Three-Body Effects in Dissociative Recombination of Molecular Ions

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Abstract. This contribution discusses possible effects of the plasma environment on dissociative recombination (DR) of two ion species, $H^+(H_2O)_4$ and $H_3^+$, for which afterglow measurements give larger recombination coefficients than beam experiments. This raises the question to what extent the apparent discrepancies reflect differing recombination mechanisms or are simply due other “errors” or “plasma complications”. $H^+(H_2O)_4$ recombination seems to be a case in which third-body effects are very strong. It also has been suggested that afterglow $H_3^+$ recombination coefficients can be reconciled with the lower storage-ring and theoretical results by invoking third-body stabilization of initially formed high Rydberg states, but the estimates presented here indicate that one should be cautious in accepting such conclusions.

1. Introduction

Experimental and theoretical studies of dissociative recombination (DR) of molecular ions with slow electrons,

$$ABC^+ + e^- \rightarrow \text{neutral fragments}, \quad (1.1)$$

have been pursued for about 60 years but there are still some nagging discrepancies. I begin by pointing out that Eq. (1.1) can be read in two ways, either as representing a binary collision or as a reaction equation that leaves unspecified the degree to which the “environment”, e.g. neighboring charged or neutral particles, influence the rate and products of the reaction. In the afterglow technique, the decay of the electron density in a plasma is measured subsequent to a brief ionizing pulse. Here, the neutral gas density (roughly from $10^{16}$ to $10^{19}$ cm$^{-3}$) and electron density ($10^9$ to $10^{10}$ cm$^{-3}$) tend to be fairly high. In recent years, experimental work on DR has shifted to merged-beam experiments, in particular ion storage rings, that yield accurate binary recombination cross sections and branching fractions with very high energy resolution. In many cases, for instance those in which diatomic ions recombine by the fast direct mechanism, the thermal rate coefficients derived from storage-ring data agree rather well with the older afterglow data. However, there are exceptions. The question is not which of the techniques gives the “correct” rate coefficient but rather which coefficient might be appropriate for a given application.

I will examine two examples: The first deals with a big “floppy” ion, a hydrated proton, $H^+(H_2O)_4$ (also written as $H_3O^+ (H_2O)_3$). I chose this ion species because there are good data from both afterglows and ion storage rings and because of its importance in the D-region of the terrestrial...
ionosphere. Recent storage-ring experiments [1] indicate that fragmentation into $4 \text{H}_2\text{O} + \text{H}$ is the
don dominant dissociation channel, but they leave open the question to what extent dissociation occurs by a
sequential process. The total energy released in this channel is moderate, only about 3.4 eV, and
much of that energy release is likely to be converted to internal rather than kinetic energy of the
fragments. In the case of an ion with numerous internal states it seems plausible that capture of an
electron results in a fairly long-lived complex that can be collisionally stabilized, similar to the well
known mechanism of electron attachment to $\text{SF}_6$.

The second example concerns the recombination of $\text{H}_3^+$, the most abundant (and most studied!)
molecular ion in the universe. It plays a crucial role in the formation of molecular species in
interstellar clouds. The long (and often controversial) history of $\text{H}_3^+$ has seen several attempts to
reconcile discrepant afterglow and beam results and to “close the books” on the subject. Invoking
third-body effects constitutes just one of these attempts. While it would be most gratifying to dispose
of the remaining discrepancies, my estimates to be discussed below indicate that the proposed third-
body mechanism fails to explain the magnitude of the observed increase of the recombination rate
with neutral density.

2. Recombination of $\text{H}^+(\text{H}_2\text{O})_4$

Afterglow measurements for the n=4 cluster are available over a wider range of gas densities than for
other cluster sizes of the same series. The equilibrium constants governing the relative concentrations
of different cluster sizes are such that it is fairly easy to produce afterglow plasmas in which the n=4
cluster dominates and to obtain good data. Fortunately, we now also have data [1] from the storage
rings on total rate coefficient and product branching fractions.

Figure 1 shows a comparison of the afterglow data [2,3,4] (all at 300K), as function of the neutral gas
density (helium or neon) to the 300 K value inferred from the storage-ring cross sections. The
observed rate coefficients initially increase with density but then approach a nearly constant value.

![Figure 1](image_url)

For other cluster sizes the storage ring data also give lower rate coefficients than the afterglows, but
the density effect is less pronounced, and there are no good afterglow data at very high densities.

We do not yet have a clear theoretical understanding why cluster ions recombine very rapidly. In
the picture outlined by Bottcher [5] the captured electron becomes temporarily bound by exciting one
or more vibrational modes and intramolecular energy transfer then renders the collision complex
relatively long-lived against auto-ionization. This lead to the possibility that in the presence of third-
body atoms, part of the energy of the complex may be transferred to the third body, thus inhibiting
auto-ionization while leaving more time for dissociation.

A simple quasi-equilibrium model suggests that the overall recombination coefficient should be
written as the sum of the binary and the three-body channel, i.e.
\[ \alpha = \alpha_1 + \alpha_2 \frac{k_s \tau[M]}{1 + k_s \tau[M]} \]  

(1.2)

where \( \tau \) is the complex lifetime, \( M \) the concentration of the third bodies, and \( k_s \) is a rate coefficient that describes collisional stabilization of the complex. In the limit of high \( M \), the rate coefficient is limited by capture rate of electrons. Equation (1.2) reproduces the experimental observations quite well for \( \alpha_1 = 5.5 \times 10^{-7} \text{ cm}^3/\text{s}, \alpha_2 = 6 \times 10^{-6} \text{ cm}^3/\text{s}, \) and taking the product \( \tau k_s \), as \( \sim 2 \times 10^{-18} \text{ cm}^3 \). If one estimates \( k_s \sim 10^{-9} \text{ cm}^3/\text{s} \), the complex lifetime would have to be on the order of 2 ns, which does not seem unreasonably long. In spite of the apparent success of this crude model, it is clearly no substitute for rigorous theory. I only wish to make the point that one should not too quickly relegate the older afterglow data to the “dust bin of history”. The storage ring data may be exactly what is needed to model very thin media like interstellar clouds, but the afterglow data may be more appropriate for models of denser plasmas.

