Recombination of H_3^+ and D_3^+ Ions with Electrons.

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Abstract. Flowing-afterglow measurements in decaying H_3^+ or D_3^+ plasmas suggest that de-ionization does not occur by simple binary recombination of a single ion species. We find that vibrational excitation of the ions fails to provide an explanation for the effect, contrary to an earlier suggestion. Instead, we suggest that collisional stabilization of H_3^{**} Rydberg molecules by ambient electrons introduces an additional dependence on electron density. The proposed mechanism would permit plasma de-ionization to occur without the need for dissociative recombination by the mechanism of potential-surface crossings.

INTRODUCTION

It is usually taken for granted that typical plasma afterglow experiments yield the binary dissociative recombination coefficient for molecular ions and that, in principle, the measured values would be the same as those inferred from beam experiments. The assumption seems plausible since the capture of an electron into a repulsive state of the neutral is thought to induce rapid dissociation[1], leaving little time for third-body interactions. The argument, however, presupposes the existence of suitable dissociation channels. If such do not exist, then perhaps long-lived Rydberg molecules can be formed and third-body interactions may be more important. The experiments described here suggest that this situation may exist in plasmas containing H_3^+ and D_3^+ ions.

Theoretical arguments [2,3] indicate that the recombination

$$H_3^+ + e^- \rightarrow H+H+H$$
$$\rightarrow H_2+ H \tag{1}$$

for vibrationally cold H_3^+ (v=0) ions by direct dissociative recombination should be slow due to a lack of suitable crossings between the ionic and neutral potential surfaces. However, vibrationally excited H_3^+ ions in $v \geq 3$ are predicted to exhibit faster recombination. This expectation disagreed with the early microwave-afterglow experiments [4,5] which gave fairly "normal" recombination coefficients ($\sim 2 \times 10^{-7}$ cm^3/s) for H_3^+ ions believed to be in v=0. This "H_3^+ dilemma" has existed for about 20 years.

The structure and energy levels of H_3^+ and H_3^* are quite well known. A brief introduction and extensive references can be found in the "thumbnail sketch

of H_3^+" by Oka and Jagod [6]. The importance of H_3^+ in astrophysical environments is discussed in reviews by Dalgarno[7] and by Tennyson et al.[8]. A fairly complete account of the history of dissociative recombination work has been given by Bates et al. [9].

One possible resolution of the H_3^+ dilemma was offered by Adams et al.[10]. They interpreted their observation of an anomalous decay of a flowing afterglow plasma by assuming the presence of two species of H_3^+ ions, one of which recombined fairly fast while the other recombined slowly ($\alpha < 2 \times 10^{-8}$ cm^3/s). By identifying the fast and slowly recombining ions as, respectively, $v > 3$ or $v = 0$ ions, theory and experiment could be reconciled. This solution, while being in conflict with the microwave afterglow results, seemed quite plausible until Amano[11,12] showed that spectroscopically identified H_3^+ ions in $v = 0$ recombined readily with electrons ($\alpha \sim 1.8 \times 10^{-7}$ cm^3/s). A repetition of the flowing-afterglow measurements by Canosa et al.[13,14] gave no evidence for the existence of two distinct types of H_3^+ ions.

Recombination cross sections for H_3^+ have been measured repeatedly in the merged-beam apparatus at the University of Western Ontario [15, 16, 17, 18]. The results showed that the cross section varied with conditions in the ion source and this was ascribed to vibrational excitation. In later work[16], the H_3^+ vibrational state was deduced from the threshold energy for electron-ion dissociative excitation. The result indicated that $v = 0$ ions recombined only slowly with electrons.

When ion storage rings became available, they were very quickly applied to H_3^+ recombination. In these instruments, vibrationally excited ions have time to relax by radiative transitions (including the $v_1 = 1$ metastable level of H_3^+ with a lifetime[19] of 1.2 s). Larsson et al.[20] and Sundström et al.[21], using the CRYRING storage ring, obtained recombination cross sections for H_3^+ ($v = 0$) over the wide energy range from 0.0025 to 30 eV. The analysis of the experimental cross sections yielded a recombination coefficient of $(1.15 \pm 0.13) \times 10^{-7}$ cm^3/s at an electron temperature of 300 K.

