A critical review of H$_3^+$ recombination studies

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Abstract: After more that 30 years of experimental and theoretical work it now appears that theory and experiment on H$_3^+$ recombination have finally converged. Since the storage ring results come very close to the latest theoretical calculations one might conclude that "the case is closed". However, some troublesome issues remain and should not be dismissed too quickly. For instance, some afterglow measurements showed faster decays at early afterglow times. It is now clear that the fast recombining species cannot be vibrationally excited ions since the same rates were found for spectroscopically identified H$_3^+$ ions in v=0. On the other hand, there is no convincing explanation for the very small rates obtained in the Prague experiments at low H$_2$ densities. It is also puzzling that some measurements find nearly the same recombination coefficients for H$_3^+$ and D$_3^+$, while others indicate that H$_3^+$ recombines much faster. It has often been stated that vibrational excitation of the H$_3^+$ ions tends to enhance recombination, but the evidence for that is far from solid; some observations suggest that the opposite is just as likely.

1. Introduction
The history of recombination studies of the H$_3^+$ ion still presents a confusing picture, even to someone who has worked on experimental studies of this ion for more than 30 years and has closely followed the “ups and downs” of experimental results and the interplay between experiment and theory. It is most gratifying that we are now at the point where the best available theory [1, 2] agrees rather well with the latest results of ion-storage-ring experiments [3]. Has the time come to close the books and to say that no further work is needed? I do not think so.

If one looks at the experimental results that were obtained over the years (see table 1 and table 2), one notices that the published thermal rate coefficients at temperatures near 300 K have varied by more than one order of magnitude. What shall we make of this large variation? Discarding the older data as “flawed” is not acceptable and may deprive us of useful insights. The variations do not seem to due to ordinary experimental errors such as calibration errors of probes etc. Almost all experimenters also studied the “benchmark ion” O$_2^+$ to test their procedures and in that case the 300 K rate coefficients agree rather well (see e.g. the references to O$_2^+$ data in [4] and [5]). It is far more likely that the poorly controlled and usually unknown internal energy of the H$_3^+$ ion (vibrational, rotational) had an effect on the measured recombination rate. Of course, the vibrational energy of the “benchmark” O$_2^+$ ions also was generally poorly controlled, but fortunately it seems to have only a small effect on the total recombination rate [6] and hence did not lead to significant discrepancies between results.
Table 1. 300 K recombination coefficients measured by afterglow techniques

| \( \alpha (300 \, K) \) \([10^{-7} \, \text{cm}^3/\text{s}]\) | Method | Reference |
|-----------------|--------|-----------|
| 2.3 ± 0.3       | SA     | Leu et al. (1973) [7] |
| 1.6             | SA     | McDonald et al. (1984) [8] |
| < 0.2           | FALP   | Adams et al. (1984) [9] |
| 1.8 ± 0.2       | SA, IR | Amano (1988) [10, 11] |
| 1.5 (1.1)       | FALP   | Canosa et al. (1991) [12], (1992) [13] |
| < 2             | IR     | Feher et al. (1994) [14] |
| < 0.3           | FALP   | Smith and Španel (1993) [15] |
| 0.5 to 2        | FALP   | Gougousi et al. (1995) [16] |
| 0.78 ± 0.23     | FALP   | Laube et al. (1998) [17] |
| < 0.4           | SA (Prague) | Kudrna et al. (2000) [18] |
| < 0.13          |        | Glosík et al. (2000) [19] |
| < 0.03          |        | Glosík et al. (2001) [20] |
| 1.5             | FALP   | Glosík et al. (2004) [21] |
| 1.6 (at 330 K)  | SA, IR | Macko et al. (2004) [22] |

Table 2. Rate coefficients inferred from beam experiments

| \( \alpha (300 \, K) \) \([10^{-7} \, \text{cm}^3/\text{s}]\) | Method | Reference |
|-----------------|--------|-----------|
| See section 3   | MB (MEIBE) | Hus et al. [23] |
| See section 3   | MB (MEIBE) | Yousif et al. [24] |
| 1.15            | ISR (CRYRING) | Larsson et al. (1993) [25] |
|                 |         | Sundström et al. (1994) [26] |
| 1±0.2 \times 10^{-7} | ISR (ASTRID) | Jensen et al. (2001) [27] |
| 0.7             | ISR (CRYRING) | McCall et al. [28] |

