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Measurements of dissociative recombination coefficients of H_3^+ , HCO^+ , N_2H^+ , and CH_5^+ at 95 and 300 K using the FALP apparatus

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Measurements are presented of the dissociative recombination coefficients α_i for reactions of electrons with H_3^+ , D_3^+ , HCO^+ , DCO^+ , N_2H^+ , N_2D^+ , and CH_5^+ ions at 95 and 300 K. The measurements were made under truly thermalized conditions using a flowing afterglow (FALP) apparatus. Contrary to previous stationary afterglow (SA) studies, $\alpha_i(\text{H}_3^+)$ was found to be immeasurably small [$\leq 2(-8) \text{ cm}^3 \text{ s}^{-1}$] at both temperatures which is consistent with recent theoretical predictions. However some evidence was obtained indicating that vibrationally excited H_3^+ recombined efficiently, which is also in accordance with the recent theory. At 300 K, $\alpha_i(\text{HCO}^+) = 1.1(-7) \text{ cm}^3 \text{ s}^{-1}$ and $\alpha_i(\text{N}_2\text{H}^+) = 1.7(-7) \text{ cm}^3 \text{ s}^{-1}$ and both were larger by a factor of three at 95 K. $\alpha_i(\text{CH}_5^+) = 1.1(-6) \text{ cm}^3 \text{ s}^{-1}$ at 300 K and $1.5(-6) \text{ cm}^3 \text{ s}^{-1}$ at 95 K. The $\alpha_i(\text{HCO}^+)$ data are compared with previous SA data and the $\alpha_i(\text{N}_2\text{H}^+)$ and $\alpha_i(\text{CH}_5^+)$ data are discussed in relation to the recombination coefficients $\alpha_e(\text{N}_2\text{H}^+)$ and $\alpha_e(\text{CH}_5^+)$ derived from merged beam (MB) cross section data. Stressed throughout the paper is the need to appreciate the chemical and physical processes which can occur in the afterglow and which may distort α_i determinations. Tentative explanations are given for the differing values of α_i and α_e obtained from FALP, SA, and MB experiments.

I. INTRODUCTION

Dissociative recombination is an important loss process for ionization in most laboratory plasmas and also in natural plasmas such as the Earth's ionosphere and interstellar gas clouds (for a discussion of these see Refs. 1-4). The temperatures [T_e (= electron), T_i (= ion), T_g (= gas)] of the component species in these natural plasmas may vary both spatially and temporally and so, for worthwhile modeling of the relative abundances of these species, the temperature dependences of the rate coefficients for the various reaction processes occurring in the plasma are required. These include the temperature dependences of the coefficients for dissociative recombination α . It is important at the onset to distinguish between the α appropriate to plasmas in which $T_e = T_i = T_g$ which we designate as α_i , and those appropriate to conditions for which $T_e > T_i$, T_g which we designate as α_e . Much work has been carried out by Biondi and his colleagues⁵⁻¹⁰ to determine both α_i and α_e for many recombination reactions using the stationary afterglow (SA) technique. Dissociative recombination has also been studied in ion trap experiments^{11,12} and merged beam (MB) experiments^{13,14} but in both of these experiments the cross sections for recombination σ_e are determined as a function of electron-ion center-of-mass energy, and then α_e values are derived from these σ_e data.

Most of the SA measurements of α_i have been obtained over the approximate temperature range 200-450 K, and those of α_e at a $T_g \sim 300$ K and up to $T_e \sim 2000$ K. Ion trap and merged beam data are obtained at center-of-mass energies in excess of about 0.1 eV. The long storage times in the

ion trap allow for internal relaxation of the molecular positive ions but the ions in the MB experiments are, in most cases, in indeterminate states of internal excitation (both rotational and vibrational¹⁴). The data obtained from these nonthermal experiments are very useful for investigating the fundamental nature of electron-ion interactions; however they cannot be used with confidence to derive α_e values appropriate to low temperatures for use in ion-chemical models of interstellar gas clouds.

Recently we have developed our flowing afterglow/Langmuir probe (FALP) technique to study electron-ion dissociative recombination¹⁵ (having previously used it for extensive studies of ion-ion recombination,¹⁶ and quite recently to study electron attachment¹⁷). The FALP technique can be applied to the study of these various reaction processes within the approximate temperature range 80 to 600 K under truly thermalized conditions. In our first studies of dissociative recombination we measured α_i for O_2^+ , NO^+ , and NH_4^+ over the temperature range 200 to 600 K.¹⁵ Now we have determined α_i at 95 and 300 K for the important interstellar ions H_3^+ (and D_3^+), N_2H^+ (and N_2D^+), HCO^+ (and DCO^+), and CH_5^+ . The data obtained are presented and discussed in this paper.

