

DETECTION OF ORGANIC MATTER IN INTERSTELLAR GRAINS

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Abstract. Star formation and the subsequent evolution of planetary systems occurs in dense molecular clouds, which are comprised, in part, of interstellar dust grains gathered from the diffuse interstellar medium (DISM). Radio observations of the interstellar medium reveal the presence of organic molecules in the gas phase and infrared observational studies provide details concerning the solid-state features in dust grains. In particular, a series of absorption bands have been observed near $3.4\ \mu\text{m}$ ($\sim 2940\ \text{cm}^{-1}$) towards bright infrared objects which are seen through large column densities of interstellar dust. Comparisons of organic residues, produced under a variety of laboratory conditions, to the diffuse interstellar medium observations have shown that aliphatic hydrocarbon grains are responsible for the spectral absorption features observed near $3.4\ \mu\text{m}$ ($\sim 2940\ \text{cm}^{-1}$). These hydrocarbons appear to carry the $-\text{CH}_2-$ and $-\text{CH}_3$ functional groups in the abundance ratio $\text{CH}_2/\text{CH}_3 \sim 2.5$, and the amount of carbon tied up in this component is greater than 4% of the cosmic carbon available. On a galactic scale, the strength of the $3.4\ \mu\text{m}$ band does not scale linearly with visual extinction, but instead increases more rapidly for objects near the Galactic Center. A similar trend is noted in the strength of the Si-O absorption band near $9.7\ \mu\text{m}$. The similar behavior of the C-H and Si-O stretching bands suggests that these two components may be coupled, perhaps in the form of grains with silicate cores and refractory organic mantles. The ubiquity of the hydrocarbon features seen in the near infrared near $3.4\ \mu\text{m}$ throughout our Galaxy and in other galaxies demonstrates the widespread availability of such material for incorporation into the many newly forming planetary systems. The similarity of the $3.4\ \mu\text{m}$ features in any organic material with aliphatic hydrocarbons underscores the need for complete astronomical observational coverage in the $2-30\ \mu\text{m}$ region, of lines of sight which sample dust in both dense and diffuse interstellar clouds, in order to uniquely specify the composition of interstellar organics. This paper reviews the information available from ground-based observations, although currently the Infrared Satellite Observatory is adding to our body of knowledge on this subject by providing more extensive wavelength coverage. The Murchison carbonaceous meteorite has also been used as an analog to the interstellar observations and has revealed a striking similarity between the light hydrocarbons in the meteorite and the ISM; therefore this review includes comparisons with the meteoritic analog as well as with relevant laboratory residues. Fundamental to the evolution of the biogenic molecules, to the process of planetary system formation, and perhaps to the origin of life, is the connection between the organic material found in the interstellar medium and that incorporated in the most primitive solar system bodies.

1. Introduction

The question of survival of any molecule in the harsh environment of the interstellar medium (ISM) was once debated quite strongly. Today we know of ~ 100 molecular species in the ISM, with at least one molecule containing 11 atoms (van Dishoeck *et al.*, 1993; Snyder, 1997). Molecules were predicted over 60 years ago (Swings and Rosenfeld, 1937), and soon after CH, CN (McKellar, 1940, 1941; Adams, 1941) and CH^+ (Douglas and Herzberg, 1941) were detected at optical wavelengths. The next detection did not occur until Weinreb *et al.* (1963) made the first radio

wavelength detection of the rotational lines of the interstellar hydroxyl radical (OH), a molecule which had been predicted a decade earlier (Shklovsky, 1953).

The first detections of ultraviolet interstellar absorption lines from atoms (Morton and Spitzer, 1966) and from H₂ molecules (Carruthers, 1970; Smith, 1973) were made by small telescopes on sounding rockets. The Copernicus satellite provided high resolution ultraviolet spectra of atomic lines such as H, D, C, C⁺, O, N, S, and Si in many different types of clouds (Spitzer and Jenkins, 1975). The molecules observed directly by the Copernicus satellite were H₂ and HD. Bands of CO and OH have also been detected at slightly longer wavelengths (1200–1500 Å). Visible wavelength detections of molecules include CH, CH⁺, CN, C₂ and NH (van Dishoeck, 1992). These atoms, ions, and molecules absorb ultraviolet radiation and re-radiate at infrared wavelengths, so the combined results from the Goddard high-resolution ultraviolet spectrograph on the Hubble Space Telescope (Cardelli *et al.*, 1991) and the Infrared Satellite Observatory (ISO) will provide deeper insight into the the physical and chemical structure of diffuse clouds.

Gas phase molecules produce rotational transitions which fall in the radio and sub-millimeter portions of the electromagnetic spectrum. Allowed rotational transitions, which result in a change in dipole moment, produce narrow, characteristic bands at these frequencies. A large fraction of the heavy elements is incorporated as solid phase molecules in interstellar grains and ices. These molecules are not free to rotate, but their vibrational transitions may be observed in the infrared portion of the spectrum. The discussion presented here will focus on the solid-state absorption features produced through the vibrational transitions in the infrared, however, there are also gas phase lines that fall in the IR part of the spectrum which are due to rotational-vibrational transitions. Gas-phase near-infrared spectra are discussed elsewhere in this volume (Chiar, 1997).

Infrared wavelengths are ideally suited to the study of the composition of interstellar dust, especially in the range between 2 and 30 μm (5000 to 330 cm⁻¹), because this spans the energy range associated with the fundamental interatomic vibrations of many molecular bonds associated with the cosmogenically most abundant species (Bellamy, 1960; Silverstein and Bassler, 1967).

Among the many spectroscopic signatures observed in the near infrared is that of an organic component, which may be the by-product of interstellar ice processing. Near infrared spectroscopic observations of the diffuse interstellar medium (DISM) have shown that absorption features near 3.4 μm (~2950 cm⁻¹) which have been attributed to the C–H stretching fundamental in aliphatic hydrocarbon grains, are present along more than a dozen sightlines through our Galaxy (Sandford *et al.*, 1991; Pendleton *et al.*, 1994) and in dust-embedded Seyfert galaxies (Wright *et al.*, 1996). Along sightlines to nearby objects (but not toward the Galactic Center), saturated aliphatic hydrocarbons, and other carbon bearing components of the interstellar medium, correlate with the amount of interstellar dust present. These features are not intrinsically related to the sources which illuminate the column

density of dust, but rather are evidence of the survival of the organic component of interstellar dust in the diffuse interstellar medium environment.

Since ground-based infrared observations are constrained by the atmospheric windows, astronomers have been unable to observe the complete 2–30 μm region. This has inhibited unique identifications of the organic materials present in the ISM. However, a good deal has been learned about the functional groups present, their contribution to the overall interstellar carbon budget, and the distribution of solid-state organic features in space. Laboratory processes, which create organics with absorption features similar to those seen in the diffuse ISM, predict related features in spectral regions inaccessible from the ground. The European Infrared Satellite Observatory (ISO) is probing those spectral regions in order to uniquely identify the organic molecules that reside on interstellar grains in the diffuse ISM (Whittet, 1997).

Advances in infrared spectrometers and detector sensitivities have allowed the ground-based studies of the organic features to expand tremendously. Until fairly recently, observations of the 3.4 μm C–H band complex were only available along the sightline towards the Galactic Center (Willner *et al.*, 1979; Wickramasinghe and Allen, 1980; Butchart *et al.*, 1986; McFadzean *et al.*, 1989), where the amount of dust is so extremely large (total visual extinction of $A_V = 31$ magnitudes), that absorption features are easily detected. In cases where the dust column density is less, the absorption features can be very weak and shallow. Improvements in detector technology have enabled observers to probe sightlines where the features are substantially weaker than along the Galactic Center sightline. The 3.4 μm interstellar feature has been detected toward the proto-planetary nebula CRL 618 by Lequeux and de Muizon (1990). Adamson *et al.* (1990) detected the 3.4 μm interstellar feature toward the bright star VI Cygni No. 12 as well as toward Galactic Center sources, and suggested that the band responsible for this feature belonged to a component along the line-of-sight, rather than to the illuminating sources themselves. Sandford *et al.* (1991) confirmed this finding with higher resolution, higher signal-to-noise spectra towards five background sources. Pendleton *et al.* (1994) extended the number of different sightlines and limits of extinction to which this feature could be seen. Wright *et al.* (1996) have extended the search for the organic component of the diffuse ISM into other galaxies, and have detected the feature towards the nucleus of heavily embedded Seyfert galaxies.

This paper contains examples of recent ground-based infrared astronomical data of the diffuse interstellar medium, and some of the laboratory comparisons that are being used to probe the composition and the processing of interstellar dust. The similarity of the 3.4 μm ($\sim 2940\text{ cm}^{-1}$) features in any organic material with aliphatic hydrocarbons underscores the need for complete astronomical observational coverage in the 2–30 μm region, of lines of sight which sample dust in both dense and diffuse interstellar clouds, in order to uniquely specify the composition of interstellar organics. However, based on the data at hand and the laboratory

experiments that can be conducted, various groups are addressing the questions of production and processing of interstellar organic material.

