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Further measurements of the $H_3^+(v=0,1,2)$ dissociative recombination rate coefficient

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A new flowing afterglow apparatus that utilizes a Langmuir probe/mass spectrometer to monitor both electron and ion decay in a hydrogen plasma has been used to measure the dissociative recombination rate coefficient of H_3^+ at two different electron temperatures. At 300 K a rate coefficient of 1.5×10^{-7} cm^3 s^{-1} was found for H_3^+ ions with a low degree of vibrational excitation ($v\leqslant2$). The rate coefficient for ground state ions H_3^+ ($v=0$) was measured as 1.1×10^{-7} cm^3 s^{-1} at 650 K. A discussion is given of the excitation states of H_3^+ ions in the afterglow in the light of slow deexcitation rates for low vibrational states. A new model for the recombination of H_3^+ is presented.

INTRODUCTION

In molecular hydrogen plasmas such as occur in interstellar clouds, planetary ionospheres, ion sources, and thermonuclear experiments, H_3^+ is usually the dominant ion. It has for example recently been detected in the atmosphere of Jupiter,[1] this representing its first detection in space using remote sensing techniques. It is formed via the reaction

$$H_2^+ + H_2 \rightarrow H_3^+(v) + H \tag{1}$$

and for many years its main destruction mechanism was believed to be dissociative recombination (hereafter DR)

$$H_3^+ + e \rightarrow \begin{cases} H + H + H & \text{(2a)} \\ H_2 + H. & \text{(2b)} \end{cases}$$

Reaction (1) is known[2] to produce vibrationally excited ions but prior to interaction with electrons, they can be relaxed to the ground vibrational state by radiative transitions,[3] if sufficient time is available, or via collisions[4,5] with H_2 if the gas density is high enough. In interstellar clouds, the first condition certainly holds and so the DR rate coefficient relevant to the ground state, $\alpha[H_3^+(v=0)]$ is of particular interest. In other situations, such as in ion sources, the recombination may well apply to vibrationally excited ions.

Given its importance, it is not surprising that many experiments have been performed to measure the recombination rate of H_3^+. An early measurement by Persson and Brown[6] produced a very small rate coefficient for electron–ion recombination in hydrogen plasmas, but in this experiment H^+ was probably the dominant ion. In 1973 Leu, Biondi, and Johnsen[7] used the stationary afterglow (SA) technique to study reaction (2) and produced the value of $2.3\pm0.3\times10^{-7}$ cm^3 s^{-1} for thermalized conditions ($T_e = T_{\text{ion}} = T_{\text{gas}}$) at 300 K. Although the vibrational state was not specified in this paper, it can be inferred from the experimental conditions that indeed the H_3^+ ions were relaxed to low v levels.

A number of other measurements of H_3^+ recombination followed, using a variety of techniques including inclined beams,[8] merged beams,[9,10] and ion trap[11] methods, but these all produced essentially the same value for α.

In 1984 however, the flowing afterglow Langmuir probe (FALP) apparatus at the University of Birmingham, in the UK was used by Adams *et al.*[12] for the study of the recombination of a number of polyatomic species and they found that the rate coefficient for H_3^+ was immeasurably small. They assigned an upper limit to its value of 2×10^{-8} cm^3 s^{-1} at 300 K. What was more, this result was supported by theoretical studies of Kulander and Guest,[13] and Michels and Hobbs[14] who indicated that the direct recombination of ground state H_3^+ was likely to be very slow due to the unfavorable position of the crossing between the initial ion state and the dissociating neutral state, through which the process was believed to proceed. The high result obtained using the ion trap and merged beam techniques was explicable due to the uncertainty concerning the excitation state of the ions used in these measurements. The situation was less clear with regards to the inclined beam experiment where considerable effort had gone into ensuring that the ions were in fact deexcited.[8,15] The disagreement with the SA measurement, was particularly perplexing, for the state of the ions should have been similar to that in the FALP measurement. The reaction was remeasured by Macdonald *et al.*[16] for a wider temperature range but the value obtained at 300 K of $\alpha(H_3^+) = 1.5\times10^{-7}$ cm^3 s^{-1} agreed quite well with previous values.

In an effort to provide a deeper insight into this problem, Hus *et al.*[17] performed a series of measurements using the merged beam technique in which the population density of vibrationally excited states in the ion beam was systematically reduced down to a low value. They found that the rate decreased by about an order of magnitude down to 2×10^{-8} cm^3 s^{-1} at 100 K as the vibrational excitation was decreased.

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Subsequent studies have indicated that in fact this value applies to H_3^+ in the $v = 0$ level.[18] The experiment was also repeated for D_3^+ yielding the same result.[19]

A new problem arose when a recalibration of the Birmingham FALP apparatus by Adams and Smith[20] led them to claim that in fact the recombination rate for H_3^+ ($v = 0$) could be revised to less than 10^{-11} cm^3 s^{-1}. In 1987 Johnsen,[21] writing in a review article, reported that the SA measurements might have produced an overestimate of the rate coefficient due to contamination of the plasma by CH_5^+ ions.

In the following year Amano,[22] using an infrared spectroscopic absorption technique, fueled the controversy by measuring a DR rate of 1.8×10^{-7} cm^3 s^{-1} for H_3^+ ($v = 0$). This measurement was criticized by Adams and Smith[23] who suggested that it was strongly influenced by collisional-radiative recombination (CRR). An extensive remeasurement by Amano[24] has since ruled out the influence of CRR and reconfirmed his earlier value. He also showed that the rate was essentially independent of the rotational state of the ions in the range from $J,K = 1,0$ to $4,4$. The range of H_3^+ recombination rates measured to date is summarized in Table I.

