Molecular ion recombination in trapped and flowing plasmas: methods, recent results, new goals, open questions

To cite this article: Nigel G Adams and Lucia M Babcock 2005 *J. Phys.: Conf. Ser.* **4** 38

View the article online for updates and enhancements.

You may also like

Molecular ion recombination in trapped and flowing plasmas: methods, recent results, new goals, open questions

Nigel G Adams and Lucia M Babcock

Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

E-mail: adams@chem.uga.edu

Abstract.   Two major techniques have been used to study electron-ion recombination, afterglows and storage rings. These have differing strengths and limitations for the determination of recombination rate constants/cross-sections, including those as a function of temperature/energy, and for the identification and quantification of the neutral products, both rovibronically excited and ground state. Here, the afterglow techniques will be reviewed (the storage ring is considered by Larsson) with emphasis on new developments. In this vein, there will be discussion of (i) rate constants for larger species, (ii) temperature dependencies of rate constants including those for some isomers, and (iii) electronically excited states; all these connect with other papers in these proceedings. New developments are discussed; in particular a means of quantifying the neutral product distributions, and possible new directions are suggested.

1. Introduction

Two major techniques have been used to study dissociative electron-ion, ei, recombination (DR): afterglows (stationary and flowing; SA and FA) and merged beams (mainly storage rings, SR). These techniques have different strengths and their combined use for a given reaction gives data, which is much more valuable than any individual study. Only the afterglow technique, and recent data obtained with it, will be discussed here to set the scene for the most recent developments described later in these proceedings. Storage rings are discussed elsewhere in these proceedings (Larsson) and will not be considered here.

In the overall recombination process,

$$XYZ + e \quad \rightarrow \quad XY^* + Z^* \tag{1a}$$
$$\rightarrow \quad X^* + YZ^* \tag{1b}$$
$$\rightarrow \quad X^* + Y^* + Z^* \tag{1c}$$

(* indicates the possibility of internal and kinetic excitation) various parameters are amenable to study. These are: (i) Recombination rate constants/coefficients (these terms are used interchangeably), α_e, at a given temperature. Here, the rate constants are for the thermal situation (if the ions are appropriately internally cooled) with the electron and ion kinetic temperatures being thermalised with the ion internal temperature. Note that this is not the case in the storage ring, where the ion internal temperature and the energy widths of the ion and electron velocity distributions, $v(E)$ are essentially constant and only the ion/electron relative energy is varied. Here, also SR cross-sections, $\sigma(E)$, are measured as a function of energy, E, yielding more detailed information than an afterglow α_e. However, a pseudo α_e can be derived from SR data using the expression

$$\alpha_{\mathrm{e}} = \int_{0}^{\infty} v(E)\sigma(E)f(E)\mathrm{d}E \tag{2}$$

where $f(E)$ is the Maxwell-Boltzmann distribution. For the reasons discussed above, this is not the true thermal value, however, note that information on the effects of ion internal energy can be gleaned by comparison of the two types of data.

(ii) α_{e} as a function of true thermal temperature, which yields values that can be related to the $\sigma(E)$ vs. E of the storage rings.

(iii) Neutral product excitation from emission spectroscopy, which gives information on rovibronically excitation of the products. This is largely the province of afterglow techniques, with equivalent information being difficult to obtain in storage rings.

(iv) Quantitative identification of the neutral products distributions. These were initially obtained spectroscopically in afterglows [1-3], but have recently been more straightforward to obtain in storage rings [4]. Now, afterglow techniques are being developed to enable neutral product distributions to be obtained mass spectrometrically (section 4). Developments in all of these areas will be discussed, as will afterglow techniques.

