

INTERSTELLAR PAH EMISSION IN THE 11–14 MICRON REGION: NEW INSIGHTS FROM LABORATORY DATA AND A TRACER OF IONIZED PAHS

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ABSTRACT

The Ames infrared spectral database of isolated, neutral and ionized polycyclic aromatic hydrocarbons (PAHs) shows that aromatic CH out-of-plane bending frequencies are significantly shifted upon ionization. For solo- and duet-CH groups, the shift is pronounced and consistently toward higher frequencies. The solo-CH modes are blueshifted by an average of 27 cm^{-1} and the duet-CH modes by an average of 17 cm^{-1} . For trio- and quartet-CH groups, the ionization shifts of the out-of-plane modes are more erratic and typically more modest. As a result of these ionization shifts, the solo-CH out-of-plane modes move out of the region classically associated with these vibrations in neutral PAHs, falling instead at frequencies well above those normally attributed to out-of-plane bending vibrations of any type. In addition, for the compact PAHs studied, the duet-CH out-of-plane modes are shifted into the frequency range traditionally associated with the solo-CH modes. These results refine our understanding of the origin of the dominant interstellar infrared emission feature near $11.2\text{ }\mu\text{m}$, whose envelope has traditionally been attributed only to the out-of-plane bending of solo-CH groups on PAHs, and provide a natural explanation for the puzzling emission feature near $11.0\text{ }\mu\text{m}$ within the framework of the PAH model. Specifically, the prevalent but variable long-wavelength wing or shoulder that is often observed near $11.4\text{ }\mu\text{m}$ likely reflects the contributions of duet-CH units in PAH cations. Also, these results indicate that the emission between 926 and 904 cm^{-1} (10.8 and $11.1\text{ }\mu\text{m}$) observed in many sources can be unambiguously attributed to the out-of-plane wagging of solo-CH units in moderately sized (fewer than 50 carbon atom) PAH cations, making this emission an unequivocal tracer of ionized interstellar PAHs.

Subject headings: infrared: ISM: lines and bands — ISM: molecules — molecular data

1. INTRODUCTION

The prominent infrared emission feature near 890 cm^{-1} ($11.2\text{ }\mu\text{m}$) discovered by Gillett, Forrest, & Merrill (1973) is one of the strong interstellar infrared emission bands observed in a wide variety of objects and under a wide variety of conditions. The other prominent members of the family fall at 3050 , 1610 , 1310 , and 1165 cm^{-1} (3.3 , 6.2 , 7.7 , and $8.6\text{ }\mu\text{m}$). Thanks in large part to the fact that the $8\text{--}13\text{ }\mu\text{m}$ region is accessible to ground-based instruments, the 890 cm^{-1} band has been the subject of extensive scrutiny. Careful observations, in particular by Roche, Aitken, and collaborators, have revealed a great deal about the detailed spectral and spatial structure of the emission in this region as a function of object type (Aitken & Roche 1983; Roche, Aitken, & Smith 1989, 1991, 1994; Cohen, Tielens, & Allamandola 1985; Witteborn et al. 1989). This, in turn, has provided important insight into the nature of the emitting species. Summing up, it was found that the 890 cm^{-1} band was generally accompanied by a second distinct, but weaker, feature near 790 cm^{-1} ($12.7\text{ }\mu\text{m}$) which often overlaps the Ne II emission line at 780 cm^{-1} ($12.8\text{ }\mu\text{m}$). Weaker features are also often present near 910 , 870 , 830 , and 740 cm^{-1} (11.0 , 11.5 , 12.0 , and $13.5\text{ }\mu\text{m}$). The observations also showed that these discrete features fell atop a broad emission plateau extending from 950 to 750 cm^{-1} (10.5 to $13.5\text{ }\mu\text{m}$). The band intensities vary with respect to one another from one object to another and spatially within objects as well as with respect to the emission plateau. While the $11.2\text{ }\mu\text{m}$ band is always prominent in spectra showing the interstellar infrared emission band spectrum, these other components are not always evident. It has also been noted that the profile of the $11.2\text{ }\mu\text{m}$ band is distinctly asymmetric, displaying a long-wavelength wing of variable intensity. This wing extends from around 880 cm^{-1} ($11.4\text{ }\mu\text{m}$) out to around 860 cm^{-1} ($11.6\text{ }\mu\text{m}$)

and displays varying degrees of substructure. In some cases, it even appears as a prominent shoulder on the $11.2\text{ }\mu\text{m}$ band (Witteborn et al. 1989).

