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# Recombination of simple molecular ions studied in storage ring: dissociative recombination of $\text{H}_2\text{O}^+$

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Dissociative recombination of vibrationally relaxed  $\text{H}_2\text{O}^+$  ions with electrons has been studied in the heavy-ion storage ring CRYRING. Absolute cross-sections have been measured for collision energies between 0 eV and 30 eV. The energy dependence of the cross-section below 0.1 eV is found to be much steeper than the  $E^{-1}$  behaviour associated with the dominance of the direct recombination mechanism. Resonant structures found at 4 eV and 11 eV have been attributed to the electron capture to Rydberg states converging to electronically excited ionic states. Complete branching fractions for all dissociation channels have been measured at a collision energy of 0 eV. The dissociation process is dominated by three-body  $\text{H} + \text{H} + \text{O}$  breakup that occurs with a branching ratio of 0.71.

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## I. Introduction

Dissociative recombination (DR) is a double-step reaction in which a molecular ion captures a free electron and in the following step dissociates into neutral fragments. Thus it plays an important role in the evolution and chemical composition of astrophysical plasmas (diffuse and dense interstellar clouds, star-forming regions, material shocked by supernova explosions, galaxies and planetary or stellar atmospheres) being one of the processes responsible for the removal of the molecular ions of these media.<sup>1–3</sup> Proper consideration of this role requires a knowledge of the absolute cross-sections, as well as the neutral product branching ratios for polyatomic DR reactions that might occur at temperatures ranging from ten to a few thousand degrees. In particular, branching ratios still remain an area of uncertainty in most cases. The complexity of the process makes it difficult to develop a general theory which would be able to predict branching ratios for DR of polyatomic molecular ions. There have been relatively few theoretical attempts at understanding the fragmentation mechanism. The model developed by Bates<sup>4,5</sup> argues that the dissociative channels involving the least rearrangements of valence bonds are favoured and thus in dissociative recombination of  $\text{XH}_n^+$  type ions a single hydrogen is most likely to be detached. However, recent experimental data on dissociative recombination of  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{CH}_3^+$ ,<sup>6</sup>  $\text{CH}_2^+$ <sup>7</sup> and  $\text{CH}_5^+$ <sup>8</sup> significantly disagree with the predictions of that model. Another approach based on phase space theory<sup>9,10</sup> is also not sufficiently quantitative and reliance must be placed

on experiment. A variety of experimental methods including microwave afterglow,<sup>11</sup> flowing afterglow Langmuir probe (FALP)<sup>12</sup> and single-pass merged-beams<sup>13</sup> techniques, have been developed in the last decades for studying the dissociative recombination process. The application of ion storage rings allows for combining of the advantages of the merged-beams technique (wide range of centre-of-mass energy at high resolution) with high-quality cooled molecular beams.<sup>14</sup> Furthermore, long storage time combined with electron cooling results in intense molecular ion beams of narrow velocity spread and well defined electronic and vibronic states, as storage time is usually long enough to allow infrared active vibrational modes to relax.

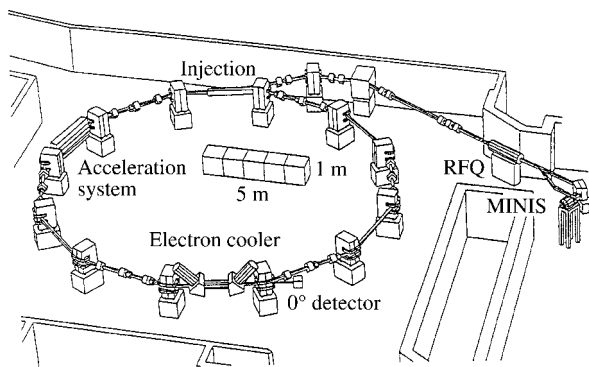
The present paper addresses dissociative recombination of  $\text{H}_2\text{O}^+$ . Since it has a well-known structure, it might be helpful in a theoretical understanding of the mechanism that allows the DR reaction to proceed. The studied process is also relevant to the oxygen chemistry of the H I zone in dense molecular clouds,<sup>3</sup> being a source of OH radicals therein.

