LECTURE 8

Organics in the ISM: Where Do They Come from?

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Abstract. Spectral comparisions of the 3.4 and 4.62 μm interstellar absorption bands to laboratory spectra of processed ices imply that interstellar organic signatures result from energetic processing of ices on grain mantles in dense molecular clouds. However, in the case of the 3.4 μm aliphatic hydrocarbon band, the interstellar feature has only been observed in the diffuse interstellar medium where no ices exist. The absence of the 3.4 μm band in any dense cloud spectrum observed to date, and the detection of the band in the outflow of an evolved carbon star, suggest the production mechanism for this particular organic species may not involve ice processing after all. The widespread distribution of the 3.4 μm carrier and the striking similarity of the interstellar band to that found in carbonaceous meteorites emphasizes the need to understand the pathway by which interstellar organics evolve. Inside dense clouds, the 4.62 μm absorption feature is seen towards embedded protostellar objects. The carrier of this band is likely the result of interstellar ice processing, and a carbon-nitrogen bearing species has been implicated. However, at least two types of energetic processing (UV photolysis and ion bombardment) can produce spectral features which similarly match the interstellar observations, so at this time the production mechanism is unclear. To produce the 4.62 μm band in the laboratory, the initial starting mixture can contain nitrogen in several forms, but if the nitrogen precursor molecule is in the form of solid state N_2, then only the ion bombardment method can break the strong bond, allowing the nitrogen

to interact with other species. The 3.4 and 4.62 μm absorption bands may be the two best indicators of the solid state organic component of the interstellar medium. Therefore, understanding the formation, evolution, and distribution of these components will help to trace the organic material that is available for incorporation into planetary systems.

1. INTRODUCTION

Until relatively recently, crucial portions of the infrared spectrum were unavailable to astronomical spectroscopists due to atmospheric limitations which hinder ground-based efforts, so despite the accumulating body of knowledge, gaps in the spectral observations have remained. The $2 - 30$ μm wavelength region is critically important for the study of organic solids and ices, and with the former Kuiper Airborne Observatory and the Infrared Space Observatory (ISO), the major gaps in the observational picture are now being filled in. The combination of moderate resolution ground-based spectroscopy with the space and airborne observations is providing a more complete inventory of the dust constituents, as well as information regarding the physical location of dust.

Stars and planetary systems form only inside the high density, low temperature environment of dense molecular clouds, therefore the composition of interstellar ices in these clouds and the effects of energetic processing on those ices is important in assessing the inventory of organic material available for incorporation into forming planetary systems. Dust in the diffuse interstellar medium (ISM) that surrounds dense clouds, must also contribute to the material found in dense regions, because new generations of dense clouds form out of swept-up diffuse ISM dust (*e.g.* [1]).

Recent observations from the Short Wavelength Spectrometer [2] on ISO [3] have provided the necessary overview of the entire near and mid-infrared, and as a consequence most of the features due to interstellar ices in the spectrum of a typical embedded protostar have now been identified (*e.g.* [4] and the contributions of Dartois and Schutte in this volume). Details concerning the processing of these ices are not so clear, however, and two absorption bands in particular are serving as probes of the dense and diffuse cloud environments. These two features, the 3.4 and 4.62 μm bands, fall in wavelength regions that can be observed from the ground. Moderate resolution, high signal-to-noise ground based data have proven to be highly complimentary to the essential information provided by ISO.

In this paper, the organic refractory components of the interstellar medium, best revealed through the 3.4 and 4.62 μm solid state absorption features, are discussed as possible tracers of the formation sites and evolution of interstellar dust. These features have been detected in diffuse and dense interstellar clouds, respectively. This paper presents the current state of the field and the puzzling questions that are apparent from the data.

2.   THE 3.4 μm BAND

Along lines-of-sight through the diffuse interstellar medium towards bright background sources, a distinct signature of hydrocarbon absorption has been detected near 3.4 μm. Spectroscopy of the 3.4 μm wavelength region reveals sub-features at 3.385, 3.420 and 3.485 μm (2955, 2925, and 2870 cm^{-1}). The positions of the 2955 and 2925 cm^{-1} sub-features are characteristic of the symmetric C–H stretching frequencies of –CH$_3$ (methyl) and –CH$_2$– (methylene) groups in saturated aliphatic hydrocarbons and the band at 2870 cm^{-1} is characteristic of the asymmetric C–H stretching vibrations of these same functional groups when perturbed by other chemical groups [5]. These distinct sub-features have now been detected along nearly a dozen different sightlines through our galaxy [6] as well as in the spectra of dust embedded Seyfert galaxies [7–9].

