SESSION 2

Laboratory experiments on cosmic dust and ices

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Abstract. The existence of cosmic dust is attested by the interstellar extinction and polarization, IR emission and absorption spectra, and elemental depletion patterns. Dust grains are efficiently processed or even destroyed in shocks, molecular clouds, or protoplanetary disks. A considerable amount of dust has to be re-formed in the ISM. In various astrophysical environments, dust grains are covered by molecular ices and therefore contribute or catalytically influence the chemical reactions in these layers. Laboratory experiments are desperately required to understand the evolution of grains and grain/ice mixtures in molecular clouds and early planetary disks. This review considers recent progress in laboratory approaches to dust/ice experiments.

Keywords. methods: laboratory,(ISM:) dust, extinction, astrochemistry

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1. Introduction

Cosmic dust grains are formed in the circumstellar shells of evolved stars (Gail & Sedlmayr 2013) and in supernovae (Matsuura *et al.* 2011). Carbonaceous and silicate grains are the major refractory materials of cosmic dust. The stardust is eventually distributed into the interstellar medium (ISM), and becomes a part of the diffuse and cold molecular clouds. The ISM is a very hazardous environment for dust. It is exposed to a very harsh irradiation field and destructive processes due to supernovae shocks such as grain-grain shattering and sputtering by ions Jones (1996). It has been estimated that only a few percent of the total mass of stardust survive these destructive processes in the ISM (Draine 2009; Zhukovska & Henning 2013; Zhukovska *et al.* 2016). However, observations of refractory elements in the ISM clearly show a depletion of these elements from the gas phase. Consequently, an efficient condensation process of dust grains in the ISM is required to balance the discrepancy between the stellar formation of dust grains and their interstellar destruction.

Cosmic dust particles play a key role in the evolutionary cycle of stars and interstellar matter. Their optical properties govern the temperature and spectral appearance of dusty regions and the radiation pressure on dust grains around stars. Experimentally derived optical properties of cosmic dust analogs prepared in laboratories on Earth are required to interpret high-quality observations. In-depth analyses of observational features are able to provide information on grain sizes and morphology, composition, structure, temperature, spatial distribution, and masses of dust grains in astrophysical environments. In addition, grains provide surfaces for astrophysically relevant reactions such as the formation of molecular hydrogen or of complex organic and prebiotic molecules in ice layers on top of

grains. Moreover, refractory grains and ices are the ingredients of planets, asteroids, and comets and therefore influence the formation of planetary systems.

Laboratory astrophysical studies are urgently required for the understanding of astrophysical processes. There are four big goals of such laboratory studies on cosmic dust analogs: i) the measurement of optical properties of dust analogs in a very broad wavelength range (VUV-mm), ii) the study of formation and processing of dust grains in different astrophysical environments iii) the investigation of chemical reactions on the surface of uncoated and ice-coated grains, and iiii) the growth of grains to mm-sized grains, pebbles, and planetesimals. In this review, we will focus on the first three topics of dust studies.

Amorphous silicates mainly exist in two different types of stoichiometry. One group corresponds to the olivine-type silicates $Mg_{2x}Fe_{2-2x}SiO_4$ and the second group is related to the pyroxene-type silicates with the general formula $Mg_xFe_{1-x}SiO_3$. Mg^{2+} and Fe^{2+} ions can replace each other in the crystalline, but also in the amorphous form. Amorphous silicates are built of the same basic structural units as the crystalline silicates, the SiO_4 tetrahedra, but without a long-range order (Bromley *et al.* 2016). In silica (SiO_2), the tetrahedra are connected between each other by corners sharing oxygen bridges between adjacent SiO_4 groups and forming a three-dimensional disordered network. The incorporation of Mg^{2+} or Fe^{2+} leads to a partial destruction of oxygen bridges and the formation of larger pores in the SiO_2 network structure. The polymerization degree of the tetrahedra is determined by the stoichiometry. However, in amorhous structures, stronger deviations from the stoichiometry in a sub-nm and nm scale can be observed.