2. Afterglow techniques

Stationary afterglows were originally used to determine α_{e}, but were superseded by flowing afterglows. However recently, Glosik *et al.* have used an Advanced Integrated Stationary Afterglow (AISA) to determine $\alpha_{\mathrm{e}}(H_3^+)$ [5]. This has dimensions of a 40 cm cube and has ultra high vacuum construction to maintain high purity. Plasma ionization is achieved by a 0.5 ms pulse of standard 2.45 GHz microwave excitation. The ions are monitored in the wall of the vessel via a pinhole orifice using a quadrupole/ion multiplier detection system. It operates at 250 K to further minimize impurities and at a pressure of ~2 Torr. The electron density, [e], is determined by a fixed Langmuir probe located in the body of the plasma, close to the mass spectrometer. The SA is inherently less versatile than the FA since all gases are exposed to the ionization source (and may thus be excited) and are present together so that the ion chemistry is more difficult to control. Since the ions are detected at the wall, they are monitored after diffusing (this is slow because of the high pressure used to inhibit diffusive loss) and, because of recombination loss, may not reflect the ion composition in the body of the plasma. The flowing afterglow is inherently more versatile since the reactant gases can be added at a series of positions in the flow enabling the chemistry to be more accurately controlled (gases are also not exposed to the microwave discharge). Details of the technique are in other reviews [6,7]. Here, ions are monitored in the body of the plasma and are not influenced by diffusion. They are, however, monitored through a sampling orifice by a downstream quadrupole/ion detector and thus in the late afterglow. To compensate for this, the plasma is modeled chemically using rate constants for ion-neutral reactions, which are generally known. Such modeling is also necessary in the SA. The FA has the further advantage that since the time variation is converted to a spatial variation, a given time in the afterglow can be monitored continuously; this is extremely valuable for detection of spectroscopic emissions where the photon counting times are long. FA's are currently used by Adams* [2,3] in Georgia, Glosik* [8] in Prague, Johnsen* [9] in Pittsburgh, Miller, Rowe* [10] in Rennes, Smith and their coworkers, where an * indicates active study of DR. All have a microwave discharge at the upstream end of a flow tube and monitor [e] as a function of distance, z, along the flow tube axis using a Langmuir probe. Individual FA's have special features. The Georgia FA is temperature variable (80-600 K) with reactant gases that can be pulse modulated and that at Pittsburgh has an optical spectrometer and a reactant gas inlet that can be moved along the flow tube axis. The Rennes FA has an axially movable mass spectrometer and that at Prague operates at high pressure (6-8 Torr) and is temperature variable. These different features make the FA's complimentary and provide several ways of determining α_{e}.
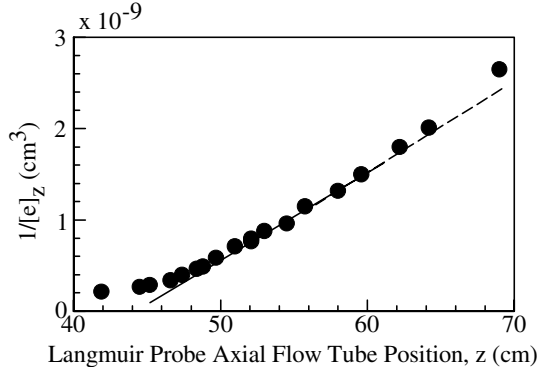
Figure 1. Variation of $1/[e]_z$ with axial position, z, in the flow for the recombination of $C_2H_5^+$, the only ion type present in the plasma [11]. The slope of the linear portion yields α_e/v_p (v_p is usually measured by modulating the plasma upstream and following the disturbance along the flow tube with the Langmuir probe).
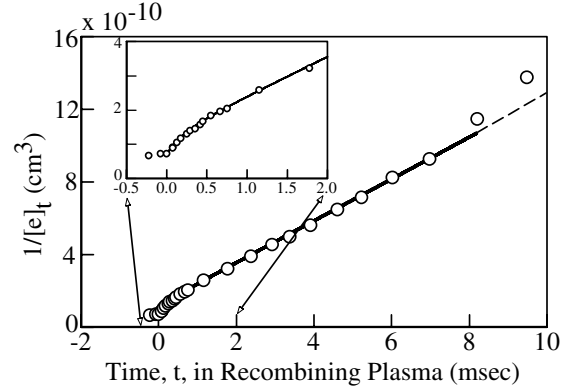
Figure 2. Variation of $1/[e]_t$ versus afterglow time, t, for the recombination of two $C_3H_3^+$ isomers with electrons [12]. Curvature of the plot, as compared with the linear decay in figure 1, indicates the differing α_e for the two recombining ion types.

The conventional means of determining α_e is when only one ion type is present in the plasma. Then the decay of [e] can be represented as

$$\frac{d[e]}{dt} = v_p \frac{d[e]}{dz} = -\alpha_e[e][+] \tag{3}$$

where [+] represents the ion density and v_p is the plasma flow velocity. Since [e] and [+] are equal this can be integrated giving

$$\frac{1}{[e]_z} - \frac{1}{[e]_0} = \alpha_e \frac{z}{v_p} \tag{4}$$

Then a plot of $1/[e]_z$ versus z ($= v_p t$) yields α_e, see figure 1.

If two ion types are present in the plasma and have a common source, then the decay of [e], = $[+_1]$ + $[+_2]$, is controlled by the separate, but coupled decays of the two ions, viz

$$\frac{d[+_1]}{dt} = -\alpha_{e1}[e][+_1] \quad \text{and} \quad \frac{d[+_2]}{dt} = -\alpha_{e2}[e][+_2] \tag{5}$$

By numerically integrating with time interval dt, the values of α_{e1}, α_{e2}, and the initial $[+_1]$ and $[+_2]$ can be varied to match the calculated variation of $[e]_t$ with t to that which can be experimentally determined. An example of this is shown in figure 2 for the simultaneous recombination of cyclic and linear (propargyl) $C_3H_3^+$. It is not possible to determine which ion type has the larger α_e without further information. Fortunately, Milligan *et al.* [13] have shown that the reaction of H_3^+ with allene ($H_2C=C=CH_2$) gives the cyclic and linear isomers in the ratio 30 to 70 and, using this source reaction, enabled the fast and slow recombining ions to be identified.

The axially movable mass spectrometer in the Rennes FA enables yet another approach to be taken [14-16]. Here α_e values can be determined for a minority ion, which is also being lost, by ion-molecule reaction with reactant gas RG (with rate constant k) and diffusion (ambipolar diffusion coefficient D_a and characteristic diffusion length Λ), with the ion decay being given by

$$\frac{d[+]}{dt} = -\alpha_e[+][e] - k[+][RG] - \frac{D_a[+]}{\Lambda^2}. \tag{6}$$

This integrates to yield

$$v_p \ln\frac{[+]_z}{[+]_{z_0}} = -\alpha_e \int_{z_0}^{z}[e]dz - \left(k[RG] + \frac{D_a}{\Lambda^2}\right)(z - z_0) \tag{7}$$

By varying the upstream electron density while monitoring [+] at a fixed z, a plot of $\ln([+]_z/[+]_{z_0})$ versus integrated electron density yields α_e/v_p as the slope. Alternatively, z can be varied in the same sort of plot, but here the reactive and diffusive loss terms are involved and need to be small for accurate α_e to be determined.

