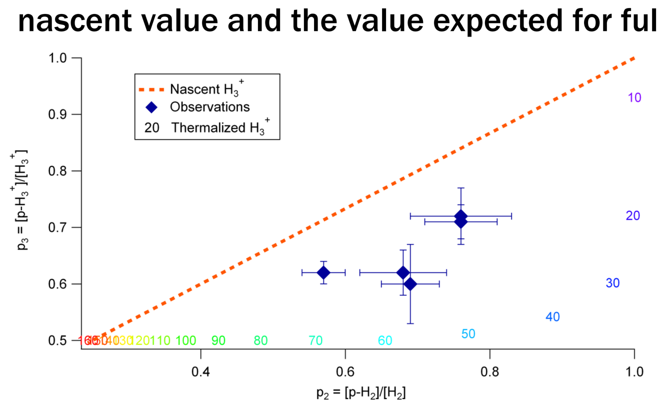
Nuclear Spin Effects in Hydrogenic Plasmas in the Laboratory and Interstellar Medium

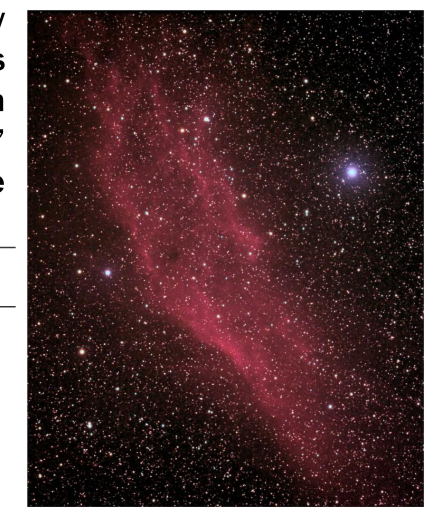
Kyle N. Crabtree, Nick Indriolo, Holger Kreckel, Carrie A. Kauffman, Eftalda Beçka, Brian A. Tom, and Benjamin J. McCall
Department of Chemistry, University of Illinois, Urbana, IL 61801

Diffuse Cloud Chemistry

In diffuse clouds, the H_2 *ortho:para* ratio is thermalized rapidly by collisions with protons (reaction A). However, H_3^+ is nonthermal, which is unexpected because of thermalization reaction D. Nuclear spin selection rules for reactions B and C enable calculation of the "nascent" H_3^+ *para* fraction (p_3), and observations show p_3 lies between the nascent value and the value expected for full thermal equilibrium.

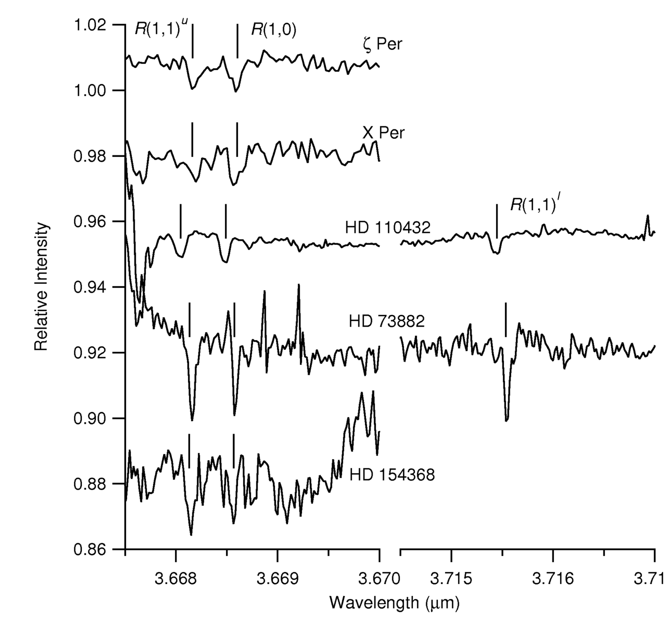


Relevant Reactions
A.) $H^+ + H_2 \rightarrow H_2 + H^+$
B.) $H_2 + CR \rightarrow H_2^+ + e^- + CR'$
C.) $H_2^+ + H_2 \rightarrow H_3^+ + H$
D.) $H_3^+ + H_2 \rightarrow H_2 + H_3^+$
E.) $H_3^+ + e^- \rightarrow H_2 + H$ or 3H