I will mainly look at data obtained using afterglow methods and the single-pass merged beam data. The cross-sections measured in ion storage rings (ISR) (see table 2) have been refined considerably over the years, but their magnitudes have not changed much. With the possible exception of the actual rotational state of the ions in the circulating beam, the experimental conditions seem now to be well controlled and characterized. However, the agreement between multiple-pass (ISR) and single-pass merged-beam data is still unsatisfactory. The ISR technique, unlike the single-pass merged beam, allows experimenters to let ions cool off vibrationally for several seconds before turning on the recombination measurement. This is an important strength of the method and may account for the better consistency of results. Since the presence of vibrationally excited ions in storage rings at small storage times has been demonstrated [29], it would be worthwhile to perform some ISR studies of recombination of vibrationally hot ions, if this is technically feasible. Additional state-selective measurements, such as those discussed by Kreckel et al. [30], would also be highly desirable.

My emphasis on measurements of rate coefficients or cross sections is not meant to distract from the extensive work that has been done on branching fractions, kinetic energy releases etc. That subject is covered by others elsewhere in this volume and I will refer to it only as needed in the context of this presentation.
2. Early stationary afterglow results

The earliest afterglow measurements in which the recombining ions were identified by mass analysis are those of Leu et al. (1973) [7] and by Macdonald et al. (1984) [8]. Measurements before 1973 probably refer to mixtures of H$_3^+$ and H$_5^+$ ions and should no longer be quoted as measurements of H$_3^+$ recombination. The rate coefficient obtained by Leu et al. at several gas temperatures below 300 K and by Macdonald et al. at elevated electron temperatures (up to 5000 K, achieved by microwave heating of the plasma electrons) appeared quite ordinary in the sense that the rate coefficient were similar to those found for other ions. This early work has withstood the test of time rather well. If one adds the data points of Macdonald et al. to the latest ISR data graph by McCall et al. [3], one finds that the electron-heated afterglow data reproduce the ISR data and the theory of Kokouline and Greene [1] quite well in the overlapping energy range. However, Macdonald’s et al. data are larger by a factor of two.

The time until 1984, which I think of as the “ignorance is bliss” period, came to an abrupt end when Michels and Hobbs [31], based on their calculations of two-dimensional potential-energy curves, predicted that the ionic ground-potential curve of H$_3^+$ does not be intersect a repulsive curve leading to neutral products. Actually, a similar prediction had been made earlier by Kulander and Guest [32]. Henceforth, it became widely accepted that recombination by the standard curve-crossing mechanism was precluded and that hence recombination of H$_3^+$ in the vibrational ground state should be extremely slow. However, Michels and Hobbs “left the door open” a little bit by pointing out that suitable curve crossings exist for H$_3^+$ ions in the third or higher vibrational states. This prediction had a strong effect on the interpretation of experimental data; it seemed natural and tempting to invoke vibrational excitation whenever an experiment showed fast recombination of H$_3^+$.

I believe that much of the “variability” of the measured H$_3^+$ recombination rates can be traced to interpretational biases introduced by trying to conform to a now outdated theory. To make this point clearer, it will be necessary to review briefly the methods of producing H$_3^+$ ions in flowing and stationary afterglows.

Ion-formation and vibrational excitation

The early stationary afterglows employed several different gas mixture and reaction schemes, but most later experiments used essentially the same reaction sequence: Helium carrier gas (at pressures near 1 Torr) is ionized and excited to the metastable state by a microwave discharge. Argon (at a pressure of typically 15% of the helium pressure) is usually (but not always) added to convert metastable helium atoms to Ar$^+$ ions by Penning ionization. To create H$_3^+$ ions, H$_2$ is introduced at densities from 10$^{14}$ to 10$^{15}$ cm$^{-3}$. The fast two-step reaction sequence

\[
\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} + 1.53 \text{ eV} \tag{1}
\]

\[
\text{ArH}^+ + \text{H}_2 \rightarrow \text{Ar} + \text{H}_3^+ + 0.57 \text{ eV} \tag{2}
\]

releases sufficient energy to produce H$_3^+$ in vibrational states up to $v=5$. However, proton transfer to Ar,

\[
\text{H}_3^+(v) + \text{Ar} \rightarrow \text{ArH}^+ + \text{H}_2 \tag{3}
\]