II. EXPERIMENTAL

Details of the FALP technique have been given in previous papers^{18,19} and in a recent review.¹⁶ The application of the technique to the determination of α_i is described in detail in a very recent paper.¹⁵ Briefly, the approach is as follows. An upstream microwave discharge in helium carrier gas (pressure ~ 0.5 to ~ 1.0 Torr) results in the production of an afterglow plasma along the length of the flow tube (~ 1 m

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long, ~ 8 cm in diameter). The upstream region of the afterglow comprises electrons, He^+ and He_2^+ ions, and neutral metastable atoms He^m , in addition to the ground state helium carrier gas atoms. It is then necessary to convert this He^+ , He_2^+ , and He^m plasma to one containing only the molecular ion for which the α_i is to be determined. This is achieved by adding a sufficient quantity of an appropriate molecular ion source gas (or vapor) to the afterglow via a downstream inlet port. Details of the ion chemistry involved in the production of each ion species included in these measurements of α_i are given in the next section. The α_i are then derived from measurements of the electron density n_e along the axis of the afterglow column (z coordinate) using a movable Langmuir probe.^{18,20} When recombination is the dominant loss process for ionization then a plot of n_e^{-1} vs z is linear and α_i is derived from the slope of the line. The reaction time is related to z via the plasma flow velocity v_p , which is readily determined.²¹ Recombination loss is enhanced and diffusion loss is inhibited by high n_e and high helium pressure, respectively. Typical initial values of n_e in these experiments were $(2-4) \times 10^{10} \text{ cm}^{-3}$ (for further details see Ref. 15). Measurements were carried out at room temperature and also at 95 K by cooling the flow tube and carrier gas with liquid nitrogen.

III. RESULTS

A. Measurement of $\alpha_i(\text{O}_2^+)$ at 95 K and general discussion of the ion chemistry

Since these studies of α_i were the first we have carried out at very low temperature, we first chose to study $\alpha_i(\text{O}_2^+)$ because it has been previously studied in detail at higher temperatures using a variety of techniques (including the FALP) and the temperature dependence has been well established between 200 and 600 K as $\alpha_i(\text{O}_2^+) \sim T^{-0.7}$.¹⁵ Measurements at 95 K had to be made very cautiously to avoid the creation of significant concentrations of O_4^+ ions in the afterglow via the three-body association of O_2^+ with O_2 . Such association reactions are promoted by low temperatures and by large number densities of the reactant gas (O_2) and the third body (He). They are potentially a source of serious errors in α_i measurements because the α_i for the dimer (cluster) ions are known to be larger than those for the common diatomic ions.⁶ The rate coefficient for the reaction



has been measured over a wide temperature range [$k(1) = 2(-29) \text{ cm}^6 \text{ s}^{-1}$ at 95 K²²] and therefore the permissible maximum concentration of O_2 in the afterglow can be determined. Careful use of the downstream mass spectrometer, which is an essential part of the FALP, confirmed for the conditions under which $\alpha_i(\text{O}_2^+)$ was determined, that O_4^+ ions were always present in the afterglow but in very small concentrations relative to O_2^+ . Of course, the relative mass spectrometer signals of O_2^+ and O_4^+ at the entrance to the downstream sampling orifice will not necessarily be representative of the relative O_2^+ and O_4^+ number densities upstream in the recombining plasma because of the differential diffusion and recombination rates of these ions. However, the flexibility of the FALP experiment is such that the reac-

tion (recombination) zone can be moved to within a few cm. of the sampling orifice by introducing the O_2 into an inlet port at this position rather than at the usual position (which is 57 cm from the sampling orifice). Also, the ionization density in the afterglow can be varied and accurately measured over several orders of magnitude (from about 10^{11} to about 10^7 cm^{-3}). Thus at low n_e , recombination of both O_2^+ and O_4^+ is insignificant and then the ion-molecule chemistry can be investigated and the O_2 flow adjusted to be sure that O_4^+ is not produced in significant concentrations in the afterglow. These kinds of checks were routinely carried out in all of the α_i studies described in this paper.

The value of $\alpha_i(\text{O}_2^+)$ obtained at 95 K was $4.8(-7) \text{ cm}^3 \text{ s}^{-1}$. This is plotted in Fig. 1 together with the previous FALP data obtained at higher temperatures. Clearly the $T^{-0.7}$ power law variation well describes $\alpha_i(\text{O}_2^+)$ over the wider temperature range 95 to 600 K. Actually the 95 K point lies slightly above the line and, although within the estimated errors, it might be the result of the presence of a very small concentration of O_4^+ . The errors on these measurements are quoted in the caption to Table I.

The determination of α_i for H_3^+ , HCO^+ , N_2H^+ , and CH_5^+ involved first the creation of H_3^+ as the dominant ion species in the afterglows, and the determination of $\alpha_i(\text{H}_3^+)$. Then the H_3^+ ions were converted to the other species via proton transfer reactions and their respective α_i determined (see later). The H_3^+ (and D_3^+) were created by adding relatively large concentrations of H_2 (or D_2) to the afterglows. At 300 K, prior to the addition of H_2 , the majority ions in the afterglow were He_2^+ together with smaller concentrations of He^+ and He^m . (The He^m concentration could be readily measured at 300 K by adding excess Ar to the afterglow and then measuring the increase in n_e using the Langmuir probe¹⁸; however this could not be done at 95 K because of Ar condensation.) On adding sufficient H_2 the following reactions occurred:

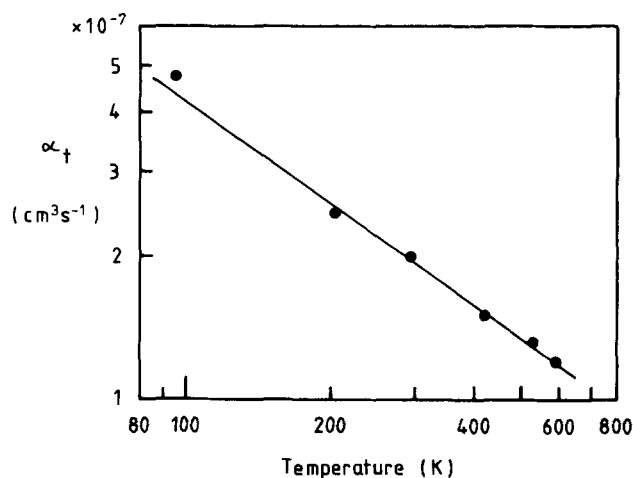
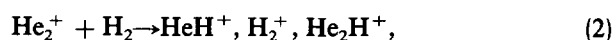


