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H_3^+: the initiator of interstellar chemistry

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Abstract: Second only to H_2, protonated molecular hydrogen, H_3^+, is the most abundantly produced interstellar molecule. Owing to its high reactivity and acidity, it plays the pivotal role in initiating interstellar chemical reactions, something which also reduces its steady-state concentration. Interstellar H_3^+ is not only destroyed in chemical reactions but also in dissociative recombination with electrons. The rate constant and mechanism of recombination have long been controversial, but great advances have been made during recent years, with the important consequence that the cosmic ray ionization rate in diffuse clouds is now believed to be higher by an order of magnitude than previously assumed.

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Introduction

A prime focus of 21st century astrophysics is the study of the molecular universe at far-infrared, millimetre and sub-millimetre wavelengths, which will provide information about the formation processes of stars and galaxies. The space mission Herschel Space Observatory and the ground-based Atacama Large Millimeter Array are examples of instruments that will be taken into operation between 2008 and 2012 to address these and other questions. During the past 50 years the picture of the interstellar medium has been transformed from something that was thought to be primarily atomic, with a few diatomic molecules present (CO, CN, CH^+), to something which is known to be primarily molecular. When Watson (1973) and Herbst & Klemperer (1973) proposed that interstellar molecules are synthesized in ion–molecule reactions, it was also clear that H_3^+ must play a pivotal role in these schemes. Although H_3^+ at that time had been known as a physically stable molecule for more than half a century (it was first discovered in Thomson's (1911) mass spectrometer), its electromagnetic spectrum was unknown. It was the skilful and persistent work by Oka and collaborators that led to the discovery of the infrared spectrum of H_3^+ (Oka 1980) and then its presence in dark (Geballe & Oka 1996) and diffuse (McCall *et al.* 1998) clouds. Oka (2006) has reviewed these and subsequent discoveries of H_3^+ in the Central Molecular Zone near the Galactic centre.

Interstellar H_3^+ is produced by cosmic ray ionization of H_2 followed by

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

This reaction is extremely efficient and leads to H_3^+ being the dominant ion in hydrogen plasma, rather than H_2^+ or H^+. Its important role in interstellar chemistry is a combination of this and its low proton affinity (4.4 eV), which results in the proton hop reaction:

$$H_3^+ + X \rightarrow HX^+ + H_2 \tag{2}$$

where X is an atom or molecule. Reactions (1) and (2) initiate a chain of reactions that produce interstellar molecules. Figure 1 shows such a network of ion–molecule reaction chemistry, with dissociative recombination as the terminating step leading to the formation of stable, neutral molecules such as water and ethanol. Dissociative recombination:

$$H_3^+ + e \underset{k_e}{\rightarrow} H_2 + H \text{ or } 3H \tag{3}$$

is the additional destruction channel to reaction (2). In order to model interstellar chemistry, the rate of reaction (3) is required, as well as the product branching ratios.

Dissociative recombination of H_3^+: a brief history

When the destruction of H_3^+ by thermal-energy electrons was measured in a pulsed-discharge (afterglow) experiment by Leu *et al.* (1973) to proceed with a rate constant of $k_e = 2.3 \times 10^{-7}\,\mathrm{cm^3\,s^{-1}}$, this could hardly have surprised anyone. After all, this was essentially the rate constant with which the atmospheric ions NO^+, N_2^+ and O_2^+ recombined. About 10 years later, based on experiments using a flowing afterglow/Langmuir probe (FALP) technique, the Birmingham group published the surprising result that the rate constant was less than $2 \times 10^{-8}\,\mathrm{cm^3\,s^{-1}}$ (Adams *et al.* 1984). This study was followed by reports in conference proceedings in which it was claimed that the rate constant could not be larger than $10^{-11}\,\mathrm{cm^3\,s^{-1}}$ (e.g. Adams & Smith 1987). There are several surprising aspects of this very small rate constant. The result was never published in a regular journal in which one could legitimately have asked for experimental

