

# The origin and evolution of interstellar organics

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**Abstract.** Over the last decade, we have made great strides in better understanding dust composition and evolution in dense clouds and the diffuse interstellar medium (ISM). Thanks to improvements in IR detector sensitivity on ground-based telescopes and the Spitzer Space Telescope mission, we are no longer limited to a handful of bright background stars in order to study dust composition in quiescent dense clouds and the diffuse ISM. More thorough sampling of lines of sight in these regions has highlighted the dichotomy of the nature and composition of dust in these environments. In addition, successes in recreating interstellar processes and dust-analogs in the laboratory have helped us to understand the differences in dust absorption features we observe in the ISM. In this article, we focus on the organic components of interstellar dust, reviewing past work and highlighting the most recent observations and laboratory experiments.

**Keywords.** Astrochemistry, molecular processes, ISM: dust, extinction, ISM: lines and bands, ISM: molecules

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## 1. Introduction

Observationally, interstellar dust is known to consist mainly of amorphous silicates as evidenced by the 9.7 and 18.5  $\mu\text{m}$  Si-O stretching and bending vibrations of this material, and graphitic carbon, responsible for the strong 2175 Å bump. Detailed models have been developed that link the measured optical properties of these materials with the grain size distribution to the observed interstellar extinction. Typically, these models conclude that both materials contribute approximately equal volumes (per H-atom) to the interstellar grain population. The well-known Draine & Lee (1984) model illustrates that graphitic and silicate grain components dominate the extinction in different wavelength regimes. Specifically, while silicates dominate the extinction beyond about 8  $\mu\text{m}$  through their strong resonances, graphitic dust controls the extinction in the visual through near-IR.

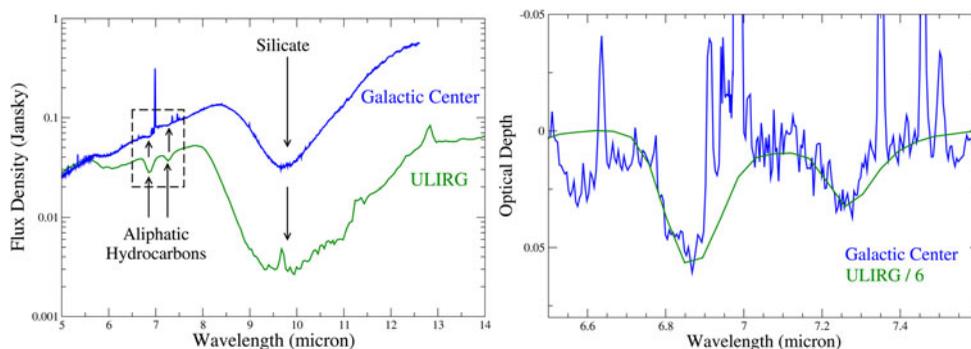
In a general sense, interstellar dust models can be separated in two distinct classes. First, in some models dust is primarily injected by stellar sources such as Asymptotic Giant Branch (AGB) stars in the form of high temperature condensates such as oxides, carbides, silicates, and graphite. These grains are slowly eroded and destroyed in the diffuse interstellar medium (ISM) by strong shock waves driven by supernova shocks. Inside dense clouds, these grains may temporarily acquire a thin ice mantle of simple molecules such as H<sub>2</sub>O and CO, but from an evolutionary viewpoint, these ice mantles have little relevance because they are rapidly photodesorbed in the diffuse ISM when they are eventually recycled (Draine & Lee 1984). In the second class of models, stardust is still an important source of dust cores. However, the ice mantles accreted by these cores are thought to be transformed by penetrating and/or cosmic-ray-created far-UV photons into an organic mantle while still residing inside the molecular cloud. In these

models, the organic mantle is thought to be a hardy, refractory material that survives both dense and diffuse cloud environments during the lifecycle of an interstellar dust grain, as does the core material itself (Li & Greenberg 2003). Hence, these two classes of models differ in the assumed character of the carbonaceous grain material and the processes that form them: soot-like dust formed at high temperatures in stellar ejecta versus polymeric organic carbon formed at low temperatures by energetic processing of simple molecules.

