ON THE ORTHO:PARA RATIO OF H$_3^+$ IN DIFFUSE MOLECULAR CLOUDS$^1$

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ABSTRACT

The excitation temperature $T_{01}$ derived from the relative intensities of the $J = 0$ (para) and $J = 1$ (ortho) rotational levels of H$_2$ has been assumed to be an accurate measure of the kinetic temperature in interstellar environments. In diffuse molecular clouds, the average value of $T_{01}$ is $\sim 70$ K. However, the excitation temperature $T(H_3^+)$ derived from the $(J, K) = (1, 1)$ (para) and (1, 0) (ortho) rotational levels of H$_3^+$ has been observed to be $\sim 30$ K in the same types of environments. In this work, we present observations of H$_3^+$ in three additional diffuse cloud sight lines for which H$_2$ measurements are available, showing that in 4 of 5 cases $T_{01}$ and $T(H_3^+)$ are discrepant. We then examine the thermalization mechanisms for the ortho:para ratios of H$_3^+$ and H$_2$, concluding that indeed $T_{01}$ is an accurate measure of the cloud kinetic temperature, while the ortho:para ratio of H$_3^+$ need not be thermal. By constructing a steady-state chemical model taking into account the nuclear-spin-dependence of reactions involving H$_3^+$, we show that the ortho:para ratio of H$_3^+$ in diffuse molecular clouds is likely governed by a competition between dissociative recombination with electrons and thermalization via reactive collisions with H$_2$.

Subject headings: astrochemistry – ISM

1. INTRODUCTION

Observations of H$_3^+$ in diffuse molecular clouds (diffuse clouds in which a significant fraction of the hydrogen is in molecular form; Snow & McCall 2006) have led to various unexpected discoveries. The very first detection of H$_3^+$ along a diffuse molecular cloud sight line (toward Cyg OB2 12) showed an abundance about 10 times greater than expected for the environment (McCall et al. 1998a). This surprising overabundance—also found toward several more diffuse cloud sight lines—led to the eventual conclusion that the ionization rate of H$_2$ due to cosmic rays, $G_2$, must be about 1 order of magnitude larger than previously thought (McCall et al. 2003; Indriolo et al. 2007). Another puzzling outcome from H$_3^+$ observations is that the average excitation temperature derived from the two lowest energy states (⟨$T(H_3^+)$⟩) $\approx 30$ K; Indriolo et al. 2007) differs significantly from the average excitation temperature derived from the two lowest rotational states of H$_2$ ($T_{01}$) $\approx 70$ K; Savage et al. 1977; Rachford et al. 2002; 2009). Given that both species are expected to be thermalized to the cloud kinetic temperature by collisions, such a discrepancy is unexpected.

Despite the fact that the $J = 0$ and $J = 1$ levels of H$_2$ are essentially different “species”—conversion between the even–$J$ para and odd–$J$ ortho nuclear spin states is only possible through reactive collisions—it has long been assumed that $T_{01}$ is a good approximation for the kinetic temperature, $T_{\text{kin}}$, in diffuse molecular clouds. This is because H$_2$ molecules are expected to experience many reactive collisions with protons during their lifetimes. As a result, the ortho and para populations of H$_2$ should be brought into thermal equilibrium with the proton kinetic temperature (Dalgarno et al. 1973).

Similarly, H$_3^+$ also has ortho and para nuclear spin states ($(J, K) = (1, 1)$ is the lowest lying para state, and $(J, K) = (1, 0)$ the lowest lying ortho state). For H$_3^+$ though, the relative population between the two states has been expected to be thermalized by reactive collisions with H$_2$ (McCall et al. 1998b; McCall et al. 2003; Gibb et al. 2010). As the average values of $T_{01}$ and $T(H_3^+)$ do not agree, this does not seem to be the case.

However, out of the 66 and 18 sight lines used to compute ($T_{01}$) and ⟨$T(H_3^+)$⟩, respectively, only 2 are shared between both samples. While previously reported values of $T_{01}$ and $T(H_3^+)$ do differ for these sight lines toward ζ Per and X Per by about 30 K (Savage et al. 1977; Rachford et al. 2002; Indriolo et al. 2007), such a small sample does not provide particularly meaningful results. In order to increase the number of sight lines with ortho and para column densities determined for both H$_2$ and H$_3^+$, we have made observations searching for H$_3^+$ absorption features along sight lines with measured H$_2$ column densities. These observations and our data reduction procedures are described in Section 2. Section 3 discusses and justifies many of the assumptions made concerning molecular hydrogen and $T_{01}$ in diffuse molecular clouds. In Section 4, we examine the H$_3^+$ + H$_2$ reaction and present steady state models to explore the temperature discrepancy between $T_{01}$ and $T(H_3^+)$. Section 5 reviews the observations and modeling, and presents our conclusions from the work.

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2. OBSERVATIONS & DATA REDUCTION
Target sight lines were selected based on $H_2$ column densities \cite{Savage1977, Rachford2002, Rachford2009} and $L$-band magnitudes. We required that the $J = 0$ and $J = 1$ column densities of $H_2$ ($N(0)$ and $N(1)$, respectively) both be known, and that the total $H_2$ column density ($N(H_2)$) be greater than $10^{20}$ cm$^{-2}$. The $L$-band magnitude was required to be brighter than 6 mag so that the necessary integration times would be relatively short. Observations focused on the $(R(1), 1)^n$, $(R(1), 0)$, and $(R(1), 1)^l$ transitions (at 3.668083 $\mu$m, 3.668516 $\mu$m, and 3.715479 $\mu$m, respectively) which arise from the $(J, K) = (1, 1)$ and $(1, 0)$ levels of the ground vibrational state of $H_2^+$, the only levels expected to be significantly populated at average diffuse cloud temperatures ($T \sim 70$ K).

Spectra in support of this project were obtained using the Phoenix spectrometer \cite{Hinkle2003} at the Gemini South Telescope and the Cryogenic High-resolution Infrared Echelle Spectrograph (CRIRES) \cite{Kaufl2004} at the Very Large Telescope (VLT). Observations at Gemini South were made in queue mode, and the Phoenix spectrometer was used with its echelle grating and 0.17" slit to produce a resolving power of about 70,000, and with the L2734 filter to select the order containing the $(R(1), 1)^n$ and $(R(1), 0)$ transitions. Observations at the VLT were made in service mode, and CRIRES was used with its 0.2" slit to provide a resolving power of about 100,000, and a reference wavelength of 3715.0 nm to cover the $(R(1), 1)^n$ and $(R(1), 0)$ transitions on detector 1 and the $(R(1), 1)^l$ transition on detector 3. The adaptive optics system was used with CRIRES to maximize starlight passing through the narrow slit. In addition to the science targets, bright, early-type stars were observed for use as telluric standards. For all observations, the star was nodded along the slit in an ABBA pattern in order to facilitate the removal of atmospheric emission lines and dark current via the subtraction of neighboring images. A log containing the observed sight lines and respective integration times is given in Table \ref{tab:1}.

Various standard IRAF\footnote{http://iraf.noao.edu/} procedures were used in the data reduction process. Given the different state of data available from Phoenix versus CRIRES, different amounts of processing were required for data from the 2 telescopes. For each night of Phoenix observations, a bad pixel map was created from the average of several dark frames, and these pixels were interpolated over in the object and flat frames. Flats were then combined to create a normalized flat field which was divided over the object frames. Neighboring AB image pairs were subtracted from each other to remove atmospheric emission and dark current. Finally, one-dimensional spectra were extracted using \textit{apall}. In the case of CRIRES observations, data were processed through the CRIRES specific pipeline, resulting in fully reduced two-dimensional spectral images for each target (given the product codes SCOM and PCOM by the pipeline). One-dimensional spectra were extracted from these images. All such spectra from both telescopes were then imported to IGOR \cite{http://www.wavemetrics.com/} where the remainder of reduction was performed.