Kohara *et al.* (2011) modeled the structure of enstatite' ($MgSiO_3$) and 'forsterite' (Mg_2SiO_4) glass employing the Reverse Monte Carlo modeling technique and the density function theory (DFT). They found that the coordination of Mg^{2+} ions is much smaller (four- and five-fold) in the amorphous form than in the crystalline environment and that the distribution of distorted SiO_4 and MgO polyhedra is irregular resulting in a poorly-defined silicate structure. However, the structural irregularities depend on the formation conditions such as temperature, quenching rates, and pressure. The inhomogeneities can have a strong impact on the spectral properties of one and the same amorphous silicate material (see for example Speck *et al.* 2011).

The spectral properties of the amorphous pyroxene and olivine stoichiometry in the MIR range are characterized by two broad bands at 10 and 18 μm corresponding to Si–O stretching and bending vibrations. The distribution of bond lengths and angles in both the SiO_4 and the MgO or FeO polyhedra in the amorhous structure determine the widths of the bands. The positions are determined by the polymerization degree of the SiO_4 units (Jäger *et al.* 2003; Sabri *et al.* 2014). The replacement of Mg^{2+} by Fe^{2+} in the crystalline silicate structure (characterized by a wealth of narrow bands) leads to a shift of the bands to longer wavelengths, which is strongly correlated with the Fe content and can be used to derive information about the composition of the silicate (Jäger *et al.* 1998). However, in amorphous silicates, this effect is merged with other shifts due to the polymerization degree, size or shape effects, which clearly limits the diagnostic value of amorphous silicate bands. However, iron ions and metallic iron have a strong impact on the UV/vis and NIR spectral data of silicates. Fe^{2+} and Fe^{3+} produce a number of bands in addition to the excitons and interband transitions between the 2p orbitals of oxygen and the 3d orbitals of Si in the VUV range. Various electronic d–d (ligand field) transitions in UV/vis and NIR are known. Amorphous silicates with pyroxene and olivine stoichiometry can be distinguished with the help of the NIR bands between 1 and 2 μm (Dorschner *et al.* 1995). Information derived from these spectral ranges could be used to restrict the silicate structure and compositions.

Temperature-dependent absorption of amorphous silicates

Special attention has to be paid to the influence of the temperature on silicate vibrational bands and on the far–infrared continuum absorption of crystalline and amorphous materials. The far IR and mm absorption is dominated by amorphous grains. First experimental studies on this problem were conducted by Agladze *et al.* (1996) and Boudet *et al.* (2005). A clear temperature dependence of the absorption cross section and of the spectral power law index (β) was found in these studies. The absorption behavior at wavelengths longer than $300\,\mu$m is related to transitions in two-level systems, which are generated by the disordered structure of amorphous silicates. Atoms or groups of atoms being able to occupy at least two energetically close configurations in an amorphous network such as the network modifier Mg^{2+}, Fe^{2+}, and H^+ contribute to the absorption processes. The temperature-dependent absorption processes can be caused by resonant and tunneling transitions. However, other structural parameter for example the porosity of the amorphous network might also influence such absorption processes.

More recent studies of differently composed and produced magnesium and magnesium–iron silicates by Demyk *et al.* (2017a) and Demyk *et al.* 2017b) have demonstrated that the mass absorption coefficients in the FIR and submm range increases with temperature and that the spectral index is characterized by complex changes at wavelengths between 200 and $700\,\mu$m. Beyond a wavelength of $20\,\mu$m, the experimentally determined absorption is considerably higher than the values calculated for interstellar silicate dust models. The results of this experimental study have strong consequences on the derived dust masses based on cosmic dust models in the FIR and submm range, which means that dust masses could be overvalued.

Optical data of silicate/ice mixtures

In interstellar environments, protoplanetary, and planetary disks, a high fraction of the dust grains is intensively mixed with ices, which mainly consist of water ice. Strong interactions between ice and grains should have a strong impact on the optical data of such mixtures. However, optical data of real dust/ice blends are missing. First experimental studies of realistic silicate/ice composites were performed by Potapov *et al.* (2018).

