THE NATURE AND EVOLUTION OF INTERSTELLAR ORGANICS

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Abstract. Infrared spectroscopy of solid state absorption features in dense and diffuse interstellar clouds has greatly advanced our understanding of the composition of dust in these regions. However, serious questions regarding the evolution of dust grains have now developed as a result of recent compositional discoveries. The creation of complex organic refractory material on or in icy mantles of grains residing in the protected environs of dense molecular clouds is thought to be the pathway by which organic carriers are formed. Two absorption features in particular, one near 3.4 μm and another near 4.62 μm have been attributed to an organic refractory residue which can be produced by ultraviolet photolysis of interstellar ices. However, even though the production site for both features is expected to occur within dense molecular clouds, these features are observed in very different physical regimes of the interstellar medium (ISM). The 3.4 μm feature is observed in the low density, low temperature portion of the diffuse ISM, and the 4.62 μm feature is observed towards embedded protostars in high density molecular clouds. Dust grains are thought to cycle between the dense and diffuse clouds fairly efficiently and on rather short timescales, thus the noteworthy absence of the diffuse ISM 3.4 μm hydrocarbon absorption band and the unique presence of the 4.62 μm band in the spectra of dense molecular cloud objects presents difficulties for the production site and/or the cycling efficiency. In this paper, we focus on comparisons between the dense and diffuse clouds which specifically address the nature and evolution of the organic component of interstellar dust. A greater understanding of the origin and distribution of interstellar organics is essential

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in any evaluation of the organic inventory available for incorporation into planetary systems and the precursor planetesimal stage.

1. Introduction

The basic building blocks of life on Earth originated in stars which formed out of interstellar gas and dust. As discussed by Tielens (this volume), the lifecycle of dust grains includes the injection of the dust into the diffuse interstellar medium (ISM) from their formation site in the circumstellar shells of evolved stars. Upon break-up of dense molecular clouds, primarily due to star formation processes, refractory grain components processed on icy grain mantles during their residence within the cloud (Greenberg 1982) are likely added to the diffuse ISM dust. New generations of dense molecular clouds form out of the swept-up combination of circumstellar dust and the recycled products from previous dense clouds. Given the expected short cycling times between the dense and diffuse ISM (McKee 1989), spectroscopic signatures indicative of refractory organic species should be observable in both the dense and diffuse ISM. In actuality, the organic solid-state features observed at near-infrared wavelengths along sightlines through dense clouds and the diffuse interstellar medium are quite different, revealing little commonality between the locales where key signature organic features are observed.

Attempts to characterize the composition of interstellar dust in both the dense and diffuse ISM have led to observations of bright background sources observed through great quantities of interstellar dust. These features are not intrinsically related to the sources which illuminate the column of dust, but rather are carried by the intervening dust along our line-of-sight. A multitude of absorption and emission features have been observed in this manner (see Whittet & Tielens 1997). Among the many spectroscopic signatures observed in the near infrared are two absorption bands that may be the strongest representatives of the processed organic component of interstellar dust. The 3.4 μm and 4.62 μm absorption bands have both been attributed to energetic processing of interstellar ices in dense molecular clouds, yet they appear in mutually exclusive locations in the ISM. The 3.4 μm absorption feature(s), attributed to the C-H stretching fundamental bands in aliphatic hydrocarbon grains (Sandford et al. 1991), are present along more than a dozen sightlines through the diffuse ISM in our galaxy (Pendleton et al. 1993) and are also seen in dust-embedded Seyfert galaxies (Bridger, Wright, & Geballe 1993). Until recently, the presence of these features in the diffuse ISM has been taken as evidence of the survival of the

organic component of interstellar dust from its formation site in the dense cloud to the diffuse interstellar medium environment. However, the noted absence of the 3.4 μm aliphatic hydrocarbon sub-features in any dense cloud spectra obtained to date raises important questions concerning the origin and/or distribution of the carrier of this band (Allamandola et al. 1992).

Likewise, the near-infrared absorption signature seen at 4.62 μm in dense cloud spectra towards bright, embedded protostellar objects also presents a problem for the standard picture of dust grain evolution. Possible identifications for this feature include some type of nitrile (CN) or isonitrile (NC) found in the residues produced through energetic processing of typical interstellar ice analog mixtures (Lacy et al. 1984; Tegler et al. 1993, 1995). See reviews by Schutte and Greenberg (this volume) for reviews of laboratory processing of interstellar ice mixtures. In laboratory experiments, the strength of the 4.62 μm band increases as the temperature is raised after the volatile components of the ices have evaporated (Bernstein, Sandford, & Allamandola 1996). For this reason, it is expected that if the observed 4.62 μm band is due to a processed ice residue, then it might survive incorporation into the diffuse ISM. However, the 4.62 μm feature, detected towards embedded protostellar sources, has thus far not been detected along diffuse interstellar medium sightlines.

Constrained by the interfering absorption of the Earth's atmosphere, ground-based infrared observations have been limited to the narrow wavelength regions through which the Earth's atmosphere is relatively transparent. The Infrared Space Observatory, launched in November 1995, is revolutionizing our understanding of the composition of interstellar dust by providing high signal-to-noise, high resolution observations along many sightlines covering the critical portion of the electromagnetic spectrum between 2–30 μm (Whittet et al. 1996). It is precisely this region which holds the key to our understanding of the composition of interstellar dust. In the diffuse ISM, the incomplete observational database has inhibited unique identifications of the organic materials present, although much 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. Greater insight has been gained regarding the ices present in dense molecular clouds, primarily because of the larger number of bright sources seen through high column densities of interstellar dust. However, the ultimate goal in our studies of interstellar dust is to understand the complete life-cycle and composition of the grains, and in that regard we have a long way to go.

In this paper, we will address problematic discrepancies in the observations of dense and diffuse clouds, and how they relate to the nature and evolution of interstellar organics. Further discussion of important dust fea-

tures is covered elsewhere in this volume (see reviews by d'Hendecourt, Schutte, and Greenberg); here we focus on those features specific to the organic component of the ISM, which may have evolved from ice mantles accreted in dense clouds.

2. Infrared Spectroscopy

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 inter-atomic vibrations of many molecular bonds associated with the cosmogenically most abundant species (Bellamy 1960; Silverstein & Bassler 1967; Allamandola et al. 1992; d'Hendecourt, Allamandola, & Greenberg 1985). Infrared spectroscopy provides the observational means for detecting absorption features of molecules in the dust. Molecules undergo both vibrational and rotational transitions; rotation is suppressed for molecules in the solid phase. For a diatomic molecule (e.g. CO), there is one allowed fundamental vibrational mode. The fundamental vibrational frequency corresponds to a bond stretch and is given by

$$\nu_{\rm F} = \frac{1}{2\pi}\left\{\frac{k}{\mu}\right\}^{\frac{1}{2}} . \tag{1}$$

where k is the force constant of the chemical bond between the atoms and μ is the reduced mass of the system (e.g., Banwell & McCash 1994).

