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Laboratory comparisons of organic materials to interstellar dust and the Murchison meteorite

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Abstract. Spectra of objects which lie along several lines of sight through the diffuse interstellar medium (DISM) reveal an absorption feature near $3.4 \mu\text{m}$, which has been attributed to saturated aliphatic hydrocarbons on interstellar grains. The similarity of the absorption bands near $3.4 \mu\text{m}$ (2950 cm^{-1}) along different lines of sight indicates that the carrier of this band lies in the diffuse dust. Several materials have been proposed as "fits" to the $3.4 \mu\text{m}$ feature over the years. A comparison of these identifications is presented. These comparisons illustrate the need for high resolution, high signal-to-noise observational data as a means of distinguishing between laboratory organics as matches to the interstellar material. Although any material containing hydrocarbons will produce features in the $3.4 \mu\text{m}$ region, the proposed "matches" to the DISM do differ in detail. These differences may help in the analyses of the chemical composition and physical processes which led to the production of the DISM organics, although ISO Observations through the $5-8 \mu\text{m}$ spectral region are essential for a definitive identification. A remarkable similarity between the spectrum of the diffuse dust and an organic extract from the Murchison meteorite suggests that some of the interstellar organic material may be preserved in primitive solar system bodies. The $3.4 \mu\text{m}$ absorption feature (in the rest frame) has recently been detected in external galaxies, indicating the widespread availability of organic material for incorporation into planetary systems.

Introduction

Observations of dust in the diffuse interstellar medium (DISM) have revealed a series of absorption bands near $3.4 \mu\text{m}$ (Wickramasinghe and Allan, 1980; Adamson *et al.*, 1990; Butchart *et al.*, 1986; Sandford *et al.*, 1991;

Pendleton, 1993). IR spectral studies are useful diagnostics because the fundamental vibrational frequencies of the common chemical bonds between the most chemically abundant elements occur in the mid-IR ($5000-400 \text{ cm}^{-1}$; $2-25 \mu\text{m}$). Until fairly recently, adequate wavelength coverage at sufficiently high resolution and good signal-to-noise ratios were not available to distinguish among several possible "fits" to the $3.4 \mu\text{m}$ feature. Consequently, the existing data were "fit" with a variety of organic materials, including plausible materials such as organic grain mantles (Greenberg, 1982; Schutte and Greenberg, 1988), and hydrogenated amorphous carbon (HAC) (Jones *et al.*, 1987) and less plausible materials, such as *E. coli* bacteria (Hoyle *et al.*, 1982). With the rapid improvement in detector technology, observational instrumentation has improved dramatically, and we are now able to see structure previously hidden in the $3.4 \mu\text{m}$ region. The new observations have demonstrated that the $3.4 \mu\text{m}$ absorption band is actually composed of several bands which correspond to the stretching modes of C-H in saturated aliphatic hydrocarbons (Sandford *et al.*, 1991; Pendleton, 1993, 1994; Pendleton *et al.*, 1994). In this paper, comparisons are made between the diffuse dust line of sight toward galactic center IRS6E and a variety of laboratory organic materials. Recently, the $3.4 \mu\text{m}$ absorption feature has been detected in other galaxies (Bridger *et al.*, 1993; Wright *et al.*, 1995, preprint). Comparisons between the extragalactic and galactic spectra reveal noticeably similar profiles. When corrected for redshift, the features of the extragalactic sources correspond exactly with the wavelengths of the absorption features in the $3.4 \mu\text{m}$ spectral region seen in our own galaxy.

Discussion

Observations of the DISM towards a variety of background illuminating sources all indicate the presence of absorption bands in the $3.4 \mu\text{m}$ region. Due to the large

amount of extinction towards the galactic center ($A_V > 30$), the strongest galactic feature appears in spectra of the galactic center sources. In order to illustrate the differences between a variety of laboratory materials produced by various processes and the diffuse interstellar dust, the figures in this paper will focus on the observational spectrum towards the galactic IR source, GC IRS 6E in the galactic center. The spectrum of GC IRS 6E was obtained at the NASA Infrared Telescope on Mauna Kea using a 32-channel near-IR grating spectrometer (CGAS).