Individual Phoenix spectra within an exposure sequence for a given target were then added together. Science target spectra from both telescopes were divided by telluric standard spectra to remove atmospheric absorption features and to normalize each spectrum. These normalized spectra were wavelength calibrated with a typical accuracy of $\sim 2$ km s$^{-1}$ using the vacuum wavelengths of the atmospheric absorption lines. Calibrated spectra were then shifted into the local standard of rest (LSR) frame, and spectra of the same target from different nights were combined using a variance-weighted mean. For each sight line the continuum surrounding the absorption features was then fit with an $n^{\text{th}}$ order polynomial ($n = 7 - 9$) and the spectrum was divided by the fit to re-normalize the continuum level. The resulting spectra for sight lines with $H_2^+$ absorption features—HD 154368, HD 73882, and HD 110432—are shown in Figure \ref{fig:1}. Although $H_2^+$ spectra for $\zeta$ Per and X Per were reported in Indriolo2007, the reduction process utilized in that study did not combine spectra using a variance-weighted mean, nor did it fit fluctuations in the continuum level with a polynomial function. For the purpose of consistency, we have reprocessed the data from both sight lines. No new data have been added, but differences in the method of processing have resulted in output spectra with slightly better signal-to-noise ratios (S/N). These spectra are also shown in Figure \ref{fig:1}.

Absorption features due to $H_2^+$ were fit with Gaussian functions in order to determine equivalent widths, velocity full-width at half-maxima (FWHM), and interstellar gas velocities. Our fitting procedure uses the functional form of a Gaussian where area (as opposed to amplitude)
is a free parameter, and includes a fit to the continuum level, \( y_0 \). In the case of the \( R(1,1)^u \) and \( R(1,0) \) lines, both absorption features are fit simultaneously and a single best-fit continuum level is found. Uncertainties on the equivalent widths (\( \delta W_\lambda \)) and continuum level (\( \delta y \))—both at the 1σ level—were output by the fitting process. To estimate the systematic uncertainties due to continuum placement, we forced the continuum level to \( y_0 + \delta y \) and \( y_0 - \delta y \) and re-fit the absorption lines. Variations in the equivalent widths due to this shift are small compared to those reported by the fitting procedure and so are not included in our analysis (i.e., \( \sigma(W_\lambda)=\delta W_\lambda \)). Assuming optically thin absorption lines and taking transition dipole moments and wavelengths from Goto et al. (2002) and references therein, column densities were derived from equivalent widths using the standard relation. All of these results are shown in Table 2.

These observations increase the total number of sight lines with both \( H_3^+ \) and \( H_2 \) detections from 2 to 5. Column densities, \( \text{para} \)-fractions, and excitation temperatures for both species along all 5 sight lines are collected in Table 3. \( H_2 \) data come from Savage et al. (1977) and Rachford et al. (2002). Uncertainties on all values are 1σ. The excitation temperatures inferred from the \( R(1,0) \), \( R(1,1)^u \), and \( R(1,1)^l \) absorption lines of \( H_3^+ \) range from 20 \( \leq T(H_3^+) \leq 46 \) K, while those reported for \( H_2 \) vary from 51 \( \leq T(H_2) \leq 68 \) K. In 4 sight lines \( T_{01} \) is greater than \( T(H_3^+) \) by about 30 K, while for X Per \( T_{01} \) and \( T(H_3^+) \) are consistent within uncertainties. Still, these observations clearly show that for the same interstellar material along 4 different diffuse molecular cloud sight lines the excitation temperatures derived from \( H_3^+ \) and \( H_2 \) do not agree.

### 3. \( H_2 \) THERMALIZATION

Given the large discrepancies between \( T_{01} \) inferred from \( H_2 \) and the excitation temperature of \( H_3^+ \), it is important to re-examine the assumption that the inferred \( T_{01} \) accurately reflects the kinetic temperature of the diffuse molecular clouds. If this assumption were incorrect, it would be conceivable that \( H_3^+ \) provides the true (lower) temperature of diffuse molecular clouds. There are at least 4 reasons this assumption could be invalid: (1) observational errors in the determination of the \( J = 0 \) and \( J = 1 \) column densities of \( H_2 \); (2) an insufficient frequency of \( H^+ + H_2 \) collisions to achieve steady state; (3) the steady state of this reaction being different from the thermodynamic equilibrium; and (4) errors caused by a varying \( J = 0 : 1 \) ratio along the line of sight. In the following subsections, we investigate each of these possibilities in turn.

#### 3.1. Observational Determination of \( H_2 \) Columns

The measurement of the column densities of \( J = 0 \) and \( J = 1 \) of \( H_2 \) is performed by profile fitting to spectra of the Lyman (\( A-X \)) band in the ultraviolet, recorded with Copernicus or FUSE. The \( H_2 \) transitions are optically thick, and are completely opaque in the line cores. Given the difficulties in accurately retrieving column densities from optically thick transitions, one might worry that the inferred \( T_{01} \) is contaminated by uncertainties caused by radiative transfer.

According to B. L. Rachford (private communication, 2010), the detailed shape of the combined profile of the \( J = 0 \) line and the two \( J = 1 \) lines is quite sensitive to the ratio of the column densities of these two rotational levels, and thus provides a very useful probe of \( T_{01} \). Because multiple vibronic bands of \( H_2 \), which are known to be relatively free of contamination by stellar lines, are used in the determination of \( T_{01} \), it is difficult to envision any systematic errors that could affect the measurements. The statistical errors in the column density measurements are typically \( \sim 0.1 \) dex, and we can therefore conclude that the ultraviolet measurements provide an accurate and fairly precise measure of the ratio of \( N(0) \) to \( N(1) \) for \( H_2 \).

#### 3.2. Frequency of \( H^+ + H_2 \) Reactions

The \( J = 0 \) and \( J = 1 \) rotational levels of \( H_2 \) belong to different spin modifications (\( \text{para} \) and \( \text{ortho} \), respectively) and are therefore not thermalized by non-reactive collisions or radiative transitions. Only chemical reactions, in which the protons are exchanged, can affect the nuclear spin modification of \( H_2 \).

Since \( H_2 \) is formed in a highly exothermic reaction on grain surfaces, its nascent rotational (and spin) distribution is presumed to represent a high temperature (Takahashi 2001). In the high temperature limit, \( H_2 \) should be formed with an \( \text{ortho}:\text{para} \) ratio of 3:1. If an insufficient number of reactive collisions occur between the formation of an \( H_2 \) molecule and its subsequent

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8 Strictly speaking, large inhomogeneous magnetic fields, such as found on the surface of paramagnetic catalysts, can also affect the nuclear spin modification of \( H_2 \), but we assume that such effects are negligible in interstellar conditions.
reactive collisions. If of an $H\beta$ destruction (by photodissociation or cosmic-ray ionization), then the average ortho:para ratio of $H_2$ may lie somewhere between the nascent value (3:1) and the thermalized value (1:2 at 60 K, for example). This could lead to $T_{01}$ overestimating the true cloud kinetic temperature.

The number of reactive collisions suffered by an average $H_2$ molecule in its lifetime can be expressed as $N_{e\gamma} \equiv \tau_{ife}/\tau_{x\gamma}$, where $\tau_{ife}$ is the average lifetime of an $H_2$ molecule and $\tau_{x\gamma}$ is the average time between reactive collisions. If $N_{e\gamma} \gg 1$, then the ortho:para ratio of $H_2$ should reflect the steady-state of the reaction in question.