Also striking is the increasing number of observations that show a distinct, sometimes prominent, feature between 926 and 904 cm^{-1} (10.8 and $11.06\text{ }\mu\text{m}$) which varies considerably with respect to the strong $11.2\text{ }\mu\text{m}$ band. Initially reported and discussed by Roche et al. (1991), there is much evidence for this in a multitude of objects. For example, TY CrA, a pre-main-sequence Ae star, shows a strong peak at $11.05\text{ }\mu\text{m}$ (Roche et al. 1991); Elias 1, another pre-main-sequence star, shows a band at $11.06\text{ }\mu\text{m}$ (Hanner, Brooke, & Tokunaga 1994); Elias 14, a young stellar object in a region of extended $12\text{ }\mu\text{m}$ emission, emits at $10.8\text{ }\mu\text{m}$ (Hanner, Brooke, & Tokunaga 1995; Greene & Young 1989). *Infrared Space Observatory* observations show that emission near $11.1\text{ }\mu\text{m}$ is common in compact H II regions (Roelfsema et al. 1996) and protoplanetary nebulae (Molster et al. 1996). Most recently, emission features between 10.8 and $11.1\text{ }\mu\text{m}$ have been shown to vary as a function of proximity to SVS 3, the exciting star in NGC 1333 (Sloan et al. 1999). Similar spatial behavior has been found in WL 16 (DeVito & Hayward 1998). When evident, this feature varies in strength from appearing as a strong, distinct feature to a weak blue shoulder on the $11.2\text{ }\mu\text{m}$ band.

In 1981, Duley & Williams suggested that the 890 cm^{-1} ($11.2\text{ }\mu\text{m}$) band position was indicative of the CH out-of-plane (CH_{oop}) bending vibrations of aromatic structural units on hydrogenated amorphous carbon particles. While the global positions of the suite of interstellar infrared emission features and the energetic constraints of the interstellar emission process are now widely believed to be more consistent with free, gas-phase polycyclic aromatic hydrocarbons (PAHs), PAH clusters, and PAH-related species, that original aromatic interpretation re-

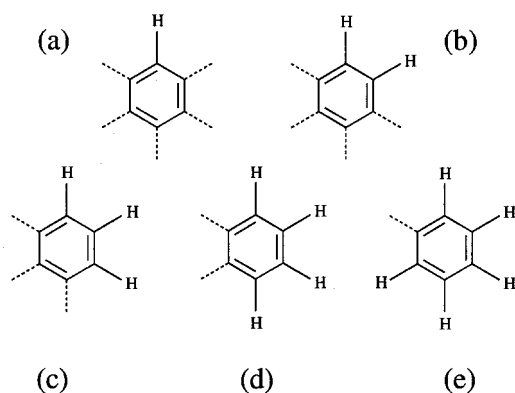


FIG. 1.—Example structures illustrating the possible adjacency classes for CH groups in aromatic molecules. (a) A CH group that has no neighboring CH groups is said to be a nonadjacent or solo-CH group; (b) two neighboring CH groups are termed doubly adjacent or duet-CH groups; (c) three neighboring CH groups are termed triply adjacent or trio-CH groups; (d) four neighboring CH groups are termed quadruply adjacent or quartet-CH groups; and (e) five CH groups that fall adjacent to each other are termed quintuply adjacent or quintet-CH groups. Dotted lines indicate bonds to the unspecified carbon skeleton of the molecule.

mains valid (e.g., Puget & Leger 1989; Allamandola, Tielens, & Barker 1989). Identification of the interstellar emission in the $910\text{--}770\text{ cm}^{-1}$ ($11\text{--}13\text{ }\mu\text{m}$) region with the CH_{oop} bending modes of interstellar aromatic compounds is entirely consistent with the typical frequencies of these modes and, furthermore, readily accounts for the observed detailed substructure in this region (e.g., Cohen et al. 1985; Witteborn et al. 1989). The frequency of an aromatic CH_{oop} bending mode is strongly dependent on the number of neighboring CH units on each benzenoid ring (e.g., Bellamy 1958). The number of neighboring aromatic CH units on a benzenoid ring is commonly indicated in terms of their “adjacency” as illustrated in Figure 1. The designation “nonadjacent” indicates a CH bond with no neighboring CH units. Likewise, “doubly adjacent” indicates two neighboring CH units on a ring; “triply adjacent” indicates three neighboring CH units; “quadruply adjacent” indicates four neighboring CH units; and “quintuply adjacent” indicates five neighboring CH units. These are also referred to as solo-CH, duet-CH, trio-CH, quartet-CH, etc., groups.

