

Influence of pressure on the formation of negative ions in water vapour

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The pulsed Townsend technique has been used to measure the mobility of negative ions in water. A strong pressure dependence of the mobility with gas pressure has been interpreted as a cascade of ion-molecule reactions leading to the formation of clusters $\text{OH}(\text{H}_2\text{O})_n$ ($n=1-3$). Using an avalanche simulator we have been able to explain the measured transients over the pressure range 2-16 Torr, $E/N=60$ Td with a single set of ion-molecule rate constants.

Water vapour plays a relevant role in atmospheric pressure plasmas and many other gas discharge applications in the biochemical and chemical synthesis fields. Despite this well know role, there is a strong lack of data for daughter ions produced in H_2O as is shown in the survey of Viehland [1]. Knowledge of ion mobilities is essential for modelling a wide range of atmospheric discharges, such as tropospheric and stratospheric TLEs (Blue Jets, Giant Blue Jets, Crawlers) [2] or other types aimed at observing the formation of ions and radicals [3].

In a previous work [4] we have reported the reduced mobility K_0 of negative ions in pure water measured with a time-resolved pulsed Townsend technique. We found a marked pressure dependence of K_0 . This is illustrated in Fig.1, displaying the measured ion currents and ion transit times T_i from which K_0 was calculated. The measurements were performed at $E/N = 60$ Td ($1 \text{ Td}=10^{17} \text{ V cm}^2$), gap distance $d = 3.1$ cm, and a pressure range from 2 to 16 Torr. Herein we show that such pressure dependence can be explained in terms of an ion-molecule reaction scheme with the same set of ion-molecule rate constants. The ionic avalanches were fitted with the simulator SIMAV-4 [5]

An inspection of Fig. 1 shows that T_i increases with pressure, this time being close to $230 \mu\text{s}$ at 2 Torr, $250 \mu\text{s}$ at 6 Torr, and $275 \mu\text{s}$ at 12 and 16 Torr. This in turn means that the velocity of the dominant ion decreases with pressure between 2 and 12 torr, and then remains essentially constant between 12 and 16 Torr (according to the present temporal resolution). The reaction scheme shown in Table 1, and used in this study, has been built from previous work [6]. H^- , H^+ and OH^- are formed in binary collisions, while the cluster species $\text{OH}(\text{H}_2\text{O})$, $\text{OH}(\text{H}_2\text{O})_2$ and $\text{OH}(\text{H}_2\text{O})_3$ result from three-body collision processes. The reaction rate constants used to fit the measured transient avalanches are also given in Table 1.

The electron drift velocity ($3.91 \times 10^6 \text{ cm s}^{-1}$) was taken from [7], while the reduced mobilities K_0 were firstly estimated from the pulsed transients over the above pressure range and then mass-identified according to the theory of Barker and Ridge [8]. These mobilities are $K_0(\text{H}^-)=K_0(\text{H}^+)=2.68$, $K_0(\text{OH}^-)=0.88$, $K_0(\text{OH}(\text{H}_2\text{O}))=0.76$, $K_0(\text{OH}(\text{H}_2\text{O})_2)=0.71$, and $K_0(\text{OH}(\text{H}_2\text{O})_3)=0.68$, all in units of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Table 1
Reaction scheme and associated reaction rate constants

Two- body reactions	Reaction rate constant	Three-body reactions	Reaction rate constant
$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{H}^- + \text{HO}$ (1)	11.5	$\text{OH}^- + 2 \text{H}_2\text{O} \rightarrow \text{OH}^-(\text{H}_2\text{O}) + \text{H}_2\text{O}$ (4)	80.0
$\text{e}^- + \text{H}_2\text{O} \rightarrow 2 \text{e}^- + \text{H}^+ + \text{HO}$ (2)	2.00	$\text{OH}^-(\text{H}_2\text{O}) + 2 \text{H}_2\text{O} \rightarrow \text{OH}^-(\text{H}_2\text{O})_2 + \text{H}_2\text{O}$ (5)	2.50
$\text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$ (3)	0.65	$\text{OH}^-(\text{H}_2\text{O})_2 + 2 \text{H}_2\text{O} \rightarrow \text{OH}^-(\text{H}_2\text{O})_3 + \text{H}_2\text{O}$ (6)	1.50
Values for 2-body reactions in units of $10^{-12} \text{ cm}^3/\text{s}$		Values for 3-body reactions in units of $10^{-31} \text{ cm}^6/\text{s}$	

