PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 2000 **358**, 2433-2444
doi: 10.1098/rsta.2000.0658

10.1098/rsta.2000.0658

Experimental studies of the dissociative recombination of H_3^+

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Despite many experimental efforts over several decades, no consensus has been reached concerning the rate of dissociative recombination of H_3^+. We review the current status concerning different experimental approaches to the measurement of the cross-section, rate coefficient and branching ratios in electron recombination of H_3^+.

Keywords: dissociative recombination; rate coefficient; cross-section

1. Introduction

Dissociative recombination (DR) of molecular ions with electrons is often the dominant neutralizing process in a plasma in which the gas temperature is a few thousand degrees or less and the electron temperature is lower than a few eV. These conditions prevail in many astrophysical plasmas, that is, in the environments where H_3^+ plays such an important role (Dalgarno 1994). Naturally, this renders the rate coefficient for dissociative recombination of H_3^+ a very important quantity, and many efforts have been devoted over the years to measure it. Despite these efforts it has been impossible to arrive at a unanimous value; in fact, it is no exaggeration to claim that the DR rate coefficient for H_3^+ has remained one of the most controversial topics in the field of electron–ion recombination. The recent discoveries of H_3^+ in dark (Geballe & Oka 1996) and diffuse (McCall *et al*. 1998; Geballe *et al*. 1999) interstellar molecular clouds have increased the interest in its recombination rate coefficient, as has the indication that chemical models of interstellar clouds may have bistable solutions that depend sensitively on how rapidly H_3^+ recombines with electrons (Lee *et al*. (1998), and references cited therein).

The most important new experimental technique to contribute to the understanding of the recombination of H_3^+ is that of ion storage rings. The use of this technique for the study of dissociative recombination has been reviewed recently by Larsson (1997, 2000). For a comprehensive review of dissociative recombination covering the period until 1990 the reader is referred to the article by Mitchell (1990). The published proceedings from four dissociative recombination conferences also provide broad overviews of the field (Mitchell & Guberman 1989; Rowe *et al*. 1993; Zajfman *et al*. 1996; Larsson *et al*. 2000).

2. Brief history of the dissociative recombination of H_3^+

The first measurement of the rate coefficient for H_3^+ was performed by means of a stationary afterglow technique and gave a value of $\alpha_{\mathrm{DR}} = 2.3 \times 10^{-7}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$

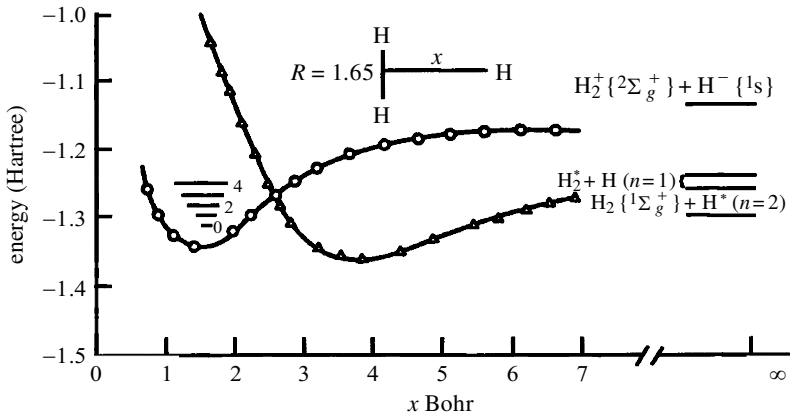

Figure 1. Potential energy curves for H_3 and H_3^+, adapted from Michels & Hobbs (1984).

at 300 K (Leu *et al.* 1973). In this experiment, hydrogen ions were created by a microwave discharge and the disappearance of mass-selected H_3^+ ions in the afterglow was measured as a function of time. It was suggested, but not proven, that the H_3^+ ions were vibrationally relaxed in the afterglow. Shortly after, inclined- and merged-beams experiments were performed (Peart & Dolder 1974*a*, *b*; Auerbach *et al.* 1977; McGowan *et al.* 1979). The results were similar to the afterglow result, and it was claimed that vibrationally de-excited H_3^+ ions were used in the experiments. The afterglow experiment was later repeated over a wide range of electron temperatures with essentially the same outcome as in the first experiment (Macdonald *et al.* 1984). At this point it seemed as if there was harmony between the different experimental results. And although the theoretical paper by Kulander & Guest (1979) primarily discussed recombination of H_3^+ at electron energies larger than 1 eV, they were not alarmed by the absence of a suitable curve crossing through the zeroth vibrational level of H_3^+ in C_{2v} geometry.