The diffuse dust observations indicate that the hydrocarbon features extend from about 3000 ($3.33 \mu\text{m}$) to 2800 cm^{-1} ($3.57 \mu\text{m}$) with subfeatures near 2955, 2925, and 2870 cm^{-1} ($3.38, 3.42, \text{ and } 3.48 \mu\text{m}$). The positions of the first two of these subfeatures are characteristic of the symmetric C-H stretching frequencies of $-\text{CH}_3$ (methyl) and $-\text{CH}_2-$ (methylene) groups in saturated aliphatic hydrocarbons (molecules with the formula C_nH_{n+2}). The relative strengths of these two subfeatures indicate that the average $-\text{CH}_2-/-\text{CH}_3$ ratio of the interstellar hydrocarbon is about 2.5 (Sandford *et al.*, 1991). However, the interstellar band profile differs from that of pure saturated aliphatic hydrocarbons in that it does not contain the two peaks near 2870 and 2850 cm^{-1} ($3.48 \text{ and } 3.51 \mu\text{m}$) characteristic of the asymmetric C-H stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively, but instead shows only a single subfeature near 2870 cm^{-1} ($3.48 \mu\text{m}$). Electronegative or other perturbing chemical groups at the end of short chain aliphatics can suppress the 2850 cm^{-1} ($3.51 \mu\text{m}$) feature without greatly affecting the positions or strengths of the other three bands. Thus, comparison of laboratory and astronomical data suggests that the 2950 cm^{-1} ($3.4 \mu\text{m}$) C-H stretch feature produced by dust in the DISM is largely due to short ($n = 2-4$) aliphatic chains like $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ attached to electronegative or other perturbing chemical groups like $-\text{O}-\text{H}$, $-\text{C}-\text{N}$, aromatics, etc.

Several materials have been suggested as candidate carriers of interstellar carbon. These include HAC (cf. Ogmen and Duley, 1988; Adamson *et al.*, 1990), quenched carbonaceous composite (QCC) (cf. Sakata *et al.*, 1987), biological materials (cf. Hoyle *et al.*, 1982) and residues produced by the irradiation of ices (cf. Schutte, 1988; Allamandola *et al.*, 1988; Sandford *et al.*, 1991; Baratta and Strazzulla, 1990; Strazzulla and Johnson, 1991).

HAC can be produced in the laboratory using one of two standard methods: (a) through inefficient hydrocarbon burning in air, and (b) by striking an arc in a controlled argon atmosphere between two amorphous carbon electrodes (cf. Borghesi *et al.*, 1987; Ogmen and Duley, 1988). QCC is synthesized from hydrocarbon, principally methane, plasmas (Sakata and Wada, 1989). Figure 1a contains a comparison of the astronomical spectrum of the line of sight toward galactic center source GC IRS 6E to the laboratory spectrum of an HAC taken from Borghesi *et al.* (1987). Figure 1b contains a similar comparison for QCC which has been heated to 450°C. The QCC spectrum was taken from Sakata and Wada (1989). A comparison of the GC IRS 6E spectrum to that of QCC at room temperature (not shown) showed that the better match occurred with the heated QCC shown

