CHEMICAL
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REVIEWS

Chemistry and physics of cosmic nano- and micro-particles

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Small solid particles represent an important and ubiquitous component of our and other galaxies and determine their overall spectral appearance. Although they constitute only a minor ingredient by mass, they control the thermal, dynamical, chemical, and ionization state of the cool and dense-phases of the interstellar medium. The grains are produced in the massive outflows of evolved stars, modified by shocks and radiative processing in the diffuse interstellar medium, and grow by accretion of ice mantles and coagulation in the dense cores of molecular clouds. The last step in their lifecycle is consumption by forming stars or their incorporation into planets. Cosmic dust particles are an extremely exciting system if one is interested in the formation routes from gas phase molecules to solids, the optical behaviour of small particles, and surface chemistry. Astronomical spectroscopy, together with dedicated laboratory studies, has led to the identification of carbonaceous solids, silicates, and different forms of ices in the Milky Way.

1 Introduction

The space between the stars is not empty, but is filled with a tenuous interstellar medium which in the Galaxy is characterized by an average density of 1 hydrogen nucleus per cm^3. This medium consists of distinct phases with very different thermodynamical properties. Most of the total mass of the galactic interstellar gas, which amounts to 6×10^9 solar masses, is contained in cool and 'dense' clouds. There are two types of such clouds: molecular clouds containing mostly molecular hydrogen, and clouds of atomic hydrogen. Molecular clouds are characterized by kinetic temperatures of 10–15 K and gas densities between a few hundred and 10^6 cm^{-3} in their dense cores. Diffuse atomic hydrogen clouds have higher average temperatures and lower densities of 80 K and 50 cm^{-3}, respectively. In addition, the interstellar medium (ISM) is pervaded by high-energy cosmic rays (MeV protons and He^{2+} ions) and exposed to an ultra-violet radiation field which has a mean flux density of 10^{10} photons m^{-2} s^{-1} nm^{-1}.

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Stars in their late evolutionary stages enrich the ISM with metals. In astronomy 'metals' include all of the elements from carbon onwards, the first element which is exclusively formed by stellar nucleosynthesis. The galactic ISM is assumed to be presently in a steady state where the consumption by star formation (a few solar masses per year) is balanced by mass injection from evolved stars and supernovae.

The presence of a general interstellar *extinction* causing reddening and weakening of stellar light was established in the early thirties of this century by Trümpler[1] and others. This was later correctly interpreted by the application of Mie's scattering theory as the result of absorption and scattering of light by small solid particles. A striking piece of evidence for the presence of such grains had already been found 150 years earlier when William Herschel detected 'holes in the sky'. However, he misinterpreted these holes as starless regions, whereas in fact they are dark clouds composed of solid particles, blocking the light of background stars.

The solid particles in the Galaxy contain about 1% of the total mass of the ISM. In astronomy the term 'interstellar dust' has been coined to describe this small-particle system. The grains have sizes between a few nanometers and several microns, whose size distribution tends to follow a power law with an exponent of -3.5. This size distribution extends into the molecular domain and sometimes even large molecules are included when the population of interstellar dust particles is considered. In this review, however, I will not follow this approach and will exclude large molecules such as polyaromatic hydrocarbons from detailed considerations (see, for example refs 2, 3 and references therein).

Based on spectroscopic evidence, the most important chemical components of interstellar dust are carbonaceous solids and silicates. Slightly elongated particles of sub-micron size with ferromagnetic or superparamagnetic inclusions aligned by magnetic fields are thought to be responsible for the observed polarization at visible and infrared wavelengths.

Although the cosmic nano- and micro-particles contain only a small amount of the total mass of the Galaxy, they are the main source of the continuous opacity in the ISM—at least at ultraviolet and optical wavelengths because of their high absorption and scattering coss-sections. This not only means that they are extremely important for the appearance of galaxies, but also implies that they strongly influence the thermal and dynamical state of the dense phases of the ISM. Very small grains and larger molecules also dominate the photoelectric heating of the interstellar gas. Furthermore, surface chemistry on dust grains contributes to the chemical state of molecular clouds and protoplanetary disks. Without these grains, an efficient formation of molecular hydrogen—the main component of molecular clouds—would not be possible.

The measurement of thermal dust radiation at infrared and sub-mm to mm wavelengths is an important analytical tool to determine the morphology, temperature and column density of matter (number of particles in a column with the cross-section of a unit area) in the environment of young and evolved stars, starburst galaxies, and active galactic nuclei (AGN). It is important to note that cosmic dust consists of different populations typical of the circumstellar shells around evolved stars, the general diffuse ISM, the molecular clouds, and the protoplanetary disks.

The interaction of light and gas with a system of small solid particles can be studied both theoretically and in the laboratory, and comparisons can be made with the results of ultra-violet, optical, and infrared spectroscopy of interstellar dust. This is often a very demanding experimental task if one considers the extreme conditions prevailing in interstellar space which include low temperatures, energetic radiation fields, and low densities. That such research can also contribute to basic chemistry was nicely demonstrated by the fullerene story[4] and the investigation of carbon chain molecules[5] and polyaromatic hydrocarbons (PAHs).[3]

There are quite a number of proceedings and review papers about interstellar dust including more than one written by the author of the present paper.[6–10] A book appropriate for graduate students has been written by Whittet.[11] In these publications the interested reader will also find extensive compilations of useful references. In this article I will not repeat the material given in these books and papers, but I will attempt to summarize the basic principles governing the chemistry and physics of solid particles in space.

2 Astrophysical constraints

The physical structure and the chemical composition of cosmic dust grains are constrained by the following factors: (a) the cosmic abundance of the elements and their depletion in the interstellar gas by the formation of solids, (b) the conditions in the mass outflows from evolved stars, (c) the wavelength dependence of extinction and polarization at ultra-violet, optical, and near-infrared (IR) wavelengths and of thermal emission at far-infrared and sub-millimetre/millimetre wavelengths, (d) the observed spectroscopic features, and (e) the results coming from the analysis of pre-solar grains preserved in ‘primitive’ (unaltered) meteorites.

