Kinetic processes in recombining $\text{H}_3^+$ plasmas

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Recombination in plasmas containing $\text{H}_3^+$ ions occurs not only by binary recombination but also by third-body-assisted mechanisms, the principal subject of this contribution. Third-body effects on recombination are of interest for model calculations of hydrogen discharges, their spectral emissions and the inference of binary recombination coefficients from plasma afterglow data.

Keywords: recombination; $\text{H}_3^+$; hydrogen plasmas; three-body recombination

1. Introduction

In a recent review of ion-storage-ring (ISR) data on the recombination of $\text{H}_3^+$ ions, Petrignani et al. [1, p. 9] conclude that ‘presently no rate coefficient measurement with a confirmed temperature below 300 K exists’. Their doubts mainly concern the abundances of rotational and para/ortho ions in the ISR collision region, and possible perturbing effects arising from residual electric fields. It was, in part, this statement that motivated me to examine what can be inferred from low-temperature plasma afterglow measurements.

Binary recombination of $\text{H}_3^+$ ions dominates in low-density environments, such as interstellar clouds. Afterglow plasmas at higher densities, however, explore additional mechanisms to return to the neutral state, as is immediately apparent when one examines historical recombination data. Figure 1 compares selected afterglow rate coefficients [2,3,5,6] to the thermal recombination coefficient inferred from earlier ISR experiments [4].

Theoretical calculations [7,8] are in good agreement with the ‘thermal’ rate coefficients of McCall et al. [4]. While the ‘raw’ afterglow data are larger by factors of 2–4, the ‘discrepancy’ is greatly reduced if one corrects for third-body effects, as was carried out by Glosík et al. [3]. The quotes around the word ‘discrepancy’ are meant to indicate that the negative connotation of the term is undeserved. The uncorrected ‘raw’ data may be just those that are needed for applications to discharge physics.

A more complete account of the history of $\text{H}_3^+$ recombination studies can be found in the review of Johnsen & Guberman [9]. This brief contribution adds some ideas on the interpretation of afterglow data, and proposed three-body

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mechanisms and a conjecture concerning the origin of the low-energy resonances observed in storage-ring measurements. These are intended to be ‘food for thought’ rather than as definite conclusions.

2. Recombination in afterglows

First of all, one should be aware that afterglow experiments are subject to complications other than third-body effects. In a ‘stationary afterglow’, one ignites a pulsed discharge in a suitable gas or gas mixture, and then observes the afterglow in the same chamber. This can lead to undesired dissociation products and internally excited (e.g. vibrationally) neutral molecules that survive into the afterglow phase. If one is not aware of this, one can draw erroneous conclusions. The ‘flowing afterglow’ avoids this problem by igniting the discharge in a flowing pure rare gas (most often helium) and adding ‘cold’ molecular gases further downstream. The gas mixture and densities have to be tailored such that the initial formation of the desired ion species is essentially completed before recombination dominates the plasma evolution. Otherwise, the ion formation (not recombination) becomes the rate-limiting step in the plasma decay.

In studies of binary recombination, one seeks to minimize the effects that ambient neutral and charged particles have on the recombination, such as collisional radiative recombination (CRR) or neutral-assisted recombination. In practice, this is not always possible. H$_3^+$ recombination appears to be particularly sensitive to third-body effects because it proceeds via intermediate Rydberg states that are easily perturbed. Possible three-body mechanisms will be discussed in the next section.

