

## Dissociative Recombination of Polyatomic Molecular Ions: Branching Ratios and Isotopic Effects

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**Abstract.** The branching ratios for the dissociative recombination of various vibrationally cold polyatomic molecular ions have been measured using the ASTRID ion storage ring. The results show that many particles are ejected during the recombination process, and that isotopic effects exist when hydrogen atoms are replaced by deuterium.

### 1. Introduction

Dissociative recombination (DR) of polyatomic ions is an important process in the interstellar medium. Polyatomic ions are produced in a sequence of ion-molecule reactions, and one of the possible ways of neutralising the ions is the process of dissociative recombination in which the molecular ions recombine with free electrons and subsequently dissociate into neutral fragments. The rate coefficient and branching ratios for dissociation into different combinations of neutral atoms and molecules thus play a decisive role for the chemical evolution in interstellar clouds. For a detailed discussion of the chemical network the papers by Smith (1992) and Sternberg & Dalgarno (1995) may be consulted.

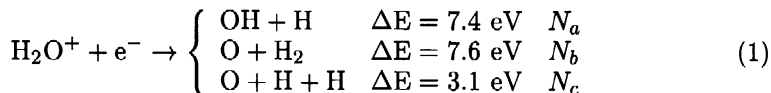
Laboratory data related to the DR reaction should consist of both the rate coefficient for the reaction as well as the branching ratios. One of the major problem in extracting such values has been the fact that the initial vibrational population of molecular ions, as produced in a standard ion source, is usually unknown. Since the DR process is known to be very sensitive to the initial vibrational state, only results obtained with fully relaxed ions can be useful for astrophysical models.

During the last 7 years, the heavy-ion storage ring technique has been used to produce intense beams of vibrationally cold molecular ions. In this technique, the molecular ions are first produced in a standard ion source (i.e. with an unknown vibrational excitation), then accelerated to an energy of a few MeV's, and subsequently stored in a heavy-ion storage ring, for a time which is longer than the vibrational (radiative) relaxation time. This method has produced a wealth of data on DR processes, from simple molecular ions such as  $\text{HD}^+$ , to polyatomic molecular ions (such as  $\text{H}_3\text{O}^+$ ) which is the subject of this paper. In

the following section, we will present the measurement technique, taking  $\text{H}_2\text{O}^+$  as an example. In Section 2 results for other molecular ions will be given, and isotopic effects will be demonstrated.

## 2. Measurement Technique: Branching Ratio for the DR of $\text{H}_2\text{O}^+$

As the measurement technique is similar for all molecular ions, we use the case of  $\text{H}_2\text{O}^+$  for demonstration purposes. For  $\text{H}_2\text{O}^+$ , the DR reaction can lead to the following products:



Once the  $\text{H}_2\text{O}^+$  beam is accelerated and stored in the ring, it is merged with a cold electron beam at the same velocity, so that the center-of-mass energy is essentially zero. The neutral fragments produced by the DR reaction exit the ring and are detected by a surface-barrier detector, which is an energy sensitive device. However, since all the products from the DR reaction hit the detector at the same time, it is impossible to obtain the branching ratio ( $N_a$ ,  $N_b$  and  $N_c$ ) from such a measurement. In order to determine the branching ratio, a grid with a known transmission is inserted in front of the detector. Particles that are stopped by the grid will not contribute to the energy signal on the detector, and thus the recombination signal will split into a series of peaks. For example, in the DR of  $\text{H}_2\text{O}^+$ , and assuming that the beam energy is  $E_0$ , the full energy peak will include contributions from all three channels, while the peak at  $(17/18)E_0$  will include contributions from channel (a) (when only OH hits the detector and the H is blocked by the grid) and from channel (c) (when O+H hit the detector, but the second H is stopped by the grid). The probability for this to happen depends only on the grid transmission  $T$  and the various branching ratios, as defined in Eq. 1. A set of linear equations connecting the number of dissociations into the different channels ( $n_a$ ,  $n_b$ ,  $n_c$ ) to the measured number of events in the different peaks ( $N(\text{O}+2\text{H})$ ,  $N(\text{O}+\text{H})$ , ...,  $N(\text{H})$ ) can then be set up:

$$\begin{pmatrix} N(\text{O} + 2\text{H}) \\ N(\text{O} + \text{H}) \\ N(\text{O}) \\ N(2\text{H}) \\ N(\text{H}) \end{pmatrix} = \begin{pmatrix} T^2 & T^2 & T^3 \\ T(1-T) & 0 & 2T^2(1-T) \\ 0 & T(1-T) & T(1-T)^2 \\ 0 & T(1-T) & T^2(1-T) \\ T(1-T) & 0 & 2T(1-T)^2 \end{pmatrix} \begin{pmatrix} n_a \\ n_b \\ n_c \end{pmatrix} \quad (2)$$

By solving this (overdetermined) set of equations, the branching ratios are readily determined after normalisation ( $N_i = n_i / \sum n_i$ ). The grid transmission  $T$  was measured using an atomic beam. An example of spectra measured for  $\text{H}_2\text{O}^+$  at 6 MeV is shown in Fig. 1. The upper panel is the spectrum measured without merging the electron beam with the ion beam, and as such represents the background due to dissociations induced by collision with the residual gas in the storage ring. The lower panel is the spectrum measured with the electrons

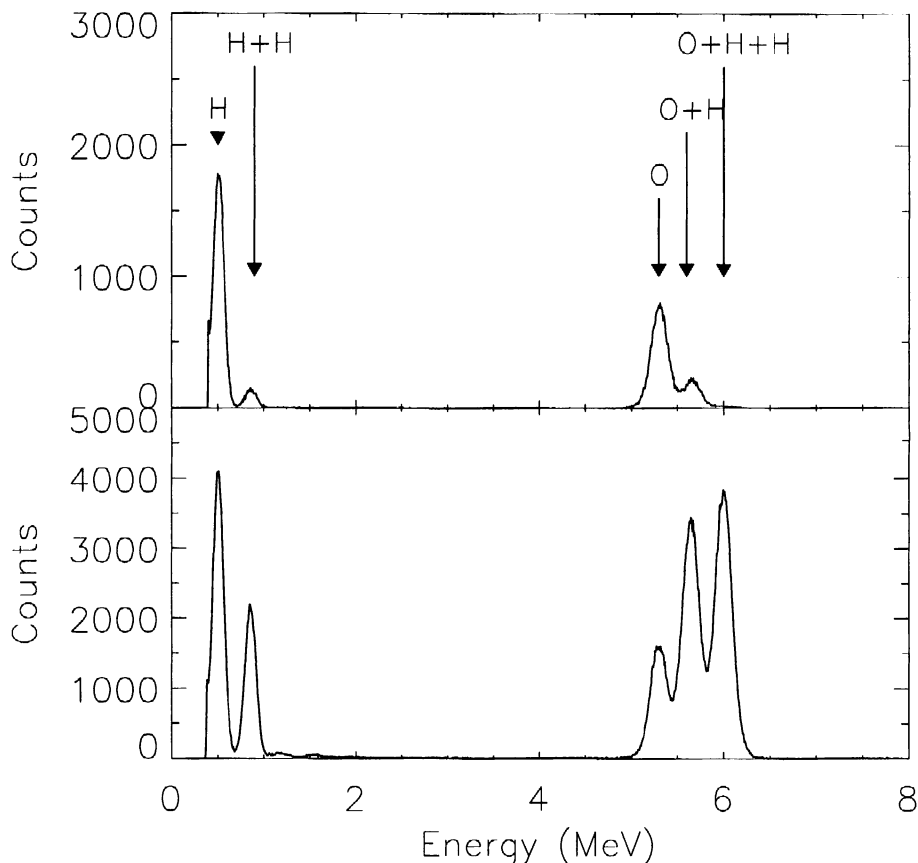


Figure 1. Energy spectra for  $\text{H}_2\text{O}^+$  without (upper panel) and with (lower panel) electrons. A grid of transmission  $T=70\%$  is located in front of the detector.

merged with the ion beam. The transmission of the grid located in front of the detector is 70%, and one can clearly observe the 5 peaks as described in Eq. 2.