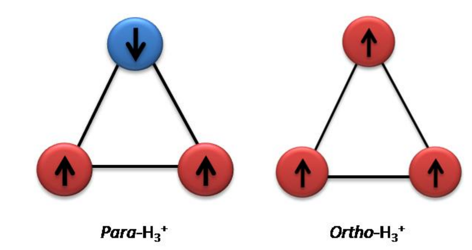


A diffuse cloud sightline towards ζ Per, the bright star pictured above.

Motivation

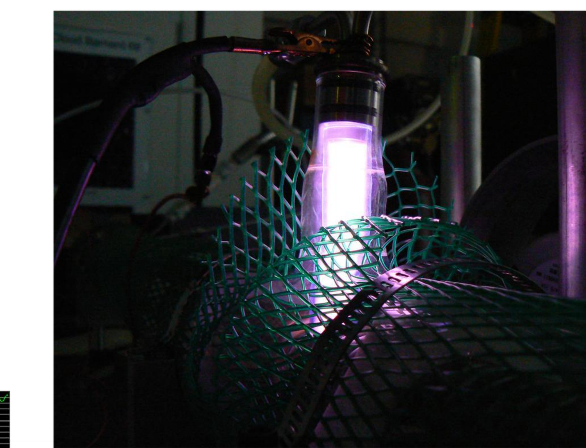


H_3^+ is the cornerstone of gas-phase chemistry in the interstellar medium (ISM). In the diffuse ISM, however, the rotational temperature derived from the H_3^+ IR spectrum disagrees with T_{01}, the temperature derived from the H_2 J=0 & 1 energy levels. We seek to understand this discrepancy by examining how nuclear spin influences thermalization in the lab and the ISM.

