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The dissociative recombination of H_3^+ – a saga coming to an end?

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ABSTRACT

Major progress has been made in the understanding of how H_3^+ recombines with thermal and sub-thermal electrons, a process of great importance to the chemistry of diffuse interstellar clouds. Two independent ion storage ring experiments with rovibrationally cold H_3^+ ions are in excellent agreement, and quantum mechanical calculations agree with the storage ring results quantitatively for the thermal rate constant, if not in all details concerning the cross section. The recombination mechanism is understood. A direct consequence of this progress is that the cosmic-ray ionization rate in diffuse clouds must be shifted upwards to a value larger than $10^{-16}\,s^{-1}$.

1. Introduction

Readers examining the literature on the dissociative recombination of H_3^+ with electrons must be genuinely puzzled by the titles they encounter: 'Enigma of H_3^+ dissociative recombination' [1], 'Dissociative recombination of H_3^+ and some other interstellar ions: a controversy resolved' [2], 'Dissociative recombination of H_3^+. Experiment and theory reconciled' [3], all published in 1993, and with further titles such as 'Is the dissociative recombination of H_3^+ really slow? A new spectroscopic measurement of the rate constant' [4], 'Mystery of an interstellar ion' [5], 'H_3^+ in the diffuse interstellar medium: the enigma related to the dissociative recombination' [6], 'Help!!! Theory for H_3^+ recombination badly needed' [7], and 'Enigma of H_3^+ in diffuse interstellar clouds' [8]. The title of a recent paper on H_3^+ in a high-profile journal is also noteworthy: 'A key molecular ion in the universe and in the laboratory' [9].

To this selection of publications should be added the fact that H_3^+ twice during the last 7 years has been the subject of Royal Society Discussion Meetings [10,11]. Thus, it is clear that H_3^+ is a molecular ion of singular importance in the laboratory and in molecular astrophysics, and that there is something enigmatic about the recombination of H_3^+ with electrons and its presence in diffuse molecular clouds.

In this Frontiers article we will describe recent progress in the understanding of H_3^+ dissociative recombination with electrons and the significance of this to the chemistry of diffuse molecular clouds and the cosmic-ray ionization rate. This is article not intended to be a full review; the reader is referred to a chapter in the book by Larsson and Orel [12] for a detailed review of electron

recombination of H_3^+, and to the article by Larsson [13] for a status report as of the year 2000.

2. The controversy regarding H_3^+ recombination

The controversy over the dissociative recombination of H_3^+ has concerned the enormous spread in the experimentally measured rate constants, the quantum state population of the H_3^+ ions used in the experiment, and the interpretation of whether a specific experimental result was supported by theory or not. A recombination rate constant for a small molecular ion such as H_3^+ that has varied over four orders of magnitude in different experiments [12,13] is an exceptional case even for a quantity which is difficult to measure with high accuracy. How was this possible and why was theory not in a better position to guide the experimentalists? After all, the lowest energy levels of H_3^+ could be predicted theoretically with spectroscopic accuracy by *ab initio* methods already in the 1980s. And how was it possible that some of the experimental results exercised such a huge influence on the modeling of interstellar diffuse molecular clouds during this same time period? The answers to some of these questions, if they are at all possible to answer, extend beyond the question of scientific results and into the realm of the sociology of science.

The dissociative recombination process for H_3^+ can be written as

$$
\begin{aligned}
H_3^+ + e &\rightarrow H + H + H \\
&\rightarrow H_2 + H
\end{aligned}
\tag{1}
$$

The primary concern here is the rate at which this reaction proceeds, which inevitably leads to the question of the mechanism of the reaction. Both of these questions reside at the center of the enigma.

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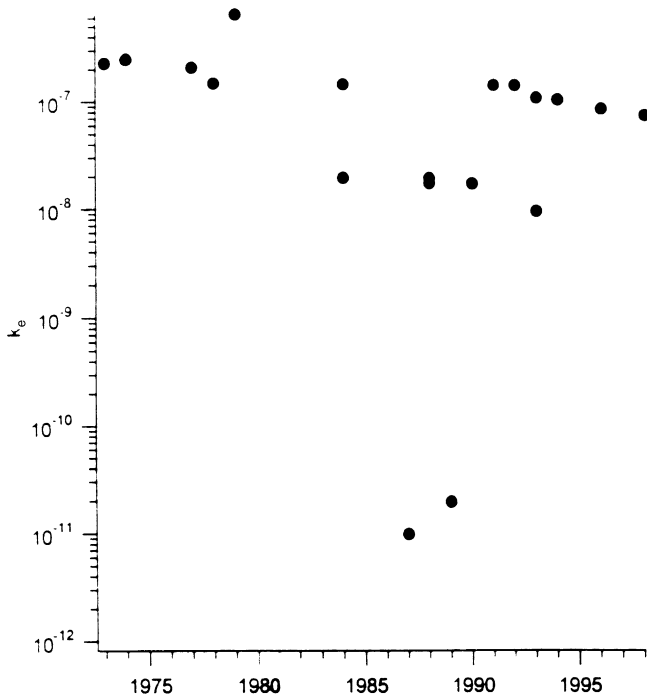 E-mail address: mats.larsson@physto.se (M. Larsson).

