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Branching fractions in the dissociative recombination of NH_4^+ and NH_2^+ molecular ions

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Abstract. Branching fractions in the dissociative recombination of NH_4^+ and NH_2^+ molecular ions with electrons were measured using the CRYRING heavy ion storage ring. We have determined complete branching fractions for NH_4^+ at 0 eV and 2 meV collision energies, and at 0 eV collision energy for NH_2^+. We found the dissociative recombination of NH_4^+ to be dominated by the two body, 'ammonia' channel. The branching fractions we obtained at 0 eV are 0.69 ± 0.03 for the NH_3 + H channel, and for the breakup into the NH_2 + H_2 and NH_2 + 2H channels 0.10 ± 0.02 and 0.21 ± 0.03, respectively. The values we obtained for 2 meV are about the same as at 0 eV. For the NH_2^+ ion we obtained 0.66 ± 0.01 for the three body N + H + H channel, 0.34 ± 0.02 for NH + H, and no breakup into the N + H_2 channel. Dissociative recombination of NH_4^+ and NH_2^+ is important as a potential source of some neutral molecules found in the interstellar clouds (NH_3, NH_2, and NH) and the measured branching fractions have important implications for modeling the chemistry of these clouds. We report also on the relative dissociative recombination cross sections for NH_4^+ and NH_2^+ for collision energies below 60 eV.

Key words: ISM: molecules – ISM: clouds – molecular processes

1. Introduction

More than 100 molecules have been identified in interstellar clouds (Dalgarno & Lepp 1996, Roueff 1997), and about one tenth of them are ions. Neutral molecules and molecular ions are formed in chains of formation and destruction reactions. In attempts to understand why the molecules and molecular ions are present in the various regions in the observed amounts, complex models have been constructed containing thousands of chemical reactions, most of them dealing with gas-phase processes (Dalgarno & Black 1976, Prasad & Huntress 1979, van Dishoeck & Black 1986, van Dishoeck 1988, Millar et al. 1991, Sternberg & Dalgarno 1995). Molecular ions are hard to observe, since their densities are low as they are subject to the very efficient process of dissociative recombination (DR), in which ions recombine with electrons and dissociate into neutral fragments. In the gas-phase theory, most polyatomic neutral molecules are assumed to form via DR reactions between polyatomic positive ions and electrons. DR reactions are usually exothermic for a variety of fragmentation channels, and relative formation rates for different sets of fragments, known as branching fractions, are required for proper modeling.

To model the abundance of the NH_3, NH_2 and NH molecules in the interstellar clouds, it is desirable to know the DR branching fractions for all the polyatomic ions of the ammonia group (NH_4^+, NH_3^+, and NH_2^+).

The theoretical 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 NH_4^+ were calculated using a theory derived by Bates (1991), which assumes that the dissociation that requires the least number of valence bonds to be rearranged is favored, and were also calculated by a statistical theory of Herbst (1978). There are no calculations for the branching fractions for NH_2^+. Experimental data are needed as guidance for the theory. Adams et al. (1991) have obtained data related to the branching fractions in DR of NH_4^+, while to the best of our knowledge no experimental data are reported for the branching fractions in DR of NH_2^+.

For the NH_2^+ ion, three DR channels (with branching fractions n_1, n_2, n_3) are energetically allowed at 0 eV energy:

$$\begin{array}{rcll} & & \mathrm{N + H_2 + 8.6\,eV} & (n_1) \\ \mathrm{NH_2^+ + e} & \rightarrow & \mathrm{NH + H + 7.4\,eV} & (n_2) \\ & & \mathrm{N + H + H + 4.4\,eV} & (n_3) \end{array} \quad (1)$$

For the NH_4^+ ion five channels (with branching fractions $n_1^{'}$, $n_2^{'}$, $n_3^{'}$, $n_4^{'}$, $n_5^{'}$) are open at 0 eV energy:

$$\begin{array}{rcll} & & \mathrm{NH_3 + H + 4.8\,eV} & (n_1^{'}) \\ & & \mathrm{NH_2 + H_2 + 4.6\,eV} & (n_2^{'}) \\ \mathrm{NH_4^+ + e} & \rightarrow & \mathrm{NH_2 + H + H + 0.1\,eV} & (n_3^{'}) \\ & & \mathrm{NH + H + H_2 + 0.6eV} & (n_4^{'}) \\ & & \mathrm{N + 2H_2 + 1.8\,eV} & (n_5^{'}) \end{array} \quad (2)$$

The given values for the kinetic energy release correspond to having the fragmentation products in their ground states. This paper reports on complete branching fractions at 0 eV and 2 meV collision energy for the NH_4^+ ion, and at 0 eV for the NH_2^+ ion.

Concerning the DR cross section for NH_4^+, the cross section was measured by DuBois et al. (1978) in the collision energy range from 0.065 to 2 eV, using the ion-trap technique. In his review paper, Mitchell (1990) presented the unpublished results of P.M. Mul for the DR cross sections for both NH_4^+ and NH_2^+. In the present work, we report on relative dissociative recombination cross sections for NH_4^+ and NH_2^+ for collision energies below 60 eV.

