Cold plasmas and ion traps for laboratory astrochemistry

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Astronomical observations reveal the rich and complex chemistry occurring in molecular clouds. The observations need to be complemented by laboratory studies in order to understand the physico-chemical processes involved. In this work, we present the use of $Ar + C_2H_2$ plasmas as a tool to study the formation of carbonaceous dust and the polymerization pathways for the charged species, and show the use of ion traps to precisely characterize specific ion-molecule reactions in astrochemically relevant conditions.

The insterstellar medium (ISM) contains dilute gas in varying conditions of density and temperature. Ice, dust and molecules have been detected in the colder and denser regions, known as interstellar clouds. In recent years, the number of molecules detected in the ISM has rapidly grown, and currently more than 300 molecules have been identified towards both galactic and extragalactic sources, including charged species and several complex organic molecules. In order to understand the physico-chemical processes leading to this rich chemistry, a combination of astronomical observations, astrochemical modeling, and theoretical and experimental efforts are required [1].

Most of these interstellar molecules are found in so-called dense clouds. In these regions, the low temperatures make ion-molecule reactions an efficient pathway to the formation of complex species, along with reactions on the surface of dust grains. However, many of these reaction pathways are not well characterized, specially when dealing with complex molecules and the formation of interstellar dust [1, 2]. In this work, we use cold plasmas and ion traps to tackle some of these problems through laboratory experiments.

Carbonaceous materials represent a significant fraction of cosmic dust and a relevant reservoir of carbon in space. 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) leads to the best agreement with observations [3], although the formation pathways, composition and structure are still not clear. 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 and Langmuir probes.

Carbonaceous dust analogues were generated in the capacitively coupled RF reactor using different sets of experimental parameters. The discharge was pulsed repetitively in periods of 20 s with varying duty cycles to allow the periodical growth of dust up to a given size and its subsequent fall on the lower electrode, 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 Scanning Electron Microscopy (SEM), to analyze the final particle composition, size and structure.

Results from the characterization of the dust can be seen in Fig. 1. The SEM image of the left panel shows that the dust grains formed are homogeneous in shape and size. The average diameter of the particles was found to be mainly influenced by the duty cycle of the discharge. The variation of the FTIR spectra of the samples with one of the discharge parameters, the coupled power, is shown on the right panel. The assignment of the bands evinces the presence of both aliphatic, aromatic and acetylenic bands, with relative intensities that depend on the plasma conditions employed for the generation of the

analogues. The features observed in the IR spectra are comparable to the astronomical observations of carbonaceous dust towards IRAS 08572+3915 [4].
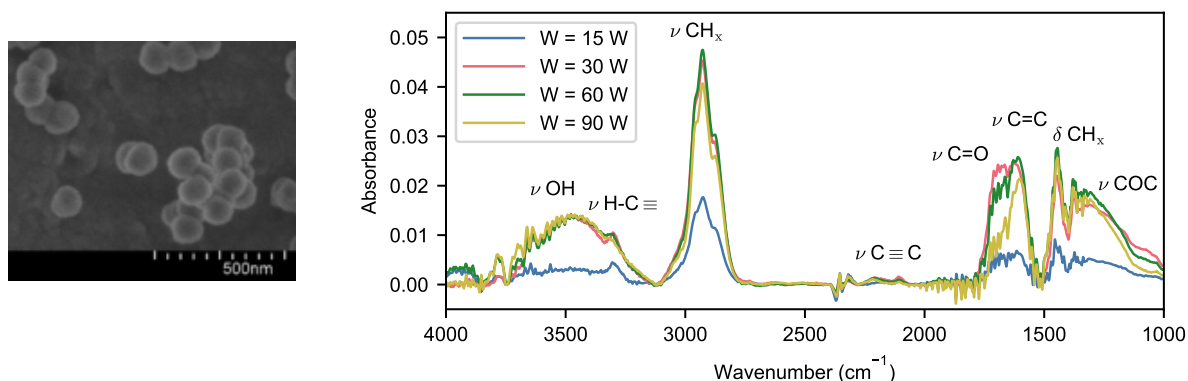

Fig. 1: Left: SEM image of a dust particle sample generated using a mixture of Ar (5 sccm) + C_2H_2 (2 sccm) with a coupled power of 15 W. The average diameter is $\sim$130 nm. Right: FTIR spectra of various dust analogues generated using different values for the coupled power in an Ar + C_2H_2 plasma.