Fig. 1. Laboratory measurements of the rate constant k_e over the years. (reproduced from Oka [6])

Fig. 1 shows the results of laboratory measurements of the rate constant k_e during more than 20 years. We do not list the references to all those measurements here; most of them are available in Refs. [7,13]. The first measurements in the early 1970s gave rate constants near 10^{-7} cm^3 s^{-1}, which is a typical rate with which dissociative recombination reactions proceed. The surprise came in 1984, when Adams et al. [14] using a flowing afterglow/Langmuir probe technique found H$_3^+$ to recombine much slower than earlier investigators found. They were only able to put an upper limit of 2×10^{-8} cm^3 s^{-1} to the rate constant, a limit that was later lowered by the Birmingham group to 10^{-11} cm^3 s^{-1} [15]. The timing was such that Adams et al. could support their measured rate constant with theoretical calculations that were done essentially simultaneously with the afterglow studies. The theoretical results of Michels and Hobbs [16] were known in Birmingham through private communication, and gave full support of a low rate constant for H$_3^+$ in its lowest vibrational level. Or did they?

Fig. 2a and b show potential energy curves for H$_3^+$ and H$_3$ in C_{2v} geometry calculated by two different groups. Fig. 2b shows the potential curves calculated by Michels and Hobbs [16], but the very similar curves of Kulander and Guest [17] shown in Fig. 2a were calculated 5 years earlier (and referenced by Michels and Hobbs). Interestingly, Kulander and Guest did not draw the same conclusions as Michels and Hobbs. The latter were explicit in their conclusion: 'We estimate that the currently accepted values of the e + H$_3^+$ recombination coefficient for interstellar conditions are two orders of magnitude too large' (p. L27 in [16]). Kulander and Guest were much more cautious. They concluded that because of the unfavorable crossing of the resonant state with respect to the equilibrium configuration of H$_3^+$, Rydberg states in H$_3$ must play an important role when low-energy electrons recombine with H$_3^+$ in its ground vibrational level. They noted that in the C_{2v} geometry, the Rydberg states are well separated from the H$_2$ (b $^3\Sigma a_u^+$) + H(1s) state dissociating to the three H(1s) atoms, but that preliminary results indicated that a coupling could occur in a collinear configuration. However, the paper by Michels and Hobbs [16] had a much larger impact on the community, and their theoretical support of a very low rate for
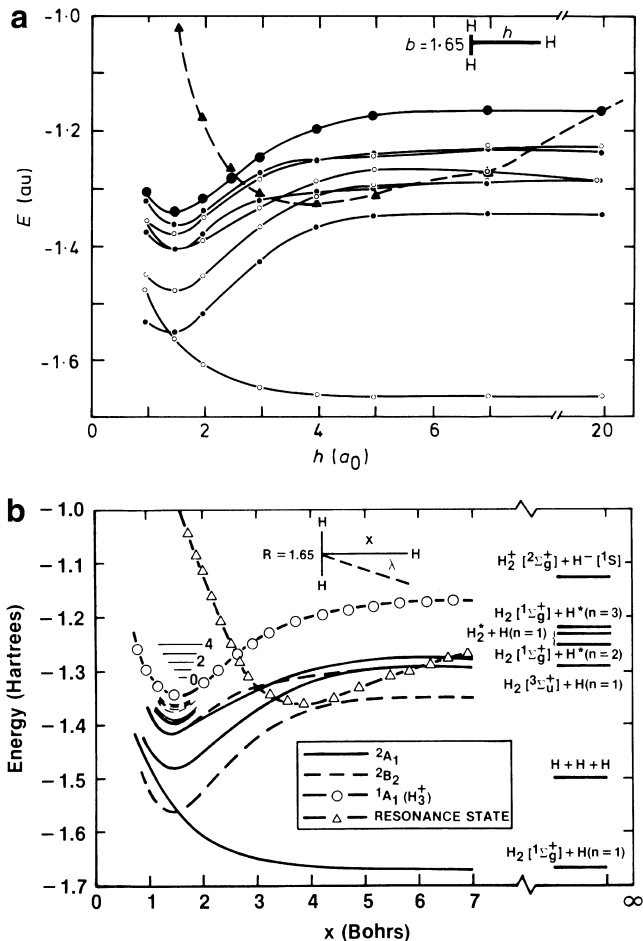