2. Experiment

The experiment illustrated in Fig. 1 was performed at the heavy ion storage ring CRYRING at the Manne Siegbahn Laboratory in Stockholm, Sweden. Only a brief description of the experiment is given here, and more details can be found in the paper of Strömholm et al. (1996). The NH_4^+ and NH_2^+ ions were created in a conventional hot filament ion source (MINIS). After extraction from the source, the ions were mass selected, injected into the storage ring, and accelerated to an energy of 6.1 MeV and 5.4 MeV for NH_2^+ and NH_4^+, respectively. In the section of the storage ring labeled as electron cooler, the ion beam was merged with a velocity-matched electron beam. The electrons in the cooler section have a small thermal energy spread. Their velocity distribution can be described by an anisotropic Maxwell-Boltzmann distribution, since the velocity spread is different along the beam and in the transverse direction (Andersen & Bolko 1990)

$$f(v_e) = \frac{m_e}{2\pi k T_{e\perp}} \left(\frac{m_e}{2\pi k T_{e_\parallel}}\right)^{1/2} \times exp\left(-\frac{m_e v_\perp^2}{2kT_{e\perp}} - \frac{m_e v_\parallel^2}{2kT_{e_\parallel}}\right). \quad (3)$$

The corresponding longitudinal and transverse temperatures are respectively $T_\parallel$ and $T_\perp$. In the present experiment $kT_\parallel \approx 0.1$ meV and $kT_\perp \approx 1$ meV. For every injection cycle and before starting the data acquisition procedure, ions were stored in the ring for a certain 'cooling' time. The electrons move with the same average velocity as the ions, and during this time the random thermal motion of the ions is reduced in many collisions with electrons. As a consequence, the ion beam shrinks in diameter. The extent of this translational cooling depends on the charge-to-mass ratio of the ions. Another cooling process that can occur during this time is the relaxation of ions through infrared emission to the ground vibrational state, but only for infrared-active vibrational modes. For NH_2^+ the 'cooling' time of 4.6 s was enough for complete vibrational relaxation. The NH_4^+ ion is a symmetric molecule having two infrared-inactive vibrational modes, and cooling for tens of seconds would be necessary for decay to the ground vibrational state (see e.g., 1978). However, the 'cooling time' was only 2 s for the measurement of branching fractions and 6 s for the DR rate measurement, which means that NH_4^+ may have been partly vibrationally excited in these measurements.

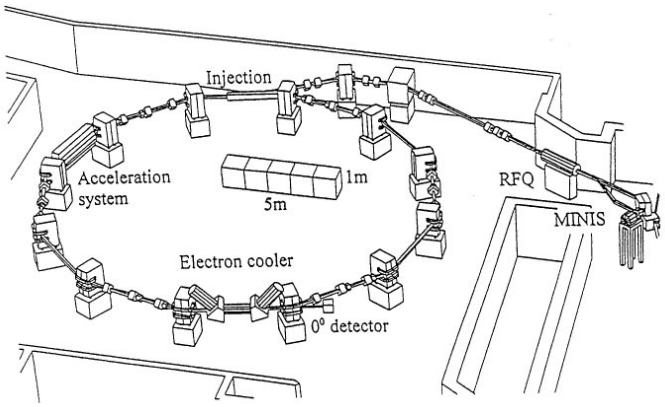

Fig. 1. View of heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory at Stockholm University. Ions stored in the ring interact with electrons in the electron-cooler section and neutral products are detected at the 0° detector.

After the cooling, the longitudinal electron velocity is tuned away from the velocity-matched condition. The detuning velocity v_d is the difference between the ion and electron velocities, and it defines the center-of-mass energy E (at least for $E > kT_\perp$), the effective collision energy

$$E = \frac{m_e v_d^2}{2}. \quad (4)$$

Following the electron cooler, the ions are bent by a dipole magnet and continue to circulate in the ring, while the neutral products from the DR process as well as those produced in collisions with the rest gas follow a straight line and hit an ion-implanted surface barrier detector, located approximately 4 m from the cooler. The diameter of the detector used in this measurement was about 4 cm. The pulse height of the signal from the detector is proportional to the total deposited energy. The spectra were recorded using a multichannel analyzer (MCA). All the fragments hit the detector at practically the same time, and the DR signal appears in the spectrum as a peak at the total beam energy, regardless of the DR channel it originates from. Neutral dissociation products from ion−rest gas collisional excitation appear as a peak at a fraction of the total energy, proportional to the ratio of their 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. The H and H_2 dissociation products can have a large kinetic energy of release and may come out at relatively large angles. The diameter of the detector was not large enough, and thus some part of the energetic H atoms from DR of NH_4^+ missed the detector. We made corrections for this particle loss in the data evaluation for both cross section and branching fractions of NH_4^+.