rapidly destroys all H$_3^+$ ions with internal energies above 0.57 eV. The remaining H$_3^+$ vibrational states are the ground state [A$_1$ (0, 0$^0$)], the $v_2=1$ bending-mode vibration [E (0, 1$^1$) at 0.3126 eV], and the $v_1=1$ breathing mode vibration [A$_1$ (1, 0$^0$) at 0.394 eV] (see Lie and Frye [33] or Oka and Jagod [5]). The radiative lifetime of the $v_1=1$ state is very long. Dinelli et al. [24] calculated a lifetime of 1.2 s for cascading to the $v_2=1$ state which then decays in 4 ms to the ground state. Thus, radiative decay of the $v_1=1$ state will not occur on the time scale of recombination (typically several hundred microseconds). Radiative decay of ions in the $v_2=1$ level is faster (~4 ms), but it is still slower than recombination under typical conditions.
In afterglows collisional destruction (quenching) of $v=1$ ions will also occur in collisions with neutrals but the rate coefficients for quenching are not reliably known. Amano's [34] absorption studies of the $v=2$ hot band indicate that the $v=1$ level is quenched by H$_2$ with a rate coefficient of approximately $3\times10^{-10}$ cm$^3$/s. If this number is true, then $v=1$ ions will be destroyed in 30 µs at [H$_2$]=1×10$^{15}$ cm$^{-3}$. On the other hand, Lee et al. [35] and Blakley et al. [36] find that some vibrationally excited ions are quenched with a far smaller rate coefficient of roughly $10^{-12}$ cm$^3$/s. Those ions would survive for 10 ms at [H$_2$]=1×10$^{14}$ cm$^{-3}$. The slowly-quenched ions are probably those in the $v=1$ level. A similar conclusion was reached by Bawendi et al. [37] who studied the absorption of H$_3^+$ hot bands in He/H$_2$ discharges. This suggests that only H$_3^+(v=1)$ ions survive long enough to undergo recombination. Observations by Lee et al. [35] indicate that ~70% of the ions may be in the vibrational ground state and 30% in an excited state. Since the $v=1$ ions are quenched rapidly, it seems very likely that the 30% long-lived ions were in the $v=1$ state.

Afterglow measurements are sensitive to an effect which one might call the “survival of the unfittest”: When two (or more) ion species are present, the fractional concentration of the slower recombining species increases with afterglow time and hence the effective recombination coefficient $\alpha_{\text{eff}} = \alpha_1 f_1 + \alpha_2 f_2$ (with $f_1+f_2=1$) eventually approaches that of the slowly recombining species. This situation can be difficult to unravel when the ion species only differ in internal state (e.g. vibrational) and when in addition quenching converts one species into the other. In modified form, the “survival of the unfittest” also occurs in multiple-pass merged-beam experiments and then leads to time-dependent apparent recombination cross section [38]. In single-pass merged-beam experiments it does not occur.

**Afterglow data after 1984**

In 1984, Adams et al. [9] applied their newly developed “Flowing Afterglow/Langmuir-Probe” (FALP) technique to the recombination of H$_3^+$ and other interesting ions. The H$_3^+$ ions were generated by Penning ionization of H$_2$ by helium metastables and subsequent reaction of H$_2^+$ with H$_2$. Adams et al. noticed that the electron density decay exhibited a deviation from the simple decay law for a single-ion afterglow. The initial electron-density decay was quite fast, compatible with a recombination coefficient near $10^{-7}$ cm$^3$/s, but then it changed to a slower decay indicating an immeasurably small ($<2\times10^{-8}$ cm$^3$/s) recombination rate coefficient. Michels’ and Hobbs’ prediction immediately offered an explanation for this effect, namely that the initial fast decay was caused by recombination of vibrationally excited ions ($v>3$) and that the slow decay should be ascribed to H$_3^+$ in $v=0$, with perhaps an admixture of $v=1$ ions. In these experiments, argon was not added to the afterglow; hence, the destruction of ($v>3$) ions by proton transfer to argon would not have occurred. Adams et al. accepted this explanation and concluded that $v=0$ ions recombine only slowly, with a rate of less than $2\times10^{-8}$ cm$^3$/s. It is this number that is usually quoted in the literature as the result of their work. What is not sufficiently appreciated is that the identification of the vibrational states was made on the basis of Michels’ and Hobbs’ prediction, not by independent experimental identification of states. Michels’ and Hobbs’ work has since been superseded by newer and far more extensive calculations that predict a fairly large recombination coefficient for H$_3^+(v=0)$. It appears to me that one should not continue to cite the work by Adams et al. as providing evidence for a slow recombination of $v=0$ ions. At one time, Adams and Smith [39] reported that the recombination rate for $v=0$ ions is even smaller ($10^{-11}$ cm$^3$/s). This very low value was later traced to an experimental problem (presence of He$^+$ ions) and has been retracted [40].