Fig. 2. (a) Potential curves of H$_3^+$ and H$_3$ calculated by Kulander and Guest [17]. The following symbols are used: (○) ^{2}A$_1$ states; (●) ^{2}B$_2$ states; (▲) resonant state; (●) H$_3^+$ ground state. (b) Potential energy curves of H$_3^+$ and H$_3$ calculated by Michels and Hobbs [16].

recombination of H$_3^+$ in its lowest vibrational level was often quoted. But theory seemingly did more than explain the very low rate measured by the Birmingham group; it also explained why other experiments gave too high a rate: contamination of vibrationally excited levels would result in a higher rate coefficient, an argument in particular applicable to the electron–molecular ion beam experiments. It also elegantly explained why H$_3^+$ was removed fast in the early part of the Birmingham afterglow apparatus; it takes some time to collisionally deactivate vibrational excitations in H$_3^+$ and as long as the afterglow contained vibrationally excited levels, recombination was fast.

The combined theoretical and experimental papers suggesting a very slow recombination of H$_3^+$ at interstellar conditions strongly influenced the leading researchers in molecular astrophysics. Interstellar H$_3^+$ is formed by cosmic-ray ionization of molecular hydrogen to form H$_2^+$, followed by the ion-molecule reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{2}$$

This reaction is so effective that H$_3^+$ is the major ion produced by discharges in hydrogen gas. In diffuse interstellar clouds H$_3^+$ is primarily destroyed by dissociative recombination, and when this destruction route was ruled out in [14–16], the abundance of H$_3^+$ was grossly overestimated [18,19], and a recombination rate constant of 10^{-10} cm^3 s^{-1} at 40 K was used in the hugely influential paper on diffuse cloud chemistry by van Dishoeck and Black [20] The first observation of H$_3^+$ in a diffuse cloud came a decade later [21],

but it is amusing to speculate what would have happened if H_3^+ had been discovered in 1988. This is how Liszt [22] expressed it: 'this led the authors [18,19] to a gross overprediction of $N(H_3^+)$, which they suggested would be observable; their suggestion seems not to have been acted upon in a timely manner, thus depriving the world of a seeming corroboration of the incorrect rate' (p. 627 in Ref. [22]). Liszt continues: 'instead, the recombination rate was corrected [4,23,25] lowering the expectations for the presence of H_3^+, and, by the time it was widely detected, this was considered surprising'.

It is correct that the infrared absorption spectroscopy measurement of the H_3^+ concentration in a decaying plasma [4], and the application of the ion storage ring CRYRING to the measurement of the cross section for reaction (1) discredited the 10^{-11} cm^3 s^{-1} rate constant. But the situation was still not satisfactory. Smith, now in team with Spanel [2,3], remeasured the recombination rate constant of H_3^+ using an improved version of the flowing afterglow/ Langmuir probe technique and found a value of $(1–2) \times 10^{-8}$ cm^3 s^{-1}, much higher than the extreme 10^{-11} cm^3 s^{-1} result but still a factor of 10 lower than the rates measured by Amano [4,25] and Sundström et al. [24]. As alluded to in the introduction, the titles of the Smith and Spanel papers are misleading; nothing was reconciled in 1993.

The experiments by Amano [4,25], Larsson et al. [23] and Sundström et al. [24] were also not free from objections. Fehér et al. [26] applied the same infrared absorption technique as Amano and concluded that only an upper limit to the rate constant could be extracted from the data. The storage ring experiments, both those of Larsson et al. [23] and Sundström et al. [24], and experiments at other storage rings such as ASTRID [27] and TARN II [28], were performed with vibrationally relaxed ions and agreed very well with each other, but the accompanying rotational distribution remained uncertain. Jensen et al. [27] estimated the rotational temperature to be somewhere between 1000 K and 3000 K, and there are reasons to believe that the rotational temperature was similar in the other ring experiments. Kreckel et al. [29] were able to measure that the H_3^+ ions in their ion storage ring experiment in the TSR contained as much as 0.3 eV of rotational excitation, and they could show that these excitations were too long lived to be removed by spontaneous emission during the half-minute storage in the Test Storage Ring. The storage ring results were supported by a flowing afterglow experiment conducted by Laubé et al. [30], which was satisfactory, but it added to confusion as to why two experiments based on the same technique would give different results [2,3,30].

Theoretical calculations prior to 1993 were restricted to the calculations of the potential energy surfaces mentioned above, or to model calculations. In 1993 the first measurements of the dissociative recombination including the high-energy region were published [23]. These were followed by calculations of the resonance-dominated process by Orel and Kulander [31]. Orel et al. [32] calculated all four states arising from the capture of an electron into the low-lying doubly degenerate e orbital while simultaneously one of the electrons in the $1a_1'$ orbital is excited:

$$H_3^+(1a_1'^2) + e^- \rightarrow H_3(1a_1' e^2) \tag{3}$$
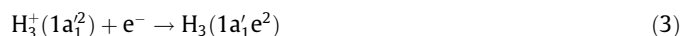
The double degeneracy of the e orbital results in four distinct electronic states. These calculations, which used a complex Kohn electron scattering calculation to obtain resonance energies and widths, and a wave packet calculation of the dissociation dynamics, gave very good agreement with the measured cross section in the high-energy region [31]. This was the first time that experimental and theoretical dissociative recombination cross sections for H_3^+ were explicitly compared, and the outcome was very encouraging. This calculation showed not only that the ion storage ring source
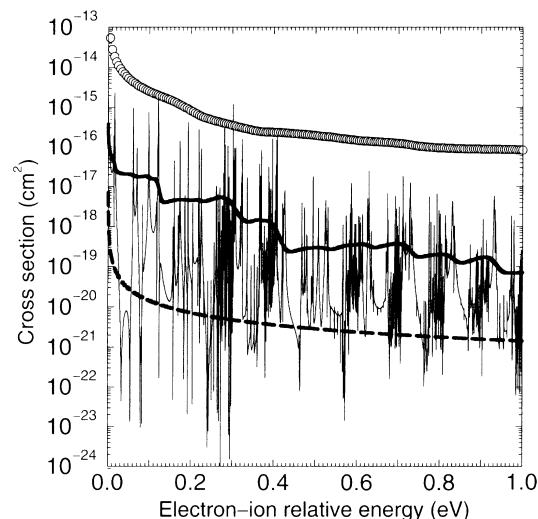
Fig. 3. Dissociative recombination of H_3^+ at low electron energy, calculated within a combined multichannel quantum defect theory/wave packet approach (restriction to the $^2B_2$ symmetry). Dashed line: cross section involving only the direct mechanism through the resonant state shown in Fig. 2. Solid narrow line: total cross section. Circles: CRYRING results from [22]. Solid broad line: total cross section, convoluted according to the anisotropic Maxwell electron-velocity distribution in CRYRING [22]. (reproduced from Schneider et al. [36])

was vibrationally cool, but also that these resonance states were not involved in the low-energy process. However, the question remained – how does H_3^+ recombine at low energies?

Some insight came from calculations by Guberman [33], and independently from Sarpal et al. [34], that had explained dissociative recombination of HeH$^+$, a molecule for which the ground electronic state is crossed by *no* repulsive neutral state. These calculations showed that in this system, nonadiabatic coupling to repulsive HeH states lying outside the classical turning point of the HeH$^+$ electronic ground state causes dissociative recombination. Was this occurring in H_3^+? Schneider and Orel [35] had studied predissociation of the 2s ($^2A_1'$), 3s ($^2A_1'$), and ($^2E'$) Rydberg states to the $^2\acute{E}$ repulsive electronic ground state of H_3. Their use of two-dimensional wave packet calculations and analytic nonadiabatic coupling elements between the 2s ($^2A_1'$), 3s ($^2A_1'$), and 3p ($^2E'$) Rydberg states and the electronic ground state, $^2E'$, produced good agreement with the experimental results of Müller and Cosby [36]. Schneider et al. [37] used the same two-dimensional model and found that the cross section for *direct* dissociative recombination, that is, coupling from the (ion + electron) system to the electronic ground state, $^2E'$, was very small. Adding the *indirect* mechanism, that is the effect of coupling to the higher-lying Rydberg states and hence to the ground state using multichannel quantum defect theory (MQDT), increased the cross section by several orders of magnitude. This large increase in the cross section was caused by this same coupling allowing a greater number of energetically accessible paths to dissociation. Nevertheless, the calculated cross section was at least two orders of magnitude smaller than that measured in CRYRING [23], as can be seen in Fig. 3.

Finally, during the last year of the millennium, a stationary afterglow experiment in Prague resurrected the very low rate constant [38]. Glosik et al. [38] could claim that their low rate was supported by theory [37]; history repeated itself.
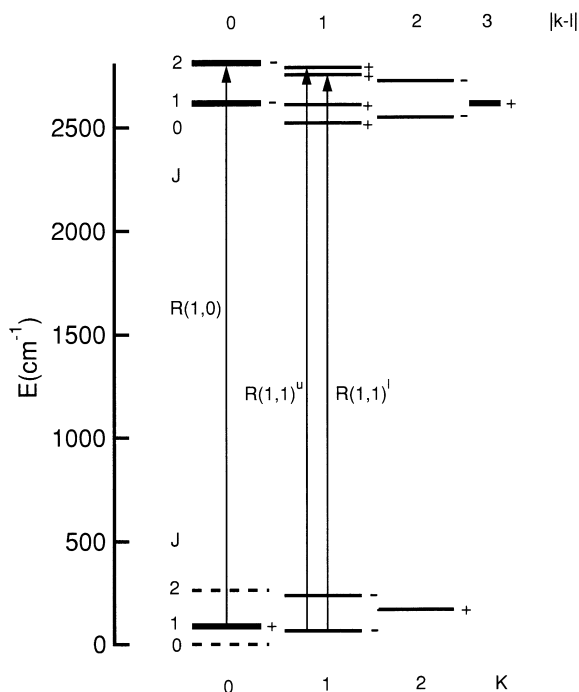
3. Experimental breakthrough