Figure 1. A comparison of afterglow H$_3^+$ recombination coefficients to ISR results. Note that the data by Glosík et al. [3] have been corrected for three-body effects.
(a) Collisional radiative recombination and collisional dissociative recombination

In the case of atomic ions, CRR is a universal recombination process that involves only hydrogenic Rydberg states. The dependence of the effective binary recombination coefficient on electron temperature $T_e$ (K) and on electron density $n_e$ ($\text{cm}^{-3}$) can be expressed by the formula of Stevefelt et al. [10]:

$$\alpha_{\text{CRR}}(\text{cm}^3\text{s}^{-1}) = 3.8 \times 10^{-9} T_e^{-4.5} n_e + 1.55 \times 10^{-10} T_e^{-0.63} + 6 \times 10^{-9} T_e^{-2.18} n_e^{0.37} \quad (2.1)$$

At low temperatures and high electron densities (e.g. $T_e < 300 \text{ K}$ and $n_e > 10^{10} \text{ cm}^{-3}$), the first, strongly temperature-dependent collisional term dominates. The formula looks simple, but the electron temperature $T_e$ is not really an independent variable because CRR releases energy that raises the electron temperature in the decaying plasma. As has been known for many years [11], under some conditions, the rate-limiting process in the plasma decay is the rate at which the electron gas is cooled by collisions with ions, not CRR as such. The cooling rate then is proportional to the square of the electron density, the same kinetic dependence as in binary recombination, not the three-body kinetics of CRR. If one is unaware of this, one may conclude that one observes binary, rather than ternary recombination. Bates et al. [12] pointed this out in their famous ‘enigma’ paper while trying to explain the experimental observations in $H_3^+$ afterglows of Amano [5].

The collisional part of CRR (the first term in equation (2.1)), when written as $A^+ + 2e^- \rightarrow A(n,l) + e^-$, looks like the inverse of electron-impact ionization, but the highly excited product neutrals (with principal and angular momentum quantum numbers $n$ and $l$) are quickly re-ionized and enter an approximate Saha equilibrium with the free electrons. The rate of electron capture into a range of high Rydberg states with principal quantum numbers is much larger (e.g. eqn (9) in [13]) than that given by the first term in equation (2.1). It rises rapidly (roughly as $n^6$) with increasing $n$. At a temperature of 300 K and an electron density $n_e = 4 \times 10^{10} \text{ cm}^{-3}$, the capture rate coefficient (into $n = 40$–80, and all $l < n$) is about $4 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}$, which is far in excess of typical binary dissociative recombination rate coefficients of simple ions. While three-body recombination involving energy transfer to atoms (e.g. helium) is less efficient, by a factor of approximately $10^7$ at $T = 300 \text{ K}$, the atom density in many experiments exceeds the electron density by a similar factor. Three-body capture involving two electrons populates all angular momentum states with similar rates because the inverse (electron-impact ionization) is fairly insensitive to the angular momentum $l$ of the Rydberg orbital. Furthermore, angular momentum mixing by electrons is much faster than collisional ionization (by roughly a factor of 100). Hence, the statistical distribution among $l$-states for a given $n$ is maintained on an even shorter time scale than the equilibrium between the free and bound electrons.

Extending the ‘universal formula’ for CRR to molecular ion cores is difficult. Collins [14] proposed that the rate of CRR is enhanced if one or more of the high molecular Rydberg states are capable of predissociation and hence cannot be re-ionized. Bates [15] estimated that this collisional dissociative recombination (CDR) process can be quite fast, but little further work has been published since. In the limit of small electron and neutral densities, the rate-limiting step in CDR is the three-body capture, and the effective CDR rate coefficient...
then should increase linearly with the neutral and electron densities. At high densities, the effective rate of CDR is limited by the rate of predissociation of high Rydberg states (with abundances proportional to \( n^2 \)) and gives the appearance of binary recombination. As Massey & Gilbody [16] remarked, CDR is difficult to distinguish (experimentally) from dissociate recombination!

(b) Neutral-assisted ternary recombination due to atoms

The extensive data collected in the afterglow measurements by the Prague group [3] leave little doubt that \( \text{H}_3^+ \) recombination can be enhanced by neutral helium atoms. The mechanism producing the enhancement is not obvious. The ‘classical’ model of neutral CRR fails because the electron–atom energy transfer is too inefficient. The angular momentum of the orbiting electron can be changed more easily by ‘\( l \)-mixing’ [17], and this can affect recombination because electrons with small \( l \) (e.g. p-electrons, with ‘penetrating orbits’) interact more efficiently with the ion core and can induce rapid predissociation of the molecular core, thereby completing recombination. The effect of \( l \)-mixing due to electrons on \( \text{H}_3^+ \) recombination was first considered by Gougousi et al. [18]. Here, we focus on proposed models in which helium atoms are the \( l \)-mixing agent.

