

The life cycle of large carbonous molecules in the interstellar medium

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The interstellar medium (ISM) contains a rich molecular inventory, where various chemical reactions can take place. This work review the recent quantum chemical computations and laboratory experiments on the study of fragmentation and molecular growth of large carbonous molecules in the ISM.

One of the most abundant carbonous molecules in the ISM are polycyclic aromatic hydrocarbons (PAHs), which lock up 10% – 20% of the carbon in the ISM and are commonly observed in a variety of astronomical objects, ranging from the Galaxy to extragalactic regions (Tielens 2008). Beside PAHs, fullerenes have been identified in the ISM (Cami *et al.*, 2010). And ~ 5 ppm of C/H, i.e., $\sim 1.9\%$ of the total interstellar C are locked on the interstellar graphene (Chen, Li, & Zhang 2017). Interestingly, both experimental and theoretical studies prove that fullerenes and graphene flakes can be formed from large PAHs through dehydrogenations and isomerizations (Berné & Tielens 2012; Zhen *et al.* 2014).

Figure 1 shows some possible carbonous reactants and their reaction pathways in the ISM. In brief, the gas-phase molecules can be ionized, isomerized, dissociated following the impacts of ions, atoms, or photons (Chen *et al.* 2014; Stockett *et al.* 2014, 2015; Zhen *et al.* 2016). Regarding ionizations, the quantum chemical calculations show that the ionization energies follow linear dependencies as functions of charge state for different size of PAHs. And the total ionization and fragmentation cross sections in ion-PAH collisions display markedly different size dependencies for pericondensed and catacondensed PAH molecules, reflecting differences in their first ionization energies. PAHs in charge states above certain limits may survive in experimental time scales due to the presence of reaction barriers (Holm *et al.*, 2011).

About dissociations, we find two types of fragmentation processes: statistical and non-statistical fragmentations. In statistical fragmentation processes, the losses of $C_{2n}H_x$ dominate the mass spectra (Chen *et al.* 2015). Non-statistical fragmentations refer to direct knock-out of atoms from a molecule, and single C-losses are commonly observed in such process (Stockett *et al.* 2014). The fragmentation of molecules lead to the formation of small molecules or isomerize to more stable structure, such as C_{60} or C_{70} (Zhen *et al.* 2014).

Beside fragmentation, small molecules may conglomerate a weakly bonded cluster, and form large molecules in the cluster following statistical or non-statistical fragmentations (Zettergren *et al.* 2013; Delaunay *et al.* 2015; Zhen, Chen, & Tielens 2018). In such reaction cycle, molecular hydrogens (Chen *et al.* 2015) and new carbonous molecules are produced, e.g., the bowl-shape molecules are found in the photodissociation experiment of bisanthenequinone cations (Chen *et al.* 2017), dumbbell C_{118} and C_{119} are formed

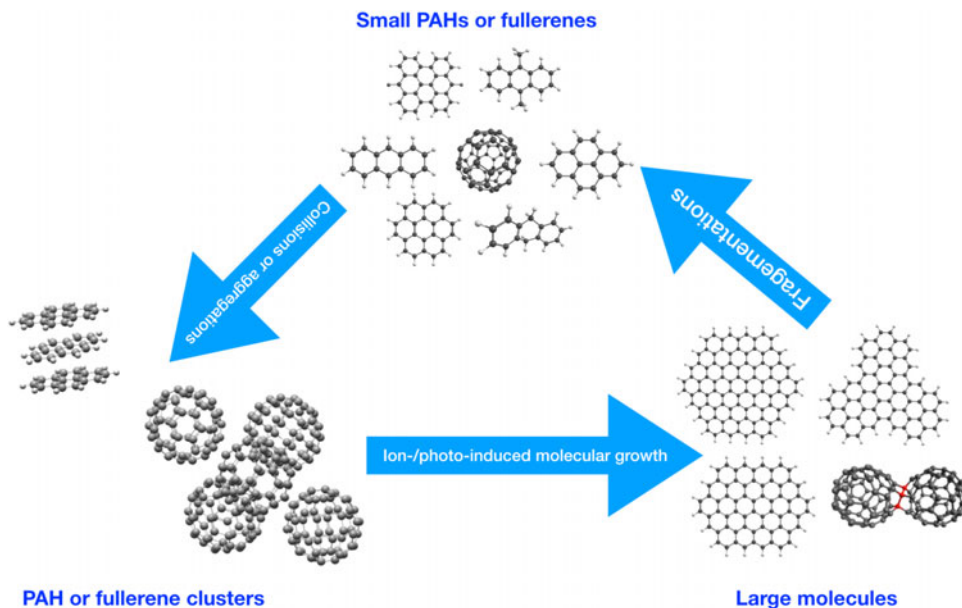


Figure 1. The life cycle of polycyclic aromatic hydrocarbons (PAHs) in the ISM. Small PAH molecules may form weakly bonded clusters through aggregations or soft collisions among molecules. Large molecules can be formed in the clusters rapidly following the impacts of ions, atoms, or photons. On the other hand, large PAHs may also dissociate to small molecules through statistical fragmentation or non-statistical fragmentation processes.

inside clusters of C_{60} by collision with α particles (Zettergren *et al.* 2013), etc. These reactions enrich the molecular inventory in the ISM.

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