Proton transfer chain in cold plasmas of H$_2$ with small amounts of N$_2$

The prevalence of NH$_4^+$

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Abstract

The ion-molecule chemistry of the astronomically relevant H$_3^+$, N$_2$H$^+$, and NH$_4^+$ ions has been investigated in the weakly ionized cold plasmas formed in glow discharges of H$_2$ with small amounts of nitrogen. The concentrations of neutrals and ions were determined by means of mass spectrometry, and electron temperatures and densities were measured with Langmuir probes. A kinetic model was used for the interpretation of the results. The selection of experimental conditions allowed the generation of ion distributions with different relative weights of the mentioned protonated species and the model calculations showed that the observed ion distributions can be explained by the occurrence of a very efficient H$_3^+$ $\rightarrow$ N$_2$H$^+$ $\rightarrow$ NH$_4^+$ proton transfer chain. The NH$_4^+$ ion, which is dominant in most of the cases studied, is ultimately derived from the small amount of NH$_3$ produced at the reactor walls. NH$_4^+$ tends to be preponderant in the ion distributions even for NH$_3$ density ratios as low as 1%. Due to the high proton affinity of ammonia, this molecule is readily transformed into NH$_4^+$ upon collision with H$_3^+$ or N$_2$H$^+$. It is conjectured that these results can be extrapolated to most of the small molecules predominant in the interstellar medium, which also have proton affinities lower than that of NH$_3$. The results support the predictions of astrochemical models indicating that NH$_4^+$ could be a preponderant ion in some warm environments like hot cores, where NH$_3$ molecules have desorbed from the grains.
1. Introduction

Gas-phase proton-transfer reactions have been intensively investigated for decades.\textsuperscript{1,2} They are of interest in basic fields, like fundamental acid base chemistry\textsuperscript{3,4} or molecular evolution in interstellar space,\textsuperscript{5-8} and also in applied research, where they are at the root of major developments in chemical ionization mass spectrometry.\textsuperscript{9-12} Studies in all these areas stress the energetic hierarchy of protonated ions dictated by the relative proton affinity of their neutral precursors,\textsuperscript{13} and the large values of typical proton transfer rate coefficients.\textsuperscript{14} An illustrative example of these characteristics is the use of $\text{H}_3\text{O}^+$ ions for the identification of trace amounts of volatile organic compounds (VOCs) in air.\textsuperscript{9,10} Hydronium is particularly well suited to this aim, since the proton affinity of $\text{H}_2\text{O}$ is larger than that of the main air components, which ensures that $\text{H}_3\text{O}^+$ will not transfer its proton to them. In contrast, VOC molecules will be protonated by hydronium virtually on every collision.

It has long been known that the simplest protonated molecule, $\text{H}_3^+$, is often the most common ion in hydrogen glow discharges.\textsuperscript{15} It is also believed that this ion is the most abundantly produced interstellar molecular species, next only to $\text{H}_2$.\textsuperscript{8} The key role of $\text{H}_3^+$ as an initiator of the ion-molecule chemical chain in molecular clouds was advanced in pioneering works on astrochemical modelling\textsuperscript{5,16} much before its actual detection in the interstellar medium (ISM). Due to its symmetry, the ion could not be observed with sensitive radio techniques and was first detected in the ISM in the nineties of the last century using infrared (IR) spectroscopy.\textsuperscript{17} Deuterated variants like $\text{H}_2\text{D}^+$ were then detected in the radio domain or in the far infrared thanks to the dipole moment induced by the D atom (see refs. 18, 19 and references therein). The $\text{H}_3^+$ ion is produced with high efficiency in the reaction of $\text{H}_2^+$ with hydrogen molecules and, given the relatively low proton affinity of the $\text{H}_2$ molecule,\textsuperscript{13} $\text{H}_3^+$ acts as an effective proton donor for many of the species likely to be found in the ISM.\textsuperscript{5,8,20} These “primordial” species are small molecules or radicals containing oxygen, carbon, and nitrogen, which are, after hydrogen and He, the most abundant atoms.

Two of the major nitrogen bearing molecules in the ISM are $\text{N}_2$ and $\text{NH}_3$, which are predicted to be present in many different media.\textsuperscript{21-26} Whereas $\text{N}_2$ is expected to be largely in the gas phase, $\text{NH}_3$ should be mostly frozen onto the surface of dust grains for temperatures lower than 100 K.