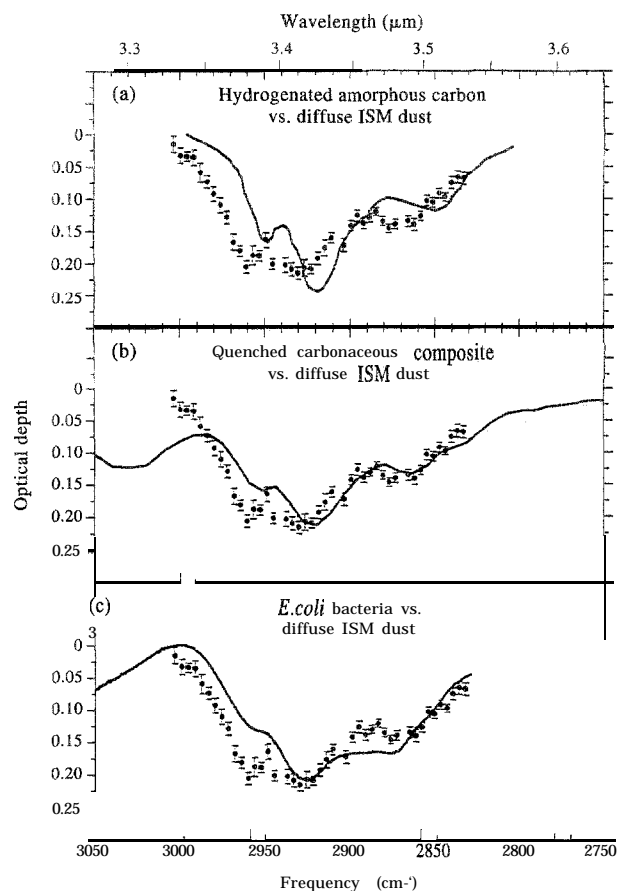


Fig. 1. A comparison of the optical depth spectrum of galactic center source IRS 6E (solid points) to: (a) the optical depth spectrum of a room temperature hydrogenated amorphous carbon (WAC) taken from Borghesi *et al.* (1987) (solid line), (b) the optical depth spectrum of a room temperature filmy quenched carbonaceous composite (QCC) taken from Sakata and Wada (1989) (solid line) and (c) the optical depth spectrum of *E. coli* suspended in a KBr pellet (solid line)

here. Since heating at these temperatures tends to aromatize the mixture, the better match between the heated QCC and the DISM is consistent with the conclusion in Sandford *et al.* (1991) that the DISM dust contains carbonaceous material other than aliphatics. HAC and QCC both provide a rough match to the interstellar C-H stretching feature; however, their spectra differ from the interstellar feature in some details. It is not surprising that both HAC and QCC fit the interstellar data to first order, since both materials contain the $-\text{CH}_3$ and $-\text{CH}_2-$ functional groups thought to be responsible for the interstellar absorption feature. Discrepancies in the positions and relative strengths of the various subfeatures are primarily due to differences in the relative abundances of $-\text{CH}_3$, $-\text{CH}_2-$ and other chemical groups in the various materials. For example, the weakness of the subfeature near 2960 cm^{-1} relative to the subfeature near 2925 cm^{-1} in the spectra of HAC and QCC when compared to the same bands in the interstellar feature suggests that the interstellar carrier is richer in $-\text{CH}_3$ groups than the particular laboratory samples of HAC and QCC shown here. Other materials (not shown here) that provide similar comparisons to the interstellar data are the ice tholins (Khare

et al., 1993) and the residue from discharge processed naphthalene (Lee and Wdowiak, 1993).

Hoyle *et al.* (1982) have suggested that the C-H stretching band of diffuse dust may be due to organic materials of biological origin. While such an identification seems extremely unlikely, a comparison between the spectrum of an *E. coli* sample and the spectrum of GC IRS 6E has been included (Fig. 1c). As with the spectra of HAC and QCC, the spectrum of *E. coli* is generally similar to the interstellar feature, just as would be expected for any material containing abundant aliphatic $-\text{CH}_3$ and $-\text{CH}_2-$ groups, but differs in detail.