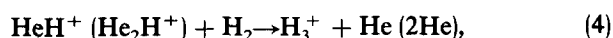
FIG. 1. FALP measurements of $\alpha_i(\text{O}_2^+)$ at several temperatures T . The solid line describes the power law relationship $\alpha_i(\text{O}_2^+) = 2(-7)(300/T)^{0.7} \text{ cm}^3 \text{ s}^{-1}$, which is a good fit to the data points over a temperature range which is unusually wide for dissociative recombination studies. The data points at temperatures of 200 K and above are from our previous FALP study (Ref. 15).

TABLE I. Values of the dissociative recombination coefficients α_i , obtained in the FALP for the ion species indicated at 95 and 300 K. The units are $\text{cm}^3 \text{s}^{-1}$ and, e.g., $2.9(-7)$ means $2.9 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$. Also given are the stationary afterglow (SA) data for H_3^+ (Ref. 7) and HCO^+ (Ref. 8) at the temperature indicated, and the derived rate coefficients α_e from merged beam (MB) data for N_2H^+ (Ref. 40) and CH_5^+ (Ref. 41). The estimated absolute errors for the FALP values of α_i (N_2H^+) and α_i (CH_5^+) are $\pm 15\%$ at 300 K and $\pm 20\%$ at 95 K. For α_i (HCO^+) the errors are somewhat greater at 300 K ($\pm 20\%$) because of the smaller range of n_e from which the α_i was obtained (see Fig. 2) and the correspondingly greater uncertainty in the slope of the reciprocal density plot (see Fig. 3). The total errors in α_i arise largely from the uncertainty in the area of the Langmuir probe ($\sim \pm 10\%$) which reflects directly into the error in n_e and therefore α_i . When this systematic error is allowed for the relative errors in the α_i values are much smaller ($\sim \pm 10\%$).

Ion	FALP data		Previous data			
	95 K	300 K	205 K	300 K	450 K	
H_3^+	$\leq 2(-8)$	$\leq 2(-8)$	$2.9(-7)$	$2.3(-7)$	$2.0(-7)$	SA
D_3^+	$\leq 2(-8)$	$\leq 2(-8)$	
HCO^+	$2.9(-7)$	$1.1(-7)$	$3.3(-7)$	$2.0(-7)$...	SA
DCO^+	$2.6(-7)$	
N_2H^+	$4.9(-7)$	$1.7(-7)$		$7.5(-7) (300/Te)^{0.5}$		
N_2D^+	$4.4(-7)$...				MB
CH_5^+	$1.5(-6)$	$1.1(-6)$		$7.0(-7) (300/Te)^{0.5}$		MB



Reaction (2) is very efficient at 300 K [$k = 5.3(-10) \text{cm}^3 \text{s}^{-1}$]²³ and, as expected, is seen to be so in our experiment at 95 and 300 K. The rate coefficient for the Penning reaction (3) varies markedly with temperature above 300 K²⁴ (the metastable atoms are mostly 2^3S and not 2^1S). $k(3)$ has been measured to be $3(-11) \text{cm}^3 \text{s}^{-1}$ at 300 K and may fall to about $1(-13) \text{cm}^3 \text{s}^{-1}$ at 95 K.²⁴ This required the presence of substantial concentrations of H_2 in the afterglow at 95 K to ensure that the He^m were totally destroyed (any source of ionization in the afterglow is readily detected using the Langmuir probe). The product ions of reactions (2) and (3) then undergo reactions with H_2 to generate H_3^+ .

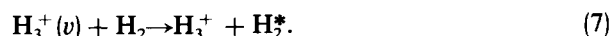


The rate coefficients for both of these reactions are large [$k(4) = 1.5(-9) \text{cm}^3 \text{s}^{-1}$ at 300 K²⁵; $k(5) = 2.1(-9) \text{cm}^3 \text{s}^{-1}$ at 300 K²⁶]. The mass spectrometer was used to confirm that H_3^+ was the dominant ionic species in the afterglow. However a small percentage of He^+ was observed to be present at 300 K. This is because He^+ is relatively unreactive with H_2 ²⁷ and because the association reaction:



is not sufficiently rapid at 300 K and at a helium pressure of 1 Torr to convert all the He^+ to He_2^+ .²⁸ However, at 95 K, reaction (6) is more rapid since $k(6)$ is larger,²⁹ the number density of He atoms in the afterglow is greater and the plasma flow velocity is smaller (the reaction time is longer) and so the He^+ ions are totally converted to molecular ions. (Indeed, a small signal at mass 12 amu, probably He_3^+ , is observed in the absence of H_2 presumably resulting from the further reaction of He_2^+ with He). So no He^+ is evident in the afterglow at 95 K and therefore on addition of sufficient H_2 , all the He_2^+ and He^m are destroyed and H_3^+ is readily produced. Note that the H_3^+ produced in reaction (5) is ini-

tially vibrationally excited^{30,31} but in the presence of H_2 it is deexcited³² via the reaction



The rate of the deexcitation of $\text{H}_3^+ (\nu)$ of course depends on $k(7)$ and the H_2 concentration in the afterglow [further referred to in relation to the $\alpha_i(\text{H}_3^+)$ estimates discussed below]. At large H_2 concentrations and at 95 K, the association reaction



was observed to occur, generating H_5^+ . The H_5^+ was detected by the mass spectrometer in increasing concentration relative to H_3^+ as the H_2 concentration was increased. In a separate SIFT experiment we measured the rate coefficient of reaction (8) to be $2(-29) \text{cm}^6 \text{s}^{-1}$ at 80 K. This number was useful in interpreting the α_i data for $\text{H}_3^+/\text{H}_5^+$ plasmas which clearly indicated that $\alpha_i(\text{H}_5^+)$ was much greater than $\alpha_i(\text{H}_3^+)$, as has previously been indicated by SA measurements (see below).