Recently, we have developed a new FALP apparatus at the University of Rennes in France. This was designed primarily for the study of the branching ratios for the DR of polyatomic ions.[25] It has also been used to measure the rate coefficient of N_2^+ ($v = 0$) DR.[26] However, we never succeeded in reproducing the FALP measurement of Adams and Smith at room temperature. Given the importance of this controversy, a new flowing afterglow apparatus was built, allowing ion density measurements to be made in the reaction zone. The rate coefficient for H_3^+ ($v \leqslant 2$) was determined as 1.5×10^{-7} cm^3 s^{-1} at 300 K and for H_3^+ ($v = 0$) as $\simeq 1.1 \times 10^{-7}$ cm^3 s^{-1} at 650 K, consistent with that of Macdonald *et al.*[16] and of Amano.[24]

EXPERIMENT

Several experiments have been performed using the apparatus shown in Fig. 1. The technique used for the first set of experiments has been described in detail elsewhere[27] and only the main features will be described below. It is directly derived from the FALP method, but with the great advantage that the reaction zone is now located in a large chamber (17 cm in diam) and this allows one to move a quadrupole mass spectrometer along the axis of the flow. An off-axis movable rod permits one to set a Langmuir probe on axis by rod rotation. Densities of both ions and electrons can therefore be obtained as a function of distance z along the flow.

A helium buffer gas is ionized by a microwave discharge and argon is injected through an upstream inlet. This results in the conversion of He_2^+ ions and He^M metastables into Ar^+ ions via the reactions

$$He_2^+ + Ar \rightarrow Ar^+ + 2He, \tag{3}$$

$$He^M + Ar \rightarrow Ar^+ + He + e\,. \tag{4}$$

At the end of the flow tube, just before the reaction zone, both He^+ and Ar^+ ions are usually present in the flow. For the highest pressure, however, nearly complete conversion of He^+ into He_2^+ ions occurs, resulting in a plasma dominated by Ar^+ ions. Hydrogen is then added through an eight needle entry port which has been designed in order to obtain very rapid mixing of the gases, without aerodynamic perturbation of the flow. H_3^+ ions are formed through the reactions

$$Ar^+ + H_2 \rightarrow ArH^+(v) + H, \tag{5}$$

$$ArH^+(v) + H_2 \rightarrow H_3^+(v') + Ar\,. \tag{6}$$

The H_3^+ ions, produced very close to the needle entry port, can be destroyed downstream by electrons and possibly by ion–molecule reaction with an impurity gas I (rate coefficient k). As discussed by Rowe *et al.*[27]

$$\ln([H_3^+]_z/[H_3^+]_0) = -\frac{k[I]z}{v} - \frac{\alpha}{v}\int [e]dz. \tag{I}$$

$[H_3^+]_z$ and $[H_3^+]_0$ are, respectively, the H_3^+ density at a distance z along the flow axis and at a chosen origin $z = 0$, downstream of the needle entry port, $[e]$ is the electron density at z position, and v is the flow velocity.

Equation (I) assumes that the formation of H_3^+ initiated by the very slow reactions [$k_7 = 1.1 \times 10^{-13}$ cm^3 s^{-1} (Ref. 28) and $k_8 = 8.3 \times 10^{-32}$ cm^6 s^{-1} (Ref. 29)]

TABLE I. Summary of the main results obtained for $\alpha(H_3^+)$ at 300 K by various authors.

Method	α(cm^3 s^{-1})	Authors
Stationary afterglow	2.3×10^{-7}	Leu *et al.* (Ref. 7)
Inclined beam	2.5×10^{-7}	Peart and Dolder (Ref. 8)
Merged beam	2.1×10^{-7}	Auerbach *et al.* (Ref. 9)
Ion trap	1.5×10^{-7}	Mathur *et al.* (Ref. 11)
Merged beam	2.1×10^{-7}	McGowan *et al.* (Ref. 10)
FALP	$<2.10^{-8}$	Adams *et al.* (Ref. 12)
Stationary afterglow	1.5×10^{-7}	Macdonald *et al.* (Ref. 16)
FALP	$\leqslant 10^{-11}$	Adams and Smith (Ref. 20)
Merged beam	2×10^{-8} ($v = 0$)	Hus *et al.* (Ref. 17)
Infrared spectroscopy	1.8×10^{-7} ($v = 0$)	Amano (Ref. 24)
Flowing afterglow	1.5×10^{-7} ($v \leqslant 2$)	This work
Flowing afterglow	1.1×10^{-7} ($v = 0$)	This work (650 K)

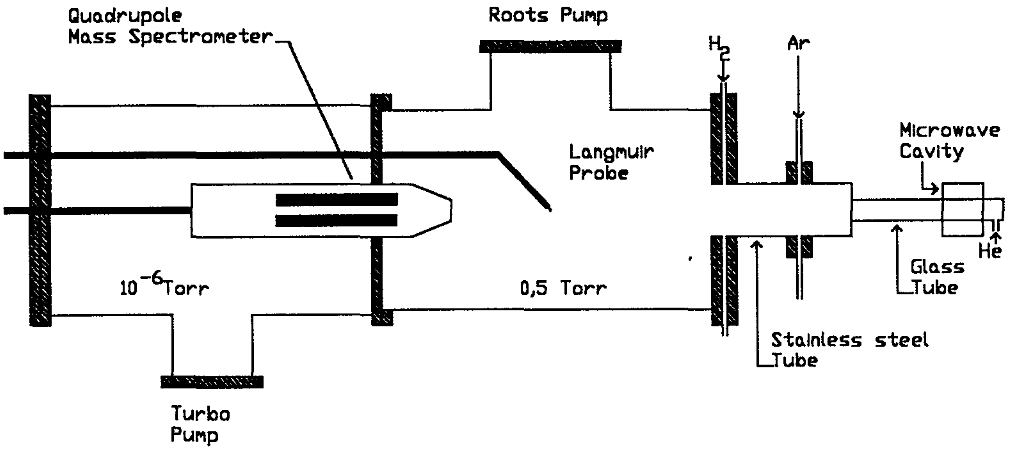

FIG. 1. Sketch of the apparatus.

$$He^+ + H_2 \rightarrow \begin{cases} H^+ + H + He & \text{(dominant channel)} \\ HeH^+ + H & \\ H_2^+ + He, & \end{cases} \qquad (7)$$

$$He^+ + 2He \rightarrow He_2^+ + He \qquad (8)$$

is negligible in the recombination zone. This point is discussed in the next section.