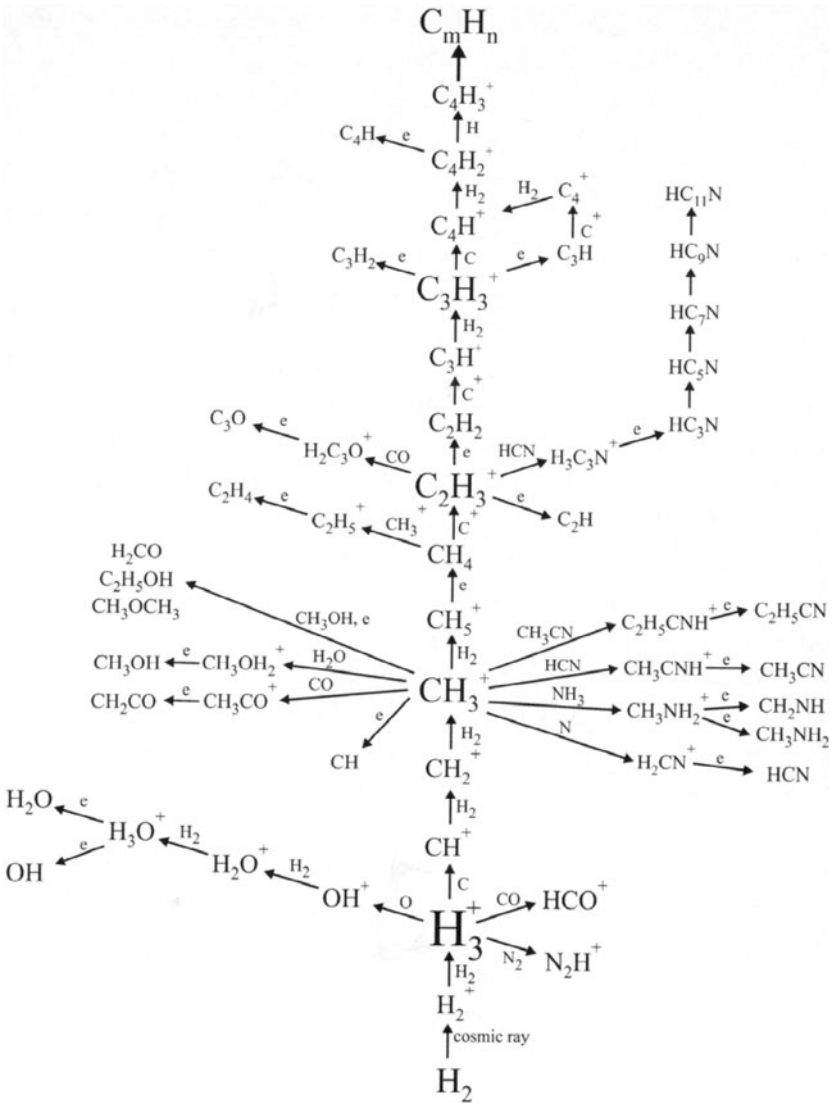

Fig. 1. Network of ion-molecule chemistry (reproduced with permission from McCall (2001)).

details; the rate constant was much smaller than what one reasonably could expect to measure with a flowing afterglow apparatus; it had a considerable impact on the community of interstellar chemists (e.g. Van Dishoeck & Black 1986), and the possibility of observing H_3^+ in diffuse clouds was discussed (where electron recombination is the main destruction process of H_3^+).

The notion of a non-recombining H_3^+ ion was so strong at the time that Amano (1988, 1990) had some difficulties in convincing the community that his measurement of a rate constant of 1.8×10^{-7} cm^3 s^{-1} was to be taken seriously. Amano measured spectroscopically the disappearance of H_3^+ in a pulsed afterglow instead of measuring, as in the FALP technique, the change in electron density along the flow tube.

