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Hydrocarbons in Meteorites, the Milky Way, and Other Galaxies

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Abstract.

The distribution, chemical structure, and formation of organic matter in the interstellar medium are important to our understanding of the overall evolution of dust. The exchange of dust between the dense and diffuse interstellar media, and the effects of processing on dust within dense clouds will affect the inventory of material available for incorporation into newly forming star and planetary systems.

A series of absorption bands near 3.4 μm has been observed towards bright infrared objects which are seen through large column densities of interstellar dust.

These aliphatic hydrocarbons carry the -CH_2- and -CH_3 functional groups in the abundance ratio $CH_2/CH_3 \sim 2.5$, and the amount of carbon tied up in this component is greater than 4% of the available cosmic carbon. The 3.4 μm band has been detected in absorption along more than two dozen lines-of-sight throughout the diffuse interstellar medium of our own Galaxy, as well as in the dusty spectra of other galaxies. Aliphatic hydrocarbons are also seen in the acid insoluble residue and organic extracts from carbonaceous meteorites, and the strong similarity between these features and those found in the diffuse interstellar dust, amid other signatures of a stellar history, suggests that interstellar organic material survives the formation of planetary systems.

Comparisons of laboratory residues to the interstellar dust features provide clues to the origin of the aliphatic component. The evidence supports an origin in the outflow of carbon stars, as well as a formation site in the diffuse ISM itself, rather than an origin within dense molecular cloud ices. Perhaps the most significant advance in the field comes from nearby ultraluminous galaxies which sometimes show greater potential for band profile studies than sources within our Galaxy. The redshift to wavelengths further removed from atmospheric interference makes ground-based observations of the entire L band of these galaxies feasible for z<0.3.

1. Introduction

One of the most intriguing tracers of the solid-phase carbon of the interstellar medium is the 3.4 μm (2940 cm^{-1}) absorption band, which arises from -CH_2- and -CH_3 groups in aliphatic hydrocarbons. Since its detection along the line-of-sight toward infrared source number 7 in the Galactic Center (Sgr A W, IRS 7) by Willner et al. (1979) and Wickramasinghe & Allen (1980), follow-up studies of the 3.4 μm band have shown that this material is a common component of *diffuse* interstellar medium (DISM) dust in the Milky Way (Butchart et al. 1986; Adamson et al. 1990; Sandford et al. 1991; Pendleton et al. 1994; Whittet et al. 1997; Ishii et al. 2003; Rawlings et al. 2003). The 3.4 μm absorption band has also been detected in several nearby galaxies (Bridger et al. 1994; Wright et al. 1996; Pendleton 1996a,b; Pendleton 1997; Imanishi et al. 1997; Imanishi & Dudley 2000; Imanishi 2000, 2002; Imanishi & Maloney 2003; Marco & Brooks 2003; & Risaliti et al. 2003; Mason 2003). Band position and profile analysis of the galactic interstellar 3.4 μm absorption feature reveal a carrier that incorporates at least 3-4% of the available interstellar carbon. The band profile shows that these aliphatic groups are likely attached to larger chemical configurations that contain at least 10% of the total available interstellar carbon (Sandford et al. 1991; Pendleton et al. 1994; Duley et al. 1998; Furton, Laiho, & Witt 1999; Mennella et al. 2002).

As a result of its diagnostic potential for tracing dust pathways and connecting interstellar to proto-solar chemistry, considerable effort has been exerted to identify the physics and chemistry that produce the 3.4 μm spectral feature. Nearly two dozen laboratory materials have been proposed as analogs of the interstellar organic refractory material, based on reasonably good matches to the 3.4 μm band. Some were produced under conditions that mimic interstellar environments and were designed to yield insight into possible interstellar production sites, while others sought only to reproduce details of the spectrum in order to identify the material. Pendleton & Allamandola (2002) compared a large, representative selection of lab residue materials suggested in the literature as possible analogs of the solid-state organic component in the DISM.

The entire 2.5-10 μm region was used in the evaluation, because the C-H stretch bands in hydrocarbons must be accompanied by the C-H bending modes, which fall in the 5-8 μm portion of the spectrum. Given the upper limits on the weak bending mode features in the DISM, and other spectral constraints related to the infrared features, comparisons of the lab spectra to the diffuse interstellar medium observations led to a significantly reduced list of matching candidates.

Hydrogenated amorphous carbon material (HACs) best fit the DISM data, regardless of the production method. The failure of the energetically processed icy materials to satisfy the DISM criteria set forth in Pendleton & Allamandola (2002), despite very good matches at 3.4 μm, indicates that the origin of the aliphatic hydrocarbons does not occur within the icy mantles of dust grains. Rather, the results support the growing body of evidence that the production of the aliphatic hydrocarbons occurs in the outflow of carbon stars (Chiar et al. 1998), or in the diffuse ISM itself (Mennella 2001).