The harmony was interrupted in 1984 and has never been fully restored since then. Adams *et al.* (1984) used the flowing afterglow/Langmuir probe (FALP) technique to measure the removal of electrons in an H_3^+ afterglow plasma and found that recombination occurred so slowly that they could only state with certainty that the rate coefficient, α_{DR} ($T = 300$ K), had an upper limit that was less than 2×10^{-8} cm^{-3} s^{-1}. This surprising result, in complete disagreement with all previous experimental results, found support in the theoretical work of Michels & Hobbs (1984). Figure 1 shows a potential energy curve diagram that illustrates why it was suggested that H_3^+ should recombine very slowly with electrons. Using the curve-crossing model originally proposed by Bates (1950), Michels & Hobbs (1984) used the vibrational overlap between different vibrational levels of the electronic ground state of H_3^+ and the H_3 $^2A_1$ resonant state to infer that the zeroth vibrational level of H_3^+ recombines very slowly with electrons. Excited vibrational levels have a more favourable vibrational overlap, and, hence, vibrationally excited H_3^+ ($v \geqslant 3$) was estimated to recombine two orders of magnitude faster than H_3^+ ($v = 0$). Moreover, the $^2A_1$ state is closed for dissociation for electron energies below 0.97 eV, and Michels & Hobbs (1984) showed that the $^2A_1$ state does not cross Rydberg states of H_3, which correlate to excited atomic or molecular products. A possible explanation for the discrepancy between the FALP result and the earlier results could then be

that vibrationally excited H_3^+ was present in the earlier experiments. Indeed, in the early part of the flowing afterglow, where vibrationally excited H_3^+ was likely to be present, a much faster disappearance of electrons was observed (Adams *et al.* 1984). The astrophysical implications of a low H_3^+ DR rate coefficient were discussed by Smith & Adams (1984).

A few years after the first FALP publication on H_3^+, several publications claiming α_{DR} ($T = 300$ K) to be 10^{-11} cm^{-3} s^{-1} followed (Adams & Smith 1987, 1988, 1989; Smith & Adams 1987). The claim was based on an extension of the FALP technique to include a comparison of the loss rates of H_3^+, He^+ and HeH^+ in the afterglow plasma. No measurable differences between the loss of these three ions were observed, and it was concluded that the two molecular ions recombined with the rate coefficient for radiative recombination of He^+. It should be noticed, however, that the FALP technique is not sufficiently sensitive to measure a rate coefficient of the order of 10^{-11} cm^{-3} s^{-1}, and the rate coefficient was inferred from theoretical estimates of the radiative recombination rate coefficient for He^+. In fact, in the FALP experiment, no measurable loss of H_3^+, He^+ and HeH^+ was observed that could be attributed to electron recombination. None of the quoted publications contains a full description of the experiment, and, in the final paper, which claims a very low rate coefficient, the upper limit was raised to $\alpha_{DR} \leqslant 10^{-10}$ cm^{-3} s^{-1} (Smith *et al.* 1990).

Experimental work following the FALP measurements discussed above is described in the next section.

3. Experimental studies of the DR of H_3^+

(*a*) *Infrared absorption spectroscopy*

Amano (1988) avoided the problem of an undetermined vibrational state distribution in H_3^+ by probing directly the loss of the ion in its zeroth vibrational level and $J = 3$, $K = 3$ rotational level in a plasma, using infrared absorption spectroscopy. The rate coefficient was determined to be $(1.8 \pm 0.2) \times 10^{-7}$ cm^{-3} s^{-1} at 210 K, in complete disagreement with the FALP result. The experiment was criticized by Adams & Smith (1989), who pointed out that due to the high electron density in Amano's plasma, collisional–radiative recombination was likely to be the main loss process of H_3^+ ions. Because of the discrepancy with the FALP measurements, and also with a merged-beams measurement (Hus *et al.* 1988), which is discussed in the next section, Amano (1990) extended his infrared spectroscopy measurements to include more rotational levels in H_3^+ ($v = 0$) and lower electron temperatures. The argument of collisional–radiative recombination being the dominant loss process was dismissed by Amano (1990) on the grounds that the ion density decayed linearly with time. However, this is not a valid argument, as pointed out by Bates *et al.* (1993). The flaw in Amano's argument is nevertheless not a problem according to Bates *et al.* (1993), who estimated the collisional–radiative rate coefficient to be smaller than 1.4×10^{-8} cm^{-3} s^{-1} at an electron temperature of 275 K, which was the highest temperature used by Amano (1990). Thus, the ion loss in Amano's infrared spectroscopy experiment is, according to Bates *et al.* (1993), dominated by dissociative recombination.