The DR rate coefficient α can be calculated from a linear plot of the left-hand side of Eq. (I) vs $\int[e]dz/v$. This can be obtained in two ways. As discussed previously,[27] if $[H_3^+]$ and $[e]$ are measured at various z values for a given initial electron density, the method is sensitive to the possible effects of impurities or of diffusion. The other way is to obtain a variation of the integral $\int[e]dz$ via a variation of the electron density for a fixed value of z. This can be achieved easily by varying the input power to the microwave cavity and by adjusting its position. The term $k[I]z/v$ is now constant and does not influence the determination of α.

The presence of impurity ions like H_3O^+ can be readily detected by the mass spectrometer in the reaction zone. Measurements were performed only when the density of these ions was found to be negligible and, in this case, both methods yielded the same α value.

A second experiment was performed using an argon–hydrogen buffer gas mixture, in order to ensure very efficient quenching of H_3^+ $(v>0)$ down to H_3^+ $(v=0)$. In this case the electron density was always found to be too small in the large chamber to permit a determination of the DR rate coefficient. A Langmuir probe was placed at a fixed z position downstream of the microwave discharge. Moving the microwave cavity along the flow tube allowed us to obtain a plot of the electron density $[e]$ vs the distance z between the cavity and the probe. The mass spectrometer showed that only H_3^+ ions were present downstream in the flow and the rate coefficient α was obtained using the standard FALP analysis.[26]

RESULTS AND DISCUSSION

Three different pressures of the helium buffer flow (respectively, 0.5, 0.8, and 1.6 Torr) were used in the first set of experiments. A typical mass spectrum of the plasma in the recombination zone is shown in Fig. 2 for the lower pressure case, when only a small conversion of He^+ into He_2^+ ions occurred in the flow tube. Figures 3 and 4 show plots of $\ln([H_3^+]_z/[H_3^+]_0)$ vs $\int[e]dz/v$ obtained using the two methods described in the previous section. The curvature observed in Fig. 3 is discussed below. Both methods yield very consistent values for H_3^+ DR rate coefficient with $\alpha = 1.5\times10^{-7}$ cm^3 s^{-1}. This shows clearly that the measurements are unaffected by effects linked to impurities or diffusion. Experiments at different pressures yielded the same results and these are in clear conflict with the values reported by Adams *et al.*[12] and Adams and Smith.[20]

A fundamental question regarding these measurements concerns the H_3^+ vibrational states. Adams *et al.* used the rate coefficient $k_q = 2.7\times10^{-10}$ cm^3 s^{-1} based upon results reported by Kim *et al.*[4] for the quenching process

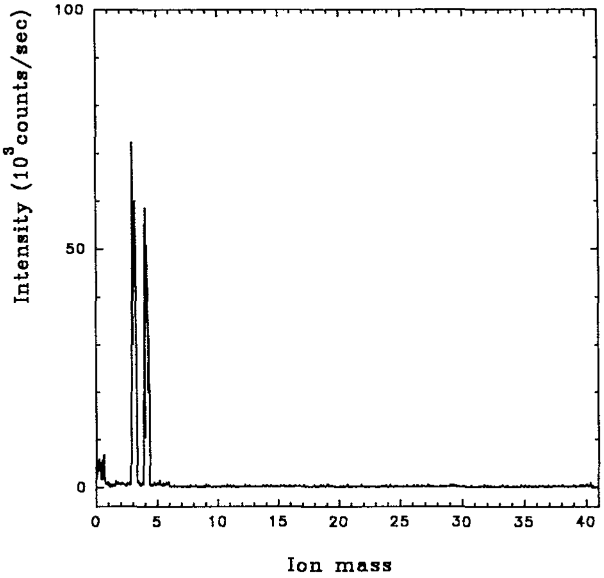

FIG. 2. A typical mass spectrum taken at 0.5 Torr.

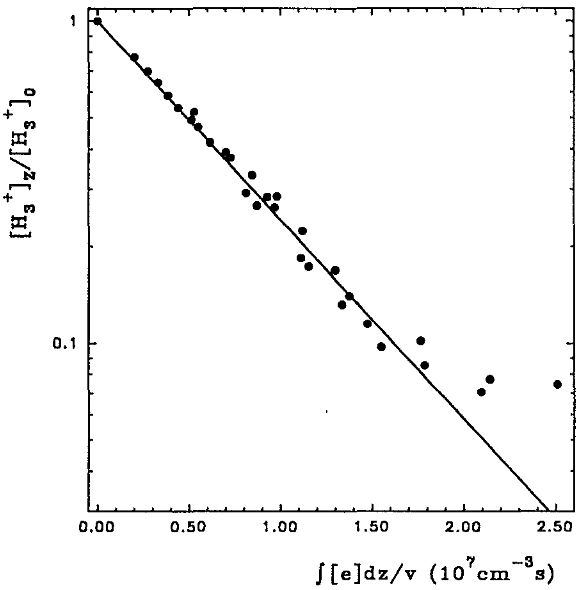

FIG. 3. The experimentally measured decrease of $[H_3^+]_z/[H_3^+]_0$ vs $\int[e]dz/v$. This integral is varied by changing z as well as $[e]$.

$$H_3^+(v) + H_2 \rightarrow H_3^+(0) + H_2 \tag{9}$$

and inferred that, in the FALP experiment, H_3^+ ions were quickly relaxed to the ground vibrational state. In the present measurements such a k_q value would imply that the excited fraction of H_3^+ ions would be less than 3×10^{-3} at the $z=0$ abscissa. Other studies[30,31] have suggested that H_3^+ is rapidly relaxed into the ground state, but this conclusion was always reached from the observation of the closure of an endothermic channel in reaction of H_3^+ with various molecules when H_3^+ had suffered a few collisions.