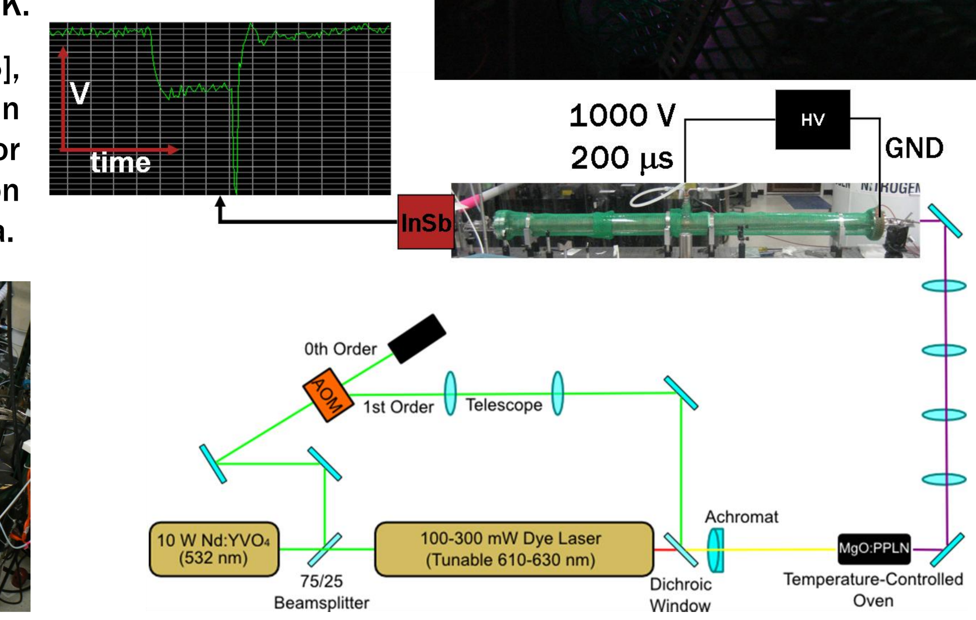


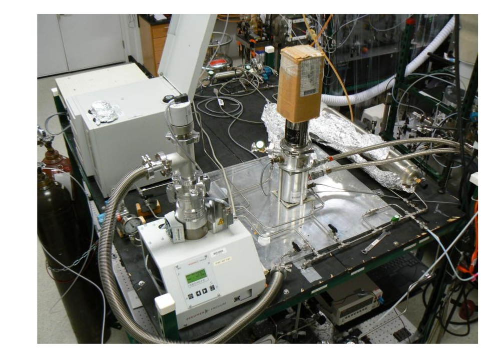
Experimental Setup

We have constructed a hollow cathode discharge cell [4] to produce pulsed hydrogenic plasmas. We perform high resolution direct absorption spectroscopy on the ν_2 fundamental band of H_3^+ using a tunable mid-infrared cw laser in a multipass configuration. By monitoring the populations of its rotational energy levels during the pulse, we can measure the kinetic and rotational temperatures of H_3^+, as well as its *ortho:para* ratio. The cell can be cooled with cryogens to reach a temperature of 130 K.



Using a *para*-H_2 converter [5], we manipulate the nuclear spin configuration of the precursor gas and observe the effects on the H_3^+ produced in the plasma.





Steady State Modeling

Using the *para*-H_3^+ formation and destruction reaction rates, we can predict the *para*-H_3^+ fraction (p_3) formed in a plasma of a certain *para*-H_2 fraction (p_2). We use the microcanonical statistical model of Park and Light [6] to calculate k_{xxxx} rate coefficients, where the subscripts refer to the nuclear spin configurations of the (H_3^+, H_2) reactant and product pairs.

$$\begin{aligned}\frac{d}{dt}[p\text{-}H_3^+] =\ & k_1\left(\tfrac{2}{3}[o\text{-}H_2]+[p\text{-}H_2]\right)[p\text{-}H_2^+] + k_1\left(\tfrac{1}{3}[o\text{-}H_2]+\tfrac{2}{3}[p\text{-}H_2]\right)[o\text{-}H_2^+]\\ & + \left\{(k_{oopp}+k_{oopo})[o\text{-}H_2] + (k_{oppp}+k_{oppo})[p\text{-}H_2]\right\}[o\text{-}H_3^+]\\ & - \left\{(k_{poop}+k_{pooo})[o\text{-}H_2] + (k_{ppop}+k_{ppoo})[p\text{-}H_2]\right\}[p\text{-}H_3^+]\\ & - k_{r(para)}[e_r^-][p\text{-}H_3^+],\end{aligned}$$

Line 1: p-H_3^+ formation. Line 2: o-$H_3^+ + H_2 \rightarrow p$-$H_3^+ + H_2$. Line 3: o-$H_3^+ + H_2 \rightarrow p$-$H_3^+ + H_2$. Line 4: p-H_3^+ destruction via electron recombination

If the reaction of H_3^+ with H_2 dominates, then at steady state, the *para*-H_3^+ fraction is given by eq. (1):

$$p_3 = \frac{(k_{oopp}+k_{oopo})(1-p_2)+k_{oppo}p_2}{(k_{oopp}+k_{oopo}+k_{poop}+k_{pooo})(1-p_2)+(k_{oppo}+k_{ppoo})p_2}$$

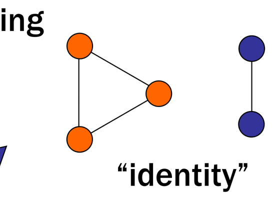
If, instead, the formation and destruction terms are significant, then eq. (2) is derived:

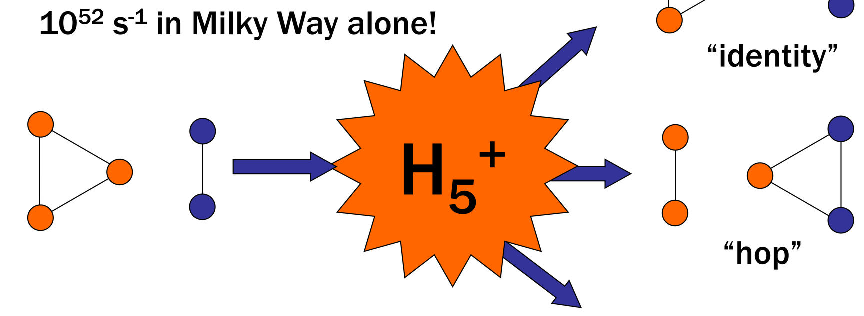
$$p_3 = \frac{k_{e,o}\frac{n(e^-)}{n(H_2)}\left(\frac{1}{3}+\frac{2}{3}p_2\right)+(k_{oopp}+k_{oopo})(1-p_2)+k_{oppo}p_2}{k_{e,p}\frac{n(e^-)}{n(H_2)}\left(\frac{2}{3}-\frac{2}{3}p_2\right)+k_{e,o}\frac{n(e^-)}{n(H_2)}\left(\frac{1}{3}+\frac{2}{3}p_2\right)+(k_{oopp}+k_{oopo}+k_{poop}+k_{pooo})(1-p_2)+(k_{oppo}+k_{ppoo})p_2}$$

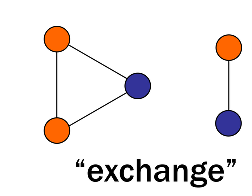
$H_3^+ + H_2$ Reaction

The *ortho* and *para* nuclear spin configurations of H_3^+ are separate species– they cannot be interconverted through radiative processes or nonreactive collisions. Reaction with H_2, however, is the most likely manner for population transfer, and therefore thermalization, to occur. This process is governed by nuclear spin selection rules and complex dynamic constraints, and its influence on the *ortho* to *para* ratio of H_3^+ at the low temperatures and densities of the ISM is unknown.

- Simplest bimolecular reaction involving a polyatomic species
- Most common bimolecular reaction: 10^{52} s^{-1} in Milky Way alone!





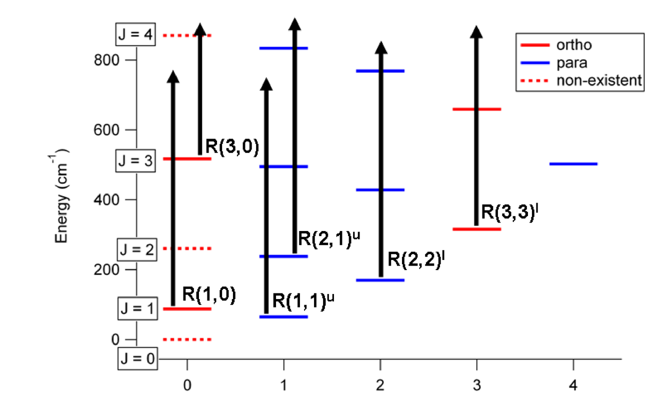


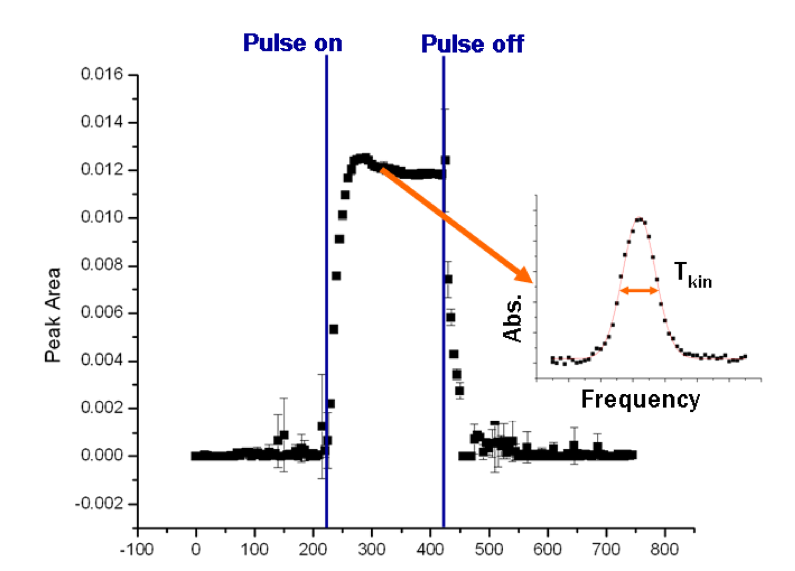
- Branching Fractions S^{id}, S^{hop}, S^{exch}
- Hop/Exchange Ratio = $\alpha = k_{hop}/k_{exch}$