Now that the basic ion chemistry which leads to the production of H_3^+ (and H_5^+) in these afterglows has been discussed, we can proceed to describe the α_i determinations for the various ionic species. It will be very evident that satisfactory interpretation of the surprising data relating to the $\alpha_i(\text{H}_3^+)$ studies relies a great deal on an understanding of the ion chemistry and the physics occurring in these plasmas.

B. The n_e vs z data: Determination of α_i for the various reactions

Having created the H_3^+ plasma, n_e was measured as a function of z and the data obtained at 300 K are shown as a $\ln n_e$ vs z plot in Fig. 2. Also shown are the data for HCO^+ , N_2H^+ , and CH_5^+ obtained under identical conditions of temperature, He pressure, and H_2 concentration but with smaller admixtures of CO, N_2 , and CH_4 as appropriate. This results in the production of the new ions via the proton transfer reactions

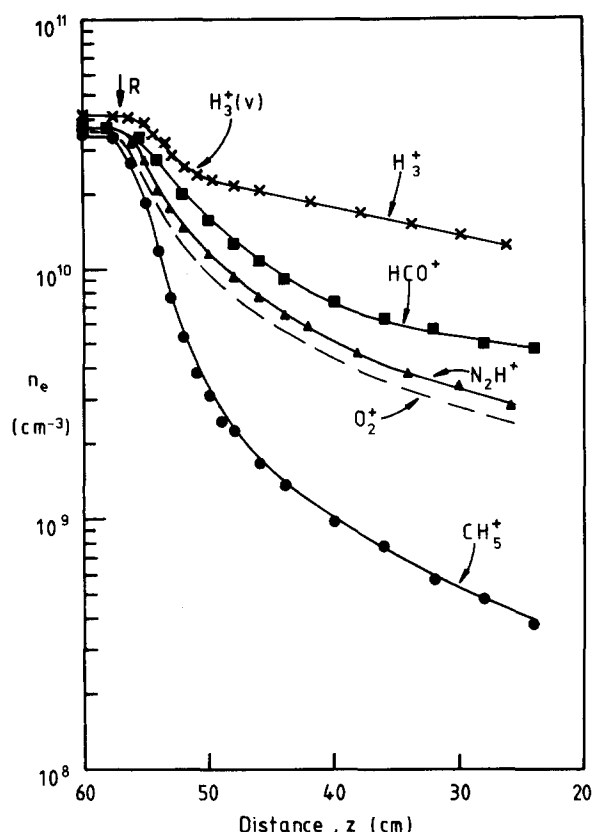
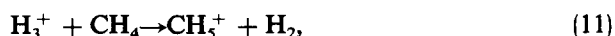
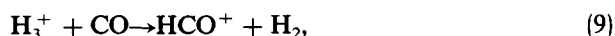


FIG. 2. Semilogarithmic plots of electron density in the afterglow n_e against z , the distance along the afterglow column as measured from the downstream mass spectrometer sampling orifice in the FALP apparatus. R indicates the position of the molecular ion source gas inlet port. The carrier gas was helium at a pressure of 1.2 Torr and the temperature was 300 K. Upstream of R , $\partial n_e/\partial z$ is small since electrons were lost from the afterglow only via ambipolar diffusion. Downstream of R , $\partial n_e/\partial z$ is larger due to the occurrence of dissociative recombination in the H_3^+ , HCO^+ , N_2H^+ , and CH_5^+ afterglow plasmas. The magnitudes of the $\partial n_e/\partial z$ for these plasmas indicate that $\alpha_i(CH_5^+) > \alpha_i(N_2H^+) > \alpha_i(HCO^+) > \alpha_i(H_3^+)$. The dashed line without points represents the data for O_2^+ (see the text).



which are rapid at 300 K³³ and also, as expected, at 80 K.³⁴ Upstream of the H_2 /reactant gas (e.g., CO) inlet port, the z gradient of n_e , i.e., $\partial n_e/\partial z$ is small since the loss of ionization is due only to the relatively slow process of ambipolar diffusion. However, as can be seen in Fig. 2, $\partial n_e/\partial z$ increases downstream of the inlet port, remarkably so for the CH_5^+ plasma. This increase is due to the onset of dissociative recombination and it is clear from Fig. 2 that the relative α_i are in the order $\alpha_i(CH_5^+) > \alpha_i(N_2H^+) > \alpha_i(HCO^+) > \alpha_i(H_3^+)$. The good linearity of the n_e^{-1} vs z plots over appreciable ranges of n_e , at least for the N_2H^+ and CH_5^+ reactions (see Fig. 3), demonstrates the dominance of recombination loss for these reactions. Note also in Fig. 2 that for small z , i.e., well downstream of the inlet port, the semilogarithmic plots become nearly linear which is characteristic of diffusive loss. A further check that recombination is indeed responsible in each afterglow for these increases in $\partial n_e/\partial z$ is made simply by considerably reducing n_e in the afterglow, thus inhibiting

