

DEUTERATED INTERSTELLAR POLYCYCLIC AROMATIC HYDROCARBONS¹

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ABSTRACT

We report infrared spectral evidence of deuterated interstellar polycyclic aromatic hydrocarbons (PAHs). Two bands are detected in the infrared emission from the ionization bar in Orion at 4.4 and 4.65 μm . The one at 4.65 μm is present at the 4.4 σ level, while the one at 4.4 μm is more tentative, with a σ equal to 1.9. An emission band at 4.65 μm is also detected in the infrared emission from M17 by Verstraete and coworkers at the 4.4 σ level. These wavelengths are highly characteristic of C-D stretching modes of deuterated PAHs and fall in a featureless region of the interstellar spectrum. The IR spectroscopic properties of deuterated PAHs are summarized, and an estimate of the deuterium fractionation between the aromatic and aliphatic carbons associated with the PAHs is given. High deuterium fractionation is implied; this is discussed in terms of interstellar PAH fractionation mechanisms.

Subject headings: astrochemistry — infrared: ISM — ISM: abundances — ISM: molecules — line: identification — techniques: spectroscopic

1. INTRODUCTION

Most interstellar objects associated with dust and gas, including H II regions, reflection nebulae, planetary nebulae, late-type stars, and the general diffuse interstellar medium (ISM), as well as galactic nuclei and active star-forming regions, show strong emission features at 3.3, 6.2, 7.7, 8.6, and 11.2 μm (Cox & Kessler 1999). These bands are generally attributed to vibrational fluorescence from UV-pumped, large polycyclic aromatic hydrocarbon molecules (PAHs; Allamandola, Tielens, & Barker 1989; Puget & Léger 1989). As a class, these interstellar species are common, having an abundance of $\sim 10^{-7}$ relative to H, and account for 5%–10% of the interstellar carbon (Allamandola et al. 1989; Puget & Léger 1989).

PAHs play important roles in the ISM. They dominate the heating of the gas through the photoelectric effect (Bakes & Tielens 1994; Verstraete et al. 1990), as well as the charge balance inside molecular clouds (Lepp & Dalgarno 1988). PAHs are thought to form in stellar ejecta through soot formation processes (Frenklach & Feigelson 1989; Cherchneff, Barker, & Tielens 1992). Subsequent interstellar processes, including deuterium exchange with hydrogen, further modify these species. As a result, the PAH family present in any object can reflect the large variety of environments experienced over its history. Deuterium provides a powerful tool to distinguish processes occurring at the low temperatures in the ISM from those occurring in high-temperature environments such as stellar atmospheres.

Since PAH fundamental vibrations involving deuterium fall close to 4.4 and 4.6 μm , wavelengths obscured by the telluric

CO₂ bands, space-borne spectroscopic observations are required to search for deuterium-enriched PAHs (Allamandola 1993). Here we report *Infrared Space Observatory (ISO)* observations that show emission bands at the predicted wavelengths. These bands are analyzed, yielding D/H ratios that are considered in light of theoretical interstellar PAH deuteration models.

2. SPECTROSCOPY OF DEUTERATED PAHs

Deuterium atoms substituted on the periphery of PAHs participate in the same characteristic types of vibrational motions as hydrogen atoms. These include C-D stretching motions, as well as in-plane and out-of-plane bending motions. However, because of the larger mass of the deuterium atom, all these vibrations are shifted to lower frequencies. For the C-D stretching modes, the frequency is lowered by a factor of ~ 1.3 (Allamandola 1993; Hudgins, Sandford, & Allamandola 1994; D. M. Hudgins, C. W. Bauschlicher, & S. A. Sandford 2004, in preparation). In addition, the vibrational motions of deuterium atoms cannot couple effectively with those of adjacent, lighter hydrogen atoms. At the low levels of deuteration expected in the interstellar PAH population, the overwhelming majority of peripheral deuterium atoms will be “nonadjacent” or “solo”—that is, they will be isolated, having no neighboring deuterium atoms with whose motion they can strongly interact (for a discussion of CH-group adjacency in PAHs, see Hudgins & Allamandola 1999).