For the study of charged species, the parameters of the discharge were adjusted to inhibit the formation of dust, since it was observed to induce the depletion of anions. The discharge was also pulsed with a frequency of 100 Hz to allow the extraction of the anions in the off part of the cycle. In these conditions, the measured ion distributions of both signs were clearly dominated by species with an even number of carbon atoms, reflecting the characteristic polyyne structures, typical of the polymerization of acetylene [5]. The ion distributions are shown in Fig. 2. For the cations, a monotonic decrease in intensity from ions with two carbon atoms till the highest number of atoms is observed. The distributions extend till 16 C atoms. The anion distributions extend further, and compounds with up to 24 C atoms are observed. In this case, the maximum signal was observed for the $C_6H_x{}^-$ group. 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 more than 6 carbon atoms.
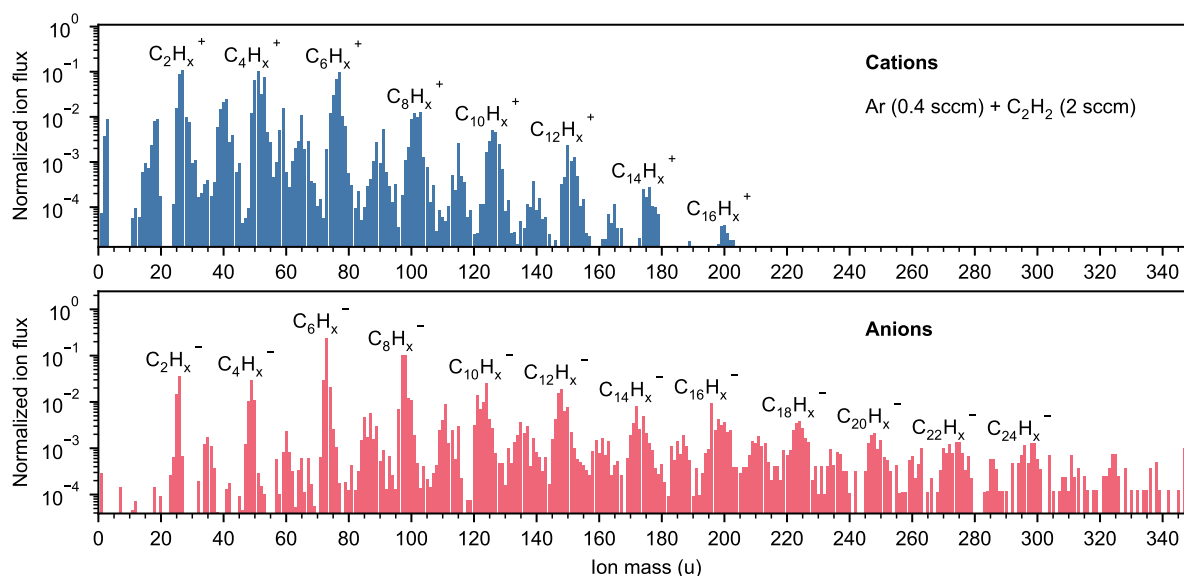

Fig. 2: Mass spectra for the charged species in the steady state of an Ar (0.4 sccm) + C_2H_2 (2 sccm) discharge with a coupled power of 50 W and a total pressure of 0.11 mbar.

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 incorporated basically radicalic and ionic polymerization mechanisms leading to polyyne structures by addition of C_2 growth precursors, accounting for the spacing of the main peaks in the mass spectra.

While cold plasmas allow us to look at the full production network for the species of interest, experiments with an ion trap are better suited for the precise characterization of the individual reactions. Radio-frequency traps allow the storage of charged particles for long times, during which they can interact with photons, electrons or neutral species [6]. Ion traps can be used to study the ion-neutral processes prevalent in interstellar environments, and, with cryogenic cooling, temperatures close to those found in such regions can be achieved. Here we show measurements of the rate coefficient at cryogenic temperatures for the reactions of CN^+, HCN^+ and HNC^+ with H_2.

HCN and its higher energy isomer HNC are presumably the two simplest isomers in chemistry. Both have been detected in a variety of interstellar environments with comparable abundances. Some of the main production channels for these molecules include ionic chemistry, with mechanisms involving HNC^+ and its higher energy isomer HCN^+. The lack of experimental studies for many of these processes hinders current astrochemical models involving HCN / HNC [7].
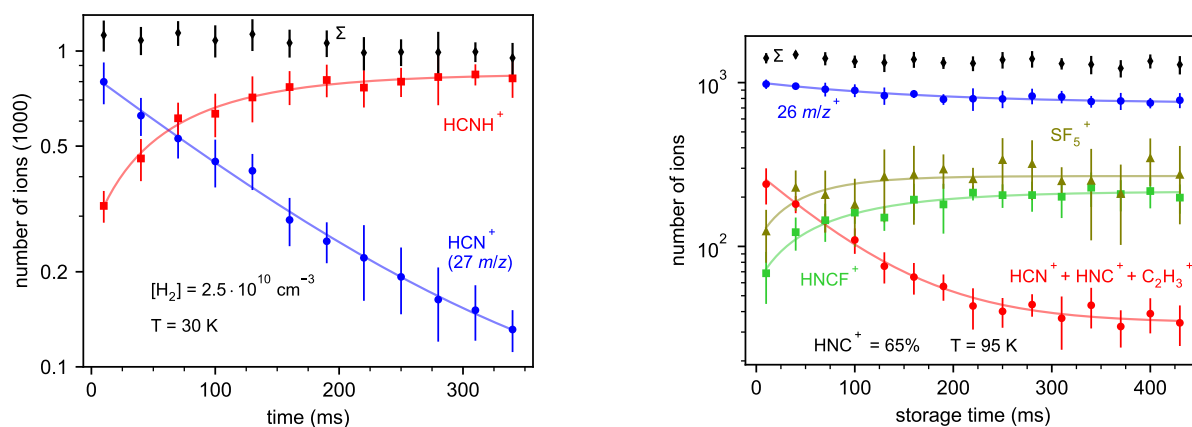

