Production of Water Molecules from Dissociative Recombination of $\mathrm{H_3O^+}$ with Electrons

L. H. Andersen,¹ O. Heber,² D. Kella,¹ H. B. Pedersen,¹ L. Vejby-Christensen,¹ and D. Zajfman²

¹Institute of Physics and Astronomy, University of Aarhus,

DK-8000 Aarhus C, Denmark

²Department of Particle Physics, Weizmann Institute of Science,

Rehovot, 76100, Israel (Received 9 July 1996)

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Water is probably the most important molecule for the thermal properties of dense, interstellar gas, and as such plays a decisive role in establishing the rate at which molecular clouds collapse towards star formation. The synthesis of water is thought to be mainly due to dissociative recombination of H_3O^+ with electrons, although experiments have, as yet, provided no evidence that H_2O is a product of the reaction. Here we present the first observation of water synthesis from the recombination of H_3O^+ , with a branching ratio of 33%. This value is in good agreement with existing observations of the $[H_2O]/[H_3O^+]$ ratio in interstellar clouds. [S0031-9007(96)01850-9]

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Chemical models of interstellar clouds are based on the knowledge of the rates and products of important reactions. Dissociative recombination, a reaction in which a molecular ion recombines with an electron and dissociates into neutral fragments, is among the least understood processes. Rate coefficients for this process have been measured by a variety of techniques [1,2], but the branching ratios for the production of neutral fragments are known completely only for two reactions ($H_3^+ + e, H_2O^+ + e$) [3,4]. On the theoretical side, a complete quantum-mechanical treatment of the dissociation process is extremely complex due to the large number of neutral potential surfaces on which the process can occur, which has caused conflicting results [5,6].

Of all the molecular species thus far detected in the interstellar medium, water is among the more important chemical compounds because of its central role in oxygen chemistry and in the cooling of interstellar clouds. Unfortunately, the abundance of this critical species is quite difficult to determine accurately. In general, H_2O does not have favorable transitions for observation by ground-based receivers, and its detection has been accomplished only through lines subject to maser emission, weak lines of isotopic species, or lines of high excitation observed from high altitudes.

The first step in the production of water is a sequence of ion-molecule reactions leading to H_3O^+ [7]:

$$H_{2} + (\text{cosmic ray}) \rightarrow H_{2}^{+} + e + (\text{cosmic ray}),$$

$$H_{2}^{+} + H_{2} \rightarrow H_{3}^{+} + H,$$

$$H_{3}^{+} + O \rightarrow OH^{+} + H_{2},$$

$$OH^{+} + H_{2} \rightarrow H_{2}O^{+} + H,$$

$$H_{2}O^{+} + H_{2} \rightarrow H_{3}O^{+} + H.$$
(1)

The H_3O^+ ion does not react with molecular hydrogen but is depleted via dissociative recombination according to

$$H_{3}O^{+} + e \rightarrow \begin{cases} H_{2}O + H & 6.4 \text{ eV } N_{1}, \\ OH + H_{2} & 5.7 \text{ eV } N_{2}, \\ OH + H + H & 1.3 \text{ eV } N_{3}, \\ O + H_{2} + H & 1.4 \text{ eV } N_{4}, \end{cases}$$
(2)

where the energy releases are for the production of ground-state products, and N_i (i = 1, 4) are the branching ratios for the dissociative-recombination reaction ($\sum N_i = 1$). Thus, one of the approaches to establish the interstellar concentration of H₂O has been through observations of H₃O⁺ [8,9]. Of course, this requires the rate coefficient for the recombination reaction depicted in Eq. (2) to be known, as well as the branching ratio N_1 for the production of water.

The dissociative recombination of H_3O^+ is critical for interstellar molecular-synthesis models, since if the fraction of the recombination resulting in OH production is small, then the dominant oxygen-containing species is H_2O , whereas if this fraction is large, the dominant species is O_2 [10,11]. Theoretical attempts to predict the branching ratios for this reaction have yielded contradictory results. Under the so-called valence-bond approach [12], Bates originally predicted that the H₂O production is dominant, the other channels being minor, whereas Herbst [5] calculated that OH production via channels N_2 (80%) and N_3 (10%) is dominant. The results depend on the appropriate crossings of the potential curve(s) for the polyatomic molecular ion and the repulsive potential energy curve(s) for the products. After reconsideration, Bates [6] concluded that channel N_2 would indeed be enhanced on the basis of more favorable crossings than first assumed.

