Branching Processes in the Dissociative Recombination of H_3^+

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We have determined the branching fractions of $H_3^+ + e$ to $H_2 + H$ or $H + H + H$ or H_3^* over the energy range 0.001 to 20 eV using the electron cooler at the storage ring CRYRING. The H_3^+ are stored and cooled at an energy of 6.5 MeV/amu. The recombined products pass through a "translucent" perforated barrier and their total energy is recorded. Thus all particles are detected. Particles passing through holes (70 μm) deposited 6.5 MeV each in the detector, while those passing through the solid (stainless steel 50 μm thick) are not stopped but give pulses of only 4.7 MeV per atom. Analysis of the pulse height spectrum gives the branching fractions directly.

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The simplest of polyatomic molecules must surely be the two electron H_3^+ ion. Acting as a proton donor, it is an important intermediate in the formation of many interstellar molecules and it has been shown to be present in the ionospheres of Jupiter [1], Saturn [2], and Uranus [3]. Its principal mode of formation is via the homogeneous reaction [4]

$$H_2^+ + H_2 \rightarrow H_3^+ + H + 1.7\ \text{eV}. \quad (1)$$

Formation of H_3^+ from purely atomic components requires three-body collisions or heterogeneous formation on, e.g., dust grains. The role of H_3^+ in astrophysics and astrochemistry has been extensively reviewed in a recent chapter by Dalgarno [5].

The principal mode of destruction of H_3^+ is via dissociative recombination (DR). The DR rate for the $v = 0$ level has now been determined over a broad energy range [6,7] and a plot of cross section versus energy taken from Ref. [6] is shown in Fig. 1. Orel and Kulander [8] are able to fit the high energy "direct" peak very well using DR of H_3^+ ($v = 0$) via four different resonance channels, the lowest one peaking at 8 eV and the highest at 10 eV. In general, however, the detailed mechanism for DR of H_3^+ is still open to much conjecture as may be judged from the title of a recent paper by Bates, Guest, and Kendall to wit: *Enigma of* H_3^+ *Dissociative Recombination* [9].

A true understanding of the process must be able to predict the branching fractions for the process, i.e.,

$$\text{fraction } \alpha \quad H_3^+ + e \rightarrow H_2 + H, \quad (2)$$

$$\text{fraction } \beta \quad \rightarrow H_2 + H, \quad (3)$$

$$\text{fraction } \gamma \quad \rightarrow H_3^*, \quad (4)$$

$$\alpha + \beta + \gamma = 1. \quad (5)$$

The results are also of practical importance in gauging the equilibrium cycle of H_3^+ since, e.g., the formation of H_2 (fraction α) is a feedstock for formation of H_3^+ [Eq. (1)], whereas the products of three-body breakup ($H + H + H$) are not readily usable for the reformation of H_3^+.

The method used in the present work is a modification of one that was first applied by Stearns *et al.* [10] to determine branching ratios in the collision induced dissociation of H_3^+. In their work, a retractable grid (~1% transmission) was inserted in front of a solid state detector which was used to measure the total energy of the particles striking it. Particles which did not pass through the holes were stopped by the grid. Since for a given transmission T, the probability of one particle getting through is $\propto T$ and of two getting through is $\propto T^2$, and of three getting through is $\propto T^3$, branching ratios could be measured. A result of the Stearns *et al.* paper was that collisional dissociation (CD) almost always led to the production of at least one ion and hence to neutral fragments of mass 1 (H) and of

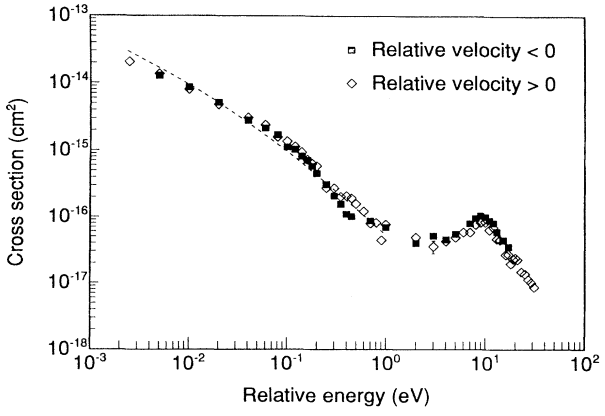

FIG. 1. Total cross section for dissociative recombination of H_3^+. Figure is from Ref. [6].