For a polyatomic molecule (such as H_2O), there are vibrational modes corresponding to either stretching or bending depending on the change of shape of the molecule. These modes are labelled as ν_N for each of the N degrees of freedom for the molecule, and are observable if the dipole moment of the molecule oscillates during vibration. Overtones occur for non-simple harmonic motion at frequencies near $2\nu_{\rm F}$, $3\nu_{\rm F}$, etc. where $\nu_{\rm F}$ is a fundamental mode. Absorption features are not directly identified with a specific molecule based solely on the wavelength coincidence of a fundamental absorption. Generally, a feature is associated with a certain bond, e.g. the O-H stretch. Laboratory data and observations at wavelengths where corresponding features should appear are necessary to assign a molecule (or a mixture of molecules), such as H_2O or CH_3OH to a particular absorption band.

3. Interstellar Dust

Interstellar dust plays a key role in physical and chemical processes in the interstellar medium. Diffuse ($T \sim 30 - 80\,$K, $n_0 = n_{\rm H} + 2n_{\rm H_2} \sim$

$100 - 800\,\mathrm{cm}^{-3}$) and dense ($T \sim 10\,\mathrm{K}$, $n_0 > 10^2\,\mathrm{cm}^{-3}$) clouds are the main contributors to the mass in the ISM. Grain cores composed of refractory materials such as silicate and amorphous carbon provide nucleation sites for the accumulation of icy mantles in dense molecular clouds (for comprehensive reviews of grain models, see e.g., Dorschner & Henning 1995; Whittet 1992). These icy mantles represent the transient interface between gaseous and solid phases. In the diffuse ISM, molecules in the mantles get desorbed back into the gas phase providing an exchange of material between the dust and the gas. Grains catalyze the production of gas-phase molecules by providing a reservoir to absorb the energy released in exothermic reactions. Mantles are also a controlling influence on the abundances of certain gas-phase species. Both theoretical models and observational evidence suggest the existence of at least two stages of mantle growth in molecular clouds, leading to the occurrence of distinct H_2O-rich (polar) and CO-rich (nonpolar) ice phases (d'Hendecourt, Allamandola, Greenberg 1985; Tielens et al. 1991).

Computational models show that the conversion of atomic to molecular hydrogen occurs within 10^6 years of cloud birth and strongly governs the evolution of grain mantles in dense clouds. At the onset of cloud collapse, when the density is low ($n_0 \sim 10^3\ \mathrm{cm}^{-3}$), the mantle formed will be H_2O-rich due to the high abundance of atomic hydrogen and oxygen in the gas phase and the ease of forming water on the grain surface. A small amount of methane (CH_4) and ammonia (NH_3) is also predicted to form on the mantles. The high probability that atomic oxygen and nitrogen will react with the abundant atomic hydrogen on the grains prevents O_2 and N_2 from forming on the mantles. As cloud collapse progresses and the density increases ($n_0 \sim 10^5\,\mathrm{cm}^{-3}$), a qualitatively different mantle layer forms. The majority of the atomic hydrogen is converted into H_2; production of polar species is inhibited, O_2 and N_2 are produced and CO is a dominant mantle constituent.

Many laboratory groups have studied the effect of energetic processing of interstellar materials (e.g. Greenberg 1963, 1979; Khare et al. 1993; Hagen, Greenberg, & Tielens 1983; d'Hendecourt et al. 1986; Schutte 1988; Allamandola et al. 1988; Ehrenfreund et al. 1991; Bernstein et al. 1995; Gerakines, Schutte, & Ehrenfreund 1996). Several materials have been suggested as candidate carriers of interstellar carbon, as attaching hydrogen atoms create similar $3.4\,\mu\mathrm{m}$ structure in their spectra. These include Hydrogenated Amorphous Carbon (HAC) (c.f. Ogmen & Duley 1988; Adamson, Whittet, & Duley 1990), Quenched Carbonaceous Composite (QCC) (Sakata et al. 1987), residues produced by the irradiation of ices (Schutte 1988; Allamandola, Sandford, & Valero 1988; Sandford et al. 1991), coal (Papoular et al. 1989, 1991), and plasma processing of polycyclic aromatic

hydrocarbons (PAHs) (Lee & Wdowiak 1993; Wdowiak et al. 1995). In many respects these materials are all variations on a theme, and the interstellar medium likely contains many of the proposed materials (see Pendleton 1997, for a review).

Spectra of astrophysical ice analogs can be compared to observational data in order to constrain the types and abundances of mantle constituents. Accurate calculation of the column densities of the carrier of the absorption features depends on an accurate calculation of the band strength (A). This is derived from laboratory spectra by taking the integral of the molecular cross section over the band of interest. The strength of the feature can be deduced from the column density (N) of the absorber in the laboratory

$$A_i = \frac{\int \tau_i(\nu) d\nu}{N} \tag{2}$$

and the depth of band i, τ_i ($I = I_0 \exp^{-\tau}$, where I_0 is the continuum intensity). Tables 1 and 2 contain information on some of the absorption features detected in dense and diffuse clouds, respectively, which are relevant to the discussion presented here.

4. Dense and Diffuse Cloud Chemistry

We will briefly discuss the ice mantle, focusing on the primary H_2O-ice and CO component. Energetic and/or thermal processing of these simple ices may result in the production of organics (such as hydrocarbons and nitriles). Table 1 compares the column density of H_2O and CO, and the optical depths of absorption features at 3.47 μm(due to sp^3-bonded hydrocarbons), 4.62 μm (possibly due to nitriles or isonitriles), and 9.7 μm (silicate) observed towards sources in and behind dense clouds. Table 2 compares optical depths and column densities of aliphatic hydrocarbons observed along several sightlines through the diffuse ISM. The 9.7 μm absorption feature has been identified with silicate material of crystalline structure in the Beta Pictoris disk (Telesco & Knacke 1991; Knacke et al. 1993) and comets (Hanner et al. 1994) and amorphous structure in dense clouds (Butchart & Whittet 1983; Aitken et al. 1988), the diffuse ISM (Mathis 1990), and dust shells of asymptotic giant branch (AGB) stars (e.g., NML Cyg; Justtanont et al. 1996). As silicates are thought to be a likely grain core component in dense molecular clouds (Greenberg 1982), evolution of the 9.7 μm absorption feature from dusty circumstellar shells to the diffuse ISM to dense clouds and comets is an important aspect to be addressed. Presently, we can compare the available observational results of some of these regions, but a major step forward awaits more conclusive results from both observations and laboratory experiments.

