New flowing afterglow technique for determining products of dissociative recombination: CH$_5^+$ and N$_2$H$^+$

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Abstract. There are discrepancies in the literature for the product distributions of electron-ion (e-i) recombination when determined using different techniques. Because of this, a new technique has been developed. This is based on the flowing afterglow, with the product neutrals detected by electron impact ionization followed by mass spectrometric detection. However, in addition to the products of recombination, there are neutrals present from ion-molecule reactions and from the gases introduced into the flow tube to create the ion of interest, which often have much greater concentrations than the products. To distinguish these products, an electron attaching gas is pulsed into the flow to transiently attach the electrons, thus quenching e-i recombination. Then the difference between the attaching gas in and out yields the product distribution. Recombination products have been detected even when their signal is as much as $\sim 10^4$ less than background. Here the details of the technique are described and the possible sources of error discussed. The viability of the technique is illustrated for the recombinations of CH$_5^+$ and N$_2$H$^+$. The latter establishes the major product as N$_2$ + H (95 to 100%) correcting an error in the literature. In the former case, the major channel detected is CH$_4$ + H (95%) which is in disagreement with a storage ring (SR) result which gave CH$_3$ as the major channel (68%). Possible reasons for this are discussed.

1. Introduction
In recent years, a large number of product distributions for dissociative electron-ion recombination have been determined [1, 2]. These are critically important in the modeling of the coupled ion and neutral chemistry in many molecular plasmas (interstellar gas clouds (ISC) [3], planetary atmospheres [4-6], and with some significance to combustion [7]). The majority of the studies have been made with storage rings (SR) with a few studies using flowing afterglows (FA). Where measurements have been made using the two different techniques, (N$_2$H$^+$, H$_2$O$^+$, H$_2$O$^+$ recombinations listed in Table 1) there is a considerable degree of disagreement and this places uncertainty on all of the measurements that have been made. This is very worrisome since these data are used in models of various plasmas and the models can make very different predictions depending on the product distributions. In the case of the ISC, this can prevent the production of several important molecules. In particular, the recombinations of CH$_3^+$ and CH$_3$OH$^+$ could, in principle, lead to the production of interstellar methane and methanol. In practice these recombinations are considered to be dissociative to a large degree [8, 9] thus preventing the production of methanol, the only known gas phase route.
Table 1. Recombination product distributions where there is disagreement between the SR and FA techniques.

| FA [10, 11] (SR [12-14]) | FA [15] (SR [12, 16-18]) |
|--------------------------|--------------------------|
| H$_2$O$^+$ + e → H + OH | 55% (22%, 30%, 20%) | H$_3$O$^+$ + e → H + H$_2$O | 5% (33%, 18%, 25%) |
| → O + H$_2$ <22% (10%, 13%, 9%) | | → OH + H$_2$ 36% (18%, 11%, 14%) |
| → O + 2H >23% (67%, 57%, 71%) | | → OH + 2H 29% (48%, 67%, 60%) |
| | | → O + H + H$_2$ 30% (1%, 4%, 1.3%) |

The determination of product distributions using these techniques (SR and FA) is complicated. In the FA, spectroscopic detection requires VUV absorption for atoms, and the very sensitive Laser Induced Fluorescence (LIF) for molecules such as OH. LIF can also be used for atoms by using chemical reactions to convert the atoms H [21] and O [15] to OH by the neutral reactions; H + NO$_2$ → OH + NO and O + GeH$_4$ → OH + GeH$_3$. Note that here the spectroscopic intensities have to be converted into number densities to compare with the electron and ion number densities, i.e., using quantitative spectroscopy. Whilst this should not cause errors, it does complicate the analysis. In the case of the SR, a detailed analysis is required using grids [22] and more recently Coulomb explosion imaging [23] to determine the product distribution. Also in some cases, corrections have to be made for collisions with the background gas in the ring [8], and for the regions where the electrons and ions are merged together and later separated [24, 25]. There is also a limitation on the energy resolution in magnetic storage rings at the higher masses; for example, in previous studies it has not been possible to fully resolve individual masses in hydrocarbons such as C$_2$H$_3^+$, C$_4$H$_5^+$, and C$_4$H$_9^+$ [26, 27], and other hydrocarbon ions [28]. However, to some extent, this situation has been alleviated by using deuterated hydrocarbons (C$_2$D$_5^+$, C$_3$D$_7^+$, and C$_4$H$_9^+$) [29, 30].