More recently, another infrared spectroscopy measurement of the H_3^+ ($v = 0$) DR rate coefficient has appeared (Féher *et al.* 1994). In this work the electron density was measured by a Langmuir probe, instead of being assumed to be approximately equal

to the H_3^+ density (Amano 1988, 1990). It was found that the electron density was different from the H_3^+ ion density, and, hence, that impurity ions were present in the plasma. Using a mass spectrometer, Féher *et al.* (1994) identified H_3O^+, H_2O^+ and H^+ as impurity ions. Thus, they concluded that their measurement of loss of H_3^+ ($v = 0$) using infrared spectroscopy could only give an upper limit of 2×10^{-7} cm^{-3} s^{-1} to the dissociative recombination rate coefficient. Whether Amano's plasma was affected by H_3O^+ and H_2O^+ impurity ions is not known, since no mass spectrometer was used.

(*b*) *Single-pass merged-beams experiments*

Whereas the early merged- and inclined-beams experiments gave results that were consistent with a rate coefficient larger than 10^{-7} cm^{-3} s^{-1}, the measurement by Mitchell and co-workers (Hus *et al.* 1988) a decade later using a single-pass merged-beams technique gave $\alpha_{\mathrm{DR}} = 2 \times 10^{-8}$ cm^{-3} s^{-1}. Thus, a result clearly larger than the FALP result (Adams & Smith 1987, 1988, 1989; Smith & Adams 1987), but smaller than existing beam results (Peart & Dolder 1974*b*; Auerbach *et al.* 1977; McGowan *et al.* 1979), stationary afterglow results (Leu *et al.* 1973; Macdonald *et al.* 1984), and the infrared spectroscopy result (Amano 1988), was obtained. The new merged-beams experiment (Hus *et al.* 1988) was performed with the same apparatus used by Auerbach *et al.* (1977) and McGowan *et al.* (1979), but with a trap ion source instead of a radio frequency ion source. Because of the long storage time in the trap source, collisional deactivation of vibrational modes was obtained. The process of dissociative excitation, i.e. $H_3^+ + e^- \rightarrow H + H_2^+ + e^-$, was used to determine the vibrational state distribution in H_3^+ to be a mixture of $v = 0$ and $v = 1$. It was suggested that the larger DR cross-sections obtained in the earlier merged-beams experiments were due to vibrationally excited H_3^+ (Auerbach *et al.* 1977; McGowan *et al.* 1979). This is quite possible, but it does not explain the inclined-beams result of Peart & Dolder (1974*a*). They expended considerable effort to ascertain that their H_3^+ ions were vibrationally de-excited (Peart & Dolder 1974*a*) using the same technique of dissociative excitation as Hus *et al.* (1988).

More recently, the single-pass merged-beams result has been modified to $\alpha_{\mathrm{DR}} = 1.2 \times 10^{-7}$ cm^{-3} s^{-1} (Yousif *et al.* 1995). In the single-pass experiment, the neutral reaction products are separated from the ion beam by means of an electric field. Yousif *et al.* (1995) noticed that when they lowered the electric field strength, the number of neutral particles arriving at the detector increased. They interpreted this as the presence of H_3 molecules in long-lived Rydberg states in the neutral product beam. The Rydberg molecules were field ionized by the electric field, and when the field was reduced, less Rydberg molecules were ionized and the cross-section increased. As will be apparent in the next section, the modified single-pass result is in agreement with ion storage-ring results. This would seem like a satisfactory situation, were it not for the fact that even stronger electric fields are involved in separating the ions from the neutrals in storage rings.