The model of Glosík et al. [3] invokes capture of p-electrons by \( \text{H}_3^+ \) ions into rotationally excited Rydberg states \( \text{H}_3^* \) (with \( n \) from 40 to 100), followed by \( l \)-mixing due to helium, and eventual decay by dissociation. The assumption is made that dissociation of high-\( l \) states is faster than autoionization, and it is implicitly assumed that it is also faster than collisional ionization by electrons. Approximate agreement with experimental data (at \( T_e \sim 300 \text{K} \)) was obtained when rather large \( l \)-mixing rates were taken for high principal quantum numbers, which may be in conflict with the lower theoretical \( l \)-mixing rates of Hickman [17], but this is not entirely clear. A more important problem is that capture of electrons into rotational resonances followed by \( l \)-mixing does not really change the thermal Saha populations of high Rydberg atoms. If, as assumed, dissociation of high-\( l \) Rydberg completes the recombination, the same should happen without the resonant capture step and \( l \)-mixing by helium, and then the extrapolation of experimental data to zero helium density (at finite electron densities) would include a contribution from CDR.

An alternative model [9] views the helium-assisted recombination process as a variation of CDR. Here, \( l \)-mixing due to helium is thought to enhance recombination by converting a well-mixed population of high \( l \)-states, initially formed by three-body capture involving two electrons, to low \( l \)-states that subsequently predissociate. The low-\( l \) states here act as a ‘sink’ that depletes the ‘reservoir’ of high-\( l \) states. If one uses the \( n^{-2.7} \) fall-off of the \( l \)-mixing rate given by Hickman [17], which strongly emphasizes states of low \( n \), one can obtain agreement [9] with experiment [3] at \( T_e = 300 \text{K} \). However, a more detailed analysis of the rate equations shows that this model overestimates the three-body rate coefficients. Briefly, the model borrowed an assumption from simplified treatments of CRR, namely that the population of Rydberg states with energies down to \(-4kT\) below the ionization limit (the ‘bottleneck’ of [11]) is approximately in Saha equilibrium. This assumption fails when states in that range are depleted by rapid predissociation. A slower decline of the \( l \)-mixing rate with increasing \( n \) would remedy this problem, but it is difficult to go
further without better information on the relevant rates. At this time, it is not clear whether \( l \)-mixing really constitutes the rate-limiting step that leads to the dependence on helium density. A complete model of CDR may provide a better explanation. Unfortunately, as Bates [15] observed many years ago, ‘The set of equations may easily be written down but serves no useful purpose because of lack of information on the rate coefficients involved’.

Neither of the two \( l \)-mixing models reproduces the temperature dependence (between 77 and 300 K) of the three-body rate observed by Glosik et al. [3] that exhibits a maximum around 150 K. The rate of CDR should simply increase with decreasing temperature since the Saha populations increase. On the other hand, there will be fewer rotationally excited \( \text{H}_3^+ \) ions at lower gas temperatures. If rotational excitation is necessary for (or at least enhances) predissociation of high Rydberg states, this might explain why the three-body rate declines below 150 K.

One brief suggestion for afterglow experimentalists: \( l \)-mixing by neon atoms should be less effective than by helium because the electron-impact cross section is smaller. It may be worthwhile to carry out experiments using neon buffer gas.

(c) **Neutral-assisted ternary recombination due to \( \text{H}_2 \)**

At low gas temperatures \( \text{H}_3^+ \) ions in \( \text{H}_2 \) can enter a cluster equilibrium with \( \text{H}_5^+ \) ions that recombine much faster (about 20 times) than \( \text{H}_3^+ \). This can give rise to \([\text{H}_2]\) density dependences that have nothing to do with three-body recombination as such. It also seems possible, though, that \( \text{H}_5^+ \) Rydberg atoms, formed by CRR or some other process, react with \( \text{H}_2 \) by associative ionization and either produce \( \text{H}_5^+ \) ions, or form transient \( \text{H}_5^+ \) complexes that subsequently predissociate. Some experimental data (e.g. Gougousi et al. [18]) have indicated a dependence on hydrogen density. Unfortunately, too little is known about this process to make reasonable estimates of its importance.