The most abundant metals—oxygen, carbon, iron, silicon and magnesium—are heavily depleted in the gas phase and form the ‘building blocks’ of the dust grains. Two main types of evolved stars produce fresh ‘stardust’. These are carbon-rich and oxygen-rich giants. In the case of carbon-rich giants, the elemental [C/O] ratio in the mass outflows is larger than 1 and the oxygen is bound to the stable CO molecule. Here, we expect the formation of carbonaceous grains, carbides, and sulfides with a chemistry very similar to what we know from soot formation in hydrogen-rich atmospheres. For the oxygen-rich stars we have the opposite case where all the carbon is bound to CO, so we expect the formation of silicates and other metal oxides. The total stardust injection rate in the Galaxy is about 5×10^{-3} solar masses per year. Supernovae may also be major suppliers of cosmic dust, but neither the efficiency of dust production nor the chemical composition are well known.

Indeed, the most abundant components of dust in the general diffuse ISM are silicates and other oxides on the one hand and various allotropes of carbon on the other. The amorphous interstellar silicates have a strong infrared feature at about 9.7 μm (stretching mode) and a weaker feature at about 18 μm (bending mode) with some evidence for the presence of hydrated silicates from features observed in the 2.75 to 3.00 μm range. In the diffuse ISM, amorphous silicates contain about 60% of the total dust volume.[12] Pure carbon materials have no strong IR signatures, in contrast to the electronic transitions they show at UV wavelengths. Solid aromatic carbon particles with some degree of disorder show C=C ring stretching modes in the range between 6.2 and 6.4 μm. In addition, spectroscopically active modes exist if hydrogen atoms are attached to the carbon network. The absorption features at 3.4 and 6.8 μm observed in the diffuse ISM are in general attributed to CH stretching and deformation modes of CH_2 and CH_3 groups in aliphatic hydrocarbons.[13] However, the hydrocarbons—which are very often assumed to be the mantles around silicate particles—form only a minor fraction of the total amount of dust in the diffuse ISM. A broad emission plateau between 6 and 9 μm observed in the spectra of quite a number of objects including the Orion Bar and post-Asymptotic Giant Branch (AGB) stars was frequently attributed to very large PAHs or hydrocarbon particles.

The most valuable information on carbon dust comes from a very strong extinction bump near 4.6 μm (217.5 nm) which is entirely due to absorption by solid particles. It can only be observed from space platforms and the most complete data set came from spectrophotometry performed with the *International Ultraviolet Observer IUE*. The feature was frequently attributed to a surface plasmon absorption in small spherical graphite particles. However, more and more evidence is accumulating that the feature is actually a π–π^* transition in a soot-like carbonaceous solid. The properties of this feature will be discussed in greater detail in Section 4.

Other dust components which are expected to be present at least in the C-rich circumstellar shells around evolved stars are carbides and sulfides. Silicon carbide was identified on the basis of a relatively broad feature peaking between 11.0 and 11.5 μm. Sulfides were proposed to be the carriers of the 21 and 30 μm features. One should stress that identifications based on a single band are and will always be a problem, especially when they are based on noisy and low-resolution spectra. (Note that in astronomy the wavelength scale instead of the wavenumber scale is frequently used.)

The spectra of young stellar objects deeply embedded in molecular cloud cores or associated with disks/envelopes and the spectra of background sources behind molecular clouds demonstrate the importance of the accretion of atoms and molecules and the formation of ice mantles around the particles. The dominant component of the ice mantles is H_2O with its well-investigated features at 3.05 and 6.0 μm while the carbon-bearing ices CO, CO_2 and CH_3OH are less abundant by at least an order of magnitude.

Direct *in-situ* evidence for the formation of distinct materials in the outflows of evolved stars and supernovae has been collected from the analysis of carbonaceous chondrites, the most primitive meteorites in our solar system, which contain primordial condensates of the solar nebula and pre-solar grains. These pre-solar grains can be identified by the isotopically anomalous proportion of both the skeleton elements and the noble gases and other minor elements they contain. This technique led to the identification of pre-solar nanodiamond, silicon carbide, graphitic, corundum and silicon nitride grains with other tiny carbide particles (TiC, ZrC, MoC) found within the graphitic grains.

3 Infrared dust spectroscopy

The infrared wavelength region from 1 to 100 μm is often called the ‘fingerprint’ region for dust spectroscopy because it covers the range of fundamental bending, stretching and skeleton modes in solids. The broad solid-state features can easily be distinguished at higher spectral resolution from the bands of gas phase molecules, which show a typical rotational-vibrational structure (see Fig. 1). Astronomical infrared spectroscopy is a ‘pencil-beam’ technique which always probes the material composition along the line of sight towards an infrared source. It is less sensitive compared to millimetre emission spectroscopy if one wants to determine molecular abundances. A more severe limitation of infrared spectroscopy is the fact that complex organic materials composed of similar compounds show very similar spectra. This makes the exact identification of carriers of broad bands such as the 3.4 μm feature ambiguous,

