

The ortho : para ratio of H_3^+ in laboratory and astrophysical plasmas

BY KYLE N. CRABTREE AND BENJAMIN J. MCCALL*

*Departments of Chemistry, Astronomy, and Physics, University of Illinois,
Urbana, IL 61801, USA*

In diffuse molecular clouds, the nuclear spin temperature of H_3^+ (approx. 30 K) is much lower than the cloud kinetic temperature (approx. 70 K). To understand this temperature discrepancy, we have measured the ratio of the hop to exchange pathways (α) in the $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$ reaction (which interconverts ortho- and para- H_3^+) using high-resolution spectroscopy of the ν_2 fundamental band of H_3^+ in a hydrogenic plasma. We find that α decreases from 1.6 ± 0.1 at 350 K to its statistical value of 0.5 ± 0.1 at 135 K. We use this result to model the steady-state chemistry of diffuse molecular clouds, finding good agreement with astronomical data provided the dissociative recombination rates of ortho- and para- H_3^+ are equal and the identity branching fraction for the $\text{H}_3^+ + \text{H}_2$ reaction is large. Our results highlight the need for further studies of the $\text{H}_3^+ + \text{H}_2$ reaction as well as state-selective measurements of H_3^+ dissociative recombination.

Keywords: hydrogen; nuclear spin; spectroscopy; interstellar clouds

1. Introduction

H_3^+ is the simplest polyatomic molecule and has been of interest since its discovery by J. J. Thomson in 1911 [1]. At that time, little was known about molecular structure, as the tenets of quantum mechanics had not yet been fully developed. Considerable debate over the existence of the molecule (and the neutral molecule H_3) ensued, and it was not until the 1930s that H_3^+ was recognized as a ‘stable’ species [2]. Over the next few decades, it was proposed that H_3^+ could be present in space, as it could be produced via cosmic ray ionization of H_2 , followed by the reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. By the early 1970s, H_3^+ was recognized as the initiator of ion–molecule chemistry in the interstellar medium [3,4]. Since its infrared spectrum was obtained in the laboratory by Oka in 1980 [5], its astronomical importance has been confirmed by its detection in a variety of environments, such as interstellar clouds [6,7], the Galactic Centre [8,9] and planetary atmospheres [10–12].

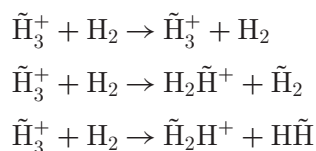
In addition to its astronomical significance, H_3^+ is of fundamental importance. As the simplest polyatomic molecule, it serves as a critical benchmark species for *ab initio* calculations [13]. Its molecular symmetry is also interesting, and

*Author for correspondence (bjmccall@illinois.edu).

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can be of pedagogical significance. Its equilibrium geometry is that of an equilateral triangle belonging to the D_{3h} point group. To treat H_3^+ with group theory [14] is a straightforward exercise that could be taught in a classroom, and the results have a practical impact on its spectroscopic properties. Owing to the Pauli exclusion principle, in its vibrational ground state, the $(J, K) = (0, 0)$ rotational level is forbidden, and spectroscopic transitions arising from that level are not observed experimentally. Another consequence of the Pauli exclusion principle is that the nuclear spin configurations ($I = \frac{3}{2}$ (ortho) and $I = \frac{1}{2}$ (para)) are linked to the rotational manifold, similar to H_2 . Also like H_2 , interconversion between ortho- and para- H_3^+ (o- H_3^+ and p- H_3^+) can only be accomplished by interaction with a strong, inhomogeneous magnetic field or by a chemical reaction.

The primary chemical reaction that can interconvert the nuclear spin configuration of H_3^+ is the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2$. On the surface, this would not appear to be a chemical reaction in the traditional sense, as the reactants and products are the same, but upon closer examination bonds are broken and formed, as can be seen from the possible outcomes of the reaction:



These are called the ‘identity’, ‘hop’ and ‘exchange’ pathways; they represent how the hydrogen atoms can be rearranged after scrambling via an $(\text{H}_5^+)^*$ collision complex. However, these scrambling processes must obey selection rules based on conservation of nuclear spin angular momentum [15,16]. These three processes can be expressed in terms of their branching fractions S^{id} , S^{hop} and S^{exch} , with $S^{\text{id}} + S^{\text{hop}} + S^{\text{exch}} = 1$. The ratio of the rates of the hop and exchange reactions ($\alpha \equiv S^{\text{hop}}/S^{\text{exch}}$) is the critical parameter that governs how exactly this reaction interconverts the nuclear spin configurations of both H_3^+ and H_2 , while S^{id} represents the fraction of collisions that do not result in hydrogen scrambling.