Some partial information on the products has been provided by the experiments of Herd, Adams, and coworkers [13,14] in which laser-induced fluorescence and VUV (vacuum ultra violet) absorption were used in an ion-flow tube and flowing afterglow. It was shown that 0.65 ± 0.15 OH radicals and 1 ± 0.2 H atoms are produced on average per recombination. Although this does not permit the extraction of the branching ratio for the production of water (N_1), it does set an upper limit of $N_1 < 0.35$. The absolute rate coefficient for the reaction depicted in Eq. (2) has been measured using many different experimental techniques, producing results in good agreement [15]. The rate coefficient at 2000 K is about 2×10^{-7} cm³ s⁻¹.

In the present Letter, we report on a direct and simultaneous measurement of the branching ratios for the dissociative recombination of H_3O^+ . The experiment was carried out at the Aarhus Storage Ring Denmark (ASTRID) [16]. Heavy-ion storage rings have become a very powerful tool in the study of dissociative recombination of simple diatomic and triatomic molecular ions [17–19]. There are many advantages of using heavy-ion storage rings. Among them is the long storage time (several seconds) that can be achieved, which makes it possible for infrared active molecular ions (such as H_3O^+) to relax vibrationally through radiative decay. This is very important as under interstellar conditions (T = 10-100 K), essentially all the molecular ions are in their ground vibrational state. Also, it is possible to store ions at MeV energies where reaction products can readily be detected, with about 100% efficiency, by standard particle detectors. In addition, the circulating molecular ion beam is easily merged with an intense, cold electron beam (from the socalled electron cooler) of the same velocity, allowing the process of dissociative recombination to be studied at low temperature.

In the present experiment, a beam of H_3O^+ was produced from water vapor and H₂ in an electron-impact ion source and injected, with an initial energy of 150 keV, into the ASTRID storage ring. The beam was then accelerated in the ring to an energy of 5.93 MeV and stored for a total time of ~ 10 s. The ion beam was merged at each turn (40 m) with the intense, cold electron beam of equal velocity, so that the center-of-mass energy was zero. The electron beam is not exactly monoenergetic and is characterized by a transversal temperature of $kT_{\perp} = 20 \text{ meV}$ and a longitudinal temperature of $kT_{\parallel} = 0.5$ meV. The electron-beam density is almost constant over its crosssectional area, which is several cm²—much larger than the cross-sectional area of the ion beam ($<1 \text{ cm}^2$). The ion beam was adjusted so as to be in the center of the electron beam and aligned with the downstream detector (see below). The dissociative-recombination products were measured by detecting the neutral fragments produced in the interaction region, using an energy-sensitive semiconductor detector mounted straight ahead of the electron cooler at a distance of ~ 6 m. After dissociation, each fragment carries a part of the beam energy which is proportional to its own mass [the kinetic-energy release is much smaller than the beam energy; see Eq. (2)]. However, because all the fragments reach the detector at the same time, the energy spectrum consists in principle of a single peak at the beam energy. Thus, it is not immediately possible to separate the four different channels in Eq. (2).