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 ± 0.016 (Datz et al. 1995). The probability that neutral fragments will

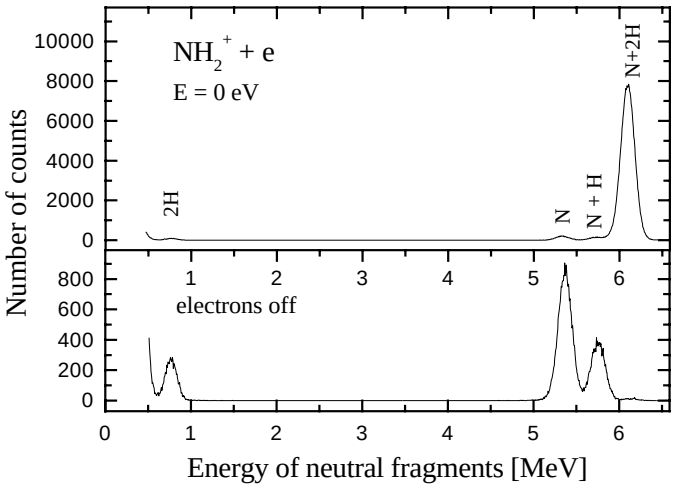

Fig. 2. MCA spectra of neutral fragments in dissociative recombination of NH_2^+ measured by the surface barrier detector. On the top the spectrum at E = 0 eV with a distinct dissociative recombination peak is shown (marked as N + 2H, mass = 16). On the bottom the background spectrum measured with the electron cooler turned off is shown. No background signal appears at full beam energy.

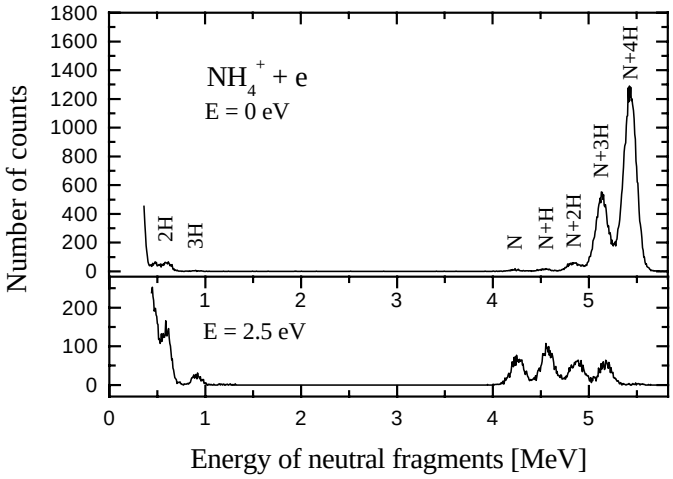

Fig. 3. MCA spectra of neutral fragments in dissociative recombination of NH_4^+ measured by the surface barrier detector. On the top the spectrum at E = 0 eV is shown. Besides the distinct dissociative recombination peak (marked as N + 4H, mass = 18), there are considerable signals in the N+3H and N+2H peaks due to light particles missing the detector. On the bottom a background spectrum measured at E = 2.5 eV (explanation given in the text) is shown.

pass the hole is equal to T, the transmission of the grid, and the probability that they will be stopped is equal to $1 - T$. Particles stopped by the grid do not contribute to the signal from the detector, and the DR signal splits over a series of peaks. The distribution of events into the peaks depends on the branching fractions and on the grid transmission, and can be used to calculate the branching fractions.

3. Data analysis

3.1. Dissociative recombination cross section

The complete data analysis procedure is described in the paper of Strömholm et al. (1996), and only the main features will be given here. In Fig. 2 a typical MCA spectrum for NH_2^+, taken at 0 eV collision energy is shown. The energies of the DR products and ion−rest gas collisions products are related to the total mass of the products, and peaks are marked with the symbols for the particles they contain. The peak at total ion energy is the DR peak, marked as N + 2H (mass = 16 product), that includes products of all DR channels: N + H_2; NH + H, and N + H + H. The small peaks at the lower energies are the background from the ion−rest gas collisions: N + H at 15/16, N at 14/16, and 2H at 2/16 of the total energy. The peak from H could not be resolved from the electronic noise. On the bottom of Fig. 2 is shown the spectrum with the background only, taken with the electron beam turned off. The maximum-energy peak practically disappeared, which means that the contribution of electron capture from the rest-gas particles to the DR signal is very small. Still, at higher energies (above 1 eV) where the DR cross section is small, the capture signal is not negligible, and the data were corrected for this small effect.

In Fig. 3 an MCA spectrum of NH_4^+, taken at 0 eV collision energy is given. The peak at total ion energy in Fig. 3 is the DR peak, marked as N + 4H (mass = 18 product), that includes products of all energetically allowed DR channels: NH_3 + H; NH_2 + H_2; NH_2 + H + H; NH + H + H_2; N + 2H_2. The background peaks appear at lower energies: N + 3H at 17/18, N + 2H at 16/18, N + H at 15/18, N at 14/18, 3H at 3/18, and 2H at 2/18 of the total ion energy. In this case, not even the 2H peak could be resolved from the electronic noise. The spectrum is also taken at 2.5 eV as shown at the bottom of Fig. 3. We used this spectrum as a background spectrum, instead of the spectrum taken with the electron beam turned off. This was done because, due to the loss of the particles from the detector, the background spectrum was not the same with and without electron beam. The energy of 2.5 eV was chosen because the DR rate has a minimum at this energy, where it is six orders of magnitude less than at 0 eV, and it is also below the threshold for the process of dissociative excitation, which could contribute to the background peaks. The DR data for NH_4^+ were also corrected for the small contribution of the electron capture from the rest-gas particles to the full energy peak.