Prior to this work, the only study of the $\text{H}_3^+ + \text{H}_2$ scrambling reaction was done by the Oka group [17]. In that work, they probed a hydrogenic plasma with high-resolution infrared spectroscopy to measure transitions arising from various o- H_3^+ and p- H_3^+ rotational levels, thereby measuring the ortho:para ratio. They did this with ‘normal’ hydrogen gas (75% o- H_2 , 25% p- H_2), and also with nearly pure p- H_2 , and they found an enhancement in the p- H_3^+ abundance in the plasma enriched with p- H_2 . This was the first observation of nuclear spin selection rules in a chemical reaction, and from the p- H_3^+ enhancement they derived $\alpha = 2.4 \pm 0.6$ at an estimated temperature of 400 K.

In this contribution, we will discuss our work on measuring the hop:exchange ratio α at lower temperatures using a liquid nitrogen-cooled plasma cell, and its implications for chemistry in interstellar space. In §2, we describe our experiment, and in §3 we discuss the results of the measurements. Section 4 covers the chemistry of diffuse molecular clouds, and how our measurements of the $\text{H}_3^+ + \text{H}_2$ reaction factor into the hydrogenic chemistry. We conclude in §5 with some

closing thoughts and future directions on the study of nuclear spin effects in the $H_3^+ + H_2$ system.

2. Experimental details

The details of the experiment have been presented previously [18], and will be summarized briefly here. The goal of the experiment is to measure the ortho : para ratio of H_3^+ (rather, the p- H_3^+ fraction p_3) in a hydrogenic plasma of known p- H_2 fraction (p_2) at a known temperature. Hydrogen gas with a known p- H_2 fraction was prepared by combining appropriate amounts of high-purity normal hydrogen and > 99.9 per cent pure p- H_2 (produced with a p- H_2 converter [19]) to give mixtures of 25, 40, 50, 66, 83 and > 99.9 per cent p- H_2 . This gas flowed into a hollow cathode plasma cell made from an approximately 4 m cylindrical copper tube encased in a glass cell evacuated with a mechanical pump. At each end were Brewster windows to allow a laser to traverse the cell, and the copper tube was wrapped in additional small tubing to allow coolant circulation. A plasma was generated throughout the length of the cell by applying a 1 kV pulse for 200 μ s duration to a stainless steel anode located a few inches above a hole in the centre of the copper cathode, which was grounded.

To measure the p- H_3^+ fraction generated in the plasma pulse, several low- J rovibrational transitions in the ν_2 fundamental band of H_3^+ were recorded with multipass direct absorption laser spectroscopy. Tunable mid-infrared light was produced by a difference-frequency-generation laser, and was passed through the hollow cathode cell four to eight times in a White configuration. After exiting the cell, the light was measured with a DC InSb detector and sent to a computer for digitization. The transitions were recorded in a step-scan mode, in which multiple pulses were averaged at each laser frequency. After processing, the integrated intensity and linewidth of each transition were recorded as a function of time. After recording a series of transitions, the linewidths were averaged to calculate the kinetic temperature of the plasma and the integrated intensities were used to calculate the rotational temperature and p- H_3^+ fraction. For each gas mixture, measurements were taken with the cell uncooled and also with liquid nitrogen cooling, and at each temperature measurements were taken at two different cell pressures.

3. Results and discussion

The results of the experiment in both the uncooled cell ($T \sim 350$ K) and in the liquid nitrogen cooled cell ($T \sim 135$ K) are plotted in figure 1. From the data, a few observations are readily apparent:

- the cell pressure has little influence on the observed p- H_3^+ fraction;
- the p- H_3^+ fraction generally is greater in plasma enriched in p- H_2 ;
- at higher temperatures, the degree of p- H_3^+ enrichment is greater at larger p- H_2 fraction compared to the low temperature data; and
- the p_3 versus p_2 trend at high temperature is nearly linear, but not at low temperature.

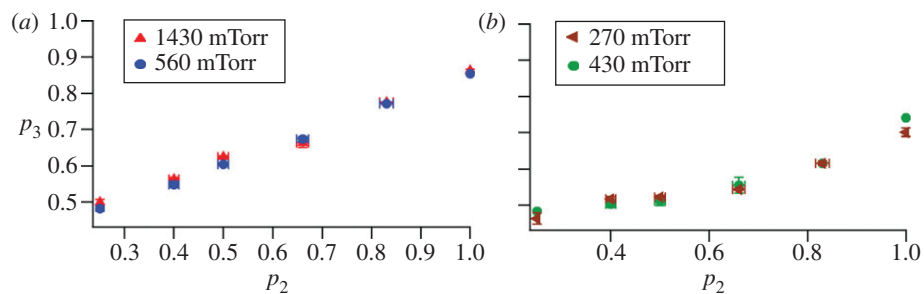


Figure 1. $p\text{-H}_3^+$ fraction versus $p\text{-H}_2$ fraction in the hollow cathode plasma. (a) Uncooled cell. (b) Liquid nitrogen cooled cell. Adapted from [18] with permission of AIP Publishing. (Online version in colour.)