The authors produced dust/ice mixtures with mass ratios of 0.8 and 2.7 by simultaneous deposition of nanometer-sized silicate grains produced by vapor-phase condensation and water ice onto 8 K cold CsI substrates. Optical data, (*n and k*), were derived from *in situ* transmission measurements at 8, 100, 150, and 200 K in the MIR spectral range using the Kramers–Kronig analysis. These optical data were compared with those calculated from the optical constants of pure silicates and water ice samples using the effective medium approaches for calculating the effective dielectric functions.

Figure 1a demonstrates the differences between the measured and the effective constants of a $MgSiO_3/H_2O$–ice mixture with a mass ratio of 2.7 at 100 K in panel a. The deviations are much stronger for high dust fractions and temperatures between 100 and 150 K. Effective optical data using an effective medium theory approach such as Maxwell Garnett mixing can provide incorrect optical data. The suppression of the water stretching vibrations could be explained by incomplete transformations from high-density to low-density amorphous water ice below 100 K and from amorphous to crystalline ice below 150 K caused by interactions with dust grains. Figure 1b shows the normalized absorption efficiencies of the two dust/ice mixtures for three temperatures. Clear systematic changes due to the composition and temperature of the composites can be observed. A trapping of water ice in/on silicate grains at 200 K was detected, which should have an impact on the desorption properties of interstellar and circumstellar ices.
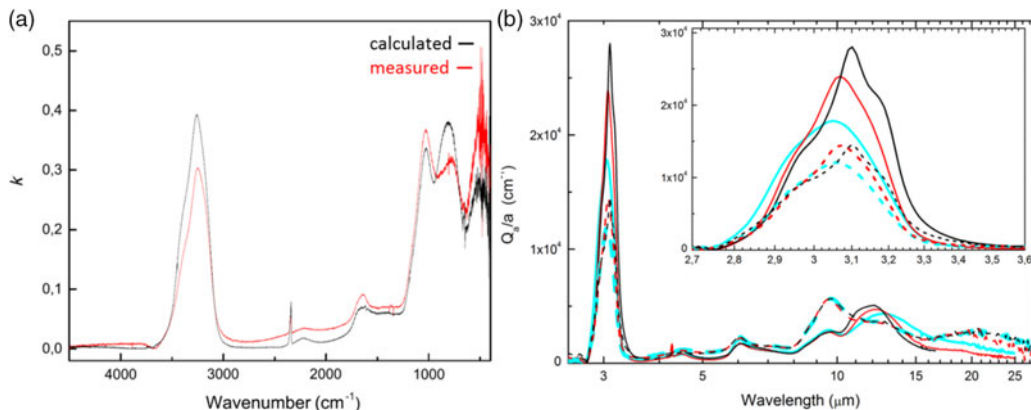
Figure 1. a) Absorption coefficients (k) of $MgSiO_3/H_2O$–ice mixtures with a mass ratio of 2.7 at 100 K. b) Normalized absorption efficiencies of silicate/ice mixtures having mass ratios of 0.8 (solid lines) and 2.7 (dashed lines) for 8 K (cyan), 100 K (red), and 150 K (black) calculated from the measured optical constants for a continuous distribution of ellipsoids in the Rayleigh limit.

2. Re-formation of dust grains in the ISM

In recent years, previous investigations of the low-temperature formation of silicates (Krasnokutski *et al.* 2014; Rouillé *et al.* 2013, 2014) and carbonaceous materials (Fulvio *et al.* 2017) were extended from the pure materials to mixed silicate/carbon systems. Gasphase precursors for the formation of carbonaceous and mixed silicate-carbon grains in the cold phase of the ISM are carbon and hydrogen atoms, small carbon-bearing molecules or clusters, polycyclic aromatic hydrocarbons, refractory elements such as Mg and Fe, and small Mg–, Fe–, and Si–bearing molecules or clusters. The precursor molecules accrete on cold host grains and can either react with each other or with surface atoms forming new solid materials.