In diffuse molecular clouds, $H_2$ is formed on grains at a rate of $R_{\text{grain}}(\text{H}_2)$, where $R$ is the grain formation rate (typically taken to be about $3 \times 10^{-17}$ cm$^3$ s$^{-1}$; e.g. Spitzer 1978, Gry et al. 2002), $n_{\text{H}} \equiv n(\text{H}) + 2n(H_2)$ is the total number density of hydrogen nuclei, and $n(H)$ is the number density of atomic hydrogen. The destruction of $H_2$ is dominated by cosmic-ray ionization and photodissociation (following absorption in the Lyman bands), and

### TABLE 2
#### Absorption Line Parameters

| Object     | Transition | $v_{LSR}$ (km s$^{-1}$) | FWHM (km s$^{-1}$) | $W_\lambda$ (10$^{-6}$ µm) | $\sigma(W_\lambda)$ (10$^{-6}$ µm) | $N(J,K)$ (10$^{13}$ cm$^{-2}$) | $\sigma(N)$ (10$^{13}$ cm$^{-2}$) |
|------------|------------|--------------------------|------------------|----------------|-------------------------------|-----------------------------|-------------|
| $\zeta$ Per | $R(1,1)$   | 7.7                      | 11.0             | 0.99           | 0.13                          | 4.99                        | 0.53         |
|            | $R(1,0)$   | 6.1                      | 9.0              | 1.00           | 0.11                          | 2.53                        | 0.29         |
| X Per      | $R(1,1)$   | 8.2                      | 9.1              | 0.80           | 0.17                          | 3.34                        | 0.69         |
|            | $R(1,0)$   | 6.3                      | 10.2             | 1.30           | 0.18                          | 3.29                        | 0.45         |
| HD 154368  | $R(1,1)$   | 5.4                      | 6.0              | 1.79           | 0.30                          | 7.43                        | 1.24         |
|            | $R(1,0)$   | 5.2                      | 5.6              | 1.12           | 0.29                          | 2.83                        | 0.74         |
| HD 73882   | $R(1,1)$   | 5.9                      | 3.9              | 1.44           | 0.21                          | 5.97                        | 0.86         |
|            | $R(1,0)$   | 5.7                      | 3.2              | 1.16           | 0.19                          | 2.94                        | 0.48         |
|            | $R(1,1)^d$ | 5.4                      | 3.5              | 1.34           | 0.15                          | 6.15                        | 0.69         |
| HD 110432  | $R(1,1)$   | -3.8                     | 6.9              | 0.74           | 0.06                          | 3.08                        | 0.24         |
|            | $R(1,0)$   | -3.3                     | 7.5              | 0.83           | 0.07                          | 2.11                        | 0.17         |
|            | $R(1,1)^d$ | -3.1                     | 8.1              | 0.69           | 0.06                          | 3.15                        | 0.28         |

### TABLE 3
#### Target Sight Line Properties

| Target | $N(1,1)$ (10$^{13}$ cm$^{-2}$) | $N(1,0)$ (10$^{13}$ cm$^{-2}$) | $p_3$ | $T(H_2^+)$ (K) | log[$N(0)$] (cm$^{-2}$) | log[$N(1)$] (cm$^{-2}$) | $p_4^f$ | $T_{01}$ (K) | $p_4^f$ |
|--------|-------------------------------|-------------------------------|-------|----------------|----------------|----------------|-------|-------------|--------|
| $\zeta$ Per     | 4.09 ± 0.53                  | 3.34 ± 0.69                  | 0.02 ± 0.04 | 28 ± 4        | 20.51 ± 0.09 | 20.76 ± 0.03 | 0.05   | 56 ± 6      | 0.05   |
| X Per          | 2.53 ± 0.29                  | 3.29 ± 0.45                  | 0.40 ± 0.04 | 46$^{+21}_{-13}$ | 20.18 ± 0.09 | 20.42 ± 0.06 | 0.15   | 57 ± 4      | 0.05   |
| HD 154368      | 2.83 ± 0.74                  | 2.94 ± 0.48                  | 0.76 ± 0.07 | 20 ± 4        | 20.50 ± 0.07 | 20.50 ± 0.07 | 0.04   | 51 ± 8      | 0.05   |
| HD 73882       | 4.93 ± 0.12                  | 2.94 ± 0.48                  | 0.76 ± 0.07 | 23 ± 3        | 20.27 ± 0.04 | 20.27 ± 0.04 | 0.04   | 68 ± 5      | 0.05   |
| HD 110432      | 6.08 ± 0.04                  | 2.94 ± 0.48                  | 0.76 ± 0.07 | 30 ± 2        | 68 ± 5        | 68 ± 5        | 0.04   | 57 ± 0.05   | 0.05   |

**Note.** — Column 3 ($v_{LSR}$) gives the interstellar gas velocity in the local standard of rest frame. Column 4 (FWHM) gives the full width at half-maximum of the absorption features. Columns 5 and 6 show the equivalent width, $W_\lambda$, and its 1σ uncertainty, $\sigma(W_\lambda)$, respectively. Columns 7 and 8 give the column density of $H_2^+$ in the state each transition probes, $N(J,K)$, and its uncertainty, $\sigma(N)$, respectively. Values for these parameters in the $\zeta$ Per and X Per sight lines were previously reported in Indriolo et al. (2007). The new values for both absorption lines toward $\zeta$ Per and the $R(1,0)$ line toward X Per are consistent with the previously published results within uncertainties. However, the new and old results for the $R(1,1)^d$ line toward X Per are inconsistent. Upon inspection, we found this to be due to a bad fit to that line during the 2007 analysis. In all cases, the values published herein should be taken to supersede those from Indriolo et al. (2007).

**Note.** — Measured column densities for the lowest lying ortho and para states of $H_2$ and $H_2^+$ are shown for the 5 sight lines with all such data available. Also shown are the para:fractions for each species and the rotational temperatures derived from a simple 2-state system analysis.

- **a** Updated analysis of $H_2^+$ data originally presented in Indriolo et al. (2007)
- **b** $H_2$ data from Savage et al. (1977)
- **c** $H_2$ data from Rachford et al. (2002)
- **d** May be affected by multiple velocity components (Crawford 1995)
- **e** $p$-$H_2^+$ fraction: $N(1,1)/(N(1,0) + N(1,1))$
- **f** $p$-$H_2$ fraction: $N(1)/(N(0) + N(1))$
has a rate of \((\zeta_2 + \Gamma)n(H_2)\), where \(\Gamma\) is the photodissociation rate. In steady state, these two rates are equal, and we can solve for \(\tau_{\text{H}^+ f e} = (\zeta_2 + \Gamma)^{-1} = n(H_2)/[Rn_H H(H)]\). By using the definition of the local molecular fraction \(f_{\text{H}_2} \equiv 2n(H_2)/n_H\) (which we will simply call \(f\)), we can rewrite this expression as \(\tau_{\text{H}^+ f e} = f/[2Rn_H (1 - f)]\).

Assuming that the reaction of \(\text{H}^+ + \text{H}_2\) dominates the interconversion of \(o\)-\(\text{H}_2\) and \(p\)-\(\text{H}_2\) (ortho- and para-\(\text{H}_2\), respectively), we can write \(\tau_{\text{H}^+ f e} = [k_{\text{ic}} n(\text{H}^+)]^{-1}\), where \(k_{\text{ic}}\) is the rate coefficient for the interconversion reaction.

