THE OPTICAL SPECTRUM OF A LARGE ISOLATED POLYCYCLIC AROMATIC HYDROCARBON: HEXA-peri-HEXABENZOCORONENE, C_{42}H_{18}

Damian L. Kokkin,1 Tyler P. Troy,1 Masakazu Nakajima,1 Klaas Nauta,1 Thomas D. Varberg,2 Gregory F. Metha,3 Nigel T. Lucas,1, and Timothy W. Schmidt1,4,5

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ABSTRACT

The first optical spectrum of an isolated polycyclic aromatic hydrocarbon large enough to survive the photophysical conditions of the interstellar medium is reported. Vibronic bands of the first electronic transition of the all-benzenoid polycyclic aromatic hydrocarbon hexa-peri-hexabenzocoronene were observed in the 4080–4530 Å range by resonant 2-color 2-photon ionization spectroscopy. The strongest feature at 4264 Å is estimated to have an oscillator strength of $f = 1.4 \times 10^{-3}$, placing an upper limit on the interstellar abundance of this polycyclic aromatic hydrocarbon at $4 \times 10^{12}$ cm$^{-2}$, accounting for a maximum of ~0.02% of interstellar carbon. This study opens up the possibility to rigorously test neutral polycyclic aromatic hydrocarbons as carriers of the diffuse interstellar bands in the near future.

Subject headings: ISM: abundances — ISM: molecules — molecular data — molecular processes

1. INTRODUCTION

Organic material such as polycyclic aromatic hydrocarbons (PAHs) are held responsible for infrared emission features in carbon rich objects (AIBs) and has been suggested to account for as much as 20% of interstellar carbon (Léger & Puget 1984; Allamandola et al. 1985; Snow & Witt 1995). In addition, PAHs are considered leading candidates as carriers of the diffuse interstellar bands (Léger & d’Hendecourt 1985; Crawford et al. 1985; Salama et al. 1999), a series of diffuse absorption features superimposed on the extinction curve of the interstellar medium (ISM). The identities of the carriers of these bands remain the longest unsolved problem of laboratory astrophysics (Herbig 1975; Sarre 2006). A scenario linking the AIBs to the DIBs is that amorphous aromatic material formed in carbon-rich stellar outflows is further processed into PAHs and eventually the DIB carriers by the interstellar photophysical environment (Goto et al. 2003; Sloan et al. 2007; Pino et al. 2008).

Despite the extensive literature reporting on PAHs in the ISM, not a single PAH species has ever been observed astronomically. This may be partly due to a paucity of laboratory data with which to compare unidentified features in astronomical spectra, or to guide astronomical searches. Obtaining optical spectra of isolated molecules at low temperature (as in diffuse clouds), in vacuo, remains a challenge of modern laboratory astrophysics (Sharp & Schmidt 2005).

Modeling of generic PAHs in the diffuse interstellar medium aims to guide the laboratory search for the carriers of the DIBs. Léger & d’Hendecourt (1985) found that species must contain no fewer than 15 atoms if they are to avoid photothermalysis, and Le Page et al. (2003) concluded that PAHs containing more than about 30 carbon atoms would be largely stable. Furthermore, it is considered that a large proportion of interstellar PAH material would exist in its ionized form(s) (Crawford et al. 1985). As such, the challenge to laboratory-based scientists is to place large PAHs into the vacuum, cool them down, permit them to ionize, and obtain their spectra. Prior to the present work, the largest neutral PAH studied spectroscopically in such a way was ovalene ($C_{32}H_{14}$), the size of which is borderline for surviving the ISM intact (Amirav et al. 1980).

An unguided laboratory search is daunting, however, as for systems containing 4–10 fused aromatic rings there are over 20,000 possible PAH structures (Dias 2004). In order to guide the laboratory search for DIB carriers, some selection mechanism is required, based on spectral intensity or structure. Recently we suggested that all-benzenoid PAHs (ABPAHs) could represent such a selection mechanism (Troy & Schmidt 2006). These ABPAHs are formed from fused benzene rings which may be drawn as being separated by single bonds. They are characterized by higher ionization potentials and more energetic electronic transitions than their non-all-benzenoid isomers. Of the more than 20,000 possible structures containing 4–10 fused rings, only 17 are all-benzenoid in character. The all-benzenoid structural motif thus provides a selection mechanism for the laboratory and perhaps the ISM. Since the ABPAHs are comparatively easy to prepare in the laboratory, it may also be that they form preferentially in the ISM. We obtained the gas-phase spectrum of the smallest member of this family: triphenylene ($C_{12}H_{14}$) (Kokkin et al. 2007). However, its small size means that even its lowest energy transitions are in the ultraviolet, far from the shortest wavelength DIBs. The ABPAHs present three optical band systems named the $\alpha$-, $\beta$-, and $\gamma$-bands in increasing intensity and energy. We found that for the strong $\beta$-band system to fall in the DIB region, it must contain no fewer than 84 carbon atoms (Troy & Schmidt 2006). However, hexa-peri-hexabenzocoronene (HBC) is known to exhibit the weaker $\alpha$-bands in the region of the DIBs. HBC, pictured in Figure 1, possesses 42 carbon atoms and is thus large enough to survive the interstellar radiation field, as modeled by Le Page et al. (2003). Since its lowest energy transitions occur in the visible region, near the strongest DIB (4429 Å in air), it was suggested as a carrier of this interstellar band by Hendel et al. (1986), who obtained spectra in a 1,2,4-trichlorobenzene solution. Furthermore, its red phosphorescence suggested that it could also be a carrier of the Red Rectangle bands, the unidentified emission features superimposed on the extended red emission of the proto–planetary nebula surrounding HD 44179 (Cohen et al. 1975; Schmidt et al. 1985).
The positive ions were extracted vertically and perpendicular to the laser and molecular beam into the time-of-flight tube. The accelerating voltage was 2050 V, applied to the bottom extraction grid. Ions were detected with a tandem microchannel plate.

