Discrepancies between $\text{H}_3^+$ recombination rate coefficients measured in ion storage rings, afterglows, and theory. Are they “real” or “apparent”? 

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Abstract. While theoretical Jahn-Teller calculations of the binary dissociative recombination of $\text{H}_3^+$ ions with electrons agree quite well with the results obtained in ion storage rings, many plasma afterglow measurements have yielded either much lower (by factors of 10 or more) or higher values (by factors of 3 to 4). This paper examines possible causes of these apparent discrepancies. Numerical afterglow simulations indicate that the very low recombination coefficients obtained in afterglows at very low concentrations of neutral hydrogen were affected by the presence of slowly recombining ion species ($\text{Ar}^+$ and $\text{ArH}^+$) and do not really pose a challenge to the storage ring data and theoretical results. On the other hand, the faster recombination observed in afterglow plasmas seems to be due to third-body assisted mechanisms that occur in addition to binary recombination.

1. Introduction

Experimental and theoretical studies of the dissociative recombination of “simple” triatomic $\text{H}_3^+$ ions have a long and controversial history. The results obtained by the storage-ring method [1,2] now agree rather well (except for some finer details) with the theoretical results based on the Jahn-Teller mechanism [3] and earlier doubts about the process have largely disappeared. The binary rate coefficients inferred from ion storage-ring data can be expressed by the power law

$$\alpha(T_e)[\text{cm}^3/\text{s}] = -1.3\times10^{-8} + 1.27\times10^{-6}T_e^{-48}$$

(1)

as a function of the electron temperature $T_e$. If one accepts the 300 K storage-ring value ($\sim7\times10^{-8}$ cm$^3$/s) as a “benchmark”, then the coefficients observed in many plasma afterglow measurements are either “too large” by factors of 2 to 3, or “too small” by factors of 10 and more. The question then arises if plasma recombination involves different or additional recombination mechanisms or if the afterglow measurements were simply “flawed”. The resolution of these apparent discrepancies is the subject of this paper. I will first discuss the unusually small values.

2. Slow recombination at low hydrogen concentrations

An extensive series of afterglow measurements by the Prague experimenters [4] seems to show that the $\text{H}_3^+$ recombination rate drops far below the binary value (by a factor of 10 and more) when the hydrogen concentration in their experiments was reduced to below about $1\times10^{12}$ cm$^3$ and similar results were obtained for $\text{D}_3^+$ ions [5]. Several suggestions have been
made to rationalize these observations: Perhaps, the equilibrium between the ortho and para spin modifications of H$_3^+$ was not maintained at low H$_2$ concentrations and the low values are due to slowly recombining ortho H$_3^+$ ions. However, this explanation is incompatible with results of both theory and other experiments: The effect of the nuclear spin states is actually rather small, at least at 300 K. Likewise, tentative suggestions that the ions in those experiments were in some excited vibrational state that recombines slowly have been ruled out by recent theoretical calculations. Considerable latitude in devising H$_3^+$ recombination mechanisms existed before the storage ring data and theory became well established, but at this time it is difficult to accept recombination mechanisms in which the presence of hydrogen is necessary for recombination. The principal function of hydrogen in afterglow measurements is simply to provide the molecules needed to produce H$_3^+$ ions. But is it obvious that the H$_3^+$ ions in the cited measurements at low [H$_2$] were formed sufficiently fast to become the dominant recombining species? The H$_3^+$ ions were produced by the reaction scheme: Ar$^+$ + H$_2$→ArH$^+$ + H followed by ArH$^+$ + H$_2$→Ar$^+$ + H$_3^+$. The reactions are quite fast (rate coefficients near $10^{-9}$ cm$^3$/s) but it takes roughly 10 msec at [H$_2$] = 10$^{11}$ cm$^{-3}$ to produce H$_3^+$ ions, while recombination of an ion with $\alpha$~ $10^{-7}$ cm$^3$/s (at $n_e$ = 10$^{10}$ cm$^{-3}$) proceeds at a time scale of $1/\alpha n_e$=1 msec. In most other experiments [H$_2$] is made sufficiently large to form H$_3^+$ ions in a time short compared to the recombination time scale!

To examine the question in some more detail, I constructed a simple numerical model that simulates the afterglow processes and the methods of analysis, called the “advanced analysis” by the Prague group [6]. They determine the recombination coefficients from graphs of the quantity

$$-(\frac{1}{n_e} \frac{dn_e}{dt} + \frac{\nu_d}{n_e})$$ (2)

vs. $1/n_e$, using experimentally measured values of the electron densities $n_e$ and the ambipolar diffusion loss rate $\nu_d$. My numerical model shows that an input value of $\alpha$ = $10^{-7}$ cm$^3$/s leads to same inferred value only if [H$_2$] is somewhat larger than 10$^{10}$ cm$^{-3}$. For [H$_2$] =10$^{11}$, the simulated data (see Figure 1) approach the input recombination rate asymptotically in the limit $1/n_e$→∞. If one extrapolates the data to $1/n_e$=0, as the authors did (see e.g. [6]) for reasons that I do not fully understand, one obtains a much smaller, incorrect value. The model also returns the relative abundance of the ions as a function of time and one sees that non-recombining Ar$^+$ and ArH$^+$ decay fairly slowly and that H$_3^+$ does not become dominant until very late in the afterglow. If one carries out simulations for much smaller assumed H$_3^+$ recombination coefficients ($\alpha$ = 2×10$^{-8}$ cm$^3$/s) one finds that H$_3^+$ dominates much earlier. In that case the experiment would have worked correctly. However, an experiment that contradicts the larger (“default”) values should be capable, in principle, to measure them! I should emphasize that the extensive data collected at higher [H$_2$] are not affected by such problems.
Figure 1 Simulation of an afterglow in an He/Ar/H$_2$ mixture for [H$_2$] = 1×10$^{11}$ cm$^{-3}$ for an H$_3^+$ recombination coefficient of 1×10$^{-7}$ cm$^3$/s. Extrapolation to $1/n_e=0$ returns a far smaller recombination coefficient.