3. Recent results

A great deal of effort has been devoted to determining α_e, their temperature dependencies and energy disposal in the recombination process in terms of excitation of the neutral products. Data in all of these areas have been the subject of several reviews [2,17-21]. Only data subsequent to these reviews will be discussed here, unless there is a specific need to mention particular data.

3.1 Room temperature recombination coefficients, α_e

The α_e that have recently been determined at room temperature can be divided into those for hydrocarbon and non-hydrocarbon ions. Consideration of the former enables the effects of hydrogenation and carbon chain length to be investigated. Such data have generally been determined using a FA in Rennes [14-16,22,23], but with some measurements in Georgia [11], Pittsburgh [24] and using SR [25-28]. α_e from 1993 onwards are compiled in table 1. What appears clear from these data is that there is no well-defined trend with increasing hydrogenation and number of C-atoms, although there does seem to be some general increase. Also, no particular technique gives consistently disparate values. However, what is emphasized by the $C_3H_3^+$ data is that there is little knowledge of the isomeric forms of the recombining ions; for $C_3H_3^+$ there is a factor of 7 difference between the α_e for the cyclic and linear (propargyl) forms. More effort needs to be devoted to this problem. Equivalent data for non-hydrocarbon ions is compiled in table 2, from the literature after 1991.

Again, no particular FA or SR technique gives consistently disparate values. The data have behavior consistent with that observed previously; α_e increase slightly with atomicity from $\sim 2.3 \times 10^{-7}$ cm^{3}s^{-1} for diatomics, although some values are very small, to $\sim 4 \times 10^{-7}$ cm^{3}s^{-1} for polyatomics. Most noticeable is the much larger α_e for cluster ions than for the other polyatomic ions (by a factor of ~ 8), a manifestation of "Super-Recombination" [50].

3.2 Temperature dependencies of recombination coefficients

Although room temperature values of α_e are very useful, much more mechanistic information can be derived by studying their temperature dependencies. Two very different types of behavior have been observed as illustrated in figure 3. In (a), there is a dependence of somewhat more than $T^{-0.5}$ at low temperatures, T, changing to somewhat less than $T^{-1.5}$ at higher T. This type of temperature behavior is reminiscent of a change from direct recombination at low T to indirect at high T, although the temperature dependencies of these mechanisms are not precisely defined. A series of reactions exhibit this behavior, as is evident from figure 3(a) and table 3. Comparison of the data with, e.g., MQDT (Multichannel Quantum Defect Theory) [51] would be very valuable for investigating the recombination.

Table 1. Values of α_e (units of 10^{-7} cm^3 s^{-1}) at room temperature measured in experimental work since about 1990, as cited in the text, for a series of hydrocarbon ions as a function of the number of C and H atoms. A line delimits the species not structurally reasonable.

C atom number	H atom number													
	2	3	4	5	6	7	8	9	10	11	13	15	17	20
1	6.4			9 7 3 11										
2		5		9 6 12										
3		7 [a] 8 [a] 1.2 [b]				8.3 19								
4				8.2				8.3		8.2				
5		9						9.5		7.2				
6			11	11	10	24					7.6			
7				7			6.5					5.5		
8						10							8.2	
10								3 8						
12								11.5	15					
14									17					
16									25 30					
32														100

[a] for c-$C_3H_3^+$
[b] for l-$C_3H_3^+$

It was hoped that all hydrocarbon ion recombinations would show this behavior, so that generic T dependencies could be used in the modeling of the Titan ionosphere [11], however, this was not the case, as shown in figure 3(b). For $C_3H_3^+$, the α_e increase slightly at higher T becoming T independent at low T. If the difference between the α_e for the cyclic and linear forms is maintained at the factor of ~7 from 170 K down to interstellar cloud, isc, temperatures, then this could partly explain the different abundances of cyclic and linear C_3H_2 observed in isc [52] (a factor of ~30), since the recombination of $C_3H_3^+$ is believed to be the source of C_3H_2. Obviously, neutral product distributions need to be determined for these recombinations to determine the percentages of C_3H_2.

3.3 Electronically excited products

As mentioned above, information on recombination products is very valuable, both for guiding theory and in applications. When the products are rovibronically excited, these can often be probed using emission spectroscopy and this has been done almost exclusively in a series of FA studies (ground state products are discussed in section 4). In the FA, a series of emissions can occur in parallel from the discharge source, and from ion-molecule and recombination reactions, and it is thus necessary to distinguish recombination out of these. This has been done by adding small quantities of a rapidly electron attaching gas (SF_6 and CCl_4 are used) not sufficient to influence the ion-molecule chemistry, but which removes the electrons thus quenching ei recombination emissions. This can be done by taking spectra with and without attaching gas addition [55] or more effectively by pulse modulating the attaching gas at a given photon wavelength and accumulating photon counts for both situations

Table 2. α_e (unit 10^{-7} cm^3 s^{-1}) at room temperature for a series of non-hydrocarbon ions as a function of atomicity [8,10,24,29-49].

Diatomic ions	
CN$^+$	3.4
CO$^+$	1.6
	1.85
HD$^+$	0.04–0.117
HeH$^+$	0.36
KrH$^+$	<0.2
	<0.12
N$_2^+$	1.75–2.6
NO$^+$	4.4
O$_2^+$	1.9–2.4
XeH$^+$	<0.4
	0.83

Triatomic ions	
CO$_2^+$	3.1
	3.5
H$_2$O$^+$	2.6
HCN$^+$/HNC$^+$	3.9
HCO$^+$	1.5-3.2 [a]
HCS$^+$	5.8
	7.9
HDO$^+$	1.5
N$_2$H$^+$	2.1
	2.8
	7.1[a]
N$_2$O$^+$	3.6

[a] Amano's values [41] of α_e for HCO$^+$ and N$_2$H$^+$, as determined using infrared absorption, are larger than average by factors of 1.6 and 3.