The diffuse medium C-H stretching feature is very similar to that produced by residues formed by the UV irradiation and subsequent warming of interstellar ice analogs (Sandford *et al.*, 1991). IR spectra of mixed molecular interstellar ice analogs containing H_2O , CH_3OH , CO and NH , reproduce many of the major spectral features attributed to ice in dense clouds (cf. Tielens and Allamandola, 1987 ; Allamandola and Sandford, 1988 ; Allamandola *et al.*, 1988). UV photolysis of ices made up of these molecules produces new, more complex compounds. Warming to 150 K leads to the evaporation of the original volatile components of the ices while leaving the more complex carbon-rich residues behind [see

Allamandola *et al.* (1988) and Bernstein *et al.* (1994, 1995) for more detailed discussions of the properties of the laboratory photolysis residues produced from CH_3OH -containing ices]. Such a process (photolysis followed by warm up) is similar to what is thought to occur to ices in dense molecular clouds. Upon break up of the cloud, due to star formation processes and/or interstellar shock waves, the refractory material produced in the dense clouds is released into the diffuse medium. This is at least one scenario that can explain the presence of the $3.4 \mu\text{m}$ aliphatic hydrocarbon feature in the diffuse dust.

Figure 2a shows a comparison between the spectrum of GC IRS 6E and the spectrum of a residue produced by the UV photolysis and subsequent warm up to 200 K of an $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3-\text{CO}$ (10 : 5 : 1 : 1) ice. The quality of the "fit" provided by this laboratory residue is similar to that of the materials discussed earlier, i.e. the overall residue feature is similar to the interstellar feature, but differs from it in detail. As with the earlier materials, we note that the lack of a stronger subfeature near 2955 cm^{-1} indicates that the abundance of $-\text{CH}_3$ groups in the laboratory residue is lower than in the carrier of the interstellar feature. This conclusion is supported by Fig. 2b, which is a comparison between the GC IRS 6E spectrum and that of a laboratory residue produced by the