3. **Afterglow measurements in pure \( \text{H}_2 \)**

The \( \text{H}_3^+ \) recombination studies by Amano [5] in pure \( \text{H}_2 \) afterglows had a profound impact when they were published because they seemed to provide the first credible evidence that recombination of \( \text{H}_3^+ \) ions in the vibrational ground state is a fast process, contrary to what others had inferred from their data. At an electron temperature of 110 K, Amano obtained a rather large recombination rate of approximately \( 4.3 \times 10^{-7} \text{ cm}^3 \text{s}^{-1} \). The ensuing controversy focused on a possible contribution by CRR. One of Amano’s arguments in favour of his interpretation that he observed binary recombination rested on the observed linear dependence of the reciprocal ion density as a function of afterglow time, exactly what is expected for binary recombination. Following up on the suggestion of Bates et al. [12], I constructed a model that includes the heat input into the electron gas from CRR and the heat loss in collisions with ions and neutrals, using standard plasma physics formulae. The result indeed confirmed the suggestion of Bates et al. At a fixed electron temperature of 110 K (Amano’s estimate of \( T_e \)), a gas temperature of 77 K and an initial electron density of \( 3 \times 10^{11} \text{ cm}^{-3} \), the effective CRR rate calculated from equation (2.1) would be very large, approximately.
7 × 10⁻⁷ cm³ s⁻¹. However, if one takes the heating into account, the electron temperature in the early afterglow would rise to approximately 160 K, and reduce the CRR rate coefficient to approximately 1.4 × 10⁻⁷ cm³ s⁻¹ and remain constant until the electron density approaches approximately 3 × 10¹⁰ cm⁻³. Hence, a fraction of Amano’s rate coefficient can be ascribed to CRR, but not all of it.

There is another problem, however: it is difficult to accept Amano’s assumption that the H⁺_3 ions did not cluster with H₂ to form H⁺_5. I made a simple numerical model that includes the H⁺_3 to H⁺_5 conversion. At a gas temperature of 77 K and [H₂] = 5 × 10¹⁶ cm⁻³, the effect on the graphs of the reciprocal H⁺_3 density as a function of afterglow time should have been drastic. But why was this not observed? My answer is somewhat speculative: the (stationary) afterglow plasma probably contained a significant population of vibrationally excited hydrogen that dissociated most H⁺_5 ions back into H⁺_3 and H₂. It is difficult to estimate the actual equilibrium fraction of H⁺_5 and to retrieve the H⁺_3 recombination coefficient from the data. A small fractional H⁺_5 population (around 5%) would suffice to double the apparent recombination coefficient. The real situation may be even more complicated because the electron and H₂ vibrational temperatures are coupled [19].

Spectroscopic observations of H₃ and D₃ emission and absorption features in H₂ (D₂) afterglows [20,21] support the conclusion that H⁺_5 recombination is one source of the observed emissions. It is less clear how much H⁺_5 contributes to the total observed recombination.