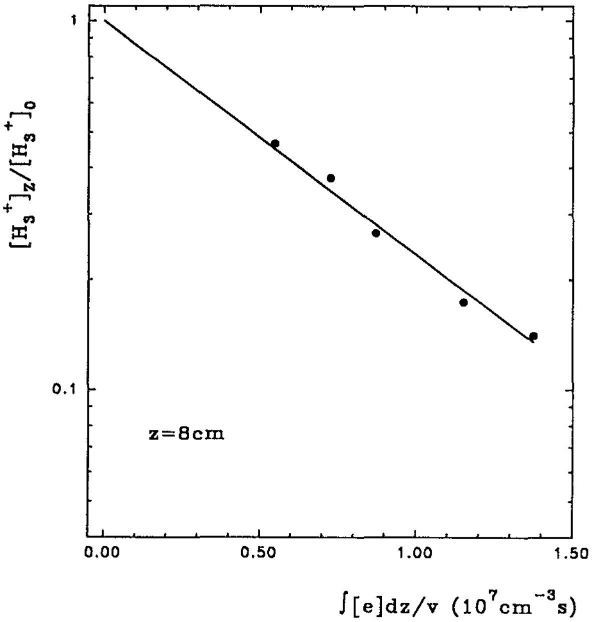

FIG. 4. The experimental measured decrease of $[H_3^+]_z/[H_3^+]_0$ vs $\int[e]dz/v$ for a given value of z (8 cm).

A further study by Blakley *et al.*[5] has shown that the quenching rate coefficient is, in fact, probably small for $v\leqslant3$ with $k_q\simeq10^{-11}$ $cm^3 s^{-1}$ and in the range 10^{-12}–10^{-11} $cm^3 s^{-1}$ for $v=1,2$. Previous studies can be interpreted as referring to the quenching of higher vibrational levels. The ions would therefore not have been fully relaxed in the FALP experiment of Adams *et al.*[12] For the hydrogen density used in the present work, a value of $k_q=10^{-11}$ $cm^3 s^{-1}$ ensures a large deactivation of the excited vibrational states. However if $k_q=10^{-12}$ $cm^3 s^{-1}$ as suggested by Blakley *et al.*,[5] then the excited state can survive into the recombination zone. It has to be noted that Amano indicates that the first vibrationally excited state of H_3^+ corresponds to one percent of the ground state ion density in his experiment.[24] Considering the time scale and the hydrogen density used, this is compatible with $k_q=10^{-11}$ $cm^3 s^{-1}$ but is inconsistent with a much lower value, unless the ions are directly created in the $v=0$ state, which is unlikely. Nevertheless, such low values of k_q concern only the $v=1,2$ states and therefore it can be concluded that, in the present experiments, only states with $v\leqslant2$ could be significantly populated. The same conclusion can be reached by considering the network of reactions that forms H_3^+ prior to recombination. The reaction

$$ArH^+(v=0) + H_2 \rightarrow H_3^+(v) + Ar \tag{10}$$

is endothermic for $v=3$. At room temperature it is fast[32] and therefore it can be concluded that it populates mainly $v\leqslant2$. For the argon density used, any H_3^+ $(v=3)$ ions immediately react back to ArH^+ $(v=0)$ via the reverse of reaction (10) and then this ion yields H_3^+ $(v\leqslant2)$ with hydrogen. In the same way, higher vibrational states (which are in fact quickly relaxed by H_2) react in a chain of forward and backward reactions leading to less and less vibrational excitation until $v\leqslant2$ is obtained. Table II summarizes typical reaction times for the various processes discussed above.

The measured values of $\alpha=1.5\times10^{-7}$ $cm^3 s^{-1}$ then certainly applies to H_3^+ $(v\leqslant2)$. From the theoretical point of view this conclusion is extremely significant since the calculation of Michels and Hobbs[14] and of Kulander and Guest[13] show that α should be extremely small for $v<4$. However, for astrochemical applications, the rate coefficient for the $v=0$ state is clearly needed. In the FALP experiment of Adams *et al.*[12] the ions were not fully relaxed and their result shows a strong curvature of the plot of $1/[e]$ vs the distance to the hydrogen inlet. This could be interpreted as an initial distribution of H_3^+ (v) reacting with very different α: close to the hydrogen inlet the H_3^+ (v) would be quickly destroyed by DR and further downstream the H_3^+ $(v=0)$ would survive and sustain the electron density. It has to be noted that the presence of any other nonrecombining ions downstream of the hydrogen entry port would lead to the same effect. In the present set of measurements and when only H_3^+ ions were present in the flow, it was never possible to reproduce such a behavior of the electron density. Under these conditions reported by Adams *et al.*[12] at 300 K, the curvature of the electron density plot vs z was observed but, in our experi-

TABLE II. Comparison of the various reaction or quenching times for two sets of plasma conditions.

Reaction	Rate coefficient ($cm^3\,s^{-1}$)	Reaction or quenching times (s)	
		$p = 1.6$ Torr	$p = 0.5$ Torr
$H_3^+(v) + H_2 \rightarrow H_3^+(0) + H$	2.7×10^{-10} [a]	5.8×10^{-6}	1.9×10^{-5}
	$1\ \times10^{-11}$ [b]	1.6×10^{-4}	5.3×10^{-4}
	$1\ \times10^{-12}$ [b]	1.6×10^{-3}	5.3×10^{-3}
$ArH^+ + H_2 \rightarrow H_3^+ + Ar$	$8\ \times10^{-10}$ [c]	$2\ \times10^{-6}$	6.6×10^{-6}
$H_3^+ + e \rightarrow$ Products	1.5×10^{-7} [d]	$>3.3\times10^{-4}$	$>1.1\times10^{-4}$

[a] Reference 4.

[b] Upper and lower limit obtained in Ref. 5.

[c] Reference 32.

[d] See Table I. The times are estimated as (rate coefficient $\times [H_2])^{-1}$ except for recombination where it is $(\alpha[e])^{-1}$. In this last case the electron density is not constant and the upper values of the reaction times are given at the onset of recombination. The plasma conditions used in the low and high pressure cases are, respectively, total pressure 0.5 and 1.6 Torr, hydrogen density 1.9×10^{14} and 6.4×10^{14} molecule cm^{-3}, initial electron density 6×10^{10} and 2×10^{10} electron cm^{-3}, plasma velocity 1.78×10^4 and 6.8×10^3 cm s^{-1}. The various times can be compared to the plasma times of flight over a typical recombination length (10 cm) which are, respectively, 5.6×10^{-4} and 1.5×10^{-3} s.

ment, it was related to the presence of a large amount of He^+ ions (detected in the recombination zone) which sustained ionization.

