Nuclear spin dependence of hydrogenic plasmas in the laboratory and the diffuse interstellar medium
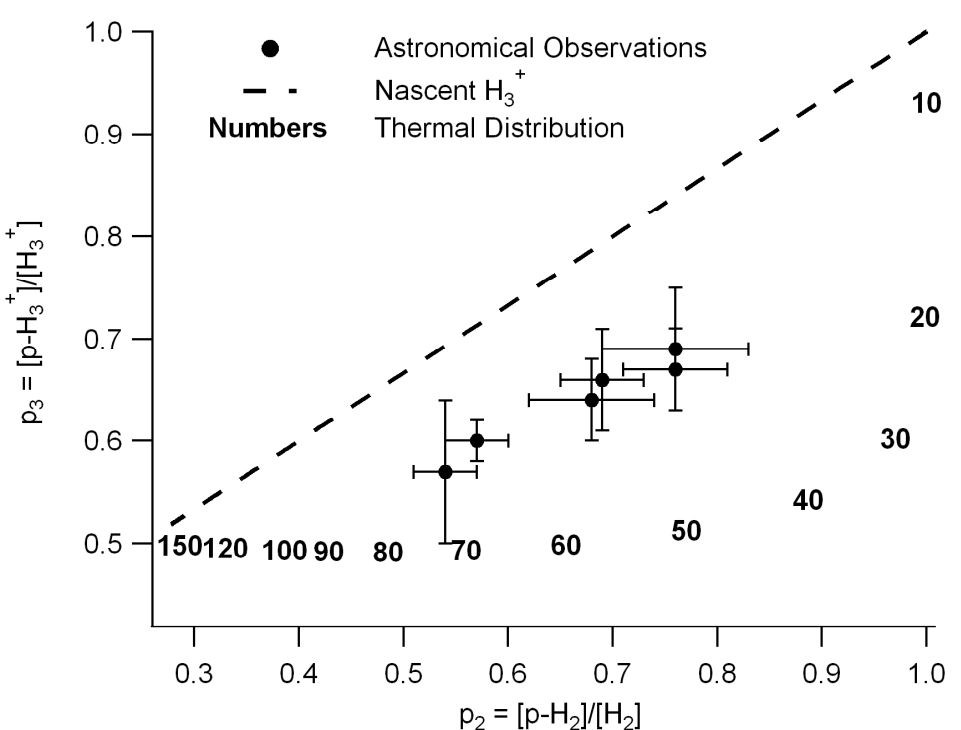
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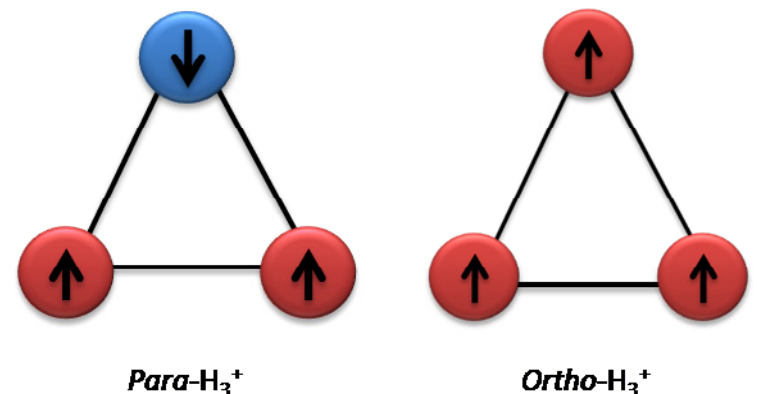
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Motivation and overview

Observations of p-H_3^+ and p-H_2 fractions in diffuse molecular clouds, highlighting the deviation from thermal equilibrium


H_3^+ is a useful probe of physical conditions in the interstellar medium (ISM), such as temperature, density, and cosmic ray ionization rate. However, in diffuse molecular clouds, the temperature inferred from H_3^+ is on average 30-40 K lower than the temperature inferred from H_2 (T_{01}), which is thought to be a good indicator of the cloud's kinetic temperature.

We have investigated the nuclear spin dependence of the reaction $H_3^+ + H_2 \rightarrow H_2 + H_3^+$, which is responsible for interconversion of o-H_3^+ ($I = 3/2$) and p-H_3^+ ($I = 1/2$). We have experimentally measured the nuclear spin dependence of this reaction at low temperature (130 K) for the first time. The results of our measurements enable modeling of the ortho/para ratio of H_3^+ in diffuse molecular clouds, and show that a competition between thermalization and dissociative electron recombination is likely responsible for the H_3^+/H_2 temperature discrepancy.