Early detections of the diffuse ISM 3.4 μm band [10–14] focused on the line-of-sight towards the galactic center, where the dust extinction is high ($A_v \approx 31$ magnitudes) and the background sources are bright in the near-infrared. Lequeux and Jourdain de Muizon [15] detected the same absorption band towards a nearby, evolved carbon star, CRL 618, and additional lines-of-sight through the galaxy later revealed the presence of the same carrier in the diffuse ISM [5, 6]. There is, however, a distinct absence of the 3.4 μm band in the spectra of dense molecular cloud dust [16, 17]. The difference in the spectra of the refractory component of dense and diffuse cloud dust was first pointed out by Allamandola *et al.* [18, 19], and the discrepancy has raised serious questions about the formation site and evolutionary history of this hardy, refractory component which is so widespread throughout our own galaxy and other galaxies. The remarkable similarity of the 3.4 μm band seen in the diffuse interstellar dust to the organic refractory material found in carbonaceous meteorites [6, 20] suggest some exchange between the dense and the diffuse medium, since meteorite parent bodies form around stars which arise from dense cloud regions.

Figure 1 displays ground-based observations of the interstellar 3.4 μm absorption band obtained at the NASA Infrared Telescope Facility and the United Kingdom Infrared Telescope. The sub-features of CH$_2$ and CH$_3$ groups are seen in absorption in the dust in our galaxy and the dust from the luminous IRAS galaxy 08572+3915 [8]. The extragalactic dust feature has been blue-shifted to account for the distance of the galaxy ($z = 0.05$). The carbonaceous material in the diffuse ISM has an average –CH$_2$–/–CH$_3$ ratio of $2.0 - 2.5$ and likely contains moderate length aliphatic chains, such as –CH$_2$–CH$_2$–CH$_3$ and –CH$_2$–CH$_2$–CH$_2$–CH$_3$, associated with electronegative chemical groups, *i.e.*, moieties like –OH, –C$\equiv$N, and aromatics [5,6]. These basic organic constituents appear to be distributed throughout galactic and extragalactic dust [7, 8, 21]. The close match in position, strength, and profile between the galactic and extragalactic dust features suggests this type of chemical arrangement may be quite common.
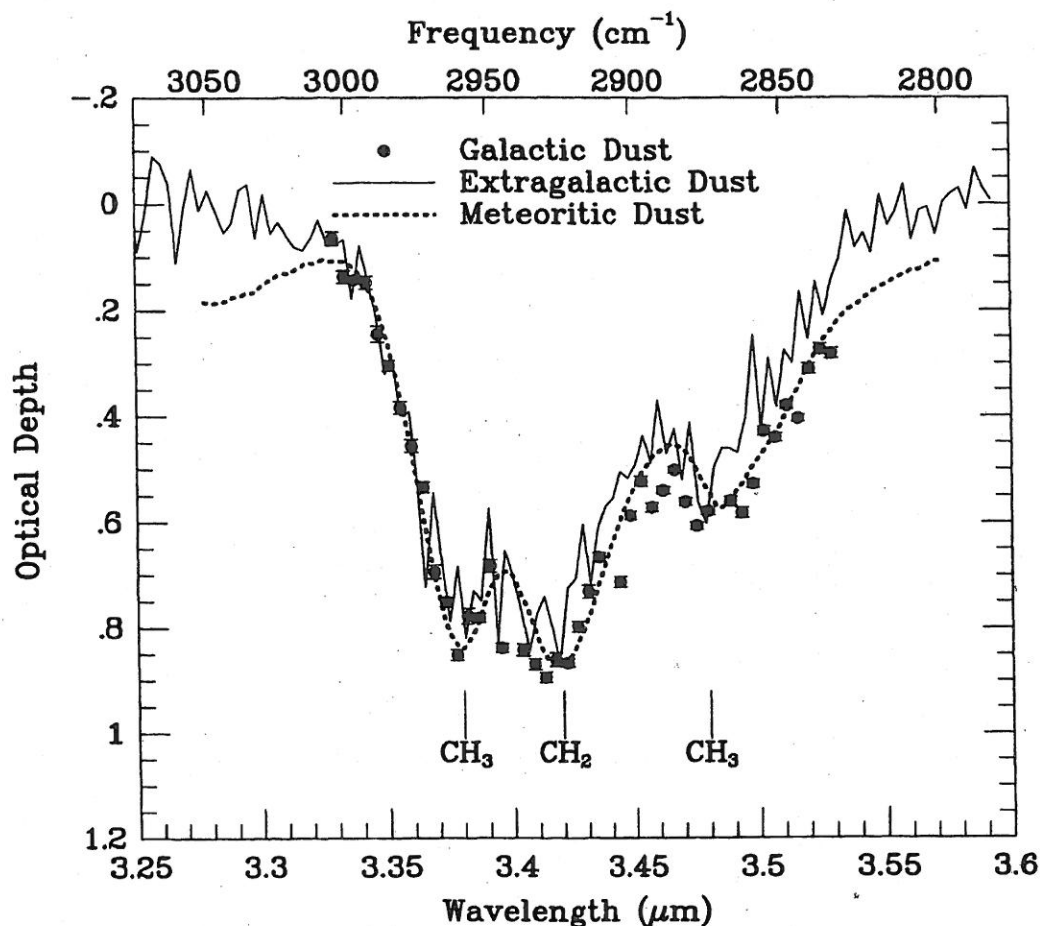
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Fig. 1. — A comparison of the aliphatic hydrocarbon feature seen in the diffuse interstellar medium in our galaxy (points), the Murchison meteorite (dashed line) and the dust of a distant galaxy (solid line; redshift of the galaxy has been accounted for). Figure taken from [9]. A similar feature has now been detected in 4 out of 13 galaxies [8].