These observations can be understood through the use of modelling based on nuclear spin statistics and steady-state kinetics. The $\text{H}_3^+ + \text{H}_2$ reaction is assumed to proceed through an $(\text{H}_5^+)^*$ collision complex in which hydrogen scrambling occurs. Under the assumption that the complex contains sufficient energy to populate any of a large number of H_3^+/H_2 product rotational states, the probability of any particular reaction outcome is proportional to its statistical weight. In the case of the $\text{H}_3^+ + \text{H}_2$ reaction, the statistical weights for each reaction channel can be calculated for each reaction ‘mechanism’: whether a hop or exchange pathway is followed [16]. By combining these mechanism-specific statistical weights into a steady-state model for the $p\text{-H}_3^+$ fraction [20], the relationship between p_3 and p_2 at steady state is

$$p_3 = \frac{\alpha + 2\alpha p_2 + 1}{3\alpha + 2}. \quad (3.1)$$

Equation (3.1) shows that the relationship between p_3 and p_2 is linear, and the slope of the line is related to α (see figure 2).

The high-temperature data are fit well by this equation, yielding $\alpha = 1.6 \pm 0.1$ at a temperature of 350 K. This is slightly lower than the value of 2.4 ± 0.6 reported previously at a temperature of 400 K. However, the data obtained in the liquid nitrogen cooled cell are clearly nonlinear, and are not well fit by equation (3.1). At the lower temperature (approx. 135 K), the assumption that any of a large number of product rotational states may be populated is less valid, as the energy-level spacing of H_2 is > 170 K. Thus, because of energetic effects, the relative probability of a particular outcome may not be proportional to its statistical weight. To model the steady-state chemistry at low temperature, nuclear spin-dependent rate coefficients for the $\text{H}_3^+ + \text{H}_2$ reaction are calculated using a microcanonical statistical model [21], taking temperature, S^{id} and α as parameters. Using these rate coefficients, at steady state

$$p_3 = \frac{(k_{\text{oopp}} + k_{\text{oopo}})(1 - p_2) + k_{\text{oppo}}p_2}{(k_{\text{oopp}} + k_{\text{oopo}} + k_{\text{pooop}} + k_{\text{poooo}})(1 - p_2) + (k_{\text{oppo}} + k_{\text{ppoo}})p_2}, \quad (3.2)$$

where, for example, k_{oppo} is the rate coefficient for the reaction $\text{o-H}_3^+ + \text{p-H}_2 \rightarrow \text{p-H}_3^+ + \text{o-H}_2$.

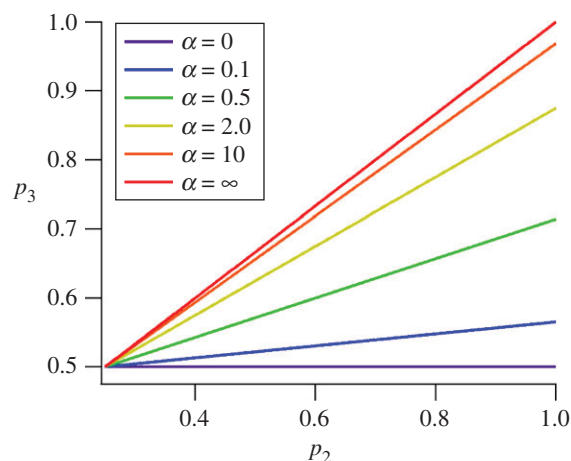


Figure 2. Plot of equation (3.1) for values of α ranging from 0 (purple, horizontal) to ∞ (red, top). Adapted from [20] with permission of AIP Publishing. (Online version in colour.)

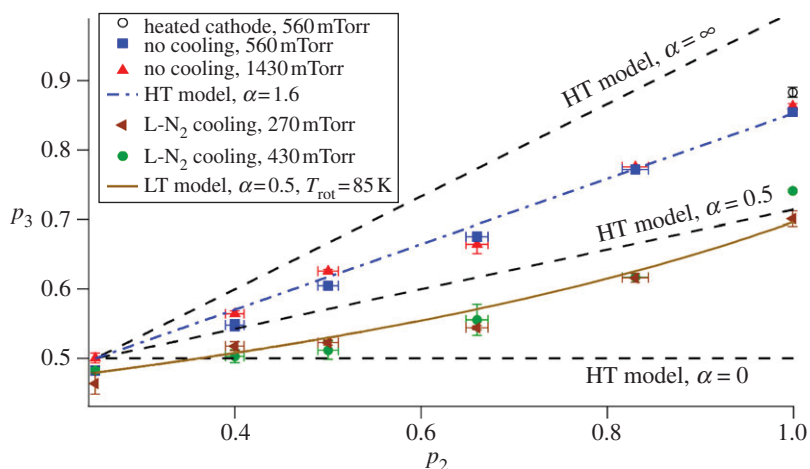


Figure 3. Summary of all data acquired in the hollow cathode, along with modelling results. Adapted from [18] with permission of AIP Publishing. (Online version in colour.)