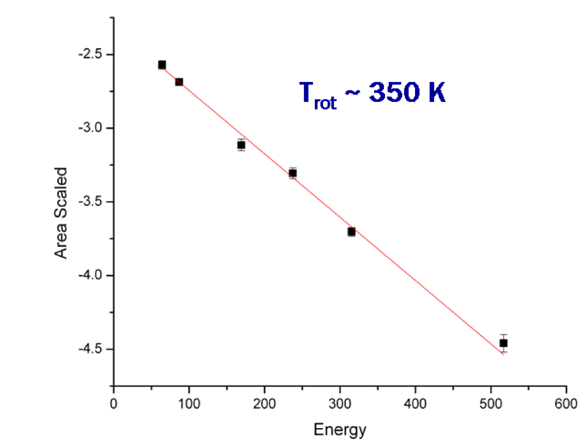
Previous measurements yield α = 2.4 at 400 K for this reaction [1], and measurements in isotopically-substituted systems show that this value decreases with temperature [2] and suggest S^{id} ~ 0.8 [3].

Experimental Results

The diagram on the right shows the observed transitions in the hollow cathode plasma. A typical absorption trace (3 scans) is shown below. Each point is the area of a Gaussian fit to the data. By comparing multiple transitions (Boltzmann plot lower right), we observe a thermal rotational distribution using a normal-H_2 feed gas.

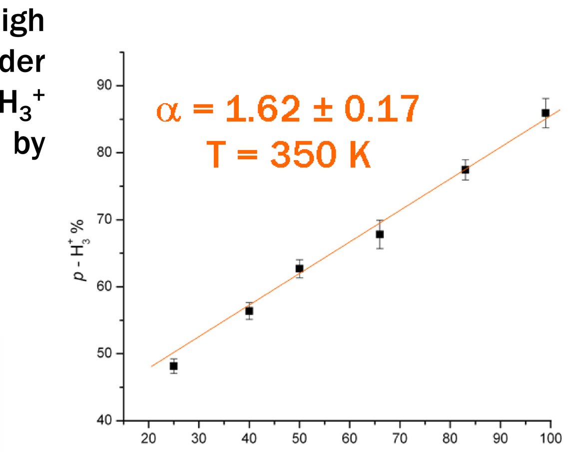






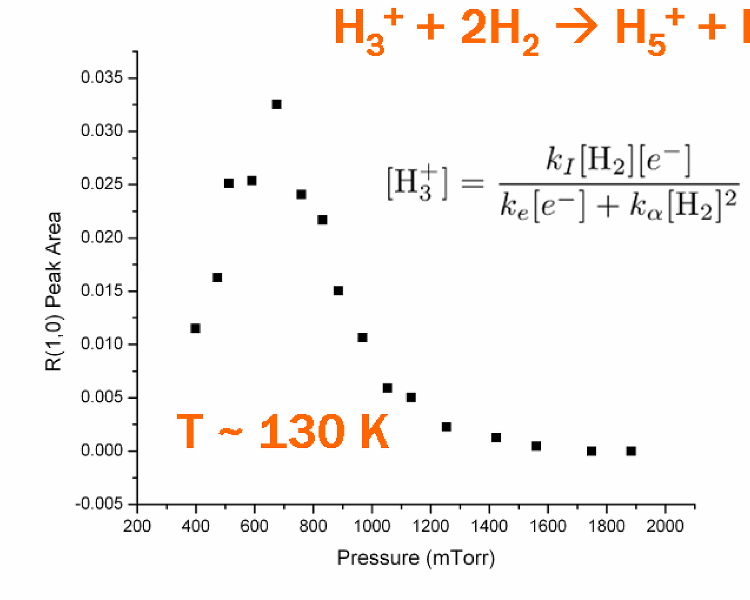
In an uncooled plasma (T~350 K), the temperature is high enough that nuclear spin selection rules dominate. Under these conditions, the steady state value of the p-H_3^+ fraction is given below. This allows calculation of α by measuring p_3 with varying *para*-H_2 enrichments.