Figure 1 also displays the infrared spectrum taken from the volatile component sublimed off of the acid insoluble residue of the Murchison meteorite (Murchison data from [22]). Spectral similarity between the light hydrocarbons of carbonaceous meteorites and the diffuse galactic dust [6, 20] have suggested that these light hydrocarbons are somehow preserved in the parent body of the meteorite.

The role of ultraviolet photolysis is one of the key questions in the chemistry of interstellar ices. Theoretical and experimental studies have long suggested that FUV photolysis of interstellar ices is important for their composition [23–31]. In the laboratory, the ultra-violet photolysis and subsequent warm-up of interstellar ice analogs produces a hardy, organic refractory residue whose spectrum is similar to the feature observed in the diffuse ISM [5]. A reasonable initial explanation for the production of the interstellar 3.4 μm band was that organic refractory material, processed in the dense
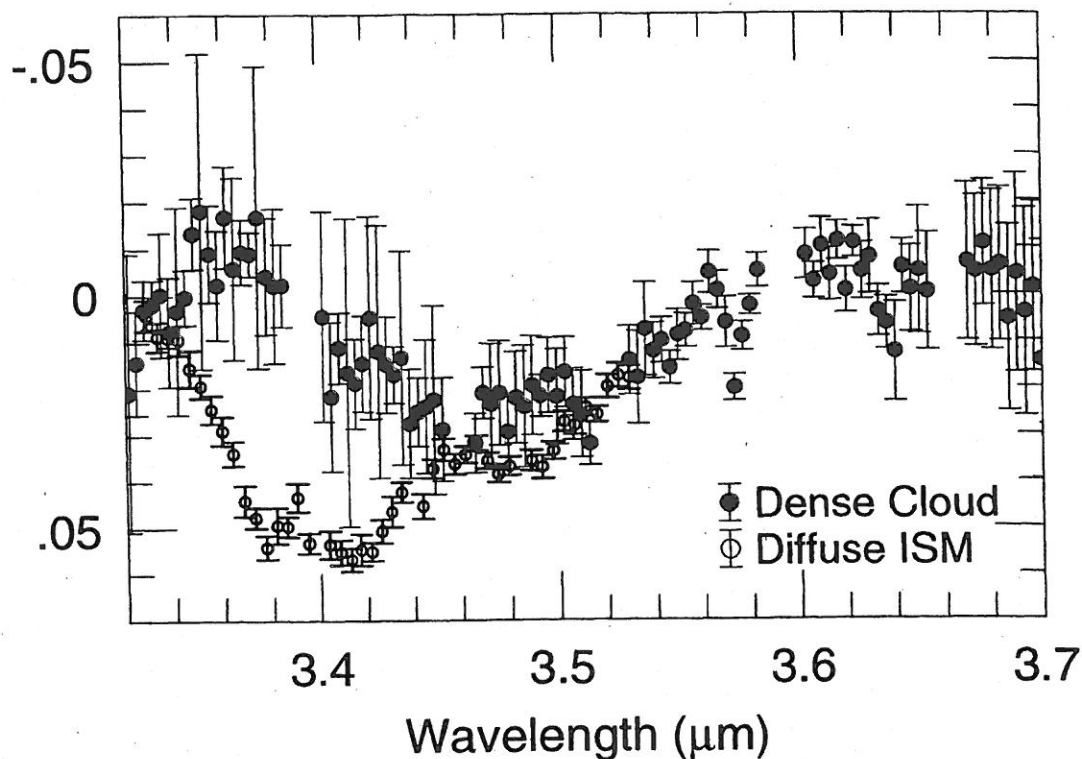
Fig. 2. — A comparison of the absorption bands in the hydrocarbon spectral region for a typical dense molecular cloud line-of-sight (solid points) and the diffuse interstellar medium (open points). Figure taken from [33].

cloud ices during exposure to UV photons and/or upon subsequent heating of the ices, remained in the diffuse ISM after the volatile components of the icy grain mantles were destroyed [32]. Laboratory studies showed that the refractory material could survive the diffuse ISM conditions and the feature was indeed observed in virtually every line-of-sight where there was enough diffuse dust to measure it. However, the apparent absence of the feature in dense cloud spectra raised new questions [9, 18, 19, 33]. Comparisons between the dust absorption features seen in dense and diffuse interstellar clouds, such as that shown in Figure 2, show the absence of the aliphatic diffuse ISM sub-features in the spectra of embedded protostellar objects.

