

## Ion chemistry in C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>/Ar cold plasmas: Anions of astrophysical interest

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Hydrocarbon anions with the general formula C<sub>2n</sub>H<sup>-</sup> (n=2-5) have been detected in circumstellar envelopes (CSEs) and cold molecular clouds in the interstellar medium [1]. These anions are coincident with the dominant negative ions observed in polymerizing acetylene cold plasmas [2, 3], where the stepwise addition of acetylenic monomers favors the formation of species with an even number of C atoms [4]. C<sub>2</sub>H<sub>2</sub> plasmas have long been of interest in the astrophysical context, where they are often used for the production of laboratory analogs of carbonaceous interstellar dust [5], but the implications of similarities and differences between the gas-phase chemistry of laboratory plasmas and astronomical environments have not been explored. Nitrile ions with a general formula C<sub>2n+1</sub>N<sup>-</sup> (n=0-4) have also been observed in CSEs and cold clouds, but as far as we know no laboratory anion distributions have been reported for N-containing acetylene plasmas. In this work we present the first results of a systematic investigation of ion distributions in C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>/Ar mixed plasmas and a comparison of these results with astronomical observations.

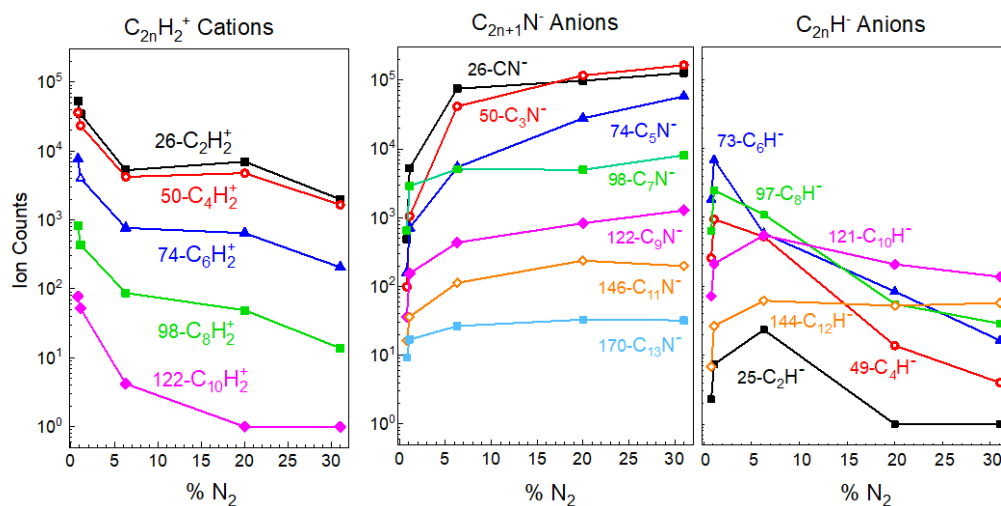


Fig 1: Evolution of characteristic ion-family distributions in RF discharges of C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>/Ar with increasing N<sub>2</sub> proportion

The experimental conditions were selected to observe incipient polymerization without particle formation. The experiments were performed in the capacitively coupled RF (13.56 MHz) reactor described in [3]. It has two electrodes, made of 20 cm diameter parallel plates, separated by 3 cm. The flows of the different gases to the reactor chamber were set with flow controllers, and the total chamber pressure was regulated with a valve connecting the chamber to the pumping system. Flows of 2 sccm C<sub>2</sub>H<sub>2</sub>, 0.2-0.4 sccm Ar, and 0.0-0.8 sccm N<sub>2</sub> were used. The total pressure before discharge ignition was 0.1 mbar, and the RF effective power was 50 W. The discharge was pulsed at 100 Hz with a 50% duty cycle, so that anions could fly out of the plasma volume in the off part of the cycle. Two differentially pumped quadrupole mass spectrometers (QMS) were used for the detection of species in the plasma. A residual gas analyzer (RGA, 0-100 u) for neutrals, and a plasma process monitor, (PPM, 0-340 u) for ions.

