

Laboratory spectroscopy and astronomical significance of the fully-benzenoid PAH triphenylene and its cation



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ABSTRACT

Triphenylene (C₁₈H₁₂) is a highly symmetric polycyclic aromatic hydrocarbon (PAH) molecule with a ‘fully-benzenoid’ electronic structure. This confers a high chemical stability compared with PAHs of similar size. Although numerous infrared and UV-vis experimental spectroscopic and theoretical studies of a wide range PAHs in an astrophysical context have been conducted, triphenylene and its radical cation have received almost no attention. There exists a huge body of spectroscopic evidence for neutral and ionised PAHs in astrophysical sources, obtained principally through detection of infrared emission features that are characteristic of PAHs as a chemical class. However, it has so far not proved possible to identify spectroscopically a single isolated PAH in space, although PAHs including triphenylene have been detected mass spectrometrically in meteorites. In this work we focus on recording laboratory electronic spectra of neutral and ionised triphenylene between 220 and 780 nm, trapped in H₂O ice and solid argon at 12 K. The studies are motivated by the potential for spectroscopic astronomical detection of electronic absorption spectra of PAHs in ice mantles on interstellar grains as discussed by Linnartz (2014), and were performed also in a cold Ar matrix to provide guidance as to whether triphenylene (particularly in its singly positively ionised form) could be a viable candidate for any of the unidentified diffuse interstellar absorption bands. Based on the argon-matrix experimental results, comparison is made with previously unpublished astronomical spectra near 400 nm which contain broad interstellar absorption features consistent with the predictions from the laboratory matrix spectra, thus providing motivation for the recording of gas-phase electronic spectra of the internally cold triphenylene cation.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in space and observed in many types of astrophysical environments (Tielens, 2013). Their presence is inferred from a number of mid-infrared emission features at wavelengths that are characteristic of C–C and C–H vibrational modes of PAHs (Allamandola et al., 1989).

It is generally accepted that excited vibrational levels of PAHs emit infrared radiation on relaxation after electronic excitation, for example in photon dominated regions (Tielens, 2013). The physical and chemical processes at play on excitation are currently a topic of intense laboratory study; PAHs can be ionized or dissociate on photon absorption (Zhen et al., 2014a; 2015), which holds the potential to enrich the interstellar medium with charged hydro-

carbons and larger hydrocarbon species that are hard to generate through bottom-up reaction schemes. Recently, it was shown experimentally that it is possible to form C₆₀ by (multi-photon) photolysis of very large PAHs (Zhen et al., 2014b), in line with model predictions for astronomically more relevant excitation schemes (Berné et al., 2015; 2016). The molecules C₆₀, C₇₀ and C₆₀⁺ have been observed in a number of astrophysical sources through their IR emission spectra (Berné et al., 2013; Cami et al., 2010; Sellgren et al., 2010). More recently, Campbell et al. (2015) have claimed the assignment of two stronger and possibly three more weaker diffuse interstellar absorption features in the 900–1000 nm region, as due to electronic transitions of C₆₀⁺ (Campbell et al., 2015; 2016a; 2016b; Walker et al., 2015). Attempts to compare optical laboratory data for gas-phase spectra of PAHs with DIB absorption features recorded through diffuse interstellar clouds have not led to identification of any PAH as a DIB carrier. A wide range of PAHs could be present including neutral, ionised, protonated, deprotonated, hydrogenated, dehydrogenated and substituted forms,

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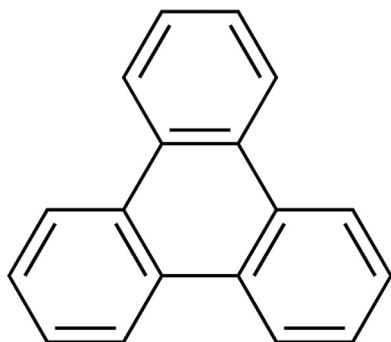


Fig. 1. Molecular structure of triphenylene ($C_{18}H_{12}$). The peripheral hydrogen atoms are omitted for clarity.

however not all of these have been explored experimentally. Surveys and critical assessments of the issues have been presented by Salama (2008) and references therein (Gredel et al. (2011); Huisken et al. (2014); Salama and Ehrenfreund (2014); Salama et al. (2011); Steglich et al. (2011)). Neutral triphenylene, $C_{18}H_{12}$, is a highly symmetric (D_{3h}) molecule containing three aromatic rings (see Fig. 1). It is a fully benzenoid PAH, which distinguishes it from many other PAHs as its aromatic rings are directly connected to each other, and all carbon atoms participate in aromatic stabilization. As benzenoid PAHs are both chemically and photochemically less reactive than non-benzenoid PAHs, this makes triphenylene particularly interesting in an astronomical context, and its cation as a potential DIB carrier. Triphenylene has been found in isomer-specific mass spectra of meteorite samples (Callahan et al., 2008) and contains six hydrogen atoms in ‘bay’ sites. Based on the interpretation of the line shapes of IR emission features, PAHs with such sites are thought to be present in the ISM (Candian et al., 2010).