Diazenylium ($\text{N}_2\text{H}^+$) and ammonium ($\text{NH}_4^+$), the protonated ions of $\text{N}_2$ and $\text{NH}_3$, can also provide crucial information for the understanding of interstellar chemistry. The $\text{N}_2\text{H}^+$ ion is usually taken as a tracer for the apolar $\text{N}_2$ molecule, which is practically impossible to observe directly using conventional spectroscopic techniques. Detections of diazenylium have been reported from many different sources.\textsuperscript{27-30} The ion is assumed to be formed almost exclusively through the
reaction of $N_2$ molecules with $H_3^+$ and to be destroyed mostly in collisions with electrons or with CO molecules.\textsuperscript{31} The existence of interstellar $NH_4^+$ is also predicted in various astrochemical models. In particular, in hot cores,\textsuperscript{23,26} and in other high temperature environments like active galactic nuclei,\textsuperscript{25} grain evaporation leads to a large increase in the gas-phase concentration of NH$_3$. Ammonia has a high proton affinity and its protonated derivative, $NH_4^+$, is predicted to become one of the dominant ions.\textsuperscript{23,26} However, the symmetric character of $NH_4^+$ precludes its observation through sensitive radioastronomic methods, and, as far as we know, $NH_4^+$ has never been detected in the ISM.

Diazeneilium and ammonium ions can be generated in the laboratory using various electrical discharges in $H_2/N_2$ mixtures. These discharges, which are of interest among other things for the synthesis of NH$_3$, have deserved the attention of different groups investigating the chemistry of cold plasmas.\textsuperscript{32-44} In our laboratory we performed a detailed diagnostics and modeling of $H_2/N_2(10\%)$ hollow cathode (HC) discharges.\textsuperscript{45,46} Special attention was dedicated to the elucidation of the heterogeneous mechanism of NH$_3$ formation at the reactor walls and to the analysis of the distinct influence of direct electron impact and ion-molecule chemistry in the relative intensities of the ion distributions.\textsuperscript{45} In the higher pressure regime ($2-8\ Pa$), corresponding to distributions dominated by ion chemistry, $NH_4^+$ was always the major ion by far. Significant amounts of $H_3^+$, $N_2H^+$ and NH$_3$ were also found. In a later work, the slow heterogeneous generation of NH$_3$ at the reactor walls was experimentally demonstrated with time resolved measurements.\textsuperscript{46} In a series of recent experiments using HC discharges of $H_2$ with small admixtures of $N_2$ and/or $O_2$\textsuperscript{47} we analyzed qualitatively the distributions of protonated ions and varied empirically the discharge conditions in order to observe the hierarchy ($NH_4^+$, $H_3O^+$, $N_2H^+$, $H_3^+$ and $O_2H^+$) of ionic species dictated by the proton affinity of the respective neutral precursors. In the present work, we focus on $H_2/N_2$ discharges and perform a detailed study of proton transfer chains in these plasmas, taking advantage of the mentioned kinetic model.\textsuperscript{45} Here, we extend our previous investigation of ionic chemistry\textsuperscript{45} to lower $N_2/H_2$ ratios and sample ion distributions with markedly different relative weights of the three protonated ions $H_3^+$, $N_2H^+$, and $NH_4^+$. It should be noted that although the exact physical conditions of interstellar media cannot be simulated in the laboratory (especially the low densities and ionization degrees), the systems investigated in this work present relevant similarities with some astronomical regions. Both are low pressure plasmas with a small ionization degree, in which ion-molecule chemistry is determined by binary collisions in a gas-phase largely dominated by $H_2$. Analogous proton transfer chains should take place in both media, but over very different space- and timescales.

The paper is organized as follows: In section 2, the experimental plasma reactor, the details of the measurements, and the kinetic model of the plasma are introduced. In section 3, the
experimental data are displayed and analyzed in the light of the kinetic model simulations. Finally, the main conclusions are summarized in section 4.

2. Experimental techniques and kinetic model

The experimental set-up for the present measurements has been described in detail in earlier works\textsuperscript{48-50} The plasmas of H\textsubscript{2} and N\textsubscript{2} in variable proportions ranging from \(~0.5\) to \(~10\%) N\textsubscript{2} are produced in DC discharges inside a grounded cylindrical stainless steel chamber (30 cm height \(\times\) 10 cm diameter) acting as a hollow cathode and provided with a central anode. The reactor, which is pumped to a base pressure of \(10^{-4}\) Pa by a 450 l s\(^{-1}\) turbomolecular pump and a dry pump, has several ports for the admittance of the fuel gases, for pressure gauges and for coupling to the diagnosis techniques, namely mass spectrometry of neutrals and ions, and double Langmuir probes made in the laboratory for the measurement of electron temperatures and densities.\textsuperscript{51,52} The quadrupole mass spectrometers (QMS) for neutrals (Balzers QMS200) and ions (Balzers PPM422) are located in differentially pumped vacuum chambers and connected to the reactor through 100 \(\mu\)m diaphragms. For the detection of neutrals, the molecules reaching the detector are ionized through electron bombardment, and then an ionic fragment with a suitable mass/charge ratio is selected for each of the species of interest (2 for H\textsubscript{2}, 16 for NH\textsubscript{3} and 28 for N\textsubscript{2}). Only stable neutral molecules are detected this way. The plasma ions are directly extracted from the discharge through the sampling orifice of the ion detector and are mass analyzed. Typical pressures in the detector chambers during operation are in the \(10^{-5}\) Pa range (1 Pa = \(2.4 \times 10^{14}\) cm\(^{-3}\)).