Related to the absence of the aliphatics in the dense clouds is the clear spectral signature of the 3.4 μm band in a nearby, evolved star CRL 618 [15, 34, 35]. The star is not far away (1.3 kpc; [36]) and the feature is too strong to attribute the absorption to dust along the diffuse ISM line-of-sight [35]. It therefore must be produced close to the evolved star. Interstellar ices cannot exist in this environment, so their processing cannot be the source of the observed aliphatics. It is suspected that the high velocity wind emanating from

this source ($\sim$200 km/s; [37–39]) plays a role in the formation of the hydrocarbons. Figure 3 is a comparison between the spectrum of the diffuse ISM dust and that of the hydrocarbons produced locally in the outflow of the evolved star CRL 618 [35].

The presence of the 3.4 μm band in the spectrum of CRL 618 suggests the aliphatics seen in the diffuse ISM might form in the outflows of carbon stars. However, even if the aliphatics are made in this way, the absence of the 3.4 μm band in the spectra of dense cloud sources remains a problem. The feature is clearly apparent throughout the diffuse ISM and the carrier should therefore find its way back into a dense cloud at some point, given the short cycling time of grains between the dense and diffuse ISM [40]. We know that dense clouds transfer a substantial amount of material to the diffuse ISM and if the diffuse ISM does not go back into making dense clouds, there simply is not enough material to keep making new stars.

One possibility that readily comes to mind is that perhaps the signature of the 3.4 μm band is hidden under layers of ice on the grains in dense, cold clouds. The problem with this solution is that the aliphatic signature is very strong and laboratory experiments have shown ice layers do not mask the telltale absorption bands [41].

Perhaps the aliphatic material is converted into some other form upon entry into a dense cloud. This possibility should be explored through laboratory experiments to test for intermediary products that we might look for observationally. The destruction of aliphatics must be extremely rapid and very complete, however, because there are currently no dense cloud spectra which reveal the presence of the distinctive aliphatic CH_2 and CH_3 sub-groups as shown in Figure 1 [42].

Carbonaceous meteorites carry a great variety of complex organic materials of varying degrees of volatility, solubility, and structural diversity [43, 44], of which the amino acids and the aliphatic components [45] are especially significant in the context of prebiotic chemistry. A poorly characterized complex of macromolecular material, the kerogen component [46] is of particular interest because it may also occur as a coloring agent on various Solar System bodies [47]. The high degree of deuteration of the complex organic molecules detected in carbonaceous meteorites and in cometary material is strong evidence for the D-fractionation having originally occurred in the interstellar medium. The remarkable similarity of the diffuse ISM aliphatic hydrocarbons to those in carbonaceous meteorites [20] suggests another puzzle that cannot be readily solved at this time. In short, if the aliphatic hydrocarbons detected in the diffuse ISM are truly absent in the dense molecular clouds, the remarkable similarity between the interstellar 3.4 μm band and that found in the meteorites may be deceptive, because it is not at all apparent that one could go from point A (the diffuse ISM) to point C (formation site of the parent body of the meteorite) without passing through point B (the dense cloud stage where the star and planetary system form). However, before disregarding the incredible match shown in Figure 1, it is worth remembering that the Murchison
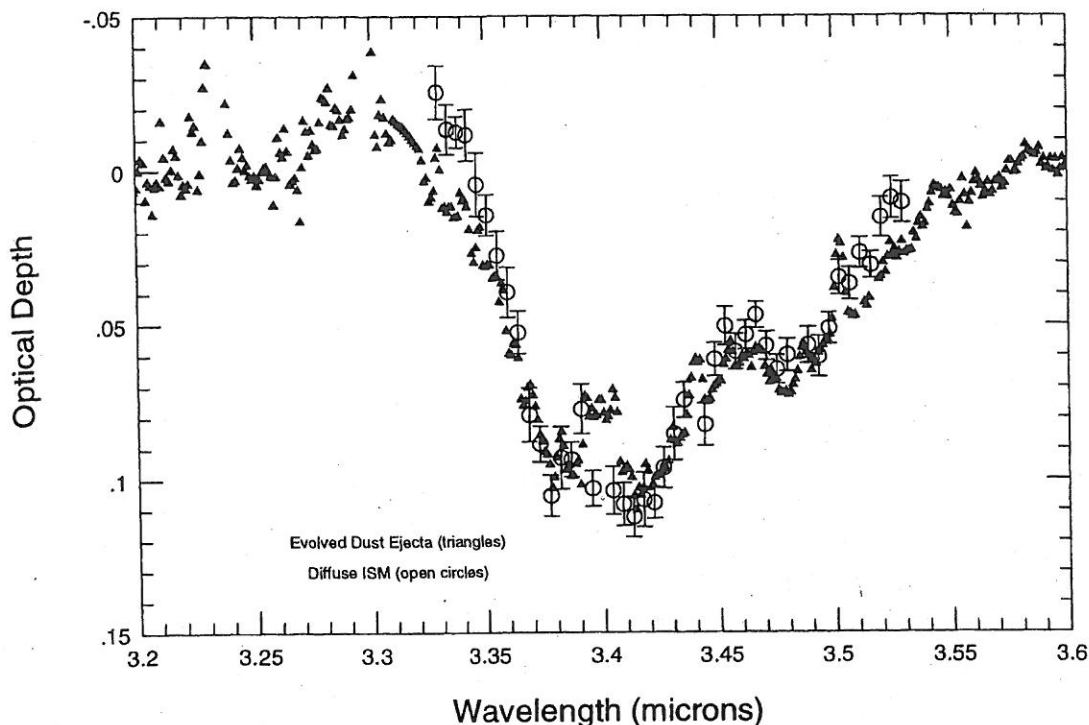
Fig. 3. — An overlay of the diffuse interstellar medium data (open points) and the aliphatic hydrocarbons seen in the outflow of an evolved star (solid points). Figure taken from [35].