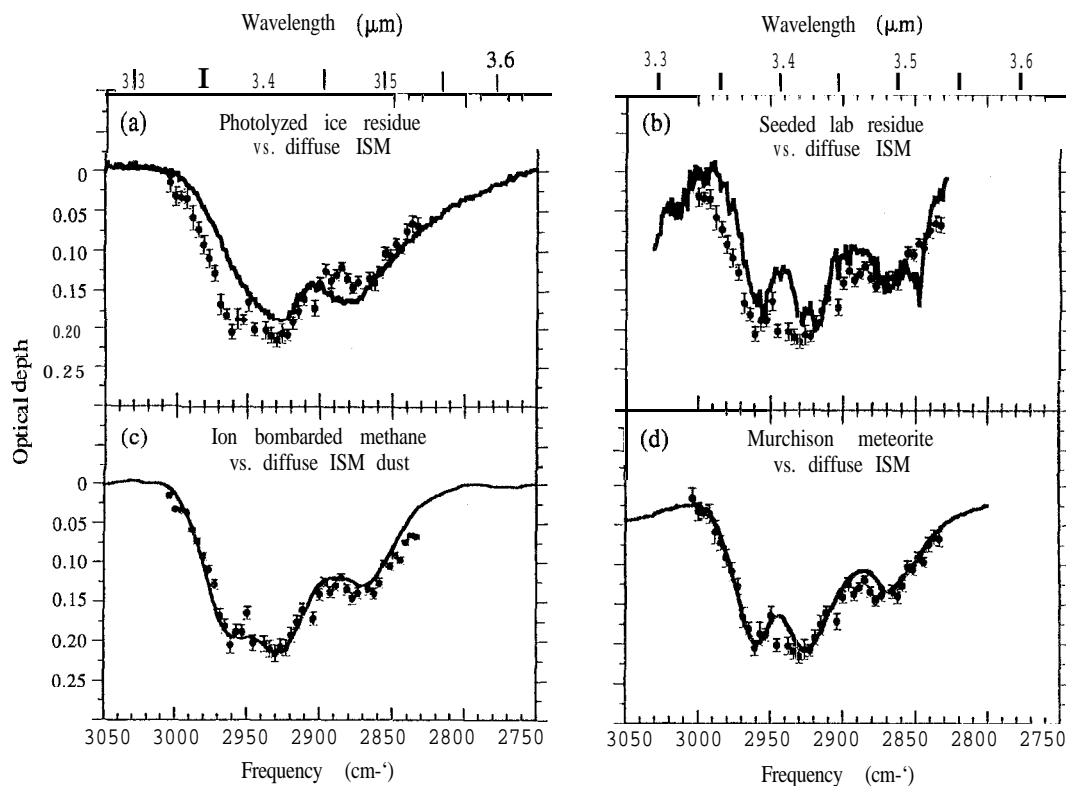


Fig. 2. A comparison of the optical depth spectrum of galactic center source IRS 6E (solid points) to : (a) the spectrum of a laboratory residue produced by the UV irradiation of a 10 K $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3-\text{CO}$ (10 : 5 : 1 : 1) interstellar ice analog followed by warm up to 200 K (solid line), (b) the spectrum of a laboratory residue produced by the UV irradiation of a 10 K $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3-\text{CO}-\text{C}_3\text{H}_8$ (10 : 5 : 1 : 1 : 1) interstellar ice analog followed by warm up to 200 K (solid line), (c) the spectrum of a laboratory residue produced by irradiating frozen (10 K) methane ice with a 180 eV/carbon atom dose of 75 keV protons (solid line) and (d) the spectrum of an organic Murchison acid residue (solid line). The photolysis residue spectra in a and b were taken from Allamandola *et al.* (1988), the spectrum of irradiated methane was kindly provided by G. Strazzulla, and the meteoritic spectrum was taken from De Vries *et al.* (1993) and was kindly provided by Dr W. Golden

UV photolysis and warm up of an $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3-\text{CO}-\text{C}_3\text{H}_8$ (10 : 5 : 1 : 1) ice, i.e. an ice enriched in $-\text{CH}_3$ groups relative to the one shown in Fig. 2a. The resulting laboratory spectrum provides an improved fit to the diffuse medium C-H stretching feature which results from the enhancement in the relative $-\text{CH}_3$ abundance,

Figure 2c is a comparison of an organic residue produced through a different process, namely ion bombardment. The laboratory data shown in this figure were kindly provided by Strazzulla and co-workers. In their experiments they have irradiated methane ice (10 K) with 75 keV protons to a total dose of 180 eV/carbon atom. The improved match to the interstellar observations could be a reflection of the different process involved in the production of this residue. The ion bombardment of a typical interstellar ice mixture, rather than pure methane, would probably lead to a greater understanding of the relative importance of the processes involved in interstellar clouds.

Despite our various attempts at reproducing the diffuse dust observations, the best overall match comes from the IR spectrum of the organic component of the Murchison carbonaceous meteorite. Some of the hydrocarbon components in primitive meteorites show strong deuterium enrichments and other isotopic anomalies, which indicate a connection to interstellar grains and molecules (Kerridge *et al.*, 1987; Ming and Anders, 1988; De Vries *et al.*, 1993; Amari *et al.*, 1994; Lewis *et al.*, 1994). The presence of isotopically anomalous diamonds, SiC, TiC and graphite in meteorites confirms that some interstellar materials were incorporated into meteorites and survived subsequent processing on the meteorite parent bodies (cf. Anders and Zinner, 1993). If the same were true for the organic component of interstellar dust, then the carbonaceous materials observed in the DISM may be one of the "parent" components from which the carbonaceous material in meteorites was derived.

Earlier comparisons of the spectra of the organic extract of the primitive CM meteorite Murchison with the interstellar C-H stretching feature demonstrated a strong similarity (Ehrenfreund *et al.*, 1991). This comparison was made prior to the availability of the high resolution, high signal-to-noise spectra of the DISM. Figure 2d shows a comparison between the spectrum of GC IRS 6E and the spectrum of a carbonaceous component of the Murchison chondrite taken by De Vries *et al.* (1993), demonstrating that the two spectra are remarkably similar in peak positions, widths and profiles.