One may ask the question why the early stationary afterglow measurements gave no hint of a slowing recombination rate during the later afterglow, from which, according to Adams et al., one should infer the correct recombination of $v=0$ ions. In a review article, Johnsen [41] suggested as one plausible explanation that the formation of impurity ions could have led to an overestimate of the H$_3^+$ recombination rate. This statement, in the context in which it was made, was true, but it has sometimes been misunderstood. In the work by Macdonald et al., the concentration (~1% at early times, rising to ~10% in the late afterglow) of 17 amu impurity ions (presumably fast recombining CH$_5^+$ with $\alpha\sim1\times10^{-6}$ cm$^3$/s) would have increased the measured recombination rate by only $10^{-8}$ cm$^3$/s in the
early afterglow but by $\sim 10^{-7}$ cm$^3$/s in the late afterglow. Since Macdonald et al. analyzed the early afterglow they given recombination coefficient of $1.6 \times 10^{-7}$ cm$^3$/s at 240 K perhaps should be adjusted slightly down to $1.5 \times 10^{-7}$ cm$^3$/s. However, the experiment would have failed to show a transition to the very slow recombination ($< 2 \times 10^{-8}$ cm$^3$/s) in the late afterglow and thus did not provide a solid argument against the findings of Adams et al.

The interpretation of Adams et al. experiment was seriously challenged by the experiment of Amano [10] who used an infrared absorption technique to monitor the decay of the $\text{H}_3^+$ ($v=0$) density in the afterglow of a radio-frequency discharge in hydrogen. Now, there could be no doubt about the state of the ion. At a gas temperature of $T=210$ K Amano inferred a recombination coefficient for $v=0$ ions of $1.8 \times 10^{-7}$ cm$^3$/s, confirming the findings of Leu et al. and Macdonald et al., but contradicting Adams et al. and Michels and Hobbs. A lively and sometimes heated debate followed in which both sides criticized aspects of the opponents’ experiments. Both Amano [10] and Smith, now working with Španel [15, 40] repeated their experiments, arriving at essentially the same conclusions as before. The work by Smith and Španel was far more extensive than that the original studies by Adams et al. The authors did find indications for the presence of vibrationally excited ions but the crucial question, which of the states recombined fast or slowly, was not clearly answered. In this set of experiments argon was added and $v>3$ ions should have been destroyed by argon. Hence, ions with sufficient vibrational energy to enable recombination by curve crossing should not have been present, certainly not with a concentration of 80%, the fast-recombining fraction seen by Smith and Španel. Judging the controversy from the current state of knowledge, in my opinion Amano’s measurements must be regarded as valid, at least those above 210 K. Amano’s conclusions have also been confirmed by a very recent optical absorption (cavity ring down) measurement by Macko et al. [22]. However, some aspects of Amano’s experiments can be questioned, one being that his decay rates at very low temperature are actually smaller than expected from collisional radiative recombination. As Bates et al. [42] have pointed out, the occurrence of collisional radiative recombination is inescapable. The second point of concern is that Amano’s measurement on the ion $\text{N}_2\text{H}^+$, using the same methods, gave far larger rate coefficients than other experiments. This is still puzzling. The third point of concern is that Amano did not carry out a simultaneous measurement of the electron densities. The measurements by Adams et al. and by Smith and Španel show quite convincingly that the electron-density decay in $\text{H}_3^+$-containing afterglow plasmas shows a peculiar deviation from a simple recombination law. However, I do not think that their data support the conclusion that $\text{H}_3^+$($v=0$) ions recombine only very slowly. The rate coefficient of $1.3 \times 10^{-7}$ cm$^3$/s that they give for excited ions probably refers to $v=0$ ions and the slower decay in the late afterglow may refer to vibrationally excited $\text{H}_3^+$, perhaps in the lowest breathing mode of vibration.

Around this time the theorists began to doubt the “conventional wisdom” that curve crossing are essential for efficient recombination of molecular ions. Experiment began to drive theory! Bates et al. [42], in their often-cited paper “Enigma of $\text{H}_3^+$ dissociative recombination”, presented an insightful review of the experiments and then proposed a multi-step mechanism to rationalize experimental results but the results were not sufficiently quantitative to persuade the community that the “enigma” had been disposed of.