meteorite provides a better match to the interstellar feature than do any of the laboratory residues produced from astrophysically plausible starting mixtures. If it is a feature so easily formed that it happened independently in several different places, one has to wonder why it is not easy to duplicate it in the laboratory.

3.   THE 4.62 μm BAND

Another solid state absorption feature attributed to an organic carrier is the 4.62 μm interstellar absorption band seen exclusively in the spectra of embedded, dense cloud objects. First reported by Soifer *et al.* [48], this feature has now been observed towards several embedded protostellar sources [49–54]. Laboratory far ultraviolet (FUV) photolysis of CO and NH$_3$ ices show a prominent absorption feature at 4.62 μm (2165 cm^{-1}) [24, 25, 28, 49, 55–57]. Ion bombardment of ices can also produce a 4.62 μm band [58, 59] as shown in Figure 4. Because different processing mechanisms can reproduce similar bands, the pathway to, as well as the exact identification of, the interstellar 4.62 μm band remains unclear.

The type of process (ultraviolet photolysis or ion bombardment) is directly relevant to the composition of the pre-processed ices on the grain mantles. If the source of the nitrogen comes from solid N_2, then ultraviolet photolysis would not break apart the N_2 bond [60], but ion bombardment could do so [58]. Ice present on bodies in the outer Solar System [61, 62] suggests that the infrared inactive N_2 ice may be hiding in the interstellar ices as well. Therefore, studies of the interstellar 4.62 μm (2165 cm^{-1}) band may provide information on both the reservoir of the solid-state nitrogen in interstellar ices and the energetic processing mechanism by which it participates in the chemistry of the X-CN feature. A comparison of the spectra of laboratory residues produced from the UV photolysis of a 12 K ice mixture of H_2O:CH_3OH:CO:NH_3 in the proportions 100:50:10:10 and subsequent warm-up to 100 K (solid line; taken from [63]) with residues produced from the ion bombardment of a mixture of H_2O:N_2:CH_4 in the proportions 1:1:1 (solid line; taken from [58]) is shown in Figure 4.

The OCN$^-$ ion has been identified with the laboratory 4.62 μm band [28, 29, 65]. It was suggested that the NCO$^-$ or OCN$^-$ ion is produced through the photolysis of icy mixtures containing CO and NH_3, which would first produce the acid HNCO. In the presence of ammonia, or some other base, an acid-base reaction (the transfer of a proton) then occurs between HNCO and NH_3 to form NCO$^-$ and NH_4^+. One problem for any ion identification is the balance of charge. For each negative ion made, a positive ion must be produced. In some of these experiments, the proposed counter-ion is NH_4^+ and a band near 6.67 μm (1500 cm^{-1}) is attributed to this ion [28]. Recent laboratory results by Demyk *et al.* [65] also attribute the 4.62 μm absorption in the spectra of UV photolyzed CO:NH_3 mixtures to OCN$^-$.

As mentioned above, an alternative way to process interstellar ice mixtures is through bombardment with high energy protons. Moore *et al.* ([59] and this volume) have shown that a band is produced at 2170 cm^{-1} (4.61 μm) upon the irradiation of a mixture of H_2O:NH_3:CH_4 (in the proportions $\simeq$ 1:3:2) after irradiation with $\simeq$ MeV protons. They also found that irradiation of mixtures H_2O:N_2:CO_2 (in the proportions $\simeq$ 1:1:1) and H_2O:N_2:CO (in the proportions $\simeq$ 5:1:1) produces a band at about 2180 cm^{-1} (4.59 μm). It is well established (*e.g.* [66–68]) that ion irradiation not only drives the formation of specific molecules, depending on the particular target, but also refractory residues. Recent work by those authors [58] which includes N_2 in the starting mixture produces a band which is similar to the interstellar 4.62 μm band. Ion bombardment, which is analogous to cosmic ray interactions with icy dust grains in dense molecular clouds, has the advantage that the high energy ions can penetrate further into icy grain mantles and can break apart materials such as solid state N_2; the resulting 4.62 μm band is discussed in [58] and is compared to the observations of the protostar W33A in Figure 4b.

