

Organic compounds as carriers of the diffuse interstellar bands

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Abstract. The diffuse interstellar bands appear as absorption features in spectra of reddened stars and lie mostly in the visible region of the spectrum. The first examples were recorded photographically nearly one hundred years ago and despite a huge amount of observational, theoretical and laboratory effort the spectra remain unassigned. Most researchers believe that organic material is responsible for the absorptions, the most popular form being polycyclic aromatic (hydro)carbon (PAH) structures. This article reviews briefly the main characteristics of the spectrum, describes some current research and outlines some lines of inquiry.

Keywords. ISM: clouds, line: identification, ISM: individual (HD 44179, V854 Cen, IRC+10216)

1. Introduction

The diffuse interstellar band problem is one that has fascinated astronomical observers for many decades and has stimulated much debate and original thinking among researchers from a wide range of scientific backgrounds. The diffuse bands are a large set of absorption features seen towards stars that are partly obscured by interstellar material in the Galaxy, in external galaxies, and towards quasars lying behind red-shifted galaxies with z up to $c. 0.5$. It is surprising that it has been so difficult to identify the carriers given that spectra of other components of the diffuse interstellar medium (ISM) such as H, Na, K and Ca^+ , diatomic molecules including H_2 , CO, CH^+ , CH and CN, and the triatomic molecules H_3^+ and C_3 , are easily obtained in the laboratory. However, after much experimental and theoretical effort not one of the $c. 300$ bands has been assigned. Using CCDs and large telescopes, spectra can be recorded towards bright moderately-reddened Galactic stars which are essentially noise-free for modest exposure times. A number of reviews have been written on the subject including those by Herbig (1995), Fulara & Krelowski (2000) and Sarre (2006).

2. Is the diffuse band problem important?

Although intriguing, one might ask if the problem is significant. A precise answer to this question is difficult to give and there will probably be some surprises; these may well include the simplicity of the eventual solution. There remains the interesting possibility that the spectrum arises from new forms of matter or dust in the interstellar medium and it is notable that new forms of carbon including fullerenes, nanotubes and graphene have only relatively recently become experimentally accessible. The diffuse bands are a good spectroscopic tracer of extinction by dust grains and this characteristic is being exploited in connection with the GAIA mission (Munari 2000, Vidrih & Zwitter 2005, Wallerstein

et al. 2007). Particularly important in the context of this Symposium is that the diffuse band carriers may be large *organic* molecules or small grains with possible links to the chemistry of life. Grains are also important more generally in astronomy in the formation of H₂ and larger molecules, in a range of physical processes in the interstellar medium, and in star and planet formation.

3. Diffuse band characteristics

Over three hundred bands have been recorded in the near-UV, visible and near-IR spectral regions with widths ranging between *c.* 2 and 100 cm⁻¹. There is no doubt that most of the reported diffuse band absorptions are interstellar rather than stellar or circumstellar in origin, and this has been confirmed through observations towards binary stars (Merrill 1936, Hobbs *et al.* 2008). There are reasonably good correlations of diffuse band strengths with E_{B-V} but with statistically significant deviations, with H I abundance, and, for some bands, with the column density of the C₂ molecule (Thorburn *et al.* 2003). Another notable property is the relative weakening of diffuse bands with respect to E_{B-V} in denser clouds, which suggests that the column density of the carriers is not determined simply by the total abundance of material but is influenced by, e.g. the UV flux. A very striking characteristic is their common occurrence; the bands are seen towards numerous Galactic and, increasingly, extragalactic optical sources. Their ubiquity is shared by the carriers of the ‘unidentified’ infrared (UIR) emission bands that are a very strong indicator of widespread polycyclic aromatic hydrocarbon material. This in itself provides circumstantial support for the idea of PAHs being closely linked with the diffuse band problem.