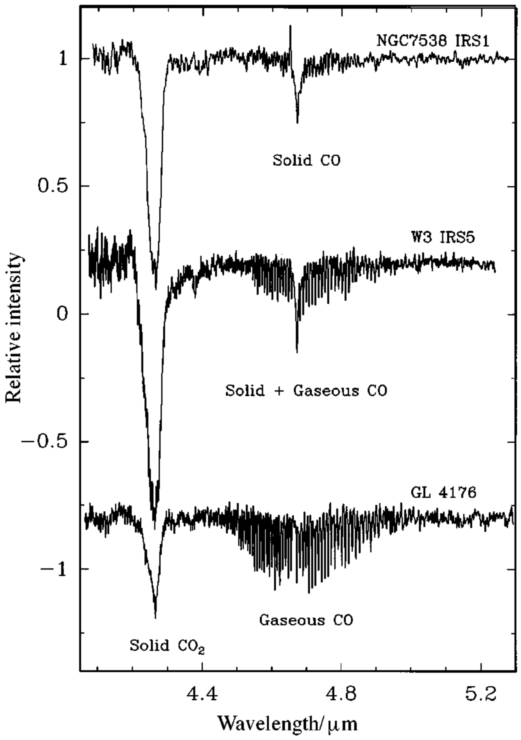

Fig. 1 Normalized infrared spectra taken with the 'Short Wavelength Spectrometer' on board the *Infrared Space Observatory* in the wavelength region of the CO_2 ν_3 and CO vibrational bands toward three embedded young stellar objects. The CO_2 is primarily in solid form, indicated by the broad line shape. The spectra have been shifted by 0.0, −1.0 and −2.25 for clarity. After van Dishoeck *et al.*[14]

and indeed, different materials fit the spectroscopic data in this case equally well.

Infrared dust 'spectroscopy' started about 30 years ago with broad-band and narrow-band photometry. The first results included the detection of the broad 10 and 18 µm silicate features[15,16] and of the SiC emission band.[17,18] Ground-based observations can only give a limited amount of information because key regions of astronomical infrared spectra are blocked by atmospheric components like water vapour, carbon dioxide and ozone. From 15 km cruising altitude of an aircraft, the broad-band atmospheric transmission is higher than 70% at most infrared wavelengths. In the pre-infrared satellite era, the 5–8 µm range and the wavelengths longward of 23 µm were almost exclusively the province of NASA's Kuiper Airborne Observatory. The KAO led to the detection of the water ice features at 6.0, 45 and 62 µm, the so-called unidentified infrared bands (UIBs) in the 5 to 8 µm range often attributed to PAHs, the hydrocarbon feature at 6.8 µm, the CH_4 ice band at 7.66 µm and the 30 µm feature in the spectra of carbon-rich evolved stars.[19]

However, there are still regions of the spectrum which are only accessible to space-based observations. Examples are the regions at 4.0–4.5 µm and 15–16 µm which are blocked by atmospheric CO_2. The low resolution spectrometer LRS (wavelength range 8–23 µm, resolution $\lambda/\Delta\lambda$ = 20–60) on board the *Infrared Astronomical Satellite IRAS* recorded about 170 000 spectra from 50 000 sources. The best 5425 spectra are compiled in the LRS Atlas[20] and many more spectra were discussed in later publications. These spectra allowed a statistical investigation of the UIBs and the silicate and carbide features to be made, and triggered many ground-based follow-up studies in the 3 µm window. Furthermore, new dust features were detected in the LRS spectra. They included the 15.2 µm feature found in the LRS spectra of a few young stellar objects attributed to solid CO_2 and the 21 µm feature present in the spectra of post-AGB stars. IRAS data also led to the detection of an excess emission in the 12 and 25 µm IRAS bands from diffuse clouds ('Cirrus' regions), due to very small grains or large molecules.

In the course of writing this paper, the 'infrared revolution' triggered by the *Infrared Space Observatory ISO* has just started. The most appropriate ISO instrument for dust spectroscopy is the short-wavelength spectrometer SWS which has a spectral resolution of 2000 and a wavelength coverage from 2.5 to 45 µm in its grating mode. The PHOT-S instrument has a spectral resolution of only 90 and a very limited wavelength coverage but is more sensitive. Early results of the ISO mission are summarized in a special issue of *Astronomy and Astrophysics*.[21] These results include: the detection of solid CO_2 as a widespread ice component in the environments of luminous and deeply dust-embedded young stellar objects; the partial crystallinity of silicates (see Fig. 2) in quite a number of objects ranging from comets over Herbig Ae/Be stars to evolved oxygen-rich objects; the detection of UIBs between 5.8 and 11.6 µm in the diffuse emission of the galactic disk; and the observations of UIBs in the spectra of other galaxies.

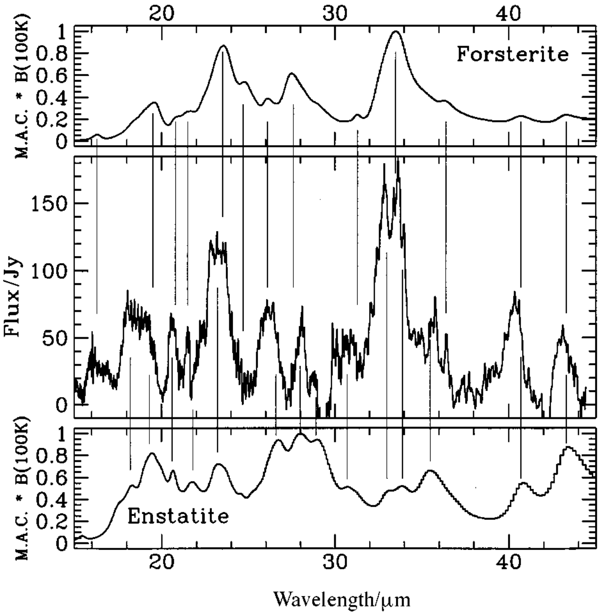

Fig. 2 Comparison of the continuum subtracted ISO SWS spectrum of AFGL 4106, a transition object between the asymptotic giant branch and the planetary nebula phase, with the mass absorption coefficients of crystalline forsterite and clino-enstatite multiplied by a Planck function of 100 K and normalized to unity. After Jäger *et al.*[24]

The large amount of new data on the UIBs will certainly revive the discussion about the real carriers of these bands. Strong UIBs are located at 3.3, 6.2, 7.7, 8.6 and 11.3 µm with a wealth of weaker features present as well. These bands are very typical of aromatic hydrocarbons.[22,23] The non-thermal nature of the emission suggests that the UIB carriers are free molecules containing between 50 and 100 C-atoms. This, together with the required stability of the molecules in regions of high UV fields, make large PAH molecules prime candidates for molecules responsible for the UIBs. The variation in the relative strengths of the UIBs may be related to different hydrogenation and ionization states of the molecules. Larger carbon clusters with a few hundred to a few thousand C-atoms should emit the non-thermal mid-infrared radiation observed in different regions of the Galaxy.