$H_3^+ + H_2 \rightarrow H_2 + H_3^+$
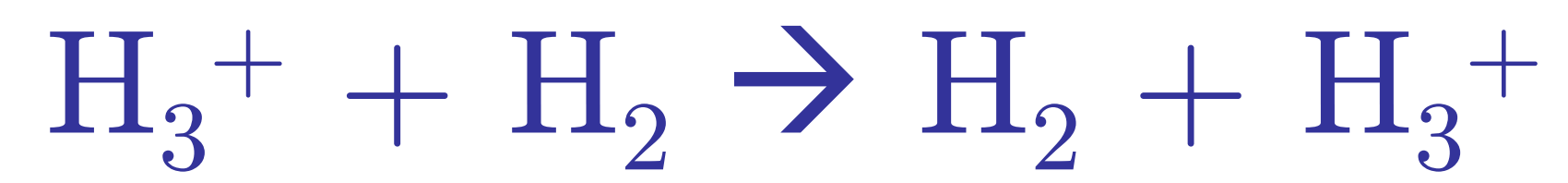
This reaction is the simplest bimolecular reaction involving a polyatomic, and is likely the most common such reaction occurring in the Universe. In the H_5^+ collision complex, proton scrambling can occur, resulting in one of the three outcomes pictured here.
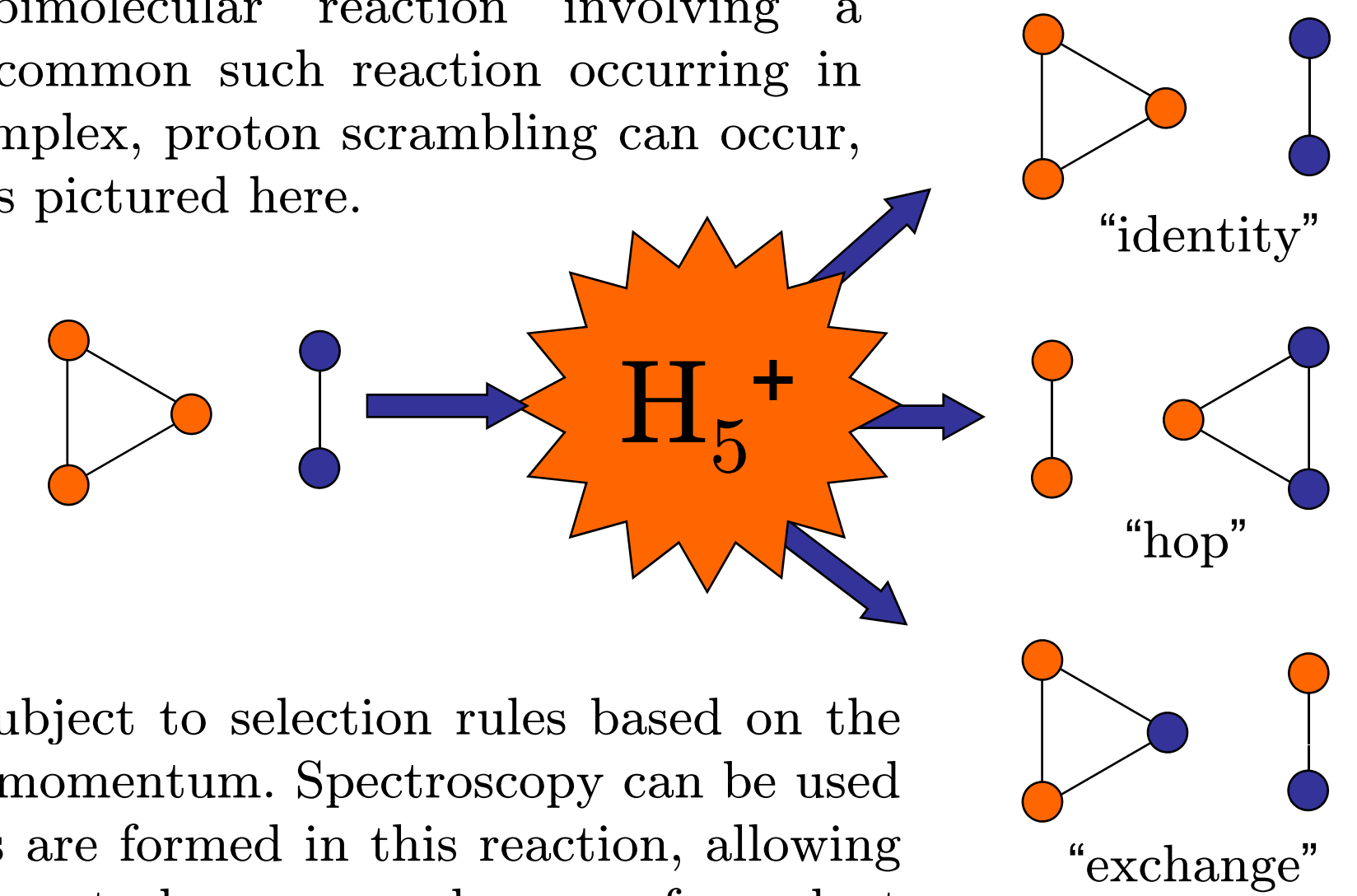
The so-called "identity" reaction is indistinguishable from a nonreactive collision, so the total nuclear spin dependence can be parameterized by the hop:exchange branching ratio fraction α.

Additionally, this entire process is subject to selection rules based on the conservation of nuclear spin angular momentum. Spectroscopy can be used to measure which nuclear spin states are formed in this reaction, allowing a measurement of α. Such measurements have never been performed at temperatures relevant for cold interstellar clouds.


Laboratory measurements

Plasma kinetics

High Temperature

In a high temperature plasma, nuclear spin statistical weights can be used to determine the probability of forming each of the nuclear spin configurations of H_3^+ and H_2 in a reaction, depending on the initial configurations and the hop:exchange ratio α.