One method, which has been very successful in discriminating among the various fragmentation patterns, is to set up a grid with a given transmission in front of the detector [20]. Such a method has been used for the study of various dissociation processes [21] and has recently been applied to extract the branching ratios for the dissociative recombination of H_3^+ [3]. When a grid with transmission T is placed in front of the detector, the probability for a single particle (atom or molecule) to pass through the grid is T, while it is T^2 for two and T^3 for three particles. The fragment(s) blocked by the grid will not reach the detector surface, and the energy deposited in the detector by the transmitted particle(s) will be lowered by an amount which is proportional to the mass of the blocked fragment(s). Thus, the energy spectrum will split into a series of peaks, the area under each of these peaks representing the number of events with the same combination of particles. For example, the peak at beam energy E_0 represents the impact of three hydrogen atoms and one oxygen atom, in any possible combination. A peak at $\frac{18}{19}E_0$ will be due to one H atom being stopped by the grid, a peak at $\frac{17}{19}E_0$ occurs when two H atoms or one H₂ molecule have been stopped, and so forth. It is possible to relate the number of counts under each of these peaks to the branching ratio, using the transmission probability: If n_1, n_2, n_3 , and n_4 are the numbers of recombination events leading to channels N_1 , N_2 , N_3 , and N_4 in Eq. (2), then the number of counts under each peak (with the grids in front of the detector) is given by

$$N(E_0) = T^2 n_1 + T^2 n_2 + T^3 n_3 + T^3 n_4,$$

$$N\left(\frac{18}{19}E_0\right) = T(1-T)n_1 + 2T^2(1-T)n_3$$

$$+ T^2(1-T)n_4,$$

$$N\left(\frac{17}{19}E_0\right) = T(1-T)n_2 + T(1-T)^2 n_3$$

$$+ T^2(1-T)n_4,$$

$$N\left(\frac{16}{19}E_0\right) = T(1-T)^2 n_4.$$
(3)

Solving the above linear equations for n_i yields immediately the values of N_i after normalization. The channels yielding $H(\frac{1}{19}E_0)$ and $2H(\frac{2}{19}E_0)$ are also available and were used to obtain the optimal solution.

Two corrections have to be made to the above scheme to extract the branching ratios. First, dissociations due to the collision of the H_3O^+ with the remaining gas in the ring are also measured by the detector and have to be subtracted from the energy spectrum. In order to ensure proper normalization, the electron beam was chopped at a rate of 50 Hz, and measurements of recombination (with electrons) and background (without electrons) were carried out simultaneously. Figures 1(a) and 1(b) show the energy spectra (without grid) as measured by the semiconductor detector for the background only (no electrons) and for



FIG. 1. Energy spectra as measured by the detector (no grids): (a) electron beam off (background), (b) electron beam on (background + recombination), and (c) recombination only.

the recombination and background (with electrons). Figure 1(c) shows the recombination signal with background subtracted. The highest peak in Fig. 1(c) (at energy E_0) corresponds to recombination events as given in Eq. (2) (all channels). The small peak on the left (at energy $\frac{18}{19}E_0$) is due to a small number of hydrogen atoms "missing" the detector. The large kinetic-energy release (in the centerof-mass frame) in the dissociative recombination can lead to spatial separation of fragments which are larger than the size of the detector ($60 \times 40 \text{ mm}^2$) after traveling the distance of ~ 6 m from the center of the electron cooler to the detector surface. It can easily be shown that the only channel that can produce enough kinetic energy so that a single H atom would miss the detector is channel N_1 . The amount of hydrogen missing the detector can be extracted from the ratio of the peaks in Fig. 1(c) and represents $(10 \pm 1)\%$ of the total recombination events. In fact, because the only channel that produces a single H atom with such a large (center-of-mass) kinetic energy is channel 1; this peak represents a direct proof that water is formed in dissociative recombination of H_3O^+ with a branching ratio which is at least 10%.

Figures 2(a) and 2(b) show the energy spectra for the background only and recombination + background, respectively, when a grid of transmission T = 0.285 is placed in front of the detector. Figure 2(c) shows the resulting energy spectrum after background subtraction. The most striking result is that only three peaks are left after background subtraction [Fig. 2(c)]. The peak at energy $\frac{16}{19}E_0$ would have corresponded to the impact of single oxy-



FIG. 2. Energy spectra as measured by the detector when a grid of transmission T = 0.285 is placed in front: (a) electron beam off (background), (b) electron beam on (background + recombination), and (c) recombination only. The solid line is the result of the fit (see text).

gen atoms. The fact that hardly any oxygen atoms were produced in the recombination process implies that channel N_4 in Eq. (2) is very small. Indeed, this will appear in the full solution of Eqs. (3).