2. Observations

Attempts to characterize the composition of interstellar dust in the diffuse ISM have employed observations along lines-of-sight where bright background sources are observed through great quantities of interstellar dust. A multitude of absorption and emission features have been observed in this manner (e.g., Whittet

& Tielens 1997; Keane et al. 2001), primarily in the icy spectra of dense cloud dust. The 3.4 μm band was first observed in the ISM by Soifer, Russell, & Merrill (1976). Polarization studies have indicated that it arises from a population of grains separate from the icy grains along the line-of-sight to the Galactic Center (Adamson et al. 1999) and it is not correlated with the ice features (e.g., Chiar et al. 2000). Detected in over two dozen sight-lines through our Galaxy (Pendleton et al. 1994; Adamson 1999; Ishii et al. 1998, 2002; Rawlings et al. 2003), the feature has now been detected in several nearby ultraluminous infrared galaxies (ULIRGs). Figure 1 shows a comparison between the dust seen towards the Galactic Center of the Milky Way and the IRAS 08572+3915 Galaxy (corrected for red shift of z=0.058). The sub-features of the distinctive aliphatic absorption bands are strikingly similar, as is the comparison from the acid insoluble residue of the Murchison meteorite, which will be discussed later.

Because hydrocarbon spectral features are weak, their clear detection requires a highly luminous source behind a very high column density of dust. It is becoming clear that the hydrocarbon bands are better seen in the dusty nuclei of some nearby galaxies, where these conditions are met exceedingly well, than in our own galactic sight-lines. Figure 2 (from Risaliti et al. 2003) is an excellent demonstration of the spectral profile information that can be obtained through extragalactic studies. Shown is the spectrum of the ultraluminous infrared galaxy IRAS 19254-7245, where the redshift of the galaxy has moved the polycyclic hydrocarbon (PAH) emission feature at 3.28 μm into a wavelength region with greatly reduced atmospheric interference and the aliphatic absorption feature profile is clearly detected. The PAH feature comes from the Starburst galaxy in this blended system, while the 3.4 μm absorption comes from the highly extinguished Active Galactic Nucleus, showing that these features can be used not only as probes of dust chemistry, but also as diagnostics of energy sources (Risaliti et al. 2003).

Star formation and the life cycle of dust require that dust be exchanged between the diffuse and dense interstellar media (Jones 1997; McKee 1989), and laboratory experiments yield residues from energetically processed ice with 3.4 μm bands remarkably similar to those detected in the diffuse ISM.

Therefore, the 3.4 μm absorption feature was initially thought to result from the processing of icy grain material within dense molecular clouds, subsequently becoming incorporated in the diffuse ISM (Greenberg 1982; Sandford et al. 1991; Pendleton et al. 1994). However, to date, the distinctive 3.4 μm hydrocarbon sub-features have not been detected in any dense cloud spectra, despite a concerted effort to find them (Allamandola et al. 1992; Brooke, Sellgren, & Smith 1996; Chiar, Adamson, & Whittet 1996; Ishii et al. 1998; Brooke, Sellgren, & Geballe 1999; and others). As first pointed out by Allamandola et al. (1992, 1993), an absence of the aliphatic hydrocarbons in dense cloud dust presents a serious challenge to theories of dust evolution and distribution between the dense and diffuse regimes.

Figure 3 illustrates the differences in 3.4 μm dust absorption between quiescent dust in the Taurus Dark Cloud (seen against the field star Elias 16; Chiar et al. 1996) and dust in the diffuse ISM. A 3.47 μm wing on the ice band has been observed in dense clouds, but it correlates with the 3.1 μm ice band, and exhibits no sub-structure at the diffuse ISM positions of 3.38, 3.42, and 3.48