Several additional flowing-afterglow measurements were carried out in Rennes and in Pittsburgh. The first study performed in Rennes [12] gave rate coefficients of $1.1 \times 10^{-7}$ cm$^3$/s at $T = 650$ K for $\text{H}_3^+$, stated to be in $v=0$, and $1.5 \times 10^{-7}$ cm$^3$/s at 300 K for ions believed to be of low vibrational excitation ($v\leq2$). The second study, performed after a modification of their flow tube, resulted in a factor-of-two lower value of $7.8 \times 10^{-8}$ cm$^3$/s at 300 K. Laube et al. [17] did not find any variation of the apparent recombination as a function of afterglow time. In contrast, Gougousi et al. [16] saw a decline of the recombination rate at late times and found that the apparent recombination rate (inferred from the early afterglow decay) increased from $1.5 \times 10^{-7}$ cm$^3$/s to nearly $2 \times 10^{-7}$ cm$^3$/s when the experimental $\text{H}_2$ concentration was raised from $1 \times 10^{14}$ cm$^{-3}$ to $15 \times 10^{14}$ cm$^{-3}$. Gougousi et al. attempted to explain their data in terms of a mixture of two different $\text{H}_3^+$ vibrational states, but
eventually preferred the explanation that the H$_3^+$ recombination proceeded by a three-body mechanism in which both electrons and neutral hydrogen play a role. In their view, their data did not provide evidence that H$_3^+$ recombination in a plasma proceeded exclusively by binary recombination. Since theories available at the time seemingly precluded fast binary recombination of $v=0$ ions, three-body mechanisms seemed viable at the time. Judging this explanation ten years later, the need for such ad-hoc explanations has been lessened considerably by the advent of more thorough theoretical explanations. However, I would not rule out that smaller three-body effects might contribute to recombination in plasmas. A second point to made about the Gougousi et al. three-body mechanism is that it requires the formation of long-lived H$_3^+$ Rydberg molecules in DR of H$_3^+$. Such have been only been found in merged-beam [43] but not in ISR experiments.

I tried to re-analyze some of the Gougousi et al. data using a two-state model in which the dominant part (around 80%) of the ion population consists of fast-recombining H$_3^+(v=0)$ ions and the remaining population recombined very slowly. Such models can be made to reproduce the data, but they rely on too many adjustable parameters, especially vibrational quenching rates, to permit firm conclusions. Nevertheless, the experimental findings are compatible with the assumption that the fast recombining ions (about 80%) were in $v=0$, while the remaining fraction consisted of slowly recombining ions. The increase of the apparent recombination rate with increasing H$_2$ concentration could then be ascribed to a more rapid quenching of vibrationally excited ions.

The recombination coefficients obtained in the second set of the Rennes experiments are somewhat smaller ($7.8 \times 10^{-8}$ cm$^3$/s) than those obtained in their earlier work and other afterglow studies. In addition, the authors did not find the decline of the recombination rate that was observed by Smith and Španel and by Gougousi et al. Perhaps, the methods of analysis used by Laube et al. provide a less sensitive test of changes in the recombination coefficient. They obtain the recombination coefficient from a graph of the kind used by the authors then will have a slope that reflects the average $\alpha$, with $n_e$ as a weighting factor. I carried out some simple model calculations, in which I assumed that the two H$_3^+$ ions were present, 80% recombining with $\alpha = 1.5 \times 10^{-7}$ cm$^3$/s, 20% non-recombining. The resulting graph of the equation above, using the electron-density range given in the Laube et al. paper, produced an acceptably straight line with slope $\alpha = 9.6 \times 10^{-8}$ cm$^3$/s, not much larger that the value $7.8 \times 10^{-8}$ cm$^3$/s obtained in the experiment. While I did not investigate the full range of conditions used in the experiment, the sample calculation indicates a possible reason why the experiment may have given a low value of $\alpha$ and showed no time dependence. On the other hand, the authors carried out a second set of experiments, in which Kr$^+$ was used as the precursor ion to make H$_3^+$ in $v=0$; the observed rate agreed well with that obtained when Ar$^+$ ions were used. It is puzzling that Laube et al. found nearly the same recombination coefficient ($6.7 \times 10^{-8}$ cm$^3$/s) for D$_3^+$ as for H$_3^+$ while most other measurements gave lower (by factors of 2 to 3) values for D$_3^+$. One possible reason may be that in the case of slowly recombining D$_3^+$, the average $\alpha$ obtained from (4) is closer to that at early times. My model calculations show that this tends to reduce the difference between the inferred D$_3^+$ and H$_3^+$ recombination rates, but I was not able to match the experimental values precisely.
3. Single-pass merged-beam data