Since the storage-ring measurements also yielded fairly large recombination coefficients for $v = 0$ ions, the problem of finding a recombination mechanism for $v = 0$ ions became more acute. New mechanisms were proposed [22, 23] that do not require crossings between ionic and neutral potential curves. It is possible that such mechanisms may play a part in the recombination of H_3^+ ions, but no detailed calculations have been made.

Not all experimentalists were willing to accept a sizable recombination coefficient for H_3^+ in $v = 0$. Smith and Spanel [24] repeated and refined the afterglow experiment of Adams et al.s' [10] and concluded that only H_3^+ ions in $v > 3$ recombined efficiently with electrons. Again, those authors found that the decay of H_3^+ plasmas was anomalous in the sense that the recombination coefficient appeared to become smaller in the late afterglow. It was, in part, this work that motivated us to carry out an additional experiment. As will be seen, we largely reproduced Smith and Spanel's [24] results that there is something peculiar about the decay of H_3^+ plasmas but our interpretation of the experiment is quite different.

To avoid ambiguities, we will use the term "recombination coefficient" (α) only for purely binary recombination. We will use the word "de-ionization coefficient" (β) to denote the quantity that is derived from plasma decay experiments. The two quantities may be equal, but this is not assumed from the onset.

A more complete description of the experiment, additional details of the analysis, and the interpretation will be given in a journal article [25].

EXPERIMENTAL METHODS

Our flow tube is a stainless-steel tube of diameter 6 cm and length 36 cm. The carrier gas was helium (at pressures near 1 Torr and temperatures near 295 K). Flow velocities ranged from 5000 cm/s to 6000 cm/s. Reagent gases are added to the flowing plasma through several movable and fixed inlets. A movable Langmuir probe [26] serves to measure electron densities n_e as a function of axial position z. A quadrupole ion mass spectrometer analyzes the ion composition at the downstream end of the flow tube.

Plasma generation and ion conversion

The techniques of recombination measurements in flow tubes are quite well known and will not be discussed here. The method consists of creating a well-characterized plasma that contains only the desired ion species and measuring the rate at which free electrons disappear. The creation of the H_3^+ plasma involves several steps:

(1) The carrier gas (helium) is partially excited to the metastable state and (to a lesser degree) ionized by passing it through a microwave discharge.

(2) Argon (~15 % of helium) is added downstream to convert metastable helium atoms to Ar^+ ions by Penning ionization. After this, the plasma contains mainly Ar^+ ions with a small admixture of He^+ and He_2^+ ions (< 0.1 % of Ar^+). The electron density at this point is typically 4×10^{10} cm^{-3}.

(3) To create H_3^+ ions, H_2 is added at densities from 10^{14} to 10^{15} cm^{-3}. The formation of H_3^+ via the reactions

$$Ar^+ + H_2 \rightarrow Ar H^+ + H \quad (+1.53\,eV) \tag{2}$$

$$ArH^+ + H_2 \rightarrow Ar + H_3^+ \quad (+0.57\,eV) \tag{3}$$
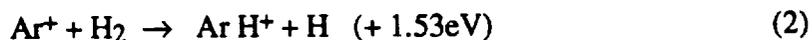
(see Radzig and Smirnov [27] for thermochemical data) takes place very rapidly compared to recombination since the rate coefficients for reactions (2) and (3) are large (~ 10^{-9} cm^3/s [28]).

Vibrational excitation and quenching of the H_3^+ ions

If the entire energy of 2.1 eV that is released in reactions (2) and (3) were to appear as vibrational excitation, which seems unlikely, then H_3^+ could be produced in vibrational states up to v=5. However, H_3^+ ions in v>1 would be destroyed rapidly by proton transfer to Ar,

$$H_3^+ + Ar \rightarrow Ar H^+ + H_2 \tag{4}$$

which is energetically possible for H_3^+ ions with internal energies above 0.57 eV. The non-reacting, surviving H_3^+ vibrational states are the ground state, the $v_2=1$ bending-mode vibration at 0.3126 eV, and the $v_1=1$ breathing mode vibration at 0.394 eV(see Lie and Frye [29] or Oka and Jagod [6]). At $[Ar]= 5x\ 10^{15}\ cm^{-3}$, $v>1$ ions would be destroyed by proton transfer $(k\ \sim 10^{-9}\ cm^3/s)$ in less than 1 μsec, a time that is far shorter than the time scale of recombination (about 1 ms).