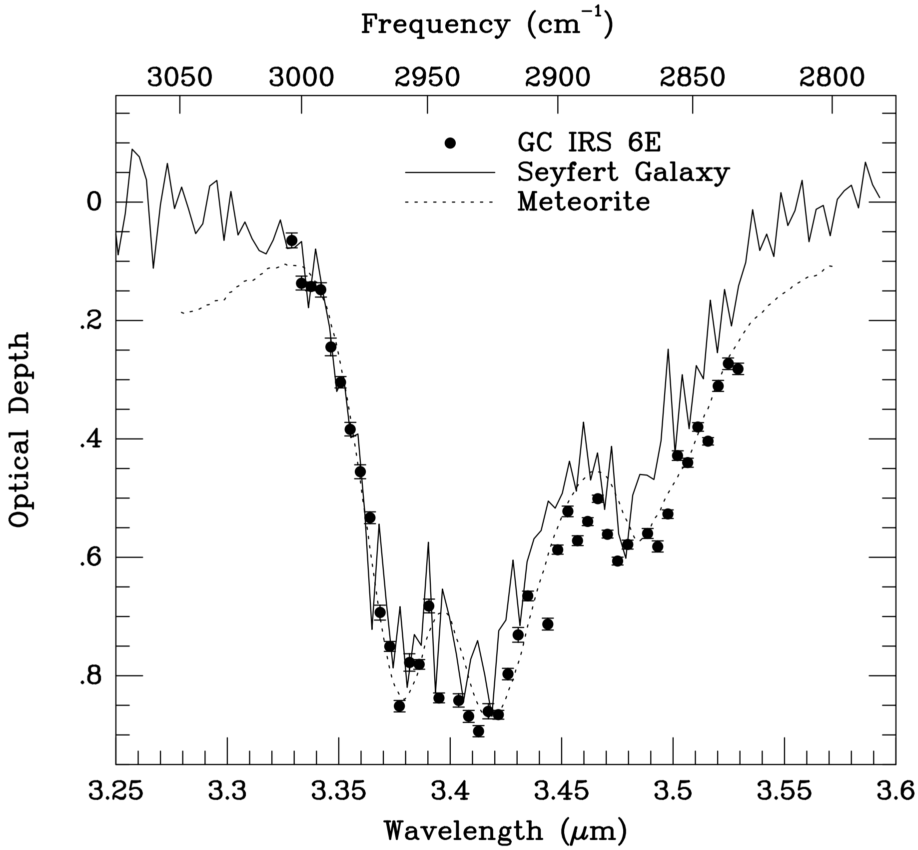

Figure 1. Aliphatic hydrocarbon features observed in galactic diffuse interstellar medium dust towards GC IRS 6E (points; Pendleton et al. 1994), the Seyfert galaxy IRAS 08572+3915 (solid line; Wright et al. 1996) & the acid insoluble residue from the Murchison meteorite (dashed line; de Vries et al. 1993). The galaxy data are corrected for red shift (z=0.058), and the other two spectra have been normalized to the optical depth of the Seyfert Galaxy at 2955 cm^{-1}. Figure from Pendleton 1997. The sub-features at 3.385 and 3.420 μm arise from symmetric C-H stretching frequencies of -CH_3 (methyl) and $-CH_2-$ (methylene), and the band at 3.485 μm comes from the asymmetric C-H stretching vibrations. Astronomical data taken with the United Kingdom Infrared Telescope (line) and the NASA Infrared Telescope Facility (points).