The various classes of C-D vibrational features in deuterated PAHs (PADs) are not all equally attractive as targets for an astronomical search for interstellar PADs. It is therefore reasonable to search for the feature or features that offer the greatest prospect for success—those whose intensity is expected to be detectable and whose spectral position minimizes ambiguity in attribution. Both criteria point to the C-D stretching vibrations of isolated deuterium atoms on PAHs as being the most promising features for which to search. As with hydrogen, deuterium atoms associated with interstellar polycyclic networks will be bonded to either aromatic carbons (those that share in the delocalized π bonding of the molecule) or aliphatic carbons (those that carry only σ or single bonds; Bernstein, Sandford, & Allamandola 1996). In the purely

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aromatic case, a deuterium atom merely replaces a hydrogen atom at the periphery of the aromatic network without altering the network. The stretching band of the resulting aromatic C-D bond falls at $4.4 \pm 0.09 \mu\text{m}$ (Hudgins et al. 1994; Bauschlicher et al. 1997; D. M. Hudgins et al. 2004, in preparation). With all the PAD aromatic C-D stretching features falling in this relatively narrow range, the composite emission of interstellar PADs is expected to give rise to a single band near this position that is analogous to the more familiar $3.3 \mu\text{m}$ C-H stretching band of interstellar PAHs. Deuterium atoms can also add to the periphery of a PAH, changing the character of the carbon atom at the addition site from aromatic to aliphatic, or replace an H atom already present on an aliphatic side group. In either structure, the stretching band of the aliphatic C-D bond on the periphery of the hexagonal C skeleton (D_n PAH) falls at $4.67 \pm 0.06 \mu\text{m}$ (D. M. Hudgins et al. 2004, in preparation). Both the aromatic and aliphatic C-D stretching bands fall in a spectral region ($4\text{--}5 \mu\text{m}$) that is free of other PAH emission features and any other known broad interstellar emission bands, thereby minimizing ambiguity in their assignment. An individual PAH molecule can possess both aromatic and aliphatic C-H bonds (e.g., Bernstein et al. 1996). Thus, any observation of emission bands at these positions in the interstellar spectrum is consistent with the PAH model and provides strong evidence for PADs.

The prospects for identifying interstellar PAD features in other parts of the spectrum are not as good. For the aromatic case, the C-D in-plane bending modes, which fall between 9.5 and $12 \mu\text{m}$, are distributed over a relatively wide range and are weak. The C-D out-of-plane bending modes, although they are generally more intense, are also problematic. Unlike the solo H modes, which tend to fall within the relatively narrow range from 10.9 to $11.4 \mu\text{m}$ (e.g., Hudgins & Allamandola 1999), the intense C-D out-of-plane features are spread out over a much wider range ($14\text{--}17 \mu\text{m}$), because of the greater structural heterogeneity of a solo deuterium atom (Bauschlicher et al. 1997; D. M. Hudgins et al. 2004, in preparation). Solo D atoms are all effectively nonadjacent by virtue of the low isotopic abundance of deuterium, not by virtue of the peripheral structure of the PAH, as is the case for solo H atoms. Consequently, on average, solo D atoms sample a wider range of molecular environments than do solo H's. As a result, C-D out-of-plane bending in interstellar PADs would be expected to produce a broad, low-contrast plateau between 14 and $17 \mu\text{m}$ that would be much more difficult to detect with certainty. Moreover, this wavelength range is also the domain of aromatic CC skeletal vibrations, introducing ambiguity of assignment due to blending with the $15\text{--}20 \mu\text{m}$ emission plateau (Moutou, Leger, & D'Hendecourt 1996; Van Kerckhoven et al. 2000). A similar situation holds for the aliphatic C-D bending (deformation) case. In this case, the bands would be expected to fall between 7 and $8 \mu\text{m}$ (Allamandola 1993; D. M. Hudgins et al. 2004, in preparation), a region overwhelmed by intense PAH emission.

3. SPECTROSCOPY OF THE ORION BAR AND M17 FROM 3 TO 5.5 μm

3.1. Observations and Data Reduction

The data presented here of the Orion Bar and M17 were obtained using the Short Wavelength Spectrometer (SWS; de Graauw et al. 1996) on board *ISO* (Kessler et al. 1996). Details of the observations are given in Table 1. The SWS grating spectra are taken in the Astronomical Observation Template 01 (AOT 01) full scan mode, speed 2 (de Graauw et al. 1996). In the AOT 01 mode, spectra are taken by scanning the grating over its full mobility range and back, yielding two independent scans (the up and down scan). Hence, in combination with the 12 detectors, 24 independent measurements of the incident spectrum are obtained. In the AOT 01 mode, each of these independent measurements is individually undersampled. However, because the measurements are obtained at slightly different wavelength offsets, they can be combined to yield a spectrum oversampled by a factor of 4. By comparing the independently reduced up and down scans for a given source, an estimate of the instrumental uncertainty can be obtained, and cosmic-ray hits can be discerned. The *ISO* SWS aperture has a size of $14'' \times 20''$ in the $3\text{--}5 \mu\text{m}$ region.

