

TOWARDS THE ELECTRONIC SPECTROSCOPY OF LARGE PAHS IN A FUEL-RICH FLAME

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Abstract.

Polycyclic Aromatic Hydrocarbons (PAHs) are considered to be an important component of the interstellar medium. However, no formal identification is possible at present, due to a lack of laboratory gas-phase spectral data for most of them.

We present an exploration of our new chemical reactor, a low-pressure flame, from which a large amount of PAHs are produced. This step is necessary, if we want to perform UV-visible electronic spectra of such large carbonaceous molecules, which could be compared to astrophysical data.

1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) seem to be an important part of the carbonaceous component in the interstellar medium (Puget & Léger 1989). They are thought to play there a prominent role in the physical and chemical processes. In particular, the Aromatic Infrared Bands (AIBs) are attributed to them (Duley & Williams 1981; Léger & Puget 1984; Allamandola et al. 1985). However the exact distribution and nature of PAHs needed to explain the positions and the profiles of these bands remain unclear. PAHs could also be responsible for the Diffuse Interstellar Bands (DIBs) (Léger & d'Hendecourt 1985; van der Zwet & Allamandola 1985) and contribute to the shape of the interstellar extinction curve and the so-called UV-bump.

In order to better understand the properties of PAHs, a set-up, the “Nanograins Experiment”, has been developed in the group “Astrophysique et édifices moléculaires” of the Laboratoire de Photophysique Moléculaire¹ in collaboration with the group “Astrochimie expérimentale” of the Institut d’Astrophysique Spatiale². The aim of the experiment is to form large PAHs-like species and to study them in interstellar-like conditions. The source is a flat laminar fuel-rich flame. This kind of reactor is known to form a wide diversity of carbonaceous structures, highly depending on the flame conditions (Homann 1998).

The species formed in the flame are characterized by their mass spectra. A large variety of flame conditions have been investigated (fuel, pressure, fresh gas velocity and C/O ratio). At first, we show evolutions in concentration profiles according to the burner distance and then we present the key parameters for the formation of large PAHs containing up to 50 carbon atoms.

2 General overview

Carbonaceous molecules are produced in a premixed flat laminar flame. This reactor has the advantage of forming large PAHs (up to 400 carbon atoms (Weilmünster et al. 1999)), directly in gas-phase. A molecular beam, seeded with species extracted from the flame, is formed by expansion and skimming. The beam is then analyzed by a Time-Of-Flight Mass Spectrometer. Characteristic mass spectra present series of peaks spaced by 12 atomic mass units (u). The main peak in each series can be associated with a specific PAH substituted or not with methyl or ethyl groups. Secondary peaks are due to hydrogenation, dehydrogenation of the the main species, presence of ¹³C isotopes or difference in the carbon skeleton. Due to the regularity of the series of peaks, the presence of oxygenated species have been ruled out.

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3 PAHs production in the "oxidation" zone

Different regimes for the formation of PAHs in rich flames have been investigated. In the first one, the species of the sooting flame are extracted at a distance corresponding to the oxidation zone. PAHs of about ten carbon atoms, corresponding to a few aromatic cycles, are formed. Evolutions in concentrations profiles versus the distance to the burner are presented in Fig. 1. The position of the concentration maximum increases with the mass of the molecule. As the distance to the burner corresponds, in such a reactor, to the timescale of the chemical evolution of the combustion in flame, this observation is relevant with the growth mechanism commonly put forward, called HACA for H-abstraction C_2H_2 -addition (Frenklach and Wang 1991).

The greater quantities of small PAHs have been detected in conditions of pressure and outflow which tend to expand the flame spatially (see Fig. 1 right panel). In these conditions, a given molecule may survive longer before to be consumed to form a bigger species, leading to an increase of the concentration.