Some additional examples of the interstellar 4.62 μm band are shown in Figures 4 and 5 (taken from [54]). The observed near-constant position for the interstellar 4.62 μm band suggests that either the carrier of the band is not very sensitive to the molecular environment, or the grain mantles towards
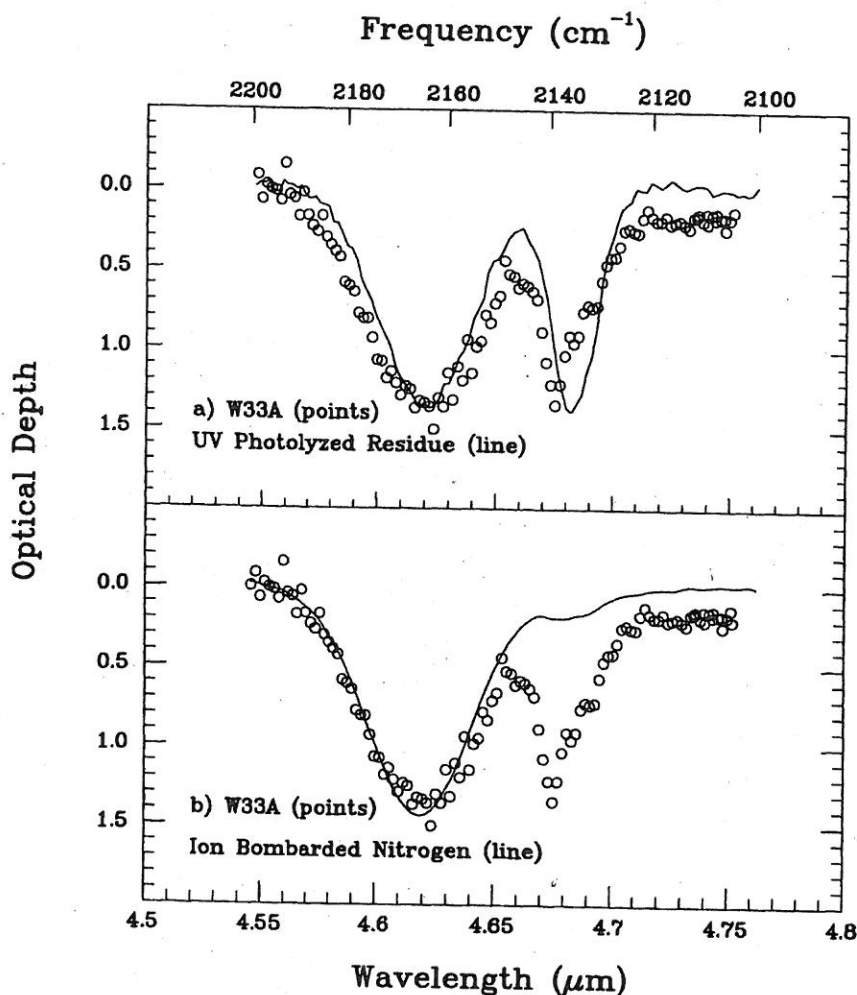
Frequency (cm^{-1})

Fig. 4. — A comparison of the 4.62 μm absorption band detected in the dense molecular cloud line-of-sight towards the protostar W33A (points [54]) to a) the organic residue produced via ultraviolet photolysis of an interstellar ice analog mixture containing ammonia (lab data from [64]; line) and b) the organic residue produced through the ion bombardment of an interstellar ice analog mixture containing solid nitrogen (N$_2$) [58]. The strong absorption band at 4.67 μm in the interstellar data and in lab data in Figure 4a is due to solid state CO. Upon warm-up, CO disappears from the laboratory spectrum, however in this case there was so much CO in the original mixture that some of it remained even at a temperature of 100 K (Bernstein, private communication). A similar 4.62 μm band can be also be produced through the ion bombardment of ammonia containing ice mixtures, however the UV photolysis of solid nitrogen containing mixtures cannot break the strong N$_2$ bond apart [60] and therefore cannot produce the 4.62 μm band.

these sources reside in very similar conditions. The latter point is unlikely due to the observed variable composition of interstellar ice mantles and the unlikely situation that all the protostars observed are at the same evolutionary stage.

The distribution of the 4.62 μm band within dense clouds may have implications for type of physical environment which favors the production of the band carrier. For instance, Tegler et al. [52] found that the 4.62 μm band did not appear in the spectrum of a background field star (Elias 16) seen through the Taurus molecular cloud, while embedded protostars seen through equivalent column densities of dust in the Taurus cloud show the feature. If these results are found to apply in general to molecular clouds, they may suggest that the production of the 4.62 μm band requires close proximity to newly forming stars. This might help constrain the production mechanism.