For both NH_2^+ and NH_4^+, the energy spectra were fitted assuming Gaussian profiles for the peaks. Then the integrated number of counts $N_{\rm DR}$ in the respective DR peaks were determined along with the integrated counts N_N in the respective background N peaks. Since the background is proportional to the rest-gas pressure, which remained constant during the experiment, the relative DR rate coefficient $< v\sigma >_{rel}$ is proportional to the ratio $N_{\rm DR}/N_N$. The brackets indicate that the obtained DR rate is an average value, because of the above mentioned electron-velocity spread Eq. (3). The values for the DR rate coefficients thus obtained were divided by the corresponding center-of-mass velocity, that is the detuning velocity v_d, to obtain cross sections. For collision energies lower than 1 meV

(the maximum energy spread in this experiment) a Fourier transform technique (Mowat et al. 1995; Strömholm et al. 1996) was used to get the cross section from the measured rate coefficient, by deconvolution of rate coefficient for the electron velocity, with the assumption of the anisotropic electron velocity distribution defined in Eq. (3).

We made corrections for a few more effects. The first was an electron energy correction for the electron space charge (Kilgus et al. 1992), including its partial neutralization by positive ions, formed from electron impact ionization of residual gas and trapped by the electron beam space charge (see, e.g., Gao 1996). Also, the DR rate was corrected for the contribution from the so-called toroidal regions at the ends of the electron cooler, where the relative velocity between the ions and the electrons (and the effective collision energy) is different from that of the straight section. An iterative procedure for this correction is described by Lampert et al. (1996). Further, at higher energies, the process of dissociative excitation starts to contribute to the background peaks. We measured the rate for this process and corrected the DR rate accordingly.

For NH_4^+, we had to estimate the portion of the counts from the DR process that appears in the background peaks because of the H and H_2 particles that missed the detector. In the first step, the integrated number of counts $N_{\rm DR}$ in the respective DR peak, and the integrated number of counts $N_{\rm N+3H}$, $N_{\rm N+2H,}N_{\rm N+H}$, and $N_{\rm N}$ in the respective N+3H, N+2H, N+H, and N background peaks were determined for every collision energy. Then, the ratios $N_{\rm N+3H}/N_{\rm N}$, $N_{\rm N+2H}/N_{\rm N}$ and $N_{\rm N+H}/N_{\rm N}$ were determined at the energy $E = 2.5$ eV, where the DR rate is very low, and its contribution to the background peaks due to missing particles is negligible. The contribution of counts from the DR process to the N background peak can be excluded in the entire range of collision energies, since for a contribution there two hydrogen molecules would have to miss the detector (also, the kinetic energy release is only 1.8 eV, see Eq. (2)). By multiplying, for every collision energy, the respective $N_{\rm N}$ with the ratios $N_{\rm N+3H}/N_{\rm N}$, $N_{\rm N+2H}/N_{\rm N}$ and $N_{\rm N+H}/N_{\rm N}$ determined for the energy $E = 2.5$ eV, the number of pure background counts in the $N_{\rm N+3H}$, $N_{\rm N+2H}$, and $N_{\rm N+H}$ peaks were obtained. The surplus of counts in the background peaks must have originated from the DR process, and be due to the missing of particles by the detector. We found that 0.28 of the DR peak was lost: 0.26 to the N + 3H peak and 0.02 to the N + 2H peak. All the data were corrected for this effect.

3.2. Dissociative recombination branching fractions

As mentioned above, inserting the grid in front of the detector splits the DR signal over a series of peaks. For example, if NH and H fragments from the DR of NH_2^+ (with branching fraction n_2) are impinging on the grid, the probability that both fragments will pass and appear in the DR peak is T^2. The probability that NH will pass and H will be stopped is $T(1-T)$, and these DR events will contribute to the N + H peak. The probability is the same for H to pass and NH to be stopped, but in this case the DR counts will appear in the H peak. For every DR channel, the number of counts that come to a certain peak are also proportional to the total number of DR events for that channel. A set of linear equations connecting the number of events in the different channels to the measured number of counts in the different peaks can then be set up. For NH_2^+ it can be written as:

$$\begin{pmatrix} N_{N+2H} \\ N_{N+H} \\ N_N \\ N_{2H} \end{pmatrix} = \begin{pmatrix} T^2 & T^2 & T^3 \\ 0 & T(1-T) & 2T^2(1-T) \\ T(1-T) & 0 & T(1-T)^2 \\ T(1-T) & 0 & T^2(1-T) \end{pmatrix} \begin{pmatrix} N_1 \\ N_2 \\ N_3 \end{pmatrix} \quad (5)$$

where N_{N+2H}, N_{N+H}, N_N, and N_{2H} are the number of counts in the corresponding peaks and N_1, N_2, and N_3 are the number of events in the different DR channels. The branching fractions n_1, n_2, and n_3 are obtained after normalization $n_i = N_i/(N_1 + N_2 + N_3)$, $i = 1, 2, 3$.