Using these statistical weights, the para-H_3^+ fraction (p_3) can be calculated from the para-H_2 fraction (p_2) and alpha:

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

High temperature model
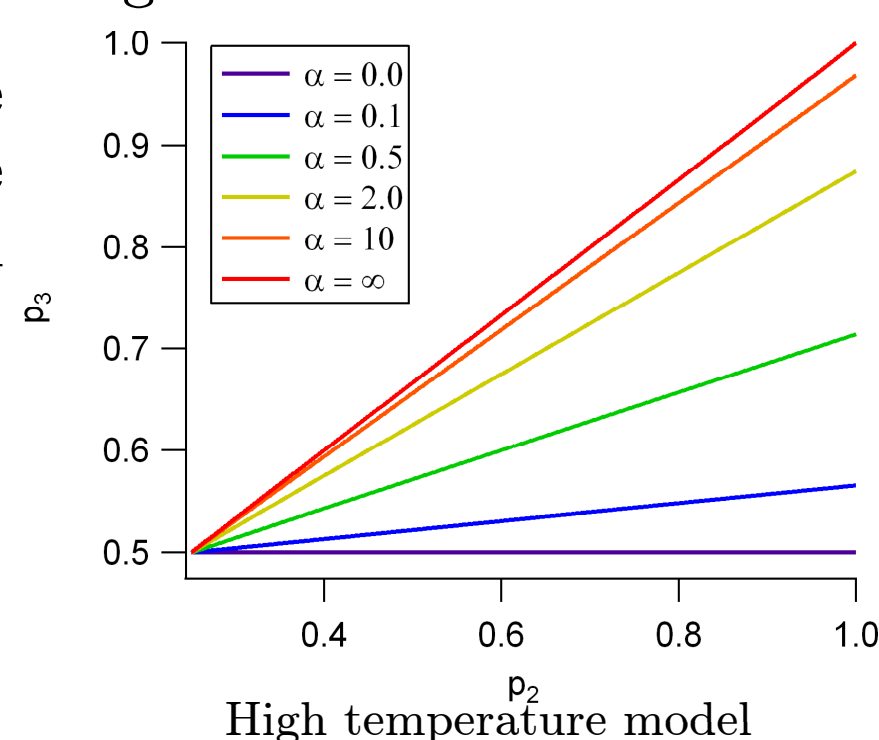
Low Temperature

At lower temperatures, some reactions with nonzero statistical weights are energetically unfavorable. For instance, reactions