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Laser induced fluorescence and vacuum ultraviolet spectroscopic studies of H-atom production in the dissociative recombination of some protonated ions

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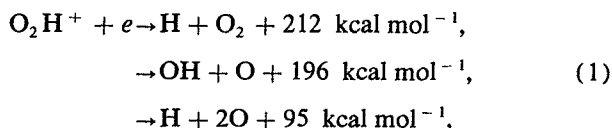
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The flowing afterglow technique, coupled with laser induced fluorescence (LIF) and vacuum ultraviolet (vuv) absorption spectroscopy, has been used to determine the fractional H-atom contributions, f_H , to the product distributions for the dissociative recombination of a series of protonated ions (N_2H^+ , HCO^+ , HCO_2^+ , N_2OH^+ , $OCSH^+$, H_2CN^+ , H_3O^+ , H_3S^+ , NH_4^+ , and CH_5^+) with electrons. The measurements were made at 300 K in two separate ways in two laboratories by (i) directly determining the H-atom number density using vuv absorption spectroscopy at the L_α (121.6 nm) wavelength and (ii) converting the H atoms to OH radicals using the reaction $H + NO_2 \rightarrow OH + NO$ followed by LIF to determine the OH number density. The agreement between the two techniques is excellent and values of f_H varying from ~ 0.2 (for $OCSH^+$) to 1.2 (for CH_5^+) have been obtained showing that in some of the cases recombination can lead to the ejection of two separate H atoms. Comparison of the oxygen/sulphur analogs, $HCO_2^+/OCSH^+$ and H_3O^+/H_3S^+ showed that the f_H values were very different. Possible reasons for these differences are discussed. Comparison is also made with the available theory.

I. INTRODUCTION

Dissociative recombination of molecular positive ions with electrons is an important process in ionized gases and plasmas, because it results both in the loss of ionization and the production of many new, and often very reactive, radical neutral species. Therefore, if the gas phase ion chemistries of media such as laser plasmas,¹ combustion flames,² interstellar gas clouds,³ and planetary atmospheres⁴ are to be understood, then rate coefficients, α , and neutral product distributions are required for the recombination of a large number of positive ions. The process of dissociative recombination is exemplified by the reaction



where several product channels are energetically possible including the total dissociation of the neutralized molecule. The α values have been determined for a wide variety of ions (see the review Refs. 5 to 7) using stationary afterglows,⁸

merged beams,⁹ and flowing afterglows¹⁰ and in some cases as a function of temperature.¹¹ However, experiments concerning the recombination products have only been performed for the ions H_3^+ ,¹¹ O_2^+ ,^{12,13} NO^+ ,¹⁴ CO_2^+ ,^{15,16} and H_2O^+ ¹⁷ and N_2^+ .¹⁸ Only in the cases of H_3^+ ($v=0$) and N_2^+ ($v=0$ and $v=1$) were the states of excitation of the recombining ion known.^{11,18} Also, only in the cases of H_3^+ and CO_2^+ has a molecular product, H_2 and CO respectively, been detected.^{11,15,16} Some theoretical effort¹⁹⁻²¹ has been devoted to predicting the products of dissociative recombination reactions, however, this is a difficult area and requires a knowledge of both the ionic and neutral potential curves, few of which are available.²² Thus, there is a great need for experimental data concerning the atomic and molecular products for ions in known states of excitation (preferably the ground vibronic state) for modeling of real plasma situations and to guide theory.

Recently, a concerted effort has been made to probe flowing afterglow plasmas using vacuum ultraviolet (vuv) absorption and laser induced fluorescence (LIF) spectroscopy. These techniques have been used to quantitatively determine the OH contribution to the product distributions for the dissociative recombination of HCO^+ , O_2H^+ , HCO_2^+ , N_2OH^+ , and H_3O^+ .²³⁻²⁵ The contributions of $OH(v=0)$ and $OH(v>0)$ have been separately determined and these combined data are reproduced in Table I (together with the

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TABLE I. H atom and OH radical fractional contributions, f_H and f_{OH} , at 300 K to the product distributions for the dissociative recombination with electrons of the protonated ions indicated. The values of f_{OH} have been taken from Ref. 24. The precursor ions from which the recombining ions were produced are indicated.

