Dear Sir

Use of ion energy distributions for the identification of species and production mechanisms in low pressure DC discharges.

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Mass spectrometry finds widespread application in the analysis of ion distributions in different kinds of plasmas. In DC discharges, the ions reaching the cathode are usually collected by means of a sampling orifice and focused with a set of electrostatic lenses onto the entrance of a mass filter. Mass spectra of ions coming directly from the plasma are not affected by the fragmentation problems at the detector that plague the mass spectrometry of neutrals, but the recorded mass distributions are not entirely free from ambiguity. In particular, ions with the same mass/charge \((m/q)\) ratio, but with different chemical composition, will contribute to the same peak. This can be a problem especially for discharges in gas mixtures that can lead to a variety of different products. Additional insight can be derived from the measurement of ion energy distributions. These energy distributions are largely determined by the acceleration of the ions in the sheath region between the plasma and the cathode, but they may also carry specific information about ion generation mechanisms within the plasma or about collisional processes in the sheath, which can in turn be of help for the identification of different ions with the same \(m/q\) ratio.

In recent works, we have investigated the ion distributions in low-pressure hollow cathode discharges of H\(_2\) and of its mixtures with CH\(_4\) and N\(_2\). The experimental set-up was already described in the mentioned references and only a brief description will be given here. The plasma reactor was a cylindrical stainless steel vessel (the cathode) with a length of 34 cm and a diameter of 10 cm with a central inner anode. Three plasma precursor mixtures (H\(_2\)/N\(_2\)(5%); H\(_2\)/CH\(_4\)(5%) and H\(_2\)/CH\(_4\)(5%)/N\(_2\)(5%)), with a total pressure of 0.02 mbar, were considered. A DC power supply of \(\approx 400\) V, 150 mA, connected to the anode through a ballast resistance of \(\approx 580\) \(\Omega\), were used in the N\(_2\)/H\(_2\) discharge. In the discharges containing methane, the current dropped by about 20% and the voltage rose in the same proportion, due most probably to a change in the characteristic resistance of the plasma. Typical residence times in the reactor were \(\approx 0.1\) s for CH\(_4\) and N\(_2\) and \(\approx 0.4\) s for H\(_2\).

A Balzers PPM421 Plasma Process Monitor (PPM), with a cylindrical mirror energy analyzer and a quadrupole mass filter, was used for the detection of ions. Within this arrangement, the ions extracted from the plasma are decelerated and focused with a set of electrostatic lenses onto the entrance of the energy analyzer formed by a semi-cylindrical capacitor. Only the ions whose entrance velocity is in an adequate relationship with the potential difference between the plates of the capacitor will pass through the filter (see Ref 6 for more detail). These ions are then mass-filtered with a quadrupole and ultimately focused on an electron multiplier. The PPM was installed in a differentially pumped chamber connected to the reactor through a 100 \(\mu\)m diaphragm. During operation the pressure in the detector chamber was in the \(10^{-7}\) mbar range. A global account of the ion chemistry in these discharges, which is dominated by protonation reactions, is given in Ref.5. In all cases, hydrogenic ions H\(_x^+\) (with \(x=1,2,3\)), and in particular H\(_3^+\), were found to be dominant. Besides these hydrogenic ions, N\(_2^+\), NH\(_4^+\) and CH\(_5^+\) were also recorded in significant amounts.

Ion energy distributions, \(f(E)\), are mostly characterized by a narrow (FWHM < 2 eV) maximum for an energy, \(E_m\), close to the value of the anode-cathode potential, which indicates that most ions are accelerated from the plasma edge towards the cathode through a largely collisionless sheath. In general “wings” of variable magnitude appear at the basis of the narrow \(f(E)\) maximum.
and in some of the minor ions, the energy distributions are broader. Illustrative examples are shown in Fig. 1. In the following, we will discuss the likely causes of the different f(E) shapes observed.

The signal at m/q = 3 corresponds to the dominant H$_3^+$ ion. In the three mixtures studied the energy distribution presents a sharp drop at the high energy side of the maximum and a smoother decline at the low energy side. Note however that the low energy decline is also very pronounced close to the maximum since f(E) falls by more than two orders of magnitude for energies $\approx 5 - 8$ eV below $E_m$, (i.e for $E \approx 0.98 E_m$) Within the plasmas considered, H$_3^+$ is produced in ion-molecule reactions and most notably in the process:

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$  \hspace{1cm} (1)

Reaction (1) has a large rate coefficient $^7$ ($k = 1.9 \times 10^{-9}$ cm$^3$ s$^{-1}$), which is nearly temperature independent over a wide T range, including the (room temperature) conditions of the present experiment. Through this mechanism, the H$_2^+$ ions, produced primarily by electron impact, are largely converted to H$_3^+$ with H$_2$ and the low experimental pressures, most of the detected H$_3^+$ ions cross the sheath region without perturbation and give rise to the mentioned sharp peak at $E_m$, which reflects somehow the narrow velocity distribution of the ions in the cold plasmas under investigation. The asymmetric low energy wing is due to energy loss processes associated with (few) inelastic collisions in the sheath, and to the detection of ions reaching the sampling orifice at the cathode wall with incidence angles lower than 90º. Most of the major ions detected (H$_2^+$, N$_2$H+, NH$_4^+$, CH$_5^+$) have energy distributions qualitatively similar to that of H$_3^+$ (not represented for clarity) with a sharp peak and a low energy tail. The magnitude and slope of this tail varies somewhat for each ion, depending on the efficiency of their respective sheath collision processes, but in all cases f(E) drops by more than an order of magnitude for $E \approx 0.98 E_m$.

