Dissociative recombination of H₃O⁺ and D₃O⁺ : absolute cross sections and branching ratios

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I. INTRODUCTION

Over the last two decades, a rich variety of molecules were discovered in interstellar clouds. To be able to understand their presence and their observed amounts, as well as to forecast the evolution of the clouds, elaborate models were developed. (see Smith[1] and Sternberg & Dalgarno[2]). However, only few molecular processes can occur due to the extreme physical conditions which prevail therein, among which is the dissociative recombination process (DR). This is the capture of a free electron by a molecular with subsequent dissociation into neutral fragments. Being a binary and very exothermic process, this is of great importance in the interstellar medium as well for comets, planetary ionospheres or ionized layers of Earth's upper atmosphere.

The determination of the branching fractions for the DR process is of great importance in astrochemistry and for polyatomic ions for instance, one might realize the complexity of that problem, due to the very large number of potential energy surfaces involved and which are unknown in most of the cases. So far, only a few theories have been used to predict the branching ratios for the hydronium ion, among them the theory derived by Bates[3-4]. The original theory predicted that the dissociations releasing a single hydrogen atom must be dominant, in obvious contradiction to what was measured afterwards using the storage ring techniques. Indeed, the three-body break up OH + H + H originating from H₃O⁺, was found to occur for 48% of the dissociations by Vejby-Christensen *et al*[5] and for 67% by us. Another theoretical approach, the so-called statistical phase-space model developed by Herbst[6], predicted that the two-body channel OH + H₂ should be dominant, but despite the revision of this model[7], this did not predict the dominance of the three-body channel.

II. EXPERIMENT

The experiment was performed at the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory in Stockholm, Sweden.

The H₃O⁺ and D₃O⁺ ions were produced in a hot filament ion source (MINIS). After extraction from the source at 30 keV, the ions are mass selected, injected into the ring, accelerated to maximum energy and stored during few seconds. The experimental protocol is the following. The infrared active ions are first cooled during short time, but long enough to allow proper internal relaxation (to reproduce the interstellar conditions) ; this is achieved by letting them interacting with the electrons at the same average velocity and thus, the random thermal motion of the ions is reduced and the ion beam shrinks in diameter. Then, the electron velocity is detuned to

$$E_{cm} = \left(\sqrt{E_e} - \sqrt{E_{cool}}\right)^2$$

, where E_e is the average laboratory electron energy and E_{cool} is the laboratory electron energy when cooling occurs.

While the ions are circulating in the ring, the neutral products created in the electron cooler section by the dissociative recombination events, as well as those produced by collisions with the rest gas, follow a straight line after the electron cooler and hit a 4cm in diameter energy-sensitive silicon detector. The spectra are recorded by a Multichannel Analyser (MCA).

III. DATA ANALYSIS PROCEDURE
A. Cross section measurements

The experimental DR rate coefficient $<v\sigma>$, at a given center-of-mass energy, is determined by : $<v\sigma> = R_b \dfrac{c}{n_e l} \dfrac{N_{DR}}{N_b}$

where c is the circumference of the ring, l the length of the electron cooler and n_e the density of the electron beam. N_{DR} is the number of counts coming from the dissociative recombination process. N_b is the number of counts coming from collision with the rest gas whereas R_b is the destruction rate per ion and per unit time. The measured rate coefficient $<v\sigma>$ is then related to the cross section by :

$$<v_{cm}\sigma> = \int_{-\infty}^{+\infty} v\sigma(v) f(v_{cm}, v_e) dv$$

where $f(v_{cm}, v_e)$ is the electron velocity distribution around the center-of-mass velocity v_{cm}. The cross sections can be extracted by deconvolution via a Fourier transform technique. Beyond this, a few corrections must be made in order to obtain the real cross sections.

B. Branching ratios measurements

To measure the branching ratios of the different dissociative recombination channels, a grid can be inserted in front of the surface barrior detector. This grid is thick enough to stop the neutral fragments that do not pass through the holes. The transmission T of the grid was measured by Datz et al[8] to be (0.312 ± 0.016). The basic principle is the following. The probability for a neutral fragment to pass through a hole is equal to T, whereas the probability not to pass is equal to (1-T). As particles stopped by the grid are not counted by the detector, the dissociative recombination signal splits into a series of peaks centered at a fraction of the full beam energy, while recording the MCA spectrum for a given center-of-mass energy. Eventually. each peak area is determined. However, we need to take into account the contribution to these peaks coming from ion-rest gas collisions. Regarding the grid properties, a set of linear equations connecting the number of dissociations into the different channels N_α, N_β, N_χ, N_δ (there are four exothermic channels for the DR of H_3O^+ and D_3O^+ at 0eV) to the measured numbers of events in the different peaks N(O+3H), N(O+2H), ..., N(H) can be set up. For the whole set of peaks, one gets :