It should be noted that another interesting comparison to the carbonaceous component of the Murchison meteorite has recently been made by Lee and Wdowiak (1993), who have obtained the spectrum of a residue produced by passing a discharge through a gaseous mixture of hydrogen and the simplest polycyclic aromatic hydrocarbon, naphthalene (C_{10}H_8). In general, the spectrum of their residue provides a good overall match to the meteoritic data throughout the mid-IR region but, like many other laboratory materials, their residue appears to have a higher ratio of $-\text{CH}_2-$ to $-\text{CH}_3$ groups than the carrier of the interstellar band. Therefore, while the spectral fit of their residue to the meteoritic data is quite impressive and provides additional support for the idea that the interstellar carrier may contain aromatic materials, it does not

provide as compelling a match to the interstellar C-H stretching feature as does the meteoritic material itself.

Virtually any material that contains substantial amounts of aliphatic $-\text{CH}_3$ and $-\text{CH}_2-$ groups will produce a feature whose overall position and profile is similar to that of the diffuse interstellar C-H stretching feature. Thus, the general fits provided by all the spectra in Figs 1 and 2 support the idea that dust in the diffuse medium contains abundant aliphatic $-\text{CH}_3$ and $-\text{CH}_2-$ groups. In this regard, it is unlikely that spectral comparisons between the astronomical and laboratory data will ever yield the "unique" identification of a single interstellar carrier. However, it is also clear that many of the analog materials proposed as the carriers of the interstellar feature on the basis of their fits to older, low-resolution astronomical data do not fit the details of the actual profile of the interstellar feature as determined by the high-resolution data. High signal-to-noise, high-resolution ($\Delta\lambda/\lambda \geq 750$) astronomical data therefore represent a means by which the spectral properties of various laboratory materials can be used to further constrain the chemical composition and "functionality" of the carrier of the diffuse C-H stretching feature. This illustrates the need for both additional high-resolution, full spectral coverage, high-quality data like that presented here for GC IRS 6E and corresponding spectroscopic laboratory data from additional, relevant, well-characterized materials having a range of appropriate compositions.

The detection of the $3.4 \mu\text{m}$ absorption feature along several sightlines in our galaxy (Sandford *et al.*, 1991; Pendleton *et al.*, 1994) provides evidence of the widespread distribution of the organic component of the DISM. The recent discovery of the $3.4 \mu\text{m}$ absorption feature in external galaxies (Bridger *et al.*, 1993) extends this result to other galaxies as well. Figure 3 is a com-

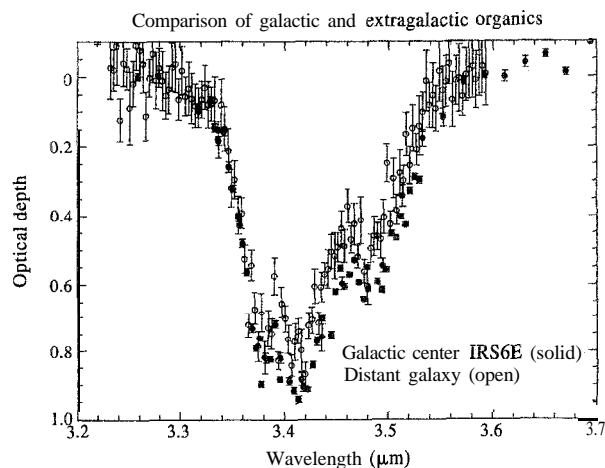


Fig. 3. A comparison of the $3.4 \mu\text{m}$ absorption feature seen toward a luminous IRAS galaxy, IRAS 08572 + 3915 (open points). The extragalactic data have been corrected for redshift so that the wavelength positions can be compared. The galactic center data have been normalized to the extragalactic at $3.4 \mu\text{m}$; the extragalactic signature is four times stronger than that from the galactic center. The galactic data were obtained at the NASA IRTF and have been published in Pendleton *et al.* (1994). The extragalactic data were recently obtained at the United Kingdom Infrared Telescope Facility and were kindly provided by Gillian Wright in advance of publication