It is also possible that the 4.62 μm band is produced via simple grain surface chemistry. An example would be a reaction occuring between acids and bases, such as the previously discussed reaction between HNCO and NH$_3$, since both of these species could be produced through grain surface chemistry. Ammonia can be formed by hydrogenation of accreted atomic N. HNCO occurs through the addition of CO+H to form HCO [69], followed by HCO+N which may rearrange itself into the lowest energy state, HNCO [70,71]. This species was proposed by Charnley [72] as the most chemically plausible carrier of the interstellar 4.62 μm band. Alternatively, the intermediate excited complex NCHO (which first forms from the addition of HCO+N) might transfer energy to the matrix rather than use that energy to rearrange the carbon and nitrogen, and the hydrogenation of NCHO would lead to NH$_2$CHO [73], a species that has been observed in the gas phase in the ISM [74], but which has no solid state 4.62 μm band.

Energetic processing of interstellar ices, either through ultraviolet photolysis, ion bombardment, or both, and grain suface chemistry are all plausible pathways by which the interstellar 4.62 μm band might arise. Identifying the production mechanism is directly related to identifications of the interstellar ice constituents which reside on the pre-processed grain mantle. The production pathways are described in more detail in [54], but they are summarized here in Table I.

4. CONCLUSIONS

Understanding the production and distribution of organic solids in the ISM aids in our understanding of the initial composition of planetary systems. The recent discovery of organic solid-state material in distant galaxies, as evidenced by the 3.4 μm hydrocarbon absorption in NGC 1068 and IRAS 08572+3915 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 own Galaxy. Comparisons of the diffuse interstellar medium 3.4 μm hydrocarbon absorption feature with the spectrum of extracts from carbonaceous meteorites has shown a remarkable similarity in profile and relative strength among the sub-features which arise from CH$_2$ and CH$_3$ groups.
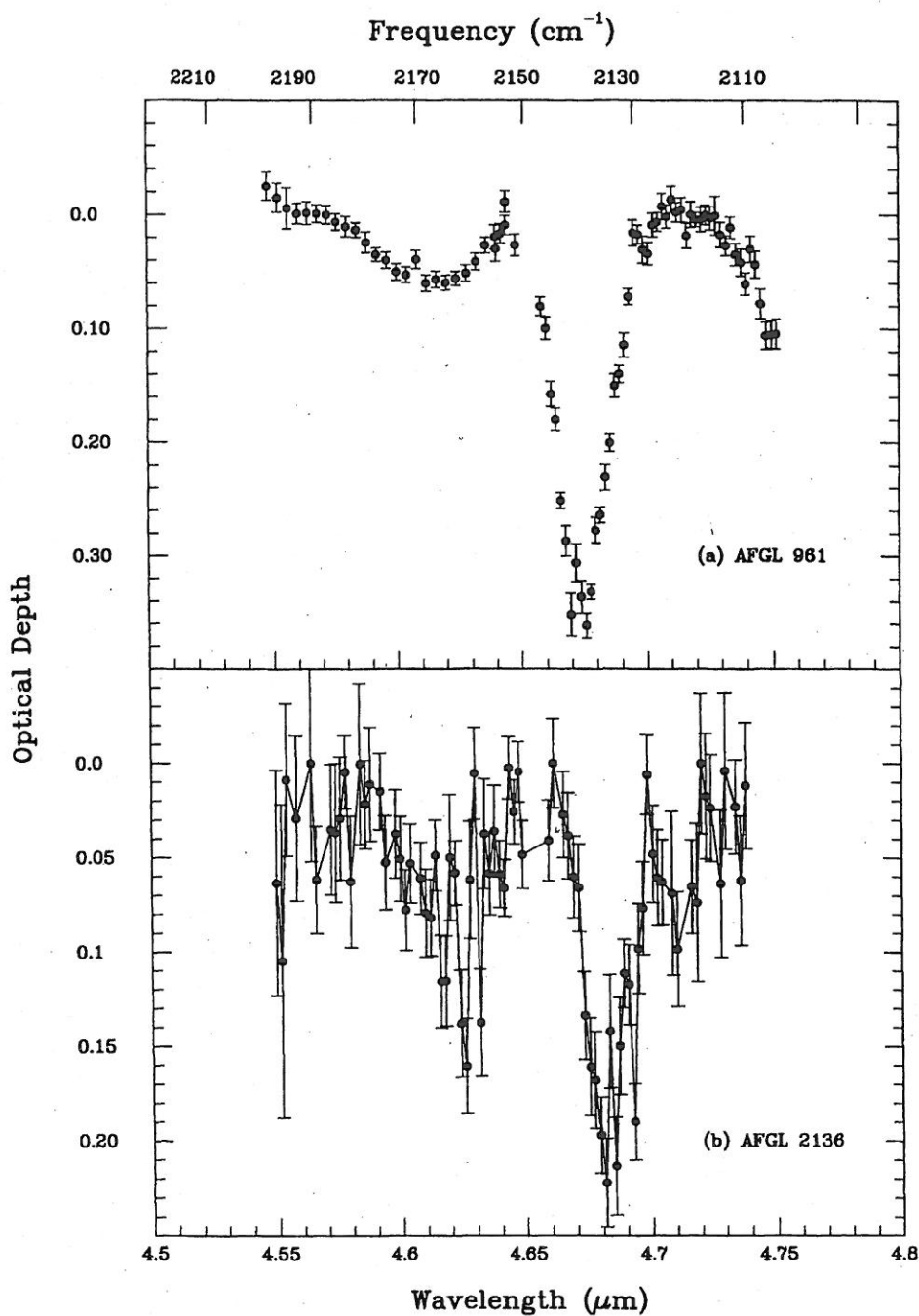
Fig. 5. — Optical depth plot from $4.5 - 4.8$ μm ($2222 - 2083$ cm^{-1}) for embedded protostars (a) AFGL 961 and (b) AFGL 2136. The absorption band at 4.62 μm is likely due to a carbon-nitrogen carrier. Where error bars are not visible, they are smaller than the points.