Precursor ions	f_{OH}				f_H		
	H_3^+	H_3^+	HCO^+	Ar^+	H_3^+	Kr^+	Xe^+
Recombining ions							
N_2H^+	...	1 ^a	^b
HCO^+	0	1 ^a
O_2H^+	0.60	0.40 ^c
HCO_2^+	0.34	0.73	0.83
N_2OH^+	0.31 ^d	0.70	0.98
$OCSH^+$	0	0.1	0.31
H_2CN^+	0.63
H_3O^+	0.65	0.80	0.87	1.14	1.16	1.04	...
H_3S^+	...	0.48 ^e	0.38	0.19	0.24 ^f
NH_4^+	0.90	...	1.03	1.36	1.03
CH_5^+	...	1.16	1.19	1.19 ^g	...
	LIF				vuv.		

^a From Ref. 25.

^b Calibration reaction for the vuv studies.

^c Deduced from f_{OH} since an H atom is a product when OH is not; see Eq. (1). This is a calibration reaction for the LIF studies.

^d This value may contain a contribution due to $NH + NO$, see text.

^e This value has been corrected for the secondary reaction $OH + H_2S \rightarrow SH + H_2O$.

^f Calibrated using the NH_4^+ recombination reaction with H_3^+ as the precursor ion.

^g Calibrated using the CH_5^+ recombination reaction with H_3^+ as the precursor ion.

results of the present study). However, this only partly specifies the product distributions and, in order for these distributions to be completely determined, the contributions of possible atomic recombination products also need to be obtained. As a step towards this goal, we have obtained the H-atom contributions to the product distributions for the above protonated ions as well as several other protonated species, ($OCSH^+$, H_2CN^+ , H_3S^+ , NH_4^+ , and CH_5^+). These measurements were made in a coordinated collaborative program carried out at the University of Birmingham, UK and the University of Rennes, France. In both laboratories, the flowing afterglow technique was used to generate plasmas containing only the recombining ions of interest and electrons. However, different spectroscopic techniques involving LIF (Birmingham) and vuv absorption (Rennes) were used to detect the H atoms.

II. EXPERIMENTAL

The basic flowing afterglow apparatus, which is common to both laboratories, has been described in detail previously and will only be briefly discussed here.^{10,13,26} A thermalized flowing afterglow plasma is created along the length of a flow tube by producing a discharge in a microwave cavity upstream in the helium carrier gas (see Figs. 1 and 2). At the pressure of 1.6 Torr used in these experiments (a lower pressure of 1 Torr was used in a few specific experiments; see Sec. II C), a plasma containing He_2^+ ions, helium metastable atoms (He^m), and electrons can readily be produced.

The He^m are destroyed by introducing a rare gas into the afterglow, thus creating atomic rare gas ions and more electrons by Penning ionization. The He_2^+ ions also react with the rare gas, again producing atomic rare gas ions, and thus a rare gas ion/electron plasma (e.g., Ar^+/e) is created. The plasma decays only slowly along the flow tube by ambipolar diffusion, as confirmed using a movable Langmuir probe to determine the electron number density, n_e , as a function of axial position, z , along the flow tube (for this situation a linear plot of $\ln n_e$ vs z is obtained). Typical n_e range from 10^{11} to 10^9 cm⁻³. Ar^+ was used as a precursor rare gas ion to the recombining ions in both the experiments employing vuv spectroscopic detection and those employing LIF and therefore, this situation will be discussed first. Hydrogen is added to the Ar^+/e plasma and an H_3^+/e plasma is rapidly created by the reaction $Ar^+ + H_2$ which gives $ArH^+ + H$ and $H_2^+ + Ar^{28}$ followed by $ArH^+ + H_2 \rightarrow H_3^+ + Ar$ and $H_2^+ + H_2 \rightarrow H_3^+ + H$. Note that, in these reactions, an H atom is produced for every H_3^+ ion. A recombining plasma composed of the ion of interest, MH^+ , is then rapidly produced by the proton transfer reaction $H_3^+ + M \rightarrow MH^+ + H_2$ following the addition of the reactant gas M (where $M = N_2$, CO, O_2 , CO_2 , N_2O , OCS, H_2O , H_2S , NH_3 , and CH_4). Sufficient M is added to vibrationally relax $MH^+(v)$ by the rapid reaction $MH^+(v) + M \rightarrow MH^+(v=0) + M$, and perhaps also by H_2 , prior to recombination.²³ Further downstream, after recombination of the MH^+/e plasma, the H-atom number density is determined in different ways