The organic material responsible for the $3.4\ \mu\text{m}$ feature seen in the diffuse interstellar medium most likely formed in icy grain mantles inside dense molecular clouds. The relatively short cycling times between the dense and diffuse clouds (McKee, 1989) would suggest the organics could be dispersed and reincorporated into the next generation of molecular clouds efficiently. There are currently two observational problems with this scenario, however, and they raise questions about both the production site of the organic material observed in the DISM, and the cycling efficiency that occurs. The discrepancies arise because we observe that (1) the aliphatic hydrocarbon absorption bands, so readily seen in the diffuse interstellar medium, do not appear in the spectra of objects seen through dense cloud material (Brooke, Sellgren, and Smith, 1996); and (2) another possible organic signature, observed near $4.62\ \mu\text{m}$ in dense clouds and thought to be the result of energetically processed interstellar ices (Tegler *et al.*, 1995), does not appear in the diffuse interstellar medium (Pendleton, Tielens, and Tokunaga, in preparation). There is some evidence that the $4.62\ \mu\text{m}$ feature arises from a triple bonded nitrogen-carbon molecule, which could result from the processing of simple interstellar ice materials which contain some form of nitrogen (such as NH_3). If so, then the only two examples of processed icy material, the hydrocarbon and nitrile (or isonitrile) bands for which we have clear evidence, do not appear to reside in the same environment. At present, the $3.4\ \mu\text{m}$ absorption band, attributed to hydrocarbons, is found only in the diffuse ISM, while the $4.62\ \mu\text{m}$ absorption band, attributed to $\text{X-C}\equiv\text{N}$, is only found in the spectra of deeply embedded protostars (Tegler *et al.*, 1995; Pendleton *et al.*, in preparation). Such a result, if upheld, will place important constraints on our understanding of the production, distribution, and evolution of the organic component of the ISM. Chiar (1997) discusses the near-infrared spectra of dense molecular clouds, including the $4.62\ \mu\text{m}$, in more detail.

2. Overview of the Interstellar Medium

The chemistry and physical conditions of the interstellar medium have been of interest for many years. During that time, the picture of the interstellar medium has evolved into a rather complex one. Conditions are such that it is not always straightforward to discuss regions as being hot or cold, dense or diffuse, ionized or neutral. There are many regions to consider, some with definitions which overlap under certain circumstances. This paper is concerned with the diffuse interstellar medium, but the literature is filled with references to a diffuse medium in which descriptions of the physical conditions vary considerably from one author to another. Therefore, in order to define clearly the region to which this paper refers, a brief overview of the interstellar medium (ISM) at large is presented. The following

discussion is based on results found in the literature concerning various aspects of the ISM (Millar and Williams, 1993; van Dishoeck and Black, 1989; McKee and Ostriker, 1977; Slavin and Cox, 1993).

While there is some argument about the relative proportions of the two main contributors to the volume of the ISM, there is no debate that hot, coronal gas and a warm, neutral medium, together compose the ISM in terms of volume. By mass, however, the two main contributors are the diffuse and dense molecular clouds. It is in these two regions that the organic component of interstellar grains forms and evolves chemically.

The hot, coronal phase ($T \sim 10^6$ K; $n \sim 10^3$ atoms/cm³) where hydrogen gas is mostly ionized, envelopes the colder regions in which a warm, ionized medium surrounds a warm, neutral medium. Typical densities and temperatures for this portion of the interstellar medium are $T \sim 10^4$ K; $n \sim 10^{-1}$ atoms/cm³. The warm medium forms the outer part of the third component in the McKee and Ostriker (1977) model, which is the cold neutral cloud regime. The cold neutral clouds are differentiated into diffuse and dense clouds. Temperatures in diffuse interstellar clouds are typically 20–100 K, and number densities range from 20–200 atoms/cm³. A recent model proposed by Slavin and Cox (1993) suggests that most of the volume of the ISM is composed of the warm, neutral medium, in which the hot, coronal gas bubbles reside. In this case, the cold, neutral medium could also exist outside of the hot, coronal gas bubbles. In either case, the diffuse and dense clouds, inside the cold, neutral medium, are themselves differentiated into several categories.

Diffuse clouds are often defined in the literature as those in which the total amount of visual extinction, A_V , is less than 1. These clouds are studied in the UV by their electronic absorption lines. The interstellar radiation field can penetrate the diffuse clouds quite readily, and the ultraviolet photons destroy most of the gas phase molecules. Very simple diatomic species are found in this primarily atomic region.

The higher densities in the translucent clouds ($A_V \approx 1-5$; $n \approx 500-5000$ cm⁻³) shield the molecules at the center of these clouds from the radiation field, although photoprocessing still plays a role at the edges of the clouds (van Dishoeck, 1992). The same conditions apply to the high-latitude cirrus molecular clouds discovered by IRAS at 100 μ m and the outer envelopes of dark, molecular clouds. Star formation is not seen in diffuse or translucent clouds, but clear evidence for the organic component of the ISM has been detected down to extinction levels of $A_V \approx 3-5$.

The sightlines presented in this paper are probably a combination of several translucent and diffuse clouds. In these cases, a background star which is bright in the near infrared, can be observed through the intervening column of interstellar dust. Hereafter, the column of intervening dust will be referred to as the *diffuse* interstellar medium. Diffuse dust lines-of-sight can obscure the background star by many magnitudes, with the upper limit in our Galaxy being the sightline toward the Galactic Center. The significant difference in these sightlines from those passing through dense molecular clouds is the absence of ice on the dust grains, although

there are many chemical and physical differences between the two regimes as well. In addition, recent studies of the diffuse medium gas have shown that the ‘cosmic’ abundance of carbon is considerably smaller than the solar value (Snow and Witt, 1995; Cardelli *et al.*, 1996). The abundance studies indicate the cosmic abundance is actually about 0.7 solar. This result is placing serious constraints on many existing dust models.

2.1. OBSERVATIONS OF THE DIFFUSE ISM

Along the sightline toward the heavily obscured Galactic Center, an $A_V \approx 31$ has been estimated. While there are indications of some dense molecular cloud absorption along this sightline (Whittet *et al.*, in preparation), arguments have been made that the majority of the interstellar dust, through which the observations are made, arises from the diffuse ISM (Roche and Aitken, 1985; Sandford *et al.*, 1991). McFadzean *et al.* (1989) have shown that while the shape of the $3.0 \mu\text{m}$ ice band varies from source to source in the Galactic Center region, the shape of the $3.4 \mu\text{m}$ feature does not. This could result from the presence of a molecular cloud close to the Galactic Center, through which we observe the Galactic Center sources. Different sources are seen through varying amounts of the dense cloud. The $3.4 \mu\text{m}$ feature, on the other hand, remains constant because for each of the Galactic Center sources, we are looking through approximately the same amount of diffuse ISM material. As illustrated in Figure 1, $2.8\text{--}3.8 \mu\text{m}$ observations toward the Galactic Center show that these spectra contain a broad ice feature at $3.0 \mu\text{m}$ (3300 cm^{-1}) and the complex CH feature near $3.4 \mu\text{m}$ (2950 cm^{-1}).

Absorption features in the $2.8\text{--}3.70 \mu\text{m}$ ($3570\text{--}2700 \text{ cm}^{-1}$) region can be produced by a variety of molecular vibrations. Stretching vibrations from O–H and C–H-bearing molecules are the most likely candidates responsible for the features seen near $3.0 \mu\text{m}$ and $3.4 \mu\text{m}$, respectively, within cosmic abundance constraints. The diffuse dust observations indicate that the hydrocarbon features extend from about $3.33 \mu\text{m}$ (3000 cm^{-1}) to $3.57 \mu\text{m}$ (2800 cm^{-1}) with subfeatures near 3.38 , 3.42 , and $3.48 \mu\text{m}$ (2955 , 2925 , and 2870 cm^{-1}). 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 $\text{C}_n\text{H}_{2n+2}$). The relative strengths of these two subfeatures indicate that the average $-\text{CH}_2-/-\text{CH}_3$ ratio of interstellar hydrocarbons is about 2.5 (Sandford *et al.*, 1991).

Pure saturated aliphatic hydrocarbons contain two peaks near 3.48 and $3.51 \mu\text{m}$ (2870 and 2850 cm^{-1}) characteristic of the asymmetric C–H stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively. The Galactic Center data show only a single subfeature near $3.48 \mu\text{m}$ (2870 cm^{-1}). Electronegative or other perturbing chemical groups at the end of short-chain aliphatics can suppress the $3.51 \mu\text{m}$ (2850 cm^{-1}) feature without greatly affecting the positions or strengths of the other three bands.

