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Graphene in the Interstellar Medium: An Astrochemical Perspective

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Abstract

The Interstellar Medium (ISM), owing to its tempestuous conditions, was never envisaged to yield any rich chemistry. In particular, the cold temperature regions erroneously seem rather inactive due to no large-scale, visible chemical activities taking place.

In this paper, we discuss and comment on recent literature as we introduce astrochemistry, talk about its wondrous avenues and delve deeper into these interactions, ones that especially take place at low temperature (Low Temperature Astrochemistry) and culminate by introducing the intriguing role carbon allotropes (like graphene) play in this interstellar matrix.

Keywords

Interstellar Medium (ISM), Graphene, Top-Down, Bottom-Up, Polycyclic Aromatic Hydrocarbons (PAHs)

Introduction

One might come across various reactions in labs which might be for synthesis, detection or identification. Often these reactions are optimized through a plethora of screening processes like temperature, pressure, solvent. In the ISM, these variables go beyond our labs into a dimension that voids human intervention, where nature's play is in its pristine form. Even a minute tinkering in the chemical recipe can present us with a product dish so unimaginable that it is almost surreal to even talk about chemistry in the stellar matrix of our being.

Astrochemistry in cold regions also called 'Low Temperature Astrochemistry', gained vigour in the late 1900's, when ammonia was first detected by *Townes et al.* as one of the first multiatomic molecules found in space [1], until when even its existence was often dismissed. Impressions in the scientific community for molecular interactions in this medium, owing to its extreme conditions and the presumed lack of activity, kept this field untouched from further research for a long time [2]. But now, as high as 256 chemical compounds have been detected in space as updated in the 2018 Census by *Mc Guire, B. A.*[3]

Since it is known for its diversity, it is natural that the ISM is not uniformly cold or hot, but its temperature in the range of millions of Kelvin. The interstellar matter also has densities varying from orders of nearly 10^{-26}g/cm^3 in the hot regions to 10^{-18}g/cm^3 in the dense molecular regions [4].
So, the components of the ISM can be broadly classified as follows:

- Interstellar Dark Clouds, consisting of cold molecular gas, with temperatures as low as 10 K-20 K.
- Interstellar Diffused Clouds, made of cold atomic gas, with approximately 100 K temperature.
- Apart from interstellar clouds, ISM constitutes the region spread between celestial bodies like stars. It is in the form of warm atomic, warm ionized and hot ionized regions found within the temperature range of 10^4 K-10^6 K.

Hence, the interstellar clouds, which tend to be the chemical reservoir for all the reactive processes to occur, are typically cold. This is because these cold regions provide an ambient environment leading to the genesis of planetary systems and other celestial bodies. So, the astrochemistry taking place in these regions is ultimately connected to the origin and evolution of the ISM the way we see it today.

Literature Studies

The recent surge in research coalescing chemistry and cosmology has led to major turning points that have now manoeuvred the curiosity of scientists in this direction. Exotic processes like formation of molecular ion complexes of noble gases in outer space, help us explore the noble gas chemistry, often sidelined as the 'inert moieties' in "on-Earth" chemistry, furthering research in this esoteric domain. The confirmation of the existence of HeH^+ (Helium Hydride) took place in 1925 when it was lab synthesized but it was only recently detected through terahertz spectroscopy at a distant planetary nebulae (NGC7027), in 2019 reported by *Gusten et al* [5]. It was theorized to have played an important role during nucleosynthesis, the formation processes of the first nuclei including hydrogen and helium which further lead to the production of other elemental species, post Big Bang. Similarly, after the detection of ArH^+ (Argonium Hydride) by rotational spectroscopy, studies talking about the possible use of argonium hydride as a tracer for monoatomic hydrogen gas, which relates to being >99.9%, have been carried out [7]. Simulation studies using quantum chemical computing also came up with plausible noble gas complexes viz. $ArCCH^+$, $ArOH^+$, $ArCN^+$, $ArNH^+$ that might exist in the ISM [8].
Now, these findings make us contemplate if astrochemistry can potentially lead or inspire chemistry we study in our labs. We might not know a lot about chemistry in space or the origin of life on Earth itself but, the intermolecular interactions taking place in the vast unknown space are universal, with foundations laid upon basic concepts guiding present day chemistry only. For instance, when large unsaturated organic molecules were first detected in cold dense clouds, it was pondered whether they could possibly be synthesized on Earth as well. The high C:H ratio in space helps in their formation while they will most likely get hydrogenated on Earth. So, simulating the conditions on Earth, after carefully studying the interstellar conditions, can possibly help us try reactions and synthesize molecules which would not be naturally found or possible otherwise.
A major significance of probing ISM is the astrobiological relevance of cold temperature astrochemistry. The evolution of any planetary system starts from diffuse ISM constituting low density cold cores. As molecular density increases due to gravitational pull, dense molecular clouds are generated. Evolving chemical composition eventually results in planetary systems via the formation of protostars. Thus, the cold ISM is likely to contain precursors, which may be used as biosignatures to study the presence or possibility of life, since the ubiquitous chemical moieties in ISM can be traced back to the beginning of the Solar System.
Carbon, the basis of life on Earth, happens to rank fourth among the other most abundant elements namely hydrogen, helium and oxygen, with <1% abundance (by mass) in the universe. But, being the key constituent of interstellar dust makes it crucial in the study of physico-chemical processes taking place in the ISM because this carbonaceous dust provides surface for the formation of molecules whose desorption leads to the enrichment of gas phase [9]. Owing to the varied amount of hybridizations carbon can exhibit, with the unique ability of catenation, one finds it