In order to circumvent some of these problems, we have developed a new flowing afterglow technique in which the products of recombination are identified by electron impact ionization followed by mass analysis, amplification in an electron multiplier and ion counting (Fig. 1). This modification means that rather than using a series of spectroscopic techniques, which have to be separately calibrated, the individual ion types are straightforwardly identified by their masses (better than 1 amu mass resolution). This allows the signals at different masses to be compared relatively, removing the need for absolute calibration. This may only seem to be a simple modification, however there are some complications that need to be overcome. Firstly, after determining the composition of the plasma, these plasma ions and electrons need to be prevented from entering the detection system, allowing only neutral species to pass through the sampling orifice. This is readily achieved by biasing the potentials on the first few lens elements of the detection system, which also prevents the passage of plasma electrons. Then, only neutral species can pass into the detection system. This includes the neutral products of recombination, but also permits passage of the gases that were introduced into the plasma as well as neutral products from ion-molecule reactions producing the recombining ions of interest. These latter contributions can be several orders of magnitude larger in concentration than the products of recombination and need to be discriminated against.

Selective detection of recombination products can be achieved in two ways, both resulting in the variation in the concentration of the recombining species (either electrons or recombining ions) and is illustrated here by the electron recombination of N$_2$H$^+$.

\[
\text{N}_2\text{H}^+ + e \rightarrow \text{N}_2 + \text{H} + 8.47 \text{ eV} \quad (1a)
\]

\[
\rightarrow \text{NH} + \text{H} + 2.25 \text{ eV} \quad (1b)
\]
This recombination was studied earlier in the FA by monitoring the H-atom production by vuv absorption [19] and later in the SR where the recombination products H, N, NH and N2H were monitored [20, 31]. In the FA, Channel (1a) was indicated to be dominant whereas the SR gave a product distribution of 36% for Channel (1a) and 64% for Channel (1b), very disparate results. Such a result is surprising since the major channel requires the breaking of the strong N≡N triple bond. However, such a distribution would be a good test of the new technique since H, N, NH and N2 can be monitored [20, 31]. In the FA, Channel (1a) was indicated to be dominant whereas the SR gave a product distribution of 36% for Channel (1a) and 64% for Channel (1b), very disparate results. Such a result is surprising since the major channel requires the breaking of the strong N≡N triple bond. However, such a distribution would be a good test of the new technique since H, N, NH and N2 can be monitored allowing the product distribution to be over determined and thus give an indication of the errors involved in the measurement. In these studies, it was not possible to follow the H+ monitor for H-atoms since there was considerable reverse mass discrimination in the quadrupole against such low mass ions. Thus, N+, NH+ and N2+ were used as monitors of N, NH and N2, respectively. Note that the use of these monitors is not perfect since some fragmentation occurs in electron impact ionization; electron impact with 70 eV electrons was generally used since most data are available for this energy [32]. These fragmentations were accounted for to determine the final percentage product distribution.

To extract product distributions from the monitor ion data, N2 was pulsed into an H3+/electron plasma created in the standard way [33, 34]. Then the proton transfer H3+ + N2 → N2H+ + H+ transiently produced the recombining ion of interest. Alternatively, a CCl4/He mix was pulsed into the afterglow causing the rapid electron attachment e + CCl4 → Cl− + CCl3. Thus, when the electron attaching gas is absent e-i recombination can occur and when it is present, e-i recombination is quenched allowing only a very small amount of i-i recombination. In this way, the difference in the monitor ions signals between the pulsed gas absent and present (in both methods) is a measure of the e-i recombination. Note that only the latter technique is illustrated here since this is the method of choice. The former technique is explained in a more detailed paper [35].

2. Experimental

For this purpose, a standard temperature variable FA [36, 37] was used with the addition of a pulse valve for pulsing gas addition into the flow tube and adding an axial electron impact ionizer to the detection system downstream of the nose cone and before the quadrupole mass spectrometer; see Fig. 1.

