The ortho:para ratio of H$_3^+$ in laboratory and astrophysical plasmas

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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 ($\alpha$) in the H$_3^+$ + H$_2$ $\rightarrow$ H$_2$ + H$_3^+$ reaction (which interconverts ortho- and para-H$_3^+$) using high-resolution spectroscopy of the $\nu_2$ fundamental band of H$_3^+$ in a hydrogenic plasma. We find that $\alpha$ decreases from $1.6 \pm 0.1$ at 350 K to its statistical value of $0.5 \pm 0.1$ 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 H$_3^+$ + H$_2$ reaction is large. Our results highlight the need for further studies of the H$_3^+$ + 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 H$_3^+$ + H$_2$ $\rightarrow$ H$_2^+$ + 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

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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 $\text{H}_3^+$ 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 $\text{H}_2$. Also like $\text{H}_2$, interconversion between ortho- and para-$\text{H}_3^+$ ($\text{o-H}_3^+$ and $\text{p-H}_3^+$) 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 $\text{H}_3^+$ 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:

\[
\begin{align*}
\tilde{\text{H}}_3^+ + \text{H}_2 & \rightarrow \tilde{\text{H}}_3^+ + \text{H}_2 \\
\tilde{\text{H}}_3^+ + \text{H}_2 & \rightarrow \text{H}_2\tilde{\text{H}}^+ + \tilde{\text{H}}_2 \\
\tilde{\text{H}}_3^+ + \text{H}_2 & \rightarrow \tilde{\text{H}}_2\tilde{\text{H}}^+ + \text{H}\tilde{\text{H}}
\end{align*}
\]

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 $S_{\text{id}}, S_{\text{hop}}$ and $S_{\text{exch}}$, 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 $\text{H}_3^+$ and $\text{H}_2$, while $S_{\text{id}}$ 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-$\text{H}_3^+$ and p-$\text{H}_3^+$ rotational levels, thereby measuring the ortho:para ratio. They did this with ‘normal’ hydrogen gas (75% o-$\text{H}_2$, 25% p-$\text{H}_2$), and also with nearly pure p-$\text{H}_2$, and they found an enhancement in the p-$\text{H}_3^+$ abundance in the plasma enriched with p-$\text{H}_2$. This was the first observation of nuclear spin selection rules in a chemical reaction, and from the p-$\text{H}_3^+$ 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 $\alpha$ 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 $\text{H}_3^+$ + $\text{H}_2$ 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 $\text{H}_3^+$ (rather, the $\text{p-H}_3^+$ fraction $p_3$) in a hydrogenic plasma of known $\text{p-H}_2$ fraction ($p_2$) at a known temperature. Hydrogen gas with a known $\text{p-H}_2$ fraction was prepared by combining appropriate amounts of high-purity normal hydrogen and > 99.9 per cent pure $\text{p-H}_2$ (produced with a $\text{p-H}_2$ converter [19]) to give mixtures of 25, 40, 50, 66, 83 and > 99.9 per cent $\text{p-H}_2$. 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 $\mu$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 $\text{p-H}_3^+$ fraction generated in the plasma pulse, several low-$J$ rovibrational transitions in the $n_2$ fundamental band of $\text{H}_3^+$ 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 $\text{p-H}_3^+$ 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 $\text{p-H}_3^+$ fraction;
- the $\text{p-H}_3^+$ fraction generally is greater in plasma enriched in $\text{p-H}_2$;
- at higher temperatures, the degree of $\text{p-H}_3^+$ enrichment is greater at larger $\text{p-H}_2$ 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.

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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 \((\text{H}_3^+)^*\) collision complex in which hydrogen scrambling occurs. Under the assumption that the complex contains sufficient energy to populate any of a large number of \( \text{H}_3^+ / \text{H}_2 \) 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

\[
p_3 = \frac{\alpha + 2ap_2 + 1}{3\alpha + 2}.
\]  

Equation (3.1) shows that the relationship between \( p_3 \) and \( p_2 \) is linear, and the slope of the line is related to \( \alpha \) (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 \pm 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 \( \text{H}_2 \) is \( > 170 \text{ K} \). 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, \( S^{\text{id}} \) and \( \alpha \) as parameters. Using these rate coefficients, at steady state

\[
p_3 = \frac{(k_{\text{oppo}} + k_{\text{opo}})(1 - p_2) + k_{\text{oppo}}p_2}{(k_{\text{oppo}} + k_{\text{opo}} + k_{\text{poop}} + k_{\text{ppo}})(1 - p_2) + (k_{\text{oppo}} + k_{\text{ppo}})p_2}.
\]  

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

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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 $\alpha$ 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 $\alpha$. This single point is consistent with $\alpha = 2.2 \pm 0.3$, consistent with the overall trend of increasing $\alpha$ with temperature and also in line with the measurements from Oka’s laboratory [17].