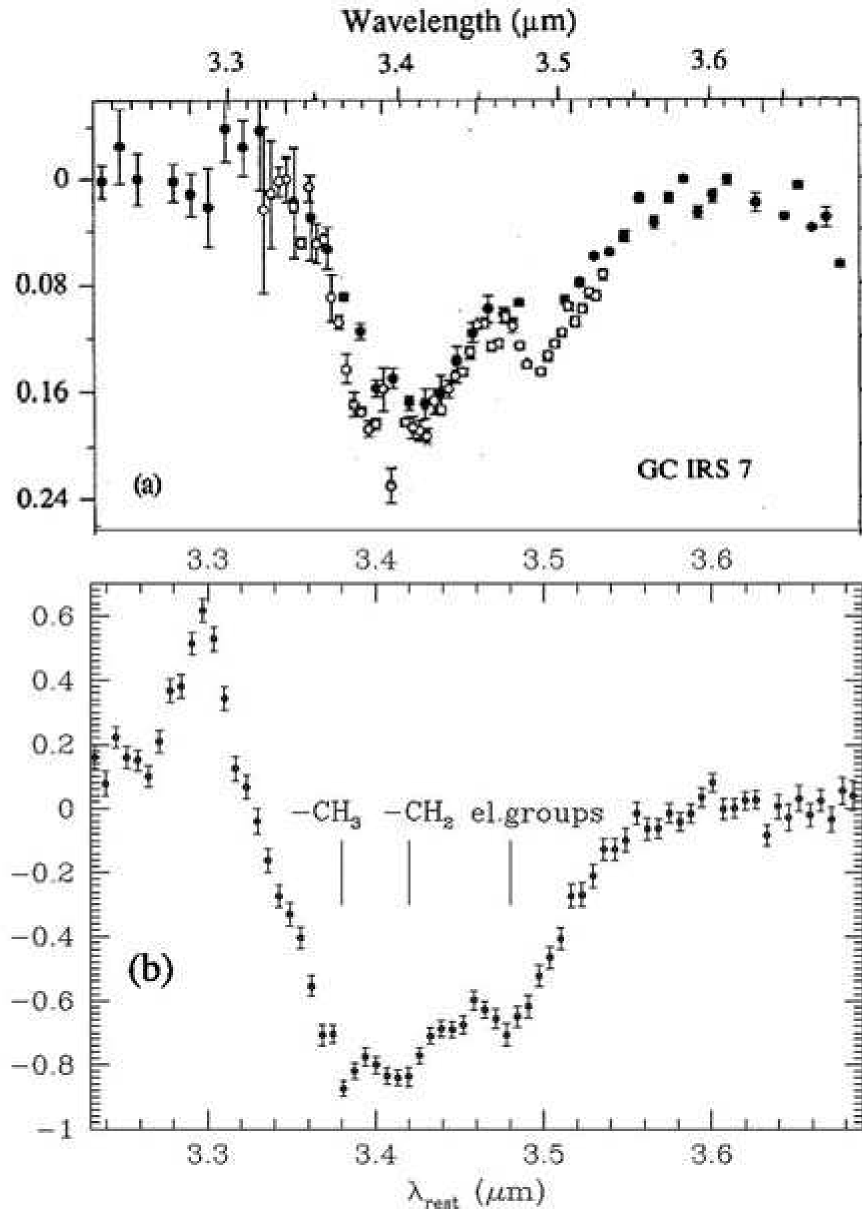

Figure 2. Figure reproduced from Risaliti et al. (2003) which shows the optical depth of the Galactic Center Source GC IRS 7 (data from Pendleton et al. 1994) and the ultraluminous IR galaxy IRAS 19254-7245 (data from Risaliti et al. 2003) corrected for redshift of z=0.062. Observations taken with the Very Large Telescope using the ISAAC instrument. The hydrocarbon chains may contain electronegative groups, denoted here in (b) and discussed in Sandford et al. 1991.

μm, even though such sub-structure is within the detection limits in many of the observations.

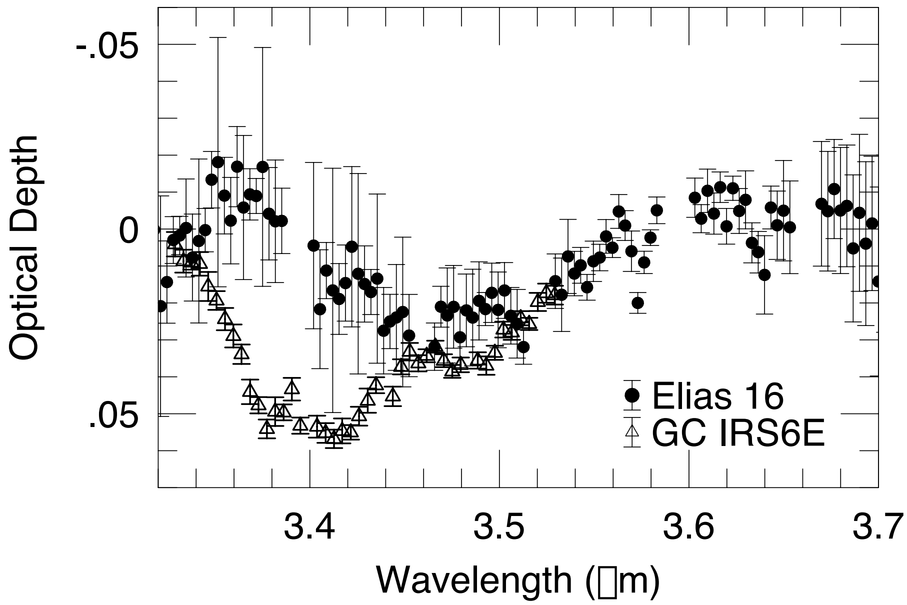

Figure 3. Absorption bands in the hydrocarbon spectral region arising from quiescent dense cloud dust as observed towards the background star Elias 16 (Chiar et al. 1996; solid points; UKIRT) and the diffuse interstellar medium dust towards Galactic Center Source IRS6E (Pendleton et al. 1994; open triangles; IRTF).

For all hydrocarbons, the C-H stretch band (3.4 μm) must have corresponding C-H bending modes (near 6.8 and 7.2 μm). The exact wavelength of the peak position will vary slightly depending on the structure of the molecule. Two interstellar lines-of-sight have been observed in the 5-8 μm region (with the Infrared Space Observatory, ISO), allowing strong upper limits to be placed upon the strength of the corresponding bending mode features for the DISM. Figure 4 shows the best data available for both the C-H stretch and C-H bending modes. Clearly we need additional information on both galactic and extragalactic dust. We await results from the Space Infrared Telescope Facility (SIRTF) for indications of 5-8 μm features and hope for new missions such as the Astrobiology Explorer (ABE) or moderate resolution spectrometers on the Stratospheric Observatory for Infrared Astronomy (SOFIA) or James Webb Space Telescope (JWST) to augment this effort.

3. Laboratory Constraints

The sub-peak positions of the C-H stretch band only indicate that there are -CH_3 and -CH_2- groups present in the material. It is the profile that gives insight into