Different aspects of dissociative recombination of  $\text{H}_2\text{O}^+$  have been previously studied by means of a variety of experimental methods. The absolute cross-sections were measured by Mul *et al.*<sup>15</sup> with a merged-beams technique over the energy range 0.005–1 eV. However, the state of excitation of the ions was not accurately determined in that experiment. Branching ratios in DR of vibrationally excited  $\text{H}_2\text{O}^+$  ions were studied by Rowe *et al.*<sup>16</sup> using a plasma flow tube experiment. Recently, dissociative recombination of  $\text{H}_2\text{O}^+$ <sup>6,17</sup> and  $\text{HDO}^+$ <sup>17</sup> in the vibrational ground state have been studied at the heavy-ion storage ring ASTRID. Absolute cross-sections were measured in the energy range from 0.1 meV to 50 eV and complete branching ratios at a collision energy ( $E$ ) of 0 eV were determined. An isotope effect favoring hydrogen atom release in DR of  $\text{HDO}^+$  was found.<sup>17</sup>

In this paper we report dissociative recombination cross-sections for  $\text{H}_2\text{O}^+$  over an energy interval from 0 eV to 30 eV and complete neutral product branching ratios measured at an energy of 0 eV.

## II. Experiment and data analysis

The experiment has been carried out at the heavy-ion storage ring CRYRING (see Fig. 1) at the Manne Siegbahn Laboratory in Stockholm, Sweden. A full description of the facility as well as the experimental method can be found elsewhere.<sup>18</sup> Here only a brief description is given. The ions, generated in a cold plasma ion source JIMIS, were extracted and after mass-selection injected into the storage ring. Then they were accelerated to the highest circulation energy possible, approximately  $0.3 \text{ MeV u}^{-1}$  and stored with a lifetime of 2.4 s. The typical ion beam current was  $0.1 \mu\text{A}$  with an uncertainty of 10%, which was measured by an inductive current transformer. The intensity of the ion beam was continuously followed by a scintillation detector by measuring the neutrals arising from collisions of the ions with residual gas in one of the straight sections of the ring. Since the count rate in the detector was proportional to the residual-gas pressure, which remained



**Fig. 1** A view of the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory at Stockholm University. The ions stored in the ring interact with the electrons in the electron cooler section and neutral products are detected on the  $0^\circ$  detector.

constant during the experiment, it was used as a measure of the relative number of circulating ions, which was monitored by a multichannel scaler as a function of time.

The stored ion beam was merged over an effective interaction length of  $l \approx 0.85$  m with a magnetically confined, monoenergetic electron beam. The electron velocity distribution in the ion rest frame is described by a flattened Maxwell function<sup>19</sup> characterized by different transverse ( $kT_{\perp} = 1$  meV) and parallel ( $kT_{\parallel} = 0.01$  meV) temperatures. A continuously renewed electron beam simultaneously served as a phase-space cooler and as a high density electron target. The cooling condition is obtained when the mean ion and electron velocities are matched, which defines the electron cooling energy as  $E_{\text{cool}} = (m_e/m_i)E_i$ . Here  $m_e$  and  $m_i$  are the electron and ion masses and  $E_i$  is the energy of the ions. The collision energy

$$E_{\text{cm}} = (\sqrt{E_e} - \sqrt{E_{\text{cool}}})^2, \quad (1)$$

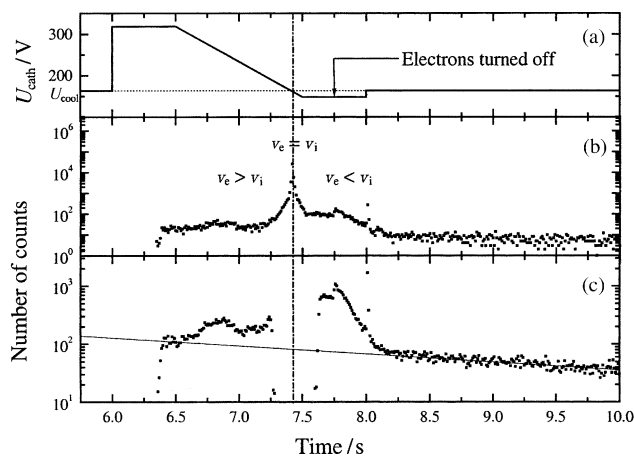
was set by detuning the electron energy  $E_e$  with respect to the cooling energy  $E_{\text{cool}}$  while keeping the ion velocity fixed. The kinetic energy of electrons in the laboratory frame was determined by the electron gun voltage, corrected for the electron space charge and its partial neutralization by positive ions that arise from the ionization of residual gas by electrons and which then get trapped by the electron space charge.<sup>8</sup> A 5 s interval between injection and the start of the measurement was long enough to vibrationally relax the ions. Neutral products created in the cooler were separated from the primary beam as they passed through the first dipole magnet following the electron cooler. Then they were detected with a 3000 mm<sup>2</sup> surface barrier detector mounted on the cooler axis beyond the magnet, at a distance of 3.5 m from the midpoint of the cooler. Since the size of the detector was larger than the transfer separation of DR products, they were detected with 100% efficiency. Each neutral fragment that arrived at the detector carried a fraction of the total ion beam energy proportional to its relative mass.