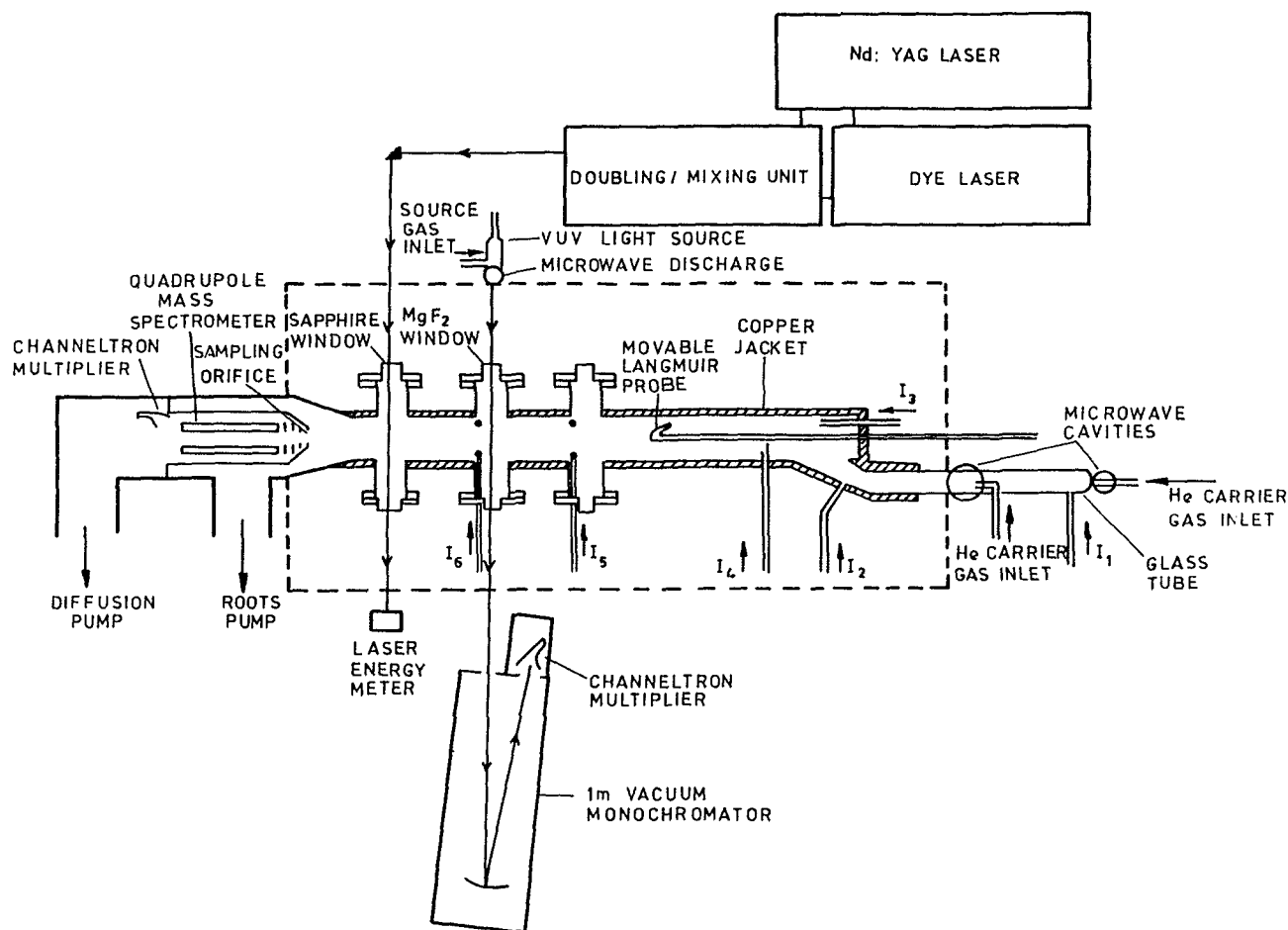


FIG. 1. A schematic diagram of the Birmingham flowing afterglow illustrating the mass spectrometer for identification of the recombining ions, a Langmuir probe to determine the electron and ion number densities, laser induced fluorescence (LIF) spectroscopy to determine the H-atom number density (via LIF on OH produced in the reaction $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$), and vacuum ultraviolet (vuv) absorption spectroscopy to calibrate the LIF detection system. The ports I_1 to I_6 are required for adding various gases to the afterglow plasma in order to produce the recombining ion of interest (see text). Different carrier gas inlet ports are used depending on whether one or two microwave cavities are in use. For further experimental details see Refs. 23 and 27.