The signal from the microchannel plate was buffered by a digital oscilloscope and processed on a desktop computer running in-house software. The synchronization and triggering of all the equipment was carried out using a multiple output programmable delay generator.

3. RESULTS AND DISCUSSION

The resonant 2-color 2-photon ionization spectrum of HBC is plotted in Figure 1. While an attempt was made to normalize the spectrum for laser power, relative intensities become increasingly unreliable toward 4100 Å. The spectrum reported here is for the 522 amu ($^{12}$C$_{42}$H$_{28}$) mass only, and as such the spectrum represents only the most abundant isotopomer (64%). A detailed analysis of the spectrum, including the other isotopomers, will be published elsewhere.

The main features are positioned at vacuum wavelengths of 4335.2 and 4264.1 Å (FWHM 1.5 Å). These are labeled $a$ and $b$ in Figure 1. The bandwidth is related to the rotational temperature which is typically 30 K in our experiments. We attribute the cluster of smaller peaks immediately to longer wavelength of these main features to "hot" bands, which are transitions arising from excited vibrational levels of the electronic ground state that remain populated by incomplete cooling in the supersonic expansion. At higher energy than these main features lie transitions involving quanta of totally symmetric vibrations built onto bands $a$ and $b$.

Preliminary quantum mechanical considerations reveal that when viewed on the central ring, the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals are the same as those of benzene, which has the same symmetry ($D_{6h}$ point group). As such, the symmetries of the lowest transitions of HBC are the same as benzene. The lowest energy transition is thus of $B_{2g} \rightarrow A_{1g}$ electronic character, induced by vibrational modes of $e_{2g}$ symmetry. An estimate of the position of the forbidden origin band is indicated by an arrow in Figure 1. A detailed quantum mechanical treatment is beyond the scope of the present article and will be presented elsewhere. We assign the bands $a$ and $b$ to false origins arising from single quanta of vibrational modes of $e_{2g}$ symmetry. An estimate of the oscillator strength of the strongest band, $b$, may be made by integrating over the molar extinction coefficient, $\epsilon(\lambda)$, of the strongest visible region band in the solution phase spectra of Hendel et al. (1986) at 4450 Å,

$$f = \frac{4.28 \times 10^{-11}}{\lambda^2} \int \epsilon(\lambda)d\lambda,$$

with $\lambda$ in m and $\epsilon$ in liters mol$^{-1}$ cm$^{-1}$. As such, the oscillator strength of $b$ is estimated to be $f = 1.4 \times 10^{-3}$.

Within the region of the spectrum plotted in Figure 1 there are several DIBs. These are plotted as negative-going peaks above the experimental spectrum with vacuum wavelengths of 4177.6, 4430.1, and 4503.0 Å. It is immediately clear that the experimental spectrum does not match any hitherto reported DIB. It is also clear that the 4177.6 and 4430.1 Å DIBs in particular are very broad compared to the observed band and it is therefore unlikely that these interstellar bands arise from transitions to the first excited state of medium-sized PAHs such
as HBC. Transitions to higher electronic states will exhibit broader bands and stronger spectra.

The nonobservation of HBC in the DIB spectrum allows us to estimate an upper limit of the column density of HBC in the DISM using

$$N_{\text{max}} = 1.13 \times 10^{20} \frac{W_{\text{max}}}{\lambda f^2} \text{ cm}^{-2},$$

with $\lambda$ and $W_{\text{max}}$ in Å. From our estimated oscillator strength, assuming a detection limit of 1 mÅ equivalent width, an upper limit on the column density of HBC may be placed at $N_{\text{max}} = 4 \times 10^{12} \text{ cm}^{-2}$. Taking the total carbon column density of $N_C = 1 \times 10^{18}$ in a typical DIB sight line, the HBC neutral represents a maximum of $2 \times 10^{-4}$ as a fraction of interstellar carbon.

However, due to the exceptional properties of HBC an astronomical search for the molecule is warranted. The next step in the laboratory is to obtain the spectrum of HBC, which is a more difficult task in the gas phase. Nevertheless, the present work makes it possible to produce cold cations in the gas phase by threshold ionization through the 4264 Å band.

4. CONCLUSIONS

We have succeeded in obtaining the excitation spectrum of hexa-peri-hexabenzocoronene ($C_{42}H_{18}$) as a jet-cooled, isolated molecule in the vacuum. Its strongest transition in the region studied was found to lie at 4264.1 Å, which does not correspond to any known diffuse interstellar band. An estimate of the oscillator strength of this band was made at $f = 1.4 \times 10^{-3}$, which afforded an upper limit on the interstellar abundance of HBC of $4 \times 10^{-12} \text{ cm}^{-2}$, or 0.02% of interstellar carbon. However, the same technique can be used to obtain the spectra of still larger and less symmetric systems which may exhibit much stronger transitions. The collection and analysis of the spectra of these all benzenoid PAH species builds up the database of gas-phase spectra required to constrain models of PAH abundances in the ISM in concert with detailed observation. In particular, an exploration of larger PAHs with strong ($f \sim 1$) transitions will provide a rigorous test of neutral PAHs as carriers of the DIBs, thus opening the door to solving the longest standing mystery in astronomical spectroscopy, or putting to bed a long-favored class of candidate.

There remains an impetus to collect spectra of cold PAH cations. The present work establishes the ability to place PAHs of 42 carbons in the vacuum by laser desorption and supersonic expansion. The next step is to produce the cold cations by threshold ionization and obtain their spectra by multiphoton dissociation (Pino et al. 2007).

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