In spectroscopic terms, there can be little doubt that the bands arise from electronic transitions, which for gas-phase molecular carriers would generally be expected to be accompanied by vibrational and rotational fine structure. Attributes commonly used in the analysis of spectra are line widths, which should be the same for one or more transitions accessing a common upper level, fine structure which can act as a label, spectroscopic patterns, combination differences, and profile variation according to rotational and vibrational temperature. To date use of these well-established approaches has not led to assignment of the diffuse band spectra. It should be noted that the widths, which for most bands greatly exceed the velocity dispersion in the cloud(s), are now generally attributed to rapid intramolecular vibrational relaxation (IVR) in the absorber following photon absorption.

4. Carrier proposals

The history of proposals as to the nature of the carriers is as long as the subject itself. It would appear that virtually every structure, charge state and size of gaseous, solid, embedded or adsorbed species has at some time been considered including H⁻, H₂, porphyrins and colour centres in crystals to name just a few. In terms of organic (i.e., carbon-based) carriers that have been suggested, these may be discussed with reference to three limiting symmetry classes: 1-dimensional carbon chains, 2-dimensional planar polycyclic aromatic (hydro)carbons or rings (i.e., necklaces), and 3-dimensional graphitic particles, nanodiamonds, fullerenes or nanotubes. Numerous variations can be considered including partially hydrogenated, dehydrogenated, ionised, organometallic and locally (partially) aromatic structures. Key issues that need be addressed are satisfying elemental cosmic abundance constraints and the fact that the observed spectrum is dominated in appearance by the order of a dozen strong ‘special’ bands, the identification of which

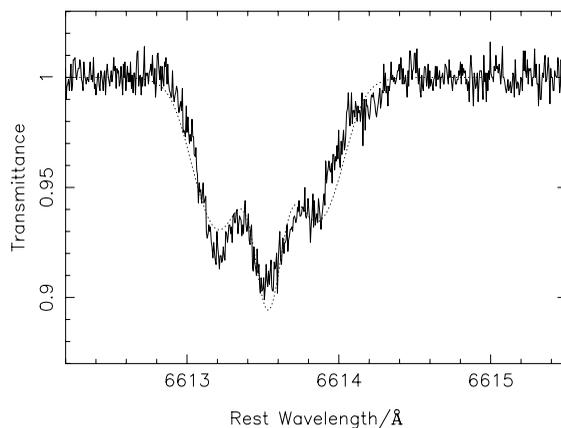


Figure 1. Profile of the $\lambda 6614$ diffuse interstellar band recorded towards μ Sgr with the Ultra-high Resolution Facility on the Anglo-Australian Telescope, with the result of molecular rotational contour fitting (Kerr *et al.* 1996).

would surely unlock much of the rest of the spectrum. There is a growing list of candidates that have appeared to be attractive possibilities but which now can be ruled out at least for the strongest diffuse bands. These include C_5 , the C_{18} necklace molecule, the PAH coronene ($C_{24}H_{12}$), and probably most neutral molecules with $n_C \leq 50$; a recent list is given by Snow & McCall (2006) in their Table 3. However, there remain a wide range of organic structures for which rather little is known of their electronic spectra including large, radical (hydrogenated and dehydrogenated) and protonated PAHs, polyenes and nanotubes. Of those molecules for which laboratory data are suggestive of a 'match', in the opinion of the writer only two are possibly viable: C_{60}^+ , for which low-temperature matrix data lie close to diffuse bands near 9577 and 9632 Å (Foing & Ehrenfreund 1997), and CH_2CN^- which has a gas-phase origin band transition in reasonable agreement with a single weak diffuse band at 8037 Å (Cordiner & Sarre 2007).