![Figure 1](image-url)  
Figure 1. The detection section of the flow tube is shown with the pulse valve, the pulsing circuitry and the pulsed data collection. The pulse valve is opened and closed by a square wave (~1Hz) from the pulse generator (PG) which also sends a trigger signal at twice the frequency to the gating/discriminator. Ion counts from the channel multiplier are amplified in the preamplifier (PA) and are accumulated into a series of bins when the counting circuit is open. Because the gating/discriminator is triggered at twice the frequency of the pulse valve, alternate counting periods occur with the pulse valve closed (A) and open (B). These are separately summed together to give the integrated counts for background and signal plus background.
These may seem minor changes but they have profound significance. To enable products of recombination to be quantitatively identified requires a detailed understanding of the pulsing process and also highly stable conditions. The recombining plasma of interest was produced in the conventional way [33, 34], by sequentially adding Ar, H₂ and the reactant gas, RG, to the He flow. After ionization of He in a microwave discharge, He⁺/He₂⁺, Ar⁺, H₃⁺ and RGH⁺ electron plasmas were successively produced (by a conventional reaction sequence) [33, 34]. The compositions of the plasmas were determined by sampling the plasma ions through the orifice in the nose cone in the conventional way with the electron impact ion source switched off. To sample neutral species in the flow, (including the products of recombination) downstream lenses were biased by ~1 V, alternately positive and negative, to prevent plasma ions and electrons from entering the detection system. In this case, the ionizer is switched on to ionize the neutrals from the plasma to be sampled by the mass spectrometer. Within these ions, to separate the monitor ions for the recombination products from the background species, a rapidly attaching gas is pulsed into the plasma to quench e-i recombination; CCl₄ is usually used producing Cl⁻ (and CCl₃). Attachment is so rapid that only small amounts of CCl₄ are used, which are insufficient to affect the positive ion chemistry. An amount of CCl₄ is added which is sufficient to attach 80 to 90% of the electrons, thus retaining a plasma which is controlled by electron/positive ion ambipolar diffusion and therefore the positive ion diffusive loss is unchanged [38]. When the electrons are present, Counter A collects 300ms bursts of monitor ions with Counter B collecting counts when negative ions are present, see Fig. 1. The difference between these for the monitor ions, when integrated, gives counts, which are proportional to the recombination products. In order to get clean square pulsed of CCl₄ into the flow tube, a weak mixture of CCl₄ in He (~1%) is introduced into the flow tube and is continuously flushed through the pulsed valve by addition of a He flush flow. To remove the CCl₄ from the flow as quickly as possible after the pulse valve has closed, a second He flush is added just after the pulse valve. To get as square a pulse of electrons as possible, the flows were optimized while monitoring the electron signal to a positively biased Langmuir probe (collecting electrons [39]) located in the region of the forming recombining ion. The electron pulse can be seen to be quite square [35], but even so, the channels do not count until 100 ms after the pulse valve opens and are terminated 100 ms before it closes. In spite of all this, and with flows that were kept extremely stable with servo valves, the counts had to be passed through a single discriminator with a single gate width and the counts in Counters A and B were only collected after this. Within the same instrument using separate counters and discriminators for the two channels, there was a difference between the counts into Channel A and Channel B even when there was no signal. This problem was due to slight differences in the discriminators and gate widths and was eliminated using the single channel before the counters. Note that such a setup, minimizes the effect of drifts that occur on a time scale greater than that corresponding to the 1 Hz frequency. In addition, random variations on a time scale less than this will be averaged out. Only drifts on time scales corresponding to ~1 Hz will contribute a background. Tests were made by having a constant CH₄ flow into the flow tube with a pulsed flow of CH₄ 10³ times less. For this situation, the counts of CH₄⁺ (a monitor of CH₄), in the A and B channels per period seemed the same, and the signal difference S (= A – B) spanned zero counts. However, when the S signal was integrated, the S built up linearly with time exactly at the rate expected for a pulsed flow of 0.1%, generating a substantial count built up in about 1 min.

3. Recombining systems studied

3.1. Electron-ion recombination of CH₅⁺

With this technique the first product distribution determined was for CH₅⁺/e recombination, with CH₄⁺, CH₃⁺, CH₂⁺ and CH⁺ as monitor ions of CH₄, CH₃, CH₂ and CH respectively. Note that these neutrals all fragment to some degree on ionization by 70 eV electrons (CH₄ → CH₄⁺ (44%), CH₃⁺ (40%), CH₂⁺ (9%), CH⁺ (5%) and C⁺ (2%); CH₃ → CH₃⁺ (75%), CH₂⁺ (18%), and CH⁺ (7%);
CH$_2$ → CH$_3^+$ (~71%) and CH$^-$ (~29%) and CH → CH$^+$ (~79%) and C$^+$ (~21%)) [32, 35, 40] and this effect has to be accounted for. All the effects that have to be taken into account can be illustrated by considering the recombination:

\[ \text{H}_3\text{X}^+ + \text{e} \rightarrow \text{H}_2\text{X} + \text{H}; \quad \text{ } \quad p_1 \quad (2a) \]
\[ \rightarrow \text{HX} + \text{H}_2/2\text{H}; \quad \text{ } \quad p_2 \quad (2b) \]
\[ \rightarrow \text{X} + \text{H}_2 + \text{H}; \quad \text{ } \quad p_3 \quad (2c) \]

where \( p_1, p_2, \) and \( p_3 \) represent the fractional product distribution. To detect these products, electron impact ionization is used with overall collision cross-sections of \( \sigma_{12}, \sigma_{11}, \) and \( \sigma_{00} \) for H$_2$X, HX and X ionization respectively. As mentioned above, electron impact ionization is considered to yield fractional monitor ion distributions of \( d_{22}, d_{21}, \) and \( d_{20} \) for H$_2$X ionization/ionization fragmentation to H$_2$X$^+$, HX$^+$ and X$^+$ respectively; similarly for HX and X fragmentation. It can now be determined what the relative monitor ion signals would be for recombination (2) and by rearrangement what the product distribution would be in terms of the relative monitor ion signals. This is analyzed in detail in a paper describing the technique [35]. The results are:

\[ p_1 \propto \frac{[\text{H}_2\text{X}^+]}{\sigma_{12}d_{22}} \quad (3a) \]

\[ p_2 \propto \frac{1}{\sigma_{11}d_{11}} \left( [\text{HX}^+] - [\text{H}_2\text{X}^+] \frac{d_{21}}{d_{22}} \right) \quad (3b) \]

\[ p_3 \propto \frac{1}{\sigma_{00}d_{00}} \left( [\text{X}^+] - [\text{H}_2\text{X}^+] \frac{d_{20}}{d_{22}} - \left( [\text{HX}^+] - [\text{H}_2\text{X}^+] \frac{d_{21}}{d_{22}} \right) \frac{d_{10}}{d_{11}} \right) \quad (3c) \]

where \([\text{H}_2\text{X}^+], [\text{HX}^+]\) and \([\text{X}^+]\) are the relative monitor ion signals and the constants of proportionality are all the same. In a similar manner, the neutral product distribution for CH$_3^+$ + e can be deduced from the monitor ion signals. The build up of the monitor ion signals with time is shown in Fig. 2 where they all increase linearly and all pass through the origin, both as expected. Note that the CH$_3^+$ and CH$_2^+$ signals are similar, but after conversion into recombination products CH$_3$ is small. This is an uncommon occurrence and happens here because of the high degree of fragmentation of CH$_4$ into CH$_3^+$ upon ionization. The curves in Fig. 2b are only plotted for illustrative purposes. In practice, only the values obtained over the whole integration period are used since these are the most accurate and contain all of the information in the data obtained at shorter times.

To be confident in the results, it is necessary to confirm that no increase in \( S \) occurs when there should be no signal. This was tested in several ways [35]. (i) A constant artificial signal was generated and data were taken. (ii) A situation was created where all of the reactant gases were present with the pulsing of the attaching gas, but with no plasma present. The neutral gases passing into the detection system were ionized and counts taken for all potential products, which are time invariant., (iii) A situation was set up in which CO$^+$ was recombining with electrons. Here no H$_2$ was added and the CO$^+$ was generated by the reaction of Ar$^+$ with added CO which produces only CO$^+$ [41]. In this case, plasma ions and electrons were prevented from entering the detection system. Since CO$^+$ dissociative recombination can only produce C + O and no CO, any signal and thus any build up of CO (as detected using CO$^+$ as the monitor ion) would be an erroneous detection of the abundant CO present in the plasma, which was not adequately discriminated against. Thus, this is a particularly stringent test. In all of these cases there was no build up of the monitor ions as expected [42]. However in this case (iii), addition of H$_2$ produces HCO$^+$ in proton transfer from H$_3^+$, which recombines to produce H + CO as a 92% channel [31].
Figure 2. Build up of the products for the e-i recombination of CH$_5^+$. (a) The integration of the monitor ions as a function of time. (b) Build up of the products of recombination obtained from (a) using equations (3a to c). Note that the signals increase quite linearly showing good statistics.