The data are processed with IA³, the SWS Interactive Analysis package (de Graauw et al. 1996), using calibration files and procedures equivalent with pipeline version 10.1. Standard data reduction techniques are used to correct for memory effects, subtract dark current, and calibrate for the responsiveness of the detectors. After manual removal of strong cosmic-ray hits and electronic jumps, the signals of the 12 detectors are all flat-fielded to the average level. Bad data are excluded based on the criterion of Chauvenet (as described in Bevington & Robinson 2003), and the data are rebinned with a constant spectral resolution of 350.

3.2. The Spectra

Both the Orion Bar and M17 are known to exhibit a wealth of PAH emission features (see Fig. 1). They show the well-known PAH bands at 3.3 , 6.2 , 7.7 , 8.6 , 11.2 , and $12.7 \mu\text{m}$ and the broad underlying plateaus associated with the 3.3 , 7.7 , and $11.2 \mu\text{m}$ bands. In addition, the *ISO* SWS spectrum of the Orion Bar shows weaker PAH bands at 3.4 , 3.5 , 5.25 , 5.7 , 6.0 , 6.7 , 11.0 , 12.0 , 13.5 , 14.2 , and $16.4 \mu\text{m}$ and a broad plateau between 15 and $20 \mu\text{m}$. In contrast, the *ISO* spectrum of M17 only shows clear emission at 3.4 , 5.25 , 5.7 , 6.0 , 11.0 , 12.0 , and $16.4 \mu\text{m}$, with a hint of a plateau between 15.5 and $17 \mu\text{m}$. The PAH emission bands dominate the mid-IR spectrum of both objects.

As discussed earlier and illustrated in Figure 1, the C-D stretching region ($4.3\text{--}5 \mu\text{m}$) falls in a very clean portion of the spectrum. In contrast, the C-D deformation ($7\text{--}8 \mu\text{m}$) and out-of-plane bending modes ($14\text{--}17 \mu\text{m}$) blend with other

TABLE 1
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Source	Position	α (J2000.0)	δ (J2000.0)	TDT ^a	Principal Investigator
Orion Bar	D5	05 35 19.81	−05 25 09.98	83101507	Drapatz
M17 ^b	IRAM 5	18 20 23.4	−16 12 31.21	09901415	Drapatz

NOTE.—Units of right ascension are hours, minutes, and seconds, and units of declination are degrees, arcminutes, and arcseconds.

^a Each *ISO* observation is given a unique TDT (target dedicated time) number.

^b Reference to first publication of complete spectrum in Verstraete et al. (1996).