3. Third-body assisted recombination

Many afterglow experiments have yielded H$_3^+$ recombination coefficients that are considerably larger than the binary value obtained in storage ring experiments. A nearly complete compilation for data obtained in helium/argon/hydrogen mixtures can be found in the paper by Glosik et al [4] and these observations strongly suggest some form of third-body assisted recombination. The well-known collisional-radiative mechanisms for atomic ions in which either electrons or neutral particles stabilize the recombination are definitely too slow (by about two orders of magnitude) to explain observations. Several ideas for more efficient three-body recombination have been proposed:

One might assume that the scattering resonances in electron/molecular-ion collisions have sufficiently long lifetimes to permit interactions with third particles (atoms, molecules, electrons) which reduce the probability of releasing the electron by autoionization. Gougousi et al [7] proposed that vibrational resonances might live long enough to be stabilized by angular-momentum changing (l-mixing) collisions and reactions with ambient H$_2$ molecules. In hindsight, the lifetimes used in their estimates were unrealistically long. Glosik et al [4] devised a mechanism in which rotational resonances undergo l-mixing in collisions with ambient He atoms and form a population of long-lived Rydberg molecules with $n>40$. This is an improvement over the earlier model, in as much as it uses more realistic, theoretically calculated lifetimes, but I think the model has several shortcomings: The l-mixing efficiency was taken as independent of principal quantum number $n$ instead of declining as $1/n^{2.7}$, as indicated by theory [8]. The final stabilizing process of the Rydberg molecules remains (a) unspecified and (b) it would have to be competitive with collisional reionization by electrons which is extremely fast for high Rydbergs.

I have explored a third possible three-body mechanism that is loosely based on the collisional dissociative mechanism of Collins [9]. I assume, as is done in the theory of collisional radiative recombination, that high Rydberg states with energies down to about $-4kT$ below the ionization limit, formed by three-body collisions and destroyed by its inverse (collisional ionization),

$$e^- + H_3^+ + M \leftrightarrow H_3^+(n) + M$$

are in thermal Saha equilibrium, i.e.

$$\frac{[H_3^+(n)]}{[H_3^+]n_e} = K(n) = n^2 \lambda_{th}^3 e^{E_i/kT}$$

where $\lambda_{th}$ denotes thermal deBroglie wavelength $\lambda_{th} = (\hbar^2 / (2\pi m_k T))^{1/2}$.

Most of the these states will have high electronic angular momenta $l$ which makes predissociation unlikely, but l-mixing due to electrons and/or atoms can reduce $l$ to small values (I took $l=0$ in my estimate) and induce predissociation. Note that the l-mixing here goes from high $l$ to low $l$. If states in a range of $n$-values are irreversibly destroyed with frequency $\nu$, the recombination rate will exceed the binary value by...
\Delta \alpha = \sum_{n_{\text{mix}}} K(n) \nu_r(n) \tag{6}

The l-mixing cross section due to the electrons [10] and the corresponding rate coefficient rise sharply with increasing \( n \)
\[ \sigma_{e, \text{mix}} = 4.4 \times \pi a_0^2 n^5 \]
while the l-mixing rate coefficient due to helium [8] falls off \( n^{-2.7} \)
\[ k_{\text{mix,He}} = 3.1 \times 10^{-5} \frac{1}{n^{2.7}} \text{[cm}^3 \text{/s]} \tag{8} \]

Both rates have to be divided by \((n^2 - 1)\) to take into account that one needs the rates from a given \( l \) state to \( l=0 \). A further consideration shows that l-mixing will cease to be the rate limiting process for \( n \) greater than about 40 because predissociation decrease with \( n \) as approximately \( 1/n^3 \).

Estimates based on this model indicate that He atoms (the carrier gas in the experiments) can have a significant effect. Fairly low Rydberg states with \( n \) from 10 to 40 are more important than higher states. The estimated three-body rate coefficient due to helium at \( T = 300 \text{ K} \) comes out to be \( 2.6 \times 10^{-25} \text{[cm}^3 \text{/s]} \) which agrees with the experimental value [4] of \( (2.5 \pm 1.2) \times 10^{-25} \text{[cm}^3 \text{/s]} \). The close agreement is almost certainly fortuitous, but it is encouraging. More detailed work is clearly needed.

4. Conclusion
I have serious doubts about the validity of the very low \( \text{H}_3^+ \) recombination coefficients that were inferred from some afterglow measurements at low \([\text{H}_2] \). Perhaps I misunderstand some aspects of the experiments, but results that contradict many other findings require stronger substantiation than has been provided. There is good experimental evidence that three-body assisted recombination of \( \text{H}_3^+ \) occurs in plasma afterglows in addition to binary recombination. The theoretical models that have been proposed to rationalize these observations are still rather tentative, but they may serve as points of departure for more accurate treatments.

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