Since the CH_{oop} bending motions of these classes of peripheral CH bonds are not all equivalent, each has associated with it a more or less unique, characteristic frequency range into which its CH_{oop} bending vibration falls. The power of this as a spectroscopic tool is illustrated in Figure 2, which shows representations of a few typical *neutral* PAHs through this region of the spectrum (*black vertical bars*). In this representation, each bar represents the position of an absorption band, while the length of that bar indicates its relative intensity. Inspection of Figure 2 shows that solo- CH_{oop} vibrations fall at the highest frequencies, roughly in the range from 900 to 860 cm^{-1} ($11.1\text{--}11.6\text{ }\mu\text{m}$), with the other classes falling at successively lower frequencies with increasing adjacency: $860\text{--}800\text{ cm}^{-1}$ ($11.6\text{--}12.5\text{ }\mu\text{m}$) for duet-CH groups, $810\text{--}750\text{ cm}^{-1}$ ($12.4\text{--}13.3\text{ }\mu\text{m}$) for trio-CH groups, and $770\text{--}735\text{ cm}^{-1}$ ($13\text{--}13.6\text{ }\mu\text{m}$) for quartet-CH groups. Quintet- CH_{oop} vibrations produce bands in two regions: $770\text{--}730\text{ cm}^{-1}$ ($13\text{--}13.7\text{ }\mu\text{m}$) and $710\text{--}690\text{ cm}^{-1}$ ($14.1\text{--}14.5\text{ }\mu\text{m}$). However, quintet-CH bands fall well below the frequency range of the interstellar emission envelope, and thus molecules with these structures are not expected to be important members of the interstellar PAH family (Cohen et al. 1985; Roche et al. 1989).

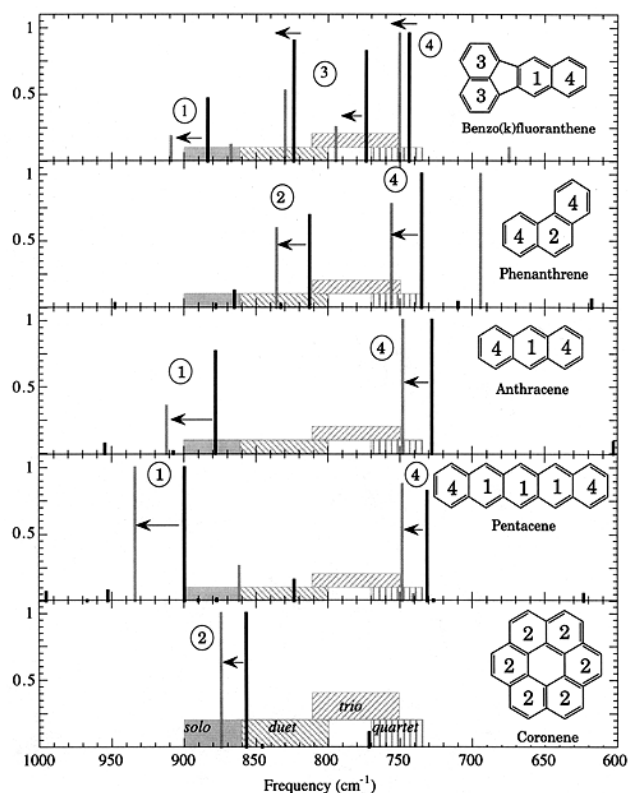


FIG. 2.—Schematized *neutral and ionized* PAH spectra in the CH out-of-plane bending region illustrating the effects of ionization. The number of adjacent CH groups are labeled within each ring and on the corresponding feature in the spectrum. The black bars reflect the positions of the spectral features of each PAH in its neutral form, while the gray bars reflect those of the corresponding PAH cation. The shaded areas indicate the *classical* ranges over which different *neutral* PAH edge structures produce bands. The blueshifts of the solo- and duet-CH modes upon ionization move them from their classical region toward and/or into the adjacent region. Spectra are from Hudgins & Allamandola (1995a, 1995b), Hudgins & Sandford (1998a, 1998b, 1998c), and Bauschlicher, Hudgins, & Allamandola (1999).