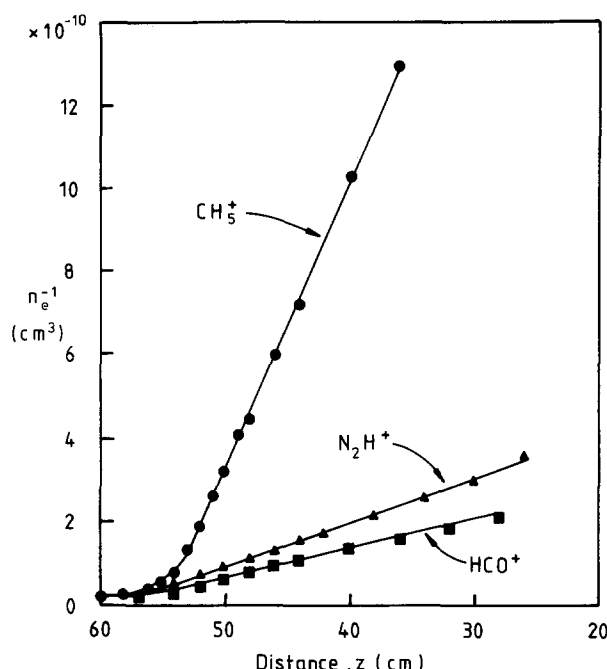


FIG. 3. Plots of reciprocal electron density, n_e^{-1} against z from the data given in Fig. 2 for the HCO^+ , N_2H^+ , and CH_5^+ afterglow plasmas. The respective α_i are obtained from the slopes of the lines. Thus $\alpha_i(CH_5^+) > \alpha_i(N_2H^+) > \alpha_i(HCO^+)$; the actual values are given in Table I.

recombination loss but without influencing diffusion loss. Under these conditions $\partial n_e/\partial z$ downstream of the inlet port reduced towards that measured upstream of the inlet port.

1. H_3^+ and D_3^+

The data obtained for D_3^+ at both 95 and 300 K were insignificantly different from those for H_3^+ . It is clear from the data in Fig. 2 that $\alpha_i(H_3^+)$ at 300 K is small, certainly considerably smaller than $\alpha_i(O_2^+)$ which at the same temperature is $2(-7) \text{ cm}^3 \text{ s}^{-1}$ [the $\alpha_i(O_2^+)$ data is represented in Fig. 2 by the dashed curve without data points]. This was a great surprise in view of previous SA data⁷ and MB data¹³ which indicated that $\alpha_i(H_3^+)$ was comparable to $\alpha_i(O_2^+)$ and that the $\sigma_e(H_3^+)$ was large. After repeating the FALP experiments several times at 300 K and also at 95 K, over a period of many weeks under a wide variety of He pressures and H_2 concentrations, we were forced to conclude that $\alpha_i(H_3^+)$ and $\alpha_i(D_3^+)$ are indeed very small at both 95 and 300 K. Recently, we have been informed by Michels³⁵ of his theoretical calculations of $\alpha_i(H_3^+)$ which indicate an infinitesimal α_i for $H_3^+(v=0)$ and that α_i only begins to become appreciable when H_3^+ is in the $v=3$ vibrational level (equivalent to about 0.9 eV of vibrational energy!) Clearly, in our experiments we expect that reaction (7) will vibrationally relax the H_3^+ and so the small $\alpha_i(H_3^+)$ indicated by our experiments is qualitatively consistent with Michels' prediction. However, recombination does occur close to the H_2 inlet port at both 95 and 300 K, albeit only to a small extent, and the question arises as to what the recombination loss is due to if it is not due to $H_3^+(v=0)$. Several factors may contribute to this small recombination loss including: (i) suprathermal electrons generated in reaction (3) which might effectively excite

H_3^+ in the interaction and hence increase $\alpha_i(\text{H}_3^+)$; (ii) vibrationally excited H_3^+ produced in reaction (5); (iii) H_3^+ ions generated in reaction (8); and (iv) impurity ions which have relatively large α_i , e.g., H_3O^+ and N_2H^+ generated from traces of H_2O and N_2 in the H_2 . At 300 K, very small signals of H_3O^+ and N_2H^+ were apparent in the mass spectrum but these represented ion densities which were far too small to be responsible for the observed recombination loss. Also production of H_5^+ at 300 K is far too slow at the concentrations of H_2 in the afterglow to account for the recombination. Electron temperature relaxation in helium at 1 Torr pressure is very efficient; we estimate that hot electrons from the Penning process will relax to thermal in about 0.1 ms.³⁶ Since recombination is apparent for about 6 cm from the inlet port (see Fig. 2), i.e., for about 0.5 ms, then "hot" electrons are not responsible and we are left with vibrationally excited H_3^+ ions as the only possible explanation. It is known that several collisions of $\text{H}_3^+(v)$ with H_2 are necessary to remove the vibrational energy from H_3^+ [reactions (7)]^{32,37} and so an equivalent rate coefficient for reaction (7) of $\sim 1(-10) \text{ cm}^3 \text{ s}^{-1}$ seems reasonable. Combining this rate coefficient with the number density of H_2 in the afterglow ($\sim 10^{14} \text{ cm}^{-3}$) indicates a time constant of ~ 0.1 ms for the vibrational relaxation process. Thus $\text{H}_3^+(v)$ could persist for a fraction of a millisecond against reaction (7) and could therefore undergo recombination on a similar timescale to that observed. Thus vibrationally excited H_3^+ could explain the observed recombination loss close to the inlet port. The occurrence of reaction (15) is direct evidence for the presence of $\text{H}_3^+(v)$.