4 Materials in interstellar and circumstellar media

4.1 Silicates and other oxides

Relatively broad features at 9.7 and 18 µm have been observed in the spectra of circumstellar dust around evolved oxygen-rich stars and young stellar objects both in absorption and emission depending on the optical depth of the regions. A deep 9.7 μm absorption feature is also present in the spectra of infrared sources with lines of sight probing the diffuse ISM. The features are attributed to asymmetric Si–O stretching and O–Si–O bending vibrations of silicon–oxygen tetrahedra. The broad bands point to the presence of highly disordered silicates with properties similar to those of silicate glasses. Apart from structural disorder, the formation of 'stardust' under non-equilibrium conditions probably also leads to a certain degree of chemical disorder such as unequilibrated components, non-stoichiometric ratios (oxygen deficiency: not all of the silicon ions form perfect SiO_4 tetrahedra), and dangling bonds. The silicate spectra show quite some variations, pointing to a considerable diversity of cosmic silicates.

The cosmic abundance of elements favours the presence of Mg/Fe silicates.The silicate-forming metals Al, Ca, Ni and Na, following Mg and Fe in elemental abundance, should only play a minor role for the chemical composition of the silicates. All these metals are indeed strongly depleted from the gas phase with nearly all the silicon locked up in silicates. There is evidence from gas phase abundance patterns and spectroscopy that in addition to silicates, iron and aluminium oxides also exist. Olivine- and pyroxene-type silicates have been widely discussed as laboratory analogues for interstellar silicates. Olivines [$(Mg, Fe)_2SiO_4$] are nesosilicates ('island' silicates) with isolated SiO_4 tetrahedra (without polymerization) connected by metal ions. Pyroxenes [$(Mg, Fe)SiO_3$] belong to the class of inosilicates ('chain' silicates) which contain chains of polymerized tetrahedra bonded over two corners by bridging oxygens. The weak hydration feature near 2.75 μm in the spectra of interstellar silicates points to a few percent by weight of OH in interstellar silicates.

The characterization of so-called GEMS (glasses with embedded metal and sulfide) in interplanetary dust grains led to the conclusion that they are of pre-accretional origin. They show striking similarities with the expected properties of interstellar silicates such as the size (0.1–0.5 μm diameter), amorphous state, composition and inclusions of iron. It has already been mentioned in the introduction that superparamagnetic inclusions are necessary for silicate grain alignment by magnetic fields to explain the observed interstellar polarization pattern.

Although some evidence for the presence of crystalline circumstellar silicates was available before the launch of ISO, the detection of prominent emission and absorption features in ISO spectra at 10.1, 11.2, 13.8, 16.3, 19.5, 21.5, 23.7, 27.9, 33.6, 35.5, 36.5, 40.5, 43.0 and 69.5 μm attributed to crystalline olivines and pyroxenes was highly suprising (see Fig. 2). A more detailed comparison of the astronomical spectra with laboratory data indicates that the pure magnesium members (forsterite and enstatite) are mainly responsible for the 'crystalline' features.

4.2 Carbonaceous materials

A detailed description of carbonaceous grains in space would require its own review and is beyond the scope of this paper (see refs 25, 26 and references therein). Here, we only concentrate on the carrier of the very strong UV bump in the interstellar extinction curve at 217.5 nm. Remarkable properties of this feature are the constancy of the peak position (variations smaller than 1%) and larger variations (up to 25%) in the peak width around a mean value of 1 μm^{-1} in wavenumbers. The variations in width are uncorrelated with the small variations in peak position.

Since its discovery in the mid-sixties the bump has been attributed to π-electron plasmon absorption in small spherical graphite particles or π–π* transitions in disordered carbonaceous grains. The graphite plasmon feature should be intrinsically very strong. Therefore, the position and shape of the feature should be sensitive to shape and size variations. The weakness of the graphite hypothesis lies in the 'fine-tuning' of the bulk optical constants and the size/shape of the grains to give a good 'fit' to the astronomical feature and the unrealistic assumption of the existence of nanometre-sized particles composed of mono-crystalline (anisotropic) graphite. Realistic carbonaceous grains show a wide range of structures due to the different hybridization states of carbon. On an intermediate scale, the sp^2-hybridized carbon atoms tend to form planar graphitic microcrystallites, so-called basic structural units (BSUs), which can be embedded between a matrix consisting mainly of sp^3-hybridized carbon. Both carbon particles with almost concentrically arranged graphitic units and particles with randomly oriented graphitic structures have been observed as products of soot formation. In these semiconducting solids, the π electrons produce the electronic density of states near the Fermi energy, and the sp^2-bonded structures determine the optical gap. Interband transitions between the binding and anti-binding π-electron bands occur mainly in the UV with a maximum between 200 and 260 nm wavelength, whereas those of the σ-electrons are located around 80 nm. The wing of the latter feature could contribute to the observed FUV rise in the extinction curve.