that convert p-H_2 to o-H_2 are endothermic by about 115 cm^{-1} (170 K), so when the temperature is low, these channels are inhibited. Using a microcanonical statistical model (Park and Light, JCP, 2007, 126, 044305), rate coefficients k_{ijkl} for reactions i-$H_3^+ + j$-$H_2 \rightarrow k$-$H_3^+ + l$-H_2 can be calculated as a function of temperature and α. These can be used to calculate p_3 as a function of p_2:
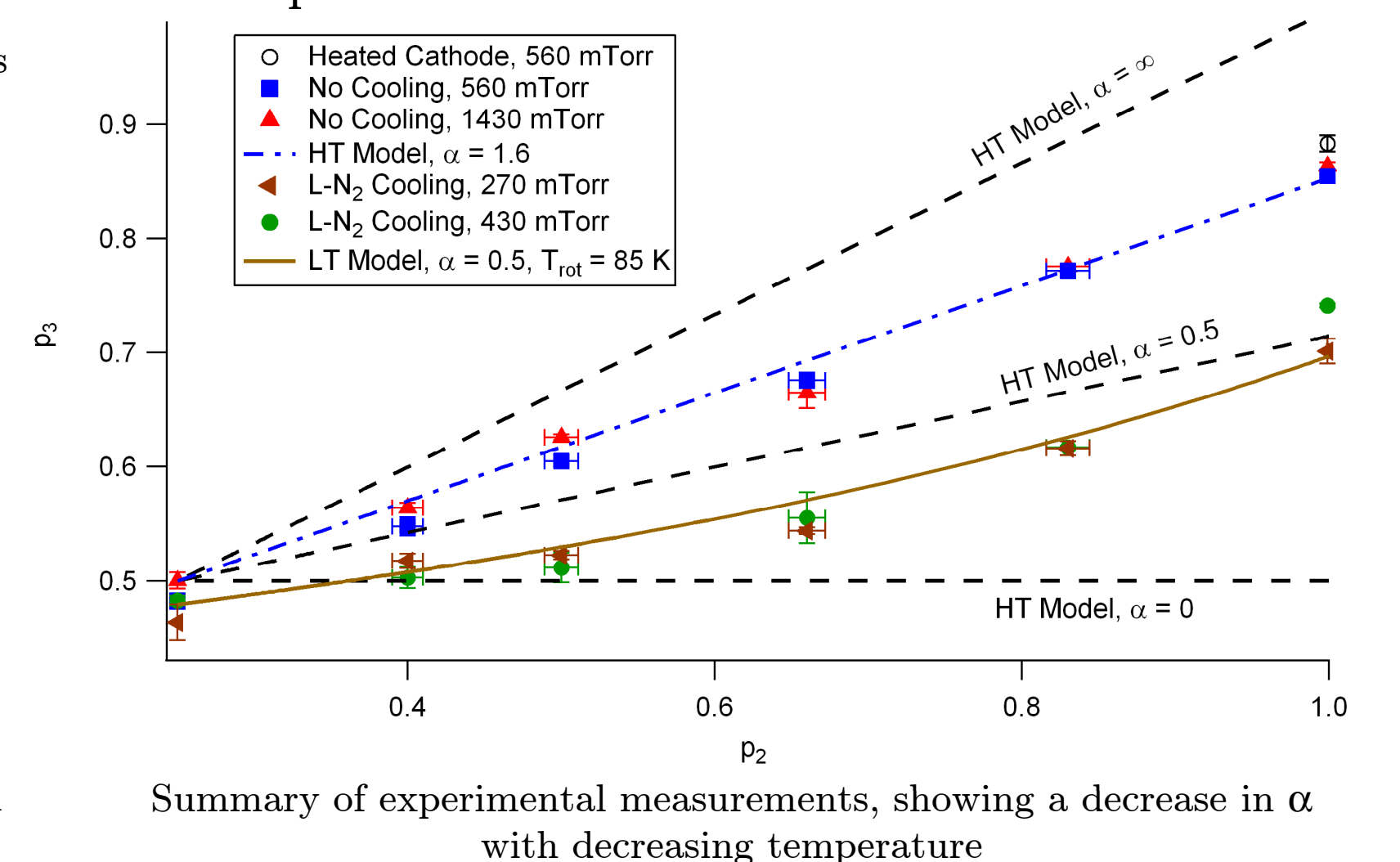
$$p_3 = \frac{(k_{oopp} + k_{oopo})(1 - p_2) + k_{oppo}p_2}{(k_{oopp} + k_{oopo} + k_{poop} + k_{pooo})(1 - p_2) + (k_{oppo} + k_{ppoo})p_2}$$
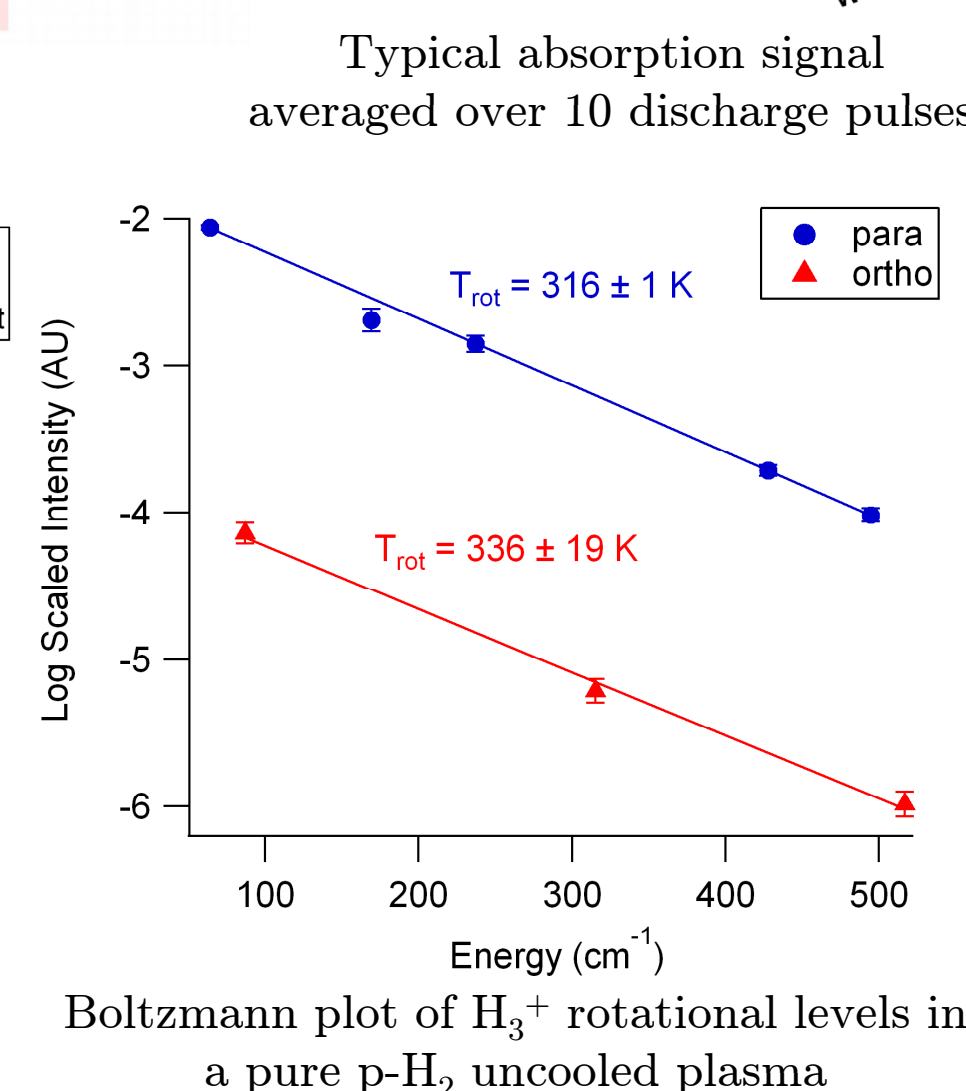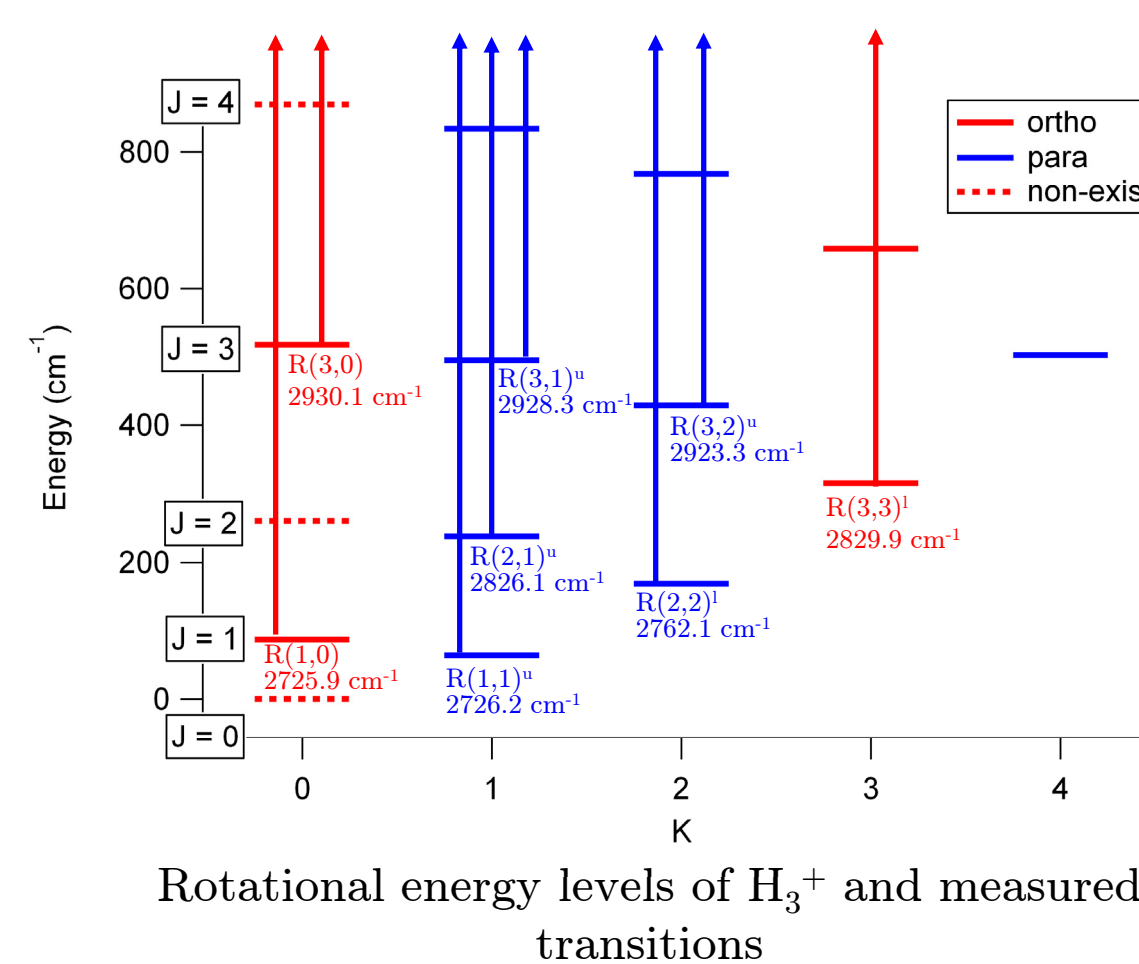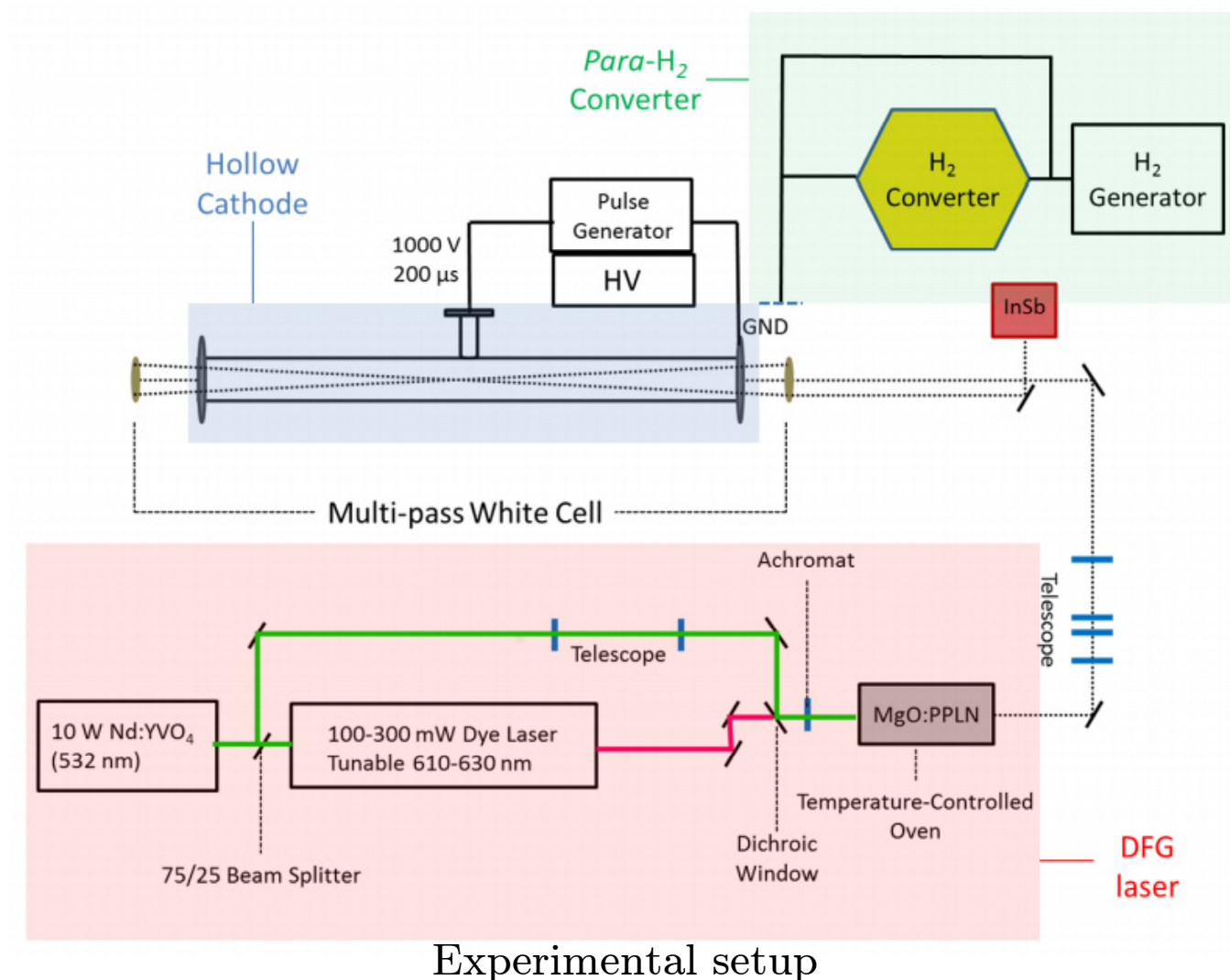
Experimental results