The characteristic frequency ranges presented above have been used extensively to draw insight into the structures of the PAHs that dominate the emitting population (e.g., Duley & Williams 1981; Jourdain de Muizon, d’Hendecourt, & Geballe 1990). However, implicit in these interpretations is the critically important assumption that the intrinsic frequencies and intensities of the various classes of CH_{oop} vibrations are more or less the same regardless of PAH charge state. In this Letter, the large body of astrophysically relevant spectral data now available in our infrared spectral database on isolated PAHs and PAH ions is used to reevaluate the classical view of the features in this region of the spectrum and the nature of the emitters.

2. RESULTS

Over the past 7 years, we have undertaken a systematic program to study the infrared absorption spectra of a wide range of PAHs and PAH ions isolated in rare gas matrices at low temperatures ($\approx 12\text{ K}$; Hudgins, Sandford, & Allamandola 1994; Hudgins & Allamandola 1995a, 1995b, 1997; Hudgins & Sandford 1998a, 1998b, 1998c). Details of the experimental procedure and a discussion of its astrophysical relevance can be found elsewhere (Hudgins & Allamandola 1995a, 1999). This work has resulted in a large and growing PAH spectral database that can be used to extend the PAH model and its

TABLE 1
COMPARISON OF CORRESPONDING CH OUT-OF-PLANE VIBRATIONAL FREQUENCIES BETWEEN NEUTRAL AND IONIZED PAHS

PAH	Nonadjacent CH			Doubly Adjacent CH			Triply Adjacent CH			Quadruply Adjacent CH		
	ν_{neutral}	ν_{cation}	$\Delta\nu_{\text{ion}}$	ν_{neutral}	ν_{cation}	$\Delta\nu_{\text{ion}}$	ν_{neutral}	ν_{cation}	$\Delta\nu_{\text{ion}}$	ν_{neutral}	ν_{cation}	$\Delta\nu_{\text{ion}}$
Naphthalene	783	759	-24
Anthracene	878	912	+34	730	748	+18
Phenanthrene	813	836	+23	735	756	+21
Pyrene	843	861	+18	747 ^a	768 ^a	+21
Benz(a)anthracene	883	911	+28	809 ^a	827 ^a	+18	749 ^a	756 ^a	+7
Benzo(c)phenanthrene	839 ^a	855 ^a	+16	758/750 ^a	756/750 ^a	-2/0
Chrysene	813	834	+21	763 ^a	761 ^a	-2
Tetracene	895	929	+34	747 ^a	758 ^a	+11
Triphenylene	744 ^a	751 ^a	+7
Benzo(e)pyrene	830	848	+18	771	?	?	750	?	?
Pentacene	900	934	+34	731	749	+18
Perylene	815/765 ^a	813/743 ^a	-2/-22
Benzo[ghi]perylene	846	864	+18	816/771	?	?
Coronene	857	875	+18
Ovalene	895 ^a	916 ^a	+21	843 ^a	857 ^a	+14
Fluoranthene	828/776	832/?	+4/?	745	?	?
Benzo(a)fluoranthene	877	908	+31	740 ^b	728 ^b	-12	740/731 ^b	743/740 ^b	+3/+9
Benzo(b)fluoranthene	887/883 ^b	905/900 ^b	+18/+17	802 ^b	798 ^b	-4	735/725 ^b	754/737 ^b	+19/+12
Benzo(j)fluoranthene	806 ^b	825 ^b	+19	753/743 ^b	750/744 ^b	-3/+1	730 ^b	734 ^b	+4
Benzo(k)fluoranthene	884	909	+25	780 ^b	786 ^b	+6	745	753	+8

^a Theoretical data from Langhoff 1996.

^b Theoretical data from Bauschlicher et al. 1999.

utility as a probe of the ISM by conducting more detailed analyses of the interstellar emission spectra than has previously been possible. Previous papers have employed the spectral database to establish the viability of the interstellar PAH model and its ability to account for the spectral variations in the interstellar emission and to constrain the size of the PAH population that dominates the emission in the 1650–1100 cm^{-1} (6–9 μm) region (Allamandola, Hudgins, & Sandford 1999; Hudgins & Allamandola 1999). Here we investigate what insight the spectral database can provide into the nature of the interstellar emission in the 950–700 cm^{-1} (9–14 μm) region of the spectrum. The data presented here do not include corrections for the matrix shift or the redshift expected between the gas-phase absorption peak frequencies and the emission frequencies of vibrationally excited PAHs (both $\approx 5\text{--}10 \text{ cm}^{-1}$) since the exact magnitude of these effects vary between molecules and between vibrational modes and both are less than the natural line width of the interstellar emitters ($\sim 30 \text{ cm}^{-1}$; Flickinger, Wdowiak, & Gomez 1991; Brenner & Barker 1992; Colangeli, Mennella, & Bussoletti 1992; Williams & Leone 1995; Joblin et al. 1995; Cook & Saykally 1998).