TABLE 1. Catalog of Dust Column Densities[a] and Visual Extinctions in Nearby Dark Clouds

Source	A_V (mag.)	N(CO) ($\times 10^{17}$ cm^{-2})	$N(H_2O)$	$\tau_{3.47}$	$\tau_{4.62}$	$\tau_{9.7}$
Elias 3*	8.4[a]	1.73[f]	9.10[i]	...	...	0.19[i]
Elias 13*	11.2[a]	0.84[f]	10.5[i]	< 0.02[l]	...	0.54[i]
Elias 16*	22.3[a]	6.40[f]	25.4[i]	0.03[l]	...	0.66[i]
Tamura 8*	18.5[b]	5.55[f]	24.5[i]	< 0.03[l]	...	...
HL Tau	6–8[c]	< 0.4[g]	14.9[i]	0.04[l]	...	0.71[i]
Elias 1	8–10[d]	0.86[f]	8.93[i]	...	...	...
Elias 18	17–20[d]	2.49[f]	14.0[i]	< 0.03[l]	...	0.43[i]
W33A	145[e]	9.10[h]	> 90[j]	0.15[j]	1.34[n]	7.84[o]
NGC 7538 IRS9	84[e]	12.59[h]	64[j]	0.10[m]	0.31[n]	4.46[o]
GL 2136		1.8	50	...	...	
GL 961 E	39[e]	3.01[h]	40[k]	0.07[m]	0.06[n]	2.11[o]
Mon R2 IRS 2	21[e]	2.73[h]	18[k]	0.05[m]	0.29[n]	2.11[e]

Note. — Asterisk (*) denotes field star located behind the Taurus Dark Cloud.

References. — (a) averaged from Elias 1978 and Smith et al. 1993. (b) Tamura et al. 1987. (c) Cohen & Kuhi 1979; Cohen 1983. (d) Elias 1978. (e) Tielens et al. 1991. (f) Chiar et al. 1995. (g) Whittet et al. 1989. (h) Chiar 1996. (i) Whittet et al. 1988. (j) Allamandola et al. 1992. (k) Smith et al. 1989. (l) Chiar et al. 1996a. (m) Brooke et al. 1996. (n) Pendleton et al. 1997. (o) Willner et al. 1982.

4.1. THE 3 μm SPECTRAL REGION

Icy grains in dense molecular clouds have been detected by the presence of the 3.0 μm absorption band along the line-of-sight towards bright infrared objects in dense molecular clouds (Merrill, Russell, & Soifer 1976; Leger et al. 1976, and many others). This feature is now easily observed toward many sources in and behind dark clouds. Although there are profile differences in terms of the width and shape of the observed 3.0 μm band from source to source, its identification with water ice (as the primary constituent) is well established. In general, the water molecule exhibits an O-H stretching mode at 3.0 μm and an H-O-H bending mode at 6.0 μm (Allamandola & Sandford 1988). Surface reactions involving oxygen atoms are the most likely processes to lead to formation of H_2O-ice on grain mantles (e.g. Jones & Williams 1984). The 3.0 μm feature is observable from ground-based telescopes whereas the 6.0 μm feature requires airborne or space-based observations. The shape of the 3.0 μm profile is a sensitive

function of the temperature and crystallinity as can be seen by comparing the spectra of the field star Elias 16 (seen through dense cloud dust) and the bright protostar BN (embedded in the Orion Molecular Cloud 1; Smith et al. 1989) in Figure 1. Elias 16 is a highly obscured red giant star located by chance alignment behind the Taurus dark cloud. Grain mantles in this sightline are relatively undisturbed by star formation in the cloud. A broad Gaussian profile (like that of Elias 16; Figure 1, top panel) is produced when water-ice is deposited at a temperature much lower than its melting point, which creates an amorphous structure. A fit to the astronomical spectrum is accomplished with a calculated model for small silicate grains coated with H_2O-ice at 23 K (Smith et al. 1989). A sharper profile, such as that observed for the embedded protostar BN (Figure 1, bottom panel), is produced when the ice is warmed: the molecules arrange themselves in a crystalline structure, the most energetically favorable solid. The BN data are fitted with a model based on a mixture of 23, 77, and 150 K (in a ratio of 3.1:1.2:1) ices, showing that there is a range of dust temperatures (as a function of distance from the embedded source) around protostars (Smith et al. 1989). Furthermore, this fit demonstrates that the spectrum is too narrow to be fit with only cold ices and that the warmest grains have temperatures greater than 100 K.

Absorption in excess of what is expected for a pure H_2O-ice profile occurs in the 3 μm spectra of many objects (e.g. Figure 1). The broad, asymmetric 3.0 μm feature is actually a blend of features due to resonances of H_2O-ice and other molecules. Of particular interest is the "long-wavelength wing" between 3.2 μm and 3.6 μm. Among the most likely candidates responsible for the wing absorption are: hydrocarbons, alcohols, O-H stretching resonances in H_2O molecules in ammonium hydrate groups (Smith et al. 1989; 1993), and H_2O_2 (Meyer et al. 1997). We will compare the H_2O-ice and "long-wavelength wing" of dense cloud sources to diffuse ISM observations in §4.3.

4.2. THE 4.67 μm (CO) ABSORPTION

Carbon monoxide is the only molecule abundant enough to collect on the mantle to a significant degree by direct condensation of pre-existing molecules in the gas phase (Duley 1974). Duley was the first to discuss the possibility that CO is a major mantle constituent of interstellar grains with a characteristic frequency that is detectable in the infrared. Solid CO exhibits the C≡O stretch at 4.67 μm; this absorption feature is observed in both the intracloud medium and in the dust around embedded objects. Lacy et al. (1984) were the first to detect the 4.67 μm CO stretch feature toward several embedded objects. Whittet, McFadzean, & Longmore (1985)

