

## Recombination of $H_3^+$ and $D_3^+$ Ions in a Flowing Afterglow Plasma

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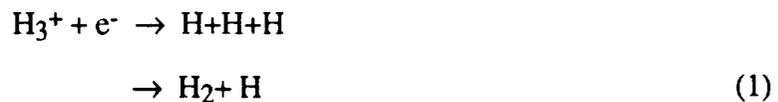
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### Abstract

The analysis of flowing afterglow plasmas containing  $H_3^+$  or  $D_3^+$  ions indicates that the de-ionization of such plasmas does not occur by simple dissociative recombination of ions with electrons. An alternative model of de-ionization is proposed in which electrons are captured into  $H_3^{**}$  autoionizing Rydberg states that are stabilized by collisional mixing of the Rydberg molecules' angular momenta. The proposed mechanism would enable de-ionization to occur without the need for dissociative recombination by the mechanism of potential-surface crossings.

### I. Introduction

The dissociative recombination (DR) of electrons with  $H_3^+$  ions



is thought to be a key process in the ionospheres of the outer planets, in interstellar plasmas, and in many electrical discharges and its recombination coefficient enters as an important parameter in models of such plasmas. Since  $H_3^+$  is the simplest polyatomic ion, it has also become a crucial test case of the theory of DR. While considerable

efforts have been devoted to this problem by theorists and experimentalists, a clear picture has not yet emerged and the experimental results still present a somewhat confusing picture. It is not even clear if binary recombination actually takes place. It was the basic goal of this work to examine the results of earlier experiments and to resolve some of the apparent paradoxes. In the course of doing this, it became necessary to repeat some earlier flowing-afterglow measurements.

We will begin with a brief review of the history of experimental work on  $\text{H}_3^+$  recombination and its interplay with theory. A recent review by Dalgarno [1] outlines the role of  $\text{H}_3^+$  in terrestrial and extraterrestrial environments and his paper contains extensive references to earlier theoretical and experimental work on this ion. The brief "thumbnail sketch of  $\text{H}_3^+$ " by Oka and Jagod [2] provides an excellent introduction to the structure and vibrational states of  $\text{H}_3^+$ . A fairly complete account of the theory and various measurements of dissociative recombination rates can be found in a paper by Bates [3]. We have compiled a list of measured rate coefficients and related information in Table 1.

From the point of view of theory, the problem is that the direct mechanism [4] of DR fails in the case of  $\text{H}_3^+$  ions. Calculations of the relevant potential surfaces [5] showed that there are no crossings between the ground-state ionic potential surface and repulsive states of the neutral molecule that would facilitate DR of  $\text{H}_3^+$  in  $v=0$ . The indirect mechanism, which is thought to involve an intermediate, autoionizing and predissociating Rydberg state, relies on the same crossings of potential surfaces and is subject to the same problem. Such arguments led Michels and Hobbs [5] to propose that  $\text{H}_3^+$  ions in  $v=0$  should not recombine with electrons efficiently, but that vibrationally excited  $\text{H}_3^+$  ions in  $v \geq 3$  might do so. Similar predictions had been made earlier by Kulander and Guest [6]. In contrast, the only experimental data (obtained by using the microwave afterglow method) that were available at that time (Leu et al. [7] and Macdonald et al. [8]) gave recombination coefficients on the order of  $2 \times 10^{-7} \text{ cm}^3/\text{s}$ ,

which is a fairly typical value for a small species. Since it appeared reasonable to assume that the experimental data referred to vibrationally unexcited  $\text{H}_3^+$  ions, the results were clearly in conflict with Michels and Hobbs' expectation. An apparent resolution of the dilemma was proposed by Adams et al.[9]. Their observations in flowing afterglow plasmas suggested that two distinguishable forms of  $\text{H}_3^+$  ions might exist, a major species that recombined fairly fast and a minor species that recombined only very slowly ( $\alpha < 2 \times 10^{-8} \text{ cm}^3/\text{s}$ ). This observation permitted the interpretation that the slowly recombining ion fraction consisted of  $\text{H}_3^+$  ( $v=0$ ) ions and it seemed natural then to identify the fast recombining fraction as  $\text{H}_3^+$  in vibrationally excited states in  $v > 3$ . This interpretation gained acceptance in spite of the fact that Adams et al.[9] had provided no independent experimental evidence for the presence of vibrational states or for their identification.

Several attempts were made to explain the discrepancy between the experimental results of the microwave-afterglow and the flowing-afterglow method. Since "impurity" ions are invariably present in afterglow plasmas, experimentalists examined their effects. Two problems can arise: Conversion of  $\text{H}_3^+$  to more complex ions tends to increase the rate of electron loss, while the presence of non-recombining ions (e.g.  $\text{He}^+$ ,  $\text{H}^+$ ) would reduce the electron loss. Since ions of mass 17 amu (most likely  $\text{CH}_5^+$  ions) were known to be present in the microwave afterglow experiment of Macdonald et al.[8], Johnsen [10] mentioned the possibility that those measurements could have been affected by impurities without giving an estimate of the magnitude of the effect. A reanalysis of those data which includes the effect of  $\text{CH}_5^+$  recombination, indicates that Macdonald et al.'s value of  $\alpha(240\text{K})$  should be corrected downwards by only about 10%. The impurity effect would have been larger at the higher electron temperatures.

The second "impurity" problem has been discussed by Canosa et al.[11,12] and by Smith and Spaniel[13]. It is one peculiarity of  $\text{He}/\text{H}_2$  afterglow plasmas that  $\text{He}^+$  ions are not efficiently removed by ion-molecule reactions, since the reaction of  $\text{He}^+$  with  $\text{H}_2$  is unusually slow ( $k = 1.1 \times 10^{-13} \text{ cm}^3/\text{s}$ )[14]. Therefore, non-recombining  $\text{He}^+$  ions can

accumulate in the late afterglow and reduce the recombination rate. It appears that the original experiments by Adams et al. [9] were somewhat affected by this problem, but later work by Smith and Spanel [13] showed that this is not the only reason why the recombination rate is reduced in the late afterglow.

The conjecture was put forth by Johnsen [unpublished, but a brief reference survives in the paper by Canosa et al. [11] that perhaps the recombination of  $H_3^+$  with electrons might produce  $H_3^*$  molecules in highly excited Rydberg states and that these molecules would be field-ionized by the Langmuir probes that are used in flowing afterglow experiment to measure electron densities. As a consequence, the current collected by the probes might be erroneously large and the recombination loss would appear to be reduced. The conjecture, however, cannot quantitatively account for the observed effects since the number of electrons that can be collected from Rydberg molecules is limited by the diffusive particle current to the probe surface. Due to the larger mass of  $H_3^*$  molecules, their thermal flux is far smaller than that of free electrons (by the factor  $[m_e/m(H_3^+)]^{1/2} = 0.04$ ). The conjecture, nevertheless, may have contained a kernel of truth. We will return to this subject in a later section (V.2).

The first clear evidence that Adams' et al. [9] identification of  $H_3^+$  vibrational states could not be upheld came when Amano [15] published results of an infrared absorption study in a decaying hydrogen plasma. He concluded that  $H_3^+$  ions in the spectroscopically-identified vibrational ground state recombined with electrons about as fast as had been measured in the microwave experiments. Several objections to Amano's results were raised, for instance that the electron density in his plasmas was sufficiently high to enable collisional-radiative recombination. A further objection was that Amano's assumption of equal electron and  $H_3^+$  densities might not have been justified, since the plasma could have contained ions other than  $H_3^+$ . Amano addressed the questions in a second paper<sup>16</sup> and pointed out that the ion density followed a hyperbolic decay (electron density proportional to reciprocal time) very well over a large range. This would not be

expected, if either of the two objections was valid. The absence of collisional radiative recombination, however, presents a puzzle. Bates et al. [3] have discussed this question in more detail. A further infrared absorption experiment in hydrogen plasmas has recently been carried out by Feher et al.[17] . Those authors only concluded that Amano's recombination rate should be considered as a upper limit which is not much of a constraint.

Additional measurements of the recombination of  $H_3^+$  in flowing-afterglow plasmas were carried out by Canosa et al.[11,12 ] Their technique was rather similar to that of Adams et al. [9] but it differed in the method of data analysis. The measured recombination coefficient were close to those obtained by Amano [15,16] and by the early microwave afterglow experiments.

Several measurements of recombination cross sections for  $H_3^+$  were made by using the merged-beam technique [18, 19, 20, 21 ]. The outstanding virtue of this technique is that the energy resolution (in the electron-ion center-of-mass system) is higher than that of plasma afterglow experiments and that fine structures in cross sections become amenable to study. Unfortunately, the only control of the internal energy of the reacting ions (e.g. vibrational energies) consists of modifying conditions in the ion source. The results of Hus et al.[18] showed that the recombination cross section of  $H_3^+$  was strongly affected by the conditions in the ion source and this was ascribed to vibrational excitation. In some measurements made with the merged-beam method (Yousif et al.[21]), the vibrational state of the recombining ions was deduced from the threshold energy for electron-ion dissociative excitation. The result seemed to indicate that the  $H_3^+$  ions were in  $v=0$  and that those recombined only slowly with electrons.

A major new innovation in experimental techniques occurred when ion storage rings [22, 23] became available for measurements of dissociative recombination. In these large-scale instruments, the residence time of ions can be made sufficiently long (8 seconds) to allow vibrationally excited ions to relax to the vibrational ground state by

radiative transitions. The authors do not explicitly state this, but presumably even the  $v_1=1$  metastable level with a calculated lifetime (Dinelli et al.[24]) of 1.2 s would have decayed by infrared transition to the  $v_2=1$  level. The work by Larsson et al. [22] and by Sundström et al.[23] using the CRYRING storage ring yielded recombination cross sections for  $H_3^+$  ( $v=0$ ) over the wide energy range from 0.0025 to 30 eV. The inferred recombination coefficient of  $(1.15 \pm 0.13) \times 10^{-7} \text{ cm}^3/\text{s}$  at 300 K (as calculated by Sundström et al. [23]) again falls in the range of the higher values. At present, the energy resolution in this technique is limited by the electron motions perpendicular to the beam. The effective "temperatures" ( $kT = 0.1\text{-}0.15 \text{ eV}$ ) are actually higher than in the afterglow experiments and it should be kept in mind that the conversion from measured cross sections to thermal rate coefficients requires an extrapolation of the cross sections to low energies.