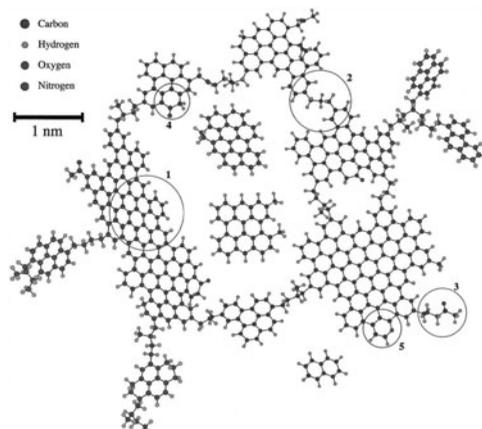
Besides the strong UV resonance at 2175 Å – characteristic for aromatic carbon – carbonaceous dust is the carrier of a number of infrared absorption features: specifically at 3.4, 6.8 and 7.2 μm. In the Milky Way, hydrocarbon bands – due to the CH stretching and deformation modes of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) groups in aliphatic hydrocarbon materials – are detected along lines of sight that probe the local diffuse ISM within 3 kpc of the Sun (Adamson *et al.* 1990, Sandford *et al.* 1991, Pendleton *et al.* 1994, Whittet *et al.* 1997) and along the line of sight toward the Galactic center (Butchart *et al.* 1986, McFadzean *et al.* 1989, Sandford *et al.* 1991, Pendleton *et al.* 1994, Chiar *et al.* 2000, 2002). These bands have also been detected in one young planetary nebula, AFGL 618 (Chiar *et al.* 1998). In recent years, ground-based and Spitzer studies have revealed that these IR absorption features are also common in the spectra of dense and dusty galactic nuclei such as associated with UltraLuminous InfraRed Galaxies (Imanishi 2000, Spoon *et al.* 2002, Mason *et al.* 2004, Imanishi *et al.* 2006, Armus *et al.*, 2007, Dartois & Muñoz-Caro 2007). A wide variety of materials have been considered as the carrier of these interstellar aliphatic bands mainly differing in their production methods (c.f., Pendleton & Allamandola 2002). These materials generally have in common that they contain aromatic and aliphatic moieties and the best-studied material which also provides the best fit to the IR observations is hydrogenated amorphous hydrocarbon (HAC, Duley 1994, Duley *et al.* 1998, Mennella *et al.* 2002). Laboratory studies have shown that HAC grains may also be responsible for the 2175 Å feature (Schnaiter *et al.* 1999).

## 2. Carbonaceous Solids in the Diffuse ISM

Aliphatic hydrocarbons are confirmed to be present in the interstellar media in our own and other galaxies, through observations of vibration absorption features centered at 3.4 μm (CH stretch), 6.85, and 7.25 μm (deformation modes) (Figure 1). Within the profile of the 3.4 μm feature, the relative depths of subfeatures at 3.338, 3.419, and 3.484 μm are indicative of short-chained hydrocarbons, with other perturbing chemical groups (Sandford *et al.* 1991). The individual chain lengths are not likely to be much longer than 4 or 5, and they are attached to electronegative chemical groups (Sandford *et al.* 1991, Pendleton & Allamandola 2002). Together, the profile of the 3.4 μm feature, the CH stretch-to-deformation mode optical depth ratio, and the absence of evidence for other types of chemical subgroups, provide indirect evidence that aromatic, *sp*<sup>2</sup> hybridized carbon domains (aromatics) are an important component of the interstellar material. Recent analysis of the dust features in the diffuse ISM toward the active galactic nucleus, IRAS 08572+3915, shows that the hydrocarbons are highly aliphatic: the aliphatic bonds outnumber the aromatic bonds by a ratio of 12.5:1 (Dartois *et al.* 2007). Based on the depth of the corresponding deformation features at 6.85 and 7.25 μm, the best candidate material is likely to be hydrogenated amorphous carbon (HAC, Chiar *et al.* 2000, Pendleton & Allamandola 2002, Mennella *et al.* 2002). Furthermore, the HAC material in the diffuse ISM possesses little nitrogen or oxygen (Pendleton & Allamandola 2002, Figure 2).