The measurements were performed under continuous flow conditions by balancing the H\textsubscript{2} and N\textsubscript{2} entrance flows, regulated with needle valves, with the total exit flow, controlled with a gate valve at the end of the reactor. Total pressures in the reactor were measured with a capacitance manometer (Leybold CTR90). A total pressure of 8 Pa was selected for the present experiments. This value was particularly appropriate for our investigation since at this pressure ion-molecule chemistry, rather than electron impact ionization, was found to determine the ion distribution in the discharges.\textsuperscript{45} The proportion of the two gases before the ignition of the discharge was set with the aid of the QMS200 mass spectrometer, whose efficiency for the measurement of H\textsubscript{2} and N\textsubscript{2} densities had been previously calibrated. The spectrometer was also calibrated for the signal of NH\textsubscript{3}, which appears as a discharge product (see below). The residence time of the gases in the chamber was found to be \(~0.75 \pm 0.15\) s. Plasma currents of 150 mA and supplied voltages of \(~400\) V were sustained during the experiments. The gas temperature, assumed to be similar to the rotational temperature, \(T_{\text{rot}}\), of the molecular species in the discharge, was obtained by means of a visible spectrometer (Jobin-Yvon FHR1000). We used the non-overlapping emission line intensities
of the R and P branches of the (0,0) band of the first negative system of \( N_2^+ \) (\( B^3\Sigma_u^+ - X^3\Sigma_g^+ \)) (wavelength interval \( \sim 388-391 \text{ nm} \)). The rotational temperature was obtained from the slope of the linear fit of \( \log \left[ I/(K'+K''+1) \right] \) vs. \( K'(K'+1) \), where the \( Ks \) are the corresponding rotational numbers. A value of \( T_r \sim 350 \text{ K} \) was derived from these plots, which agrees with the temperatures obtained in former experiments with similar discharges for other gas precursors.\(^{51,53}\) The temperatures of positive ions in this kind of plasmas are assumed to be similar or slightly higher than those of the neutral species. For the model simulations, we used rate coefficients from the literature, which correspond usually to 300 K.

Electron temperatures, \( T_e \sim 2.8 \pm 0.5 \text{ eV} \), and electron densities, \( N_e \sim 3.0 \pm 0.5 \times 10^{10} \text{ cm}^{-3} \), were determined with the Langmuir probe. Individual ion densities in the plasma were derived from the ion fluxes recorded with the PPM422 mass spectrometer. The calibration of this spectrometer showed that its detection efficiency was roughly proportional to the inverse square root of the ion mass. The comparison of the present set of measurements with previous data\(^{45}\) shows a smaller production of \( \text{NH}_3 \) in the discharges, most likely due to changes in the wall condition of our reactor, but these surface changes are only relevant for heterogeneous processes and have no direct influence on the gas-phase ion-molecule chemistry to be discussed below.

The steady-state experimental data could be successfully reproduced and interpreted using a kinetic model described in full detail in ref.\(^{45}\). Comparison of model predictions with time-resolved measurements was also encouraging.\(^{46}\) The main characteristics of the model and the discharge chemistry are briefly reviewed here. The model is based on the integration of a set of coupled differential equations accounting for the processes taking place in the plasma glow and at the reactor walls. The solution of the system of equations provides the time evolution of the neutral and ionic species from the ignition of the discharge till the attainment of the steady state. The gas-phase processes considered are electron impact ionization, dissociation and neutralization, as well as ion-molecule reactions. Wall processes include ion neutralization, which is assumed to take place with unit efficiency, and surface reactions between neutral atoms and radicals, which are the only processes relevant for neutral chemistry in the reactor, since binary gas-phase reactions have low probabilities (\( k \sim 10^{-12} \text{ cm}^3 \text{ s}^{-1} \)) at room temperature, and three body reactive collisions (with typical rate coefficients of \( \sim 10^{-32} \text{ cm}^6 \text{ s}^{-1} \)) are too rare at the low pressure of our discharges.