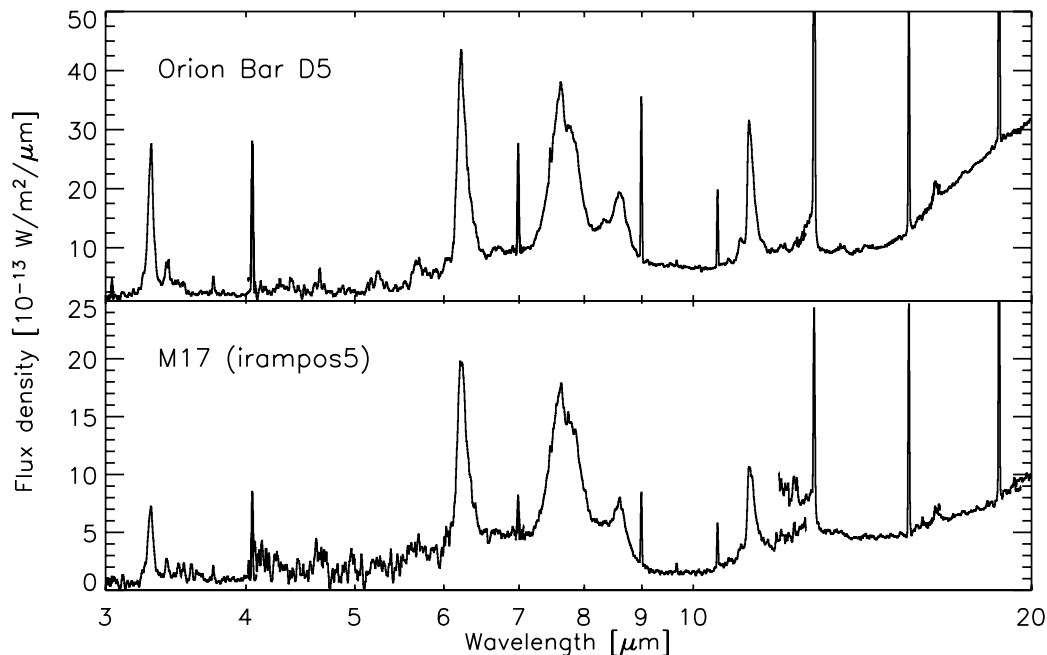


FIG. 1.—The 3–20 μm ISO SWS spectrum of the Orion Bar at position D5 and of M17 at IRAM position 5. The pointing of both observations is given in Table 1.

very prominent interstellar features. The spectrum between 4.2 and 5.5 μm of the Orion Bar (Fig. 2, *left*) shows weak continuum emission. This continuum is possibly due to a small fraction of dust inside the H II region, heated to high temperatures by resonantly scattered Ly α radiation. Alternatively, these are larger (~ 500 C atoms) PAH-like structures stochastically heated by a single- or multiphoton event. On top of the dust continuum, there is evidence for new weak emission

features centered near 4.4 and 4.65 μm , as well as the 5.2 μm PAH emission band and hydrogen recombination lines. The 4.65 μm feature overlaps the Pf β emission line at 4.652 μm . To determine the intensity of the underlying broad 4.65 μm feature, the contribution from the Pf β line is removed. This removal is based on the theoretical ratio of the Pf β hydrogen recombination line to the Br α line, calculated assuming the conditions of case B in Storey & Hummer (1995), with