Substituting into the equation for \(N_{\text{r}x\text{n}}\), we find

\[
N_{\text{r}x\text{n}} = \frac{k_{\text{ic}} n(\text{H}^+) f}{R / n_H [2(1 - f)]}.
\]

To estimate the number density of \(\text{H}^+\), we consider the steady state of its formation and destruction. \(\text{H}^+\) is formed by cosmic-ray ionization of \(\text{H}\) atoms, at a rate of \(\zeta_2 n(H)\), where \(\zeta_2\) is the cosmic-ray ionization rate of \(H\) \((2.3 \zeta_2 \approx 1.5 \zeta_2\); Glassgold & Langer 1974). Given the abundances of various species in diffuse clouds and the rate coefficients for reactions between \(\text{H}^+\) and such species, chemical models (e.g. Woodall et al. 2007) predict that \(\text{H}^+\) is destroyed predominantly by charge transfer to atomic oxygen, with a rate of \(k_{\text{ct}} n(\text{H}^+) n(O)\).

Equating these rates of formation and destruction and solving for \(n(\text{H}^+)\), we find \(n(\text{H}^+) = \zeta_2 (1 - f)/[k_{\text{ct}} x(O)]\), where \(x(O) = n(O)/n_H\). Finally, substituting this into the expression for \(N_{\text{r}x\text{n}}\) gives

\[
N_{\text{r}x\text{n}} = \frac{k_{\text{ic}} \zeta_2}{R / k_{\text{ct}} 2n_H x(O)} f / [2(1 - f)].
\]

Adopting values of \(k_{\text{ic}} = 2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\) (Gerlich 1990), \(R = 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}\), \(\zeta_2 = 4 \times 10^{-16} \text{ s}^{-1}\) (Indriolo et al. 2007), \(k_{\text{ct}} = 7.31 \times 10^{-10} (T/300)^{0.23} \exp(-225.9/T) \text{ cm}^3 \text{ s}^{-1}\) (Woodall et al. 2007), \(x(O) \approx 3 \times 10^{-4}\) (Cartledge et al. 2004; Jensen et al. 2005), and typical diffuse cloud values of \(f = 0.1\) and \(n_H = 100 \text{ cm}^{-3}\) (Snow & McCauley 2006), we find that at \(T \approx 70 \text{ K}\), \(N_{\text{r}x\text{n}} \approx 1400\). Thus, the typical \(\text{H}_2\) molecule will experience over 1000 reactive collisions during its lifetime, and we can safely assume that the initial ortho-to-para ratio of \(\text{H}_2\) is irrelevant; instead, the observed ortho-to-para ratio should reflect the steady state of the reactive collisions.

3.3. Steady State of \(\text{H}^+ + \text{H}_2\) Reactions

From a thermodynamic perspective, one would expect that the steady state of the \(\text{H}^+ + \text{H}_2\) reaction would represent a thermal distribution of \(o\)-\(\text{H}_2\) and \(p\)-\(\text{H}_2\), if no other processes influence the spin modifications. This expectation has been confirmed by a phase space theoretical calculation by Gerlich (1990), who found that the ortho-to-para ratio could be expressed at low temperatures \((30-80 \text{ K})\) by the expression 9.35 \exp(-169.4/T), quite close to the thermodynamic expectation of 9 \exp(-170.4/T). Evidently the nuclear spin selection rules for this chemical reaction, which suppress the ortho-to-para conversion by a factor of 6, do not significantly impact the final distribution.

3.4. Line of Sight Integration Effects

One remaining concern regards the estimation of \(T_{01}\) in a diffuse molecular cloud from the column densities of \(J = 0\) and \(J = 1\), which are integrated quantities along the line of sight. If some of the \(\text{H}_2\) resides in hotter, mostly atomic gas where \(\text{H}^+_1\) is not abundant, that hot \(\text{H}_2\) would cause the observed line-of-sight \(T_{01}\) to exceed \(T_{01}\) in the molecular cloud. We expect that such contamination would not be a major effect, as \(\text{H}_2\) is known to self-shield very effectively from the interstellar radiation field; thus, the amount of \(\text{H}_2\) in primarily atomic (and presumably warmer) gas is likely to be quite small compared to the amount of \(\text{H}_2\) in the molecular cloud itself.

To estimate the magnitude of this effect more quantitatively, we take a simple cloud model with a hotter outer region and cooler inner region. Assuming that \(T_{01} = 100 \text{ K}\) in the outer region (based on Copernicus observations of diffuse atomic clouds; Jenkins et al. 1983), we varied \(T_{01}\) in the inner region between 10 K and 100 K for a set of models where the outer region contained 1/2, 1/4, 1/8, and 1/16 of the material in the cloud. We then computed the line-of-sight \(T_{01}\) that would be derived considering both regions of gas. The result of this analysis is shown in Figure 2.

Taking the diffuse cloud model of Neufeld et al. (2005) with a constant density \((n_H = 100 \text{ cm}^{-3})\) and standard UV radiation field \((\chi_{\text{UV}} = 1)\) illuminating the cloud from one side, we then determined the amount of \(\text{H}_2\) expected to be in the outer region for comparison with observed \(\text{H}_2\) column densities in diffuse clouds. We define the transition from the outer to inner regions to be...
at $E(B-V) = 0.04$ ($N_H \approx 2.3 \times 10^{20} \text{ cm}^{-2}$), about half of the total color excess (hydrogen column density) found to supply self-shielding effects in H$_2$ [Savage et al. 1977; Gillmon & Shull 2000]. Integrating $n(H_2)$ in the outer region gives $N_{\text{outer}}(H_2) = 6 \times 10^{19} \text{ cm}^{-2}$. Because this model effectively only treats one side of a cloud, we compare this value to half of the total H$_2$ column densities reported in Table 3. The two extreme cases are HD 110432 and HD 154368, where the outer region accounts for about 1/4 and 1/12 of the total cloud, respectively. Taking the observed values of $T_{\text{ex}}$ and using the appropriate curves on Figure 2, we estimate the temperature of the inner cloud region for each of the 5 sight lines considered herein. The results are marked in Figure 2 as cross hairs, and show that the line-of-sight values of $T_{\text{ex}}$ overestimate the inferred inner cloud values of $T_{\text{ex}}$ by only about 5–10 K. As such, the observed values of $T_{\text{ex}}$ should be relatively close to the true values of $T_{\text{ex}}$ in molecular clouds. We therefore assume for the remainder of this paper that the line of sight $T_{\text{ex}}$ does represent the diffuse molecular cloud kinetic temperature.

### 3.5. Summary on H$_2$ Temperature

From the preceding discussions, we conclude that UV measurements accurately measure the column densities of $J = 0$ and $J = 1$ of H$_2$ in diffuse clouds, that the chemical reaction between H$_2^+$ and H$_2$ occurs $\sim 10^3$ times during the life of an average H$_2$, and that the steady state of this chemical reaction leads to an ortho:para ratio that closely reflects the kinetic temperature of the gas. Furthermore, we conclude that it is unlikely that the integration along the line of sight introduces significant contamination of the inferred $T_{\text{ex}}$. In summary, then, measured values of $T_{\text{ex}}$ in diffuse molecular clouds should accurately reflect the cloud kinetic temperature. Consequently, the excitation temperature of H$_2^+$, which is significantly lower than $T_{\text{ex}}$, must not always reflect the kinetic temperature.

### 4. ORTHO AND PARA H$_2^+$

Having shown that the temperature discrepancy between $T_{\text{ex}}$ and $T(H_2^+)$ in diffuse molecular clouds is real and that $T_{\text{ex}}$ accurately reflects the cloud kinetic temperature, we now consider the processes related to H$_2^+$ thermalization in diffuse molecular clouds to examine why $T(H_3^+)$ might not match the kinetic temperature.

#### 4.1. Nascent and Thermalized Para-H$_3^+$ Fractions

H$_3^+$ is produced by the reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H,$$

which follows the cosmic-ray ionization of H$_2$ to form H$_2^+$. The nuclear spin modification of the product H$_3^+$ depends on the nuclear spin modifications of the reactant H$_2$ and H$_2^+$ according to the selection rules given by Oka (2004). It is most convenient to express the nuclear spin modifications in terms of the para-fractions, rather than the ortho:para ratios, so we define

$$p_2 \equiv \frac{n(p-H_2)}{n(p-H_2) + n(o-H_2)}$$

and

$$p_3 \equiv \frac{n(p-H_3^+)}{n(p-H_3^+) + n(o-H_3^+)}.$$

As the cosmic-ray ionization of H$_2$ is not expected to affect the nuclear spin modification, we can further assume that the para-fraction of H$_3^+$ is also given by $p_2$. Table 4 demonstrates, using these reactant fractions and the nuclear spin branching fractions, that the para-fraction of newly formed H$_3^+$ is $p_3 = (1/3) + (2/3)p_2$, assuming that the rate for the H$_3^+$ + H$_2$ reaction is independent of nuclear spin configuration. In diffuse molecular clouds, the vast majority of the H$_2$ population lies in the lowest ortho and para states, as the temperature of 70 K is well below the energy of the next states (the $J = 2$ state lies 510 K above $J = 0$, and $J = 3$ lies 844 K above $J = 1$). Therefore, to derive $p_2$ from astronomical observations we use the formula $p_2 = N(0)/[N(0) + N(1)]$. H$_3^+$ on the other hand does have energetically accessible para states, as the (2,2) and (2,1) states lie only 151.3 and 249.2 K above the (1,1) ground state. However, the (2,2) and (2,1) states are expected to quickly undergo radiative decay to the (1,1) state at the temperatures and densities of the diffuse molecular clouds (Oka & Epd1 2004). Furthermore, the vast majority in the next ortho state, (3,3) has not been observed in these environments (Oka et al. 2004), so the postulated ortho state (3,3) should fall in the range of 40–50 K, and this should have about the 80 K difference between $T_{\text{ex}}$ and $T(H_3^+)$. In summary, the temperature ranges discussed here, the para-fractions of H$_3^+$ and H$_2$ are nonlinear with respect to these excitation temperatures. In terms of $p_3$, all $T(H_3^+)$ above about 40 K should have about the same $p_3$, while $p_3$ changes substantially when $T(H_3^+)$ falls below 40 K, as can be seen in Figure 3. Spontaneous emission will raise the apparent $p_3$ (as derived from the N(1,1):N(1,0) ratio) relative to the thermalized $p_3$ and consequently lower $T(H_3^+)$ with respect to $T_{\text{ex}}$. However, Figure 3 illustrates that the magnitude of this effect cannot account for the discrepancy observed in the astronomical observations in these environments in terms of the para-fractions, with the possible exception of X Per.

#### 4.2. The Reaction of H$_3^+$ with H$_2$

As in the case of H$_2$, the nuclear spin modifications of H$_3^+$ cannot effectively be changed by radiative transitions or by non-reactive collisions; only chemical reactions can do so. In this case, the reaction H$_3^+$ + H$_2$ → (H$_3^+$)* → H$_2$ + H$_3^+$ is the most efficient mechanism for interconverting
change reaction (4) to occur. The dissociation energy 

\[ \text{H}_2^+ \rightarrow \text{H}^+ + \text{H} \] 

calculations is available for the \( \text{H}_2^+ \) spin angular momentum. For instance, in order for a reaction between

\[ ^3\text{H}_2 + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H} \]

obey nuclear spin selection rules (Quack 1977; Oka 2004). Like reaction 1, the hop and exchange pathways must

actions 3 and 4 the configuration may change. However,

\[ ^3\text{H}_2 + ^3\text{H}_2 \rightarrow (1 - p_2)^2 \]

\[ ^3\text{H}_2 + ^1\text{H}_2 \rightarrow (1 - p_2)^2 \]

\[ ^1\text{H}_2 + ^1\text{H}_2 \rightarrow (1 - p_2)^2 \]

\[ ^1\text{H}_2 + ^3\text{H}_2 \rightarrow (1 - p_2)^2 \]

Total

\[ - \rightarrow (1/3) + (2/3)p_2 \]

\[ \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H}_2 \] (identity),

\[ ^3\text{H}_2 + ^3\text{H}_2 \rightarrow ^3\text{H}_2^+ + ^3\text{H}_2 \] (hop), and

\[ ^3\text{H}_2 + ^1\text{H}_2 \rightarrow ^3\text{H}_2^+ + ^1\text{H} \] (exchange). (4)

In the case of reaction 2, the nuclear spin configurations of the \( ^3\text{H}_2^+ \) and \( \text{H}_2 \) remain unchanged, while in reactions 3 and 4 the configuration may change. However, like reaction 1, the hop and exchange pathways must obey nuclear spin selection rules (Quack 1977; Oka 2004). For instance, in order for a reaction between \( ^3\text{H}_2^+ \) and \( \text{H}_2 \) to form \( ^3\text{H}_2^+ \) the reaction must be an exchange, and \( ^3\text{H}_2^+ \) must also be formed to conserve the total nuclear spin angular momentum.

A potential energy surface based on high-level \textit{ab initio} calculations is available for the \( \text{H}_2^+ \) system (Xie et al. 2003). Based on the surface stationary points, a barrier of 52.2 cm\(^{-1}\) must be overcome for a hop reaction (3) to occur, and a barrier of 1565.9 cm\(^{-1}\) for an exchange reaction (4) to occur. The dissociation energy \( D_c \)

is calculated to be 2903 cm\(^{-1}\); therefore (\( \text{H}_2^+ \))\(^+\) formed from association of \( \text{H}_2^+ \) with \( \text{H}_2 \) has sufficient energy to overcome these barriers. As such, the complex may undergo many hop and exchange processes over its lifetime, and given sufficient time, the product distribution may approach a statistical limit. As the statistical weights for the hop and exchange reactions are 3 and 6, respectively, the branching ratio \( \alpha \equiv \frac{^3\text{H}_2^+}{^1\text{H}_2^+} \) is 0.5 in the statistical limit. Quantum reactive scattering calculations are presently unavailable on this potential energy surface, so experimental data are necessary for determining the value of \( \alpha \), as well as its temperature dependence.

The only experimental determination of \( \alpha \) for the \( \text{H}_2^+ + \text{H}_2 \) system was performed by Cordonnier et al. (2000). This study was done by spectroscopically measuring the \textit{ortho-para} ratio of \( \text{H}_2^+ \) formed in a discharge of pure \( \text{H}_2 \) at 400 K, and under these conditions, the value \( \alpha \) was 2.4 was derived. No measurements at lower temperatures have been reported for this system, but the isotopically-substituted reaction \( \text{D}_2^+ + \text{H}_2 \) has been studied at a variety of collision energies using an ion trap/guided beam technique (Gerlich 1993). It was observed that \( \alpha \) varies substantially with the \( \text{D}_2^+ + \text{H}_2 \) collision energy. As this energy decreases, \( \alpha \) approaches the statistical value of 0.5, and the value 2.4 is reached at an energy corresponding to the average collision energy at \( \sim 440 \) K, in general agreement with the study by Cordonnier et al. (2000). However, a direct comparison of these results to \( \text{H}_2^+ \) in the interstellar medium is problematic owing to the endothermicity of the reaction channel and the nonthermal reactant internal state distribution in the experimental measurement.