In the present study, the H_3^+ density and the electron density can be directly measured in the recombination zone. As shown by Eq. (I), the plot of $\ln([H_3^+]_z/[H_3^+]_0)$ vs $\int[e]dz/v$ has to be linear as long as there are no sources of H_3^+ ions downstream of the hydrogen inlet. Nonlinearity can also be interpreted as being due to various vibrational states of H_3^+ ions recombining with different rate coefficients. A curvature of the plot was sometimes observed, as shown in Fig. 3, which summarizes a large number of different experiments under various flow conditions. This behavior however was never obtained in the high-pressure case when only a few He^+ ions were present. The observed curvature corresponds to situations where the H_3^+ density has decayed to a very small fraction of the total ion density ($\sim5\%$). A small production rate of H_3^+ may therefore balance destruction by recombination. In fact, evaluation of the convection term in the transport equation shows that it is not completely negligible. By taking this term into account and the creation by the very slow reactions (7) and (8) (the products of which react with Ar and H_2 to form H_3^+), the rate of production of H_3^+ ions in this part of the recombination zone can be estimated to be 4.2×10^{12} ions $cm^{-3}\,s^{-1}$, the recombination being 9.9×10^{12} ions $cm^{-3}\,s^{-1}$. Such evaluations however are subject to large uncertainties. Therefore, although the calculated production terms do not strictly balance recombination, there is a qualitative agreement with above explanations.

In order to strengthen our conclusions, it was decided to perform a further experiment using the second experimental protocol described in the previous section.

An argon–hydrogen mixture ($P = 0.5$ Torr) was used as buffer gas and flowed directly through the microwave discharge. Figure 5 displays plots of the variation of the electron density $[e]$ vs distance to the microwave cavity z, respectively close to and far from the discharge. In the second case, the initial electron density has fallen to a low value and its decrease is therefore mainly due to diffusion loss. The downstream part of this plot yields a value of the ambipolar diffusion coefficient of 540 $cm^2\,s^{-1}$ Torr in excellent agreement with the value of 500 $cm^2\,s^{-1}$ Torr reported by von Engel[33] in pure hydrogen at 300 K, (argon was only 26% of the total buffer density in the present experiment). Close to the discharge, the initial electron density is much higher and

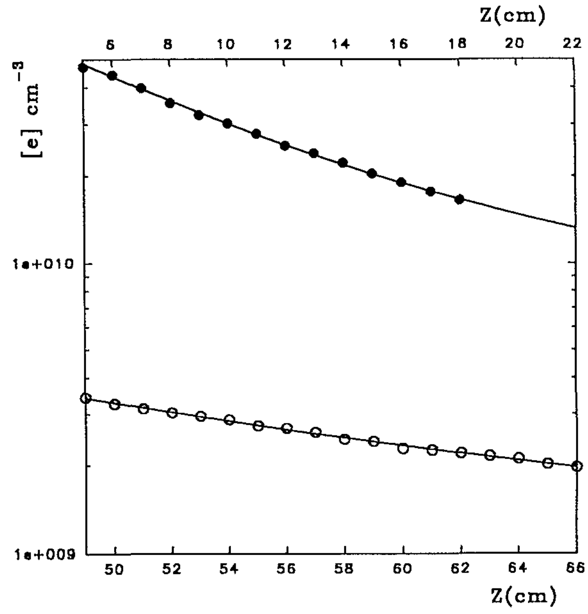

FIG. 5. Variation of the electron density vs distance to the discharge in an hydrogen buffer plasma. Open circle: far from the discharge ($z = 49$–66 cm), filled circle: close to the discharge ($z = 5$–18 cm).

the much larger decrease can only be attributed to recombination. An equivalent ambipolar diffusion coefficient of 2160 $cm^2 s^{-1}$ Torr has been estimated from the initial slope of this upstream plot. Assuming that the ion temperature was close to room temperature, this value would imply an electron temperature of 2300 K. This value would even be higher if we assume electron–ion thermal equilibrium. Although Langmuir probe measurements of the electron temperature are tedious they can be accurate if performed with sufficient care. In the present experiment, the temperature has been found to range from 650 K close to the discharge to 450 K far downstream. Such values therefore cannot explain the data of Fig. 5 in terms of pure ambipolar diffusion. A plot of $1/[e]$ vs z is shown in Fig. 6 and yields $\alpha(H_3^+) = 1.1 \times 10^{-7}$ $cm^3 s^{-1}$. Such a determination assumes that only H_3^+ ions are present in the flow. A mass spectrum obtained downstream is shown in Fig. 7. Clearly H_5^+ ions are not formed and H_3O^+ remains negligible. Assuming a temperature dependency for α of $T^{-0.5}$, the 1.1×10^{-7} $cm^3 s^{-1}$ measured value yields 1.6×10^{-7} $cm^3 s^{-1}$ at 300 K in very good agreement with the first experimental protocol.