In order to study the simultaneous formation of silicates and carbonaceous refractory solids, matrices of 6 K cold Ne ice were doped with atoms and molecules that are potential precursors of complex silicates (Mg, Fe, SiO, SiO_2) and of carbonaceous materials (C_n, n = 2–10). In addition, they contained ice-forming species such as CO, CO_2, C_3O, H_2O, and O_3. The doping process could be realized by simultaneous laser ablation of carbonaceous and siliceous targets. The formed species were identified using UV/vis and IR spectroscopy. In a second step, the neon matrices were annealed up to a temperature of 12 K to trigger the diffusion and reactions between the cold dopants in the ice. The condensation process could be monitored by *in situ* IR spectroscopy. The disappearance of the molecular bands and the rise of a broad feature at 10 μm in the IR spectra could be observed that is due to the Si–O stretching band typical for amorphous silicates (see Fig. 2a). In addition, a very small amount of magnesium carbonate was formed. High-resolution electron microscopy (HRTEM) investigations revealed the formation of amorphous carbon and silicates as two distinct types of grains. As in the case of pure silicate and carbon condensation, the grains were characterized by a porous aggregate structure of the nanoparticles. The carbonaceous grains can be described by a fullerene-like structure. The formation of both condensates occured via barrierless reactions. The formation of SiC was not observed, neither with IR spectroscopy nor with HRTEM analysis combined with energy-dispersive X-ray spectroscopy. More details on these studies can be found in Rouillé *et al.* (2019).

The co-condensation of silicates and carbonaceous molecules can result in redox reactions taking place either between oxygen-bearing and reducing carbon-bearing molecular
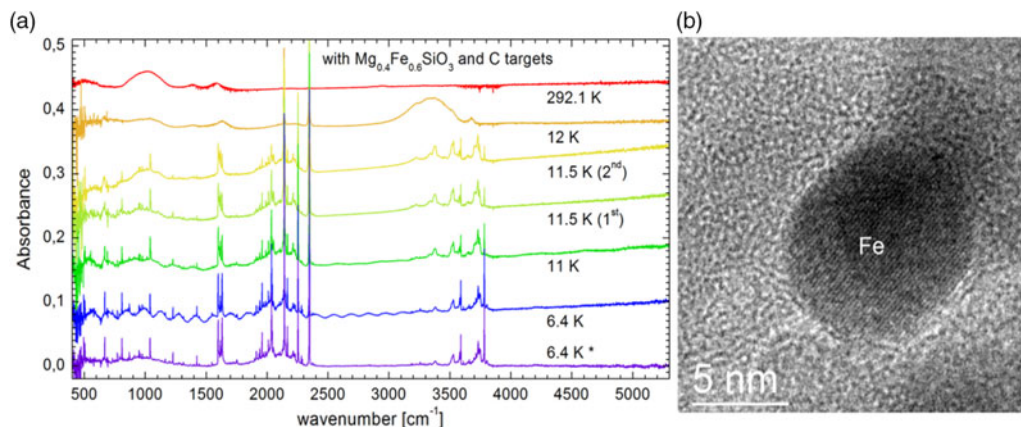
Figure 2. Spectral evolution of a Ne matrix doped with carbonaceous and siliceous species (* Interferences subtracted). The band at $1000\,cm^{-1}$ ($10\,\mu m$) formed upon annealing to 11.5 K is due to silicate. b) A HRTEM micrograph of a metallic iron nanoparticle formed during the condensation process in an amorphous silicate matrix.

species or between reducing and oxidizing solid components. The oxidation process of carbonaceous molecules or materials requires the reduction of a metallic silicate component. The simultaneous condensation of Mg-Fe-silicates with carbonaceous species lead to the reduction of ferrous ions and the formation of metallic Fe particles (see Fig. 2a). The experimental results demonstrate that complex silicate and carbonaceous grains can be re-formed as two distinct grain populations in the cold ISM.

