

# Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Nitrogen Heterocycles (PANHs)

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## Abstract

The mid-infrared spectra of the nitrogen-containing heterocyclic polycyclic aromatic compounds 1-azabenz[a]anthracene; 2-azabenz[a]anthracene; 1-azachrysene; 2-azachrysene; 4-azachrysene; 2-azapyrene, and 7,8 benzoquinoline in their neutral and cation forms were investigated. The spectra of these species isolated in an argon matrix have been measured. Band frequencies and intensities were tabulated and these data compared with spectra computed using density functional theory at the B3LYP level. The overall agreement between experiment and theory is quite good, in keeping with earlier results on homonuclear polycyclic aromatic hydrocarbons. The differences between the spectral properties of nitrogen bearing aromatics and non-substituted, neutral polycyclic aromatic hydrocarbons will be discussed.

## 1. Introduction

The past decade has witnessed renewed interest in the molecular physics and infrared spectroscopic properties of polycyclic aromatic hydrocarbons (PAHs). Motivated in large part to understand the widespread interstellar infrared emission attributed to mixtures of neutral and ionized PAHs in different interstellar environments. The matrix isolation technique has also been particularly effective in providing the infrared An ongoing project at the NASA Ames Astrochemistry laboratory has combined matrix isolation spectroscopy of polycyclic aromatic hydrocarbons with theoretical computations using density functional theory to generate an infrared spectral database of neutral, cationic, and anionic PAHs. These data are available from our website at [www.astrochem.org/pahdata/index.html](http://www.astrochem.org/pahdata/index.html). This database is expanded here with the first reported IR spectra of neutral and ionized, nitrogen substituted PAHs (aza-PAHs). The argon matrix isolated spectra of the nitrogen substituted PAHs (PANHs): 1-azabenz[a]anthracene; 2-azabenz[a]anthracene; 1-azachrysene; 2-azachrysene; 4-azachrysene; 2-azapyrene, and 7,8 benzoquinoline in their neutral and cation forms are discussed.

## 2. Experimental

The experimental technique will be described briefly, a detailed description of the procedure is available elsewhere [1, 2]. Samples were prepared by vapor co-deposition of the PAH/PANH of interest with an over abundance of argon onto a 14K CsI window suspended in a high-vacuum

chamber. In general, samples were vaporized from heated Pyrex tubes while argon was admitted through a length of liquid nitrogen cooled copper tubing. Such conditions yield an Ar/PANH ratio, in excess of 1000/1 [3]. Once a sufficient amount of material has been deposited, the infrared spectrum of the sample is recorded. Comparison of the original (neutral) spectrum to that obtained after the sample is exposed to ionizing radiation permits identification of PAH/PANH ion features, which appear upon photolysis. To distinguish between the bands of PAH/PANH cations and anions, as well as spurious photoproducts, experiments were conducted in which the argon matrix was doped with an electron acceptor,  $\text{NO}_2$ , at a concentration of approximately 1 part in 1000. The presence of an electron acceptor quenches the formation of PANH anions, permitting the unambiguous identification of PANH cations.

All calculations were performed using the Gaussian 98 computer code. For the species treated here, the geometries are optimized and the harmonic frequencies computed using density functional theory (DFT). Specifically, the hybrid [4] B3LYP [5] functional was utilized in conjunction with the 4-31G basis sets [6]. Calibration calculations, which have been carried out for selected systems, show that a single scale factor of 0.958 brings the B3LYP harmonic frequencies computed using the 4-31G basis set into excellent agreement with the experimental fundamental frequencies.

### 3. Results

This section presents a brief overview of the mid-infrared spectra of neutral PANHs (For a detailed analysis see; A. L. Mattioda, D. M. Hudgins, C. W. Bauschlicher, Jr., Rosi, M., L. J. Allamandola, *J. Phys. Chem*, submitted). As with all polycyclic aromatic species studied to date, the vibrations can be grouped into the following categories: CH stretching modes (centered near  $3050\text{ cm}^{-1}$ ), CC stretching and combinations between CC stretching and CH in-plane bending vibrations (between  $1650$  and  $1100\text{ cm}^{-1}$ ), and CH out-of-plane bending modes (between  $900$  and  $500\text{ cm}^{-1}$ ). However, for species as complex as these, the notion of a fundamental vibration involving only these separate motions is not strictly valid. Nonetheless these motions dominate the vibrations that give rise to the bands that fall in these regions and they can be used to understand the influence of nitrogen insertion as described below.

Nitrogen insertion induces several interesting new spectroscopic trends for this family of molecules. For the neutral species nitrogen inclusion causes unusual intensity enhancements for the different classes of vibration and induces significant, new IR activity for a specific mode. Computed dipole moments are also presented for these species in their neutral and ionized forms, enabling a search for individual interstellar PANHs. There are two features which set the spectra of nitrogen bearing aromatics apart from the general spectral properties of non-substituted, neutral polycyclic aromatic hydrocarbons. First, the addition of nitrogen induces a remarkable enhancement of the bands between  $1650$  and  $1100\text{ cm}^{-1}$ , reminiscent of the changes which occur upon ionization [7,8]. The bands which are enhanced the strongest by nitrogen inclusion are those which involve the skeletal CC and CN stretching vibrations, those bands falling between  $1600$  and  $1100\text{ cm}^{-1}$ . The second unique influence of nitrogen substitution is the appearance of a significant new band near  $1400\text{ cm}^{-1}$  for 1-azabenz[a]anthracene, 4-azachrysene,

and 7,8 benzoquinoline. In most (not all) cases, this band is associated with structures in which the nitrogen is located in a pendant ring, at one of the vertices adjacent to the fused bond. A requirement for this feature to appear prominently is the presence of a hydrogen atom at the para-position to the nitrogen.

The overall calculated dipole moments for the neutral and cation forms of the PANH molecules are as follows: 7,8-benzoquinoline, 1.84 (2.38 for the cation) Debye; 2-azapyrene, 3.1597 (3.49 for the cation) Debye; 1-azabenz[a]anthracene, 1.66 (2.20 for the cation) Debye; 2-azabenz[a]anthracene, 3.00 (5.34 for the cation) Debye; 1-azachrysene, 2.43 (3.72 for the cation) Debye; 2-azachrysene, 3.37 (4.24 for the cation) Debye and 4-azachrysene, 1.88 (2.17 for the cation). This compares with 1.85 Debye for H<sub>2</sub>O and 2.34 for H<sub>2</sub>CO and indicates these molecules should be accessible to microwave or radio searches.

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