The f(E) of the H$^+$ ion (m/q =1 in Fig. 1) deserves special comment, since, in addition to the peak and low energy wing just discussed, has a shoulder extending to energies 10-15 eV higher than $E_m$. This shoulder corresponds to H$^+$ generated by dissociative electron impact ionization of H$_2$:

$$H_2 + e \rightarrow H + H^+ + 2e$$  \hspace{1cm} (2)

Reaction (2) is a direct Franck-Condon process in which the H$^+$ ions are formed with a high translational energy. Part of these translationally excited ions are not thermalized in the plasma and reach the cathode with their “excess” energy.

The energy distributions of the ions discussed (m/q=1 and 3), do not change significantly with the gas mixture considered, but interesting differences are observed in some of the minor ions. Fig 1 shows that the energy distributions of the ions with m/q = 14 and 15 are different for each of the three mixtures investigated. In the H$_2$/N$_2$ mixture (upper panel), the signal at m/q =14 is due to the atomic ion N$^+$. The corresponding f(E) has a comparatively broad maximum with an average E larger than $E_m$. In fact, the high energy side of the energy distribution is similar in shape to the broad shoulder already discussed for the f(E) of H$^+$, which indicates that N$^+$ is mostly formed with a high translational excitation in the Franck-Condon electron impact dissociative ionization of N$_2$:

$$N_2 + e \rightarrow N + N^+ + 2e$$  \hspace{1cm} (3)

A contribution of H$^+$ + N$_2$ to the production of N$^+$ atoms is unlikely. At the comparatively low collision energies within the plasma, proton encounters with diatomic molecules lead preponderantly to inelastic or charge transfer processes (see Ref 7 and references therein).

In the same plasma, the signal at m/q=15 corresponds to the molecular ion NH$^+$, but the energy distribution parallels that of the N$^+$ atomic ion. The most likely route for the production of NH$^+$ is the reaction of the translationally excited N$^+$ ions with the H$_2$ molecules prevailing in the gas mixture:
\[ N^+ + H_2 \rightarrow NH^+ + H \] (4)

At the thermal energies of the present experiments, collisions of \( H_2^+ \) with \( N_2 \) lead preponderantly to \( N_2H^+ \) (see Refs 5 and 7) and are not expected to contribute appreciably to the formation of \( NH^+ \).

Reaction (4), mediated by long range attractive interactions, has a large room temperature rate coefficient \( k = 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \), with a weak temperature dependence for the collision energies relevant to our experiments. The reaction takes place through a “stripping” mechanism in which the ion picks up a hydrogen atom from the molecule without significantly changing its initial velocity.

In the \( H_2/CH_4 \) plasma (middle panel), the signals \( m/q=14 \) and \( m/q=15 \) are due to \( CH_2^+ \) and \( CH_3^+ \) respectively. The corresponding energy distributions have a narrow peak centred at \( E_m \), but lack the high energy part extending beyond this value observed in the \( H_2/N_2 \) discharge. In the \( H_2/CH_4 \) plasma, the two \( f(E) \) have noticeable tails below \( E_m \). It is worth noting that whereas the peak at \( E_m \) is dominant for \( CH_3^+ \), most of the \( CH_2^+ \) signal is concentrated in a broad maximum at somewhat lower energy (between 0.91 \( E_m \) and 0.98 \( E_m \)). As commented on above, the low energy tails in these distributions are most likely associated with collisions in the sheath and with non perpendicular ion incidence angles, but the exact collisional mechanisms cannot be determined from the present data.

In the \( H_2/N_2(5\%)/CH_4(5\%) \) plasmas (lower panel in Fig. 1), the \( m/q=14 \) and 15 signals correspond to the sum of the carbon- and nitrogen-containing ions discussed above. This is clearly shown in Fig. 2 for the case of \( m/q=14 \), where the \( f(E) \) directly measured in the discharge is compared, in a linear intensity scale, with the distribution obtained by adding up the \( m/q=14 \) signals from the \( H_2/N_2(5\%) \) and \( H_2/CH_4(5\%) \) plasmas (note that the energy scales have been conveniently shifted). The case of mass 14 is particularly illustrative because both \( N^+ \) and \( CH_2^+ \) ions are present in comparable amounts (\( \approx 50\% \)). A similar comparison can be performed for \( m/q=15 \). For this signal, the \( f(E) \) in the discharge of the ternary mixture is largely determined by \( CH_3^+ \), but a shoulder beyond \( E_m \) corresponding to \( NH^+ \) is clearly appreciable in the lower panel of Fig. 1. A fit of this shoulder with the \( f(E) \) shape of the \( NH^+ \) ion (not displayed for clarity) shows that its contribution to the total \( m/q=15 \) signal in this plasma is roughly 5%.

In general, the different ions tend to have distinct energy distributions and, although a rigorous explanation of the detailed \( f(E) \) shapes is usually not possible, given their complex dependence on many different factors like collision processes and detector parameters, the measured distributions can be often used as a signature of the various ions present in the plasma. Note that in this respect the procedure is not restricted to the few selected cases discussed in the previous paragraphs.

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**Yours**

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References


Figure captions

**Figure 1.** Energy distributions, f(E), of the ions reaching the cathode. Note that the energy interval at the horizontal axis has been shifted in such a way that the position of the peaks coincide vertically for the three panels. Upper panel: H2/N2(5%), discharge; middle panel: H2/CH4(5%), discharge; lower panel: H2/N2(5%)/CH4(5%) discharge.

**Figure 2** Energy distributions, in a linear intensity scale, for m/q=14 in the discharges investigated. Upper panel: distributions in the discharges of the binary mixtures H2/N2(5%), and H2/CH4(5%). Lower panel: Comparison of the energy distribution recorded in the discharge of the ternary mixture with that obtained from addition of the curves of the upper panel. The signals have been normalized to one at the maximum of the distribution of the ternary mixture.
Figure 1
Figure 2