Kinetic processes in recombining H_3^+ plasmas

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Recombination in plasmas containing 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.

Key words: Recombination, H_3^+, hydrogen plasmas, three-body recombination

1. Introduction

In a recent review of ion-storage-ring (ISR) data on the recombination of H_3^+ ions Petrignani et al (2011) 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 perhaps 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 H_3^+ ions dominates in low-density environments, such as interstellar clouds. An afterglow plasma at higher densities, however, explores 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 (Leu et al 1973, Macdonald et al 1984, Amano 1990, Glosík 2009) to the thermal recombination coefficient inferred from earlier ISR experiments (McCall 2004).

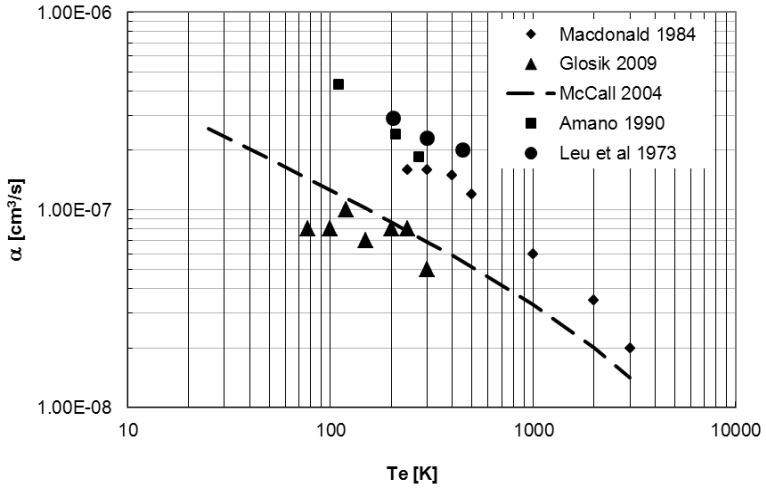

Fig 1. Comparison of afterglow H_3^+ recombination coefficients to ISR results. Note that the data by Glosik et al (2009) have been corrected for three-body effects.

Theoretical calculations (Kokoouline and Greene 2003, Fonseca dos Santos et al, 2007) are in good agreement with the "thermal" rate coefficients of McCall (2004). While the "raw" afterglow data are larger by factors of 2 to 4, the "discrepancy" is greatly reduced if one corrects for third-body effects, as was done by Glosik et al (2009). 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.

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 becomes the rate-limiting step in the plasma decay, not recombination.

In studies of binary recombination one seeks to minimize effects ambient neutral and charged particles 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.

(a) Collisional radiative recombination (CRR)

CRR is a universal recombination process that involves only hydrogenic Rydberg states. The strongly temperature dependent "effective" binary recombination coefficient can be expressed by the universal formula of Stevefelt et al. (1975):

$$\alpha_{\mathrm{CRR}}[\mathrm{cm^3 s^{-1}}] = 3.8\times10^{-9} T_e^{-4.5} n_e + 1.55\times10^{-10} T_e^{-0.63} + 6\times10^{-9} T_e^{-2.18} n_e^{0.37} . \qquad (1)$$

Under the conditions of interest here (electron temperatures T_e < 300 K, and electron densities $n_e > 10^9$ cm^{-3}), the first (collisional) term dominates. The formula looks simple but the electron temperature T_e is not really an independent variably because CRR releases energy that raises the electron temperature in the decaying plasma. As has been known for many years [Byron et al 1962], 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 (1993) pointed this out in their famous "enigma" paper while trying to explain the experimental observations in H_3^+ afterglows of Amano (1990). The validity of the "universal formula" for CRR in the case of molecular ions is not certain. Collins (1965) proposed that the rate of CRR is enhanced if one or more of the high molecular Rydberg states are capable of predissociation.

A further point should be made. CRR, when written as $A^+ + 2e^- \rightarrow A + e^-$, looks like the inverse of electron-impact ionization, but the neutral is initially formed in high Rydberg states that are quickly ionized again. A better picture to have in mind is that the plasma contains a population of high Rydberg atoms, in approximate Saha equilibrium with the free electrons. For electrons bound by energies of a few kT_e, the equilibrium is established on a time scale of the reciprocal ionization rate for high Rydbergs, times on the order of nanoseconds to microseconds. All angular momentum states are populated according to their statistical weights, since the inverse (electron-impact ionization) is fairly insensitive to the angular momentum *l* of the Rydberg orbital. This is one reason why additional "*l*-mixing" of high Rydbergs (e.g. with n>40 due to ambient atoms (e.g. He) cannot enhance recombination, as has been proposed (Glosik et al 2009). Mixing a population in statistical equilibrium cannot have an effect. We will return to this later.

(b) Neutral-assisted ternary recombination due to atoms

The extensive data collected in the afterglow measurements by the Prague group (Glosik et al 2009) leave little doubt that H_3^+ recombination can be enhanced by neutral helium atoms. However, the mechanism producing the enhancement is not obvious. The "classical" model of neutral-assisted recombination, in which an atom acts as the energy–removing third body, fails because the electron-atom energy transfer is too inefficient. The angular momentum of the orbiting electron can be changed more easily, an effect called "*l*-mixing", and this can affect recombination because only electrons with small *l* (e.g. *p*-electrons) interact with the ion core and can induce predissociation of the molecular core, thereby completing recombination. A random redistribution of the angular momenta, of course, favors states of high *l* with larger statistical weights.

