POSTERS

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Interstellar polycyclic aromatic hydrocarbons: Spectroscopy, photofragmentation and photoproducts

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Abstract. Ubiquitous strong mid-infrared emission bands are observed towards many objects and are attributed to interstellar Polycyclic Aromatic Hydrocarbons (PAHs). PAHs are ionized, or even dissociate, when exposed to strong interstellar radiation fields. By means of ion trap mass spectrometry, light-induced dissociation patterns of PAH cations are measured and the mid-infrared spectroscopic signatures of the parent ion and its dissociation products are characterized. These results are then combined with density functional theory (DFT) calculations to obtain insight into the dissociation characteristics of interstellar PAHs at a molecular level.

Keywords. astrochemistry, methods: laboratory, techniques: spectroscopic, molecular processes

1. Introduction

A distinctive set of mid-infrared (mid-IR) emission bands located at 3.3, 6.2, 7.7, 8.6 and 11.3 μm are detected towards a variety of galactic and extragalactic sources. It is generally accepted that these emissions bands are caused by PAHs relaxing to the ground state by IR fluorescence after they have been excited by the interstellar radiation field (Allamandola *et al.* (1989)). It has been estimated that about 15% of the total cosmic carbon budget is locked-up in aromatic molecules, emphasizing their importance in the cosmic cycle of matter. Interstellar PAHs can dissociate upon excitation by an intense radiation field and the induced chemical transformations are reflected in the IR emission bands. It has been suggested that dissociation of large aromatics eventually results in the formation of interstellar fullerenes (Berné & Tielens (2012)). The underlying chemical processes involved in the dissociation of aromatics are not well understood. We apply a combined experimental and computational approach to shed light on the PAH dissociation mechanisms.

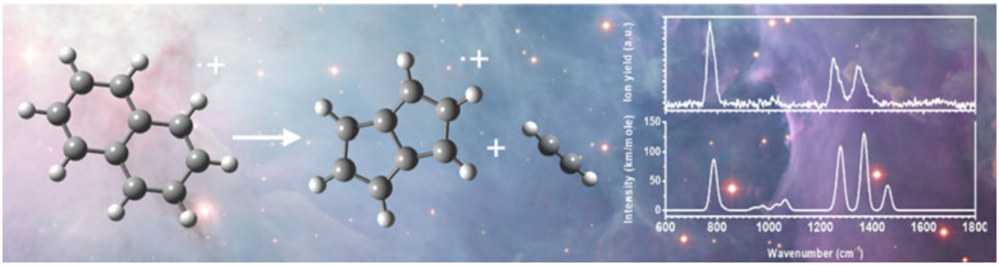

Figure 1. Mid-infrared spectroscopic evidence for the formation of pentalene$^{\cdot+}$ from the dissociative ionization of naphthalene. Figure is based on data from Bouwman *et al.* (2016).

2. Method

Experiments are performed on a Paul-type quadrupole ion trap time-of-flight (TOF) mass spectrometer. Ions are generated by electron ionization or 193 nm ArF excimer laser multiphoton ionization. Ions are transferred into the ion trap by means of electrostatic lenses, where they are trapped in a Radio Frequency (RF) field and mass-selected species can be isolated. Next, the mass-selected ions are exposed to laser radiation originating from a dye laser to induce dissociation and the fragmentation pattern is measured as a function of laser fluence by means of TOF mass spectrometry. Mid-IR spectroscopic measurements are performed with the ion trap connected to the free electron laser for infrared experiments (FELIX) at Radboud University. Quantum chemical computations using density functional theory (DFT) are performed using the supercomputer LISA at SURFsara to obtain molecular insight.

3. Results and Conclusions

IR spectroscopy: We performed mid-IR action spectroscopy on a series of PAH cations ranging from small species such as naphthalene up to sizes that are astronomically relevant, with the largest species being dicoronylene ($C_{48}H_{20}$). The PAHs studied in our experiments were selected to span various symmetry groups and degrees of compactness to investigate the effect of these parameters on the appearance of their respective IR spectra (Bouwman *et al.* (2019)). From these studies we concluded that the most compact PAHs with the highest symmetry have IR spectra that best resemble the observed mid-IR bands, while PAHs with lower symmetry exhibit modes at frequencies that do not correspond to the main IR emission bands.

Dissociation patterns and dissociation products: Our studies of the light-induced dissociation of PAHs reveals that large symmetric PAHs (i.e., larger than ∼24 C-atoms) dissociate via full dehydrogenation followed by loss of C_2-units. Dissociation of such large PAHs cations results in bare carbon clusters, which are likely in the form of fullerenes (Zhen *et al.* (2014)). Small and irregular PAHs tend to loose C_2H_2-units or carbon chain ions from the (partly dehydrogenated) parent ion. IR spectroscopic studies of dissociation products formed form small (nitrogen-containing) PAHs revealed that pentagon are included in the hexagon-containing aromatic structure (de Haas *et al.* (2017), Bouwman *et al.* (2016) and Fig. 1). This is a critical step in fullerene formation that suggests that top-down formation of fullerenes from PAHs may occur in the ISM.

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