The vibrational state of H_3^+ ions is directly linked to the vibrational state of H_2 and to the characteristic time of the quenching reaction (9). Simple thermodynamic considerations show that excitation of the vibrational levels of H_2 remained small since a power of 130 W was used in the microwave discharge for a hydrogen flow rate of 1.04×10^{-2} mol/s. Assuming that all the discharge energy goes into producing $H_2(v=1)$ yields a $[H_2(v=1)]/[H_2(v=0)]$ ratio of 0.33. Assuming a Boltzmann distribution and again all the power available for vibrational excitation, yields: $[H_2(v=1)]/[H_2(v=0)] = 0.2$, $[H_2(v=2)]/[H_2(v=0)] = 0.04$, $[H_2(v=3)]/[H_2(v=0)] = 0.01$, and $[H_2(v=4)]/[H_2(v=0)] = 0.003$ at a vibrational temperature of 3600 K. Such values obviously are extreme upper limits. Langmuir probe measurements of the electron temperature are in fact strongly indicative of a very low vibrational excitation of H_2. If the vibrational excitation would have been high, the electron temperature could have been substantially increased above room temperature close to the discharge by exchanges between the electron gas and the excited H_2. The relaxation of the electron temperature by vibrationally excited H_2 could be extremely efficient as shown by the values at threshold of the cross section for vibrational excitation by slow electrons.[34] A detailed balance calculation yields a relaxation time of 0.5 μs. On the other hand, the relaxation of electron energy into translational–rotational energy of H_2 is also very efficient. Based on the work of Koura[35] we estimated the relaxation time to be 1 μs under our experimental conditions. The electron temperature must therefore have a value between the neutral translational and vibrational temperature. Using the estimated translational–rotational relaxation time, the vibrational excitation and de-excitation rate coefficients of H_2 by slow electrons and assuming a neutral translational temperature of 300 K, a simple numerical calculation of the electron temperature at steady state led to a very low ratio $[H_2(v=1)]/[H_2(v=0)] \approx 0.03$ to reproduce the measured electron temperature of 650 K. This ratio would even be smaller if the translational temperature was higher. Due to the very large hydrogen density in this experiment, $H_3^+(v)$ was quickly relaxed by $H_2(v)$ downstream of the discharge. Assuming the very low limit of $k_q = 10^{-12}$ $cm^3 s^{-1}$ for reaction (9), the characteristic relaxation time of $H_3^+(v)$ was 80 μs (corresponding to a characteristic distance of 3 cm). Some H_3^+ $(v = 1,2)$ ions could therefore still be present at a distance of $z = 5$ cm where Langmuir probe measurements are started. However, the recombination

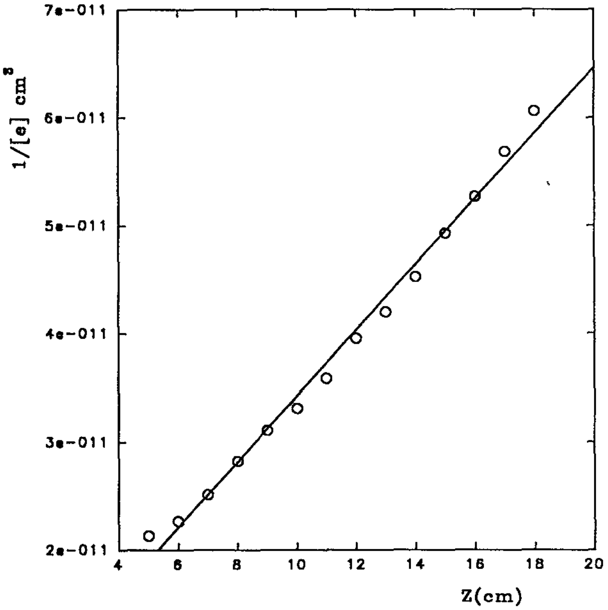

FIG. 6. Plot of $1/[e]$ vs z yielding a value of $\alpha(H_3^+) = 1.1 \times 10^{-7}$ $cm^3 s^{-1}$.

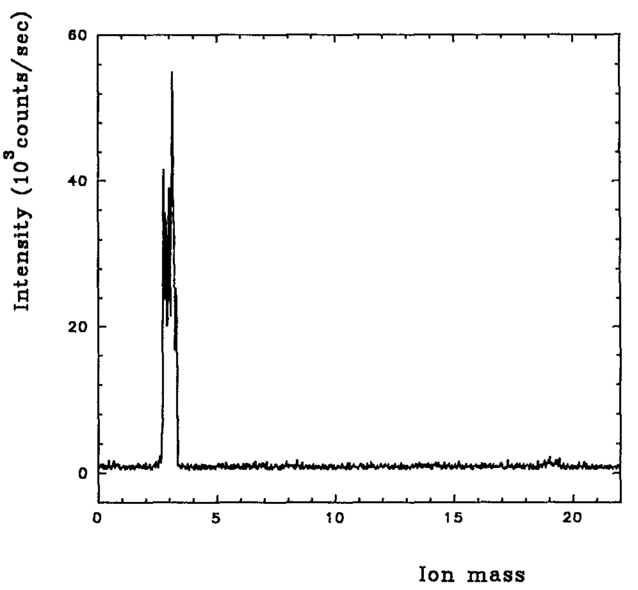

FIG. 7. A spectrum of the hydrogen plasma far downstream of the discharge.

characteristic time was greater than 200 μs so that H_3^+ (v) ions were relaxed to their ground state prior to DR.

The results presented in this section are therefore in agreement with the work of Macdonald *et al.*[16] and of Amano.[22,24] They contradict the extremely small α value obtained using the Birmingham FALP apparatus.[12,20]

A MODEL FOR H_3^+ RECOMBINATION

To summarize the experimental results, H_3^+ ($v = 0$) is found to recombine with electrons with a rate coefficient of 1.1×10^{-7} cm^3 s^{-1} at 650 K and $H_3^+(v \leqslant 2)$ close to 1.5×10^{-7} cm^3 s^{-1} at room temperature. Figure 8 shows a sketch of the potential energy curves for H_3 and H_3^+ indicating the resonant $^2A_1$ state of H_3^+, calculated by Michels and Hobbs[14] and by Kulander and Guest.[13] It can be seen that the crossing of this curve with the ground state of H_3^+ occurs far from the $v = 0$ level. In fact one has to go to $v > 3$ before a satisfactory overlap of the two states is achieved. Assuming that the position of the resonant state has been accurately calculated, then one must conclude that H_3^+ in low vibrational states must recombine by means of a mechanism other than via a direct transition from the ion state to an intersecting, dissociating state.

