Branching Ratios in Dissociative Recombination Measured in a Storage Ring

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Short review of branching ratios measurements in dissociative recombination process of polyatomic molecules by means of storage ring is given, with the main advantages of this experimental technique.

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 plasma of (dark) interstellar molecular clouds, inner coma 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. It is a complex problem, since a large number of potential energy surfaces have to be considered, and only model calculations can be performed. In his theoretical model Bates (3) assumes that the dissociation which requires the least number of valence bonds to be rearranged is favored. Herbst (4) used a statistical phase space theory to make predictions of DR branching ratios.

Before storage ring measurements, the DR branching ratios were measured mostly by spectroscopic techniques, for thermalized polyatomic ions in flowing afterglow plasmas (5). These methods are quite complicated and the complete set of branching ratios cannot be obtained in one measurement. The uncertainties from normalization of data from different measurements increase the uncertainty of the obtained branching ratios.

By use of the single-pass merged-beam technique (6), measurements were improved in a sense that complete set of DR branching ratios is obtained in one measurement, and branching ratios can be obtained for a range of energies. However, densities of merged electron and ion beams are limited, for the electron beam in order to avoid the possible space-charge effect, and for the ion beam by ion source production of a particular molecular ion. This results in long time for a data collection. The problem is also that in this type of experiments the ion-electron interaction occurs a short time after ion extraction from a source, and ions are typically vibrationally excited, which makes it difficult to compare obtained results with a theory and with results of other experiments.

A storage ring, which in spirit is a combination of merged-beam and ion trap technique, with use of a grid technique (which will be explained later in the text) becomes an excellent tool for measuring branching ratios in dissociative recombination. It provides energy dependent DR measurements, down to an interaction energy that corresponds to low temperatures in interstellar molecular clouds or inner coma of comets. It also provides interaction with vibrationally cold ions, and from one measurement complete branching ratios in DR process can be obtained.

EXPERIMENTAL TECHNIQUE

Branching ratios in DR were measured at two storage rings up to now: ASTRID at the University of Aarhus, Denmark, and CRYRING at Stockholm University, Sweden. The main idea of the measurement will be given on the example of the CRYRING storage ring, ilustrated in Fig. 1 (7). Molecular ions produced in ion source MINIS are injected into the ring, accelerated, and kept circulating by a periodic structure of bending and focusing magnets. The pressure in the ring is very low, about 10^{-11} Torr, and ions can be stored for a time

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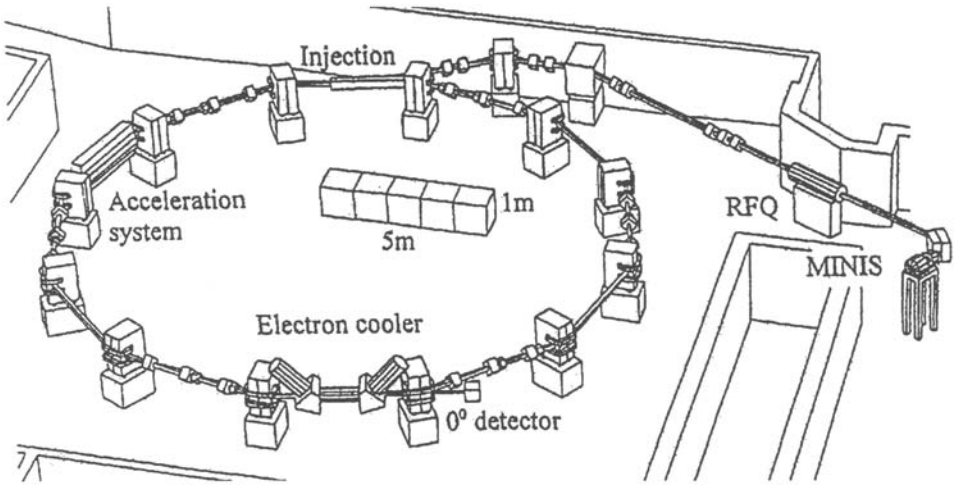

FIGURE 1 The CRYRING facility at the Manne Siegbahn Laboratory, Stockholm

longer than vibrational relaxation time for most of molecular ions. In the section of the storage ring labeled as "electron cooler", the ion beam is merged along the distance of about 1 m with an electron beam, which serves as a target. For every injected ion beam, interaction repeats many times during the beam circulation in the ring, and the data gathering is as many times faster than in the single-pass merged beam experiment. By tuning the electron energy, the interaction energy can be changed (center-of-mass energy). 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 energy spectrum of neutral fragments the peak formed by DR usually dominates.

Peak position scales with the mass of the corresponding particles impinging the detector and the background from the collisions of molecular ion with the rest-gas appears as peaks at lower energies. High ion beam energy and ultra high vacuum reduces the background.

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 grid transmission. The spectrum shown in Fig. 2 illustrates the grid effect. This is the spectrum of neutral fragments from DR of the NH_2^+ ion at 0 eV

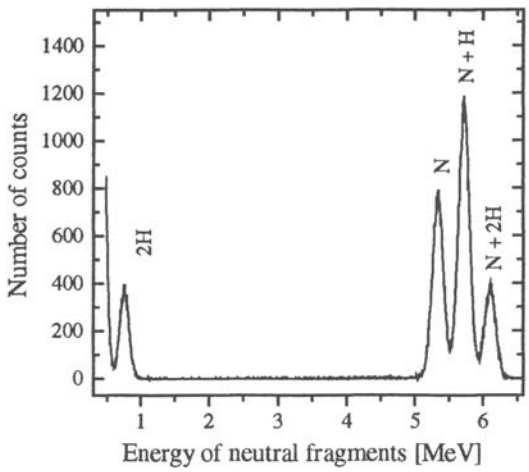

FIGURE 2. The spectrum of neutral fragments in dissociative recombination of the NH_2^+ ion at 0 eV interaction energy, obtained with a grid in front of the detector.

collisional energy, obtained with a grid in front of the detector. Without the grid, 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 can be calculated.

RESULTS AND DISCUSSIONS

Up to now DR branching ratios have been measured for these molecular ions: H_3^+, H_2D^+, H_2O^+, H_3O^+, CH_2^+, CH_3^+, CH_5^+, NH_2^+, NH_4^+ (8, 9, 10, 11, 12,13).

For the investigated molecular ions two- and three-body DR fragmentation channels were energetically opened, and for most of the ions, DR was dominated by three-body break-up. For the H_3^+ molecular ion at low energy (< 0.1 eV) 75% of the DR events finish in the three-body H + H + H channel. For the H_2O^+, CH_2^+ and NH_2^+ ions also three-body channel was found to be dominant: 68% in O + H + H (10), 63% in the C + H + H (11), and 66% in N + H + H (13). However, for the molecules with larger number of atoms the obtained branching ratios are more different. The difference can be seen comparing the respective two-body branching ratios. For DR of H_3O^+ 33% goes into the two-body H_2O + H channel (10), for CH_5^+ only 5% goes into the two-body CH_4 + H channel (12), and for NH_4^+ 69% into the two-body NH_3 + H channel (13). Herbst and Lee (4) suggested that the dominance of the three-body channels (for CH_5^+ and H_3O^+) could be explained by secondary fragmentation of vibrationally or electronically excited molecular products of the two-body channels.

The fragmentation patterns are at this point not really understood. Regularity seems to be missing, since for some of the more complex ions greater fragmentation occurs, while in other complex species, less fragmentation results. A question is whether all the generated products are result of the primary or of further dissociation. One may anticipate that these results may guide efforts to obtain a general theoretical explanation for fragmentation in the DR process.

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