## 3. Processing of grains and reactions on grain surfaces

In cold and high-density astrophysical environments, dust grains are covered by molecular ices (Boogert *et al.* 2015). The molecules can be simply physisorbed or they can form chemical bonds with surface atoms. Consequently, chemically active molecules are concentrated for a long time in a small volume, which enables slow reactions to occur, and the excess energy released from exothermic association reactions is dissipated to the grain surfaces. These ices are a source of complex organic molecules (COMs) observed in the ISM or in protoplanetary disks.

The formation of COMs in ice analogs has already been studied for a long time (van Dishoeck 2014; Öberg 2016) with great success. In the recent years, such laboratory experiments has been supplemented by studies on the formation of potential prebiotic molecules. The formation of sugars and their derivates under interstellar conditions was reported by Fedoseev *et al.* (2017) and Nuevo *et al.* (2018). Very recently, propanal and prebiotically relevant 1-propanol could be synthesized at a temperature of 10 K by Qasim *et al.* (2019). The formation of peptide-like molecules, which are possible precursors of amino acids, were synthesized in CH_4:HNCO ice mixtures upon UV processing (Ligterink *et al.* 2018).

However, dust grain surfaces may also play an active role, either by influencing the desorption properties of molecules or as a catalyst for the formation of complex or prebiotic organic species. However, such studies are still rare and more experiments are required.

In addition, reactions at the interface between grains and ices can be of particular importance for the production of precursor molecules of COMs such as CO and CO_2. The formation of CO and CO_2 by bombardment or irradiation of hydrogenated carbon grains covered by water ice with He^+ ions or Ly-α photons respectively, was already studied by Mennella *et al.* (2004) and Mennella *et al.* (2006). Further experiments were
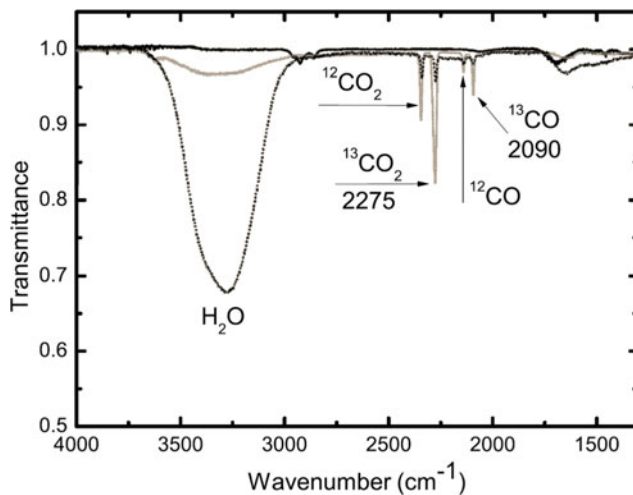
Figure 3. IR spectra of amorphous ^{13}C grains (solid line), amorphous ^{13}C with H$_2$O ice (dotted line) or with O$_2$ ice deposition (gray solid line) upon bombardment with 200 keV H$^+$.

performed on water and O$_2$ ice layers covering amorphous carbon foils by bombardment or irradiation with protons or UV photons respectively (Raut *et al.* 2012; Fulvio *et al.* 2012).

The formation of CO and CO$_2$ in water and O$_2$ ices on top of hydrogenated fullerene-like carbon grains by proton bombardment at a temperature of 16 K was studied by Sabri *et al.* (2015). Hydrogenated fullerene-like carbon grains composed of ^{13}C atoms were prepared by gas-phase condensation. The grains were covered with H$_2$O and O$_2$ ice and finally bombarded with 200 keV protons. The formation of new molecular species was analyzed using *in situ* IR spectroscopy. Under proton bombardment, CO and CO$_2$ molecules were formed in the ice (see Fig. 3). The formation cross sections of solid ^{13}CO and ^{13}CO$_2$ were determined from the increase of the column density as a function of the proton fluence. ^{13}CO and ^{13}CO$_2$ were formed efficiently at the interface between ice and solid carbon grains at the expense of solid carbon leading to intense grain erosion. In addition, the carbon grains were strongly graphitized upon ion bombardment in a surface layer. The formation of CO and CO$_2$ at the expense of solid carbon material corresponding to an erosion rate of 1.13×10^{-15} nm/ion should influence the formation pathways to more complex molecules in astrophysical environments.