In fact there are several pieces of evidence that suggest that this is so. In a paper published in 1967 Chupka *et al.*[36] showed, using a technique that involved the photoionization of a molecular hydrogen target, that H_3^+ ions could be produced via the associative ionization process

$$H(n=2) + H_2(^1\Sigma_g^+) \rightarrow H_3^+ + e.$$

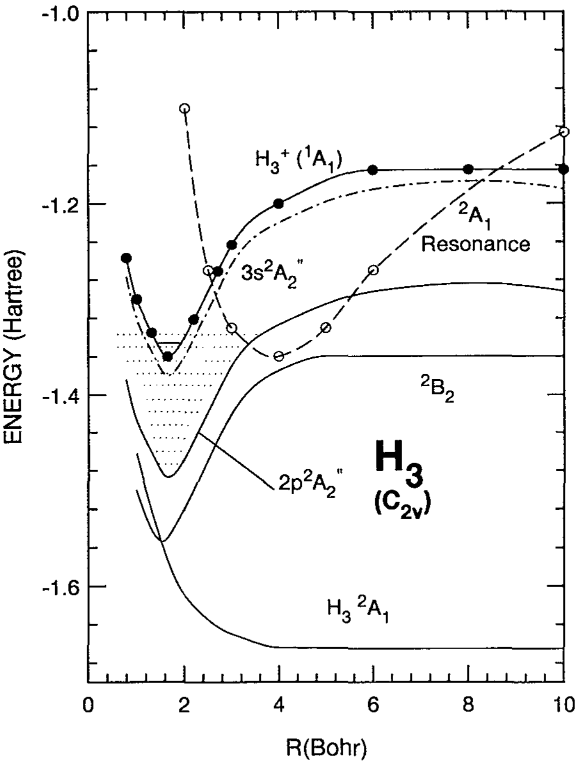

FIG. 8. Potential energy curves of H_3^+ and H_3.

It was found that this process occurred when the reactants had essentially zero collision energy and that the cross section fell off as the collision energy increased. Chupka *et al.*[36] argued that this indicated that the potential energy curve along which the reactants approached each other was either nonrepulsive at large internuclear separations or that it was attractive. Since the $H(n = 2) + H_2(^1\Sigma_g^+)$ asymptote lies at -1.29 hartrees, this implies the latter for, according to theory,[2,3] the lowest intersection of a neutral state with the H_3^+ ground state occurs at -1.271 hartrees. Chupka *et al.* result indicates that H_3^+ is most likely produced in a level with $v < 3$. Associative ionization is just the inverse of dissociative recombination and so the implication is that indirect recombination involving transitions between the ion state and attractive neutral Rydberg states is the driving mechanism.

Further evidence for the importance of the indirect mechanism for H_3^+ recombination comes from merged beam experiments. Preliminary results of a study of the product branching ratios,[37] indicated that a decay channel yielding H_3^* states with lifetimes exceeding 10^{-7} s accounted for about 8% of the total recombination cross section at a collision energy of 0.01 eV. It would seem not unreasonable to suggest that the observed dissociation channels might be the daughters of shorter lived H_3^* Rydberg states. High-resolution studies of H_2^+ ion recombination[38,39] found that the cross section displayed deep window resonances which correlated extremely well with structures predicted by theory incorporating both the direct and indirect processes. Such resonances have also been found in a high-resolution examination of D_3^+ recombination.[19]

Indirect dissociative recombination is a process in which the kinetic energy of the incoming electron is converted in a resonant excitation process into nuclear motion. Thus, when the energy is sufficient, the electron can induce a transition of the nuclear motion to a higher rotational or vibrational state, and having lost its kinetic energy, the electron is temporarily captured into a Rydberg state. This idea was originally proposed by Stabler who calculated that for electron–ion collisions the rotational excitation cross section[40] and thus the electron capture rate[41] was very large. For example, he calculated capture rates of the order of 1×10^{-7} cm^3 s^{-1} for several diatomic ions, including N_2^+, O_2^+, and He_2^+. In itself, however, this is not the recombination rate since the nuclear excited Rydberg state thus formed has an energy greater than the ionization potential and it must lose this energy in order for the recombination to be stabilized. When there is a suitable curve crossing, the Rydberg state can be rapidly predissociated before it has time to autoionize. This is the case for N_2^+ and O_2^+ and these ions display fast recombination rates,[42] although this can in fact mostly be attributed to the direct recombination process. For He_2^+ there is no suitable curve crossing and this ion exhibits a low recombination rate.[43]

Bardsley[44] examined the indirect process in more detail and analyzed the situation where the direct and indirect processes would compete with each other. He showed that, except for very low energies (<0.001 eV), rotational excitation would play a very minor role, although indirect capture involving vibrational excitation could be important provided there existed Rydberg states within the energy range of the incoming electrons which decayed via predissociation faster than via autoionization.

Giusti,[45] Giusti *et al.*,[46] Hickman,[47] and Nakashima *et al.*[48] have studied the competition between direct and indirect recombination in situations where there is an optimal or close-to-optimal curve crossing between the ion state and the dissociating resonant state. These authors find that the indirect process leads to the production of window resonances in the cross section. This is due to the fact that when the collision energy is such that there is the possibility of exciting a vibrationally excited Rydberg state, the wave function describing the system becomes localized in that state, rather than in the unbound direct resonance. The nuclear coupling to the Rydberg resonant state is much weaker than the electronic coupling to the unbound state and so the recombination process is much weaker leading to dips in the cross section. In these calculations however, it was assumed that the vibrational excitations leading to the formation of the neutral Rydberg states would only involve changes of $v = 1$. The reason for this is that the transfer of electronic motion to the nuclear motion involves a violation of the Born–Oppenheimer principle. Studies of autoionization processes in molecules reveal the existence of a propensity rule[49] where only small changes of vibrational energy are involved.

In 1981, O'Malley[50] introduced the idea that transitions involving large changes in vibrational energy might play a significant role in the recombination process. In particular, he envisaged the interference of low n, high v resonances with the dissociation process which again would lead to a weakened recombination rate. Hickman[47,51] has studied the influence of this, so-called full-direct process[52] in calculations of H_2^+ recombination taking full account of the direct and indirect processes. He found that for the $v = 1$ case, where there is a good overlap between the ion state and the dissociating state, both the indirect and the full-direct processes lead to resonant dips in the cross section which is dominated by the direct process. For the $v = 0$ case, the overlap is nonoptimal and the full-direct mechanism produces a large enhancement of the transition probability.

