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Large effects of small pressure changes in the kinetics of low pressure glow discharges

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Low pressure glow discharges produce cold plasmas, far from thermal equilibrium. Typical electronic temperatures in this kind of plasmas range between 1 and 10 eV, whereas those of the heavier species (neutrals and ions) remain close to room temperature (< 0.1 eV). Cold plasmas are useful for a large number of scientific studies, like spectroscopy of excited levels or kinetics of highly reactive species (radicals and ions), which play a key role in the gas phase chemistry of combustion or in remote regions of interstellar space and planetary ionospheres. Cold plasmas find also widespread application in elemental analysis and in a variety of technological processes, like sputtering, thin film processing, plasma sterilization, and controlled fusion devices, where they are used for wall conditioning and cleaning [1].

Glow discharges are stable over a pressure range determined by the suitable conditions for electron acceleration and multiplication in collisions with gas particles. Gas pressure determines electron temperature and density, the frequency of binary collisions, the importance of surface vs gas-phase processes and the characteristics of the plasma sheath. The composition of glow discharges evolves often gradually with pressure, but sometimes abrupt changes are observed within a comparatively small pressure interval. In this work, we will show that these more sudden changes can provide valuable clues about the variation in the relative importance of the key physicochemical mechanisms determining the discharge properties. To this aim, we will use results derived from the diagnostics and modeling of hollow cathode DC glow discharges of air and of H_2, both pure or in H_2/Ar and H_2/N_2 mixtures. All the plasmas studied correspond to pressures in the ≈ 0.5-10 Pa range and were generated in a cylindrical (10 cm diameter x 30 cm length) stainless steel reactor. The main diagnostics techniques used were mass spectrometry of neutrals and ions and Langmuir probes. Optical emission spectroscopy was also used in some cases. For more details see refs [2-4]. Simple zero-order kinetic models of the plasma glow with the different precursors were used for the rationalization of the results and for identification of the most relevant processes. In the following, we comment briefly on relevant traits of the various discharges.

The left hand side of Figure 1 shows the mole fraction composition of neutrals in a DC glow discharge of air as a function of pressure. The experimental data and the predictions of the kinetic model are both displayed [2]. As expected, N_2 is always the dominant neutral species, but the concentrations of NO and O_2 have opposite trends and, in the low pressure regime, NO even does replace O_2 as the second most abundant constituent. NO is almost exclusively produced in heterogeneous wall reactions, and its production rate is increased at low pressures thanks to the enhanced N_2 and O_2 dissociation caused by the moderate growth in T_e (typically from 3 to 4 eV). At low pressures the ionic composition of the plasma, dominated by N_2^+ and NO^+ (Fig. 1, right), is

largely determined by the concentration of the neutrals and by the relative magnitude of their electron impact ionization cross sections.

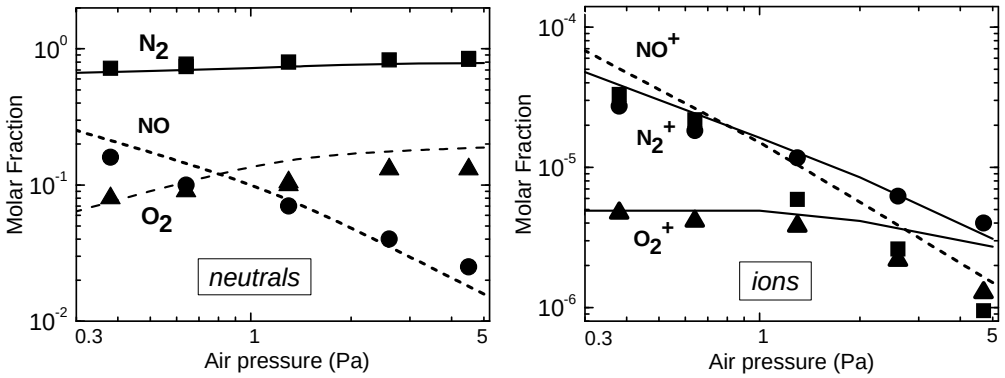

Fig. 1: Mole fraction composition of neutrals (left) and ions (right) in a DC glow discharge of air as a function of pressure. Symbols and lines are the experimental data and model results, respectively.

