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Using cold plasma to investigate the mechanisms involved in cosmic dust formation: Role of the C/O ratio and metals

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Abstract. Using a cold plasma reactor in which we inject an organosilicon molecular precursor, we investigate chemical mechanisms that can be involved in dust formation in evolved stars. By injecting metal atoms into the gas-phase, we investigate the role of metals on dust composition. We show the formation of composite particles made of pure metal (silver) nanoparticles embedded in an organosilicon dust. We study the impact of oxygen and show that it can inhibit dust formation, likely through the destruction of nucleation seeds.

Keywords. astrochemistry, dust, stars: AGB and post-AGB, methods: laboratory, plasmas

1. Introduction

The processes related to nucleation, growth and processing of dust particles are of interest for both laboratory cold plasmas and astrochemistry. At the end of their life, evolved stars expel elements, in particular hydrogen, carbon, oxygen, silicon as well as metals such as titanium, magnesium and iron. The presence of these elements in an environment with favourable temperature and density conditions, results in dust formation. It is admitted that the gas-phase composition, in particular the C/O ratio has an impact on the type of formed dust (Ebel 2000). Metals also have a role as they are found to be involved in the final dust composition. Our objective is to get insights into the underlying mechanisms by using a dusty cold plasma.

2. Synthesis of the cosmic dust analogues

Our experiment is based on a capacitively-coupled axially-asymmetric radiofrequency (RF, 13.56 MHz) argon (p = 5.3 Pa) discharge. A complete description of the set-up can be found elsewhere (Despax & Raynaud 2007). The plasma is ignited between two different in size parallel electrodes. The top electrode (smaller) is the driving one. The bottom electrode and reactor walls are grounded. Consequently, a self bias voltage is created on the top electrode allowing for sputtering of a metallic target (silver). The used molecular precursor is hexamethyldisiloxane (HMDSO, $Si_2C_6OH_{18}$). From its decomposition, we expect to have fragments containing Si, C, O and H, which are key elements to build cosmic dust analogues. HMDSO is pulse injected in the reactor. For our experiments,

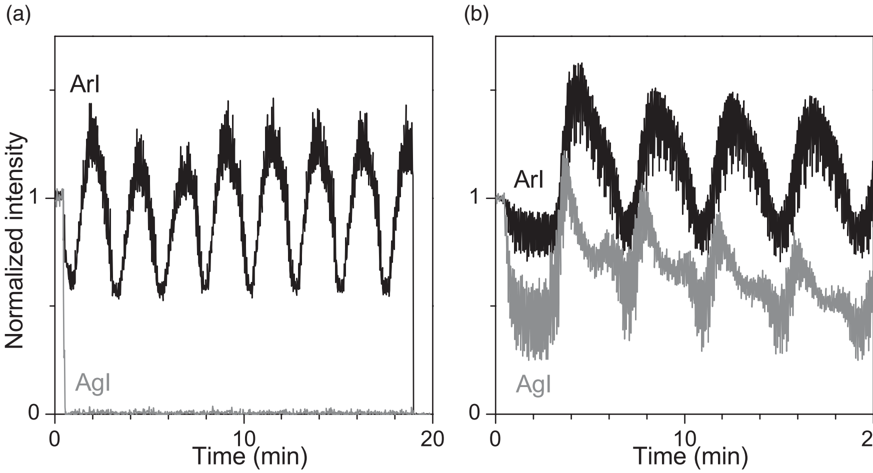

Figure 1. Time-resolved OES of argon (549.6 nm) and silver (546.5 nm) lines. Dust synthesis (a) without silver sputtering (P=10 W, HMDSO average flow = 0.28 sccm), and (b) with silver sputtering (P=30W, HMDSO average flow = 0.12 sccm).

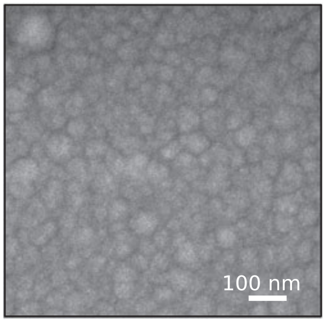

Figure 2. SEM image of collected dust (P=10 W, HMDSO average flow = 0.28 sccm).

the pulse period (5 s) and the amplitude (1 V) are fixed. The amount of HMDSO is controlled by the pulse duration.

The plasma is monitored by optical emission spectroscopy (OES). More specifically we perform a time-resolved analysis on two spectral lines: the argon line at 549.6 nm and the silver line at 546.5 nm. When HMDSO is injected inside the argon plasma, we observe oscillations of the argon line intensity at two frequencies (Fig. 1 (a)). The higher frequency corresponds to the pulsed injection of HMDSO whereas the lower frequency is related to dust formation in the plasma. The correlation between the argon line variation and dust formation have been demonstrated by light scattering studies (Despax *et al.* 2012). On the other hand, one can observe that the silver line disappears after HMDSO injection (Fig. 1 (a)). This is due to the growing deposit of the molecular precursor on the target, which prevents the sputtering of the metal. We however successfully manage to create dust with silver by increasing the RF power and reducing the HMDSO average flow, by reducing the pulse duration (Fig. 1 (b)).