An alternative formation pathway of organic molecules could be surface reactions on uncoated dust particles. In the ISM or in protoplanetary disks, dust grains are exposed to bombardment with abundant atoms such as C, H, O, and N. COM formation on uncoated carbonaceous dust grains was experimentally studied by Potapov *et al.* (2017). Fullerene-like carbon grains produced by laser ablation of graphite (Jäger *et al.* 2009) and cooled down to a temperature of about 10 K were exposed to oxygen and hydrogen atoms generated in a microwave-driven atomic source from the molecules. Two different mixtures of O$_2$:H$_2$ (1:60 or 10:70) were employed. The grains were exposed to atoms for 30 minutes with a final fluence of 1.8×10^{20} atoms cm^{-2}. The results are displayed in Fig. 4. Many different molecules were produced under O and H exposure including CO, CO$_2$, H$_2$CO, H$_2$O, and H$_2$O$_2$. The relative amounts of these products were strongly governed by the mixing ratio of the two gases. The experimental study has demonstrated, that the bombardment of interstellar carbon grain analogs by O and H atoms at about 10 K causes the formation of CO molecules from surface atoms of the grains. The CO molecules can be further hydrogenated resulting in the formation of formaldehyde on
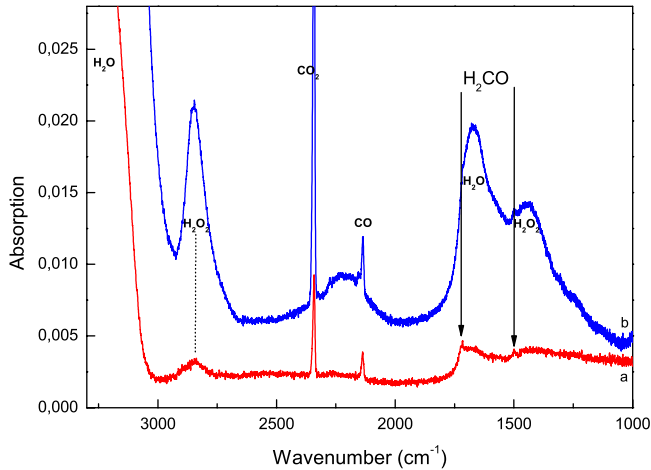
Figure 4. Difference spectra before and after O/H bombardment of carbon grains. Spectra a) and b) correspond to O_2/H_2 ratios of 1/60 and 10/70, respectively.

the surface. Formaldehyde can be the precursor for many interesting molecules such as methanol or sugar molecules (Fedoseev *et al.* 2017, see also Ligterink *et al.* 2018).

4. Summary and Outlook

Over the last years, enormous progress was made in understanding refractory dust components in various astrophysical environments. Laboratory astrophysics provided important data on optical properties for the interpretation and understanding of observations. However, we also learned that amorphous structures of silicates and other amorphous materials are not well defined and may lead to very complex spectral behavior, which was already observed in the MIR/FIR range, but in particular in temperature-dependent measurements in the submm spectral range.

Studies on the formation and processing of refractory materials are required to understand re-formation processes in various astrophysical environments such as the interstellar medium and protoplanetary and planetary disks. The re-formation of interstellar refractory dust was simulated in the laboratory under conditions prevailing in the ISM. The barrierless formation of silicates and carbonaceous grains at temperatures around 10 K was experimentally proven. The simultaneous deposition of both types of molecular precursors, leads to the formation of distinct silicate and carbonaceous grains.

Carbon grains can be a further source for simple, but also for more complex molecules. In particular, the number of CO and CO_2 molecules generated by erosion of grains can have a strong impact on astrochemical processes in ices or in the gas phase.

The formation of complex organic and prebiotic molecules in ice coatings on carbonaceous and siliceous particles was only addressed in a very limited number of laboratory studies so far. However, first interesting studies in this field clearly demonstrate the catalytic effect of dust surface on astrochemical processes in ices (Potapov *et al.* 2019).

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