Heterogeneous neutral chemistry leads to the recycling of the parent species, \( \text{H}_2 \) and \( \text{N}_2 \), and to the production of appreciable amounts of \( \text{NH}_3 \). Under the comparatively high flux of atoms and radicals to the wall characteristic of the plasma, Eley-Rideal reactions are found to predominate, but a Langmuir-Hinshelwood mechanism must also be considered for the synthesis of \( \text{NH}_3 \). In order to account for the already mentioned smaller production of ammonia detected in the present measurements, some of the heterogeneous chemistry parameters of the original model had to be
modified. The new set of preferred parameters is listed in Table 1. For comparison, the older values from ref. 45 are also listed in parentheses. The reason for the changes in the heterogeneous chemistry with respect to the previous experiments is not entirely clear. It is certainly not an effect of the total pressure since the same pressure was also used in some of the previous experiments. It might be somewhat related to the smaller fractions of N₂ in the present measurements but, as indicated above, the most likely explanation is a change in the surface conditions of the reactor in the lapse of time (months) between the former experiments an those of the present work. The rest of the rate coefficients in the model are the same as in ref. 45.

**Table 1.** Rate coefficients (probabilities) for sticking and Eley-Rideal wall processes used in the plasma model. Fs represents a free surface site. The designation “s” in parentheses corresponds to surface species. The values of the rate coefficients used in ref. 45 are also included (in parentheses) for comparison. Processes W₁₁ and W₁₅ correspond to Langmuir-Hinshelwood reactions, that are modeled with Arrhenius type equations. They are included for completeness of the list of heterogeneous reactions (see ref. 45 for details).

<table>
<thead>
<tr>
<th>Heterogeneous reactions</th>
<th>Rate coefficients (γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W₁  H  + Fₛ → H(s)</td>
<td>1</td>
</tr>
<tr>
<td>W₂  H  + H(s) → H₂ + Fₛ</td>
<td>3.5x10⁻³ (1.5x10⁻³)</td>
</tr>
<tr>
<td>W₃  N  + Fₛ → N(s)</td>
<td>1</td>
</tr>
<tr>
<td>W₄  N  + N(s) → N₂ + Fₛ</td>
<td>1.2x10⁻² (6x10⁻³)</td>
</tr>
<tr>
<td>W₅  NH + Fₛ → NH(s)</td>
<td>1</td>
</tr>
<tr>
<td>W₆  NH₂ + Fₛ → NH₂(s)</td>
<td>1</td>
</tr>
<tr>
<td>W₇  N  + H(s) → NH(s)</td>
<td>6x10⁻³ (1x10⁻²)</td>
</tr>
<tr>
<td>W₈  H  + N(s) → NH(s)</td>
<td>5x10⁻³ (8x10⁻³)</td>
</tr>
<tr>
<td>W₉  H  + NH(s) → NH₂(s)</td>
<td>5x10⁻³ (8x10⁻³)</td>
</tr>
<tr>
<td>W₁₀ NH + H(s) → NH₂(s)</td>
<td>6x10⁻⁴ (1x10⁻²)</td>
</tr>
<tr>
<td>W₁₁ NH(s) + H(s) → NH₂(s) + Fₛ</td>
<td>-</td>
</tr>
<tr>
<td>W₁₂ H  + NH₂(s) → NH₃ + Fₛ</td>
<td>5x10⁻³ (8x10⁻³)</td>
</tr>
<tr>
<td>W₁₃ NH₂ + H(s) → NH₃ + Fₛ</td>
<td>6x10⁻³ (1x10⁻²)</td>
</tr>
<tr>
<td>W₁₄ H₂ + NH(s) → NH₃ + Fₛ</td>
<td>5x10⁻⁴ (8x10⁻⁴)</td>
</tr>
<tr>
<td>W₁₅ NH₂(s) + H(s) → NH₃ + 2Fₛ</td>
<td>-</td>
</tr>
</tbody>
</table>
The ion-molecule chemistry is restricted to the gas-phase. Ions are produced or transformed in the plasma, and eventually accelerated through the plasma sheath toward the cathode wall, where they are neutralized upon impact. As mentioned before, a pressure of 8 Pa was selected in this work because for this pressure the measured ion distributions are largely determined by ion-molecule reactions in the glow,\(^{45,47}\) which are the objective of the present research. Under our experimental conditions, ions undergo on average several collisions before leaving the glow region. There are certainly differences between the collision frequencies and diffusion properties of the various ions, especially between the lighter ions (i.e those with just H atoms) and the heavier ones (i.e. those containing N atoms). These differences are naturally accounted for by the model. The ion-molecule processes and their corresponding rate coefficients are listed in Table 2. These values have not been modified with respect to those of the original model, but are included here for convenience, since they are relevant for the discussion below. In spite of the large values of the rate coefficients, ion chemistry has little influence in the concentrations of neutrals, given the very low ion concentrations in our plasmas, with typical ionization degrees of $\sim 10^{-5}$.