At this time, it appeared that the problem had been resolved in favor of the larger recombination rates. The conflict between theory and experiment, sometimes referred to as an "enigma" [3], appeared to fade into the background when new recombination mechanisms [25, 26] were proposed that seemed capable of accommodating higher recombination rates for  $H_3^+$  ( $v=0$ ) ions. The situation changed again when Smith and Spanel [13] presented new data in support of Adams et al.s' [9] contention that only  $H_3^+$  ions in  $v>3$  recombined efficiently with electrons and that  $v=0$  would recombine only slowly. Their experiments included many corroborating tests and the conclusions seemed to be well-founded. Our work was, in part, motivated by that experiment.

In the article, we will present new results of flow-tube measurements on the recombination of  $H_3^+$  and  $D_3^+$  ions. While we were able to reproduce some of Smith and Spanel's [13] experimental results, we will show that their interpretation of the anomalous decay of  $H_3^+$  plasmas cannot be correct. We were eventually led to conclude that the peculiar decay of  $H_3^+$  plasmas probably has little to do with vibrational excitation of the ions. A different and more interesting explanation will be offered.

In the following, we will make a distinction between the customary "recombination coefficient" of a specified ion (denoted by " $\alpha$ ") and the "de-ionization coefficient" (denoted by " $\beta$ ") of a plasma. The de-ionization coefficient is meant to represent the total measured volume loss (excluding diffusion) of free electrons. It may refer to a mixture of ions and it may include other processes, for instance re-ionization of recombination products. This distinction does not bias the discussion in favor of a postulated recombination process, and it avoids the use of ill-defined concepts, such as a time-dependent recombination coefficients. It will be seen later that this distinction is important in the case of  $H_3^+$  plasmas.

## II. Experimental Methods

The flowing afterglow method to determine electron-ion recombination coefficients and products of recombination is quite well developed [9]. The emphasis in this paper is on the anomalous features of the decay of  $H_3^+$  plasmas. Therefore, we will devote more space to questions of vibrational excitation of  $H_3^+$  ions and the methods of data analysis.

Our flow tube (see Fig. 1) is a stainless steel tube (diameter 6 cm, length = 36 cm) with two attached long quartz windows for spectroscopic observations (not used in the present experiment). As is customary, reagent gases are added through several movable and fixed reagent inlets. A movable Langmuir probe (diameter = 25  $\mu$ m, length = 0.28 cm) serves to measure electron densities. We have given a detailed discussion of the use of Langmuir probes in flow tubes in a recent publication [27]. A quadrupole ion mass spectrometer samples plasma ions from the downstream end of the flow tube. All gas pressures, flow rates were measured by capacitance manometers and calibrated gas flow meters. The carrier gas was helium (at pressures near 1 Torr). Flow velocities ranged from 5000 cm/s to 6000 cm/s. The gas temperature was typically 295 K.

## II. 1 Method of plasma generation and ion conversion

A plasma in the pure carrier gas helium is generated in an upstream microwave discharge. Argon gas (at a pressure of typically 15 % of the helium pressure) is added at a downstream gas inlet to convert metastable helium atoms to argon ions by Penning ionization and to reduce the rate of ambipolar diffusion. In the region downstream from the argon inlet, the plasma then contains mainly thermalized electrons,  $\text{Ar}^+$  ions and some  $\text{He}^+$  and  $\text{He}_2^+$  ions (< 0.1 % of  $\text{Ar}^+$ , as measured by the mass spectrometer). Such a plasma is essentially non-recombining. At the position of the reagent inlet, the electron density was typically  $4 \times 10^{10} \text{ cm}^{-3}$ .

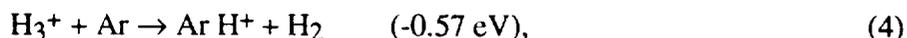
To create  $\text{H}_3^+$  ions,  $\text{H}_2$  is added at the reagent inlet at densities of  $10^{14} \text{ cm}^{-3}$ . The following reaction sequence occurs:



The exoergicities refer to  $\text{Ar}^+$  in the  $^2\text{P}_{3/2}$  fine structure state and ground vibrational and electronic states for the molecular species. Thermochemical data were taken from Radzig and Smirnov [28]. The rate coefficients for reactions 2 and 3 are on the order of  $10^{-9} \text{ cm}^3/\text{s}$  [29].

## II.2 Vibrational excitation and quenching

The question of vibrational excitation in the  $\text{H}_3^+$  ions needs to be examined in detail. If it is assumed, which however seems unlikely, that the entire energy of 2.1 eV that is released in the two-step process appears in vibrational excitation of the  $\text{H}_3^+$  product, then  $\text{H}_3^+$  could be produced in vibrational states up to  $v=5$ . However, the more highly excited  $\text{H}_3^+$  ions will be destroyed quickly by proton transfer to Ar,



which becomes energetically possible for  $\text{H}_3^+$  ions with internal energies above 0.57 eV. There are only three  $\text{H}_3^+$  vibrational states below 0.57 eV, the ground state [ $A_1 (0, 0^0)$ ], the  $\nu_2=1$  bending-mode vibration [ $E (0, 1^1)$  at 0.3126 eV], and the  $\nu_1=1$  breathing mode vibration [ $A_1 (1, 0^0)$  at 0.394 eV] (see Lie and Frye [30] or Oka [2]). The corresponding energies for  $\text{D}_3^+$  are 0.2275 eV ( $\nu_2=1$ ) and 0.2856 eV ( $\nu_1=1$ ).

Since the density of argon in the experiment is typically  $5 \times 10^{15} \text{ cm}^{-3}$ , and exo-ergic proton transfer is invariably fast ( $k \sim 10^{-9} \text{ cm}^3/\text{s}$ ), destruction of the higher vibrational states would occur in a time of less than 1  $\mu\text{sec}$ . This time is far shorter than the time over which recombination occurs.

One may wonder, however, if vibrationally excited  $\text{H}_3^+(\nu > 1)$  might enter a reaction equilibrium with vibrationally excited  $\text{ArH}^+$  ions (via reaction 3 in both directions) and thus would be constantly regenerated. It seems very unlikely that vibrational excitation would persist very long in such a process since in each proton transfer some vibrational energy will be converted to translational energy. Furthermore,  $\text{ArH}^+$  ions should then be detected by the mass spectrometer, but there is no experimental evidence for a significant presence of  $\text{ArH}^+$  ions. The conclusion is that  $\text{H}_3^+$  ions in  $\nu > 1$  can be excluded from further consideration.

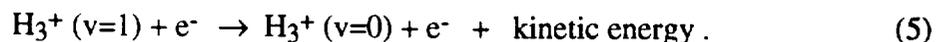
The radiative lifetime of the  $\nu_1=1$  level is very long since a direct transition to the ground state is dipole forbidden. Dinelli et al. [24] calculated a lifetime of 1.2 s for cascading to the  $\nu_2=1$  level which then decays in 4 ms to the ground state. Thus, radiative decay of the  $\nu_1=1$  level will not occur on the time scale of recombination (it takes about 1 ms for the electron density to decay from  $4 \times 10^{10} \text{ cm}^{-3}$  to 1/8 of that value if the recombination coefficient is  $\alpha = 2 \times 10^{-7} \text{ cm}^3/\text{s}$ ). Radiative decay of ions in the  $\nu_2=1$  level

is faster ( $\tau = 4$  ms), but unless quenching occurs some could survive into the late afterglow.

Collisional destruction (quenching) of  $v=1$  ions in collisions with  $H_2$  will be considered next. Amano's [31] absorption studies of the  $v_2$  hot band indicate that the  $v_2=1$  level is quenched rapidly, with a rate coefficient of approximately  $3 \times 10^{-10}$   $cm^3/s$ . This eliminates ions in this state from further consideration, since they will be destroyed in  $30 \mu s$  at  $[H_2] = 1 \times 10^{14}$   $cm^{-3}$ . On the other hand, there is considerable evidence (see Lee et al. [32], Blakey et al. [33], and Smith and Spanel [13]) that some vibrationally excited ions are quenched with a far smaller rate coefficient of roughly  $10^{-12}$   $cm^3/s$ . Those ions would survive for 10 ms at  $[H_2] = 1 \times 10^{14}$  (1 ms at  $[H_2] = 1 \times 10^{15}$   $cm^{-3}$ ) and could be present during the recombination phase of the afterglow. 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. [34] who studied the absorption of  $H_3^+$  hot bands in He/ $H_2$  discharges. They ascribed the slow quenching of the  $v_1=1$  state to the lack of a dipole moment for transition to the ground state.

The foregoing discussion shows that  $H_3^+$  ( $v_1=1$ ) ions may survive long enough to undergo recombination. An estimate of their relative abundance clearly would be of interest. The for the present purpose most relevant estimate is that of Lee et al. [32]. It refers to a flowing afterglow plasma of the same gas composition as that in our experiment, but of lower electron density. Their studies of ion-molecule reactions of  $H_3^+$  indicated that 70% of the ions were in the vibrational ground state and 30% in an (unidentified by them) excited state. Since the  $v_2=1$  ions are quenched rapidly, we suggest that the 30% long-lived ions were in the  $v_1=1$  state.