We studied the $H_3^+ + H_2$ reaction by monitoring the populations of several low-energy rotational levels of H_3^+ in a pulsed hollow cathode plasma with variable temperature and p-H_2 fraction using direct absorption spectroscopy. The kinetic and rotational temperatures along with the p-H_3^+ fraction were calculated from the spectroscopic measurements.

By performing these measurements at a variety of temperatures and p_2 values, we found that the value of α decreases from 1.6 ± 0.1 at 350 K to 0.5 ± 0.1 at 130 K. At temperatures below 130 K (relevant for the ISM), we expect α to remain at its statistical value of 0.5. This is the first study of the $H_3^+ + H_2$ reaction at low temperature.

Experimental setup

Typical absorption signal averaged over 10 discharge pulses

Rotational energy levels of H_3^+ and measured transitions

Boltzmann plot of H_3^+ rotational levels in a pure p-H_2 uncooled plasma

Summary of experimental measurements, showing a decrease in α with decreasing temperature

Diffuse molecular cloud observations and modeling

We have observed H_3^+ in 6 diffuse molecular cloud sightlines that have published UV measurements of H_2 (T_{01}). In all targets, $T(H_3^+)$ is substantially lower than T_{01}. Because H_2 is thermalized efficiently by abundant protons in these environments, the observations show that the nuclear spin configurations of H_3^+ are not in thermal equilibrium.

| Target	Obs.	p_3	p_2	$T(H_3^+)$	T_{01}
ζ Per	UKIRT	0.65(4)	0.68(4)	25(3)	58(6)
X Per	UKIRT	0.66(5)	0.69(4)	24(4)	57(4)
HD 154368	Gem. S.	0.69(6)	0.76(7)	22(4)	51(8)
HD 73882	VLT	0.67(4)	0.76(5)	23(3)	51(6)
HD 110432	VLT	0.60(2)	0.57(3)	30(2)	68(5)
λ Cep	UKIRT /Keck	0.57(7)	0.54(3)	34(10)	73(4)

Observed p-H_3^+ and p-H_2 fractions and temperatures in diffuse molecular cloud sight lines. H_2 data come from Copernicus or FUSE measurements.

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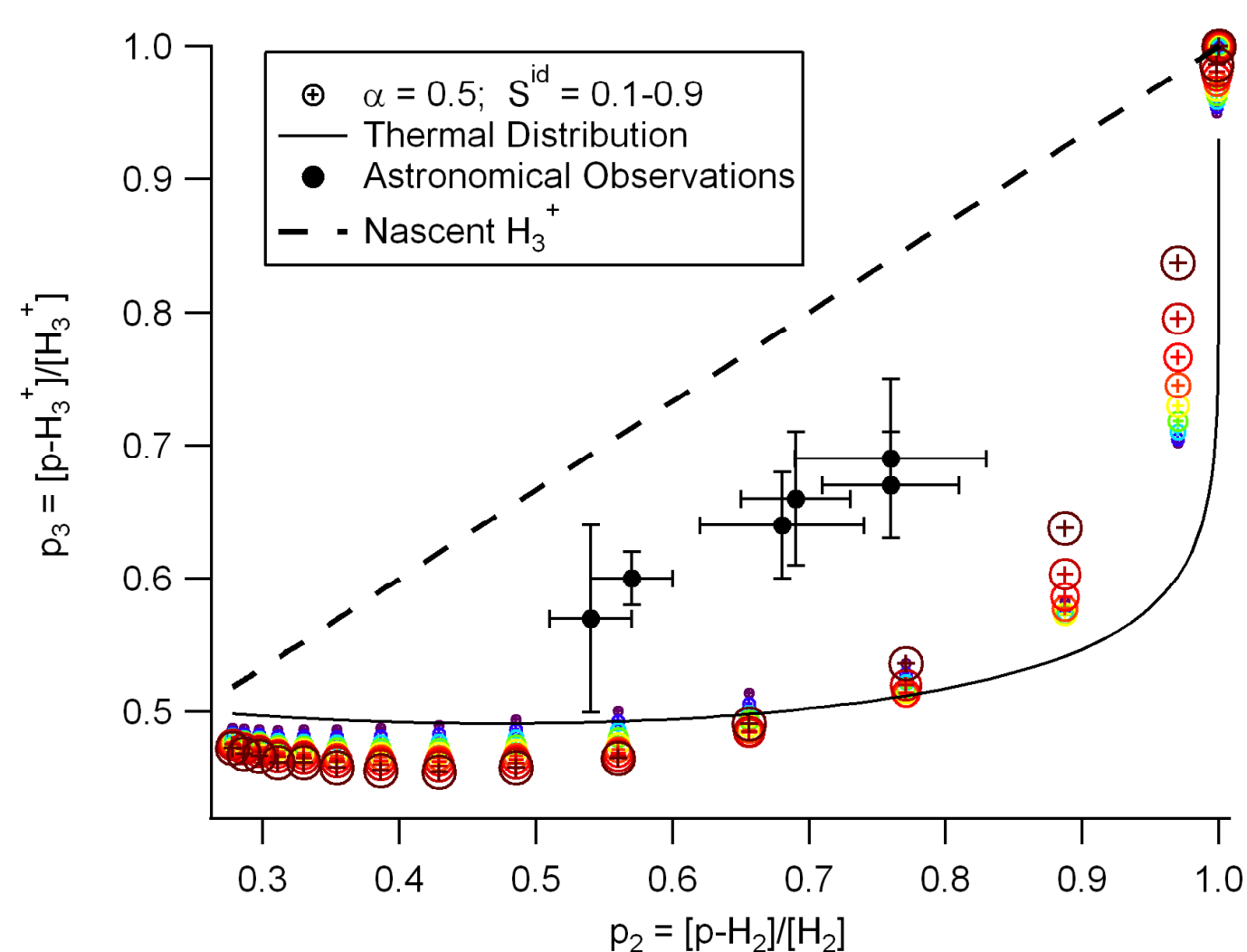$$- k_{r(para)}[e_r^-][p\text{-}H_3^+].$$

