Ionic and neutral kinetics in C_2H_2/Ar RF plasmas during the first stages of formation of interstellar carbonaceous dust analogues.

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Carbonaceous materials represent a significant fraction of cosmic dust and a relevant reservoir of carbon in space, particularly, they have been found in the interstellar medium, in the Milky Way and in some external galaxies. Besides, cosmic dust plays a key role in the chemistry and physics of dense clouds in the interstellar medium. In fact, the formation routes of many molecules discovered in space are presently assumed to include heterogeneous reactions of volatile species on the surfaces of these particles.

Interstellar carbonaceous dust originates characteristic IR absorption bands, revealing the presence of aliphatic and aromatic functional groups in variable proportions. Among the various products investigated in the laboratory as possible carriers of these bands, hydrogenated amorphous carbon (a-C:H or HAC) leads to the best agreement with observations [1,2], although the formation pathways, composition and structure are still not clear.

In this work, we have used capacitively-coupled RF plasmas of C_2H_2/Ar mixtures to study the gas-phase formation of a-C:H particles as interstellar dust analogues. The diagnostics of the gas phase has been performed by mass spectrometry of neutrals and ions, visible emission spectroscopy and Langmuir probes (Fig.1). The formation of dust has been monitored by Mie scattering.

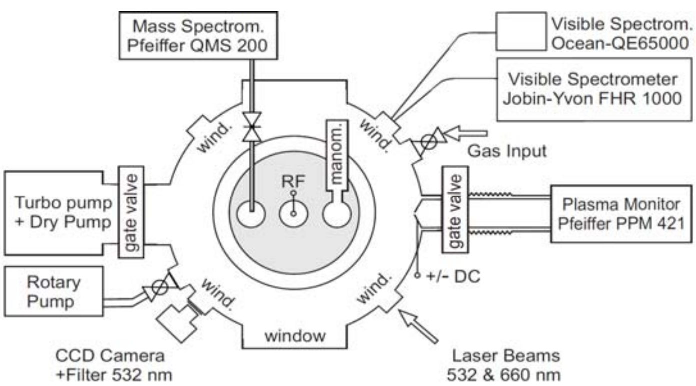

Figure 1. Experimental set up of the RF discharge and the diagnostics equipment.

For the study of charged species, special attention has been paid to the first stages of polymerization before the onset of particle formation, since it was observed that the appearance of dust induces the depletion of anions. Therefore, the gas mixture proportions, total pressure and applied power were empirically adjusted to favor it, by testing the disappearance of light scattering. In these conditions, the measured distributions of cations and anions were clearly dominated by species with an even number of carbon atoms, reflecting the characteristic polyyne structures, typical of the polymerization of acetylene. The ion distributions are shown in Figure 2. They reveal a monotonic decrease in intensity from ions with two carbon atoms till the highest number of atoms detected. For cations, the distributions extend till 12 C atoms. The anion distributions extend further, and compounds with 20 C atoms are observed. Both, for cations and anions, the C_nH_x peak profiles were found to be highly specific for each C_n group. From the measured mass spectra, it was not possible to decide on the possible presence of charged aromatic species with six or more carbon atoms.

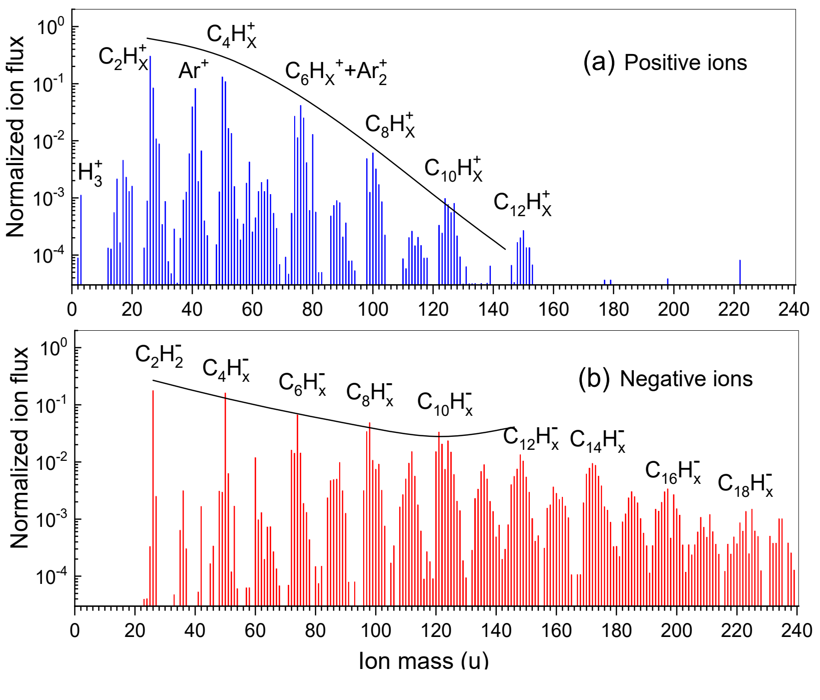

Figure 2. Experimental steady-state distributions of positive (a) and negative (b) ions in a 50 W discharge of C_2H_2 (2 sccm)/Ar (1.25 sccm) at 0.10 mbar. The discharge was pulsed at 100 Hz with a 50% duty cycle, so that the anions could flow out of the plasma volume in the *off* part of the cycle. The lines above the spectra correspond to the envelopes of the $C_nH_x{}^{+/-}$ distributions calculated with the model (assuming T_e = 3.3 eV and $n_{cations} = 8\times10^8$ cm^{-3}) [3].