(*c*) *Merged-beams experiments in ion storage rings*

Ion storage rings represent the most recent development of the merged-beams technique. The major improvements are the long storage time, which allows vibrational excitations to be removed by radiative vibrational relaxation, the high beam

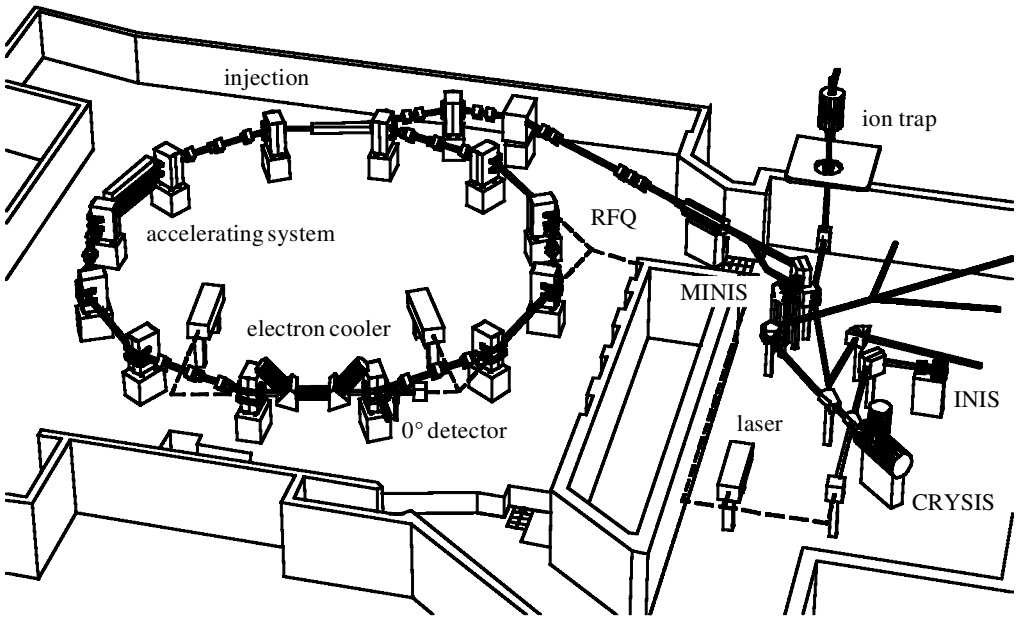

Figure 2. The CRYRING heavy-ion storage-ring facility at the Manne Siegbahn Laboratory, Stockholm University. The storage ring is 51.6 m in circumference. Molecular ions are produced in the ion source MINIS, accelerated and mass selected, further accelerated in the radio frequency quadrupole (RFQ) field, injected into CRYRING, further accelerated by an RF system, and finally stored for *ca.* 10 s. During the storage phase, the ion beam is translationally cooled by a velocity-matched electron beam in the electron cooler section, and vibrationally cooled by radiative relaxation. During the dissociative recombination experiment, which starts after *ca.* 10 s, neutral reaction products are detected by the 0^0-detector. CRYSIS is an ion source for highly charged ions and INIS is an ion injector to this source.

energy (typically 1–10 MeV amu^{-1} for light ions), the ultra-high vacuum conditions, which radically increase the signal-to-noise ratio, and the circulation of the ion beam, which increases the effective beam current. In the H_3^+ experiments discussed below, the recombination signal was measured against a *zero* background.

Figure 2 shows the ion storage-ring facility CRYRING at the Manne Siegbahn Laboratory at Stockholm University. The cross-section measurements in CRYRING gave a thermal rate coefficient of 1.15×10^{-7} cm^{-3} s^{-1} (Larsson *et al.* 1993; Sundström *et al.* 1994). These measurements were followed by a series of experiments that exploited the full potential of the ion storage-ring technology: branching ratio measurements by means of a new translucent grid technique that took advantage of the high beam energy (Datz *et al.* 1995*a*); measurements of cross-sections and branching ratios of H_2D^+ (Datz *et al.* 1995*b*; Larsson *et al.* 1996), which required phase-space cooling of the stored H_2D^+ ions in order to measure the degree of impurity D_2^+ in the beam in combination with additions to the translucent grid technique; and a measurement of the cross-section of D_3^+ with an electric field added to the interaction region (Larsson *et al.* 1997; Le Padellec *et al.* 1998). The results are summarized in table 1.