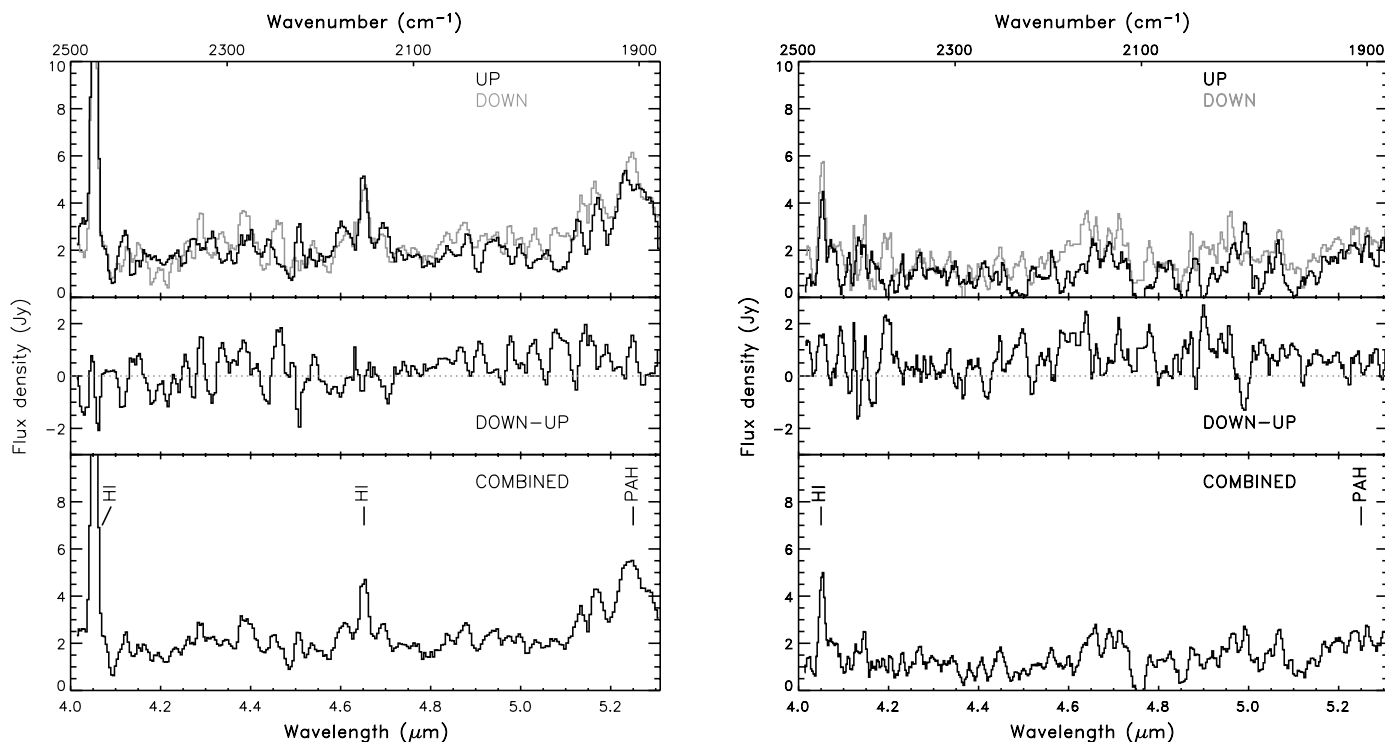


FIG. 2.—ISO SWS spectrum of the Orion Bar (*left*) and M17 (*right*) in the 4–5.3 μm region. The top panels show the independently reduced up and down scans, the middle panels the difference between the up and down scans, and the bottom panels the final (combined) spectrum.

$T = 7500$ K and $n_e = 10^4$ cm $^{-3}$. The derived Pf β /Br α flux ratio is rather weakly dependent on T and n_e in this regime, giving rise to a 1% uncertainty at most. Since the wavelengths of the Br α and Pf β emission lines are close, no extinction correction was applied to the theoretical line ratios. Subsequently, a Gaussian of width equal to the instrumental resolution element and with a flux equal to the derived Pf β flux is then subtracted from the spectrum. This analysis shows that there is additional emission at 4.65 μ m (see Fig. 3). The uncertainty of the Pf β intensity introduces an uncertainty of less than 1% to the 4.65 μ m flux. The fluxes of the two candidate features together with the flux of the bands near 3.3 and 5.25 μ m are given in Table 2. The uncertainties have been determined by comparing the independently reduced up and down scans. These uncertainties are dominated by uncertainty in the dark-current subtraction, resulting in some wavelength-dependent error as well. Taking this into account, we conclude that the 4.4 and 4.65 μ m features are present in this spectrum of the Orion Bar at the 1.9 and 4.4 σ levels, respectively.

Similarly, Figure 2 (right) shows the spectrum of M17 between 4.0 and 5.3 μ m. As already reported by Verstraete et al. (1996), on top of the weak dust continuum a clear feature is present at 4.65 μ m. However, there is no evidence for emission at 4.4 μ m. For this position, the contribution of the Pf β line to the 4.65 μ m feature is negligible (see also Fig. 2).

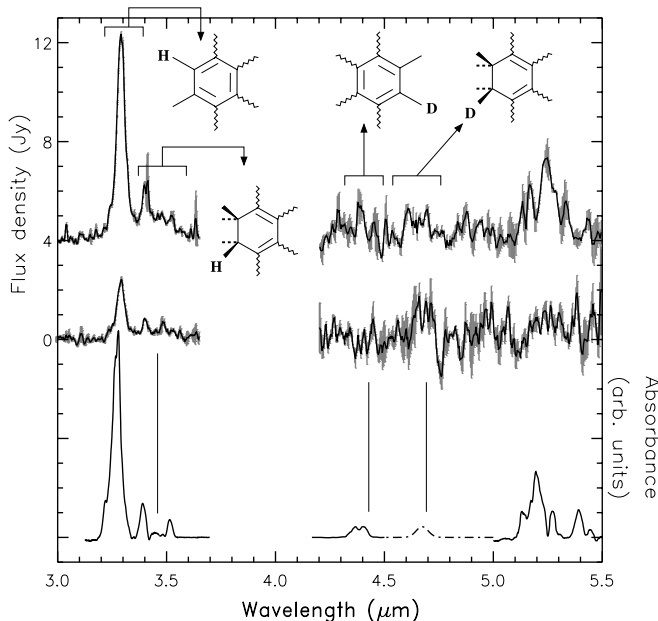


FIG. 3.—Comparison of the 3.0–5.5 μ m continuum-subtracted *ISO* SWS spectrum of the Orion Bar (top trace) and M17 (middle trace) to the absorption spectrum of a partially deuterated PAH mixture (lower trace, solid line) and the computed absorption spectrum of a D_n PAH (lower trace, dashed line). The C-H and C-D bonds shown on the chemical structures give rise to the spectral features indicated by the brackets. The aromatic and aliphatic C-H stretches produce the bands in the 3 μ m region, the C-D stretches in PADs and D_n PAHs produce the bands at 4.4 and 4.65 μ m, respectively, and the 5.2 μ m feature is due to overtones of C-H bending vibrations. The agreement in wavelength between the expected features from PADs and the two weak, new features reported here at 4.4 and 4.65 μ m supports their assignment as PADs (see footnote 5). The PAH mixture spectrum is produced by co-adding the spectra of individual fully deuterated PADs and fully hydrogenated PAHs in a D/H = 1/20 ratio and contains naphthalene, phenanthrene, pyrene, chrysene, 7,8-dihydrobenzo[a]pyrene, d $_8$ -naphthalene, d $_{10}$ -phenanthrene, d $_{10}$ -pyrene, and d $_{12}$ -chrysene. The computed spectrum of the D_n PAHs contains dihydro-pyrene, dihydrocoronene and dihydrocircumcoronene (D. M. Hudgins et al. 2004, in preparation).

