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The weakness of diffuse bands in nebular environments

Possible impact on the PAH$^+$ hypothesis

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Abstract. It has been widely suggested that PAH cations (PAH$^+$) may be the carriers of the diffuse interstellar bands, so it is of interest to probe diffuse band behavior in regions suspected of having high abundances of PAHs. Here we examine the strengths of several of the visible-wavelength diffuse interstellar bands in two nebular environments where infrared emission and ultraviolet indicators show that PAHs are abundant. One might expect the PAHs to be predominantly positively ionized in these regions, yet the diffuse bands are systematically weak. This led us to examine the ionization balance for PAHs for conditions appropriate for our observed nebulae, to see whether the weakness of the diffuse bands might rule out PAH cations as the carriers. We find that this conclusion is ambiguous, however, due to the very rapid rates for recombination of PAHs: under conditions that may reasonably represent our observed nebulae, the PAHs might be in predominantly neutral form. If so, this would explain the weakness of the diffuse bands, but leaves open some very perplexing questions about where the PAHs might be dominantly in cation form, hence where the diffuse bands do arise if they are due to PAH$^+$.

Key words: ISM:general – ISM:molecules – ISM:reflection nebulae

1. Introduction

The carriers of the diffuse interstellar bands have eluded astronomers for some 60 years, since they were originally recognized as unidentified interstellar features by Merrill (1934). The bands consist of numerous (as many as 200 by some reckoning) interstellar absorption features, all of which are too broad to be atomic lines, but whose carriers are unknown. Solid-state absorption in grains or grain mantles has been proposed (e.g. Shapiro & Holcomb 1986 and references cited therein), as have molecular transitions (e.g. Russell 1935; Douglas 1977), but even today there is a lack of agreement about whether the carriers are in the dust or the gas in the diffuse interstellar medium. A review of the arguments on this question was published years ago (Smith *et al.* 1977) and is still relevent today; in addition, a comprehensive review of the diffuse bands will soon appear (Herbig 1995), as will a compendium of results from a recent symposium on the subject (Tielens & Snow 1995), both of which provide further insight into the arguments. Recent work on emission features seen in the Red Rectangle have demonstrated that at least some of the diffuse bands must be molecular in origin (Sarre 1991; Fossey 1991; Scarrott *et al.* 1992; Miles & Sarre 1993).

The suggestion a decade ago that polycyclic aromatic hydrocarbon (PAH) molecules might be abundant in the diffuse interstellar medium (Léger & Puget 1984) led almost immediately to the proposal that PAH ions (PAH$^+$) could be the carriers of the diffuse bands (Crawford *et al.* 1985; Léger & d'Hendecourt 1985; van der Zwet & Allamandola 1985), because the cations of moderate-sized PAHs have their primary electronic absorption spectra at visible wavelengths. Since then, further impetus for this proposal has come from laboratory experiments on PAH$^+$ species, which have produced results suggesting wavelength coincidences between PAH$^+$ transitions and diffuse bands (Salama & Allamandola 1992a, 1992b; Léger *et al.* 1995). In a recent study, Salama *et al.* (1995) have demonstrated general feasiblity of the PAH$^+$ hypothesis. On the other hand, a search for features expected from ionized coronene ($C_{24}H_{12}$) and ionized ovalene ($C_{32}H_{14}$) has proven negative (Ehrenfreund *et al.* 1995).

Unfortunately, to date measurement of PAH$^+$ spectra have been constrained to solid-state experiments, in which the PAH cations are embedded in matrices (argon or neon), so there are unknown shifts in both wavelength and width of the features. Thus no *definitive* identification of any diffuse band with a specific PAH$^+$ species has yet been made. It is also true that the general PAH hypothesis remains unproven; recent laboratory results on infrared emission bands have, in fact, led to some criticism of the entire PAH picture (Schlemmer *et al.* 1994), although their spectral mismatches occur for small PAHs (N_{carbon} = 10 and 16), whereas the expected mean carbon number for interstellar PAHs is larger than this.

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2. PAHs in the nebulae associated with HD 37903 and HD 200775

The presence of PAHs in circumstellar and nebular environments is inferred from a series of infrared emission features (known as the Unidentified InfraRed bands, or simply the UIRs). These are the emission features seen at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7μm, and they are found in many kinds of environments where there is a source of photons sufficiently energetic to excite the emitters (most of the excitation comes from UV photons, but some is attributed to visible-wavelength photons as well; Buss *et al.* (1994); Sellgren *et al.* 1990. The identification of the UIRs with PAHs has become widely accepted; the emission bands are interpreted as due to stretching and bending modes of the C-H and C-C bonds in aromatic structures (Léger & Puget 1984; Allamandola *et al.* 1985).