The ion storage ring studies of H_3^+ (Larsson *et al.* 1993; Sundström *et al.* 1994) giving a rate constant of 1.15×10^{-7} cm^3 s^{-1} started to tip the scale towards a higher rate, but the situation at the time of the Royal Society Discussion Meeting on H_3^+ (Herbst *et al.* 2000) was confusing. Larsson (2000) has reviewed this in detail, and the reader is referred to this article for many more references than given here. One year later, at the symposium entitled 'Dissociative Recombination of Molecular Ions with Electrons' (Guberman 2003), it was not inconceivable that the recombination rate constant rate constant for H_3^+ at interstellar conditions (i.e. $T_e < 100$ K) could be as small as 10^{-8} cm^3 s^{-1}. What had happened, and what was the way forward to come to grips with this elusive rate constant?

From confusion to clarity: almost

The mechanism for the dissociative recombination of H_3^+ remained a problem for a long time. The lowest vibrational level of ground state H_3^+ is remote from the doubly excited resonant state of H_3 which can drive recombination of vibrationally excited levels in H_3^+. Schneider *et al.* (2000) investigated the effect of indirect recombination through the manifold of H_3 Rydberg states converging to ground state

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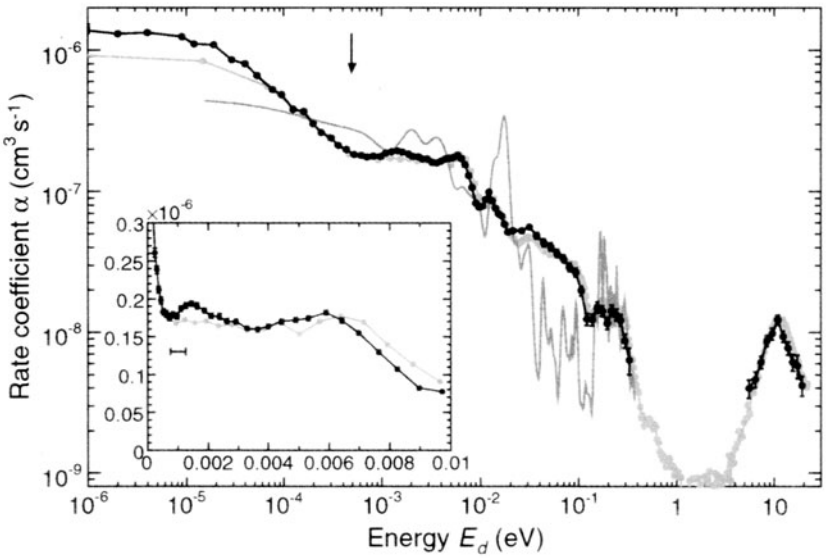

Fig. 2. Comparison of results for dissociative recombination of H_3^+. The interconnected black dots display the results from TSR (Kreckel *et al.* 2005), the interconnected grey dots display the results from CRYRING (McCall *et al.* 2003), and the continuous grey line shows the theoretical results of Kokoouline & Greene (2003a,b). The small difference between the experimental data of CRYRING and TSR is due to the colder electron beam used in the TSR experiment (reproduced with permission from Kreckel *et al.* (2005)).

H_3^+ and found it to be substantial, but nevertheless unable to give a rate constant larger than $10^{-9}\,cm^3\,s^{-1}$. Without the indirect mechanism, the rate was lower by a factor of a hundred.

Around the year 2000 a new stationary afterglow experiment (Glosik *et al.* 2000) produced results in good agreement with the theoretical result. There was accumulating evidence that experiments at ion storage rings had been successful in determining the rate constant for H_3^+ in the zeroth vibrational level, but with considerable rotational excitations, and there were indications that the rotational excitations affected the rate constant (Jensen *et al.* 2001; Kreckel *et al.* 2002; Larsson *et al.* 2003).

Greene's group in Boulder found that a hitherto overlooked mechanism, Jahn–Teller distortion of the H_3^+ ion as a result of the incoming low-energy electron, increased the recombination rate (Kokoouline *et al.* 2001), but only by about a factor of ten as compared with the result of Schneider *et al.* (2000). Greene concluded in his talk at Guberman's meeting in 2001:

> "The rate and cross-section of the dissociative recombination of H_3^+ are found to be in the range of the microwave afterglow results [i.e. about $10^{-8}\,cm^3\,s^{-1}$] and about an order of magnitude smaller than the storage ring experiments." (Greene *et al.* 2003).