Four-atomic ions	
H$_3$O$^+$	8
HCNH$^+$	2.8
HCO$_2^+$	4.6
HN$_2$O$^+$	4.5
HSO$_2^+$	2.7
N$_2^+$.N$_2$	26

Polyatomic ions	
CH$_3$CNH$^+$	3.3
D$_3$O$^+$.D$_2$O	17
CH$_3$CHOH$^+$	3.9
H$^+$(HCOH)$_2$	33
NH$_4^+$.NH$_3$	48
C$_2$H$_5$CNH$^+$	4.7
H$^+$(CH$_3$CN)$_2$	28
NH$_4^+$(NH$_3$)$_2$	48
	14[b]
H$^+$(CH$_3$COH)$_2$	14
H$^+$((CH$_3$)$_2$CO)$_2$	14
H$^+$(CH$_3$COCH$_3$)$_2$	34[c]
	70[d]

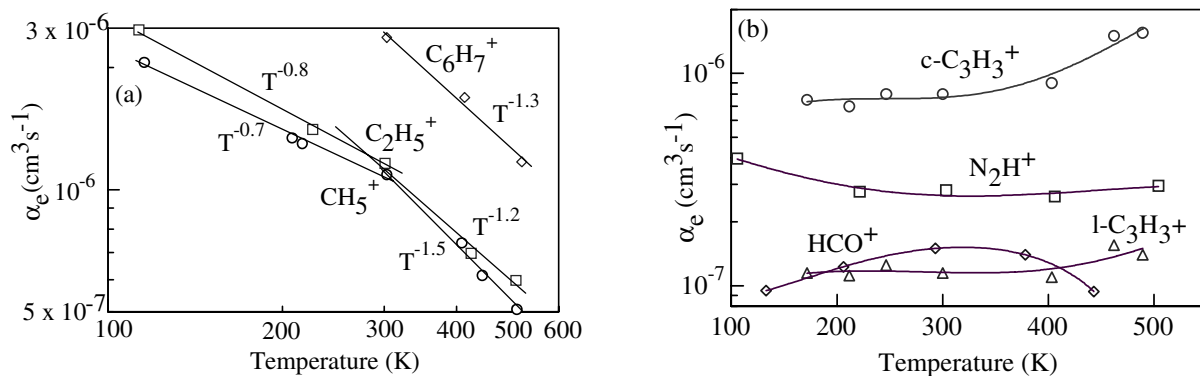[b] Obtained at 600 K
[c] Obtained at 580 K
[d] Obtained at 450 K

Figure 3. Temperature dependencies of α_e for the ions indicated. (a) shows temperature dependent behavior [11], whereas in (b), the α_e for important interstellar ions are quite temperature invariant (C$_3$H$_3^+$ [12]; N$_2$H$^+$ and HCO$^+$ [43]).

Table 3. Temperature dependencies of α_e as observed with various methods (FALP: Flowing Afterglow / Langmuir Probe; MB: Merged Beam; SR: Storage Ring).

Recombining ion	Exponent n of T^n dependence	Temperature range		Technique	Reference
		T (K)	T_e (K) [b]		
O_2^+	−0.65		300–2000	FALP	[38]
	−0.7	100–500		FALP	[11]
NO^+	−0.85		300–2000	FALP	[38]
HNC^+ [a]	−0.96		100–5000	MB	[40]
HCO^+	−1.2		−	MB	[53]
	~ 0	100–500		FALP	[43]
N_2H^+	~ −0.2 / 0 [c]	100 (200) 500		FALP	[43]
$HCNH^+$	−0.65		< 1000	SR	[54]
CH_5^+	−0.7 / −1.5 [c]	100 (300) 500		FALP	[11]
	−0.52		200–1000	SR	[26]
$c-C_3H_3^+$	0 / +0.7 [c]	160 (350) 500		FALP	[12]
$l-C_3H_3^+$	0 / +0.2 [c]	160 (350) 500		FALP	[12]
$C_2H_5^+$	−0.8 / −1.2 [c]	100 (300) 500		FALP	[11]
$C_6H_7^+$	−1.3	300–500		FALP	[11]

[a] vibronically excited

[b] Subscript e refers to electron temperature

[c] Two values given as n_1 / n_2 with transition temperature given in parentheses in next column

until the difference is statistically significant [56]. The effectiveness of this approach has been shown by determining the photon count rates from specific emission lines versus [e]. A very well defined dependence of count rate on [e]² has been observed for a series of lines as expected for recombination emissions from equation (3) [63]. This has enabled vibrational populations of electronically excited states, and in some cases the percentage contribution of that state to the full product distribution [44,58-62], to be determined. Recent data are listed in table 4.
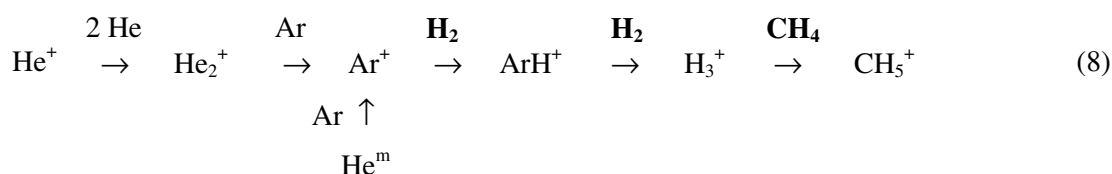
4. New developments