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mass 2 (H_2 or H + H), i.e.,

$$H_3^+ + B \rightarrow H + H_2^+ \quad (6)$$

$$\rightarrow H + H^+ + H^+ \quad (7)$$

$$\rightarrow H_2 + H^+ \quad (8)$$

$$\rightarrow H + H + H^+ . \quad (8)$$

Very little mass 3 (H_2 + H or H + H + H) was observed and the cross section dropped precipitously over their energy range (0.1–1 MeV). Hence at the energy of this experiment (19.5 MeV) the mass 3 yield from collisions in the residual gas should be vanishingly small. Mitchell *et al.* [11] used this grid method with 400 keV H_3^+ ions to measure the branching ratio in DR of H_3^+, but a serious problem arose because of background due to CD on residual gas. For example, if the DR product is H + H_2 and H is stopped in the grid, the H_2 product would be mixed with the H_2 background peak; if the H_2 is stopped in the grid, the H peak would be mixed with the background H peak. The result was a signal-to-noise ratio of $\leq 1 : 100$. In addition, the vibrational population in the H_3^+ beam was not defined. Nonetheless, the authors were able to state that over the energy range from 0.01 to 0.05 eV the H + H + H exit channel "dominates." In a later publication Mitchell [12], ostensibly using the same method, reports that of a total cross section of 3.6×10^{-15} cm^2 at $E =$ 0.01 eV, the fraction going to H_2 + H (α) is 0.40 ± 0.10, the fraction going to H + H + H (β) is 0.51 ± 0.15, and the fraction going to H_3^0 (γ) is 0.09 ± 0.04. The vibrational state is not specified.

In the present work which covers the range of 0.001 to 20 eV, we have overcome these two difficulties. The H_3^+ ions are injected into the CRYRING heavy ion storage ring [13] at an energy of 300 keV/amu and accelerated to an energy of 6.5 MeV/amu. The beam is "cooled" by a merged electron beam tuned to the velocity of the stored ion beam and is contained for a period of 9 sec before measurement begins. This storage time permits radiative relaxation of the H_3^+ to its vibrational ground state [6,14]. The energy of the merged electron beam is then shifted to achieve a given relative energy [15]. Neutral species formed by either DR or CD in the straight section containing the merged electron beam, exit the ring in a straight line through the first bending magnet, and strike a solid state detector which records to total energy deposited in a given event. To determine the branching ratio, we use a barrier which does not stop the projectile. The barrier is introduced in front of the solid state detector, and it is thin enough to merely degrade the particle energy so as to decrease the pulse height from the entering particle when it strikes the detector. The method is best illustrated by the conditions of the experiment. The barrier is a 50 μm thick stainless steel sheet with ~70 μm diameter electroetched holes [16]. The transmission (i.e., the fraction of open area) T is 31%. The beam energy is 6.5 MeV/amu. A proton passing through the barrier material will lose ~1.8 MeV. The detector is located ~4 m from the end of the recombination region and thus only 0.002 eV transverse recoil energy is required for two fragments to be separated enough so as not to pass through the same hole.

Peaks appear in the energy spectrum whose values depend on whether all three atoms have passed through holes (P_3), two atoms have passed through holes and one through the solid (P_2), one atom has passed through a hole and two through the solid (P_1), or none through the hole and all three through the solid (P_0).

A typical spectrum is shown in Fig. 2. The contribution of the three exit channels and corresponding peak energies are given by

$$P_3 = \alpha T^2 + \beta T^3 + \gamma T, \qquad 19.5 \text{ MeV}, \quad (10)$$

$$P_2 = (1 - T)[\alpha T + 3\beta T^2] \qquad 17.7 \text{ MeV}, \quad (11)$$

$$P_1 = T[\alpha(1 - T) + 3\beta(1 - T)^2] \qquad 15.9 \text{ MeV}, \quad (12)$$

$$P_0 = \alpha(1 - T)^2 + \beta(1 - T)^3 + \gamma(1 - T) \qquad 14.1 \text{ MeV}. \quad (13)$$