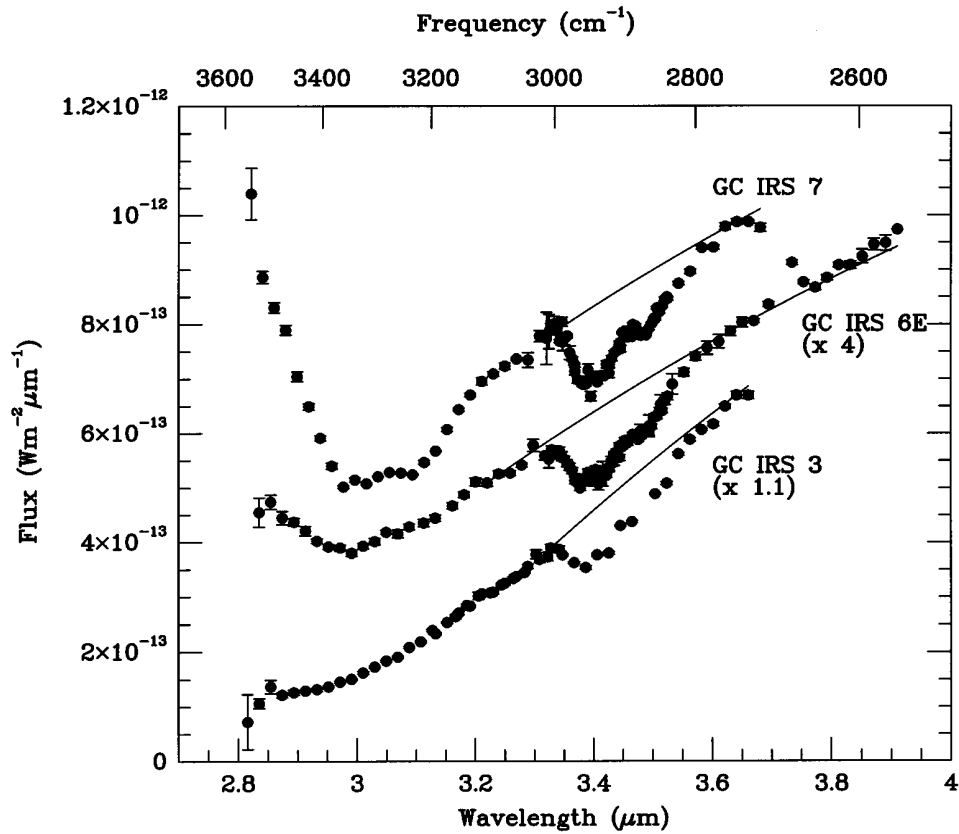


Figure 1. The 2.8–4.0 μm (3570–2500 cm^{-1}) fluxed spectra of sight lines towards Galactic Center sources IRS 7, IRS 6E, and IRS 3. The low resolution data have a resolution of 0.018 μm per detector [$\lambda/\Delta\lambda$] = 155–220 over the 2.80–4.0 μm (3570–2500 cm^{-1}) range. High resolution data points between 3.33 and 3.55 μm (3000 and 2820 cm^{-1}) are superposed for GC IRS 6E and GC IRS 7 (taken from Pendleton *et al.*, 1994). Where error bars are not showing, error bars are smaller than the points.

Observations of the 3.4 μm feature along sightlines other than that towards the Galactic Center are shown in Figure 2 for stars which have diffuse interstellar extinction values which are substantially lower than that of the Galactic Center. The features are correspondingly weaker, but the peak wavelength and general shape of the bands match very well with the Galactic Center spectra. The data in Figure 2 are the resultant optical depth plots, which are derived from the flux data similar to that shown in Figure 1 (see Sandford *et al.*, 1991 and Pendleton *et al.*, 1994 for a discussion of the choices for a continuum baseline to the flux data).

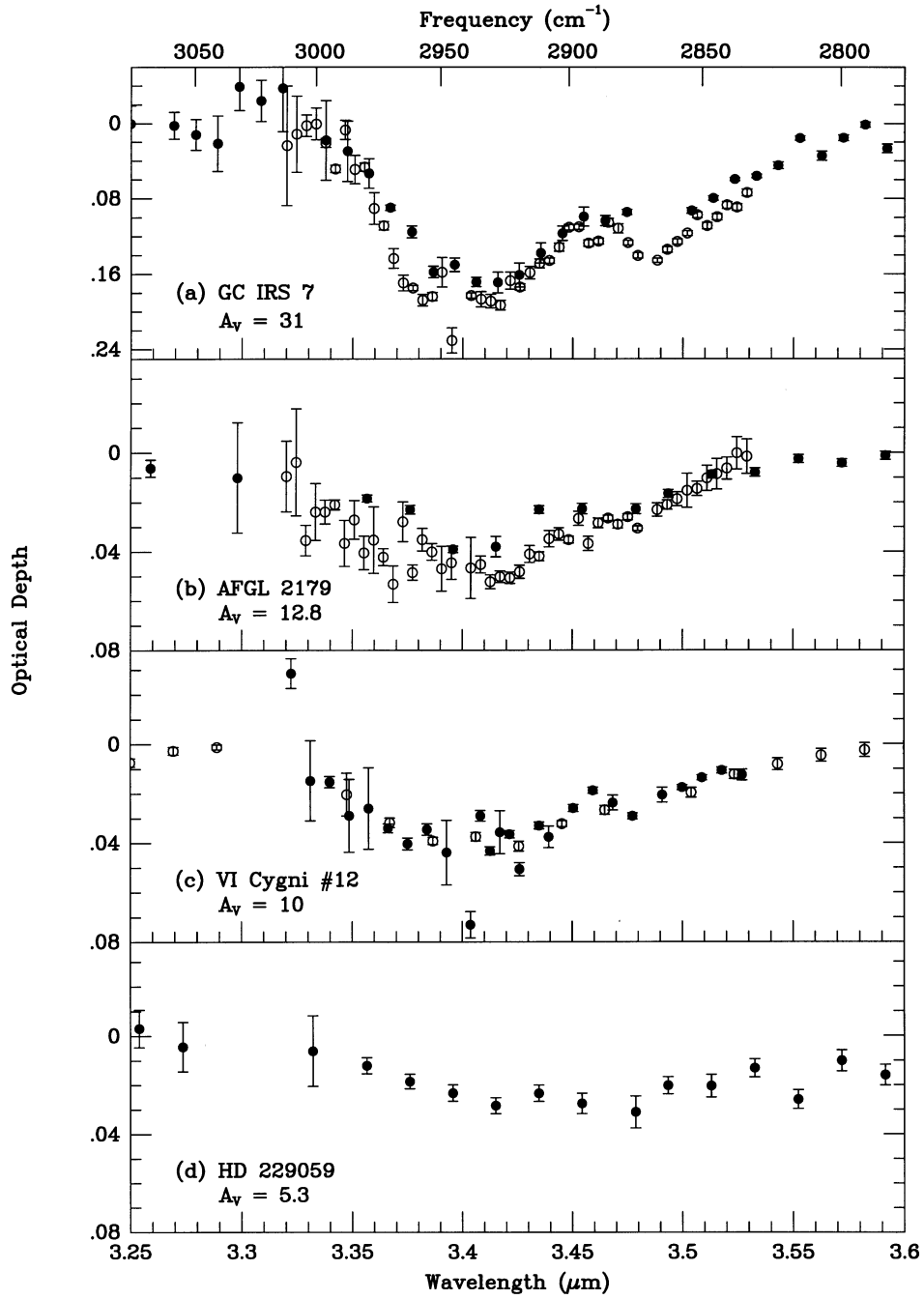


Figure 2. Optical depth plots from 3.25–3.6 μm (3077–2778 cm^{-1}) for (a) GC IRS 7, (b) the WC star AFGL 2179, (c) the supergiants VI Cygni No. 12, and (d) HD 229059. High resolution data are displayed as open points; low resolution data are displayed as solid points (taken from Pendleton *et al.*, 1994).

3. Laboratory Comparisons

The interstellar processes that produce organic materials include gas-grain, ion-molecule, and solid state reactions. Many laboratory groups have studied the effect of energetic processing of interstellar materials (Greenberg, 1963; Donn and Jackson, 1970; Greenberg and Yench, 1973; Khare and Sagan, 1973; Khare *et al.*, 1993; Greenberg, 1979; Hagen *et al.*, 1980; d'Hendecourt *et al.*, 1986; Schutte, 1988; Allamandola *et al.*, 1988; Ehrenfreund *et al.*, 1991; Bernstein *et al.*, 1995; Gerakines *et al.*, 1996; Henning *et al.*, 1995; and others). Several materials have been suggested as candidate carriers of interstellar carbon. These include Hydrogenated Amorphous Carbon (HAC) (cf. Ogmen and Duley, 1988; Adamson, Whittet and Duley, 1990), Quenched Carbonaceous Composite (QCC) (cf. Sakata *et al.*, 1987), residues produced by the irradiation of ices (cf. Schutte, 1988; Allamandola, Sandford and Valero, 1988; Sandford *et al.*, 1991; Baratta and Strazzulla, 1990, Strazzulla and Johnson, 1991), coal (Papoular *et al.*, 1989; Papoular *et al.*, 1991), and the plasma processing of polycyclic aromatic hydrocarbons (PAHs) (Lee and Wdowiak, 1993; Wdowiak *et al.*, 1995). In many respects these materials are all variations on a theme, and the interstellar medium may contain many of the proposed materials. The similarity of the $3.4\ \mu\text{m}$ band complex among these candidate materials underscores the need for astronomical data from other wavelength regions to finally determine the structure and composition of the organic component in the ISM. Here we review the current state of several candidate matches, based on the available comparative data.