Buss *et al.* (1994) found, in a small sample of hot stars, that there is a strong correlation between "excess" UV extinction in the 8.5 - 10.5 μm^{-1} wavelength range and "excess" IR emission as indicated by the ratio of the 12- and 100-μm *IRAS* bands in emission. The correlation shows the expected relationship between energy that is absorbed in the UV by PAHs and that which is emitted in the IR by PAHs. The two stars HD 37903 and HD 200775 (which excite reflection nebulae NGC 2023 and NGC 7023, respectively) have high values in the Buss *et al.* study for both the *excess* UV absorption and the *excess* nebular I_{12}/I_{100} emission close to the stars (the actual I_{12}/I_{100} values of about 0.05 for these nebulae within molecular clouds are typical for other B1.5–B5 V reflection nebulae [Buss *et al.* (1994); *cf.* Jenniskens & Désert (1993)] and are comparable to the values typically seen in the diffuse interstellar medium).

The hydrogen densities and temperatures, as well as dust reddenings for these two stars in reflection nebulae, also indicate that a large portion of the line-of-sight material lies within the region where the UV radiation field is strong enough to excite PAH emission; i.e. for these two stars at least half, if not most, of the total foreground material must lie close to the stars (Buss *et al.* 1994; Jaffe *et al.* 1990; *cf.* Howe *et al.* 1991).

3. PAH ionization in nebular environments

Significantly, the wavelengths of the infrared emission bands are almost independent of the ionization state. The main effect of ionization is in the relative intensities of the bands; i.e. neutral and ionized PAHs have very similar spectra, but the relative intensities of the bands are affected by the ionization. It has been shown that a mixture of neutral and ionized PAHs provides the best fit to the relative strengths of the UIRs in some sources (Szczepanski & Vala 1993; De Frees *et al.* 1993). This leads to the expectation that in nebular environments where PAH emission features are seen, there is likely to be a significant abundance of positive ions, suggesting that the diffuse bands ought to be formed in such regions if PAH cations are responsible. We have explored this possibility more quantitatively.

Using the formalism of Bakes & Tielens (1994), we have calculated the ionization balance for selected PAHs in environments such as reflection nebulae, which are close to hot stars. We used pentacene ($C_{22}H_{14}$) and coronene ($C_{24}H_{12}$) as our model PAHs. The ionization cross section for these molecules was taken from Verstraete *et al.* (1990); we used experimentally measured electron affinities and ionization potentials.

The results show, perhaps surprisingly, that the high electron affinities for $PAH^+ + e^-$ recombination prevent PAH^+ from being dominant in the denser portions of nebular environments, even for radiation field intensities as high as a few hundred times the average interstellar value. For example, using the conditions for NGC 2023 adopted by Black & van Dishoeck (1987), namely a particle density of 10^4 cm^{-3} and a radiation field intensity 300 times the average interstellar value, we find that the neutral forms of both pentacene and coronene dominate over the positively ionized forms by a large factor. On the other hand, in ordinary diffuse interstellar regions, again the neutral PAHs dominate over the positive ions, despite the lower densities, because the radiation field intensity is low. This makes it a challenge to find *any* conditions under which PAH^+ should be dominant, which in turn presents a challenge to the general hypothesis that these are the carriers of the diffuse bands.

The calculations show that the ratio of PAH^+/PAH is highest in intermediate regions, where the density is dropping off but the radiation field intensity remains high. Specifically, for both pentacene and coronene, our calculations show that for a radiation field intensity of 300 times the average interstellar value, the PAH^+/PAH ratio is greater than 1 for any density below about 10^3 cm^{-3}. Thus we would expect high PAH^+ abundances in regions near hot stars, but where the density is moderate to low.

For environments such as reflection nebulae, the crux of the question of whether and where PAH^+ are reasonably abundant depends on the competing rates at which the density and the radiation field intensity drop off with distance from the exciting star. If the density n falls off more rapidly than the radiation field I, then there will be a zone with a high value of PAH^+/PAH; on the other hand, if I drops off faster than n, then the PAHs will remain neutral out to substantial distances from the exciting star.