$$p_3 = \frac{\alpha + 2\alpha p_2 + 1}{3\alpha + 2}$$



$H_3^+ + 2H_2 \rightarrow H_5^+ + H_2$

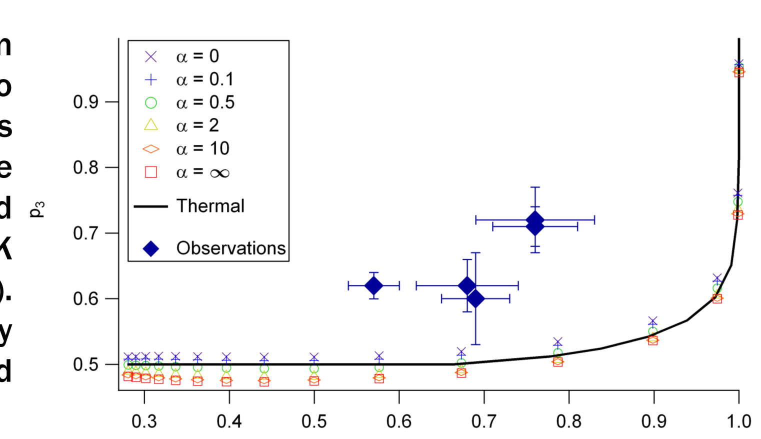
$$[H_3^+] = \frac{k_I[H_2][e^-]}{k_e[e^-]+k_\alpha[H_2]^2}$$