4. Afterglows in rare-gas/H₂ mixtures

Afterglows in helium–argon–hydrogen mixtures are the subject of the paper by Dohnal et al. [22], presented at this meeting. The authors present evidence that para-H⁺_3 ions recombine much faster than ortho-H⁺_3 by both the binary and the three-body mechanisms. Their paper should be consulted for details. However, I would like to make two brief comments at this point. The binary recombination coefficient is taken as that obtained by extrapolating measured rate coefficients to zero helium density. But should one not also extrapolate to zero hydrogen density? In many of their measurements, the Prague group found that the effective recombination coefficients of H⁺_3 (and of D⁺_3) declined sharply (to < 10⁻⁸ cm³ s⁻¹) when the H₂ (D₂) densities were reduced from 10¹² cm⁻³ to 10¹¹ cm⁻³, which is difficult to reconcile with the theoretical results and the ISR data. As discussed in more detail by Johnsen & Guberman [9], this observation probably does not indicate a true dependence of the recombination coefficient on [H₂], but more likely resulted from slow formation of H⁺_3 at low H₂ concentrations. However, other explanations (J. Glosík & R. Plašil 2012, personal communication), for instance that the H⁺_3 ions at low [H₂] are in one or more slowly recombining states, cannot be entirely ruled out at this time.

In principle, one should also extrapolate the observed recombination coefficients to very low electron densities, but again this cannot be done in practice. Most available data indicate that the electron density (in the experimental range) has little effect. An element of doubt remains, however (see [18]).
5. A conjecture concerning resonances in storage-ring measurements

The afterglow data on para- and ortho-H$_3^+$ suggest that the low-energy peaks around 0.01 eV that are seen in storage rings should be due to para-H$_3^+$, while storage-ring measurements are not the subject of this contribution, I would like to share one observation that I made while trying to understand three-body effects in afterglow recombination.

The helium-assisted process, proposed by the Prague group [3] and two theoretical colleagues, invokes long-lived electron–ion rotational resonances as the first step. Their paper contains an interesting graph of calculated lifetimes for the rotational resonance from the (1, 1) to the (2, 1) state of para-H$_3^+$ as a function of electron energy. It is then argued that the states with the longest autoionizing lifetimes have the best chance of being $l$-mixed (see §2b), but this is a viable proposal only if those states do not rapidly predissociate, in which case dissociative recombination would be the fastest decay mode. It occurred to me that, if, contrary to expectation, these resonant states actually do predissociate in some fashion, this should leave a signature in the high-resolution-storage-ring data. Strangely enough, this seems to be true. If one examines the storage-ring data [1], one finds three, currently unassigned, peaks in the range around 0.005–0.02 eV, at the same energies where the lifetimes of the rotational resonances are the largest. In Petignani et al. [1, fig. 5] the peaks are labelled C and E (the next higher peak should be ‘G’ but is not labelled as such). The correlation could be due to coincidence, of course, but perhaps it indicates that these rotational resonances actually lead to dissociative recombination. The largest experimental peak in that energy range (at 6 meV, labelled ‘A’) does not have a counterpart in the lifetime graph and probably has a different origin. The storage ring data by Kreckel et al. [23, fig. 8] may provide a clue: the central part of peak ‘A’ remained nearly unchanged when para-enriched rather than normal hydrogen was fed to the ISR ion source, possibly because the actual abundance of the responsible species did not change when para-enriched H$_2$ was substituted. Perhaps peak ‘A’ reflects a resonance from the (2, 1) target rotational state to the (3, 1) rotational state.

The Rydberg states formed by the rotational capture would have high principal quantum numbers. Petignani et al. [1] suggest that something ‘problematic’ may be happening to some of the theoretically predicted dissociative recombination resonances that appear to be missing in the experimental data. One potential such problem that comes to mind is that $l$-mixing by stray fields may lengthen their predissociation lifetime sufficiently to enable them to survive the flight to the separation magnet, at which point they suffer rapid field ionization in the motional electric field. This would affect mainly Rydbergs in very high states.

There are some interesting questions here, but I leave them to those who are more familiar with theory and the intricacies of ISR experiments.

6. Conclusions

Larsson et al. [24] asked whether the ‘saga’ of H$_3^+$ recombination had come to an end and conclude that it is not quite finished. Further surprises may indeed come, but I think we now have a better idea where the remaining pieces of the puzzle belong. A theoretically well-founded assignment of the prominent low-energy
peaks in the ISR data remains an important task. While it is encouraging that afterglow and ISR data can be reconciled to some extent, a better understanding of $\text{H}_3^+$ recombination in the plasma environment is also still needed. The two problems may be linked.

References