In the diffuse ISM for which the UV bump is a characteristic feature, structural changes in the carbonaceous grains can be expected by UV and ion irradiation. Indeed it was demonstrated experimentally that irradiation leads to structural changes and to UV bumps located close to the position of the astronomical feature.[27] Narrow features can be produced by isolated particles, whereas the widening of the bump can be attributed to particle clustering.[28] In Fig. 3 a comparison between the profile of the interstellar extinction bump and a measurement of isolated nanometre-sized hydrogenated carbon grains can be found.

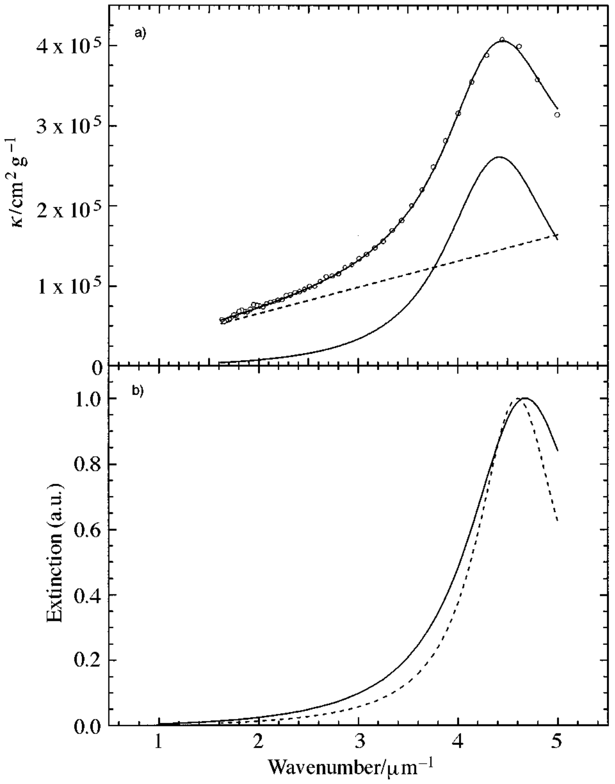

Fig. 3 (*a*) Decomposition of the spectrum of nanometre-sized and isolated hydrogenated carbon grains in a linear component (dashed line) and a Drude profile (solid line); (*b*) comparison of the measured and matrix-corrected profile with the Drude component of the mean interstellar extinction curve (dashed line). After Schnaiter *et al.*[28]

4.3 Molecular ices

Spectroscopic evidence for molecular ices has been found in the infrared spectra of background stars behind molecular clouds, deeply dust-enshrouded young stellar objects, and cool oxygen-rich stars. Here we will only discuss the properties of ices in molecular clouds (see, for example ref. 29).

Observations with the *Infrared Space Observatory* resulted in a complete inventory of molecular ices in molecular clouds (see Fig. 4). The most abundant component is H_2O ice, followed by CO and CO_2 on the 10% level, relative to H_2O. Water ice has infrared features at 3.05 μm (OH stretching mode), 6.00 μm (HOH bending mode) and 13.3 μm (libration mode) with lattice modes at far-infrared wavelengths (45 and 62 μm), all of which are observed. The diagnostic feature of CO ice is located at 4.67 μm (CO stretching mode), whereas the CO_2 ice features are observed at 4.27 μm (CO stretching mode) and 15.3 μm (OCO bending mode). The observed 6.0 and 6.6 μm features seem to be a blend of different features. The blue emission wing of the 6.0 μm feature cannot be attributed to H_2O ice and was tentatively identified with the C=O stretching vibration of an organic acid (*e.g.* formic acid HCOOH). Methanol ice contributes to the 6.8 μm feature, but the real carrier remains to be identified. The same is true for the 4.62 μm feature which is probably caused by an ice component containing a nitrile group ('XCN'). Minor ice components such as CH_4, CH_3OH and XCN are present at the level of a few percent relative to H_2O. The detailed analysis of the spectroscopic results suggests that CO-bonded carbon atoms are more abundant than CH-bonded carbon atoms in the molecular ices. Together with the low limits for the abundance of NH_3 ice (less than 5% relative to water), this suggests that the accreted gas was mostly of molecular composition (high CO/C and N_2/N ratios).

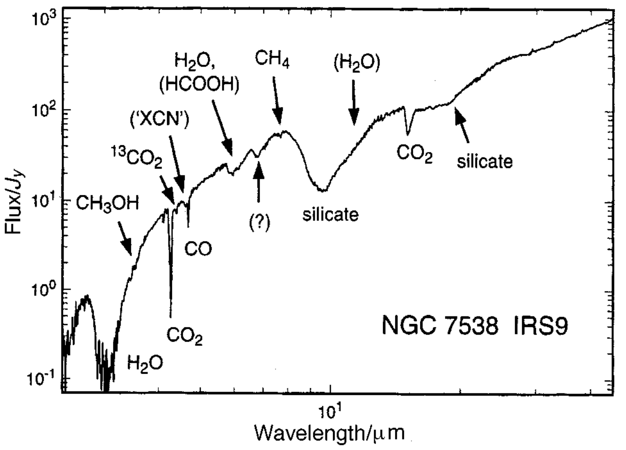

Fig. 4 ISO SWS spectrum of the young stellar object NGC 7538-IRS9, covering the full SWS range from 2.4 to 45 μm at a spectral resolution of about 500. Various absorption features due to solid ice and silicates can be identified. After Whittet *et al.*[30]

If the density becomes high enough in molecular clouds, atoms and molecules collide with dust grains and stick to their surface. However, only the CO molecule has a high enough gas phase abundance to form an ice mantle by direct freeze-out. The presence of other ice components, especially of H_2O and CO_2 ice, cannot be explained by the accretion of these molecules from the gas phase, but is clearly an indication of hydrogenation and oxidation reactions on grain surfaces. The composition of the ice mantles very probably depends on the actual H/H_2 ratio. If atomic hydrogen is available, hydrogenated species such as H_2O, CH_4, H_2CO and CH_3OH can form. At higher densities the H/H_2 ratio decreases and oxidation reactions become important, including the formation of CO from CO_2. Different H/H_2 ratios can also be an explanation for the occurrence of both 'polar' (H_2O-rich) and 'non-polar' (H_2O-poor and CO/CO_2-rich) ices.