prevailing in diverse multi-atomic configurations, generally referred to as allotropes. Many of these carbon allotropes are known to be present in the ISM (*Jäger et al. 2011*) [10]. Due to this ability, carbon contributes to the molecular diversity of ISM. Hence, the study of molecular configurations in which these carbon atoms are present in the ISM can give immense information in the prebiotic context of development of organic molecules as well (*Henning & Salama* 1998).

Graphene, being one of the simplest and most versatile carbon allotropes, becomes a molecule of great interest to unfurl the chemistry of the more known entities like Polycyclic Aromatic Hydrocarbons (PAHs) and Complex Organic Molecules (COMs) which exist in different parts of ISM. Graphene is linked to them all, and thought to be a non-excludable part in the growth of such molecular species owing to the proposed Top-Down & Bottom-Up synthesis approaches. Yet, interestingly, it has still not been specifically identified in the ISM contrary to its closely related counterparts viz. fullerenes and presolar nanodiamonds [11]. Consequently, though it has almost been a decade

since fullerene was detected, the mechanisms exploring C_{60} synthesis are still being studied in-silico, by the means of chemical modeling and simulation based models, through UV photon irradiation of circumovalene ($C_{66}H_{20}$), discussed ahead in the Top-Down pathway. This makes graphene even more intriguing, as an allotrope, to study.

Materials viz. graphene, fullerene, are often synthesized through multiple techniques that can be largely classified as a.) Top-Down Pathway b.) Bottom-Up Pathway

Top-Down Pathway

Top-Down approach takes into account the formation route for interstellar carbonaceous dust starting from larger PAHs undergoing dehydrogenation to form graphene morphologies. These graphene sheets further undergo isomerization, fragmentation or cyclization leading to the enrichment of carbon dust in the ISM [11].

The unusual infrared emission features ranging from about 6 μm to 20 μm, accounting for the possible detection of planar graphene in the Magellanic Cloud planetary nebulae *(García-Hernández et al., 2011)*, point towards the likelihood of C_{24} being synthesized through this approach via the dehydrogenation of larger PAHs [12].These observations yearn for further analysis and study of graphene in astronomical bodies like meteorites.

It has been under discussion that, in the diffuse ISM, Top-Down formation pathways should be considered as per efficiency because of the requirement of high density and temperature conditions otherwise, as discussed ahead in the Bottom-Up approach. *Berne and Tielens* (2012) found a rise in C_{60} and simultaneous decrease in PAHs abundances with increasing UV field in NGC 7023 nebula, via the formation and folding of graphene finally producing fullerene [13]. This points towards the fact that the graphene sheets synthesized from PAHs, via the

Top-Down approach, can create fullerene following the discussed folding mechanism in UV field which goes on to decide its fate in the ISM after it has been produced. So, herein, graphene can also be thought of as a species useful to study the ultraviolet field present in the region based on its abundance. Also, while discussing the sensitivity of the model it was found that, for NGC 7023 nebula under study, the time span of dehydrogenation was so much smaller than the cage formation and shrink timescale that it is equivalent to start the calculations with planar C_{66} graphene flakes rather than $C_{66}H_{20}$ [14]. Hence, graphene flakes might be effectively used as precursors to study

Top-Down Formation pathways in ISM in general.

Bottom-Up Pathway

The growth of carbon nanostructures viz. graphene, fullerene, quantum dots, from simpler chemical moieties like methane, acetylene, benzene, and small PAHs, support this synthesis model which is thought to be a more pragmatic route for carbon dust formation when talking about the dense interstellar conditions in the high temperature regions. *Biennier et al.* found that XRD analysis of carbonaceous dust as a bulk sample, produced from the pyrolysis of acetylene, led to the detection of amorphous matrix containing small, organized aromatic islands composed of two graphene layers connected via aliphatic linkages [15]. The ubiquity of PAHs is not something new so the possibility of these PAHs to form larger graphene sheets cannot be overlooked. In that sense, these PAHs can find useful application in the study of graphene formation under conducive conditions while they can also be explored as possible tracers for graphene rich environments. Lab experimentation has already witnessed methane forming carbon clusters up to C_{20}, apart from its omniscient role in the formation of various organic molecules upon irradiation [16], hinting at the plausible synthesis of graphene as well.

Using their model, based on quantum-chemical computations and experimentations, related to the UV absorption and IR emission studies, *Chen et al.* estimated that an upper limit of almost 2% of the total amount of carbon in ISM can be possibly applied for graphene's enrichment in the interstellar space [17]. Due to the non-detection of prominent features in the IR emission spectra in comparison to that standard spectra observed in the ISM, an upper limit of C:H ratio was estimated to be nearly 5 ppm for the same .

Nanoscale graphene morphologies have been reportedly seen in the carbonaceous chondrites, belonging to the CV3 category, namely QUE 94366 and Allende meteorites [18]. The morphologies discovered here might as well belong to the carbonaceous materials, in the nebular zones surrounding the proto-Sun, dating back to the time the Sun was in its initial phase of formation. But no such specific observation has been made in the cold ISM regarding the presence of graphene or even graphene-like morphologies, as in the above case which happens to be the hot temperature ISM. Though chemical processes in the cold ISM eventually lay ground for the molecular diversity found in the planetary and stellar medium, these are relatively understudied. Thus, the cold regions in the ISM including interstellar dust, or carbonaceous molecules embedded in icy mantles, should also be studied as these regions can provide necessary conditions for atoms to interact over a span of time, and diffuse in the ice matrix after being processed by energetic sources like cosmic rays, UV photons, to produce a stable form they can exist in.

Though there is a lack of graphene being observed, laboratory experimentation has shown the possibility of its presence in cold temperatures, when the reaction temperatures were kept as low as 4 K to 300 K as the experiment proceeded, as discussed ahead. Recently, *Sivaraman et al.* proposed a possible pathway for graphene formation even in cold ISM conditions, as reported in 2023 [19]. They explore the synthesis of N-doped graphene by the Vacuum Ultraviolet (VUV) irradiation of benzonitrile ice film using 9 eV photons. The ice film using LiF and KBr as substrate supports was formed by benzonitrile deposition at 4 K. The photon irradiation was carried out for around 9 hours, followed by warming the sample to 300 K uniformly and analyses by IR and VUV spectroscopy. This work is first of its kind which brings together synthesis of Quantum Dots (QDs) and doped graphenes at these interstellar temperatures opening new avenues for research and study.

Discoveries like these are inspiring researchers around the globe to tinker in their laboratories with experiments which might lead us to an enhanced understanding of the pathways behind such findings.

Conclusion

As evident from the discussion, one potential way might be to study ices of derivatized aryls through irradiation and comparing their reactivities and products to look out for other graphene analogues. Due to their higher reactivity compared to their unsubstituted counterparts, upon irradiation these might lead to a more convenient formation of graphene-based moieties owing to their varied physico-chemical properties.

This exploratory irradiation of ices, made from specific chemicals can also find application in more mainstream industries and academia as a developmental procedure for small scale synthesis of exotic molecules. Here too, various parameters like the duration of irradiation, extent of rewarming, purity of the ices and even multilayered ices, are likely to play a role in the product that is aimed to be synthesized.

Also, nebular carbon materials like those discussed by *Giri et al.,* have been claimed to be of enormous significance in redshift astronomy and astrophysics related studies. Carbon rich species are contemplated to be promising candidates for the variety of anonymous spectroscopic features observed in different parts of ISM hence, studying their formation pathways will give greater insights into the physical conditions of the ISM [20].

Sivaraman et al. have shown the possibility of existence of QDs even in the harsh interstellar conditions based on their experimental findings. This opens new avenues in the observational astronomy field to explore this multifaceted carbon nanochemistry for promising breakthroughs in future.

Discussions about the specifically detected C_{60} and C_{60}^{+} fullerenes (in ISM) by *Berne et al.* as the investigators of the chemical dynamics of carbon derived species have piqued scientific interest, as they offer a new methodology to probe the physico-chemical conditions of the ISM. Hence on the same note, graphene, the parent allotrope of the carbon family, can also potentially be used as a tracer of the interstellar environment to probe the rich carbon chemistry non-existent on earth, yet dominant in the chassis of our universe.

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