3.1. PROCESSING OF INTERSTELLAR ICES BY UV PHOTOLYSIS

The ambient interstellar radiation field does not affect more than the outer edges of a molecular cloud, once the amount of extinction exceeds $A_V \approx 7$ (Tielens and Allamandola, 1987), and the ultraviolet photons emitted by a newly formed star do not penetrate very deeply into the surrounding molecular cloud. Therefore, in order for UV photolysis to occur on a large scale throughout a dense molecular cloud, there must be another source of UV photons.

The reaction responsible for the additional UV photons is the decay process of the H_2 molecule, which is excited to higher electronic states by cosmic rays penetrating the cloud. While the background radiation field produced through this process ($10^3\ \text{photons cm}^{-2}\ \text{s}^{-1}$ with a typical energy of $\approx 10\ \text{eV}$; Prasad and Tarafdar, 1983) is much less than the average flux field in the diffuse ISM (10^8 photons), it is sufficient to process the simple molecules residing in the icy grain mantles. Radicals which are heated by the UV photons can diffuse through the icy mantle and react with other molecules. In this way, complex chemistry occurs in the mantle at a more rapid rate than could transpire via surface reactions alone. Various conditions within the cloud can lead to warm-up of the icy mantles (break-up of the cloud after the onset of star formation, stellar outflow winds, shock waves,

etc.). The more volatile components of the icy mantle are lost upon warm-up while the more refractory organic material remains. A more complete overview of ultraviolet photolysis of interstellar ices is given elsewhere in this volume (Tielens and Charnley, 1997).

Ultraviolet photolysis of interstellar ice analogs has proven to be a plausible pathway for the production of organic residues, and several laboratory groups have contributed to the advancement of this field. Figures 3a and b compare the organic residue produced through UV photolysis by the Allamandola and Sandford group at NASA Ames Research Center. As with many comparison materials, the lack of a stronger subfeature near 2955 cm^{-1} , in Figure 3a, indicates the abundance of $-\text{CH}_3$ groups is higher in the carrier of the interstellar feature than in the laboratory residue. This conclusion is supported by Figure 3b, which is a comparison between the GC IRS 6E spectrum and that of a laboratory residue produced by the UV photolysis and warm up of an $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO}:\text{C}_3\text{H}_8 = 10:5:1:1:1$ ice, i.e., an ice enriched in $-\text{CH}_3$ groups relative to the one shown in Figure 3a.

Recently, infrared spectra have been obtained for laboratory residues of photoprocessed low-temperature ices which have been exposed to long-term solar ultraviolet radiation on the EURECA satellite (Greenberg *et al.*, 1995). The initial ice mixtures were similar to those used in the Allamandola and Sandford work (Figures 3a and 3b), and the EURECA samples were also exposed to UV processing in the laboratory prior to launch. Unfortunately, there is no record of the sample as it appeared prior to space exposure, so any the differences attributed to additional processing are difficult to assess. The EURECA samples were put into space on the ERA platform of the EURECA satellite at an altitude of 500 km, and were exposed to additional irradiation by the full solar spectrum for a total of four months (Innocenti and Mesland, 1995). While the Sun may not be an ideal representation of the interstellar radiation field, this experiment extended the long-term irradiation substantially over that achieved in the laboratory and it allowed simultaneous irradiation of several samples. One of those samples is shown here in Figure 3c.

3.2. ION BOMBARDMENT OF INTERSTELLAR ICES

Figure 4 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 colleagues. In their experiments they have irradiated methane ice (10 K) with 75 keV protons to a total dose of 180 eV/C-atom. As with the EURECA residue, the improved match to the interstellar observations over some of the other carbonaceous materials, is striking. This improvement could be a reflection of the different process involved in the production of this residue, or it could be the result of starting with pure methane. Ion bombardment may play an important role in the molecular cloud environment, and the stronger, deeper penetration allowed by this process can affect chemical changes that the UV photolysis may not provide. The ion bombardment of a typical interstellar ice

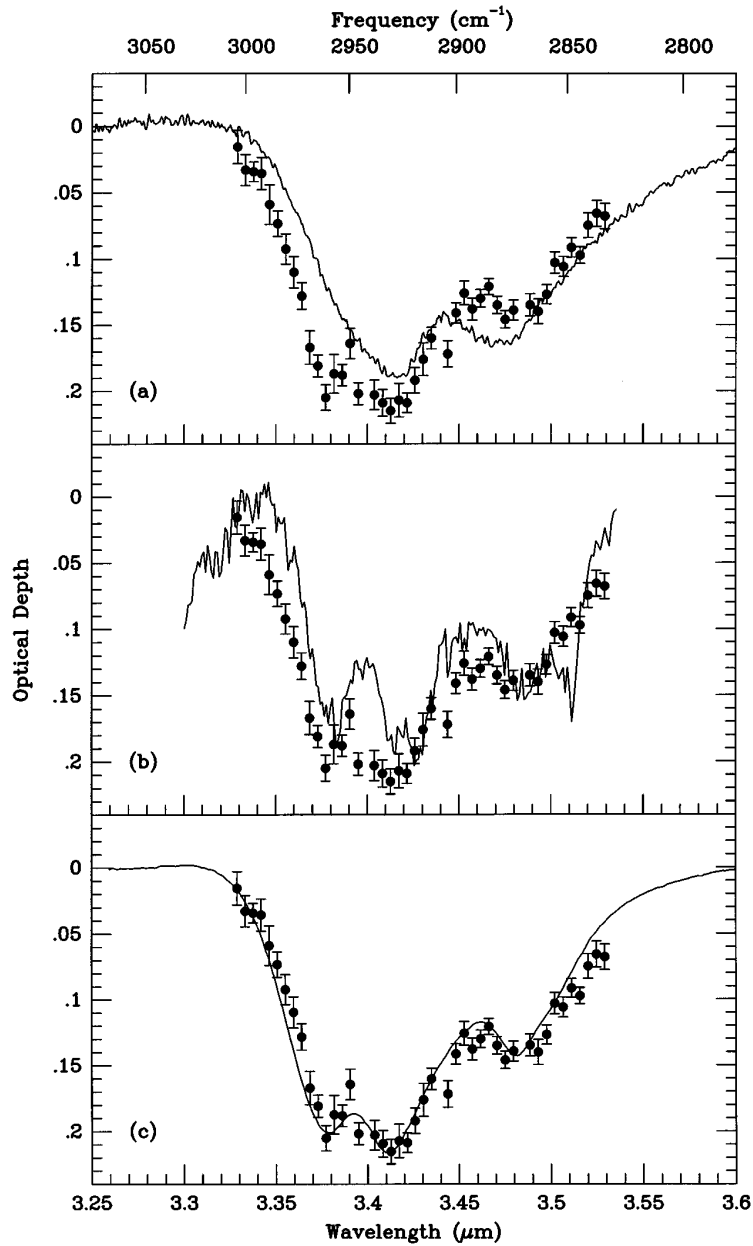


Figure 3. A comparison of the optical depth spectrum of Galactic Center source IRS 6E (solid points) to (a) the spectrum of a laboratory residue produced by the UV irradiation of a 10 K $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO} = 10:5:1:1$ interstellar ice analog followed by warm 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), and (c) the spectrum of a laboratory residue produced by the UV irradiation of an interstellar ice analog with an initial mixture of $\text{H}_2\text{O}:\text{CO}:\text{NH}_3:\text{C}_2\text{H}_2 = 5:2:2:1$, followed by warm up to 200 K and exposure to irradiation in space for 4 months (solid line). Observational data from Pendleton *et al.* (1994); laboratory data in (a) and (b) from Allamandola, Sandford and Valero (1988); laboratory data in (c) from Greenberg *et al.* (1995).