5. Fine structure in some of the bands

The discovery that some of the narrower bands have a high level of fine structure and asymmetric profiles (Sarre *et al.* 1995, Ehrenfreund & Foing 1996) is probably one of the best indicators that the carriers are molecular in nature. One example is shown in Figure 1 where the $\lambda 6614$ diffuse band shows three (possibly four) components. The dashed line is a χ^2 minimisation fit assuming an oblate symmetric top molecule about the size of coronene at a derived rotational temperature of 20 K and this is discussed further by Kerr *et al.* (1996). The band shape is reminiscent of P, Q and R rotational branch structure which is a common attribute of molecular electronic spectra. Such a fit is by no means unique to an oblate top as illustrated by others (Schulz *et al.* 2000), and an alternative description in terms of isotope structure has been put forward (Webster 1996). An even greater challenge to interpretation is presented by the $\lambda 5797$ band which exhibits considerable ultra-fine structure (Kerr *et al.* 1998) as illustrated in Figure 2.

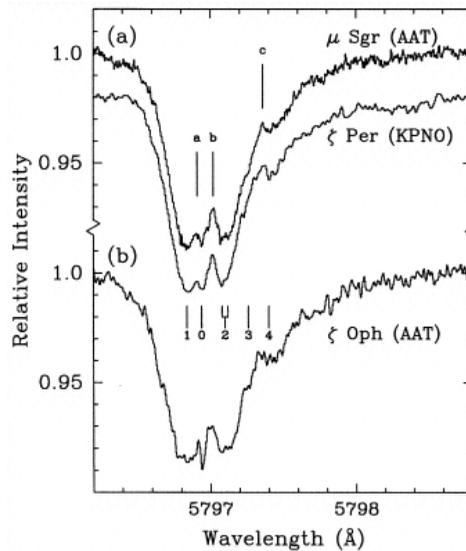


Figure 2. Observations of the $\lambda 5797$ diffuse band obtained with the Ultra-high Resolution Facility on the Anglo-Australian Telescope (AAT) and at Kitt Peak National Observatory (KPNO). Data recorded towards three stars are shown and illustrate the consistency of the fine structure of the features (Kerr *et al.* 1998).

6. Circumstellar Environments

Although the diffuse band spectrum is commonly observed in absorption along lines-of-sight towards reddened stars, the data obtained often represent the superposition of absorptions due to more than one cloud, each with its own density, ionisation and velocity structure. Consequently some attention has been paid to more localised carbon-rich circumstellar and nebular environments in the hope that not only would the formation regions for diffuse band carriers be identified, but that spectra might be observed under different and warmer conditions than hold for the diffuse ISM. Three cases are of particular interest: carbon-rich circumstellar shells such as IRC+10216, the Red Rectangle, and the R Coronae Borealis (RCB) star V854 Cen.

6.1. The circumstellar shell of IRC+10216

Given that most researchers consider that the diffuse band carriers are carbon-based molecules, it has been widely thought that these could be formed initially in the outflows of mass-losing carbon stars. Based on observations this does not appear to be the case, at least in the sense of diffuse band carriers being present in exactly the same chemical form as seen in the diffuse ISM. A search for absorptions arising in the circumstellar shell of the mass-losing carbon star IRC+10216 using a background star revealed no evidence for circumstellar diffuse band carriers (Kendall *et al.* 2002), and a similar result has been found for observations directly towards post-AGB stars (see contribution by Luna *et al.*, this volume). Additionally no diffuse band spectra were seen towards stars in the background of circumstellar material of the Helix nebula (Kendall & Maunon 2004).

6.2. The Red Rectangle

The Red Rectangle displays a strong set of UIR (PAH) bands which provides very strong evidence for organic aromatic material in the nebula. There is also emission from silicates which is thought to be confined largely to a circumbinary disk. Prominent unidentified optical bands appear near 5800, 6380 and 6615 Å and have a pronounced X-shaped spatial distribution in the nebula, falling along the bicone interfaces (Schmidt & Witt 1991). The peak wavelengths of the optical bands (and also ERE) shift to shorter wavelength with increase in offset as would be expected in moving towards cooler conditions.

