

Observations of the photochemical evolution of carbonaceous macromolecules in star-forming regions

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Abstract. The goal of this contribution is to illustrate how spatially resolved spectroscopic observations of the infrared emission of UV irradiated regions, from star forming regions to the diffuse ISM, can be used to rationalize the chemical evolution of carbonaceous macromolecules in space, with the help of astrophysical models. For instance, observations with the Spitzer space telescope lead to the idea that fullerenes (including C_{60}) can form top-down from Polycyclic Aromatic Hydrocarbons in the interstellar medium. The possibility that this process can occur in space was tested using a photochemical model which includes the key molecular parameters derived from experimental and theoretical studies. This approach allows to test the likelihood that the proposed path is realistic, but, more importantly, it allows to isolate the key physical processes and parameters that are required to capture correctly the evolution of carbonaceous molecules in space. In this specific case, we found that relaxation through thermally excited electronic states (a physical mechanism that is largely unexplored, except by few teams) is one of the keys to model the photochemistry of the considered species. Subsequent quantum chemical studies stimulated by the (limited) astrophysical model showed that a detailed mapping of the energetics of isomerization and de-hydrogenation is necessary to understand the competition between these processes in space.

Such approaches, involving experimentalists and theoreticians, are particularly promising in the context of the upcoming JWST mission, which will provide access to the signatures of carbonaceous species in emission and in absorption at an angular resolution that will enable to reach new chemical frontiers in star and even in planet forming regions.

Keywords. astrochemistry, ISM: molecules, ISM: clouds, ISM: fullerenes; methods: observations and modeling

1. Introduction

Spectroscopic observations of the infrared emission of UV irradiated regions, in star forming regions, reveal spectroscopic signatures at 3.3, 6.3, 7.7, 11.2 and 12.7 μm (Fig. 1). These signatures have been attributed to gas-phase macromolecules belonging to the family of Polycyclic Aromatic Hydrocarbons (PAHs, Léger & Puget (1984); Allamandola *et al.* (1985), see structures in Fig. 1). More recently, specific bands at 7.0, 17.4 and 18.9 μm have been attributed to the C_{60} buckyball (i.e. Buckminsterfullerene) in the NGC 7023 reflection nebula by Sellgren *et al.* (2010) and in an evolved star by Cami *et al.* (2010).

2. Variations in the infrared spectra

One particular aspect of these infrared bands when observed in nearby star-forming regions is that they show some spatial variations. In the case of the NGC 7023 nebula, the

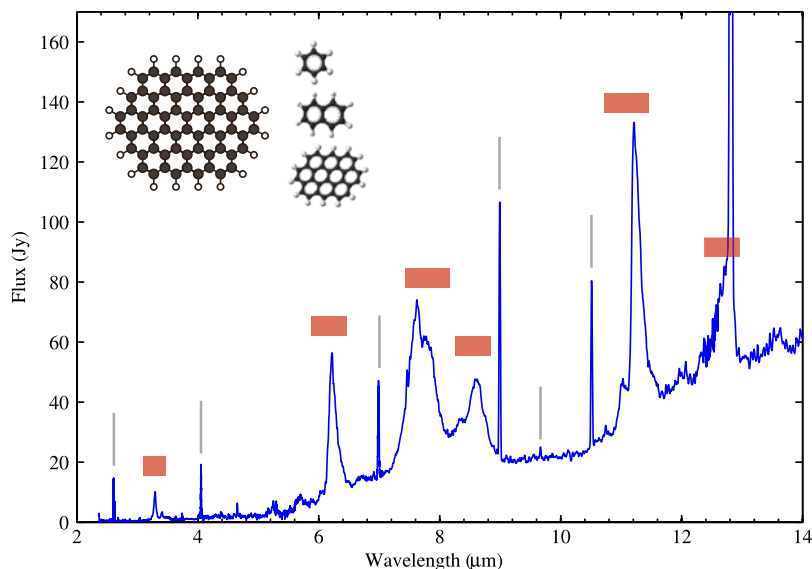


Figure 1. Mid-infrared spectrum of the Orion Bar, obtained with the ISO satellite. The broad bands observed at 3.3, 6.3, 7.7, 11.2 and 12.7 μm marked with red labels have been attributed to PAH emission. The narrow lines are due atoms or small molecules present in the gas. Upper left hand corner: a few molecular structures belonging to the PAH family are represented (with Carbon in black and Hydrogen in white).