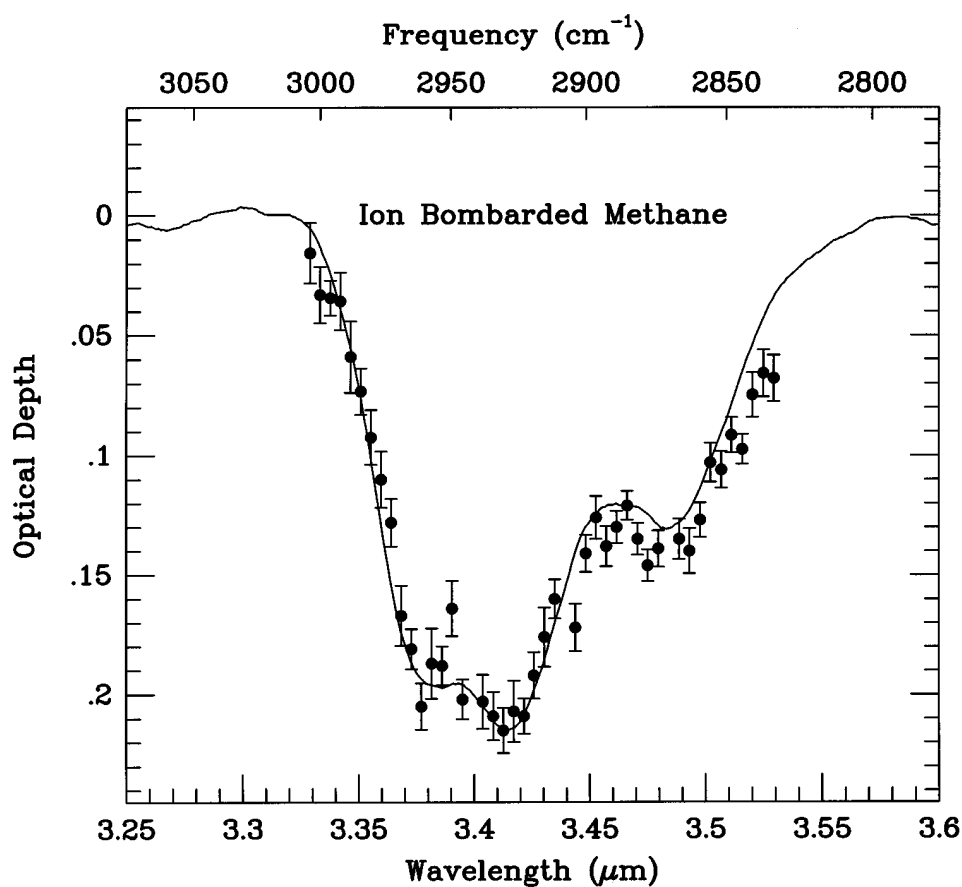


Figure 4. A comparison of the optical depth spectrum of Galactic Center source IRS 6E (solid points) to the spectrum of a laboratory residue produced by irradiating frozen (10 K) methane ice with a 180 eV/C-atom dose of 75 keV protons (solid line) (laboratory spectrum provided by G. Strazzulla).

mixture, rather than pure methane, would probably lead to a greater understanding of the relative importance of the processes in interstellar clouds. Several groups are actively pursuing the bombardment of interstellar materials with electrons and ions, including the Goddard group led by Marla Moore and the Italian group led by Giovanni Strazzulla. A combination of the UV photolysis and ion bombardment experiments, performed in succession, could lead to insight into the conditions under which dust grains survive and evolve.

3.3. HYDROGENATED AMORPHOUS CARBONS

In recent years, amorphous carbon has been the focus of several laboratory groups as the search for the carbonaceous components to the ISM moved away from

graphite as the explanation for many astrophysical phenomena. Hydrogenated Amorphous Carbon (HAC) can be produced in the laboratory: a) through inefficient hydrocarbon burning in air, b) by striking an arc in a controlled Ar atmosphere between two amorphous carbon electrodes (cf. Borghesi, Bussoletti and Colangeli, 1987; Ogmen and Duley, 1988; Duley, 1994), or by c) the decomposition of a gas-phase precursor with a DC electric field (Furton and Witt, 1996). During the latter process, the plasma glows and the residue condenses on the relatively cool substrate in the form of a film. There are many forms in which amorphous carbon can exist, however, all are characterized by microcrystallinity produced by graphitic platelets which are randomly oriented in larger grains. Compared to graphite, amorphous carbon has the same C–C distance, but the interlayer distance is larger. Amorphous carbon has more chemically active sites than does graphite, with unsaturated C atoms sitting on the periphery of the crystallites. These sites can be occupied by single H atoms, which would lead to bonds of CH, –CH₂–, or –CH₃. The excitation mechanisms for HACs in space are not entirely clear, although there are probably multiple pathways by which the interstellar HAC can be produced. What is clear is the fact that hydrogenated amorphous carbon is a continuum of materials whose properties can be altered by processing in interstellar space through chemical exposure as well as radiation.

HAC is thought by many to be the best candidate material to explain an astrophysical phenomenon known as the extended red emission (ERE), which is the photoluminescence radiation emitted by interstellar dust. The ERE has been observed in the spectrum of various galactic objects: reflection nebulae (Witt and Boroson, 1990), planetary nebulae (Furton and Witt, 1992), HII regions (Sivan and Perrin, 1993), the dark nebula L1780 (Mattila, 1979, Chlewicki and Laureijs, 1987), and high latitude cirrus (Guhathakurta and Tyson, 1989). Recently, the first detection of ERE outside of our Galaxy was reported based on observations of the dusty halo of the M82 galaxy (Perrin, Darbon and Sivan, 1995). The extended red emission consists of a broad emission bump about 1000 Å wide (FWHM), centered between 6500 and 7500 Å. The bump has been explained either by fluorescence from isolated PAH molecules (d’Hendecourt *et al.*, 1986, Leger *et al.*, 1988) or by fluorescence from solid state materials such as QCC or HAC. Duley (1985) and Witt and Schild (1988) both suggested the luminescence of hydrogenated amorphous carbon grains may be the source of this ‘extended red emission’ (ERE). Recent results demonstrate that the luminescence efficiency of the ERE in various environments, which is the ratio of ultraviolet photons absorbed to the luminescence photons emitted, compares favorably to the efficiencies of laboratory HAC samples (Witt, Ryutov and Furton, 1997), and HAC samples offer a comparably good match to the near-infrared observations of the diffuse medium organics. Figure 5 compares the HAC film produced by Furton and Witt (1996) to the diffuse medium hydrocarbon features. All HACs exhibit a prominent 3.4 μm band, however the relative strengths of the features vary considerably; the match shown here is one of the best fits to the observations.

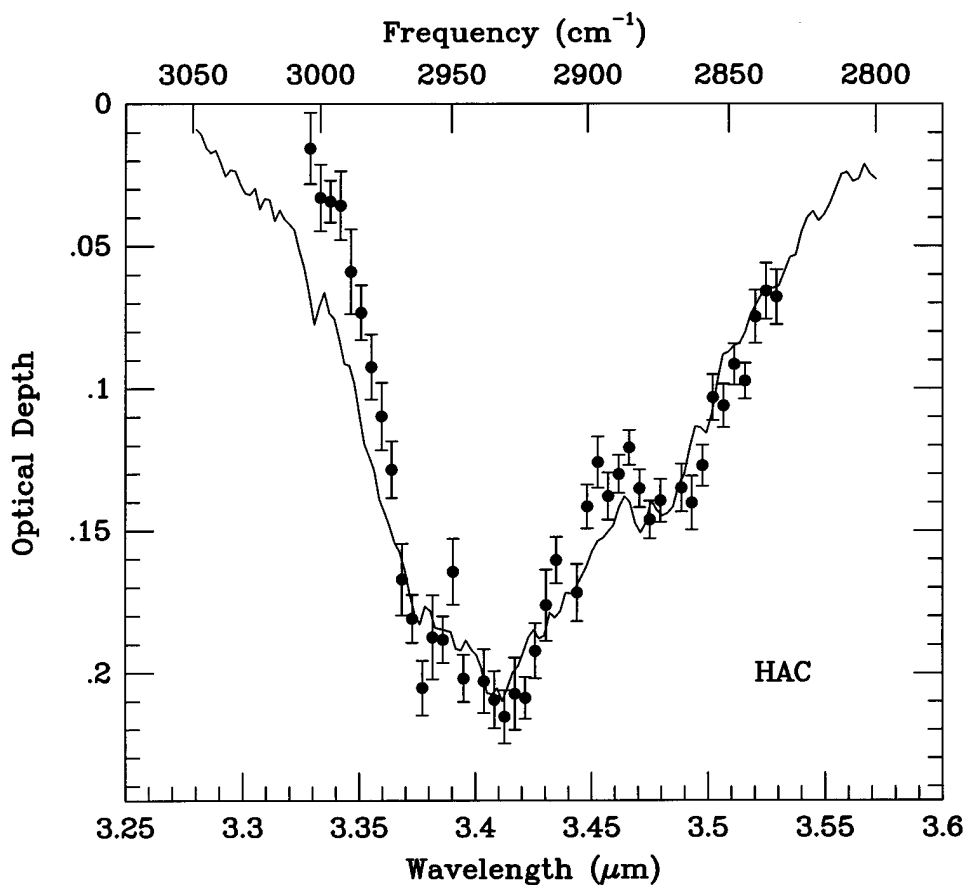


Figure 5. A comparison of the optical depth spectrum of Galactic Center source IRS 6E (solid points) to the spectrum of a hydrogenated amorphous carbon produced through the decomposition of a gas-phase precursor with a DC electric field (solid line) (from Furton and Witt, 1996).