The single-pass merged-beam method, in the form of the MEIBE apparatus that existed at the University of Western Ontario, was used several times to study $\text{H}_3^+$ recombination. In single-pass measurements, the ions do not have sufficient time to relax vibrationally or rotationally before merging with the electron beam. Hence, it is not surprising that the experimenters noticed pronounced dependences of the inferred DR cross sections on the type of ion source used and its operating parameters. The observed effects were quite drastic: Hus et al. [23] found a nearly 20 times larger cross DR cross section when the “rf source” was used rather than the “trap source”. The studies of greatest interest for the present discussion are those of Hus et al. and Yousif et al. [24] in which the authors sought to determine which of the vibrational states were present in the beam by measuring the threshold energy for the electron impact excitation of $\text{H}_3^+$ from $^1\text{A}_1'$ to the dissociating state $^3\text{E}'$, i.e. the process

$$e^- + \text{H}_3^+ \rightarrow e^- + \text{H} + \text{H}_2$$

(5)

In the Yousif et al. experiment, the ions were produced in a radio-frequency trap source, the same source that in the experiments of Hus et al. produced slowly recombining ions. They observed a sharp rise of the cross section at 15 eV, the expected threshold for $v=0$ ions, and concluded that the ion beam contained predominantly $v=0$ ions. This was seen as evidence that large DR cross sections (implying 300 K rate coefficients near $1\times10^{-7}$ cm$^3$/s) were only obtained when the beam contained vibrationally excited ions. However, the observed sharp observed rise of the excitation cross sections above threshold is difficult to reconcile with theory [44] and was not seen in later measurements of the same excitation process [45].

With the benefit of hindsight, I do not think that Yousif’s et al. main conclusion (low DR rate for $v=0$) can be upheld. How to explain the dependence on ion source conditions is a different matter. Again, I see no viable alternative to the assumption that some vibrational (or perhaps rotational) states of $\text{H}_3^+$ recombine slowly but this explanation creates a conundrum. It would imply that the ion sources used in those experiments sometimes produced nearly pure sample of $\text{H}_3^+$ in non-recombining excited states, but sometimes produced nearly pure samples of fast recombining ions. Small admixtures of excited ions to a predominantly $v=0$ ion population cannot explain the large observed variation of the DR cross-sections.

The merged-beam experiment may have been subject to other effects. Mitchell (in Mitchell and Johnsen [46]) describes a merged-beam experiment in which the deflection field used to separate product neutrals from the ions in the post-collision region was varied. It was found that the measured DR product signal increased by a factor of five (approaching that obtained in ISR experiments) when the field strength in that region was reduced from 3000 V/cm to 200 V/cm. Mitchell suggested that this effect was caused by field ionization of $\text{H}_3$ Rydberg molecules that are produced by DR of $\text{H}_3^+$. At the high field strength, but not at the lower, a substantial fraction of the recombination products would be re-ionized and would not be counted as DR products. Mitchell pointed out one difficulty with his suggestion, namely that field-ionization should have been equally effective in the bending magnet in ISR experiments. The motional electric field in the magnet is even larger than 3000 V/cm. His suggestion also implies that $\text{H}_3$ Rydberg molecules account for at least 80% of the DR products. Otherwise, a factor-of-five reduction of the product yield under high-field conditions should not have been seen. Such a high product fraction for $\text{H}_3$ Rydberg molecules is hard to reconcile with other measurements of product yields. Mitchell’s statement that the observed DR cross sections at the low separation fields were close the ISR values appears to be the origin of Larsson’s [47] statement that the merged-beam and CRYRING had now been reconciled. This conclusion does not seem to be fully justified at this time.
4. The recent afterglow data obtained in Prague