A simple kinetic model that included aliphatic species up to 12 C atoms and assumed a homogeneous discharge was developed to rationalize the experimental data. The model includes the main types of ions observed, and incorporates basically radicalic and ionic polymerization mechanisms leading to polyyne structures by addition of C_2 growth precursors. It stresses the important role of the vinylidene anion (H_2CC^-) and predicts that in the steady state a large fraction of the negative charge (60−75%) resides in the anions. It can account for the measured ion distributions with reasonable values of charge density and electron temperature (see continuous lines on the mass spectra in Figure 2). Supplementary studies on the transient behavior of neutrals and ions at the ignition of the discharge are in progress for a better comprehension of the kinetics at the early stages of the ionic aggregation processes.

Additional experiments were performed with C_2H_2/Ar plasmas at discharge conditions appropriate for the efficient production of carbonaceous dust in the capacitively coupled RF reactor. In this case, the discharge was pulsed repetitively with on/off cycles of 14 s/6 s to allow the periodical growth of dust up to a given size and its subsequent fall on the lower electrode [4], which was grounded. The dust was collected on Si and Al substrates placed on this lower electrode. The samples were extracted later and characterized ex-situ by means of Fourier Transform Infrared (FTIR) spectroscopy and field emission Secondary Electron Microscopy (SEM), to analyze the final particle composition, size and structure.

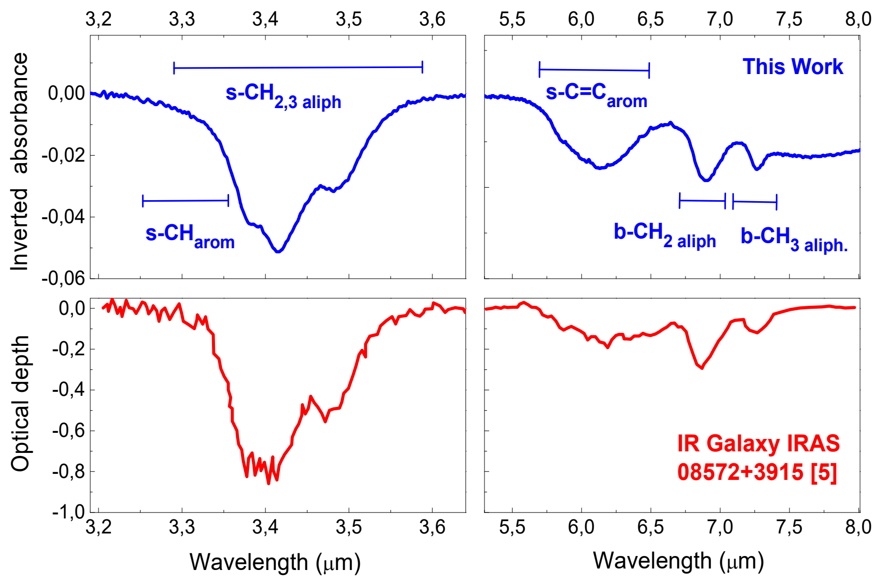

Figure 3. Upper panel: IR spectrum of a-C:H dust grown in a modulated RF discharge with C_2H_2 (2 sccm)/Ar (5 sccm), 0.3 mbar, on/off cycles of 14 s/6 s and 15 W, applied during 80 min. Lower panel: Spectral survey of the infrared galaxy IRAS 08572+3915 [5].

Figure 3 displays the two most characteristic mid infrared spectral regions of the dust grown in our laboratory, and a comparison with the observations reported for IRAS 08572+3915 [5]. The assignment of the bands evinces the presence of both, aliphatic and aromatic bands. Our experimental results show a good agreement with those of the astronomical survey.

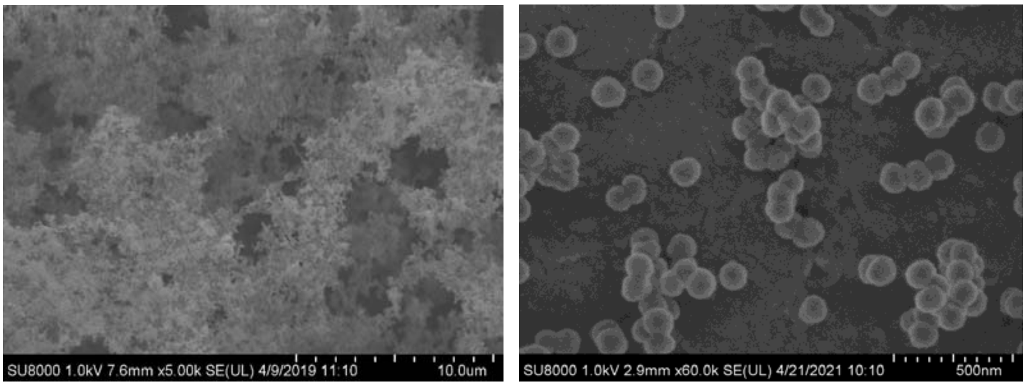

Figure 4. SEM images of the dust grown on Al plates in the same conditions of Fig. 3, taken at $5\cdot10^3$ and $6\cdot10^4$ amplification factors. The left panel evinces a spongy structure of the dust. The right panel allows to estimate a quite homogeneous shape and particle size, with average diameters of some 130 nm.

The final goals of these last experiments were to study the interaction of the cosmic dust analogues grown in the RF plasma with volatile species under astrophysical conditions [4], employing an ice chamber available in our laboratories, and also to irradiate the dust with UV photons and high energy electrons, to simulate its processing by cosmic radiation [6]. Further experiments are in progress in this direction, but they are out of the scope of this contribution.

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