The radiative lifetimes of the $v_1=1$ and $v_2=1$ levels (1.2 s and 4 ms, respectively) [19] are too long for radiative relaxation to be important. Quenching of $v=1$ ions in collisions with H_2 is more effective. Amano's [30] absorption studies of the v_2 hot band indicate that the $v_2=1$ level is quenched by H_2 with a rate coefficient of approximately $3x10^{-10}\ cm^3/s$. This eliminates $v_2=1$ ions; they will be destroyed in 30 μs at $[H_2]= 1x10^{14}\ cm^{-3}$. On the other hand, there is evidence [31,32] for slower quenching $(k\sim 10^{-12}\ cm^3/s)$ of other vibrational states. It seems very likely that the slowly-quenched ions are those in the $v_1=1$ level. A similar conclusion was reached by Bawendi et al. [33] who studied the absorption of H_3^+ hot bands in He/H_2 discharges.

The foregoing considerations indicate that only H_3^+ ($v_1=1$) ions live long enough to undergo recombination. Smith and Spanel [24] did not consider the destruction of the higher vibrational levels by proton transfer with argon and consequently believed that most H_3^+ ions would be in states $v\geq3$. We do not agree with this conclusion; others have expressed the same criticism earlier [13,14]. This is an important point, since Smith and Spanel's proposed reconciliation of theory and experiment rests on the assumption that vibrationally excited ions dominate.

There is no *a priori* reason to expect that *para* and *ortho* H_3^+ ions should recombine equally fast. According to Oka [34], *ortho-para* equilibration by proton exchange with H_2 is rapid. We assume that the proton-transfer rate is sufficiently large $(k>10^{-10}\ cm^3/s$ would suffice at $[H_2] = 10^{14}\ cm^{-3})$ to keep the para-to-ortho ratio at a constant value in the recombining plasma.

DATA ANALYSIS

The most common method of deducing β from the slope of a graph of the reciprocal of the electron density $n_e(z)$ *vs.* axial position z (V being the plasma velocity),

$$\frac{1}{n_e(z)} = \frac{1}{n_e(z=0)} + \beta\frac{z}{V} \tag{6}$$

provides quick, but only only approximate values of a z-averaged de-ionization coefficient. Since we are looking for deviations from a simple decay law, we were forced to employ a more rigorous approach (for details see ref. 25): It consisted of solving numerically the continuity equation for the electron density $n_e(r, z)$ in a flowing plasma with a parabolic velocity field. The computed solutions were then used to validate a computationally faster, approximate method that could be used for routine data analysis. The approximate method extracts a z-dependent de-ionization coefficient $\beta(z)$ from the measured electron density $n_e(z)$. This form of

analysis was shown to be sufficiently accurate by using the exact model to generate simulated $n_e(z)$ values and then analyzing the simulated data by the approximate method. In addition, tests were made on experimental data obtained in O_2^+ plasmas. As expected, no systematic variation of $\beta(z)$ with z was found and the measured β agreed with the known recombination coefficient $\alpha(O_2^+)$.

EXPERIMENTAL RESULTS

40 decay curves $n_e(z)$ were recorded for $[Ar] = 4 \times 10^{15}$ cm^{-3} to 8×10^{15} cm^{-3}, and $[H_2] = 1 \times 10^{14}$ cm^{-3} to 1.7×10^{15} cm^{-3}. Even the simplest form of data analysis (based on Eq. (9)) showed that β increased noticeably with increasing H_2 concentration (see Fig. 1). A similar, but less scattered graph was obtained when the average values of $\beta(z)$ in the first 4 cm were plotted as a function of $[H_2]$.

Figures 2 and 3 show examples of the electron density $n_e(z)$ and $\beta(z)$ for two different H_2 concentrations. It is apparent that β is not constant but that it decreases with increasing z. This finding reproduces the observations of Smith and Spanel[24]; the decay of the plasma clearly does not follow a simple recombination law.