We calculate the steady state p-H_3^+ fraction resulting from cosmic-ray ionization of H_2, the reaction of H_3^+ with H_2, and dissociative recombination (DR) of H_3^+ with electrons. As was done in our experiment, we calculate rate coefficients k_{ijkl} using a microcanonical statistical model.

$$p_3 = \frac{k_{e,o}\frac{2x_e}{f}\left(\frac{1}{3} + \frac{2}{3}p_2\right) + (k_{oopp} + k_{oopo})(1 - p_2) + k_{oppo}p_2}{k_{e,p}\frac{2x_e}{f}\left(\frac{2}{3} - \frac{2}{3}p_2\right) + k_{e,o}\frac{2x_e}{f}\left(\frac{1}{3} + \frac{2}{3}p_2\right) + (k_{oopp} + k_{oopo} + k_{poop} + k_{pooo})(1 - p_2) + (k_{oppo} + k_{ppoo})p_2}$$
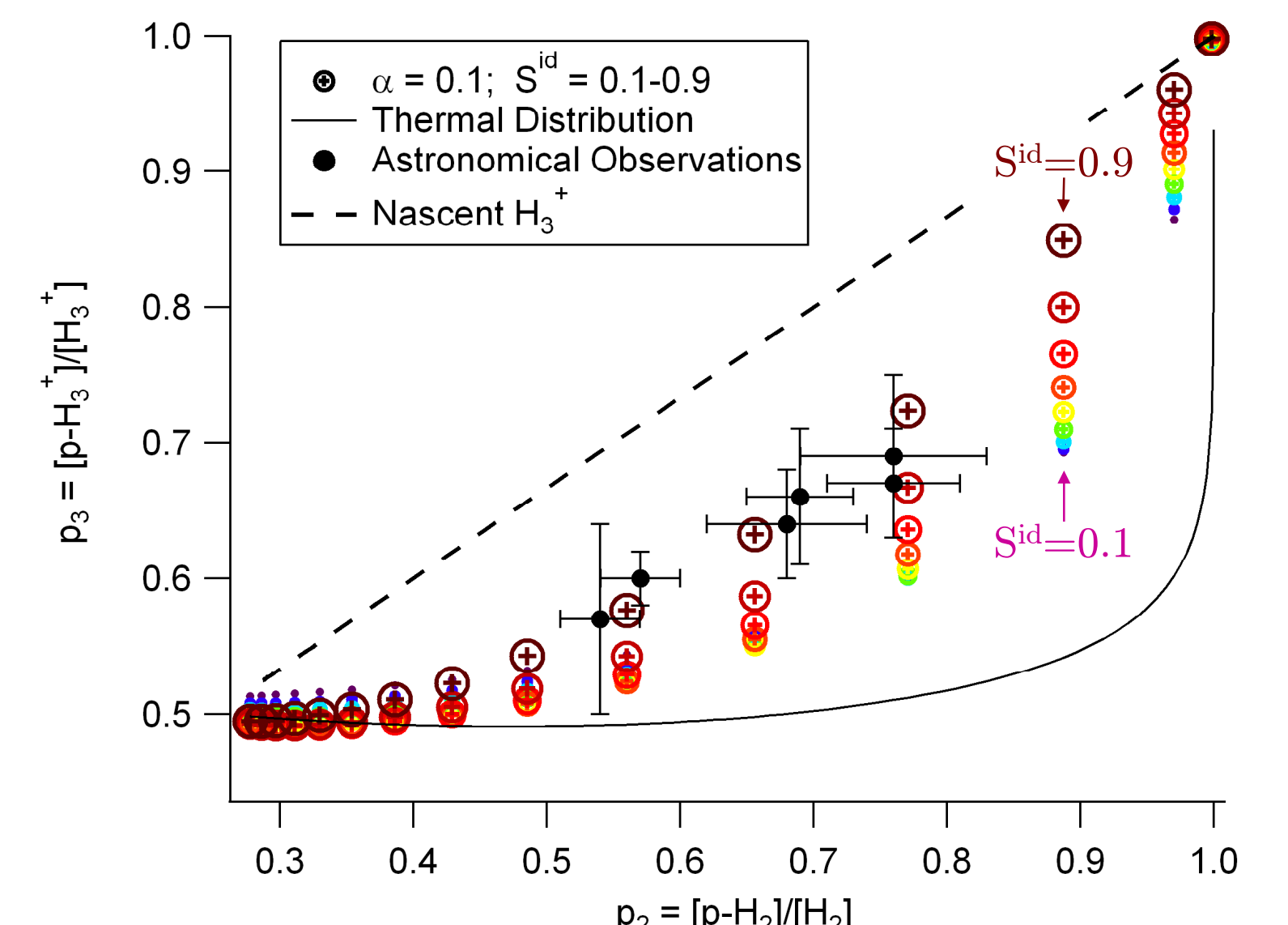
Our final equation depends on the fractional ionization and molecular fraction of the cloud, the p-H_2 fraction, the DR rates of o-H_3^+ and p-H_3^+, and the rate coefficients k_{ijkl} for the $H_3^+ + H_2$ reaction. The latter rate coefficients are calculated as a function of temperature and the branching fractions for the identity, hop, and exchange processes (S^{id}, S^{hop}, and S^{exch}, respectively). Using the hop:exchange ratio $S^{hop}/S^{exch} = \alpha = 0.5$ as found in our laboratory measurements, we calculate rate coefficients for each value of p_2 at the corresponding kinetic temperature T_{01}, and assume a fractional ionization of 10^{-4} and molecular fraction of 