**Table 2.** Rate coefficients for ion-molecule reactions in the plasma.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$ $H^+ + NH_3 \rightarrow NH_3^+ + H$</td>
<td>$5.20 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_2$ $H_2^+ + H \rightarrow H_3^+ + H$</td>
<td>$6.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_3$ $H_2^+ + H_2 \rightarrow H_3^+ + H$</td>
<td>$2.00 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_4$ $H_2^+ + NH_3 \rightarrow NH_3^+ + H_2$</td>
<td>$5.70 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_5$ $H_3^+ + N_2 \rightarrow H_3^+ + N_2H^+ + H$</td>
<td>$2.00 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_6$ $H_3^+ + N \rightarrow NH^+ + H_2$</td>
<td>$2.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_7$ $H_3^+ + N \rightarrow NH_2^+ + H$</td>
<td>$3.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_8$ $H_3^+ + NH_3 \rightarrow NH_4^+ + H_2$</td>
<td>$4.40 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_9$ $H_3^+ + N_2 \rightarrow N_2H^+ + H_2$</td>
<td>$1.86 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_{10}$ $N^+ + NH_3 \rightarrow NH_2^+ + H$</td>
<td>$5.00 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{11}$ $N^+ + NH_3 \rightarrow NH_2^+ + NH$</td>
<td>$0.20 \times 2.35 \times 10^{-9} = 4.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{12}$ $N^+ + NH_3 \rightarrow NH_2^+ + N$</td>
<td>$0.71 \times 2.35 \times 10^{-9} = 1.67 \times 10^{-9}$</td>
</tr>
<tr>
<td>$T_{13}$ $N^+ + NH_3 \rightarrow NH_2^+ + N_2H^+ + H_2$</td>
<td>$0.09 \times 2.35 \times 10^{-9} = 2.12 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{14}$ $NH^+ + H_2 \rightarrow H_3^+ + N$</td>
<td>$0.15 \times 1.23 \times 10^{-9} = 1.85 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{15}$ $NH^+ + H_2 \rightarrow NH_2^+ + H$</td>
<td>$0.25 \times 1.23 \times 10^{-9} = 6.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{16}$ $NH^+ + NH_3 \rightarrow NH_2H^+ + NH$</td>
<td>$0.25 \times 2.40 \times 10^{-9} = 6.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{17}$ $NH^+ + NH_3 \rightarrow NH_4^+ + N$</td>
<td>$6.50 \times 10^{-10}$</td>
</tr>
<tr>
<td>$T_{18}$ $NH^+ + N_2 \rightarrow N_2H^+ + N$</td>
<td>$1.95 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
3. Results and discussion

The distributions of neutrals and ions measured for a H$_2$ + 5.7% N$_2$ discharge are shown in Figure 1, together with the results of the model calculations. The absolute densities of the neutral species have been determined by equating the sum of the calculated distributions (which includes also the atoms and radicals) to the density corresponding to the total chamber pressure ($\sim 2 \times 10^{15}$ cm$^{-3}$). For the comparison between experiment and calculations, the respective sums of the signals of the stable molecules (H$_2$, NH$_3$ and N$_2$) have been put to scale. It is worth noting at this point that estimates based on the model and on previous measurements in the same experimental set-up show that virtually all H$_2$ and N$_2$ molecules are dissociated and recycled at the walls within the typical residence time in the reactor. The estimation of the absolute ion concentrations was done by equating the sum of the measured ion signals to the total electron density measured with the Langmuir probe ($\sim 3.0 \times 10^{10}$ cm$^{-3}$). This procedure excludes implicitly an appreciable presence of negative H$^-$ ions. As discussed in previous work, the concentration of negative hydrogen ions is deemed negligible in our plasmas, where the estimated amount of H$_2$ molecules in high vibrational levels is very low. Sheath collisions might distort somewhat the ion signals recorded at the detector, especially that of H$_3^+$, which may suffer symmetric charge exchange in collisions with H$_2$; however this effect is expected to be small and to influence more the shape of the energy distribution of H$_2^+$ than its concentration.
Figure 1 Concentrations of ions (a) and neutrals (b) in the steady-state of a H$_2$/N$_2$ (5.7 \%) discharge. Experimental measurements (white columns with error bars), model calculations (grey columns).

