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CHAPTER 3

Dissociative Recombination of H_3^+ Ions with Electrons: Theory and Experiment

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Abstract

Four decades of experimental and theoretical studies of the dissociative recombination of the seemingly “simple” H_3^+ ions with electrons have often given strongly disagreeing results. The literature on the subject abounds in terms like *enigma* and *puzzles*, and several authors have asked if the “saga” is finally approaching a satisfactory ending. Fortunately, recent progress in theory and experiment has greatly reduced many of the apparent contradictions. In this review, we attempt to reconcile the remaining discrepancies, in particular those between beam experiments and those employing plasma afterglow techniques. We conclude that there are no true contradictions between those results if one examines the conditions under which the data were taken and includes effects arising from third-body-assisted recombination. The best available theoretical treatments of purely binary recombination now agree rather well with state-of-the-art ion-storage ring results, but we think that further refinements in the complex theoretical calculations are required before it can be said that the mechanism of the recombination is understood in all details and that the “saga” has truly come to an end.

1. INTRODUCTION

H_3^+ , the simplest of all polyatomic molecular ions, consists of three protons arranged in an equilateral triangle, held together by two electrons. The physics and chemistry of this ion has occupied a special niche in the molecular physics community for many years, and it is a fair question to ask why it continues to be of interest today and what progress has been made in understanding its basic properties. The apparent simplicity of this ion makes it attractive as a test case for *ab initio* quantum-chemical calculations and that certainly has stimulated much theoretical work. A second important motivation comes from astrophysics: H_3^+ is perhaps the second most abundant molecular species (after H_2) in interstellar clouds, in the ionospheres of the outer planets, and plays a central role in determining the ionization balance and in building more complex ions that determine the physical properties in these star-forming regions (Herbst, 2007; McCall, 2006; McCall et al., 2002). While the ion is quite stable, the relatively small proton affinity of H_2 (4.2 eV) enables efficient proton transfer to other molecules. However, if H_3^+ ions recombine efficiently with electrons and dissociate into H_2 and/or H atoms in the process, the same species from which they were formed by several slow steps, the reaction chain is essentially terminated, and recombination limits the rate of molecule formation. The effect of H_3^+ on

01 the interstellar chemistry can be quite complicated and lead to bistable
02 chemical evolutions, as has been discussed in detail by Pineau Des Forêts
03 and Roueff (2000).

04 In this review, we focus on the dissociative recombination (DR) of H_3^+
05 ions with electrons, a process that can be symbolically represented as



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10 Anticipating later discussions, we note that Equation (1) may be read
11 either as representing an ion–electron binary collision or as a reaction
12 equation that describes a more complex process in an ionized gas. We
13 adopt the first interpretation but note that other electron–ion recombina-
14 tion mechanisms exist in which part of the energy released by recombina-
15 tion is transferred to third bodies (atoms, molecules, or other electrons)
16 or is removed by emission of radiation. We will discuss such third-body-
17 assisted recombination only to the extent that it affects the interpretation
18 of experimental data.

19 All experimental studies of DR face the problem that two charged
20 species, ions and electrons, must be brought together in a controlled
21 manner with a small relative velocity. Theorists have an equally and
22 perhaps even more difficult task. A slow electron that is captured by a
23 molecular ion can give rise to numerous excited states of the molecule,
24 and it requires extensive quantum mechanical calculations to decide
25 which of those states eventually lead to dissociation. The task is further
26 complicated by the fact that recombination is sensitive to the rotational
27 and vibrational states of the ion and that the ion exists in two nuclear spin
28 modifications, denoted as para- H_3^+ (two of the three proton spins
29 aligned) and ortho- H_3^+ (three proton spins aligned).

30 As in other fields of physics and chemistry, experiment and theory
31 sometimes have often given conflicting answers to some of the basic
32 questions. For many years there was considerable doubt that efficient
33 recombination of H_3^+ actually occurred! Many open and once difficult
34 questions have been clarified in recent years by advances in theory and
35 by new and powerful experimental techniques, especially ion-storage
36 rings that supply more detailed information than the plasma-based
37 experimental methods. Progress in theory has been commensurate with
38 that in experiment: what Bates (1993), the “founding father” of DR, once
39 described as an “enigma” has largely been solved, but some finer details
40 may still need to be worked out.

41 This review is intended to present a critical but not necessarily
42 complete analysis of all experiments and theories. We seek to reconcile
43 experiment and theory as far as possible given the current state
44 of knowledge, and to see if remaining discrepancies are “real” in

01 the sense that they indicate deficiencies in our understanding as
 02 opposed to incomplete or erroneous interpretations of experimental
 03 observations.

04 The literature on DR is extremely large and H_3^+ is certainly not the
 05 only ion of interest. Several excellent reviews on DR in general have
 06 appeared in the last few years that include extensive lists of measured
 07 rate coefficients and other data (Florescu-Mitchell & Mitchell, 2006;
 08 Larsson & Orel, 2008). A previous review of H_3^+ recombination mea-
 09 surements by Johnsen (2005) contains much additional material that we
 10 will not repeat here, and some proposed solutions of apparent contra-
 11 dictions have now been ruled out by new experimental and theoretical
 12 work.

13

14

15 2. BASIC DEFINITIONS

16

17 We begin by reviewing some basic definitions, most of which are com-
 18 mon in the physics of atomic collisions, but others are specific to parti-
 19 cular experiments and require a few words of explanation.

20 Consider an ion that moves in a region containing uniformly distrib-
 21 uted free electrons at density n_e (cm^{-3}). The recombination coefficient α is
 22 defined by the probability dP that the ion captures an electron during
 23 time dt and dissociates before releasing it by autoionization, i.e.,

24

$$25 \quad dP = \alpha n_e dt. \quad (2)$$

26 This defines a “raw” or “effective” recombination coefficient that
 27 still depends on the distribution of the relative ion–electron speeds
 28 $f(v_{\text{rel}})$. If the recombination is purely binary, one can define a recombi-
 29 nation cross section $\sigma(v_{\text{rel}})$, which is related to the rate coefficient by the
 30 average

31

$$32 \quad \alpha = \langle \sigma(v_{\text{rel}}) v_{\text{rel}} f(v_{\text{rel}}) \rangle, \quad (3)$$

33 where the brackets indicate averaging over all v_{rel} . If $f(v_{\text{rel}})$ is sufficiently
 34 narrow to be reasonably approximated by a delta function centered at
 35 $\langle f(v_{\text{rel}}) \rangle$, the cross section is closely given by the ratio

36

$$37 \quad \sigma(v_{\text{rel}}) \cong \frac{\alpha}{\langle v_{\text{rel}} \rangle}. \quad (4)$$

38

39 This approximation is fairly good in merged-beam experiments, but
 40 fails at very low v_{rel} . For that reason merged-beam experimenters often
 41 report their raw results not as cross section but as a nonthermal recombi-
 42 nation coefficient as a function of the “detuning energy.” However, they
 43 usually deconvolute the recombination coefficient to obtain the cross
 44 section, and then compute the thermal recombination coefficient by

convolving the cross section again with a Maxwell distribution. The deconvolution may require extrapolation to very low energies.

Plasma afterglow experiments directly yield the thermal recombination coefficient, although often only over a narrow range of temperatures. Those results are typically given in the form of a power-law dependence

$$\alpha(T_e) = \alpha(300K) \left(\frac{T_e}{300} \right)^{-x}, \quad (5)$$

as a function of the electron temperature T_e . In such experiments, the ion translational ion temperature T_i is almost always the same as the gas temperature T_g , but T_e can be greater than T_i . It can hardly ever be assumed that the internal degrees of freedom of the ions, especially their vibrations, are in thermal equilibrium at the translational temperature.

Theoretical calculations usually generate cross sections for a set of discrete collision energies. To facilitate comparison to experiment, theorists often calculate (a) the thermal rate coefficient and (b) an “effective” rate coefficient that should be measured in beam experiments with a finite energy resolution. The procedure “washes out” some of the finer structure in the theoretical cross section but, unlike the thermal rate coefficient, retains some of its structure.

3. EXPERIMENTAL TECHNIQUES

The experimental techniques used to study DR can be divided into two broad categories, plasma afterglow experiments and merged-beam experiments.

In afterglow experiments, electron-ion recombination rate coefficients and product yields are derived from observations of ion and electron densities, optical emissions, and neutral products during the afterglow phase of a plasma. The analysis of afterglow plasmas can be complicated by reaction processes that occur in addition to electron-ion recombination, and it also is not always obvious that recombination in a plasma involves only simple binary recombination. However, what is regarded as a “complication” in the context of recombination may be of great interest to the physics of ionized gases in general and this should be kept in mind.

Merged-beam and ion-storage ring methods, while requiring far greater experimental effort, are closer to the theorists’ ideal experiment and can provide more detailed information. The outstanding progress that has been made in refining these techniques now permits studies with very high energy resolution as well as determinations of the chemical

01 identity of neutral reaction products and their kinetic energy. Such data,
02 of course, provide far more sensitive tests of theoretical calculations of
03 recombination than the thermally averaged rate coefficients obtained by
04 afterglow techniques.

05

06 3.1 Afterglow Techniques

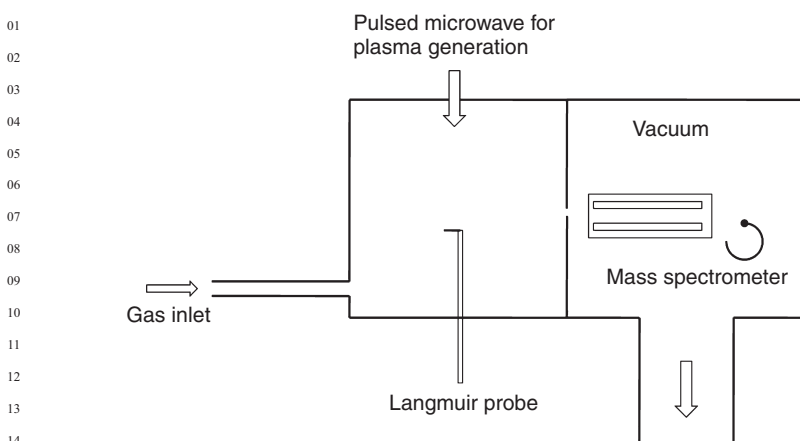
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08 The two principal subcategories, “stationary” or “flowing” afterglows,
09 have much in common, but they differ in the way that the plasma is
10 produced and observed. We will discuss them together while pointing
11 out relative strengths and weaknesses.

12 In the stationary afterglow, more appropriately called a “pulsed” after-
13 glow, a plasma in a pure gas or gas mixture is created by repeated pulses
14 of microwaves, high voltages applied to discharge electrodes, ultraviolet
15 light, or other ionizing radiation (see Figure 1). All afterglow observations
16 are carried out in the same volume as a function of time.

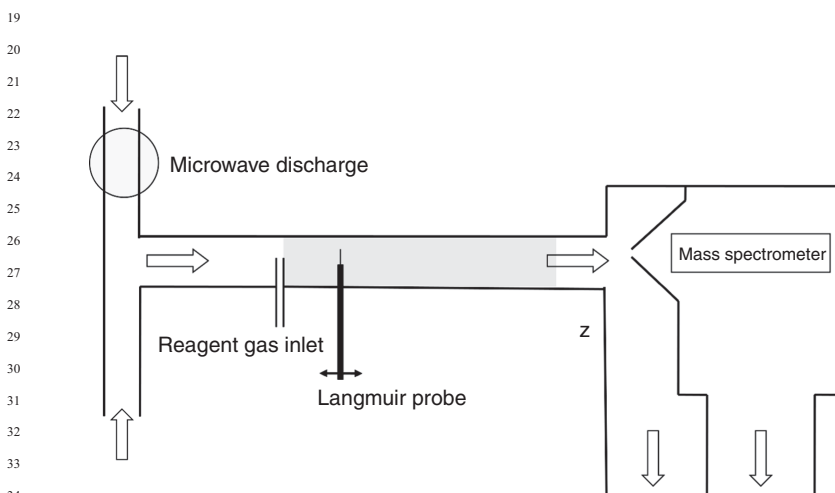
17 In the flowing afterglow method (see Figure 2), a pure gas (helium
18 most often) is first ionized, usually in a microwave discharge, and then
19 flows at high speed down the flow tube and is eventually discharged into
20 a fast pump. At some point, reagent gases are added that convert the
21 primary ions and metastable atoms to the desired molecular ion species.
22 Recombination occurs in the region downstream from the reagent inlet,
23 and observations are carried out as a function of distance from the gas
24 inlet. The flow tube method has the advantage of greater chemical flex-
25 ibility and it avoids exposing the molecular gases directly to an intense
26 discharge, which can lead to undesired excitation or dissociation. It also
27 has some disadvantages: There is only an approximate correspondence
28 between time and distance since the gas flows faster at the center of the
29 tube than it does near the wall and the spatial distribution of particles in
30 the plasma is not necessarily uniform. Also, the mixing of gases at the
31 reagent inlet is not instantaneous and this can complicate the data
32 analysis.

33 A frequently employed method to convert the active species flowing
34 out of the discharge to ions consists of adding argon at a point upstream
35 from the reagent inlet. This converts metastable helium to argon ions,
36 which are subsequently used as precursors for the ion–molecule reactions
37 that generate the desired ion species. What is often ignored is that along
38 with the argon ions some undesired energetic particles and ultraviolet
39 photons also enter the region downstream from the reagent inlet, for
40 instance metastable argon atoms (see, e.g., Skrzypkowski et al., 2004)
41 that are produced by collisional radiative recombination of argon ions.
42 Ultraviolet photons, in particular “trapped” helium resonance radiation,
43 can enter the reaction zone unless one adds a sufficient amount of argon
44 to destroy them by photoionization of argon. Fortunately, such effects do



15 **Figure 1** Schematic diagram of a stationary or pulsed afterglow apparatus.

16 A Langmuir probe or a microwave frequency method is used to record the decay of
17 the electron density subsequent to an ionizing pulse. Typical linear dimensions of the
18 plasma chamber are 10–40 cm



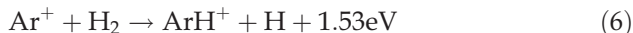
35 **Figure 2** Schematic diagram of a flowing afterglow Langmuir probe apparatus
36 (FALP). A movable Langmuir probe records the electron density as a function
37 of distance from the reagent inlet

38
39
40 not interfere much with measurements of recombination coefficients, but
41 they can be important in spectroscopic studies of reaction products.

42 Different afterglow experiments employ different reaction sequences
43 to produce H_3^+ ions. One frequently used scheme makes use of the fast
44 two-step reaction sequence

01

02



03

04 followed by

05

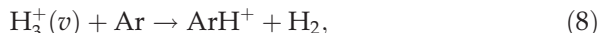
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08 which releases sufficient energy to produce H_3^+ in vibrational states up
09 to $v=5$. If argon is present in sufficient concentration, subsequent proton
10 transfer to Ar,

11



12

13 destroys all H_3^+ ions with internal energies above 0.57 eV, leaving
14 only those in the ground state [$A_1(0, 0^0)$], in the $v_2=1$ bending-mode
15 vibration [$E(0, 1^1)$ at 0.3126 eV], and in the $v_1=1$ breathing-mode vibra-
16 tion [$A_1(1, 0^0)$ at 0.394 eV]. The radiative lifetime of the $v_1=1$ state is very
17 long (~ 1.2 s). Radiative decay of ions in the $v_2=1$ level is faster (~ 4 ms),
18 but does not necessarily occur at the time scale of recombination
19 measurements.

20

21 The electron density can be measured by several methods: Langmuir
22 probes return local values of n_e , while microwave methods have low
23 spatial resolution and yield a “microwave-averaged electron density.”

24

25 The flow tube has the significant practical advantage that the gas is
26 exchanged rapidly, on a time scale of milliseconds. In stationary after-
27 glows, outflow of gases occurs only through the small sampling orifice
28 used for mass spectrometric sampling of ions, but the gas exchange time
29 is usually on the order of many minutes. For this reason, impurity
30 problems tend to be less serious in flow tubes than in stationary
31 afterglows.