In low pressure plasmas of pure hydrogen, the concentrations of neutrals, H_2 and H, correspond to a balance between electron impact dissociation and wall recombination, and the H/H_2 ratio (≈ 0.1) does not exhibit large variations over the pressure range studied. However, remarkable changes were found in the ionic concentrations, with an inversion of the major ion from H_2^+ to H_3^+ for a discharge pressure $p \approx 1$ Pa, as shown in the left panel of Figure 2 [3]. Below this pressure, the H_2^+ ion has the highest concentration, but beyond it, H_2^+ is transformed to H_3^+ through the very effective $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction ($k = 2 \cdot 10^{-9}$ cm^3 s^{-1}) [5]. The production of H_3^+ is favored by the increase in collision frequency, but the model analysis demonstrates that the decisive factor for the predominance of the H_3^+ ion is rather determined by the decrease of T_e with increasing pressure. The higher electronic temperatures (up to 8 eV) at the lower pressure values (see right panel of Figure 2) result in an appreciably enhanced rate of H_2^+ generation.

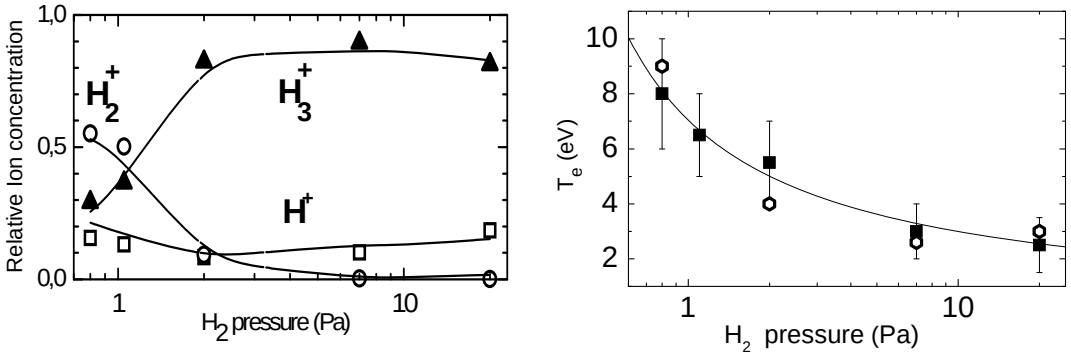

Fig. 2: Left: Relative concentrations of ions in the H_2 plasma. Symbols and lines depict the experimental data and model results, respectively. Right: Electron temperatures. Black squares: Langmuir probe data. Open circles: values used in the model for best fit to the experimental concentrations of atoms and ions. The line in this panel is only to guide de eye.

Adding a relatively small proportion of Ar to the H_2 plasmas discloses new discharge features [4]. In this case, a significant change in the ionic composition takes place in the p ≈ 0.7-2 Pa interval (see Figure 3). Increasing pressure in this range leads to a crossing of the H_2^+/H_3^+ ionic ratio, analogous to that described for pure H_2 plasmas, and to a marked decline in the Ar^+ relative concentration. In the H_2/Ar plasmas studied, the electronic temperatures measured in the Ar/H_2 plasma are lower, roughly by a factor of two, than those obtained previously in the same reactor for a pure H_2 plasma at the same pressures; and the changes in the proportion of H_2^+ vs H_3^+ are theoretically justified by a small fraction (< 3%) of high energy (> 50 eV) non-thermal electrons, whose presence is evinced by the presence of Ar^{2+}. Model estimates also show that the decline of Ar^+ is caused by attenuation in the plasma sheath through the asymmetric charge exchange process $Ar^+ + H_2 \rightarrow H_2^+ + Ar$, which is unimportant at the thermal collision energies of the glow region, but whose probability is high for the ion energies up to 300 – 500 V in the cathode sheath. The cathode sheath lengths are typically ≈ 1 – 2 cm.

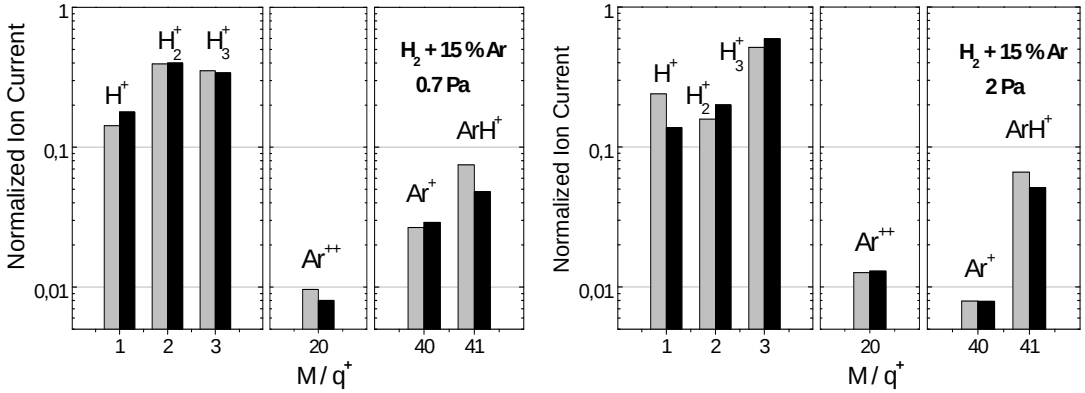

Fig.3: Left: Grey bars: Measured fluxes (normalized to one) of the ions reaching the cathode in a hollow cathode DC discharge of H_2 + 15% Ar for a pressure of 0.7 Pa. Black bars: Ion fluxes calculated taking into account the Maxwellian electrons at T_e = 3.5 eV, a 2.3% fraction of high energy electrons, and attenuation of the Ar^+ flux in the cathode sheath by asymmetric charge exchange. Right: Same as the left panel, but for a pressure of 2 Pa and T_e = 2.5 eV. In this case, the fraction of high energy electrons used in the calculations was 0.7%.

Plasmas of H_2/N_2 mixtures have again distinct characteristics. Their ionic distributions, represented in Figure 4, display also marked variations over the 0.7-2 Pa pressure range, with a remarkable growth in the amount of NH_4^+ and a relative decrease of most other ions. The ammonium ion is produced in collisions of H_2^+, H_3^+ and N_2H^+ with NH_3, which is in turn formed in wall reactions involving N and H atoms. NH_3 reaches relative concentrations ≈ 5% in the plasmas studied. The rate coefficients for the ion-molecule reactions of H_2^+, H_3^+ and N_2H^+ with NH_3 are very high ($5.7 \cdot 10^{-9}$, $4.4 \cdot 10^{-9}$ and $2.3 \cdot 10^{-9}$ cm^3 s^{-1} respectively) [5] and when the collision frequency increases to a given point, these ions are transformed readily to NH_4^+. For the dimensions of our reactor, this happens precisely within the pressure interval considered.

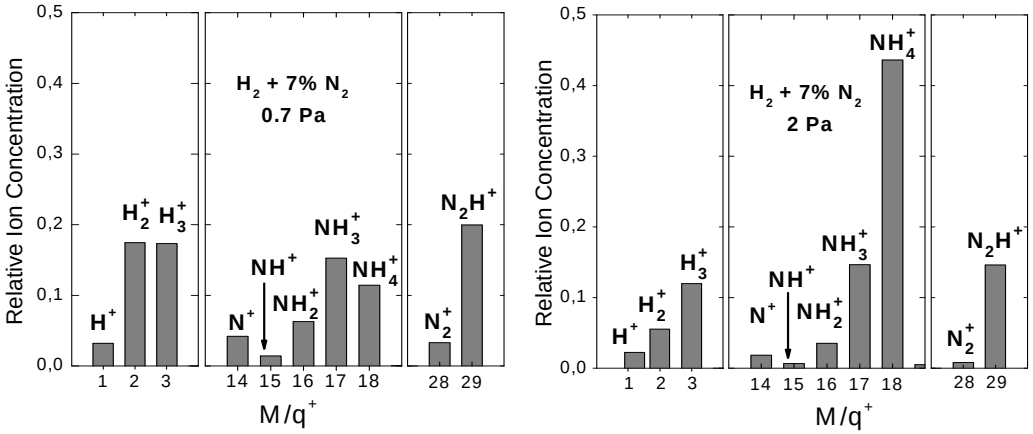

Fig.4: Left: Relative ion concentrations measured in a hollow cathode DC discharge of H_2 + 7% N_2 for a pressure of 0.7 Pa (normalized to one). Right: The same as the left panel, but for a pressure of 2 Pa.

In the previous paragraphs we have shown various examples of characteristic changes in the chemical composition of glow discharges with pressure, due to different causes, including dissociation and wall reactions (air plasmas), a marked variation in electronic temperature (H_2 plasmas), relevance of non-thermal electrons and sheath collisions (H_2/Ar plasmas) or the selection of a dominant ion by increasing collision frequency (H_2/N_2 plasmas). On closing, we would like to emphasize the usefulness of analyzing distinctive composition changes, like those described above, for the identification of key features in the plasma chemistry of low pressure discharges.

Aknowledgements

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References

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