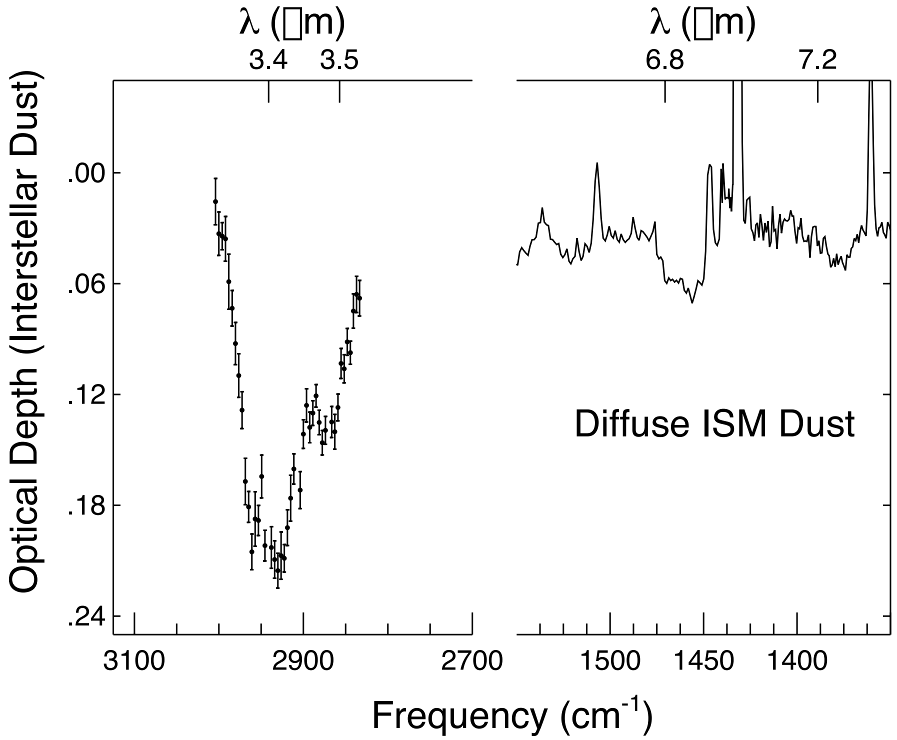

Figure 4. Comparison of the near and mid-infrared features evident in the diffuse interstellar medium as seen towards the Galactic Center (points from Pendleton et al. 1994, NASA IRTF, and thin line from Chiar et al. 2000, ISO SWS spectra.

the nature of the material. The entire mid-infrared spectrum, however, gives deeper insight into the overall nature of the hydrocarbon than does the 3.4 μm band alone. For example, materials which are primarily pure alkanes absorb much more strongly in the C-H stretch band than in the C-H deformation band.

From the 2.5-10 μm spectral comparisons made in Pendleton & Allamandola (2002), many laboratory residues that match the 3.4 μm absorption bands fairly well fail in comparison of the C-H bending mode bands. In fact, all residues produced through the energetic processing of ices yield features in the bending mode region that far exceed (in optical depth) those seen in the diffuse ISM. Conversely, every hydrogenated amorphous carbon (HAC) material produced by plasma processing (details of the processing varying from one experiment to the other), yields spectra consistent with the interstellar data. None of the energetically processed ice mixtures contained PAHs, however, and that is an important laboratory investigation to pursue.

Based on the interstellar data, the following four spectral criteria were used in Pendleton & Allamandola (2002) to evaluate analog materials: i) comparisons of the profile and sub-peak positions of the 3.4 μm aliphatic CH stretching-mode band, ii) the ratio of the optical depth (O.D.) of the aliphatic C-H stretch to the O.D. of the O-H stretch near 3.1 μm, iii) the ratio of the O.D. of the aliphatic C-H stretch to the O.D. of the carbonyl band near 5.9 μm, and iv) the ratio of the O.D. of the aliphatic C-H stretch feature to the O.D. of the C-H deformation modes near 6.8 μm and 7.25 μm. Figure 5 presents one sample from each of three production categories of laboratory analog materials. See Pendleton & Allamandola (2002) for a more complete representation.

4. Discussion

The schematic shown in Figure 7 represents a molecular structure consistent with existing observations of the DISM organic component. Relative numbers of aromatic and aliphatic carbon-hydrogen bonds, as well as their sub-classification within type, are all consistent with the observed spectra, including the aliphatic -CH_3 to -CH_2- ratio, and the relative numbers of solo, duo, trio, and quartet hydrogens deduced from the interstellar IR emission bands (Hony et al. 2001). The volume of this molecular fragment is $\sim 10^{-19}$ cm^3, thus a 0.1 μm dust grain would contain approximately 10^4 fragments.