For NH_4^+ the set of equations can be written as:

$$\begin{pmatrix} N'_{N+4H} \\ N'_{N+3H} \\ N'_{N+2H} \\ N'_{N+H} \\ N'_N \\ N'_{3H} \end{pmatrix} = \begin{pmatrix} T^2 & T^2 & T^3 & T^3 & T^3 \\ T(1-T) & 0 & 2T^2(1-T) & T^2(1-T) & 0 \\ 0 & T(1-T) & T(1-T)^2 & T^2(1-T) & 2T^2(1-T) \\ 0 & 0 & 0 & T(1-T)^2 & 0 \\ 0 & 0 & 0 & 0 & T(1-T)^2 \\ 0 & T(1-T) & T^2(1-T) & T(1-T)^2 & 2T(1-T)^2 \end{pmatrix} \begin{pmatrix} N'_1 \\ N'_2 \\ N'_3 \\ N'_4 \\ N'_5 \end{pmatrix}$$

where N'_{N+4H}, N'_{N+3H}, N'_{N+2H}, N'_{N+H}, N'_N, and N'_{3H} are the number of counts in the corresponding peaks and N'_1, N'_2, N_3, N'_4, and N'_5 are the number of events in the different DR channels. The branching fractions n'_1, n'_2, n'_3, n'_4, and n'_5 are obtained after normalization, e.g., $n'_i = N'_i/(N'_1 + N'_2 + N'_3 + N'_4 + N'_5)$, $i = 1, 2, 3, 4, 5$.

The first three linear equations in the matrix, which include N'_{N+4H}, N'_{N+3H}, and N'_{N+2H}, were corrected for the missing of particles by the detector, using the values for the portion of the DR counts missed by the detector estimated in the cross section data analysis. The number of DR counts cannot be found explicitly from the spectra obtained by using the grid, because it splits over the DR and the background peaks. Therefore, its implicit value is used:

$$N_{\rm DR} = N'_1 + N'_2 + N'_3 + N'_4 + N'_5. \quad (6)$$

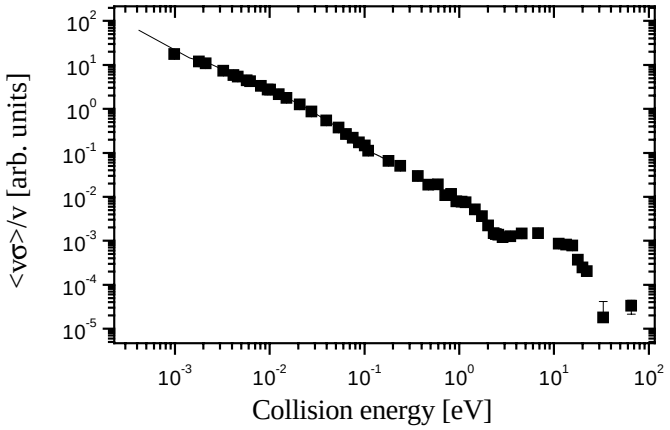

Fig. 4. Relative cross section for dissociative recombination of NH_2^+ as a function of collision energy. Solid squares show cross sections obtained by dividing measured rate coefficient by the electron velocity. The solid line is a cross section deconvoluted with the assumption of an anisotropic Maxwell-Boltzmann electron velocity distribution and using a Fourier transform technique.

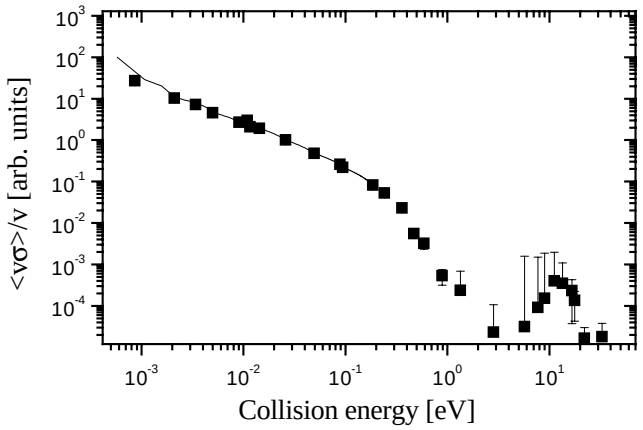

Fig. 5. Relative cross section for dissociative recombination of NH_4^+ as a function of collision energy. Solid squares show cross sections obtained dividing measured rate coefficient by the electron velocity. The solid line is a cross section deconvoluted with assumption of an anisotropic Maxwell-Boltzman electron velocity distribution, and using a Fourier transform technique.