Fig. 3: Number of ions in the trap as a function of storage time for two of the processes studied. Left: time evolution of HCN^+ ions reacting with H_2. Right: determination of the branching ratio of the $CN^+ + H_2$ reaction using SF_6 as a chemical probe. SF_5^+ ions are formed from HCN^+, while $HNCF^+$ is produced from HNC^+. The sum of all the ions in the trap is denoted by Σ.
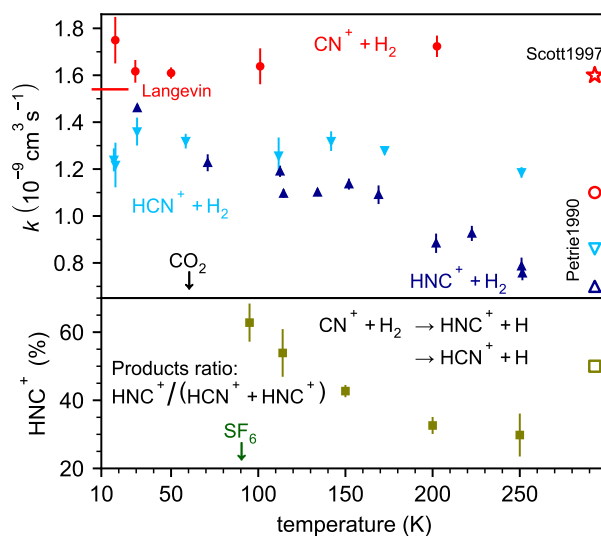

Fig. 4: Upper panel: rate coefficients of the reactions of CN^+ / HCN^+ / HNC^+ with H_2 as a function of temperature. Lower panel: branching ratio of the $CN^+ + H_2$ reaction as a function of temperature.

A 22 pole trap setup [8] was used to determine the reaction rate coefficients for production and destruction of HCN^+ and HNC^+ in collisions with H_2 in the range of $17 - 250$ K, using chemical probing to differentiate the two ionic isomers [9]. The ions are produced in a storage ion source and mass selected by passing through a first quadrupole mass filter. After a set storage time in the 22 pole trap, the ions are mass selected in a second quadrupole and subsequently detected.

In order to determine the rate coefficient of the reactions of interest, the trap is filled with H_2 at various densities, and the rate at which the primary ions disappear is determined as shown in the left panel of Fig. 3. Regarding isomer production, the high energy isomer HCN^+ was the major ion produced in the ion source ($\sim 90\%$), and isomerization to HNC^+ could be achieved in the trap by adding a sufficient amount of CO_2. The ratio of both isomers in the trap could be determined by analyzing the different products obtained when reacting with O_2 or SF_6, as shown in the right panel of Fig. 3.

The measured rate coefficients are shown in Fig. 4. The rate coefficients for the CN^+ and HCN^+ reactions with H_2 are stable with temperature and close to the Langevin value, while the one for $HNC^+ + H_2$ presents a noticeable increase at lower temperatures. The product branching ratios for the $CN^+ + H_2$ reaction also show a marked temperature dependence, favoring the production of HNC^+, the lower energy isomer, at lower temperatures.

References

[1] E. F. van Dishoeck, *Faraday Discuss.* **168** (2014) 9–47.

[2] J. Cernicharo, *ApJ* **608** (2004) L41–L44.

[3] E. Kovačević, I. Stefanović, J. Berndt, Y. J. Pendleton, and J. Winter, *ApJ* **623** (2005) 242.

[4] E. Dartois, T. R. Geballe, T. Pino, A.-T. Cao, A. Jones, D. Deboffle, V. Guerrini, P. Bréchignac, and L. d'Hendecourt, *A&A* **463** (2007) 635–640.

[5] M. Jiménez-Redondo, I. Tanarro, and V. J. Herrero, *Plasma Sources Sci. Technol.* **31** (2022) 065003.

[6] D. Gerlich and M. Smith, *Phys. Scr.* **73** (2005) C25–C31.

[7] F. Fontani, L. Colzi, E. Redaelli, O. Sipilä, and P. Caselli, *A&A* **651** (2021) A94.

[8] P. Jusko, M. Jiménez-Redondo, and P. Caselli, *Mol. Phys.* (2023) e2217744.

[9] P. Dohnal, P. Jusko, M. Jiménez-Redondo, and P. Caselli, *J. Chem. Phys.* **158** (2023) 244303.