TABLE 2
FLUXES AND UNCERTAINTIES FOR THE INTERSTELLAR FEATURES
(AFTER CONTINUUM SUBTRACTION)

WAVELENGTH (μ m)	ORION BAR		M17	
	Flux (W m $^{-2}$)	σ	Flux (W m $^{-2}$)	σ
3.3 ^a	1.1E10 $^{-13}$	45	3.0E10 $^{-14}$	20
3.4 ^a	1.4E10 $^{-14}$	12	3.6E10 $^{-15}$	5
3.5 ^a	4.0E10 $^{-15}$	6.5
4.4.....	7.2E10 $^{-15}$	1.9
4.65.....	1.5E10 $^{-14}$	4.4	1.2E10 $^{-14}$	4.4
5.25.....	4.6E10 $^{-14}$	9.4	2.1E10 $^{-14}$	3.4

^a The 3.2–3.65 μ m plateau under the 3.3, 3.4 and 3.5 μ m bands is considered to be independent of these bands and hence does not contribute to their fluxes.

The fluxes with their uncertainties for the features associated with M17 are given in Table 2.

We also checked the *ISO* SWS spectra of many other sources, primarily H II regions, but also reflection nebulae, planetary nebulae, and galaxies. However, the Orion Bar and M17, discussed here, are the only two sources that show detectable emission in the 4 μ m region expected from PADs. We attribute this to the inherent weakness of the features, in combination with the low flux of most sources and the high noise level in band 2a of *ISO* SWS. This is supported by the fact that, for all spectra taken at different positions within M17 and the Orion Bar, these new features are only evident in regions with the strongest PAH intensities.

3.3. The Identification

Figure 3 compares the 3.0–5.5 μ m spectrum of the Orion Bar with the Pf β line removed (top trace) and M17 (middle trace) to the absorption spectrum of a partially deuterated PAH mixture (solid line, lower trace) and the computed absorption spectrum of a D_n PAH (dotted line, lower trace). The solid line portion of the lower trace in Figure 3 presents the spectrum produced by combining the laboratory absorption spectra of a variety of individual PADs, PAHs, and H_n PAHs. Here the aromatic C-H stretches produce the 3.3 μ m band, the aliphatic C-H stretches and the overtones and combinations of CC modes produce the weak features between 3.4 and 3.5 μ m, and the complex structure centered near 5.2 μ m is due to overtones and combinations of the longer wavelength C-H bending vibrations. The band centered near 4.4 μ m in the spectrum arises from the aromatic C-D stretches of the PADs within the molecular mixture. The dashed-line portion of the lower trace presents the computed position of the aliphatic C-D stretch in D_n PAHs with one aliphatic deuterium atom (D. M. Hudgins et al. 2004, in preparation).⁵ The computed values of the corresponding 3.3 and 4.4 μ m bands (not shown in Fig. 3) are in good agreement with the laboratory spectra (D. M. Hudgins et al. 2004, in preparation). The good correspondence in position between the predicted PAD features and the two potential interstellar features adds credibility to their detection. The

⁵ The composite absorption spectrum has not been shifted to take into account the approximately 10–15 cm $^{-1}$ redshift inherent in the emission process (Cherchneff & Barker 1989; Flickinger & Wdowiak 1990; Brenner & Barker 1992; Colangeli, Mennella, & Bussoletti 1992; Joblin et al. 1995; Cook & Saykally 1998). If this redshift is included, the agreement is quite good.

center of the aliphatic C-D band position here ($4.65 \mu\text{m}$) is consistent with that very recently reported by Grishko & Duley (2003) for the corresponding aliphatic C-D stretch band ($4.5\text{--}4.75 \mu\text{m}$) in deuterated amorphous carbon. Interestingly, the width of this feature for amorphous carbon is ~ 4 times greater than that observed here. This reflects the broader range in environments that the vibrating deuterium atom experiences in solid amorphous material versus that for a free molecule. This is also consistent with the interstellar features arising from free molecules, not particles.