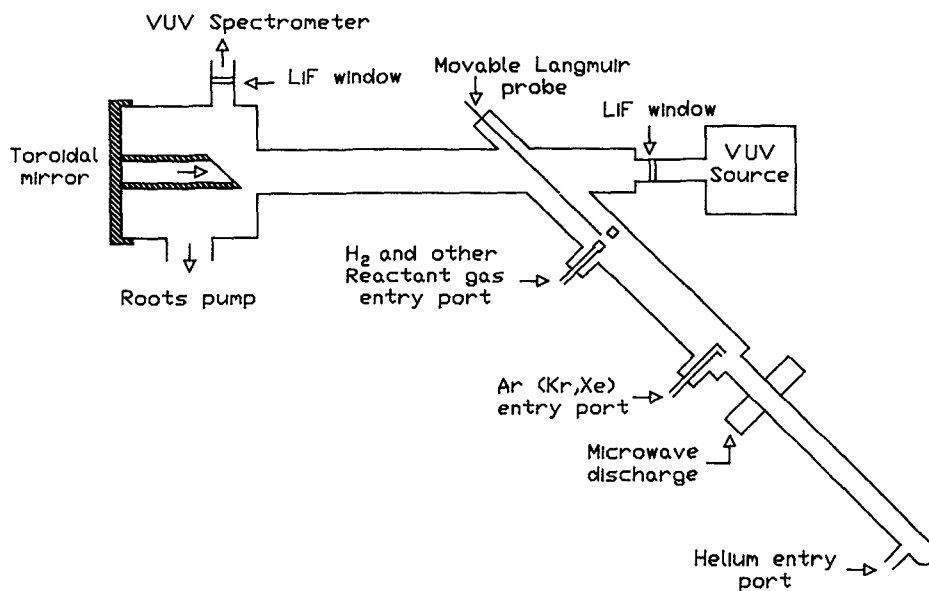


FIG. 2. A schematic diagram of the Rennes flowing afterglow illustrating the vacuum ultraviolet (vuv) absorption technique which enables the H-atom number density to be determined using a ~ 110 cm absorption path length. The toroidal mirror can be replaced by a mass spectrometer (not illustrated) to enable the ion composition of the afterglow plasma to be determined. The upstream section of the flow tube can also be connected directly to the pumping chamber close to the roots pump side arm to enable the ion composition to be determined near to the port at which gas M is introduced. For further details on the technique see Ref. 29.

in the two laboratories. All measurements were made at 300 K.

A. Detection of H atoms using LIF

In order to determine the H-atom number density in the flow tube, the H atoms are converted to OH via the reaction $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ by adding NO_2 downstream after the MH^+ / e plasma has recombined. The vibrationally excited OH produced in this reaction is rapidly relaxed to the ground vibrational state by excess NO_2 . The $\text{OH}(v=0)$ number density is then determined using LIF. Since the technique for detecting OH has been described in detail previously,²³ it will only be discussed briefly here. Laser radiation at ~ 281 nm is directed across the flow tube exciting $\text{OH } X^2\Pi(v''=0)$ radicals into the $A^2\Sigma(v'=1)$ state and fluorescence is detected at ~ 312 nm due to the $A^2\Sigma(v'=1) \rightarrow X^2\Pi(v''=1)$ transition using an interference filter in front of a photomultiplier. The intensity of the LIF for a particular transition is related to the OH number density as follows. For this calibration, a large number density of H atoms is generated in the flow tube by passing H_2 through the upstream microwave discharge. Ionization due to the presence of H_3^+ in the flow tube was removed by addition of N_2 followed by the reactions $\text{H}_3^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}_2$ and $\text{N}_2\text{H}^+ + e \rightarrow \text{N}_2 + \text{H}$. These H atoms are convected downstream and their number density determined by absorption of L_α radiation directed across the flow tube. (The basic technique used here has been reported previously²³ and is almost identical to that discussed below for the direct detection of H atoms from the MH^+ / e recombination; see Sec. II B). The absolute H-atom number densities in this situation were $\sim 10^{11} \text{ cm}^{-3}$ which is substantially greater than those produced in the MH^+ / e recombinations. Addition of sufficient NO_2 to the H-atom swarm then converts all of the H atoms to $\text{OH}(v''=0)$ which are detected using the LIF facility and this provides the calibration of the OH number density, $[\text{OH}]$. Using this procedure, the contributions of OH to the product distributions given in Table I were determined.