How can $\alpha_i(\text{H}_3^+)$ be estimated from the n_e vs z data? The above argument implies that the reduction in n_e near to the inlet port is due to recombination of $\text{H}_3^+(v)$ and diffusion of both $\text{H}_3^+(v)$ and H_3^+ . The relative number density of $\text{H}_3^+(v)$ is reducing both via recombination and via collisional relaxation to H_3^+ . This very complicated situation cannot be disentangled but an estimate of an "effective recombination coefficient" α_{eff} can be obtained assuming a recombination rate law of the form $v_p \partial n_e / \partial z = \alpha_{\text{eff}} n_e n_{\text{H}_3^+(v)}$. The density of $\text{H}_3^+(v)$ is estimated as the difference between the n_e values ($n_{\text{H}_3^+(v)} + n_{\text{H}_3^+}$) at large z and the values n_e at small z ($= n_{\text{H}_3^+}$) projected back to large z . Thus, $\alpha_{\text{eff}} \sim 7(-8) \text{ cm}^3 \text{ s}^{-1}$ and this clearly must exceed $\alpha_i(\text{H}_3^+)$ and be smaller than $\alpha(\text{H}_3^+(v))$. An upper limit to $\alpha_i(\text{H}_3^+)$ can be estimated by assuming that the decrease in n_e downstream of the recombination zone is due entirely to recombination of H_3^+ . This indicates $\alpha_i(\text{H}_3^+)$ to be $\leq 2(-8) \text{ cm}^3 \text{ s}^{-1}$. Actually, the $\ln n_e$ vs z plot is almost linear at small z which is indicative of diffusive loss alone and indeed the exponential loss rate is very close to that expected on the basis of the known diffusion coefficient for H_3^+ ions in helium.³⁸ This implies that very little recombination of H_3^+ is occurring in the afterglow even at these large n_e and therefore that the upper limit to $\alpha_i(\text{H}_3^+)$ is certainly less than $2(-8) \text{ cm}^3 \text{ s}^{-1}$. Unfortunately, we cannot further quantify this. It seems therefore that Michels' conclusion that $\alpha_i(\text{H}_3^+)$ is infinitesimal is vindicated.

At 95 K, and for low concentrations of H_2 , a similar reduction in n_e occurred near to the inlet port which we

again attribute to the presence of a small fraction of $\text{H}_3^+(v)$ in the afterglow. Thus, a small $\alpha_i(\text{H}_3^+)$ is indicated at this temperature also [$\leq 2(-8) \text{ cm}^3 \text{ s}^{-1}$]. However, on the addition of larger flows of H_2 , n_e reduced more rapidly with z and this correlated with the appearance of H_5^+ at the mass spectrometer. Clearly H_5^+ was being produced via reaction (8) and recombining at a more rapid rate than H_3^+ which is in qualitative agreement with the previous SA findings.⁷ With the present configuration of the FALP reactant gas flow system we were not able to add sufficient H_2 to convert all the H_3^+ to H_5^+ and so were not able to determine $\alpha_i(\text{H}_5^+)$ to a worthwhile accuracy. A crude, approximate analysis of the n_e vs z curve at the maximum H_2 concentration which could be obtained ($7 \times 10^{14} \text{ cm}^{-3}$) together with our measured value of the rate coefficient for reaction (8) indicates only a lower limit for $\alpha_i(\text{H}_5^+)$ of $\sim 2(-7) \text{ cm}^3 \text{ s}^{-1}$ at 95 K. The SA value⁷ for $\alpha_i(\text{H}_5^+)$ at 205 K is $(3.6 \pm 1.0)(-6) \text{ cm}^3 \text{ s}^{-1}$. The major difference between the FALP and SA values for $\alpha_i(\text{H}_3^+)$ is perplexing. We have no convincing explanation for this except to tentatively suggest that the presence of a small fraction of H_5^+ ions in the SA could have resulted in a larger $\alpha_i(\text{H}_3^+)$ because of the much larger $\alpha_i(\text{H}_5^+)$ (production of H_5^+ is promoted by the high pressures at which the SA experiments were carried out).

The emission spectra of H_3 and D_3 have been identified by Herzberg³⁹ from hollow cathode discharges in H_2 and D_2 , respectively. These were assumed to originate from recombining H_3^+ and D_3^+ . If this were the case then the recombining ions were probably vibrationally excited. However it was noted that the emission intensities from H_3 and D_3 were greatly enhanced when the cathode was cooled with liquid nitrogen and so we suggest that the H_3 and D_3 were most probably produced from the dissociative recombination of H_5^+ and D_5^+ , e.g.,