3.4. QUENCHED CARBONACEOUS COMPOSITE

Quenched Carbonaceous Composite (QCC) is synthesized from hydrocarbon, principally methane, plasmas (Sakata and Wada, 1989). Sakata *et al.* (1992) have suggested that a material similar to QCC may be a major component of interstellar dust, and they note an interesting similarity between the fluorescence spectrum of QCC and the broad emission feature (6500–7000 Å) observed in regions of dust known as reflection nebulae, which are illuminated by nearby stars (Sellgren *et al.*, 1985) and planetary nebulae (Furton and Witt, 1990). The components of QCC have features similar to the 220 nm extinction ‘bump’ (Sakata *et al.*, 1983, 1994) and to the unidentified infrared emission features which occur in many different types of interstellar environments (Sakata *et al.*, 1990 and references therein). The unidentified infrared emission features have also been strongly identified with poly-

cyclic aromatic hydrocarbons (Leger and Puget, 1984; Allamandola *et al.*, 1985, 1989 and references therein), and have also been proposed as an explanation for the extended red emission discussed in the previous section. Figure 6 compares the astronomical spectrum of the line of sight toward Galactic Center source GC IRS 6E to the laboratory spectrum of QCC after heating to 723 K. The QCC spectra was taken from Sakata and Wada (1989). A spectrum of room temperature QCC did not match the interstellar spectrum as well. Since heating tends to aromaticize the mixture, the better match between the heated QCC and the DISM from that of room temperature QCC (not shown) is consistent with the conclusion in Sandford *et al.* (1991) that the DISM dust contains carbonaceous material other than aliphatics. QCC has been proposed as a candidate material for the unidentified emission features, as well as the infrared absorption features, and investigations into the conditions under which this material remains a plausible candidate for the interstellar observations are ongoing by the Japanese group led by S. Wada.

The ultimate goal of comparisons between astronomical and laboratory organics is to answer the following questions: what is the chemical composition of the interstellar organic material, how was it formed, and how did it evolve? The general fits provided by all the spectra in Figures 3–6 support the idea that dust in the diffuse medium contains abundant aliphatic $-\text{CH}_2-$ and $-\text{CH}_3$ groups. A unique identification of the interstellar carrier will probably only arise after a complete 2–30 μm spectrum of several interstellar sightlines has been obtained. The results from the 3.4 μm ground-based observations do, however, show 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 (Sandford *et al.*, 1991; Pendleton *et al.*, 1994). High signal-to-noise, high resolution ($\lambda/\Delta\lambda = 750$) astronomical data therefore represent a means by which the spectral properties of various laboratory materials can be used to further constrain the chemical composition of the carrier of the diffuse C–H stretching feature. This illustrates the need for both additional high resolution, full spectral coverage, high quality observational data and corresponding spectroscopic laboratory data from additional, relevant, well-characterized materials having a range of appropriate compositions.

3.5. THE GALACTIC DISM, DUST IN DISTANT GALAXIES, AND THE MURCHISON METEORITE

Recent detection of the 3.4 μm absorption band complex in other galaxies has opened a new window of opportunity in the observational study of spectral absorption features. The two best detections of the 3.4 μm feature obtained to date are in NGC 1068, which has an active nucleus heavily obscured by dust (Bridger *et al.*, 1993), and in the ultraluminous IRAS galaxy, 08572+3915 (Wright *et al.*, 1996) in which the band complex is unusually strong. In both NGC 1068 and IRAS

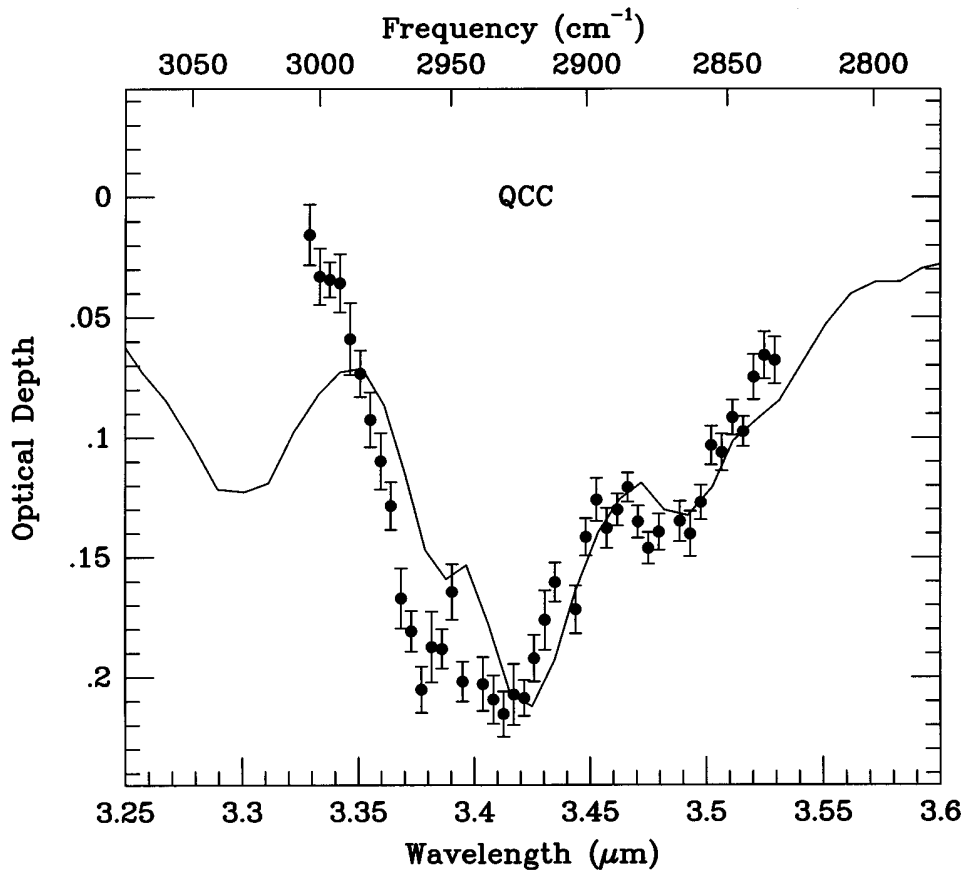


Figure 6. A comparison of the optical depth spectrum of Galactic Center source IRS 6E (solid points) to the optical depth spectrum of filmy Quenched Carbonaceous Composite (QCC) taken from Sakata and Wada (1989; solid line).

08572+3915, the detailed shape of the $3.4 \mu\text{m}$ absorption band complex is amazingly similar to that seen from the diffuse ISM in our Galaxy. The relative strengths of the 3.38 and $3.42 \mu\text{m}$ sub-features are approximately the same, indicating that the extragalactic dust has a similar $-\text{CH}_2-$ to $-\text{CH}_3$ ratio. The surprising strength of the overall band complex in IRAS 08572+3915, nearly four times greater than that observed in our own Galaxy, suggests that a great deal of information can be learned about the profile and peak positions of dust absorption features through the study of dust in other galaxies. Also, features which fall in wavelength regions which are unobservable in our own Galaxy, by ground-based telescopes, may be Doppler shifted in distant galaxies, into a spectral region that enables ground-based studies. The Seyfert galaxies in which the hydrocarbon features have been detected are seen almost face-on, therefore it is unlikely that the absorption arises from the

diffuse ISM in the disks of these galaxies. It is more plausible that the absorption arises in the dusty tori surrounding the active cores (Wright *et al.*, 1996).

Carbonaceous chondrites, such as the Murchison meteorite, contain interstellar signatures, and the organic features correspond closely with the interstellar bands. The enhanced deuterium abundance in the organic component and other isotopic anomalies, ensures that the material is extraterrestrial (Kerridge, Chang and Shipp, 1987; Ming and Anders, 1988; Lewis, Amari and Anders, 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. A more detailed account of the composition of the Murchison meteorite can be found in Cronin, Pizzarello and Cruikshank (1988), Khare *et al.* (1996), and Bernatowicz *et al.* (1996).