The experimental results are shown together with the modelling results in figure 3. The low-temperature data are well described by equation (3.2) using rate coefficients calculated with $\alpha = 0.5$ and $T = 135$ K. Overall, the observed trend is that α increases with increasing temperature. To test this, the hollow cathode cell was heated to 450 K by flowing hot ethylene glycol through the coils, and the p- H_3^+ fraction was measured in a pure p- H_2 plasma. As can be seen in figure 3, the observed p_3 value is even greater than that at 350 K, suggesting a larger value of α . This single point is consistent with $\alpha = 2.2 \pm 0.3$, consistent with the overall trend of increasing α with temperature and also in line with the measurements from Oka's laboratory [17].

Physically, the results suggest that the hop: exchange ratio α is determined by the lifetime of the $(\text{H}_3^+)^*$ complex formed by the collision between H_3^+ and H_2 . The lifetime is important because, semiclassically, the hop pathway only requires that a single hydrogen move from H_3^+ to H_2 , while in order for an exchange to occur, the complex must at least undergo a hop, internal rotation and another hop. At higher temperatures, the average complex lifetime is shorter owing to the higher collision energy, and the hop pathway is favoured simply because fewer complexes exist for sufficient time to allow the exchange to occur. When the complex lifetime is sufficiently long, the complex can fully scramble, leading to the statistical outcome $\alpha = 0.5$. At 135 K, the statistical value of 0.5 is already observed, so, barring any quantum effects at extremely low temperatures, we would expect that α will remain at that value at even lower temperatures.

4. Diffuse cloud modelling

The $\text{H}_3^+ + \text{H}_2$ reaction is of particular importance in interstellar clouds, where it is responsible for thermalizing the ortho:para ratio of H_3^+ . Of particular interest are diffuse molecular clouds, because the chemistry is very simple and yet the ortho:para ratio of H_3^+ is not well understood. Diffuse molecular clouds are regions of space with densities around 10^2 cm^{-3} , most hydrogen in molecular form and most carbon in the form of C^+ [22]. Temperature in these environments is generally determined by measuring the ortho:para ratio of H_2 (called T_{01}), which is very rapidly thermalized through collisions with abundant protons [23]. A survey of diffuse molecular clouds yields $\langle T_{01} \rangle \sim 70 \text{ K}$ [24–26], but $\langle T(\text{H}_3^+) \rangle$, the temperature derived from observations of the ortho:para ratio of H_3^+ , is approximately 30 K [27].

Recent observations¹ [23] provide a total of six clouds in which ortho:para ratios of both H_3^+ and H_2 have been measured. For H_3^+ , spontaneous emission brings all p- H_3^+ into its lowest $(J, K) = (1, 1)$ rotational state faster than the collisional time scale. In the case of o- H_3^+ , its lowest-energy $(1, 0)$ state is the only state significantly populated at diffuse cloud temperatures, so the measurement of the ratio of column densities $N(1, 0)/N(1, 1)$ gives the ortho:para ratio of H_3^+ directly. The ratios observed in diffuse clouds are plotted in figure 4 in terms of their para fractions, and the data are shown in table 1. From the observations, it can be seen that the p- H_3^+ fraction is not in thermodynamic equilibrium with its environment, as measured by the p- H_2 fraction.

The chemistry of H_3^+ in diffuse molecular clouds is simple. As discussed in §1, it is formed from cosmic ray ionization of H_2 , followed by the reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$, and is destroyed primarily through dissociative recombination (DR) with electrons. Because the nuclear spin configurations of H_2 are rapidly brought into thermodynamic equilibrium, the p- H_2 fraction can be treated as a constant, and it is straightforward to calculate the nascent p- H_3^+ fraction as it is formed from H_2 (see table 2 and the dashed line in figure 4). The observed p- H_3^+ fractions fall between their nascent values and their equilibrium values, implying that H_3^+

¹The data presented in this paper differ from those in [23]. The raw data have been re-reduced to correct some recently discovered errors, and one additional H_3^+ detection has been added. Further details are available in [28].