## II.A. Cross-sections

All the neutrals arising from a single DR event reached the detector with a time separation much shorter than its integration time and thus were recorded at the total ion beam energy. Similarly, neutral bound or fragmented water molecules, created *via* electron capture (EC) from the rest-gas atoms, were recorded at full energy. Other neutral products created in the ion-rest gas collisions or in electron induced dissociative excitation reactions were detected at a fraction of the total energy and thus could be distinguished from the DR + EC signal. However, the energy resolution of the detection system was not sufficient to resolve fully the DR + EC peak from the background. Thus only a part of the DR + EC pulse height distribution, free of background, was selected to be monitored as a measure of the total DR + EC ( $C_{\text{DR+EC}}$ ) rate.

The measurement for the DR cross-section was performed by scanning the electron energy<sup>20</sup> over the range which corresponds to collision energies of between 0 and 30 eV. A detailed structure of the electron energy scan is shown in Fig. 2a. The cathode voltage was first rapidly jumped to the highest value and kept constant over 0.5 s in order to estimate the EC rate ( $C_{\text{EC}}$ ), which was expected to be dependent on the local changes of the vacuum in the cooler due to the ions trapped in the electron beam space charge potential. At these high collision energies, the DR cross-section is vanishingly small. Then, the ramping voltage was decreased to its lowest value, crossing the cooling voltage closely to the end of the ramping interval. Thus, a part of the energy region being the subject of study was covered once with the electron velocity higher than the ion velocity. Finally, after 0.5 s, during which time the voltage remained unchanged, it was ramped back to the cooling voltage. Before reaching the cooling voltage the electron beam was turned off by setting the electron gun power supply to zero. Thus the EC contribution arising from the collisions with the residual gas in the absence of electrons could be measured.

The data were collected continuously within the 7 s measurement window, distributed over 1000 energy channels. After each injection of ions the cycle started again. The data were taken over 400 full cycles. The measured spectrum is shown in Fig. 2b. In order to accurately estimate the EC contribution, the same procedure was applied with a higher ion beam current, after blocking the detector within the time window corresponding to the collision energy range close to 0 eV (see Fig. 2c). The absolute  $C_{\text{DR+EC}}$  and  $C_{\text{EC}}$  rates were then obtained by multiplying the number of counts in each energy window by a correction factor  $f = N_i/N_f$ . Here  $N_i$  and  $N_f$  are the number of



**Fig. 2** (a) The electron energy scan as a function of time. (b) Full DR spectrum measured over the whole energy scan. (c) DR spectrum measured with a high ion beam current in order to determine the background contribution coming from electron capture reactions.

counts over the whole area of DR + EC peak and its background-free fraction, respectively. Both numbers were obtained from pulse-height spectra, which were recorded over the same time interval. The pure DR count rate ( $C_{\text{DR}}$ ) at a given energy window was obtained by subtraction of the  $C_{\text{EC}}$  contribution according to the following formula:

$$C_{\text{DR}} = C_{\text{DR+EC}} - \frac{C_{\text{b}}^{\text{e}} - C_{\text{n}}^{\text{e}}}{C_{\text{b}} - C_{\text{n}}} C_{\text{EC}}, \quad (2)$$

where  $C_{\text{b}}$  and  $C_{\text{b}}^{\text{e}}$  are the background rates measured with a scintillation detector, while keeping the electron beam off and on, respectively, and  $C_{\text{n}}$  and  $C_{\text{n}}^{\text{e}}$  are the respective noise levels in the detector.