The final consideration for this reaction is the fraction of reactions that lead to no change in the nuclear spin modification, \( S^{id} \). A large value for \( S^{id} \) would indicate that nuclear-spin-changing collisions are a small fraction of the total number of \( \text{H}_2^+ + \text{H}_2 \) collisions, and the thermalization process would be slower than the collision rate. In fact, there is experimental evidence for this, as studies of the \( \text{H}_2^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 \) reaction give a rate coefficient of \( 3.5 \times 10^{-10} \) cm\(^3\) s\(^{-1}\) (Gerlich et al. 2002), much slower than the Langevin rate coefficient 1.7 \times 10^{-9} \) cm\(^3\) s\(^{-1}\). These results lead to \( S^{id} \sim 0.8 \), but

\[ \begin{array}{|c|c|c|c|}
\hline
\text{Reaction} & \text{Collison Fraction} & \text{Branching Fraction} & \text{p-H}_2^+ \text{ Fraction} \\
\hline
\text{p-H}_2^+ + \text{p-H}_2 & (p_2)^2 & 1 & p_2^2 \\
\text{p-H}_2^+ + \text{o-H}_2 & p_2(1 - p_2) & 2/3 & (2/3)(1 - p_2)p_2 \\
\text{o-H}_2^+ + \text{p-H}_2 & (1 - p_2)^2 & 2/3 & (2/3)(1 - p_2)p_2 \\
\text{o-H}_2^+ + \text{o-H}_2 & (1 - p_2)^2 & 1/3 & (1/3)(1 - p_2)^2 \\
\hline
\text{Total} & - & - & (1/3) + (2/3)p_2 \\
\hline
\end{array} \]

\textbf{Note}. — This table presents the calculation of the nascent p-H\textsubscript{2}\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{2}\textsuperscript{+} formation, and are derived from nuclear spin selection rules (Quack 1977; Oka 2004). The final column presents the calculation of the nascent p-H\textsubscript{2}\textsuperscript{+} fraction.

Fig. 3.— The nascent (dashed line) and thermalized (numbers, in K) p-H\textsubscript{2}\textsuperscript{+} fraction as a function of the p-H\textsubscript{2} fraction. The circles represent the observations of diffuse molecular clouds summarized in Table 3 with 1\( \sigma \) uncertainties.

\( \text{H}_3^+ \) and \( \text{p-H}_3^+ \). When \( \text{H}_3^+ \) and \( \text{H}_2 \) collide, there are three possible reaction outcomes:

\[ \text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2 \] (identity),

\[ \text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2\text{H}^+ + \text{H}_2 \] (hop), and

\[ \text{H}_3^+ + \text{H}_2 \rightarrow \text{HH}_2^+ + \text{H} \] (exchange). (4)
it is possible that $S_{id}$ could be different for the purely hydrogenic system, which is thermoneutral rather than exothermic.

4.3. Steady State Para-$H_3^+$ Fraction from $H_3^+ + H_2$: “Bimolecular Reactive Equilibrium”

After taking into account its chemical physics, does the steady state of the $H_3^+ + H_2$ chemical reaction lead to a completely thermalized $p_3$ in the interstellar medium? To consider this question, we have constructed a simple steady-state model for ortho and para-$H_3^+$, in terms of nuclear-spin-dependent rate coefficients $k_{xxx}$ for each potential sub-reaction (e.g., $k_{appc}$: $o-H_3^+ + p-H_2 \rightarrow p-H_3^+ + o-H_2$). The derivation of this model, which we shall call the “bimolecular reactive equilibrium” (BRE) model, is presented in the Appendix, and the resulting expression for $p_3$ is given in the Appendix as equation (B4).

The rate coefficients themselves were computed using the prescription of Park & Light (2007), which takes into account both the nuclear spin branching fractions as well as energetic considerations at the state-to-state level, using a microcanonical approach. This work has since been extended by Hugo et al. (2009) to deuterated versions of this chemical reaction, and the latter authors report quantitative agreement between the two sets of calculations. We therefore judge these rate coefficients to be reliable within the context of this theoretical approach.

The Park & Light code (provided by K. Park, private communication 2009) requires five input parameters: the kinetic temperature, the rotational temperature of $H_3^+$ and $H_2$, and the three branching fractions $S_{id}$, $S_{hop}$, and $S_{exch}$. For these calculations, the rotational temperature was held at 10 K in each nuclear spin manifold in order to have the vast majority of $o-H_3^+$ in (1,0) and $p-H_3^+$ in (1,1). Therefore, we express the inputs to the model in terms of only three parameters: $T = T_{kin}$, $S_{id}$, and $\alpha$, as $S_{id} + S_{hop} + S_{exch} = 1$ and $\alpha = S_{hop}/S_{exch}$. The code then outputs all of the rate coefficients required in equation (B4). For a single set of branching fraction values, the rate coefficients were calculated for $10 \leq T \leq 160$ K in steps of 10 K, and $p_2$ was set to its thermal value for each calculation.

Figure 4 shows the results of the BRE model for a fixed value of $\alpha = 0.5$ for various values of $S_{id}$ ranging from 0.1-0.9; similarly, Figure 5 shows results for fixed $S_{id} = 0.5$ and various $\alpha$ ranging from 0-\infty. The results of the calculation are not particularly sensitive to the fraction of collisions that are reactive (as traced by $S_{id}$) or the ratio of the hop to exchange outcomes ($\alpha$). Since in all cases $p_3$ falls near its thermal value, these results suggest that regardless of the values of $\alpha$ or $S_{id}$, the $H_3^+ + H_2$ reaction should essentially thermalize the $H_3^+$ nuclear spin species. This stands in clear contradiction to the reported astronomical observations in diffuse molecular clouds, with the exception of X Per. The discrepancy between $T_{mol}$ and $T(H_3^+)$ cannot be explained by the BRE model, and must then be explained by a lack of equilibration via this chemical reaction.

An interesting aspect of these results is that the steady state $p_3$ at some temperatures is actually below the value of 0.5 expected based on statistical weights alone (often called the “high-temperature limit”). This appears to be a robust result for $\alpha > 0.5$, at least in the range of $S_{id}$ explored here. This effect may have been observed experimentally in our group’s recent measurements of supersonically expanding hydrogen plasmas. Tom et al. (2010) reported $p_3 = 0.491 \pm 0.024$ for a normal hydrogen ($p_2 = 0.25$) plasma at $\sim 80$ K, and Kreckel et al. (2010) reported $p_3 = 0.479 \pm 0.02$ in a warmer ($\sim 200$ K) normal hydrogen and argon plasma. Finally, in work outside our laboratory, Kreckel et al. (2007) have reported $p_3 = 0.4$ in a low-temperature ion trap. All of these measurements suggest that it is in fact possible to achieve $p_3 < 0.5$, and lend some evidence to support the calculated results.

Recent measurements in our laboratory have confirmed, with higher statistical significance, $p_3 < 0.5$ in hollow cathode plasmas containing normal hydrogen. These results will be reported elsewhere, but it should be noted that $p_3$ in these plasmas may be influenced by three-body collisions due to the higher number densities.
4.4. Steady State Para-\(H_3^+\) Fraction from \(H_3^+ + H_2\) and \(H_3^+ + e^-\)

We now consider whether there are enough reactive collisions within the lifetime of an average \(H_3^+\) in diffuse molecular clouds to bring the spin modifications into BRE. The destruction of \(H_3^+\) in such clouds is dominated by dissociative recombination (DR) with electrons, and the lifetime is simply 
\[
\tau_{\text{dr}} = \frac{k_{\text{dr}} n(e^-)}{k_{\text{dic}} n(H_2)} \sim T^{70 K}
\]
where \(x_e\) is the electron fraction, typically \(1.5 \times 10^{-4}\), and \(T\) is the temperature in steady state. The destruction rate is closer to the nascent fraction, as this represents the fraction of H\(_3^+\) that will be produced in the gas and will experience a lifetime of (Cardelli et al. 1996; Sofia et al. 2004). If we adopt the smaller reactive rate coefficient \(k_{\text{rxn}}\), where
\[
k_{\text{rxn}} = (k_{\text{dr}} n(e^-))^{-1}
\]
the steady state fraction is the same for both nuclear spin modifications of Gerlich et al. (2002), we find that \(n_{\text{rxn}} \sim 20\). However, if we instead adopt the smaller reactive rate coefficient \(3 \times 10^{-10}\) cm\(^3\) s\(^{-1}\) of Adams & Smith (1987), we find that \(n_{\text{rxn}} \sim 5\). With such a small number of collisions in the lifetime of \(H_3^+\), \(P_3\) may not reach the value predicted by equation (4). In the appendix we derive a more complete steady state expression (equation [7]) including the effects of both the \(H_3^+ + H_2\) reaction and nuclear-spin-dependent DR rates \((k_{\text{e,p}}\) and \(k_{\text{e,o}}\) for \(p-H_3^+\) and \(o-H_3^+\)).