In addition, the different sublimation temperatures of pure and embedded ice components may play a role in determining the ice composition. Under interstellar conditions, the sublimation temperatures of CO and H_2O are 20 K and 90 K, respectively. The release of mantle material by thermal heating or even the destruction of grain cores by shocks associated with energetic outflows from young stars can trigger a completely new and complex gas phase chemistry in the so-called hot cores associated with very young massive stars.

Ultra-violet photoprocessing is another process which has been widely considered to be of importance for the chemical evolution of molecular ices. It was proposed that photodissociation (*e.g.* dissociation of H_2O) can lead to radicals (*e.g.* OH) and the subsequent formation of simple molecules (CO_2) as well as more complex molecules (CH_3OH, H_2CO) by radical–radical and radical–molecule reactions. Experiments have demonstrated that prolonged periods of ultra-violet irradiation and warm-up can lead to the production of even more complex molecules. Finally extended UV photoprocessing (and ion irradiation) may lead to macromolecular carbonaceous mantles. Laboratory experiments indicate that the 4.62 μm feature can be produced by UV irradiation of ices containing nitrogen, and OCN^- may be a good candidate for the carrier of this feature. However, there is no strong evidence for complex molecules in the ices from infrared spectroscopy, which casts some doubt on the importance of ultra-violet photolysis.

5 Laboratory astrophysics and astrochemistry

5.1 Grain formation

Grain formation in cool outflows from evolved stars takes place in a temperature and pressure regime which is different from the conditions we usually have in laboratory experiments. During the expansion of the outflow, matter cools and complex molecules and clusters can form. Efficient cluster formation and growth is expected at temperatures around 1000 K and gas densities between 10^8 and 10^{10} cm^{-3}. In astrophysics the grain formation process has been often described by classical nucleation theory. The main goal of this theory is to predict the formation rate of 'critical' clusters formed by monomer additions (clusters with less monomers are unstable). This theory was actually developed for the description of water droplet formation but fails when applied to soot formation or condensation of refractory materials from the gas phase. In the case of metal oxide and soot formation, the monomers are not present in the gas phase, and chemical bonds have to be broken during the nucleation and growth process. Therefore, a chemical kinetic description is much more appropriate, but the difficulty often lies in the lack of kinetic data for individual reactions, especially in the case of the oxygen-rich chemistry.

Relatively few experiments have been performed to study the formation of clusters in a metal-SiO gas mixture, which is the relevant chemical composition for the outflows of oxygen-rich stars. The Goddard group found that above 950 K, Mg and Fe do not join SiO_x clusters and only these clusters are stable at high temperatures.[31] At lower temperatures the clusters with their large surface areas deplete the gas phase of refractory metals such as Fe or Mg and also provide a substrate for additional reactions with oxygen and oxygen-bearing molecules. A thorough understanding of the formation of metal oxides in oxygen-rich outflows is hampered by a lack of experimental data on the relevant reaction rates.

The formation of carbonaceous materials in the outflows of evolved C-rich stars is assumed to be similar to soot formation in hydrocarbon flames.[32,33] The study of this process relies heavily on the large amount of information coming from the investigation of soot nucleation in combustion. The most abundant precursor molecule for the formation of carbon grains in the outflows is acetylene. Grain formation should start with the production of the first aromatic rings, involving the replacement of the acetylenic triple bond by a double bond.

Further chemical growth of the aromatic ring molecules consists of the formation of radical edge sites through hydrogen abstraction and addition of hydrocarbons—especially acetylene—to the radical sites. Coalescence of larger aromatic units finally leads to soot particles with turbostratic structures. Surface growth on the periphery of aromatic planes may lead to cross-linking by aliphatic hydrocarbon chains resulting in a material which resembles hydrogenated amorphous carbon (a-C : H). The temperature window for the chemical growth process is rather small (1100–800 K). For temperatures below 1100 K the addition of acetylene becomes an irreversible reaction starting the growth process. For temperatures below 800 K, the endothermicity of the hydrogen abstraction reduces the formation rate of radical sites and stops the growth process. This leads to low PAH formation yields of 10^{-4}–10^{-5} for distances from the star larger than two stellar radii. A somewhat different scenario for the formation of carbonaceous grains starts with the formation of carbides which later act as condensation nuclei. Carbon grain formation also takes place in hydrogen-deficient atmospheres of carbon-rich Wolf–Rayet stars and R Coronae Borealis stars. In this case, it should be very similar to the route of fullerene formation *via* smaller linear carbon chains, cyclic C_{10}, larger monocyclic and bi-tri-cyclic rings finally leading from fullerenes to carbon dust particles.

5.2 Surface reactions

The importance of surface reactions to produce molecular hydrogen in space was realized even before interstellar molecular hydrogen was detected.[34] Radiative association of two hydrogen atoms [H(1s) + H(1s)] is extremely slow because H_2 has no permanent dipole moment, and so would have to involve forbidden rotational–vibrational transitions. Collisions with a third gas-phase species, which would ‘absorb’ the excess energy, are extremely rare under the molecular cloud conditions. It is now generally accepted that the formation of the most abundant molecule in space, molecular hydrogen, occurs on grain surfaces. However, there are only very few experimental studies of this process under conditions relevant to astrophysics (low kinetic energy of incoming H atoms, low substrate temperature, appropriate substrate material) (see, for example ref. 35). We already touched on the importance of grain surface chemistry when we discussed the chemical composition of interstellar ices (see Section 4), a second area where surface reactions have to be considered.