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Physically, the results suggest that the hop: exchange ratio $\alpha$ is determined by the lifetime of the $(H_3^+)^*$ 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 $\alpha$ will remain at that value at even lower temperatures.

4. Diffuse cloud modelling

The $H_3^+ + H_2$ 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 $(T_{01}) \sim 70$ K [24–26], but $(T(H_3^+))$, the temperature derived from observations of the ortho:para ratio of $H_3^+$, is approximately 30 K [27].

Recent observations$^1$ [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 $H_2^+ + H_2 \rightarrow H_3^+ + H$, 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 $H_3^+$

$^1$The 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].
Ortho: para H® in plasmas

Figure 4. Observed para fractions of H® + and H2 in diffuse molecular clouds. The dashed line shows the p-H® + fraction formed from the H® + + H2 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® + data are from [28] and references therein. All H2 data are from [25] except those of ζ Per, which are from [24].

<table>
<thead>
<tr>
<th>target</th>
<th>p2</th>
<th>p3</th>
<th>T01</th>
<th>T(H® +)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ζ Per</td>
<td>0.68 ± 0.06</td>
<td>0.65 ± 0.04</td>
<td>58 ± 6</td>
<td>25 ± 3</td>
</tr>
<tr>
<td>X Per</td>
<td>0.69 ± 0.03</td>
<td>0.66 ± 0.06</td>
<td>57 ± 3</td>
<td>25 ± 5</td>
</tr>
<tr>
<td>HD 73882</td>
<td>0.76 ± 0.05</td>
<td>0.68 ± 0.05</td>
<td>51 ± 4</td>
<td>23 ± 4</td>
</tr>
<tr>
<td>HD 110432</td>
<td>0.57 ± 0.03</td>
<td>0.59 ± 0.03</td>
<td>69 ± 3</td>
<td>31 ± 4</td>
</tr>
<tr>
<td>HD 154368</td>
<td>0.76 ± 0.07</td>
<td>0.69 ± 0.07</td>
<td>51 ± 6</td>
<td>22 ± 5</td>
</tr>
<tr>
<td>λ Cep</td>
<td>0.54 ± 0.03</td>
<td>0.57 ± 0.09</td>
<td>72 ± 4</td>
<td>34 ± 13</td>
</tr>
</tbody>
</table>

does not undergo sufficient collisions with H2 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® + [23]. The result is

\[
p_3 = \left[ \frac{k_{e,o}}{f} \left( \frac{1}{3} + \frac{2}{3} p_2 \right) + (k_{oopp} + k_{oppo})(1 - p_2) + k_{oppo} p_2 \right] \left[ \frac{k_{e,p}}{f} \left( \frac{2}{3} - \frac{2}{3} p_2 \right) + \frac{k_{e,o}}{f} \left( \frac{1}{3} + \frac{2}{3} p_2 \right) \right] + (k_{oopp} + k_{oppo} + k_{oop} + k_{poo})(1 - p_2) + (k_{oppo} + k_{pooo}) p_2, \tag{4.1}
\]

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Table 2. Calculation of the nascent p-H\textsubscript{3}\textsuperscript{+} fraction formed in diffuse molecular clouds from the H\textsubscript{2}\textsuperscript{+} + H\textsubscript{2} reaction, assuming that cosmic ray ionization of H\textsubscript{2} to form H\textsubscript{2}\textsuperscript{+} does not affect its nuclear spin configuration. The collision fraction represents the fraction of total H\textsubscript{2}\textsuperscript{+} + H\textsubscript{2} collisions with the specified nuclear spin configurations. The branching fractions are for p-H\textsubscript{3}\textsuperscript{+} formation, and are derived from nuclear spin selection rules [15,16]. The final column presents the calculation of the nascent p-H\textsubscript{3}\textsuperscript{+} fraction. Adapted from [23] with permission of the American Astronomical Society.