Now that the OH number density can be determined, the H-atom number density, $[\text{H}]$, in the MH^+ / e recombining plasma is obtained (as stated above) by converting the H atoms to OH using the same $\text{H} + \text{NO}_2$ reaction. Note that the H atoms in the carrier gas arise from several sources: (a) the $\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}$ and $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reactions, (b) the recombination of $\text{H}_3^+(v>0)$ in the gas phase and $\text{H}_3^+(v=0)$ at the walls, (c) the recombination of MH^+ , and (d) from any impurities in the helium carrier gas, such as H_2O , which can be dissociated in the microwave discharge. (Impurities were minimized by baking the flow tube prior to the measurements and passing the helium and hydrogen through zeolite filled traps cooled to liquid nitrogen temperature and the argon through a zeolite trap cooled to 200 K). To account for background H atoms produced by (a), (b), and (d) and hence determine the H-atom contribution to the MH^+ / e product distribution [in (c)], further calibration experiments were carried out using an $\text{O}_2\text{H}^+ / e$

recombining plasma [reaction (1)] produced by addition of O_2 ($= \text{M}$). First, the total OH number density, $[\text{OH}]$, was determined using LIF by adding NO downstream of the recombination region, but upstream of the laser beam, to relax any vibrationally excited OH to $v''=0$. This gave the fraction, f_{OH} , of the recombinations which lead to OH production as 0.6. Hence, it follows that the fraction of H atoms per recombination, f_{H} , is 0.4, since if OH is not produced then an H atom has to be [see Eq. (1)]. Introduction of NO_2 in place of NO additionally generates OH from H atoms produced by (a), (b), (c), and (d) above and, since the contribution from (c) is known in this case, the background H-atom number density can be deduced. Following this, other gases, M, can be added to generate other MH^+ ions and the values of f_{H} deduced for their recombination with electrons. Taking account of all of the possible sources of error, the f_{H} are considered to be accurate to within $\pm 30\%$.

B. Detection of H atoms using vuv absorption

H atoms resulting from processes (a) to (d) were directly detected by using a bent flow tube (see Fig. 2) and passing L_α from a vuv light source along the length of the downstream part of this flow tube. In this way, an optical path length of ~ 110 cm was obtained giving an absorption of typically 10% compared with about 1% for the 8 cm path length (used in preliminary studies) available when the radiation was directed across the flow tube.¹⁷ A toroidal mirror was used to reflect the L_α into a 3 m vuv spectrometer equipped with a vuv photomultiplier. The $[\text{H}]$ was then obtained from the L_α absorption as previously described.²⁹ The profile of the L_α emission line from the vuv source, which is required for this technique, was obtained using the 10 m vuv spectrometer at Meudon in collaboration with Launay (see Ref. 17). To check the ion composition of the plasma, the toroidal mirror could be replaced by a mass spectrometer. It is also possible to connect the upstream section of the flow tube directly to the pumping chamber close to the Roots pump side arm (see Fig. 2). In this way, the ionic composition of the plasma close to the entry port for M could also be determined. To calibrate the technique and to determine the absorption due to (a), (b), and (d), N_2 was added to produce a recombining $\text{N}_2\text{H}^+ / e$ plasma. It is known from previous studies that $\text{N}_2\text{H}^+ + e$ gives only $\text{H} + \text{N}_2$ even though the product channel $\text{NH} + \text{N}$ is energetically possible.²⁵ (Corroborating evidence was obtained by adding NO to the recombining plasma whilst monitoring $\text{OH } X^2\Sigma(v''=0)$ using LIF. If NH were present, then it would react rapidly with NO giving $\text{OH} + \text{N}_2$.³⁰ No OH fluorescence was observed, indicating that NH is not produced in this recombination reaction.) Then, knowing the background $[\text{H}]$ and by separately adding other gases, M, the f_{H} for the recombination of the various MH^+ ions were determined. These are listed in Table I. Since the quality of the result depends on the conditions being stable between the calibration and the measurement, a calibration was made immediately before each measurement. Uncertainties in the absorption measurements are of the order of $\pm 10\%$ and this results in an uncertainty in f_{H} of about $\pm 20\%$.