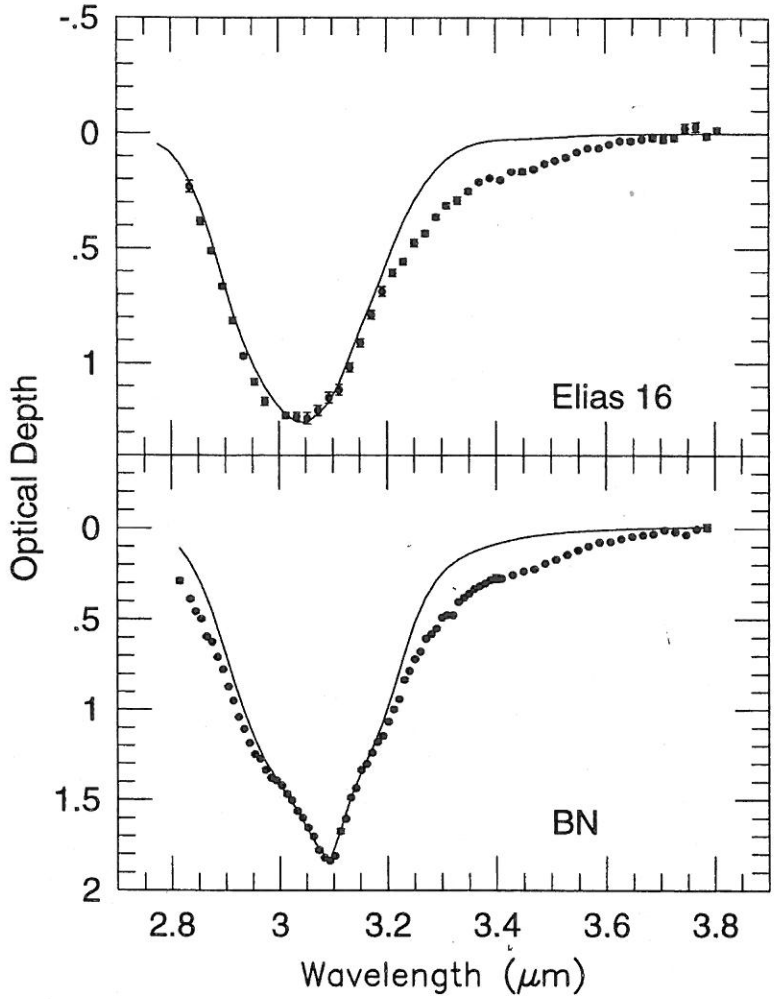

Figure 1. [*Top*] H_2O-ice spectrum of the field star Elias 16, which samples the quiescent cloud medium in Taurus. The points are the astronomical data and the solid line is the calculated model spectrum for pure H_2O-ice mantles at 23 K. [*Bottom*] Spectrum of protostar BN, which samples warm conditions around an embedded object. The solid line is the calculated spectrum for a mixture of pure H_2O-ice mantles at temperatures between 23 – 150 K. (Figure from Smith et al. 1989).

were the first to detect solid CO absorption in a dark cloud environment towards background stars. Since then, there have been many studies of solid CO in molecular clouds.

Laboratory studies have shown that the solid CO absorption profile is affected by a number of factors such as the composition of the host matrix, and its thermal history (e.g. Sandford et al. 1988; Palumbo & Strazzulla 1993). Recent studies of solid CO absorption (Tielens et al. 1991; Kerr et al. 1991, 1993; Chiar et al. 1995) show that the feature consists of two overlapping components, (1) a broad, shallow component (at $\sim 4.682\,\mu$m) attributable to CO in a matrix dominated by H_2O, and (2) a narrow component (at $\sim 4.673\,\mu$m) produced by either pure CO, CO in a nonpolar

matrix (such as CO mixed with CO_2, N_2 or O_2), or CO in a weakly polar matrix (i.e., CO mixed with a small amount of H_2O). These components are referred to as the polar and nonpolar components, respectively. In most cases, the nonpolar component dominates the feature. While the two components are blended with each other, they are indicative of the polar and nonpolar phases of mantle growth (see Chiar 1997 for a recent review). The CO profiles observed in different clouds have been compared with laboratory data for both the broad and narrow components in an effort to account for their existence in terms of the chemical and physical state of the cloud (e.g., Tielens et al. 1991; Kerr et al. 1991, 1993; Chiar et al. 1995; Chiar 1996).

4.3. THE 3.4 μm HYDROCARBON REGION

4.3.1. *Diffuse Interstellar Medium*

Along the sight-line toward the heavily obscured Galactic Center, the total visual extinction, A_V, has been estimated to be ≈ 31 mag (Becklin et al. 1978; Henry et al. 1984; Sellgren et al. 1987 and others). While there are indications of some dense molecular cloud absorption along this sightline (Whittet & Tielens 1997), arguments have been made that the majority of 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 μm ice band varies from source to source in the Galactic Center region, the shape of the 3.4 μm 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 μm 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 2, 2.8 – 3.8 μm observations toward the Galactic Center show that these spectra contain a broad ice feature at 3.0 μm (3300 cm^{-1}) and a complex hydrocarbon feature near 3.4 μm (2950 cm^{-1}). Absorption features in the 2.8 –3.70 μm (3570–2700 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 μm and 3.4 μm respectively, within cosmic abundance constraints. The diffuse interstellar medium observations indicate the presence of hydrocarbon features which extend from about 3.33 μm (3000 cm^{-1}) to 3.57 μm (2800 cm^{-1}) with sub-features near 3.38, 3.42, and 3.48 μm (2955, 2925, and 2870 cm^{-1}). The positions of the first of these sub-features are characteristic of symmetric and asymmetric C-H stretching

TABLE 2. Hydrogen, Carbon, $-CH_3$, and CH_2 Column Densities (in units of cm^{-2}), and the Percent of Cosmic Carbon in the Aliphatic Hydrocarbon Component of the Diffuse Medium Dust

Object	A_V	$\tau^a_{9.7}$	$N(H)^b$ ($\times 10^{22}$)	$N(C)^b$ ($\times 10^{18}$)	$N(CH_3)$ ($\times 10^{16}$)	$N(CH_2)$ ($\times 10^{16}$)	Percentage Carbon^c
GC IRS 7	31	3.6±0.4	5.9	22	29	57	3.9
GC IRS 6E	31	3.6±0.4	5.9	22	31	62	4.2
GC IRS3	31	36.6±0.4	5.9	22	35	71	4.9
HD 229059	5.3	...	1.0	3.7	3.5	8.5	3.2
HD 194279	3.9	...	0.74	2.7	2.0	5.0	2.6
BD+40 4220	6.2	...	1.2	4.4	4.0	7.5	2.6
CygOB2#12	10	0.58±0.1	1.9	7.0	6.0	13	2.7
AFGL 2104	12.0	0.64 ± 0.05	2.3	8.4	5.6	13	2.2
AS 320	5.2	0.26	0.99	3.7	2.7	6	2.4
AFGL 2179	12.8	0.65 ± 0.05	2.4	9.0	7.0	16	2.6
Ve 2-45	6.5	0.36 ± 0.05	1.2	4.6	4.6	6.0	2.2

[a]Silicate optical depths were taken from Roche & Aitken 1984, 1985.

[b]$N(H)$ and $N(C)$ were calculated assuming $N(H) = 1.9 \times 10^{21} A_V$ (Bohlin et al. 1978) and $N(C)/N(H) = 3.7 \times 10^{-4}$ (Allen 1973).

[c]This is a lower limit for the percent of cosmic carbon which is tied up in the $-CH_3$ and $-CH_2$ groups combined, $[N(CH_3) + N(CH_2)]/N(C)$.

frequencies of -CH_3 (methyl) and -CH_2- (methylene) groups in saturated aliphatic hydrocarbons (molecules with the formula C_nH_{2n+2}). The relative strengths of these sub-features indicate that the average -CH_2-/-CH_3 ratio of interstellar hydrocarbons in the diffuse ISM is about 2.5 (Sandford et al. 1991).

Observations of the 3.4 μm feature along sightlines which have diffuse interstellar extinction values which are substantially lower than that of the Galactic Center are shown in Figure 3. 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 3 are the resultant optical depth plots, which are derived from the flux data similar to that shown in Figure 2 (see Sandford et al. 1991 and Pendleton et al. 1994 for a discussion of the choices for a continuum baseline to the flux data).