**Figure 1.** [left] Mid-IR spectrum of the line of sight toward the Galactic Center taken with the Infrared Space Observatory's SWS (upper spectrum, Chiar *et al.* 2000). Mid-IR spectrum of the ULIRG F00183-7111 taken with the Spitzer Space Telescope's IRS (lower spectrum, Spoon *et al.* 2004). Both the galactic and extragalactic spectra show absorption features due to HACs (6.85 and 7.25  $\mu\text{m}$ ) and silicates (9.7  $\mu\text{m}$ ). [right] The 6.5 to 7.5  $\mu\text{m}$  region, showing the HAC absorption features in more detail. The ULIRG spectrum (smooth line) has been divided by a factor of 6 for presentation purposes.



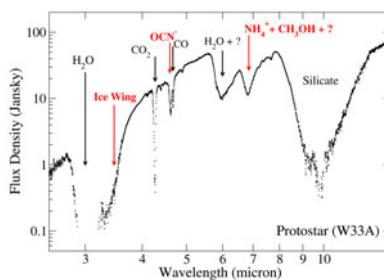
**Figure 2.** The basic structural and molecular character of carbonaceous, interstellar dust in the diffuse interstellar medium. The specific geometries of the aromatic plates and aliphatic components simply represent what is likely. The structure is somewhat splayed out to reveal the molecular structural details; we envision the actual structure somewhat more closed in. The approximate volume of this fragment is on the order of  $10^{-19} \text{ cm}^3$ . Thus, a typical 0.1  $\mu\text{m}$  DISM carbonaceous dust grain would contain approximately  $10^4$  of these fragments. The encircled sections signify the different structural unite: 1. aromatic network, 2. aliphatic bridge, 3. aliphatic carbonyl, 4. aromatic carbonyl, 5. aromatic nitrogen. From Pendleton & Allamandola (2002).

The 3.4  $\mu\text{m}$  band resulting from experiments that produce HAC material in the laboratory show excellent agreement with the astronomical feature profile. The differences are in the production route of the HACs. Experiments show that the IR spectral behavior of hydrocarbons produced by laser pyrolysis of acetylene is similar to that observed in the diffuse ISM (Schnaiter *et al.* 1999). These results point toward production of hydrocarbon grains in the AGB/PN phase of stellar evolution. The detection of the aliphatic hydrocarbon absorption feature in the outflow of an evolved star (Lequeux & Jourdain de Muizon 1990, Chiar *et al.* 1998) is indirect evidence that the diffuse ISM hydrocarbons originate, at least partially, in these environments (i.e. as stardust). On the other hand, the 3.4  $\mu\text{m}$

profile can also be reproduced in the laboratory by hydrogenation of carbon particles, suggesting that the  $3.4\ \mu\text{m}$  carrier forms in situ in the diffuse ISM (Mennella *et al.* 2002). The prevalence of HACs in the galactic and extragalactic diffuse ISM is suggestive of this sort of widespread HAC production. The survival of HACs in the diffuse ISM and their absence in dense clouds is puzzling, but experiments by Mennella (2006) shed some light on this issue. In the diffuse ISM there is an equilibrium situation between hydrogenation of carbon particles and their destruction by UV photons. However, in dense clouds the reduction of H-atom flux and an activation energy for H-atom formation inhibits CH formation in these cold regions.