The outline of this paper is as follows. In the next section the motivation for the experiments is discussed and the experimental details are given in Section 3. Section 4 summarizes what is known about triphenylene and its cation in the literature. This information is linked with the experimental data in Section 5. The final section concludes with a discussion of the astronomical relevance of these findings.

2. Experimental-astronomical motivation

2.1. PAHs in water ice

PAHs are expected to freeze out, as do many other volatile species, on cold dust grain in interstellar and circumstellar media. As water forms the main constituent of ice in space, the study of PAHs in water ice is of particular interest. In the laboratory, where specific PAHs can be selected, IR and UV–vis studies have provided much information on the physical and chemical properties of such species embedded in water ice (e.g. Bernstein et al. (2005, 2007); Bouwman et al. (2011); Cuyille et al. (2014); Guennoun et al. (2011); Sandford et al. (2004)). In astronomical infrared ice surveys, however, many PAHs have similar vibrational modes, causing spectral features to overlap. It is here that optical electronic solid state spectra of PAHs in a low temperature water matrix can offer an attractive potential alternative (Linnartz, 2014). Water itself does not absorb in the UV–vis, and a significant number of electronic transitions of neutral and ionised PAHs have much higher transition strengths and are more molecule-specific than their vibrational spectra. This means that in laboratory studies of optical spectra highly diluted mixtures of PAHs embedded in water ice can be used, which are more representative of real astronomical conditions. Optical absorption spectroscopy of PAHs embedded in interstellar ice analogues was introduced in 2003 by Gudipati

and Allamandola (Gudipati and Allamandola, 2003; 2004; 2006) and has more recently been applied to a number of cases in Leiden (Bouwman et al., 2011; 2009; Cuyille et al., 2014). A range of PAHs embedded in various matrix environments (mainly H_2O , NH_3 and Ne/Ar) has been studied, along with their spectroscopic dependence on a number of parameters, including temperature, ice morphology and concentration. The present study adds to this research through the study of triphenylene and its cation embedded in water ice. With the discovery that radical cations of PAHs can be stable in water ice for extended periods of time, i.e. more than several weeks (Gudipati and Allamandola, 2006), the potential astrochemical relevance of these trapped ions became clear. This same study showed that up to 70% of the embedded neutral PAH sample can be ionised by VUV radiation. As the electrons and radical cations remain separated in the ice, both species can participate in subsequent reactions. Regeneration of the parent neutral PAH is not significantly observed on the heating of ice-embedded PAH cations (Gudipati and Allamandola, 2006). Recent IR studies show the formation of alcohols (PAH-OH) and ketones (PAH=O) (Cook et al., 2015; Guennoun et al., 2011) in vacuum UV (VUV) irradiated PAH-containing water ices at 14 K temperatures. Generally observed is that critical to the lifetime of the radical ion is the morphology of the ice where, upon heating, the transition from amorphous to crystalline ice initiates the end of its lifetime. Up to that point, the stability argument suggests that astrophysical ices may be enriched with ions, and, as the main constituents of ice are transparent to visible light, these species may thus be detected by their absorption features in direct or scattered light.

2.2. PAHs as diffuse band carriers

PAHs have been discussed as potential carriers of some, possibly many, of the diffuse interstellar absorption bands for many years. However, to date none of the PAH neutrals, radical cations or protonated PAHs that have been studied spectroscopically in matrices or in the gas-phase has been found to have a definitive correspondence with spectra observed towards reddened background stars. It is clear that the strongest diffuse bands do not originate in small PAH species, but this does not rule out PAHs as an entire class contributing to interstellar absorption. The recent claim of C_{60}^+ as a diffuse band carrier by Campbell et al. (2015) using dissociation spectroscopy of small helium tagged C_{60}^+ -complexes was built initially on matrix absorption experiments by Fulara et al. (1993) that are very similar to those reported here for the triphenylene cation ($C_{18}H_{12}^+$). The matrix results inspired astronomical observations by Foing and Ehrenfreund (1994) in the relatively unexplored and observationally challenging spectral region near 950 nm which revealed new diffuse bands in possible correspondence with the matrix data of Fulara et al. (1993). The recent recording of complementary gas-phase spectra of $He_nC_{60}^+$ Kuhn et al. (2016), confirms the laboratory rest wavelengths published Campbell et al. (2015, 2016a). Currently, several astronomical groups focus on the interpretation of the astronomical data that are situated in a wavelength domain where telluric pollution by water features causes a serious issue (Cordiner et al., 2017; Galazutdinov et al., 2017; Walker et al., 2016).

3. Experimental details

The spectra of triphenylene and its cation were measured using OASIS, our Optical Absorption Setup for Ice Spectroscopy. The setup has been used in a number of comparable studies previously, and details are available in Bouwman et al. (2009) and Allodi et al. (2013). Dilute ice mixtures of PAH and water/argon (between 1:3,000 and 1:8,000) were prepared by sublimating triphenylene and co-depositing this with H_2O or Ar onto a UV–vis-transparent

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