We call this model simply the “steady state” model, and we adopt the values \(f = 0.9\) and \(x_e = 1.5 \times 10^{-4}\) as before. Figure 8 shows the results of this steady state model if we assume that the DR rate coefficient is the same for both nuclear spin modifications (we have adopted the temperature-dependent value of McCall et al. 2004). In this case, the values of \(P_3\) depend quite sensitively on \(S^{id}\), as this represents the fraction of \(H_3^+ + H_2\) collisions that are nonreactive during the relatively short lifetime of \(H_3^+\). Consequently with higher values of \(S^{id}\) (larger circles in Figure 6), the \(p-H_3^+\) fraction in steady state is closer to the nascent fraction. For \(S^{id} = 0.9\), which corresponds to a reactive rate coefficient of \(k_{\text{rxn}} = 1.9 \times 10^{-10}\) cm\(^3\) s\(^{-1}\), the calculated \(P_3\) are in reasonable agreement with most of the observations. The upper range of the X Per uncertainty is consistent with \(S^{id} = 0.7\).

In Figure 8 we instead consider the calculated DR rate coefficients for ortho and para-\(H_3^+\) presented in dos Santos et al. (2007). Their prediction is that \(p-H_3^+\) is destroyed considerably faster by electrons at low temperatures than \(o-H_3^+\); consequently, for large values of \(S^{id}\), the steady state \(P_3\) does not approach either the nascent or astronomically-observed values. In the absence of the \(H_3^+ + H_2\) reaction (\(S^{id} = 1\)), \(P_3\) would be governed by a steady state determined by the competition between the formation and the spin-dependent DR processes, and this is shown in Figure 8.

---

**Figure 6.** Steady state calculations of the para-\(H_3^+\) fraction as a function of the para-\(H_2\) fraction, under the influence of both the \(H_3^+ + H_2\) reaction and dissociative recombination. The plotted quantities are analogous to those in Figure 4. In this case, the \(o-H_3^+\) and \(p-H_3^+\) DR rate coefficients \(k_{\text{e,o}}\) and \(k_{\text{e,p}}\) are assumed to be equal and taken from McCall et al. (2004). Each vertical cluster of points represents a calculation at a single temperature, beginning at 160 K in the lower left and decreasing by 10 K each point moving to the right.

**Figure 7.** Same as Figure 6 except using the spin-dependent dissociative recombination rate coefficients from dos Santos et al. (2007).

**Figure 8.** Steady state calculations of the para-\(H_3^+\) fraction as a function of the para-\(H_2\) fraction, under the influence of formation and dissociative recombination only. The solid line shows the thermal limit, and the dotted line represents the results of our calculations, where we have used the spin-dependent dissociative recombination rate coefficients from dos Santos et al. (2007). Also plotted are the nascent \(H_3^+\) distribution (dashed line) and the astronomical observations.
If the calculated rate coefficients of dos Santos et al. (2007) are correct, it is difficult to explain the observed $p_3$. This is because, with the exception of X Per, the observed $p_3$ are higher than the curve resulting from the steady state of $H_3^+$ formation and destruction using these DR rate coefficients, and inclusion of the $H_3^+$ + $H_2$ reaction further drives $p_3$ toward the value expected for thermal equilibrium. Recent storage ring experiments by Tom et al. (2009) and Kreckel et al. (2005) both saw an increased DR cross-section when $H_3^+$ is produced from $p$-$H_2$; however, recent imaging results presented in Kreckel et al. (2010) suggest that the ions in these experiments have been heated during extraction from the ion sources, and the difference between the $o$-$H_3^+$ and $p$-$H_3^+$ may therefore have been overestimated. Further experimental work is clearly needed to pin down the enhancement (if any) in $p$-$H_3^+$ DR, and confirmation of the theoretical predictions would also be quite helpful.

To summarize, according to our models the reaction of $H_3^+$ with $H_2$ is expected to effectively thermalize the nuclear spin configurations of $H_3^+$ at steady-state, provided that sufficient collisions occur within the lifetime of an $H_3^+$. In diffuse molecular clouds, however, the average number of reactive collisions with $H_2$ suffered by an $H_3^+$ is small, indicating that the formation and destruction rates of the two nuclear spin species should be important. A more complete model which takes these factors into account reaches reasonable agreement with observations in 4 of 5 sight lines provided $S^{ad}$ is on the order of 0.9 and $o$-$H_3^+$ and $p$-$H_3^+$ are destroyed at equal rates owing to DR. Reconciling the observations with the spin-dependent theoretical rates of dos Santos et al. (2007) is difficult, and accurate experimental measurements of the spin-dependent DR rates of $H_3^+$ at low temperature are needed.

5. CONCLUSIONS

While all evidence seems to suggest that $T_{01}$ inferred from ultraviolet spectroscopy of $H_2$ accurately reflects the kinetic temperature of diffuse molecular clouds, the observed excitation temperature of $H_3^+$ is clearly non-thermal in 4 of the 5 measured sight lines. Based on the microcanonical model of Park & Light (2007), we have constructed a steady state model to predict the $para$-$H_3^+$ fraction ($p_3$) if reactive collisions between $H_3^+$ and $H_2$ control the spin modifications of $H_3^+$. Those results show $p_3$ slightly below the limit expected for full thermalization, and far from the observations. However, a steady state model that incorporates both the $H_3^+$ + $H_2$ reaction as well as the $H_3^+$ formation (following cosmic-ray ionization) and destruction (by electron recombination) can reproduce the observed $p_3$ if the reactive collision rate is somewhat slow and the dissociative recombination rates for $ortho$ and $para$ $H_3^+$ are comparable. Our interpretation, given the currently available data, is that $H_3^+$ suffers relatively few spin-changing collisions with $H_2$ in its lifetime, and is thus incompletely equilibrated by this reaction. The observed $para$-$H_3^+$ fraction therefore lies between the nascent fraction and the nearly-thermal fraction that would be reached with sufficient reactive collisions. If our model is correct (and the spin-dependent DR rates of $H_3^+$ are nearly equal at low temperature), this marks the first determination of the reactive rate coefficient of the $H_3^+$ + $H_2$ reaction, and suggests a value on the order of $10^{-10}$ cm$^{-3}$ s$^{-1}$.

Fully quantum reactive scattering calculations of the $H_3^+$ + $H_2$ reaction would be highly desirable, as they would pin down the state-to-state rate coefficients needed to predict the interstellar $para$-$H_3^+$ fraction. Further experiments and theoretical calculations to elucidate the dependence (if any) of the dissociative recombination on the nuclear spin modification of $H_3^+$ are also urgently needed. Once the effects of the reactive collisions and dissociative recombination are fully understood, the $para$-$H_3^+$ fraction in diffuse molecular clouds can be calculated as a function of the kinetic temperature and the ratio of the molecular fraction to the electron fraction. This, in turn, suggests that $H_3^+$ may become a useful “thermometer” for diffuse molecular clouds with high extinction, where ultraviolet measurements of $H_2$ are not feasible. However, the calibration of this thermometer will require further experimental and theoretical efforts.