Glosík and his coworkers in Prague have an active research program on H$_3^+$ and D$_3^+$ recombination, using both a flow tube and an advanced stationary afterglow apparatus (AISA). Details of their techniques and results are presented by Glosík and also by Plasil elsewhere in this volume. As far as the flowing afterglow data are concerned, there is no particular discrepancy with earlier work. The same is true for the results obtained in the AISA system when the measurements were done in the presence of high concentrations of H$_2$ (>10$^{12}$ cm$^{-3}$). However, Glosík and his coworkers made the very interesting observation that the DR rate coefficient fell of rapidly (down to ~1×10$^{-9}$ cm$^3$/s) when the H$_2$ concentration was reduced to below 10$^{12}$ cm$^{-3}$. It is one unique feature of the AISA apparatus that, due to its large size and hence small diffusion losses, the afterglow can be followed for much longer times. The decline of the DR rate coefficient to very small values at low H$_2$ (or D$_2$) concentrations was observed for both H$_3^+$ and D$_3^+$. A convincing explanation of this finding has not yet been given. If we accept that (a) the experimentally measured electron-density decays are due to H$_3^+$ recombination, that (b) they refer to H$_3^+$ (v=0) ions, and that (c) the true binary rate coefficient of H$_3^+$ at 300 K is at least as large as that inferred from the ISR experiments and theory (~ 7×10$^{-8}$ cm$^3$/s), then we have indeed a “very interesting problem”. Of the three assumptions, (b) can be challenged. Perhaps, quenching of vibrationally excited H$_3^+$ becomes very ineffective at low H$_2$ concentrations. If excited ions recombine more slowly, as I have tentatively suggested throughout this paper, this might explain the findings. An additional problem may be that the neutral H$_2$ molecules in the experiment become vibrationally excited in the discharge. It is known that this happens in nitrogen discharges. This may prevent vibrational cooling of the ions. Assumption (a) is also far from certain. It is true that the experimenters conclusions are supported by model calculations and that the mass spectrometer showed the presence of H$_3^+$ ions. However, model calculations of afterglow plasmas are notoriously difficult and the mass spectrometer samples ions only from the edge of the plasma. Fortunately, the Prague group has embarked on an ambitious program to use optical absorption (using a cavity-ring-down technique) to verify the existence of H$_3^+$ in v=0 in their afterglow. First results (using a test chamber rather than the complete AISA system) have been most encouraging and I hope that the Prague group will pursue this project until a clear conclusion is reached.

5. Conclusions

It appears that the “discrepancies” between experimental results on the DR coefficient of H$_3^+$ are not nearly as serious as is sometimes stated. Early theoretical predictions that H$_3^+$ “cannot recombine” often led experimenters to interpret their observation in such a way as to conform to theory. If one makes allowance for such biases, then the recombination coefficients obtained in afterglows, with exception of the AISA data from Prague at low H$_2$, span only about factor of 2.5 (from 7×10$^{-8}$ cm$^3$/s to about 2×10$^{-7}$ cm$^3$/s) and are not much larger than those obtained by ISR techniques and calculated by the best available theory. I think that there are some good reasons to suspect that some vibrationally excited H$_3^+$ ions recombine more slowly than those in v=0. If this were so, it would explain a number of observations in afterglows and in merged-beam experiments. This conjecture may turn out to be false but it has the virtue that it can be tested by theory and/or experiment.