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Table I. — Production pathways.

Starting Molecule	Product	Comments	References
UV Photolysis of Ices			
CO, NH$_3$, H$_2$O, CH$_3$OH ices	XCN probable	Band at 2165 cm^{-1} correlates with band near 1700cm^{-1}, presumably due to a carbonyl stretch which explains shifted peak with respect to typical nitrile; C,N,O are implicated in the carrier.	Hagen 1982; d'Hendecourt et al. 1986 Allamandola et al. 1988 Sandford & Allamandola 1990 Bernstein et al. 1997 Elsilia, Allamandola & Sandford 1997
N$_2$-mixtures	no 2165 cm^{-1} band.		van IJzendoorn et al. 1983 Jacox & Milligan 1964 Bernstein 1998
Grain Surface Reactions			
Hydrogenation/Nitrogen Addition			
H+CO	HCO	Stabilization of the excited NCHO* to its lowest energy level form, HNCO. Gas phase HNCO has band at 2269 cm^{-1}, HNCO in solid argon has band at 2259 cm^{-1}.	Tielens & Hagen 1982 Kuan & Snyder 1996
N+HCO	NCHO* to HNCO		
	NCHO* to NCHO	If NCHO is the final product, hydrogenation will occur to NH$_2$CHO. NH$_2$CHO observed in gas phase in ISM.	
Acid-Base Chemistry			
CO, NH$_3$		In conjunction with UV Photolysis: band assigned to OCN$^-$	Grim 1988; Grim & Greenberg 1987b;1989; Schutte & Greenberg 1997
H$_2$O,NH$_3$, HNCO		Without UV. Deposition onto 12K substrate yields OCN$^-$ and NH$_4^+$, band at 2171 cm^{-1} grows during warm-up.	Keane & Schutte 1998
Ion Bombardment of Ices			
H$_2$O:NH$_3$:CH$_4$	XCN probable	($\simeq$ 1:3:2); MeV protons; produces 2170 cm^{-1} band.	Moore et al. 1983
H$_2$O:N$_2$:CO$_2$	XCN probable	($\simeq$ 5:1:1 and 1:1:1); Band at 2180 cm^{-1}.	Moore et al. 1983
H$_2$O: CH$_4$: NH$_3$ or N$_2$ ices (2:1:1)	R-O-CN	30-60 keV helium, argon ions; produces 2165 cm^{-1} band. R is a species belonging to the refractory residue.	Palumbo et al. 1998

Ultraviolet photolysis, ion bombardment, and thermal processing all probably play a role in the interstellar chemistry of ices, although each mechanism may have greater relevance under specific astrophysical conditions. Recent studies of the evolution of dust between the dense and diffuse interstellar medium are probing the physical conditions under which refractory species are observed.

Production of the 3.4 μm band in the outflow of the evolved carbon star CRL 618 suggests that the carrier of this band is not formed by the energetic processing of interstellar ices. Even so, the incorporation of the hydrocarbons into the next generation of molecular clouds should occur, and the absence of the 3.4 μm band in dense cloud spectra remains a serious concern.

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.

Laboratory results clearly indicate that ice processing leads to the production of some types of organic material, and the 4.62 μm absorption band observed in dense molecular clouds towards embedded protostellar objects is a likely example. Organic residues produced by energetic processing of astrophysically plausible initial ice mixtures reproduce the 4.62 μm (2165 cm^{-1}) band quite well in both peak position and profile. Ion bombardment has the advantage that it would allow N$_2$, possibly the dominant nitrogen reservoir in molecular clouds, to participate in the chemistry of the ices. Ions are more energetic than UV photons and can break apart the strong N$_2$ bond.

The eventual identification of the interstellar 4.62 μm band may reveal an important clue to the production, evolution, and distribution of interstellar organic matter. Whatever identification laboratory studies eventually reveal for the carrier of the interstellar 4.62 μm band, it is now clear that the spectrum of the carrier will not exhibit any other strong bands in the mid-infrared as, ISO has shown there are none in the interstellar data. The formation site of the hydrocarbon 3.4 μm band and the carrier and process which results in the interstellar 4.62 μm band are important to the study of organic material in planetary systems, since these compounds may well have been preserved in some form in meteorites and comets.

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