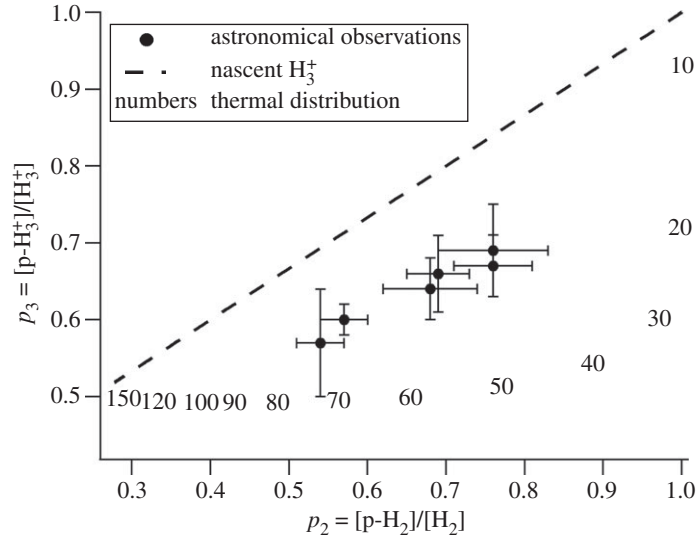


Figure 4. Observed para fractions of H_3^+ and H_2 in diffuse molecular clouds. The dashed line shows the $p\text{-}H_3^+$ fraction formed from the $H_2^+ + H_2$ reaction, and the numbers show the para fractions at thermodynamic equilibrium for the temperature given by the number at that point. Adapted from [23] with permission of the American Astronomical Society.

Table 1. Diffuse molecular cloud sight lines, observed para fractions and temperatures. All H_3^+ data are from [28] and references therein. All H_2 data are from [25] except those of ζ Per, which are from [24].

target	p_2	p_3	T_{01}	$T(H_3^+)$
ζ Per	0.68 ± 0.06	0.65 ± 0.04	58 ± 6	25 ± 3
X Per	0.69 ± 0.03	0.66 ± 0.06	57 ± 3	25 ± 5
HD 73882	0.76 ± 0.05	0.68 ± 0.05	51 ± 4	23 ± 4
HD 110432	0.57 ± 0.03	0.59 ± 0.03	69 ± 3	31 ± 4
HD 154368	0.76 ± 0.07	0.69 ± 0.07	51 ± 6	22 ± 5
λ Cep	0.54 ± 0.03	0.57 ± 0.09	72 ± 4	34 ± 13

does not undergo sufficient collisions with H_2 during its lifetime to thermalize its nuclear spin prior to its destruction via DR.

To model the chemistry occurring in diffuse molecular clouds, we have built a steady-state chemical model that takes into account the nuclear spin dependence of the relevant reactions involving H_3^+ [23]. The result is

$$p_3 = \left[k_{e,o} \frac{2x_e}{f} \left(\frac{1}{3} + \frac{2}{3} p_2 \right) + (k_{oopp} + k_{oopo})(1 - p_2) + k_{oppo} p_2 \right] / \left[k_{e,p} \frac{2x_e}{f} \left(\frac{2}{3} - \frac{2}{3} p_2 \right) + k_{e,o} \frac{2x_e}{f} \left(\frac{1}{3} + \frac{2}{3} p_2 \right) + (k_{oopp} + k_{oopo} + k_{pooop} + k_{poooo})(1 - p_2) + (k_{oppo} + k_{ppoo}) p_2 \right], \quad (4.1)$$

Table 2. Calculation of the nascent p-H₃⁺ fraction formed in diffuse molecular clouds from the H₂⁺ + H₂ reaction, assuming that cosmic ray ionization of H₂ to form H₂⁺ does not affect its nuclear spin configuration. The collision fraction represents the fraction of total H₂⁺ + H₂ collisions with the specified nuclear spin configurations. The branching fractions are for p-H₃⁺ formation, and are derived from nuclear spin selection rules [15,16]. The final column presents the calculation of the nascent p-H₃⁺ fraction. Adapted from [23] with permission of the American Astronomical Society.

reaction	collision fraction	branching fraction	p-H ₃ ⁺ fraction
p-H ₂ ⁺ + p-H ₂	$(p_2)^2$	1	p_2^2
p-H ₂ ⁺ + o-H ₂	$p_2(1 - p_2)$	$\frac{2}{3}$	$\frac{2}{3}(1 - p_2)p_2$
o-H ₂ ⁺ + p-H ₂	$(1 - p_2)p_2$	$\frac{2}{3}$	$\frac{2}{3}(1 - p_2)p_2$
o-H ₂ ⁺ + o-H ₂	$(1 - p_2)^2$	$\frac{1}{3}$	$\frac{1}{3}(1 - p_2)^2$
total	—	—	$\frac{1}{3} + \frac{2}{3}p_2$

where $k_{e,o}$ and $k_{e,p}$ are the DR rate coefficients for o-H₃⁺ and p-H₃⁺, respectively, x_e is the fractional abundance of electrons (typically approx. 1.5×10^{-4}) and f is the local molecular fraction ($2n(\text{H}_2)/[n(\text{H}) + 2n(\text{H}_2)]$; we adopt a value of 0.9 as the gas is thought to be highly molecular in these regions). Equation (4.1) is similar to equation (3.2), with the addition of terms related to H₃⁺ formation and destruction particular to diffuse molecular clouds. The k_{xxxx} rate coefficients are calculated using the aforementioned microcanonical statistical model [21]. Because of the low temperatures in these environments (< 130 K), we compute these rate coefficients using $\alpha = 0.5$. The kinetic temperature at which they are calculated is determined by the value of p_2 , as the p-H₂ fraction is in thermodynamic equilibrium with the environment. Finally, the k_{xxxx} rate coefficients are calculated assuming a rotational temperature of 10 K because H₃⁺ undergoes spontaneous emission faster than the collisional time scale at such low densities. By doing this, we ensure that the rate coefficients we compute have all p-H₃⁺ in the (1,1) state and all o-H₃⁺ in the (1,0) state, so the extra rotational energy of (2,2) and (2,1) (which decay spontaneously between collisions) is not included.