After solving Eq. 2, the measured branching ratio for the DR of  $\text{H}_2\text{O}^+$  is (Jensen et al. 1999)

$$\begin{aligned}
 N_a(\text{OH} + \text{H}) &= 0.30 \pm 0.05 \\
 N_b(\text{O} + \text{H}_2) &= 0.13 \pm 0.03 \\
 N_c(\text{O} + \text{H} + \text{H}) &= 0.57 \pm 0.06
 \end{aligned}
 \tag{3}$$

The branching ratio for the DR of vibrationally hot  $\text{H}_2\text{O}^+$  has been measured previously using the flowing afterglow methods (Rowe et al. 1987). However, these numbers ( $N_a(\text{OH} + \text{H}) = 55\%$ ,  $N_b(\text{O} + \text{H}_2) < 21\%$  and  $N_c(\text{O} + \text{H} + \text{H}) > 24\%$ , see Eq. 3) cannot be directly compared to the results of the present experiment, which were obtained for fully relaxed  $\text{H}_2\text{O}^+$  ions. For cold  $\text{H}_2\text{O}^+$ , the three-fragment channel represents about 60% of the dissociation products and

is thus the dominant channel. Thus, the simplest break-up process (hydrogen release, channel  $N_a$  in Eq. 1) is not the most important route for the dissociation process, in disagreement with the original theory derived by Bates (1986).

### 3. Branching Ratios for the DR of Molecular Ions of Astrophysical Interest

In this section, we provide the results for the branching ratios of various molecular ions as measured using storage rings and the grid technique. Although some variation in the grid methods have been used (for example the translucent grid, as presented by Datz et al. 1995), they all rely on the same basic principle of using a grid of known transmission. All these measurements have been made using the ASTRID ring in Aarhus, Denmark, and the CRYRING ring, Stockholm, Sweden.

Theoretically, the determination of the branching ratios is a complex problem where a large number of potential energy surfaces have to be considered. Only few general theories which predict the branching ratios have been developed during the last years, among them the theory derived by Bates (1986). By assuming that dissociations which require the least number of valence bonds to be rearranged are favored, Bates was led to the conclusion that dissociations releasing a single hydrogen atom should dominate. Bates later revised his theory (Bates 1991) in view of some previous experimental data and took into account that also favorable curve crossings are needed for the process to proceed. It was argued that, for example, in the case of dissociative recombination of the hydronium ion it should also be possible to form  $\text{OH} + \text{H}_2$ , and  $\text{OH} + \text{H} + \text{H}$ . In the former case the two ejected H-atoms are in an attractive singlet state, while in the latter case they are in a repulsive triplet state. For the methyl ion, recombination into  $\text{CH} + \text{H} + \text{H}$  was predicted to be negligible, and dissociation into  $\text{CH} + \text{H}_2$  was believed to play only a minor role. For both ions, the three-body channel  $\text{X} + \text{H}_2 + \text{H}$  was ignored ( $\text{X}=\text{O}$  or  $\text{C}$ ). Another theoretical point of view, the so-called statistical phase-space model by Herbst (1978), predicted that the two-body channel  $\text{XH} + \text{H}_2$  should be dominant. A modified version of the model with more adjustable parameters was later compared with experimental data, but even though it was possible to fit the data with this model, it was concluded that the model did not possess any predictive power (Galloway & Herbst 1991).

The results in Table 1 demonstrate the complexity of the DR process. For all molecules, strong fragmentation is occurring, and the assumption that the release of a single hydrogen atom is the dominant process is not confirmed by the data.

On the other hand, a rather strong isotopic effect (H versus D) is clearly observed. For all cases measured so far, the H-release is the preferred two-particle break-up process. It is possible to explain such an effect using a simple model. During the DR process, an excitation to a repulsive potential surface occurs. If the potential surface has two possible dissociation pathways (for example  $\text{OD} + \text{H}$  and  $\text{OH} + \text{D}$  for the DR of  $\text{HDO}^+$ ), then, the dissociation dynamics will be influenced by the nuclear dynamics, since the H fragment moves faster than the D fragment. Since DR processes occur on a doubly excited state, it competes

Table 1. Branching ratios for the dissociative recombination of molecular ions.