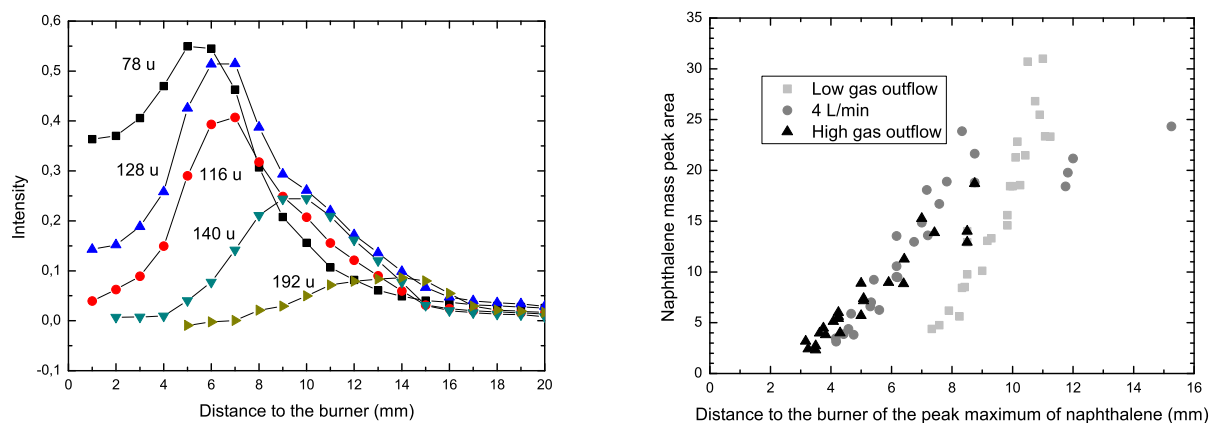


Fig. 1. Left panel : Spatial distribution of small PAHs in an acetylene flame. Right panel : Correlation between the area of the naphthalene mass peak and the distance to the burner at the maximum concentration.

4 PAHs production in the sooting zone

The second regime is characterized by a greater C/O ratio and a higher pressure in the source chamber. The species are extracted at the edge of the flame. In this region, a large amount of PAHs are formed and molecules with up to 50 carbon atoms have been detected. In the case of direct ionization of the species by an F_2 excimer laser at 157 nm (7.9 eV), we notice that the even number of C atoms have a higher concentration than those with an odd number (Fig. 2). This is not the case with 2 photon ionization at 295 nm. In the last case results may be affected by fragmentation resulting from events where more than 2 photons are absorbed. Thus we consider spectra taken at 157 nm to be more representative of the neutral species distribution.

As shown in Fig. 2, the produced PAHs are roughly compact ones, which are the more stable species in the flame. The species above the compact PAHs line are due to fragmentation. Astro-PAHs are also thought to be compact according to the C-H bending modes ratio observed in astrophysical IR spectra. The species we produce are therefore interesting analogues.

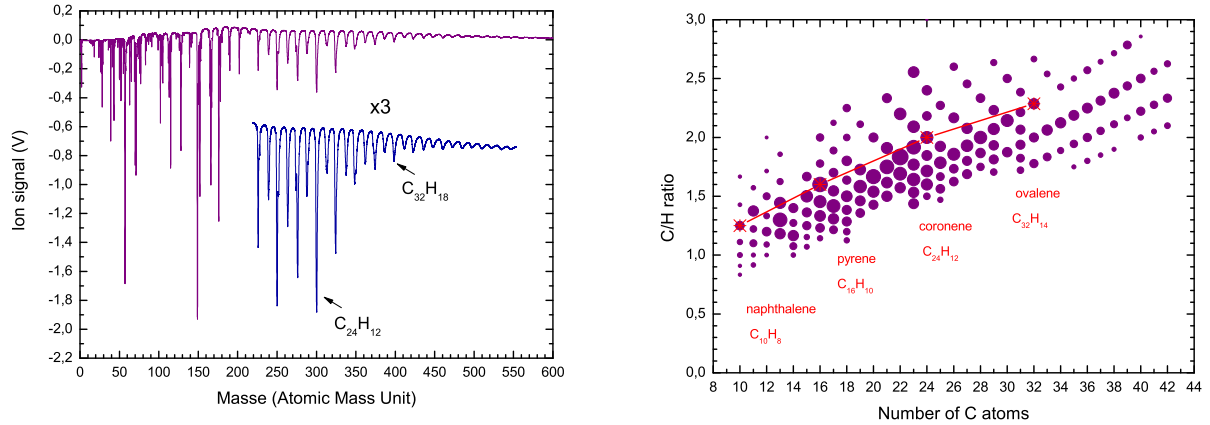


Fig. 2. Left panel : Large PAHs-rich mass spectrum of an ethylene flame. Right panel : C/H ratio of large PAHs versus the number of C atoms (The point size varies with the logarithm of the ion signal). Such diagrams are used by geochemists to characterize the aromaticity of the materials. The line figures the PAHs of high compactness (whose names are recalled) for comparison.

5 Outlook

We succeeded in optimizing our source for the formation of large gas-phase PAHs. We now produce species in enough abundance to perform UV electronic spectra of the species. In the future, the spectra will be extended to the visible wavelengths in order to compare them with the Diffuse Interstellar Bands (DIBs) (Herbig 1995).

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