In the first equation 0.28 $N_{\rm DR}$ is multiplied by the transmission function T^2 and added to $N^{'}_{N+4H}$. In the second equation 0.26 $N_{\rm DR}$ is multiplied by the transmission function T^2 and subtracted from $N^{'}_{N+3H}$. Finally, in the third equation 0.02 $N_{\rm DR}$ is multiplied by the transmission function T^2 and subtracted from $N^{'}_{N+2H}$.

4. Results and discussion

4.1. Dissociative recombination cross section

The relative DR cross sections for NH_2^+ and NH_4^+, measured in the collision energy interval from 0.001 to 65 eV for NH_2^+ and from 0.001 to 33 eV for NH_4^+, are shown in Fig. 4 and Fig. 5, respectively. The solid lines are the cross sections deconvoluted as described above. The error bars in the graphs are purely statistical at the one sigma level. The energy dependence of the cross section is important for our understanding of the dynamics of the DR process. We have found that the energy dependence of the DR cross section for NH_2^+ is

$$\begin{aligned} &E^{-0.9} \quad \text{in the energy range } \ 0.001\,\text{eV} \ < E < \ 0.025\,\text{eV},\\ &E^{-1.4} \quad \text{for } 0.028\,\text{eV} < E < 0.1\,\text{eV}, \text{and}\\ &E^{-1.3} \quad \text{for } 0.1\,\text{eV} < E < 1\text{eV}. \end{aligned} \tag{7}$$

In the first energy interval the cross section approximately follows the E^{-1} dependence (Wigner 1948), typical of the direct DR mechanism. The obtained energy dependence in the interval 0.028 eV $< E <$ 0.1 eV agrees with the value given by Mitchell (1990): $E^{-1.35}$ for $E >$ 0.05 eV. The broad peak at 7 eV could be from the capture to the Rydberg states associated with the ionic core that dissociates to NH + H^+.

For the energy dependence of the DR cross section for NH_4^+ we obtained

$$\begin{aligned} &E^{-0.97} \quad \text{in the energy range } 0.001 \ < E < 0.05\ \text{eV},\\ &E^{-1.5} \quad \text{for } \ 0.08 < E < 0.24\,\text{eV}, \text{and}\\ &E^{-3.3} \quad \text{for } 0.36 < E < 2.8\,\text{eV}. \end{aligned} \tag{8}$$

In the first energy interval, the cross section follows the E^{-1}dependence. The obtained energy dependence in the second and the third energy range agree very well with the energy dependence data obtained by DuBois et al. (1978) in the same energy ranges, $E^{-1.4}$ and $E^{-3.4}$, respectively. It is important to note that in the measurement of DuBois et al. (1978) the storage time was 90 min, enough for decay of all four vibrational modes, and in the present measurement it was only 3 s. However, the obtained energy dependence does not reflect any difference due to possible vibrational excitation of the NH_4^+ ion in the present measurement. The broad peak in the cross section at 11 eV could be from the capture to the Rydberg states associated with the ionic core which dissociates to NH_3 + H^+.

4.2. Dissociative recombination branching fractions

The spectrum of neutral fragments from DR of the NH_2^+ ion, obtained with a grid in front of the detector, is shown in Fig. 6. The spectrum at E = 0 is given on the top, and the background spectrum measured with electron cooler turned off on the bottom. After the background subtraction from the top spectrum, and solving the set of equations Eq. (5) that connects the number of events in the different peaks to the number of events in the different DR channels, we obtained the branching fractions in DR for NH_2^+

$$\begin{aligned} &n_1 \ = \ 0.00 \pm 0.01;\ n_2 = 0.34 \pm 0.02\,;\\ &n_3 \ = \ 0.66 \pm 0.01. \end{aligned} \tag{9}$$

The obtained branching fractions are similar to those obtained for CH_2^+ (Larson et al. 1998), which is also dominated by the three-body C + H + H channel (0.63).

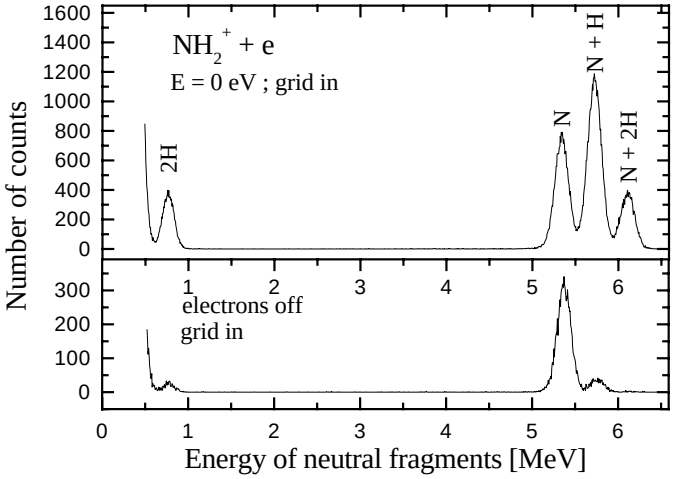

Fig. 6. MCA spectrum of neutral fragments in dissociative recombination of NH_2^+ detected with a grid in front of the detector. On the top the spectrum at E = 0 is shown. On the bottom background spectrum measured with the electron cooler turned off is shown.