A further, but seldom mentioned vibrational quenching may occur by superelastic collisions with electrons

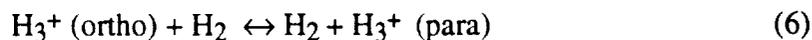


The reaction would involve the same intermediate  $H_3^{**}$  compound states that are invoked in indirect dissociative recombination, but it would be terminated by autoionization, rather than by dissociation. Unfortunately, nothing appears to be known for this type of quenching in the case of  $H_3^+$ , but Guberman [35] has carried out calculations for the corresponding process of  $N_2^+(v=1)$  ions. The surprising result was that the quenching rate exceeded the rate of dissociative recombination by a factor of 18. If the same were true for  $H_3^+(v=1)$  then most  $v=1$  ions would be quenched before suffering recombination. It is interesting to note that  $v=1$  ions account for only about 4 to 6 % of all ions in He/ $H_2$  discharges [34]. Thus, the abundance of 30% given by Lee et al.[32] may be an upper limit that refers to plasmas of low electron densities where electron quenching is unimportant.

In their discussion of the same reaction sequence, Smith and Spanel [13] did not consider the destruction of the higher vibrational levels via reaction (4). They concluded that most  $H_3^+$  ions would be highly vibrationally ( $v \geq 3$ ) excited. We reach the opposite conclusion that only a few (at most 30%) might be excited to  $v_1=1$ . Experimental tests pertaining to vibrational excitation will also be discussed in Sec. III.

### II. 3 Para and ortho $H_3^+$ .

There is no *a priori* reason to expect that the para (three proton spins aligned) and the ortho (two proton spins aligned) forms of  $H_3^+$  should have the same recombination coefficients. In an afterglow experiment, two distinct recombination coefficients would be observable only if the para/ortho equilibration time is longer than the time scale of recombination. In the opposite case of rapid equilibration, the concentration-weighted average of the two coefficients would be measured. According to Oka [36], the conversion from one form into the other by proton exchange with  $H_2$ ,



is a rapid process, but unfortunately no rate coefficient is given. We assume that the proton-transfer rate is sufficiently large ( $k > 10^{-10} \text{ cm}^3/\text{s}$  would be sufficient at  $[\text{H}_2] = 10^{14} \text{ cm}^{-3}$ ) to maintain the para-to-ortho ratio at its 1:1 equilibrium value.

#### II.4 Presence of $\text{H}_5^+$ ions

There is no reason to be concerned about formation of  $\text{H}_5^+$  ions at room temperature since the equilibrium constant for three-body association



has the small value of  $2 \times 10^{-19} \text{ cm}^3$  at 300 K [37]. At the highest  $\text{H}_2$  concentrations used in our experiments ( $1.7 \times 10^{15} \text{ cm}^{-3}$ ) the  $\text{H}_5^+/\text{H}_3^+$  ratio would be only  $3 \times 10^{-4}$ . Vibrationally excited  $\text{H}_3^+$  ions should not associate with  $\text{H}_2$ , even at reduced temperatures, since the binding energy of  $\text{H}_5^+$  (0.35 eV) [37] is very close to the vibrational quantum in  $\text{H}_3^+$ .

#### II.5 Impurity estimates

Gaseous impurities can be a problem in afterglow experiments. Their effect is more severe in studies of  $\text{H}_3^+$  ions since the ions readily transfer protons to many common impurities and the resulting ions may have large recombination coefficients. In this work, the mass spectrometer indicated that  $\text{H}_3\text{O}^+$  ions formed by the fast ( $k = 4.3 \times 10^{-9} \text{ cm}^3/\text{s}$ ) proton transfer



were the principal offending ions. Hence, all efforts were made to reduce the H<sub>2</sub>O concentration by placing cold traps into the gas supply lines, but some water vapor remained. Since the mass spectrometer is located far downstream from the recombination region, the mass spectra reflect conditions in the late afterglow, rather than in the recombination zone and some computations are required to find out how many H<sub>3</sub>O<sup>+</sup> ions are present in the recombination region. Model calculations were made which included proton transfer, recombination of both H<sub>3</sub><sup>+</sup> (using  $\alpha = 2 \times 10^{-7} \text{ cm}^3/\text{s}$ ) and H<sub>3</sub>O<sup>+</sup> ( $\alpha \sim 1 \times 10^{-6} \text{ cm}^3/\text{s}$ ) [38] and ambipolar diffusion in the region from the H<sub>2</sub> inlet to the mass spectrometer. The residual H<sub>2</sub>O concentration then was deduced by fitting the ratio H<sub>3</sub>O<sup>+</sup>/H<sub>3</sub><sup>+</sup>, as measured by the mass spectrometer, to that predicted by the model. This procedure yielded a residual water concentration of  $3 \times 10^{10} \text{ cm}^{-3}$ . The model also shows that such a concentration of water will only have a small effect on the electron density decay in the recombination region (an additional 5% reduction during the first factor-of-ten decline of the electron density).

## II. 6 Data analysis

Several different methods were used to derive de-ionization coefficients from the measured electron densities  $n_e(z, r=0)$ . The customary method of deducing  $\beta$  from the slope of a graph of

$$\frac{1}{n_e(z)} = \frac{1}{n_e(z=0)} + \beta \frac{z}{V} \quad (9)$$

was used to obtain approximate values of the de-ionization coefficient. In this simple approach, diffusion in axial and radial directions is neglected. A more rigorous approach is needed if one wishes to determine the dependence of  $\beta$  on  $z$ . It then becomes necessary

to analyze the shape of the decay curves in detail and one is forced to include diffusion in both axial and radial directions.

A rigorous analysis of a recombining flowing afterglow plasma is a rather difficult task. The continuity equation for the electron density  $n_e(r, z)$  in the flow tube with a parabolic velocity field (Poiseuille flow) is given by

$$\frac{\partial n_e(r, z)}{\partial z} = \frac{1}{V_0[1 - (\frac{r}{R})^2]} \{-\beta n_e^2 + D_a[\frac{\partial^2 n_e}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r}(r \frac{\partial n_e}{\partial r})]\}. \quad (10)$$

Here,  $V_0$  is the gas flow velocity on the axis of the tube, and  $r$  and  $R$  denote the radial variable and the flow tube radius, respectively.  $D_a$  is the ambipolar diffusion coefficient of ions and electrons. It was deduced from measured mobilities using Einstein's relation between mobility and diffusion. A series of measurements in  $H_3^+$  plasmas at very low electron densities ( $< 2 \times 10^9 \text{ cm}^{-3}$ ) showed that the calculated diffusion loss agreed with the measured diffusion loss to an accuracy of better than  $\pm 10\%$ .

Numerical solutions of Eq. (10) were obtained for a few conditions of interest, but the computing time was found to be impractically long for fitting a large set of experimental data. Hence, the computed solutions were used only to validate a simpler, approximate method that was employed for routine data analysis. In the approximate method, the gas flow velocity is taken to be radially independent and the assumption is made that the radial variation of  $n_e(z, r)$  is given by fundamental diffusion mode in a cylinder. The approximate continuity equation for the electron density on axis ( $r=0$ ) then can be written as

$$\frac{\partial n_e(r=0)}{\partial z} = \frac{1}{V_{eff}} [-\beta n_e^2 + D_a(\frac{\partial^2 n_e}{\partial z^2} - \frac{n_e}{\Lambda^2})]. \quad (11)$$

Here,  $\Lambda = R / 2.405$  is the fundamental diffusion length for a cylinder of diameter  $R$  and  $D_a$  is the ambipolar diffusion coefficient. The effective flow velocity  $V_{\text{eff}}$  is close to the gas velocity on the axis of the flow tube. Estimates showed that axial diffusion (the second-derivative term in Eq. 11) can have a significant effect in the early afterglow and that it should be retained even at this level of approximation.

The  $z$ -dependent de-ionization coefficient  $\beta(z)$  was obtained by putting Eq. 11 in the form

$$\beta(z) = \frac{1}{n_e^2} \left[ D_a \left( \frac{\partial^2 n_e}{\partial z^2} - \frac{n_e}{\Lambda^2} \right) - V_{\text{eff}} \frac{\partial n_e}{\partial z} \right]. \quad (12)$$

If  $n_e(z)$  is known from the measurement, all quantities on the right-hand-side are known and, at least in principle,  $\beta(z)$  can be computed. If only a single ion with recombination coefficient  $\alpha$  is present, the procedure should return a constant value of  $\beta(z) = \alpha$ . In practice, differentiating experimental data is a poor procedure and it was found preferable to fit the reciprocal values of  $n_e(z)$  to a polynomial. The needed derivatives then were obtained analytically. A third-order polynomial fit to  $1/n_e(z)$  results in a second-order polynomial expansion of  $\beta(z)$ . Higher-order polynomials were tried, but they tended to introduce undesirable oscillations that were not present in the data.

The approximate model was tested by using the exact model to generate simulated  $n_e(z)$  values for known recombination coefficients and typical experimental conditions. The computer-generated data were then analyzed using Eq. 12. We found that the approximate method reproduced the input recombination coefficients (see Fig. 2) to an accuracy of about 3% when the effective flow velocity was taken as 100% of the gas flow velocity on the axis of the flow tube. When the same method was applied to reduce experimental data obtained in recombining  $\text{O}_2^+$  plasmas (made by adding  $\text{O}_2$  at the reagent inlet), the  $\beta(z)$  curves exhibited only random deviations of <10% from an the

average value of  $1.85 \times 10^{-7} \text{ cm}^3/\text{s}$ . The average value of  $\beta(\text{O}_2^+)$  is only 6% smaller than the recombination coefficient given Mehr and Biondi [39] ( $\alpha = 1.95 \times 10^{-7} \text{ cm}^3/\text{s}$ ). This discrepancy may reflect, in part, a systematic error in the absolute values of  $n_e(z)$  that are obtained from the Langmuir probes.

During the data fitting it was noted that the  $\beta(z)$  curves at large  $z$  were very sensitive to small experimental errors in the  $n_e(z)$  data at large  $z$ . This is not a flaw in the method of analysis. It merely reflects the fact that recombination becomes less important in the late afterglow.

### III. Experimental results

A total of 40 decay curves  $n_e(z)$  were recorded for different argon densities (from  $4 \times 10^{15} \text{ cm}^{-3}$  to  $8 \times 10^{15} \text{ cm}^{-3}$ ) and different  $\text{H}_2$  densities (from  $1 \times 10^{14} \text{ cm}^{-3}$  to  $1.7 \times 10^{15} \text{ cm}^{-3}$ ). The absence of significant impurities was checked in each case by the mass spectrometer before the data were taken.