C. Other techniques for generating MH^+/e plasmas

In the plasmas discussed above, the background H-atom number density is larger than that resulting from the recombination since one H atom is generated per recombining ion in process (a) and other H atoms are generated in process (b). To reduce the background H-atom number density, several other methods of producing MH^+/e plasmas were employed.

In the LIF studies, a second microwave cavity was positioned downstream of the cavity generating the plasma (see Fig. 1). This second cavity was only weakly energized in order to heat away the plasma electrons and ions by increasing their loss due to ambipolar diffusion (a lower helium pressure of 1 Torr was also used in these measurements to further increase the diffusive loss of ionization), ensuring that He^m was the dominant reactive species downstream. The Penning reaction $He^m + CO \rightarrow CO^+ + e + He$ was used to create a CO^+/e plasma and addition of H_2 then generated an HCO^+/e plasma via the reaction $CO^+ + H_2 \rightarrow HCO^+ + H$. Since no H_3^+ is produced, then process (b) cannot be a source of H atoms. Gas M was then added to create an MH^+/e plasma by proton transfer from HCO^+ . Note that it was not possible to remove all of the He^+ ions in this way. Some He^+ ions remained and produced C^+ in the $He^+ + CO$ reaction at a level of about 15% of HCO^+ . Fortunately, C^+ reacts with NH_3 and H_2O and secondary reactions produced NH_4^+ and H_3O^+ as the terminating ions. In the H_2CN^+ recombination reaction, the only other case in which this technique was used, the reaction of HCN with C^+ does not result in the production of H_2CN^+ . In this case, the presence of C^+ and the products of its reactions had to be accounted for. Alternatively, for some MH^+ studies, Ar could be added producing Ar^+ via the reaction $He^m + Ar \rightarrow Ar^+ + e + He$. Then, addition of M such as H_2O resulted in the production of H_3O^+ by the consecutive reactions $Ar^+ + H_2O \rightarrow H_2O^+ + Ar$ and $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$, thus minimizing H-atom production. The f_H were determined by adding NO_2 as before and are given in Table I.

In some of the vuv absorption studies, Kr or Xe was added to the afterglow in place of Ar without H_2 being introduced, thus creating Kr^+ (and Xe^+)/ e plasmas. Addition of M then resulted in reactions such as $Kr^+(Xe^+) + NH_3 \rightarrow NH_3^+ + Kr(Xe)$ and $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ again minimizing H-atom production. Sufficiently large flows of M were used to ensure that recombination (for example, of NH_3^+) did not compete with the second reaction, but were also kept sufficiently small to prevent clustering from occurring; e.g., $NH_4^+ + NH_3 + He \rightarrow NH_4^+ + NH_3 + He$. The f_H were again determined as in Sec. B and are also given in Table I.

III. RESULTS AND DISCUSSION

The combined data from all of the f_H measurements for the dissociative recombination of N_2H^+ , HCO^+ , O_2H^+ , HCO_2^+ , N_2OH^+ , $OCSH^+$, H_2CN^+ , H_3O^+ , H_3S^+ , NH_4^+ , and CH_5^+ are given in Table I. Also included are the