Using spin-independent low-temperature dissociative rate coefficients measured using the storage ring technique [29], we obtain the results plotted in figure 5*a*. The agreement with the astronomical observations is particularly good for $S^{\text{id}} \sim 0.9$. The identity branching fraction is not well constrained from current experimental data, as only the hop : exchange ratio α could be determined. If S^{id} really is 0.9, that would imply that a large fraction of collisions included in the total collisional rate coefficient (the Langevin rate $1.91 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) do not form scrambling complexes. However, more recent storage ring measurements of the H₃⁺ DR rate have shown that the o-H₃⁺ and p-H₃⁺ rates are not equal, but differ by a factor of 2 ($k_{e,p} \approx 2k_{e,o}$) [31,32]. However, the latest storage ring measurements call into question the results of the prior studies [33]. Recent theory agrees with this general trend, but predicts that for the lowest states of H₃⁺ $k_{e,p} \approx 10k_{e,o}$ [30], and recent flowing afterglow measurements [34] are consistent with the theoretical results. In all, the uncertainty in the DR rate coefficients is just as large a problem as the uncertainty in S^{id} (see figure 5*b*), highlighting the

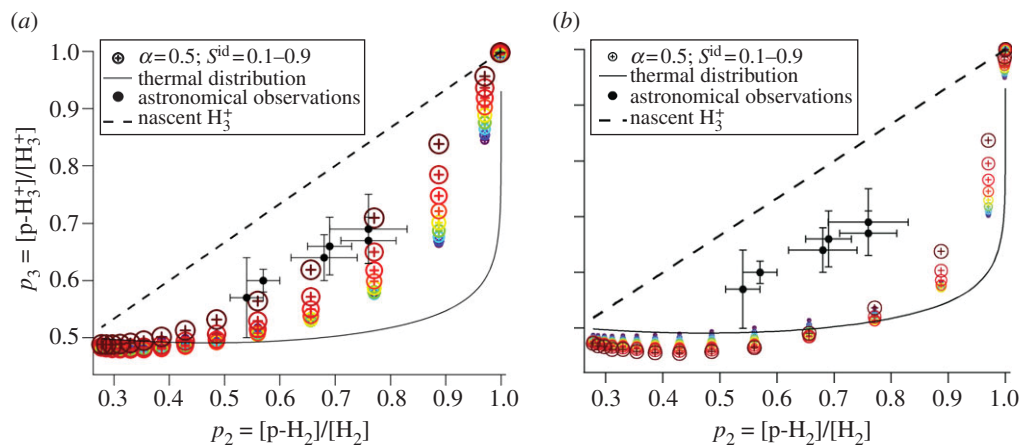


Figure 5. Results of equation (4.1). (a) Results using dissociative rate coefficients from [29]. The clusters of points are calculated from 10 to 160 K in steps of 10 K from right to left. Within each cluster, the identity branching fraction S^{id} varies from 0.1 (small purple symbols) to 0.9 (large brown symbols). (b) Results using the theoretical dissociative rate coefficients from [30]. If S^{id} is set to 1, the model still does not come into agreement with the astronomical data. Adapted from [23] with permission of the American Astronomical Society. (Online version in colour.)

need for further experimental studies of these reactions before the diffuse cloud chemistry can completely be understood.

5. Perspectives

We have measured the hop: exchange ratio α of the $H_3^+ + H_2$ reaction for the first time at low temperature, and found that at 135 K, it is at its statistical value of 0.5. The value of α increases with temperature because the $(H_5^+)^*$ collision complex has a shorter lifetime, favouring the hop pathway over the exchange. We would expect α to remain at its statistical value at even lower temperatures, but further experimental work is needed for verification. One way of performing such measurements is to use the ion trap/laser-induced reaction method [35], which has the potential of reaching temperatures as low as 10–20 K. Such measurements may also provide absolute rate coefficients, thereby determining the value of S^{id} .

Our experimental results have guided efforts at understanding the $H_3^+ - H_2$ temperature discrepancy in diffuse molecular clouds. Using steady-state modelling, we are able to explain this discrepancy provided that o- H_3^+ and p- H_3^+ have nearly equal DR rates, and that the value of S^{id} is of the order of 0.9. However, there is no experimental justification for $S^{\text{id}} = 0.9$, and equal o- H_3^+ and p- H_3^+ DR rates would contradict the most recent experimental and theoretical results, so at present the model only represents an early step towards understanding the observed temperature discrepancy. Further experimental measurements of the $H_3^+ + H_2$ reaction as well as state-specific H_3^+ DR rates would help validate or falsify our model. On the astronomical front, we are in the process

of searching for H_3^+ in eight more diffuse molecular cloud sight lines in which H_2 measurements are available. Additional H_3^+ detections would provide additional data points to more firmly establish the relationship between the ortho:para ratios of H_3^+ and H_2 .