Apart from the intrinsic importance of assigning these bright emission features, the peak wavelengths of the most prominent bands fall close to the absorption wavelengths of some of the diffuse interstellar absorption bands (Sarre 1991, Fossey 1991). The wavelengths and widths of the bands both decrease with offset *towards* the individual diffuse band characteristics as discussed by Scarrott *et al.* (1992) and Sarre, Miles & Scarrott (1995). However, even at the highest offsets of *c.* 15'' (Glinksi & Anderson 2002) and 22'' (Van Winckel *et al.* 2002) there remains a small difference between the peak wavelength of, e.g. the 5800 Å emission feature and the λ5797 diffuse interstellar band. In their paper Glinksi & Anderson (2002) concluded that the hypothesis that the same molecule may be the carrier of the 5800 Å Red Rectangle band and the λ5797 DIB was contradicted by their observations. In Figure 3, high-quality data from Van Winckel *et al.* (2002) has been taken and, under the assumption of linear behaviour, least-squares fitted for the region beyond 10''. By extrapolation it is found that the peak wavelength of the Red Rectangle emission band would reach the diffuse absorption band wavelength at an offset of $58 \pm 19''$ from HD 44179. Hence the best available published data are not inconsistent with the same carrier being responsible for the 5800 Å emission feature and the λ5797 diffuse interstellar band, with the ultimate proof or otherwise likely only to be obtained when the spectra are recorded in the laboratory and assigned.

The major part of the shift in peak wavelength occurs within 10'' of the star and may be due to overlapping *vibrational* sequence structure as mentioned by Sarre *et al.* (1995) and more recently taken up by Sharp *et al.* (2006). A possible explanation for the band behaviour beyond 10'' could be that it reflects the influence of a slowly decreasing *rotational* 'temperature' with offset. The likely link between the Red Rectangle optical emission bands and a sub-set of diffuse interstellar bands provides the third example of spectral evolution of emission bands of the Red Rectangle towards an absorption counterpart in the ISM, the other two being the 3.3 and 11.2 μm PAH infrared bands.

It may be of interest to note that a long-standing close association between the λ6614 diffuse band as recorded in absorption (Herbig 1975) and the Red Rectangle (Cohen *et al.* 1975) can be found at the back of the hard copy of the *Astrophysical Journal* volume 196 (1975). Plate 2 from Herbig (1975) shows the λ6614 diffuse band recorded towards bright stars and on the facing page is Plate 3 which contains a Red Rectangle image from Cohen *et al.* (1975). On closing the journal volume the information in the two plates lies in touching distance and continues to do so in many libraries worldwide!

6.3. V854 Cen

To date the only object other than the Red Rectangle to exhibit the unidentified optical emission bands is the RCB star V854 Cen observed at minimum light (Kameswara-Rao & Lambert 1993). V854 Cen also presents a display of UIR (PAH) bands though these are unusual in their relative strengths with features at 3.3, 6.3, 11.3 and 13.5 μm being the most prominent; the commonly observed UIR bands at 7.7 and 8.6 μm are very weak in V854 Cen (Lambert *et al.* 2001). The optical bands in the, e.g. 5800 Å region are broad compared with their equivalents at high offset in the Red Rectangle and also have different

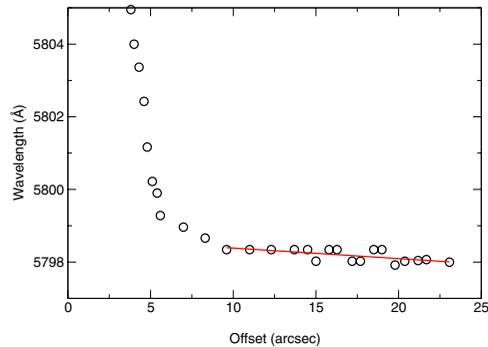


Figure 3. Peak wavelength of the ‘5800’ Å (F1) emission feature of the Red Rectangle as a function of offset from HD 44179. The data are taken from Van Winckel *et al.* (2002).

relative strengths, the strongest in the 5800 Å set being the 5829 Å feature. The reason for this is unclear. Lambert *et al.* (2001) noted that the UIR band spectrum of V854 Cen is broadly similar to that of the carbon-rich PPN IRAS 22272+ 5435. However, there is no evidence for optical diffuse bands arising in absorption from circumstellar material of this star (Luna *et al.* 2008).