In addition to determining excitation in the product states, it is critical to quantitatively identify the ground state products both for applications and to constrain, test and guide theory. Such studies were initially made with FA for diatomics, H_2O^+ and H_3O^+ [1,64], but detection was spectroscopic and was thus time consuming, restricting the rate at which systems could be studied. With the more straightforward product detection techniques in SR, this rapidly provided a body of data, however, discrepancies were found with the earlier FA studies. In order to provide alternatives, a new FA technique is being developed which does not rely on spectroscopic detection and this is illustrated in figure 4. Ionization is produced in the usual way upstream and reactant gases are added to the flow to generate recombining ions. At the downstream mass spectrometer, residual ions are prevented from entering the detection system by application of suitable potentials to the detection lenses. Neutral He, reactant gases and products of ion-molecule and recombination reactions are unimpeded and pass directly into the detection system where they are ionized by electron impact and detected. The ionized neutrals from recombination can often not be distinguished mass spectrometrically from the background due to other ionized neutrals. However, this can be achieved by pulse modulating an attaching gas (SF_6 or CCl_4) into the flow at a point just downstream of where the recombining ions are

Table 4. Population distributions for vibrational states (relative) and electronic states (%) determined in the FA using emission spectroscopy. Cases where emission was not seen are marked by "NS".

Ion	Product state and population	Vibrational population (relative)										Ref.
		$v=0$	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$	$v=6$	$v=7$	$v=8$	$v=9$	
HCO^+	CO a	1	0.33	0.17	0.16	0.17	0.03	0.04				[57]
DCO^+	CO a	1	0.33	0.17	0.16	0.17	0.03	0.04				[57]
CO_2^+	CO A 0.33%	1	0.58	0.09								[58]
	CO d 40%	1	1.54	2		1.94	0.6	0.1	0.09			[59]
	CO e 0.83%			1		10						[59]
	CO a' 60%				1	2	1.8	0.7	0.18	0.05	0.04	[59]
	CO a 29%											[60]
	CO a' 5.3%											[61]
	CO d 5.7%											[61]
	CO e ~0.09%											[61]
N_2H^+	N_2 B	NS	NS	1	0.31	0.3	0.17	0.07	0.02	0.01	0.007	[57]
		NS	NS	1	0.8	0.42	0.38	0.41	0.13	0.09	0.035	[43][b]
	N_2 B 19%	NS	0.9–1.0	1	0.45–0.52	0.38–0.45	0.26–0.48	0.14–0.17	0.03–0.07			[44][a]
N_2D^+	N_2 B	NS	NS	1	0.31	0.3	0.16	0.04	0.02	0.01	0.007	[57]
		NS	NS	1	0.36	0.3	0.28	0.07	0.07	0.04	0.03	[43][b]
H_2O^+	OH A 7.6%	1	0.89									[62]
CS_2^+	CS A	1	1.08	0.8	0.5	0.5						[63]
	CS a	1	1.2	1.4								[63]
HCS_2^+	CS A	1	1.26	0.95	0.64	0.76						[63]
	CS a	1	0.9	0.9								[63]

[a] Range in vibrational product populations due to the range of axial positions monitored.
[b] Data obtained at 100 K.

generated. Electron attachment is so rapid that the concentrations that have to be added are insufficient to affect the ion chemistry. The rapidly recombining electron/ion plasma is thus converted to the more slowly recombining ion/ion plasma and the products of ei recombination are quenched.

By integrating the ion counts over many pulses, with (B Counts) and without (A Counts) the attaching gas present until the difference (A − B) between these counts is statistically significant, provides a measure of the contribution of this mass to the recombination products, see figure 5. The time required for counting depends on the magnitude of the background relative to the signal.

To illustrate the technique, consider the recombination of CH_5^+, which is produced in the reaction sequence:

$$He^+ \xrightarrow{2\,He} He_2^+ \xrightarrow{Ar} Ar^+ \xrightarrow{H_2} ArH^+ \xrightarrow{H_2} H_3^+ \xrightarrow{CH_4} CH_5^+ \qquad (8)$$
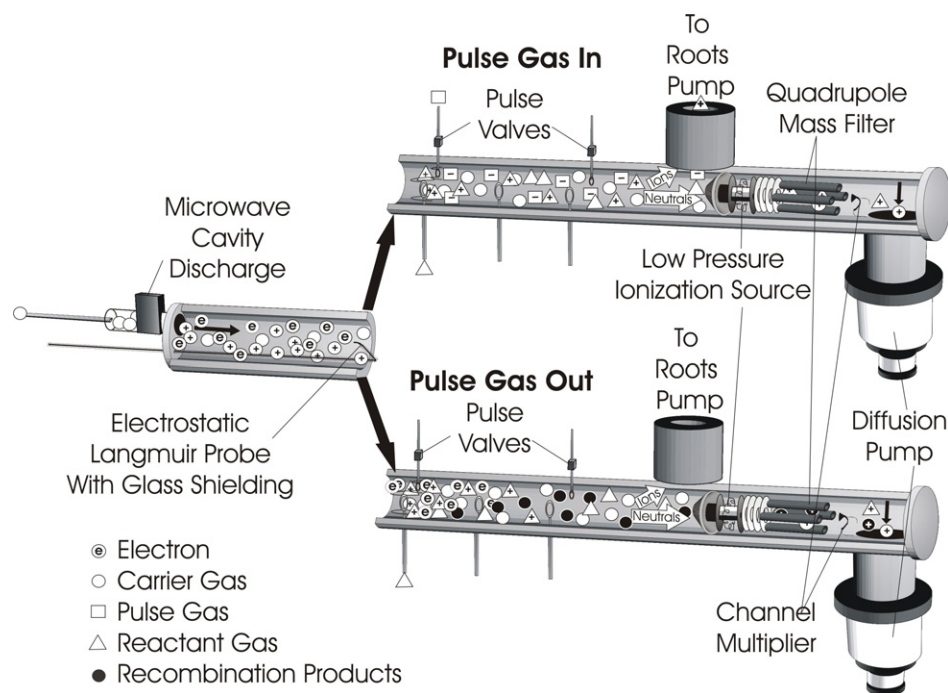
$$Ar \uparrow$$