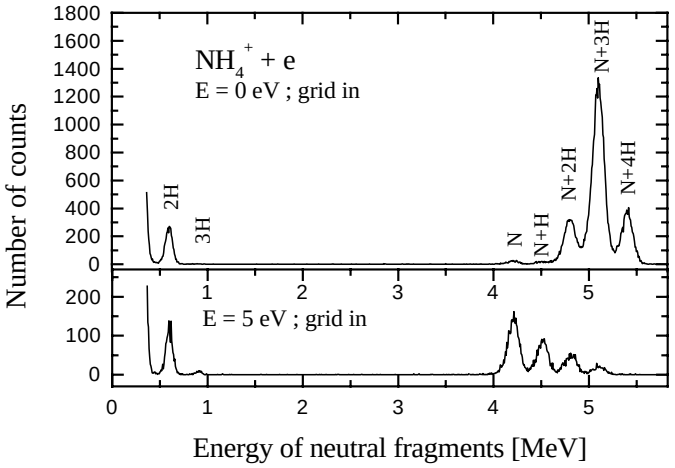

Fig. 7. MCA spectrum of neutral fragments in dissociative recombination of NH_4^+ detected with a grid in front of the detector. On the top the spectrum at E = 0 is shown. On the bottom the background spectrum measured at energy E = 5 eV is shown.

The energy spectrum of neutral fragments from DR of the NH_4^+ ion, detected with a grid in front of the detector, is shown in Fig. 7. On the top the spectrum at E = 0 is shown, and on the bottom the background spectrum as measured at energy E = 5 eV. The spectrum taken at 5 eV could be used as a background spectrum, as the DR rate is small at this energy, and measurement with the grid was not done at 2.5 eV. After the background subtraction from the peaks on the top spectrum, and solving the set of equations for NH_4^+ Eq. (6), we obtained the branching fractions in DR for NH_4^+ at 0 eV:

$$n_1^{'} = 0.69 \pm 0.03;\ \ n_2^{'} = 0.10 \pm 0.02;$$
$$n_3^{'} = 0.21 \pm 0.03;\ \ n_4^{'} = 0.00 \pm 0.01;$$
$$\text{and} \quad n_5^{'} = 0.00 \pm 0.01. \tag{10}$$

The same procedure with the data taken at 2 meV energy resulted in the following branching fractions:

$$n_1^{'} = 0.67 \pm 0.03;\ n_2^{'} = 0.09 \pm 0.02;$$
$$n_3^{'} = 0.24 \pm 0.03;\ \ n_4^{'} = 0.00 \pm 0.01;$$
$$\text{and} \quad n_5^{'} = 0.00 \pm 0.01. \tag{11}$$

The uncertainties in the branching fractions were calculated taking into account the uncertainties of fitting the peaks, the uncertainties in the estimation of number of particles missed by the detector, the uncertainty of the grid transmission and the uncertainty corresponding to the background substraction. The uncertainties are added in quadrature. There is no difference between the obtained branching fractions for NH_4^+ at 0 eV and at 2 meV within the uncertainties.

Bates (1991) presented NH_4^+ data of Adams et al. (1991), obtained by use of the flowing afterglow technique, in the form of equations connecting branching fractions

$$n_1' + 2n_3' = 1.08 \text{ and}$$
$$n_2' - n_3' = -0.08. \tag{12}$$

These are in very good agreement with our results

$$n_1' + 2n_3' = 1.11 \pm 0.07, \text{and}$$
$$n_2' - n_3' = -0.11 \pm 0.04. \tag{13}$$

Comparing with the theoretical data, there is no agreement with the obtained experimental results. Herbst (1978) obtained at a temperature of 10 K that the fraction of the ammonia-forming channel (with branching fraction $n_1^{'}$ in Eq. (2)), is only 0.24. On the opposite extreme, Bates (1991) predicted that all DR proceeds through the ammonia-forming channel.

Our results show that two body ammonia-channel is dominated in DR of NH_4^+ with $n_1^{'}$= 0.69. Among the polyatomic molecular ions experimentally investigated so far, this is the ion with the least degree of fragmentation. Thus, in the storage ring measurement of DR for H_3O^+ Vejby-Christensen et al. (1997) obtained 0.33 for the H_2O + H channel. In a flowing afterglow measurement Williams et al. (1996) obtained only 0.05 for the same channel. Semaniak et al. (1998) obtained also only 0.05 for the CH_4 + H channel in DR for CH_5^+. Herbst and Lee (1997) suggested that the dominance of the three body channels could be explained by secondary fragmentation of vibrationally or electronically excited molecular products of the two body channels. The energy release in DR of the CH_5^+ ion for the three-body CH_3 + H + H channel is 3.51 eV, the energy release in DR of the H_3O^+ ion for the three-body OH + H + H channel is 1.3 eV, and in DR of the NH_4^+ the three-body NH_2 + H + H channel is very close to thermoneutral, with the energy release 0.1 eV (Bates 1991). The importance of the three-body channel in DR seems to depend on this surplus energy: the obtained DR fractions for the three-body channels are 0.70 for CH_5^+, 0.48 for H_3O^+, and 0.21 for NH_4^+. One may conjecture from these values that the vibrational energy in the molecular products caused the secondary fragmentation.