A smaller set of data was taken for D_3^+ ions. The observations largely mirrored those for H_3^+. Again, the recombination coefficient increased with increasing D_2 concentration, but the D_3^+ de-ionization coefficients were significantly smaller (from 0.7×10^{-7} cm^3/s to 1.3×10^{-7} cm^3/s in the range $[D_2] = 1$ to 14×10^{14} cm^{-3}).

INTERPRETATION OF RESULTS

The interpretation should explain the enhancement of β upon hydrogen addition, the decline of $\beta(z)$ with increasing position z, and if possible, it should elucidate the recombination mechanism. We attempted to explain the peculiar decay of the plasma by two different models. The first model assumes the presence of H_3^+ ions in two different states. The second model invokes an entirely different explanation in terms of Rydberg molecules.

Two - state model

The assumption that the z dependence of β is caused by the presence of H_3^+ ions in $v=0$ and in $v_1=1$ leads to

$$\beta(z) = \alpha_0 f_0(z) + \alpha_1 f_1(z) \tag{6}$$

where α_0 and α_1 denote the recombination coefficients of $v=0$ and $v_1=1$ ions, and f_0 and f_1 are their fractional concentrations. Quenching of $v_1=1$ ions to $v=0$ by H_2 (rate coefficient k_q) and differing recombination losses make the concentrations z-dependent. It is not difficult to construct a kinetic model that yields a fit to the measured $\beta(z)$ curve at $[H_2] = 1.3 \times 10^{14}$ cm^{-3}. Figure (2) shows fits for $\alpha_0 = 2.2 \times 10^{-7}$ cm^3/s, $\alpha_1 = 4 \times 10^{-8}$ cm^3/s, $f_0 = 0.7$, and two quenching coefficients of $k_q = 1 \times 10^{-12}$ cm^3/s and $k_q = 1 \times 10^{-13}$ cm^3/s. However, when the same values are

used to compute a fit to the data at $[H_2] = 1.7 \times 10^{15}$ cm^{-3}, the model (see Fig. 3) indicates that $\beta(z)$ should now increase with z. A decline of $\beta(z)$ can be forced by reducing the quenching rate to $k_q = 1 \times 10^{-13}$ cm^3/s, but the model fails to reproduce the observation that β at z=0 (only 1 cm from the reagent inlet)is larger at the larger H_2 concentration. We eventually concluded that the two-state model does not provide a consistent explanation of the experimental findings.

De-ionization by Rydberg molecule stabilization

We now return to the subject that was mentioned in the Introduction, namely de-ionization mechanisms which involve interactions with third bodies. The $\beta(z)$ data suggest that the de-ionization coefficient is larger at higher electron densities and higher H_2 densities. Is it possible that these particles affect the mechanism of de-ionization directly, rather than changing the state of the recombining ions? At first sight, this does not seem to be viable proposition. Electron-stabilized and neutral-stabilized recombination are known to be too slow (by several orders of magnitude)[35] to have an effect on recombination in low-density ($n_e < 10^{11}$ cm^{-3}) plasmas. Third-body effects are inefficient because electron capture requires energy transfer to a third particle during the brief electron-ion encounter.

In the following, we will argue that additional stabilization mechanisms exist in the case of molecular ions, especially those that do not undergo fast dissociative recombination. Theory indicates the H_3^+ ions may fall into this category. Non-dissociating, long-lived Rydberg states may be formed in collisions of electrons with molecular ions. These can be stabilized not only by energy-removing collisions but also by angular-momentum changing (l-mixing and possibly m-mixing) collisions.

The following sequence may occur: In the first step, an electron of low angular momentum (s or possibly p) is captured into a ro-vibrational level of a Rydberg state of H_3,

$$e^- + H_3^+ \rightarrow H_3^{**} \ (v=1, n, s\ ). \tag{7}$$

The n=7 state should be favored since excitation to the $v_2=1$ state (0.3126 eV) in n= 7, l=0 is resonant at an electron energy of +0.0309 eV (1.2 kT at 300 K).