The simplest form of data analysis consisted of deducing average de-ionization coefficients from the slope of  $1/n_e(z)$  vs.  $z$  graphs. The results indicated that  $\beta$  increased noticeably with increasing  $\text{H}_2$  concentration as is shown in Fig. 3. A similar graph was obtained when the average values of  $\beta(z)$  in the first 4 cm were plotted as a function of  $[\text{H}_2]$ . No such variation was found when the argon concentration was varied.

Figures 4 and 5 show typical examples of the electron density  $n_e(z)$  for two different  $\text{H}_2$  concentrations. In the lower part of the figures, we show  $\beta(z)$  as calculated from Eq. 12. It is apparent that  $\beta$  decreases with increasing  $z$ . This finding qualitatively reproduces the observations of Smith and Spanel[13]. Actually, if their published data (Fig. 2 in ref.[13]) are processed by using Eq. 12, the resulting  $\beta(z)$  curves look remarkably similar to those in our Fig. 4 and those shown by Smith and Spanel (their Fig.4). The decay of the electron density in this plasma clearly is anomalous in the sense that it cannot be described by a simple recombination law.

Two comments should be made at this point: The  $\beta(z)$  curves shown in Figs. 4 and 5 may give the impression of higher accuracy than is justified by the original data. The initial values of  $\beta(z)$  are reasonably insensitive to the choice of diffusion constants that enter in the analysis; the values at  $z=10$  cm would be in error by  $\pm 20$  % if the diffusion losses have an error of  $\pm 10$  %. We also concede that the late-afterglow decay curves observed by Smith and Spanel [13] are intrinsically more accurate than ours. The reason is simply that the flow tube used by those authors had a larger cross section and that their experiment was done at a higher pressure. As a consequence, the diffusion losses were smaller (by a factor of 4) and the late afterglow data were superior.

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 (see Fig.3), but the  $D_3^+$  de-ionization coefficients were significantly smaller (from  $0.7 \times 10^{-7}$  cm<sup>3</sup>/s to  $1.3 \times 10^{-7}$  cm<sup>3</sup>/s in the range  $[D_2] = 1$  to  $14 \times 10^{14}$  cm<sup>-3</sup>).

#### IV. Search for excited states

Several auxiliary measurements were carried out to find evidence for the presence of excited  $H_3^+$  ions. The ideas for those were, in part, based on the tests performed by Smith and Spanel.

In one such test, carbon monoxide was added through a reagent inlet located about 6 cm downstream from the  $H_2$  inlet. At that location, most of the fast recombining fraction of  $H_3^+$  should have recombined, but the slowly recombining fraction should still be present. The reaction with CO,



would convert the non-recombining  $H_3^+$  ions to recombining  $HCO^+$  ( $\alpha = 2.4 \times 10^{-7}$  cm<sup>3</sup>/s) [40] ions. As a consequence, the electron density should fall off more rapidly after

CO addition. Smith and Spanel observed a distinct enhancement of the electron loss upon adding CO. We tried to duplicate this experiment, but we found no effect; substitution of  $\text{HCO}^+$  ions for  $\text{H}_3^+$  ions did not measurably enhance the electron loss. We do not consider our failure to observe the effect of CO additions as being in conflict with Smith and Spanel's findings. The diffusion losses in our tube were higher, which makes it more difficult to observe subtle effects in the late afterglow. Addition of methane at the downstream location, however, did result in a clear enhancement of the electron loss rate. This is not surprising since the proton transfer with methane produces  $\text{CH}_5^+$  ions ( $\alpha = 1.1 \times 10^{-7} \text{ cm}^3/\text{s}$ ) [41] which recombine much faster than  $\text{H}_3^+$ . The test with methane also shows that  $\text{H}_3^+$  ions were still present at that point in the afterglow. If the plasma at that point had contained mainly  $\text{H}_3\text{O}^+$  impurity ions, adding methane would not have had the observed effect.

An attempt was also made to use methane addition as a detector for  $\text{H}_3^+(\nu \geq 3)$ , even though there are strong reason to doubt their presence. The idea again was borrowed from Smith and Spanel, who give more details. It relies on the fact that  $\text{H}_3^+(\nu \geq 3)$  reacts with  $\text{CH}_4$  to form  $\text{CH}_3^+$  which then reacts again with  $\text{CH}_4$  to form  $\text{C}_2\text{H}_5^+$ . In contrast,  $\text{H}_3^+(\nu < 3)$  reacts with  $\text{CH}_4$  to form  $\text{CH}_5^+$ . If  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  had different electron-ion recombination coefficients, this could be exploited as a means to diagnose the vibrational state distribution of the  $\text{H}_3^+$  ions. As a preliminary step, we measured the recombination coefficients of both ions, however using  $\text{Ar}^+$  ions reacting with  $\text{CH}_4$  to make  $\text{CH}_3^+$  which then reacted further to make  $\text{C}_2\text{H}_5^+$ . To our dismay, we found only a 10 % difference between the recombination rates of  $\text{CH}_5^+$  ( $\alpha \sim 1 \times 10^{-6} \text{ cm}^3/\text{s}$ ) and  $\text{C}_2\text{H}_5^+$ , while Smith and Spanel had found that  $\text{CH}_5^+$  recombined significantly faster. In view of this problem, we discontinued the search for  $\text{H}_3^+(\nu \geq 3)$  by this method.

Smith and Spanel also described a rather interesting method of detecting  $\text{H}_3^+$  ions in  $\nu=1$  which seemed worth repeating. They noted the presence of a small amount of  $\text{ArH}^+$  ions in the downstream plasma. This was found to be surprising since all  $\text{ArH}^+$  ions

should have been destroyed in reactions with the abundant  $\text{H}_2$ . Their explanation for the persistence of  $\text{ArH}^+$  was that those ions entered an equilibrium with vibrationally excited  $\text{H}_3^+$  ( $\nu=1$ ) ions via the reaction



The observation of  $\text{ArH}^+$  then was seen as evidence for the existence of vibrationally excited ions. We repeated this measurement in the hope that we might learn more about the abundance of  $\text{H}_3^+$  in  $\nu=1$ . To avoid complications due to recombination reactions of  $\text{ArH}^+$  and  $\text{H}_3^+$ , we used our selected-ion drift tube apparatus [42] rather than the plasma flow tube. In this experiment, short pulses (10  $\mu\text{s}$ ) of mass selected  $\text{Ar}^+$  ions were injected into an ion drift tube of length 36 cm, filled with helium buffer gas with additions of argon and  $\text{H}_2$ . The reactions taking place are the same as those in the flow tube. A second mass spectrometer, located at the opposite end of the tube, analyzes the ions that have traversed the drift tube. The arrival time spectra of the ions were recorded with a time resolution of about 0.25  $\mu\text{s}$ . If two ion species, e.g.  $\text{H}_3^+$  ( $\nu=1$ ) and  $\text{ArH}^+$ , react back and forth many times while traversing the drift tube, their arrival spectra should be nearly identical. This was indeed observed. The  $\text{ArH}^+$  signal, while far smaller (<1% of  $\text{H}_3^+$ ), exhibited to an extraordinary degree of precision the same time dependence as that of  $\text{H}_3^+$ . At first, this seemed to indicate an equilibrium process. However, it was discovered rather quickly that the ratio of the  $\text{ArH}^+$  and  $\text{H}_3^+$  intensities did not vary linearly with the  $[\text{Ar}]/[\text{H}_2]$  concentration ratio, as would be required for an equilibrium process. Further tests showed that  $\text{ArH}^+$  signal depended critically on the small bias voltages that were applied to the ion extraction electrodes and it became clear that the vast majority of  $\text{ArH}^+$  ions were produced by proton transfer from non-thermal  $\text{H}_3^+$  ions during the extraction of ions from the drift tube into the mass spectrometer. We suspect, but cannot prove, that the same complication was present in the flow tube experiments of

Smith and Spanel. The equilibrium "constants" given by them (actually they varied by a factor of four) may have little to do with the reaction equilibrium of reaction 14 and no conclusions about the existence of excited  $H_3^+$  ions can be drawn.

## V. Interpretation of Results

The interpretation of the data should provide an explanation for the enhancement of the de-ionization coefficient due to hydrogen addition and the decline of the rate of recombination with position  $z$ . In the following section, we will examine two different models. The first model assumes the presence of  $H_3^+$  ions in two different states. The second model will invoke an entirely different explanation in terms of Rydberg molecules.

### V.1. Two-state model

In view of our discussion in Sec. II, it is natural to seek an explanation of the  $z$  dependence of  $\beta$  by assuming that  $H_3^+$  ions in  $v=0$  and in  $v_1=1$  are present. If this were the case, then the de-ionization coefficient for a mixture of  $v=0$  and  $v_1=1$  ions would be given by

$$\beta(z) = \alpha_0 f_0(z) + \alpha_1 f_1(z) \quad (15)$$

where  $\alpha_0, \alpha_1$  denote the recombination coefficients of  $v=0$  and  $v_1=1$  ions, and  $f_0$  and  $f_1$  are the fractional concentrations ( $f_0 + f_1 = 1$ ). Here the  $\alpha_i$  are constants, but the fractions  $f_0$  and  $f_1$  will change with  $z$  as a result of recombination and quenching of excited ions.