As first pointed out by Ehrenfreund *et al.* (1991), there is a strong similarity between the 3.4 μm feature seen in the solvent-soluble, acid-insoluble extracts of the Orgueil and Murchison carbonaceous chondrites and the Galactic Center spectrum (observational data from Butchart *et al.*, 1986). Cronin and Pizzarello (1990) have shown that the aliphatics in the Murchison meteorite are primarily a structurally diverse suite of branched, alkyl-substituted cycloalkanes, ranging in C number from about 15 to 30. These are one-, two-, and three-ring condensed alicyclic compounds. Comparisons of higher resolution astronomical observations to the *sublimate* of the acid insoluble residue of the Murchison meteorite (Pendleton *et al.*, 1994; meteoritic data from DeVries *et al.*, 1993), reveals that the excellent match in the 3.4 μm region is consistent with the hypothesis that light hydrocarbons are responsible for the interstellar feature. Through heating, the more volatile light hydrocarbons are captured in the sublimate. The close match between the ISM observations and the Murchison meteorite, and the known presence of cyclic aliphatics in the meteoritic feature, suggest the presence of cyclic rather than linear aliphatics in the interstellar medium. At present, it is not possible to discriminate between cyclic and linear aliphatic hydrocarbons through observational methods; however, this is an important question as it is related to the structure and survivability of interstellar organics. The Ehrenfreund (1991) work has also prompted comparisons between laboratory residues and the Murchison meteorite, such as that presented in Figure 7, where the organic soluble extract of Murchison (benzene-methanol 9:1) (Cronin and Pizzarello, 1991) was compared to hydrogen plasma-processed naphthalene (Wdowiak *et al.*, 1995). The comparison shows good agreement throughout the near-IR, however, in detail the 3.4 μm band complex is deficient in methyl groups, as is the case in nearly all of the comparisons other than those to the Murchison meteorite. Recent experiments by the Wdowiak group have produced a much improved spectral match in this region which are attributed to improvements in

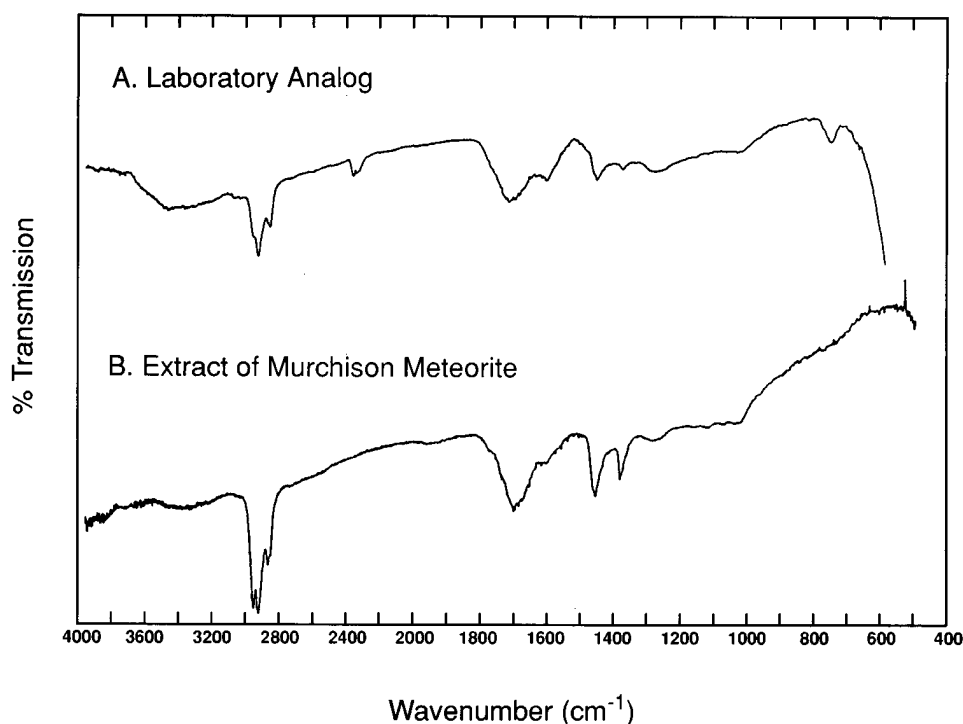


Figure 7. Comparison of FTIR (spectrum A) of the deposited film from hydrogen plasma processed naphthalene to organic extract of Murchison meteorite (from Cronin and Pizzarello, 1990); figure reproduced from Lee and Wdowiak (1993) and Wdowiak *et al.* (1995) with permission.

the laboratory apparatus, including better gas handling and access to the interior of the discharge tube. Preliminary results indicate enhanced CH_3 contributions over that exhibited in Figure 7a. The new residues also exhibit ultraviolet features that correlate with interstellar extinction features (Wdowiak, private communication).

The comparisons made with higher resolution astronomical data (data from Pendleton *et al.*, 1994) and the sublimate from the acid insoluble residue of the Murchison meteorite (data from DeVries *et al.*, 1993), are shown with the new data from the highly luminous Seyfert galaxy IRAS 080572+3915 in Figure 8 (Pendleton, 1996; Wright *et al.*, 1996). The three spectra are quite similar in peak positions, widths, and profiles. A correction for the redshift of the IRAS galaxy has been applied to the spectrum shown in Figure 8. In the original spectrum, the sub-peaks of the galactic interstellar features can be seen at 3.57, 3.61 and 3.70 μm .

3.6. HYDROCARBONS AND SILICATES IN OUR GALAXY

Comparisons between the total visual extinction, A_V , and the optical depth of diffuse dust absorption features, τ , reveals that although the optical depth of the 3.4 μm feature scales linearly with extinction for the local diffuse medium, the

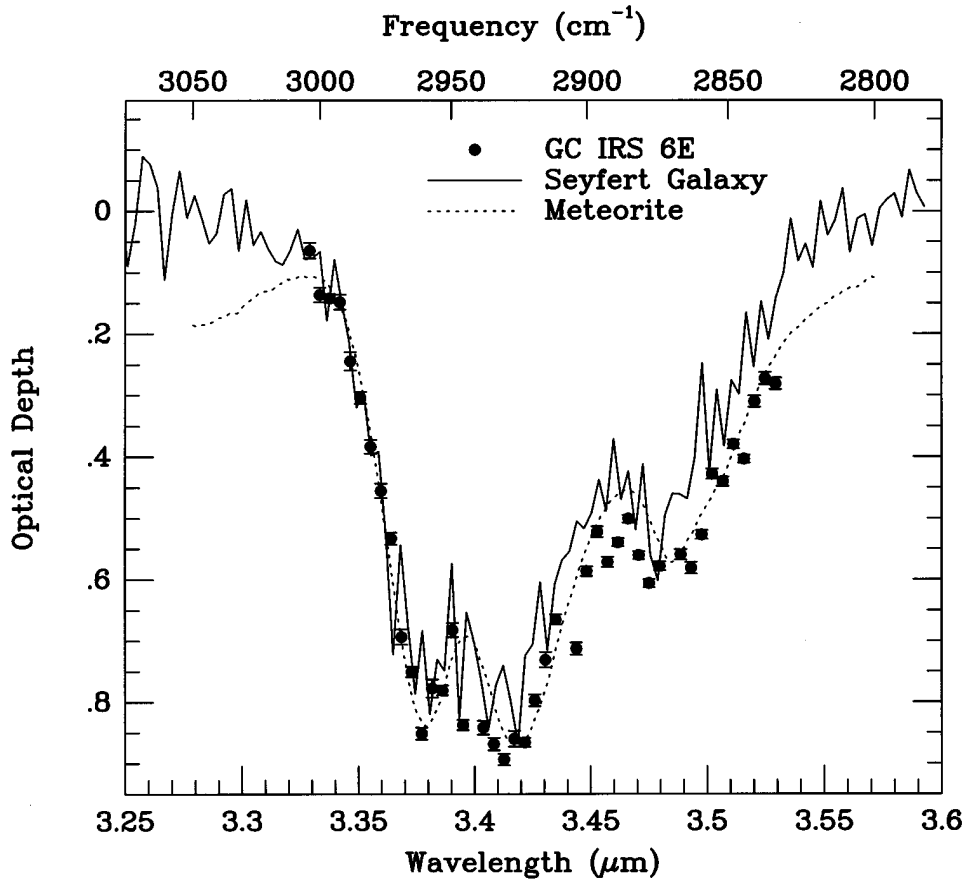


Figure 8. A comparison of the optical depth spectrum of Galactic Center source IRS 6E (solid points), the sublimate from the acid-insoluble component of the Murchison meteorite (thick line; from DeVries *et al.*, 1993), and the redshift corrected $3.4\ \mu\text{m}$ feature in the embedded Seyfert Galaxy IRAS 08572+3915 (thin line; from Wright *et al.*, 1996, and Pendleton, 1996).

ratio of $A_V/\tau(3.4)$ is lower toward the Galactic Center (Sandford, Pendleton and Allamandola, 1995). A similar trend has been observed previously for silicates in the diffuse medium (Roche and Aitken, 1985), suggesting that the silicate and carbonaceous materials in the DISM may be physically correlated (Figure 9). This result also suggests that the composition of interstellar dust or the galactic dust grain population may vary throughout the Galaxy (Sandford, Pendleton and Allamandola, 1995). The similar behavior of the C–H and Si–O stretching bands illustrates the possibility that these two components may be coupled, perhaps in the form of silicate-core, organic-mantled grains, as proposed by Greenberg (1982). Comparisons of the $3.4\ \mu\text{m}$ and $9.7\ \mu\text{m}$ absorption bands in other galaxies will provide an additional view of this complex situation.