On the basis of the band-position correspondence between the interstellar and the laboratory model spectra shown in Figure 3, we attribute the possible new interstellar feature near $4.4 \mu\text{m}$ from the Orion Bar to the aromatic C-D stretch from interstellar PADs. The second broader feature centered near $4.65 \mu\text{m}$, evident in both the Orion Bar and M17 spectra, falls precisely where the aliphatic C-D stretch is predicted. The sum of the intensities of these features provides a measure of the amount of deuterium in the PAH population. The D/H ratio of the emitting PAH population can be estimated by taking the ratio of this sum to the analogous sum of the $3.3 \mu\text{m}$ and weaker satellite band intensities, which provide a measure of the hydrogen in the PAH population. Assuming that the integrated absorbance values of the corresponding C-H/C-D modes are similar, we estimate that the D/H ratio distributed over the aromatic and aliphatic carbons within the family of interstellar PAHs in the Orion ionization ridge is 0.17 ± 0.03 and 0.36 ± 0.08 in M17. Within this framework, the aliphatic groups have a much higher deuterium fraction than the aromatic groups, as implied by the high $4.65/3.4$ intensity ratio compared to the $4.4/3.3$ intensity ratio; in particular, M17 does not show deuteration of the aromatic groups.⁶ It is interesting that variable deuterium enrichments have been invoked by Draine (2004) to account for the observed variation in the gas-phase D/H ratio in the local ISM (Linsky 2003, 2004). In particular, Orion is a region with a low gas-phase D/H ratio (Jenkins et al. 1999), consistent with deuterium enrichment in heavier species. If borne out by further observations, this difference in D/H fractionation may provide important insight into the isotopic fractionation processes at work with interstellar PAHs.

4. DISCUSSION

Deuterium fractionation occurs because of the different zero-point energies of C-H and C-D bonds, which results in slightly more stable C-D bonds. Therefore, dehydrogenation is slightly favored over dedeuteration, and, with the passage of time, PAHs will become deuterium-enriched (Allamandola et al. 1989; Tielens 1997; Millar et al. 2000). Because the C-H and C-D bond energy differences are small (~ 500 K), high deuteration is generally a sign of chemistry at low temperatures. Thus, while PAHs may be formed in high temperature stellar ejecta, any deuterium enrichment must reflect a later chemical exchange with cold interstellar gas. This is consistent with the low deuterium abundance in stellar ejecta due to nucleosynthetic processes during the lifetime of the star. For PAHs, there are at least four distinctly different astrochemical

processes that could drive deuterium enrichment in the ISM (Sandford, Bernstein, & Dworkin 2001). First, PAH deuterium enrichments can result from low-temperature ($T < 50$ K) ion-molecule reactions occurring in the gas phase (Tielens 1997; Millar et al. 2000). Second, PAHs can become deuterium-enriched in ice mantles in dense interstellar clouds. Gas-grain chemistry should produce large deuterium enrichments in grain mantles where reduction is occurring because of the high atomic deuterium fractionation of the accreting gas (Tielens 1992; Charnley, Tielens, & Rodgers 1997). Third, additional deuterium enrichment can occur for PAHs within ices rich in species such as HDO, NH_2D , and CH_2DOH when they are processed by UV and cosmic-ray radiation (Sandford et al. 2000). In this case, both aromatic and aliphatic C-D bonds are produced. Finally, deuterium enrichment by unimolecular photodissociation can also occur for PAHs in the gas phase (Allamandola et al. 1989). In contrast to the previous processes, this does not require low temperatures and is expected to be most significant for PAHs in the size range from about C_{10}H_8 (naphthalene) to $\text{C}_{42}\text{H}_{18}$ (hexabenzocoronene), the portion of the interstellar PAH population expected to dominate the emission in the $3\text{--}5 \mu\text{m}$ region of the spectrum. With time, interstellar PAHs could become highly enriched in deuterium by any or all of the above processes. Measured deuterium fractionations of simple interstellar molecules are typically $0.01\text{--}0.1$ (e.g., Markwick, Charnley, & Millar 2001), but much higher deuterium fractions have occasionally been measured. In particular, deuterated methanol is more abundant in the warm gas around the low-mass protostar IRAS 16293–2422 than fully hydrogenated methanol (Parise et al. 2002). Since PAHs are considerably more stable and, as a family, more abundant in the ISM than many of the smaller species that show deuterium enrichments ($\text{PAH}/\text{H}_2 \sim 10^{-7}$ compared to $\text{HCN}/\text{H}_2 \sim 10^{-8}$) and PAHs carry more H atoms per molecule than simpler molecules, PAHs may well represent a large reservoir of deuterium-enriched interstellar materials.