### 3. Carbonaceous Solids in Dense Molecular Clouds

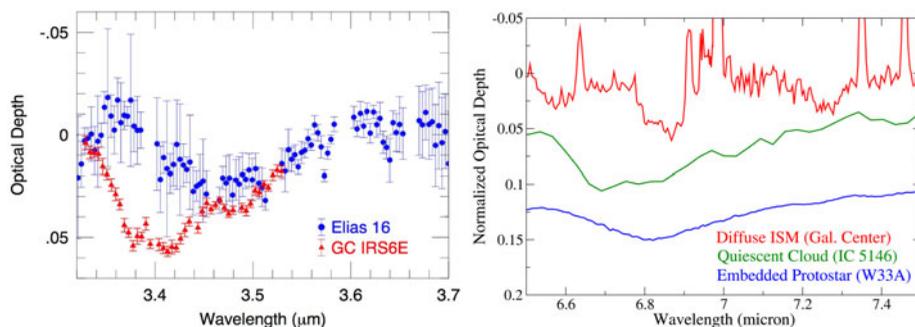
The infrared spectra of objects embedded in or located behind molecular cloud material are characterized by strong absorption features due to simple molecules in a mixed molecular ice (Figure 3, Gibb *et al.* 2004). These species are formed through hydrogenation and oxidation reactions among gaseous species on grain surfaces (Tielens & Hagen 1982). However, there are a number of absorption features that defy this simple model. Notably, absorption was discovered at  $4.62\ \mu\text{m}$  in the spectra of, particularly, high-mass protostars (Lacy *et al.* 1984, Tegler *et al.* 1993, Pendleton *et al.* 1999, Gibb *et al.* 2000). Recently, this band has also been observed to be common in the spectra of low mass protostars (van Broekhuizen *et al.* 2005). These data reveal the presence of (at least) two components at  $4.62$  and  $4.60\ \mu\text{m}$ . The  $4.62\ \mu\text{m}$  absorption feature has now unambiguously been attributed to the  $\text{OCN}^-$  ion (Schutte & Greenberg 1997, Demyk *et al.* 1998). Early photolysis experiments on ices revealed that this band grows immediately upon photolysis (Lacy *et al.* 1984). It persists even after the ice evaporates and is associated with an inorganic salt (Grim & Greenberg 1987, Schutte & Khanna 2003). The  $4.62\ \mu\text{m}$  band has long been considered a key indicator of the importance of UV photolysis in the evolution of interstellar dust (Li & Greenberg 2003). However, besides photolysis, the  $4.62\ \mu\text{m}$  profile can also be produced by ion irradiation of ices (Palumbo *et al.* 2000). Moreover, recent studies have shown that simple warm up of mixtures containing HNCO and  $\text{NH}_3$  also results in the formation of the  $\text{OCN}^-$  ion (van Broekhuizen *et al.* 2004) and this thermal evolution is a viable alternative to energetic processing.



**Figure 3.** The infrared spectrum of the luminous protostar, W33A, shows infrared absorption features due to ices including  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_4$  (Gibb *et al.* 2004). In addition, these spectra contain the (possible) signature of processed ices.

The assignment of the  $4.62\ \mu\text{m}$  band to an anion has given rise to a “hunt” for the absorption features associated with the counterion in interstellar spectra. The  $6.85\ \mu\text{m}$  band is the most promising of these (Figure 4). Analysis of moderate resolution SWS spectra of high mass YSOs revealed that this band consists of (at least) two components: one component at  $6.75\ \mu\text{m}$  that is carried by a volatile ice molecule and a component

at  $6.95 \mu\text{m}$  which is more refractory (Keane *et al.* 2001). This identification of multiple contributors to the  $6.85 \mu\text{m}$  band is confirmed by the analysis of the large sample of protostars and background sources studied with the IRS on the Spitzer Space Telescope in the c2d program (Boogert *et al.* 2008). While these spectra are low resolution, the large sample allows a reliable segregation in these two components. Laboratory studies have assigned the  $6.85 \mu\text{m}$  band to the  $\text{NH}_4^+$  cation (Schutte & Khanna 2003). A key issue is buried here: An abundance of 7% is inferred for  $\text{NH}_4^+$  relative to  $\text{H}_2\text{O}$  from the  $6.95 \mu\text{m}$  band; in contrast, the inferred abundance of the  $\text{OCN}^-$  ion is less than 1% (van Broekhuizen *et al.* 2008). Clearly, other ions must be hidden in the spectra. The  $\text{HCOO}^-$  ion is often considered but its abundance is less than 0.3% (Boogert *et al.* 2008). A number of other components have been identified in the  $6.0 \mu\text{m}$  band – possibly due to  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  – of protostellar spectra but these do not really correlate well with the  $\text{NH}_4^+$  band (Boogert *et al.* 2008). This ion mismatch throws somewhat of a pall on the otherwise success story of ions in ices.