$$He^m$$

Figure 4. Schematic diagram of a new FA technique for quantitatively identifying the neutral products of recombination. The upper and lower representations of the downstream flow tube show the situations with and without the attaching pulse gas added.

Thus H_2 and CH_4 recombination products, yielding H_2^+ and CH_4^+ on electron impact, have large backgrounds; that for CH_3 is also large since fragmentation on electron impact ionization of CH_4 to give CH_3^+ is large for 70 eV electrons. Backgrounds on H are much smaller, since it is only produced in the reaction of Ar^+ with H_2 and is thus only present in a concentration similar to that of the ions, and those for CH and CH_2 are very small. However, as stated above, accumulation of data for sufficient time on all ions should produce statistically significant results. Preliminary data illustrating this are given in figures 5 and 6. Analysis of these data shows relative contributions to the product distribution for CH_3, CH_2, CH and H (taken as being the contributions of CH_3^+, CH_2^+, CH^+ and H^+) of 27, 16, 4, 53 compared with the values 27, 9, 2 and 62 obtained in the SR [26]. Thus, this technique is showing a great deal of promise. Corrections need to be made for relative diffusion of the recombination products and differing ionization efficiencies and fragmentations, but these appear small.

5. Future goals

The studies summarized above have suggested new directions and new goals that could profitably be pursued. (i) Detailed information is needed on recombinations of particular applied or theoretical interest. (ii) Complimentary techniques need to be developed to compare with previous results and reveal new features. This is beginning with the development of a new FA technique for obtaining product distributions to compare with the results of the very productive SR measurements. Comparison of T dependencies of α_e obtained with both techniques could be very revealing since the FA varies the ion internal temperature whereas the SR does not. This requires α_e versus T to be determined from SR variations of σ with E. (iii) Effects of isomeric structure on α_e, $\alpha_e(T)$, neutral product distributions and product excitation need to be investigated. This has been started with the Rennes hydrocarbon ion studies and the $C_3H_3^+$ investigations. Many isomers exist; $C_3H_3^+$ has two experimentally known and five theoretically (P. Bera and H F Schaefer, priv. com. 2004), and these need to be separately characterized. (iv) In conjunction with theory, operative reaction mechanisms need to be identified, both in terms of comprehensive theories and simple mechanisms (direct, indirect,
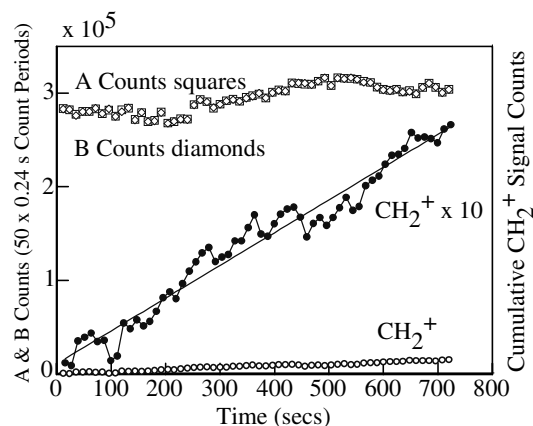
Figure 5. Accumulation of CH_2^+ signal counts (accumulated A – B Counts) over integration periods up to 700 s for CH_5^+ recombination. Also shown are the total A and B counts for shorter count periods to show the stability.
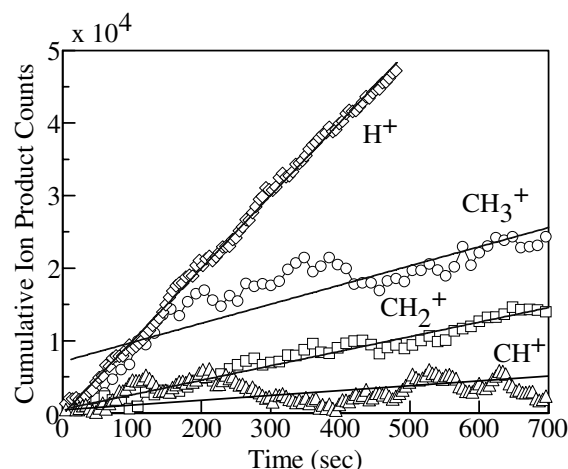
Figure 6. Accumulation of signal counts (A – B Counts) for the ions indicated over integration periods up to 700 s in the CH_5^+ recombination with electrons.

tunneling) or a combination of these. (v) Finally, a longer term goal would be to follow the recombination through the reaction intermediates and explore the competing reaction pathways as is being done with gas phase neutral reactions [65]. Coulombic explosion, as started with the SR [66], could perhaps explore some of this and could maybe tell whether three body fragmentation occurs in one step or is sequential. There are many exciting discoveries waiting to be explored in this developing area of science.