This suggests that appropriate conditions might prevail in transition zones at the outer boundaries of reflection nebulae and H II regions. This would imply that lines of sight intersecting such transition zones should have strong diffuse band absorption, if the carriers of the bands are PAH cations. For pentacene and coronene, the ideal conditions lie within a range of 10 to 100 times the average interstellar radiation field intensity, with n_H in the range between 100 and 1000 cm^{-3}.

4. Diffuse bands in nebular environments

There is an extensive literature on diffuse bands in nebular regions, starting with the observation by Morgan (1944), who found that the 4430Å band is deficient in the Trapezium region of the Orion nebula. This was followed by the work of Walker (1963) and then A'Hearn (1971), who reached similar conclusions. Other kinds of regions localized around hot stars are also known to be deficient in diffuse bands; e.g. Snow & Wallerstein (1972), Snow (1973), and Seab (1995 and references cited therein). The general thrust of this literature is that the bands are either weak or absent in circumstellar regions of all descriptions, including both hot star and cool star envelopes.

In their study of diffuse band absorption in reflection nebulae, Josafatsson & Snow (1987) carried out correlation analyses, probing the dependence of the diffuse bands on other interstellar quantities, including the color excess $E(B-V)$.

Among the stars included in their sample were HD 37903 and HD 200775, the exciting stars of the two reflection nebulae described earlier in this paper, which have since been studied in detail for their infrared emission and UV extinction properties (Buss *et al.* 1994). The spectral types are B1.5V and B3Ve, respectively, and both have visual extinctions due to dust of about $A_V = 1.45$. The circumstellar contribution to E(B-V) for the Be star HD 200775 due to free-free scattering by electrons has been removed (see Pfau *et al.* 1987), and the tilted circumstellar disk surrounding this star does not contribute to the line-of-sight extinction (Brown *et al.* 1995) or to the diffuse bands.

The measurements of diffuse bands in both nebulae show that the bands are significantly weak relative to extinction (Snow *et al.* 1977; Walker *et al.* 1980; Josafatsson & Snow 1987; Pfau *et al.* 1987). In the study of Josafatsson & Snow, the six observed bands were found to be weak by 1-2σ in HD 37903 and up to 5σ in HD 200775. Walker *et al.* find no evidence for any diffuse bands in the spectrum of HD 200775, except for the features at 6284Å and possibly the one at 5780Å, in the entire spectrum between 5550 and 6750Å. In addition, Pfau *et al.* report that the 4430Å band is also weak in this line of sight; these authors quote the catalog of Snow *et al.* (1977), but appear to refer also to additional observations of their own. In any event, there is little doubt that in the spectra of these two stars the diffuse bands are systematically weak relative to normal diffuse interstellar medium behavior.

Another star in the Josafatsson & Snow paper may be of interest. This is HD 38087, which is associated with reflection nebulosity in the Orion region, and for which Witt *et al.* (1986) discovered scattering in the 2175Å extinction feature, which was attributed to the presence of unusually large dust grains (the ratio of total to selective extinction for this line of sight is $R_V = 4.86$, according to Aiello *et al.* 1988). Further information on this line of sight comes from an analysis of *IUE* spectra by Snow & Witt (1989), who show that the depletions of some elements onto the dust is enhanced, suggesting that the grain growth has occurred partly through the accretion of gas particles onto dust. This is clearly another environment where the UV radiation field is high, and one in which the infrared PAH features are moderately strong (Sellgren *et al.* 1990), comparable to those of HD 200775 and HD 37903 (Jenniskens & Désert 1993). Yet again the diffuse bands are normal or weak (cf. Jenniskens *et al.* 1994); they are certainly not enhanced (Josafatsson & Snow find five of the six bands to have negative deviations, which range up to about 2σ). According to Snow & Witt, only about 25 percent of the total column density toward HD 38087 lies within the reflection nebulosity, which may explain why the diffuse bands are at most only moderately weak, in contrast with HD 37903 and HD 200775, for which a large majority of the foreground material lies within the nebulosity.

5. Results and Discussion

The weakness of diffuse band absorption in environments known to have strong PAH emission and strong UV radiation fields could be interpreted as a serious criticism of the general hypothesis that the bands are carried by PAH$^+$ molecules. But the sensitivity of this result to physical conditions, and the resultant ambiguity of intepretation, leaves the door open, at least for now. It is possible that toward the two particular reflection nebulae under discussion here, the trade-off between density and radiation field intensity favors density, allowing the PAHs to remain neutral.