<table>
<thead>
<tr>
<th>reaction</th>
<th>collision fraction</th>
<th>branching fraction</th>
<th>p-H\textsubscript{3}\textsuperscript{+} fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-H\textsubscript{2}\textsuperscript{+} + p-H\textsubscript{2}</td>
<td>(p\textsubscript{2})\textsuperscript{2}</td>
<td>1</td>
<td>p\textsubscript{2}</td>
</tr>
<tr>
<td>p-H\textsubscript{2}\textsuperscript{+} + o-H\textsubscript{2}</td>
<td>p\textsubscript{2}(1 − p\textsubscript{2})</td>
<td>2/3</td>
<td>2/3(1 − p\textsubscript{2})p\textsubscript{2}</td>
</tr>
<tr>
<td>o-H\textsubscript{2}\textsuperscript{+} + p-H\textsubscript{2}</td>
<td>(1 − p\textsubscript{2})p\textsubscript{2}</td>
<td>2/3</td>
<td>2/3(1 − p\textsubscript{2})p\textsubscript{2}</td>
</tr>
<tr>
<td>o-H\textsubscript{2}\textsuperscript{+} + o-H\textsubscript{2}</td>
<td>(1 − p\textsubscript{2})\textsuperscript{2}</td>
<td>1/3</td>
<td>1/3(1 − p\textsubscript{2})\textsuperscript{2}</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td>1/3 + 2/3p\textsubscript{2}</td>
</tr>
</tbody>
</table>

where k\textsubscript{e,o} and k\textsubscript{e,p} are the DR rate coefficients for o-H\textsubscript{3}\textsuperscript{+} and p-H\textsubscript{3}\textsuperscript{+}, respectively, x\textsubscript{e} is the fractional abundance of electrons (typically approx. 1.5 × 10\textsuperscript{-4}) and f is the local molecular fraction (2n(H\textsubscript{2})/[n(H) + 2n(H\textsubscript{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 H\textsubscript{3}\textsuperscript{+} formation and destruction particular to diffuse molecular clouds. The k\textsubscript{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 α = 0.5. The kinetic temperature at which they are calculated is determined by the value of p\textsubscript{2}, as the p-H\textsubscript{2} fraction is in thermodynamic equilibrium with the environment. Finally, the k\textsubscript{xxxx} rate coefficients are calculated assuming a rotational temperature of 10 K because H\textsubscript{3}\textsuperscript{+} 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-H\textsubscript{3}\textsuperscript{+} in the (1,1) state and all o-H\textsubscript{3}\textsuperscript{+} 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 5a. The agreement with the astronomical observations is particularly good for S\textsuperscript{id} ∼ 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\textsuperscript{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 × 10\textsuperscript{-9} cm\textsuperscript{3}s\textsuperscript{-1}) do not form scrambling complexes. However, more recent storage ring measurements of the H\textsubscript{3}\textsuperscript{+} DR rate have shown that the o-H\textsubscript{3}\textsuperscript{+} and p-H\textsubscript{3}\textsuperscript{+} rates are not equal, but differ by a factor of 2 (k\textsubscript{e,p} ≈ 2k\textsubscript{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 H\textsubscript{3}\textsuperscript{+} k\textsubscript{e,p} ≈ 10k\textsubscript{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\textsuperscript{id} (see figure 5b), highlighting the

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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 $\alpha$ of the $\text{H}_3^+ + \text{H}_2$ 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 $\alpha$ increases with temperature because the $(\text{H}_3^+)^*\text{H}_2$ collision complex has a shorter lifetime, favouring the hop pathway over the exchange. We would expect $\alpha$ 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 $S^{\text{id}}$.

Our experimental results have guided efforts at understanding the $\text{H}_3^+ - \text{H}_2$ temperature discrepancy in diffuse molecular clouds. Using steady-state modelling, we are able to explain this discrepancy provided that $\text{o-H}_3^+$ and $\text{p-H}_3^+$ have nearly equal DR rates, and that the value of $S^{\text{id}}$ is of the order of 0.9. However, there is no experimental justification for $S^{\text{id}} = 0.9$, and equal $\text{o-H}_3^+$ and $\text{p-H}_3^+$ 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 $\text{H}_3^+ + \text{H}_2$ reaction as well as state-specific $\text{H}_3^+$ DR rates would help validate or falsify our model. On the astronomical front, we are in the process.
of searching for \( \text{H}_3^+ \) in eight more diffuse molecular cloud sight lines in which \( \text{H}_2 \) measurements are available. Additional \( \text{H}_3^+ \) detections would provide additional data points to more firmly establish the relationship between the ortho:para ratios of \( \text{H}_3^+ \) and \( \text{H}_2 \).

The ortho:para ratio of \( \text{H}_2 \) is also a critical parameter in deuterium fractionation because \( \text{o-H}_2 \) acts as an energy reservoir capable of reversing fractionation reactions involving \( \text{H}_3^+ \). 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 \( \text{H}_2 \) ortho:para ratio as is done in diffuse clouds. \( \text{H}_3^+ \), on the other hand, is readily observed in these environments. Given that a simple relationship between the \( \text{H}_3^+ \) and \( \text{H}_2 \) 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-\( \text{H}_2 \) 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 \( \text{H}_2 \) ortho:para ratio from measurements of \( \text{H}_3^+ \).

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