Dust is collected and observed by scanning electron microscopy (SEM). An exemple is presented in Fig. 2. Dust particles have a round shape with a reproducible average size and dispersion, which depend on the experimental conditions. We should note here that the dust particles are connected by a matrix made of the same elements as the dust.

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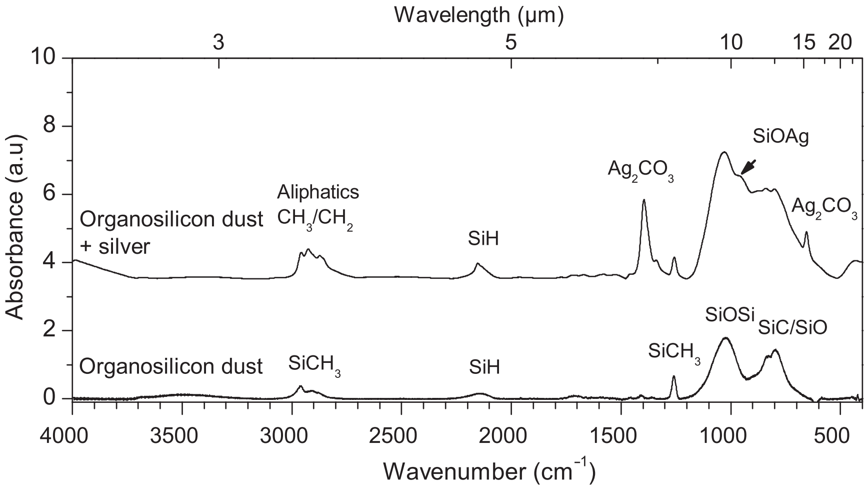

Figure 3. Infrared spectra of collected organosilicon dust with and without silver.

3. Impact of metal atoms

The IR spectrum of the collected dust (Fig. 3) has been studied using the ESPOIRS set-up (Demyk *et al.* 2017). Without silver, the dust has a typical organosilicon structure with a characteristic band at around 10 μm corresponding to SiOSi (+$SiOCH_x$, x=[2,3]) bonds. Bands of $SiCH_x$ are also evidenced around 3.4 μm and at 8 μm.

In presence of silver atoms, the IR spectrum reveals an organosilicon structure and new bands involving silver. We observe the formation of silver carbonate which indicates an interaction of the metal with CO species in the gas phase. In addition, the AgOSi vibration is an indication of an organosilicon-silver interaction inside the dust. We note changes in the aliphatic bands indicating a modification of the carbonaceous structure of the dust. Using in addition TEM analysis, we conclude that the addition of metal atoms in the plasma leads to the formation of silver crystalline nanoparticules embedded in the organosilicon dust. We also investigated the molecular content associated with the collected dust using the laser desorption ionisation mass spectrometry available on the AROMA set-up (Sabbah *et al.* 2017). We found the presence of numerous hydrocarbon species including aromatics, which are not observed in the sample without silver. This suggests a role of silver atoms in the formation of these species in the gas phase.

4. Impact of oxygen

In relation with the C/O ratio, we investigate the impact of oxygen on dust formation by progressively adding O_2, which dissociates in the plasma. The experiment is followed by OES and presented in Fig. 4. In the presence of dust in the plasma, we progressively increase the oxygen flow. At a certain amount of oxygen, dust formation is not observed anymore. When the oxygen flow is decreased, dust formation reappears again. This shows a correlation between the oxygen amount and dust formation in the plasma. We identify a transition regime between the presence and absence of dust. Oxygen can either affect nucleation seeds or dust growth. The injection of another compound that would serve as nucleation seeds may help further progress in addressing this issue.

5. Conclusion and Perspectives

In this exploratory work, we successfully use a cold plasma reactor to investigate the impact of gas-phase composition on the formation of dust containing key elements

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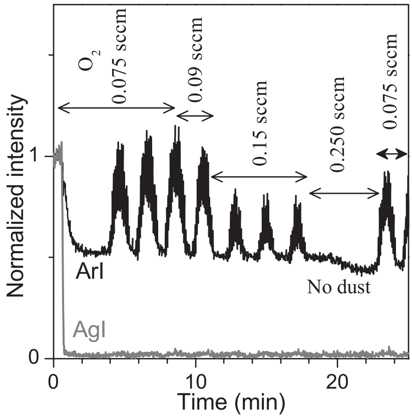

Figure 4. Time resolved OES following the impact of oxygen flow on dust formation.

involved in stardust (C, O, Si, H, metal). We show that a large amount of oxygen in the mixture prevents dust formation. When metal atoms are injected in the plasma, different chemical mechanisms enter into competition leading to the formation of crystalline metallic nanoparticles embedded in the amorphous organosilicon dust. This also impacts the gas-phase carbon chemistry with the formation of new molecular species including aromatic molecules. Further investigation is needed to fully understand the role of silver on the molecular composition. Other, more astrophysically relevant metals such as iron will be considered in future experiments.

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