Ion	Channel	Energy release (eV)	Branching ratio	Ref.
$\text{H}_3^+$	H+H+H	5.2	0.75	Datz et al. (1995)
	$\text{H}_2$ +H	10.1	0.25	
$\text{H}_2\text{D}^+$	H+H+D	5.2	0.73	Larsson et al. (1996)
	$\text{H}_2$ +D	10.1	0.07	
	HD+H	10.1	0.20	
$\text{H}_2\text{O}^+$	OH+H	7.5	0.30±0.05	Jensen et al. (1999)
	O+ $\text{H}_2$	7.6	0.13±0.03	
	O+H+H	3.1	0.57±0.06	
$\text{CH}_2^+$	CH+H	5.8	0.25±0.04	Larson et al. (1998)
	C+ $\text{H}_2$	6.8	0.12±0.02	
	C+H+H	2.3	0.63±0.06	
$\text{NH}_2^+$	N+ $\text{H}_2$	8.6	0.±0.01	Vikor et al. (1999)
	NH+H	7.4	0.34±0.02	
	N+H+H	4.4	0.66±0.01	
$\text{HDO}^+$	OD+H	7.5	0.21±0.03	Jensen et al. (1999)
	OH+D	7.5	0.10±0.04	
	O+HD	7.6	0.10±0.04	
	O+H+D	3.1	0.59±0.07	
	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$ +H	6.4	
	OH+ $\text{H}_2$	5.7	0.18±0.07	
	OH+H+H	1.3	0.48±0.08	
$\text{CH}_3^+$	O+ $\text{H}_2$ +H	1.4	0.01±0.04	Vejby-Christensen et al. (1997)
	$\text{CH}_2$ +H	5.0	0.40±0.1	
	CH+ $\text{H}_2$	5.2	0.14±0.1	
	CH+H+H	0.7	0.16±0.15	
$\text{D}_3\text{O}^+$	C+ $\text{H}_2$ +H	1.6	0.30±0.08	Jensen et al. (2000)
	$\text{D}_2\text{O}$ +D	6.4	0.25±0.02	
	OD+ $\text{D}_2$	5.7	0.15±0.01	
	OD+D+D	1.3	0.57±0.04	
	O+ $\text{D}_2$ +D	1.4	0.02±0.02	
$\text{D}_2\text{HO}^+$	$\text{D}_2\text{O}$ +H	6.4	0.16±0.06	Jensen et al. (2000)
	HDO+D	6.4	0.12±0.04	
	OD+HD	5.7	0.13±0.01	
	OH+ $\text{D}_2$	5.7	0.02±0.02	
	OD+H+D	1.3	0.4±0.04	
	OH+D+D	1.3	0.15±0.03	
	OH+ $\text{D}_2$ +D	1.4	0.004±0.004	
	O+HD+D	1.4	0.016±0.005	
	$\text{C}_2\text{H}_2^+$	$\text{C}_2\text{H}$ +H	5.8	
CH+CH		1.2	0.13±0.01	
$\text{C}_2$ +H+H		0.2	0.30±0.05	
$\text{CH}_2$ +C		2.4	0.05±0.01	
$\text{C}_2$ + $\text{H}_2$		5.1	0.02±0.03	
$\text{NH}_4^+$	$\text{NH}_3$ +H	4.8	0.69±0.03	Vikor et al. (1999)
	$\text{NH}_2$ + $\text{H}_2$	4.6	0.10±0.02	
	$\text{NH}_2$ +H+H	0.1	0.21±0.03	
	NH+H+ $\text{H}_2$	0.6	0.0±0.01	
	N+ $\text{H}_2$ + $\text{H}_2$	1.8	0.0±0.01	
$\text{CH}_5^+$	$\text{CH}_4$ +H	8.0	0.049±0.013	Semaniak et al. (1998)
	$\text{CH}_3$ + $\text{H}_2$	7.99	0.048±0.002	
	$\text{CH}_3$ +H+H	3.51	0.698±0.008	
	$\text{CH}_2$ + $\text{H}_2$ +H	3.18	0.172±0.016	
	CH+ $\text{H}_2$ + $\text{H}_2$	3.29	0.033±0.011	

with autoionization. Due to the nuclear dynamics, the dissociation time for the OH+D channel is longer, thus, there is a higher probability for autoionization in this channel than in the OD+H channel. Hence, it is expected that the channels where an hydrogen atom is released will have higher probability to survive autoionization, than the channel where a deuterium is released. More details about this mechanism, as well as others which could influence the DR of deuterated species can be found in Jensen et al. (1999).