previously published data for f_{OH} .²³⁻²⁵ This is the most comprehensive study of the products of recombination that has ever been undertaken, yet much remains to be done. Note that for HCO^+ , where no OH is observed, and therefore the product must be H atoms, the expected f_H of 1 was obtained. It is gratifying to see that there is good agreement between the two different detection techniques. When there is a difference (still within the combined errors associated with the two experiments), the vuv technique generally gives the larger value for f_H , perhaps an indication that the contribution due to background H atoms has not been completely taken into account. The differences are most marked for $OCSH^+$ and N_2OH^+ . However, f_H is small for $OCSH^+$ and thus the relative effect of background H atoms would be largest. In the case of N_2OH^+ , it is possible that there could be a contribution to the total f_{OH} due to the exothermic recombination channel $NH + NO + 150 \text{ kcal mol}^{-1}$. There would be such a contribution if NH is produced since, when NO is added to the afterglow plasma to relax $OH(v'')$, the reaction $NH + NO \rightarrow OH + N_2$ will also occur on a similar time scale, because it has a rate coefficient similar to that for the quenching reaction.³⁰ This could be checked using LIF to detect NH in the absence of added NO. In the LIF studies of the recombination of H_3S^+ , the secondary neutral-neutral reaction $OH + H_2S \rightarrow SH + H_2O$ occurred giving an erroneously small value for f_H . Addition of further H_2S , while monitoring the OH LIF, enabled a rate coefficient of $4.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ to be obtained for this reaction in excellent agreement with the recent previous value of $4.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.³¹ This reaction has been taken into account to obtain the value of f_H quoted for H_3S^+ in Table I. No equivalent reaction occurs in the case of $OCSH^+$. (The rate coefficient for the reaction $OH + OCS \rightarrow SH + CO_2$ is very small.)³² For the case of HCO_2^+ , f_{OH} and f_H sum to close to 1 indicating that the exothermic channel $O + HCO + 88 \text{ kcal mol}^{-1}$, in which neither H atoms nor OH are produced, is not very significant.

It is interesting to compare the product distribution for the sulphur/oxygen analogs HCO_2^+ and $OSCH^+$ and also H_3O^+ and H_3S^+ . For $HCO_2^+/OCSH^+$, the difference in f_{OH} is large (f_{OH} being larger for HCO_2^+), however, this is not unexpected since theoretical calculations have shown that in $OCSH^+$ the proton is bonded somewhat more strongly to the S atom than to the O atom³³ and therefore the structural form $OCSH^+$ is more likely. The difference in f_H is also large for the two pairs of systems with f_H being smaller for the thioanalog. This may be merely a manifestation of differences in the potential curves between the analogous systems. However, it should be noted that analogous channels are energetically possible for H_3O^+/H_3S^+ with similar exothermicities. LIF studies of SH would be of value for these reactions.

For H_3O^+ , f_H and f_{OH} sum to ~ 1.5 indicating that the channel $OH + 2H + 30 \text{ kcal mol}^{-1}$, although fairly small, is significant (indeed a more detailed analysis shows that this channel is of the order of 20% of the product distribution). Although theoretical efforts to predict the products of dissociative recombination are in the development phase,

some comparison with experiment is possible. The situation for H_3O^+ has been discussed in detail previously.²⁴ For NH_4^+ , both the earlier phase space calculations of Herbst¹⁹ and the recent theoretical suggestions of Bates²¹ indicate that the $\text{NH}_2 + \text{H}_2$ channel is large. However, experiment shows that $f_H \sim 1$ and thus, unless the $\text{NH}_2 + 2\text{H}$ channel is large (which is unlikely since it is close to thermoneutral), the $\text{NH}_2 + \text{H}_2$ channel is expected to be small. The earlier theoretical ideas of Bates,²⁰ as expounded by Millar *et al.*,³⁴ who quoted $\text{NH}_3 + \text{H}$ as the only channel, are more consistent with experiment. However, note that the present experiments cannot distinguish between the $\text{NH}_3 + \text{H}$ and the $\text{NH} + \text{H}_2 + \text{H}$ channels. For CH_5^+ , Millar *et al.* predict an f_H of ~ 0.9 which is not much smaller than the experimentally determined value (see Table I). That the experimental value is greater than 1 indicates that the $\text{CH}_3 + 2\text{H}$ channel is significant, a feature of the product distribution which was not predicted theoretically.

IV. CONCLUSIONS

A comprehensive study of the H-atom contribution to the product distributions for the electron-ion dissociative recombination of a series of ground state protonated ions has been carried out. The good agreement between the results obtained using two very different experimental techniques gives a large measure of confidence in the experimental results. Comparison with theory has shown that much more development of the theory is required. In particular, calculations are needed of the potential energy curves for the ground state recombining ions and for the neutralized dissociating molecule. Further experimental work is also required to provide complete product distributions for the recombination reactions. It should be noted that a complete product distribution has yet to be obtained for a polyatomic ion (except for the simple cases of N_2H^+ and HCO^+).

The data presented here are of great relevance to molecular synthesis in interstellar clouds. This aspect of the work will be presented in a separate publication.

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