2. HCO^+ and DCO^+

The addition of relatively small concentrations of CO to the H_3^+ (and D_3^+) afterglows resulted in an immediate enhancement of the n_e gradient. CO addition initiates the fast proton transfer reaction (9) which has a rate coefficient at both 80 and 300 K of $1.8(-9) \text{ cm}^3 \text{ s}^{-1}$,³⁴ and so H_3^+ is rapidly converted to HCO^+ (similarly for DCO^+). Clearly $\alpha_i(\text{HCO}^+) > \alpha_i(\text{H}_3^+)$ [and indeed $\alpha_i(\text{HCO}^+) > \alpha_{\text{eff}} > \alpha_i(\text{H}_3^+)$]. A plot of n_e^{-1} vs z for the HCO^+ data at 300 K is shown in Fig. 3. The range of linearity of this plot is limited because of the relatively small $\alpha_i(\text{HCO}^+)$ of $1.1(-7) \text{ cm}^3 \text{ s}^{-1}$ and this is reflected in the somewhat greater uncertainty we place on $\alpha_i(\text{HCO}^+)$ at 300 K (see Table I). At 95 K, $\alpha_i(\text{HCO}^+)$ and $\alpha_i(\text{DCO}^+)$ are measured to be $2.9(-7)$ and $2.6(-7) \text{ cm}^3 \text{ s}^{-1}$, respectively.

Our $\alpha_i(\text{HCO}^+)$ at 300 K is significantly smaller than the SA value⁸ (see Table I) but not greatly so when the combined errors of both experiments are taken into account. However, our value at 95 K is slightly smaller than the SA value at the higher temperature of 205 K. The larger value derived from the higher pressure SA experiment may be due

to the production of small concentrations of the association ion HCO^+ . CO which presumably will have a larger α_i . This suggestion arises from our observation that for large flows of CO in our experiment, small signals of HCO^+ . CO were detected by the mass spectrometer. This prompted us to measure with our SIFT the rate coefficient for the reaction

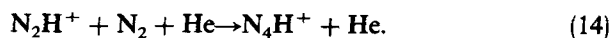


At 80 K, $k(13) = 1.1 (-29) \text{ cm}^6 \text{ s}^{-1}$. Knowing this rate coefficient we were able to estimate the maximum permissible value of the CO concentration in the afterglow for insignificant production of $\text{HCO}^+ \cdot \text{CO}$. Safeguards of this kind are very important in this type of work since it is all too easy to fail to detect mass spectrometrically small signals of weakly bonded ions such as $\text{HCO}^+ \cdot \text{CO}$ because these ions are so readily collisionally dissociated in the mass spectrometer sampling system.

Within the limitations of only two data points and assuming a power law dependence, the present data indicate that $\alpha_i(\text{HCO}^+)$ varies approximately as T^{-1} between 95 and 300 K.

3. N_2H^+ and N_2D^+

The addition of small concentrations of N_2 to the H_3^+ (or D_3^+) plasmas again resulted in an obvious enhancement in the n_e gradient (see Fig. 2). This is a result of the production of N_2H^+ (or N_2D^+) via the fast reaction (10). The plot of n_e^{-1} vs z for the N_2H^+ data at 300 K is shown in Fig. 3 and the linearity of the plot is indicative of recombination loss. The value of $\alpha_i(\text{N}_2\text{H}^+)$ thus obtained is $1.7 (-7) \text{ cm}^3 \text{ s}^{-1}$. At 95 K, $\alpha_i(\text{N}_2\text{H}^+)$ and $\alpha_i(\text{N}_2\text{D}^+)$ are measured to be $4.9 (-7)$ and $4.4 (-7) \text{ cm}^3 \text{ s}^{-1}$, respectively. That $\alpha_i(\text{N}_2\text{D}^+)$ is somewhat smaller than $\alpha_i(\text{N}_2\text{H}^+)$ is not significant within error but it is intriguing that $\alpha_i(\text{DCO}^+)$ is also smaller than $\alpha_i(\text{HCO}^+)$ by about the same percentage at the same temperature. Perhaps there is a small isotope effect in these cases. $\alpha_i(\text{N}_2\text{H}^+)$ at 95 K is three times greater than the 300 K value and so a $\sim T^{-1}$ variation for $\alpha_i(\text{N}_2\text{H}^+)$ is also indicated. Again it must be pointed out that large flows of N_2 promoted the association reaction



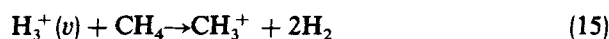
We determined $k(14)$ using the SIFT to be $2.8 (-29) \text{ cm}^6 \text{ s}^{-1}$ at 80 K [i.e., about three times greater than the corresponding $\text{HCO}^+ + \text{CO}$ reaction (13)]. In this case the strongly bound N_4H^+ ion is produced. Again, $k(14)$ sets the upper limit to the concentration of N_2 which is permissible in the afterglow.

No SA value has been published for $\alpha_i(\text{N}_2\text{H}^+)$ but electron recombination of N_2H^+ has been studied using the MB technique.⁴⁰ A much larger value for $\alpha_e(\text{N}_2\text{H}^+)$ at 300 K of $7.5 (-7) \text{ cm}^3 \text{ s}^{-1}$ has been derived from these MB $\sigma_e(\text{N}_2\text{H}^+)$ data. While it is not too profitable to compare these ion beam data with truly thermal data, a larger value of $\sigma_e(\text{N}_2\text{H}^+)$ might be expected if vibrationally excited N_2H^+ has a relatively large σ_e since it is known that N_2H^+ is readily vibrationally excited (from drift tube studies of endoergic proton transfer⁴²) and so it is very likely that $\text{N}_2\text{H}^+(v)$ is a major component of the ion beam. In the FALP, $\text{N}_2\text{H}^+(v)$ is

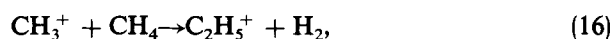
rapidly relaxed in proton transfer reactions analogous to reaction (7).