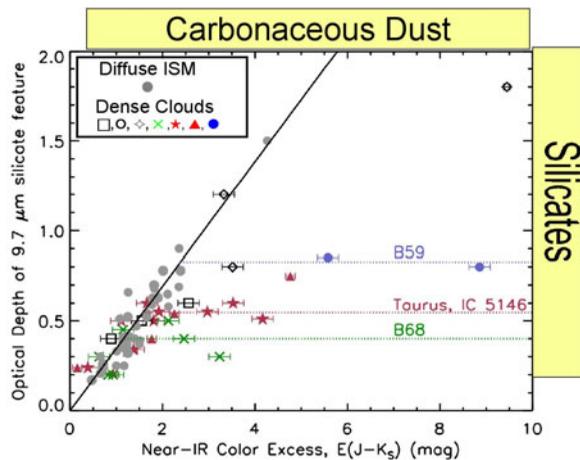


**Figure 4.** [right] Mid-IR spectra in the  $6.5$  to  $7.5 \mu\text{m}$  region showing the distinct differences between diffuse ISM [top: Chiar *et al.* 2000], dense cloud [middle: Chiar *et al.*, in prep.] and YSO dust [lower: Gibb *et al.* 2000]. [left] Contrasting absorption features in the  $3.32$  to  $3.7 \mu\text{m}$  region of dust in dense clouds and diffuse ISM (Chiar *et al.* 1996).

#### 4. Processing of Interstellar Dust

Models of molecular cloud evolution indicate that there is rapid cycling of material between dense clouds and the diffuse ISM (e.g., McKee 1989) that should result in similar grain properties in both environments. However, current observations have contributed to the mounting evidence that there are distinct and surprising differences in dust components in these environments, challenging old ideas about dust evolution. Particularly, the properties of the primary refractory dust components – silicates and carbonaceous dust – show variations between the diffuse ISM and dense clouds. The distribution of silicate dust in the ISM can be traced by measuring the absorption feature at  $9.7 \mu\text{m}$ , whereas the carbonaceous dust is roughly traced by the near-IR extinction or color excess. In the diffuse ISM, these quantities show a tight correlation over a wide range of extinction values (Figure 5, Roche & Aitken 1984, Whittet 2003) indicating that the silicate and graphitic dust components are well-mixed and vary little in relative abundance. In dense molecular clouds, these grain components evolve and exist independently from each other as shown by the failing of the silicate-carbonaceous dust correlation trend (Figure 5, Whittet *et al.* 1988, Chiar *et al.* 2007).

HACs are a widespread and independent dust component in the diffuse ISM. Their prevalence is demonstrated by the widespread detection of the  $3.4 \mu\text{m}$  feature, and now, thanks to Spitzer, the  $6.85$  and  $7.25 \mu\text{m}$  features in the galactic and extragalactic



**Figure 5.** Optical Depth of the  $9.7 \mu\text{m}$  feature traces the silicate dust whereas the near-IR color excess traces the carbonaceous dust abundance. In the diffuse ISM, these components are well-mixed as evidenced by the tight correlation between the quantities. In the dense ISM, the correlation fails at high extinction, due to changes in the dust properties (Chiar *et al.* 2007).

diffuse ISM. The properties of HACs also seem to be robust wherever HACs are observed: the ratio of the stretching and deformation modes is consistent in both galactic and extragalactic sightlines. In addition, spectropolarimetry data of both galactic and extragalactic sightlines show a clear lack of polarization across the  $3.4 \mu\text{m}$  feature, indicating that the carrier is best explained by a population of small, unaligned carbonaceous grains with no physical connection to the silicates (Mason *et al.* 2007, Chiar *et al.* 2006, Adamson *et al.* 1999). This finding also supports the idea that the HACs originate, at least partially, in the outflows of evolved stars (e.g., Chiar *et al.* 1998, Schnaiter *et al.* 1999).