A careful survey of the CH_{oop} absorption band frequencies in the 950–650 cm^{-1} (10.5–15 μm) for each PAH/PAH⁺ pair in the database has been carried out to determine the effect of ionization. These frequencies are listed in Table 1, and the effect is illustrated in Figure 2. The table reflects neutral frequency, cation frequency, and ionization shift for each class of CH_{oop} bend in the molecule. The trio- and quartet- CH_{oop} features are, in some cases, interspersed with and difficult to distinguish from low-frequency skeletal deformation bands. To avoid this complication, only those PAHs for which all the CH_{oop} modes can be unambiguously identified have been included in the table. Also, in those cases in which the experimental data are incomplete, theoretically calculated frequencies are given (indicated by footnote).

The first column in Table 1 shows that the solo- CH_{oop} modes for ionized PAHs are consistently blueshifted by 18–34 cm^{-1} , with the average being 27 cm^{-1} . These modes fall between 934 and 900 cm^{-1} (10.7 and 11.1 μm), with about 910 cm^{-1} (11.0 μm) being typical of the majority. Interestingly, the average

solo- CH_{oop} ionization shifts in the table that are taken from theoretical calculations (ovalene, benzo[b]fluoranthene, $\langle \Delta\nu \rangle = 19 \text{ cm}^{-1}$) are about 40% lower than those that are taken from experimental measurements ($\langle \Delta\nu \rangle = 31 \text{ cm}^{-1}$). Indeed, a comparison involving those molecules for which both data sets are available (anthracene, benz[a]anthracene, tetracene, pentacene, benzo[a]fluoranthene, benzo[k]fluoranthene) shows that the theoretical calculations consistently underestimate the magnitude of the solo- CH_{oop} blueshift by an average of 5 cm^{-1} .

As with the solo-CH modes, the duet-CH modes are also consistently blueshifted, although to a somewhat smaller degree. These fall within the reasonably broad range from 875 to 825 cm^{-1} (11.4 to 12.1 μm), a range similar in magnitude to that covered by the neutral species albeit somewhat higher in frequency. This class of CH_{oop} bend is found to blueshift by 14–23 cm^{-1} with an average shift of 18 cm^{-1} . For these modes, the magnitudes of the theoretically predicted and experimentally measured shifts are in good agreement. Interestingly, a closer inspection of the data reveals that the positions divide naturally into two subgroups that seem to correlate with the structures of the molecules. The duet- CH_{oop} modes for PAHs with compact, highly symmetric structures (pyrene, benzo[ghi]perylene, coronene, ovalene) fall consistently at the highest frequencies (i.e., 875–857 cm^{-1} , 11.4–11.7 μm), while those modes in the less symmetric, noncompact PAH cations (phenanthrene, benz[a]anthracene, benzo[c]phenanthrene, chrysene, benzo[e]pyrene, and benzo[j]fluoranthene) fall consistently at lower frequencies (855–825 cm^{-1} , 11.7–12.1 μm).

Inspection of Table 1 shows that the behavior of the trio- and quartet- CH_{oop} modes upon ionization is somewhat ambiguous. The trio-CH modes are the most difficult to pin down, showing a wide range of both redshifting and blueshifting ($|\Delta\nu| \approx 1\text{--}22 \text{ cm}^{-1}$). The quadruply adjacent modes tend to be blueshifted, but to varying degrees ($|\Delta\nu| \approx 0\text{--}21 \text{ cm}^{-1}$). Interestingly, despite the varying frequency shifts, the resultant PAH cation quartet- CH_{oop} modes tend to group within a tight frequency range that is half that of the associated neutral modes. For ionized PAHs the range appears to be 761–734 cm^{-1} ($\Delta\nu = 27 \text{ cm}^{-1}$, $\langle \nu \rangle = 750 \text{ cm}^{-1}$), whereas for neutral PAHs the range is 783–725 cm^{-1} ($\Delta\nu = 58 \text{ cm}^{-1}$, $\langle \nu \rangle = 743 \text{ cm}^{-1}$).

