

BRANCHING FRACTIONS IN DISSOCIATIVE RECOMBINATION OF NH₄⁺ AND NH₂⁺ MOLECULAR IONS

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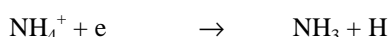
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More than 100 molecules have been identified in the interstellar clouds [1, 2] and among them only a few molecular ions. Formed in the chains of reactions, they are hard to observe, as they are subject to a very efficient process of dissociative recombination (DR), in which molecular ion recombines with an electron and dissociates into neutral fragments. DR reaction is usually exothermic for variety of fragmentation channels, and relative formation rates for different sets of fragments, known as branching fractions, are required.

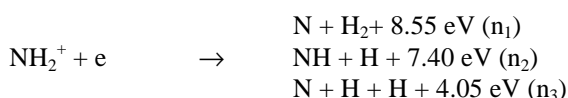
It was only recently confirmed that DR of the NH₄⁺ ion may be important for the interstellar ammonia synthesis [3]. Namely, in the reaction between H₃⁺ and N in the interstellar clouds the major ion product of the reaction would be NH₂⁺, which is converted to NH₄⁺ in the presence of H₂ in the interstellar medium by the sequence of reactions. Created NH₄⁺ recombines with an electron in DR process, and it is very important to know the fraction of this reaction which ends up with the NH₃ molecule as the product:



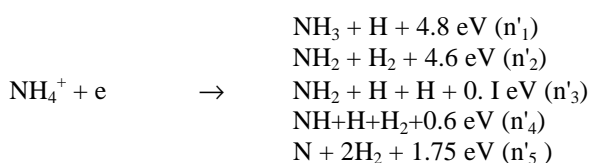
It should be noted that NH₂⁺ formed in the reaction between H₃⁺ and N can be subject of DR process, instead to be converted to NH₄⁺, and it is desirable to find the DR branching fractions for both NH₄⁺ and NH₂⁺ molecule.

Theoretically, the determination of the branching fractions for polyatomic ions is a complex problem, since a large number of potential energy surfaces has to be considered. The branching fractions for NH₄⁺ ion were calculated using a theory derived by Bates [4] which assumes that dissociation which require the least number of valence bonds to be rearranged are favoured, and by a statistical theory of Herbst [5]. There are no calculations for the branching fractions for NH₂⁺. Experimental data are needed as more reliable, and also as a guidance for the theory. Adams et al. [6] have obtained data related to the branching fractions of DR for NH₄⁺, while for the NH₂⁺ ion there are no published experimental results.

For NH₂⁺ three DR channels (with branching fractions n₁, n₂, n₃) are energetically allowed at 0 eV energy:



For NH₄⁺ five DR channels (with branching fractions n'₁, n'₂, n'₃, n'₄, n'₅) are energetically allowed at 0 eV energy:



In the present work we report on the complete branching fractions for dissociative recombination at 0 eV energy for the NH₂⁺ and NH₄⁺ ions. The experiment was performed at the heavy ion storage ring CRYRING at the Manne Siegbahn Laboratory in Stockholm, Sweden. The experiment and data analyses have been previously described in detail [7, 8], and here is given only a brief description. The NH₂⁺ or NH₄⁺ ions created in a conventional hot filament ion source were mass selected, injected into the storage ring and accelerated to an energy of 5.4 MeV for NH₄⁺ and 6.1 MeV for NH₂⁺. In the section of the storage ring known as electron-cooler the ion beam was merged with a velocity-matched electron beam. The electron beam is prepared in a way that the electrons have small thermal energy spread. The thermal energy spread is different along the beam and in the transversal direction, and it was 0.1 meV and 1 meV, respectively. For every injection cycle, before starting the measurement, the ions were stored in the ring for a 'cooling time', when the random thermal motion of the ions reduces by the interaction with electrons, the ion beam shrinks in diameter and the ions can also be relaxed through infrared emission to the ground vibrational state. For NH₂⁺ cooling time was 4.6 s and it was enough for complete vibrational relaxation. For NH₄⁺ cooling time was 2 s. As NH₄⁺ has two infrared

inactive vibrational modes it would need tens of seconds for complete relaxation and it possibly remained partly vibrationally excited.

The neutral products from the DR process as well as the neutrals produced in collisions with the rest gas in the cooler were detected by an surface barrier detector. The pulse height of the signal from the detector is proportional to the total deposited energy. The spectra were recorded using a multichannel analyser. All the fragments hit the detector practically in the same time, and the DR signal appears in the spectrum as a peak at the full beam energy, regardless on the DR channel it originates from. The neutral product of the ion - rest gas collision appears as peak at the fraction of the full beam energy, defined by the ratio of its mass to the total ion mass. The intensity of the peak in the spectrum is proportional to the number of events in the corresponding process.

In order to determine the branching fractions a grid with a known transmission was inserted in front of the detector. The transmission of the grid has been measured to be 0.312 [9]. Particles that are stopped by the grid do not contribute to the energy signal on the detector, and thus the DR signal splits into a series of peaks depending on the branching fractions and on the grid transmission. The number of dissociations into different channels (proportional to the branching fractions) and the measured numbers of events in the different peaks can be connected by the set of linear equations, through the simple functions of the grid transmission. The number of dissociations into different channels is determined solving this set of equations, and branching fractions are obtained after the normalisation for the sum for all the channels to be equal to one.

In this way we obtained for NH_2^+ $n_1 = 0.00 \pm 0.02$; $n_2 = 0.34 \pm 0.05$ and $n_3 = 0.66 \pm 0.01$. This has similar tendency as the branching fractions obtained for CH_2^+ [10], where the three-body $\text{C} + \text{H} + \text{H}$ channel have also been found to be the dominant one (63%).

For NH_4^+ , we obtained: $n'_1 = 0.69 \pm 0.07$; $n'_2 = 0.10 \pm 0.05$; $n'_3 = 0.21 \pm 0.07$; $n'_4 = 0.00 \pm 0.01$ and $n'_5 = 0.00 \pm 0.01$. That means that ammonium is the main product of DR.

Bates [4] presented data of Adams et al. [6] in the form of equations connecting branching fractions:

$$\begin{aligned}n'_1 + 2 n'_3 &= 1.08 \\n'_2 - n'_3 &= -0.08\end{aligned}$$

which is in good agreement with the our results:

$$\begin{aligned}n'_1 + 2 n'_3 &= 1.11 \pm 0.16 \\n'_2 - n'_3 &= -0.11 \pm 0.09\end{aligned}$$

Regarding the theoretical data, there is no agreement with the obtained experimental results. Herbst [5] obtained at a temperature of 10 K (practically equivalent to our 0 eV) that fraction of the 'ammonium' channel is only 24%, and Bates [4] predicted that all the DR proceeds through the 'ammonium' channel.

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