The question was thus unavoidable: perhaps the rate constant was increased by a factor of 10 by rotational excitations?

Oka (2003), being well aware that the observation of H_3^+ in diffuse clouds (McCall *et al.* 1998) favoured a low recombination rate constant, insisted that:

> "Finally a word of caution. This astronomical mystery should not be taken to constrain the value of k_e in any definitive way. The assumed canonical astrophysical parameters may be wrong. It is even possible that clouds containing H_3^+ are indeed very large. *What we need is the TRUE value of k_e, and not a value which explains the problem quickly*. To this end scientists in different disciplines need to work together. Physicists, chemists and astronomers of the world, unite!" (Oka 2003).

The past five years have seen remarkable progress towards an understanding of dissociative recombination of H_3^+. In a collaborative effort between groups in Stockholm, Berkeley and Urbana-Champaign, a supersonic expansion discharge ion source was built and tested, and was found to be able to produce rotationally cold H_3^+. This source was connected to the ion storage ring CRYRING in Stockholm and used as injector. McCall *et al.* (2003, 2004) found a decrease of the rate constant as a result of the rotational cooling of H_3^+ to about 40 K, but only to $6.8\times10^{-8}\,cm^3\,s^{-1}$ from the rotationally 'hot' value of $1.15\times10^{-7}\,cm^3\,s^{-1}$.

Using a different procedure of rotationally cooling H_3^+, namely with a cryogenically cold ion trap, Kreckel *et al.* (2005) used the test storage ring in Heidelberg with the trap as injector and obtained very good agreement with the results from CRYRING.

Kokoouline & Greene (2003a,b) discovered a factor of ten error in their preliminary calculations (Kokoouline *et al.* 2001; Greene *et al.* 2003), and managed to overcome a number of technical hurdles in order to calculate a fully quantum mechanical cross-section. The rate constant derived from their cross-section was in excellent agreement with the storage ring results. Figure 2 shows the storage ring and theoretical results. The agreement between the theoretical and experimental cross-sections has been improved in a recent theoretical work (Fonseca dos Santos *et al.* 2007), but is still not

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perfect. It is not clear why the theoretical cross-section is more highly structured than the experimental one.

Thus, the situation concerning the recombination rate constant for H_3^+ changed radically during the span of a few years. Now nobody seriously questions that the rate constant at an electron temperature of 300 K and a rotational temperature of 30–50 K is about 7×10^{-8} cm^3 s^{-1}. This has two consequences: it requires a revision of a canonical astrophysical parameter, the cosmic ray ionization rate, and an explanation of the conflicting results derived from plasma experiments.

McCall *et al.* (2003) explained the observed column density of H_3^+ in the diffuse cloud towards ζ Persei by an enhanced cosmic ray ionization rate, from the dark cloud canonical value of 3×10^{-17} to 1.2×10^{-15} s^{-1}. The latter value, which is the ionization rate of molecular hydrogen, corresponds to a cosmic ray ionization rate per hydrogen atom of 5.2×10^{-16} s^{-1}. In a more comprehensive analysis, this rate was reduced to 3.2×10^{-16} s^{-1} (Indriolo *et al.* 2007), still an order of magnitude larger than the canonical value. Indriolo *et al.* also investigated H_3^+ in other diffuse clouds and found an average value of 2×10^{-16} s^{-1}. The need for an upward revision of the cosmic ray ionization rate based on the detection of large abundances of H_3^+ in diffuse clouds and the recombination rate constant derived from storage rings and theory has also been pointed out by Dalgarno (2006).

The last piece of the H_3^+ puzzle is an understanding of the various afterglow experiments, of which only a few have been briefly discussed here. A comprehensive review of all plasma experiments up to the end of 2006 can be found in a very recently published research monograph by Larsson & Orel (2008). Glosik's group in Prague, in collaboration with Greene and Kokoouline (Glosik *et al.* 2008), have made an ambitious attempt to explain the result of all plasma experiments. If they are correct, plasma experiments which yield very low rates can be explained by formation of long-lived H_3 Rydberg states acting as storage reservoir for H_3^+ ions.

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