The insight that the storage ring experiments were performed on rotationally hot H_3^+ ions [29], and the realization that the

rotational temperature influenced the dissociative recombination rate constant [39], made it clear that a decisive experiment would have to be performed with H_3^+ ions populating only a few rotational levels of the ground vibrational state. Fig. 4 shows the rotational levels in the ground vibrational state and in the first excited state of the asymmetric stretch. At interstellar cloud conditions, only the two lowest rotational levels are populated, and hence it is the $R(1, 0)$ and the two $R(1, 1)$ lines that are observed in absorption towards diffuse molecular clouds [20]. Because of the great importance of H_3^+ in astrophysics the goal was clear: measure the recombination cross section for H_3^+ ions populating only $J = 1$ (the $J = 0$ level is forbidden by the Pauli principle).
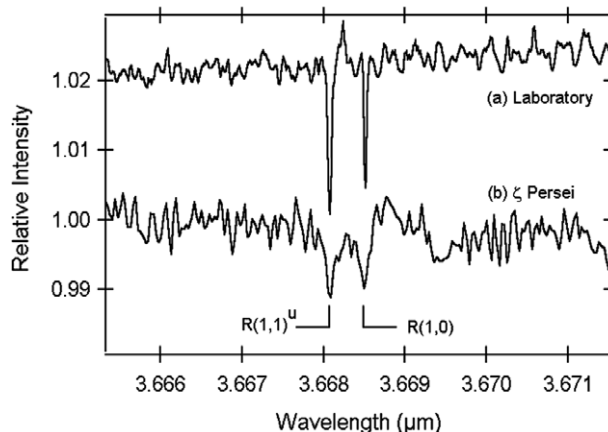
The geometric structure of H_3^+ being an equilateral triangle is both a disadvantage and an advantage for an experimenter who wants to study recombination of rotationally relaxed H_3^+ in an ion storage ring. It is certainly a disadvantage that spontaneous emission from rotationally excited levels is extremely slow owing to the symmetric geometry of H_3^+. On the other hand, if H_3^+ can be produced rotationally cold, it would not interact with the blackbody radiation from the vacuum pipes constituting the storage ring system, and the ions would remain cold even after tens of seconds of storage.

Two different approaches to producing rotationally cold ions were chosen at the storage rings CRYRING and TSR. The effort at CRYRING was carried out in collaboration between research groups in Stockholm and Berkeley. A discharge pinhole supersonic jet expansion was built at Berkeley, characterized by cavity ring-down infrared spectroscopy, and shipped to Stockholm and used as injector for experiments at CRYRING [41–43]. Fig. 5 compares a cavity ring-down spectrum of rotationally cooled H_3^+ with an absorption spectrum towards the diffuse interstellar cloud towards ζ Persei, showing that the supersonic discharge source was capable of producing ions at interstellar conditions.

The TSR team used a cryogenically cooled radiofrequency multipole trap in which the H_3^+ ions from a relatively hot rf storage ion

Fig. 5. Spectra of two H_3^+ transitions arising from the two lowest rotational levels, $J = 1$, $K = 0$ and 1, which are the only levels with significant population in diffuse clouds. $R(1, 0)$ is inherently slightly stronger than $R(1, 1)^u$, and the $J = 1$, $K = 0$ level is somewhat less populated than the $J = 1$, $K = 1$ level by the Boltzmann factor, so the two absorption lines appear with nearly equal strength. The top trace shows the cavity ring-down absorption spectrum of the supersonic expansion source. In this source, H_3^+ number densities of $\sim 10^{11}$ cm^{-3} were produced in the plasma downstream of a 500-µm pinhole through which hydrogen gas at 2.5 atm expanded supersonically into the vacuum. Based on relative intensity measurements of the two lines, the rotational temperature of the plasma was estimated to be 20–60 K depending on conditions. The bottom trace shows a spectrum of a diffuse cloud towards ζ Persei obtained with the CGS4 infrared spectrometer at the United Kingdom Infrared Telescope (UKIRT). (reproduced from McCall et al. [40])

source were trapped and cooled by a buffer gas. The cryogenic trap was then used as injector to the TSR. Fig. 6 shows the first preliminary results from the TSR experiment and the CRYRING results for comparison. One of us (ML) remembers how this result came as a revelation, and an extremely satisfactory confirmation of the CRYRING result. The final results of the TSR experiment [44] are shown in the next section together with the CRYRING results and theoretical results.