The ortho:para ratio of H_2 is also a critical parameter in deuterium fractionation because o- H_2 acts as an energy reservoir capable of reversing fractionation reactions involving H_3^+ . Deuterium fractionation is most commonly observed in cold, dense molecular clouds, where the visual extinction is too high to allow for UV measurements of the H_2 ortho:para ratio as is done in diffuse clouds. H_3^+ , on the other hand, is readily observed in these environments. Given that a simple relationship between the H_3^+ and H_2 ortho:para ratios in diffuse clouds exists, it is possible that such a relationship also exists in dense clouds. The chemistry in dense clouds is much more complicated, and the steady-state assumption may not be valid because the p- H_2 fraction can no longer be assumed constant, so modelling is comparatively more difficult. Nevertheless, with some additional modelling work, it may be possible to infer the H_2 ortho:para ratio from measurements of H_3^+ .

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References

- 1 Thomson, J. J. 1911 Rays of positive electricity. *Philos. Mag.* **21**, 225–249. (doi:10.1080/14786440208637024)
- 2 Kragh, H. 2010 The childhood of H_3 and H_3^+ . *Astron. Geophys.* **51**, 6.25–6.27. (doi:10.1111/j.1468-4004.2010.51625.x)
- 3 Herbst, E. & Klemperer, W. 1973 The formation and depletion of molecules in dense interstellar clouds. *Astrophys. J.* **185**, 505–534. (doi:10.1086/152436)
- 4 Watson, W. D. 1973 The rate of formation of interstellar molecules by ion-molecule reactions. *Astrophys. J.* **183**, L17. (doi:10.1086/181242)
- 5 Oka, T., 1980 Observation of the infrared spectrum of H_3^+ . *Phys. Rev. Lett.* **45**, 531–534. (doi:10.1103/PhysRevLett.45.531)
- 6 Geballe, T. R. & Oka, T. 1996 Detection of H_3^+ in interstellar space. *Nature* **384**, 334–335. (doi:10.1038/384334a0)
- 7 McCall, B. J., Geballe, T. R., Hinkle, K. H. & Oka, T. 1998 Detection of H_3^+ in the diffuse interstellar medium toward Cygnus OB2 No. 12. *Science* **279**, 1910–1913. (doi:10.1126/science.279.5358.1910)
- 8 Goto, M., McCall, B. J., Geballe, T. R., Usuda, T., Kobayashi, N., Terada, H. & Oka, T. 2002 Absorption line survey of H_3^+ toward the galactic center sources. I. GCS 3-2 and GC IRS3. *Pub. Astron. Soc. Jpn.* **54**, 951–961.
- 9 Goto, M. *et al.* 2008 Absorption line survey of H_3^+ toward the galactic center sources. II. Eight infrared sources within 30 pc of the galactic center. *Astrophys. J.* **688**, 306–319. (doi:10.1086/591657)
- 10 Drossart, P. *et al.* 1989 Detection of H_3^+ on Jupiter. *Nature* **340**, 539–541. (doi:10.1038/340539a0)
- 11 Trafton, L. M., Geballe, T. R., Miller, S., Tennyson, J. & Ballester, G. E. 1993 Detection of H_3^+ from Uranus. *Astrophys. J.* **405**, 761–766. (doi:10.1086/172404)
- 12 Geballe, T. R., Jagod, M.-F. & Oka, T., 1993 Detection of H_3^+ infrared emission lines in Saturn. *Astrophys. J.* **408**, L109–L112. (doi:10.1086/186843)