Peaks from background gas dissociation are labelled B_0–B_4. For dissociation giving a mass 2 product B_2, B_3, B_4 [Eq. (8) or (9)] peaks appear at 9.4, 11.2, and 13.0 MeV. For a mass 1 background [Eq. (6) or (7)] the peaks appear at 6.5 or 4.7 MeV depending on whether or not the single hydrogen atom has passed through the hole (B_1) or has gone through the material (B_0). The transmission T can be separately and accurately determined from the spectrum simply from the ratio $B_1/(B_1 + B_0)$ from which we obtain $T = 0.312$, $\delta T/T = 0.13\%$. Since all particles are recorded, it is not necessary to make measurements both with and without barrier. (Note that with

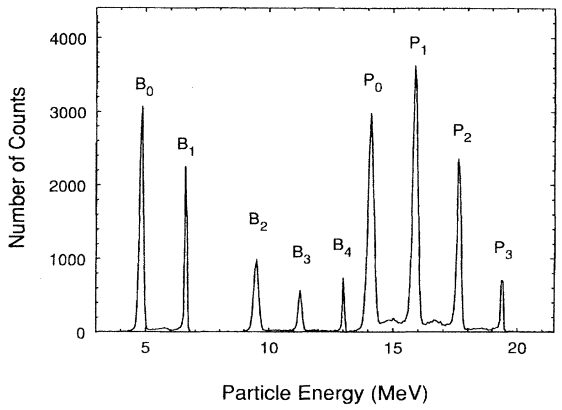

FIG. 2. Pulse height spectrum observed from solid state detector. Peaks marked P_3, P_2, P_1, and P_0 correspond to Eqs. (10)–(13), respectively. Peaks marked B_0–B_4 arise from dissociative ionization and excitation in collision with background gas (see text). The low shoulders that appear on some of the peaks arise from particles that have passed through a hole but which have struck an edge on the way through.

the electron beam off, there is no measurable background in the mass 3 region.) Since there are four equations and three unknowns, the systems is overdetermined. The product yields could be readily determined by a least squares analysis.

Measurements were made in the energy range 0.001 to 20 eV. The results are plotted in Fig. 3. First, it can be stated that the contribution of H_3^* (channel γ) is immeasurably small. Such an entity has been postulated [17]. But at least on the time scale of our experiment, ~100 nsec from formation to detection, and with the reactant H_3^+ in the $v = 0$ state, none is observed. If some components of the neutral beam are found and remain in high Rydberg states, they could be field ionized and lost by passing through a bending magnet (0.9 T) with a resultant motional field of 3.25×10^5 V/cm. For a hydrogenic system, this corresponds to a maximum bound state of $n \cong 7$. The agreement of our total cross-section measurements, where they overlap with those of Mitchell and Yousif [17] who used much weaker fields, would seem to indicate that these high Rydberg states do not contribute much. The value of α, the fraction in the $H_2 + H$ channel (Fig. 3), is remarkably constant at ~0.25 at collision energies of 0.001 to 0.5 eV; it then rises and displays peaks at ~1.4, and 15 eV. None of these features correspond to the broad "direct" peak seen in the total cross section (Fig. 1).

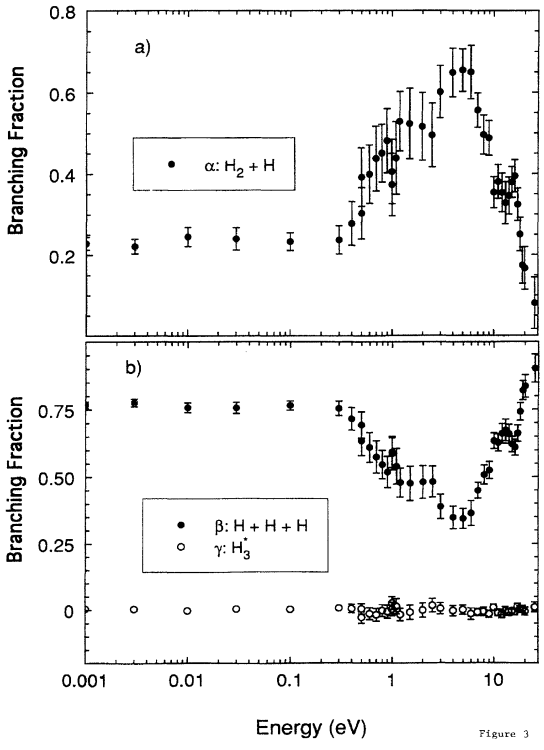

FIG. 3. Branching fractions for $H_3^+ + e$, (a) product $H_2 + H$ (α), (b) ● product $H + H + H$ (β), and ○ product H_3^0 (γ).