A reaction model that reproduces the measured  $\beta(z)$  curve obtained at  $[H_2] = 1.3 \times 10^{14} \text{ cm}^{-3}$  can be constructed easily. It consists of recombination of ions in  $v=0, v_1=1$ , and quenching of  $v_1=1$  ions to  $v=0$  in collisions with  $H_2$ . Four quantities enter:  $\alpha_0$  and

$\alpha_1$ , the initial fraction  $f_0(z=0)$ , and the quenching coefficient  $k_q$  of the  $v_1=1$  state with  $H_2$ . An adequate fit (see Fig.4 ) can be obtained by using  $\alpha_0= 2.2 \times 10^{-7} \text{ cm}^3/\text{s}$  for the recombination coefficient of  $v=0$  ions,  $\alpha_1= 4 \times 10^{-8} \text{ cm}^3/\text{s}$  for that of  $v=1$  ions, and  $f_0 = 0.7$ . This choice of  $f_0$  was suggested by the results of Lee et al.[32]. Two trial values for the quenching coefficient were used,  $k_q= 1 \times 10^{-12} \text{ cm}^3/\text{s}$  and a ten times larger value (it does not enter critically at low  $H_2$  concentrations). As may be seen in Fig.4, the two-state model reproduces the measured de-ionization coefficients fairly and we initially believed that this model had some merit.

A problem arises, however, when we use the same values to compute a fit to the data at a higher  $H_2$  concentration,  $[H_2]= 1.7 \times 10^{15} \text{ cm}^{-3}$ . The model calculations (see Fig. 5 ) indicate that  $\beta(z)$  should increase with  $z$  and remain nearly constant thereafter when the higher value of  $k_q$  is used. This happens because quenching of the  $v_1=1$  state now occurs much earlier in the afterglow. We can force a decline of  $\beta(z)$  by reducing the quenching rate to  $k_q=1 \times 10^{-13} \text{ cm}^3/\text{s}$ . If such a small value of  $k_q$  is taken, however, it is hard to explain why the measured  $\beta$  at  $z=0$  (only 1 cm from the reagent inlet) should be larger than at the lower  $H_2$  concentration. We eventually concluded that the two-state model does not really provide a consistent explanation of the experimental findings. In the absence of independent evidence for the presence of excited states of  $H_3^+$ , it would not seem justified to introduce additional  $H_3^+$  states or other quenching mechanisms into the model in an attempt to explain the data.

It is noteworthy that our value of  $\beta(z=0) = 2.2 \times 10^{-7} \text{ cm}^3/\text{s}$  at  $[H_2] = 1.7 \times 10^{15} \text{ cm}^3/\text{s}$  is very close to that by Leu et al. [7] ( $2.3 \times 10^{-7} \text{ cm}^3/\text{s}$ ). We should not have observed such high values if the plasma had contained a sizable fraction of non-recombining ions. The experiment of Leu et al. made use the very accurate microwave afterglow method which is free of many complications that are present in flowing plasmas. In retrospect, Leu et al.s' claim that their  $H_3^+$  ions were  $v=0$  was well justified

since it is now known that discharges in He/H<sub>2</sub> mixtures contain very few  $v=1$  ions (about 6% of  $v=0$ )[34].

## V.2 De-ionization by Rydberg molecule stabilization (RMS).

The interpretation of our data in terms of two states of the H<sub>3</sub><sup>+</sup> ion did not result in a consistent picture. If it had done so, we still would have had the problem of explaining how H<sub>3</sub><sup>+</sup> ions in  $v=0$  undergo recombination in the absence of suitable crossings of potential surfaces while those in  $v_1=1$  do not. The task now will be to find a de-ionization mechanism that is compatible with the anomalous decay without invoking binary recombination.

Our data contain a clue about the de-ionization mechanism. The slow decay of the plasma at late times (low electron densities) and the effect of H<sub>2</sub> suggest that both electrons and H<sub>2</sub> molecules in some way influence the process of recombination as such, rather than affecting the identity of the recombining ion species. Such considerations and information obtained from other experiments motivated us to explore an entirely different de-ionization mechanism. The process discussed in the following departs significantly from previous models of de-ionization in plasmas. In judging its merits, it should be kept in mind that no previous theory has provided a quantitative explanation of H<sub>3</sub><sup>+</sup> recombination.

The basic idea is that de-ionization of H<sub>3</sub><sup>+</sup> plasmas occurs by a very efficient form of three-body recombination which involves both electrons and neutral atoms as third bodies. The dominant part of the recombination energy is disposed of in the form of radiation or by a reaction with H<sub>2</sub>.

Three-body recombination, in which electrons act as stabilizing third bodies, is usually considered only in plasmas containing atomic ions (for a recent review of three-body recombination, see Flannery [43]). In this mechanism, the captured electron transfers part of its kinetic energy to a second electron while being accelerated in the ion's

field. The process is quite well understood. Its recombination coefficient [44] is given by

$$\alpha [\text{cm}^3/\text{s}] = n_e 2.5 \times 10^{-19} (300/T)^{9/2} \quad (16)$$

which implies small values of  $\alpha = 2.5 \times 10^{-9} \text{ cm}^3/\text{s}$  at  $n_e \sim 10^{10} \text{ cm}^3/\text{s}$  and  $T=300 \text{ K}$ . When molecular ions are present, dissociative recombination tends to be far more rapid and for this reason little attention has been paid to electron-stabilized recombination in plasmas that contain molecular ions. The same is true for neutral-stabilized recombination, which is less efficient by 6 to 7 orders of magnitude than electron-stabilized recombination. A special case arises, however, when a plasma contains molecular ions that do not undergo dissociative recombination. Long-lived autoionizing states can then be formed in collisions of electrons with molecular ions, and redistribution of angular momenta (l-mixing) can further enhance the lifetimes of such states.

The following sequence may occur in  $\text{H}_3^+$  plasmas: In the first step, an electron of low angular momentum (s or possibly p) is captured into a  $v=1$  Rydberg state of  $\text{H}_3$ , i.e.,



There is nothing new in invoking this resonance. It is the first step in the indirect recombination mechanism [45]. Excitation to the  $v_2=1$  state (0.3126 eV) in  $n=7, l=0$ , would be resonant at an electron energy of +0.0309 eV (1.2 kT at 300 K), very close to the maximum of a thermal distribution. For  $\text{D}_3^+$ , capture into  $n=8, l=1$  would be resonant at  $\sim 0.5 \text{ kT}$ , which is somewhat less efficient.

When there are no crossings between Rydberg states and repulsive states, predissociation will be rather slow and most doubly-excited states will decay by autoionization. If there were such crossings, then of course we would have a ready explanation for recombination, but this is not the case [3,5].

It is now known from studies of dielectronic recombination [46] and zero-electron-kinetic-energy (ZEKE) spectroscopy [47] that redistribution of angular momenta of Rydberg electrons (*l*-mixing) due to electric microfields and collisions can reduce the rates of predissociation and autoionization by several orders of magnitude, the basic reason being that high-*l* electrons do not penetrate to the core of the molecule. We propose that ambient plasma electrons, neutral atoms (He), and perhaps ions rapidly induce *l*-mixing in the  $H_3^{**}$  molecules and render them stable (or long-lived) against autoionization. Since the statistical weight of states increases with *l*, most  $H_3^{**}$  will not autoionize so that their average lifetime is drastically increased. A mixing of nearly degenerate *l*-states and their magnetic sublevels requires only momentum exchange but very little energy exchange with third particles and thus should occur very rapidly. The expected mixing efficiency will be discussed next.

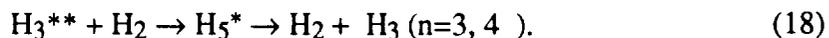
If *l*-mixing is to be effective, it must occur during the lifetime of the autoionizing resonance. The lifetime of some  $H_3^{**}$  autoionizing states have been measured to be extremely long (of the order of  $10^{-7}$  s)[48]. In particular, autoionizing states formed by  $e^- + H_3^+$  collisions in an ostensibly field-free vacuum region must survive for  $10^{-8}$  to  $10^{-7}$  s to explain observations in the merged-beam experiment of Yousif et al. [21] and those of Mitchell et al.[49]. Unfortunately, the state of the long-lived  $H_3^{**}$  molecules that are observed in the beam experiments, is not well known. It seems possible that the electron is captured into a state of low angular momentum and then exchanges angular momentum with the ion-core. Perhaps, this may be the reason that the lifetimes are so long. It is also not entirely clear whether or not the observed lifetimes really refer to molecules that have not interacted in any way with the small electric stray fields (estimated by Mitchell [49])

to be  $< 1\text{V/cm}$ ) that are always present in beam experiments. Perhaps, some  $l$ -mixing occurs even in small, static fields of  $< 1\text{ V/cm}$ . If this were the case, however, then we would argue that  $l$ -mixing in a plasma should be at least as efficient but probably far more efficient. The electric microfields in a plasma at  $n_e=2 \times 10^{10}\text{ cm}^{-3}$  due to nearest-neighbor charge (distance of a few  $\mu\text{m}$ ) are also of the order of  $1\text{V/cm}$  and the fields have high-frequency components up to  $10^{11}\text{ Hz}$ .

Measurements of Gallagher et al.[50] on sodium Rydberg atoms in  $n= 5-10$  indicate that  $l$ -mixing in collisions with helium atoms proceeds with a rate coefficient of  $\sim 10^{-8}\text{ cm}^3/\text{s}$  if  $l>2$ . At 1 Torr of He, this gives a mixing time of 3 ns which is shorter than the lifetime of the  $\text{H}_3^{**}$  resonance. However, for  $l=0$  and 1, mixing due to heavy-particle perturbers is not observed. The reason for the lack of  $l$ -mixing of the  $s$  and  $p$  states is that those states have larger quantum defects (lower energy), and that heavy particles can transfer only a minute fraction of their energy to electrons. The quantum defects for  $\text{H}_3$  Rydberg states have been calculated by King and Morokuma [51] to be approximately 0.06 ( $s$ -states) and 0.025 ( $p$ -states), which means that an  $n=7$   $s$ -state would lie  $0.005\text{ eV}=kT/5$  below states of high  $l$  values. The transfer from  $s$  to  $p$  and higher states is the point where  $l$ -mixing due to electrons may play a crucial and rate-controlling role. The energy barrier of  $kT/5$  is no hindrance for thermal electron collisions and a single electron collision can transfer sufficient energy. Estimates of  $l$ -changing cross sections [52] for  $25\text{eV}$  electrons with  $n=25$  atoms indicate very large values of  $10^{-10}$  to  $10^{-9}\text{ cm}^2$ . Of more direct relevance are the experiments by Devos et al. [53]. They showed that the  $l$ -changing efficiency of thermal electrons in collisions with helium Rydberg atoms ( $n= 8$  to  $17$ ) is so large that mixing of  $l$ -states occurs in an immeasurable time (less than a few ns) at electron densities of  $2 \times 10^{11}\text{ cm}^{-3}$ . This implies an  $l$ -changing rate coefficient for thermal electrons of  $>10^{-3}\text{ cm}^3/\text{s}$ ! An estimate of the three-body coefficient for forming  $\text{H}_3^{**}$  in high  $l$ -states from  $\text{H}_3^+$  and two electrons would be given by the product of the capture rate coefficient ( $\sim$ a few  $10^{-7}\text{ cm}^3/\text{s}$ ), the lifetime of the

resonance ( $\sim 10^{-8}$  to  $10^{-7}$  s), and the l-mixing coefficient due to electrons ( $> 10^{-3}$  cm<sup>3</sup>/s). The resulting rate coefficient ( $\sim 10^{-17}$  cm<sup>6</sup>/s) would be larger than in Eq. 16 by two orders of magnitude.

We will now turn our attention to decay modes of H<sub>3</sub>\*\*( $n=7, v=1, l$ ) molecules other than autoionization. They can be re-ionized by slow electron collisions which change their l-value back to the autoionizing state (s, or p). In addition, they may descend to lower energy states by collisional energy loss with neutral atoms or electrons, slow predissociation (if it occurs), by radiating to a lower state, or by reacting with an H<sub>2</sub> molecule. Collisional energy loss (n-changing) with helium atoms is not important at  $n=7$  (Bates and Khare [54]) 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. [52] to be  $\sim 10^{-5}$  cm<sup>3</sup>/s which yields a destruction rate of  $2 \times 10^5$  s<sup>-1</sup> at  $n_e = 2 \times 10^{10}$  cm<sup>-3</sup>. Radiative decay rates for  $n=7$  hydrogenic states are close to  $1 \times 10^6$  s<sup>-1</sup> for s-states,  $2 \times 10^7$  s<sup>-1</sup> for p-states, and about  $2 \times 10^6$  s<sup>-1</sup> for a statistical mixture of l-values up to  $l=6$  [51, 55]. Therefore, radiation is likely to be the dominant decay mode under the conditions of our experiment, but electron quenching will dominate at higher electron densities. Destruction in collisions with H<sub>2</sub> will be a two step process, formation of an H<sub>5</sub>\* complex, followed by predissociation,

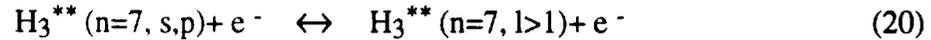


The second step is essentially the same as dissociative recombination of H<sub>5</sub><sup>+</sup> ions which is known to occur rapidly. Reaction (18) is important for the interpretation of our experiment, since it provides the needed enhancement of the loss rate of electrons in the presence of H<sub>2</sub>. The reaction will compete with radiative decay if it occurs on a time scale of  $< 1 \mu\text{s}$ . At  $[\text{H}_2] = 1 \times 10^{15}$  cm<sup>-3</sup>, this requires a rate coefficient of  $\sim 1 \times 10^{-9}$  cm<sup>3</sup>/s for reaction 18, which is not unreasonable.

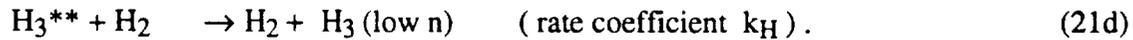
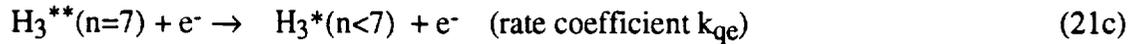
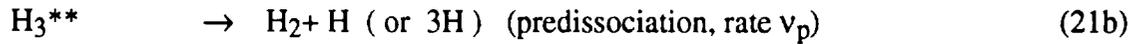
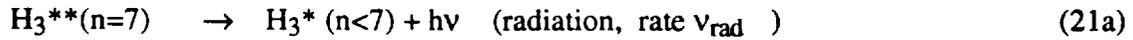
In the following, we present a simple rate model for the de-ionization process and compare it to our data. The capture and autoionization step



is described by a capture coefficient  $k_c$  and an autoionization rate  $v_a$ . Stabilization by l-mixing due to electrons



and its reverse reaction are described by rate coefficients  $k_s$  and  $k_l$  in the forward and reverse directions, respectively. Helium does not enter as a third body, since we have assumed that the electrons control the rate-limiting step in the l-mixing from s or p to higher l and back. The main destruction reactions for  $\text{H}_3^{**}$  are:



In order to allow for the possibility that the rate coefficients for  $\text{H}_3^{**}$  in the autoionizing state (s,p) differ from those in higher l-states, we treat their destruction separately and attach the subscripts "0" and "l" to the respective rate coefficients. It is a simple matter to show that this reaction scheme gives a de-ionization coefficient

$$\beta = -\frac{1}{n_e^2} \frac{dn_e}{dt} = \frac{k_c}{1 + \frac{1}{\frac{n_e k_s v_i}{(n_e k_i + v_i) v_a} + \frac{v_0}{v_a}}} \quad (22)$$

where

$$v_0 = v_{\text{rad},0} + v_{\text{p},0} + k_{\text{qe}} n_e + k_{\text{H}} [\text{H}_2] \quad (23a)$$

and 
$$v_1 = v_{\text{rad},1} + v_{\text{p},1} + k_{\text{qe}} n_e + k_{\text{H}} [\text{H}_2]. \quad (23b)$$

In the limit of large  $n_e$  and high values of  $v$ ,  $\beta$  approaches the constant value  $k_c$ . This means that all captured electrons recombine irreversibly. In the limit of vanishing  $n_e$ , the deionization rate coefficient  $\beta$  approaches the value

$$\beta = \frac{k_c}{1 + \frac{v_a}{v_0}}. \quad (24)$$

This value still depends on the  $\text{H}_2$  concentration through Eq. 23a. In the limit of vanishing  $[\text{H}_2]$ ,  $\beta$  should approach a small value that depends on the ratio  $v_a/v_{\text{rad},0}$ . The ratio may be on the order of ten to hundred and  $\beta$  would then would be 1 to 10 % of  $k_c$ .

### V.3 Comparison of the RMS model to experimental data

The functional form of Eq. 22 fits our data quite well, and it is possible to find a set of rate coefficients such that Eq. 22 provides a reasonable fit. Fig. 6 shows a comparison to experimental values of  $\beta (n_e)$  (the same data as shown in Fig. 4 and 5, but plotted as a function of the electron density). The rate coefficients used were:

$$k_c = 4.4 \times 10^{-7} \text{ cm}^3/\text{s}$$

$$v_a = 1.3 \times 10^8 \text{ s}^{-1}$$

$$k_s = 1.25 \times 10^{-2} \text{ cm}^3/\text{s}$$

$$k_i = 3.1 \times 10^{-4} \text{ cm}^3/\text{s}$$

$$v_{\text{rad},0} = 1.1 \times 10^6 \text{ s}^{-1}$$

$$v_{\text{rad},1} = 1.1 \times 10^6 \text{ s}^{-1}$$

$$v_{p,0} = v_{p,1} = 0$$

$$k_H = 4.5 \times 10^{-9} \text{ cm}^3/\text{s}$$

$$k_{qe} = 1 \times 10^{-5} \text{ cm}^3/\text{s}$$

This set of numbers is not necessarily unique but the values are quite close to those that were estimated earlier. Detailed balancing suggests that the ratio  $k_s/k_i$  should be close to  $n^2-1=48$  (assuming that only the  $l=0$  state autoionizes), where  $n=7$  is the principal quantum number of the Rydberg state, since  $l$ -mixing from  $s$  to  $l>0$  states requires little energy exchange (0.2 kT). The ratio  $k_s/k_i=40$  fits the data quite well.

Our model is crude in many respects. For instance, we treat all Rydberg molecules with  $l>1$  as a single entity which is probably not justified. We also do not wish to give the impression that our experimental data provide sufficient evidence for the validity of this model. More detailed studies would be needed to do that. On the other hand, the estimates underlying the model seem sound and the rate coefficients are reasonable.

#### V. 4 Consequences of the proposed de-ionization mechanism and relation to other work.

If the proposed de-ionization mechanism occurred, it would immediately solve the theoretical dilemma of having to account for "binary recombination" of electrons with  $\text{H}_3^+$  ions. This process is not needed to explain the observed de-ionization. It is only required that the  $\text{H}_3^{**}$  Rydberg molecules decay to lower states by radiation, slow

predissociation, or collisional quenching, and this will certainly occur. Radiation alone would suffice to explain the observed rate coefficients.

In support of our model, we adduce several pieces of supporting experimental evidence. The first of those is somewhat indirect but it shows that "loosely bound" electrons (Rydberg molecules) can persist in some plasmas. The presence of "loosely bound electrons" in pure-helium afterglows has actually been a puzzle for many years.  $\text{He}_2^+$  ions dominate such plasmas, and they are known not to undergo rapid dissociative recombination. The situation may be quite similar to that in  $\text{H}_3^+$  plasmas. Experiments by Kaplafka et al. [56] showed that exposure of a helium afterglow plasma to a rather weak pulse of microwave radiation (capable of heating free electrons by several hundred K) enhanced the free electron density by factors of up to three. This would indicate that the plasma contained more loosely-bound electrons than free electrons. Similar observations have been made by Castell [57]. It seems very likely that the "loosely bound electrons" are  $\text{He}_2^*$  Rydberg molecules formed by collisional stabilization of  $\text{He}_2^{**}$  autoionizing complexes, the same process that we invoke in the case of  $\text{H}_3^+$  plasmas. It can be shown from the equations given earlier that the concentration of Rydberg molecules can approach or exceed that of free electrons if the electron density is sufficiently high.

To our knowledge, no search for loosely bound electrons has been carried out in plasmas containing  $\text{H}_3^+$  ions. There is, however, one puzzling spectroscopic observation that could be explained readily by postulating the presence of Rydberg molecules. Both Amano [58, 59] and also Miderski and Gellene [60] noted that  $\text{H}_3$  (or  $\text{D}_3$ ) absorption and emission lines (from  $n=3$  states) in  $\text{H}_2$  ( $\text{D}_2$ ) plasmas exhibited line profiles that indicated high, non-thermal energies (about 0.3 eV) of the absorbing or emitting  $\text{H}_3$  molecules. As noted by the authors, the energy is close to that expected if the excited ( $n=3$ )  $\text{H}_3$  molecules were formed by recombination of  $\text{H}_5^+$ . But, as Amano noted, the plasma should not have contained any  $\text{H}_5^+$  ions under his experimental conditions. The solution to the seeming contradiction may be that the fast, excited  $\text{H}_3$  species were produced from

$H_3^* + H_2$  collisions, Eq. 18, which has nearly the same energetics as  $H_5^+$  recombination. Thus, spectroscopic observations may give the appearance of  $H_5^+$  recombination even though these ions are not present in the plasma. Actually, there may be two excitation mechanisms for  $H_3(n)$  states, decay from  $H_3^{**}$  (no excess translational energy) and reaction (18). At high  $n_e$  and low  $T$ , collisional radiative recombination (Eq. 16) should provide an additional mechanism of population Rydberg states. Spectroscopic studies may be able to distinguish the different excitation mechanisms.

The most direct observation that indicates production of  $H_3^{**}$  molecules from  $H_3^+$  recombination comes from the merged-beam experiments of Mitchell [49]. He found that the apparent  $H_3^+$  recombination cross sections could be increased by about a factor of five when a "deflection field" (used to deflect unrecombined ions out of the beam before they strike the detector) was reduced in magnitude. This would suggest that majority of  $H_3^+ + e^-$  "recombination" events produces long-lived  $H_3^{**}$  Rydberg molecules. The role of electric fields in beam experiments may be quite complicated and probably deserves some more analysis.

The proposed mechanism, if it is valid, has also one disturbing consequence: Observation of plasma de-ionization coefficients on the order of a few  $10^{-7}$   $cm^3/s$  cannot be taken as sufficient evidence for a dissociative mechanism. Most ions that have been studied in the past probably do recombine dissociatively, but there is very little direct evidence in support of that assumption. Stabilization of Rydberg molecules is likely to be more important in polyatomic ions and in may, in part, explain the large recombination rates of those. It may also play a role as an additional recombination channel in some simpler ions, possibly  $HCO^+$ ,  $HeH^+$  and other hydride ions, and it may also give rise to some reaction products that cannot be produced by binary recombination. Thus, it can probably not be taken for granted that the product yields measured in afterglow experiments are applicable to environments at low densities, such as many astrophysical plasmas.

## VI. Conclusions

Our experimental observations, in part, are very similar to those of Smith and Spaniel [13] and we concur with them that the decay of  $H_3^+$  plasmas is indeed anomalous in the sense that it does not obey a simple recombination law. However, our interpretation of the experimental findings is entirely different.

We attempted to explain the anomalous plasma decay by assuming the presence of ions in the  $v=0$  and  $v_1=1$  state, but we did not find that this resulted in a consistent description of the experimental data. An alternative de-ionization model is proposed that invokes collisional stabilization of  $H_3^{**}$  Rydberg molecules. If this model is correct, then it is quite possible and even likely that the binary recombination of electrons with  $H_3^+$  ions is a very slow process, as was predicted by the early theory of Michels and Hobbs [5].

Our measurements indicate that de-ionization coefficients in the range from 1.5 to  $2.5 \times 10^{-7} \text{ cm}^3/\text{s}$  at 300 K may be appropriate for modeling of  $H_3^+$  plasmas of reasonably high density, for instance those in electrical discharges and perhaps in some planetary ionospheres. The  $T^{-0.5}$  dependence of  $\alpha(H_3^+)$  on gas temperature that was measured by Leu et al.[7] may be of some practical value to scale this "recombination coefficient" to other gas temperatures. The de-ionization coefficient of  $D_3^+$  appears to be significantly smaller than that of  $H_3^+$ .

It is an entirely different question which recombination coefficient should be used in environments of very low densities, e.g. in the interstellar medium. Here, the "true" binary recombination coefficient at low temperatures is needed. It is conceivable that the recombination cross sections measured in ion-storage ring experiments are close to the true values, but this is far from obvious since the presence of electric fields in the interaction region may also lead to l-mixing effects. The recent observations by Mitchell

and coworkers [49] indicate that the interpretation of beam experiments may be far more complicated than had been thought.

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Table I

Recombination coefficients observed in earlier experiments. The abbreviations of methods refer to: SA (Stationary Afterglow), FALP (Flowing Afterglow/Langmuir Probe), IR (Infrared absorption in afterglow plasmas), MB (Merged Beam), ISR (Ion Storage Ring). The cross sections measured in beam experiments (MB and ISR) have been converted to 300 K rate coefficients.

| $\alpha$<br>[ $10^{-7}$ cm <sup>3</sup> /s] | T<br>[K]  | Method | vibrational<br>state | reference |
|---|-----------|--------|----------------------|-----------|
| 2.3±0.3                                     | 300       | SA     | 0                    | 7         |
| 1.6   | 300       | SA     | 0                    | 8         |
| <0.2  | 300       | FALP   | 0                    | 9         |
| 1.8±0.2                                     | 210       | IR     | 0                    | 15        |
| 1.5 (1.1)                                   | 300 (650) | FALP   | ≤3 (0)               | 11, 12    |
| <2  | 510       | IR     | 0                    | 17        |
| 1.3 (0.3)                                   | 300       | FALP   | ≥3 (1, 2)            | 13        |
| 0.2   | (300)     | MB     | 0                    | 21        |
| 1.15  | (300)     | ISR    | 0                    | 22        |

## Figure Captions

**Fig.1** Schematic diagram of the flow tube used in these experiments. The main section of the tube has a length of 34 cm and an internal diameter of 6 cm.

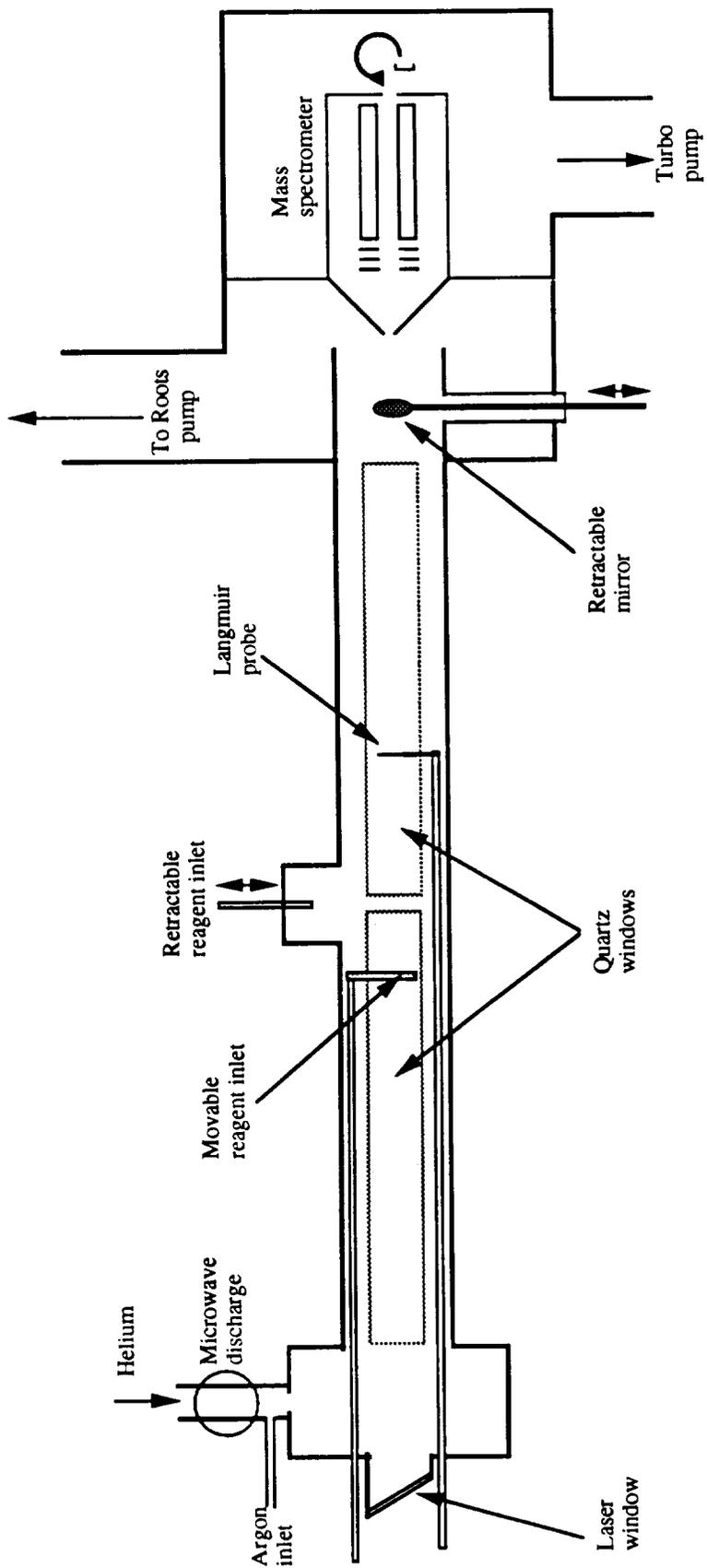
**Fig. 2** Values of  $\beta(z)$  (filled squares, right-hand scale) derived from simulated  $n_e(z)$  data (open circles, left-hand scale) by the procedure described in the text. Line drawn through the  $n_e(z)$  data represents a third order polynomial fit. A recombination coefficient of  $2 \times 10^{-7} \text{ cm}^3/\text{s}$  was used in the simulation. The arrow indicates the position where the reagent is added in the simulation.