The data displayed in Figure 1 show clearly that the gas-phase is mostly composed of H$_2$ molecules, with a density close to 1.7 \times 10^{15} \text{cm}^{-3}. The densities of the rest of the species are orders of magnitude lower, with neutrals in the $10^{13}$-$10^{14}$ \text{cm}^{-3} range and ions in the $10^8$-$10^{10}$ \text{cm}^{-3} range. Interestingly, the maximum in the ion distribution corresponds to NH$_4^+$, which is ultimately derived from the small amount (\textasciitilde 1\%) of NH$_3$ produced in the discharge. The ions H$_3^+$ and N$_2$H$^+$ are also found in significant amounts. These ions are stable toward H$_2$, which is by far the preferential collision partner, and tend to predominate in the ion distribution. Other minor ions (NH$_3^+$, NH$_2^+$, H$_2^+$ and H$^+$) are detected too.

In Figure 2, we extend the comparison of experiment and model results to three representative ion distributions, covering the whole range of H$_2$/N$_2$ ratios sampled in the experiments. The corresponding distributions of neutrals are qualitatively similar to that shown in Figure 1 and have been omitted.
In all cases the protonated derivatives of the stable neutral molecules (H$_3^+$, N$_2$H$^+$ and NH$_4^+$) dominate the distributions, but in the first of them (panel a), H$_3^+$ is the major ion. In the second case (panel b), the three ions are present in comparable amounts and the third one (panel c) is dominated by NH$_4^+$. The rest of the ions are only present as minor species. The global agreement between measurements and simulations is good, but it is worth noting that the model predictions tend to overestimate the amount of NH$_3^+$ and to underestimate somewhat that of H$_3^+$. 

The relative concentrations of H$_3^+$, N$_2$H$^+$ and NH$_4^+$ as a function of the proportion of N$_2$ in the discharge fuel gas are represented in Figure 3. The relative concentrations of neutrals in the same discharges are also represented, for reference, in the lower panel of this figure. The fraction of H$_3^+$ in the plasma is found to decrease steadily with growing nitrogen content. In spite of the large excess of H$_2$ in all the discharges investigated, only for initial proportions of N$_2$ lower than 2% is
H$_3^+$ the dominant ion. In contrast, for N$_2$ ratios higher than 4%, NH$_4^+$ is the major ion, although its precursor, NH$_3$, is always the least abundant neutral molecule.

**Figure 3.** Evolution of the relative fractions of protonated ions in the plasma as a function of the initial fraction of N$_2$ in the H$_2$/N$_2$ discharge mixture (three upper panels). The measured values are represented by symbols. The solid lines are the full model predictions. The dashed lines show the results of the model without including the reaction between N$_2$H$^+$ ions and NH$_3$ molecules leading to the production of NH$_4^+$ (reaction T$_{25}$ of Table 2). In the lowest panel, the changes in the relative concentrations of the corresponding neutral molecules are represented for reference.
The evolution of the ion densities portrayed in Figure 3 is dictated by a balance between the different chemical stability of the ions and the relative importance of their respective production pathways in the media considered, which is in turn controlled by the selected experimental conditions. The three ions are very stable with respect to their neutral precursors. Their respective proton affinities are 422.3 kJ mol⁻¹ for H₂, 493.8 kJ mol⁻¹ for N₂ and 853.6 kJ mol⁻¹ for NH₄⁺. Note that the sequence of proton affinities favors the production of N₂H⁺ with respect to H₃⁺, and of NH₄⁺ with respect to the other two ions, but the final proportion of the three ions depends on the dimensions of our reactor, on the experimental pressure that constrain the global collisional regime, and on the proportion of the initial gas mixture, which establishes the collision frequency of the various reactive partners. The evolution of the relative concentrations of protonated ions with the initial amount of N₂ is globally well predicted by the kinetic model (solid lines in Figure 3). The agreement between measurements and model calculations is best for NH₄⁺ and somewhat worse for the other two ions. Although the ion chemistry is restricted to the gas phase, surface processes are indirectly crucial for the determination of the final ion distributions since they control the production of NH₃.

