

Electronic spectroscopy of PAHs and PAH derivatives in supersonic jet

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Abstract. Polycyclic Aromatic Hydrocarbon (PAHs) molecules are attracting much attention in the astrophysical and astrochemical communities because of their ubiquitous presence in space due to their ability to survive in the harsh environmental conditions of the interstellar medium (ISM). The objective of this work is to provide gas phase, high-resolution spectroscopic data on the electronic and vibronic transitions of PAHs and their nitrogenated derivatives measured in astrophysically relevant conditions.

Keywords. Astrochemistry, ISM: molecules, PAHs, electronic transitions, absorption, Methods: laboratory, CRDS

1. Introduction

High-resolution laboratory measurements of PAHs are of particular interest for astrophysicists since these molecules are suggested as possible carriers of the diffuse interstellar bands (DIBs). In the UV, visible and near infrared regions, PAHs exhibit a unique set of electronic transitions, which give each molecule a unique absorption signature. Providing the intrinsic electronic band profiles and peak positions of PAHs and their derivatives in astrophysically relevant conditions (i.e., gas phase molecules and ions at low temperature) is a powerful tool to search for specific PAHs and ions in interstellar spectra.

Recent infrared spectroscopy studies have suggested that nitrogen-substituted PAHs (PANHs) could also be present in the interstellar medium as nitrogen is one of the most abundant atoms after hydrogen, helium, and carbon (Spitzer (1978)). Here we study the effect of nitrogen insertion in the benzenoid skeleton on the electronic spectra of PAH molecules seeded in argon supersonic jet expansions. We examine the case of the substitution of carbon atoms by nitrogen atoms in the benzenoid skeleton of phenanthrene ($C_{14}H_{10}$), a prototype non-compact PAH (Bejaoui & Salama (2019)).

2. Experiment

High-resolution absorption spectra of phenanthrene (Phen) and phenanthridine (PhenN, $C_{13}H_9N$) seeded in supersonic jet expansions have been measured using the COSmIC setup (Salama *et al.* 2018) which combines a pulsed discharge slit nozzle (PDN) with a high-sensitivity cavity ring-down spectrometer (Biennier *et al.* (2003, 2004)). Phen and PhenN samples (Sigma Aldrich, > 98%) are introduced at the bottom of the reservoir, heated up to 120° C and the vapor is carried with an argon buffer. The gas expanding through a 10-cm rectangular slit generates a 10 Hz pulsed collision-free planar expansion. Cavity ring-down spectra of Phen and PhenN are recorded at 2 mm downstream the slit nozzle where the measured rotational temperature is of the order of 52 K (Tan & Salama (2005)). The laser is tuned over the 315-345 nm spectral region to probe the vibronic

transitions of the $2^1A_1(S_1) \leftarrow X^1A_1(S_0)$ electronic absorption band system of neutral Phen and PhenN seeded in the supersonic expansions.

3. Results

The comparison between the electronic CRDS spectra of Phen and PhenN show that the PhenN spectrum exhibits more absorption transitions (106 bands) compared to Phen (74 bands). The substitution of C-H bond with N atom reduces the symmetry of Phen and induces non-bonding electrons (a pair of electrons in the valence shell of each N atom) which affects the geometry of the molecule. Theoretical studies show that the lengths of the PhenN chemical bonds and the angles between the adjacent bonds are different compared to the parent molecule in both the ground and excited singlet states (Deperasinska & Prochorow (2003)). This deformation doesn't only affect the ring where the N atom is introduced but extends to the other aromatic rings. The lower symmetry of the benzenoid skeleton of N-substituted PAH increases the vibrational activity of PhenN due to favorable Franck-Condon factors that enable additional non-totally symmetric planar vibrations. Additionally, the absorption spectrum of PhenN is blue-shifted compared to Phen and the two strongest bands of both molecules are shifted by 277 cm^{-1} to higher energies. A close comparison between the band profiles of these two bands shows similar bandwidths (Bejaoui & Salama (2019)). No broadening induced by the insertion of one nitrogen in the skeleton has been observed in the S_1 system of PhenN.

The comparison of the laboratory spectra of Phen and PhenN with DIBs features observed with the ESO Diffuse Interstellar Bands Large Exploration Survey (EDIBLES) is in progress.

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