While the IR bands at  $3.4$ ,  $6.8$  and  $7.2 \mu\text{m}$  are ubiquitous in the diffuse ISM of the Milky Way, they have never been observed in the denser molecular cloud material. The synergy between UV irradiation and hydrogenation that exists in the diffuse ISM to provide the ideal environment for HAC production, does not exist in dense clouds where hydrogenation cannot counteract destruction of HACs by UV and cosmic-rays (Mennella 2006). Thus, in dense clouds, the  $3.4 \mu\text{m}$  absorption feature is not detected. In contrast, the latter regions show absorption features at  $3.47$  and  $4.62 \mu\text{m}$  (as well as bands due to ice molecules such as  $\text{H}_2\text{O}$  and  $\text{CO}$ ) that conversely – are never observed in the diffuse ISM. This dichotomy in the IR characteristics of the diffuse and dense ISM may thus provide an important means to follow the evolution of carbon dust in the ISM.

New sensitive ground-based and Spitzer spectra have demonstrated that processed ices are a ubiquitous component around young stars in dense clouds. The  $4.62$ ,  $6.0$  and  $6.8 \mu\text{m}$  features, attributed to some form of “processed” ices whether it be thermal or energetic, are now widely detected in low mass and high mass YSOs (§3). Given the lack of UV photons or sources of thermal radiation in the more quiescent regions of dense clouds, it is not too surprising that the  $4.62 \mu\text{m}$  band is not detected there. A limit of  $\tau_{4.62 \mu\text{m}} < 0.05$  has been placed for the line of sight toward Elias 16 in the Taurus dark cloud (Tegler *et al.* 1995, Whittet *et al.* 2001). More curious, though, is that the  $4.62 \mu\text{m}$  feature is missing in the diffuse ISM, implying that it is not a major constituent of refractory dust (Whittet *et al.* 2001). Prior to Spitzer, absorption features at  $6.0$  and  $6.8 \mu\text{m}$  were associated with processed ice around massive YSOs. However, Spitzer IRS observations revealed the presence of these features along the lines of sight toward field

stars that probe quiescent dust in dense clouds (Knez *et al.* 2005). One of the carriers of the 6.85  $\mu\text{m}$  band,  $\text{NH}_4^+$ , can therefore not be produced by energetic processing alone, pointing towards low-temperature reactions as the mechanism for production (Boogert *et al.* 2008). Further evidence for ions in ices is given by the 4.62  $\mu\text{m}$  feature attributed to  $\text{OCN}^-$ . Recent observations have shown that this feature is present around high- and low-mass YSOs and that its strength is highly variable, suggesting that electron-, proton-, UV, or thermal-processing could play a role in its production and evolution (van Broekhuizen *et al.* 2005).

## 5. Key Questions and Future Directions

Over the last decade, ground-based and space-based IR spectra have provided new and exciting insight into the carbonaceous and silicate components of interstellar dust. These new data have also raised several questions concerning the relationship between dense cloud and diffuse ISM dust. First, what is the connection between diffuse ISM hydrocarbons, meteoritic kerogen and other Solar System organic components? Second, what is the connection between diffuse ISM HACs, identified by features at 3.4, 6.85 and 7.25  $\mu\text{m}$ , and dense cloud “salts”, identified by features at 3.47 and 6.8  $\mu\text{m}$ ? And, finally, why don't these dust components mix or survive in the two environments?

With the present sensitivity of IR detectors along with the availability of 8 to 10 meter-class telescopes, mapping dust components in quiescent and star-forming clouds is now possible. Current instrumentation should also allow us to trace where the conversion from HAC to processed ices in dense clouds occurs. Of primary importance in solving this question will be probing the transition region on the outskirts of dense clouds where subtle changes in the ice and refractory dust properties and, therefore, their spectral profiles occur. NASA's James Webb Space Telescope, scheduled to launch in 2013, will be able to observe relevant dense cloud sources with unprecedented sensitivity. SOFIA may open up the opportunity to carry out detailed polarimetric observations of various ice features that could tell us which dust components reside together on the same grains.

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## Discussion

SNOW: Where is the line between dense and diffuse clouds?

PENDLETON: The transition from diffuse to dense cloud is probably represented by a quiescent cloud region where we don't see active star formation happening and the lowest extinction has a value of  $A_v = 3-4$ . At higher  $A_v$ , you're starting to see the formation of ice and perhaps the chemistry that's happening in the absence of star formation and we have to rely on cosmic rays to do some of that processing. I think the quiescent cloud region is the key to connect the dense and diffuse clouds.

When we get the COS instrument on the HST, we can look at the region where  $A_v$  is high enough to get an infrared absorption feature but low enough that you will still see the ultraviolet absorption and emission so that we can maybe compare the dust grains and the region and see if there are in fact the same ones.

NITTLER: I am all confused in the terminology of what a hydrogenated amorphous carbon actually is. You said laboratory analogs match the 3.4 micron spectrum. You said Murchison IOM matches the spectrum. Does that mean Murchison IOM is a HAC? Is molecular model that you show a HAC?

PENDLETON: From an observational standpoint, it seems that the three materials that you mentioned have strong similarities but I know in details that they are quite different. But it was not too long ago that we thought that the aliphatic hydrocarbons we see in the diffuse ISM actually come from the processing of ices on dense cloud grains. What we have been able to show quite clearly is that is not how they are produced. The fact that HAC produced in the laboratory matches the diffuse ISM was such a great step forward in helping us understand that part of the puzzle.

VAN DISHOECK: I think your comment about is not due to processing or UV processing of water-rich ices is fully correct. What I tried to do is using carbon-rich ices and they provide a good match with the 3.4 micron feature. As for the 6.8 micron feature, there are many different types of processing, e. g., thermal processing, UV and cosmic ray processing and they all have quite different signatures. The whole 5 to 8 micron region can actually be divided into more than just these two components, more like five independent components. Some of them are due to normal regular ices such as water ices and some of which may have something to do with processing.

PENDLETON: I only call out 6.0 and 6.8 micron features because I was trying to make comparison to the diffuse ISM. In fact, I did not mean to in any way imply the cosmic ray is responsible for producing the 6.0 and 6.8 features.

PATHAK: I just want to point out that in the laboratory we can see 3.4 micron band if we just take the singular carbon nano tube and bombard the hydrogen atoms. In order to make the singular nano tube in the laboratory all you have to do is just take any hydrocarbons and have the ion heat to 800 degrees or 900 degrees C. If take the infrared spectrum of the singular nano tube, you don't see any feature because they are extremely weak. In Raman spectrum you can see strong peak from singular carbon nano tube. So in addition to amorphous carbon, there are carbon nano tubes coming from carbon stars as well. In fact, there are carbon nano tubes in meteorites as well.

PENDLETON: The one thing that I am absolutely convinced is that when we go through the inventory, it's going to be a wide distribution of materials. I've tried to highlight just a few and simplify it down to a few of things that we've learnt along the way. On Friday, Vito Mennella will be talking about the laboratory work that he's done. One of the pioneering thoughts that he puts forward is while aliphatic hydrocarbons are made in the outflow carbon stars, they are also destroyed there. The very fact that we see them in the diffuse ISM must mean that the destruction versus formation occurs even in the diffuse ISM itself and somehow formation must win because we actually see the feature. There must be all kinds of nano particles being thrown out by carbon stars into the ISM but we are just unable to detect them.



Scott Sandford showing a piece of aerogel like that flown on the Stardust spacecraft during the press conference (photo by Sze-Leung Cheung).