We postulate that in the second step the angular momentum of the Rydberg molecule is randomized in collisions with ambient electrons (l-mixing and possibly m-mixing). It is known from studies of dielectronic recombination[36] and zero-electron-kinetic-energy (ZEKE) spectroscopy [37] that redistribution of angular momenta of Rydberg electrons (l-mixing) due to electric microfields and collisions can increase predissociation and autoionization lifetimes by several orders of magnitude. The basic reason is that the wave functions of high-l states do not interact with the ion core. Since the lifetimes of some H_3^{**} autoionizing states are quite long (of the order of 10^{-7} s) [38, 39] and the l-mixing efficiency of thermal electrons is extremely large (rate coefficients $>10^{-3}$ cm^3/s) [40], l-mixing should occur in less than 10^{-7} s under the conditions of our experiment ($n_e = 4 \times 10^{10}$ cm^{-3}).
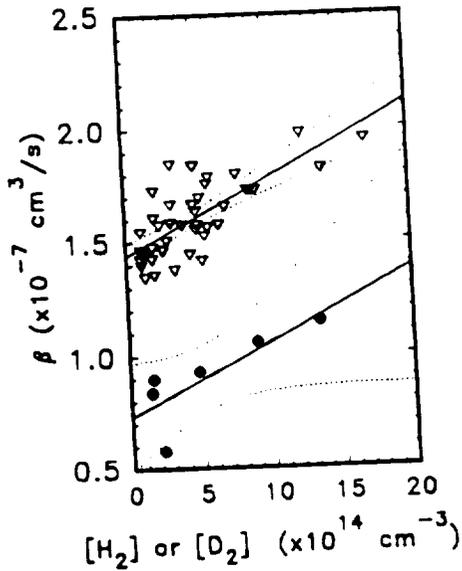
FIGURE 1. β-values in H_3^+ or D_3^+ plasmas (from the $1/n_e$ vs. z plots), as a function of $[H_2]$ (triangles) or $[D_2]$ (filled circles). Lines: Least-squares fit to the data. Dotted lines: 95% confidence limits the least-squares fit.
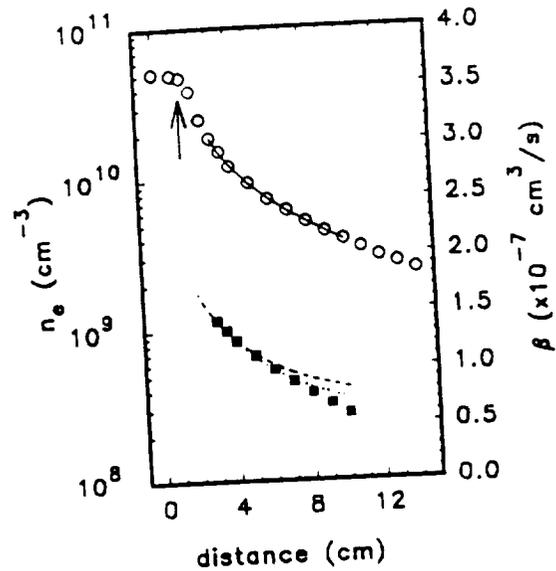
FIGURE 2. $\beta(z)$ values (filled squares) derived from $n_e(z)$ data (open circles) at $[H_2] = 1.3 \times 10^{14}$ cm^{-3}. Lines through $\beta(z)$ points: Model calculations for $k_q = 1 \times 10^{-12}$ cm^{-3}/s (dashed) and $k_q = 1 \times 10^{-13}$ cm^3/s (dotted). Arrow: Position of the H_2 gas inlet.
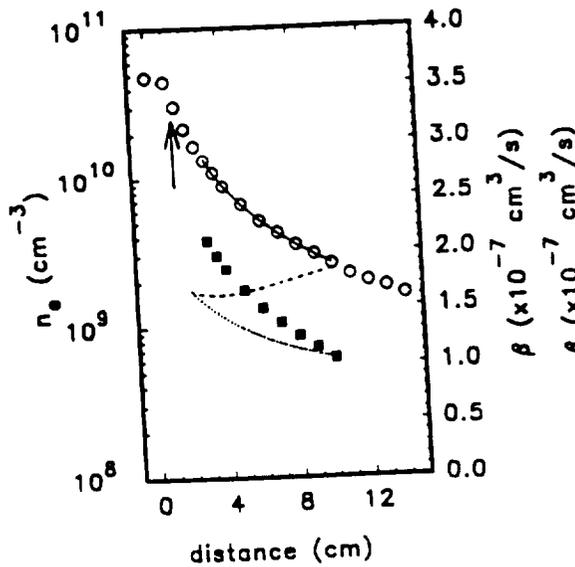
FIGURE 3. Same as Fig. 3, but for $[H_2] = 1.7 \times 10^{15}$ cm^{-3}.
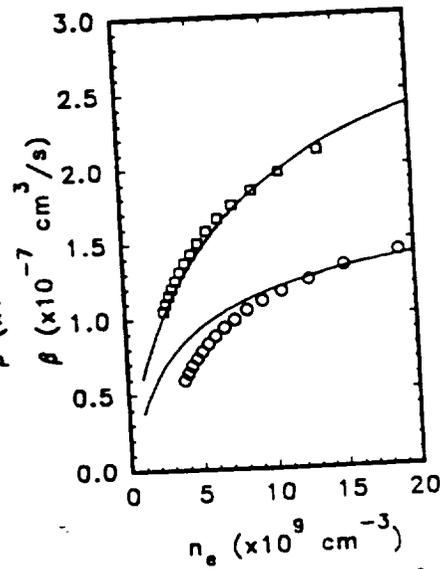
FIGURE 4. Comparison of observed values of $\beta(n_e)$ at $[H_2] = 1.3 \times 10^{14}$ cm^{-3} (circles) and $[H_2] = 1.7 \times 10^{15}$ cm^{-3} (squares) to the model calculations described in the text.