References

[1] Kokouline V and Greene C H 2003 Phys. Rev. A 68 012703
[2] Kokouline V and Greene C H 2003 Phys. Rev. Lett. 90 133201
[3] McCall B J, Huneycutt A J, Sakally R J, Geballe T R, Djuric N, Dunn G H, Semaniak J, Novotny O, Al-Khalili A, Ehlerding A, Hellberg F, Kalkori S, Neau A, Thomas R, Österdahl F and Larsson M 2003 Nature 422 500
[4] Gougousi T, Golde M F and Johnsen R 1997 Chem. Phys. Lett. 265 399
[5] Peverall R, Rosen S, Peterson J R, Larsson M, Al-Khalili A, Vikor L, Semaniak J, Bobbenkamp R, Le Padellec A, Maurellis A N, van der Zande W 2001 J. Chem. Phys. 114 6679
[6] Petrignani A, Hellberg F, Thomas R D, Larsson M, Cosby P C and van der Zande W 2005 J. Phys.: Conf. Series this volume
[7] Leu M T, Biondi M A and Johnsen R 1973 Phys.Rev. A 8 413
[8] Macdonald J A, Biondi M A and Johnsen R 1984 Planet. Space Sci. 32 651
[9] Adams N G, Smith D and Alge E 1984 J. Chem. Phys. 81 1778
[10] Amano T 1988 Ap. J. 329 L121
[11] Amano T 1990, J. Chem. Phys. 92, 6492
[12] Canosa A, Rowe B R, Mitchell J B A, Gomet J C and Rebrion C 1991 Astron. Astrophys. 248 L19
[13] Canosa A, Gomet J C, Rowe B R, Mitchell J B A and Queffelec J L 1992 J. Chem. Phys. 97 1028
[14] Feher M, Rolubacher A, Maier J P 1994 Chem. Phys. 185 357
[15] Smith D and Spanel P 1993 Int. J. Mass Spectrometry and Ion Processes 129 163
[16] Gougousi T, Johnsen R and Golde M F 1995 Int. J. Mass Spectr. and Ion Proc. 149/150 131
[17] Laube S, Le Padellec A, Sidko O, Rebrion-Rowe C, Mitchell J B A and Rowe B 1988 J. Phys. B 31 2118
[18] Kudrka P, Spanel R, Glosik J, Tichy M, Poterya V and Rusz J 2000 Czechoslovak Journal of Physics 50 329
[19] Glosik J, Spanel R, Poterya V, Kudrka P and Tichy M 2000 Chem. Phys. Lett. 331 209
[21] Macko P, Bano G, Hlavenka P, Spanel R, Poterya V, Pysanenko A, Votava O, Johnsen R, Glosik J 2004 Int. J. Mass Spectrom. Ion Processes 233 299
[23] Hus H, Yousif F B, Sen A and Mitchell J B A 1988 Phys. Rev. A 38 658
[24] Yousif F B, Van der Donk P J T, Orakzi M and Mitchell J B A 1991 Phys. Rev. A 44 5653
[25] Larsson M, Danared H, Mowat J R, Sigray P, Sundström G, Broström L, Filevich A, Källberg A, Mannervik A S, Rensfelt K G and Datz S 1993 Phys. Rev. Lett. 70 430
[26] Sundström G, Mowat J R, Danared H, Datz S, Broström L, Filevich A, Källberg A, Mannervik S, Rensfelt K G, Sigray P, af Ugglas M and Larsson M 1994 Science 263 785
[27] Jensen M J, Pedersen H B, Safran C P, Seiersen K, Urbain X and Andersen L H 2001 Phys. Rev. A 63 052701
[28] McCall B J, Huneycutt P J T, Orakzi M and Mitchell J B A 1991 Phys. Rev. A 44 5653
[29] Krohn S, Kroth S, Lammich L, Levin J, Scheffel M, Schwalm D, Tennyson J, Vager Z, Wester R, Wolf A and Zajfman D 2002 Phys. Rev. A 66 052509
[30] Krochel et al. 2005 J. Phys.: Conf. Series this volume
[31] Michels H H and Hobbs R H 1984 Astrophys. J. 286 L27
[32] Kulander K C and Guest M F 1997 J. Phys. B 12 L501
[33] Lie G C and Frye D 1992 J. Chem. Phys. 96 6784
[34] Amano T 1993 in Dissociative Recombination: Theory, Experiment and Applications ed Rowe B R, Mitchell J B A and Canosa A (Plenum Press, New York)
[35] Lee H S, Drucker M, Adams N G 1992 Int. J. Mass Spectrom. Ion Processes 117 101
[36] Blakley C R, Vestal M L and Futrell J H 1977 J. Chem. Phys. 66 2392
[37] Bawendi M G, Rehfuss B D and Oka T 1990 J. Chem. Phys. 93 6200
[38] Kroth S, Amiray Z, Baer A, Zajfman D, Lange M, Knoll L, Levin J, Schwalm D, Wester R and Wolf A 2000 Phys. Rev. A 62 032713
[39] Adams N G and Smith D 1988 in Rate coefficients in astrochemistry ed Millar T J and Williams D A (Kluwer, Dordrecht) p 173-192
[40] Smith D and Španel P 1993 Chem. Phys. Lett. 211 454
[41] Johnsen R 1987 Int. J. Mass Spectrom. Ion Processes 81 67
[42] Bates D R, Guest M F and Kendall R A 1993 Planet. Space Sci 41 9
[43] Mitchell J B A, Forand J L, Ng C T, Levac D B, Mitchell R E, Mull P M, Claes W, Sen A and McGowan J Wm 1983 Phys. Rev. Lett. 51 885
[44] Orel A E 1992 Phys. Rev. A 46 1333
[45] Jensen M J, Pedersen H B, Safran C P, Seiersen K, Urbain X and Andersen L H 2001 Phys. Rev. A 63 052701
[46] Johnsen R and Mitchell J B A 1998 Advances in Gas Phase Chemistry 3 49
[47] Larsson M 1995 Int. J. Mass Spectrom. Ion Processes 149/150 403