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APPENDIX

REACTIONS AND RATES

In this appendix, we derive the formulas for the bimolecular reactive equilibrium and steady-state $para$-$H_3^+$ fractions. We consider 4 processes: cosmic ray ionization of $H_2$, formation of $H_3^+$, the $H_3^+$ + $H_2$ reaction, and dissociative recombination of $H_3^+$. If all nuclear spin configurations are considered, this gives a total of 28 reactions. The chemical reactions used in the model and their rate expressions are summarized in Table 5. It should be noted that for this section, we employ the chemist’s notation of using square brackets to refer to the number density of the respective
gives the final result:

$\zeta_2 [H_2]$ for all species. For $H^+ + p$ presented in Table 4. Under these conditions, the full rate equation can be solved for $p^+$. Assuming steady state, equation (3) is equal to 0. The right side can then be divided by $[H_3^+][H_2]$ in order to express the rate in terms of $p_2$ and $p_3$ as follows:

$$0 = \{(k_{oopp} + k_{oppo}) (1 - p_2) + (k_{opoo} + k_{popp}) p_2\} (1 - p_3) - \{(k_{poop} + k_{popp}) (1 - p_2) + (k_{poop} + k_{popp}) p_2\} p_3.$$  

(B2)

The resultant equation can be solved for $p_3$:

$$p_3 = \frac{(k_{oopp} + k_{oppo})(1 - p_2) + (k_{opoo} + k_{popp}) p_2}{(k_{oopp} + k_{oppo} + k_{poop} + k_{popp})(1 - p_2) + (k_{opoo} + k_{popp} + k_{poop} + k_{popp}) p_2}. \tag{B3}$$

Owing to nuclear spin selection rules, the rate coefficients $k_{oppo}$ and $k_{popp}$ are rigorously 0. Removal of these terms gives the final result:

$$p_3 = \frac{1}{(k_{oopp} + k_{oppo} + k_{poop} + k_{popp})(1 - p_2) + (k_{opoo} + k_{popp}) p_2}. \tag{B4}$$

DERIVATION: STEADY STATE MODEL

Consider now the case in which $H_3^+$ formation and DR compete effectively with the $H_3^+ + H_2$ thermalization reaction. We make the assumption that formation of $p^+ - H_3^+$ from $H_3^+ + H_2$ is governed only by the nuclear spin branching fractions presented in Table 3. Under these conditions, the full rate equation for $p^+ - H_3^+$ is:

$$\frac{d}{dt} [p^+ - H_3^+] = k_1 [p^+ - H_2][p^- - H_3^+] + \frac{2}{3} [p^+ - H_2][o^+ - H_3^+] + \frac{2}{3} [o^+ - H_2][p^- - H_3^+] + \frac{1}{3} [p^+ - H_2][o^+ - H_3^+].$$

(C1)

From Table 3 we can reduce the first line in this equation to $k_1 [H_2][H_3^+] \{(1/3) + (2/3)p_2\}$. We now invoke steady state arguments for all species. For $H_3^+$, $\zeta_2 [H_2] = k_1 [H_2][H_3^+]$, therefore $k_1 [H_2]$ can be replaced by $\zeta_2$. Setting the resultant equation equal to zero and dividing by $[H_3^+][H_2]$ as before gives:

$$0 = \frac{\zeta_2}{[H_2]} \left( \frac{1}{3} + \frac{2}{3} + \frac{2}{3}p_2 \right)$$

TABLE 5

| Number | Reaction | Rate | Comments |
|--------|----------|------|----------|
| 1 | $H_2 + CR \rightarrow H_3^+ + e^- + CR^-$ | $\zeta_2 [H_2]$ | Cosmic ray ionization |
| 2 | $H_2 + H_3^+ \rightarrow H_3^+ + H$ | $k_1 [H_2][H_3^+]$ | $H_3^+$ formation (see Table 4) |
| 3 | $i-H_3^+ + j-H_2 \rightarrow m-H_3^+ + n-H_2$ | $k_{ij,mn} [i-H_3^+][j-H_2]$ | Thermalization reaction for $H_3^+$ |
| 4 | $p-H_3^+ + e^- \rightarrow H_2 + H (or) 3H$ | $k_{e,p}[p-H_3^+][e^-]$ | $p-H_3^+$ DR |
| 5 | $o-H_3^+ + e^- \rightarrow H_2 + H (or) 3H$ | $k_{e,o}[o-H_3^+][e^-]$ | $o-H_3^+$ DR |

Note. — The branching fractions for $o-H_3^+$ and $p-H_3^+$ in reaction 2 are assumed to be given by nuclear spin statistics. In reaction 3, $i$, $j$, $m$, and $n$ represent the nuclear spin configurations of the respective species ($o$ or $p$). Some of these 16 reactions are forbidden by nuclear spin selection rules, and others are not used directly in the derivation because they do not result in a change in the $H_3^+$ nuclear spin configuration. Square brackets refer to the number density of the species.
\[ \zeta_2 [H_2] = (e^-)(k_{e,p}[p-H_2^+] + k_{e,o}[o-H_2^+]). \] (C3)

Dividing both sides of equation \([\text{C3}]\) by \([H_2^+] [H_2]\) results in an expression for \(\zeta_2/[H_2^+]:\)

\[ \frac{\zeta_2}{[H_2^+]} = \frac{\langle e^- \rangle}{[H_2]}(k_{e,p}p_3 + k_{e,o}(1 - p_3)). \] (C4)

Substituting this relation into equation \([\text{C2}]\) gives:

\[
0 = \frac{\langle e^- \rangle}{[H_2]}(k_{e,p}p_3 + k_{e,o}(1 - p_3))(\frac{1}{3} + \frac{2}{3}p_2) + \{(k_{oopp} + k_{opp}) (1 - p_2) + (k_{oppo} + k_{opp}) p_2\} \{1 - p_3\} - \{(k_{poopo} + k_{poop}) (1 - p_2) + (k_{pooop} + k_{poop}) p_2\} p_3 - k_{e,p} \frac{\langle e^- \rangle}{[H_2]}p_3. \] (C5)

Solving for \(p_3\) and removing the \(k_{opp}\) and \(k_{poo}\) terms yields:

\[ p_3 = \frac{k_{e,o} \frac{\langle e^- \rangle}{[H_2]}(\frac{1}{3} + \frac{2}{3}p_2) + (k_{oopp} + k_{oppo})(1 - p_2) + (k_{oppo} p_2)}{k_{e,p} \frac{\langle e^- \rangle}{[H_2]}(\frac{2}{3} - \frac{2}{9}p_2) + k_{e,o} \frac{\langle e^- \rangle}{[H_2]}(\frac{1}{3} + \frac{2}{3}p_2) + (k_{oppo} + k_{oppo} + k_{poop} + k_{poo})(1 - p_2) + (k_{oppo} + k_{poop}) p_2}. \] (C6)

Finally, the ratio \(\langle e^- \rangle/[H_2]\) can be replaced by \(2x_e/f\), which results in equation \([\text{C7}]\):

\[ p_3 = \frac{k_{e,o} 2x_e}{f(\frac{2}{3} - \frac{2}{9}p_2) + k_{e,o} \frac{\langle e^- \rangle}{[H_2]}(\frac{1}{3} + \frac{2}{3}p_2) + (k_{oppo} + k_{oppo} + k_{poop} + k_{poo})(1 - p_2) + (k_{oppo} + k_{poop}) p_2}. \] (C7)

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