variations as a function of the distance of the star show that C_{60} emission increases when approaching the star while PAH emission decreases (Fig. 2). This observation presented in Berné & Tielens (2012) was interpreted as evidence of the formation of C_{60} in the interstellar medium, at low temperature and low density (typically, $T = 10$ to 100K, with densities at most of $n_H = 10^3 \text{ H/cm}^{-3}$). At such low densities, classical formation routes, which build-up the C_{60} bottom-up from small carbon containing units are inefficient. This observation and evidence from laboratory experiments that direct transformation of graphene into fullerenes is possible (Chuvilin *et al.* 2010) lead Berné & Tielens (2012) to propose that the buckyball is being formed top-down in the ISM, by photochemical processing of large PAH molecules.

3. Building a photo-physical model of the evolution of large carbonaceous molecules in space

The proposed top down scenario (Fig. 3) was later rationalized using a detailed photo-chemical model by Berné *et al.* (2015). In this model, a template PAH (i.e. circumovalene, $C_{66}H_{20}$) is exposed to UV radiation (the UV field generated by the star in NGC 7023). After UV absorption, the molecule can relax through different mechanisms, mainly: emission of radiation, dissociation, ionization and isomerization.

If these various chemical paths can be characterized theoretically or experimentally in terms of molecular parameters (such as activation energy), they can be inserted in an astronomical model, and the time-dependent evolution of the species can be computed. This is what has been done in Berné *et al.* (2015), using the molecular parameters available in the literature for the key reactions described in Fig. 3. Using this model, the authors show that the top-down formation of C_{60} is possible in strong UV environments ($G_0 = 10^5$, in units of the Habing field Habing (1968)), over typical time scales of 10^5 years, i.e., comparable to the age of the NGC 7023 nebula. One important aspect of this