Distributions of neutrals, cations and anions were recorded for  $N_2$  mixing ratios ranging from 0.8 to 31%. It was not possible to reach lower  $N_2$  concentrations due to a residual  $N_2$  impurity in acetylene. Among the neutral species formed in the discharge, HCN is worth mentioning. Its concentration increased appreciably with growing  $N_2$  proportion. Changing the  $N_2$  concentration in the discharges from 1.1 % to 6.3 % produced a drastic decrease in the total amount of detected cations and a corresponding growth in the global anion concentration (see Fig.1). Further increase in the  $N_2$  mixing ratio up to 31% had a less drastic effect. Carbonaceous cations in the discharges are dominated by families of the  $C_{2n}H_x^+$  type and their distributions are not much altered with growing  $N_2$  proportion. In the case of anions,  $N_2$  addition leads to significant changes in the more complex  $C_nN_mH_x^-$  distributions. We focus here on the two anion families detected in space. For the lowest  $N_2$  concentrations investigated (0.8% and 1.1 %) the  $C_{2n}H^-$  ( $n=2-5$ ) intensities are larger or comparable to those of the adjacent  $C_{2n+1}N^-$  ( $n=1-4$ ). For  $N_2$  mixing ratios larger than 6.3 % nitrile anions dominate all distributions.

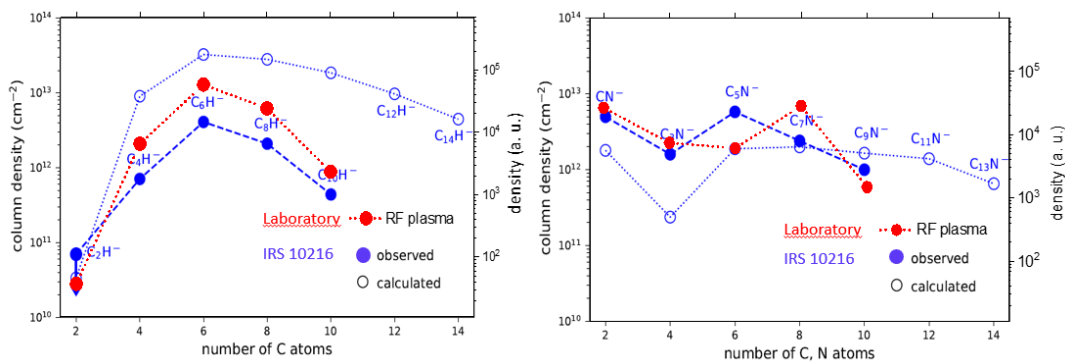


Fig 2: Comparison of laboratory  $C_{2n}H^-$  and  $C_{2n-1}N^-$  anion distributions (red, right y-axis) with astronomical observations and astrochemical calculations from [1] (blue, left y-axis) of the IRS+10216 circumstellar envelope. The laboratory data are for  $C_2H_2$  (83.6%),  $N_2$  (1.1%), Ar (15.3%)

Figure 2 shows a comparison between astronomical observations and laboratory measurements for a plasma containing a small  $N_2$  proportion (1.1%). The astronomical results shown correspond to a CSE, but the anion distributions found in cold clouds are alike. The similitude between the measurements and observations is worth noting, especially for the  $C_{2n}H^-$  family. This result is particularly puzzling if one considers the contrasting chemical mechanisms usually assumed for the two very different environments considered. Astrochemical models take a neutral polymerization route, initiated by UV photons, for the formation of  $C_{2n}H$  and then, radiative electron attachment to produce  $C_{2n}H^-$ . In contrast, models of cold plasmas assume anionic polymerization usually driven by  $C_2H^-$  formed in turn by dissociative electron attachment to  $C_2H_2$ . Both astrochemical and plasma models have some controversial issues and we are presently working on the chemistry of these systems in an attempt to clarify the reasons for the observed similarities in the anion distributions.

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