Of our two nebulae, NGC 7023 would give rise to higher expected diffuse band strengths under the PAH$^+$ hypothesis, because models show a somewhat lower density than in NGC 2023 (see Choksi *et al.* 1988; Fuente *et al.* 1992; and Black & van Dishoeck 1987), which would suggest a higher proportion of positive ions in NGC 7023. It is interesting that the diffuse bands are even weaker in NGC 7023 (i.e. toward HD 200775) than in NGC 2023 (HD 37903).

One could speculate that the weakness of diffuse band absorption in the circumstellar regions that favor the presence of PAH cations could be due to emission filling in the absorption bands, but a close look at the data on HD 37903 and HD 200775 appears to rule this out. The spectra shown by Josafatsson & Snow (1987) show completely normal absorption profiles for the diffuse bands, with no hint of emission cores or of displaced emission wings. Some displacement would be expected, in view of the demonstration that diffuse band carriers do appear in emission in the Red Rectangle (Sarre 1991; Fossey 1991), with wavelengths shifted substantially (by 2 to 4 Å). The data of Josafatsson & Snow show no signs of emission at the same wavelengths where emission is seen in the Red Rectangle.

The present discussion regarding PAH$^+$ ions as the carriers for the diffuse bands strictly applies only to the six yellow-red bands (including the well-studied 5780 and 5797Å features) included in the Josafatsson & Snow paper; possibly many other diffuse bands in the yellow-red (as reported by Walker *et al.* 1980); and probably also the 4430Å band (as indicated by Pfau *et al.* 1987). To date there has been no specific suggestion that any of the six diffuse bands studied by Josafatsson and Snow are due to PAH$^+$ cations, but the recent paper by Léger *et al.* (1995) does claim such an origin for the 4430Å band, as was suggested by an earlier study by Salama & Allamandola (1992b). The specific PAH ion proposed by Léger *et al.* was methyl pyrene, which we have not specifically modelled.

Our discussion might apply equally well to other proposals for diffuse band origins in ionized molecular species, although the same uncertainties raised here would also apply. For example, ionized buckminsterfullerene ($C_{60}{}^+$) has been suggested as a carrier of diffuse bands (Léger *et al.* 1988), and has recently been identified as the probable source of two newly-discovered infrared features (Foing & Ehrenfreund 1994). Like PAHs, fullerenes have very high electron affinities, so it is possible for them to remain neutral in nebular regions having high electron densities.

A viable proposed candidate for the diffuse band carriers must not only satisfy the observational fact that the bands are weak in nebulae subjected to high radiation fields, but must also be consistent with the finding that the diffuse bands are weak in dense clouds (Wampler 1966; Snow & Cohen 1974; Adamson, Whittet, & Duley 1991). Ionized molecules should fit the latter condition rather easily, since recombination (possibly to the negative ion stage) should occur readily in dark clouds.

Neutral molecules could satisfy this as well, if they become negatively charged in dense regions, or if they are destroyed or altered in chemical reactions in such regions. Neutral diffuse band carriers with low ionization potentials are favored by Herbig's (1993) analysis of correlations among diffuse bands and other interstellar features, which showed that the diffuse bands in general correlate better with neutral gas-phase atomic species than with simple molecules such as H_2. It is noteworthy that some recent suggestions regarding diffuse band formation by large carbonaceous neutral molecules (e.g. Fulara *et al.* 1993; Thaddeus 1995) may be favored by our analysis, particularly if the molecules are unsaturated (Freivogel *et al.* 1994), since these species would be expected to evolve rapidly to more complex molecules in dark clouds. Neutral molecules in general have low oscillator strengths, which could present a problem from the point of view of abundances needed in order to produce the observed diffuse band spectrum, but as seen in the Freivogel *et al.* paper, this may not be a problem for certain classes of molecules.

Perhaps the most significant result from this study is the tight constraints that we appear to have placed on the environments where diffuse bands can form, *if* they are produced by PAH cations. If so, we have established that the bands will be favored only in regions where the radiation field intensity is relatively high while the density is relatively low. This should provide some useful predictions of diffuse band behavior, specifically of their environmental dependencies, that can be tested observationally.

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