Acknowledgements

References

[1] Rowe B R and Queffelec J L 1989 Experimental Studies of Dissociative Recombination Branching Ratios *Dissociative Recombination: Theory, Experiment and Applications* eds J B A Mitchell and S L Guberman (Singapore: World Scientific) p 151

[2] Adams N G 1992 *Adv. Gas Phase Ion Chem.* **1** 271

[3] Adams N G 1993 Flowing Afterglow Studies of Electron-Ion Recombination using Langmuir Probes and Optical Spectroscopy *Dissociative Recombination: Theory, Experiments and Applications* eds B R Rowe and B A Mitchell (New York: Plenum Press) p 99

[4] Larsson M 2001 *Adv. Gas Phase Ion Chem.* **4** 179

[5] Glosik J, Plasil R, Poterya V, Kudrna P and Tichy M 2000 *Chem. Phys. Lett.* **331** 209

[6] Adams N G and Smith D 1988 Flowing Afterglow and SIFT *Techniques for the Study of Ion-Molecule Reactions* eds J M Farrar and J W H Saunders (NY: John Wiley & Sons, Inc.) p 165

[7] Smith D and Adams N G 1988 The Selected Ion Flow Tube (SIFT): Studies of Ion-Neutral Reactions *Advances in Atomic and Molecular Physics* eds D R Bates and B Bederson (New York: Academic Press) p 1

[8] Glosik J and Plasil R 2000 *J. Phys. B* **33** 4483

[9] Skrzypkowski M P, Johnsen R, Rosati R E and Golde M F 2004 *Chem. Phys. Lett.* **296** 23

[10] Mostefaoui T, Laube S, Gautier G, Rebrion-Rowe C, Rowe B R and Mitchell J B A 1999 *J. Phys. B.* **32** 5247

[11] McLain J L, Poterya V, Molek C D, Babcock L M and Adams N G 2004 *J. Phys. Chem. A* **108** 6704

[12] McLain J L, Poterya V, Jackson D M, Adams N G and Babcock L M 2004 *J. Phys. Chem. A* submitted

[13] Milligan D B, Wilson P F, Freeman C G, Meot-Ner M and McEwan M J 2002 *J. Phys. Chem. A* **106** 9745

[14] Abouelaziz H, Gomet J C, Pasquerault D and Rowe B R 1993 *J. Chem. Phys.* **99** 237

[15] Lehfaoui L, Rebrion-Rowe C, Laube S, Mitchell B A and Rowe B R 1997 *J. Chem. Phys.* **106** 5406

[16] Rebrion-Rowe C, Lehfaoui L, Rowe B R and Mitchell J B A 1998 *J. Chem. Phys.* **108** 7185