4.1. Relationship to PAHs

Aliphatic and polycyclic aromatic hydrocarbons (D'Hendecourt 1997; Leger & Puget 1984; Allamandola et al. 1985, 1989; Joblin, Leger, & Martin 1992) no doubt coexist in the diffuse ISM, so we might expect to see the PAHs, as well as aliphatics, in absorption. However, the C-H stretch absorption feature of aromatic hydrocarbons (near 3.28 μm), will be weak in comparison to the aliphatic bands, since the aromatics contain fewer hydrogen atoms per carbon atom (H/C < 1) than do aliphatics (H/C > 2). This causes the intrinsic strength of the aromatic C-H stretching band to be 2-3 times lower than its aliphatic counterpart. A tentative detection of the 3.28 μm feature in absorption towards the Galactic center (Pendleton et al. 1994), suggested that the aromatic abundance fraction could be as large as $\sim$10% of the available carbon. Part of this fraction could be the absorption counterpart of the infrared emission (Geballe 1997), and/or be due to aromatic hydrocarbon dust grains that are too large to emit in the near IR. Sellgren et al. (1994) reported a more secure detection of PAH absorption in dense clouds, based on an absorption feature near 3.25 μm (3080 cm^{-1}). The exact position of the C-H stretching absorption varies depending upon the molecule in question, so that a mixture of aromatics would be expected to produce a band centered in the 3.25 μm - 3.28 μm region. PAH absorption in extragalactic dust may be easier to detect. The relevance of extragalactic observations to this problem can clearly be seen from Figure 2, where the redshift of the galaxy and the degree of dust and illumination source make detection of weak absorption features at the edge of ground based atmospheric windows more feasible.

4.2. Evolution of the 3.4 μm band from diffuse to dense clouds

Aliphatic hydrocarbons are clearly made in the outflow of evolved carbon stars (Lequeux & Jourdain de Muizon 1990; Chiar et al. 1998). The subsequent

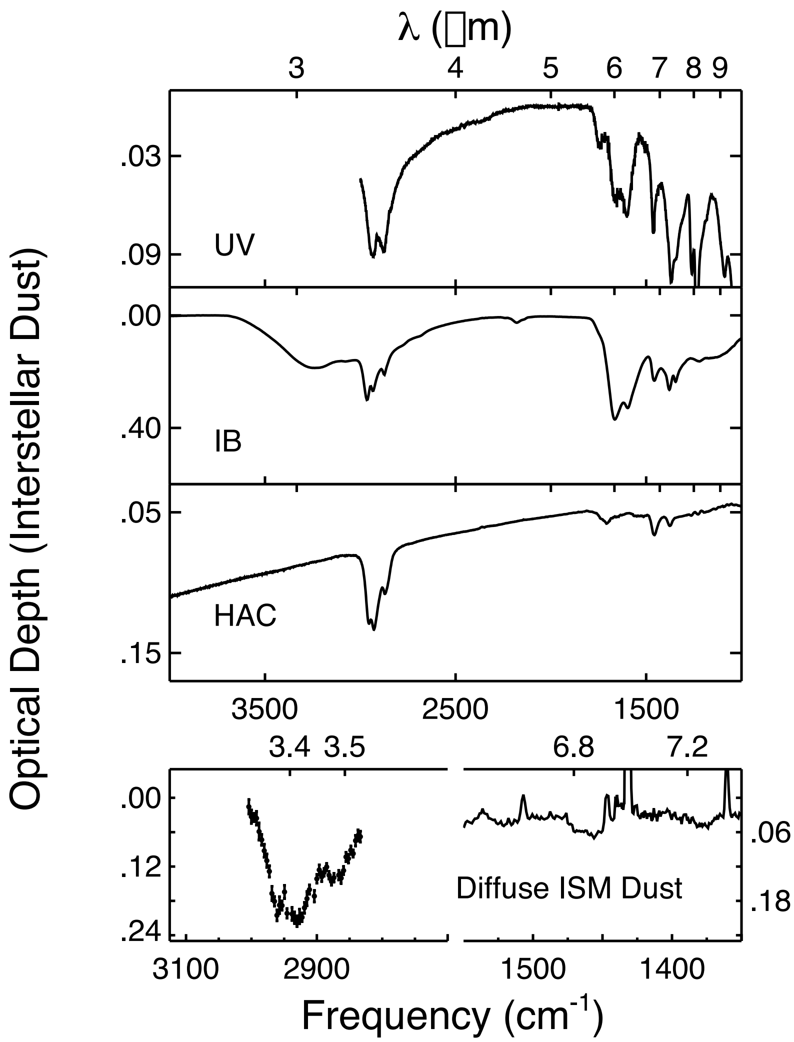

Figure 5. Laboratory residues from the ultraviolet photolysis (UV) and ion bombardment (IB) of interstellar ice analogs, and plasma processed hydrogenated amorphous carbon (HAC). Representative samples top to bottom: (UV): H_2O:CH_3OH:CO:NH_3 ice (100:50:10:10), data from Allamandola, Sandford, & Valero 1988; (IB): H_2O:N_2:CH_4 ice (∼0.06:1:1), data courtesy of Marla Moore, and (HAC): hydrogenated, laser desorbed amorphous carbon, data from Mennella et al. 1999. Bottom panel: dust towards the Galactic Center as shown in Figure 4.