4. CH_5^+

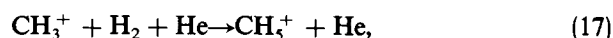
The addition of small concentrations of CH_4 to the H_3^+ plasma resulted in a rapid increase in the n_e gradient (Fig. 2). The mass spectrometer indicated that CH_5^+ was the dominant ion ($> 95\%$) but also small signals of CH_3^+ and C_2H_5^+ were evident. The CH_5^+ is formed via the proton transfer reaction (11) and the appearance of CH_3^+ was a clear indicator of the presence of $\text{H}_3^+(v)$, since it is known that the reaction



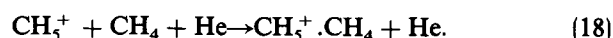
is rapid.⁴³ This then is direct evidence for the existence of small concentrations of $\text{H}_3^+(v)$ which we deduced earlier in relation to the $\alpha_i(\text{H}_3^+)$ studies. The C_2H_5^+ ions are formed via the rapid two-body reaction



which has a rate coefficient of $1.2 (-9) \text{ cm}^3 \text{ s}^{-1}$ at 300 K⁴⁴ and presumably also at 95 K. CH_3^+ is also converted to CH_5^+ by the three-body association reaction



which thus enhances the CH_5^+ population in the plasma. Reaction (17) is known to be quite rapid at 80 K⁴⁵ and therefore at 95 K at the pressure conditions (~ 1 Torr) of the present experiments. Again, it must be mentioned that association of the ion under study (CH_5^+) with its parent (CH_4) occurs at low temperatures:



The rate coefficient for reaction (18) is $2.5 (-28) \text{ cm}^6 \text{ s}^{-1}$ at 80 K, as measured in the SIFT,⁴⁶ and so again the concentration of CH_4 in the plasma at the low temperature had to be minimized.

It is worthy of note here that association reactions of HCO^+ and N_2H^+ with H_2 are very slow [$< 5 (-30) \text{ cm}^6 \text{ s}^{-1}$ in He at 80 K] and that association of CH_5^+ with H_2 has not been observed even at 80 K in our SIFT. So for the concentrations of H_2 used in these experiments these reactions are unimportant.

The n_e^{-1} vs z data at 300 K are plotted in Fig. 3 and $\alpha_i(\text{CH}_5^+)$ obtained from the slope is $1.1 (-6) \text{ cm}^3 \text{ s}^{-1}$. At 95 K, $\alpha_i(\text{CH}_5^+)$ has increased to $1.5 (-6) \text{ cm}^3 \text{ s}^{-1}$. This relatively small increase in $\alpha_i(\text{CH}_5^+)$ and the correspondingly weak temperature dependence ($\sim T^{-0.3}$) is typical of α_i which are relatively large such as those for cluster ions.^{9,10} It is perhaps significant that the value for $\alpha_e(\text{CH}_5^+)$ at 300 K derived from MB data is rather close to our $\alpha_i(\text{CH}_5^+)$ [actually slightly smaller, $\alpha_e(\text{CH}_5^+) = 7 (-7) \text{ cm}^3 \text{ s}^{-1}$].⁴¹ This unusually good agreement between FALP data and MB predictions may be due to the relatively weak temperature (energy?) dependence of α_i (and α_e) and because any residual excitation in the CH_5^+ ion beam would presumably not greatly influence the σ_e value for this particular ion since, on the basis of the FALP data, σ_e would be expected to be large even for ground state ions.

IV. SUMMARY AND CONCLUSIONS

The very small α_i for ground vibrational state H_3^+ ions (and D_3^+ ions), indicated by these experiments runs contrary to previous experimental results but is consistent with recent theoretical predictions by Michels. Thus H_3^+ is only the second molecular ion which has so far been shown to recombine very slowly, the other well-known case being He_2^+ .⁵ However, recombination of H_3^+ ions does occur when they are vibrationally excited, again in accordance with theoretical predictions. Emission spectra of neutral H_3 and D_3 molecules have been observed from H_2 (and D_2) discharges. This could be due to recombination of H_3^+ (ν) but was most likely due to recombination of H_5^+ (and D_5^+). That $\alpha_i(H_3^+)$ is so small is contrary to the usual assumptions made in interstellar ion-chemical models and has major effects on the predictions of these models.^{34,47,48}

The α_i for HCO^+ , N_2H^+ , and CH_5^+ have magnitudes as expected on the basis of previous SA data for a variety of ionic species. The $\alpha_i(CH_5^+)$ is the largest of the three and increases more slowly with decreasing temperature than do $\alpha_i(HCO^+)$ and $\alpha_i(N_2H^+)$. These data illustrate a trend which is gradually emerging, i.e., fast recombination reactions have weaker inverse temperature dependences than slower reactions. Discrepancies between data obtained from collision-dominated thermal experiments such as the SA and the FALP and the nonthermal merged beam data are not unexpected not least because of the different internal states of the recombining ions. The agreement between the SA and FALP results for individual reactions is generally good, except possibly at low temperatures when the SA values are sometimes a little larger. This might be due to the presence of small fractional concentrations of cluster ions in the SA which is operated at higher pressures than the FALP and which promotes the formation of association ions (as does low temperature). The major discrepancy between the $\alpha_i(H_3^+)$ determined in the SA and the FALP is difficult to explain. Clearly, further work and thought are necessary to resolve this perplexing discrepancy.

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