For the lowest initial amounts of N₂ (< 1%), the production of H₃⁺ through reaction T₃ (see Table 2) still prevails over its various chemical destruction pathways, but NH₄⁺ and N₂H⁺ overcome H₃⁺ in the plasma as soon as the initial N₂ concentration is increased to 2-3%. These two ions are efficiently produced from their respective neutral precursors, at the cost of H₃⁺, in reactions T₈ and T₉ of Table 2. The rate coefficient for the formation of NH₄⁺ in collisions with H₃⁺ (reaction T₈) is more than twice the corresponding coefficient for the production of N₂H⁺ (reaction T₉), and compensates the lower plasma concentration of NH₃ as compared with N₂. Given their higher stability, ammonium and diazenylium do not revert to H₃⁺. With further growth in the proportion of initial N₂, the amount of NH₃ in the plasma, though relatively small, is enough to efficiently transform N₂H⁺ into NH₄⁺ through reaction T₂₅. This leads to a predominance of NH₄⁺ over the rest of the ions. The relevance of reaction T₂₅ is also illustrated in Figure 3, where the model results, with and without this reactive channel, are displayed. The upper panel of the figure shows that reaction T₂₅ has no influence in the evolution of H₃⁺. Without this reaction, H₃⁺ is equally depleted in collisions with either N₂ or NH₃, but the relative proportions of ammonium and diazenylium change dramatically due to the mentioned process. At the lowest N₂ ratios, the conversion of N₂H⁺ into NH₄⁺ is still small, due to the very low concentrations of ammonia in the plasma. However, for the higher proportion of N₂ investigated (∼ 10%) the model results indicate that more than half of the NH₄⁺ observed is produced through reaction T₂₅. The gradual increase in the contribution of this channel to the production of NH₄⁺ can be intuitively grasped by considering the changes of the
relevant mean free path with increasing ammonia concentration. The mean free path for reactive collisions of $\text{N}_2\text{H}^+$ with $\text{NH}_3$ at thermal energies can be estimated from the rate coefficient for reaction T$_{25}$ ($k = 2.3 \times 10^{-9}$ cm$^3$ s$^{-1}$). For the lowest amounts of $\text{NH}_3$ considered ($\sim 0.1\%$), which correspond to molecular densities of $\sim 2 \times 10^{12}$ cm$^{-3}$, the reactive mean free path is of the order of 5 cm. (Note that this is just a rough estimate based on the cross section derived from the rate coefficient, but it is meaningful for the present discussion). For the highest $\text{NH}_3$ concentration ($\sim 2 \times 10^{13}$ cm$^{-3}$), the mean free path is approximately an order of magnitude lower. For the dimensions of our reactor, with a radius of 5 cm, the conditions sampled evolve from a situation where the $\text{N}_2\text{H}^+$ ions have a high probability of being neutralized at the wall before colliding with $\text{NH}_3$, to a point where $\text{N}_2\text{H}^+$ has an appreciable probability of undergoing a reactive collision with $\text{NH}_3$ before leaving the plasma volume.

Figure 4 shows the model predictions for the time evolution, between $10^{-7}$ s and 10 s, of the three protonated ions and their neutral precursors in the plasmas with the two extreme $\text{N}_2$ concentrations considered. The model assumes that, at the beginning of the discharge, the positive charge is concentrated in the primary positive ions $\text{H}_2^+$ and $\text{N}_2^+$ formed in the electron impact ionization of the corresponding neutral molecules. Immediately after the ignition, $\text{H}_3^+$, formed in reaction T$_3$, dominates the ion distribution. For the $\text{H}_2/\text{N}_2 (9.6\%)$ mixture (left panels of Fig. 4), the $\text{N}_2\text{H}^+$ ion, formed in reaction T$_9$ at the expense of $\text{H}_3^+$, becomes the main positive charge carrier within $\sim 2 \mu$s and remains so for the next $\sim 0.1$ s. After that time $\text{NH}_3$, which is formed through a comparatively slow multistep wall mechanism, grows to appreciable concentrations in the gas phase, and the ion-molecule chemistry becomes much more complex, with the participation of the various $\text{NH}_x$ species associated with the presence of $\text{NH}_3$ (see Table 2). For simplicity, we have only represented the two main ions of the $\text{NH}_x^+$ family. These ions are $\text{NH}_3^+$, with different formation pathways listed in Table 2, and mostly $\text{NH}_4^+$, produced also in different reactions and notably in reaction T$_{25}$, which leads in turn to an appreciable decrease of $\text{N}_2\text{H}^+$, as commented on in the discussion of Figure 3. Approximately 0.5 s after the beginning of the discharge, the steady state is reached with ammonium as the prevailing ion in the plasma. The predicted slower evolution of $\text{NH}_3$, portrayed in the lower panels of Figure 4, has been experimentally verified in recent work by our group. For the $\text{H}_3/\text{N}_2 (0.55\%)$ mixture (right panels of Fig. 4), the evolution of the various ions is slower due to the smaller collision frequency between the relevant species. $\text{N}_2\text{H}^+$ and $\text{NH}_4^+$ reach their maximum values approximately $10^{-4}$ s and 2 s respectively after the ignition. It is worth noting that for the two examples shown, the “quasi” steady state concentration of $\text{H}_3^+$ is fixed early. Once $\text{N}_2\text{H}^+$ reaches its maximum, the relative amount of $\text{H}_3^+$ remains nearly constant; the later increase of $\text{NH}_4^+$ takes place almost exclusively at the expense of $\text{N}_2\text{H}^+$. For the $\text{H}_2/\text{N}_2 (0.55\%)$
discharge, which corresponds to the lowest N₂ fraction studied, the steady-state results lead to a predominance of H₃⁺, in accordance with the measurements. The time resolved predictions show however that H₃⁺ and N₂H⁺ are present in comparable amounts for the time interval between \(\sim 10^{-4}\) and 0.5 s after the ignition. Only after the production of NH₃ at the walls and after the ensuing N₂H⁺ depletion in favour of NH₄⁺, does H₃⁺ recover its preponderance. Qualitatively similar results are obtained for the different H₂/N₂ mixtures investigated, with H₃⁺, N₂H⁺ and NH₄⁺ being produced sequentially. The timescales and relative concentrations of the ions in the final distribution are of course determined by the initial N₂ content. The findings of this section can in principle be scaled to other low pressure environments dominated by binary collisions.