Aromatic	
C atoms	400
C-H bonds	140

Aliphatic	
C atoms	70
C-H bonds	150
Methyl $-CH_3$	40
Methylene $-CH_2-$	100
Tertiary CH	5

Figure 6. Numbers of aromatic and aliphatic carbon atoms, as well as the total number of C-H bonds and the distribution of hydrocarbons for the interstellar dust fragment shown in Figure 7.

balance between hydrogenation and UV-dehydrogenation may follow the path suggested by Mennella et al. (1999, 2001, this volume), which offers an explanation for the absence of the aliphatics in dense cloud dust. While this is certainly a strong possibility, it is also true that the quiescent regions within dense clouds have not been thoroughly explored. Now that ground based telescopes and instrumentation are making that possible, surveys of field stars behind dense cloud dust must be conducted to thoroughly search for this critical component. Several photometric surveys (Ladaet al. 1999; Kramer et al. 2003; 2MASS, and others), provide J,H,K photometry of likely targets for the 3.4 μm search. Also, SIRTF offers hope of finding the corresponding 5-8 μm bands along some of these sight-lines.

4.3. Meteoritic Comparisons

Comparisons between the spectra of carbonaceous meteorites and DISM dust are important to the investigation of the delivery of organic material to the early Earth and to our general understanding of the processes that govern the evolution of interstellar and solar system dust. Meteorites contain materials produced in the outflow of carbon stars (Ott 1993 & others), and so the question of interstellar organic connections naturally arises. The literature contains a wealth of information concerning processed meteoritic material. Which of these, if any, is appropriate for interstellar dust comparisons is a key question. Figure 8 presents the 3 - 10 μm data of two samples from the Murchison meteorite that were processed differently. The 3.4 μm absorption band in both is similar to that of the diffuse interstellar dust, but the corresponding mid-IR signatures in the 5-8 μm region appear to be markedly different. Once again, the 5-8 μm features prove critical to any spectral analysis.

Figure 8 is a comparison of the Murchison meteoritic spectra from de Vries et al. (1993) (dashed curve) and Cronin & Pizzarello (1990) (solid curve). In Cronin & Pizzarello (1990), the soluble hydrocarbons were extracted directly from a powdered Murchison sample with a 9:1 mixture of benzene:methanol,

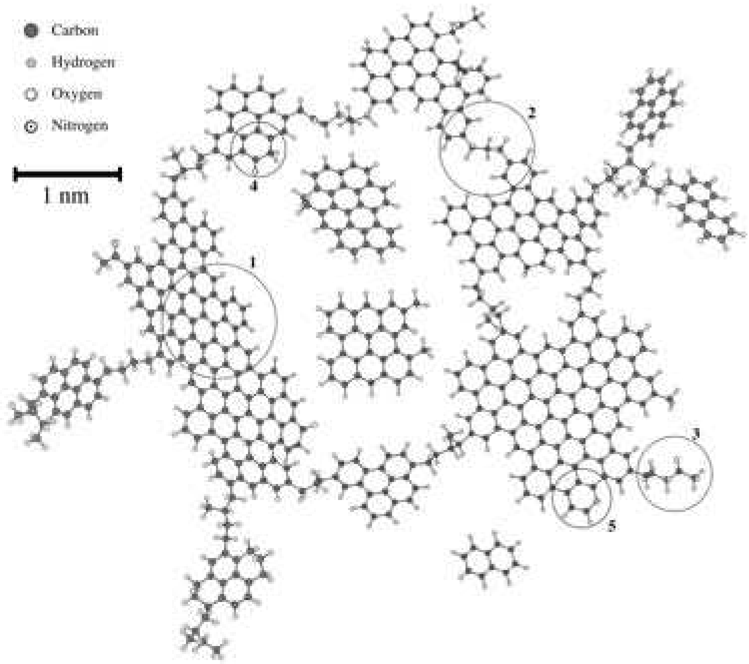

Figure 7. The basic structural and molecular character of carbonaceous interstellar dust in the diffuse interstellar medium consistent with spectroscopic constraints from interstellar data (including emission data from Hony et al. 2001). The encircled components are examples of an: 1) aromatic network, 2) aliphatic bridge, 3) aliphatic carbonyl, 4) aromatic carbonyl, and 5) aromatic nitrogen. Figure courtesy of J. Dworkin and M. Bernstein; taken from Pendleton & Allamandola (2002).

and no acid digestion was involved. In contrast, the de Vries et al. (1993) sample isolated the macromolecular carbon by digesting the silicates with HF, leaving an acid insoluble residue. In addition to dissolving the mineral components, the acid solution also dissolves small polar molecules, (e.g., amino acids). Nonetheless, organic solvent extraction cannot remove all of the small-to-medium sized organics. de Vries (1993) and Wdowiak et al. (1988 & 1995) have shown this to be the case, because if the acid residue is heated, the sublimate (shown here as the dashed curve) clearly contains recondensed hydrocarbons. A compendium of spectra in the $2 - 10$ μm region, resulting from different extraction and digestion processes, would be very useful to the astrophysicist attempting to compare carbonaceous meteoritic material to interstellar dust, interplanetary dust, or cometary spectra. Mutschke et al. (1995) have discussed these issues with regard to interstellar diamonds, addressing the effects of processing on the resulting spectra. There is a definite need for additional, cross-disciplinary, discussion to further understanding of the stardust/meteorite connection such as that undertaken by Wdowiak (1988) and Lee & Wdowiak (1993).