7. Some lines of inquiry

In this section three possible contributors to the diffuse band spectrum are considered. It has been suggested that PAH-based anions could play a role as many of these molecules are predicted to have electronic absorption spectra that lie in the visible spectral region. The suggested transitions, not yet observed experimentally for PAH anions, occur between a stable ground electronic state and a shallow dipole-bound higher electronic state which lies just below the electron detachment threshold (Sarre 2000). This proximity in energy means that the electron affinity of the neutral molecule (i.e., the ionisation energy of the anion) is a very good approximation to the transition energy for the ground to dipole-bound state excitation. As an illustration, DFT B3LYP calculations with X. Liu on the phenoxy radical, C_6H_5O , yield an electron affinity of 2.15 eV in reasonable agreement with the experimental value of 2.253(6) eV; this falls in the diffuse band range at approximately 550 nm. A high electric dipole moment for the neutral is a prerequisite for the existence of the dipole-bound state and this is met for C_6H_5O with a calculated value of 4.0 Debye. These properties of C_6H_5O extend to numerous larger polar polyaromatic molecules and laboratory spectra are needed to explore this proposal. One argument against molecular anions as candidate carriers is their susceptibility to electron photodetachment.

Secondly, although discussed at various times over the years in the literature, the possible rôle of heteroatoms incorporated in or on the periphery of PAH molecules has probably been underestimated but there is little experimental data with which to make comparison with astronomical data.

Finally, the discovery of carbon nanotubes warrants some consideration. A recent paper by Zhou *et al.* (2006) presents calculated transition energies for nanotubes with $n_C \sim 80$ –200. These transitions are polarised along the tube axis and are found to have a high f value and fall in the 1–2 eV range. An alternative type of transition in carbon nanotubes has been observed in the condensed phase through excitation spectra (Weisman & Bachilo 2003) resulting in over sixty (n,m) assigned spectra for single-walled nanotubes, many of which fall in the visible spectral region. A complementary set of DFT calculations on both semiconducting and metallic nanotubes reveals spectra in the diffuse band spectral region (Barone *et al.* 2005b, Barone *et al.* 2005a). However, an examination of the available experimental data suggests there is no consistent correspondence of these transitions in carbon nanotubes with the diffuse band spectrum.

Acknowledgements

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Discussion

HENNING: If your nanotube explanation would be correct, why should nature select the special diameter for your nanotube? Because if you change the diameter, the band position would immediately change. So nature would have to fine tune the nanotube size distribution.

SARRE: I think that's really a key issue. I put it in for completeness. There is the issue of variability of the diameter, the question of length and there's the question of chirality. As you probably know when you try to make nanotubes, you make a soup of them, so nature would have to select. But on the other hand, there would be equivalent selection problems for PAHs when you get to very large systems. So I don't think we wish to rule it out at this point.

SALAMA: I have a question about your search for diffuse bands in carbon stars. It is based on a search for one band or a few bands?

SARRE: No, we looked for about six in all. It was done as a broad band survey, not just for a particular section. So we looked for 5797, 5780, 6284, etc., all those standard candidates.

SPECK: Have you looked at any of the carbon stars that actually show UIR bands? Hardly any carbon stars have them, but at least three of them show UIR bands.

SARRE: I have to say no, we haven't. There has been some work on detection of diffuse bands *towards* carbon stars, but that's not actually the question. So it sounds like that would be worth doing if they optically bright enough.

GARCIA-LARIO: Regarding DIBs in the circumstellar envelopes of evolved stars, I would like to draw your attention to our poster paper (p. 217) where we surveyed a number of post-AGB stars with various chemistry conditions. We show the lack of this feature as formed in the circumstellar shells; all the features we have found can be explained as from the interstellar medium between the stars and ourselves. So there is a real depletion of these features in the envelope of evolved stars, independent of whether they are carbon rich or oxygen rich.