The experiment was carried out with two different grids. The exact transmissions were calibrated by storing an atomic beam of the same mass (¹⁹F⁺) and energy ($E_0 = 5.93$ MeV) as H₃O⁺ and measuring the time-normalized count rates of the electron-capture process with and without grids. The resulting transmissions obtained are $T = 0.285 \pm 0.02$ for the first grid and $T = 0.635 \pm 0.02$ for the second grid.

The energy spectrum shown in Fig. 2(c) was fitted using a sum of four Gaussian functions (solid line) in order to extract the areas under each of these peaks. After correcting for the 10% of hydrogen atoms missing the detector, Eqs. (3) were solved for the value of n_i . Normalizing this value to unity yields the following branching ratios for the dissociative recombination of H₃O⁺:

$$N_1 \quad (H_2O + H) = 0.33 \pm 0.08, N_2 \quad (OH + H_2) = 0.18 \pm 0.07, N_3 \quad (OH + H + H) = 0.48 \pm 0.08, N_4 \quad (O + H + H_2) = 0.01 \pm 0.04.$$
(4)

More details about the precise analysis of the results, including all the peaks present in the spectra, will be given in a forthcoming paper [22]. However, it might be important to point out that the above solution was also tested by including more peaks from the energy spectrum (the hydrogen peaks) and more unknowns (such as the O + H + H + H channel, which is energetically forbidden). No differences were found in the results, and the forbidden channels were found to have a very small contribution to the branching ratios. Also, in order to check for vibrational relaxation effects, the measurement was carried out at different storage times. The results were found consistent with each other. The branching ratios given in Eq. (4) are valid for an electron temperature of 20 meV. Also, the state of excitation of the various fragments produced in the recombination is unknown.

The above branching ratios can be compared with the partial measurement by Adams [14], where the average OH production per dissociation was found to be 0.65 ± 0.15 . in excellent agreement with the present value of N_2 + $N_3 = 0.66 \pm 0.11$. Also, the production rate of single hydrogen atoms found here $(N_1 + 2N_3 + N_4 = 1.3 \pm$ 0.14) is slightly higher than the value of 1 ± 0.2 found by Herd [13]. Interstellar implications of the above branching ratios, and more specifically the 33% water production, can be evaluated using the scheme proposed in 1987 by Sternberg, Dalgarno, and Lepp [11] who made a detailed analysis of the predictions for the abundance of H_3O^+ , H₂O, OH, and a series of hydrocarbons in dense clouds. Based on the previously assumed 35% for the fraction of water molecules produced upon H₃O⁺ recombination, the ratio $[H_2O]/[H_3O^+]$ was calculated to be $\approx 500-2000$ [23]. The almost identical branching ratio such as measured here (33%) should yield basically the same values.

Observations of $H_2^{18}O$ by Jacq *et al.* [24] in OMC-1 (Orion molecular cloud) and Sgr B2 (Sagittarius), together with observation of H_3O^+ by Wooten *et al.* [8], suggest the ratio $[H_2O]/[H_3O^+]$ to be between 1500 and 6000. More recent observations by Zmuidzinas [25] give a ratio of 300 for Sgr B2. This value, although slightly lower than the lower limit of the model prediction (using the branching ratio of 35% for the water production), is still in qualitative agreement with the branching ratio measured in this experiment, and the astrophysical models. A more detailed measurement of the H₂O is planned in early 1997 with the Submillimeter Wave Astronomy Satellite (SWAS) which will study the chemical composition of interstellar galactic clouds to help determine the process of star formation. Approximately half of the SWAS mission will be spent observing H₂O and O₂ towards cloud cores [26], and it is expected that these results, together with the present ones, will help to understand the formation of interstellar matter.

The branching ratios for the dissociative recombination of H_3O^+ show that considerable fragmentation occurs, while most of the astrophysical models assume generally two-body dissociation. A measurement made for the dissociative recombination of CH_3^+ shows the same pattern, the three-body dissociation channels being important [22]. Implications of this fragmentation have to be investigated, using chemical models of molecular synthesis in interstellar clouds.

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