Recent detection of the 3.4 μm absorption band complex in other galaxies (Bridger et al. 1993; Wright et al. 1996) has revealed the same substructure and relative strength of the features as found in the spectra of the diffuse ISM in our own galaxy. Figure 4 compares the 3.4 μm hydrocarbon absorption feature in our own galaxy to that observed in a distant galaxy (the embedded Seyfert galaxy, IRAS 08572+3915). The surprising strength of the overall band complex in the dusty torus of the extragalactic source indicates that dust in other galaxies may provide valuable spectral

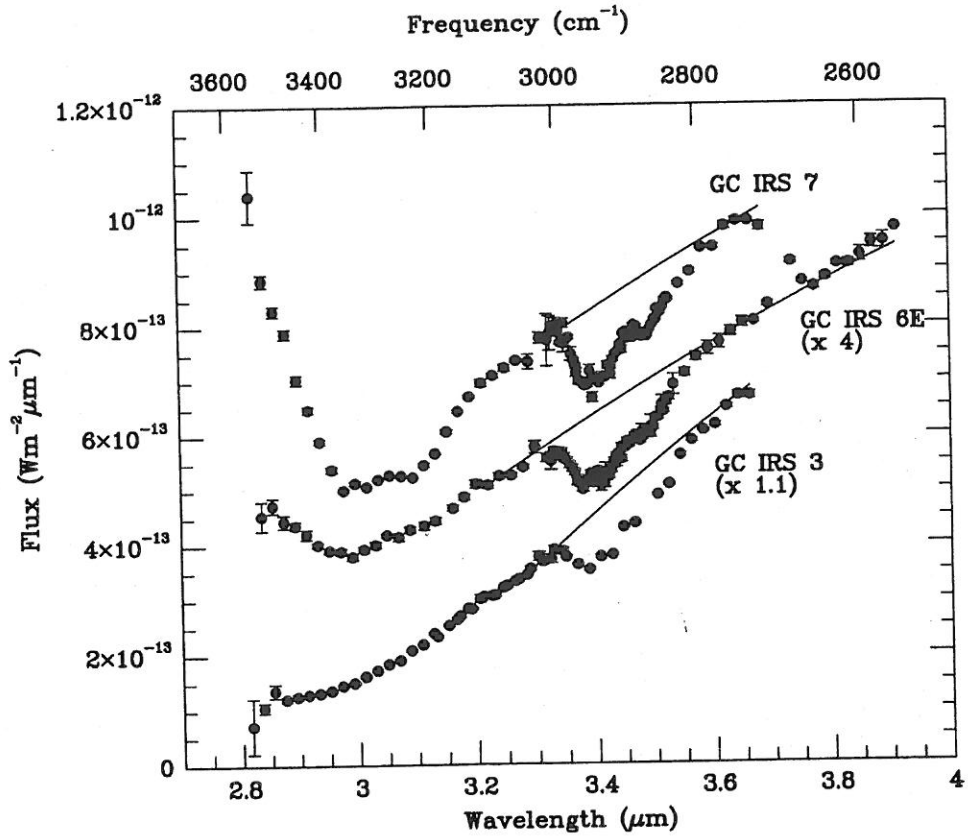

Figure 2. The 2.8 - 4.0 μm (3570 - 2500 cm^{-1}) fluxed spectra of sight lines towards Galactic Center sources IRS 7, IRS 6E, and IRS 3. The low resolution data have a resolution of 0.018 μm per detector $[\lambda/\Delta\lambda]$ = 155 - 220 over the 2.80 - 4.0 μm (3570 - 2500 cm^{-1}) range. High resolution 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.

profile information despite the great distances to the illuminating source. In addition, the spectral features may appear at wavelengths that are red-shifted into regions that are more accessible from the ground. Figure 4 also compares the diffuse ISM and extragalactic features to organics found in the Murchison meteorite. As first pointed out by Ehrenfreund et al. (1991), there is a strong similarity between the 3.4 μm feature seen in the Orgueil and Murchison carbonaceous chondrites and the diffuse ISM spectra. In the meteorite, the aliphatics that produce this feature are primarily cyclic aliphatics (Cronin and Pizzarello 1990). Observationally, we cannot distinguish between cyclic or chain-like aliphatic (CH_2 and CH_3) groups at this time, but it will be interesting to investigate the nature of the interstellar aliphatics in light of the meteoritic results. At present, we can simply note that the comparison between the three spectra (the diffuse ISM in our galaxy, the dusty region in the distant galaxy, and the Murchison mete-

