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Measurement of the Branching Ratio for the Dissociative Recombination of $H_3^+ + e$

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The dissociative recombination of H_3^+ with electrons can have two exit channels, namely $e + H_3^+ \rightarrow H + H + H$ (channel I), and $e + H_3^+ \rightarrow H_2 + H$ (channel II). A new technique has been developed which has been used to determine the relative contributions of channels I and II to the overall recombination process. Over the energy range from 0.01 to 0.05 eV it has been found that channel I dominates.

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The identification of the products of dissociative recombination is of vital importance not only to our understanding of electron-ion recombination mechanisms and the structure of the molecular system under study but also to complement the modeling of the chemistry of ionized systems. For example, many reaction schemes have been proposed to explain the presence of large organic molecules such as polyacetylenes in interstellar space[1,2] or to explain the energy balance of the Jovian atmosphere.[3,4] These depend critically upon the branching ratios for the final channels of dissociative recombination.

Peart and Dolder[5,6] have measured the cross sections for ion pair ($H^+ + H^-$, $H_2^+ + H^-$) formation during the recombination of electrons with H_2^+ and H_3^+ ions, and the excitation states of atomic products formed during dissociative recombination have been measured for H_2^+ and D_2^+,[7,8] for O_2^+,[9] for Xe_2^+, Kr_2^+, and Ar_2^+,[10-12] and for NO^+.[13]

Kinetic modeling of pulse radiolysis experiments with organic gases[14-16] has been used to predict the major dissociation channels for a variety of organic ions, while Herbst[17] has used a statistical phase-space theory to estimate the neutral-product branching ratios for $HCNH^+$, H_3O^+, CH_3^+, and NH_4^+.

In this paper we have successfully used a technique which follows from a suggestion of Berkner *et al.*[18] in 1971, which allows us to identify the individual exit channels for the dissociative recombination of H_3^+ with electrons. This is the first direct measurement of neutral-product branching ratios for polyatomic-ion recombination.

For the measurements we have used the merged electron-ion beam apparatus (MEIBE-I) which has been described in detail previously.[19,20] Briefly, H_3^+ ions, formed in an rf ion source at a pressure 0.1 Torr of hydrogen gas, are accelerated and interact with an electron beam which is made to merge with the ion beam. By matching the electron and ion velocities, very low center-of-mass interaction energies can be obtained. The neutral products formed in the interaction region are detected with an energy-sensitive surface-barrier detector.

The main reactions which occur in the interaction region are as follows:

$$\text{signal} \quad e + H_3^+ \rightarrow H + H + H, \qquad (I)$$

$$\rightarrow H_2 + H; \qquad (II)$$

$$\text{background} \quad H_3^+ + X \rightarrow H^+ + (H + H) + X, \qquad (III)$$

$$\rightarrow H_2^+ + H + X, \qquad (IV)$$

$$\rightarrow (H + H) + H + X^+. \qquad (V)$$

(Recombination to H_3^* requires radiative stabilization which is very slow and so can be neglected.)

Following these dissociation reactions, the resulting fragments continue to move with approximately the same velocity as the primary beam. Therefore the kinetic energy of the initial ions is divided between the neutral fragments according to their mass.

The surface-barrier detector used to detect the neutrals is energy sensitive. The output pulse-height spectrum for the signal plus background neutral products from an H_3^+ beam interacting with the electron beam and the background gas is shown in Fig. 1(a). An example of the signal distribution is given in Fig. 1(b).

H atoms from Reaction IV arrive at the detector with one-third of the total energy. H_2 molecules or 2H atoms from Reaction III carry two-thirds of the energy while Channels I, II, and V which yield all neutral hydrogen products give rise to pulses whose energy corresponds to the total

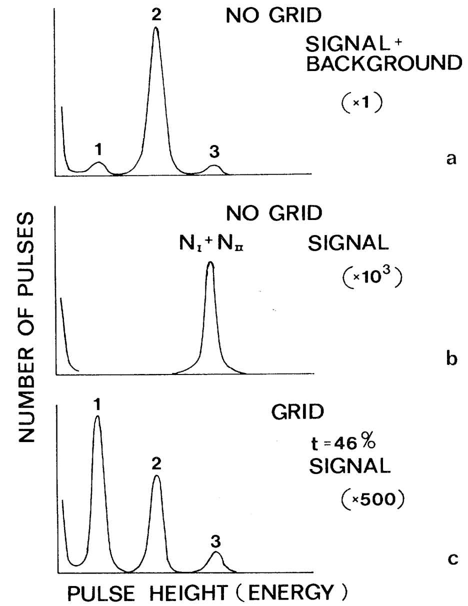

FIG. 1. Pulse-height distributions of detector pulses for (a) H_3^+ beam, no grid, signal plus background. (b) H_3^+ beam, no grid, signal only. (c) H_3^+ beam, 46% transmission grid, signal only.

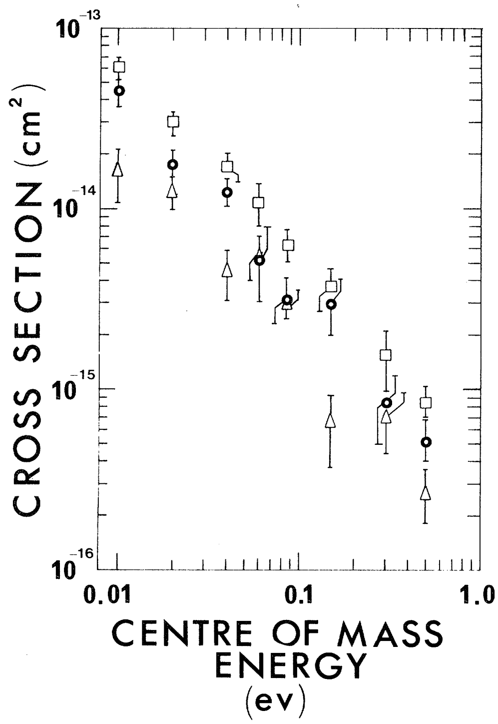

FIG. 2. Cross sections for the dissociative recombination of $H_3^+ + e$ leading to H + H + H (circles), H_2 + H (triangles), and total cross section (squares).

beam energy. This is because the products arrive at the detector almost simultaneously and so are indistinguishable from a single full-energy mass-3 neutral, which incidentally is not expected to exist.

