4.4. BRANCHING FRACTIONS IN DISSOCIATIVE RECOMBINATION OF NH_4^+ AND NH_2^+

L. Vikor[a] , A. Al-Khalili[a], H. Danared[b], N. Djuric[c], G. H. Dunn[c], M. Larsson[a], A. Le Padellec[a], S. Rosén[a], M. af Ugglas[b]

[a] *Department of Physics, Stockholm University, Box 6730, S-113 85 Stockholm, Sweden*

[b] *Manne Siegbahn Laboratory*

[c] *JILA, University of Colorado, Campus Box 440, Boulder, CO 80309-0390 USA*

1. Introduction

Dissociative recombination (DR) is a process in which molecular ions recombine with electrons and dissociate into neutral fragments [1, 2]. It takes place in plasmas of (dark) interstellar molecular clouds, inner comas of comets, planetary ionospheres, and in the ionized layers of Earth's upper atmosphere.

In the DR process molecular ions are neutralized and destroyed, and for a polyatomic ion it is important to know probabilities for producing different sets of neutral fragments, known as branching ratios. For modeling the chemistry of interstellar molecular clouds, the branching ratios data are necessary, but in the long list of gas phase reactions, given at the University of Manchester Astrophysics Group homepage (http://saturn.ma.umist.ac.uk:8000/) for branching ratios are usually given only assumed values in the lack of measured or calculated data.

The DR branching ratios are basically difficult to measure, because the DR products are neutral particles, and electric and magnetic field cannot be used to separate the different decay channels. The theoretical determination of the branching ratios is also difficult, since a large number of potential energy surfaces have to be considered, and only model calculations can be performed (Bates [3], Herbst [4]).

We measured branching fractions in dissociative recombination of NH_2^+ and NH_4^+ ions, using the CRYRING heavy ion storage ring. Dissociative recombination of NH_2^+ and NH_4^+ ions 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. A storage ring provides DR measurements down to an interaction energy that corresponds to low temperatures in interstellar molecular clouds or inner comas of comets, and also provides interaction with vibrationally cold ions. Using a very simple technique of passing of DR fragments through a grid before the detection, complete branching ratios in DR process can be obtained from one measurement. 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^+.

2. Experimental technique and results

Branching ratios in DR of NH_2^+ and NH_4^+ ions are measured at CRYRING. The experimental details can be found in [5]. Molecular ions, produced in the ion source MINIS, are injected into the ring, accelerated to 6.1 MeV for NH_2^+, and 5.4 MeV for NH_4^+, and kept circulating for a few seconds (4.6 s for NH_2^+ and 2 s for NH_4^+), to relax through infrared emission to the ground vibrational state. For NH_2^+ this time was enough for complete vibrational relaxation, while for NH_4^+ one vibrational mode remained excited.

In the "electron cooler" section of the storage ring, the ion beam is merged with an electron beam along the distance of about 1 m, which serves as a target. By tuning the electron energy, the interaction energy can be changed. Following the electron cooler, the ions are bent by a 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 energy-resolving surface barrier detector. In the spectrum of neutral fragments, peak position scales with the mass of the corresponding particles impinging the detector. The peak formed by DR, at maximum energy, usually dominates the spectrum. The background peaks, corresponding to neutral products from the collisions of molecular ion with the rest-gas, have lower intensities due to high ion beam energy and ultra high vacuum.

In order to determine the branching ratios, a grid with a known transmission is inserted in front of the detector. The probability for neutral fragments to pass the hole is equal to grid transmission T**,** and the probability to 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 ratios and on the

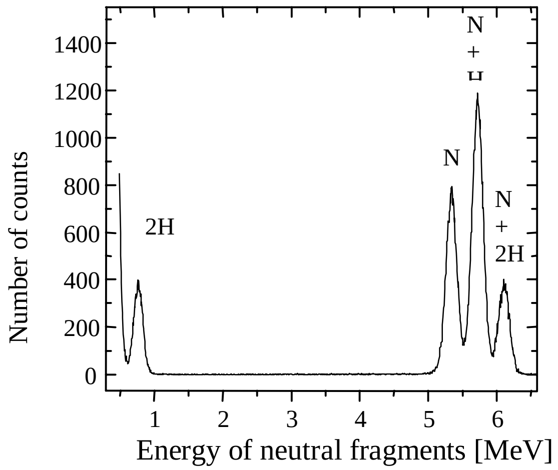

Figure 1. The spectrum of neutral fragments in dissociative recombination of the NH_2^+ ion at 0 eV interaction energy, obtained with a grid in front of the detector.

grid transmission. The spectrum shown in Fig. 1 illustrates the grid effect. This is the spectrum of neutral fragments from DR of the NH_2^+ ion at 0 eV collisional energy. Without the grid, all the DR products would appear at the full beam energy, that was 6.1 MeV. The peaks are well separated, because of the high energy of the ion beam. From the integrated number of counts in the peaks and with the known grid transmission T, branching ratios were calculated. In this experiment a grid with a transmission of 0.312 was used.

We have found that the recombination of NH_4^+ at 0 eV relative energy is dominated by the two-body NH_3 +H channel (69 %). For the break-up into the NH_2 +H_2 and NH_2 + H + H we obtained 10 % and 20 %, respectively. The values we obtained for 2 meV are about the same as at 0 eV.

For the NH_2^+ ion we obtained 66 % for the three body N + H + H channel, 34 % for NH + H, and no breakup into the N + H_2 channel.

Among the polyatomic molecular ions experimentally investigated so far, NH_4^+ is the ion with the least degree of fragmentation. In the storage ring measurement of DR for H_3O^+ Vejby-Christensen et al. [6] obtained only 33% for the two-body H_2O + H channel, and Semaniak et al. [7] obtained only 5% for the CH_4 + H channel in DR for CH_5^+. Herbst and Lee [4] 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.

3. References

[1] Bates, D. R., Phys. Rev. **78** (1950) 492.

[2] Larsson, M., Annu. Rev. Phys. Chem. **48** (1997) 151.

[3] D. Bates, J. Phys. B: At. Mol. Opt. Phys. **24** (1991) 3267.

[4] Herbst, E., Lee, H.-H., Astrophys. J. **485** (1997) 689.

[5] L. Vikor L., A. Al-Khalili, H. Danared, et al., Astron. Astrophys. (1999) (in press).

[6] L. Vejby-Christensen, L.H.Andersen, O. Heber, et al., Astrophys. J. **483** (1997) 531.

[7] J. Semaniak, Å. Larson, A. Le Padellec, et al., Astrophys. J. **498** (1998) 886.