While interstellar PAHs are expected to be enriched in deuterium, the extent of the enrichment depends on the local environment and history, making the PAH D/H ratio a particularly useful new interstellar probe. In particular, PAHs freshly ejected by stars would be expected to contain little deuterium, since most of the parent star's original deuterium would have been destroyed during nucleosynthesis. In contrast, PAHs in dense clouds have experienced a long period of interstellar evolution and will have had ample opportunity to become enriched in deuterium by ion-molecule and unimolecular photodissociation reactions occurring in the gas phase and by radiation-driven exchange reactions in ice mantles. Some of the highest D/H ratios in gas-phase PAHs might be expected in the transition zones, such as the Orion Ionization Ridge studied here, where H II regions are exposing fresh dense cloud material to the strong stellar radiation field. These environments drive rapid gas-phase enrichments, and this is where deuterium-enriched PAHs frozen in ice grains will be released into the gas phase as well. Here, the PAH D/H ratio may serve as a probe of past interstellar heritage and age. If borne out, the differences in fractionation between aromatic and aliphatic hydrogen suggested by the Orion Bar and M17 data may reflect that they derive largely from different processes. In particular, enriched D_n PAHs and methylated PAHs may result from exchange reactions and photochemistry in ice mantles (in the dense-cloud phase). In contrast, the fractionation of aromatic H atoms may be

⁶ This high aliphatic-to-aromatic C-D ratio raises the issue of band identity. The only other interstellar species of which we are aware that could contribute in this region are the cyanopolynes. Individual members of this C-chain family have bands that are evenly distributed between 4.4 and $4.8 \mu\text{m}$ (Allamandola et al. 1999). It seems unlikely that only two lines would show in this region if cyanopolynes were responsible.

controlled by ion-molecule and unimolecular photodissociation reactions in the gas.

This interstellar chemistry may have also played an important role in determining the inventory of organic compounds present during the formation of the solar system and preserved today in meteorites and interplanetary dust particles (IDPs) collected in the stratosphere. Of particular interest is that the analysis of these extraterrestrial organics, in combination with observations of the interstellar PAH D/H ratio as presented here, may make it possible to evaluate the relative contributions of the different interstellar processes described above to the establishment of the organic species incorporated into the solar system. Isotopic studies of the D/H ratio in primitive carbonaceous meteorites and IDPs reveal a large deuterium excess, which implies they carry significant amounts of presolar, interstellar materials (Kerridge, Chang, & Shipp 1987; Zinner 1997; Messenger 2000). Interestingly, the deuterium enrichments are only associated with the amorphous organic material in these extraterrestrial samples (Kerridge et al. 1987; Keller, Messenger, & Bradley 2000), material that is dominated by PAHs and closely related aromatic structures (Clemett et al. 1993; Cody, Alexander, & Tera 2002). Further, recent mass spectral studies of the PAH populations in the Allende and Murchison meteorites strongly suggest that the PAHs in these meteorites have a presolar, interstellar origin, with a composition largely undisturbed by solar nebula processing (Plows et al. 2003). Thus, interstellar PADs represent the first family of compounds that can be directly observed in different interstellar environments and that can also be subjected to laboratory studies of meteorites and IDPs. As such, they provide a unique and direct link between

the ISM and the solar system, a link that can be exploited to more deeply understand both.

5. CONCLUSIONS

Infrared emission features have been detected at 4.4 and 4.65 μm in the spectrum of the Orion Bar and at 4.65 μm in the spectrum of M17. These peak positions are characteristic for aromatic and aliphatic C-D bonds, analogous to the well-known emission bands at 3.3 and 3.4 μm . We attribute these features to deuterated PAHs and D_n PAHs. Infrared spectroscopy of deuterated interstellar species offers the ability to probe the extent of deuteration of an entire chemical family, rather than the deuteration in one species. Since the PAH infrared emission features are ubiquitous throughout the cosmos, observations at these frequencies can serve as probes of the PAH D/H ratio in a very wide variety of Galactic and extragalactic objects. Within the Galaxy, the deuterium distribution between the aromatic and aliphatic components reflects the fractionation processes at play during the interstellar lifetime of the emitting species. Since deuterated PAHs are present in meteorites, follow-up observations may also allow a better understanding of the connections between the interstellar medium and the solar system.

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