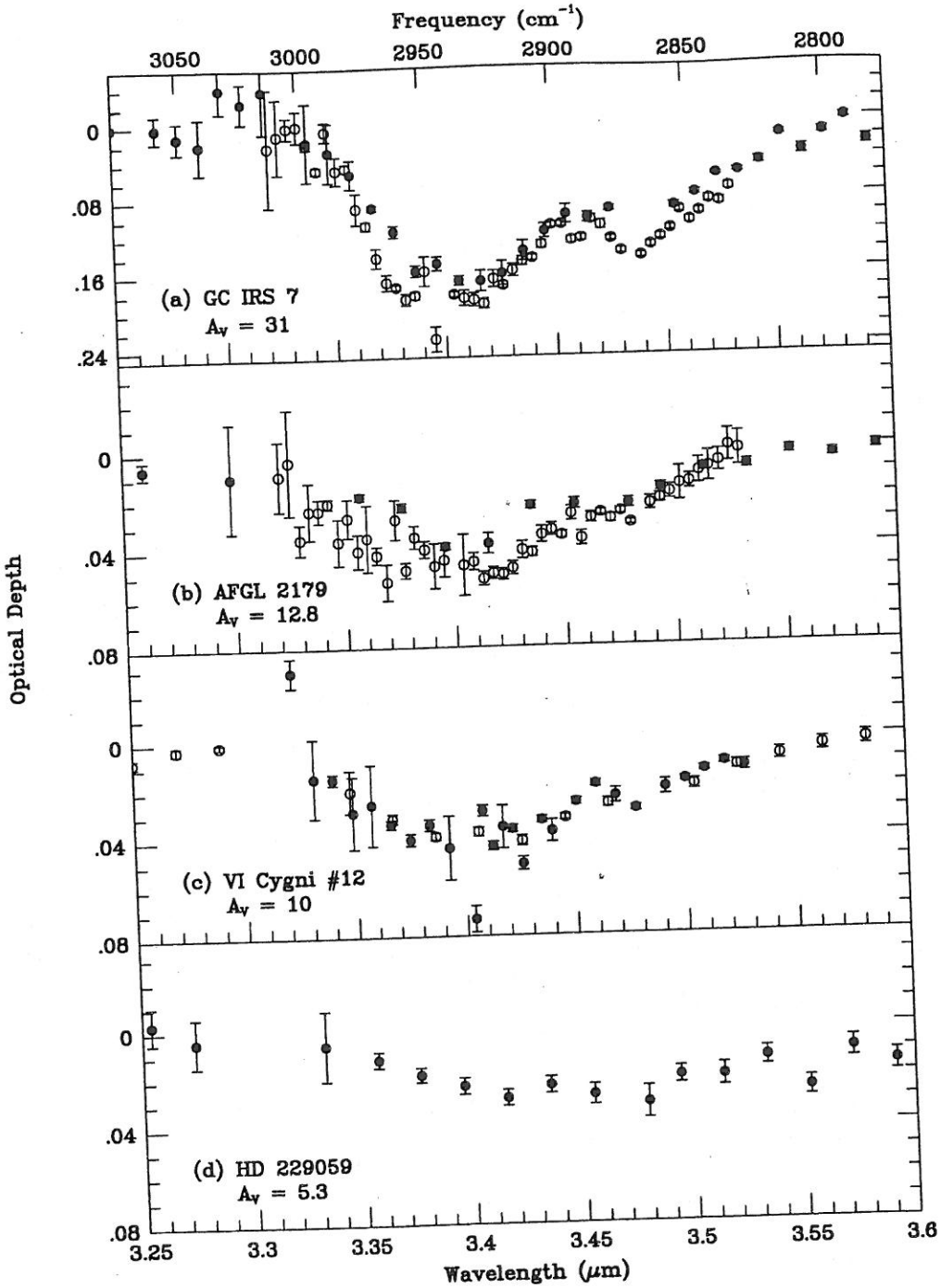

Figure 3. Optical depth plots from 3.25 - 3.6 μm (3077-2778 cm^{-1}) for (a) GC IRS 7, (b) the WC star AFGL 2179, (c) the supergiants Cyg OB2 #12, and (d) HD 229059. High resolution data are displayed as open points; low resolution data are displayed as solid points (taken from Pendleton et al. 1994).

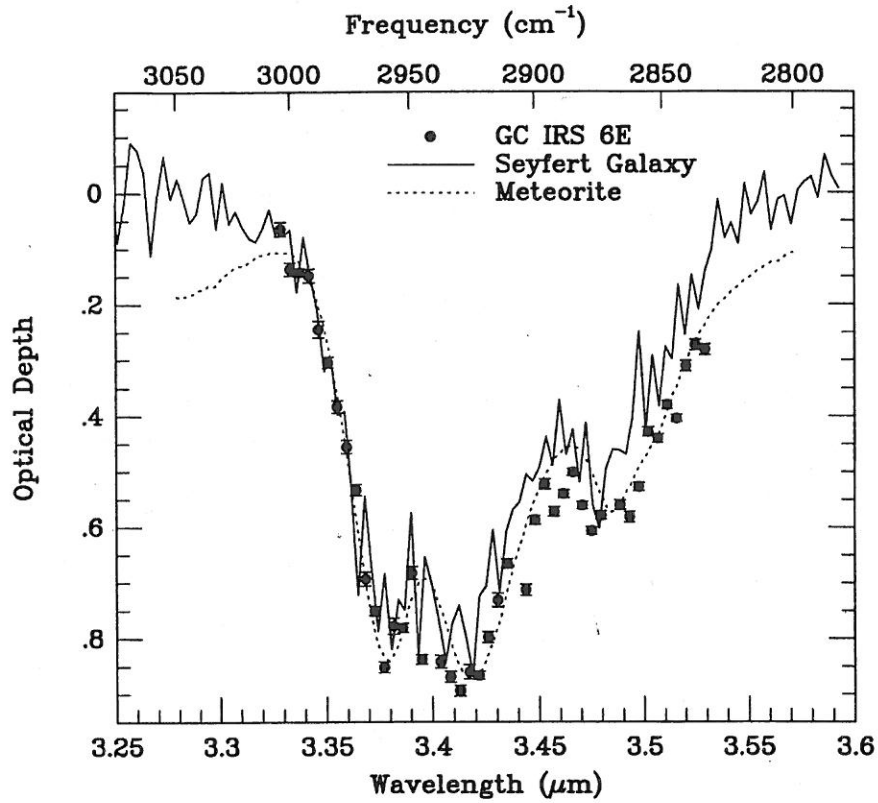

Figure 4. A comparison of the optical depth spectrum of the Galactic Center source IRS 6E (solid points), the sublimate from the acid-insoluble component of the Murchison meteorite (dotted line; from DeVries et al. 1993), and the redshift corrected 3.4 μm feature in the embedded Seyfert Galaxy IRAS 08572+3915 (solid line; taken from Wright et al. 1996).

orite) is remarkable. The spectral features shown in Figure 4 are different than the 3.4 μm feature observed in dense clouds; we discuss the differences in the following section.

The 3.28 μm Aromatic Hydrocarbon Region: It is important to point out the relationship between the aliphatic hydrocarbon features and the polycyclic aromatic hydrocarbons (PAHs; Leger & Puget 1984; Allamandola et al. 1985, 1989; Joblin, Leger, & Martin 1992). While the aromatic hydrocarbons likely coexist in the diffuse ISM where the CH_2 and CH_3 group (aliphatic) hydrocarbons are found, and while the C-H stretching absorption feature of aromatic hydrocarbons falls near 3.28 μm (3050 cm^{-1}), only a weak aromatic feature is expected compared to the aliphatic bands, since the aromatics contain fewer hydrogen atoms per carbon atom (H/C$<$ 1) than do aliphatics (H/C$>$ 2), making the intrinsic strength of the aromatic C-H stretching band 2-3 times lower than its aliphatic counterpart. A suggestive detection of the 3.28 μm feature in absorption towards the Galactic center has been reported (Pendleton et al. 1994). They concluded that the aromatic abundance fraction could be as large as $\sim$10% of the C along

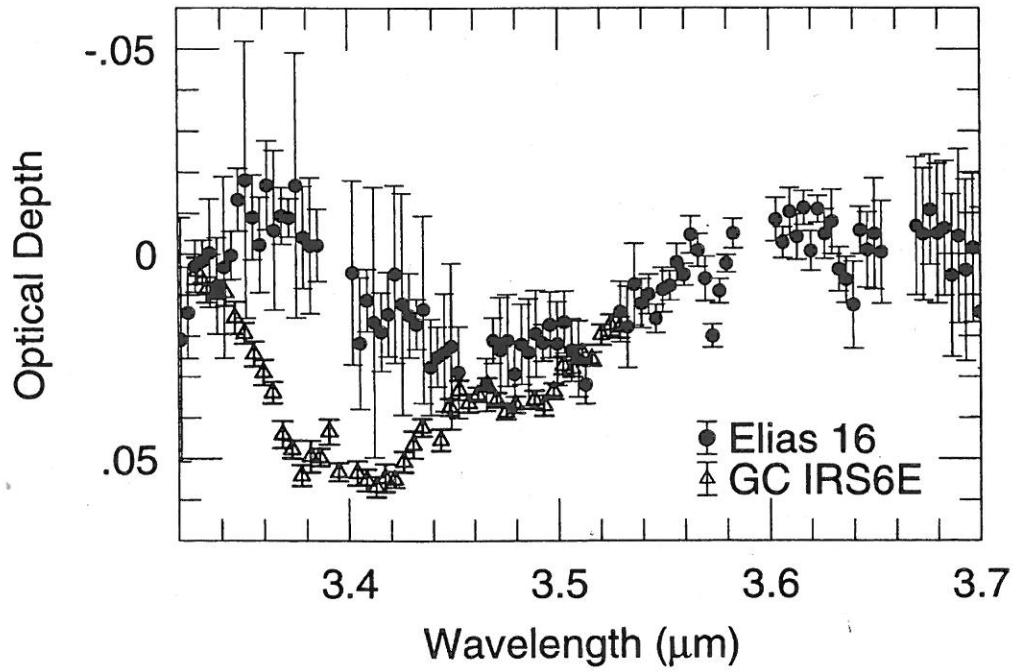

Figure 5. The 3.4 μm absorption feature towards the Galactic Center source GC IRS6E (from Pendleton et al. 1994; triangles) and Elias 16 (Chiar et al. 1996; circles) scaled to the depth of the 3.47 μm feature in Elias 16.