The DR rate coefficients  $\langle\sigma v\rangle$  were obtained from the expression:

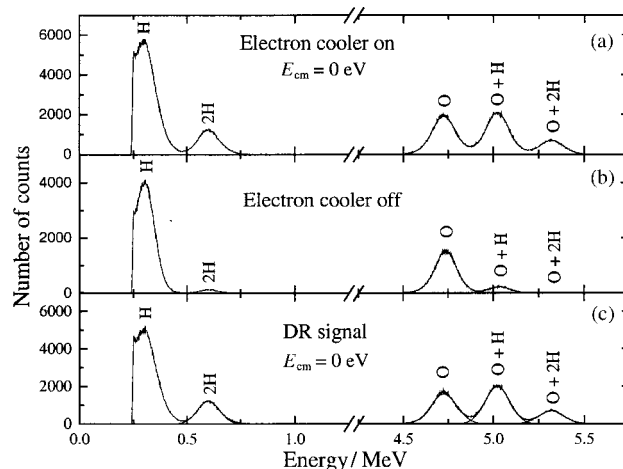
$$\langle\sigma v\rangle = R_{\text{b}} \frac{c}{n_{\text{e}} l} \frac{C_{\text{DR}}}{C_{\text{b}}^{\text{e}}}, \quad (3)$$

where  $\sigma$  is the DR cross-section,  $v$  the relative velocity,  $c$  the circumference of the ring (51.6 m),  $n_{\text{e}}$  electron density and  $l$  the length of the electron cooler section. In an independent measurement the absolute ion beam current was measured and related to the ion breakup on the residual gas through a factor  $R_{\text{b}}$ .

The measured DR rate coefficient is the velocity weighted cross-section, averaged over the velocity distribution of the electron beam. Since the velocity distribution is known,<sup>19</sup> a Fourier transform procedure<sup>18</sup> could be used to obtain the cross-section. However, this procedure sometimes results in the creation of artificial structures. Here, the DR cross-sections were derived by dividing the measured rate coefficient by the detuning velocity  $|v_{\text{e}} - v_{\text{i}}|$  between the electrons and the ions. This simple method is justified since for most of the experimental points, the detuning velocity is larger than the electron velocity spread.

The measured cross-section was also corrected for the contribution arising from the toroidal regions of the electron cooler. In these regions, the ion and electron beams separate and electron-ion collisions occur with relative energies higher than in the straight part of the cooler. These contributions have been calculated using an iterative procedure<sup>21</sup> and subtracted from the measured cross-section.

A total uncertainty in the DR cross-sections was estimated to be approximately 20% at the  $1\sigma$  level. This is dominated by the uncertainty of the ion beam current (10%), the electron density (5%), the effective length of the electron cooler (10%) and the statistical uncertainty of the mea-

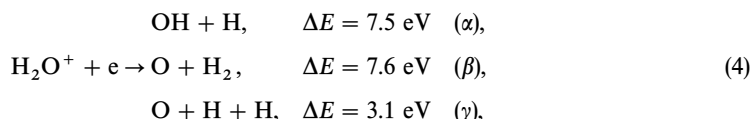


**Fig. 3** Energy spectra of neutral fragments of  $\text{H}_2\text{O}^+$  measured with a grid in a front of the detector. (a) The spectrum measured with an electron beam at a collision energy of 0 eV. (b) The background spectrum collected after turning the electron beam off. (c) A “pure” DR spectrum obtained after subtraction of the background.

sured count rates, which were typically below 5% (with the exception of the rates at energies above 20 eV where the uncertainties were up to 30%).

## II.B. Branching ratios

The neutral product branching ratios for DR of  $\text{H}_2\text{O}^+$  were obtained from the energy spectra measured with a grid inserted in front of the detector. The grid is made of stainless steel, 50  $\mu\text{m}$  thick, with holes of 70  $\mu\text{m}$  diameter. The transmission of the grid was measured in independent experiment using a proton beam of energy ranging from 0.3 MeV to 1.7 MeV. The transmission  $T$  was found to be  $0.297 \pm 0.015$  (the uncertainty is given at the  $3\sigma$  level) and energy independent. Each single particle could pass through the grid with a probability of  $T$ . Particles stopped by the grid (with a probability of  $(1 - T)$ ) did not contribute to the signal. For example, the products of two-body DR breakup can be detected with a probability of  $T^2$  or  $T(1 - T)$ , with the energy carried by the fragments passing through the holes. Thus the DR peak, the position of which was originally independent of the fragmentation pattern (see previous section), is now distributed over a series of peaks. For DR of  $\text{H}_2\text{O}^+$ , three dissociative recombination channels (with branching ratios  $\alpha$ ,  $\beta$ ,  $\gamma$ ) are energetically allowed at 0 eV collision energy:



The given values for the kinetic energy release were calculated assuming that the neutral products are in their ground states. Fig. 3 shows the energy spectra measured using the grid: the top panel shows the spectrum measured at collision energy of 0 eV, the middle panel shows the background collision distribution as measured after turning the electron beam off and the bottom panel shows the background-subtracted DR signal. The background subtraction was done similarly to the procedure described in the previous subsection (see eqn. (2)). The number of counts over each of the peaks  $N_{\text{H}}$ ,  $N_{\text{O}}$ ,  $N_{\text{O+H}}$  and  $N_{\text{O+2H}}$  in the DR spectrum were obtained by fitting the spectrum with a set of Gaussians as shown in Fig. 3c. The peak areas are related to the contribution of different dissociation channels  $N_{\alpha}$ ,  $N_{\beta}$  and  $N_{\gamma}$  through a set of equations which can be found in ref. 17. The branching ratios ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) were determined after normalization of the number of events appearing in a given channel to the total number of events in all dissociation channels. In this paper we report on the complete branching fractions at a collision energy of 0 eV.

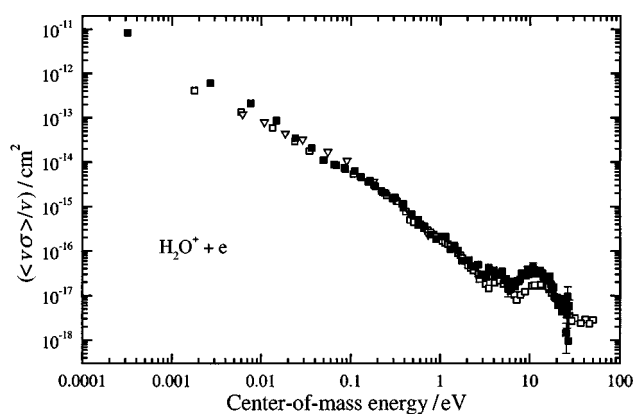
### III. Results and discussion

#### III.A. Cross-sections

The absolute cross-sections for  $\text{H}_2\text{O}^+$  have been measured over the collision energy interval between 0 eV and 30 eV. The data are shown by the solid squares in Fig. 4. They are compared with the results obtained in a single-pass merged beam experiment performed by Mul *et al.*<sup>15</sup> and the storage ring data reported recently by Jensen *et al.*<sup>17</sup> The cross-sections originally taken from ref. 15 had to be divided by a factor of 2 because of an error in their calibration procedure.<sup>22</sup> Since the state of excitation of the ions in that experiment was not accurately determined, the data cannot be directly compared to the present results. Nevertheless, in the energy range between 0.1 eV and 1 eV, they are in a very good agreement with the present data, as well as the results obtained at ASTRID. The systematic difference between the CRYRING and the ASTRID data at energies below 30 meV arise from the difference between the temperatures of the electron beams, being 1 meV and 25 meV, respectively. At collision energies above 2 eV our cross-sections agree qualitatively with those measured by Jensen *et al.*,<sup>17</sup> but they are systematically larger. The positions of two peaks found at energies of 4 and 11 eV are shifted towards low energies by about 1 and 4 eV, respectively, with respect to the ASTRID data.

The origin of these resonances can be explained by electron capture to Rydberg states converging to electronically excited ionic states, followed by (pre)dissociation. As has been concluded by Jensen *et al.*,<sup>17</sup> the first of the observed peaks can be attributed to electron capture to the series of Rydberg states with an ionic  $\text{H}_2\text{O}^+$  core in a second excited state  $\tilde{\text{B}}^2\text{B}_2$ .<sup>23</sup> These Rydberg states, which are originally bound against dissociation,<sup>24–26</sup> can be predissociated by other Rydberg states converging to excited ionic states lying around 9–20 eV.<sup>24</sup> The peak observed at a collision energy of 11 eV can be explained by electron capture to those Rydberg states. The positions of both peaks coincide with the features in the cross-sections for dissociative excitation of  $\text{H}_2\text{O}^+$  measured by Jensen *et al.*<sup>17</sup> A sharp threshold for the H channel was found at 5 eV. The peak found at 12 eV in the O channel is suggested to be due to a resonant coupling to one of the highly excited states.

The energy dependence of the cross-section in the low energy range can also be significant for understanding of the mechanism of the DR process. The energy dependence of the DR cross-section for  $\text{H}_2\text{O}^+$  found in the present experiment was found to be  $E^{-1.24}$  at energies below 0.1 eV. It is significantly more steep than the  $E^{-1}$  behaviour,<sup>27</sup> typical of the direct DR mechanism. In the energy interval between 0.1 eV and 2 eV the DR cross-sections decrease much faster with an  $E^{-1.55}$  energy dependence. A similar drop in the DR cross-section in the energy region 0.3–0.4 eV was observed in the ASTRID experiment.<sup>17</sup> The authors suggested that the drop is related to the competitive depletion mechanism that arises from the opening of a new autoionization channel of the neutral system (formed by electron capture) into a vibrationally excited state of the ion.



**Fig. 4** Absolute cross-sections for dissociative recombination of  $\text{H}_2\text{O}^+$  (solid squares) as a function of center-of-mass energy. Typical statistical error bars are shown for a few experimental points. The other results of Mul *et al.*<sup>15</sup> (divided by 2) and Jensen *et al.*<sup>17</sup> are shown as opened triangles and squares, respectively.

In order to obtain the thermal rate coefficient, which can be directly applied to modelling of media considered in thermodynamical equilibrium, the measured cross-section was convoluted with an isotropic Maxwellian velocity distribution yielding  $(4.3 \pm 0.6) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at 300 K.

### III.B. Branching ratios

The neutral product branching ratios in DR of  $\text{H}_2\text{O}^+$  at a collision energy of 0 eV have been obtained as follows:

$$\begin{aligned} \text{OH} + \text{H}, \quad \alpha &= 0.20 \pm 0.05, \\ \text{H}_2\text{O}^+ + \text{e} \rightarrow \text{OH} + \text{H}_2, \quad \beta &= 0.09 \pm 0.04, \\ \text{O} + \text{H} + \text{H}, \quad \gamma &= 0.71 \pm 0.06. \end{aligned} \quad (5)$$

The dissociation is dominated by the three-body breakup. A similar tendency has been found in dissociative recombination of  $\text{H}_3^+$ ,<sup>28–30</sup>  $\text{CH}_2^+$ ,<sup>7</sup>  $\text{CH}_5^+$ ,<sup>8</sup>  $\text{H}_3\text{O}^+$ ,<sup>6,31</sup>  $\text{CH}_3^+$ ,<sup>6</sup>  $\text{H}_2\text{O}^+$ .<sup>6,17</sup> The branching ratios reported in the present work show that there is more three body fragmentation than has been previously found in other experiments. Branching ratios measured by Rowe *et al.*<sup>16</sup> in a flowing-afterglow experiment indicated a dominance of two-body breakup as follows:  $\alpha = 0.55$ ,  $\beta < 0.24$  and  $\gamma > 0.24$ . However, these results cannot be directly compared with the present data, since they have been obtained for vibrationally and electronically excited ions. Similar fragmentation patterns to those observed in our measurement were reported in the experiment performed at the storage-ring ASTRID. However, recent experimental data reported by Jensen *et al.*<sup>17</sup> ( $\alpha = 0.30$ ,  $\beta = 0.13$  and  $\gamma = 0.57$ ), show slightly different redistribution of the flux over the OH + H and O + H + H dissociation channels. Our data are found to be in a perfect agreement with the earlier results reported by the ASTRID group.<sup>6</sup>

The present data and that of other experimental results on neutral product branching ratios in DR of polyatomic molecular ions<sup>6–8,17,31</sup> show a general tendency to be dominated by three-body breakup. This is in disagreement with the theory derived by Bates,<sup>4,5</sup> for which it is suggested that dissociative recombination of  $\text{XH}_n^+$  type molecular ion favours the dissociation pathways which involve the least rearrangement of valence bonds. Thus, according to that theory, the channels in which a single hydrogen atom is released are most likely. Thus, a detailed theoretical explanation of the fragmentation mechanism in DR of polyatomic ions still remains a challenge. One possible mechanism explaining the dominance of the three-body breakup could be that it arises from a secondary fragmentation of the vibrationally excited molecular products in two-body channel.<sup>32</sup>

## IV. Conclusion

The absolute cross-sections for dissociative recombination of  $\text{H}_2\text{O}^+$  ions have been measured over the energy range between 0 eV and 30 eV. The energy dependence of the cross-section in the low-energy range indicates the DR yield is more efficient than those predicted by the direct mechanism. Neutral product branching ratios for DR of water ions have been determined at a collision energy of 0 eV. The three-body O + H + H channel was found to dominate with a branching fraction of 0.71.

## V. Acknowledgements

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