Thus, if PAHs containing quartet-CH groups are an important part of the interstellar PAH population, clear structure is expected to be evident in the $750\text{--}740\text{ cm}^{-1}$ ($13.3\text{--}13.5\text{ }\mu\text{m}$) region.

3. ASTROPHYSICAL IMPLICATIONS

The ionization shifts of the solo- and duet-CH_{oop} modes have two important ramifications for the astrophysical problem. First, the $\approx 870\text{ cm}^{-1}$ ($\approx 11.4\text{ }\mu\text{m}$) emission wing has traditionally been assumed to have a common origin with the dominant $11.2\text{ }\mu\text{m}$ feature and has been attributed to anharmonicity in the solo-CH out-of-plane bending modes of vibrationally excited PAHs (Witteborn et al. 1989). However, the data presented here suggest an alternative explanation. As discussed above, the positions of the duet-CH_{oop} features in the compact PAH cations all fall in the range $875\text{--}857\text{ cm}^{-1}$ ($11.4\text{--}11.7\text{ }\mu\text{m}$), precisely the range covered by the red wing in the typical interstellar emission spectrum. Consequently, it is reasonable to suggest this wing (or shoulder, as the case may be) and any substructure therein is attributable to the duet-CH_{oop} modes of compact PAH cations in the emitting population. Interestingly, PAH stability is directly related to the degree of structural compactness (i.e., more compact = more stable). Thus, the PAH cations that appear to be contributing the most in this region ($11.4\text{--}12.1\text{ }\mu\text{m}$) are precisely the ones best suited for survival in the energetic emission zones. It is also worth noting that, based on a more limited data set of PAH cation spectra, Szczepanski & Vala (1993) suggested that the dominant $11.2\text{ }\mu\text{m}$ interstellar emission band itself might arise from the duet-CH_{oop} modes of PAH cations. However, the more extensive set of data presented Table 1 do not seem to bear out this possibility.

The second consequence of these data is the natural and necessary emergence of features near 910 cm^{-1} ($11.0\text{ }\mu\text{m}$). As discussed earlier, a feature of widely varying intensity has been observed at just this position in a large number of astronomical objects. Since this feature falls at a frequency significantly higher than those classically attributed to aromatic CH_{oop} bends of any type, its appearance has remained a challenge to the PAH model. This difficulty is, however, alleviated by the data

presented in Table 1, which shows that the positions of the solo-CH_{oop} bending features of the PAH cations in the database are in good agreement with that of the interstellar feature. Therefore, based on these data, we propose that the $11.0\text{ }\mu\text{m}$ component of the interstellar emission spectrum is an unambiguous tracer of moderately sized (fewer than 50 carbon atom) PAH cations that contain solo-CH groups.

4. CONCLUSION

We have shown that the prominent PAH CH out-of-plane bending frequencies are significantly shifted upon ionization. For solo- and duet-CH groups, the shift is pronounced and consistently to higher frequencies with averages of 27 and 18 cm^{-1} , respectively ($\approx 0.3\text{ }\mu\text{m}$). This is a large shift, requiring a reassessment of the interstellar emission band assignments in the $1000\text{--}770\text{ cm}^{-1}$ ($10\text{--}13\text{ }\mu\text{m}$) region. As a consequence, the solo-CH modes are shifted to frequencies *above* those normally associated with aromatic CH out-of-plane bends. Likewise, the duet-CH modes shift toward—and for the most stable, compact PAH cations into—the frequency range traditionally associated with the nonadjacent modes. Consequently, the puzzling emission between 926 and 904 cm^{-1} (10.8 and $11.1\text{ }\mu\text{m}$) observed in many sources can be unambiguously attributed to the out-of-plane bending vibrations of solo-CH units on the periphery of moderately sized (≤ 50 carbon atom) PAH cations and is an unequivocal tracer of ionized interstellar PAHs. Furthermore, the variable $880\text{--}860\text{ cm}^{-1}$ ($11.4\text{--}11.6\text{ }\mu\text{m}$) emission wing on the dominant 890 cm^{-1} ($11.2\text{ }\mu\text{m}$) interstellar feature is consistent with the positions of the duet-CH out-of-plane bending features of PAH cations. Thus, the intensity and topology of this wing may provide a second, albeit marginally resolved, probe of the ionized aromatic species in the emission regions.

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