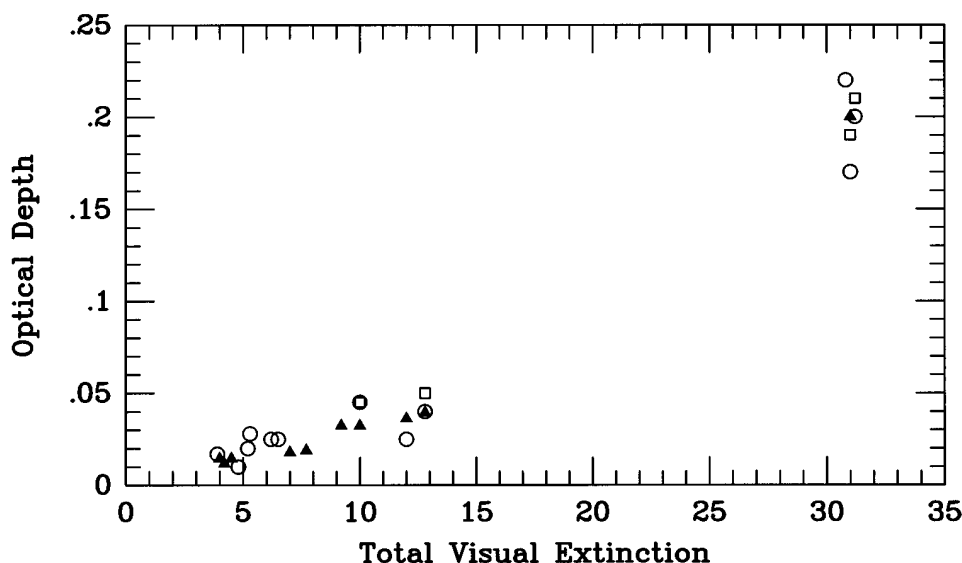


Figure 9. Plot of the optical depth of the C–H and Si–O stretching bands, due to dust in the diffuse medium, vs. optical extinction. The low-resolution C–H data points (open circles) and the high-resolution C–H data points (open squares) are taken from Pendleton *et al.*, 1994. The optical depths of the Si–O band, from Roche and Aitken (1984), shown as triangles, have been scaled by a factor of 1/18 to normalize them to the strength of the 2925 cm^{-1} –CH₂– feature at the Galactic Center. The various points associated with different sources in the Galactic Center have been slightly offset from each other in visual extinction for clarity. For discussion of this relationship, see Sandford, Pendleton and Allamandola (1995).

3.7. AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are thought to be ubiquitous in space and are likely to be responsible for the infrared emission features seen in the spectra of many galactic and extragalactic objects associated with UV rich regions (cf. Leger and Puget, 1984; Allamandola *et al.*, 1985, 1989). In general, the infrared emission spectra observed in many different classes of objects contain intense, well-defined bands, weaker minor bands, and underlying broad features. Researchers have proposed that there are at least two classes of materials which contribute to the spectra. Free, molecule-sized PAHs, which account for the narrower emission bands, and clusters of PAHs or amorphous carbon particles rich in aromatics, which account for the broader emission underlying the narrow features (Allamandola, Tielens and Barker, 1989). The narrow emission features have been dealt with elsewhere, so in this section the nature of the carrier of the broad, underlying feature will be addressed.

There is tentative evidence for an absorption feature near $3.25\ \mu\text{m}$ (3080 cm^{-1}) in the spectra of dense clouds (Sellgren, Smith and Brooke, 1994) and near $3.28\ \mu\text{m}$ (3050 cm^{-1}) in the diffuse medium (Pendleton *et al.*, 1994), which may be due to PAHs and aromatic material in general. 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 $3.25\text{--}3.28\ \mu\text{m}$ ($3080\text{--}3050\ \text{cm}^{-1}$) region. Compared to the aliphatic bands, only a weak aromatic feature is expected since aromatics contain fewer H atoms per C atom ($\text{H/C} \leq 1$) than do aliphatics ($\text{H/C} \geq 2$) and because the intrinsic strength of the aromatic C–H stretching band is 2–3 times lower than its aliphatic counterpart. The aromatic abundance fraction could be $\sim 10\%$ of the C along the line of sight to the Galactic Center (Pendleton *et al.*, 1994), which may be larger than that estimated from galactic observations of the infrared *emission* features (C about 1–18%; Leger and Puget, 1984; Allamandola *et al.*, 1985, 1989; Joblin, Leger and Martin, 1992). This suggests that a comparable amount or slightly more aromatic carbon exists in large PAHs, PAH clusters, and aromatic grains than in the form of gas phase molecules. A significant fraction of the carbon in meteorites is also in the form of aromatics (cf. Hyatsu and Anders, 1981; Basile, Middleditch and Oro, 1984; Mullie and Reisse, 1987). The aromatics in meteorites (Krishnamurthy *et al.*, 1992; Cronin and Chang, 1994) and interplanetary dust particles (Clemett *et al.*, 1993) are often enriched in deuterium, indicating an interstellar connection. The strong telluric methane lines in this same region make a definitive detection of the $3.28\ \mu\text{m}$ ($3050\ \text{cm}^{-1}$) band from ground-based observations difficult, but the possibly large abundance of aromatics in the interstellar medium, and the intriguing connection to PAHs in meteoritic material, make this an important area for further study. Results from the Infrared Satellite Observatory (ISO) promise to address this important issue.

4. Summary

While radio observations reveal the presence of organic molecules in the gas phase of the interstellar medium, near-infrared observations reveal the solid-state features that arise from interstellar dust grains. There is excellent evidence for an organic component in the dust of the diffuse interstellar medium. The infrared absorption band complex near $3.4\ \mu\text{m}$ ($2950\ \text{cm}^{-1}$), observed in the spectra of stars which are seen through interstellar dust, is attributed to carbonaceous dust through comparisons of the high resolution, high signal-to-noise astronomical data, and a variety of laboratory spectra of organic residues which contain abundant aliphatic $-\text{CH}_2-$ and $-\text{CH}_3$ groups. However, the similarity of the $3.4\ \mu\text{m}$ features in any organic material with aliphatic hydrocarbons underscores the need for complete astronomical observational coverage in the $2\text{--}30\ \mu\text{m}$ region, of lines of sight which sample dust in both dense and diffuse interstellar clouds, in order to uniquely specify the composition of interstellar organics. The interstellar $3.4\ \mu\text{m}$ bands require at least 4% of the cosmic carbon available. Recent reports of extragalactic observations reveal the organic feature seen in our own Galaxy is prevalent in other galaxies as well. The discovery of the $3.4\ \mu\text{m}$ absorption band complex in dusty

Seyfert galaxies has illustrated the ubiquitous distribution of the carbonaceous component throughout our Galaxy and in others. The surprising strength of the feature in a distant galaxy has revealed the possibility of studying features which are unavailable to ground-based observational work due to telluric absorption features. The Doppler shift of the distant galaxies can translate these features into atmospheric windows, thus opening up a new arena for the study of dust composition.

Comparisons of near-infrared laboratory spectra to astronomical galactic and extragalactic near-infrared observations, illustrates that material containing substantial amounts of aliphatic $-\text{CH}_2-$ and $-\text{CH}_3$ groups will produce a feature whose overall position and profile is similar to that of the diffuse interstellar C–H stretching feature. The distribution of the carbonaceous component of the diffuse interstellar medium is not uniform throughout our Galaxy, as noted by the fact that the strength of the C–H stretching band does not scale linearly with the amount of visual extinction towards the Galactic Center. Extragalactic observations are not yet able to trace the distribution of the carrier in the distant galaxies.

The efficient cycling of dust between dense and diffuse clouds in our galaxy suggests that the organic component so clearly seen in the diffuse medium should be apparent in the dense molecular clouds where it is thought to originate. Such is not the case, however, and the absence of the aliphatic hydrocarbon signature in the dense cloud spectra is not well explained at this time. Furthermore, spectra of embedded protostars in several dense molecular clouds reveal an absorption band near $4.62\ \mu\text{m}$ which is likely the result of a $\text{C}\equiv\text{N}$ bond. As suspected in the case of the aliphatic hydrocarbon $3.4\ \mu\text{m}$ feature, the ‘ $\text{X}-\text{C}\equiv\text{N}$ ’ band is also a probable product of energetic processing of interstellar ice in the molecular cloud environment. If so, the cycling of dust between the dense and diffuse clouds would suggest the $4.62\ \mu\text{m}$ feature appear in the diffuse interstellar medium, but as yet that has not been the case.

Finally, the striking similarity of the near-infrared spectrum of the Murchison carbonaceous meteorite to the interstellar observations suggests that the carbonaceous component of dust in the diffuse interstellar medium and the meteoritic material may be closely related, and that the light hydrocarbons in the carbonaceous fraction of primitive meteorites may provide one of the best analogs for the organic fraction of dust in the diffuse interstellar medium.

While it is not possible to assign a unique identification to the carrier of the interstellar organic component based on comparisons of the $3\text{--}4\ \mu\text{m}$ region alone, these studies demonstrate the utility of comparing high signal-to-noise, high-resolution astronomical infrared spectra over a broad wavelength range with the spectra of laboratory analog materials. The complete and uninterrupted spectral region from 2 to $30\ \mu\text{m}$, observed at high signal-to-noise and high spectral resolution ($\lambda/\Delta\lambda \geq 750$), holds the key to identifying the interstellar organic materials. Investigations into the effect of further processing of organic residues and sequen-

tial combinations of processing techniques will be illustrative of the astrophysical conditions to which interstellar organics are subject.

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