4. Theoretical breakthrough

The final theoretical breakthrough came with the work of Kokoouline et al. [45], in which they identified a new mechanism that had not been included in previous work: the Jahn-Teller distortion of the H_3^+ ion induced by the incoming electron. They showed that this Jahn-Teller coupling of electronic and nuclear motion is by far the most important mechanism for electron recombination in this system at thermal energies. Just as the addition of couplings to Rydberg states increased the cross section by orders of magnitude, the Jahn-Teller coupling, which again allowed access to a greater number of dissociative paths, caused a large increase in the cross section. Their first calculation was not quantitative, but was able to establish upper and lower limits to the cross section. Their upper limit corresponded to a rate coefficient of 1.2×10^{-8} cm^3 s^{-1} at 300 K.[1] This was followed [46,47] by a fully quantum mechanical treatment of dissociative recombination of H_3^+. These calculations included a full, three-dimensional treatment of the dynamics, including the Jahn-Teller symmetry breaking effects that had not earlier been included in treatments of dissociative recombination, a correct treatment of indirect recombination via intermediate Rydberg states, and the effect of rotational excitations. This was accomplished by transforming the problem from typical internuclear distance coordinates (r_1, r_2, r_3) into hyperspherical coordinates (R, θ, ϕ) involving the hyperradius R defined by $R^2 = (r_1^2 + r_2^2 + r_3^2)/\sqrt{3}$ and the two hype-

Fig. 4. Rovibrational energy level diagram of H_3^+ showing transitions observed in interstellar clouds. The rotational levels at 2500 cm^{-1} belongs to the $v_2 = 1$ vibrational level (the superscript u stands for 'upper' and l for 'lower'). The $J = 0$, $K = 0$ and $J = 2$, $K = 0$ levels (dashed) in the ground state are forbidden by the Pauli principle. Only $J = 1$, $K = 0$ (*ortho*) and $J = 1$, $K = 1$ (*para*) are populated in cold clouds. (reproduced from McCall [39])
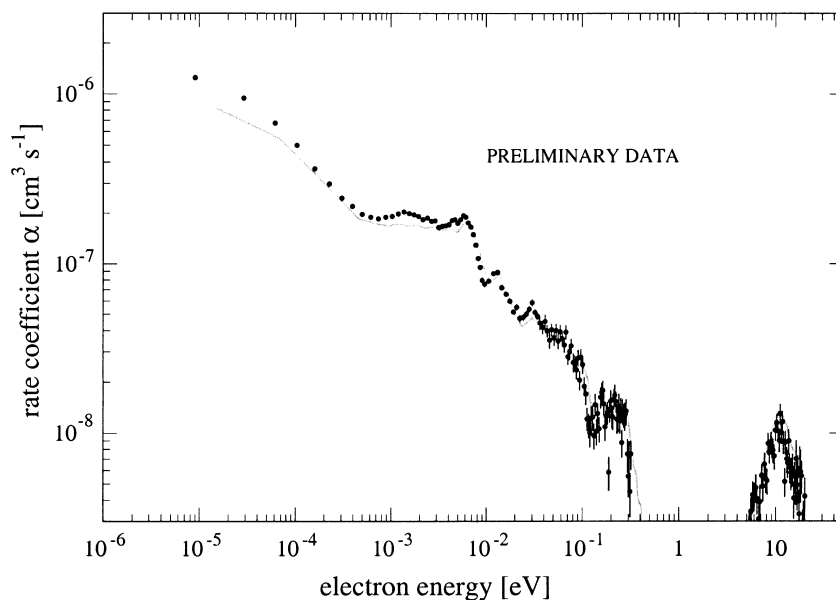
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[1] There is a factor π^2 error in Ref. [45], so the correct upper limit should be 1.2×10^{-7} cm^3 s^{-1} at 300 K (see Refs. [46,47]).

Fig. 6. Preliminary results (•) for dissociative recombination of H_3^+ obtained at the TSR with the cryogenic ion trap as injector. The thin grey line shows the CRYRING result [40–42]. The small difference below 10^{-2} eV is due to the lower electron temperature used in the TSR experiment, 0.5 meV as compared with the 2.0 meV used in CRYRING. (H. Kreckel, private communication 2005)

rangles θ and ϕ. This allowed MQDT to be applied to the problem, with the hyperradius used as the one-dimensional adiabatic parameter, replacing the usual parameter, the internuclear distance in a diatomic molecule.