[17] Johnsen R 1987 *Int. J. Mass Spectrom. Ion Proc.* **81** 67
[18] Adams N G and Smith D 1988 Laboratory Studies of Dissociative Recombination and Mutual Neutralization and their Relevance to Interstellar Chemistry *Rate Coefficients in Astrochemistry* eds T J Millar and D A Williams (Dordrecht: Kluwer) p 173
[19] Mitchell J B A and Rebrion-Rowe C 1997 *Int. Rev. Phys. Chem.* **16** 201
[20] Adams N G 1994 *Int. J. Mass Spectrom. Ion Proc.* **132** 1
[21] Adams N G and Babcock L M 2000 Identity and Degree of Excitation of the Products of Dissociative Electron-Ion Recombination. *Dissociative Recombination: Theory, Experiment and Applications IV* eds M Larsson, J B A Mitchell and I E Schneider (Singapore: World Scientific) p 190
[22] Hassouna M, LeGarrec J L, Rebrion-Rowe C, Travers D and Rowe B R 2003 Reactions of Electrons with Hydrocarbon Cations: From Linear Alkanes to Aromatic Species *Dissociative Recombination of Molecular Ions with Electrons* ed S L Guberman (New York: Kluwer) p 49
[23] Rebrion-Rowe C, LeGarrec J L, Hassouna M, Travers D and Rowe B R 2003 *Int. J. Mass Spectrom.* **223-224** 237
[24] Gougousi T, Golde M F and Johnsen R 1997 *Chem. Phys. Lett.* **265** 399
[25] Larson A, Le Padellec A, Semaniak J, Stromholm C, Larsson M, Rosen S, Peverall R, Danared H, Djuric N, Dunn G H and Datz S 1998 *Ap. J.* **505** 459
[26] Semaniak J, Larson A, Le Padellec A, Stromholm C, Larsson M, Rosen S, Peverall R, Danared H, Djuric N, Dunn G H and Datz S 1998 *Ap. J.* **498** 886
[27] Ehlerding A, Arnold S, Viggiano A A, Kalhori S, Semaniak J, Derkatch A, Rosén S, af Ugglas M and Larsson M 2003 *J. Phys. Chem. A* **107** 2179
[28] Kalhori S, Viggiano A A, Arnold S T, Rosen S, Semaniak J, Derkatch A M, af Ugglas M and Larsson M 2002 *Astron. Astrophys.* **391** 1159
[29] Canosa A, Rowe B R, Mitchell J B A, Gomet J C and Rebrion C 1991 *Astron. Astrophys.* **248** L19
[30] Abouelaziz H, Queffelec J L, Rebrion C, Rowe B R, Gomet J C and Canosa A 1992 *Chem. Phys. Lett.* **194** 263
[31] Le Padellec A, Mitchell J B A, Al-Khalili A, Danared H, Kallberg A, Larson A, Rosen S, af Ugglas M, Vikor W S L and Larsson M 1999 *J. Chem. Phys.* **110** 890
[32] Geoghegan M, Adams N G and Smith D 1991 *J. Phys. B* **24** 2589
[33] Laube S, Lehfaoui L, Rowe B R and Mitchell J B A 1998 *J. Phys. B* **31** 4181
[34] Lange M, Levin J, Gwinner G, Hechtfischer U, Knoll L, Schwalm D, Wester R, Wolf A, Urbain X and Zajfman D 1999 *Phys. Rev. Letts.* **83** 4979
[35] Le Padellec A, Laube S, Sidko O, Rebrion-Rowe C, Rowe B R, Sarpal B and Mitchell J B A 1997 *J. Phys. B* **30** 963
[36] Peterson J R, Le Padellec A, Danared H, Dunn G H, Larsson M, Larson A, Peverall R, Stromholm C, Rosen S, af Ugglas M and van der Zande W J 1998 *J. Chem. Phys.* **108** 1978
[37] Canosa A, Gomet J C, Rowe B R and Queffelec J L 1991 *J. Chem. Phys.* **94** 7159
[38] Spanel P, Dittrichova L and Smith D 1993 *Int. J. Mass Spectrom. Ion Proc.* **129** 183
[39] Peverall R, Rosen S, Peterson J R, Larsson M, Al-Khalili A, Vikor W S L, Semaniak J, Bobbenkamp R, Le Padellec A, Maurellis A N and van der Zande W J 2001 *J. Chem. Phys.* **114** 6679
[40] Sheehan C, Le Padellec A, Lennard W N, Talbi D and Mitchell J B A 1999 *J. Phys. B* **32** 3347
[41] Amano T 1990 *J. Chem. Phys.* **92** 6492
[42] Rowe B R, Gomet J C, Canosa A, Rebrion C and Mitchell J B A 1992 *J. Chem. Phys.* **96** 1105
[43] Poterya V, McLain J L, Adams N G and Babcock L M 2004 *J. Chem. Phys. A* in preparation
[44] Rosati R E, Johnsen R and Golde M F 2004 *J. Chem. Phys.* **120** 8025
[45] Glosik J, Plasil R, Zakouril P and Poterya V 2003 Dissociative Recombination of Protonated Dimer Ions *Dissociative Recombination of Molecular Ions with Electrons* ed S L Guberman (New York: Kluwer) p 67
[46] Skrzypkowski M and Johnsen R 1997 *Chem. Phys. Lett.* **274** 473
[47] Glosik J, Plasil R and Poterya V 2001 *J. Phys. B* **34** 2781
[48] Plasil R, Glosik J and Zakouril P 1999 *J. Phys. B* **32** 3575
[49] Glosik J, Bano G, Plasil R, Luca A and Zakouril P 1999 *Int. J. Mass Spectrom.* **189** 103
[50] Bates D R 1994 Dissociative Recombination: Crossing and Tunneling Modes. *Advances in Atomic, Molecular and Optical Physics, Volume 34* eds B Bederson and H Walther (San Diego: Academic Press) p 427
[51] Giusti A 1980 *J. Phys. B.* **13** 3867
[52] Irvine W M 1995 *Adv. Space Res.* **15** 35
[53] Le Padellec A, Sheehan C, Talbi D and Mitchell J B A 1997 *J. Phys. B* **30** 319
[54] Semaniak J, Minaev B F, Derkatch A M, Hellberg F, Neau A, Rosen S, Thomas R, Larsson M, Danared H, Paal A and af Ugglas M 2001 *Ap. J. Suppl. Ser.* **135** 275
[55] Johnsen R, Skrzypkowski M, Gougousi T and Golde M F 2000 Spectroscopic Emissions from the Recombination of N_2O^+, N_2OH^+/HN_2O^+, CO_2^+, CO_2H^+, HCO^+/COH^+, H_2O^+, NO_2^+, HNO^+ and LIF Measurements of the H Atom Yield from H_3^+. *Dissociative Recombination: Theory, Experiment and Applications IV* eds M Larsson, J B A Mitchell and I E Schneider (Singapore: World Scientific) p 200
[56] Adams N G, Mostefaoui T and Babcock L M 2003 Technique for Distinguishing and Determining the Origin of Photon Emissions from He^+/Ar^+ Plasmas. *Dissociative Recombination of Molecular Ions with Electrons* ed S L Guberman (New York: Kluwer) p 37

[57] Butler J M, Babcock L M and Adams N G 1997 *Mol. Phys.* **91** 81
[58] Tsuji M, Nakamura M, Nishimura Y and Obase H 1995 *J. Chem. Phys.* **103** 1413
[59] Tsuji M, Nakamura M, Nishimura Y and Obase H 1998 *J. Chem. Phys.* **108** 8031
[60] Skrzypkowski M, Gougousi T, Johnsen R and Golde M F 1998 *J. Chem. Phys.* **108** 8400
[61] Rosati R E, Johnsen R and Golde M F 2003 *J. Chem. Phys.* **119** 11630
[62] Sonnenfroh D M and E. C G 1993 *J. Chem. Phys.* **98** 2872
[63] Plasil R, McLain J L, Molek C D, Adams N G and Babcock L M 2003 *J. Phys. Chem. A* in preparation
[64] Williams T L, Adams N G, Babcock L M, Herd C R and Geoghegan M 1996 *Mon. Not. Roy. Astr. Soc.* **282** 413
[65] Zewail A H 1993 *J. Phys. Chem. A* **97** 12427
[66] Zajfman D, Krohn S, Lange M, Kreckel H, Lammich L, Strasser D, Schwalm D, Urbain X and Wolf A 2003 *Nucl. Instrum. Meth. in Phys. Res.* **B205** 360