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Fluorescence Spectroscopy of Gas-phase Polycyclic Aromatic Hydrocarbons

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ABSTRACT

The purpose of this investigation was to produce fluorescence spectra of polycyclic aromatic hydrocarbon (PAH) molecules in the gas-phase for comparison with blue luminescence (BL) emission observed in astrophysical sources Vijn et al. (2004, 2005a,b). The BL occurs roughly from 350 to 450 nm, with a sharp peak near 380 nm. PAHs with three to four rings, e.g. anthracene and pyrene, were found to produce luminescence in the appropriate spectral region, based on existing studies. Relatively few studies of the gas-phase fluorescence of PAHs exist; those that do exist have dealt primarily with the same samples commonly available for purchase such as pyrene and anthracene. In an attempt to understand the chemistry of the nebular environment we also obtained several nitrogen substituted PAHs from our colleagues at NASA Ames. In order to simulate the astrophysical environment we also took spectra by heating the PAHs in a flame. The flame environment counteracts the formation of eximers and permits the spectroscopy of free-flying neutral molecules. Experiments with coal tar demonstrate that fluorescence spectroscopy reveals primarily the presence of the smallest molecules, which are most abundant and which possess the highest fluorescence efficiencies. One gas-phase PAH that seems to fit the BL spectrum most closely is phenanthridine. In view of the results from the spectroscopy of coal tar, a compound containing a mixture of PAHs ranging from small to very large PAH molecules, we can not preclude the presence of larger PAHs in interstellar sources exhibiting BL.

1. Introduction

Dust is a ubiquitous catch-all term used when referring to the multitude of known and unknown particles larger than molecules in the universe; it has been studied a great deal,

yet the true nature and composition has eluded astronomers for some time. One component of dust known to exist is polycyclic aromatic hydrocarbon (PAH) molecules.

This study was undertaken in response to a recently discovered blue emission feature Vijn et al. (2004) in nebulae, known to contain PAHs from infrared observations of the aromatic emission features. The blue luminescence (BL) can be seen in Figure 1; the spectrum was measured at the wavelengths of the hydrogen Balmer lines, denoted with the triangles. The BL spans the spectral region from 350 to 500 nm with peaks near 375 and 390 nm. The luminescence has been interpreted as arising from photo-induced fluorescence by small, neutral PAH molecules Vijn et al. (2004).

Only a small handful of readily available PAHs have been studied in the gas phase. With the few existing gas-phase spectra, it was found that PAH with three to four rings best fit the BL. It is important to study these molecules in the gas phase because of the matrix shift. A matrix shift is the shifting of the spectral features to different wavelengths, which depends upon the phase and environment of the sample. For example, molecules in a solution will have the same spectral features as the same molecules in the gas phase; however, the wavelengths of the features and their relative strengths will be different: this makes identification of molecules in astrophysical environments nearly impossible based on data taken in solution. To that end we have studied a number of PAHs in the gas phase. Many of the spectra were acquired for the commonly studied PAHs, and our spectra agreed well with those in the literature. In addition to the commonly studied PAHs we also studied several nitrogen heterocyclic PAHs, these samples were provided by Lou Allamandola.

2. Experiment

The laser induced fluorescence of gas-phase PAHs was studied with a helium-cadmium laser operated at 326 nm. In some cases a flame was utilized to provide a high temperature environment for both high temperature spectra and to dissociate PAH eximers (a cluster of two or more molecules). The fluorescence was observed with a CCD spectrometer.

3. Discussion

Figure 2 is a concise presentation of the relevant data collected through the course of this research. PAHs that exhibit gas-phase fluorescence in the peak region of the BL, from 375-390 nm, have masses between 178 and 252 g mole⁻¹.

Small molecules tend to be more efficient at fluorescing, which implies that in a mixed environment small PAHs will be preferentially detected over large PAHs with relatively lower fluorescence efficiencies. Coal tar provides a crude mixture of large and small PAHs. Through our experiments with coal tar we showed that there is indeed a preference for small PAHs

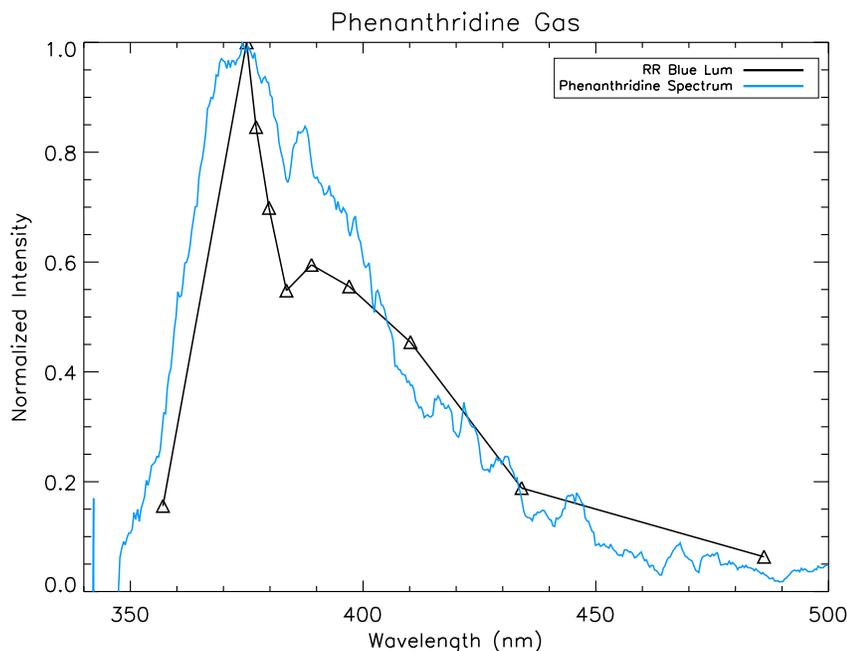


Fig. 1.— Phenanthridine gas phase fluorescence spectrum fit to the blue luminescence (BL). The BL spectrum is from the Red Rectangle (Vijh et al. 2005a), denoted by black triangles. The phenanthridine shown as the solid blue curve is from this study. This sample came from Lou Allamandola at NASA Ames.

to be detected through the observation of their fluorescence. This implies that large PAHs would be hard to observe in a mixture containing both small and large PAHs.

In both pure samples and mixtures we observed the formation of eximers. Eximer fluorescence occurs at longer wavelengths than the monomer (or single molecule) fluorescence. In our study of coal tar we found that the relative fluorescence efficiencies of these clusters was lower than the fluorescence efficiencies of smaller monomer PAHs. Comparing the spectral region in which the eximer fluorescence commonly occurs to that of the BL one can see that fluorescence by eximers is unlikely to be the source of the BL. Eximers are also unlikely to be responsible for the extended red emission.

Figure 1 shows a spectrum of phenanthridine (a three ringed PAH with a single nitrogen substitution); it can be seen that its peak falls on the first BL peak, demonstrating the ability of PAHs to fluoresce over the entire spectral region covered by the BL. It should be pointed out that this is not a spectral identification, because the fluorescence efficiency of phenanthridine is low when compared to other PAHs similar in size. Therefore, it is most likely a mixture of small neutral monomer PAHs that are responsible for the BL.

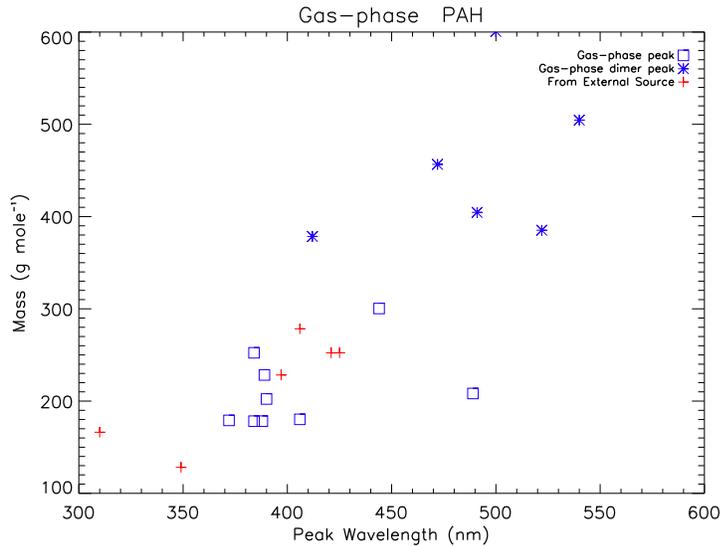


Fig. 2.— This plot shows the trend of the peak wavelength of fluorescence increasing with mass. The open blue squares were measured in this study with our setup. The blue stars represent the peak fluorescence for those molecules that formed eximers were assumed to be dimers (two molecules). To make the graph the molecular weight was doubled. The red crosses are values from Mastral et al. (2004), also done in the gas phase.

4. Conclusions

We have demonstrated that small PAHs could be responsible for the BL. If correct, the BL is most likely due to a mixture of small neutral monomer PAH (3-4 rings), and not a single PAH. We can also conclude that small PAH may not be the most prevalent PAH in nebulae, but their luminescence is easier to detect due to their higher fluorescence efficiencies.

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