It is interesting to note the similarity of the breakup of the NH_4 molecule in DR of NH_4^+ and the photodissociation

of the isoelectronic CH_4 molecule. With photons of 121.6 nm CH_4 dissociate to CH_3 + H in about 50% of the events (Mordaunt et al. 1993).

In the standard set of reaction rates provided by the University of Manchester Institute of Science and Technology (UMIST, see the UMIST Astrophysics Group homepage at http://saturn.ma.umist.ac.uk:8000/) for NH_2^+ it is given that $n_2 = n_3 = 0.50$, and for NH_4^+ that $n_1' = n_3' = 0.50$.

5. Summary

The complete branching fractions for DR of the NH_2^+ ion have been measured at 0 eV collision energy. The three body N + H + H channel was found to dominate DR with a branching fraction of 0.66; for the NH + H channel the measured fraction was 0.34; and no breakup into the N + H_2 channel has been measured.

The complete branching fractions for DR of the NH_4^+ ion have been measured at 0 eV and 2 meV collision energies. The DR of this molecular ion was found to be dominated by the two body, 'ammonia' channel. The branching fractions we obtained at 0 eV are 0.67 for the NH_3 + H channel, 0.09 for the NH_2 + H_2, and 0.24 for the NH_2 + 2H channel. There is no difference of the obtained branching fractions at 0 eV and 2 meV within the errors. Our results are in good agreement with the data of Adams et al. (1991), presented by Bates (1991) in the form of equations connecting branching fractions.

The relative dissociative recombination cross sections have been measured for the NH_2^+ molecular ion in the collision energy interval from 1 meV to 65 eV and for the NH_4^+ molecular ion in the interval from 1 meV to 33 eV.

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References

Adams N.G., Herd C.R., Geoghegan M., et al., 1991, J. Chem. Phys. 94, 4852
Andersen L.H., Bolko J., 1990, Phys. Rev. A 42, 1184
Bates D., 1991, J. Phys. B: At. Mol. Opt. Phys. 24, 3267
Datz S., Sundström G., Biedermann Ch., et al., 1995, Phys. Rev. A 52, 2901
Dalgarno A., Black J.H., 1976, Rep. Prog. Phys. 39, 573
Dalgarno A., Lepp S., 1996, In: Drake G.W.F. (ed.) Atomic, Molecular, & Optical Physics Handbook. American Institute of Physics, New York, p. 919
DuBois R.D., Jeffries J.B., Dunn G.H., 1978, Phys. Rev. A 17, 1314
Gao H., 1996, Low energy electron-ion recombination at CRYRING. Ph.D. Thesis, Stockholm University
Herbst E., 1978, ApJ 222, 508
Herbst E., Lee H.-H., 1997, ApJ 485, 689
Kilgus I., Habs D., Schwalm D., et al., 1992, Phys. Rev. A 46, 5730
Lampert A., Wolf A., Habs D., et al., 1996, Phys. Rev. A 53, 1413
Larson Å., Le Padellec A., Semaniak J., et al., 1998, ApJ 505, accepted for publication
Mitchell J.B.A., 1990, Phys. Rep., 186
Millar T.J., Rawlings J.M.C., Bennet A., et al., 1991, A&AS 87, 585
Mordaunt D.H., Lambert I.R., Morley G.P., et al., 1993, J. Chem. Phys. 98, 2054
Mowat J.R., Danared H., Sundström G., et al., 1995, Phys. Rev. Lett. 74, 50
Prasad S.S., Huntress W.T., 1979, ApJS 43, 1
Roueff E., 1997, Bulletin de la S.F.P. 109, 7
Semaniak J., Larson Å., Le Padellec A., et al., 1998, ApJ 498, 886
Sternberg A., Dalgarno A., 1995, ApJS 99, 565
Strömholm C., Semaniak J., Rosén S., et al., 1996, Phys. Rev. A, 54, 3086
Vejby-Christensen L., Andersen L.H., Heber O., et al., 1997, ApJ 483, 531
Van Dishoeck E.F., 1988, In: Burton W.B., Wolstencroft R.D. (eds.) Millimetre and Submillimetre Astronomy. Kluver, Dordrecht, p. 117
van Dishoeck E.F., Black J.H., 1986, ApJS 62, 109
Wigner E.P., 1948, Phys. Rev. 73, 1002
Williams T.L., Adams N.G., Babcock L.M., et al., 1996, MNRAS 282, 413