If we examine now the situation for H_3^+, as shown in Fig. 8, it can be seen that the $v = 10$ level of the $2p\,^2A_2''$ state lies just above the $v = 0$ level of the H_3^+ ground state. One could propose therefore a transition to this state which in turn could be predissociated by the H_3^* ground state. (Note that in D_{3h} symmetry, the $^2B_2$ state which dissociates to three ground state hydrogen atoms and the $^2A_1$ state which dissociates to $H_2 + H$ are degenerate.) The question is, how likely is a $\Delta v = 10$ transition and would this state be more likely to be autoionized than predissociated. Jungen[53] has discussed the competition between autoionization and predissociation in diatomic molecules and has applied multichannel quantum defect theory (MQDT) to this problem. In this approach, the molecular system under study is treated in terms of two regions. In one region, the system is intact and is described by bound-state wave functions. In the other, the system is either predissociated or autoionized so that it is described by continuum wave functions. MQDT allows a smooth coupling of these two situations to be described so that autoionization and predissociation transition probabilities can be calculated. Indeed such a theory has been used by Giusti,[45] Giusti *et al.*,[46] and Nakashima *et al.*[48] in their treatments of the dissociative recombination of diatomic ions.

If we consider the H_3^+ recombination process in these terms, one can envisage the electron approaching the ion in the distant region. In this region, the Born-Oppenheimer approximation will not hold for the electron is far from the ion core and, during the time it takes to reach the ion core, the nuclei can have undergone a considerable movement. Due to the long-range nature of the Coulomb interaction however, the incoming electron can severely perturb the electron orbitals of the H_3^+ ion, leading to a substantial nuclear rearrangement. Thus a large transition such as $\Delta v = 10$ is not inconceivable. When the electron has entered the inner region, it becomes bound to the highly excited nuclear core, forming, for example, the $2p\,^2A_2''$ state. Now however, the Born–Oppenheimer approximation is valid so that a transfer of nuclear to electronic motion is unlikely. This means that the autoionization rate for this highly excited state will be very small (see, for example, Ref. 53, Table VI).

Bordas and Helm[54] have recently obtained some very pertinent results from a study in which a beam of metastable $2p\,^2A_2''(N=0,K=0)$ molecules is produced via charge transfer between a H_3^+ beam and a cesium target and these molecules are excited to high lying Rydberg states via laser excitation. The spectrum of these high Rydberg states is examined using field ionization detection and it is found that window resonances appear in this spectrum at values of $n = 61$, 64, 86, and 129. Analysis of this phenomena has shown that these resonances appear because these states are predissociated via a large v transition to a low n state, (probably an $n = 2$, E' state in this case) which is then predissociated by the ground state of H_3. This is essentially the same mechanism as outlined above for H_3^+ recombination.

Another possible mechanism for H_3^+ recombination involves much smaller v transitions to states with $n = 3$ and above (see Fig. 8). Dehmer and Chupka[55] have shown that for H_2, autoionization will be the dominant decay mechanism for high n states which can ionize via a $\Delta v = -1$ transition. For states involving ionizing transitions with $\Delta v > 1$, predissociation or radiation can often compete successfully with autoionization even though the lifetime for such events can be longer than typical allowed autoionization lifetimes. It is possible that such $\Delta v > 1$ transitions can occur in the manner described above leading to the production of long lived, nonautoionizing Rydberg states which can subsequently either radiate down to the repulsive ground state of the H_3 molecule or be predissociated if there is sufficient coupling to that state. Kulander and Guest[13] did indicate in their 1979 paper that they had performed preliminary calculations that indicated coupling between the higher Rydberg states and the excited $H_2(b\,^3\Sigma_u^+) + H(1s)$ state in colinear configurations.

As mentioned in the previous section, the results presented in this paper are about a factor of 5 higher than results obtained using the merged beam technique.[17] In that experiment, the cross section was seen to decrease as the vibrational population of the ions was lowered. The state of excitation of the ions was monitored by examining the position of the threshold for the dissociative excitation of H_3^+. A recent reanalysis of this experiment has provided strong confirmation that ground-state ions were used for the recombination.[18] In addition, high-resolution studies of D_3^+ recombination[19] revealed the presence of window resonances and these were seen to be smeared out as the ion source conditions were changed so that the beam contained excited vibrational states. The recombination cross section for H_3^+ has been remeasured several times using a different merged beam apparatus in the same laboratory, lending confidence to the observation that the measured cross section does decrease with decreasing internal energy. The answer to this dilemma may lie in the fact that the flowing afterglow and the merged beam techniques measure different things. In the flowing afterglow, the electron and ion densities in a recombining afterglow are studied as a function of distance along the flow, and therefore of time, in order to determine the total recombination rate. In the merged beam experiment, the products of the recombination process are separated from the primary ion beam, detected and counted using nuclear counting techniques.

When the merged beam results were compared with the null result of Adams and Smith[20] the problem was to explain why the merged beam experiment did not yield a low result. One possible explanation put forward[56] was that the long-lived H_3^* molecules, formed in the recombination process would be detected in the merged beam case, but would be ionized when in contact with a Langmuir probe thus apparently yielding a low recombination rate.

The problem now, however, is to explain why the merged beam technique measures a low product yield. The reason for this may again perhaps be traced to their being a considerable fraction of long-lived H_3^* molecules formed in the recombination process. If these were formed in high n states, then they may be ionized on passing through the electric field used to separate the ions from the neutrals. In the MEIBE I apparatus, this field has a strength of about 6 kV/cm. This is sufficient to field-ionize states with n greater than $n=18$. An experiment is planned to study the effects, on the measured recombination cross section, of varying the electric field experienced by the neutrals over a very wide range. This experiment will use a field ionizer[57] capable of producing fields up to 150 kV/cm which will ionize states greater than $n=9$.

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