Several models to explain efficient He-assisted recombination invoke *l*-mixing. One such model (Glosik et al 2009) invokes electron-capture by H_3^+ ions into long-lived rotationally excited Rydberg atoms with n>40, followed by *l*-mixing due to helium. The final fate of the long-lived states was not specified. This model produces rough agreement with experimental data, but only if an unrealistically large *l*-mixing rate is taken for high values of n, which is in conflict with the expectation that the *l*-mixing rate declines rapidly as $n^{-2.7}$ [Hickman1978]. The second problem, mentioned earlier, is that *l*-mixing of high Rydberg states due to helium atoms cannot have an effect since the population is *l*-mixed to begin with. The effect of *l*-mixing on recombination is probably limited to a range of Rydberg states (10 to 20 perhaps) that lie low enough to be mixed by helium collisions, but high enough to be subject to re-ionization by collisions or autoionization (otherwise recombination has already taken place). One final remark: *l*-mixing by other rare gases (neon, argon) should be less effective since the electron-impact cross sections are smaller and exhibit Ramsauer minima. This could be tested by experiment.

An alternate model (Johnsen and Guberman 2010) views the He-assisted recombination process as a variation of the collisional dissociative recombination, originally proposed by Collins (1965). Here, *l*-mixing due to helium is thought to enhance recombination by converting high *l*-states, initially formed by CRR, into low *l*-states that subsequently predissociate. This tentative model also gives rough agreement with experiment. Neither of the two models reproduces the observed temperature dependence of the three-body effect. Something essential is clearly missing!

(c) Neutral-assisted ternary recombination due to H_2

At low gas temperatures H_3^+ ions in H_2 can enter a cluster equilibrium with H_5^+ ions that recombine much faster (about 20 times) than H_3^+. This may (but does not always) give rise to $[H_2]$ density dependences, that have nothing to do with three-body recombination as such. It also seems possible, though, that H_3* Rydberg atoms, formed by CRR or some other process, react with H_2 by associative ionization and produce either H_5^+ ions, or form a transient H_5* complexes that subsequently predissociate. Some experimental data (e.g. Gougousi et al 1995) 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 H_2

The H_3^+ recombination studies by Amano (1990) in pure H_2 afterglows had a profound impact when they were published, because they seemed to provide the first credible evidence that H_3^+ recombination for 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 ~ 4.3×10^{-7} cm^3/s. The ensuing controversy focused on a possible contribution by CRR. One of Amano's arguments in favor 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 [1993], 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 formulas. 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 3×10^{11} cm^{-3}, the effective CRR rate calculated from Eq. (1) would be very large, ~ 7×10^{-7} cm^3/s. However, if one takes the heating into account, the electron temperature in the early afterglow would rise to ~ 160 K, and reduce the CRR rate coefficient to ~ 1.4×10^{-7} cm^3/s and remain constant until the electron density approaches ~3×10^{10} 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 H_2 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 $[H_2] = 5\times10^{16}$ cm^{-3}, the effect on the graphs of the reciprocal H_3^+ density on 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 H_2. 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 population (around 5%) would suffice to double the apparent recombination coefficient. The real situation may be even more complicated since the electron- and H_2 vibrational temperatures are coupled (Osiac et al. 2007)

Spectroscopic observations of H_3 and D_3 emission and absorption features in H_2 (D_2) afterglows [Miderski, and Gellene 1988, Amano and Chan 2000] 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 H_2 mixtures

Afterglows in Helium-argon-hydrogen mixtures are the subject of the paper by Dohnal et al (2012), 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 (correctly) 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 rate coefficients declined sharply (to $<10^{-8}$ cm^3/s) when the H_2 density was reduced to below 10^{12} cm^{-3}, and this is often mentioned as serious problem since a "binary" coefficient cannot vary with hydrogen density. As discussed in more detail by Johnsen and Guberman (2010), this observation probably does not indicate a true dependence of the recombination coefficient on $[H_2]$, but more likely resulted from slow formation of H_3^+.

In principle, one should also extrapolate the observed recombination coefficients to very low electron densities, but again this cannot be done in practice. Available data indicate that the electron density (in the experimental range) has little effect. An element of doubt remains, however.

5. A speculation 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 He-assisted process proposed by the Prague group in collaboration with two theoretical colleagues (Glosik et al 2009) 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 states with the longest auto-ionizing lifetimes have the best chance of being *l*-mixed (see Sec 2b) and to subsequently recombine, 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 (Petrignani et al 2011) one finds three, currently unassigned, peaks in the range around 0.005 to 0.02 eV, at the same energies where the lifetimes of the rotational resonances are the largest. In Fig. 5 of Petrignani et al (2011) the peaks are labeled C and E (the next higher peak should be "F" but is not labeled). 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, labeled A) does not have a counterpart in the lifetime graph and probably has a different origin. The storage ring data by Kreckel et al (2010) (see their Fig.8) may provide a possibly useful clue: The central part of peak "A" remains nearly unchanged when para-enriched rather than normal hydrogen is fed to the ISR ion source, possibly because the actual abundance of the responsible species is not changed when para-enriched H_2 is fed to the ion source. Perhaps peak "A" reflects a rotational resonance from the (2, 1) to the (3, 1) rotational state. The Rydberg states formed by the rotational capture would have high principal quantum numbers (20 to 40). Petrignani et al (2011) suggest that something "problematic" may be going on in the storage rings, including perhaps destruction or *l*-mixing of high Rydbergs by stray fields. There are some interesting questions here, but I leave them to those who are more familiar with the intricacies of ISR experiments.

6 Conclusions

Larsson et al (2008) 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 clear assignment of the prominent low-energy peaks in the ISR data to theoretically well-founded mechanisms remains an important task. While it is encouraging that afterglow and ISR data can be reconciled to some extent, a better understanding of recombination in the plasma environment is still needed.

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