32

33 The methods to measure recombination coefficients are essentially the
34 same in both types of afterglows. In the simplest case, when only a single
35 ion species is present and the plasma is quasi-neutral, e.g., $n_e = n_i$, the
36 electron continuity equation is given by

37

38

$$\frac{\partial n_e(t, \vec{r})}{\partial t} = -\alpha n_e^2(t, \vec{r}) + D_a \nabla^2 n_e(t, \vec{r}), \quad (9)$$

39

40 where D_a is the ambipolar diffusion coefficient of the ion. If diffusion is
41 sufficiently slow that it can be ignored, the reciprocal electron density
42 varies with time as

43

44

$$\frac{1}{n_e(t, \vec{r})} = \frac{1}{n_e(0, \vec{r})} + \alpha t, \quad (10)$$

45

46 and hence the recombination coefficient can be obtained directly from the
47 slope of a graph of the measured reciprocal electron densities as a func-
48 tion of time. This simple form of analysis yields reasonably accurate

recombination coefficients only if the diffusion current of ions into or out of the volume in which n_e is measured is very small compared to the volume loss rate of electrons due to recombination. A frequently used, but not entirely satisfactory, approximation “corrects” for the diffusion loss of electrons by fitting the observed electron density decays to an equation of the form

$$\frac{dn_e(t)}{dt} = -\alpha n_e^2(t) - \frac{D_a n_e}{\Lambda^2}, \quad (11)$$

in which Λ^2 is the fundamental diffusion length of the plasma container, and the electron density is measured at the center of the container (or points on the axis of a flow tube). The equation is correct only in the limits when either of the two loss terms greatly outweighs the other since it ignores the fact that quadratic recombination loss tends to “flatten” the spatial distribution of electrons and ions. As a consequence, the diffusion current away from the center is reduced, and Equation (11) overestimates the diffusion loss, but underestimates the recombination loss. The pulsed microwave afterglow measurements often employed numerical solutions of the continuity equations to analyze the data while the analysis of flow tube data is usually carried out using Equation (11).

The time scale of recombination experiment is of practical interest. From Equation (10), it follows that the electron density during the afterglow decays by a factor of 2 from its value at time t whenever the time increases by the “half-time” $\tau_{1/2}$, given by

$$\tau_{1/2} = \frac{1}{\alpha n_e(t)}. \quad (12)$$

Accurate determinations of recombination coefficients require observation of n_e over a significant range, a factor of 4 or preferably more. Hence, for an initial electron density of $n_e(t=0) = 10^{10} \text{ cm}^{-3}$ and a typical recombination coefficient $\alpha = 10^{-7} \text{ cm}^3/\text{s}$, one must measure $n_e(t)$ over a time of at least $(1+2) = 3 \text{ ms}$, longer if the initial electron density is only 10^9 cm^{-3} . Obviously, the ion–molecule reactions that form the desired ions should go essentially to completion in a time short compared to the time scale of recombination, and the ions under study must not convert to a different type during this time by reacting with any of the gases in the afterglow plasma or impurity gases. We will show later (see Section 6.1) that serious errors ensue when these requirements are not fulfilled.

The gas temperature in afterglows can be adjusted fairly easily over a limited range from liquid-nitrogen temperature (77 K) to roughly 600 K by heating the entire apparatus. This is more useful as a means to control equilibrium concentrations of weakly bound ions (for instance shifting the chemical equilibrium from H_3^+ to H_5^+ ions) than as a means to measure the

01 temperature variation of recombination coefficients. Much higher electron
02 temperatures (up to 10,000 K) can be reached by microwave heating of the
03 electron gas, a technique that was used extensively in stationary afterglows
04 and that has provided data on many important ion species, including H_3^+ .
05 The technique is subject to complications in the presence of molecular
06 additives (Johnsen, 1987). In the afterglow measurements on H_3^+ , such
07 effects are not important and we will not discuss this subject further.

08 Higher gas temperatures (up to nearly 10,000 K) can be reached by
09 employing shock heating of the afterglow plasma (Cunningham et al.,
10 1981), a technique that has been applied to several recombination pro-
11 cesses of atmospheric interest but not to H_3^+ .

12

13 3.2 Single-Pass Merged-Beam and Ion-Storage Ring Experiments

14

15 With the development of ion-storage rings, experiments on DR were
16 transformed from small-scale “table-top” experiments to large-scale mul-
17 tiuser type operations that made use of technologies from nuclear and
18 high-energy physics. The impact of these new machines cannot be over-
19 stated: the considerable investment in the experimental facilities revital-
20 ized and revolutionized experimental studies of DR. We will only
21 summarize the basic principles and current capabilities since extensive
22 reviews have been written by authors who are more familiar with experi-
23 mental details (Larsson & Orel, 2008).

24 The predecessor of the storage rings, the single-pass merged-beam
25 method was developed at the University of Western Ontario (see, e.g.,
26 Auerbach et al., 1977). While it was an important step forward and
27 resulted in many important results, the single-pass merged beam has
28 been superseded by the more powerful ion-storage ring technique. Both
29 have in common that recombination of ions and electrons takes place
30 between parallel ion and electron beams of nearly the same velocity. In a
31 single-pass merged beam, the ion beam passes through the electron target
32 beam once and is then discarded; in a storage ring the ions circulate in the
33 ring and pass through the interaction region (see Figure 3) many times. It
34 is not the more “efficient” use of ions in storage rings that makes them
35 preferable but the fact that the longer storage time (up to 10 seconds) in a
36 ring removes all excited ions that radiate on that time scale, for instance
37 infrared active vibrationally excited ions.

38 In merged beams, the relative velocity between the two beams can be
39 made very small. More importantly, the velocity spread in the electron
40 target gas can be greatly reduced by accelerating the (initially “hot”)
41 electrons to a high velocity that closely matches that of the ions. The
42 narrowing of the electron velocity distribution in the direction of the
43 beam (but not transverse to it) is a purely kinematic effect that follows
44 from the classical equations of motion. However, at finite electron

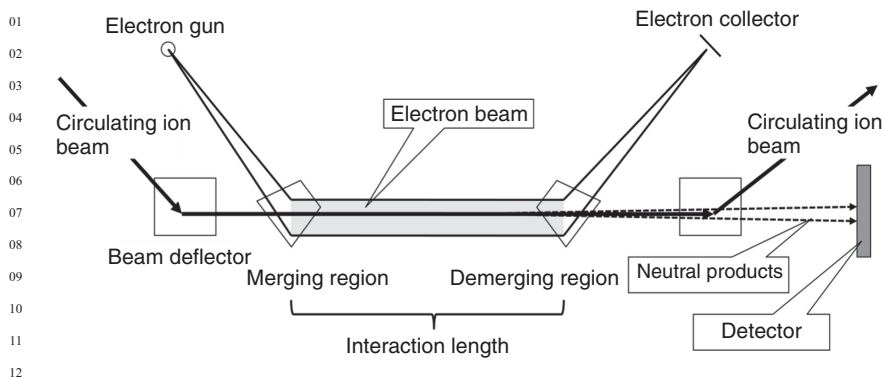


Figure 3 Schematic diagram of the electron cooler and interaction region of an ion-storage ring. The length of the interaction region is typically on the order of 1 m

densities Coulomb interactions between electrons occur and the actual velocity spread in the beam direction is somewhat larger than that calculated from the kinematic equations. In addition, the effective energy resolution for ion–electron collisions depends also on the velocity components transverse to the beam. It is common practice to model the electron velocity distribution by a two-temperature Maxwellian function with temperatures T_{\parallel} for the parallel velocity component and T_{\perp} for the two transverse components.

Several methods are available to reduce the transverse velocity spread and thereby improve the energy resolution: In the single-pass merged-beam apparatus (Auerbach, 1977), improvements in the energy resolution were made by using trochoidal analyzers to merge electron and ion beams, while storage rings employ “electron coolers” in which the electrons are cooled by expansion in a magnetic guiding field. Cooling and recombination can be accomplished either in the same section of the ring or in the two separate sections. In addition, the coolers also cool the ion beam by a “friction” effect and reduce the diameter of the ion beam.

In all merged-beam techniques, recombination events are detected by counting recombination products using an energy-sensitive barrier detector. The detector ideally registers one count of full pulse height when all products from a single event strike the detector simultaneously. In that case the number of counts received for a single traversal of a single ion through the electron target is

$$N = \alpha n_e \Delta t. \tag{13}$$

Here α is the recombination rate coefficient appropriate to the experimental velocity distribution, n_e the electron density, and Δt the time of traversal of an ion through the interaction region. If the ion beam is much narrower than the electron beam, which is the case in storage rings, there

01 is no need to consider overlap factors. To obtain absolute values of α , one
02 needs to know the ion beam current, which can be measured either by
03 collecting ions or using a current transformer.

04 While ion-storage rings come very close to the theorist's perception of
05 an ideal experiment, there are some, fortunately minor, imperfections
06 that should be mentioned. Ion-electron collisions also occur in the mer-
07 ging and demerging regions (magnets in storage rings) where the ion and
08 electron beams are obviously not parallel and their relative velocities are
09 larger than those in the straight part of the interaction region; however,
10 this "toroidal correction" is not large and can be taken into account.

11 In addition to providing high-resolution recombination cross sections,
12 storage rings have an outstanding ability to determine the relative abun-
13 dance of recombination products by placing grids in front of the detector
14 and analyzing the pulse-height spectra (for details, see Larsson & Orell,
15 2008). The single-pass merged beam also has been employed for such
16 studies but the small event rate made quantitative product determina-
17 tions tedious and time consuming.

18

19

20 4. THEORY

21

22 4.1 DR Mechanisms

23

24 If all internuclear distances in a polyatomic molecule are held constant
25 except for the dissociation coordinate, a potential curve similar to that for
26 a diatomic molecule can be used to illustrate the fundamental features of
27 DR. Figure 4 shows such a slice through the potential surfaces of the ion,
28 Rydberg, and dissociative states. ϵ denotes the electron energy at which
29 capture takes place into a repulsive state of the neutral molecule from an
30 ion in some vibrational level. Note that any electron energy will do, even
31 zero, since varying the electron energy only varies the point of capture.
32 Once in the repulsive state, the neutral molecule can emit the captured
33 electron or dissociate. If dissociation takes the internuclear distance
34 beyond the crossing point of the neutral and ion curves, electron emission
35 (autoionization) is no longer possible and dissociation is completed. This
36 is the direct mechanism for DR originally proposed by Bates (1950).
37 Superexcited states of the neutral molecule are generally found at the
38 same total energies as that for the ion ground state. Electron capture also
39 occurs into these superexcited states and competes with capture into
40 the dissociative state. Among these states are the vibrationally excited
41 Rydberg states that have the ground state of the ion as core. The $v=0$
42 ground core Rydberg levels all lie below the ion, but the $v=1$ ion level is
43 the energetic limit of an infinite number of Rydberg levels as are the other
44 excited ion vibrational levels. Capture into one of these levels at electron

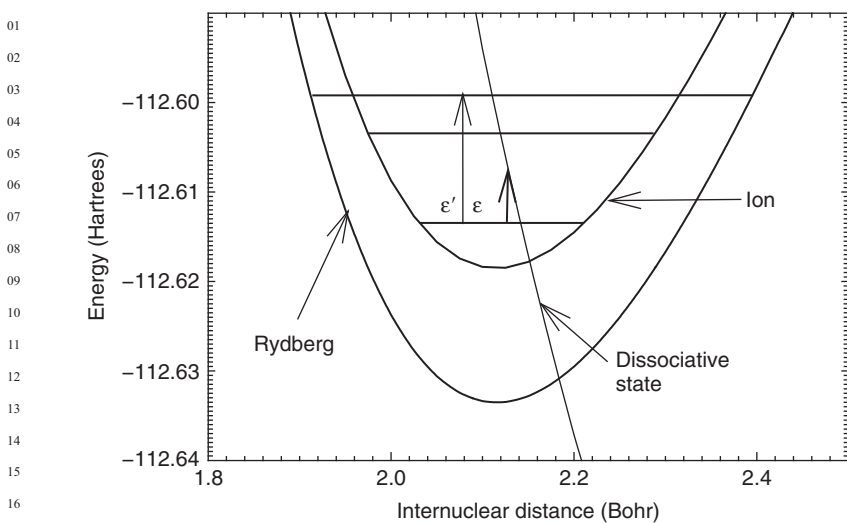
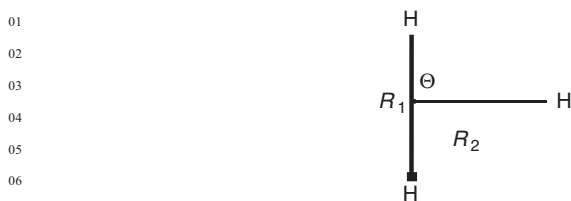


Figure 4 The direct (at electron energy ϵ) and indirect (at electron energy ϵ') mechanisms of dissociative recombination

energy ϵ' is shown in Figure 4. After capture, the electron can be emitted or the Rydberg level can be predissociated by the dissociative state of the direct mechanism. This is the indirect DR mechanism, first introduced by Bardsley (1968). Both the direct and indirect mechanisms are paths to the same dissociation products and can interfere with each other. Any technique for calculating the DR cross section must account for this interference. A recent addition to the indirect DR mechanism, Rydberg states having an excited ion core (Guberman, 2007), will not play a role in H_3^+ DR at low electron energies since the first excited ion states lie too high above the ground state (Shaad & Hicks, 1974). A second-order mechanism (Guberman & Giusti-Suzor, 1991; Hickman, 1987; O'Malley, 1981) also can take place in which the neutral repulsive state acts as an intermediate between the electron-ion and a bound Rydberg state. In this manner, an electron can be captured by an electron-electron interaction into a Rydberg state.

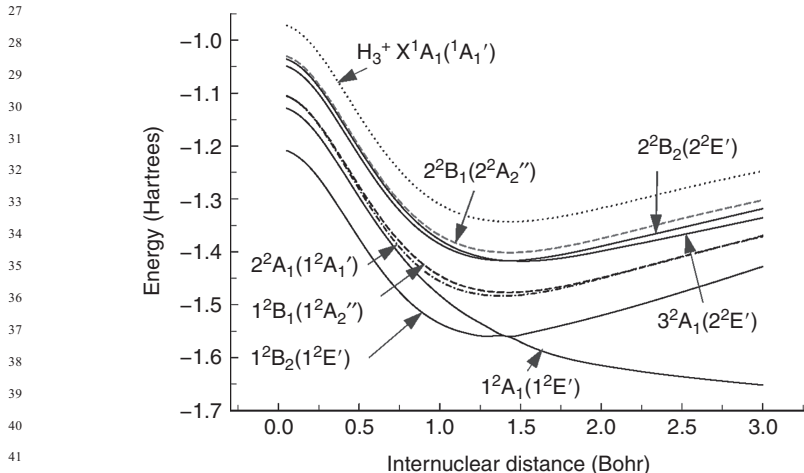
4.2 H_3^+ Potential Curves and Surface

Figure 6 has potential curves for H_3^+ and for several H_3 states that are important for DR. These states have been calculated in C_{2v} symmetry with the nuclear configuration shown in Figure 5, i.e., R_1 , the distance between two H atoms has been kept constant at the equilibrium separation, $1.63 a_0$. The remaining atom moves along R_2 , which is perpendicular



08 **Figure 5** Jacobi coordinates for H_3

11 to R_1 and intersects R_1 at its midpoint. The potential curves are calculated
 12 with [4s, 3p, 2d, 1f] Gaussian basis sets centered on each H atom. For the
 13 description of Rydberg surfaces, this basis set is supplemented with six
 14 diffuse s and six diffuse p basis functions placed at the center of mass.
 15 Orbitals are determined in Hartree-Fock (HF) calculations on H_3^+ , and
 16 the final energies are obtained from CI wave functions calculated by
 17 taking all single and double excitations to the virtual orbitals from a
 18 large reference set of configurations. The potential curves are identified
 19 by the symmetries in C_{2v} as well as the symmetries at the equilateral
 20 triangle configuration in D_{3h} . It is clear from Figure 6 that no neutral state
 21 potential curves cross the X^1A_1 ground-state ion curve ($X^1A'_1$ at the
 22 equilateral triangle configuration), the highest potential curve in the
 23 figure. The two possible dissociative routes are the lowest curves, 1^2A_1
 24 and 1^2B_2 . These curves are degenerate at the equilateral triangle position
 25 where they have $1^2E'$ symmetry, and they have asymptotes that lie below

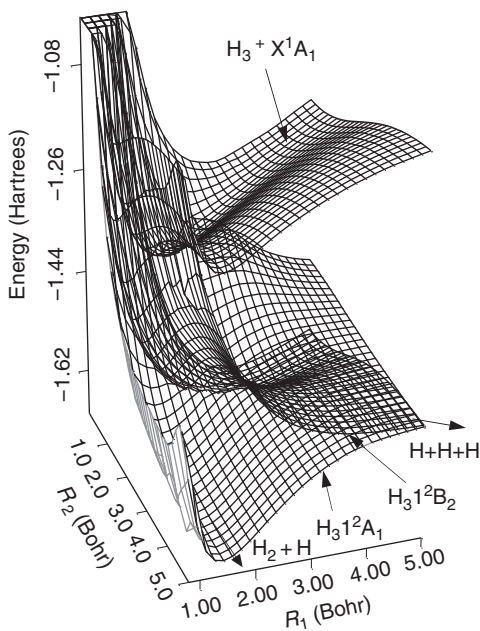


43 **Figure 6** Potential curves for the approach of one H in C_{2v} geometry along R_2 (as in
 44 Figure 5) to the midpoint of the other two H atoms held at $R_1=1.63 a_0$

01 the ground vibrational state of H_3^+ . No other states can provide DR
 02 routes at low electron energies. These states consist of a $2p_x$ or $2p_y$ orbital
 03 bound to the ion ground state where the xy plane is the plane of the
 04 molecule. Because these states do not cross the ion, DR was initially
 05 thought to be slow for H_3^+ . This is discussed further below. The neutral
 06 curves shown in Figure 6 are qualitatively similar to those shown in
 07 Figure 3 of Petsalakis et al. (1988). A precise comparison is not possible
 08 due to the different geometries used in their figure. However, at the
 09 equilateral triangle geometry, the curves in Figure 6 are about 0.12 eV
 10 lower than those of Petsalakis et al. (1988).