- 13 Morong, C. P., Gottfried, J. L. & Oka, T. 2009 H_3^+ as the benchmark for rigorous *ab initio* theory. *J. Mol. Spectrosc.* **255**, 13–23. (doi:10.1016/j.jms.2009.02.010)
- 14 McCall, B. J. 2001 Spectroscopy of H_3^+ in laboratory and astrophysical plasmas. PhD thesis, University of Chicago.
- 15 Quack, M. 1977 Detailed symmetry selection rules for reactive collisions. *Mol. Phys.* **34**, 477–504. (doi:10.1080/00268977700101861)
- 16 Oka, T. 2004 Nuclear spin selection rules in chemical reactions by angular momentum algebra. *J. Mol. Spectrosc.* **228**, 635–639. (doi:10.1016/j.jms.2004.08.015)
- 17 Cordonnier, M., Uy, D., Dickson, R. M., Kerr, K. E., Zhang, Y. & Oka, T. 2000 Selection rules for nuclear spin modifications in ion-neutral reactions involving H_3^+ . *J. Chem. Phys.* **113**, 3181–3193. (doi:10.1063/1.1285852)
- 18 Crabtree, K. N., Kauffman, C. A., Tom, B. A., Bečka, E., McGuire, B. A. & McCall, B. J. 2011 Nuclear spin dependence of the reaction of H_3^+ with H_2 . II. Experimental measurements. *J. Chem. Phys.* **134**, 194311. (doi:10.1063/1.3587246)
- 19 Tom, B. A., Bhasker, S., Miyamoto, Y., Momose, T. & McCall, B. J. 2009 Producing and quantifying enriched para- H_2 . *Rev. Sci. Instrum.* **80**, 016108. (doi:10.1063/1.3072881)
- 20 Crabtree, K. N., Tom, B. A. & McCall, B. J. 2011 Nuclear spin dependence of the reaction of H_3^+ with H_2 . I. Kinetics and modeling. *J. Chem. Phys.* **134**, 194310. (doi:10.1063/1.3587245)
- 21 Park, K. & Light, J. C. 2007 Microcanonical statistical study of ortho–para conversion in the reaction $H_3^+ + H_2 \rightarrow (H_5^+)^* \rightarrow H_3^+ + H_2$ at very low energies. *J. Chem. Phys.* **126**, 044305. (doi:10.1063/1.2430711)
- 22 Snow, T. P. & McCall, B. J. 2006 Diffuse atomic and molecular clouds. *Annu. Rev. Astron. Astrophys.* **44**, 367–414. (doi:10.1146/annurev.astro.43.072103.150624)
- 23 Crabtree, K. N., Indriolo, N., Kreckel, H., Tom, B. A. & McCall, B. J. 2011 On the ortho : para ratio of H_3^+ in diffuse molecular clouds. *Astrophys. J.* **729**, 15. (doi:10.1088/0004-637X/729/1/15)
- 24 Savage, B. D., Bohlin, R. C., Drake, J. F. & Budich, W. 1977 A survey of interstellar molecular hydrogen. I. *Astrophys. J.* **216**, 291–307. (doi:10.1086/155471)
- 25 Rachford, B. L. *et al.* 2002 A Far Ultraviolet Spectroscopic Explorer survey of interstellar molecular hydrogen in translucent clouds. *Astrophys. J.* **577**, 221–244. (doi:10.1086/342146)
- 26 Rachford, B. L. *et al.* 2009 Molecular hydrogen in the Far Ultraviolet Spectroscopic Explorer translucent lines of sight: the full sample. *Astrophys. J. Suppl. Ser.* **180**, 125–137. (doi:10.1088/0067-0049/180/1/125)
- 27 Indriolo, N., Geballe, T. R., Oka, T. & McCall, B. J. 2007 H_3^+ in diffuse interstellar clouds: a tracer for the cosmic-ray ionization rate. *Astrophys. J.* **671**, 1736–1747. (doi:10.1086/523036)
- 28 Indriolo, N. & McCall, B. J. 2012 Investigating the cosmic-ray ionization rate in the galactic diffuse interstellar medium through observations of H_3^+ . *Astrophys. J.* **745**, 91. (doi:10.1088/0004-637X/745/1/91)
- 29 McCall, B. J. *et al.* 2004 Dissociative recombination of rotationally cold H_3^+ . *Phys. Rev. A* **70**, 052716. (doi:10.1103/PhysRevA.70.052716)
- 30 dos Santos, S. F., Kokoouline, V. & Greene, C. H. 2007 Dissociative recombination of H_3^+ in the ground and excited vibrational states. *J. Chem. Phys.* **127**, 124309. (doi:10.1063/1.2784275)
- 31 Kreckel, H. *et al.* 2005 High-resolution dissociative recombination of cold H_3^+ and first evidence for nuclear spin effects. *Phys. Rev. Lett.* **95**, 263201. (doi:10.1103/PhysRevLett.95.263201)
- 32 Tom, B. A. *et al.* 2009 Dissociative recombination of highly enriched para- H_3^+ . *J. Chem. Phys.* **130**, 031101. (doi:10.1063/1.3065970)
- 33 Kreckel, H. *et al.* 2010 Storage ring measurements of the dissociative recombination of H_3^+ : a closer look. *Phys. Rev. A* **82**, 042715. (doi:10.1103/PhysRevA.82.042715)
- 34 Varju, J., Hejduk, M., Dohnal, P., Jílek, M., Kotrčík, T., Plašil, R., Gerlich, D. & Gloščík, J. 2011 Nuclear spin effect on recombination of H_3^+ ions with electrons at 77 K. *Phys. Rev. Lett.* **106**, 203201. (doi:10.1103/PhysRevLett.106.203201)
- 35 Kreckel, H. 2007 Electron collisions and rovibrational action spectroscopy of cold H_3^+ molecules. *J. Phys. Conf. Ser.* **88**, 012064. (doi:10.1088/1742-6596/88/1/012064)