This *ab initio* calculation by Kokoouline and Greene [46,47] yielded a value for the dissociative recombination rate of $\alpha(300\,K) = (7.2 \pm 1.1) \times 10^{-8}\,\mathrm{cm^3\,s^{-1}}$, in good agreement with the new storage ring results. The theoretical cross section for D_3^+ [47] was also calculated and is in excellent agreement with the results from CRYRING [48,49], but the agreement between theory [51] and experiment [52,53] for D_2H^+ is distinctly poorer In the electron energy range 0.02–0.1 eV for H_3^+ the agreement is less satisfactory [42,43,47,50], with the experimental cross section being higher than the theoretical value. This calculation was improved [54]; the final comparison with experimental results from CRYRING [41] and TSR [44] is shown in Fig. 7. The influence of this disagreement on the deduced thermal rate coefficients, however, is small. In addition, this must be put into context with the state of theory with regard to dissociative recombination cross sections. This level of agreement is as good as, and in many cases better than, that of calculations on dissociative recombination of diatomics. At the time there were no other calculations in the literature for polyatomics treating the full-dimensionality of these systems. This was the first, and currently only one other exists [55]. In addition, this calculation is one of the few in the literature that supplied information about the final products of the dissociative recombination reaction. The branching ratio calculated for the three-body channel by Kokoouline et al. [45], 0.70 ± 0.07, is in very good agreement with the CRYRING storage ring results [42] (see also Ref. [56]); the peak in the vibrational distribution of $H_2(v)$ was found to occur at $v = 5$–6 [45], which agrees very well with the TSR experiment [56].

This calculation also included the effect of rotational excitation. Therefore, it was possible to vary this as a parameter and assess its effect, corroborating the speculation that rotational excitation played a significant role in observed differences among the experimental results. The cross section for rotational temperatures at 600 K was found to be slightly below that of the experiment of Jensen et al. [27], in which the rotational temperature was estimated to be in the range 1000–3000 K. This supplies solid evidence that the early results obtained at CRYRING [23,24] and ASTRID [27],
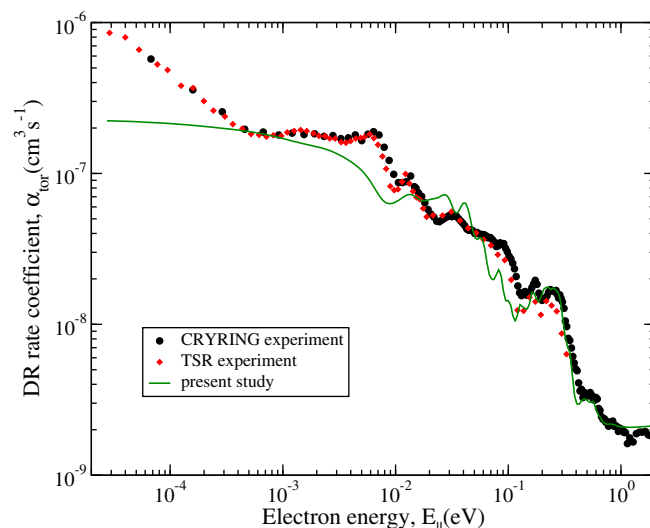
Fig. 7. Comparison of the calculated cross section for dissociative recombination of H_3^+ by dos Santos et al. [51] to the experimental results from CRYRING [35–37] and TSR [38]. The theoretical result is obtained by assuming a rotational temperature of 1000 K. This smoothens the theoretical cross section and makes the agreement with experiment better. The experimental results were obtained for rotational temperatures at least a factor of 10 lower, so the agreement looks better than it probably is. (reproduced from dos Santos et al. [50])

which gave results just above or at $10^{-7}\,\mathrm{cm^3\,s^{-1}}$, were slightly too high because of rotational excitations. The FALP-MS result of Laubé et al. [30], for which the rotational temperature was likely to be 300 K, is in very good agreement with the theoretical result.

This convergence of theory and experiment seems to indicate that the 'Mystery of an interstellar ion' [5] has been solved. However, this has only led to further complications in the astrochemical models that use this cross section.

5. Interstellar implications

The initial detection [21] of H_3^+ in diffuse molecular clouds, where abundant electrons are produced by the photoionization

of atomic carbon by starlight, came as quite a surprise, as it was expected that dissociative recombination would reduce the H_3^+ abundance to unobservable values. (For a review of diffuse clouds, see Ref. [57].) In fact, this detection led many prominent scientists to speculate that the storage ring measurements indicating a high recombination rate [23,24,27,28] must be 'wrong' in the sense of not applying to interstellar conditions. In fact, it was this astrophysical result that provided the impetus for the experiments described in Section 3. Now, given that the recombination rate of H_3^+ really IS fast, how can we interpret the observations?

As mentioned in Section 2, interstellar H_3^+ is produced by a two step process: first, H_2 is ionized by a cosmic-ray (usually a proton with energy of ~2–100 MeV) to form H_2^+; second, the H_2^+ reacts with another H_2 to form H_3^+ and H. Because the second step proceeds quickly at the Langevin collisional rate, the formation of H_3^+ is rate-limited by the ionization step. We can therefore write the formation rate as $\zeta_2\, n(H_2)$, where ζ_2 is the ionization rate per H_2 molecule and $n(H_2)$ is the number density of H_2 molecules. In diffuse molecular clouds, H_3^+ is predominantly destroyed by dissociative recombination, at a rate of $\alpha(T_e)\, n(e)\, n(H_3^+)$. If we assume that the formation and destruction of H_3^+ are in steady state, then we can equate these two rate expressions: $\zeta_2\, n(H_2) = \alpha(T_e)\, n(e)\, n(H_3^+)$. We can rewrite this expression in terms of the H_3^+ number density, as