There is a clear isotope effect in that the rate coefficient scales with the number of deuterium atoms. The branching ratio data show that no H_3 Rydberg molecules reach

Table 1. *Results from dissociative recombination experiments in CRYRING*

molecule	quantity	result	reference
H_3^+ $(v=0)$	α_{DR} (300 K)	1.15×10^{-7} cm^{-3} s^{-1}	Sundström *et al.* (1994)
H_2D^+ $(v=0)$	α_{DR} (300 K)	6×10^{-8} cm^{-3} s^{-1}	Larsson *et al.* (1996)
D_3^+ $(v=0)$	α_{DR} (300 K)	2.7×10^{-8} cm^{-3} s^{-1}	Le Padellec *et al.* (1998)
H_3^+ $(v=0)$	branching ratio	H + H + H: 0.75 H + H_2: 0.25	Datz *et al.* (1995*a*)
H_2D^+ $(v=0)$	branching ratio	H + H + D: 0.73 HD + H: 0.19 H_2 + D: 0.09	Datz *et al.* (1995*b*)

the detector. Whether this is because the Rydberg molecules decay by dissociation or by autoionization before they reach the detector, or because they are field ionized by the motional electric field in the dipole magnet, cannot be determined in the experiment. For D_3^+, an electric field of 30 V cm^{-1} was added to the electron–ion interaction region. This had no measurable effect on the DR cross-section.

Finally, it is worth noting that the experimental cross-section for electron energies of *ca.* 9–10 eV (Larsson *et al.* 1993) agree very well with theoretical calculations by Orel & Kulander (1993). The comparison of experiment with theory also suggested that H_3^+ was vibrationally cold in the CRYRING experiment.

The corroboration of results obtained in one storage ring by experiments in another storage ring is an important part of the search for systematic errors. During the last year, experiments with H_3^+ have been carried out in the storage rings TARN II (Tanabe *et al.* 2000) and ASTRID (L. H. Andersen 2000, personal communication). The TARN II results are in very good agreement with the data from CRYRING, and also the results from ASTRID are essentially in agreement with the those obtained in CRYRING within the combined error bars. Finally, a very important piece of information has emerged from a recent Coulomb explosion imaging experiment by means of an extracted H_3^+ beam at the Test Storage Ring (TSR) in Heidelberg. The Coulomb explosion imaging technique allows the population of vibrational levels in a molecule to be monitored. The technique has been used to measure DR cross-sections for vibrationally excited levels in HD^+ (Amitay *et al.* 1998). When applied to H_3^+ it was found that the most long-lived vibrational level in H_3^+ had a lifetime of *ca.* 0.5–1.0 s (D. Zajfman 2000, personal communication). This is in very good agreement with the theoretical calculations of Dinelli *et al.* (1992).

(*d*) *Flowing afterglow experiments*

Bearing in mind the consistent absence of dissociative recombination of H_3^+ $(v=0)$ in previous FALP experiments (Adams & Smith 1987, 1988, 1989; Smith & Adams 1987), the result from a new FALP apparatus supplied with a mass spectrometer was surprising. The rate coefficient for H_3^+ $(v=0)$ was measured to be 1.1×10^{-7} cm^{-3} s^{-1} at an electron temperature of 650 K (Canosa *et al.* 1992). The addition of a movable mass spectrometer to the FALP apparatus allowed the ions in the afterglow to be monitored. The new FALP–MS result inspired Smith & Španel (1993*a*, *b*) to remeasure the rate coefficient with a modified version of the FALP apparatus that previously had given the result that DR of H_3^+ in its lowest vibrational

level is immeasurably small. A quadrupole mass spectrometer was added to the FALP apparatus, but, in contrast to the apparatus used by Canosa *et al.* (1992), where the relative abundance of mass-selected ions was measured along the afterglow with a movable quadrupole, the ions were only monitored at a fixed position at the end of the afterglow. Smith & Španel (1993*a*, *b*) went to great lengths to identify possible systematic errors in their experiment, and concluded that H_3^+ ($v = 0$) recombined with a rate coefficient of $1\text{–}2 \times 10^{-8}\,\mathrm{cm^{-3}\,s^{-1}}$ at 300 K. The titles of the two papers by Smith & Španel (1993*a*, *b*) are misleading. The controversy is not resolved by their work, and there is a misunderstanding concerning the rate coefficient measured in CRYRING. However, the claim for an immeasurably small rate coefficient was no longer upheld in the work of Smith & Španel (1993*a*, *b*).