**Figure 4.** Model prediction for the time evolution of the most relevant ionic (a), (b) and neutral (c), (d) species after the ignition of the discharges. The initial gas mixtures were H₂/N₂ (9.6%) for the left panels and H₂/N₂ (0.55%) for the right panels.

The results of this work provide direct information on the generation and interconversion of protonated ions in a low density gas dominated by H₂. In analogy with many interstellar media, the protonation chain is initiated by H₃⁺ and is then propagated in encounters of the newly formed ions with minor neutral species. The study is limited to nitrogen containing compounds at room temperature, but the key chemical generation of NH₄⁺ through collisions of NH₃ with H₃⁺ and N₂H⁺ observed in the experiments, should also take place with most of the protonated ions likely to be found in the ISM, which are derived from molecules with proton affinities lower than that of
ammonia. Once \( \text{NH}_4^+ \) is formed, it will not be further transformed through reactions with the most common interstellar molecules (\( \text{CO}, \ \text{H}_2\text{O}, \ \text{CH}_3\text{OH}, \ \text{HCN}, \ \text{CH}_4 \ldots \)) being solely destroyed in collisions with electrons. As electron densities are orders of magnitude lower than those of molecular species, multiple ion-molecule reaction pathways will replenish the \( \text{NH}_4^+ \) content. It is thus likely that in some interstellar media a large fraction of the positive charge will be carried by ammonium ions.

The results of the present work are most meaningful for high temperature environments like hot cores and protoplanetary disks, where ammonia has desorbed from the grains. Incidentally, it can be noted that the alternative dominance of the different protonated ions after the ignition of the discharge (upper panels of Figure 4) bears a certain formal resemblance with the predictions of core collapse in stellar formation. In particular, the final rise of \( \text{NH}_4^+ \) in the laboratory plasmas is also associated with a delayed desorption of \( \text{NH}_3 \) from a surface, although the physical origin is different in the two cases. In the plasma reactor, \( \text{NH}_3 \) desorption represents the final step in the heterogeneous production of the molecule, whereas in interstellar space the release of \( \text{NH}_3 \) is due to the heating of the grains. Given the already mentioned unsuitability of \( \text{NH}_4^+ \) for radio astronomic detection, a search for this ion should be probably based on IR spectroscopy (see ref. 55 and references therein).

**Summary and Conclusions**

The neutral and ionic compositions of low pressure plasmas of \( \text{H}_2 \) with small amounts (~0.5-10\%) of \( \text{N}_2 \) have been experimentally investigated in a hollow cathode reactor, and theoretically simulated by means of a kinetic model. Our study has been focused on the protonated species \( \text{H}_3^+ \), \( \text{N}_2\text{H}^+ \), and \( \text{NH}_4^+ \) that dominate the ion distributions in the plasmas.

The selection of experimental conditions has allowed a sampling of collisional regimes favoring different relative weights of the three protonated ions. The distributions observed range from those dominated by \( \text{H}_3^+ \) for the lowest (~1\%) \( \text{N}_2 \) proportions, to those where \( \text{NH}_4^+ \) is predominant for \( \text{N}_2 \) ratios higher than 4\%. For relative concentrations of \( \text{N}_2 \) between 2 and 4\%, the densities of the three ions are comparable. It is worth noting that ammonium ions are ultimately derived from the small amounts of \( \text{NH}_3 \) produced at the reactor walls. This efficient concentration of the positive charge in the ammonium ion can be traced back to the high proton affinity of \( \text{NH}_3 \) as compared with \( \text{H}_2 \) and \( \text{N}_2 \), and to the fact that virtually any collision of \( \text{H}_3^+ \) and \( \text{N}_2\text{H}^+ \) with \( \text{NH}_3 \) will lead irreversibly to the production of \( \text{NH}_4^+ \). The results of the present work support the asserts from recent astrochemical models indicating that \( \text{NH}_4^+ \) might be a preponderant ion in later stages of core collapse, where the temperature rise leads to a desorption of \( \text{NH}_3 \) from the grains.
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