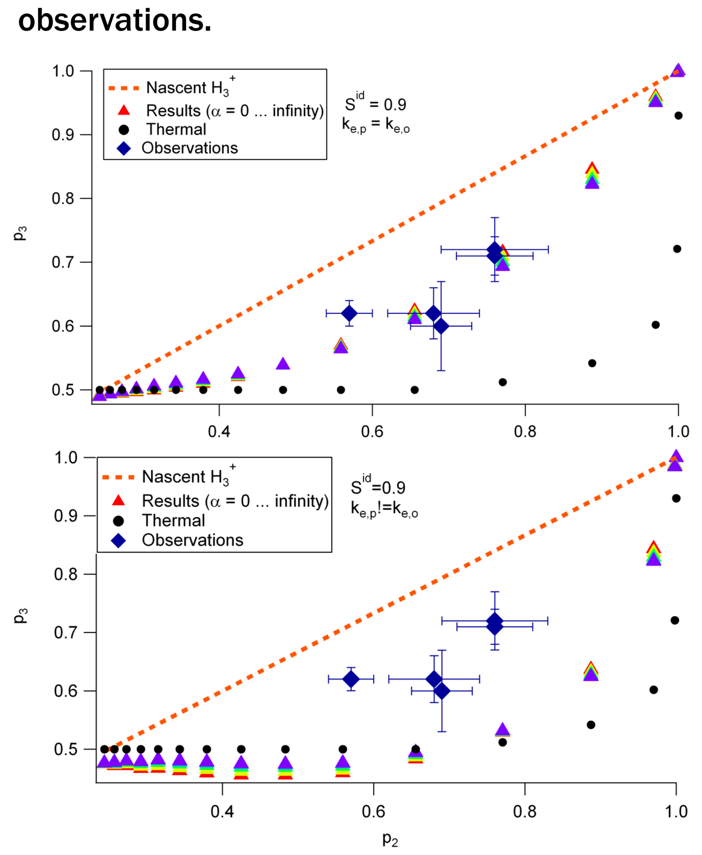


Upon cooling with liquid nitrogen, an obvious pressure dependence of the line intensities was observed. This is likely due to the influence of the three-body reaction $H_3^+ + 2H_2 \rightarrow H_5^+ + H_2$. After re-examination of the uncooled plasma data, the same effect was observed, though it was not as dramatic. Consequently, the data likely cannot be interpreted as a probe of the branching ratio of the $H_3^+ + H_2$ reaction, but is instead a blend of that and the three-body reaction. Pressure-dependent studies may provide further insight into both processes.

Modeling Results

Calculation of rate coefficients k_{xxxx} depends on the parameters S^{id}, α, and T. We constrain p_2 to its thermal value, as in diffuse clouds it is rapidly thermalized via proton collisions. On the left are the results of eq. (1) with S^{id} held constant at 0.1, and T varying from 10-160 K (10 K increments, markers from right to left). With this model, H_3^+ is expected to be roughly thermalized, in contrast to diffuse cloud observations.





The best agreement between the modeling and diffuse cloud observations comes when S^{id} is 0.9 (corresponding to a "reactive" $H_3^+ + H_2$ rate coefficient of 1.5 x 10^{-10} cm^3 s^{-1}), and the *ortho* and *para* H_3^+ electron recombination rate coefficients are held equal at 2.0 x 10^{-7} cm^3 s^{-1} (upper right).

However, there is theoretical [7] and experimental [8] evidence that the electron recombination rate for *para*-H_3^+ is faster than that of *ortho*-H_3^+. Using the theoretical rate coefficients in [7], the p_3 curve shifts downward, as expected for the higher p-H_3^+ destruction rate. This curve cannot be brought into agreement with the observations even with S^{id} = 1. Note that all of this is insensitive to the value of α used. These efforts highlight the need for more conclusive experimental measurements of state-selective recombination rates to validate or invalidate this model.

Conclusions & Outlook

Using steady state chemical modeling and astronomical observations, we have for the first time inferred a reactive rate coefficient for the $H_3^+ + H_2$ reaction. We have also made progress toward understanding the temperature discrepancy observed in diffuse clouds between H_2 and H_3^+. Moving forward, we will pursue a three-pronged approach to further understand these processes:

1. In the diffuse ISM, we will continue our search for H_3^+ in sightlines for which measurements of H_2 are available. We will also pursue measurements of H_2 in sightlines where only H_3^+ data are available.
2. We will continue our modeling efforts by calculating rate coefficients with a higher identity reaction branching fraction, and pursue more definitive experimental measurements of the o-H_3^+ and p-H_3^+ dissociative recombination rates.
3. In the laboratory, we will study hydrogenic plasmas at more temperatures and pressures in order to understand both two- and three-body processes in the plasma. A collaboration to study this reaction at lower temperatures in an ion trap is envisioned.

References & Funding

[1] M. Cordonnier *et al.*, *J. Chem. Phys.* 111, 3181 (2000).
[2] D. Gerlich, *J. Chem. Soc. Faraday Trans.* 89, 2199 (1993).
[3] D. Gerlich *et al.*, *Planet. Space Sci.* 50, 2175 (2002).
[4] T. Amano, *J. Opt. Soc. Am. B*, 2, 790 (1985).
[5] B. Tom *et al.*, *Rev. Sci. Inst.* 80, 016108 (2009).
[6] K. Park & J. Light, *J. Chem. Phys.* 126, 044305 (2007).
[7] S. F. Dos Santos *et al.*, *J. Chem. Phys.* 127, 124309 (2007).
[8] B. Tom *et al.*, *J. Chem. Phys.* 130, 031101 (2009).