Rydberg states below the ionization limit, which are likely to be involved in dissociative recombination of H_3^+, have been investigated in some detail [18–24]. In these experiments, high Rydberg states are populated by means of laser excitation from the $v = 0, N = 0, K = 0$ level of the H_3 $2p^2A_2$ state, generated by charge transfer of an H_3^+ beam in cesium vapor. This technique allows Rydberg states lying within a few meV below the $H_3^+ + e$ threshold to be studied. The high Rydberg states are indirectly predissociated by interaction with interlopers which are part of the $n = 2$ manifold; the interloper states are in turn predissociated by the $2p\,^2E^1$ state [20]. The high Rydberg states are populated in low vibrational levels embedded in a dense manifold of highly excited vibrational levels of Rydberg states with $n = 2$. The interaction between the high Rydberg states and the interlopers thus relies on a coupling between widely different vibrational modes of the ionic core. It has been proposed [24] that a similar mechanism may be operative for dissociative recombination, and it has been pointed out that this mechanism does not rely on a potential curve crossing. Recently several features observed in the charge transfer optical-optical double resonance spectrum [22] were accounted for by means of quantum defect calculations of H_3 Rydberg dynamics [25]. The charge transfer technique has also been used to investigate the three-body/two-body product branching ratio for dissociating H_3 $2s\,^2A_1'$ and $2p\,^2A_2''$ levels [25]. It was found that the two-body channel dominates for these low-lying levels with respect to the $H + H + H$ limit, see Fig. 4. But, it was also found that the three-body channel increased with increased amount of vibrational excitation contained in the nascent H_3^+ ions. These observations are consistent with time-dependent quantum-mechanical calculations of the dissociation of H_3 Rydberg states [26,28]. In the absence of a favorable curve crossing in H_3^+, it is obvious that Rydberg states, above the ionization limit, must play an important role in the DR of H_3^+. Although no calculations have been performed for the above-ionization-limit Rydberg states operative in dissociative recombination, it is conceivable [25–27] that the amount of vibrational excitation involved in the intermediate interloper states leads to a dominance of the three-body channel. This agrees with our experimental results for moderate electron energies. When the electron energy is sufficient to excite the first vibrational level of the core (~0.3 eV), the two-body channel increases in importance, something which continues until about 4.5 eV. The threshold of formation $H_2 + H$ ($n = 2$) is 0.97 eV above H_3^+ ($v = 0$); our measured two-body yield shows a narrow dip at ~1 eV. When the energy is increased above the $H^+ + H_2$ limit at 13.6 eV which corresponds to 4.4 eV relative to H_3^+ ($v = 0$), the three-body channel becomes increasingly important. In the above paragraph, we do not pre-

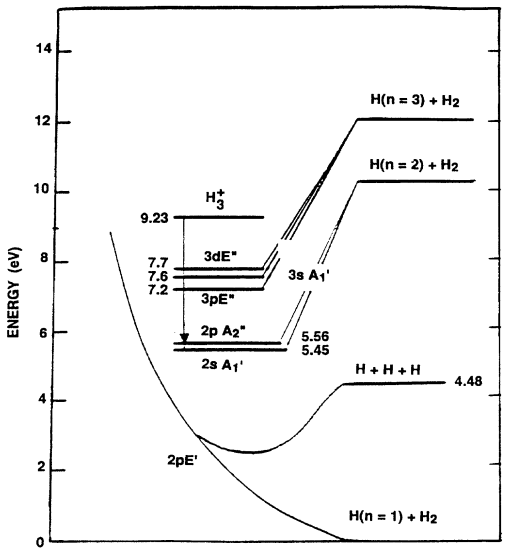

FIG. 4. Schematic potential energy diagram of H_3 and H_3^+. The arrow indicates electron capture transition. Figure is from Ref. [25].

tend to make a complete explanation of the experimental results. There are, however, some striking relationships between energetically possible transitions and changes in the two-body to three-body ratios. A detailed theoretical explanation of the DR process for H_3^+ remains open for conjecture.

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