrophysical sources like white dwarf stars and central stars of planetary nebulae. Electronic spectra of C_{60}^- and C_{70}^- have been recorded in the past using matrix-isolation spectroscopy [204,205], however, these spectra lack spectral resolution. Gas phase messenger spectroscopy offers high-resolution spectra of these species [206]. In general, the formation of helium-tagged anions is challenging due to the increased electron repulsion between the He tag and the anion caused by the additional electron(s). However, thanks to the lower temperature in HNDs compared to current cryogenic ion trap setups, our helium-tagging messenger spectroscopy setups can overcome this issue [206].

Regarding fullerene cations in higher charge states, electronic and vibrational spectra of $C_{60}^{2+/3+}$ have been measured in neon matrices across a broad spectral range encompassing IR, NIR, and UV-visible regions [207]. Furthermore, an electronic gas-phase spectrum of C_{70}^{2+} is already available [208].

Apart from fullerenes and fullerene analogues, it is important to investigate electronic transitions of larger carbon-containing molecules like carbon chains and polycyclic aromatic hydrocarbons (PAHs). While numerous spectral studies have been dedicated to PAHs, no experimental absorption spectrum has matched any DIBs to date. However, many PAHs and PAH-related species remain for laboratory spectroscopic studies.

In addition to monomer ions, charged oligomers composed of fullerenes [209,210], aliphatic or aromatic carbon structures are the focus of future investigations. The use of HNDs is particularly advantageous in this context, as both homo- and heterogeneous clusters can be easily formed in HNDs through sequential pickup.

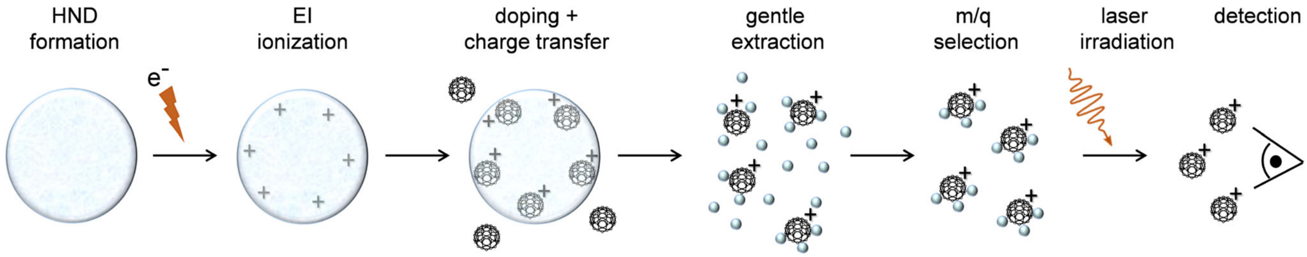

Fig. 34 Formation of He-tagged molecular ions by using HNDs [60]

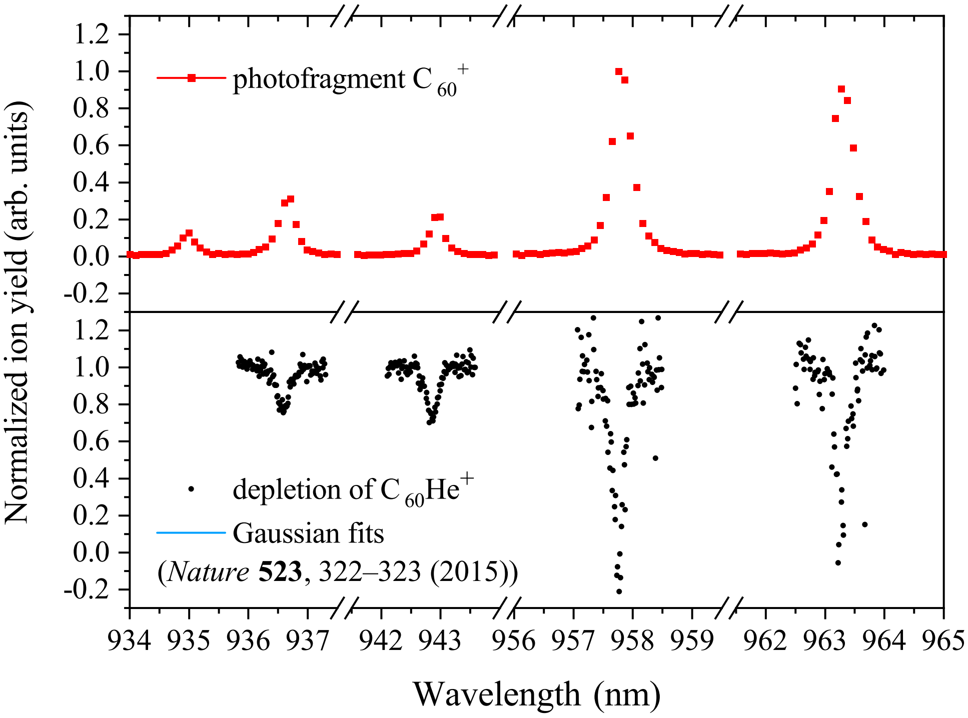

Fig. 35 The upper graph, depicted in red, displays the absorption spectrum of the precursor ion $C_{60}He_2^+$. This spectrum was obtained using the novel setup [60], where we recorded the yield of the photofragment C_{60}^+. The lower graph shows the gas phase absorption spectrum of $C_{60}He^+$ measured by Campbell et al. [36]

Concluding remarks

Helium-tagging messenger spectroscopy represents a powerful and effective tool that provides high-quality absorption spectra, which are indispensable for the search for nC species in astronomical observational data. The formation of helium-tagged ions through the use of superfluid helium nanodroplets has demonstrated its effectiveness and versatility. In this contribution, we have discussed various promising candidates that we intend to investigate using our messenger spectroscopy setups at the University of Innsbruck.

Acknowledgments

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23 Characterizing hydrogenated nanocarbon from the gas to the solid using vibronic spectroscopies

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Status

This contribution details the study of nanocarbons in the PIIM laboratory in Marseille using two types of complementary UV–visible laser spectroscopies: the

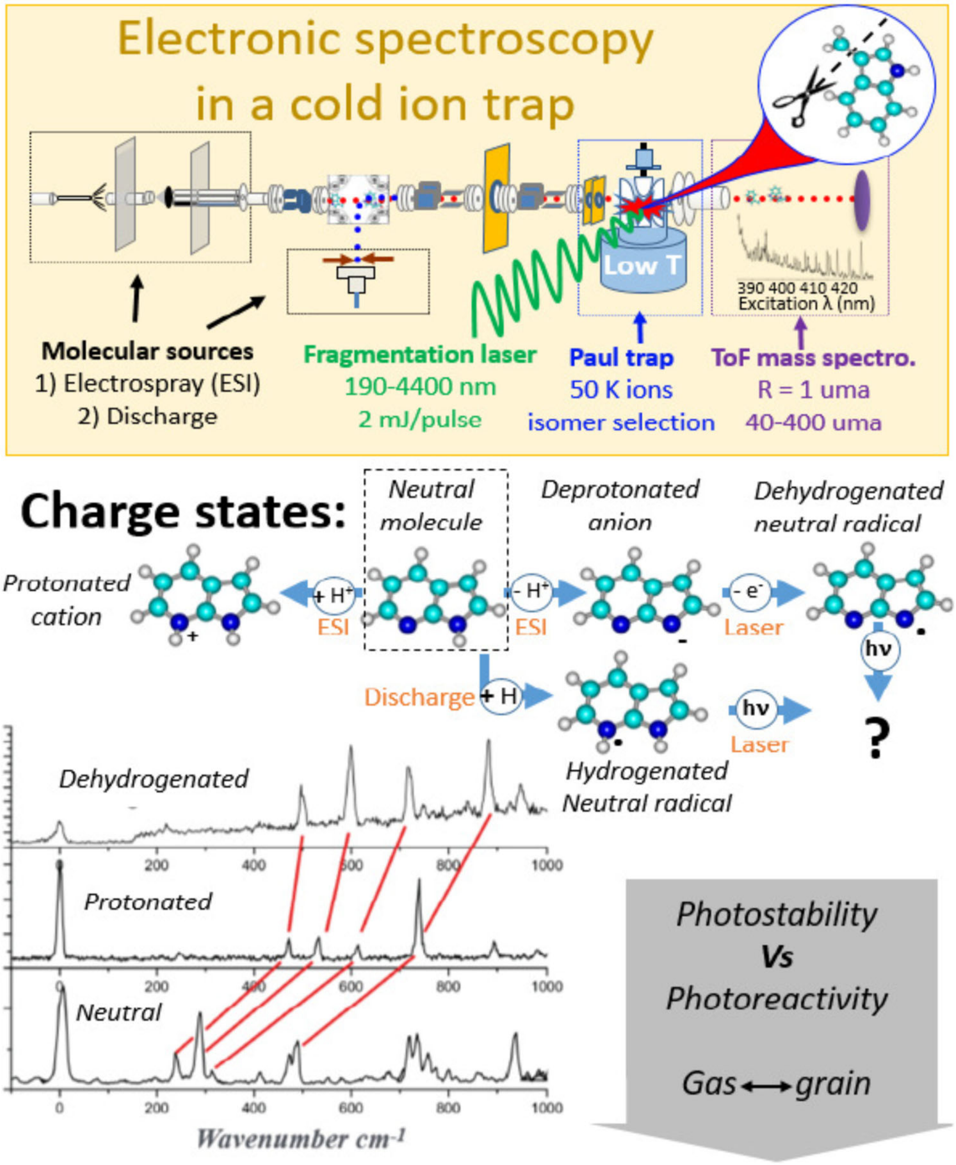

Fig. 36 Electronic spectroscopy in a cryogenic ion trap as a probe of carbonaceous molecules: technique especially sensitive to molecular structure and to charge state

vibronic spectroscopy of small aromatic molecules in varying charge states in the gas phase (Fig. 36), and the Raman spectroscopy of graphitic and amorphous solid nanocarbon (Fig. 37). We describe the state of the art in each domain before outlining the future challenge of combining these techniques to study the influence of charge and hydrogenation state on the nature of solid nanocarbons produced by deposition of small photoexcited aromatic molecules on graphite.

Electronic spectroscopy of charged molecular ions in cold ion traps or of neutral molecules in molecular beams has been widely used to study the molecular physics of aromatic molecules for decades. However, in the five years since the first radioastronomy detection of an aromatic molecule in the interstellar medium [96], the study of small aromatics, and particularly those bearing a cyano group, by the laboratory astrophysics community has been significantly boosted. The recent demonstration of the recurrent fluorescence mechanism in the cyanonaphthalene radical cation (see section 19), potentially explaining the photostability of cyanonaphthalene under interstellar conditions and thus its higher than expected abundance in TMC-1, is an excellent example of the insights currently being made in this field by laboratory studies [178]. The use of action spectroscopies to study the non-radiative pathways of small aromatics (i.e., typically 1–4 aromatic rings) can give indications as to their photostability and their potential indirect contribution to the interstellar aromatic fraction, i.e., producing fragments that act as precursors to build up larger aromatics [211] (see also Sect. 6). Figure 36 illustrates the cryogenic ion trapping experiment in the PIIM laboratory, where electronic spectroscopy of simple aromatic ions is performed using tuneable UV–visible-IR lasers coupled to mass spectrometry. Thanks to our combination of experimental setups and sources, we can produce and study (de-)protonated and (de-)hydrogenated charge states, characterizing the electronic excited states and relaxation dynamics as a function of the presence and position of heteroatoms or functional groups in the structure. In the example shown, the vibronic structure of the first excited state of azaindole is seen to shift in wavenumber as a function of the charge on the molecule. As will be discussed below, these simple aromatics could be used as precursors to grow larger nanocarbons.

Multiwavelength Raman microscopy has proven to be a powerful and non-destructive tool for the characterization of carbon materials containing both aromatic domains and defects, from graphene to nanocarbons (see Sect. 35) and amorphous carbons [212] including nano-onions (see Sect. 8) (complementary to other characterization techniques like nanoIR—Sect. 13, REELS—Sect. 24, LIBS—Sect. 25, SEM—Sect. 27). Due to electronic resonances, Raman microscopy not only delivers vibrational information on the carbon skeleton. It also allows the characterization of defects, delivering details about structure, including indirect information about the edges decorating the aromatic skeleton. It has been shown that the H content in amorphous carbon is related to the relative intensity ratio of two bands (the "graphitic" G and "defect" D bands, see Fig. 37) [213], allowing processing effects such as heating to be investigated [214]. Depending on the way nanocarbonaceous particles form, they could experience porosities with a wide range of active surfaces.

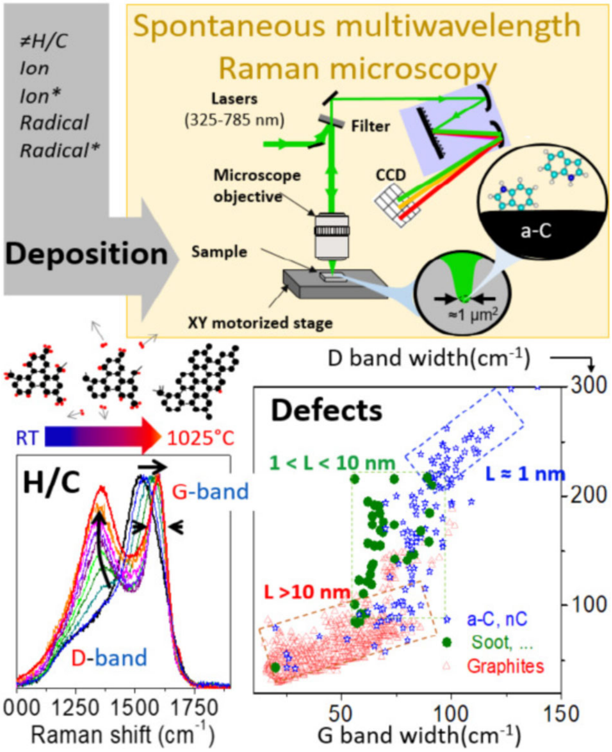

Fig. 37 Raman microspectroscopy as a probe of carbonaceous solids: technique especially sensitive to H/C ratio and to local defects at the nanoscale. Part of the figure has been adapted from [212]

Current and future challenges

Carbon in non-terrestrial environments cycles though multiple gas, solid and plasma phases, while being subjected to processing by means of heat, hydrodynamic shocks, cosmic ray interactions, and photons at energies across the electromagnetic spectrum. The question we wish to answer is: to what extent does processing and reactivity of nanocarbon in the gas phase impact the role of deposited macroscopic solids in non-terrestrial environments? Our experimental approach, detailed in the following, will specifically test how the H content, charge state, molecular size and geometry, and chemical composition of gas phase aromatic building blocks affect thermal properties and stability of the nanocarbonaceous solid formed.

A current challenge for laboratory astrophysicists is determining the formation route to molecular hydrogen in the interstellar medium. Polycyclic aromatic hydrocarbons are expected to become hydrogenated at intermediate stages during this process, and we can study singly hydrogenated aromatic neutral radicals with a discharge source in our molecular beam experiment [215]. By photodetachment of an electron from a deprotonated anion, we can produce the singly dehydrogenated neutral radical [216]. However, very few of such species have been studied to date and we aim to survey the spectroscopy and photophysical properties of these almost unknown families, looking at how the presence of heteroatoms like O and N impact their stability.

Raman spectroscopy analyses of amorphous carbons are well established for hydrogenated carbons, but this is not the case for amorphous carbons containing O and N. For these materials, a current challenge is to repeat what was already achieved for hydrogenated amorphous carbons. Indeed, in carbonaceous solids, the presence of elements other than H atoms (like O, N,...) bonded to the edges of aromatic rings affects Raman spectra by indirectly modifying the underlying carbon skeleton. The Raman cross section of the carbon skeleton is much more intense than that related to chemical bonds like C-O, C-H or C-N. Information retrieved for H, O and N content is thus indirect, obtained by interpreting a signature coming from the carbon skeleton. The issue is that this could lead to an incorrect interpretation and the challenge is thus to disentangle the different contributions to the Raman spectral bands. Three different but complementary strategies could be undertaken:

- *Producing solids with different H/O/N compositions by selective tuning of the molecules used as precursors.*
- *Performing an isotopic study as chemical bonds are dependent on the reduced masses, for a given precursor.*
- *Using Tip Enhanced Raman Scattering (TERS) or Surface Enhanced Raman Scattering (SERS) that could be more sensitive to the C-O, C-H and C-N bonds than classic Raman spectroscopy.*

Having identified the current challenges in each domain, we intend to go a step further and combine our experimental expertize in characterizing the geometry, electronic structure and dynamics of aromatic molecules in varying charge states and degrees of hydrogenation with our expertize in characterization of nanocarbon materials by Raman microspectroscopy. We will isolate and characterize simple aromatic molecules in our ion trap or molecular beam, then deposit them onto graphite substrates and reanalyze the resulting nanocarbon formed. We will investigate how the charge state and degree of hydrogenation of the simple precursor impacts the nature of the carbon layers deposited into the solid phase. Precursors may have a higher N or O content, to provide samples to benchmark the influence of these heteroatoms on the Raman signal. They may be deposited as radicals, to study the competing reaction pathways of dimerization versus grafting to the substrate versus polymerization upon the surface. Equally the gas phase precursors could be photoexcited to electronic or vibrationally excited states to investigate the role of internal energy in determining the branching ratio of products in the solid phase. Their thermal and photostability can be studied during Raman microscopy measurements (see Fig. 37).

Concluding remarks

The existing expertize in molecular photophysics of gas phase aromatics and spectral characterization of carbonaceous solids in our group will be combined to study to what extent does processing of nanocarbon in the gas phase impact the structure of deposited macroscopic carbonaceous solids in non-terrestrial environments. The key question we will address is how the degree of hydrogenation of small gaseous aromatics impacts their reactivity and the nature of the solid nanocarbon they form.

Acknowledgments

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24 Optical properties of nC species derived from reflection electron energy loss spectroscopy spectra

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Status

The optical constants and dielectric function are defined by the response of electrons of a solid to an external electric field. Such information has fundamental importance in both theoretical studies and applied physics. So, there is a continuous interest and effort for a long time to determine accurately the optical constants of solids. Along this line, traditional optical techniques, such as reflectance and absorption spectroscopy with ellipsometry measurements, were extensively used to obtain optical constants. Many of these available data was collected and synthesized as a database of optical constants for various materials [217]. However, most of the dielectric or optical properties lack data points in the energy range between 20 and 50 eV. Furthermore, the available data of a solid usually consist of different pieces measured by several research groups using different samples under different experimental conditions. Therefore, it is a real challenge to use them as potential applications. For this reason the electron energy loss spectroscopy (EELS) was introduced for deriving optical constants [218–221]. One of the main advantages of this technique was the simplicity in experiment requirements. In contrast with the optical measurements it also holds the opportunity to get the optical constant for nonzero momentum transfers.

Current and future challenges

Great progress in deriving the electron energy loss function (ELF) and thereby to get the optical constants of the samples from experimentally measured reflection electron energy loss spectroscopy (REELS) spectra have been made since the past decades. The precise description of the energy dissipation processes, the combined effects of multiple elastic scattering as well as bulk and surface inelastic scattering of an electron interacting with the sample system, is of crucial importance. Most of the previous works used either the original or the modified algorithm developed by Tougaard and Chorkendorff [222] aiming at extracting a single inelastic scattering distribution from REELS, where a measured REELS spectrum is described by multiple convolutions of single inelastic scattering distribution including differential inverse inelastic mean free path (DIIMFP) and/or differential surface excitation probability (DSEP) for surface excitations. These attempts promised advances in understanding of the electron-solid interaction and provide valuable optical data of insulators and metals. However, the algorithm has serious limitations. The most noticeable is that neither the *f*-sum rule regarding to the oscillator strength nor the *ps*-sum rule for perfect screening are fulfilled.

Advances in science and technology to meet challenges

In recent years, we have developed a high-precision method based on energy loss spectroscopic measurements of electrons backscattered from the examined sample [223]. We named the method reverse Monte Carlo method. Our method combines accurate simulation of backscattered electron loss spectra with a global optimization procedure. The authors of this section have shown the efficiency of the new method to extract the optical constants for solid materials from experimentally measured reflection electron energy loss spectroscopy (REELS) spectra [224,225]. As an example, they present results for iron but the method could be applicable to carbonaceous solid materials, and the corresponding optical constants (n and k indices) could be used to model astronomical spectra. The absolute value of the ELF can be extracted with the new model with a very low relative error and at the same time the *f*- and *ps*-sum rules also fulfilled with very high accuracy. The RMC model takes into account the elastic scatterings and both the surface and bulk excitation effects in the inelastic interaction while electrons crossing an interface between vacuum and solid by using a spatially varying DIIMFP under semi-classical framework.

For the characterization of the elastic process the Mott's elastic cross section is used by applying the partial-wave expansion method. For the description of the inelastic processes we have used the dielectric function formalism. In the procedure of RMC, an initial ELF was parameterized by several dozens of arbitrarily Drude-Lindhard functions as:

$$\mathrm{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right] = \sum_{i=1}^{N} A_i \left[\frac{-1}{\epsilon(q,\omega:\omega_{pi},\gamma_i)}\right] \tag{3}$$

where the $3N$ oscillator parameters, A_i, ω_{pi} and γ_i are, respectively, the oscillator strength, the energy and the width of the i-th oscillator. They are initially arbitrarily selected at the long wavelength limit, $q \rightarrow 0$. For finite q-values, the dielectric function $\epsilon(q,\omega)$ is extended with the scheme of Ritchie and Howie [226]. By the help of the ELF, the REELS spectrum can be simulated by employing the Monte Carlo (MC) simulation method for the electron transport. A goodness function of the ELF can be defined as the summed difference between the simulated spectrum and the experimental spectrum. Consequently, the problem to find the accurate ELF of a sample becomes the question to find the optimum set of the $3N$ oscillator parameters, which yields minimum value of the goodness function. So, using the successive approximation, the oscillator parameters was improved by minimizing the differences between a simulated and a measured REELS spectrum. The iteration was stopped when the simulated spectrum agreed with the corresponding measured spectrum with high accuracy. We note that for samples with complex ELF, like for the case of transition metals, fifty or more Drude-Lindhard type functions are needed for accurate description of the ELF. Determination of the ELF of the sample thus turns into a task of global optimization procedure to get the best oscillator parameters in a multi-dimensional hyperspace. To solve this, we used a Markov chain Monte Carlo (MCMC) sampling procedure, i.e., Metropolis importance sampling by adopting a simulated annealing method for adjusting the parameter set. As an example, the results of the calculation steps applying the RMC for iron sample are shown in Fig. 38. The optimized ELF is shown in red curve.

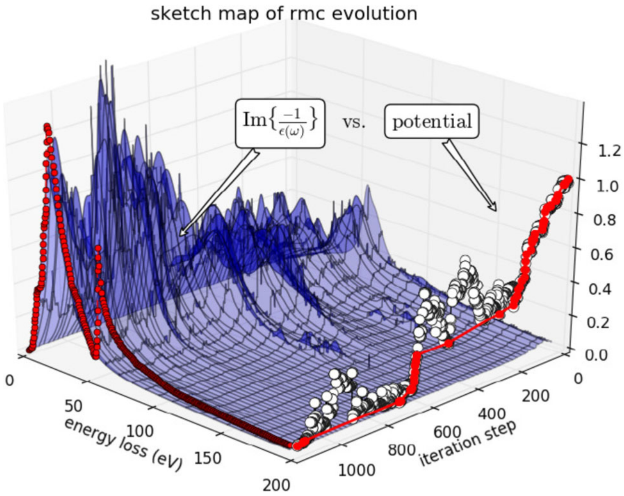

Fig. 38 Schematic diagram of the improvement of the ELF during the RMC simulation. Blue waves denote the updating of the trail ELFs with MCMC steps. True ELFs obtained finally by RMC are depicted in red dots on left. Variation of potentials of the trial ELFs are displayed on right with white dots and a decreasing line with red dots

Once the final ELF, $\mathrm{Im}\left[-1/\epsilon(\omega)\right]$, is obtained by the RMC method, the corresponding real part, $\mathrm{Re}\left[-1/\epsilon(\omega)\right]$, can be deduced via Kramers-Kronig relation. Then the complex dielectric function can be expressed as:

$$\begin{aligned}\epsilon_1 &= \frac{-\mathrm{Re}\left[-1/\epsilon(\omega)\right]}{\mathrm{Im}\left[-1/\epsilon(\omega)\right]^2 + \mathrm{Re}\left[-1/\epsilon(\omega)\right]^2}\\ \epsilon_2 &= \frac{\mathrm{Im}\left[-1/\epsilon(\omega)\right]}{\mathrm{Im}\left[-1/\epsilon(\omega)\right]^2 + \mathrm{Re}\left[-1/\epsilon(\omega)\right]^2}\end{aligned} \tag{4}$$

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ can be calculated as:

$$n = \sqrt{\frac{\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}}{2}},$$
$$k = \sqrt{\frac{-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}}{2}}. \quad (5)$$

Finally, to minimize the uncertainties of the obtained ELF the calculations were performed using various incident energies and the obtained ELFs are averaged for different energies to get the final ELF. Figure 39 shows the refractive index n and extinction coefficient k of Fe in the energy range of 0–180 eV with the widely quoted database of Palik.

Concluding remarks

We have shown the efficiency of our method by using various samples with the calculation of the ELF, the optical constants and the electron inelastic mean free paths, verifying the accuracy of the derived energy loss function with the f- and ps-sum rules [228, 229]. Our works clearly show and provide a new solution for mining fundamental optical constants (n, k) buried in REELS spectra. We show evidences that our present model behaves as the most adequate treatment to obtain optical constants from REELS. Although we present results for iron case it is generalizable for other elements. We are working on the new data base for elements used in practical applications, based on the method published in the recent work.

Acknowledgments

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25 Long-wave infrared laser-induced breakdown spectroscopy of complex carbon molecules in the vicinity of a laser-induced plasma

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Status

The study of laser-induced plasmas (LIPs) has advanced significantly, providing insights into rapidly expanding, hot, and partially ionized vapor plumes. These plasmas are of intense research interest due to their unique properties and potential applications. The field of laser-induced plasma research is crucial for its wide-ranging applications, particularly in the simulation of space plasmas and the analysis of carbon nanostructures. Laser-Induced Breakdown Spectroscopy (LIBS) has emerged as a powerful analytical technique within this field, offering a rapid and comprehensive method for elemental and molecular analysis. LIBS serves as a fast and versatile tool invaluable for quality control, ground truth analysis, and environmental monitoring [230–233]. In space research, laser-induced plasma can simulate conditions analogous to cosmic environments, such as those found in planetary atmospheres or interstellar regions. By generating high-energy plasmas, this technique enables the study of material interactions, elemental compositions, and processes under extreme temperatures and pressures, providing critical insights into astrophysical phenomena and advancing space exploration technologies. Furthermore, the field holds significant importance in the study of carbon nanostructures. The recent exploration of Mid- to Long-wave infrared (IR) emissions from laser-induced plasma has opened up new possibilities for detecting larger carbon molecules [230, 231, 234, 235], which are crucial for the advancement of nanomaterial science. This development has direct implications for the creation of carbon-based nanotechnologies and materials with novel properties. In our recent experiments, we tested anthracene and successfully observed the IR LIBS signatures of anthracene molecules and their breakdown products. This achievement highlights the potential of LIBS in analyzing complex carbon compounds and contributes to our understanding of molecular interactions within plasmas. Anthracene is a well-known and extensively studied organic compound in the field of organic chemistry. It serves as a model compound for investigating the properties and reactivity of larger, more complex polycyclic aromatic hydrocarbons (PAHs). The IR LIBS spectrum of anthracene provides crucial insights into its functional groups and molecular vibrations in the plasma plume. By analyzing this spectrum, we can identify and characterize various chemical bonds in the anthracene molecule, such as C-H, C-C, and C=C bonds. IR LIBS spectroscopy is instrumental in identifying the structural features of anthracene, including the presence of aromatic rings and the positioning of substituents on these rings. Understanding the IR LIBS spectrum of anthracene is essential for comprehending its chemical properties, reactivity, and practical applications in research and industry. Figure 40 presents the

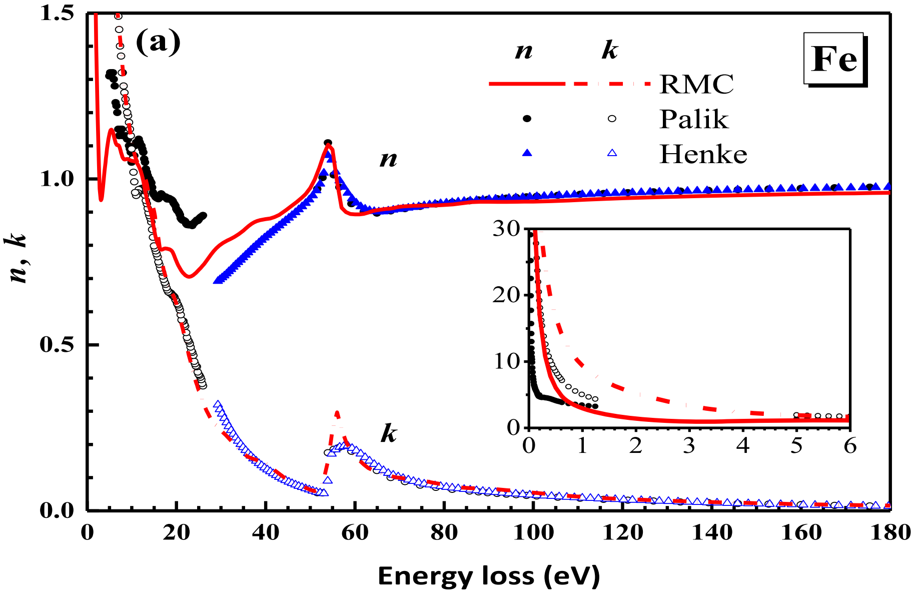

Fig. 39 Optical constants of refractive index n and extinction coefficient k of Fe obtained by RMC method together with the Palik's data (circles for n and open circles for k [217]) and with the Henke's data (triangles for n and open triangles for k [227])

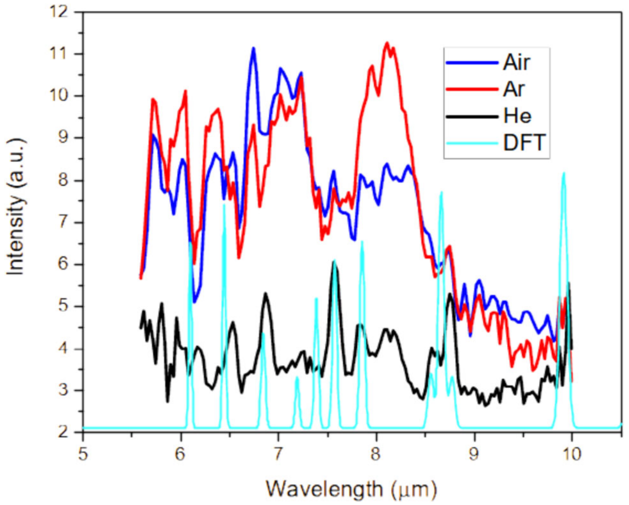

Fig. 40 IR LIBS spectra of anthracene under three different atmospheres: ambient air, Ar, and He. DFT calculated vibrational spectrum of gas anthracene is also plotted

IR LIBS spectra of anthracene under three different atmospheres: ambient air, argon (Ar), and helium (He).

The delay times were fixed at 3 μs with an integration time of approximately 220 μs. The spectrum obtained under He appears noticeably different from those obtained under air and Ar, both of which exhibit similar appearances. To evaluate the vibrational frequencies of anthracene gas molecules, density-functional theory (DFT) model calculations were performed using the ORCA quantum chemistry computational program package [236]. The application of DFT with the B3LYP exchange-correlation functional and the def2-TZVP electronic wave function basis set showed good agreement with the IR LIBS experiments (Fig. 40). Within the He spectrum, vibrational signatures of intact anthracene molecules in the gas phase are readily observed and identified, including aromatic CC stretching and CH bending bands located at 6, 6.5, 6.86, 7.23, 7.4, 7.56, 7.84, 8.5, 8.7, and 9.9 μm. However, within the air and Ar spectra of anthracene, numerous intense emission features are present alongside those from the intact anthracene gas molecules, with the most prominent non-anthracene features identifiable around 7 and 8.1 μm.

Current and future challenges

To fully understand these IR LIBS spectral features, we need to explore the IR emission signatures of potential carbon-containing molecular products of plasma. One of the challenges lies in the limited availability of IR signature databases for carbon compounds in high-temperature environments. Addressing this challenge will be crucial for advancing our understanding of the chemical processes occurring in laser-induced plasmas and their applications in various fields.

Advances in science and technology to meet challenges

The study of polycyclic aromatic hydrocarbons (PAHs) using IR LIBS presents unique challenges due to the complex nature of these molecules and the environments in which they are studied. One major challenge is the lack of comprehensive databases for IR signatures of carbon compounds in high-temperature environments, which are crucial for accurate identification and analysis of PAHs and their breakdown products in laser-induced plasmas. To mitigate these challenges, several approaches can be taken. First, investing in the creation and expansion of databases containing IR signatures of carbon compounds, specifically focusing on high-temperature environments, is essential. Collaborating with international research groups and institutions to compile and standardize these databases would enhance their accessibility and use. Additionally, utilizing and developing advanced computational methods, such as density-functional theory (DFT) and machine learning algorithms, can provide a theoretical basis for experimental validation and identification of PAHs.

Improving the spectral resolution of IR LIBS systems is also critical to distinguish between closely spaced spectral features, enabling better identification of specific functional groups and molecular structures in PAHs. Conducting experiments under controlled atmospheric conditions, such as inert gas environments like helium, can reduce interference from air and enhance the detection of intact PAH molecules and their breakdown products. Moreover, developing standardized sample preparation techniques is crucial to ensure consistent and reproducible results, particularly for solid-state PAH samples.

Effective advancements in science and technology are crucial for addressing these challenges. The design and fabrication of advanced IR LIBS instruments with enhanced detection capabilities are imperative. These improvements include better laser sources, detectors, and optical components. Our recent innovation is a state-of-the-art 2D MCT array detection system. It is capable of quickly capturing a broad spectrum of atomic and molecular LIBS emissions in the long-wave infrared region (LWIR, approximately 5.6 to 12 μm) in under a second [237]. This technological breakthrough significantly boosts our ability to analyze PAHs and other compounds by providing rapid and detailed spectral information. Additionally, our ongoing development of sophisticated data analysis tools and software is crucial. These tools, which incorporate machine learning and artificial intelligence, are essential for handling complex spectral data and enabling automated feature recognition and interpretation.

Fostering interdisciplinary collaboration between chemists, physicists, material scientists, and engineers is crucial to address the multifaceted challenges in PAH analysis using IR LIBS. Establishing standardized protocols and reference materials for IR LIBS analysis of PAHs will ensure consistency and comparability of results across different laboratories and studies. By addressing these challenges and implementing these mitigations, the field of IR LIBS study on PAHs can advance significantly, leading to a deeper understanding of these complex molecules and their behavior in various plasma environments.

Concluding remarks

The field of laser-induced plasmas (LIPs) and Laser-Induced Breakdown Spectroscopy (LIBS) remains an essential and dynamic area of research. The challenges associated with analyzing polycyclic aromatic hydrocarbons (PAHs) using IR LIBS, such as the need for comprehensive databases of IR signatures for carbon compounds at high temperatures, are being met with innovative solutions and collaborative efforts. Our recent introduction of a state-of-the-art 2D MCT array detection system is a testament to the ongoing advancements in enhancing the capabilities of IR LIBS instruments. This system enables swift and detailed spectral analysis of PAHs and other compounds in the long-wave infrared region, paving the way for new research opportunities and applications. As we continue to advance in the field of laser-induced plasma research, we expect to deepen our understanding of the intricate physical and chemical processes within these plasmas. Refining analytical techniques and broadening the spectrum of detectable emissions will lead to more precise and comprehensive elemental and molecular analyses. Exploring the infrared emissions from laser-induced plasma may reveal the presence of larger carbon molecules, which would have profound implications for nanomaterial science and carbon-based nanotechnologies. Moreover, advancements in simulating space plasma conditions could yield significant breakthroughs in space exploration and enhance our comprehension of the cosmos.

Acknowledgments

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26 Mutual neutralization in collisions between oppositely charged ions in space

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Status

Mutual Neutralization (MN) between cations and anions; $A^+ + B^- \rightarrow A + B$, is a fundamental charge-recombination process, which is significant for plasma environments cool enough to accommodate an anion population. Two examples of space environments where this occurs are in dark interstellar and circumstellar clouds where carbon containing anions have been identified [88], and in stellar atmospheres where detailed

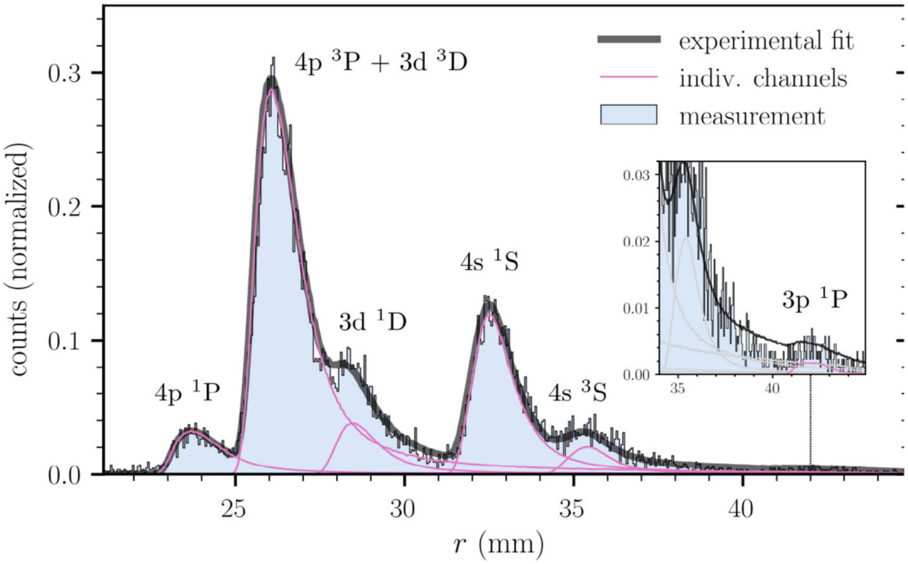

Fig. 41 Distribution of measured mutual distances of neutral MN products at detection. Each channel gives a contribution determined by its related kinetic-energy release and the coefficients of the linear combination of such contributions giving the best fit to the data are the measured branching fractions. Figure reproduced from Ref. [240]

knowledge of the reactions with the abundant atomic hydrogen anions have proven to be essential for deducing correct stellar metal abundances from astronomical observations [238]. For detailed understanding of the role of such processes, experimental studies with final-quantum-state selectivity are essential for sub-eV collisions in the center of mass frame. This has been achieved in a single-pass merged-beams setup at Université Catholique de Louvain [239] and in the cryogenically cooled Stockholm University double storage-ring facility, DESIREE [166, 240]. A wide range of studies of MN interactions involving atomic collision partners have been reported using these devices. An example is shown in Fig. 41, where the final states in $Mg^+ + D^- \rightarrow Mg + D$ reactions are clearly resolved and may thus be used to benchmark theory and models [238].

Recently, MN experiments have been carried out at DESIREE with molecules ranging in sizes from the simplest diatomic [241] to triatomic [242] and complex ones such as, e.g., Polycyclic Aromatic Hydrocarbons (PAHs) and fullerenes [243]. In these studies, the reaction rates and final state distributions may be monitored as the ions cool when they are stored on timescales exceeding minutes. This is key to mimic the conditions in, e.g., interstellar molecular clouds where MN processes may be important for the ionization balance that defines the chemistry in such environments [88, 244]. Here, parallel advances in theory and modeling are of equal importance. The first such combined experimental and theoretical study of an MN reaction involving two oppositely charged complex molecular ions (fullerenes) [243] demonstrates the importance of considering the polarizabilities, the finite sizes, and the final states of the collisions partners for reliable estimates of MN rates. Studies of these types may significantly advance the understanding of the formation and destruction of molecules in space, including a wide range of carbon molecular nanostructures discussed in this roadmap (see e.g., Sects. 4, 14, 18, 19, 20, 33, 35).

Current and future challenges

Major challenges in future studies of MN reactions involving molecular and cluster ions include:

- Identify key molecular systems to be studied in the laboratory: More than 300 molecular species have been identified in space and the list is ever expanding. Thus, studying MN for all combinations of two of them or with all possible atomic collision partners is not feasible.
- Produce the ions in well-defined or narrow ranges of rotational and vibrational quantum-states: This is particularly important for complex molecules that cool too slow in isolation to equilibrate in cryogenic storage devices.
- Prepare isobaric and isomerically pure ion beams: Key to study how the molecular structure affects MN rates in interactions with, e.g., biomolecules including the building blocks of life.
- Detect two or more neutral reaction products with high efficiency and to determine their masses: This allows disentangling non-destructive MN reactions from bond-breaking and bond-forming reactions.
- Resolve close-lying states of the reaction products: A situation that is common for complex molecules such as, e.g., PAHs and fullerenes.
- Measure absolute reaction cross sections and rates as a function of center-of-mass collision energy: So

far this has only been achieved in single-pass experiments [239].
- Test and validate models that have been developed and successfully used for atomic MN: Key step to further refine or develop new models for molecular MN, which is significantly more demanding.

Advances in science and technology to meet challenges

Most molecules and clusters have forbidden or weakly allowed ro-vibrational transitions with radiative lifetimes exceeding those of beams stored in cryogenically cooled devices. Production of pre-cooled ions is therefore often necessary to achieve quantum level control of the ro-vibrational states of the reactants in mutual neutralization experiments. Recent developments of He-droplet [203, 245] and supersonic expansion techniques allow for producing cold ions directly and are expected to be important to overcome this challenge, while conventional ion sources may also be used for this purpose if they are combined with cooled ion traps [246]. Pre-trapping may then be used to accumulate ions outside the storage device while a cold ion bunch is being stored for the actual experiment. This allows using ionization methods that typically produce low ion currents such as, e.g., laser desorption and electrospray ionization. Combined with isomer selection techniques [247] this will open up for studying MN processes with, e.g., biomolecular system in unprecedented detail. Improved sensitivity means that beam impurities (isobars) may contribute significantly to the measured reaction rates. Here, methods to resolve and get rid of such impurities are needed as have recently been developed at the Cryogenic Storage Ring (CSR) in Heidelberg [248].

Detection of neutral products with keV energies in the laboratory reference system are an essential part of merged-beams experimental studies. Current technology based on electron-multiplying devices yield the necessary time and position information, but do not reveal the identity of individual detected particles. To achieve that, μ-calorimeter techniques are required in which the kinetic energies are determined and related to the mass of the particles through their known velocities. A μ-calorimeter array with properties adequate for use in DESIREE is being developed in collaboration with, and based on earlier work by, groups at the Kirchhoff Institute and the Max-Planck Institute for Nuclear Physics, both in Heidelberg [249]. The ability to determine the identity of each detected particle will open new avenues of opportunities in merged-beams experiment: This will for examples enable the distinction between pure electron-transfer processes and chemical reactions and offer direct detection of processes in which the two oppositely charged molecular ions are fused to a single compound.

Final states of MN processes are separated by the physical separations of the products, which are determined by the kinetic-energy releases characteristic of each channel. The resolution is then limited by the uncertainty in the position at which the reaction took place and therefore limited due to the finite length of the interaction region. One way to improve the resolution drastically is to analyze the light emitted from neutrals formed in MN processes, and in DESIREE a parabolic mirror, which significantly increases the efficiency of the light collection has been installed recently. Detecting such photons in coincidence with the reaction products allows for background free measurements and more detailed information on the reaction dynamics.

Applications in, e.g., astrophysics of results of MN experiments most often need absolute reaction cross sections and rates to enter in models. Often such absolute numbers are provided by theory, with the role of the experiment being only to validate the theory by verifying other predictions of the calculation as, e.g., the branching fractions into possible final-state channels. While this is a valid procedure, it is desirable to be able to measure absolute cross sections directly for a range of bench-marking collision systems. In order to extract absolute cross sections from the measured rates, it is necessary to measure the ion intensities and the effective overlap of the two beams. The latter is represented by the so-called form factor and is challenging to determine, in particular with stored ion beams where narrow slits can not be applied. For many atomic ions, storage prior to the MN reactions is not necessary and for such systems absolute cross sections can be measured in single-pass mode. From comparisons between single-pass and stored beams studies in DESIREE for the same collision systems and overall conditions, the information needed in order to extract absolute cross sections from experiments with stored and relaxed molecular ions can become available.

Concluding remarks

Recent experimental advances allow studies of mutual neutralization reactions with internally relaxed molecular ions under conditions mimicking those in space. This is key to unravel the significance of such processes for, e.g., the ionization balance in interstellar clouds that determines the evolution of molecules therein. Close collaborations with astronomers and theoreticians are needed to address current and future challenges to answer such open questions. This involves guiding the technical and instrumental developments as well as identifying key molecular systems to be studied in the laboratory. The NanoSpace COST Action CA21126 provides the ideal platform for such collaborative efforts.

Acknowledgments

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27 Engineered nanostructured materials with nanostriped surfaces: bridging the gap between Space and Earth

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Status

Advanced materials, such as nanostructured materials play an important role in terrestrial environments, since they have distinctive properties and offer various applications, like air filtration, water purification and soil remediation because of their increased surface area and reactivity. Besides, nanostructured materials contribute to the development in energy storage devices, sensors and coatings, that enhance performance in different terrestrial applications. These include naturally occurring, as well as engineered ones. Nanostructured materials, such as graphene, carbon nanotubes, nanostructured clay minerals, silicate, metal, magnetic and ice nanoparticles are found in both Space and on Earth and have similar characteristics, related to low dimensions and structure-derived specificities. Yet, in contrast to terrestrial environments, space nanomaterials behave differently under conditions such as vacuum, cosmic radiation and microgravity. Investigating both terrestrial and space-based nanostructured materials is vital for revealing the fundamental building blocks of the Universe, the elaboration of innovative technologies on Earth, inspiring novel applications for nanostructured materials on Earth. However, while those on Earth are created for various applications, those in space influence the formation and evolution of celestial bodies, having an impact on astronomical phenomena and cosmic structures. In contrast to naturally occurring nanostructured materials in Space and on Earth, artificially synthesized ones can be nanoengineered with precise control over their structure and geometry at the nanometer scale and can play an important role in linking up Space and Earth, contributing to advances in industry, medicine and environment.

Current and future challenges

Advanced materials are confronted with various challenges that hinder their widespread application. Firstly, there is the cost issue. The development and production of advanced materials are costly, thereby hindering its widespread adoption. Scalability is another challenge to address here. Although some materials appear to hold promise in laboratories, it is problematic producing them on an industrial scale. Matters become more complicated because of complex manufacturing processes. Efficient production may be slowed down by the need for delicate processes in making high-tech materials. Also, ensuring that they will last and work well in real-life conditions is not an easy thing to do. Besides, different environmental stresses will occur wherein long-term performance should still be ensured. Efficient production may be slowed down because of lack of sophisticated techniques that are required for the production of advanced materials. Besides, ensuring the long-term performance and reliability of these materials in various applications is a significant challenge. Also integration of advanced materials with the already existing technologies may also be a challenge due to compatibility issues that might arise. At the same time environmental aspects also play a key role here. Because of this purpose ranging from exfoliation to production and ultimate disposal must be managed closely so as to reduce any adverse environmental impacts. Innovative solutions are needed to resolve these issues. Furthermore, looking forward into what lies ahead for advanced nanomaterials there are several challenges that need addressing. One is customization and tailoring; since industries are growing continuously, there is an increasing demand for application-specific advanced materials. Another one is multifunctionality that should be considered as a major target. This has given rise to development of multi-functional nanocomposites which have exhibited superior performance over an extensive range of applications, thus driving innovation in nanomaterial synthesis. One more challenge is the efficient integration of nanomaterials into larger structures preserving their distinctive properties. For this, advanced fabrication techniques and a good knowledge of nanoscale phenomena are required. In the light of sustainability, the development of ecologically clean materials, as well as processes becomes important. It should be noted that biocompatibility is an essential feature especially in medical applications. Addressing these issues may have significant implications for nanostructured materials with nanostriped surfaces among other advanced materials that could transform industries and impact human lives.

Advances in science and technology to meet challenges

The above-mentioned challenges concerning advanced materials require a comprehensive approach. Nanostructured materials with nanostriped surfaces constitute advanced materials that possess unique enhanced electronic, optical and other properties, as well as functionalities due to the presence of narrow stripes with

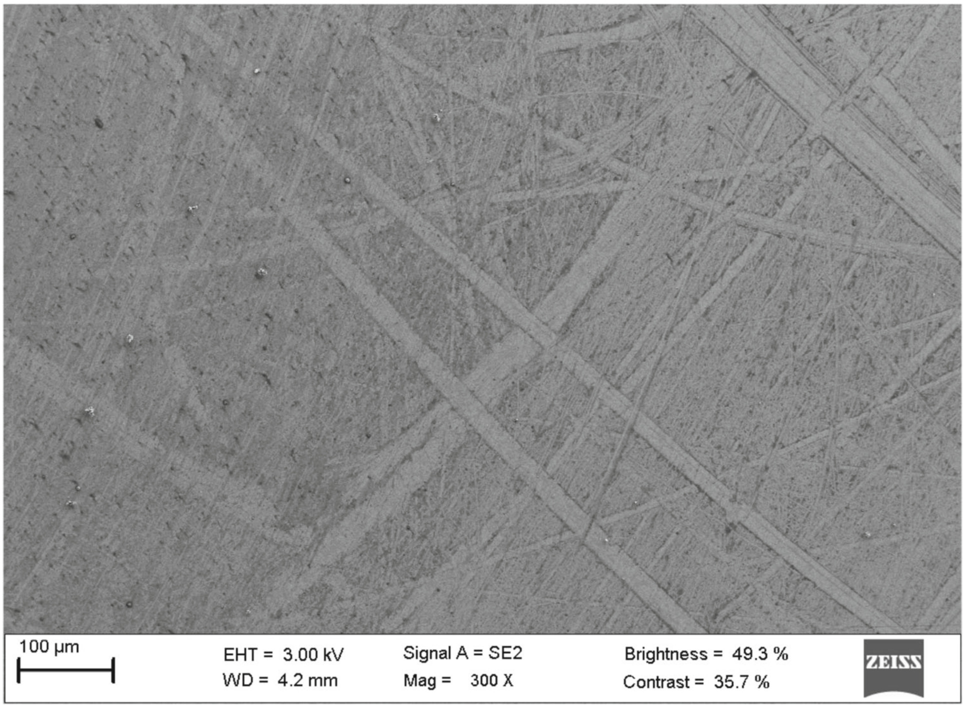

Fig. 42 Scanning electron microscope (SEM) image of mono-and few layer graphene sheet consists of the nanostripes on Si/SiO$_2$ substrate with atomically flat surface achieved using pressure of $\sim$ 200 Pa at rubbing (with bulk graphite powder) circular cycles of 500. The rubbings are performed manually. Figure adapted from [250]

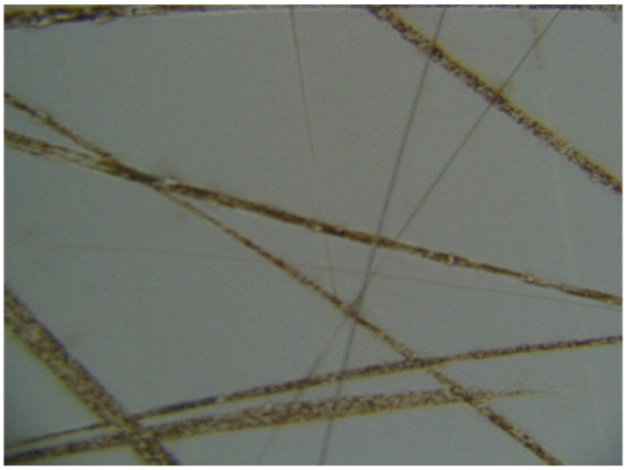

Fig. 43 Optical image (20x) of graphene (thick) and h-BN (thick) nanostripes on Si/SiO$_2$ wafer at applied pressure of $\sim$ 200 Pa. The rubbings are performed manually. The number of rubbing circular cycles is 1000 for 200 ng bulk h-BN powder with 184 nm (commercial quality) crystallite size and 800 for graphite powder. Figure adapted from [250]

widths in the range of a few nanometers on the surface. These nanostripes can be nanoengineered through various techniques to alter the surface properties for various applications.

The recently developed Substrate rubbing technology (SRT) [250–253], which is very simple (one-step), extremely fast (60 s), very cheap, transfer-free, highly productive, ecologically clean and universal, allows obtaining 2D sheets with nanostriped surfaces, heterostructures and nanocomposites based on them and nanoengineered biostructures which can be applied in various fields. These nanostripes can be obtained manually or mechanically by rubbing layered bulk materials on different substrates at atmospheric pressure conditions without using any template and technique. The nanostripes are mono-, few- and multiple atomic layers of exfoliated flakes organized in self-assembled narrow bands of nanosized quantum dots. Due to their 2D nature, these distinctive novel nanostriped nanosheets (see Fig. 42) and structures (Fig. 43) are unique as they have a high quality, large area and unique structure (composed of arrays of self-assembled nanosized quantum dots). More so, they have novel electrical, mechanical, thermal, and optical characteristics, which can lead to a variety of applications. The discovered groundbreaking one-step rubbing process allows creating unique 2D nanostructures with different nanoarchitecture of unique nanostripes with exceptional properties. SRT allows also nanoengineering the size, shape and surface morphology of nanostriped nanostructures at the nanoscale with enhanced properties and functionalities that would meet human needs in many areas. Nanostriped surfaces of engineered nanostructured materials are in a position to help solve the gap between terrestrial and space-based natural nanostructured materials, thus establishing a connection between nanomaterials existing in Space and those on Earth. Naturally occurring and engineered materials exhibit unique properties at nanoscale which make them highly adaptable to the challenges experienced in space exploration, as well as on Earth. Engineered nanostructured materials could play an important part in space exploration. Being lightweight and possessing enhanced mechanical strength and thermal stability, they would be perfect candidates for constructing durable and lightweight spacecraft components. Also, the use of nanostructured materials with nanostriped surfaces can help in creating more efficient advanced propulsion systems which can make space travel faster. Moreover, these materials can enhance the performance of spacecrafts by providing improved shielding against radiation, as well as micrometeoroids while also allowing for comfort and greater flexibility for astronauts. On Earth engineered nanostructured materials with nanostriped surfaces can be applied in diverse fields, such as electronics, energy, healthcare, and environmental remediation. Nanostructured materials used in electronics have made it possible to produce smaller chips and devices that are faster and energy-efficient, such as transistors and sensors. As for healthcare they can be used in drug delivery systems, diagnostic devices, tissue engineering, etc. Furthermore, nanostructured materials with nanostriped surfaces contribute to the development of renewable energy technologies by increasing the efficiency and durability of solar cells and batteries. Besides, they also play an important role in environmental sustainability through the development of efficient pollution sensors, water purification membranes and catalysts for clean energy generation.

Concluding remarks

The study of natural terrestrial and space nanostructured materials, as well as artificially synthesized and nanoengineered ones with nanostriped surfaces is necessary to understand the Universe's basic building blocks, as well as the creation of innovative technologies on Earth, that may give impetus for new applications of nanostructured materials on Earth. In summary, these nanoengineered nanostructured materials with nanostriped surfaces serve as a bridge between Space and Earth thereby providing innovative solutions to problems faced by both. Their remarkable properties make them indispensable in terms of technological advancement, enhancing human life and Space exploration.

Acknowledgments

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28 Ballistic conduction of carbon molecules

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Description of the state of the art

Carbon stands out among the elements. It is the essence of life. What makes C special is that it is the smallest element having four valency electrons. Besides bonding with other life-producing elements including H, 0, N, P and S on Earth, C also bonds with itself. In the diamond, it uses all its valence electrons for bonding, whereas in graphite or fullerenes, three electrons suffice, leaving one delocalized electron to hop from one C atom to another. Molecules contributing delocalized electrons are called sp^2 or Π systems.

The Hückel tight-binding model assumes that the different electron orbitals can be added to give an approximation to the Hamiltonian. Recall that the Hamiltonian H^M of the molecular graph (or Π-system) M having n–carbon atoms, is $\alpha\mathbf{I} + \beta\mathbf{A}$, where $\mathbf{A}$ is the $n \times n$ adjacency matrix of the carbon skeleton of the molecular graph associated with M. An ij entry of $\mathbf{A}$ is 1 of there is a σ bond between atoms i and j of M and 0 otherwise. The Coulomb parameter α and the resonance integral β are set to zero, and 1, respectively, to give the normalized effective Hamiltonian $\mathbf{A}$.

The tight–binding quantum mechanical model simplifies Schrödinger's equation, describing the electron density function ψ, to $\mathbf{A}\psi = E\psi$, yielding the allowed quantized energy levels, E, for the molecule [254]. The vector ψ gives an orbital which is the density function in the molecule measured by the probability that the delocalized electrons of the molecule occupy the associated energy level E [255,256].

Carbon is important for life as we know it. Carbon compounds are the foundation of life on Earth, and CH_3^+ plays an important role. The simple organic ion having just one carbon atom and three hydrogen atoms, reacts with other molecules to form more complex ones related to living bodies [257]. Recent NASA research shows that the James Webb Space Telescope detected the methyl cation (CH_3^+) and other polycyclic aromatic hydrocarbons (PAHs) in a young star system, located about 1,350 light-years away in the Orion Nebula [257]. NASA's discovery shows that there are basic building blocks for life in space. Healthy human cells conduct electrical currents. We think, move and feel thanks to electric flow through the nervous system that enables signals to be sent throughout the body and to the brain.

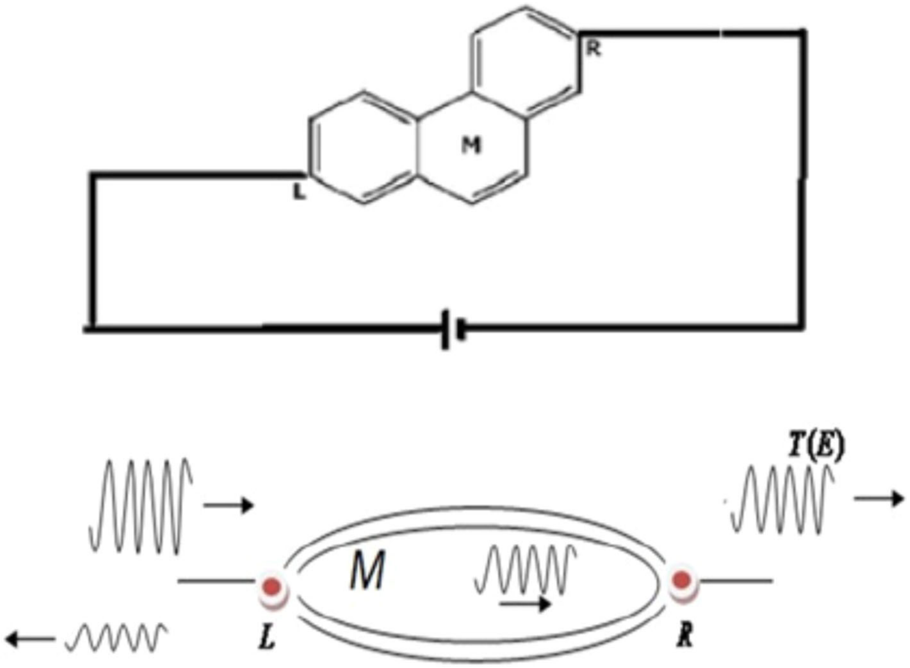

Fig. 44 (i) A molecule M connected across a voltage at two atoms L and R. (ii) The SSP model for a ballistic electron entering at energy E via atom L

However C is hardly ever mentioned as the source of electric current in living cells.

The topological structure of carbon material lies within the nanoscale and forces ballistic electrons to flow within a confined space. The mean free path of the energetic electrons is much longer than the size of the electrical contact atomic points. In such situations, quantum mechanics can be applied to ballistic conduction using electron wave functions which exhibit coherent interference. A spectral graph theoretic treatment predicts possible reactivity and transformation pathways of nano–carbon (Fig. 44).

Challenges and new directions: Progress beyond the state of the art

The source and sink potential (SSP) model describes ballistic molecular conductivity. Introduced by Ernzerhof et al. in 2004, the SSP model predicts the fractional transmission $T(E)$ of an electron through a hydrocarbon or carbon molecule as a function of energy E [258, 259].

As shown in Fig. 1, the molecule with two prescribed connection carbon (C) atoms (L and R terminals) forms a molecular electronic device (MED) connected in a circuit by two semi–infinite wires across a small bias voltage [260, 261]. A graph theoretical treatment considers the 0–1–adjacency matrix $\mathbf{A}$ of the molecular graph which is the C–framework where the edges are the C–C sigma bonds. The molecules are $\pi-$systems, that is each C atom of the neutral (uncharged) molecule contributes a delocalized electron. These are the electrons which may produce a flow of electricity through the molecule. The number of non–bonding orbitals in the molecule is the nullity of $\mathbf{A}$ [256]. The rational function $T(E)$ involves the characteristic polynomials of the molecular graph and three of its subgraphs that depend on the connection vertices. The transmission $T(0)$ at the Fermi level of energy leads to selection rules that distinguish 11 possible cases depending on the nullities of the molecular graph and its three subgraphs [262]. The presence of the delocalized electrons may lead one to expect all MEDs to be conductors. This is not the case. A molecule conducts or acts as an insulator depending on the underlying molecular graph and its connection atoms. We showed that in general, a molecule can change its transmission properties from conduction to insulation by using appropriate connection atoms for the desired electrical behavior [255, 260]. By considering all the possible MEDs, a clear classification of which topologies of carbon molecules allow ballistic interaction can predict carbon structures likely to be produced in space.

Advances in science and technology to meet challenges

Most molecules exhibit mixed (X) conductance. However we showed that omni–conducting (C) and omni–insulating (I) molecules exist. In these molecules the electric behavior is independent of the connecting atomic terminals [262]. Our goal is to obtain a complete classification in which every possible single-molecule, two-lead MED based on the carbon framework of any conjugated π system has its place within the structure. A refinement of the selection rules considers terminal vertex pairs at an odd distance, a non–zero even distance or the zero distance apart. Conductance or insulation depends on whether the nullity of the molecule is 0, 1 or more than one [263]. The electrical behavior is expected to be omni–conducting (C), omni–insulating (I) or mixed (X). The combinations of the electrical behavior and the nullity type for the three different distance categories give 81 possible cases. We have proved that 42 cases are mathematically impossible. Examples of molecules populating another 35 cases have been found among relatively small molecular graphs. To resolve the remaining four open cases, new methodologies need to be devised [263].

Concluding remarks

There are many questions we need answers for. Does predicted ballistic conduction explain mechanisms of interaction with carbon in space? Unexpected emission and absorption spectral lines, that have been observed recently, need to be identified. Are the electrical (quantum mechanical) properties and structure of nano-carbon molecules altered in the absence of Earth's atmosphere? Do carbon molecules, known to be conducting, remain so in space? Using data bases of emission and absorption spectra of molecules in space, which distortion, shifting or splitting of energy levels may account for unexplained spectra? Is there distortion of the bonds for degenerate energy levels explained by the Jahn-Teller effect? At the Fermi level, nut fullerenes have non-zero spin at every carbon atom so that each atom is predicted to participate in reactions [256]. Do these exist in space? Analysis of data bases of emission and absorption spectra of molecules in space may lead to the discovery of carbon molecules unknown to us. Are there molecules which are unstable in our atmosphere but occur in space? At present there are more questions than answers. Full use of the mathematical, scientific and technological expertize available can lead to significant progress.

Acknowledgments

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29 Catalytic properties of fullerenes in non-terrestrial environments

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Status

Fullerenes have been identified as diffuse interstellar band carriers [36]. There are studies which have found fullerenes to be effective catalysts in processes like hydrogenation, hydroformylation, etc. While these properties make them attractive for catalytic applications, it also points out the potential to play a significant role in astrochemistry, the formation of organic molecules, and the study of origin of life chemistry. In this regard, below we present a brief summary of the current studies about various categories of molecules.

PAHs: Fullerenes are shown to serve as excellent catalysts for H-transfer reactions, such as hydrogeneration and hydrodealkylations. They are also efficient in converting methane into higher hydrocarbons. Doping with elements like potassium and manganese can enhance their selectivity for C_2 and higher hydrocarbon species. Additionally, due to their resilience to gamma radiation fullerenes can play a role in various astrochemical activities and potentially lead to the synthesis of amino acids. Furthermore, fullerenes are capable of absorbing polycyclic aromatic hydrocarbons (PAHs) and are effective catalysts for hydrocracking coal extracts that contain PAHs. They also seem to have a role in the formation of PAHs in the interstellar medium as catalysts. The two main hypothesis in the origin of life are iron-sulfur theory [264] and RNA world hypothesis [265]. PAH world hypothesis is a precursor of RNA world hypothesis. Fullerenes are the degradation products of PAHs and therefore fullerenes might also have a role in the PAH world hypothesis.

Tholins: Tholins are organic molecules generated when simple carbon-containing compounds are irradiated with solar UV or cosmic rays. Fullerenes play a role in activating the C-H bond of methane and promoting its conversion into higher hydrocarbons. They can also trap, adsorb, and desorb methane and have catalytic activity in the production of hydrogen (H_2) from methane (CH_4). Furthermore, fullerenes can trap ethane and adsorb water [266], although these compounds have not been extensively studied in terms of catalysis. Additionally, the interaction between fullerenes and molecules like carbon dioxide (CO_2) and nitrogen (N_2) has not been explored much in the context of catalysis.

Other molecules regarding origin of life: Fullerenes have the capacity to trap ammonia, formaldehyde, hydrogen cyanide, and acetylene [267]. There is also the possibility of amination of fullerenes [267]. These interactions with life-related molecules have not been extensively studied in the context of catalysis with fullerenes. Furthermore, acetylenes can produce fullerenes, where acetylene itself acts as a catalyst in the process. Acetylene can bond to C_{60} with the assistance of Wilkinson's catalyst, and cyanoacetylene can transform into cyclic cyanide in the presence of C_{60}^{2+}.

As summarized above, many aspects of fullerenes catalytic behavior and interactions with specific molecules remain unexplored and offer opportunities for research from which significant insight could in astrochemistry and astrobiology studies.

The life began in a prebiotic soup as the Miller-Urey experiment describes, and the prebiotic reactions' intakes might be sourced from both terrestrial or exogenic sources. Our own research focuses on the catalytical effects of fullerenes on the Miller-Urey chemistry.

Current and future challenges

Numerous challenges surround the utilization of fullerenes [268], particularly in the context of catalysis. One pressing challenge is comprehending the new chemical reactivity of C_{60}, prompted by its unique 3D geometry, which offers a rich landscape for diverse chemical reactions. However, essential reactions that involve transition metal catalysts for transforming fullerenes into more advanced structures have not been thoroughly explored, making predictions regarding reactions with fullerene derivatives an ongoing challenge. Moreover, creating supramolecular architectures involving fullerenes that closely mimic natural photosynthetic processes is an area of exploration but also a challenge. Bridging the gap between scientific discovery and practical implementation is an overarching challenge, particularly in considering the timeframe for applications. In the realm of photocatalysis, combining fullerenes with semiconductor materials demonstrates the potential for enhancing efficiency.

Nevertheless, understanding the underlying mechanisms, particularly for visible light catalysis, remains a significant challenge. Practical considerations, such as selectivity in complex solutions, chemical stability, and the quantitative impact of fullerene size and thickness on composite systems, are also key challenges. The purification of fullerenes, due to their cost and complexity, necessitates advanced technologies. Moreover, the utilization of theoretical calculations to gain insights into photo-catalytic mechanisms and optimize fullerene-semiconductor composite structures poses challenges. The configuration control of fullerene-modified composite catalysts, including the development of simpler synthesis methods for mass production, is an area demanding further research. Furthermore, exploring the broader range of fullerene types and their derivatives for environmental catalysis is encouraged. Attention should be given to the treatment of diverse pollutants beyond organic dyes and heavy metal ions, including persistent organic pollutants and gas phase pollutants, and the environmental risks associated with photocatalysis, necessitating in-depth examination. Thus, the challenges encompassing fullerenes and nanocarbons in catalysis range from understanding their surface chemistry to clarifying their roles as catalysts, investigating the relationship between active sites and reactivity, and advancing architectural engineering.

Advances in science and technology to meet challenges

Focusing on our own expertize; theoretical studies involving quantum mechanical simulations, molecular dynamics calculations and emerging field of machine learning techniques has gained importance in interpreting the experimental and observational results if not simply guiding their direction.

Figure 45 represents one such result from our studies where fullerene existence has been shown to reduce the reaction barrier hence pointing out a catalytic effect on one of the key reactions in Miller-Urey experiment.

The integration of quantum mechanical simulations [269] and machine learning techniques has opened new possibilities in recent years especially in the catalysis studies. The quantum mechanical simulations has provided valuable insights into the catalytic behavior of fullerenes. This advancement has facilitated the design of more efficient and selective fullerene-based catalysts. Besides, the advances in techniques of characterization, synthesis, catalysis, spectroscopy, and theoretical modeling for nanocarbons might also be applicable for fullerenes. The innovations in synthetic methodologies and surface functionalization have expanded the range of tailor-made fullerene catalysts, granting precise control over their activity and selectivity. The emerging 3D printing techniques in the catalysis provides broad and multidisciplinary applications [270].

In space exploration, advancements in additive manufacturing techniques for in situ nanocarbon production [271] enable autonomous fabrication and assembly of nanocarbon-based structures. Integrating state-of-the-art spectrometers and sensors on space platforms might allow real-time monitoring of nanocarbon reactivity and structural changes under space conditions, leading to a deeper understanding of their behavior in extraterrestrial environments.

Concluding remarks

The catalytic properties of fullerenes offer exciting opportunities with unique properties like high surface area and electron affinity, especially in non-terrestrial environments, making it a promising candidate for the origin of life. Understanding and controlling their unique chemical reactivity due to variable 3D geometries is though complex. The chemical reactivity of endohedral fullerenes remains largely unexplored, and taming weak forces like hydrogen bonding for stable supramolecular structures is challenging. While many uncharted territories remain, this research direction

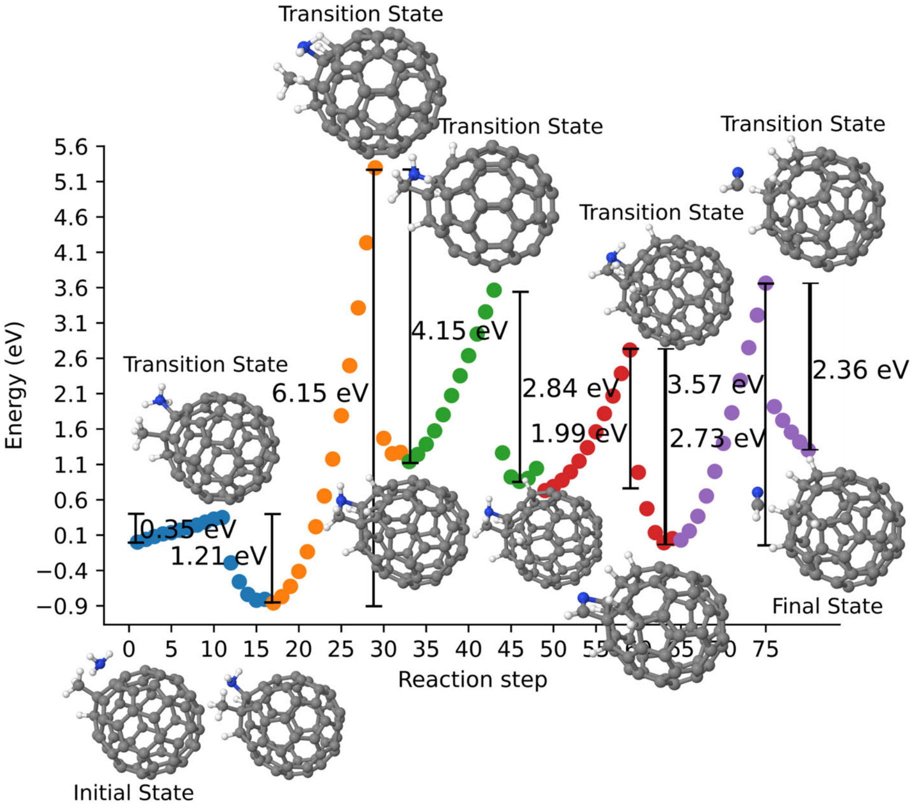

Fig. 45 Theoretical calculation of the reaction barrier of hydrogen cyanide and three molecular hydrogens via methane and ammonia under C_{60} catalysis. The barriers without and with the existence of fullerene are 6.24 eV and 5.30 eV, respectively

holds both scientific curiosity and boundless potential and might shed light on panspermia and astrochemistry.

Acknowledgments

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30 Theoretical prediction of electron impact partial ionization cross sections

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Status

Since electrons are found everywhere in the Universe, electron-atom/molecule collisions occur in environments like planetary atmospheres, interstellar medium, stellar and technological plasmas, and biological systems. Electrons play a crucial role in the astrophysical environments and the comprehension of how electrons interact with molecules aids scientists in unravelling the chemical evolution of the Universe, indirectly enhancing our understanding of the available raw materials for planetary systems [272]. Various elastic and inelastic collision processes are possible when the projectile interacts with the molecules in these environments. Total ionization cross section (TICS) is an inelastic process which is quite well studied both experimentally and theoretically. The recent Astrochemistry Low-energy Electron Cross-Section (ALeCS) database is a one-stop solution to find ionization cross sections of several molecules relevant to astrochemistry along with their ionization rates and reaction network coefficients [273]. In addition to modeling electron-induced processes in dense environments, exact electron impact partial ionization (PICS) is necessary to perform a quantitative analysis of mass spectrum data from on-board mass spectrometers of space probes sent on deep space or sample collection missions from comets.

Binary encounter Bethe (BEB) [274], Deutsch-Märk (DM) [275] and complex scattering potential ionization contribution (CSP-ic) [276] methods are some of the well-known semi-empirical models to predict the TICS giving good agreement with the experimental data. However, the estimation of partial ionization cross section (PICS) is not much explored which may be partly

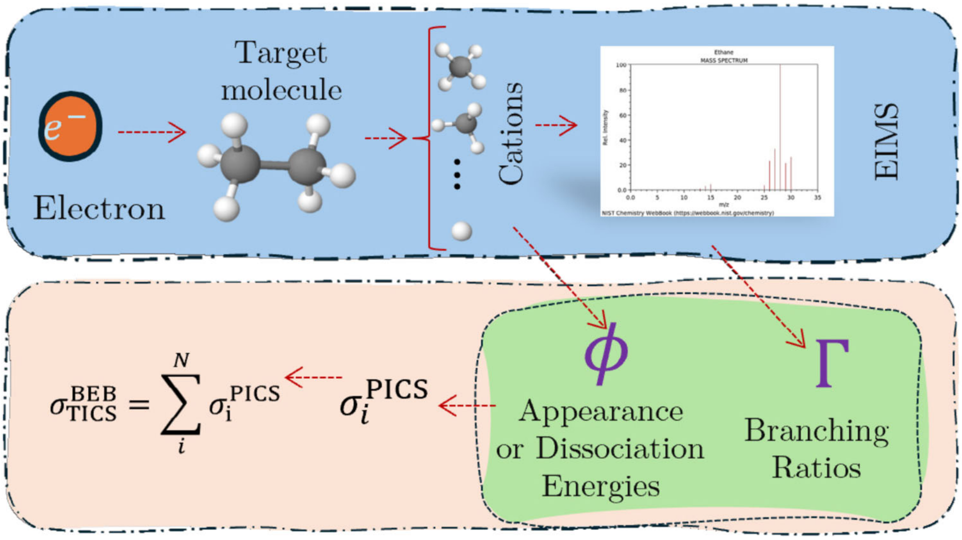

Fig. 46 Simple schematic diagram depicting the workflow of predicting the partial ionization cross sections

due to the challenges in studying the fragmentation of molecules [247]. Only in recent years the study of PICS using the combination of the BEB method with experimental mass spectrum data is being explored and the estimation of the PICS is being made for several molecules [277]. The electron impact mass spectrometry (EIMS) technique can be used to know the abundance of cations concerning their mass-to-charge ratio and then using the TICS from the BEB model one can predict the PICS of cations. However, in the absence of experimental EIMS data, it isn't easy to estimate PICS.

On the other hand, to predict the EIMS theoretically, the quantum chemical mass spectrometry (QCxMS) [278] method can be used. Mass spectrum data (MSD) [279] and modified BEB (mBEB) [277] are the two methods currently explored to predict PICS. Here, we require the branching ratios and the appearance energies of the cations. The branching ratios are obtained from the relative abundances of the cations from the mass spectrum which is the ratio of the relative intensity of the cation to the total ion intensity, typically these are measured at a specific incident energy either 70 eV or 100 eV. Then the appearance energies (AEs) for the most prominent cations are estimated by fitting the ion abundance curves in the extended Wannier law. They can also be calculated theoretically if we know the fragmentation pathways of the molecule. Huber et al. [280] and Graves et al. [279] have provided a scheme for calculating the dissociation energies of the cationic fragments. Graves et al. [279] recently developed a software, Relative and Absolute Partial Ionization and Dissociation - Cross Sections (RAPID-CS) to calculate the PICS of small single-centered diatomic/triatomic/polyatomic molecules by electrons and positrons [281].

In a recent study [282] we predicted the PICS of biomolecules using the MSD and mBEB method in combination with the experimental EIMS data. A simple schematic of the workflow to predict PICS is shown in Fig. 46. As an example and application of the MSD and mBEB methods, one can refer to our recent work [282], where we predicted the PICS of biomolecules using the MSD and mBEB methods in combination with experimental EIMS data and compared them with the measured cross sections. Some of the limitations in calculating the PICS using the MSD and mBEB methods are as follows.

- Since the TICS calculation depends on the accurate estimation of the orbital binding and kinetic energies, it is very important to use accurate quantum chemistry methods to predict the orbital parameters.
- The magnitude of TICS/PICS is sensitive to the ionization energy/AE. Hence obtaining accurate AEs of the fragments is necessary to obtain a reliable PICS.
- The detection of lighter fragments in the experiment is sometimes missed which may lead the MSD and mBEB methods to underestimate the ionization cross section.

Current and future challenges

To determine the PICS of the target we are heavily dependent on the availability of the experimental mass spectrometry data of the target and the appearance energies of the cations originating from the parent molecule. Many complex species, molecules of astrophysical interest and biomolecules of applied interest do not have the experimental mass spectrum data that hinders one from investigating the PICS of such targets. Theoretically, QCxMS can be used to get the mass spectrum data of the cationic fragments but with limited success and the calculation of appearance energies for major fragments is not an easy task. Further development in the QCxMS to provide accurate mass spectrum data along with appearance energies may pave the path for calculating the PICS of the major fragments soon. Integrating the current methods (MSD and mBEB) to calculate PICS with QCxMS may be an important and interesting problem to investigate in the future where one can obtain all the information regarding the mass spectrum data, appearance energies and PICS theoretically for any target molecule. Also, the development of machine learning models is coming up rapidly to determine the total ionization cross section [283]. Soon, it may be interesting to work on efficient models like the physics-informed neural networks implementing the current methods to determine PICS that pose some challenges for further development in this direction.

Advances in science and technology to meet challenges

On the experimental front, only a few groups like Rehman et al. [284], and Lopes et al. [285] are working to measure the PICS of the molecular targets that are not sufficient enough to meet the demand of the various scientific communities where the cross-section data are required. Hence more stress has been placed on developing simple theoretical models that can predict the cross sections efficiently in a reasonable time. In our recent work, we have showcased the capabilities of the present theoretical models in predicting PICS by comparing them with the recent experimental results. As the need for cross section data is growing especially for biomolecules and complex species, the need for improvement in the existing methods is inevitable to predict accurate cross sections. The recent development of a generalized BEB (GBEB) [286] model that includes acceleration correction overcomes the shortcomings of the effective charge experienced by the ejected electrons which were not considered in the original BEB model. Such advancement in the development of the BEB model led to a better agreement of the theoretical data with experiments. The GBEB method shows better agreement with the experimental results for the complex molecules. More investigation using the GBEB method is desirable in future for a variety of targets to check its applicability. Moreover, it may be interesting to use the GBEB method in combination with the existing MSD/mBEB methods to investigate the PICS for the cations originating from the parent molecule in future.

Concluding remarks

We have seen decent progress in the theoretical front to calculate the PICS using the modified BEB model in combination with experimental EIMS data. However, there seems to be a dip in the measurement of PICS and this needs to be addressed by experimental groups. There are plenty of complex species and biomolecules of applied interest that need experimental investigation and hence more development to measure TICS and PICS is an urgent need for the scientific community working in these areas of research and related topics. Moreover, with the advancement in Machine Learning and Deep Learning models to predict the TICS of atomic and molecular targets, it is not far enough that we will soon have such models to predict the PICS of any molecular targets. However, to train such machine learning models, we need an abundant amount of reliable experimental data to train the model for the prediction of PICS of unknown targets with accuracy. For this to happen, more data must be made available to researchers all around the world through open-source repositories.

Acknowledgments

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31 Metadynamics assembly of fullerene-like nanoparticle from a random aggregation of carbon atoms in space

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Status

Carbon has a variety of metastable phases, each of which has unique physicochemical properties ranging from superhard and insulating (e.g., diamond) to ultrasoft semimetallic (e.g., graphite) and even superconducting (e.g., fullerenes) [287,288]. Therefore the search for novel carbon phases with special properties like excellent electrical conductivity or ultrahardness is of great significance in materials science [287,289]. Nowadays classical molecular dynamics simulations are used in novel carbon material research [290], however Tangarife et al. [291] caution that classical molecular dynamics simulations of carbon phases could lead to unphysical results due to incorrectly set simulation parameters like interatomic potential. On the other hand, ab initio simulations have a proven track record of prediction success including the prediction of novel carbon phases like T-carbon, as well as simulated XRD patterns and simulated energy-loss near-edge spectroscopy, which are in agreement with experimental data [289]. Additionally, Gruber et al. [292] have reported highly accurate ab initio predictions for equilibrium phase boundaries of carbon allotropes. Another promising recent advancement in the field is the use of metadynamics to find stable and metastable phases of carbon [293].

Current and future challenges

The SCF method in use is a type of DFT tight binding, known as DFTB. It's parameter set is the default in the computational package CP2K 2023.1. The structure reforming methods are cell optimization (which includes simultaneous geometry optimization of the system), molecular dynamics and metadynamics.

One of the main questions we address is the preferred hybridization of carbon clusters originating in space. Another is what are the preferred structures: linear, linear branched, rings, condensed rings, 3D nanoparticles (NP), polymers, etc. A similar question is how complex can the structures really get.

One of the initial aggregates consists of 25 carbon atoms with random interatomic orientation and distances. The simulation cell has dimensions 15 x 15 x 15 Å.

I The first computational step is geometry optimization. The stabilization results in a nearly planar molecule, of tangled polycyclic type. The most dominant hybridization is sp^2, followed by sp^3. Roughly 3 times more atoms are in sp^2. We employ dynamics to test stability and enable energy minimization through spontaneous chemical changes. The thermostat is set to 400K. The calculation is carried out in NVT ensemble. The simulation length is 20 ps. No reactions occur. The product is labeled CNPI. It appears to have potential for assembly of closed-cage structures.

II The next computational step is metadynamics. The goal is to bind two CNPI clusters into a structure, which resembles a half-fullerene. The first three bonds between the molecules appear without a barrier. The formation of the fourth and final bond has free energy barrier of 11 kcal/mol, because of a small C-frame twist. The product (2xCNPI) consists of 16 atoms in side chains and 34 atoms in its main, bowl-shaped fragment. Additional interfragment bonds form without CV definitions. The energy pit of the product is only partially examined. However, the discovered 37 kcal/mol free energy barrier of the reverse reaction, points out that 2xCNPI is significantly more stable than the reagents.

The following computational step is once again metadynamics. The goal is to bind two 2xCNPI clusters into a molecule with a complete semi-spherical C-framework. The fragment-binding reactions occur practically without a barrier. It is possible that the minimal apparent barriers (1.5–2.5 kcal/mol) occur, only because of the time required for the reacting atoms to meet. There is a good chance that the fragment-binding reactions are probably barrierless. Additional coupling bonds are formed without CV guidance. The final product (C71SC) has a closed-cage core of 71 atoms. Once again, there is no need to completely examine the product's energy pit. The discovered free energy barrier of the reverse reaction is 37 kcal/mol. The results states that the product is the more stable of the two forms, by at least an order of magnitude. Some gaps (large rings) exist in the structure of C71SC and an additional MTD step is used to reduce their size through intramolecular cyclization. A total of 4 CVs are defined. The discovered activating free energies: 0.5, 2.5, 7 and 24 kcal/mol. The quasi-spherican carbon core of the resulting fullerene-like molecule (C72SC) can be labeled as C72[4,5,6,7,8,10]fullerene (Fig 47). The spherical core is not as symmetrical as the geometry of classical fullerenes, but considering the modeled process initiated with 25 randomly positioned atoms, the discovered mechanism has scientific significance.

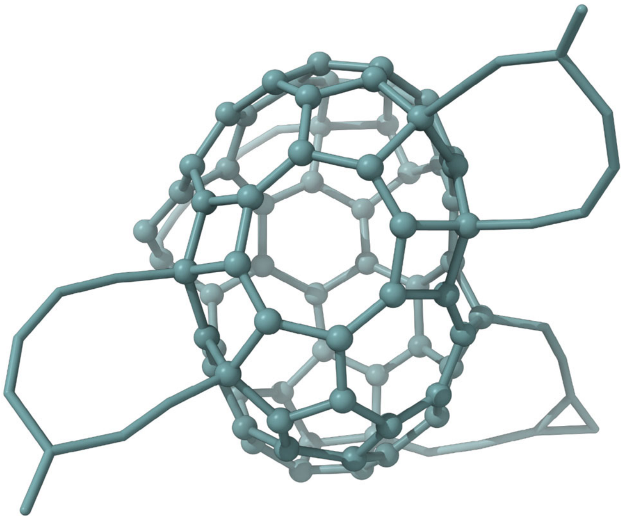
Fig. 47 C72SC geometry

It is hypothesized that cosmic UV radiation can cleave linear carbon fragments [294], therefore the quasi-spherical core of C72SC (C72) is of interest, as a molecule of its own. The theoretical IR spectrum of both nanoparticles resembles the theoretical spectrum of fullerene C_{70}. There are claims that C_{60} and C_{70} have been found in the interstellar space. The possibility exists that asymmetrical closed-cage molecules, similar to the one in this study, can be misclassified as commonly known fullerenes.

The spherical core is not as symmetrical as fullerenes C_{60} or C_{70}, but considering the process started with randomly positioned 25 carbon atoms, the final result is significant.

Advances in science and technology to meet challenges

Molecular dynamics (MD) is a method of exploring the potential energy surface in which the system naturally evolves in time according to Newton's equations of motion. Temperature is taken into account to model the translational, rotational and vibrational degrees of freedom by recalculating the nuclei's speeds at given time intervals. MD enables the recovery of the entropy and hence the free energy with higher physical fidelity than static calculations. Born-Oppenheimer molecular dynamics (BOMD) has a mixed approach in which the nuclei are treated as classical particles, while the electrons are modeled with quantum mechanics. The method enables time-feasible, realistic simulation of chemical reactions.

Metadynamics (MTD) is a simulation in which the processes are guided to model a chosen chemical reaction. Collective variables (colvars, CVs) are defined over molecular degrees of freedom to bias the system toward selected changes. Penalty potentials (hills) are periodically spawned for current values in the CV space to raise the free energy and reach unexamined geometries. When a TS is crossed over the study of the new minimum begins, once again starting at the bottom of the energy pit. Reversing the bias potential peaks gives us the relative stability of each geometry - the free energy surface of the reaction. With the raise in energy unguided changes are free to occur, giving us realistic insight over the studied processes.

Ab initio dynamics and metadynamics are state of the art methods for modeling the reactive behavior of molecular species.

Concluding remarks

If randomly clumped, small collections of carbon atoms in space tend to form sp^2-dominant clusters resembling the C-skeleton of polycyclic aromatic hydrocarbons. Almost all atoms would participate in condensed rings. Such molecules resemble fragments of closed-cage carbon species. Our research proves that similar carbon clusters can easily bind into fullerene-like structures. The calculated IR spectrum of the modeled quasi-spherical nanoparticle is close to that of C_{70}. Perhaps, such lower structures of lower symmetry can be mistaken for commonly known fullerenes, in IR-based studies of the cosmos.

Acknowledgments

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32 Atomistic machine learning for simulating the structure of disordered hydrogenated carbon materials

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Status

The field of atomistic modeling of materials dates back to the mid-20th century. Its main tasks are to elucidate i) the structure of materials, ii) the properties derived thereof or iii) both simultaneously. Fulfilling these tasks usually starts by building a mathematical model describing the potential energy surface (PES), i.e., the total energy and atomic forces as a function of all the atomic positions. Acquiring a quantitatively accurate solution to this problem from first principles is far from trivial, as it relies on solving the many-body Schrödinger equation for the system at hand. The approximation most used in atomistic materials modeling is due to Kohn and Sham [295], who introduced a single-particle ansatz for Hohenberg and Kohn's density-functional theory (DFT) [296]. Efficient and massively parallel software implementations of DFT have enabled accurate modeling of the PES of amorphous carbon (a-C) materials and used this accuracy to try to infer its structure [297]. However, when it comes to complex materials like a-C and a-C:X (where X stands for a dopant at high concentration, like H) an accurate description of the PES is only one of the two necessary ingredients. The other one is sufficient sampling of configuration space to generate realistic structures.

The real process whereby a-C:X materials grow experimentally is some variant of the deposition mechanism, in which energetic atoms/ions interact with the growing material, aggregating (or "depositing") on it. "Energetic" refers to any energy significantly higher than the thermal kinetic energy under the given thermodynamic conditions, from energies of 100 eV/atom and higher used to grow high-density "diamond-like" a-C, down to the energies in the vicinity of 1 eV/atom (and lower) that might be encountered in the interstellar medium. Simulating this process from first principles for a representative number of atoms (needed to properly recreate the structural disorder in a-C) is simply computationally intractable. Therefore, scientists resorted to more crude -but much more computationally cheap- approximations of the underlying PES than that afforded by DFT. So-called interatomic potentials or force fields use simple mathematical formulas to describe the energy and forces as a function of the atomic coordinates, and were used to model the growth of a-C [298]. However, these simplified models typically fail to describe the formation and breaking of chemical bonds, as well as non-standard atomic environments (such as those that might be encountered in a-C), with quantitative accuracy. Fortunately, in recent years machine learning (ML) techniques have been introduced to this field. ML interatomic potentials (MLPs) [299,300] use highly flexible mathematical models that capture the intrinsic symmetries of atomistic systems, and can be trained from DFT data to achieve accuracy, flexibility and computational efficiency (see Fig. 48).

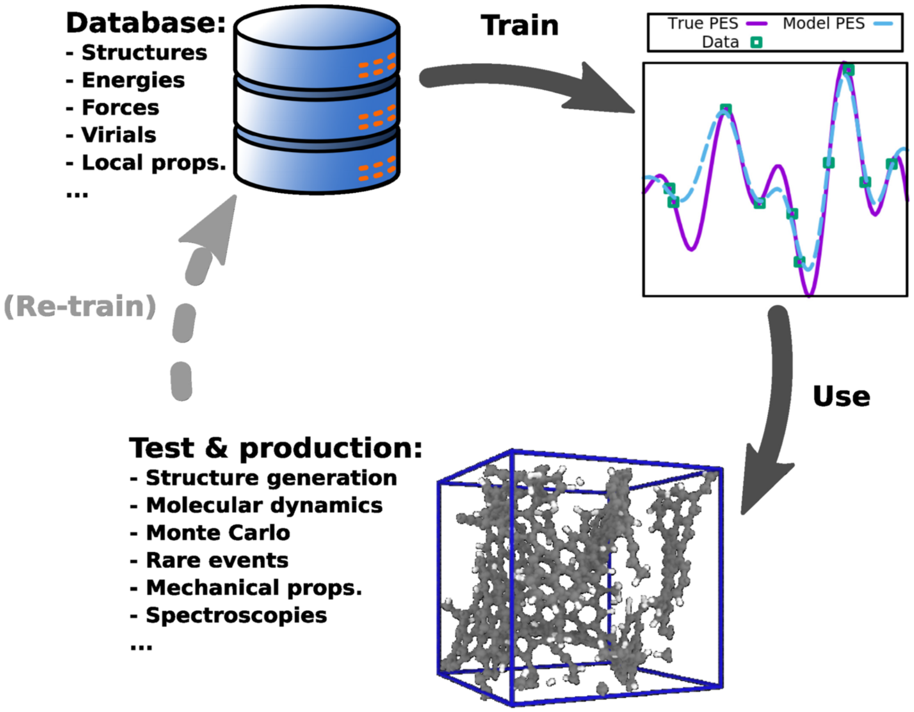

Fig. 48 A typical MLP training workflow involves data generation and curation, fitting of the model itself and possibly a retraining step based on tests of the model performance (e.g., whenever the accuracy is insufficient)

These atomistic ML techniques have revolutionized atomistic materials modeling and have enabled accurate studies of chemically pure (i.e., undoped) a-C [301] and its growth process [302] with quantitative agreement with available experimental observables.

Current and future challenges

Current developments in MLP technology have focused on improving the accuracy and computational efficiency of MLPs. Indeed, MLPs for a-C based on more sophisticated architectures than that used in the seminal papers [301,302] on ML-driven a-C modeling are appearing [303]. These enable even more accurate simulation, which might be particularly relevant to model the transition states that determine the chemical reaction rates during the aggregation process. They also enable more comprehensive sampling, for instance longer simulation times in molecular dynamics (MD) studies and larger system sizes. One of the existing challenges is the development of accurate multispecies MLPs for a-C:X materials. In MLP development, the cost of evaluating the energy and forces increases with the number of chemical elements that the particular MLP can handle. More critically, the complexity of the training database of structures required to fit an accurate multispecies MLP for disordered materials explodes as a function of the number of species. In the case of a-C:X materials, hydrogen, oxygen and nitrogen are the most relevant impurities. Our group has started to develop these tools for single impurities, e.g., a-C:O [304] and a-C:H.

The main challenges for the future thus include i) developing accurate MLPs that can simultaneously handle several impurities and ii) devise effective strategies to navigate the vast configuration space and PES spanned by this increasingly complex range of chemical compositions to derive realistic atomic-scale models of disordered carbons and their properties. This is also relevant in terms of recreating the physical conditions and chemical reaction pathways under which a-C:X and complex hydrocarbons form in the interstellar medium. Another issue that plagues MLPs is their “shortsightedness”. MLPs are based on an atom-wise decomposition of the total energy of the system. Thus, they are local and are generally unable to account for long-range correlations in the electronic structure of materials.

Advances in science and technology to meet challenges

The field of MLP development is advancing very rapidly, with continuous major developments in the last ten years and an explosion of the field in the last two years. These advances have been mostly driven by improving the accuracy of the fits versus DFT or even beyond-DFT electronic structure reference methods. To address the shortsightedness problem highlighted above, the inclusion of long-range interactions is necessary. These are implicitly incorporated in new-generation MLP architectures based on message-passing neural networks, which have been termed by some "semi-local" MLPs. However, the computational cost of these models explodes with the number of layers and thus the effective range of the interactions. A direct brute-force incorporation of long-range interactions is also impractical because the number of atoms within a given distance of another atom grows as the cube of this distance, with the computational cost to evaluate these interactions growing accordingly. Other approaches are reverting to the inclusion of long-ranged physics-based models with short-range parametrization. Examples of these are van der Waals corrections, partial charges, and charge equilibration models. These are still under active development and we expect big improvements in the coming years. It is less clear whether more complicated correlations in the electronic structure of matter can be incorporated using these types of effective models which overlook the quantum nature of interatomic interactions. Of relevance to the modeling of hydrocarbons and a-C:H are phenomena such as aromatic stabilization and π-conjugation taking place over distances larger than the explicit cutoff of the MLP. A promising avenue to explore in this regard is the integration of quantum-mechanical models with ML, e.g., in the flavor of computationally efficient tight-binding models of the electronic structure using an ML-based parametrization of the Hamiltonian matrix elements (as a function of the local atomic environments). Such hybrid models could bring us one step closer to MLPs able to describe interatomic interactions quantitatively over all relevant length scales. A second issue is how to leverage the power and flexibility of ML for structure generation. This is particularly attractive for amorphous or highly complex compounds, where experimental determination of the atomistic structure is not straightforward. A promising strategy to tackle this issue is incorporating experimental information directly into the structure optimization by combining an MLP with on-the-fly prediction of experimental observables, coupled to a direct feedback into the simulation. This has recently been achieved for a-C:O with X-ray photoelectron spectroscopy (XPS) as the experimental technique of choice [304] and will likely be extended to other techniques in the near future. Of relevance to complex hydrocarbons are X-ray diffraction (XRD), Raman spectroscopy and infra-red (IR) spectroscopy, among others. These techniques are all amenable to these extended MLP architectures and we can expect proof-of-concept studies within the next couple of years.

Concluding remarks

Overall, the field of atomistic materials modeling is advancing very fast driven by the recently introduced MLPs. MLP-based simulations are enabling a new degree of understanding of the atomistic structure of complex materials and compounds. Mature examples exist in the literature for the study of chemically pure carbon materials, and recent work is also starting to tackle the study of doped or alloyed carbon-based materials. It is likely that MLPs will play a crucial role in improving our understanding of the structure and formation mechanisms of a-C:H in the near future, including processes specifically relevant to spontaneous synthesis taking place in the interstellar medium.

Acknowledgments

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33 Vacuum ultraviolet photo-processing of cosmic polycyclic aromatic hydrocarbons

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Status

Investigating the interplay between vacuum ultraviolet (VUV) photons and polycyclic aromatic hydrocarbon (PAH) molecules holds significant importance for gaining insights into the physics and chemistry of photodissociation regions (PDRs) associated with star-forming regions [90]. This interaction plays a crucial role in influencing the chemical inventory by triggering various unimolecular processes, as illustrated in Fig. 49.

The energy-dependent nature of VUV radiation can activate diverse reaction pathways, resulting in a range of products. These resulting products may exhibit specific reactivity patterns that, in turn, influence the broader chemical dynamics within the environment. Additionally, VUV radiation is widely acknowledged as the primary catalyst for initiating the ubiquitous infrared (IR) emission commonly referred to as the aromatic infrared band (AIB), observed toward many astronomical objects [?]. The AIBs serve as valuable local probe of cosmic PAH population compositions, which are expected to change in response to local factors like the VUV radiation field. VUV photons can trigger dissociation and ionization, competing with PAH recombination and reactions with gas phase species, resulting in varying charge and hydrogenation states within different environments [305]. These states significantly impact the IR spectra of PAHs and are crucial for models of interstellar extinction. Variations in IR spectra in photodissociation regions reflect these charge state changes. Nevertheless, fully interpreting the AIBs faces two main challenges: i) the difficulty of recording laboratory IR spectra for large PAHs that are resilient to harsh VUV radiation, and ii) the fact that PAHs can transform into transient structures or isomers after photo-processing, which may not be stable

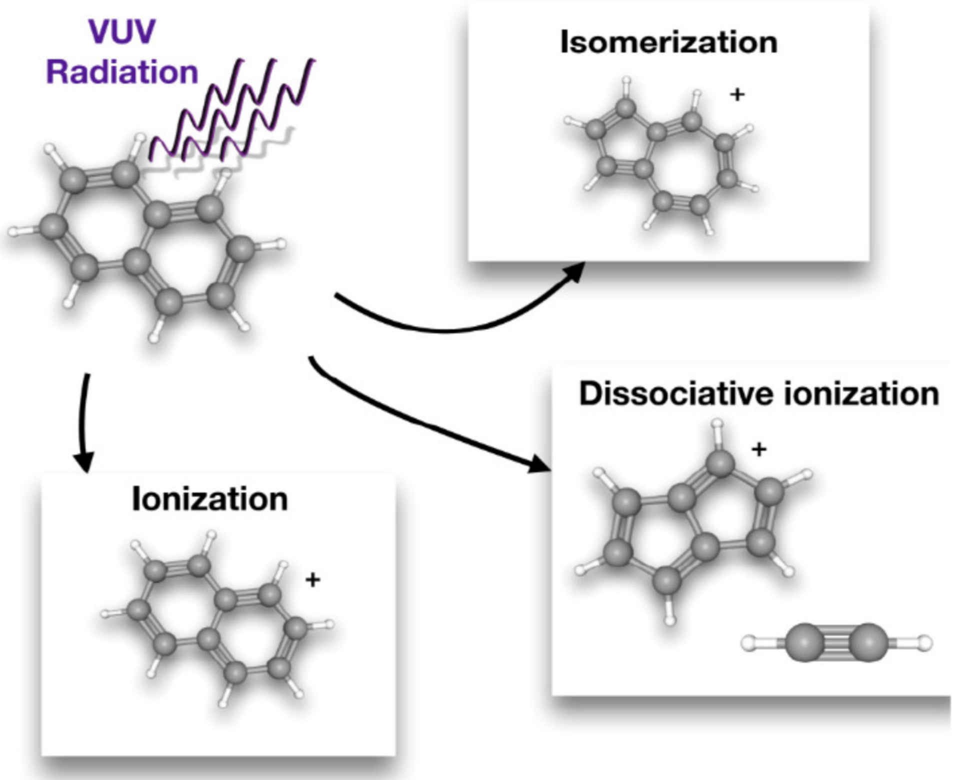

Fig. 49 Unimolecular reactions triggered by VUV radiation

in a laboratory setting and therefore must be generated in situ and isolated to be studied.

VUV photo-processing experimental investigations have primarily concentrated on either the ionization or fragmentation aspects from neutral PAH precursors. As these two processes are in direct competition, and it is imperative to consider both aspects simultaneously. During the last decades these aspects started to be investigated for cationic PAHs, revealing that ionization prevails for the larger PAH cation, while it competes with fragmentation for the smaller PAH cation. Consequently, the variations in PAH ionization characteristics may be equally significant as kinetic fragmentation parameters in the chemical modeling of the interstellar PAH population. This highlight the importance of incorporating both photo-fragmentation and photo-ionization into models.

The question of how cosmic PAHs react after absorbing a VUV photon has, for the most part, been answered without precise control over the internal energy or even the structure of the reacting ionized PAHs. Recently, it has become evident that the reactivity of ionized PAHs and the resulting products from dissociative ionization are significantly impacted by the energy of the incoming photon, defining the internal energy imparted to the molecular system.

Recent observations made by the James Webb Space Telescope (JWST) in the infrared spectral range, offering unrivalled spatial and spectral resolution, clearly motivate the need for additional laboratory data. Indeed, understanding the fate of PAHs after the photoabsorption of VUV photons is an almost obligatory step in elucidating the mechanism at play that leads to AIBs.

Current and future challenges

The vacuum ultraviolet VUV photo-processing of neutral PAHs is arguably the most comprehensively understood. Major dissociation pathways for neutral PAHs typically involve the ejection of atomic or molecular hydrogen and C_2H_2 [306], with dissociative ionization resulting in a quasi-balanced branching ratio, especially for smaller PAHs like naphthalene ($C_{10}H_8$), and a shift toward H/H_2 loss as the PAH size increases. These experiments are commonly conducted at synchrotron facilities, where broadly tuneable VUV radiation sources are available. The incorporation of spectrometers capable of recording coincidences between photo-ions and photo-electrons has enabled the retrieval of breakdown curves with precisely defined internal energy [307]. This is a crucial aspect as it facilitates the modeling of the obtained results using kinetic calculations such as the Rice-Ramsperger-Kassel-Marcus (RRKM) approach. In certain cases, coupling RRKM calculations with quantum chemical computations allows for the extraction of structural details regarding the ionized fragments formed. The primary challenge lies in the ability to synthesize PAHs with distinctive structures (involving defects in the carbon framework) and effectively introduce sizable PAH molecules into the gaseous phase.

The study of cationic PAH photo-processing has been relatively limited due to the necessity of combining an ion trap with a VUV light source. Data predominantly originate from two experimental setups. One allows for tuning the energy of VUV photons, with mass-selected ions stored in a room-temperature trap [308]. One drawback is that the ion trap is operated with a pressure of 10^{-3} mbar of buffer gas, allowing ions to dissipate energy through collisions at a much higher rate than in outer space. The other involves cryogenically cooled traps with a backing pressure better than 10^{-8} mbar to replicate conditions closer to those found in PDRs, but employs only tabletop laser-generated photons at 10.5 eV [309]. In both cases, significant challenges include the inability to unequivocally retrieve information about the structure of ionic fragments.

Understanding the chemical reactivity of ionized PAHs is essential for unravelling the aromatic chemistry occurring in space. Additionally, the identification of non-reactive PAH species holds significance since they can serve as reservoirs for accumulating carbon matter. Many past and ongoing ion-molecule investigations have been conducted without precise control over the internal energy of ionized PAHs. At best, the ions are brought to a known thermal equilibrium before reactions take place. Conversely, by employing a tunable VUV light source, it becomes possible to modulate the photon excitation energies. This gradual increase in energy results in increased internal energy within the ions, thereby affecting their chemical reactivity or inducing structural changes that, in turn, have a broad impact on the chemical behavior of these molecular ions. Ion-molecule chemistry serves as a valuable tool for monitoring isomerization reactions in PAHs. In this process, reactivity changes are tracked as a function of photoexcitation energy [310]. The increase in photon energy produces ions with higher internal energy and eventually drives unimolecular isomerization reactions, where the newly formed isomer might exhibit different reactivity with the neutral target. Therefore, changes in reactivity can be used as proxies for the formation of new isomers.

Advances in science and technology to meet challenges

The main technological advances needed for the VUV photo-processing of neutral PAHs reside in the sample production of large molecules, i.e., optimizing the transfer from solid phase to gas phase, and then subsequent cooling of the large PAHs. This would necessitate the development of a more reliable oven and pick-up chamber coupled to supersonic expansion.

In order to improve the VUV photo-processing experiment involving ionic PAHs, a two-pronged approach can be pursued. Firstly, it involves the integration of a cryogenic ion trap with a tuneable VUV light source. Secondly, there is the addition of a diagnostic tool aimed at providing insight into the structures of the photo-fragments generated. An ideal choice for this diagnostic tool would be the inclusion of IR action spectroscopy.

In the realm of ion-molecule reactions, where ions are formed using VUV radiation, the grail already exists; it consists of preparing ions using ion-electron coincidence, ensuring that ions are generated in a single chosen quantum state. Nonetheless, the duration of such experiments is not well-suited to the stringent time constraints associated with beamtime availability in synchrotron sources. This situation presents two viable alternatives: the first is to improve the performance of the apparatus used at synchrotron facility to speed up the acquisition time, and the second is to couple a tandem mass spectrometer including an ion-electron coincidence source to a tabletop VUV laser system.

Concluding remarks

Although VUV radiation is ubiquitous in space and is one of the driving forces behind the astrochemical network, laboratory data remains scarce in this spectral range compared to others. This scarcity can be explained by the difficulty of accessing a tuneable VUV light source. In my opinion, the development of a larger number of tabletop VUV laser systems would enable considerable gains to be made. In addition, the robustness of current commercial OPO laser systems enables us to build VUV laser systems with a resolution of a few cm^{-1} while obtaining a tunability of a few eV.

Acknowledgments

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34 Ionization tolerance of carbon allotropes in space: fullerenes

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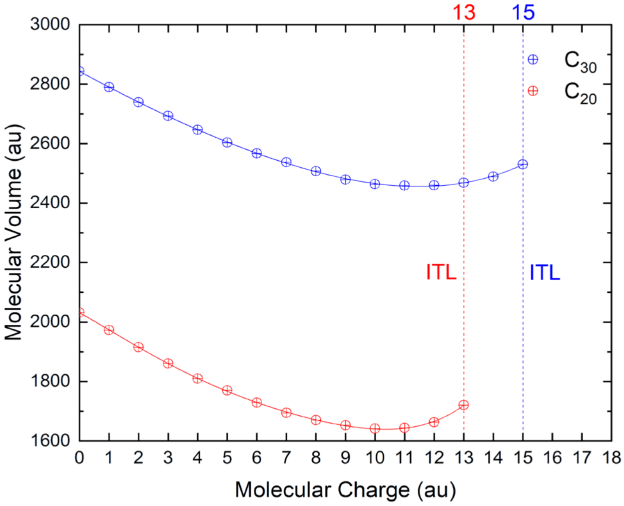

Fig. 50 Changes in molecular volume upon ionization in C_{20} and C_{30} Fullerenes. Computations were performed at B3LYP/PC1 model. Molecular volumes have been calculated via QTAIM

Status

Ionization is one of the most common phenomena in space which alters the chemical behavior of molecular species via interaction with radiation. As a result, the molecular electron density and the spatial positions of atomic nuclei undergo energy perturbation and relaxation. Such a complicated physical picture of ionization is viewed as a cleavage of old and the formation of new chemical bonding. The faith of a molecule depends on the structural change at the final episode of this showdown, the Ionization Tolerance Limit (ITL).

By applying quantum chemical calculations, we have proved that one of the allotropes of carbon identified in space, i.e., C_{60} fullerene, shows extremely high resilience toward structural change led by ionization and by accommodating a huge amount of net positive charge up to +26 [311,312]. Our prediction is supported by laboratory gas phase mass spectrometry data of the detection of highly positively charged C_{60}^q with $q = +1$ to +14.

We also provided a mechanistic approach of single photon stepwise ionization as the plausible pathway to the formation of these highly ionized forms of C_{60} fullerene in the condition of space [311]. Our calculations demonstrated that the energy of photons necessary to initiate and lead the process of C_{60} ionization to its ITL is within the vacuum to extreme UV range [311]. This spectrum of energy is viable in the space environment.

Our preliminary theoretical results on two small size fullerene C_{20} and C_{30} demonstrate that tolerating the high degree of ionization is a part of the chemistry of fullerenes (Fig. 50).

The observed trends in profiles of volume change versus charge follow a similar parabolic shape observed for C_{60}. At the charge of +10 and +11, the volume of both fullerenes shrinks to its smallest value. The ILT values stand at +13 and +15 for C_{20} and C_{30} separately.

Current and future challenges

To understand the relationship between the size of fullerene and its ITL, we expanded our study to include some small members of the C_n fullerene family with the number of carbon atoms, n, less than 60. The main issue here is the generation of a relatively large number of structures (isomers) for the neutral form of a specific C_n fullerene molecule. For instance, in comparison with one known isomer of C_{60} fullerene, C_{36}, and C_{40} neutral form structures are expanded to 15 and 39 isomers, respectively [313]. Searching for all structurally related isomers of fullerene and finding the lowest energy among them to start with, is a stunning theoretical task, which consumes extensive computational power and time [314]. The molecular structures of some of the isomers of C_{40} fullerene are presented in Fig. 51.

In addition to the theoretical challenges, the scarcity of experimental data to deduce the errors of computed values of ionization for specific fullerene is another main problem in studying ITL.

Advances in science and technology to meet challenges

The advances in artificial intelligence science and its capability to look for possible solutions to complicated problems is one of the options to apply for tackling the structural isomerism in fullerenes [314]. If it is trained properly such an approach can provide as many molecular structures as possible for specific fullerene. However, the quantum chemical calculations still would need to be conducted on all of the delivered structures.

With the recent leap in measuring attosecond phenomena [315], the gates to study the details of fast processes in which electrons are directly involved such as the ionization of a molecule or ion-molecule are opened. The laboratory techniques which will be emerged soon can monitor the changes in electron density of gas phase fullerenes upon ionization and measure the ITL of fullerenes. The vital information from such experiments can potentially lead to more accurate quantum chemical models.

Concluding remarks

To understand how elemental carbon in molecular form is distributed in various ways to different corners of the Universe, it is necessary to study their chance of surviving various physicochemical processes throughout space. Ionization is a common process that all molecular

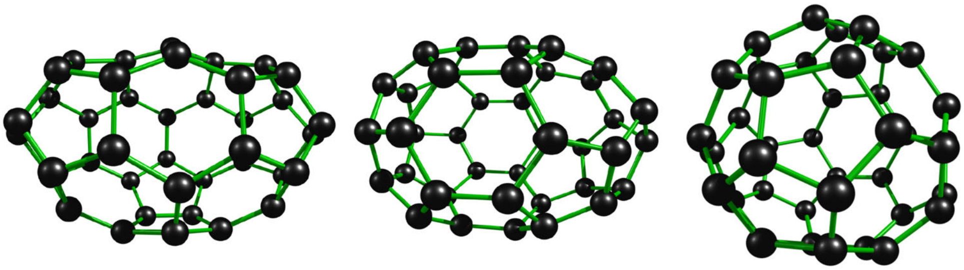

Fig. 51 Molecular structure of some isomers of C_{40}. Isomers from Atlas of Fullerenes [313]

species are prone to within the harsh radiation conditions of space.

Carbon in its fullerene form has enough carbon atoms confined in a complex cage structure that can serve as the precursor of other moderately sized and structurally complex carbon backbone compounds.

Based on our findings, some of the members of the fullerene family such as C_{20}, C_{30}, and Buckminsterfullerene C_{60} show a high degree of resiliency in the hostile radiation environment. Therefore we propose to extend the study to further include other fullerenes within the framework of the presented road map.

Acknowledgments

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35 Endohedral fullerenes as reaction sites for the chemistry of space

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State of the art

The idea that fullerene nanocages could form a protected site for non-conventional elementary chemical reaction pathways to occur, under the typical conditions of the interstellar medium, is a new one that has been inspired by the discovery of both neutral and cationic C_{60} in space [36]. This speculation, which has only partially been explored so far, but without specific application to astrochemistry [316,317], is in line with the broad objective of exploring new routes to molecule formation in space, focusing on the role of carbon nanostructures (Fig. 52).

So far, hypotheses for the role of fullerenes in astrochemical kinetic models, alongside the traditional two categories of gas phase processes and chemistry involving dust grains and ices, have been in connection to possible surface catalytic properties of C_{60}, e.g., in the formation of polycyclic aromatic hydrocarbons (PAH) and complex organic matter (COM), as well as water adsorption and a potential role in amino acid formation (see e.g., contributions 17 and 23, present roadmap).

The endohedral chemistry of carbon nanotubes, a closely related carbon allotrope, is an active research area with the emphasis on the synthesis of new hybrid materials with novel properties. The confinement of molecules inside nanotubes can significantly influence the chemical reactions that they can undergo and the surrounding carbon cage can protect the product from the ambient atmosphere. For example, stable polyynes, sp^1 hybridized carbon chains, can be synthesized within nanotubes and graphene nanoribbons have been produced from confined PAHs [318]. The limited studies of fullerene endohedral chemical reactions published to date have been, e.g., concerned with the theoretical study of successive hydrogenation of an encapsulated N atom via proton or H transfer through the cage to produce NH_3 and NH_4^+ [316]. Another study involved proton transfer reactions between H_2O and hydrogen halide molecules within C_{70} to form conjugate acid–base ion pairs within the cage, reactions that do not normally occur in the absence of the cage [317]. The latter provides evidence for a significant non-covalent interaction between the encaged species and the inside of the carbon cage. The predicted difference in bond lengths for $(H_2O.HF)@C_{70}$ complexes inside the cage compared to isolated $H_2O...HF$ was in agreement with experimental observations of encapsulated species prepared by the so-called "molecular surgery" technique whereby the cage is chemically opened to insert small molecules and then chemically re-closed [319]. Multiple capture within C_{60} has been observed for high flux Li^+ irradiation of solid state fullerenes [320]. $He_2@C_{70}$ has been observed with very low yield under high temperature, high He pressure treatment of C_{70} and $He_2@C_{60}$

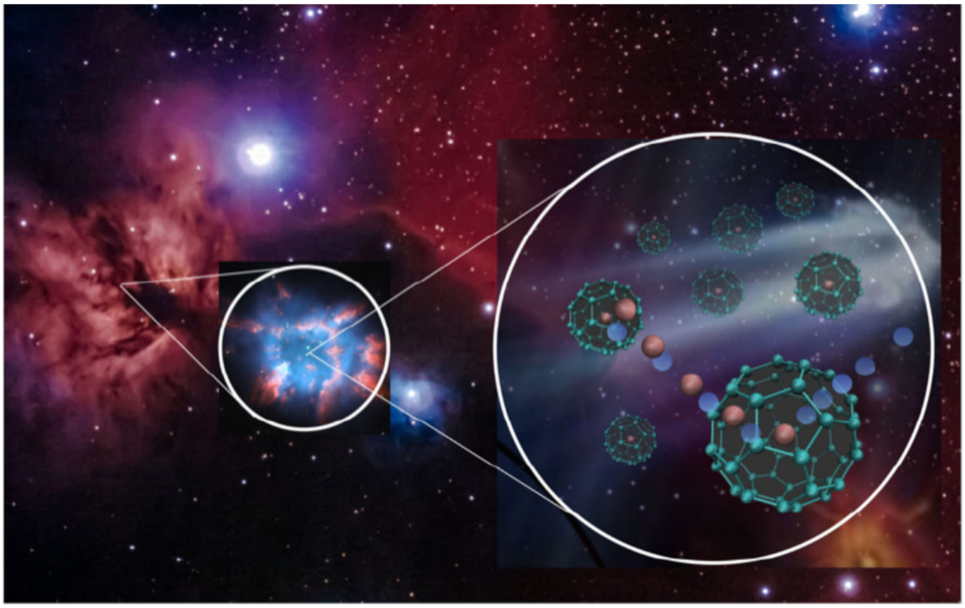

Fig. 52 Schematic illustration of diatomic molecular formation inside fullerene cages from atomic precursors. Background figure from https://www.openaccessgovernment.org/investigate-planetary-nebulae/101876/@copyrightXamad

was formed in controlled explosions carried out in a sealed chamber containing fullerenes and He [321,322].

The space environment The most likely means of encapsulating species within fullerenes under the conditions of space would be low energy barrier processes, akin to those discussed in [316], or hyperthermal collisions. At centre of mass collision energies of a few eV it is possible for small atomic species such as He or Li^+ to overcome the potential barrier for penetration through a hexagon or pentagon and enter the cage without destroying it [320]. The translational energy of the captured species is eventually transferred to cage vibrations thus greatly reducing the probability for the captured atom or ion to escape. Although hyperthermal collisional capture of atoms or ions has been reported for a variety of systems, predominantly rare gases, nitrogen atoms and alkali metal ions [320], there has been no report, to our knowledge, of multiple capture in the gas phase under sequential single collision conditions, an important precursor to reactions occurring inside the cage in an astrochemical environment.

To date there have been no reports of $H@C_{60}$ formation in single collision experiments, although there have been many theoretical studies of hydrogen implantation in nanocarbon, mainly related to questions of hydrogen storage. The most stable configuration at low interaction energies appears to be an exohedrally bound H with the cage penetration barrier for neutral H estimated to be in the same few-eV range as for $Li^+ + C_{60}$ or $He + C_{60}^+$. H atoms with kinetic energies in the appropriate range can be produced, e.g., within dark clouds via electron impact excitation of excited repulsive electronic states of H_2 [323] and have been observed in the expansion shell of a young carbon-rich planetary nebula [324].

Current and future challenges

The systematic theoretical and experimental study of the potential for endohedral fullerene reactions to be a significant contributor to molecular formation in space could provide important new insights into the formation of small molecular species. The presence of the cage could substantially increase the lifetime of otherwise unstable reaction intermediates and provide a route via vibrational energy transfer or perturbation of the captured species to stabilize excited reaction products. The study of the endohedral reactivity of fullerenes is challenging from both the experimental and theoretical points of view. From the theoretical point of view, a practical medium-term goal would be the structural, kinetic and dynamic properties of some $A + X@C_{60}$ prototype systems where X and A are both first or second row atoms. This task presents some non-trivial aspects. For example, for the determination of interaction energies, the size of the system forces the level of quantum chemical calculations to be limited to those less demanding in terms of computing time, but potentially less accurate. Accordingly, all previous studies of $X@C_{60}$ use classical MD or DFT calculations with a wide range of penetration barriers reported even for the simple prototypical $H + C_{60}$ system. Moreover, *a priori* the $A + X@C_{60}$ interaction can proceed through several channels: physisorption or chemisorption inside or outside the cage, quantized translation inside the cage etc. and all competing processes need to be accounted for by models. Finally, the electronic structure and spectroscopy of atoms and molecules inside the fullerene and of the fullerene itself will be modified, as shown by recent spectroscopic studies of endohedral fullerenes produced via the molecular surgery route [325]. Due to the complexity of the calculations, the relevance for astrochemistry and the feasibility of experiments, the H + $H@C_{60}^{+} \rightarrow H_2@C_{60}^{+}$ would seem an appropriate system to begin with before moving on to more complex systems.

Experimentally it will be necessary to work with at least one charged partner in collisions to control the centre of mass collision energy and be able to use the established ion trapping and/or storage techniques to cool and monitor the spectroscopy of reaction products. Challenges lie in producing sufficiently high density of $X@C_{60}^{+}$ to provide a chance of detecting the sequential capture of another atom and probing the reaction products by a combination of mass spectrometry and spectroscopic techniques to determine reaction cross sections/rates. It may prove advisable to start with more complex collision partners produced via molecular surgery such as $He@C_{60}$, $X_2@C_{60}$ or $XY@C_{60}$ colliding with atoms/ions to provide first proof of principle of endohedral reactivity, which may be more challenging to study theoretically. Spectroscopic studies of species produced via the molecular surgery route can also provide a useful pointer to the spectroscopic fingerprint of potential endohedral products.

Advances in science and technology to meet challenges

The current level of the experimental technology, such as ion traps, cryogenic storage rings, molecular beams and spectroscopy, is, in principle, able to meet the challenge. However, this will require the development and construction of more complex apparatus to combine sequential collisional formation with high sensitivity product detection and characterization. A feasible approach would involve firstly, the formation and trapping of $X@C_{60}^{+}$ either in situ which would require the ability to tune the centre of mass collision energy between X and C_{60}^{+} or by initially preparing $X@C_{60}$ using molecular surgery followed by evaporation/ionization to produce a gas phase source of $X@C_{60}^{+}$ as a precursor to ion trapping and stabilization through cooling in the trap. The stabilized endohedral ion would then be collided at a controlled and tuneable centre of mass collision energy with reactant A, formed, e.g., via photodissociation of a gaseous molecular precursor. A second trap will collect and cool the final products which can then be studied using conventional action spectroscopy (see e.g., contributions 5 and 13, present roadmap). Alternatively, the final endohedral fullerene product could be dissociated via photo- or collisional excitation with subsequent mass spectrometric detection of endohedral reaction products.

Concluding remarks

The search for new chemical routes, to expand the inventory of reactions and feed kinetic models, is boundless in astrochemistry. The discovery of C_{60} in space provides the rationale for the hypothesis that fullerenes are additional chemical routes, capturing and stabilizing atoms and molecules inside the cage. This class of processes has to be characterized by theoretical and experimental studies to assess their contribution to molecule formation, including them in astrochemical models.

Acknowledgments

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36 Catalytic formation of molecules on the surface of cosmic dust grain analogues

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Status

It is well-known that in astrophysical environments, such as the interstellar medium (ISM), cold and hot prestellar cores, protostellar envelopes, and planet-forming disks, surface reaction pathways lead to a greater complexity of molecular species. The surface is provided by mainly carbon- and silicate-based dust grains. In addition to providing a meeting place for reactants, dust grains allow for dissipation of excess energy released in bond formation (third-body action), may play a catalytic role by lowering activation barriers for reactions and diffusion, and can directly participate (by atoms and/or functional groups) in surface reactions. The role of cosmic dust grains in physical and chemical processes on their surfaces was recently discussed in a review paper [326].

However, laboratory astrochemical research has largely focused on chemical processes in/on the molecular ices that cover the dust grains in cold and dense astrophysical environments, which are known to have rich chemistry. This is due to the typical view of grains in such environments as a compact refractory (mainly carbon- or silicate-based) core covered by a thick (tens or hundreds of monolayers) ice layer. This view, however, does not take into account the potentially high (or very high, up to 90% according to some results) porosity of dust grains, despite of considerable supporting evidence from laboratory experiments on cosmic dust analogues (e.g., [327]), dust evolution models (e.g., [328]), and analysis of cometary particles (e.g., [329]). The interested reader is referred to a recent research paper [330] for a detailed discussion and references. Examples of porous dust grains are presented in Fig. 53. High porosity means physical mixing of dust moieties with ices and availability of a much larger dust surface area (and thus a much greater number of binding/reactive sites) as compared to a compact dust core [330]. The first evidence of dust/ice mixing in cold astrophysical environments obtained by comparing laboratory and observational spectra was recently presented [331]. Also, pathways to molecular complexity in low-density regions of the ISM (with low or no ice coverage) have started to be studied in the recent years.

Catalytic formation of molecules on dust grains (when dust plays a role of a classical catalyst) as relevant to various astrophysical environments is attracting more and more attention following a few pioneering studies. Some examples of such studies: low-temperature formation of H_2 [332] and H_2O [333] as relevant to the low-density ISM chemistry; low-temperature formation of ammonium carbamate [327], a complex organic molecule, as relevant to the high-density ISM chemistry; high-temperature catalytic formation of CH_4, NH_3 and complex organic molecules as relevant to atmospheric chemistry of exoplanets [334]. More examples and references can be found in the review of Potapov & McCoustra [326].

Current and future challenges

The last 25 years have seen surface science methodologies making rapid ingress into studying physicochemical processes involving dust. There has been significant progress in our understanding of thermal and non-thermal desorption, small molecule formation and ice growth, and building chemical complexity through thermal and non-thermal chemistry in ices. This needs to continue to develop a fully rounded picture of the chemical evolution of grains and ices.

However, it is time to look at the role of the grain surface in a wider range of environments and explore uncharted territory. There are reports of surface reactions leading to the formation of direct precursors of prebiotic molecules, such as amino acids and nucleobases. Investigations of such reactions are directly linked to the big scientific question - the origin of life on Earth - and reinforce its exogenous hypothesis. Those reactions may proceed on dust grains more efficiently and on much shorter timescales than it is currently thought due to reduction of activation barriers for diffusion and reaction, as in the case of ammonium carbamate.

We should consider that grains, in addition to carbonaceous and siliceous materials, may contain iron and other first row transition metals as widely used in industrial catalytic processes. These metals are heavily depleted from the gas phase into silicate minerals and carbonaceous dust as single atoms and small atom-number clusters. In addition, space weathering of the metallo-silicate minerals themselves might nucleate the formation of nanoparticles. These single atom and nanocluster materials are consequently present in astrophysical environments and available to heterogeneously catalyze chemical reactions such as Fischer-Tropsch and Diels-Alder processes. Such work is at the cutting edge of catalytic research and opens the door to astrocatalysis.

In this context, it is worth mentioning Wächtershäuser's hypothesis of the origin of life, with iron sulfides as the key catalytic elements. The energy released from redox reactions of these sulfides could be available for the synthesis of organic molecules and for the formation of polymers especially in aqueous environments. This clearly suggests that we must take our catalytic investigations into exploring liquid–solid heterogeneous catalysis as may occur in the cores of appropriately warmed asteroids, icy moons, and minor planets. Evidence from the meteoritic record clearly supports water alteration (observation of clays and carbonate minerals) as well as the necessary inventory of prebiotic complex organic materials.

Advances in science and technology to meet challenges

Laboratory techniques combining production of cosmic dust grain analogues with astrochemical experiments are required to study the catalytic formation of molecules on dust surfaces. Moreover, high sensitivity of detection techniques (molecular spectroscopy, mass spectrometry) is necessary as the formation yields of complex organic and prebiotic molecules can be very low. Additionally, detection of species formed in surface reactions should be done in situ as ex situ analysis may lead to undesirable chemical reactions in the sample with the ambient environment and to lose of the direct link to the processes of interest taking place under astrophysically relevant conditions. Currently however, prebiotic molecules produced in interstellar ice analogues have been unambiguously identified only by ex situ methods. We also need to address the issue of higher pressure and liquid phase processes that are heterogeneously catalyzed. This will blur the distinction between in situ and ex situ measurements.

Of course, quadrupole mass spectrometry and Fourier transform infrared spectroscopy will continue to be utilized in these studies. However, they have well known limitation in terms of identifying molecules as the size and molecular complexity increases.

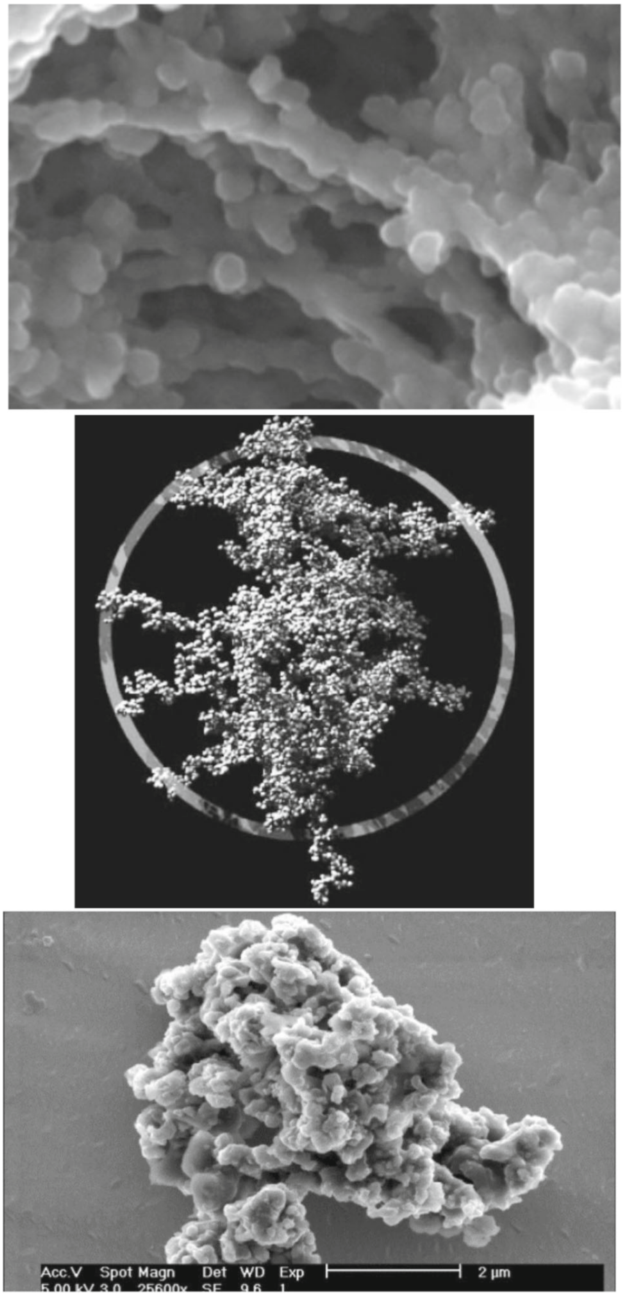

Fig. 53 Top frame: Laboratory analogue of dust grains. Reproduced from [327] with permission ©AAS. Middle frame: Dust aggregate, simulation. Reproduced with permission from [328], ©AAS. Bottom frame: Interplanetary dust particle [329]. Reproduced from NASA catalog, ©NASA

One technique that allows for sensitive in situ detection of originally formed large molecules is Matrix-Assisted Laser Desorption Ionization (MALDI) combined with high-resolution mass spectrometry providing for exact mass, and hence molecular formula, determination. This technique is widely used in biology and medicine and has great potential in astrochemistry. Currently, only a team at Caltech have used the MALDI technique to identify molecules that are formed in astrophysically relevant ices ([335] and references therein). Such an experimental setup is now being developed at the Max Planck Institute for Astronomy.

Another approach is a combination of an in situ gas phase chirped-pulse Fourier transform microwave spectrometer detection and a low temperature surface desorption experiment [336,337]. Such a combination should allow for studies of complex organic molecules produced on and desorbed from the surface of cosmic ice analogues giving unambiguous information about the molecular composition, the molecular structure, and the transition frequencies of molecules needed for their detection by radio telescopes in various astrophysical environments. It might also permit measurements of chiral excess than cannot be achieved with mass spectrometry which would open a window on the symmetry breaking in prebiotic chemistry.

The remaining challenge is to combine an astrochemical experiment having high-sensitivity detection coupled to in situ production of dust grains. Technically, this can be done. However, for now, collaborative projects between groups having these complementary techniques in hand are the simplest approach to research in the direction discussed in the present paper.

Concluding remarks

Investigations of the catalytic formation of molecules on the surface of cosmic dust grains will be directly linked to the questions of our astrochemical heritage and existence of other habitable planets, presenting interest not only for astrophysical/astrochemical communities but for a much wider public auditory. Moreover, this research direction may potentially lead to new applications of carbonaceous and siliceous nanoparticles in industrial processes.

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37 Energetic-ion triggered chemistry on the surface of cosmic dust grain analogues

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Status

The chemistry in the interstellar medium (ISM) is a key to understanding galactic, stellar, and ultimately planetary evolution. Within dense regions of the ISM, dust particles are common and interact with the other constituents of the medium in several ways that are decisive for the local environment. They absorb and emit stellar light, provide surfaces for chemical reactions, and are the building blocks of comets, asteroids, planetesimals and planets.

Astronomical observations clearly show that in the cold, dense environments, the dust is mixed with molecular ices. Many of the laboratory experiments simulating physical and chemical processes on the surface of these cosmic dust grains have been performed on ices covering standard substrates, such as gold, copper or potassium bromide (KBr), which are not characteristic of cosmic dust grains [338–340]. For reviews, see [341,342]. This is due to the typical view of dust as comprising a compact core surrounded by a thick ice mantle. Physical and chemical processes occurring on and in such ices are considered independent of the properties of the dust surface.

However, recent laboratory studies have shown that bare dust material is available for surface processes in cold astrophysical environments. The experiments on the agglomeration of H_2O molecules on the dust surface [343,344] and on the thermal desorption of H_2O and CO ices mixed with dust grains [330,345] clearly demonstrate this finding. Cosmic dust grains may be covered by a sub-monolayer or few layer quantities of ice due to their fractal nature, high porosity and corresponding large surface area [330]. In addition, agglomeration of H_2O molecules may result in grain surfaces presenting both wet and dry areas even for a "thick" ice mantle [344].

Thus, we believe that the role of dust surfaces in the formation of molecules has been underestimated and studies involving reliable dust analogues are required to understand the physico-chemical picture of cold astrophysical environments. In addition to providing a meeting place for reactants, dust grains show catalytic effects which include: (i) dissipation of energy excess released in bond formation (i.e., acting as a third body); (ii) lowering of diffusion barriers for reactants and activation barriers of reactions; and (iii) direct participation (by atoms or functional groups) in surface reactions (see reference [326] for a review) (Fig. 54).

Current and future challenges

The main triggers of dust grain surface chemistry in cosmic environments are photon irradiation, cosmic ray interactions (both processes dissociate molecules producing reactive radicals), thermal processing (allowing for reaction barriers to be surmounted), and atom addition from the gas phase. The catalytic formation of molecules on cosmic grain analogues triggered by UV, atoms, and heat have been studied by several groups (see [326] for a review), however, chemistry on dust triggered by cosmic rays presents practically uncharted territory.

In [346], the abundances of new molecular species, characterized by FTIR spectroscopy, formed from formamide irradiated with 200 keV protons at low temperatures, were compared for amorphous olivine (MgFeSiO4) grains and inert silicon surfaces. The comparison showed that the presence of dust grains reduces the overall yield of synthesized species (NH_3; CN^-; NH_4^+ OCN^-, CO_2, HNCO, CO). This result was linked to the larger surface area of silicate grains compared to that of the silicon substrate, which may enhance desorption of formamide and to the possible charge exchange due to the presence of iron and magnesium metals in silicates.

Mennella et al. irradiated H_2O ices on hydrogenated amorphous carbon grains by 30 keV He^+ ions at 12 K [347]. The formation of CO and CO_2 was observed. The authors estimated from the experimental results that from a few to tens of percent of the carbon of carbonaceous particles can be converted to CO and CO_2 during a dense cloud timescale.

Another study was devoted to the synthesis of CO_2 on carbon foils covered by H_2O ice and triggered by 100 keV protons at 20 and 120 K [348]. The authors concluded that reactions of OH radicals and oxygen atoms with the carbon surface can be a significant source of CO_2 in interstellar grains.

Similarly, the synthesis of CO and CO_2 on the surface of amorphous carbon grains covered by H_2O and O_2 ices under 200 keV proton irradiation at 17 K has been observed [349]. The results reinforced the previous conclusion that the formation of CO and CO_2 strongly restricts the lifetime of the solid carbon material in cold astrophysical environments and demonstrated the graphitization of carbonaceous grains by proton bombardment.

Thus, previous experiments on the formation of new species involving dust materials have been devoted to binary systems (carbon + water or O_2) and low-energy particles (30 - 200 keV). The outcomes were the formation of only two simple molecules, CO and CO_2. Finding the origins of more complex molecules present in molecular clouds remains a challenge to solve.

The heavy ion fraction in cosmic rays (most have energies between 10 MeV/u and 1000 MeV/u) yields non-negligible contributions to radiolysis due to their high electronic energy loss, even if protons and alpha particles are significantly more abundant. Interactions with dust and ice materials should lead to the efficient production of reactive radicals and, possibly, much greater molecular complexity than we know from UV and low-energy-particle experiments. We might expect the catalytic formation of complex organic and prebiotic molecules.

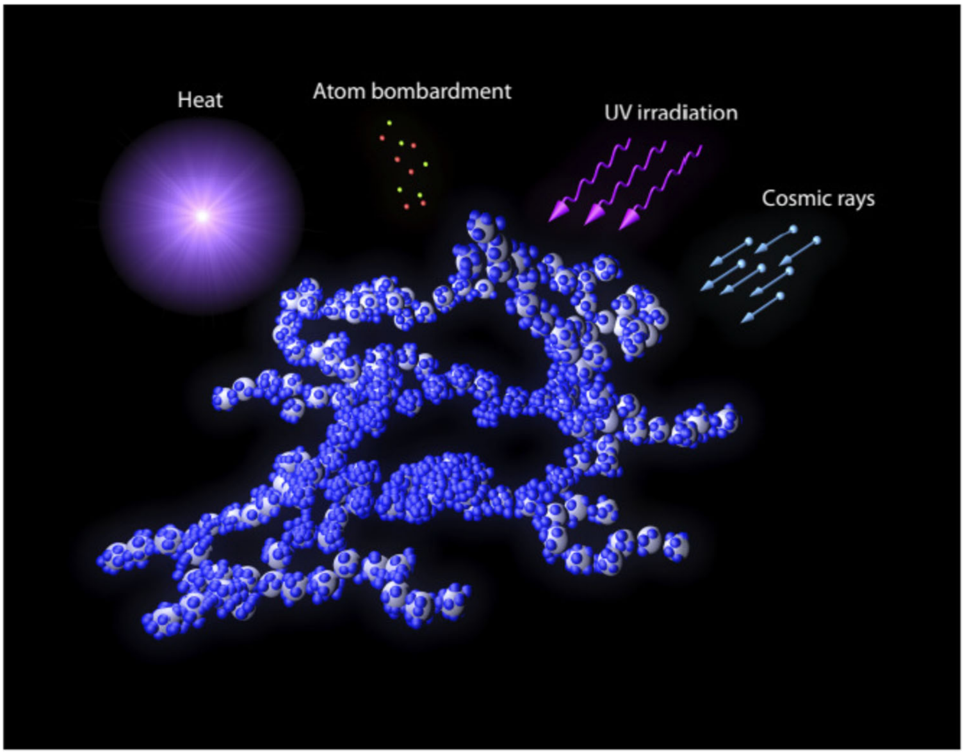

Fig. 54 Schematic showing dust grains (gray) mixed with ice molecules (blue) and the main sources of their processing in astrophysical environments. Figure reproduced from [330]

Advances in science and technology to meet challenges

With the realization, that through their complex, highly porous shape, the surface of dust grains is available for ice molecules to interact with, we aim to perform a set of experiments using such grains as substrate instead of the typical, chemically inert substrates. Relevant materials for the dust grain analogues are amorphous carbon and silicates such as pyroxenes and olivines of nanometric sizes. These grains can be produced using an existing laser ablation setup [345].

High energy (MeV-GeV range) ion irradiation at the GSI ion accelerator facility will serve as a trigger for reactions in key molecular ices abundant in astrophysical environments (H_2O, CO, CO_2, NH_3, CH_4, CH_3OH) on the surface of carbon and silicate nanoparticles (analogues of cosmic dust grains). Figure 55 shows the cryogenic spectroscopy chamber at the M-Branch at GSI UNILAC, which has been employed for a number of investigations into astrochemical questions, such as the sputtering and radiolysis of ices as well as complex molecules by using ion beams to simulate cosmic radiation, see , e.g., [350].

During irradiations at temperatures typical of cold, dense astrophysical environments, the evolution of the mixture of ice and dust grains will be monitored by FTIR spectroscopy and mass spectrometry. The main aims are to explore (i) the level of molecular complexity that emerges in astrophysical environments through cosmic ray interactions with icy dust grains, and (ii) the catalytic effect of the dust in solid-state astrochemistry.

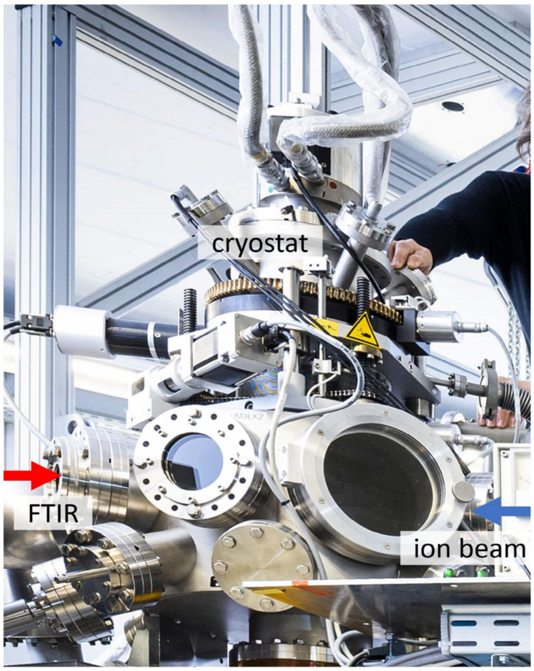

Fig. 55 Cryogenic spectroscopy chamber at the M-Branch at the GSI UNILAC ion accelerator

Concluding remarks

We aim to explore a new route in the laboratory study of chemical processes in cold, dense astrophysical environments by investigating energetic-ion triggered chemistry in mixtures of cosmic dust grain analogues with ices at low temperatures. We expect to extend the existing knowledge on the chemistry in these environments. Through the introduction of a setup that enables the particle surface to act as a catalyst, we might observe the formation of complex organic and prebiotic molecules, which will link our research to a big scientific question, the origin of Life on Earth.

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38 Quantum chemistry studies of prebiotic molecules on interstellar ices: the case of glycine

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Status

Glycine (NH_2CH_2COOH) is regarded as the basic building block leading to life [351]. Since its discovery in the Murchison meteorite , e.g., [352] it has been suggested that its formation could occur in the interstellar medium (ISM). Identification of Glycine in samples of cometary dust from comet 81P/Wild 2, in the coma of the Churyumov-Gerasimenko comet, in samples collected on the Ryugu asteroid and finally the recent joint experimental and astrochemical modeling study, have strengthened this hypothesis. However, despite many observational searches for gas phase glycine in interstellar sources with a first claimed detection in 2003 [353], refuted in 2005 [354], glycine has not yet been detected in the ISM.

Current and future challenges

From the standpoint of astrochemical modeling, the formation of glycine is investigated considering its both gas phase and solid-state chemistries, see , e.g., [355]. From this modeling there are more arguments for the solid-state mechanism and for solid glycine being the reservoir for gas phase glycine. However, if these authors [356] and [355] have concluded to the efficient formation of glycine upon interstellar ices, they disagree on the amount of glycine released in the gas phase. For instance, using a higher binding energy, it has been shown [357] that the formed glycine should be quickly destroyed by radicals such as NH or CH_3O present on the ice, before it fully evaporates into the gas phase. It was therefore concluded that there is a crucial need of a better knowledge of the binding energy of glycine on the ice, a key parameter that affects its abundance in the gas phase [356]. This claim has motivated our present computational study devoted to the calculation of accurate binding energies for NH_2CH_2COOH, COOH and NH_2CH_2 not yet available in the literature.

Advances in science and technology to meet challenges

We initially started extensive computations from a slab model [358] of the ice grain using a QM/MM hybrid approach and have concluded to a minimum size cluster of 34-water molecules to be described at the quantum level for accurate binding energy calculations. A prospection of the number of water molecules close to the adsorbed species NH_2CH_2COOH, COOH and NH_2CH_2, showed the importance of the closest four water molecules to which the molecules make close bonds which allowed us to leave the 30 remaining waters frozen. We employ density functional theory by means of M062X with two basis sets namely 6-311++g(d,p) and 6-31+g(d) to calculate binding energies of the fragments and of the two conformers of glycine on the 34-water grain model. M062X is parametrized to mimic short- and intermediate-range dispersion effects and has been shown to lead to reasonably good binding energies at near equilibrium energies [359]. All calculations were performed with Gaussian 16 software [106].

We define the binding energy of a given species with a grain model or a molecular cluster as $E_{\text{bind}} = -[E(\text{cluster} + \text{species}) - E(\text{species}) - E(\text{cluster})]$, where $E(\text{cluster} + \text{species})$ is the energy of the grain modeled by the cluster including the adsorbed species, $E(\text{species})$ is the energy of free species in gas phase and $E(\text{cluster})$ is the energy of the bare molecular cluster. For all calculations, the selected four water molecules being the closest to the adsorbed species (the four water molecules highlighted in green in Figs. 56, 57) are computed with M062X/6-311++g(d,p), the remaining 30 water molecules are computed with M062X/6-31+g(d) through the gen keyword.

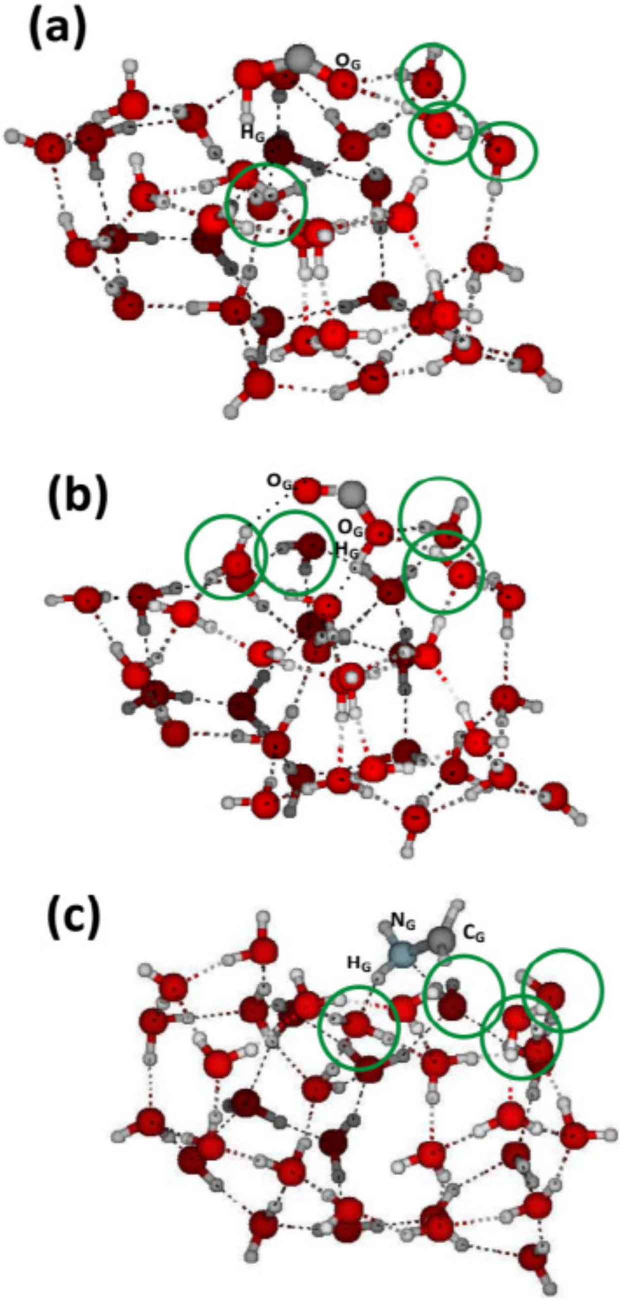

Fig. 56 Adsorbed COOH from glycine-*trans* (**a**), COOH from glycine-*cis* (**b**), NH_2CH_2 (**c**) on the 34-water model cluster

For the NH_2CH_2 fragment (a less hydrophilic molecule) the energy difference is less important between our calculated B.E of 5913 K and the 5530 K and 4680 K values reported in Ref. [356] and Ref. [355], respectively. From the astrochemical modeling standpoint, our BEs calculations for glycine tend to confirm the one used by Garrod (10100K), however their BE used for COOH is considerably smaller than ours. To compensate for the use of a mixed basis set approach, the Basis Set Superposition Error (BSSE) has been calculated by using the counterpoise (CP) correction. We give below a table (Table 1) comparing our computed binding energies on the 34-water model grain with those from [355,356]. We report with **G** index indicating the atoms belonging to glycine and respective fragments, the hydrogen bonds accommodating the species at the equilibrium geometry on the 34-water model cluster: O_G-H=1.96 Å, O_GH_G-O=1.46 Å, N_GH_G-O=2.53 Å, and N_G-H=1.87 Å, for glycine-cis, and O_G-H = 1.82 Å, O_GH_G-O= 1.54 Å, N_G-H= 1.78 Å, and N_GH_G-O = 3.2 Å for glycine-trans. Also, we give those relevant to the adsorption of COOH-cis: H_G-O=1.33 Å, and O_G-H=1.89, 2.09 Å, for COOH-trans: H_G-O=1.42 Å, and OG-H=2.13, 1.88 Å, and for NH_2CH_2: HG-O=1.95 Å, N_G-H=1.87 Å, and C_G-H=2.4 Å.

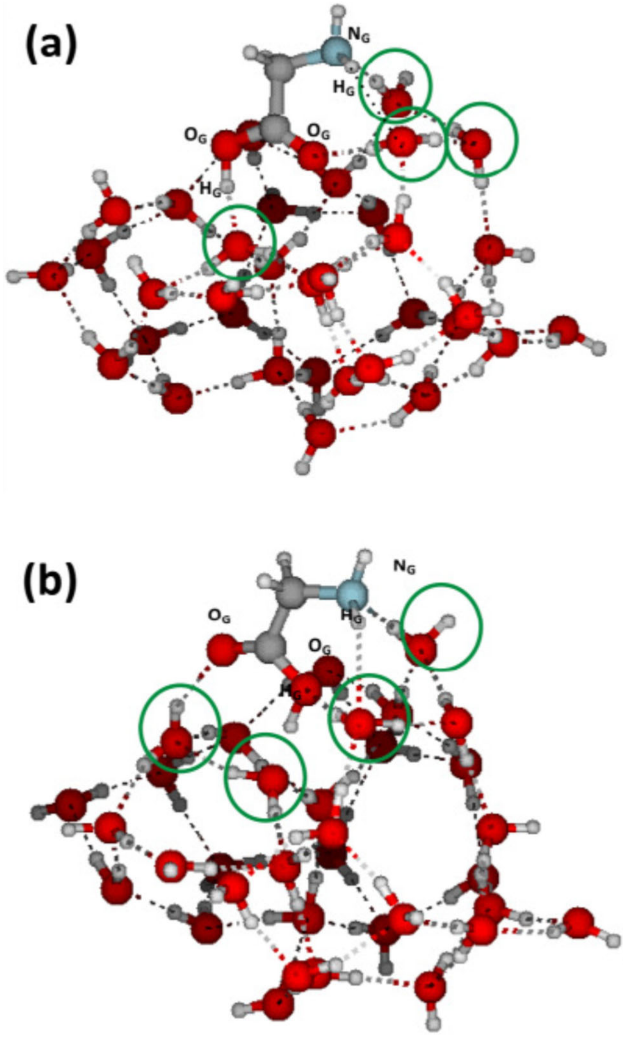

Fig. 57 Adsorbed glycine-trans (**a**), glycine-cis (**b**) on 34-water model cluster

It is worth noting that while in the gas phase our two lowest optimized conformers of glycine do correspond to the two lowest conformers of Ref. [360], i.e., (cis: *102*) and (trans:*011*), however, on the 34-water cluster our {energetically most stable} optimized cis and trans conformers become the *002* and *012* of the same reference (Table 1).

Table 1 M062X/gen computed ZPE, and BSSE corrected B.E: (Z.B.E), and (Z.B.E, BSSE) in kelvin, respectively, for COOH, NH_2CH_2, and glycine on the 34-water model cluster

Species	COOH -cis	COOH -trans	NH_2CH_2	Gly -cis	Gly -trans
Z.B.E.	9931	11756	6888	11213	13732
(Z.B.E BSSE)	7975	10369	5913	9440	11670
Garrod [355]	5120	–	4680	–	10100
Suzuki et al. [356]	2000	–	5530	–	–

Concluding remarks

We employ a 34-water molecules water cluster to be used as a grain model for accurate binding energy calculations. We calculate the B.E of COOH, NH_2CH_2 and of the two conformers of glycine. Within such a model, our calculated B.E for the two lowest trans and cis conformers of glycine are, respectively, 11670 K and 9440 K. As expected for a hydrophilic molecule we calculated high binding energies for the two COOH configurations: 7975 K for the COOH reactant associated to glycine-cis and 10369 K for the one associated to glycine-trans. These binding energies are much higher than the ones reported, 5120 K and 2000 K in [355, 356], respectively. Such high binding energies for COOH are likely to affect their rate of diffusion with consequences on the glycine formation. We hope that our calculated binding energies for both conformers of glycine, COOH and NH_2CH_2 will motivate new astrochemical modeling to investigate further this hypothesis of solid-state glycine as a reservoir for gas phase glycine.

Acknowledgments

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39 Surface interactions between ice and dust in planet-forming regions

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Status

Astronomical observations have revealed that the Universe is rich in molecules. More than 300 molecules have been identified in the interstellar and circumstellar medium. The formation and evolution of these species in star-forming regions are the key questions in astrochemistry. This requires input from astronomical observations, models, laboratory, and theoretical calculations. Carbon-based molecules have received the most attention due to their versatile hybridized bonds and their role in the building blocks of life. The goal of this research is to better understand how interstellar dust and gas evolve from diffuse clouds to planetary systems, shedding light on the composition of early planets.

In molecular clouds shielded from external radiation, atomic species, such as H, O, C, N, and S, start accreting onto the submicron-sized dust grains made of carbonaceous or siliceous material in the temperature range of 10–20 K. Dust grains act as a surface concentrator, allowing species to meet and providing a third body to dissipate the excess energy after exothermic reactions. In addition, the dust temperature is key in determining whether the newly formed molecules remain on the grains or desorb to the gas phase. H_2 has a relatively low binding energy on dust surfaces, so it is highly expected to desorb upon formation. In contrast, O atoms react with two H atoms ($O \rightarrow OH \rightarrow H_2O$), eventually forming a layer of H_2O-rich ice.

The accumulated ice layer covering dust grains with an average thickness of $\sim 0.005 \mu m$ forms the so-called interstellar ice mantle [361]. Laboratory and theoretical studies show that the energetic processing of interstellar ice further increases the molecular complexity, including the formation of aldehydes, alcohols, amino acids, and nucleobases through radical-radical reactions or radical-molecule associations (see review by Öberg 2016 [342]). It is important to note that the impacting photons or highly energetic particles are not completely absorbed (attenuated) by the ice layer due to the relatively small absorption cross section. As a result, the chemistry is not limited to the ice layer. The possible scenario is that such energetic processing triggers complex solid-state mechanisms in three different reaction regions from the outer to the inner ice mantle: bulk ice chemistry, ice-dust interface reactions, and probably dust alternation.

One of the research interests in the astronomical laboratory is to investigate the possible interactions between H_2O ice and carbonaceous dust upon impact by energetic particles or photons. Previous experimental results show significant erosion of carbon material, leading to the formation of volatile carbon-bearing molecules such as CO_2 and CO. For example, Mennella et al. (2004, 2006) estimated a better conversion ratio of carbon atoms bound in dust to newly formed CO and CO_2 of 1–8% after 30 keV He^+ radiolysis or UV photolysis of H_2O ice on (hydrogenated) amorphous carbon grains (HAC), depending on the sample material used [363,364]. Furthermore, Raut et al. (2012) used 100 keV protons to study the H_2O-carbon dust interface reactions and demonstrated the temperature dependence of the CO_2 yield but did not detect CO [348]. For the first time, the experimental work provided direct evidence for carbon erosion by labeling the dust with ^{13}C isotopes. Since only oxygen atoms resulting from the H_2O dissociation are incorporated into the products, Fulvio et al. (2012) investigated the possible role of carbon dust processing by O_2 ice to explain the CO_2 formation after UV irradiation [365]. A similar work by Sabri et al. (2015), using 200 keV protons, reported a destruction rate of 1.1×10^{-15} nm ion^{-1} for O_2 ice on amorphous carbonaceous (aC) dust and presented the microscopic images, including high-resolution transmission electron microscopy (HRTEM) and field emission scanning electron microscopy (FESEM), of dust samples before and after erosion [349]. All these experimental results clearly show the conversion of carbon atoms from refractory material to volatile species at the ice-dust interface upon energetic processing, enriching the carbon content in the molecular inventory.

Current and future challenges

Several possible reaction mechanisms have been proposed to explain the formation of CO_2 and CO in the interface chemistry. One hypothesis is the direct dissociation of carbonaceous dust to single carbon atoms, which can react with O atoms resulting from the ice layer (e.g., H_2O or O_2 ice) to form CO. Subsequent reactions with O or OH radicals lead to the formation of CO_2 (i.e., $CO+O\rightarrow CO_2$ or $CO+OH\rightarrow CO_2+H$). However, the absence of hydrocarbons and carbon oxides in this formation model has been questioned.

An alternative model has been suggested by Shi et al. (2015), which suggests the direct release of CO_2 molecules by the double oxygenation of carbon atoms bound to dust surfaces. The CO_2 is then dissociated into CO and O [366]. Chuang et al. (2023) experimentally proved the O-atom attachment mechanism using the selectively isotope-labeled oxygen molecules ($^{16/18}O_2$) on amorphous ^{13}C dust samples upon X-ray irradiation [362]. In Fig. 58, the IR spectrum (a) obtained from the experiment of $^{16}O_2$ ice on a-^{13}C dust shows the corresponding $^{13}C^{16}O_2$ and $^{13}C^{16}O$ with a relatively broad feature of the carbonyl group (i.e., refractory-$^{13}C{=}^{16}O$), which also remains as residue on the dust sample at 300 K. The X-ray irradiation of $^{18}O_2$ ice on the same carbon dust sample results in the formation of a $^{13}C{=}^{18}O$ functional group and a series of isotope-labeled $^{13}C^{18}O_2$ and $^{13}C^{16}O^{18}O$ (IR spectrum (b)). The experimental findings confirm the double oxygenation mechanism (i.e., sequential $^{16/18}O$-atom attachment to form $^{13}C^{16}O^{18}O$). Moreover, the essential intermediate carbonyl group bound to the dust surfaces is correspondingly transferred from refractory-$^{13}C{=}^{16}O$ to -$^{13}C{=}^{18}O$ in the residual spectra at 300 K. This mechanism is also consistent with the obtained product kinetics, which shows that CO_2 is formed more efficiently and earlier than CO, implying that CO_2 is the first-generation product.

Advances in science and technology to meet challenges

H_2O ice forms on interstellar grain surfaces and is expected to be exposed to cosmic rays or UV photons in star-forming regions. The chemistry in the ice mantle is complex due to the presence of different ice/dust phases. Furthermore, H_2O-coated dust is inherited by later planet-forming stages and coagulates in different geometries, sizes, and morphologies in the midplane of protoplanetary disks where EUV or X-rays from the central stars dominate the photochemistry. More laboratory work is desired to better understand how these high-energy photons interact with the icy mantles and whether interfacial chemistry occurs. Chuang et al. (2023) report similar products, CO_2 and CO formation resulting from the H_2O (O_2) ice on aC dust triggered by soft X-rays (250-1250 eV) at 13 K, along with the apparent graphitization of the dust sample [362]. The experimental findings also indicate that the product yield depends on the dust thickness, probably due to a larger ice-dust contact area. A follow-up study on the wavelength dependence (e.g., K-shell absorption of C: $\sim$ 284 eV and O: $\sim$ 543 eV) is planned to use a synchrotron light source. Besides the photon emission, the heat of the star also provides a radial gradient of temperatures ranging from 10 to a few hundred Kelvin. Icy grains can exist over a relatively wide tem-

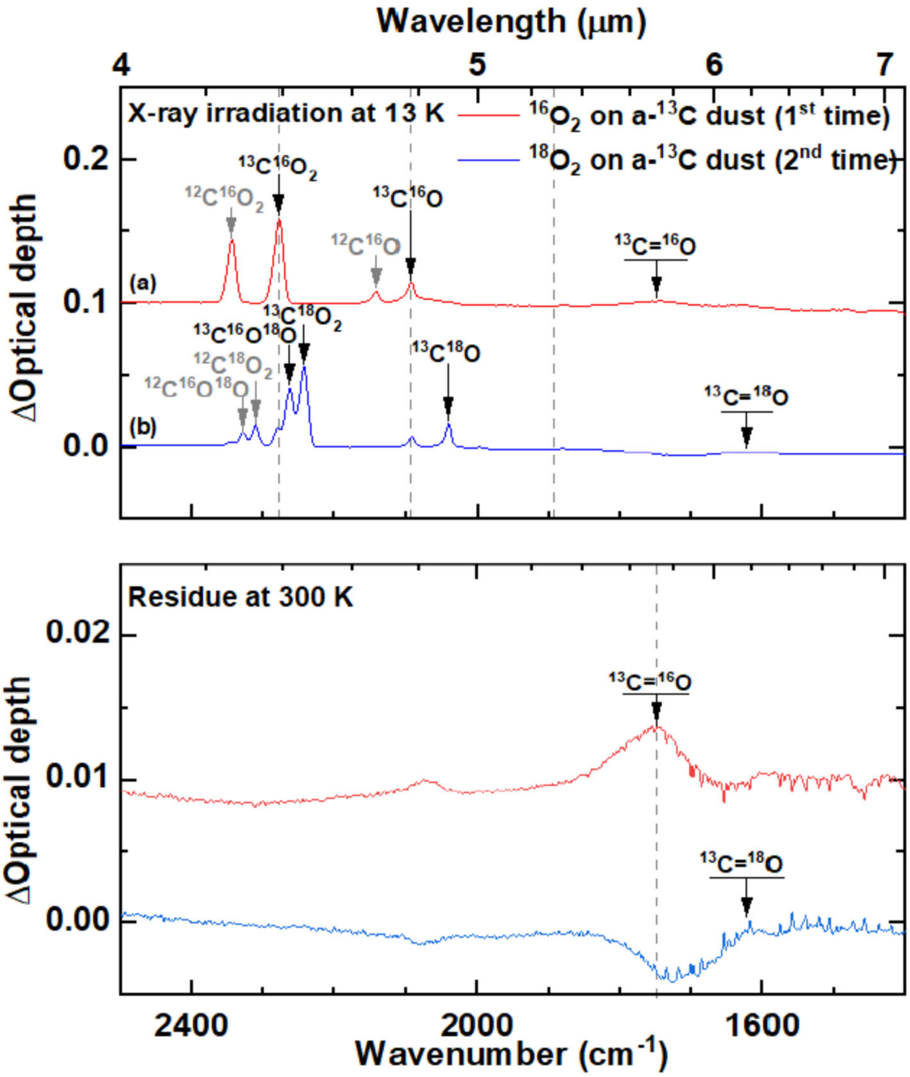

Fig. 58 Upper: the IR difference spectra obtained after X-ray irradiation of (**a**) $^{16}O_2$ and (**b**) $^{18}O_2$ ices on the same a-^{13}C dust analog at 13 K for 60 min. Bottom: the corresponding residual IR spectra measured at 300 K. Figure adapted from [362]

perature range (< 150 K). However, the newly formed CO_2 may remain in the ice or sublimate to the gas phase, depending on the dust temperature. Moreover, the vertical mixing of icy grains between the midplane and the elevated layers that suffer from enhanced X-ray flux is also desired to probe the comprehensive chemistry in protoplanetary disks.

Concluding remarks

In addition to passively providing a surface for species to react, cosmic grains can also chemically participate in interfacial reactions. Oxygen attachment has been extensively investigated in the laboratory with different energy sources, resulting in the common production of CO_2 and CO, which could influence the C/O or refractory/volatile ratios in protoplanetary disks. There are still open questions, such as whether other molecules could also induce carbon erosion and how carbonaceous dust is destroyed by harsh irradiation in the inner disks. With several advanced techniques used in astrochemistry, it is time to explore the unprecedented details of ice and dust chemistry in planet-forming regions.

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40 On the probability to form amino acids in space

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Status

Anaxagoras, (c. 510–428 BC) proposed that life was universal and introduced the term panspermia from the greak ”$\pi\alpha\nu$” (pan), ”all” and ”$\sigma\pi\epsilon\rho\mu\alpha$” (sperma) ”seed”. In the 1920s, Oparin formulated the theory of the prebiotic soup [367]. Methane, ammonia, hydrogen, and nitrogen, along with water in the early atmosphere, formed the building blocks for the origin of life through chemical reactions due to atmospheric electrical discharges, UV rays and sunlight. This theory is considered the beginning of many modern theories on the origin of life. In 1979 the idea appears that life could have originated in hydrothermal systems of the primitive Earth, whose characteristics are favorable for the abiotic synthesis of organic molecules [368]. However, it highlights the extraterrestrial origin of life. Extraterrestrial objects as a source of organic compounds from the early Earth, mainly carbonaceous chondrite meteorites. Both nitrogen and phosphorus are essential elements for life. The nitrogen compounds formed depend on the oxidation state of the atmosphere; a neutral atmosphere reduces nitrogen oxides to ammonia. Furthermore, the extraterrestrial material could have been a source of ammonia on early Earth. In the case of phosphorus, its presence in the terrestrial environment is limited, but carbonaceous chondrites contain it.

Carbonaceous chondrites (CCs) are fragments of primitive asteroids that contain abiotic organic material and provide a natural sample of extraterrestrial organic chemistry and chemical evolution before terrestrial life in the solar system. Analysis over 50 years have determined that these meteorites have a complex organic composition and contain diverse structures such as macromolecules and simpler soluble compounds such as amino acids. Many of these compounds have their equivalent in the biosphere, such as amino acids in proteins, and isotopic compositions that verify their formation in presolar environments and their subsequent evolution. It is not known if this evolution resumed on Earth to promote biogenesis.

Most amino acids, protein and non-protein, are chiral, i.e., they exist in two forms, L- and D- enantiomers, one being the mirror image of the other. To build proteins, life only uses the L-enantiomers. Therefore, biology exhibits homochirality and the reason why, is unknown, as the abiotic mechanisms that generate proteins and nucleic acids result in racemic mixtures, i.e., equal. However, some chiral amino acids from carbonaceous chondrites have enantiomeric excesses that have the same L-configuration as terrestrial amino acids, and this is not due to terrestrial contamination. These non-racemic amino acids from meteorites provide the only example of molecular asymmetry measured outside the biosphere. Therefore, because existing life requires homochirality for the structure and function of biopolymers, these discoveries imply the possibility that prebiotic properties were established in abiotic chemical evolution and contributed to the origin of life.

Current and future challenges

Amino acids are the building blocks of proteins, consisting of an amino (-NH_2) and carboxyl (-COOH) group together with a specific side chain for each amino acid. In addition, most amino acids in proteins bond a hydrogen atom to the α-carbon that is adjacent to the carboxyl.

One of the most important experiments for the synthesis of abiotic amino acids is the Miller-Urey experiment [369]. By activating an electrical discharge in a highly reducing gaseous mixture of CH_4, NH_3 and NH_2, at that time representative of the primitive atmosphere, protein amino acids including Gly, Ala and Asp were produced along with two non-protein ones. This result provided experimental support for Oparin's prebiotic soup theory. Recent analyses of the Miller-Urey experiments detected 23 amino acids, many more than the initial five [370].

Amino acids have also been synthesized from gas mixtures using UV, X-ray, and proton irradiation. The synthesis of α-amino acids, those that make up proteins and have the amino group attached to the carbon adjacent to the carboxy, occurs through a variant of the Strecker reaction [371]. This reaction begins with the gas phase production of HCN and aldehydes, followed by the condensation of these molecules with NH_3, to form α-aminonitrites in aqueous solution. Subsequent hydrolysis of the nitrile group to the carboxyl group generates α-amino acids (Fig 59) [351].

The irradiation with ultraviolet light in the laboratory of different gas mixtures (H_2O, CO, CO_2, CH_4, CH_3OH, NH_3), similar to those of interstellar ice, produces complex organic compounds, such as amino acids. These compounds are analyzed using chemical techniques such as gas chromatography coupled to mass spectrometry, GC-MS. Protein amino acids, such as alanine Al, and non-protein amino acids, such as 2,3-diaminopropanoic acid DAP, were found [372]. These amino acids have also been detected in carbonaceous chondrites [373].

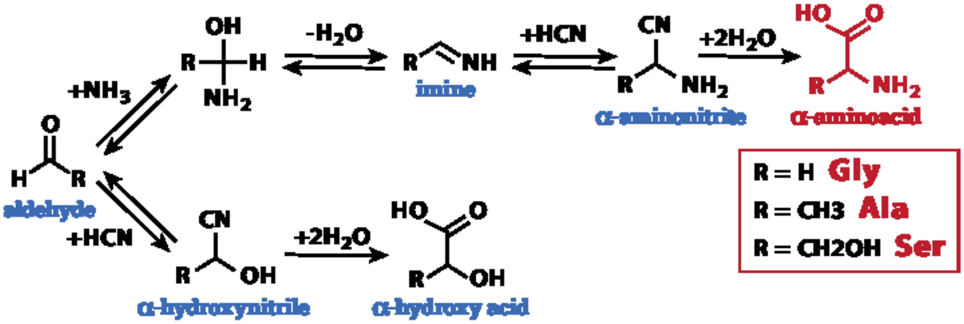

Fig. 59 Formation of α-amino acids. Figure adapted from [351]

Schlesinger and Miller [374] examined the effect of gas composition on the yield and variety of amino acids, demonstrating that gas mixtures of CH_4, H_2 and N_2 generate amino acids with excellent yields, while the opposite occurs with CO_2 and N_2. They also showed the relationship between the yield of amino acids and the pH of the solution.

Recently, the reaction of UV radiation, naphthalene ($C_{10}H_8$), NH_3, and H_2O has produced 13 amino acids [375]. However, we still do not know what is the probability that these reactions will occur.

In addition, it has been found that amino acids can survive a radiation dose of 14 MGy although they are reduced to 1/4-1/5 of their original value that they had at the beginning of the history of the Solar System [376].

Radioastronomy has enabled the identification of over 256 species not just in our backyard, interstellar clouds in the neighborhood of our Sun, but throughout our Galaxy, the Milky Way, in nearby galaxies and some distant quasars. Powerful new equipment like the Atacama Large sub-Millimeter Array (ALMA) and the James Webb Space Telescope promise to deliver more insight into the composition of molecular clouds and maybe even of water-ice grains.

Advances in science and technology to meet challenges

The challenge, as chemists, is to produce credible routes by which the simplest and abundant molecules like water, ammonia, carbon monoxide, hydrogen cyanide, etc can be transformed into more complex species at fast enough rates over the 1-to-50-million-year lifetimes of molecular clouds.

Some authors argued that the acid-induced autocatalytic addition of water to nitriles would lead to the formation of complex organic molecules (COMs or iCOMs) containing a peptide bond (-N(H) -C(O)-). These bonds link two *amino acids* together and long chains of amino acids form *proteins* – the foundations of life on Earth (and elsewhere?). This reaction is well-known to laboratory organic chemists and features in undergraduate textbooks but is perhaps not as well known outside that sphere. Of course, in the laboratory the reaction is conducted in the liquid state in solution whereas we are envisaging it taking place on amorphous water-ice grains in the interstellar medium under vastly different conditions.

Current suggestions in the astrochemical literature for radical-radical reactivity, and charged pathways also represent a promising mechanism to explain the formation of complex molecules. For example, the presence of the acid, hydronium H_3O^+, is absolutely crucial to the whole process and has very recently been considered [377].

We aim to establish the chemical routes through Density Functional (DFT) investigations. Establishing these pathways is a major accomplishment but do these reactions take place at sufficiently fast rates in the ISM to be significant? We now have to compute the kinetics of these reactions for which the minimum energy path has to be traced out and we have to include multi-dimensional quantum effects through the small-curvature tunnelling approximation in the case of small barrier-reactions or apply sophisticated variants of capture theory in the case of barrierless reaction mechanisms.

Concluding remarks

Experimental investigations of the formation and reactions of organic molecules in the interstellar medium is a complex and costly task. In recent years, the use of sophisticated DFT methodologies has become widely used to study chemical reactions of gaseous amino acids and related compounds. Amino acids have been found in meteorites and have been created in the laboratory; however, extensive search in the ISM has not yet provided any firm detection. Despite significant advances in computational chemistry, the characterization of several mechanisms by which amino acids can form in Space remains largely incomplete. This claim has motivated us to study by employing sophisticated tools of computational chemistry several aspects, such as energetically favorable reaction pathways, dust particles compositions and reaction mechanisms not yet available in the literature.

This observation can be made both for processes in the gas phase and for the elementary mechanisms involved at the interface between gas and interstellar dust grains.

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