$$n(H_3^+) = \frac{\zeta_2}{\alpha(T_e)} \frac{n(H_2)}{n(e)}. \tag{4}$$

We assume here that all of the quantities in Eq. (4) are constant throughout a diffuse cloud (i.e., they have the same value in the interior and exterior). This assumption is surely incorrect, but it is likely not too bad of an approximation. We also assume that $T_e = T$, where T is the kinetic temperature of the gas. We can then convert Eq. (4) into observable quantities, using the fact that the observed column density $N(X) = n(X) \cdot L$, where L is the absorption path length through the cloud. With a little algebra, we can isolate the 'unknowns' with the result that

$$\zeta_2 L = \alpha(T) N(H_3^+) \frac{N(e)}{N(H_2)}. \tag{5}$$

In favorable cases, everything on the right hand side of Eq. (5) is known. The kinetic temperature T is inferred from the ratio of $J = 0$ and $J = 1$ of H_2, which can be measured by UV spectroscopy, and the recombination rate $\alpha(T)$ is then known from the storage ring measurements using rotationally cold H_3^+ ions. The column density of H_3^+ is known from infrared observations of the $R(1, 0)$ and $R(1, 1)^u$ transitions. The column density $N(e)$ is approximately equal to $N(C^+)$, which is measured by UV spectroscopy, and $N(H_2)$ is also measured by UV spectroscopy. In less favorable cases, some of these quantities must be assumed or inferred from other information.

Assuming that the experimental and theoretical determinations of $\alpha(T)$ are indeed correct, it is then possible to directly infer the product of the ionization rate and the path length. In a recent survey of diffuse cloud sightlines [58], the product $\zeta_2 L$ was found to have values between ~5000–25000 cm/s. Given an estimate of the total gas column density, and an estimate of the gas number density (e.g., from the observed rotational excitation of C_2), one can estimate the absorption path length L and thereby infer the cosmic-ray ionization rate ζ_2. The recent survey [58] yielded a range of $\zeta_2 \sim 1$–$7 \times 10^{-16}\,s^{-1}$, which is considerably higher than the conventionally adopted value of ~$3 \times 10^{-17}\,s^{-1}$.

Thus, the resolution of a long-standing mystery in chemical physics (the rate of H_3^+ dissociative recombination) has spawned a new mystery in astrophysics: why is the cosmic-ray ionization rate so large in diffuse molecular clouds? This higher ionization rate has already been reconciled with some chemical models of diffuse clouds [59–61], and a potential explanation in terms of magnetohydrodynamic effects has been presented [62]. Indeed, this higher rate has now been generally accepted by the astrophysics community [63], and there is hope that a complete physical and chemical understanding of this rate and its implications is on the horizon.

6. Conclusions

There have been significant advances in the qualitative understanding of the dissociative recombination of H_3^+ and equally significant quantitative progress. The recombination rate constant can be applied with confidence at interstellar conditions. This has generated a new mystery in astrophysics – the high cosmic-ray ionization rate in diffuse clouds – but one which is bound to provide very important insights in astrophysics when it has been solved. The problem has moved from microcosmic to macrocosmic in less than a decade.

Does this mean that H_3^+ recombination is a completely solved problem? No, it does not. One remaining problem is to understand the plasma afterglow experiments. The Prague group no longer claims that the rate constant is very low [64], but the details of the plasma chemistry in these experiments as well as in other afterglow experiments need to be worked out. Why do some afterglow experiments agree with theory and the ion storage rings whereas others do not? The critical review by Johnsen [65] provides a lot of insight but not a final answer.

Theory has made striking progress, but the poor agreement with experiments for D_2H^+ suggests that significant theoretical improvements are still needed [51].

The storage ring experiments [41–44] were quantum state resolved to a remarkable degree, but one can even go one more step in quantum resolution: the lowest rotational state, $J = 1$, has two non-degenerate levels, $K = 1$ and 0 (see Fig. 4). The $K = 0$ level is characterized by the three nuclear spins being aligned in the same direction (*ortho*-H_3^+), whereas for the $K = 1$ level, two nuclear spins are in one direction and the third in the opposite direction (*para*-H_3^+). Theory predicts a radically larger rate constant for *para*-H_3^+ below 300 K [54]. Preliminary experiments with *para*-H_3^+ [43] show the same trend but much less so than predicted theoretically. The *para/ortho* issue is the subject of ongoing research at both the TSR and CRYRING, but we are hesitant to draw any conclusions at this point.

We have chosen an 'astrophysics' style for the title of this article, and the answer to the question posed must be: 'Yes, the saga is coming to an end; but slowly.'

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