11 Also shown in the figure are the 3^2A_1 and 2^2B_2 states, which are the
 12 components of the $2^2E'$ doubly degenerate state at the equilateral triangle
 13 configuration. These states are too high in energy to be dissociative
 14 channels at low electron energies.

15 Figure 7 shows a two-dimensional surface for 1^2A_1 , 1^2B_2 and the ion
 16 ground state. In the plot, both R_1 and R_2 are varied and Θ , as shown in
 17 Figure 5, is fixed at 90° . Both neutral surfaces intersect at the equilateral
 18 triangle configuration. As shown in the figure, the 1^2A_1 surface leads to
 19 $H_2 + H$ and both 1^2A_1 and 1^2B_2 can generate $H + H + H$.



43 **Figure 7** Potential surfaces for H_3 and H_3^+ using the coordinates of Figure 5 with
 44 $\Theta = 90^\circ$

4.3 Vibrational and Rotational Considerations

The nuclear configuration of the ground state of H_3^+ is an equilateral triangle and belongs to symmetry group D_{3h} . The normal modes are shown in Figure 8, labeled using the notation of Herzberg (1945). The first normal mode, labeled ν_1 , is the symmetric stretch or breathing mode. The remaining normal modes, ν_{2a} and ν_{2b} , are degenerate, i.e., they have the same frequency. Indeed, ν_{2a} and ν_{2b} , as shown in Figure 8, are not unique. An infinite number of pairs of modes can be obtained by taking orthogonal linear combinations of ν_{2a} and ν_{2b} , and they are all equally valid. If one degenerate mode is superposed upon another with different phases for the vibrational motion, the H atoms will move in ellipses (Herzberg, 1945). If the motion in the two modes is out of phase by 90° (i.e., when the atoms in one mode are passing through the equilibrium position, the atoms in the other mode are at the maximum displacement), the H atoms will move on circles and the motion can be described with a vibrational angular momentum quantum number, ℓ . Instead of describing the vibrational state of the molecule with quantum numbers, v_1 , v_2 , and v_3 , it is now common practice to use (v_1, v_2^ℓ) . For H_3^+ (Watson, 2000), $\ell = -v_2, -v_2 + 2, \dots, v_2 - 2, v_2$.

Since H_3^+ is a symmetric top (i.e., two of its moments of inertia are equal), the quantum numbers specifying the rotational energy levels are N^+ , the total angular momentum, and K^+ , the projection of N^+ , upon the molecular symmetry axis. Each proton has a spin of $1/2$ and the total nuclear spin, I , can be $3/2$ (ortho) or $1/2$ (para). For the ortho states, $K^+ = 3n$, where n is an integer (Pan & Oka, 1986). For the para states, $K^+ = 3n \pm 1$ (Pan & Oka, 1986). It can be shown that the state with $(N^+, K^+) = (0, 0)$ does not exist. The lowest energy rotational state is for $(1, 1)$ and is ortho. The second level, at 23 cm^{-1} above $(1, 1)$, is $(1, 0)$ and is ortho. The $(1, 0)$ level is highly metastable since an ortho–para transition is forbidden. The lowest ortho levels are $(1, 0)$, $(3, 3)$, $(3, 0)$, and $(4, 3)$. The lowest para levels are $(1, 1)$, $(2, 2)$, $(2, 1)$, and $(3, 2)$. It is interesting to note, especially for the

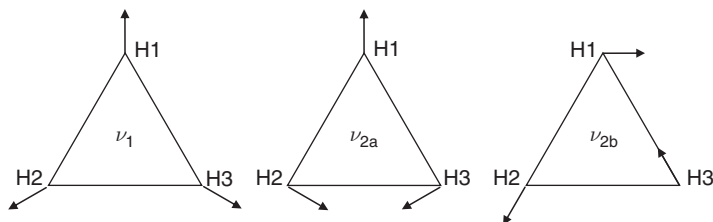


Figure 8 The three normal mode vibrations of the ground state of H_3^+

01 interpretation of DR experiments, that all of these levels have very
 02 long lifetimes (Pan & Oka, 1986). The radiative lifetimes are 1.2×10^6
 03 seconds for (2, 2), 15×10^6 seconds for (2, 1), 3.3×10^4 seconds for
 04 (3, 2), 2.2×10^4 seconds for (3, 0), and 2.2×10^4 seconds for (4, 3) (Pan & Oka,
 05 1986). Once generated, these ions will not decay by photoemission during
 06 DR experiments.

07

08 4.4 One- and Two-Dimensional Theory

09

10 4.4.1 Direct Recombination

11 The direct recombination cross section for vibrational level v' , $\sigma_{v'}$, is given
 12 by (Bardsley, 1968; Flannery, 1995; Giusti, 1980)

13

$$14 \quad \sigma_{v'} = \frac{2\pi}{k^2} r \frac{\Gamma_{v'}}{(1 + \sum_v \Gamma_v)^2} \quad (14)$$

15

16 where $\Gamma_{v'} = \pi^2 |(\Psi_d X_d | H | \Psi_i X_{v'})|^2$, r is the ratio of the statistical weights of
 17 the neutral and ion states, k is the wave number of the incident electron, v
 18 runs over the open ion vibrational levels, X_d and $X_{v'}$ are dissociative and
 19 bound vibrational wave functions, respectively, Ψ_d and Ψ_i are electronic
 20 wave functions of the dissociative and the ion states, respectively, and H is
 21 the electronic Hamiltonian. Equation (14) does not account for the inter-
 22 mediate Rydberg levels. In the expression for $\Gamma_{v'}$, the integration is over the
 23 electronic and nuclear coordinates. If the dissociative potential curve does
 24 not cross within the turning points of the ion vibrational level, the small
 25 vibrational overlap will lead to a small $\sigma_{v'}$. Figure 6 shows that the
 26 dissociative potential curves, 1^2A_1 and 1^2B_2 , in a one-dimensional view,
 27 do not cross the ion. This feature alone led theorists (Kulander & Guest,
 28 1979; Michels & Hobbs 1984) to predict that the DR rate constant for H_3^+ is
 29 small. At the time, the direct recombination process was thought to be
 30 much more important than the indirect process.

31

32 4.4.2 Multichannel Quantum Defect Theory

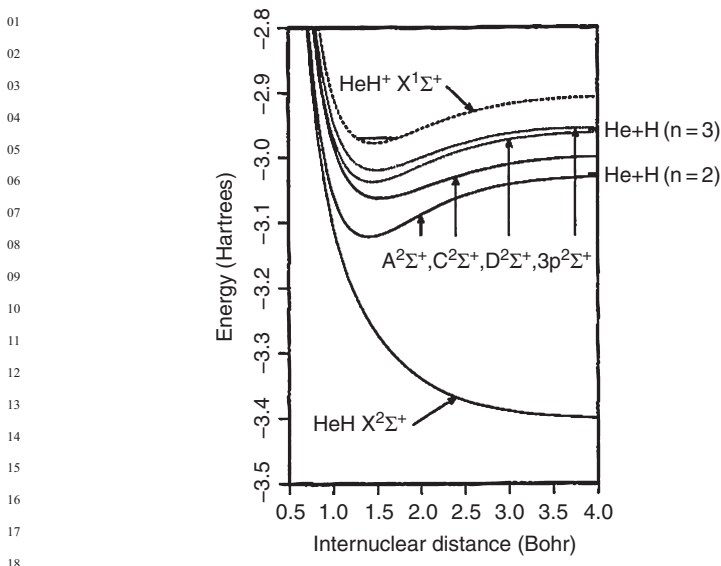
33

34 Because of the large literature on Multichannel Quantum Defect Theory
 35 (MQDT), a full description of the technique is not given here. Instead we
 36 guide the reader to the most relevant literature. The primary advantages of
 37 MQDT for the study of DR is that one can account for interference between
 38 direct DR and indirect DR with both being treated equally and one can treat
 39 entire Rydberg series rather than concentrating upon individual states as
 40 would be the case with a scattering theory approach. The pioneering
 41 studies which introduced MQDT to the study of DR were those of Lee
 42 (1977) and Giusti (1980). The approach of Giusti (1980) modified by
 43 Nakashima et al. (1987) to incorporate Seaton's (1983) closed-channel
 44

01 elimination procedure for the S matrix is the approach used today by most
02 theorists. The theory involves a K or reaction matrix which contains the
03 interaction matrix elements between all channels. The K matrix is calculated
04 perturbatively from the Lippmann–Schwinger equation. The first papers
05 used a K matrix limited to first order. The usage of a second-order K matrix
06 was introduced by Guberman and Giusti-Suzor (1991). The original
07 approach has been revised to include rotation (Schneider et al., 1997; Takagi,
08 1993; Takagi et al., 1991), derivative couplings (Guberman, 1994), Rydberg
09 states with excited cores (Guberman, 2007), and spin–orbit coupling
10 (Guberman, 1997). An excellent reference on MQDT is the volume by
11 Jungen (1996) and the papers contained therein.

13 4.4.3 Dissociative Recombination of HeH^+ and One-Dimensional H_3^+

14 A clue that the theoretical view of H_3^+ could be wrong came in calculations
15 on a diatomic molecule that shares the noncrossing features of H_3^+ .
16 Because we can think of HeH^+ as H_3^+ with two of the protons super-
17 posed, they are expected to have similar recombination mechanisms.
18 Figure 9 shows the ground-state potential curve for HeH^+ and curves
19 for seven HeH states (Guberman, 1994, 1995). All the HeH states in
20 Figure 9 are Rydberg with the exception of the ground state. None of
21 the states cross the ion curve. For this case, it was shown that electron
22 capture could occur by breakdown of the Born–Oppenheimer principle,
23 which also drives indirect DR. Because all the states found to be involved
24 in DR are adiabatic Rydberg states, there are no electronic couplings
25 between these states. Instead, derivative couplings were introduced to
26 drive DR between the adiabatic states. The cross section was calculated
27 for ^3HeH up to 0.3 eV, using the MQDT approach (Giusti, 1980; Guber-
28 man & Giusti-Suzor, 1991), and over most of this region, the indirect
29 process was much more important than direct recombination. Indeed,
30 inclusion of the indirect mechanism increased the cross section by a factor
31 of 49 (Guberman, 1995). For ^3HeH , it was also found that $\text{He} + \text{H}(2s)$ are
32 the main dissociation products at low electron energies. The total rate
33 coefficient at 300 K was $2.6 \times 10^{-8} \text{ cm}^3/\text{s}$, giving a clear example of how
34 DR, dominated by the indirect mechanism, can have a high rate coefficient.
35 Indeed, the rate would have been higher if it had been calculated
36 for the true analog of H_3^+ , the unphysical ^2HeH . The potential curves
37 shown in Figure 8 apply also to ^2HeH , but the lower mass, compared to
38 ^3HeH , raises the vibrational levels in the well leading to higher overlap
39 with the $\text{C}^2\Sigma^+$ dissociative state. Other calculations (Sarpal et al., 1994)
40 for ^4HeH using an R -matrix approach did not report a rate coefficient but
41 also found that indirect recombination dominated the cross section. The
42 main dissociation products were $\text{He} + \text{H}(1s)$ at low electron energies.
43 This was surprising since the identity of the dissociation products found
44



19 **Figure 9** Potential curves for HeH and HeH⁺ from Guberman (1995). Reprinted by
 20 permission from the AIP Press

21
 22 with the MQDT approach was a qualitative and not a quantitative result.
 23 Experiments (Strömholm et al., 1996) have since verified that the main
 24 products are He + H (2s).

25 Takagi (2003) reported a one-dimensional MQDT treatment of DR
 26 using the potential curves of Michels and Hobbs (1984). He found that
 27 the rate coefficient of the recombining ion was highly sensitive to the
 28 initial rotational level with the $N \geq 4$ levels of the vibrational ground
 29 state having large rate coefficients.

31
 32 **4.4.4 Derivative Couplings for H_3^+**

33 In a study of the predissociation of H_3 (Schneider & Orel, 1999), d/dR_1
 34 and d/dR_2 (see Figure 5 in their paper) derivative couplings connecting
 35 the lowest 2A_1 dissociative state with $2s^2A_1$ and $3s^2A_1$ were reported. For
 36 the $2s$ state, the d/dR_1 coupling at the ion equilibrium separation
 37 ($R_1=1.65 a_0$ and $R_2=1.43 a_0$) is $0.15 a_0^{-1}$ and that for d/dR_2 is -0.20
 38 a_0^{-1} . (The phase of the coupling is arbitrary since it depends upon the
 39 phases of the orbitals and the total wave function.) The largest d/dR_1
 40 coupling is $0.75 a_0^{-1}$ at $R_1=1.15 a_0^{-1}$ and $R_2=0.92 a_0^{-1}$ and for $|d/dR_2|$
 41 it is >0.95 near $R_1=1.15-1.85$ and $R_2=0.93$. The largest coupling in this
 42 case is for R_1 near the equilibrium separation but for R_2 smaller than the
 43 equilibrium separation. The couplings with the $3s$ Rydberg state, as
 44

01 expected, are much smaller. Tashiro and Kato (2002) have reported
 02 derivative couplings calculated in hyperspherical coordinates between
 03 the two $2pE'$ (1^2A_1 and 1^2B_2 states in C_{2v}) dissociative states and the
 04 $2s^2A_1$. They found a large coupling that peaks at $5 a_0^{-1}$ for a hyperradius
 05 of $1.5 a_0$ and hyperangles of $\theta=1/2$ and $\phi=\pi/6$ radians and for the
 06 upper $2pE'$ state (1^2B_2). Couplings with the lower $2pE'$ state (1^2A_1) were
 07 found to be much smaller in agreement with the results of Schneider and
 08 Orel (1999).

09

10

11 4.4.5 Two-Dimensional Cross Sections

12 Using a combined wave packet MQDT approach and derivative cou-
 13 plings, a two-dimensional calculation (varying R_1 and R_2 as in Figure 5)
 14 was performed for DR along the 2B_2 surface (Schneider et al., 2000). For
 15 direct recombination, they found that the calculated cross section is 4–5
 16 orders of magnitude below the experimental cross section (Larsson et al.,
 17 1997). However, the inclusion of Rydberg states coupled together by the
 18 R_1 and R_2 dependence of the quantum defect led to a dramatic increase
 19 in the cross section although the theory was still two orders of magni-
 20 tude less than the experimental cross section. The authors concluded that
 21 the Rydberg channels, via the indirect mechanism, played a crucial role
 22 in the DR of H_3^+ . They attributed the difference between theory and
 23 experiment to the lack of a full three-dimensional treatment and to the
 24 absence of the 2A_1 dissociative state in the theoretical treatment. They
 25 also tested the proposal of Bates that DR in H_3^+ may occur via inter-
 26 connected Rydberg states in which the connection is mainly between
 27 states differing by $\Delta v=1$. They found that $\Delta v \geq 1$ connections are also
 28 very important.

29

30

31 4.5 Three-Dimensional Treatments of H_3^+ DR

32

33 The first three-dimensional theoretical treatment of the DR of a poly-
 34 atomic molecule (Kokoouline et al., 2001) combined several new theoret-
 35 ical methods for the study of DR with aspects of the MQDT approach. In
 36 these pioneering calculations, a new driving mechanism, not present in
 37 diatomic molecules, was introduced. The next section contains a brief
 38 description of the adiabatic hyperspherical approach. Section 4.5.2 describes
 39 the role of Jahn–Teller (JT) coupling in the DR of H_3^+ . Section 4.5.3 sum-
 40 marizes the role of the nuclear spin. The approach to calculating the
 41 cross sections used in the first paper (Kokoouline et al., 2001) is given
 42 in Section 4.5.4. The revised approach used in later papers is discussed
 43 throughout and described further in Section 4.5.5. The last section
 44 contains suggestions for future theoretical research.

4.5.1 Hyperspherical Coordinates and the Adiabatic Approximation

The calculations describe the nuclear motion with hyperspherical coordinates consisting of a hyperspherical radius, R , and two hyperangles, θ and ϕ . The coordinates can be defined in terms of the distances between the H atoms. Taking r_i to be the distance between atom i and the center of mass, the hyperradius is given by $R^2 = \sqrt{3} (r_1^2 + r_2^2 + r_3^2)$ (Kokoouline et al., 2001). In later papers (Kokoouline & Greene, 2003a,b), the expression for R remains the same but r_i is taken to be the distance between atoms j and k and the coordinates are given by

$$r_1 = 3^{-1/4} R \sqrt{1 + \sin \theta \sin \left(\phi + \frac{2\pi}{3} \right)}, \quad (15)$$

$$r_2 = 3^{-1/4} R \sqrt{1 + \sin \theta \sin \left(\phi - \frac{2\pi}{3} \right)}, \quad (16)$$

and

$$r_3 = 3^{-1/4} R \sqrt{1 + \sin \theta \sin \phi}. \quad (17)$$

From Equations (15)–(17) one can derive expressions for θ and ϕ , which become intuitively meaningful by consulting Figure 6 in the work of Kokoouline and Greene (2003a) for a valuable demonstration of the meanings of these angles. [For further discussion of hyperspherical coordinates, the reader is referred to the review by Lin (1995)]. The general idea is that the hyperradius describes the overall size of the molecule, whereas the hyperangles, which are not explicitly defined in the first paper, describe the shape of the molecule. These considerations lead to the adiabatic hyperspherical approximation in which motion in R is considered to be much slower than the motion in the hyperangles, i.e., as the atoms traverse the potential surface, the shape of H_3^+ changes more rapidly than the overall size of the molecule. With the motion in the hyperangles separated from the motion in R , a Schrödinger equation at a single value of R can be written in which the eigenvalue is a point on the potential curve. The hyperradius, R , is identified as the polyatomic analog to the familiar diatomic internuclear distance. But is this analogy appropriate? The familiar Born–Oppenheimer approximation is an adiabatic treatment of the nuclear motion and is justified by the great difference in the electron and nuclear masses. However, in the adiabatic hyperspherical approach for H_3^+ , the particles are all of equal mass. This approach is tested (Kokoouline & Greene, 2003a and 2003b) by solving for the nuclear vibrational energies within the generated potential curves. The eigenvalues for several low-lying levels differ by less than 23 cm^{-1} from a full three-dimensional

01 diagonalization (Jaquet et al., 1998), and the results support the use of this
02 approximation. In later work (Fonseca dos Santos et al., 2007), this approx-
03 imation is partially dropped (see below).

04 While the adiabatic hyperspherical approximation for H_3^+ appears to
05 be successful for the vibrational energies, there have been no reported
06 tests of the accuracy of the amplitudes of the vibrational wave functions.
07 Inaccuracies in the amplitudes may significantly affect the values of
08 important matrix elements between Rydberg states. It is interesting to
09 note that the adiabatic hyperspherical approach fails for H_2D^+ and D_2H^+
10 (Kokoouline & Greene, 2005).

11

12

13 4.5.2 Potential Surfaces and Jahn–Teller Coupling

14 The potential surface of H_3^+ used by Kokoouline et al. (2003) is from
15 Cencek et al. (1998) and Jaquet et al. (1998), and the H_3 surfaces are from
16 the work of Siegbahn and Liu (1978), Truhlar and Horowitz (1978), and
17 Varandas et al. (1987). These surfaces need to be interpolated to be
18 converted to a grid in hyperspherical coordinates, but this is not covered
19 in the published papers.

20 The main driving force for DR, introduced for the first time in these
21 calculations, is the JT coupling (Jahn & Teller, 1937), a coupling which
22 does not occur in diatomic molecules. Figure 6 shows that the two lowest
23 states of H_3 intersect. The intersection point is at the equilateral triangle
24 configuration where the molecule has D_{3h} symmetry. The two lowest
25 states have two electrons distributed in the three H 1s orbitals and one
26 electron that is either in a $2p_x$ or $2p_y$ orbital where the molecule is in the
27 xy plane. As R_2 (see Figure 5) moves away from the equilateral triangle
28 value ($1.43 a_0$) but with Θ fixed at 90° , the molecular symmetry is lowered
29 to C_{2v} and the degeneracy is split. The splitting is known as the static JT
30 effect. The degeneracy at the D_{3h} configuration appears as a point of
31 conical intersection when the potential surfaces are plotted in normal
32 coordinate space, not Cartesian coordinate space. A further splitting of
33 the energies of the original vibrational levels (in the wells of the $2p_x$ or $2p_y$
34 electronic states) occurs when the levels are determined in the mixed
35 state. This splitting arises from the dynamic JT effect. An excellent
36 description of the JT effects can be found in the work of Herzberg (1966).

37 For H_3 (Greene et al., 2003), the JT mixing has used the K -matrix form
38 of Staib and Domcke (1990) and the JT mixing parameter and quantum
39 defects, μ , of Mistrík et al. (2000), which was obtained from a fit to *ab initio*
40 surfaces. The nature of the conical intersection allows one to represent the
41 coupling with two parameters [see Equation (4.7) of Mistrík et al. (2000)].
42 This is an enormous simplification compared to other situations where a
43 non-JT coupling may need to be represented by a surface of derivative
44 couplings. Of further importance, Staib and Domcke (1990) reported that

01 the fit to the *ab initio* results of Nager and Jungen (1982) shows that the
 02 conical shape of the potential surfaces is close to a true cone, although
 03 data to support this observation were not reported. This observation
 04 means that higher JT interaction terms beyond linear may not be needed
 05 and that the interaction of the np series with the ns or nd series is not
 06 important since if they were important a distorted conical shape would
 07 occur. Here, n is the principal quantum number. These observations
 08 provide some justification for the use of only an $\ell = 1$ partial wave for
 09 the incoming electron in the calculations of Kokouline and Greene
 10 (2003). On the other hand, Mistrík et al. (2000, 2001) found evidence for
 11 strong mixing of the ns and nd Rydberg states with 3p, 4p, and 5p states
 12 built on H_3^+ cores having the degenerate asymmetric vibrational motion.
 13 A point on the $5pE'$ surface was found to have only 80% p character.

14 The JT coupling parameter and the quantum defects used (Kokouline
 15 et al., 2003a, b) are for the $4p\pi$ state of H_3 (Mistrík et al., 2000). Ideally,
 16 the best coupling parameters and the best quantum defects would vary
 17 with the Rydberg or continuum orbital energy. However, these are not
 18 available. In addition, for $n \geq 3$ the quantum defect varies only slightly
 19 with n but that for $n = 2$ differs considerably from those for $n \geq 3$.
 20 Because the MQDT approach requires a single coupling parameter and
 21 a single quantum defect surface, one must choose a compromise
 22 value. Usage of the $n = 4$ quantum defects (Kokouline et al., 2003)
 23 should produce only very small errors in the positions of resonances,
 24 but the $n = 2$ states will suffer the largest shift in energy from the true
 25 positions.

26 The JT interaction is generally thought of as that between states having
 27 the same n^* . Here n^* is the effective principal quantum number, i.e.,
 28 $n^* = n - \mu$, and μ is the quantum defect. In the MQDT approach used by
 29 Greene and coworkers, the JT interaction not only describes the interac-
 30 tion between the two E' states having outer orbitals $2p_x$ and $2p_y$ but also
 31 accounts for the mixing of Rydberg states with different n^* , the mixing of
 32 Rydberg states with continuum states, and the mixing of the Rydberg
 33 and continuum states with the $2pE'$ dissociative states. This assumes that
 34 these mixings are symmetry allowed. Rydberg orbitals of differing n^* ,
 35 although orthogonal to each other, are quite similar near the nuclei
 36 except for a normalization factor of $1/n^{*3/2}$. Since it is the Rydberg
 37 amplitude near the nuclei that is most important, the JT effect will
 38 occur between Rydberg states and the two dissociative states, scaled by
 39 the $1/n^{*3}$ factor. The normalization constant is squared since the width
 40 [see the expression below Equation (14)] has the square of the interaction
 41 matrix element. If the incoming electron is in a p_x continuum orbital, it
 42 can be captured into an np_y orbital also scaled by the $1/n^{*3}$ factor.
 43 For two different Rydberg states having effective principal quantum
 44 numbers of n_1^* and n_2^* , the connecting width would scale as $1/(n_1^*n_2^*)^3$.

01 The couplings mix the Rydberg and continuum states with the lowest
02 $n = 2$ dissociative states along which DR is finalized.

03 The mixing of all the Rydberg states with each other and that of the
04 continuum state with all the Rydberg states means that many possibilities
05 for DR can occur. The continuum electron can be directly captured into
06 the $2p_{x,y}$ states followed by dissociation, or it can be captured into a
07 higher state which, via couplings to other intermediate levels, can even-
08 tually lead to the dissociative levels. The mechanism is remarkably simi-
09 lar to one originally proposed by Bates et al. (1993).

10

11 4.5.3 Nuclear Spin

12
13 The nuclear spin has been included in prior theoretical studies of homo-
14 nuclear diatomic DR whenever molecular rotation is considered. The
15 calculations reported by Greene and coworkers also include nuclear
16 spin in the theory. Nuclear spin cannot be ignored because in H_3 , the
17 nuclei are fermions and the total wave function must change sign for an
18 interchange of any two protons. (The exchange is equivalent to a rotation
19 by 180° around an axis perpendicular to the main symmetry axis.) This
20 requirement places restrictions upon the allowed values for the rotational
21 quantum numbers and requires that the total symmetry (i.e., the product
22 of the symmetries of the vibrational, rotational, nuclear spin and electro-
23 nic wave functions) be that of the A'_2 or A_2'' representations of D_{3h} . The
24 ortho and para states have total nuclear spin of $3/2$ and $1/2$, respectively.

25

26 4.5.4 Calculation of the DR Cross Section and Rate Coefficient

27
28 The first paper (Kokoouline et al., 2001) reported preliminary calculations
29 which made use of the hyperspherical adiabatic approach and an expres-
30 sion derived by O'Malley (1966) for the direct DR cross section, σ , of
31 diatomic molecules:

32

$$33 \quad \sigma = \sum_{\beta} \frac{\pi^2}{E_{el}} \frac{\Gamma_{\beta} R_{\beta}}{|U'_{\beta} R_{\beta}|} |\Psi R_{\beta}|^2 \quad (18)$$

34

35

36 In Equation (18) β is an index that runs over the dissociative routes, E_{el}
37 is the electron energy, R_{β} is the value of the hyperradius for the β^{th}
38 dissociative route at an energy, E_{el} , above the ion rovibrational level
39 undergoing DR, Γ_{β} is the width for capture into the β^{th} dissociative
40 route, U_{β} is the slope of the β^{th} dissociative route, and $\Psi(R_{\beta})$ is the
41 dissociative nuclear wave function. The use of this expression follows
42 from the observation that when the potential curves are plotted as a
43 function of the hyperradius, all the Rydberg states cross the ion ground
44 state.

Equation (18) omits the survival factor [the denominator within parentheses in Equation (14)] and thereby does not account for autoionization. There are several other caveats to consider. This expression was derived for diatomic molecules and its use for H_3^+ entails replacing the internuclear distance by the hyperradius. This replacement is not likely to lead to quantitative results. In diatomics, the nuclear configuration depends solely upon the internuclear distance, and the Franck–Condon factor in Γ_β has a rigorous dependence upon this distance. In a triatomic, in hyperspherical coordinates, the Franck–Condon factors will depend upon both the hyperradius and the hyperangles. Since the hyperradius is often viewed as a measure of the size of the molecule, taking Γ_β to depend only upon R_β is making the approximation that the Franck–Condon factors depend more upon molecular size than upon the details of molecular shape. This approximation is not expected to be reliable. It is probably for these reasons that the results (Kokoouline et al., 2001) are referred to as preliminary and approximate. Both upper and lower bound cross sections were reported. The lower bound cross sections included only the 2p states. Both the 2p and higher np states are included in the upper bound cross section. In a later paper (Kokoouline & Greene, 2003b), it is noted that the cross sections reported in the first paper (Kokoouline et al., 2001) need to be multiplied by a factor of π^2 due to inconsistencies in the literature concerning the definition of the K matrix. Surprisingly, if one multiplies the 2001 results by π^2 , the upper bound cross section is in quite good agreement with the storage ring results (Jensen et al., 2001). The calculated cross sections are structureless as are the experimental results to which they were compared. Using only the 2p states, it is estimated that 70% of the DR events lead to $\text{H} + \text{H} + \text{H}$ compared to the experimental result (Datz et al., 1995a, b) of $75\% \pm 8\%$. For the $\text{H} + \text{H}_2$ channel, the peak H_2 vibrational distribution occurs at $v = 5\text{--}6$ compared to the broad distribution found experimentally, which peaks at $v = 5$ (Strasser et al., 2001). The upper bound thermal rate coefficient at 300 K is $1.2 \times 10^{-7} \text{cm}^3/\text{s}$ after correction by the π^2 factor and compares well to the storage ring results of $1.0 \times 10^{-7} \text{cm}^3/\text{s}$ (Jensen et al., 2001) and $1.15 \times 10^{-7} \text{cm}^3/\text{s}$ (Sundström et al., 1994). The usage of Equation (18) to calculate these results would lead one to conclude that this agreement must be fortuitous. However, the agreement reported not only for the cross section and rate constant but also for the branching fraction and vibrational distribution argues otherwise.

4.5.5 Improved Cross Sections

The lack of structure in the calculated cross section was corrected in a later detailed paper (Kokoouline & Greene, 2003b), which used an MQDT approach instead of Equation (18). The use of the adiabatic

01 hyperspherical approximation has been described above as has the K
02 matrix having the JT coupling.

03 The calculated rate coefficients are reported (Kokoouline & Greene,
04 2003a and 2003b) to be accurate to better than 20% due to the incomplete
05 set of states that are included in the calculations. The states are character-
06 ized by the quantum numbers $[I, \Gamma, N^+, N]$, where I represents the two
07 values for the total nuclear spin, $3/2$ (ortho) and $1/2$ (para), Γ denotes the
08 total molecular symmetry (A_2' or A_2''), and N^+ and N denote the rotational
09 quantum number for H_3^+ and H_3 , respectively. (The total molecular
10 symmetry is determined by the need to have the total wave function
11 change sign upon a swap of any two nuclei.) In the first detailed report of
12 the calculations (Kokoouline & Greene, 2003b), 17 sets of these quantum
13 numbers were used, each with 8–12 vibrational wave functions (includ-
14 ing the continuum) and 50–100 hyperspherical potential curves. A tabu-
15 lation of the levels is not included.

16 In the most recently reported calculations (Fonseca dos Santos et al.,
17 2007), several improvements were incorporated into the cross section and
18 rate constant calculations. The adiabatic hyperspherical approximation
19 was relaxed by including couplings between the adiabatic channels. The
20 slow variable discretization approach was used to incorporate these
21 couplings, but the details of these new calculations are not reported.
22 A comparison of the calculated vibrational energies for 26 low-lying
23 vibrational states with a full three-dimensional diagonalization (Jaquet
24 et al., 1998) shows a clear improvement over the earlier full adiabatic
25 approach (Kokoouline & Greene, 2003b). The positions of the Rydberg
26 resonances are improved with this revision.

27 However, the physical interpretability of these calculations is some-
28 what problematic. Potential curves plotted as a function of the hyperradi-
29 us are much more difficult to interpret than the more familiar surfaces
30 plotted as a function of Cartesian coordinates. Furthermore, if one
31 improves upon the adiabatic hyperspherical approach by including
32 more couplings between the curves, the concept of a potential curve as
33 a function of the hyperradius becomes weak. In the limit of completely
34 dropping the adiabatic hyperspherical approximation, potential curves
35 are no longer meaningful. These considerations must be balanced against
36 the reasonable agreement that has been obtained to date between these
37 calculations and experiment. This is discussed further below.

38 An important additional improvement in the most recent calculations
39 (Fonseca dos Santos et al., 2007) is the addition of more resonance states.
40 Rotational states up to $N^+ = 5$ are included compared to the prior calcula-
41 tions which included levels up to $N^+ = 3$ (but not $K^+ = 1$) and (4, 3) for the
42 ground vibrational level. A detailed accounting of the included vibra-
43 tional levels is not presented, which makes it difficult to assess whether
44 or not the theoretical treatment is adequate at particular electron energies.

4.5.6 Toroidal Correction

In the storage ring experiments, a beam of molecular ions circulates in a large ring (51.6-m circumference) (Strömholm et al., 1996) and merges with a beam of electrons in only a small section (0.85 m) (Strömholm et al. 1996) of the ring known as the electron cooler (the region between the merging and demerging regions in Figure 3). The electron beam is bent by a toroidal magnetic coil at the beginning and end of the overlap region. Collisions between the continuously renewed electron beam and the ions serve to reduce the random motions of the ions leading to a high energy resolution. The ion beam is generally a few mm in diameter compared to the electron beam which is a few cm in diameter.

The cooler is also the location where DR takes place. For measurements at “zero” center of mass energy, the electron beam is velocity matched with the ion beam. For other center of mass energies, the electron beam energy is shifted up or down from the “zero” energy measurement. For most of the length of the cooler, the electron beam is very closely collinear with the ion beam and the intended center of mass energy is appropriate. However, in the merging and separating regions at both ends of the cooler, the ion and electron beams are not parallel and the center of mass energy changes with the angle between the two beams. The result is that a measurement of the DR rate constant at a single center of mass energy (appropriate in the straight section of the electron beam cooler) is actually an average of rate constants for different center of mass energies over the length of the cooler from the beginning of the merging region to the end of the separating region. The bending region comprises only about 15% (Amitay et al., 1996) of the full length of the overlap of electron and ion beams and was thought to not play a significant role in deriving the value of the rate constants. However, an important recent study by Kokoouline and Greene (2005) on H_3^+ indicates that the experimental data deviate considerably from the theoretical values near 0.03 eV, 0.1 eV, and above 0.8 eV. In the latter region the difference between experiment and theory is over an order of magnitude. If the theoretical results are averaged over the full cooler length, accounting for the higher relative center of mass energies at the ends of the cooler, the theory agrees with experiment above 0.8 eV and shows improved agreement at 0.03 and 0.1 eV. The results indicate that raw storage ring data must be corrected to remove the effect of the electron bending regions. The deconvolution procedure for accomplishing the correction (Lampert et al., 1996) introduces considerable uncertainty because the rate constants needed at higher energies have often not been measured, and in the case of those that have been measured, they too must be corrected. The result is an iterative procedure which is usually carried out to first order (i.e., a single iteration) (Strömholm et al., 1996).

4.5.7 Breit–Wigner Cross Sections

If one assumes that all electron captures into Rydberg states lead to dissociation in one way or another and that there is no direct dissociative channel that would interfere with the dissociation through the Rydberg states (as is the case for H_3), the Breit–Wigner expression can be used for calculating DR cross sections. An important innovative approach along these lines has been reported by Jungen and Pratt (2009). They treated the linear JT effect, restricting capture into $v_2 = 1$ Rydberg levels (from the ion ground state). Capture into $v_1 = 1$ Rydberg levels was not considered. Using spectroscopic data for the $3pE'$ state and previously determined JT coupling parameters, they show that after averaging over the closely spaced $v_2 = 1$ resonances, a simple cross section expression results which is independent of n^* and structureless.

4.5.8 Comparison of Theory and Experiment

For the four isotopomers, Jungen and Pratt (2009) show that there is a factor of two disagreement with the experimental rate coefficient at some energies for D_3^+ and a factor of 2–3 disagreement for D_2H^+ . For H_2D^+ and H_3^+ the agreement is even better except near 0.006 eV for H_3^+ . The resulting rate coefficients show remarkable agreement with experimental results for the four isotopomers considering the simplicity of the cross section expression. Figure 14 has the latest results of Greene and coworkers (Fonseca dos Santos et al., 2007), Jungen and Pratt (2009), and the CRYRING (McCall, 2004) data for H_3^+ . The theoretical results of Fonseca dos Santos et al. (2007) show much more structure than the CRYRING data. Although the theory and experiment are in generally good agreement, there is clearly room for improvement.

4.5.9 Suggestions for Future Theory

The pioneering research of Greene, Kokoouline, and coworkers has made an enormous contribution to our understanding of the DR of H_3^+ . Nevertheless, many of the details remain to be uncovered. We still do not know which Rydberg states drive DR. The identities of the important states will change with electron energy as will the details of the mechanism. An important contribution in this regard has been the theoretical work of Tashiro and Kato (2002, 2003) on the predissociation lifetimes of H_3 Rydberg states. They found that the $2s^2A_1'$ state has a large coupling with the upper $2pE'$ state (see Section 4.4.4) and may be a feeder state for DR from higher Rydberg states. They propose that in DR, initial electron capture occurs into high n ($n = 6$ or 7) states with low vibrational excitation followed by coupling to lower n states with higher vibrational

01 excitation. The coupling eventually leads to the $2s^2A_1'$ state, which is
02 predissociated mostly by the upper $2pE'$ state. They propose that if
03 electron capture involving a single vibrational quantum is most impor-
04 tant, the $6s^2A_1'(1, 0^0)$ and $7p^2E'(0, 1^1)$ are important for DR at electron
05 energies just above the lowest vibrational level of H_3^+ . By propagating a
06 wave packet from $7pE'(0, 1^1)$, they find that the predissociation involves
07 the intermediate states $5p^2E'$, $4s^2A_1'$, $3s^2A_1'$, $3p^2E'$, $2s^2A_1'$, and finally DR
08 via $2pE'$. However, the precise identification of these states requires
09 greater accuracy in the quantum chemical determinations of their posi-
10 tions and widths and would be a valuable contribution. Note that the
11 $2s^2A_1'$ state and those for $n > 2$ are not included in the calculations of
12 Greene, Kokoouline, and coworkers or those of Jungen and Pratt (2009)
13 and should be considered for future work.

14 Future theoretical studies should explore the role of the $\ell = 0$ and 2
15 partial waves. The work of Tashiro and Kato (2002) indicates that the $\ell = 0$
16 wave may be more important than $\ell = 2$. The calculations of Greene,
17 Kokoouline, and coworkers and Jungen and Pratt (2009) treated only
18 $\ell = 1$. The inclusion of the $\ell = 0, 2$ partial waves may account for some
19 of the differences between theory and experiment.

20 The JT coupling explored by Greene and coworkers is probably the
21 dominant coupling that drives DR. But other derivative couplings
22 that have been identified in prior calculations (Schneider & Orel, 1999;
23 Schneider et al., 2000; Tashiro & Kato, 2002) need to be included in future
24 three-dimensional calculations.

25 The failure of the adiabatic hyperspherical approach for H_2D^+ and D_2H^+
26 leads one to ask if it is entirely adequate for H_3^+ . Instead of calculating
27 vibrational energies to determine the accuracy of this approach, it may
28 be more meaningful to compare the values of S matrix elements resulting
29 from the adiabatic hyperspherical approach to elements calculated by
30 relaxing this approach.

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33 5. HISTORY OF EXPERIMENTAL H_3^+ RECOMBINATION 34 STUDIES

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36 As may be seen in Figure 10, the measured recombination coefficients
37 have varied considerably over the years. While all afterglow measure-
38 ments carried out before 1973 probably refer to mixtures of H_3^+ and H_5^+
39 ions (and impurity ions), the recombining H_3^+ ions were clearly identi-
40 fied by mass analysis in the microwave afterglow studies by Leu et al.
41 (1973). The measured recombination rates were very similar to those
42 found for many other ions and nothing unusual was noted. Subsequent
43 studies used either an inclined-beam (Peart & Dolder, 1974) or single-pass
44 merged-beam (Auerbach et al., 1977) measured recombination cross

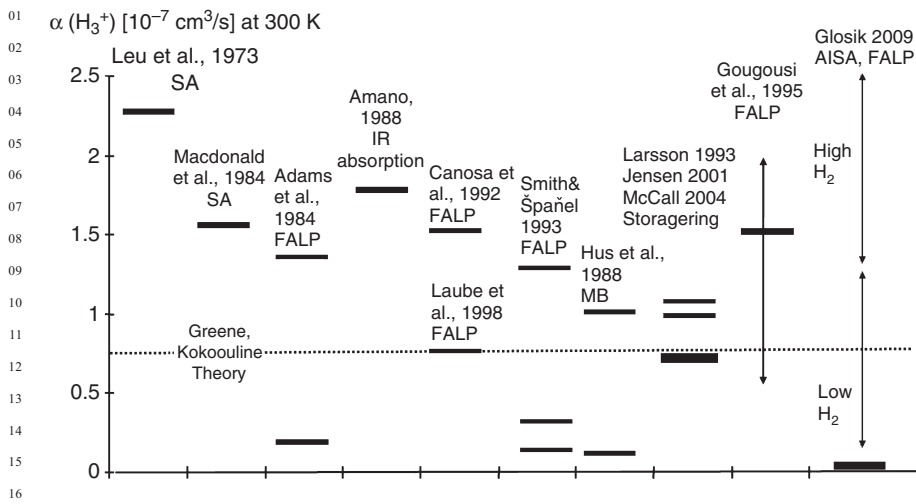


Figure 10 H_3^+ recombination coefficients inferred from different types of experiments, at electron temperatures near 300 K

sections over a wider range of energies, confirming the afterglow data within about a factor of two. Macdonald et al. (1984) extended the microwave measurements to higher electron temperatures up to 5000 K by microwave heating of the plasma electrons. While the measured 300 K rate coefficients were somewhat smaller than those of Leu et al. (1973), the temperature dependence was quite close to that expected from the merged-beam results.

Not much attention was paid at that time to a theoretical argument by Kulander and Guest (1979) that the usual curve-crossing DR mechanism would not be applicable in the case of H_3^+ . The situation changed when Michels and Hobbs (1984) again calculated one-dimensional potential-energy curves of H_3^+ and showed that the ionic ground-state curve of H_3^+ in the lowest vibrational states does not intersect a repulsive curve leading to neutral products. However, suitable curve crossings, were found for H_3^+ ions in the third or higher vibrational states. Hence, Michels and Hobbs suggested that the experimental data referred to vibrationally excited H_3^+ ions. Their argument was seemingly strengthened by new experimental data of Adams et al. (1984), who used their new “Flowing Afterglow Langmuir Probe” (FALP) technique to study the recombination of H_3^+ . They noticed that the initial electron-density decay was quite fast, compatible with a recombination coefficient near $10^{-7} \text{ cm}^3/\text{s}$, but also that it changed in the later afterglow to a slower decay indicating a much smaller ($<2 \times 10^{-8} \text{ cm}^3/\text{s}$) recombination rate coefficient. Michels’ and Hobbs’ prediction offered a ready explanation for this

01 observation, namely that the initial fast decay was due to recombination
02 of vibrationally excited ions ($v \geq 3$) and that the slow decay should be
03 ascribed to H_3^+ in $v=0$. Later, Adams and Smith reported that the
04 recombination rate for $v=0$ ions might be even smaller ($\sim 10^{-11}$ cm^3/s).
05 Larsson and Orel (2008) provide a brief account of these experiments,
06 which were not published in detail. While this very low value may have
07 been due to an experimental problem (presence of nonrecombining He^+
08 ions) it became generally (with some exceptions) accepted that H_3^+ in the
09 vibrational ground-state recombined only slowly.

10 The interpretation of Adams et al. experiment became highly question-
11 able when Amano (1988, 1990) used infrared absorption to monitor the
12 decay of the H_3^+ ($v=0$) density in the afterglow of a radio-frequency
13 discharge in pure hydrogen. At a gas temperature of $T=210$ K Amano
14 measured a recombination coefficient for $v=0$ ions of 1.8×10^{-7} cm^3/s ,
15 fairly close to the data of Leu et al. and Macdonald et al. The ensuing debate
16 at times became rather contentious. Responding to some criticism, Smith
17 and Špaňel (1993) repeated the original studies by Adams et al. (1984) in
18 much greater detail and arrived at the conclusion that $v=0$ ions recombined
19 with $\alpha = (3.6 \pm 1) \times 10^{-7}$ cm^3/s , somewhat faster than their previous result.

20 The measurements by Amano suggested that curve crossing might not
21 be as essential for recombination as had been thought. Bates et al. (1993),
22 in a paper entitled “Enigma of H_3^+ dissociative recombination,” pro-
23 posed a multistep mechanism to rationalize experimental results, but
24 the theory was not sufficiently quantitative to dispose of the “enigma.”

25 Additional flowing-afterglow measurements were carried in attempts to
26 settle the question. One study (Canosa et al., 1992) gave rate coefficients of
27 1.1×10^{-7} cm^3/s at $T=650$ K for H_3^+ , thought to be in $v=0$, and 1.5×10^{-7}
28 cm^3/s at 300 K for ions believed to be of low vibrational excitation ($v \leq 2$).
29 A further study in the same laboratory by Laubé et al. (1998) resulted in a
30 factor-of-two lower value of 7.8×10^{-8} cm^3/s at 300 K. This value is often
31 quoted as the afterglow measurement that agrees best with the storage ring
32 results. However, the authors also carried out an identical experiment for
33 D_3^+ and found essentially the same recombination coefficient as for H_3^+ ,
34 and this does not agree with the storage ring data.

35 Gougousi et al. (1995), using the flowing afterglow techniques,
36 observed a decline of the recombination rate at late times and found
37 that the apparent recombination rate (inferred from the early afterglow
38 decay) increased from 1.5×10^{-7} cm^3/s to nearly 2×10^{-7} cm^3/s when
39 the experimental H_2 concentration was raised from 1×10^{14} cm^{-3} to
40 15×10^{14} cm^{-3} . They attempted to explain their data by a model in
41 which H_3^+ recombination occurred by a three-body mechanism in
42 which both electrons and neutral hydrogen play a role.

43 Later studies using the single-pass merged-beam method did not lead
44 to consistent results. For instance, Hus et al. (1988) found a nearly

01 20 times larger cross DR cross section when the “rf source” was used
02 rather than the “trap source” to produce ions. In single-pass measure-
03 ments, the ions do not have sufficient time to relax vibrationally or
04 rotationally before merging with the electron beam, and hence it seemed
05 possible that the observed effects were due to vibrational excitation of the
06 ions, as was suggested by the authors. Mitchell [unpublished, brief
07 accounts are contained in a paper by Johnsen and Mitchell (1998) and
08 by Mitchell and Rogelstad (1996)] also carried out a merged-beam experi-
09 ment in which the deflection field used to separate product neutrals from
10 the ions in the post-collision region was varied. The measured DR pro-
11 duct signal increased by a factor of 5 (approaching that obtained in
12 storage-ring experiments) when the field strength in that region was
13 reduced from 3000 V/cm to 200 V/cm. Mitchell ascribed this effect to
14 field ionization of H_3 Rydberg molecules that are produced by DR of
15 H_3^+ . At the high field strength, but not at the lower, a substantial fraction
16 of the recombination H_3 Rydberg products would be re-ionized in the
17 demerging region of the apparatus and would not be counted as DR
18 products. The problem with this suggestion is that it does not really
19 remove the discrepancy between the merged-beam and storage ring
20 data since field ionization should also occur in the bending magnet of
21 storage ring experiments. A convincing explanation of these observations
22 has not yet been given.

23 Since then, afterglow measurements on H_3^+ and D_3^+ have been carried
24 out almost exclusively by Glosik and coworkers in Prague, who use both a
25 flow tube and an advanced stationary afterglow apparatus (AISA). The
26 Prague group systematically studied the dependence of the apparent rate
27 coefficients as a function of gas densities and temperature. A nearly complete
28 set of their data has been presented in a recent paper (Glosik et al., 2009a).

29 The Prague group (Macko et al., 2004) also carried out a series of
30 afterglow measurements in which the $H_3^+(v=0)$ ion density during the
31 afterglow was measured by optical absorption using a cavity ring-down
32 technique. These results confirmed the spectroscopic measurements by
33 Amano (1988 and 1990) and show that vibrationally cold ions recombine
34 with coefficient of about $\sim 1.5 \times 10^{-7} \text{ cm}^3/\text{s}$.

35 The most interesting and startling observations made by the Prague
36 group (see, e.g., Plašil et al., 2002) were that the DR rate coefficients seem
37 to fall off rapidly (down to $\sim 1 \times 10^{-9} \text{ cm}^3/\text{s}$) when the H_2 concentration is
38 reduced to below 10^{12} cm^{-3} . It is this observation that challenges the now
39 generally accepted rate coefficient of $\sim 1 \times 10^{-7} \text{ cm}^3/\text{s}$ and seemingly poses
40 a serious problem. We will show later (see Section 6.1) that those afterglow
41 data do not really support the very low inferred recombination rates.

42 The modern era of DR studies of H_3^+ and D_3^+ (and many other ion
43 species) began with the extensive work using ion-storage rings, the
44 CRYRING in Stockholm, the ASTRID ring in Aarhus, and the TSR in

01 Heidelberg. Unlike the afterglow and single-pass merged-beam work,
 02 this technique produced remarkably consistent results. Steady improve-
 03 ments in the energy resolution, control and characterization of vibrational
 04 and rotational states, and beam quality were made over the years, but
 05 the conclusions never changed significantly. The latest results of the
 06 CRYRING and TSR rings show a nearly identical dependence of the
 07 rate coefficient (or cross section) on energy, including the finer structures
 08 that will be discussed later. The thermally averaged (Maxwellian) rate
 09 coefficient as a function of electron temperature, derived from the
 10 CRYRING results (McCall et al., 2004), can be expressed by an analytical
 11 fit of the form

$$12 \quad a(T_e)[\text{cm}^3/\text{s}] = -1.3 \times 10^{-8} + 1.27 \times 10^{-6} T_e^{-0.48}, \quad (19)$$

13
 14 which gives a recombination coefficient of $6.9 \times 10^{-8} \text{ cm}^3/\text{s}$ at $T_e = 300 \text{ K}$.
 15 This value refers to ions in the lowest vibrational state, and at a rotational
 16 temperature of about 30 K.

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23 6. RECONCILING AFTERGLOW AND STORAGE RING 24 RESULTS

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32 6.1 Afterglow Measurements That Yielded Very Low Recombination 33 Coefficients

34 We will discuss the unusually low values first. There are good reasons to
 35 believe that plasma recombination can be enhanced by third-body-
 36 assisted recombination, but it is difficult to envision a mechanism that
 37 suppresses binary H_3^+ recombination in the plasma environment. One
 38 might surmise that the H_3^+ ions in the experimental plasmas were of a
 39 particular type, for instance in a nonrecombining vibrational state or
 40 perhaps in different spin modification, e.g., ortho or para H_3^+ . At this
 41 time, it appears very unlikely that vibrationally excited H_3^+ ions recom-
 42 bine more slowly than those in the ground state, as was suggested in
 43 a previous review by one of the present authors (Johnsen, 2005).

01 New theoretical calculations by Fonseca Dos Santos et al. (2007) for the
 02 E (0, 1¹) and A₁ (1, 0⁰) vibrationally excited states actually indicate
 03 the opposite so that this “loop hole” has essentially been closed. Like-
 04 wise, recent storage ring experiments (Tom et al., 2009) and theory
 05 (Fonseca dos Santos et al., 2007) indicate that both the ortho and para
 06 spin modifications of H₃⁺ recombine at nearly the same rate, at least at
 07 300 K. The storage ring results show that the ortho form recombines
 08 somewhat more slowly, but only by about a factor of 1.5.

09 The most puzzling findings that need to be examined in some detail
 10 are those made in the extensive series of stationary- and flowing-after-
 11 glow measurements by the Prague group (Glosik et al., 2009a; Plašil et al.,
 12 2002). Their experiments seemed to indicate that the H₃⁺ recombination
 13 rate dropped to values far below the binary value (by a factor of 10 and
 14 more) when the hydrogen concentration in the experiments was reduced
 15 from about 1 × 10¹² cm⁻³ to 1 × 10¹¹ cm⁻³. Very similar results were
 16 consistently obtained by the two different afterglow methods, at different
 17 temperatures, and also for D₃⁺ ions (Glosik et al., 2009b). This finding is
 18 often mentioned as a serious problem since it is in conflict with both
 19 recent theory and experiments.

20 It is always difficult to reanalyze experimental data that were taken by
 21 others. However, if one examines the experimental conditions, one rea-
 22 lizes that the expected recombination rate of about 10⁻⁷ cm³/s could
 23 not have been observed at low H₂ concentrations. While the two reactions
 24 in the sequence Ar⁺ + H₂ → ArH⁺ + H and ArH⁺ + H₂ → Ar + H₃⁺ are
 25 fast (rate coefficients near 10⁻⁹ cm³/s), it will still take roughly 10 ms
 26 at [H₂] = 10¹¹ cm⁻³ to produce H₃⁺ ions, but recombination of an ion
 27 with α = 10⁻⁷ cm³/s (at n_e = 10¹⁰ cm⁻³) proceeds at a time scale of
 28 1/(αn_e) = 1 ms. This means that the loss rate of electrons in the plasma
 29 is not limited by recombination, but by the rate at which the ion is
 30 formed. Since our criticism affects a large set of published data, we
 31 constructed a simple numerical model that simulates the afterglow pro-
 32 cesses and the methods of analysis that were employed by the Prague
 33 group. The authors determine recombination coefficients using a form of
 34 data analysis in which one constructs a graph of the measured values of
 35 the quantity

$$36 \quad - \left(\frac{1}{n_e^2} \frac{dn_e}{dt} + \frac{\nu_D}{n_e} \right) \quad (20)$$

37
 38
 39 as a function of the reciprocal electron density. Here ν_D describes the
 40 loss of ions and electrons due to diffusion in the fundamental diffusion
 41 mode. If the plasma contains only one recombining ion species from the
 42 very beginning, or if this condition is approached rapidly, then a graph of
 43 this kind indeed approaches the value of the recombination coefficient in
 44 the limit of n_e → 0 (i.e., the late afterglow). In practice, the asymptotic

01 value is attained in a short time if the reactions forming H_3^+ go to
 02 completion rapidly, which is the case in most afterglow measurements
 03 when the H_2 density is sufficiently high. However, this is not true when
 04 the H_2 density is very low.

05 Our numerical model returns the values in the expression above as a
 06 function of the reciprocal electron density. To keep the model simple, we
 07 ignore depletion of the neutral H_2 due to the ion–molecule reactions, even
 08 though it is not negligible, but including it would make the situation only
 09 worse. The model shows that an input value of $\alpha = 10^{-7} \text{ cm}^3/\text{s}$ and initial
 10 electron densities of $1 \times 10^{10} \text{ cm}^{-3}$ leads to same inferred recombination
 11 coefficient only if $[\text{H}_2] > 10^{12} \text{ cm}^{-3}$. At $[\text{H}_2] = 1 \times 10^{11} \text{ cm}^{-3}$ (see Figure 11)
 12 graphs of the same kind show that the asymptotic value is never
 13 approached on the time scale of the experiment (about 40 ms). The authors'
 14 method of recovering the recombination coefficients employed a linear
 15 extrapolation (sometimes done approximately on a logarithmic graph)
 16 toward $1/n_e \rightarrow 0$. The procedure returns a much smaller and incorrect
 17 value of the recombination coefficient. The asymptotic value approached
 18 in the limit $n_e \rightarrow 0$ should have been used, but in practice this value cannot
 19 be obtained at low $[\text{H}_2]$, even by curve-fitting, with any reasonable degree
 20 of precision, since diffusion becomes the dominant loss in the late afterglow.
 21 Another way of illustrating the cause of the problem is to examine the
 22 evolution of the ion composition during the afterglow, an example of which

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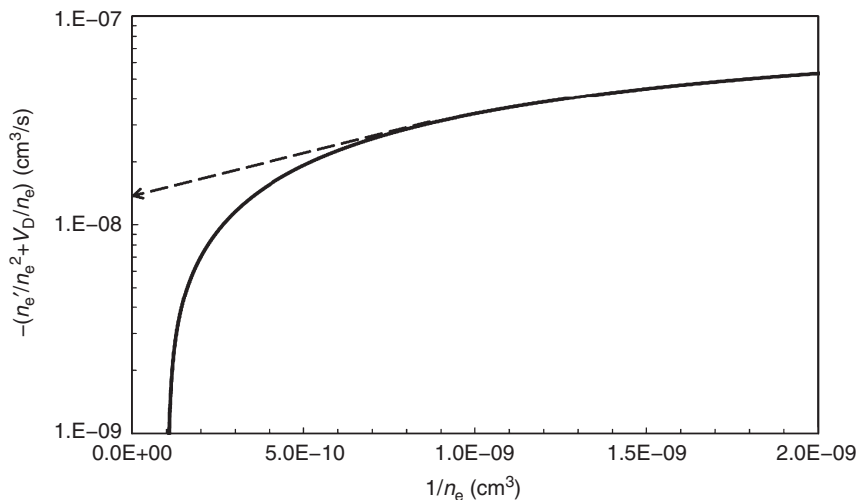
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41 **Figure 11** Numerical simulation of an afterglow in an helium/argon/hydrogen mixture
 42 at a hydrogen concentration of $1 \times 10^{11} \text{ cm}^{-3}$ for an assumed H_3^+ recombination
 43 coefficient of $1 \times 10^{-7} \text{ cm}^3/\text{s}$. The arrow indicates the extrapolation to $1/n_e=0$, from
 44 which a far smaller recombination coefficient is obtained

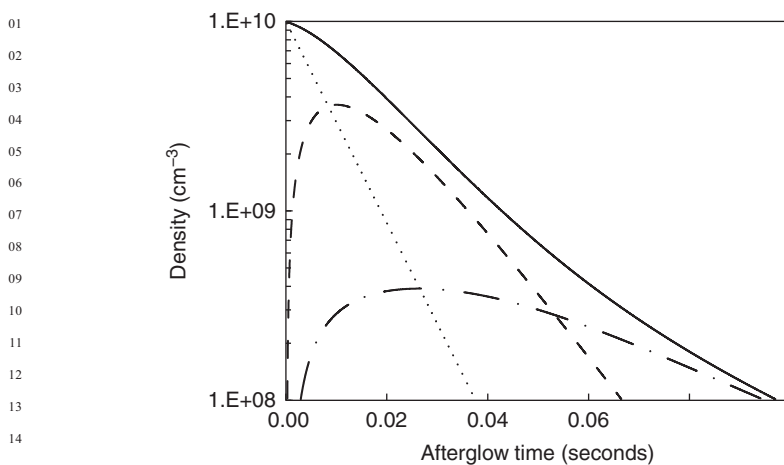


Figure 12 Numerical simulation of an afterglow in a helium/argon/hydrogen mixture at a hydrogen concentration of $1 \times 10^{11} \text{ cm}^{-3}$ for an assumed H_3^+ recombination coefficient of $1 \times 10^{-7} \text{ cm}^3/\text{s}$. The lines indicate the evolution of density of electrons (thick line), Ar^+ ions (dotted line), ArH^+ ions (dashed line), and H_3^+ ions (dash-dotted line)

is given in Figure 12. Even at an afterglow time of 40 ms, H_3^+ accounts for only 1/3 of all ions, which makes it impossible to obtain accurate H_3^+ recombination coefficients. The authors did carry out simultaneous mass spectrometric observations that seemed to indicate that the plasma was dominated by H_3^+ ions. However, the mass spectrometer samples ions from a region near the wall of the plasma container where the electron density and recombination loss of H_3^+ is lower, and hence the relative abundance of this ion is higher than it is in the center of the plasma.

We conclude that the observations of very low recombination rates at low $[\text{H}_2]$ are probably in error and that consequently there is no need to search for explanations in terms of H_3^+ recombination mechanisms. In reality, the situation may be more complicated. A slower increase of the recombination coefficient with H_2 concentration is consistently observed at much higher $[\text{H}_2]$ and this effect must have a different origin (see Section 6.3). While attempting to fit some of the published data samples, we also noticed that better fits were obtained when the model H_2 concentration was reduced to values below the stated concentrations. This may indicate that a fraction of the H_2 was dissociated during the discharge phase of the experiment in the stationary afterglow experiments. Some dissociation of H_2 can also occur in flowing afterglow measurements due to metastable argon atoms that enter the recombination region. These remarks are speculative. It may be worthwhile to conduct some experiments to clear up such questions.

01 A further observation of very low recombination rates was made by
02 Adams et al. (1984) in an afterglow experiment. This observation had a
03 great impact and for a while since it was believed to provide evidence
04 that H_3^+ ions in their vibrational ground state recombined only slowly.
05 Their experiments showed that the electron density in an H_3^+ afterglow
06 initially decayed quite fast (indicating a recombination rate of about
07 $1.3 \times 10^{-7} \text{ cm}^3/\text{s}$) but then decayed much more slowly. No such effects
08 were found when the plasma contained O_2^+ ions. At the time when the
09 experiments were done, it was believed that H_3^+ in the vibrational
10 ground state recombined very slowly. Hence the experimenters drew
11 the natural conclusion that the initial decay was due to vibrationally
12 excited H_3^+ and that the later slower decay was due to ground state
13 ions. The lowest 300 K recombination coefficient derived in a later repetition
14 of this experiment by Smith and Špaňel (1993) was $3 \times 10^{-8} \text{ cm}^3/\text{s}$,
15 lower by a factor of 2.3 than the storage ring value. The authors believed
16 that this value referred to a mixture of $v=0$ and $v=1$ ions. However, the
17 accuracy of this value must be regarded as questionable. It was obtained
18 by fitting the observed decay to a model that has too many adjustable
19 parameters, the relative abundance of the two (or possibly three) states,
20 two recombination coefficients, the quenching coefficient from the higher
21 to the lower state, an estimated impurity concentration, and a diffusion
22 rate. Also, the deviation of the decay curve from that corresponding to a
23 simple (single-ion) decay is actually very small (only a few %), which
24 makes it difficult to determine several coefficients by curve-fitting. While
25 a good fit to the data was obtained, it does not necessarily result in a
26 unique value of the recombination coefficient in the late afterglow. We
27 constructed a simple numerical model similar to the one used by the
28 authors and found that equally good fits could be obtained for higher
29 recombination rate coefficients (up to about $6 \times 10^{-8} \text{ cm}^3/\text{s}$) in the late
30 afterglow. If one simply fits the $1/n_e(t)$ graph in the paper by a straight
31 line, one obtains an upper limit of the recombination coefficient in the
32 later afterglow of about $8 \times 10^{-8} \text{ cm}^3/\text{s}$. While the data show that there is
33 indeed something “unusual” about the decay curve, the low inferred
34 value of $\alpha(v=0,1) = 3 \times 10^{-7} \text{ cm}^3/\text{s}$ is not sufficiently accurate to be
35 considered a challenge to the storage ring data. In an attempt to reduce
36 the vibrational state to $v=0$, Smith and Špaňel carried out a second set of
37 measurements in which they used Kr^+ ions to produce H_3^+ and, using a
38 different fitting procedure, arrived at an even lower estimated value α
39 ($\text{H}_3^+, v=0$) $\sim (1-2) \times 10^{-7} \text{ cm}^3/\text{s}$. However, the authors also found evi-
40 dence that the plasma contained both H_3^+ and KrH^+ in apparent chemi-
41 cal equilibrium, and it is not at all obvious which of the two ions was
42 responsible for the observed recombination loss.

43 Similar observations of a reduced recombination rate in the later after-
44 glow were later made in flowing-afterglow measurements by Gougousi

01 et al. (1995). Given the considerable uncertainty of the data analysis, the
02 lowest values are not in conflict with the storage ring value at 300 K.
03 Those authors attempted to explain their observations by a three-body
04 mechanism in which ambient electrons induce l -mixing in the autoionizing
05 states. The model may have contained a kernel of truth, but it relied
06 on unrealistically long lifetimes, taken from a merged-beam experiment,
07 that are not supported by either theory or other measurements.

08 The explanation for the observed faster decay at early afterglow times
09 may actually be that proposed by Smith and Spaňel, but in somewhat
10 modified form. We now know from theory (Fonseca dos Santos et al.,
11 2007) that vibrational excitation enhances recombination, even for low
12 vibrational states. Unfortunately, there are no direct measurements of
13 such rates that would help to put this conjecture on a firmer basis.

14 We conclude in this section that there are no afterglow measurements
15 that give strong support for H_3^+ ($v=0$) recombination coefficients sig-
16 nificantly smaller than those found in storage rings. Those afterglow
17 measurements, in which the state of the ion was identified by spectro-
18 scopy, consistently yielded higher values. We now turn our attention to
19 the question why many afterglow measurements have yielded higher
20 recombination rates.

21

22 6.2 Afterglow Measurements That Yielded High Recombination 23 Coefficients 24

25 Most afterglow measurements, provided sufficient H_2 was present in
26 the gas mixture, yielded recombination coefficients that were higher by
27 factors of 2–3 than those found in the storage ring experiments. The
28 extensive compilation of data presented in the recent paper by Glosik
29 et al. (2009a) shows quite clearly that the observed rate coefficients
30 tend to increase with increasing neutral density (largely helium), which
31 suggests that the recombination is enhanced in the presence of third
32 bodies. The problem is that the conventional three-body collisional-
33 radiative recombination mechanisms for atomic ions, in which either
34 neutrals or electrons act as stabilizing agents, are far too slow to
35 explain the observed three-body rate coefficients. In the next section
36 we will explore more efficient third-body-assisted recombination
37 mechanisms.

38

39 6.3 Third-Body Stabilized Recombination of H_3^+ 40

41 There are several possible mechanisms that could make third-body
42 effects on recombination more efficient in the case of molecular ions
43 that recombine indirectly via intermediate resonant states that involve
44 capture into high Rydberg orbitals. High Rydberg states are easily

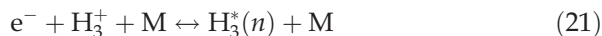
01 perturbed by neighboring particles, in particular the electronic angular
02 momentum can be altered by l -mixing collisions and the decay by dis-
03 sociation strongly depends on the electronic angular momentum. The
04 resonant states that play a role in the binary recombination are primarily
05 those in which the ion core is vibrationally excited by the JT interaction.
06 Here the relevant electronic states have relatively low principal quantum
07 numbers (around 6–8), and low angular momentum which makes pre-
08 dissociation fairly efficient compared to autoionization. If one assumes
09 that all captured electrons predissociate, as is done in some simplified
10 treatments (Jungen & Pratt, 2009), then electron capture is the rate limit-
11 ing step and any additional third-body stabilization mechanism will have
12 no effect. On the other hand, if autoionization is not negligible, then
13 l -mixing by third-body interactions may lead to states that are no longer
14 capable of autoionization, but can be stabilized by further collisions. That
15 would enhance recombination. A mechanism of this kind was once
16 proposed (Gougousi et al., 1995) to explain H_3^+ recombination at a time
17 when the binary recombination mechanism was not as well established
18 as it is now. The l -mixing due to electrons was thought to be the most
19 important ingredient. In hindsight, the proposed mechanism employed
20 unrealistically long resonance lifetimes, which were based on experimen-
21 tal observations in merged-beam experiments.

22 A different mechanism for a more efficient third-body-assisted recom-
23 bination process has recently been proposed by Glosik et al. (2009a,b).
24 It shares some features (like l -mixing) with the model of Gougousi et al.,
25 but it focuses on resonant states formed by capture into rotationally
26 excited core states, which form Rydberg states with higher principal
27 quantum number ($n = 40$ – 80) and invokes l -mixing due to ambient neu-
28 tral atoms (helium in particular). These states do not usually contribute
29 much to recombination since they tend to decay quickly by autoioniza-
30 tion, but they can have fairly long lifetimes (e.g. >10 ps) and are thus good
31 candidates for l -mixing. If one now had a further mechanism that stabilizes
32 the population of these Rydberg molecules, i.e., renders them incapable of
33 reverting to an autoionizing state, the overall recombination rate would be
34 enhanced and the neutral density would be one controlling factor in the
35 recombination in the afterglow plasma. Using theoretically calculated life-
36 times of the initially formed autoionizing states and estimates of the
37 l -mixing efficiency due to helium atoms, and assuming that a large number
38 of Rydberg states (principal quantum numbers from 40 to 100) contribute,
39 the authors succeeded in deriving a three-body rate coefficient that comes
40 close to the experimental value. However, the assumptions underlying his
41 model are not realistic: Firstly, the authors' estimate assumes a very high
42 l -mixing efficiency of the helium atoms, that is appropriate only for small
43 principal quantum numbers, while theoretical calculations (Hickman,
44 1978, 1979) show that the efficiency of l -mixing due to helium falls off

01 rapidly with principal quantum number as $n^{-2.7}$ for $n > \sim 15$. Secondly, if
 02 one invokes l -mixing due to helium atoms as the rate limiting step, one
 03 should also consider l -mixing by electrons, which is known to be faster by
 04 many orders of magnitude than that due to helium atoms, and its effi-
 05 ciency rises with the fifth power of the principal quantum number (Dutta
 06 et al., 2001). In the range $n = 40$ – 80 , in typical afterglows with ionization
 07 fractions of about 3×10^{-7} , l -mixing by electrons would be more efficient
 08 by factors from 10 to 10^4 than by helium atoms. Thus, one would also
 09 expect a very efficient electron-assisted recombination process, for which,
 10 however, there is little experimental evidence. The relevant rate coefficients
 11 will be discussed later. The third problem is that this model leaves unan-
 12 swered the question how the l -mixed states are eventually stabilized.
 13 Collisional stabilization by stepwise n -reducing collision with either elec-
 14 trons or atoms may occur, but the efficiency of such collisions is not
 15 expected to be higher than for atomic systems such that the overall process
 16 is not likely to be faster than collisional radiative recombination of atomic
 17 systems.

18 The model also has a more basic deficiency. It focuses on the lifetime of
 19 the initially formed rotational autoionizing resonances in low l -states and
 20 then assumes that higher l -states are exclusively populated by l -mixing.
 21 A more complete model should include three-body capture of electrons
 22 into all l -states by rotationally excited H_3^+ ions and its inverse, collisional
 23 ionization. For high n -states (with binding energies below ~ 4 KT) collisional
 24 ionization occurs on a time scale that is much shorter than the time
 25 scale of recombination in an afterglow plasma such that an equilibrium
 26 population of l -mixed states is always present. Any additional l -mixing
 27 mechanism hence is of no consequence.

28 We will now consider a third mechanism for an efficient three-body
 29 mechanism that is an extension of the collisional dissociative process of
 30 Collins (1965), who realized that three-body capture of electrons into
 31 high Rydberg states of molecules can sometimes lead to predissociating
 32 states. Hence, the slow collisional and radiative descent from high- n to
 33 low- n states, the only stabilization route open to atomic systems, can be
 34 bypassed thus enhancing the overall recombination rate. Collins only
 35 treated a hypothetical model system with a single dissociative state, and
 36 did not consider effects of orbital angular momentum on the rate of
 37 predissociation, which should be included in a fuller treatment. In our
 38 model, we also invoke l -mixing but in the direction from high to low
 39 angular momenta and stabilization by predissociation of low l -states.
 40 We assume that in the plasma an equilibrium population of high Ryd-
 41 berg states, denoted by H_3^* , is maintained by three-body capture and its
 42 inverse, collisional ionization, i.e.,



01 and that the equilibrium constant $K(n)$ of this reaction is approximately
02 given by the Saha equilibrium

$$03 \quad \frac{[H_3^*(n)]}{[H_3^+]n_e} = K(n) = n^2 \lambda_{th}^3 e^{E_n/kT}, \quad (22)$$

06 where n is the principal quantum number and λ_{th} is the thermal de
07 Broglie wavelength of the electrons at temperature T , i.e.,

$$09 \quad \lambda_{th} = \frac{h^2}{(2\pi m_e kT)^{1/2}} \quad (23)$$

11 and E_n is the ionization potential of the Rydberg state. The assumption is
12 made that three-body capture populates all l and magnetic substates m_l
13 evenly. This seems justified since the inverse process, collisional ioniza-
14 tion, depends only weakly on angular momentum of the Rydberg state.
15 In the traditional theory of collisional radiative recombination of atomic
16 ions, one now considers the departures from the thermal equilibrium
17 due to the downwards collisional and radiative cascading transitions
18 (Stevelfelt et al., 1975). Under the conditions of the afterglow experiments
19 discussed here (electron densities $<4 \times 10^{10} \text{ cm}^{-3}$, helium densities
20 $<3 \times 10^{17} \text{ cm}^{-3}$), the effective binary rate coefficients due to either electron
21 or helium stabilized recombination at 300 K are on the order of $10^{-9} \text{ cm}^3/\text{s}$,
22 and make a negligible contribution to the binary recombination coeffi-
23 cient of $\sim 10^{-7} \text{ cm}^3/\text{s}$. Since we are seeking a three-body mechanism that
24 is far more efficient, we ignore all collisionally induced and radiative
25 transitions. Instead, we focus on other mechanisms that stabilize $H_3^*(n)$.
26 Any process, that stabilizes $H_3^*(n)$ with frequency ν_s , will enhance the
27 overall recombination by the amount

$$29 \quad \Delta\alpha(n) = K(n)\nu_s(n). \quad (24)$$

31 If many such states exist, the overall recombination rate will exceed the
32 binary rate by the sum of $\Delta\alpha$ over a range of n

$$34 \quad \Delta\alpha = \sum_{n_{\min}}^{n_{\max}} K(n)\nu_s(n), \quad (25)$$

36 and the effect may become comparable to the binary rate coefficient. The
37 range of n will be discussed further below. For exploratory purposes, we
38 assume that only s-states within a range of n predissociate on a time scale
39 faster than l -mixing so that l -mixing becomes the rate limiting step. Let us
40 first consider l -mixing due to electrons. It is known that electrons are very
41 efficient in inducing l -mixing. The cross section for the process at an
42 electron energy of 5 meV is approximately (Dutta et al., 2001)

$$44 \quad \sigma'_{e, \text{mix}} = 4.4 \times \pi a_0^2 n^5, \quad (26)$$

01 slightly smaller (by a factor of ~ 0.65) for electrons with thermal energy at
 02 300 K. The corresponding rate coefficient is taken as

$$03 \quad k'_{e,\text{mix}} = v_e \sigma'_{e,\text{mix}}. \quad (27)$$

04
 05 This rate coefficient describes the transfer from a given l, m_l state into
 06 any one of the other $n^2 - 1$ states. What we need for our purpose is the
 07 rate of transfer from any of the $n^2 - 1$ states to a particular state, namely
 08 $l = 0$, which will be smaller by the factor $1/(n^2 - 1)$. For simplicity, we take
 09 the factor as $1/n^2$.

10 Hence, the needed l -mixing rate $k_{e,\text{mix}}$ is taken as $k'_{e,\text{mix}}/n^2$ and rises
 11 with n as n^3 . Inserting the relevant numbers leads to an estimate of
 12 $k_{e,\text{mix}} = n^3 \times 2.7 \times 10^{-9}$ [cm^3/s]. The actual mixing rate v_{mix} , i.e., the product
 13 $n_e k_{e,\text{mix}}$ [1/s], is not necessarily equal to the rate limiting stabilization
 14 frequency in Equation (24), at least not for all values of n . If one made
 15 that assumption, the summation in Equation (25) would diverge strongly!
 16 One needs to take into account that the rate of predissociation of the
 17 s-states will be a declining function of n . A crude estimate may be based
 18 on the classical expectation that the rate at which an electron in an s-state
 19 will “collide” with the ion core is proportional to the classical orbiting
 20 frequency, which scales as $1/n^3$. This means that the l -mixing frequency
 21 increases as n^3 , while the predissociation frequency declines as $1/n^3$. If one
 22 views l -mixing and predissociation as two “conductances” in series, the
 23 combined inductance would rise as n^3 at low n , but fall off as $1/n^3$ at
 24 high n , but we do not know *a priori* where the “crossover” might be.
 25 Experimental measurements of $\text{H}_3(n)$ predissociation spectra (Mistrík
 26 et al., 2001) show that predissociation rates of s-states fall below 10^6 [1/s]
 27 around $n = 40$, which is to be compared to the expected l -mixing rate at an
 28 electron density of 10^{10} [cm^{-3}] of about 1.7×10^6 [1/s]. The exact numbers
 29 are not critical but it seems plausible that the summation in Equation (25)
 30 should be cut off somewhere around $n = 40$. If one now performs the
 31 summation from $n_{\text{min}} = 12$ to $n_{\text{max}} = 40$, one finds that electron stabilized
 32 recombination makes only a fairly small contribution to the overall recom-
 33 bination. At the highest electron densities that are commonly used in
 34 afterglow experiments, $n_e = 4 \times 10^{10} \text{ cm}^{-3}$, the effect would be to increase
 35 the binary rate by only about $1 \times 10^{-8} \text{ cm}^3/\text{s}$, larger than the enhancement
 36 by purely collisional radiative recombination, but still only a small part of
 37 the binary rate coefficient. Our estimates indicate that the electron density
 38 will play only a minor role in typical afterglow experiments of H_3^+ recom-
 39 bination. This agrees with experimental observations.

40 The situation is quite different when one considers helium atoms as
 41 third bodies. The estimates follow very much the same scheme as for
 42 electrons, but the l -mixing rate is now taken as

$$43 \quad k_{\text{mix, He}} = 3.1 \times 10^{-5} \frac{1}{n^2} \frac{1}{n^{2.7}} [\text{cm}^3/\text{s}]. \quad (28)$$

This value is obtained from the cross sections given by Hickman (1978, 1979, and 1981), multiplied with the average velocity for H_3^+/He collisions at thermal energy (300 K). The fast fall-off with increasing n makes the summation in Equation (25) convergent at high n so that the high- n cutoff does not matter much. However, it is not obvious where to cut off the summation at low n . We chose a low- n cutoff at the value of n for which the ionization potential of that state exceeds thermal energy by a factor of 4 or greater. The summation then leads to the estimate that the recombination rate at $n(He) = 3 \times 10^{17} \text{ [cm}^{-3}\text{]}$ (10 Torr at 300K) would exceed the binary rate by $8 \times 10^{-8} \text{ [cm}^3/\text{s}]$ (see Figure 13). The corresponding three-body rate coefficient with helium at 300K would be $2.6 \times 10^{-25} \text{ [cm}^6/\text{s}]$, which agrees with the experimental value of $(2.5 \pm 1.2) \times 10^{-25} \text{ [cm}^6/\text{s}]$ (Glosik et al., 2009a), far better than one has a right to expect. The corresponding rate coefficient for D_3^+ would be $(2.2 \pm 1.2) \times 10^{-25} \text{ [cm}^6/\text{s}]$, very similar to the measured values of $(1.8 \pm 0.6) \times 10^{-25} \text{ [cm}^6/\text{s}]$ (Glosik et al., 2009b). Our model would predict only a small increase of the three-body coefficient at reduced temperatures, by about 50% at 100K.

We note that helium is particularly effective in inducing l -mixing because the electron-helium momentum transfer cross section is large and nearly independent of energy. By comparison, neon should be far less effective (see Hickman, 1978). There is only a single measurement (Macdonald et al., 1984) of H_3^+ recombination in neon buffer gas (at 20 Torr) which actually yielded a significantly lower recombination rate than a very similar measurement in helium.

We also consider a third stabilization mechanism that involves the hydrogen gas that is usually present in afterglow experiments of H_3^+ recombination. It is known that H_5^+ ions recombine much more rapidly

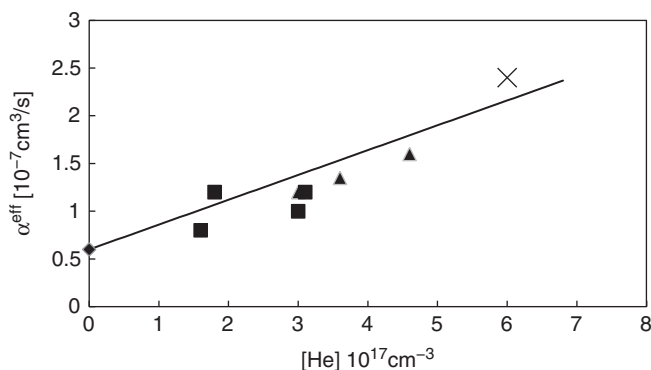


Figure 13 Observed dependence of the H_3^+ recombination coefficient at $T=300 \text{ K}$ on the experimental helium density. Squares and triangles: data from Glosik (2009a). Cross: data from Leu et al. (1973). The line indicates the density dependence expected from the model described in the text

01 with electrons with a 300 K rate of $a(\text{H}_5^+) = 1.8 \times 10^{-6}$ [cm^3/s]
 02 (Macdonald et al., 1984). While the equilibrium concentration of H_5^+
 03 is small compared to that of H_3^+ , transient H_5^* Rydberg molecules
 04 could be formed in collisions of H_3^* with H_2 , i.e., a reaction of the
 05 type



07
 08
 09 The forward rate coefficient should be comparable to that of fast
 10 ion-molecule reactions, i.e., $k(\text{H}_2) \sim 2 \times 10^{-9}$ cm^3/s . Once formed,
 11 these H_5^* probably predissociate very rapidly, since the recombina-
 12 tion of H_5^+ ions is extremely fast (Macdonald et al., 1984). If one adds
 13 this as an additional stabilization mechanism to H_3^+ recombination,
 14 the effective stabilization frequency that enters Equation (24) would
 15 be given by $[\text{H}_2]k(\text{H}_2)$. The proper choice of n_{max} in the summation
 16 over n is not obvious in this case. To reproduce the large experimental
 17 value (Gougousi et al., 1995) of the three-body rate of about
 18 2.5×10^{-23} cm^6/s , the summation would have to include n values
 19 up to about 70 and this does not seem to be unreasonable. This may
 20 also explain the rather high value obtained by Amano (1990), how-
 21 ever, that experiment also employed very high electron densities
 22 (5×10^{11} cm^{-3}), and it is difficult to separate possible effects of elec-
 23 trons from those of H_2 . The experiment did not show a measurable
 24 effect of H_2 on the observed recombination rate.

25 The foregoing estimates indicate that H_3^+ recombination in an after-
 26 glow plasma, at least in part, involves a mechanism in which the neutral
 27 gas density plays a role. This agrees with experimental findings. Helium
 28 seems to particularly effective in promoting recombination.

29 One would not expect a significant effect of the electron density if it is
 30 below 4×10^{10} cm^{-3} . Again, this agrees with experiments in the range of
 31 electron densities commonly present in afterglows.

32 The three-body model that we propose is by no means complete:
 33 The assumption that the equilibrium concentrations of the Rydberg
 34 states are only slightly perturbed is a serious simplification and ignores
 35 competition between different stabilization mechanisms. Constructing a
 36 more rigorous model, however, looks like an exceedingly complicated task.

37

38

39 7. COMPARISON OF STORAGE RING DATA

40

41 The storage ring measurements have yielded remarkably consistent data
 42 over the years. While some of the early measurements (Jensen, 2001;
 43 Larsson et al., 1993) gave slightly higher cross sections than was found
 44 in later work, those were shown to be due to rotational excitation of the

ions. Nearly complete control of the rotational population was eventually achieved by using either a supersonic jet expansion ion source (CRYRING) or a cryogenically cooled radio-frequency multipole trap (TSR). The actual rotational populations were verified by optical absorption measurements, and it was shown that only the two lowest rotational states were populated. As far as is known from experiment, the rotational populations in the circulating beam do not differ significantly from those injected from the ion source.

If one compares the two results obtained in the CRYRING (McCall et al., 2004) and in the TSR (Kreckel et al., 2005), one is immediately struck by the fact that the observed energy dependence is nearly identical in both experiments. It should be noted, however, that the TSR data were normalized to the CRYRING data at an energy of 10 eV. The absolute magnitude of the cross sections and the overall dependence on energy are well reproduced by theory which seems to say that the binary recombination cross section has been firmly established. However, if one compares the finer structure of the measured and calculated cross sections (see Figure 14), one notices that the theoretical results show several narrow peaks that are not present in the experimental data. It is not clear at this time if this discrepancy is due to approximations made in the theory or if it indicates a possible systematic problem in the

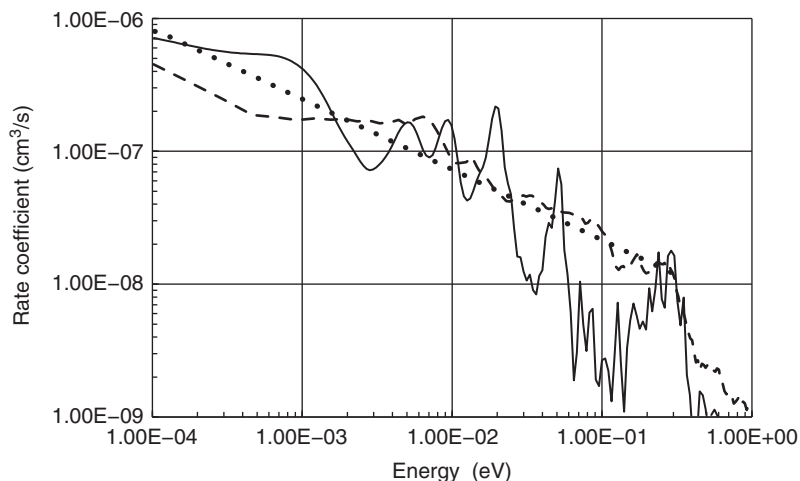


Figure 14 Comparison of the experimental CRYRING data of McCall et al. (2004) (dashed line) to the theoretical results of Fonseca dos Santos (2007) (solid line), for a rotational temperature of 13 K. The theoretical data have been convoluted with the experimental energy resolution and have been corrected for the “toroidal effect.” Drawn from data supplied by M. Larsson and V. Kokoouline. The dotted line represents results of the approximate Jahn–Teller theory of Jungen and Pratt (2009)

01 measurements. Third-body-assisted recombination of the kind that seem
 02 to occur in afterglows can almost certainly be excluded since the relevant
 03 particle densities are lower by many orders of magnitude. Such effects
 04 have been considered in storage ring experiments of dielectronic recom-
 05 bination to explain the higher-than-expected recombination cross sec-
 06 tions in the limit of very energies (Pajek and Schuch, 1997, 1999). Since
 07 DR is much faster than dielectronic recombination, it should be much less
 08 affected by third-body effects and such effects are probably negligible.

09 One may also ask if the magnetic field in the interaction region of storage
 10 rings (570 mT in the TSR, 300 mT in the CRYRING) and small electric stray
 11 fields (estimated to be on the order of 1 V/cm) have an effect on the
 12 recombination. Wolf et al. (2006) mention such effects without reaching a
 13 conclusion as to their importance. Several possibilities exist: If for some
 14 reason l -mixing due to small fields were to occur on a time scale comparable
 15 to that of autoionization or predissociation, this could affect the relative
 16 importance of the two decay channels and alter the recombination rate. If
 17 l -mixing should produce long-lived high- l states of H_3 , those presumably
 18 would be field-ionized in the demerging magnets and the net effect would
 19 be that the observed recombination rate would be too small. If, on the other
 20 hand, l -mixing enhances the rate of predissociation, then the observed rates
 21 would come out larger than they would be in the absence of fields. One
 22 experiment (Larsson et al., 1997) et al. has been performed (for D_3^+) in which
 23 small electric fields (on the order of 30 V/cm) were deliberately added and
 24 those gave negative results. The negative finding is not totally conclusive as
 25 was mentioned by the authors of that study. Ideally one should remove all
 26 stray fields, rather than adding to them, which in practice, of course, is
 27 impossible to achieve. Some theoretical calculations have been made to
 28 assess l -mixing due to small static fields (Chao et al., 1998) in the context
 29 of ZEKE spectroscopy. It appears that small fields on the order of a few V/
 30 cm can induce l -mixing in Rydberg states, but the time constants are found
 31 to be on the order of 1–10 ns, which is much longer than likely lifetimes of H_3
 32 autoionizing states. Hence, in the absence of evidence to the contrary, we do
 33 not believe that stray fields will have significant effects but the question may
 34 deserve further scrutiny. The same conclusion has been reached by the
 35 storage ring experimenters (Wolf, private communication).

36

37

38 8. H_3^+ PRODUCT BRANCHING

39

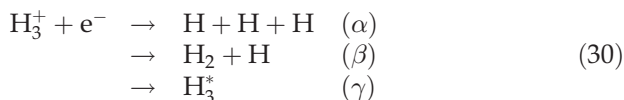
40 The first measurements of the product branching ratios

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01 were carried out by an extension the MEIBE merged-beam apparatus in
02 which a grid was placed in front of the energy-sensitive detector. These
03 experiments (Mitchell et al. 1983) were extremely challenging, suffered
04 from fairly poor signal-to-noise ratio, and the vibrational state of the
05 recombining ion was not known very well. Florescu-Mitchell and
06 Mitchell (2006) provide a synopsis of the results of this work: channel
07 α accounted for typically 52%, channel β for 40%, and surprisingly
08 channel γ for the remaining 8%. In later work it was found that the
09 third channel appeared to increase when the field strength in the demer-
10 ging region of the experiment was reduced which seems to indicate that
11 a fraction of the H_3^* were field-ionized in that region. If that interpreta-
12 tion is correct, which is still not clear at this time, then the lifetime of
13 these metastable particles must have been on the order of or larger than
14 about 100 ns, the flight time from the interaction region to the detector. It
15 was this observation that motivated Gougousi et al. (1995) to propose
16 that the recombination of H_3^+ in afterglow plasmas involved stabiliza-
17 tion of metastable H_3^* by subsequent reactions with hydrogen
18 molecules.

19 Later work by Datz et al. (1995) using the CRYRING provided more
20 detailed and presumably more accurate energy-resolved branching
21 fractions for H_3^+ recombination. At energies below 0.3 eV, decay
22 channel α into three H-atoms was found to account for 75% of the
23 total, channel β for 25 %, and channel γ was not observed at all. Datz
24 et al. state that metastable H_3^* Rydberg molecules with principal
25 quantum numbers below about 7 should have survived without
26 being field-ionized while passing through the demerging magnet
27 and hence should have been detectable. The authors concluded that
28 formation of high Rydberg states probably does not contribute much
29 to the recombination. The branching fractions observed by Datz et al.
30 are very well reproduced by the statistical model of Strasser et al.
31 (2003). Very detailed two-dimensional investigations of the kinematics
32 of the dissociation into three H atoms and vibrational distributions of
33 the H_2 product were also reported by Strasser et al. (2001, 2002a, and
34 2002b).

35 It is difficult to determine precise branching fractions for H_3^+
36 recombination afterglow measurements since there are numerous
37 extraneous sources of H atoms. In the only such experiment (Johnsen
38 et al., 2000) that has been performed, the H atom yield was mea-
39 sured by converting the H atoms to OH by reacting H with NO_2 and
40 then measuring the OH concentration using laser-induced fluores-
41 cence. The results indicated that branch α accounts for 63% of the
42 total, roughly compatible with the storage ring data. It was not
43 possible to measure the H_2 yield directly or to find evidence of
44 long-lived H_3^* .

9. ISOTOPE EFFECTS

It is difficult to perform afterglow studies of the recombination of H_2D^+ and HD_2^+ , but several storage ring measurements have been published. A detailed discussion and references to theoretical papers can be found in the book by Larsson and Orel (2008). It appears that the agreement between theory and experiment is less satisfactory, especially for HD_2^+ , and that more theoretical work is needed. D_3^+ has been studied by both afterglow (Glosik et al., 2009b; Gougousi et al., 1995; Laubé et al., 1998) and storage ring methods (Larsson et al., 1997). Most of the experimental data indicate that D_3^+ recombines more slowly than H_3^+ by a factor of 2–3, although one afterglow experiment (Laubé et al., 1998) gave nearly the same value for both ions. Arguing from a simplified theoretical treatment, Jungen and Pratt (2009) suggest that the recombination coefficient of D_3^+ should be smaller than that of H_3^+ by a factor of $\sqrt{2}$, a weaker isotope effects than predicted by the theory of Kokoouline and Greene (2003).

10. CONCLUSIONS

Largely motivated by applications to ionospheric physics, astrophysics, and technical applications of cold, nonequilibrium plasmas, studies of DR have been an ongoing communal effort for many years. In the case of H_3^+ , results have often been difficult to reconcile, and while the discussions have been contentious at times, most often they were conducted in the spirit of collegiality, and we have now reached a state that is close to a consensus. Larsson et al. (2008), in their concise and well-presented review of the status of H_3^+ recombination studies, ask the question if “the saga has come to an end.” They conclude that the “saga” is not quite finished but that it is approaching a satisfactory finale in which experiment and theory converge to a common picture of this important process. We largely concur with their assessment. As far as binary recombination is concerned, the consistency of storage ring data obtained in different experiments strongly suggests that the data are reliable and are applicable to conditions in the interstellar medium. The absolute magnitude of the coefficients is well reproduced by theory, but it would be highly desirable to refine the theoretical treatments to the point where they accurately reproduce the finer structure of the observed energy dependence of the cross section.

Larsson et al. in their review point to the outstanding problem of reconciling the afterglow and storage ring measurements, in particular those that yielded coefficients far below the binary value. We have examined the data in some detail and find that those measurements

were not performed under conditions that permit an unambiguous inference of substantially lower recombination coefficients. We also conclude that recombination in a plasma containing substantial densities of neutral and charged particles involves additional third-body-assisted mechanisms that should be taken into account in applications other than those to highly dilute interstellar media. In this we agree with the conclusion of Glosik et al. (2009a and 2009b) that neutral particles play an important part in such processes, but we propose an alternate, although still very approximate, model that seems to fit observations fairly well.

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