For low energies I and II are the only electron-ion processes which can occur.[21] Hence when the background is subtracted out, the pulse-height distribution at the detector is as shown in Fig. 1(b).

If a grid with known transmission t is placed in front of the detector then the probability that all three particles from Channel I will reach the detector is no longer the same as for the two particles from Channel II. This can be used to separate out the contributions from these two channels. If $N_{\rm I}$ and $N_{\rm II}$ are the number of neutral counts arising in a given time from Channels I and II respectively and if N_1, N_2, and N_3 are the number of counts under peaks 1, 2, and 3, then it is easily shown that

$$N_3 = t^3 N_{\rm I} + t^2 N_{\rm II}, \tag{1}$$

$$N_2 = 3t^2(1-t)N_{\rm I} + t(1-t)N_{\rm II}, \tag{2}$$

$$N_1 = 3t(1-t)^2 N_{\rm I} + t(1-t)N_{\rm II}. \tag{3}$$

This is illustrated in Fig. 1(c) which shows the signal pulse-height distribution with a 46% grid in place.

Equations (1)–(3) can be rearranged to yield three sets of expressions for $N_{\rm I}$ and $N_{\rm II}$, namely ($t \neq 0, 1$),

$$N_{\rm I} = \frac{tN_2 - (1-t)N_3}{2t^3(1-t)}, \tag{2a}$$

$$= \frac{(1-t)N_3 - tN_1}{t^2(4t-3)(1-t)}, \quad t \neq 0.75, \tag{2b}$$

$$= \frac{N_1 - N_2}{3t(1-t)(1-2t)}, \quad t \neq 0.5, \tag{2c}$$

and

$$N_{\rm II} = \frac{3(1-t)N_3 - tN_2}{2t^2(1-t)}. \tag{3a}$$

These equations can be used to calculate the respective cross sections for Reactions I and II.

A most important parameter in Eqs. (2) and (3) is the transmission t. This must be known to very high accuracy. Two methods were used to determine t. One was an optical measurement of the ratio of open area to total area of the grid using a calibrated microscope. This yielded a value of $t = (45 \pm 5)\%$. The second method exploits the redundancy of information in Eqs. (2) and (3) where three experimentally measured variables N_1, N_2, and N_3 are used to determine two quantities N_I and N_{II}. Because of this redundancy t can be treated as a variable and a self-consistent analysis performed to find a value of t which gives the closest agreement between all the equations. This analysis yielded a value of $t = (44 \pm 2)\%$ which was finally adopted for evaluating N_I and N_{II}.

Figure 2 shows our experimental results for σ_I, σ_{II}, and $\sigma_I + \sigma_{II}$ versus center-of-mass energy. The error bars shown represent the neutral counting statistics, the uncertainty in ion and electron currents, and the uncertainty in the measurement of the grid transmission t. Other systematic errors due to the determination of the form factor and other experimental parameters though not shown contribute an additional overall uncertainty in the magnitude of the cross-section curve of ±15%.

It can be seen that over the measured energy interval from 0.01 to 0.50 eV, the channel leading to three hydrogen atoms dominates over the one leading to $H_2^* + H$. Also, the data suggest that the ratio $(H_2 + H)/3H$ may be electron-energy dependent. The exact dependence will be determined in subsequent experiments.

Recent theoretical calculations by Kulander and Guest[22] have indicated that if the sum of the internal energy of the H_3^+ ions and the kinetic energy of the electrons is greater than about 1 eV above the ground vibrational state of H_3^+, then the dominant dissociation channel will lead to $H_2(^1\Sigma_g^+) + H(2s \text{ or } 2p)$. For energies less than this, indirect recombination via capture into Rydberg levels of the neutral model is predicted to dominate leading to dissociation into three hydrogen atoms.

An estimate of the distribution of vibrational states in our H_3^+ beam can be obtained by comparison with studies by Blakly, Vestal, and Futrell,[23] who used an electron-impact ion source to produce H_3^+ ions. By examining low-energy ion-molecule reactions they were able to demonstrate that at a source pressure of 0.1 Torr, more than 75% of their beam was vibrationally excited. Our rf source, being larger (diameter 2.5 cm), has a longer mean residence time and at 0.1 Torr, their analysis indicates that about 65% of the H_3^+ ions are excited. Approximately 10% have internal energies in excess of 1 eV.

Given this analysis it would appear that there is at least qualitative agreement between our findings and the theoretical predictions of Kulander and Guest although their analysis does not include contributions due to dissociation to $H_2 + H(1s)$.

A consideration of the vibrational modes of H_3^+[24] shows that A and E states are fairly evenly populated. The A states perform symmetric stretch vibrations which are likely to couple to states dissociating to 3H atoms. E states are degenerate with one mode favoring dissociation to 3H atoms and another favoring $H_2 + H$. Hence given a highly vibrationally excited H_3^+ beam, it is perhaps not surprising that the dominant mode of dissociative recombination would lead to 3H atoms.

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