On the other hand, the change from hydrogen to deuterium does not seem to change the "overall" branching ratio. This is clearly seen in the  $\text{H}_3\text{O}^+$  and  $\text{D}_3\text{O}^+$  results, where the branching ratio is left unchanged. Also, changing one hydrogen atom by a deuterium, and thus splitting a DR channel in two (such as the OD+H and OH+D channels for the DR of  $\text{HDO}^+$ , which correspond to one channel in  $\text{H}_2\text{O}^+$ ) does not change the overall branching ratio: the sum of the branching ratios for the split channels in the deuterated species is equivalent to the single channel in the hydrogenated molecular ions.

However, as pointed out above, there is not yet a general picture for the DR of polyatomic molecular ions. More detailed theoretical work is needed, and we hope that the data which have been collected so far will provide guidelines for such work.

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## Discussion

*T. Geballe:* How do you expect that branching ratios and rate coefficients vary with relative speed of the merged beams (i.e. with collision energy) ?

*D. Zajfman:* Nothing is really known, except for one case measured at CRYRING where the branching ratio was left exchanged when the relative speed was changed. The cross section goes  $\sim E^{-1}$  where  $E$  is the collision energy.

*B. Rowe:* Two questions: (1) Your results show a trend toward multiple fragmentation. Do you expect the same fragmentation pattern for more complex ions (PAHs) ? (2) In the experiment by Williams, Adams et al. (1996, MNRAS 282, 413) how do they know that  $\text{H}_3\text{O}^+$  is vibrationally cold? To my knowledge, it is very difficult to ensure that protonated ions are vibrationally cold in a flowing afterglow experiment.

*D. Zajfman:* (1) I have no ideas, but this could be an interesting experiment ! (2) This could be a central reason for the difference between our results and Williams, Adams et al. result.

*E. Herbst:* Many interstellar ions consist of multiple-bonded heavy atoms and 1 or 2 H atoms. I would expect that such ions will recombine mainly via two-body channels. Do you agree ?

*D. Zajfman:* Not necessary: A measurement made at CRYRING for  $\text{C}_2\text{H}_2^+$  showed that for this ion again many-body channels dissociation is important.

*E.F. van Dishoeck:* (1) Can you elaborate on the discrepancy between the various experiments on the products of DR of  $\text{H}_3\text{O}^+$  ? (2) Are you able to measure the electronic states in which the atoms are formed, e.g.  $\text{C}(^3\text{P})$  or  $\text{C}(^1\text{D})$  in the case of  $\text{CH}_2^+ + e \rightarrow \text{C} + \text{H}_2$  or  $\text{C} + \text{H} + \text{H}$ .

*D. Zajfman:* (1) The experiment by Williams, Adams et al. (1996) show a much smaller production of water than ours. In our case, the branching ratio is measured a few microseconds after the interaction with the electron, while in the Williams, Adams et al. case, it is a much larger time. If the  $\text{H}_2\text{O}$  produced in the DR is highly excited, it could dissociate, although it is difficult to imagine that it would need such a long time. Another point is that the Williams, Adams et al. results came from three independent measurements of rate coefficients, which is more difficult to normalize than the present result where the branching ratio is measured in one single experiment. (2) Yes, we could do it, and for  $\text{H}_2\text{O}^+$  there is a preliminary result for the  $\text{O} + \text{H} + \text{H}$  channel by S. Datz on CRYRING.

*C. Qi:* Is there any difference between recombination reactions in the gas and on the grains? Have you ever investigated the DR reactions on the grain? Eric Herbst mentioned that they have calculations of the recombination reactions of  $\text{HCO}^+$  on grains. Can you explain more about it ?

*D. Zajfman:* No, we haven't made any experimental investigations. With grains, the interaction will be with a bound electron, which may lead to very different results.