0.9. The results are shown in the plots on the right. Good agreement is seen when $S^{id} = 0.9$ and the DR rates of o-H_3^+ and p-H_3^+ are equal, but no agreement is found when using recent theoretical predictions of the DR rates, in which p-H_3^+ DR is 10 times faster than o-H_3^+ DR. While further study of H_3^+ DR is needed, our modeling suggests that the ortho:para ratio of H_3^+ in diffuse molecular clouds is determined by a competition between the $H_3^+ + H_2$ reaction and DR.
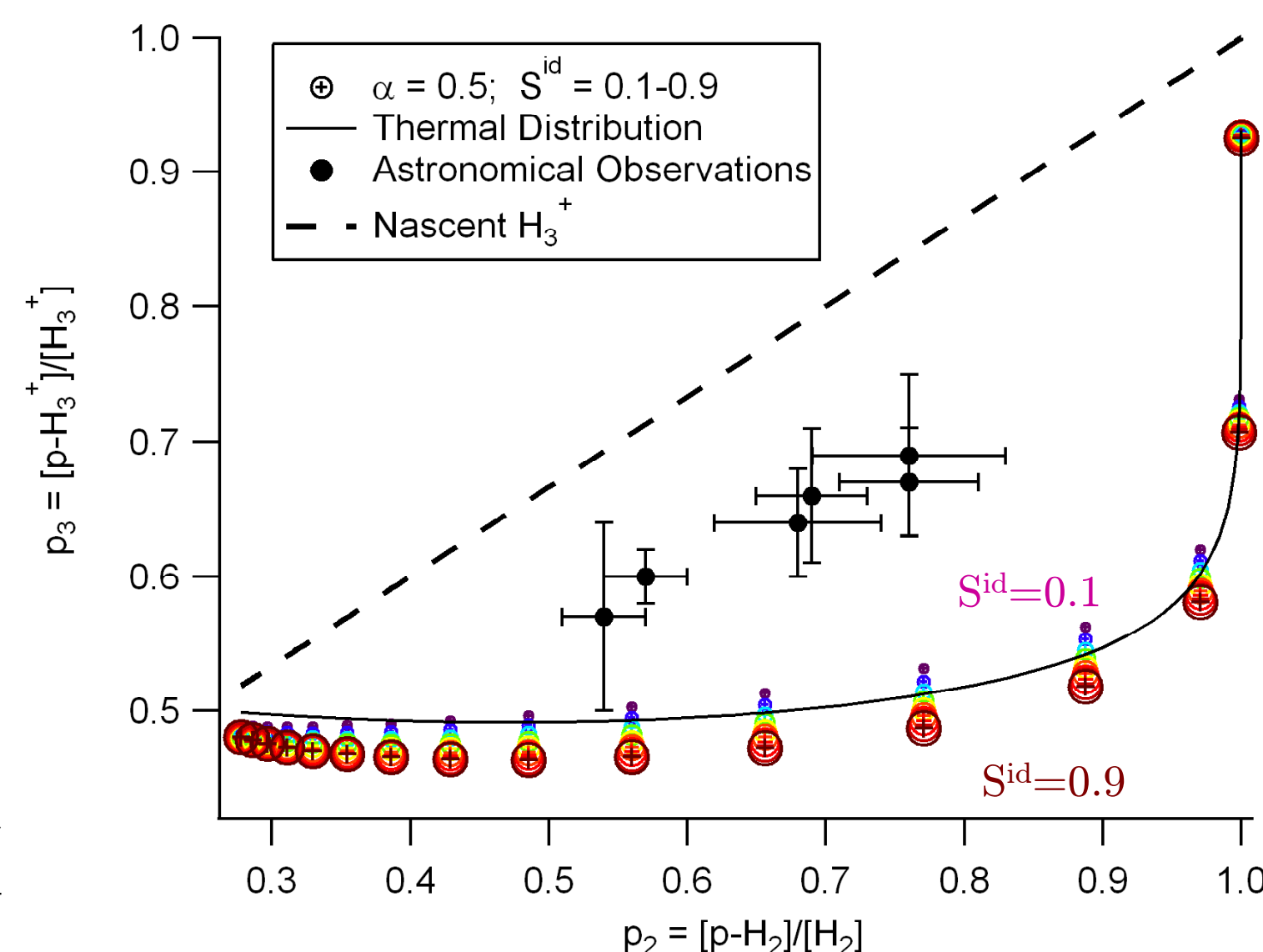
Results of model calculations excluding H_3^+ formation and DR, instead only considering H_3^+ reacting with H_2. No matter the value of S^{id} used, the p-H_3^+ fraction approaches its thermal value (shown by the solid line).

Results of model calculations using H_3^+ DR rate coefficients from storage ring measurements [o- and p-H_3^+ DR rates equal, B. J. McCall et al. Nature 422, 500 (2003)]. Good agreement is observed when $S^{id} = 0.9$. This may imply that many $H_3^+ + H_2$ collisions are nonreactive.

Results of model calculations using recent theoretical DR rate coefficients [dos Santos et al., J. Chem. Phys. 127, 124309 (2007)]. No agreement is observed. The values of the DR rates of o- and p-H_3^+ at low temperature are still under investigation [Kreckel et al., Phys. Rev. A 82, 042715 (2010)].

Further info and funding