As soon as the H$_2$ was added, the CO$^+$ monitor ion immediately started to accumulate as expected.[42] This very clearly shows that background signals, even much larger than those due to recombination, can be cleanly discriminated against.

Note that when CCl$_4$ is pulsed in, negative ions are produced and thus some i-i recombination involving Cl$^-$ can occur. This is expected to make only a small contribution since this recombination, especially involving atomic ions, is slow. Such a contribution would yield negative signal counts and when it occurred at the same mass as a monitor ion for e-i recombination products, it would erroneously reduce this observed contribution. There are many energetically possible channels for this i-i recombination of CH$_5^+$ + Cl$^-$ including: 1) CH$_4$ + HCl + 8.9 eV, 2) CH$_4$ + H + Cl + 4.4 eV, 3) CH$_3$ + H$_2$ + Cl + 4.4 eV, 4) CH$_3$(Cl + H$_2$ + 8.0 eV, 5) CH$_3$ + H + HCl + 4.4 eV, 6) CH$_3$Cl + 2H + 3.5 eV, 7) CH$_2$ + H$_2$ + HCl + 4.0 eV, 8) CH$_2$Cl + H$_2$ + H + 3.7 eV. Note that channels (2 and 3) could occur with the conventional mechanism of long-range electron transfer, but that some such recombinations have been observed which require an intimate interaction [43]. To test for any i-i recombination the monitor ions Cl$^+$, HCl$^+$, and CH$_3$Cl$^+$ were observed and the signal followed; these are reproduced in Fig. 3. Note that the signals are very small compared with CH$_4^+$ and CH$_3^+$, but that the integrated signals do still increase in an approximately linear way within the counting statistics. CH$_3$Cl$^+$ is essentially zero, but Cl$^-$ and HCl$^+$ (marginally) are slightly negative showing that a little i-i recombination maybe occurring, however it is only a few percent. This small signal is not surprising since the plasma chemistry was optimized to keep this at a minimum. Thus this would not significantly affect the product distribution determined for the CH$_5^+$ + e recombination. This does however introduce the possibility that product distributions for i-i recombination could be determined using this technique by maximizing this recombination process. Such recombination is increasing in importance with the detection of C$_6$H and C$_8$H$^+$ in interstellar clouds [44, 45] and the indication that
Figure 3. Build up of the monitor ions for the products of e-i and i-i recombination. Note that CH$_4^+$ increases very rapidly with time because of the much more sensitive scale than in Fig. 2. This is evident from the more pronounced statistical variations than in Fig. 2. Monitor signals, which are negative going, imply that they are products of i-i recombination (Cl$^+$ and HCl$^+$). C$^+$ and CH$_4$Cl$^+$ signals are at the limit for this count period of 100 sec showing that they are varying statistically about the zero and are not products.

there are negative ions in the atmosphere of Titan [46]. Note that since CH$_4$Cl$^+$ cannot be a product of e-i recombination; its signal represents the magnitude of the statistical errors which are very small indeed. That Cl seems to be a product is not surprising since long-range electron transfer would occur, following conventional thought on i-i recombination.

The DR data of CH$_5^+$ in Fig. 2 and using equation (3) determines the product distribution in Table 2. This can be compared with the distribution previously obtained by Semaniak et al. in the SR [8]. These distributions are radically different with CH$_4$ dominating in the FA (95%) and CH$_3$ dominating in the SR (68%). Sheehan and St-Maurice [47] in a single pass merged beam experiment obtained the same rate coefficient as the SR (2.9 x 10$^{-7}$ relative to 2.8 x 10$^{-7}$ cm$^3$ s$^{-1}$) with ions that were vibrationally excited. Based on this, they suggested that the SR ions were also excited. This seems unlikely since the CH$_5^+$ could relax vibrationally in the 2 sec in the SR before recombination [8], Larsson (priv. com. 2007). However, there is no radiative mechanism for completely rotationally relaxing the ions and such excitation is possible. The effect of rotational excitation can be tested by studying the recombination in the FA at elevated temperatures and such studies are planned. Another possibility is that the ions at mass 17 amu could have been $^{13}$CH$_4^+$ as well as CH$_5^+$, but, if this were the case, then a $^{12}$CH$_4^+$ signal 90 times larger (the isotope ratio of $^{12}$C to $^{13}$C) would be expected and this was not observed Larsson (priv. com. 2007). A further possibility is that there is some fragmentation of the CH$_4$ product to CH$_3$ in the 10$^{-6}$ sec time scale between recombination and product detection in the SR.