parison of the galactic center GC IRS6E spectrum with that of an ultraluminous IRAS galaxy, IRAS 08572+3915, which may be a buried QSO. This galaxy lies at a redshift of $z = 0.058$, so the feature has been blueshifted for comparison to the galactic center. The remarkably similar profiles show the same type of substructure attributed to CH, and CH₃ groups. The exact agreement in wavelength peak with redshift confirmed that this feature originates from dust in the Seyfert galaxy. The spectrum of IRAS 08572+3915 was obtained using the CGS4 instrument at the United Kingdom Infrared Telescope Facility (Wright and co-workers). The strength of the extragalactic feature is four times that seen toward the galactic center. This work illustrates the likelihood that we may now conduct detailed near-IR spectral studies of portions of the spectrum unavailable to us from the ground for galactic sources, by looking toward our extragalactic neighbors.

In addition to high-resolution, high signal-to-noise data in the 3 μm region, it is important to obtain spectral information at longer wavelengths. The CH and OH deformation modes, the C=O and C=C stretching modes, and the C-O, C-N and C-C stretching and bending modes of interstellar dust can only be investigated in the 5-9 μm region. Unfortunately, this spectral region is unavailable from ground-based observatories. To date, the best spectra available from the Kuiper Airborne Observatory (KAO) do not have sufficient resolution to allow for detailed studies of the diffuse dust features that appear in this spectral region. Presently, observations have been limited to the galactic center region and VI Cygni no. 12, a luminous B5 star which suffers 10 magnitudes of extinction (Humphreys, 1978). No other sources with diffuse dust along the line of sight are bright enough to observe in this wavelength region with the KAO. Figure 4 contains the KAO spectrum (Pendleton and co-workers) obtained along the line of sight to the galactic source VI Cygni no. 12. The spectrum shows an absorption near 6.85 μm , as would be expected from the hydrocarbons. The higher resolution possible with ISO will allow much more detailed information to be extracted from spectra of DISM sources.

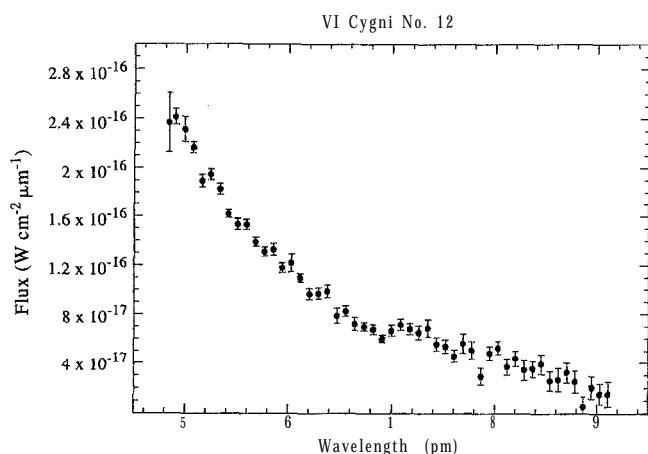


Fig. 4. The 5-9 μm spectrum towards VI Cygni no. 12 taken from the Kuiper Airborne Observatory using the spectrometer HIFOGS ($R \sim 250$)

Summary

The 3.4 μm absorption feature attributed to saturated aliphatic hydrocarbons has been detected along several sightlines through our galaxy as well as in other galaxies. Such widespread distribution supports the assertion that the organic component of the interstellar dust is available for incorporation into newly forming planetary systems. The remarkable similarity of the diffuse dust spectra to the Murchison meteoritic spectrum suggests the possibility that the organic component of the carbonaceous meteorites may be in part the remnants of the interstellar dust. High-resolution, high signal-to-noise data obtained along the line of sight toward the galactic center have allowed detailed comparisons to be made between the various organic residues produced in the laboratory. While definitive identifications must await spectral information from the longer wavelength (5-8 μm) region, the high-resolution, high signal-to-noise 3.4 μm data enable comparisons to be made which may help in our understanding of the processes involved in the production of the organic material seen in the DISM.

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