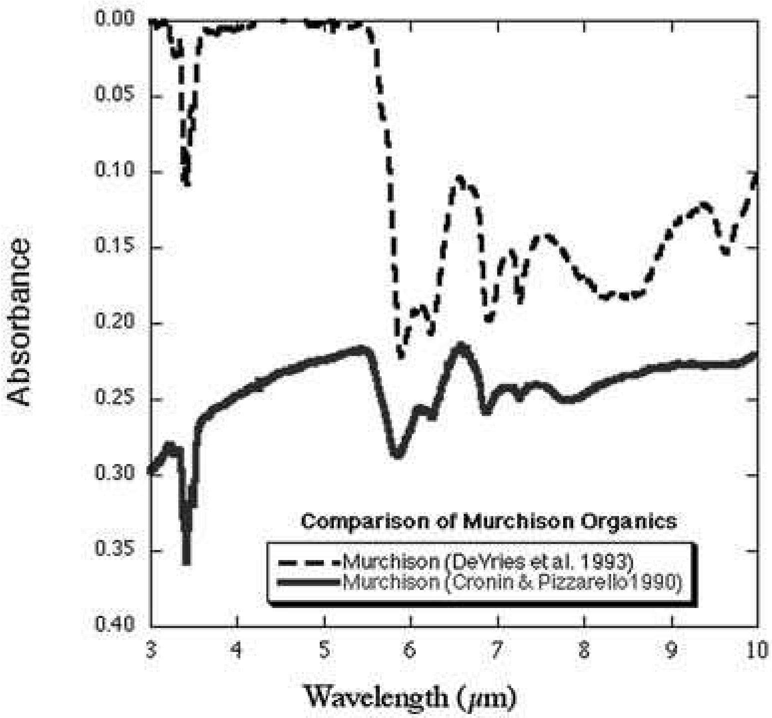

Figure 8. A comparison of the Murchison meteoritic data from de Vries et al. (1993) (acid insoluble residue; dashed curve) and Cronin and Pizzarello (1990) (organic extract; solid curve). The Cronin & Pizzarello (1990) sample closely matches hydrogenated amorphous carbon materials (Lee & Wdowiak 1993), and is therefore consistent with the DISM dust features shown in Figure 4.

5. Summary

The spectroscopic evidence currently available indicates that the organic refractory material in the diffuse interstellar medium is predominantly hydrocarbon in nature, possessing little nitrogen or oxygen, with the carbon distributed between the aromatic and aliphatic forms. Long alkane chains $H_3C\text{-}(CH_2)_n-$ with n much greater than 4 or 5 are not major constituents of this material. Comparisons to laboratory analogs indicate the DISM organic material resembles plasma processed pure hydrocarbon residues much more so than energetically processed ice residues. This result is consistent with a birthsite for the carrier of the 3.4 μm band in the outflow region of evolved carbon stars.

Comparisons of dust from our own galaxy with that of distant galaxies suggests that the organic component of interstellar dust is widespread and may be an important universal reservoir of prebiotic organic carbon. In addition, several nearby ultraluminous galaxies show greater potential for band profile studies than sources within our Galaxy. The redshift to wavelengths further removed from atmospheric interference makes ground-based observations of the entire L band of these galaxies feasible for $z<0.3$.

Currently, observations and laboratory experiments indicate that the material responsible for the 3.4 μm wing in the spectra of **dense** molecular cloud sources is different from the carrier of the aliphatic hydrocarbon 3.4 μm bands in the **diffuse** ISM, and further observations of dense cloud sightlines using background stars are important to fully evaluate this situation. Paradoxically, the meteoritic aliphatic signature is more similar to that in the diffuse rather than the dense ISM, even though the solar nebula emerged as a condensation in a dense molecular cloud. The spectral similarity is a critical result to verify, because the absence of the aliphatics in dense cloud dust will indicate the similarity between the diffuse dust aliphatics and the carbonaceous meteorites is simply coincidental. Also, if aliphatic hydrocarbons are truly absent in dense clouds, then the scenario suggested by Mennella et al. (1999, 2001, this volume) of the C-H bond destruction, and the prohibition of re-hydrogenation, would be strongly supported. On the other hand, if the connection between the organic extract of carbonaceous meteorites and the diffuse ISM dust can be established, then the ubiquitous aliphatic hydrocarbons are readily available for incorporation into planetary systems forming throughout our own and other dusty galaxies.

Finally, the importance of obtaining corresponding 5-8 μm data for sightlines where the 3.4 μm absorption band is detected cannot be overemphasized. As demonstrated by the questions arising from the information that has been garnered thus far, there is a great need to obtain data on the C-H bending mode region for other positions within our Galaxy, in other galaxies, and in laboratory studies of primitive Solar System material.

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Suzanne Madden and little Elianna Jones Madden are ready to learn about diamonds. Photo credit: Uma Vijh.