$$\begin{pmatrix} N(O+3D) \\ N(O+2D) \\ N(O+D) \\ N(O) \\ N(3D) \\ N(2D) \\ N(D) \end{pmatrix} = \begin{pmatrix} T^2 & T^2 & T^3 & T^3 \\ T(1-T) & 0 & 2T^2(1-T) & T^2(1-T) \\ 0 & T(1-T) & T(1-T)^2 & T^2(1-T) \\ 0 & 0 & 0 & T(1-T)^2 \\ 0 & 0 & 0 & T^2(1-T) \\ 0 & T(1-T) & T^2(1-T) & T(1-T)^2 \\ T(1-T) & 0 & 2T(1-T)^2 & T(1-T)^2 \end{pmatrix} * \begin{pmatrix} N_\alpha \\ N_\beta \\ N_\chi \\ N_\delta \end{pmatrix}$$

By solving this set of equations, one can obtain the branching ratios after normalization to the total number of dissociations : $n_i = \dfrac{N_i}{\sum_i N_i}$ with $i = \alpha, \beta, \chi, \delta$

IV. RESULTS AND DISCUSSION
A. Absolute cross section and thermal rate coefficient

The measured DR cross sections as a function of collision energy are shown in Fig. 1 for H_3O^+ and D_3O^+. The cross section is monotonically decreasing and the slope becomes steeper for energies higher than 0.1 eV.
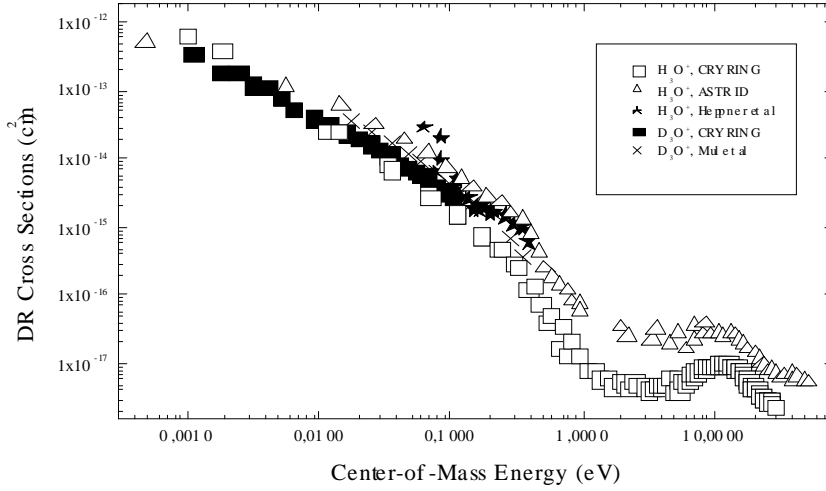

Fig 1 : Cross sections for H_3O^+ and D_3O^+ (different experiments).

The E^{-1} energy dependance is often characteristic of the so-called direct dissociative recombination process for polyatomic ions in the low energy range, according to the Wigner threshold law[9]. Our results are in good agreement with those from Mul *et al*[10]. Fig 1 shows also the cross sections that were measured for H_3O^+ by Vejby-Christensen et al[5] , as well as the first absolute measurements by Heppner et al[11]. The H_3O^+ cross sections are in the same order than those for D_3O^+, and no clear isotop effect could be highlighted.

B. Branching ratios

At 0eV, one obtains for H_3O^+:

$n_\alpha (H_2O + H) = 0.18 \pm 0.05$
$n_\beta (OH + H_2) = 0.11 \pm 0.05$
$n_\chi (OH + H + H) = 0.67 \pm 0.06$
$n_\delta (O + H_2 + H) = 0.04 \pm 0.06$

The equivalent ratios for D_3O^+ are :

$n_\alpha (D_2O + D) = 0.13 \pm 0.05$
$n_\beta (OD + D_2) = 0.11 \pm 0.02$
$n_\chi (OD + D + D) = 0.76 \pm 0.02$
$n_\delta (O + D_2 + D) = 0.00 \pm 0.01$

As was already found for other systems, the three-body breakup is dominating, in contrary to what was generally considered in previous astrophysical models (dominance of the two-body fragmentation). The production of (heavy) water is also found to be non completely negligible. Our results also show that atomic oxygen is a minor product of the DR of H_3O^+ and deuterated species. In addition, there seems to

be not more isotop effect in the branching fractions than was found for the cross sections.

V. CONCLUSION

Absolute cross sections and complete branching ratios for the DR of H_3O^+ and D_3O^+ were measured. The main finding is that the three-body break up is by far the most dominant.

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