The FALP–MS apparatus was used in an extensive set of measurements (Laubé *et al.* 1998) that was performed in order to try to resolve the discrepancy between the two FALP experiments (Canosa *et al.* 1992; Smith & Španel 1993*a*, *b*). This did not meet with success, and although the new value, $\alpha_{\mathrm{DR}}\ (300\ K) = (7.8 \pm 2.3) \times 10^{-8}\,\mathrm{cm^{-3}\,s^{-1}}$, was lower than the previous one (Canosa *et al.* 1992), it was also significantly higher than the result of Smith & Španel (1993*a*, *b*). The major criticism levelled by Smith & Španel (1993*a*, *b*) against the FALP–MS experiment by Canosa *et al.* (1992) was that their H_3^+ were not vibrationally cold. Laubé *et al.* (1998) used KrH^+ as a precursor ion in the production of H_3^+, which, because of the slight endothermicity of the reaction $KrH^+ + H_2 \rightarrow H_3^+ + Kr$ (Smith & Španel 1993*a*, *b*), supposedly produced H_3^+ ions populating only the zeroth vibrational level.

In between the conflicting FALP experiments described above, Gougousi *et al.* (1995) performed a FALP experiment that gave results similar to those of Smith & Španel (1993*a*, *b*); the difference, however, is that Gougousi *et al.* (1995) give a very different interpretation of their results. Just as in Smith & Španel's (1993*a*, *b*) FALP apparatus, Gougousi *et al.* (1995) monitored the ions with a quadrupole mass spectrometer at the downstream end of the flow tube. They observed a rapid deionization of the plasma in the early part of the afterglow, and a slower deionization further downstream. Whereas Smith & Španel (1993*a*, *b*) interpreted this as the presence of vibrationally excited H_3^+ in the early part of the afterglow, Gougousi *et al.* (1995) argued that H_3^+ ($v \geqslant 2$) is destroyed so rapidly by proton transfer to Ar that only H_3^+ ($v = 0, 1$) need be considered. They suggested instead that the rapid deionization in the early part of the afterglow was due to the formation of H_3 in a Rydberg state by electron capture, followed by stabilization of the capture process by interaction with a third body, which could be either molecular hydrogen or an electron. A consequence of their interpretation is that binary dissociative recombination of H_3^+ ($v = 0$) must be very slow. Although Gougousi *et al.*'s (1995) FALP apparatus was not equipped to observe radiation from H_3 Rydberg molecules, it was part of the data analysis; in fact, it was even stated that radiation alone would explain the observed deionization rate. However, in a more recent experiment, with the apparatus equipped to allow the monitoring of the afterglow by optical spectroscopy, no emission from H_3 plasmas was observed (Johnsen *et al.* 2000). Laser-induced fluorescence probing of atomic hydrogen, on the other hand, indicated that each recombination event of H_3^+ produced, on average, 2.2 ± 0.3 H atoms. This is in very good agreement with the 2.5 measured in CRYRING (see table 1).

Of the many FALP measurements of deionization of an H_3^+ plasma, only those indicating a very low rate coefficient (Adams & Smith 1987, 1988, 1989; Smith &

Adams 1987) are clearly wrong (Smith & Španel 1993*b*), a probable reason being the presence of non-recombining He^+ in the afterglow. The more recent FALP measurements discussed in this paper do not show consensus, although the range of measured rate coefficients is narrowed. It is extremely difficult to point at a flaw in any of the most recent FALP experiments. It is inescapable, however, that the FALP–MS apparatus provides a possibility to measure, mass selectively, the ion composition in the afterglow, which gives a better control of the plasma conditions compared with the apparatuses with a mass spectrometer in a fixed position at the end of the flow tube.