3. Three-body effects in the DR of \( \text{H}_3^+ \)?

I will skip a discussion of the rather convoluted history of \( \text{H}_3^+ \) studies since I reviewed it not too long ago [6]. At this time theoretical and experimental results strongly favor acceptance of a moderately large 300 K binary recombination rate coefficient of about \( 7-8 \times 10^{-8} \text{ cm}^3/\text{s} \).

However, most afterglow experiments (if sufficient hydrogen is present) give rates that are higher by about a factor of two or more. Although the data are quite scattered, there is a roughly linear increase with the neutral densities, compatible with a three-body coefficient of about \( 3 \times 10^{-25}/\text{cm}^6/\text{s} \). Głosik et al [7] show a graph of the data and propose a three-body mechanism that expands on an earlier conjecture by Gougousi et al. [8]. The recombination is thought to involve resonant capture of low-angular momentum electrons into high Rydberg states, followed by \( l \)-mixing in collisions with neutral atoms, which inhibits auto-ionization and increases stabilization.

Does such a mechanism really explain the observed density dependence and thus reconcile afterglow and beam data?

To simplify the discussion, I will assume that only \( p \)-states are formed initially. Binary recombination occurs by predissociation of the \( \text{H}_3^+(n,p) \), while the three-body mechanism is thought to proceed via \( l \)-mixing, and subsequent “stabilization”, which includes any process that irreversibly destroys \( \text{H}_3^+(n,l) \). \( l \)-mixing is an essential part of the scheme since it multiplies the statistical weight by a large factor (about of 1000 for a Rydberg population from \( n=25 \) to 80) and hence the stabilization step can be relatively slow. The efficiency of the three-body mechanism may be estimated if one applies detailed balancing to obtain the equilibrium constant

\[ K_{eq}(p) = \frac{[\text{H}_3^+(n,p)]}{[\text{H}_3^+]} = \frac{\alpha_{cap} \tau_c}{[\text{H}_3^+]} \]  

(1.3)

Figure 2 Electron capture and \( l \)-mixing scheme. Boxes labeled \( \text{H}_3^+(n,p) \) represent high Rydberg states with principal quantum numbers \( n \) in \( p \)-states. \( \text{H}_3^+(n,l) \) denotes statistical mixtures of all possible \( l \)-states.
Here, \( \alpha_{cap} \) represents the rate of electron capture into \( p \)-states of high Rydbergs. The three-body recombination coefficient is then limited by the value

\[ \alpha_3 = K_{eq}(p)k_i \] (1.4)

where \( k_i \) denotes the rate coefficient for inducing \( l \)-mixing in collisions with the neutral atoms (helium in most cases). Glosik et al [7] estimate \( K_{eq}(p) \sim 3.5 \times 10^{-17} \text{ cm}^3 \) from theoretical average lifetimes \( \tau_a \sim 100 \text{ ps} \) for a range of Rydberg states with \( n \) from 25 to 80, and an estimated value of \( \alpha_{cap} \sim 3.5 \times 10^{-7} \text{ cm}^3/\text{s} \) (Note: a slightly lower estimate for \( K_{eq}(p) \) can be obtained from the Saha equation).

To reproduce the (very approximate) experimental value \( \alpha_3 \sim 3 \times 10^{-25} \text{ cm}^3/\text{s} \) using Eq. (1.4) one needs mixing rate coefficients \( k_i \) on the order of \( 10^{-8} \text{ cm}^3/\text{s} \) or larger. The problem is that such large \( l \)-mixing coefficients in rare gases are compatible with theory [9] and experiment only for Rydberg states near \( n=10 \). For higher \( n \) the rate coefficients fall off rapidly as \( n^{-2.7} \). Thus I conclude that \( l \)-mixing for the high \( n \)-states (25 to 80) cannot be fast enough to explain the observed three-body rates. One should keep in mind, however, that an \( n=80 \) Rydberg state is very large! At a pressure of 1 Torr, several thousand atoms reside within its volume making the use of \( l \)-mixing rate coefficients somewhat dubious! It is also possible that at high ambient electron density \( l \)-mixing due to plasma electrons (those mixing cross sections are extremely large and increase as \( n^5 \)) may speed up the mixing, but there is a further problem. Even if complete \( l \)-mixing were to occur, one still needs a mechanism to "stabilize" the \( l \)-mixed population. A gradual removal of energy by \( n \)-reducing collisions with neutral atoms encounters the same "bottleneck" that makes three-body recombination of atomic ions very slow. Stabilization by predissociation may help, but its efficiency is hard to estimate because we do not know the needed predissociation rates for the many states involved.

4. Conclusions

While experimental findings suggest that some dissociative recombination processes are enhanced by the plasma environment, a satisfactory theoretical picture has not yet emerged. The question is not purely "academic" and should be pursued further. Realistic modelling of plasmas may involve more than the purely binary recombination mechanism!

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