**Fig. 3** Measured de-ionization coefficients  $\beta$  in  $\text{H}_3^+$  and  $\text{D}_3^+$  plasmas obtained from the  $1/n_e$  vs.  $z$  plots, as a function of  $\text{H}_2$  ( $\text{D}_2$ ) concentration. Heavy line: Least-squares fit to the data. Dotted lines represent the 95% confidence limits of the least-square fit.

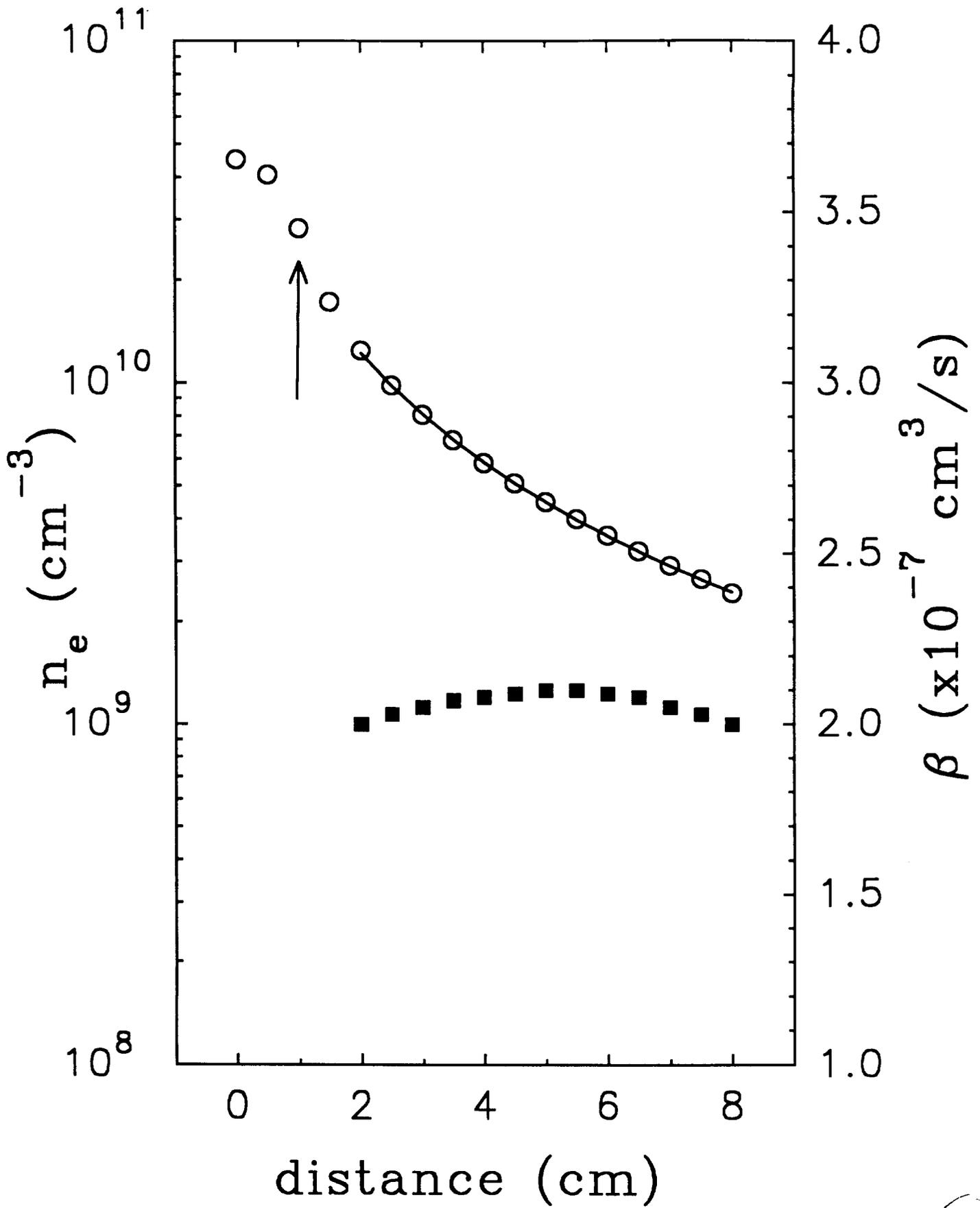
**Fig. 4** Values of  $\beta(z)$  (filled squares, right-hand scale) derived from measured  $n_e(z)$  data (open circles, left-hand scale) at  $[\text{H}_2] = 1.3 \times 10^{14} \text{ cm}^{-3}$ . Line drawn through the  $n_e(z)$  data represents a third-order polynomial fit. The arrow indicates the position where the reagent is added in the simulation. Lines through  $\beta(z)$  points represent model calculations using the two-state model for a quenching coefficient of  $k_q = 1 \times 10^{-12} \text{ cm}^3/\text{s}$  (dashed line) and  $k_q = 1 \times 10^{-13} \text{ cm}^3/\text{s}$  (dotted line).

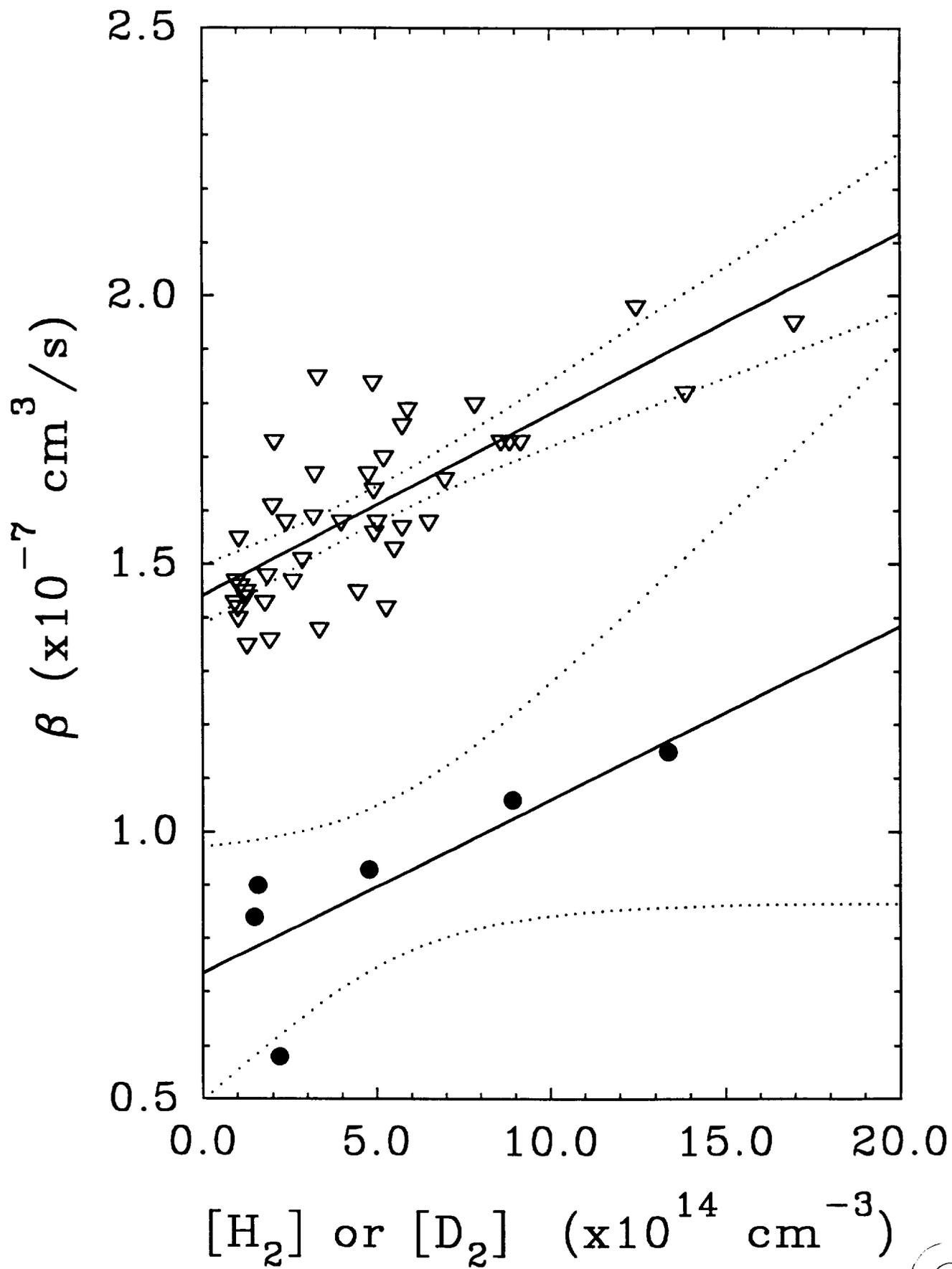
**Fig. 5** Values of  $\beta(z)$  (filled squares, right-hand scale) derived from measured  $n_e(z)$  data (open circles, left-hand scale) at  $[\text{H}_2] = 1.7 \times 10^{15} \text{ cm}^{-3}$ . Line drawn through the  $n_e(z)$  data represents a third-order polynomial fit. The arrow indicates the position where the reagent is added in the simulation. Lines through  $\beta(z)$  points represent model calculations using the two-state model for a quenching coefficient of  $k_q = 1 \times 10^{-12} \text{ cm}^3/\text{s}$  (dashed line) and  $k_q = 1 \times 10^{-13} \text{ cm}^3/\text{s}$  (dotted line).

**Fig. 6** Comparison of observed values of  $\beta(n_e)$  at  $[\text{H}_2] = 1.3 \times 10^{14} \text{ cm}^{-3}$  (circles) and  $[\text{H}_2] = 1.7 \times 10^{15} \text{ cm}^{-3}$  (squares) to the model calculations described in the text.



(1)





(3)