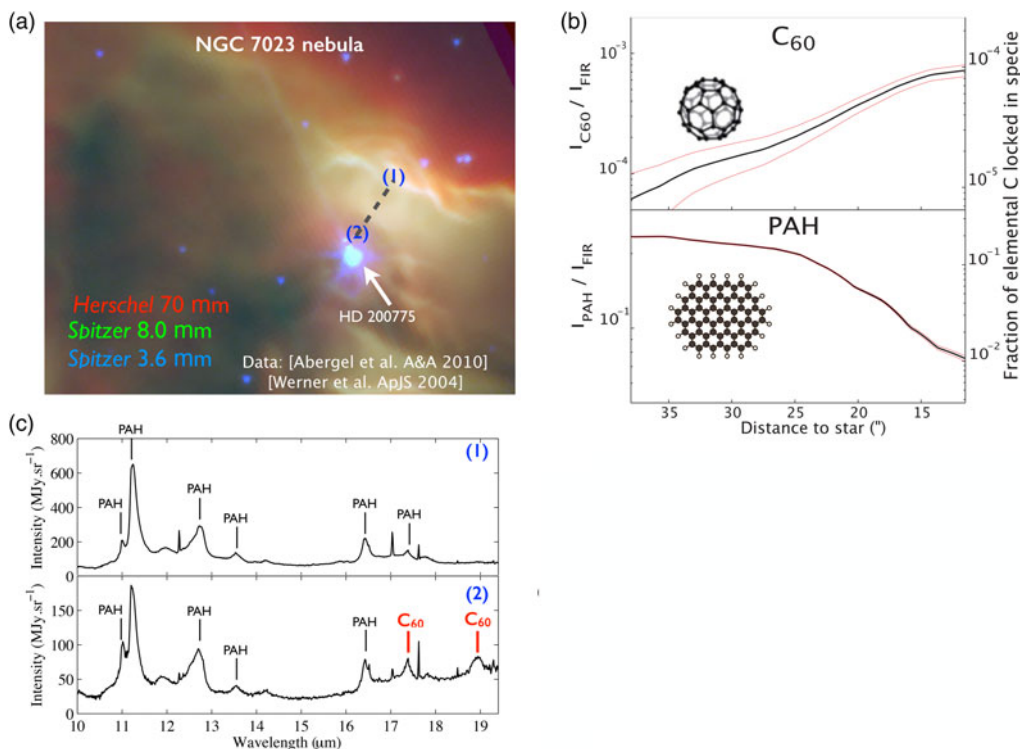


Figure 2. Upper left panel : RGB image of the NGC 7023 nebula. Lower left panel : Spitzer IRS spectra taken at positions (I) and (II) shown in the image. PAH and C₆₀ bands are labeled. Upper right panel : abundance profile for PAHs and C₆₀ along the cut between position (I) and (II), and derived from the IRS and Herschel data. Figures taken from [Berné & Tielens \(2012\)](#).

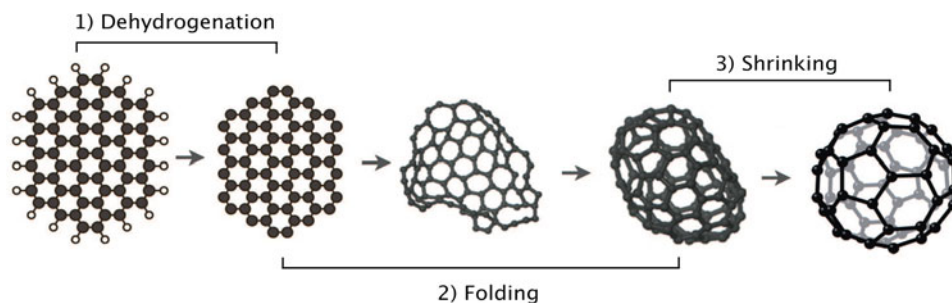


Figure 3. Schematic view of the evolution of PAHs into C₆₀ under UV irradiation from massiv stars. Figure taken from [Berné et al. \(2015\)](#).

study is that it shows that the main relaxation mechanism competing with isomerization, and thus limiting the efficiency of fullerene formation, is a relatively unexplored physical process called delayed fluorescence, or Poincaré fluorescence (emission from electronic levels populated after the molecule has been highly excited vibrationally, a mechanism which was proposed for PAHs by [Léger et al. \(1988\)](#)). The direct characterization of this mechanism for large molecules has been elusive, and thus, the description that is given in the model of [Berné et al. \(2015\)](#) is somewhat limited by the absence of laboratory measurements of the efficiency of this radiative process. This illustrates how

astrochemical models are intrinsically limited by the knowledge available on fundamental processes, and underlines the importance of experimental and theoretical characterization. Another example concerns the sequence proposed in Figure 3. Recent quantum chemical calculations performed by Parneix *et al.* (2017) suggest that the formation of pentagonal defects which provides curvature and can lead to folding may in fact occur before dehydrogenation (contrary to what is depicted in the scenario of Fig. 3). This does not mean that the model of Berné *et al.* (2015) is incorrect, but that it needs to be refined to include paths where defect formation competes efficiently with H loss. Again, this shows how theory (in this case) is necessary to rationalize correctly (in models) information that is obtained through observations.

4. Taking the next step in the JWST era

Many more observations of the kind described in Fig. 2 will be obtained with the upcoming JWST mission, and thus the already existing and fruitful synergy between molecular physicists and astronomers will prove useful to probe in even greater details the paths that lead to chemical complexity in space. This is also one of the aims of the early release science program “radiative feedback from massive stars as Traced by Multiband Imaging and Spectroscopic Mosaics” (Berne *et al.* 2017) that will make spectral maps of a star-forming region with unprecedented spatial resolution, allowing to probe new chemical frontiers.

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