Surface reactions in the ISM include: (i) sticking and accommodation of gas phase atoms and molecules on the grain surface, (ii) scanning of the surface to find a co-reactant, and (iii) ejection of the newly formed species. Two different reaction schemes for grain-surface reactions were considered in astrochemistry.[36] These are the ‘accretion-limited’ and the ‘reaction-limited’ regimes. In the first case, the migration time of a species on the surface is shorter than the accretion time. This means that the surface chemistry is limited by the accretion rate rather than by the co-reactant collision rate. This implies that the rate coefficients play only a limited role, and a Monte Carlo approach is more appropriate to describe the chemistry. ‘Reaction-limited’ chemistry deals with the case that the surfaces contain many reactive species (large surfaces instead of the small grains) and the reactions are limited by the co-reactant collision rates. Such models can be treated by conventional rate equations and are very similar to gas phase models. The ‘accretion-limited’ regime seems to be more appropriate to surface chemistry in molecular clouds because gas-phase species are accreted at an average rate of about 1 species per day. The migration time scales of the lighter species (H, C, N, O) are short compared with this accretion time scale. Besides atom–radical reactions, atomic hydrogen addition reactions are the most important reaction channels, since atomic hydrogen rapidly tunnels through activation barriers.

In most of the models for grain surface chemistry, a diffusive approach has been considered. In this mechanism, also known as the Langmuir–Hinshelwood mechanism, reactions between species in thermal equilibrium with the surface occur. Another mechanism, the so-called Eley–Rideal process, was widely ignored. Here a chemisorbed and a non-chemisorbed species react. This means that the gas-phase reactant does not equilibrate with the surface and the reactions can be far more exothermic than their Langmuir–Hinshelwood counterparts. A known example of such a reaction is the hydrogen abstraction from a diamond surface.

Only in the case of the weakly bounded H_2 molecule is desorption easily possible at the low grain temperatures in quiescent molecular clouds. Non-thermal desorption processes such as cosmic-ray spot heating, cosmic-ray induced thermal desorption and explosive heating by chemical reactions have been invoked to explain the release of heavier species into the gas phase. However, the efficiencies of these processes have not been very reliably determined.[29]

5.3 Spectroscopy

The identification of interstellar dust components relies heavily on the comparison of astronomical spectra with spectroscopic measurements performed on cosmic dust analogue materials in the laboratory. Such measurements should provide optical data for well-characterized materials (chemical composition, degree of disorder) over a broad wavelength range—in the ideal case from the vacuum UV to the far infrared. In addition, possible variations of the optical behaviour with temperature in the range appropriate to cosmic grains (10–1500 K) have to be investigated.

Optical data for materials relevant to astronomy (*e.g.* silicate glasses of cosmic elemental composition, carbonaceous grains, irradiated materials) are often not available. There is a number of active laboratory groups producing and measuring such specific materials. A wide variety of production techniques to produce small particles important for astronomy have been applied, including mechanical dispersion methods, condensation techniques (arc discharge, sublimation from resistively heated rods), chemical vapour deposition methods (laser induced chemical vapour deposition, plasma discharges) and ablation techniques (laser ablation, sputtering).

Two different approaches have usually been applied to the characterization of the optical properties of the materials. These are the measurements of absorption and scattering on small particle systems and the measurement of the wavelength-dependent optical constants (complex dielectric function, complex refractive indices). Both methods have their own pros and cons. In the case of measurements on small-particle systems, size, shape and clustering effects are difficult to evaluate. Limitations of the second approach are that no bulk equivalent of the small particles may exist or that the optical constants of very small particles become size-dependent. Comparisons between these methods can be performed when using scattering calculations to obtain absorption and scattering efficiencies from the complex refractive indices. Such calculations can also be used to evaluate the size, shape and clustering effects. The simplest case of scattering calculations are those performed on the basis of Mie scattering theory for spherical particles. Meanwhile, more sophisticated methods are available for non-spherical and agglomerated grains (see the excellent text by Bohren & Huffman).[37]

The effects of particle clustering and wide size distributions can only be circumvented by spectroscopy on isolated small particles with a narrow range of sizes. Molecular beam techniques coupled with mass spectroscopy and matrix-isolation spectroscopy have recently been applied to characterize the optical properties of nanometre-sized dust analogue grains.[28]

Optical data for cosmic dust analogues have been produced by the NASA Ames and Leiden Astrochemistry groups for ices, by the Naples group for carbonaceous solids, by the Goddard group for silicates, and by the Jena Laboratory Astrophysics group for carbonaceous solids, oxides (including silicates) and other refractory materials. Electronic data bases exist for ices and refractory solids and can be accessed by http://www.strw.leidenuniv.nl (ices) and http://www.astro.uni-jena.de (refractory solids).

6 Outlook

Astronomical spectroscopy will continue to contribute to our knowledge of the physical conditions in the ISM in our own and other galaxies. The airborne observatory SOFIA and infrared space telescopes such as FIRST will allow sensitive and high-resolution spectroscopy in the far-infrared, a wavelength region where bending modes of pure carbon clusters and vibrational bands of PAHs are located. NASA's *Stardust* mission will bring back cometary and interstellar grains to Earth for a detailed chemical and physical analysis around the year 2006. Spectroscopy on mass-selected isolated small particles in the laboratory is required for a better understanding of the observed astronomical features. The formation of refractory grains can only be better understood when kinetic reaction rates become available. Surface chemistry taking into account the specific conditions in interstellar space has to be added to the gas phase chemistry in molecular clouds in order to explain grain mantle composition and the production of complex molecules.

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8 References

1 R. Trümpler, *Lick Obs. Bulletin*, 1930, **420**
2 L. J. Allamandola, in *The Cosmic Dust Connection*, ed. J. M. Greenberg, Kluwer, Dordrecht, 1996, p. 81.
3 F. Salama, in *Low Temperature Molecular Spectroscopy*, ed. R. Fausto, Kluwer, Dordrecht, 1996, p. 169.
4 H. Kroto, *Science*, 1988, **242**, 1139.
5 J. P. Maier, *Chem. Soc. Rev.*, 1997, **24**, 21.
6 *Molecules and Grains in Space*, ed. I. Nenner, AIP Conf. Proc. 312, AIP Press, New York, 1994.
7 *Dust and Chemistry in Astronomy*, ed. T. J. Millar and D. A. Williams, Institute of Physics Publ., Bristol and Philadelphia, 1993.
8 J. Dorschner and Th. Henning, *Astron. Astrophys. Rev.*, 1995, **6**, 271.
9 Th. Henning, *The Cosmic Dust Connection*, ed. J. M. Greenberg, Kluwer, Dordrecht, 1996, p. 399.
10 Th. Henning, in *Molecules in Astrophysics: Probes and Processes*, IAU Symp. No. 178, ed. E. F. van Dishoeck, Kluwer, Dordrecht, 1997, p. 343.
11 D. C. B. Whittet, *Dust in the Galactic Environment*, Institute of Physics Publ., Bristol, Philadelphia, New York, 1992.
12 D. C. B. Whittet and A. G. G. M. Tielens, in *From Stardust to Planetesimals*, ASP Conf. Ser. 122, ed. Y. J. Pendleton, A. G. G. M. Tielens, San Francisco, 1997, p. 161.
13 Y. J. Pendleton and J. E. Chiar, in *From Stardust to Planetesimals*, ASP Conf. Ser. 122, ed. Y. J. Pendleton, A. G. G. M. Tielens, San Francisco, 1997, p. 179.
14 E. F. van Dishoeck, F. P. Helmich, W. A. Schutte, P. Ehrenfreund, F. Lahuis, A. C. A. Boogert, A. G. G. M. Tielens, Th. de Graauw, P. A. Gerakines and D. C. B. Whittet, in *Star Formation with the Infrared Space Observatory*, ASP Conf. Ser. 132, ed. J. Yun and R. Liseau, San Francisco, 1997, p. 54.
15 N. J. Woolf and E. P. Ney, *Astrophys. J.*, 1969, **155**, L181.
16 F. J. Low and K. S. K. Swamy, *Nature*, 1970, **227**, 1333.
17 J. A. Hackwell, *Astron. Astrophys.*, 1972, **21**, 239.
18 R. Treffers and M. Cohen, *Astrophys. J.*, 1974, **188**, 545.
19 E. F. Erickson and J. A. Davidson, in *Proceedings of the Airborne Astronomy Symposium on the Galactic Ecosystems: From Gas to Stars to Dust*, ed. M. R. Haas, J. A. Davidson and E. F. Erickson, ASP Conf. Ser. 73, San Francisco, 1994, p. 707.
20 IRAS Science Team, ed. F. M. Olnon and E. Raimond, *Astron. Astrophys. Suppl. Ser.*, 1986, **65**, 607.
21 Special ISO Issue of Astronomy and Astrophysics, 1996, *Astron. Astrophys.*, **315**, No. 2.
22 J. L. Puget and A. Léger, *Ann. Rev. Astron. Astrophys.*, 1989, **27**, 161.
23 L. J. Allamandola, A. G. G. M. Tielens and J. R. Barker, *Astrophys. J. Suppl. Ser.*, 1989, **71**, 733.
24 C. Jäger, F. Molster, J. Dorschner, Th. Henning, H. Mutschke and R. Waters, *Astron. Astrophys.*, 1998, in the press.
25 Th. Henning and F. Salama, *Science*, 1998, submitted.
26 Th. Henning and M. Schnaiter, in *Laboratory Astrophysics and Space Research*, ed. P. Ehrenfreund, H. Kochan, C. Krafft, V. Pirronello, Kluwer, Dordrecht, 1998, sin the press.
27 V. Mennella, G. A. Baratta, L. Colangeli, P. Palumbo, A. Rotundi, E. Bussoletti and G. Strazzulla, *Astrophys. J.*, 1997, **481**, 545.
28 M. Schnaiter, H. Mutschke, J. Dorschner, Th. Henning and F. Salama, *Astrophys. J.*, 1998, **498**, 486.
29 W. Schutte, in *The Cosmic Dust Connection*, ed. J. M. Greenberg, Kluwer, Dordrecht, 1996, p. 1.
30 D. C. B. Whittet, W. A. Schutte, A. G. G. M. Tieleus, A. C. A. Boogert, Th. de Graauw, P. Ehrenfreund, P. A. Gevakines, F. P. Helmich, T. Prusti and E. F. van Dishoeck, *Astron. Astrophys.*, 1996, **315**, L357.
31 J. A. Nuth, III, in *The Cosmic Dust Connection*, ed. J. M. Greenberg, Kluwer, Dordrecht, 1996, p. 205.
32 I. Cherchneff, in *The Molecular Astrophysics of Stars and Galaxies*, ed. T. W. Hartquist, D. A. Williams, Oxford University Press, Oxford, 1998, in the press.
33 M. Frenklach and E. D. Feigelson, *Astrophys. J.*, 1989, **341**, 372.
34 R. J. Gould and E. E. Salpeter, *Astrophys. J.*, 1963, **138**, 393.
35 V. Pirronello, C. Liu, L. Shen and G. Vidali, *Astrophys. J.*, 1997, **475**, L69.
36 A. G. G. M. Tielens and D. C. B. Whittet, in *Molecules in Astrophysics: Probes and Processes*, IAU Symp. No. 178, ed. E. van Dishoeck, Kluwer, Dordrecht, 1997, p. 45.
37 C. R. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, J. Wiley, New York, 1983.

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