7

In the third step, the long-lived H_3^{**}(n=7, v=1, l>1) can be returned to the autoionizing state (s, or p) by further collisions, they may be quenched to lower n-states by neutral atoms or electrons, they may undergo slow predissociation, radiate to a lower state, or react with an H_2 molecule. Some of the decay rates are known or can be estimated. Collisional energy loss (n-changing) with helium atoms is not important [41] compared to radiative decay. The rate coefficient for n-changing collisions of electrons with n=7 Rydberg atoms (electron quenching) has been measured by Devos et al. [43] to be $\sim 10^{-5}$ cm^3/s. Radiative decay rates for n=7 hydrogenic states are close to 1×10^6 s^{-1} for s-states , 2×10^7 s^{-1} for p-states, and about 2×10^6 s^{-1} for a statistical mixture of l-values up to l=6 [42]. The reaction with H_2

$$H_3^{**} + H_2 \rightarrow H_2 + H_3^* \qquad (8)$$

provides the needed enhancement of the loss rate of electrons in the presence of H_2. It will compete with radiative decay if it occurs on a time scale of $<1\mu s$. At $[H_2] = 1 \times 10^{15}$ cm^{-3} , this requires a rate coefficient of $\sim 1 \times 10^{-9}$ cm^3/s for reaction (8), which is not unreasonable.

The set of reaction equations is easily solved to obtain an effective de-ionization coefficient. The capture and autoionization step

$$H_3^+ + e^- \leftrightarrow H_3^{**} \ (n=7, s,p) \qquad (9)$$
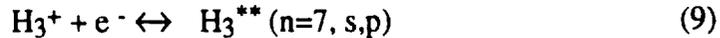
is described by a capture coefficient k_c and an autoionization rate v_a . Stabilization by l-mixing due to electrons

$$H_3^{**} (n=7, s, p) + e^- \leftrightarrow H_3^{**} (n=7, l>1) + e^- \qquad (10)$$
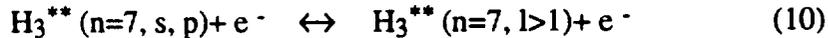
and its reverse are described by rate coefficients k_s and k_i, respectively. The following destruction reactions for H_3^{**} were included:

H_3^{**}(n=7)	$\rightarrow$ H_3^* (n<7) + hν	(radiation, rate v_{rad})	(11a)
H_3^{**}	$\rightarrow$ H_2+ H (or 3H)	(predissociation, rate v_p)	(11b)
H_3^{**}(n=7) + e$^-$	$\rightarrow$ H_3^*(n<7) + e$^-$	(rate coefficient k_{qe})	(11c)
H_3^{**} + H_2	$\rightarrow$ H_2 + H_3 (low n)	(rate coefficient k_H) .	(11d)
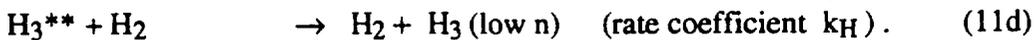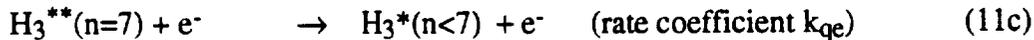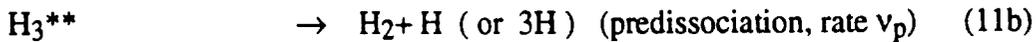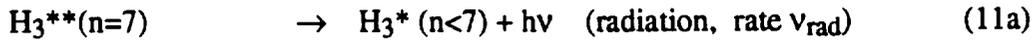
To allow for the possibility that the rate coefficients for H_3^{**} in the autoionizing states (s, p) differ from those in higher l-states, we treat their destruction separately and attach the subscripts "0" and "1" to the rate coefficients. After some algebra, the effective de-ionization coefficient can be put in the form

$$\beta = -\frac{1}{n_e^2}\frac{dn_e}{dt} = \frac{k_c}{1 + \dfrac{1}{\dfrac{n_e k_s v_l}{(n_e k_i + v_l)v_a^-} + \dfrac{v_0}{v_a}}} \qquad (12)$$

where $v_0 = v_{rad,0} + v_{p,0} + k_{qe} n_e + k_H [H_2]$

and $v_1 = v_{rad,1} + v_{p,1} + k_{qe} n_e + k_H [H_2]$.

It is possible to find a set of plausible rate coefficients so that Eq. (12) gives a reasonable fit to the data. Fig. 4 shows a comparison to experimental values of β (n_e) for the following set of rate coefficients:

$$k_c = 4.4 \times 10^{-7} \, cm^3/s, \quad v_a = 1.3 \times 10^8 \, s^{-1}, \quad k_s = 1.25 \times 10^{-2} \, cm^3/s$$

$$k_i = 3.1 \times 10^{-4} \, cm^3/s, \quad v_{rad,0} = v_{rad,1} = 1.1 \times 10^6 \, s^{-1}$$

$$v_{p,0} = v_{p,1} = 0, \quad k_H = 4.5 \times 10^{-9} \, cm^3/s, \quad k_{qe} = 1 \times 10^{-5} \, cm^3/s$$

We do not claim that this set of model parameters is unique or that the agreement with the data is sufficient proof for the validity of the model. More detailed studies would be required to prove that this model is valid. It is interesting, however, that the fitting parameters are quite close to those that were estimated earlier. If this model is correct, it would solve the theoretical dilemma of having to account for fast "binary recombination" of electrons with H_3^+ ions since this process would not be needed to explain the observed plasma de-ionization.

Our model is compatible with the most recent merged-beam observations of Mitchell and coworkers [43]. They found that the apparent H_3^+ recombination cross sections decreased by about a factor of five when a "deflection field" in the post-collision region was increased in magnitude. The effect is ascribed to field-induced re-ionization of autoionizing H_3^{**} molecules that were formed in electron-H_3^+ collisions. The role of electric fields in such experiments is not yet perfectly understood, but the observations demonstrate that long-lived H_3^{**} states can be produced in such collisions. The nature of these states and the reasons for their unexpectedly long life-time, however, are not at all clear.

CONCLUSIONS

We reach the tentative conclusion that the recombination of H_3^+ plasmas does not exclusively occur by binary recombination. If this is true, then the results of afterglow measurements may be compatible with the theoretical expectation that binary recombination of H_3^+ ions in v=0 should be rather slow.

The "true" binary recombination coefficient of H_3^+ is needed for some applications, e.g. for models of the interstellar medium. It is conceivable that the recombination cross sections measured in merged-beam or ion-storage ring experiments are close to the true values, but the effects of residual electric fields in such experiments need to be examined more closely.

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