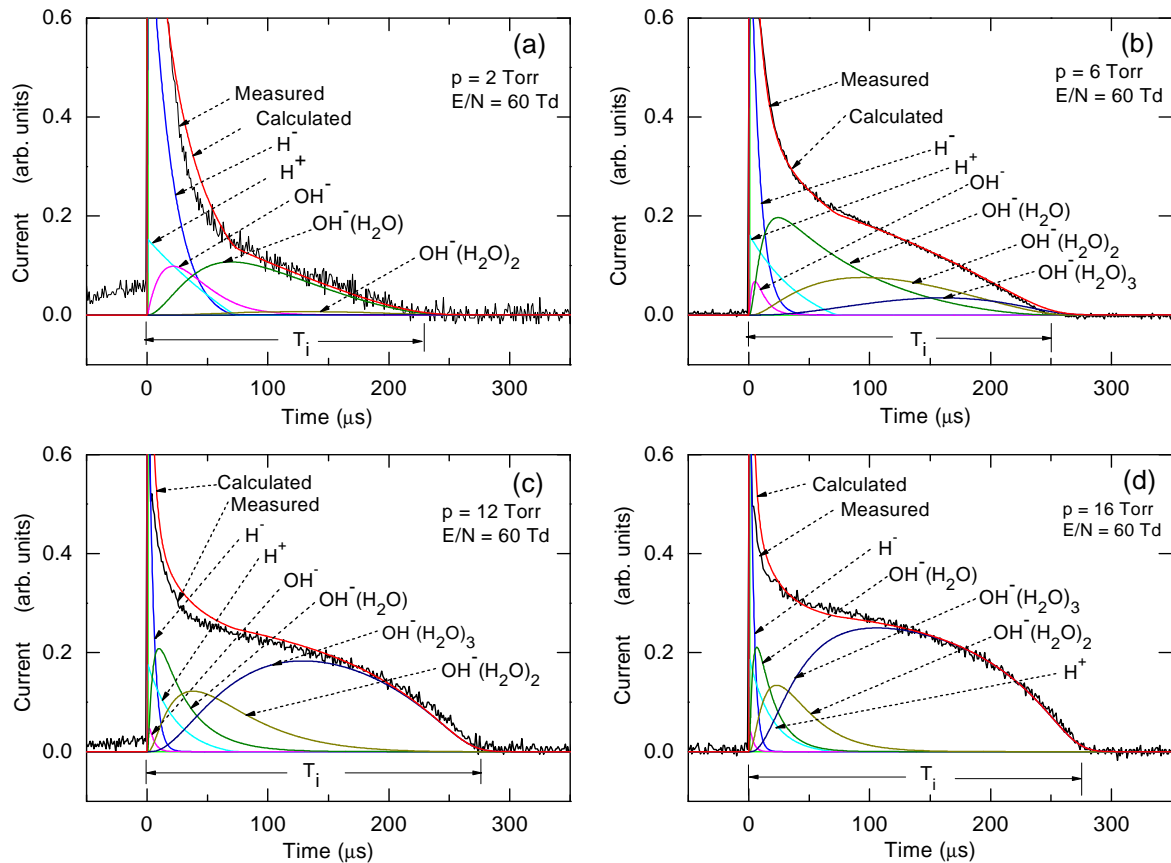


Figure 1. Measured (rigged black curve) and simulated (solid, red curve) currents at $E/N=60$ Td and $d = 3.1$ cm in pure H_2O , for pressures of (a) $p=2$ Torr, (b) $p=6$ Torr, (c) $p=12$ Torr, (d) $p=16$ Torr. The ion transit time T_i is shown. In Fig. (d) the contribution of the OH^- current is too small to be indicated (pink curve).

Figure 1 shows the measured and simulated total and partial currents for each pressure and fixed $E/N=60$ Td. The agreement between measurement and simulation is good in all cases. An inspection of the individual currents shows that the dominant ion at $p=2$ Torr is clearly $OH^-(H_2O)$, while at pressures of 12 and 16 Torr it is $OH^-(H_2O)_3$. It is interesting to see that at the intermediate pressure of 6 Torr, there occurs the transition between the predominant ion $OH^-(H_2O)$ and $OH^-(H_2O)_3$ through the intermediate $OH^-(H_2O)_2$.

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