Table 2. Previous and present product distributions for the e-i recombination of CH$_5^+$.

| Reaction                      | Present FA | Previous SR$^a$[8] |
|-------------------------------|------------|--------------------|
| CH$_5^+$ + e → CH$_4$ + H     | 95 ± 5%    | 2 ± 2%             |
| → CH$_3$ + H$_2$/2H           | ≤ 8%$^b$   | 68 ± 1%            |
| → CH$_2$ + H$_2$ + H          | ≤ 1%       | 25 ± 4%            |
| → CH + 2H$_2$                 | ≤ 1%       | 5 ± 4%             |
a) values at an energy of 37 meV. b) use of the earlier FA data for H-atoms (117.5%) implies that the CH$_3$ plus 2 H channel is dominant over the CH$_3$ plus H$_2$ channel.

In the FA, in addition to the discounted effect of i-i recombination on the product distribution the often radical products can be lost in neutral-neutral reactions or by relative diffusion. Generally the former can be quite slow with the rate coefficients: CH$_3$ + CH$_3$ $\rightarrow$ C$_2$H$_6$; 4.6 x 10$^{-11}$ cm$^3$ s$^{-1}$ [48], CH$_3$ + CH$_2$ $\rightarrow$ C$_2$H$_4$ + H; 2.1 x 10$^{-10}$ cm$^3$ s$^{-1}$ [48], CH + H$_2$ $\rightarrow$ CH$_2$ + H; 2.3 x 10$^{-11}$ cm$^3$ s$^{-1}$ [49], CH + CH$_4$ $\rightarrow$ Products; 5.4 x 10$^{-11}$ cm$^3$ s$^{-1}$ [50]. To account for diffusive loss, the worst-case condition was taken with 100% loss at the walls being assumed for radicals with obviously no loss for CH$_4$. Modeling of this reactive and diffusive loss would modify a Semaniak et al. [8] distribution for CH$_4$, CH$_3$, CH$_2$ and CH from 2%, 68%, 25% and 5% to 3%, 68.3%, 27.3% and 1.4%, an insignificant change relative to the difference between the FA and SR results.

3.2. Electron-ion recombination of N$_2$H$^+$

Another recombination that has been included in these initial studies is that of N$_2$H$^+$ because of the drastic difference between FA and SR results as mentioned earlier. The results of this study have recently been published [42] and so will only be briefly mentioned here. The same techniques and tests were used as described above for CH$_5^+$ recombination and confirmed, consistent with the earlier FA study, that the NH + N channel was 0-5% with the N$_2$ + H channel being very dominant. These data caused a repeat of the SR experiment, which showed that in the original measurement the H$_2$ in the source had been depleted and the recombination of the ion at 29 amu was for $^{14}$N$^{15}$N$^+$ and not N$_2$H$^+$. A repeat of the measurement with H$_2$ and N$_2$ in the source showed that the NH + N channel is consistent with the FA, having a value of $\sim$10% (Larsson, priv. com. 2007).

4. Summary

Detailed analysis has shown that, with some modification, the FA can be used to obtain accurate product distributions for e-i recombination. The addition of a pulse valve discriminates greatly in favor of recombination neutral products with electron impact ionization to make the products detectable by mass spectrometry. The technique has required highly stable gas flows of high purity gases, with very reproducible pulsing of the attaching gas. The need for accurate, identical and stable pulse amplitude discriminators and counting gate widths is essential for meaningful product distributions to be obtained. Initial studies have established the major product of the N$_2$H$^+$ electron recombination as being 95 to 100% N$_2$ + H, with the NH + N channel being minor (0 to 5%) if present at all. The CH$_5^+$ recombination has shown that the technique can be used with more polyatomic species, although is does reveal a discrepancy between FA and SR results. The technique can now be used with confidence to study other e-i recombinations. It has also revealed that it is possible to identify the products of i-i recombination, which is becoming increasingly important in several plasmas.

Acknowledgements

Funding from the NSF and NASA is gratefully acknowledged.

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