4. Conclusions

The secrets of the dissociative recombination of H_3^+ have not yet been completely unravelled, and there is not yet consensus among the different experimental approaches. The results from the ion storage rings are internally consistent and lend strong support for a rate coefficient of $10^{-7}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ at 300 K. This value is essentially in agreement with the results obtained with the FALP–MS technique and by infrared absorption spectroscopy. The two FALP experiments by Smith & Španel (1993*a*, *b*) and Gougousi *et al.* (1995) cannot be dismissed, and as long as no valid criticism against the two FALP experiments is levelled, an element of doubt must remain concerning the DR rate coefficient of H_3^+.

We stress that even if the rate coefficient were as low as $1\text{–}2 \times 10^{-8}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, recombination through the $^2A_1$ resonant state is much slower. Thus, another mechanism must be sought even if the FALP result of Smith & Španel (1993*a*, *b*) is correct. It is likely that this mechanism is similar to the one giving rise to DR of HeH^+ (see Larsson (1997, 2000) for a discussion of experimental and theoretical results), i.e. coupling by the nuclear kinetic energy operator of the HeH^+ ground state to close-lying, but non-crossing, Rydberg states. The theory of DR of H_3^+ is discussed in this issue by Orel *et al.*

I thank A. Le Padellec for valuable discussions, A. Suzor-Weiner and I. F. Schneider for comments on the draft manuscript, and L. H. Andersen and D. Zajfman for communicating unpublished results. This work was supported by the Swedish Natural Science Research Council (NFR).

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Discussion

D. Smith (*University of Keele, UK*). The flowing afterglow/Langmuir probe (FALP) method directly provides dissociative recombination coefficients of ions with electrons under thermalized conditions at given kinetic temperatures. The storage-ring experiments provide cross-sections as a function of the electron–ion interaction energy, which must be well defined at very low energies to allow meaningful calculations of rate coefficients for dissociative recombination at the low temperatures appropriate to interstellar clouds. We therefore consider that the FALP measurements are inherently more reliable for interstellar ion chemical models. Thus, we find that the dissociative recombination coefficient for H_3^+ ions in their lowest vibrational state is $1–2\times10^{-8}$ cm^3 s^{-1} at 300 K. This measure coefficient increases slowly with decreasing temperature, T, the increase being consistent with the often-assumed $T^{-0.5}$ dependence for dissociative recombination coefficients.

A. Suzor-Weiner (*Université Paris-Sud, Orsay, France*). In the storage-ring experiments on H_3^+ dissociative recombination, can you exclude the presence of ions in an excited *metastable* (triplet) state with a lifetime larger than the storage time? Such states could recombine much faster than the ground-state ion.

M. Larsson. If the excited triplet state were populated, we would have seen some signature of it in dissociative excitation measurements, which we have performed for D_3^+ (Le Padellec 1998). One must also bear in mind that prior to a cross-section measurement, the ion beam is electron cooled for maybe 10–15 s. During the electron-cooling phase, because of the velocity matching conditions between electron and ion beams, dissociative recombination will remove a state with a large cross-section for recombination. Recent Coulomb explosion imaging experiments at TSR (D. Zajfman, personal communication) would also provide a sensitive test of possible contamination of triplet state population. No such populations have been reported, however, a definitive answer would have to await the complete analysis of the TSR data.

P. Španel (*Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic*). Since HCO^+ is 1.2×10^{-7} cm^3 s^{-1}, it follows that H_3^+ is much smaller (for ions in their lowest vibrational state). H_3^+ for vibrationally excited ions appears to be significantly greater, at about 1.5×10^{-7} cm^3 s^{-1}, which is close to the value inferred from the storage-ring experiment. These FALP experiments also indicate that D_3^+ is *ca.* 30% lower than H_3^+.

J. B. A. Mitchell (*PALMS, Université de Rennes, France*). You presented the inclined beam results of Peart & Dolder (1974*a*, *b*) and it must be realized that when these were made, they were state of the art. Most of the data that came from this apparatus are in very good agreement with other experiments. For example, H_2^+ recombination and H_3^+ recombination to form H_2 and H^-. (Our measurements on the latter reaction indicated that the ions in the Peart & Dolder experiment were in $v = 1$ and $v = 0$.)

Their H_3^+ dissociative recombination results are two orders of magnitude higher than the storage ring and the single-pass merged-beam results. This cannot be explained simply by vibrational excitation. I believe that what is going on in this region around 1 eV could be very important to our understanding of this problem.

A second area which requires understanding is that of the recombination of D_3^+.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES