Dust Evolution from the Laboratory to the Interstellar Medium

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Abstract. There is increasing observational evidence that the composition of interstellar dust varies with interstellar environment. Irradiation from UV photons and cosmic rays, as well as chemical interactions with the interstellar gas, play a crucial role for grain transformation. The analysis of "laboratory analogues" represents a powerful tool to better understand the nature and evolution of cosmic materials. In particular, the study of grain processing under simulated dense and diffuse interstellar conditions is fundamental to outline an evolutionary pathway for interstellar dust.

We review the results of experiments aimed at studying the variations of the composition of nano-sized carbon particles in response to UV and ion irradiation and H atom exposure. These results give us the opportunity of reconciling the dichotomy of the 3.4 μm band in the spectrum of diffuse and dense clouds through an evolutionary transformation of the aliphatic component caused by grain processing. Moreover, we discuss formation of CO and CO₂ molecules by ion irradiation of water-ice covered hydrogenated carbon grains. This result indicates that the composition of the refractory component can influence the chemical evolution of ice mantles during energetic processing in dense clouds.

1. Introduction

Only 1% of the interstellar medium mass resides in small dust grains, yet they play a basic role in many physical and chemical processes. Dust dominates the energy balance through absorption and emission of radiation and strongly interact with gas. It favours molecular formation and influences the birth of stars. The wavelength dependence of the interstellar extinction and polarization and specific UV and IR signatures indicate that silicate and carbon grains are the main components of dust in diffuse interstellar regions. In dense molecular clouds an ice mantle, composed primarily of water, accretes on grains forming core-manlte structures. However, the exact nature and evolution of solid particles in space remain not completely clear.

Astronomical observations have shown significant variations of carbon grain properties with environment. A correlation between the width of the UV interstellar extinction bump with environment has long been known [1]. Concerning the aliphatic organic component, a dichotomy between dense and diffuse clouds is well established [2,3,4,5]. Recently, silicates with amorphous and crystalline structure have been observed in different regions with ISO [6,7,8]. A solid interpretation of these changes should rely on an evolutionary physical-chemical scheme of solid materials under processing. In fact, dust grain composition evolves through exposure to UV photons, heat, gas and cosmic rays. In this context the role of laboratory is getting more and more important and significant progress has been achieved in this field. Nowadays,
simply assignment of a spectral feature on the basis of the similarity to that of an analogue material is considered only the starting point for an accurate identification of the interstellar carrier. Experiments aimed at studying the spectral and structural modifications of cosmic dust analogue under simulated interstellar medium conditions are indispensable to disclose the nature of dust grains. In the case of silicates, processing induces phase transformations: thermal annealing actives the amorphous to crystalline transition [9,10,11,12], while ion irradiation can amorphize crystalline silicates [13,14,15]. Important structural and spectroscopic variations take place also in carbonaceous material due to energetic processing. Here, we consider the problem of the evolution of this component. A brief review of the experimental work done to outline a model for the origin and evolution of the organic component of interstellar dust is reported. Moreover, we discuss the experimental results indicating that grain composition can influence the chemical evolution of ice mantles during energetic processing.

2. The evolution of the organic component of interstellar dust

The IR spectrum of dust in the diffuse interstellar medium is characterized by the aliphatic 3.4 μm absorption band with its three typical subfeatures due to the C-H stretching modes in the methyl (CH₃) and methylene groups (CH₂) [2]. The C-H bending modes at 6.85 and 7.25 μm, associates to the stretching bands (see Figure 1), have been observed with ISO along the line of sight towards the Galactic center source Sgr A* (IRS 7) [16]. In contrast, the band is absent in the spectra of source embedded in molecular clouds [3,4,17]. The 3.4 μm band has been observed in the spectrum of the C-rich protoplanetary nebula CRL 618 [18], while it has not been detected in the spectrum of C-rich AGB stars that are considered the progenitors of objects such as CRL 618. Spectropolarimetric observations have shown that the C-H stretching feature is not polarized [19].

![Figure 1. C-H stretching (3.4 μm) and bending (6.85 and 7.25 μm) bands observed with ISO towards the Galactic center source Sgr A* (thin line) [16] compared with those of activated in carbon grains after atomic hydrogen exposure.](image)

To identify the nature of the aliphatic material responsible for the interstellar absorption feature some simply criteria should be adopted: 1) One should produce an analogue material able to match the spectral profile of the interstellar band. 2) The material should be compatible with the conditions of the diffuse medium. 3) The difference between dense and diffuse interstellar regions should be explained. 4) The amount of carbon atoms locked in the candidate carrier of the feature should be compatible with the cosmic abundance of this element [20,21,22]. Since the discovery of the band, more than twenty materials have been proposed as candidate on
the basis of the spectral profile similarity. However, this approach indicates that an univocal identification of the carrier is not possible. Different C-based materials containing CH₂ and CH₃ functional groups can reproduce the band profile with different degrees of approximation. An extensive analysis of the spectrum of interstellar dust and that of analogue materials has reduced the number of candidate materials and indicated that the carrier is much more similar to plasma processed hydrocarbon materials than energetically processed ice residues [23].

Cycling of material between diffuse and dense regions links the two environments from the evolutionary point of view. The absence of the C-H modes in the spectrum of dense regions suggests that a C-H bond destruction mechanism is active. On the other hand, C-H bonds should form in diffuse regions, since the 3.4 μm feature is associated to diffuse dust. Alternatively, hydrogenated carbon grains of circumstellar origin could give rise to the observed C-H bonds [18]. In this case, however, their destruction should take place in time interval longer than the cloud life time. According to these general considerations, it is necessary to identify the processes active in the interstellar medium and quantify their effects by means of the cross sections obtained in simulation experiments.

The evolution with UV processing of the 3.4 μm band of hydrogenated carbon grains has been studied under simulated diffuse and dense interstellar medium conditions [24]. In the first case bare grains were considered, while to emulated dense cloud conditions, grain samples covered with an ice layer were irradiated. In both cases a strong decrease of the 3.4 μm band intensity with UV irradiation takes place. From the decrease of the band intensity with UV fluence, the destruction cross section of C-H bonds by UV photons can be estimated. A value of \( 1 \times 10^{-19} \) cm² is representative of the cross-section for both experiments. The result agrees with the cross sections estimated for hydrocarbon molecules [25].

Similar experiments have been carried out with 30 keV He⁺ ions to simulate cosmic ray processing of the interstellar carrier [26]. As in the case of UV irradiation experiments, bare hydrogenated carbon grains and grains with a water ice cap have been irradiated. Also in this case, the spectral evolution is characterised by a strong decrease of the band intensity with ion bombardment. From the decrease of the band intensity with ion fluence the C-H bond destruction cross section for these ions has been estimated. Taking into account the dependence of the stopping power on energy and ion mass, the destruction cross section for 1 MeV protons of \( 9.4 \times 10^{-16} \) cm² has been derived [26]. It was used to discuss the influence of cosmic ray irradiation on the evolution of the interstellar aliphatic component.

These experiments indicate that both UV and ion irradiation easily destroy the C-H bonds present in hydrogenated carbon grains. Using the cross sections estimated in the simulation experiments, the values \( 8 \times 10^7 \) photons cm⁻² s⁻¹ and 1.8 protons cm⁻² s⁻¹, respectively, for the UV Galactic field and 1 MeV protons [26,27], the C-H bond destruction rates have been evaluated for diffuse clouds. In these regions the effects of ion irradiation are negligible and the destruction is determined by UV photons. The destruction of the aliphatic bonds should take place in \( 10^4 \) yr, a time interval three orders of magnitude smaller than the typical diffuse cloud time scale of \( 3 \times 10^7 \) yr. The origin of the carrier of the aliphatic features cannot be circumstellar.

The presence of the 3.4 μm band in the spectrum of diffuse clouds implies that a process able to form C-H bonds and counteract their destruction must be active. This mechanism has been identified in the interaction of H atoms with carbon grains [28,29]. Exposure of hydrogen-free nano-sized carbon grains to atomic hydrogen, produced by microwave discharge dissociation of molecular hydrogen, determines the formation of aliphatic C-H bonds. In Figure 1 you can see the remarkable similarity between the C-H modes observed toward the Galactic center and those of H processed carbon grains. This material requires the lowest amount of carbon to reproduce the intensity of the observed features in the local diffuse medium [29]. The C-H bond formation cross section, as estimated by the increase of the 3.4 μm optical depth with H atom fluence, is
The knowledge of the formation and destruction cross sections allow a complete formal description of the evolution of the interstellar aliphatic component [26]. In the diffuse medium bare carbon grains are processed by H atoms, UV photons and cosmic rays. Competition between destruction and formation of C-H bonds determines an equilibrium value for grain hydrogenation. From the evolutionary point of view, the C-H bonds in the CH$_2$ and CH$_3$ groups responsible for the 3.4 $\mu$m stretching band and the associated bending features at 6.85 and 7.25 $\mu$m form in situ in the diffuse interstellar medium.

In dense regions an ice layer, consisting primarily of H$_2$O covers grains. The presence of the ice mantle, which prevents H atoms from interacting with the carbon grain, and the reduced amount of atomic hydrogen with respect to the diffuse regions inhibit hydrogenation. However, despite the presence of the ice layer on grains destruction of C-H bonds can proceed [24,25,26]. A breakdown of the equilibrium reached in the diffuse medium takes place and grain hydrogenation decays exponentially with time from its diffuse medium equilibrium value. The decay rate is the sum of terms due to the attenuated Galactic field, the internal radiation field and cosmic rays.

In conclusion, the difference of the 3.4 $\mu$m band in diffuse and dense clouds is due to evolutionary transformations of carbon grains caused by processing. C-H bond destruction occurs in both the dense and diffuse regions. Grain hydrogenation takes place in the diffuse clouds and is inhibited in dense molecular clouds.

3. The evolution of carbon core - mantle structures during energetic processing

In dense regions, the formation of core-mantle structures and the changes of gas properties with respect to diffuse clouds determine the conditions for a gradual dehydrogenation of the carbon particles. Processing is important not only for the evolution of refractory dust grains, but also for that of ice mantles. It is well known that energetic processing modifies the composition of ices. Much laboratory work has been carried out to characterize the infrared spectra of ices of astrophysical interest and their modifications under thermal processing and UV and ion irradiation [30,31,32]. However, laboratory studies have been performed on ices deposited on inert substrates. These experiments have been very useful to understand many fundamental aspects of the nature of interstellar ices. The chemical nature of grains can influence the formation and evolution of ices and can modify their chemical composition due to reactions at the grain-ice interface during energetic processing.

Only recently specific experimental information on the evolution with energetic processing of ices deposited on interstellar dust analogs has been obtained [33]. In particular, the formation of CO and CO$_2$ molecules induced by ion irradiation of hydrogenated carbon grains covered with a water ice layer has been observed. The evolution of the CO$_2$ band at 2339 cm$^{-1}$ and the CO feature at 2136 cm$^{-1}$ is shown in Figure 2.

The presence of CO ice in grain mantle is generally interpreted in terms of direct condensation of CO molecules from gas phase. On the contrary, it is thought that CO$_2$ forms in solid phase through surface reactions and/or energetic processing of ice mantles. A common aspect of these formation models is the presence of C atoms in C-bearing molecules (mainly CO) in the ice mantles. The results of irradiation of carbon grains covered with water ice show that CO and CO$_2$ molecules can also be directly formed from carbon atom of the grains during energetic processing.

The formation cross sections of these molecules, obtained from the band intensity increase with ion fluence are equal within the errors: $(7.3 \pm 0.5) \times 10^{-16}$ and $(7.7 \pm 0.3) \times 10^{-16}$ cm$^2$, respectively, for CO and CO$_2$. Moreover, at least about 2% and 3% of carbon atoms initially in the carbon grains are transformed by ion irradiation to CO and CO$_2$ molecules. These conversion factors and an estimation of the amount of carbon locked in carbon grains in dense molecular clouds allow the evaluation of the contribution of CO and CO$_2$ produced by cosmic
Figure 2. The CO$_2$ and CO bands of hydrogenated carbon grains covered with a water ice layer after ion irradiation at fluences of $7.3 \times 10^{14}$ and $3.8 \times 10^{15}$ ions cm$^{-2}$. The spectrum before ion irradiation is shown for comparison. The spectra are offset from each other in ordinate for the sake of clarity. They are arranged by increasing fluence from bottom to top.

ray irradiation of carbon particles to the observed column densities of these molecules for clouds whose visual extinction is known. The amount of CO and CO$_2$ molecules produced by cosmic ray irradiation of carbon particles can account for 3 - 7% and 3 - 36% of the observed CO$_2$ and CO, respectively. In the case of CO$_2$ oxidation of CO molecules of mantles by oxygen atoms and/or energetic processing of mantles are predominant for the formation of these molecules in dense clouds. It should be noted, however, that no quantitative estimation of the contribution of these processes has been reported so far.

Pontodoppian et al. [34] have recently shown that the solid CO band profile observed toward low-mass forming clouds is composed of three components. The red component at 2136.5 cm$^{-1}$ has a FWHM of 10.5 cm$^{-1}$ and accounts for 10 - 60% of the total CO. This component is not consistent with the available water-rich mixture of CO and the carrier has not been identified. The good correspondence of the profile of CO produced by ion irradiation of water-covered carbon grains with that of the interstellar CO red component and the estimated contributions to the total CO column densities motivated the assignment of the red component to CO formed on carbon grains [34].

It is worth noting that the formation of CO and CO$_2$ molecules on carbon grains and cycling of materials between dense and diffuse interstellar regions, where desorption of mantles takes place, determine a chemical erosion of these particles. The expected particle mass reduction is of about 10% during the particle lifetime.

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