the line-of-sight to the Galactic Center. This tentative absorption feature could be due to the absorption counterpart of the infrared emission and/or aromatic hydrocarbon dust grains which are too large to emit in the near IR (cf. d'Hendecourt, this volume; Geballe 1997). In dense clouds, evidence for an absorption feature near 3.25 μm (3080 cm^{-1}) which may be due to aromatic material has been reported (Sellgren et al. 1994). 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 (3080 – 3050 cm^{-1}) region. Given the large potential abundance of aromatics implied by these observations, it is clearly important to resolve the presence of the 3.25 μm – 3.28 μm absorption feature in diffuse and dense cloud sources.

4.3.2. *Dense Clouds*

In dense molecular clouds, absorption in the 2.8 μm – 3.8 μm region is dominated by the H_2O-ice band near 3.0 μm as discussed above. Additional absorption between 3.2 and 3.6 μm, termed the "long wavelength wing," can be seen in Figure 1. Figure 5 shows the spectra of the Galactic Center source IRS6E (Pendleton et al. 1994), which samples diffuse ISM dust, and

Elias 16 (Chiar et al. 1996), which samples dense molecular cloud dust. The structure near 3.4 μm seen in the diffuse ISM profiles is apparently missing in dense cloud spectra. Thus far, none of the dense cloud detections have shown subfeatures like those in the diffuse ISM spectra. Smith et al. (1993) discussed the most likely scenarios for the absence of the aliphatic sub-structure in the dense cloud spectra. Among the possibilities that were ruled out was the idea that the aliphatic hydrocarbons are part of the grain core which becomes mantled with ice in the dense cloud. Baratta & Strazzulla (1990) have investigated this point, and find that even substantially thick ice layers atop a hydrocarbon residue still reveal pronounced sub-structure near 3.4 μm in the laboratory spectra.

Further evidence that the 3.4 μm wing in dense cloud spectra arises from material in the grain mantle, rather than the core, comes from correlation studies comparing the optical depth of the "long-wavelength wing" with other dense cloud absorption features. Allamandola et al. (1992) detected a broad band at 3.47 μm in luminous protostellar objects, which they attributed to sp^3-bonded hydrocarbon material. This structural difference means that in these materials, hydrogen is bonded to a carbon atom which is bonded to three other carbons. This differs significantly from the structure of the diffuse ISM 3.4 μm feature where a carbon atom is attached to either two or three hydrogen atoms (i.e., CH_2 or CH_3, respectively). The dense cloud 3.47 μm feature has since been detected in other protostellar sources (Sellgren et al. 1994; Brooke et al. 1996), in low-mass embedded objects (HL Tau) and in the quiescent cloud medium in the Taurus dark cloud (Elias 16; Chiar et al. 1996). There is little correlation between the 3.47 μm feature and the 9.7 μm silicate feature; the latter is known to be associated with the grain core. In contrast, the optical depths of the 3.47 μm feature and 3.0 μm H_2O-ice feature are strongly correlated (Brooke et al. 1996; Chiar et al. 1996). This strong correlation supports the conclusion that the carrier of the 3.47 μm feature resides in the mantle material, because the 3.0 μm water ice feature is clearly associated with grain mantles. Such a correlation also suggests that the carrier of the 3.47 μm feature does not exist in the core (or an inner mantle layer) beneath the H_2O-ice layer. The conclusion that seems most apparent from observations and laboratory experiments is 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.

4.4. THE 4.62 μm (X–C≡N?) BAND

Nitriles (compounds containing the –C≡N group) play a vital role in the formation of prebiotic molecules (Matthews 1992). The discovery of an

interstellar absorption feature near 4.62 μm has prompted laboratory comparisons of nitriles and isonitriles (such as CH_3NC) to the interstellar observations. This unidentified feature, commonly referred to as the X−C≡N) band, is seen in the spectra of several young stellar objects (e.g. Figure 6; see also Lacy et al. 1984, Tegler et al. 1993; 1995, Weintraub et al. 1994, Pendleton, Tielens, & Tokunaga 1997). Infrared laboratory spectra of ultraviolet photolyzed interstellar analog ice mixtures show a prominent absorption feature at 4.62 μm (2160 cm^{-1}). See Pendleton et al. (1997) for a review of possible identifications of the 4.62 μm feature. Although the identification of this feature is by no means secure, it is interesting to contemplate the implications of an identification of the 4.62 μm absorption band with the product of some type of interstellar ice processing inside dense molecular clouds. Laboratory studies have shown that nitriles produced in the residues of UV processed ice mixtures survive temperature increases up to about 200K. While this component is not quite as hardy as the aliphatic hydrocarbon component produced under similar conditions, the survivability of the laboratory band produced near 4.62 μm is consistent with the environment such material would be exposed to in the diffuse ISM. Therefore, it is difficult to understand why the 4.62 μm band is not seen in any of the diffuse ISM observations. Presently, none of the possible identifications for this band can adequately explain this discrepancy, and we are missing another piece of the puzzle of the interstellar dust picture.

The 4.62 μm band detections within dense clouds have thus far been limited to bright, embedded protostellar sources. The lack of detection in the quiescent cloud medium, as evidenced by observations of a bright background field star, Elias 16, seen through large amounts of dense cloud dust, is taken as evidence that ice in the vicinity of embedded sources contains the carrier of the 4.62 μm band whereas the general intracloud material does not (Tegler et al. 1995). If identification of the 4.62 μm band with an a −C≡N molecule is confirmed, then the possible connection to primitive Solar System bodies may become clearer. Detections of the −C≡N stretch first overtone, at 2.2 μm, in some Solar System objects, have been made by several authors (e.g. Jewitt et al. 1982; Bell et al. 1985; Cruikshank et al. 1991). It is important to determine whether these same organic molecules are also present in dust grains in the ISM, as these grains may accrete to form cometary bodies, and comets may have delivered vast quantities of organic materials to the early Earth.

5. Summary

The incorporation of organic solids into planetesimals is of prime importance in the evaluation of the materials that were likely delivered to the

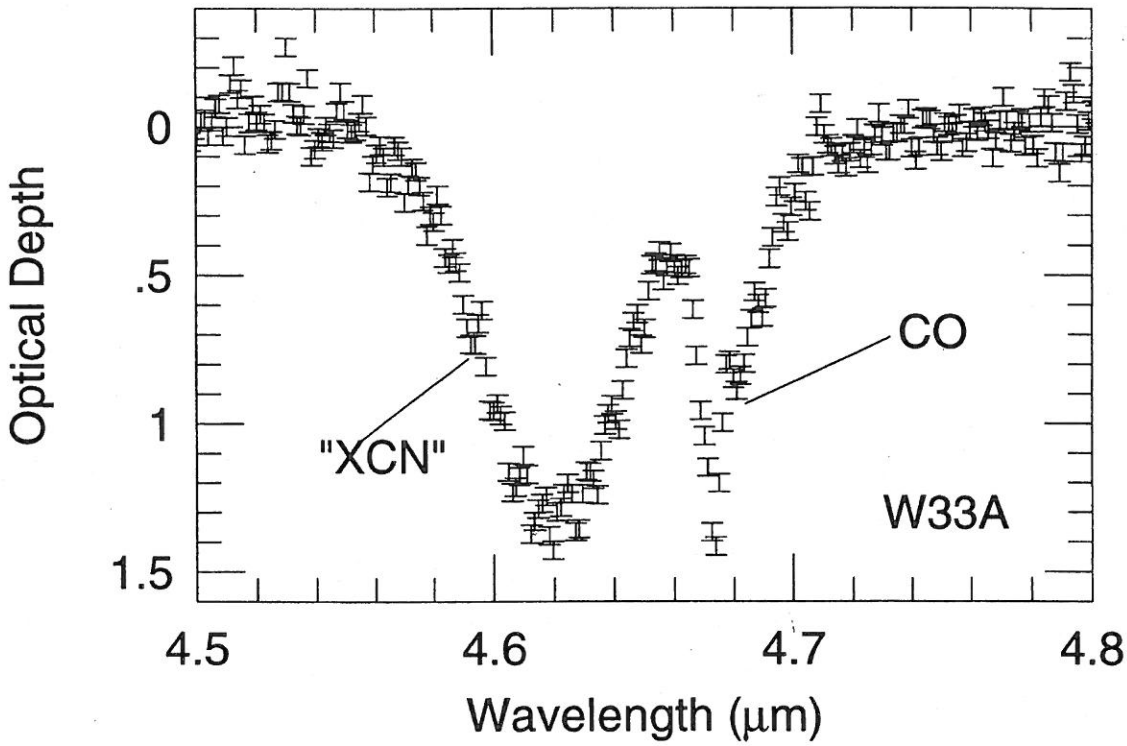

Figure 6. The 4.5-4.8 μm spectrum of the young stellar object, W33A. The feature at 4.62 μm and the CO feature at 4.67 μm are shown.

early Earth by comets and asteroids, as these building blocks may have played an important role in the emergence of life on our planet. Planetesimals formed from the material available in the solar nebula, which originated in the interstellar medium. Understanding the production and distribution of organic solids in the ISM, therefore, aids in our understanding of the initial composition of those bodies that would later bombard planets with ices and organic material. The recent discovery of organic solid-state material in distant galaxies, as evidenced by detection of 3.4 μm hydrocarbon absorption (§4.3) points out the ubiquitous nature of the carrier, which has now been detected along more than a dozen lines-of-sight through the diffuse interstellar medium in our Galaxy. Comparisons of the diffuse interstellar medium 3.4 μm absorption feature with extracts from carbonaceous meteorites have shown a remarkable similarity in profile and relative strength among the sub-features which arise from CH_2 and CH_3 groups. The evolution of dust grains and, in particular, the evolution of the organic component of the dust, is central to the issue of the interstellar material incorporated in primitive Solar System bodies. Processing of icy grain mantles in dense molecular clouds and the cycling of the refractory dust components between the dense and diffuse ISM are key aspects of the inventory of material during planetesimal formation. Temperatures in the dense molecular cloud regions are sufficiently cold, and the grains

are well enough shielded from the harsh environment outside the cloud, that icy mantles form easily on grain cores. The accretion of ice mantles on dust grains in dense molecular clouds is confirmed by the detection of the 3.0 μm absorption band, attributed to H_2O and the 4.67 μm absorption band, attributed to solid CO, in many dense molecular clouds.

Laboratory studies have shown that energetic processing of simple ice mixtures, including H_2O and CO, reproduce many of the spectral features observed in dense molecular clouds. In the laboratory, warm-up of interstellar ice analogs reveals the presence of an organic refractory residue which remains after the volatile ice component has been removed. If the initial laboratory mixture includes some type of nitrogen-bearing component, refractory residues form which exhibit an absorption band in the 4.62 μm region, a feature which is seen in observations of embedded protostellar objects (Lacy et al. 1984; Tegler et al. 1993, 1995) . This interstellar feature has been named the "X-CN" band, because of the connection to a nitrogen bearing component. The 3.4 μm aliphatic hydrocarbon feature is also produced in the laboratory through UV photolysis of ices. If these interstellar bands (at 4.62 and 3.4 μm) are produced through ultraviolet photolysis of ices, the carrier is a hardy, refractory material that would be expected to survive long after the volatile materials are gone. Upon the break-up of a star-forming cloud, surviving refractory material could become incorporated into the surrounding diffuse ISM. Although this theory is supported by observations of the 3.4 μm absorption feature in the diffuse medium, it is refuted by the absence of this feature in dense clouds and the absence of the 4.62 μm feature in the diffuse ISM. If these two features are produced via energetic processing of icy grain mantles, as the laboratory studies suggest, then we might expect to see both features in the spectra of dense and diffuse cloud objects. The fact that we do not presents a problem in our current understanding of the evolution of interstellar dust.

Studies presented in this review suggests that the interstellar hydrocarbon feature may be primarily produced via an alternative mechanism, such as in the outflow of carbon stars in the diffuse ISM itself. Another interesting point is that searches for the 4.62 μm absorption band have so far revealed the feature only in spectra of heavily embedded sources which are associated with the molecular cloud (§4.4). Spectra of background field stars seen through equivalent amounts of dense cloud dust do not reveal the 4.62 μm absorption band. This suggests that the carrier is not interspersed throughout the dense cloud, but is localized near the embedded object. A more thorough comparison of embedded and background objects must be made in order to confirm this very interesting result, but taken at face value it suggests that close proximity to the forming star is a requirement for production of the 4.62 μm band. If the identification of the band

as a nitrile or isonitrile is confirmed, then the 4.62 μm absorption band is another aspect of the organic component of interstellar dust that must be better understood in order to evaluate the material that went into the early solar nebula and planetesimals.

Finally, the remarkable comparison of the diffuse ISM feature to that found in the Murchison meteorite underscores the need to fully understand the nature and evolution of interstellar organic solids. Is the similarity an indicator of unaltered interstellar organics in the meteorite? We must know where these materials are made, how they are created, how they are distributed throughout the interstellar medium, and what type of processing they have endured. Only then will we have a chance to learn about the true availability of these organic constituents for incorporation into planetary systems during the star and planet formation processes.

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