Experimental Measurements of the $H_3^+ + H_2 \rightarrow H_3^+ + H_2$ Reaction in a Hollow Cathode

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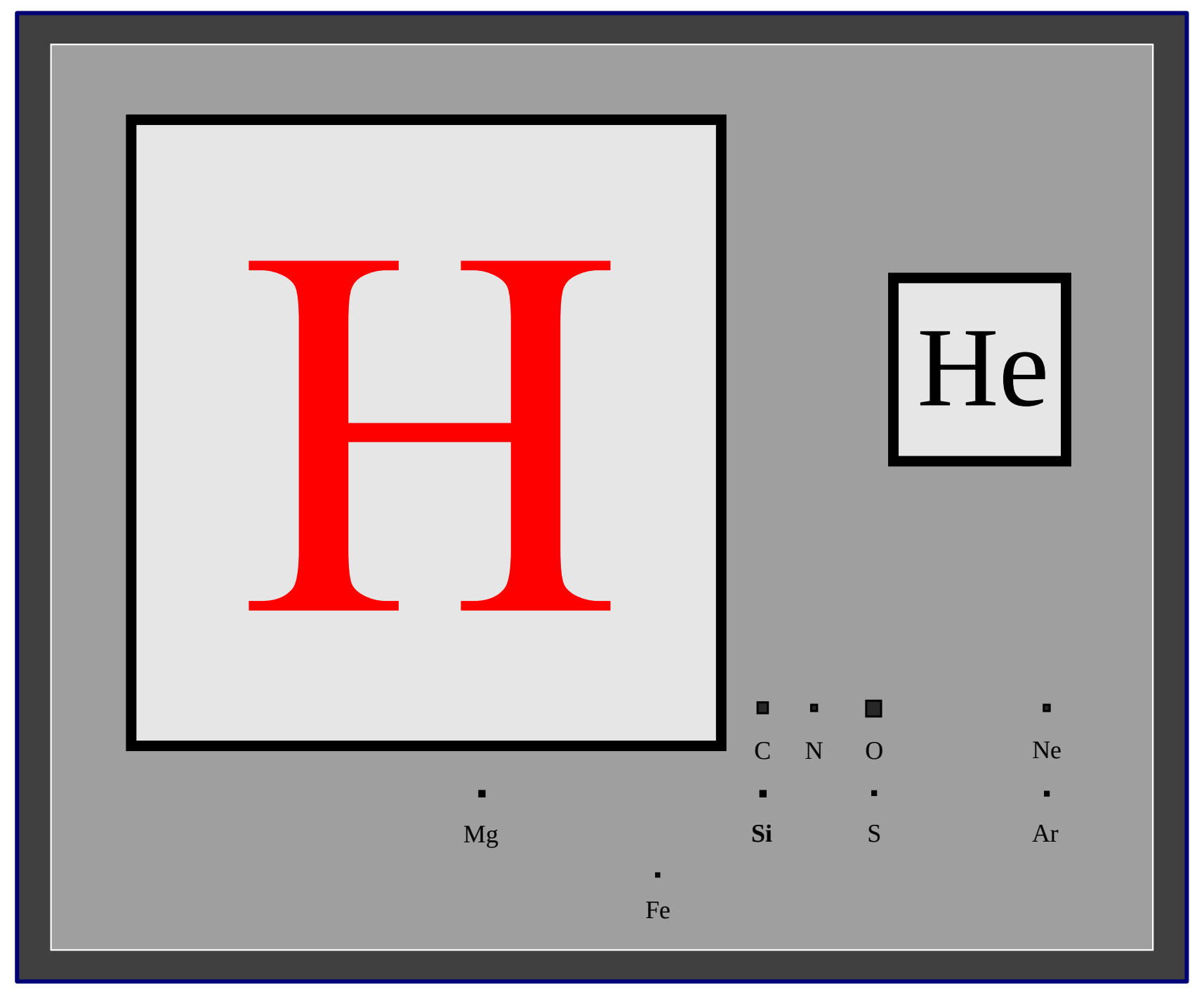
Motivation

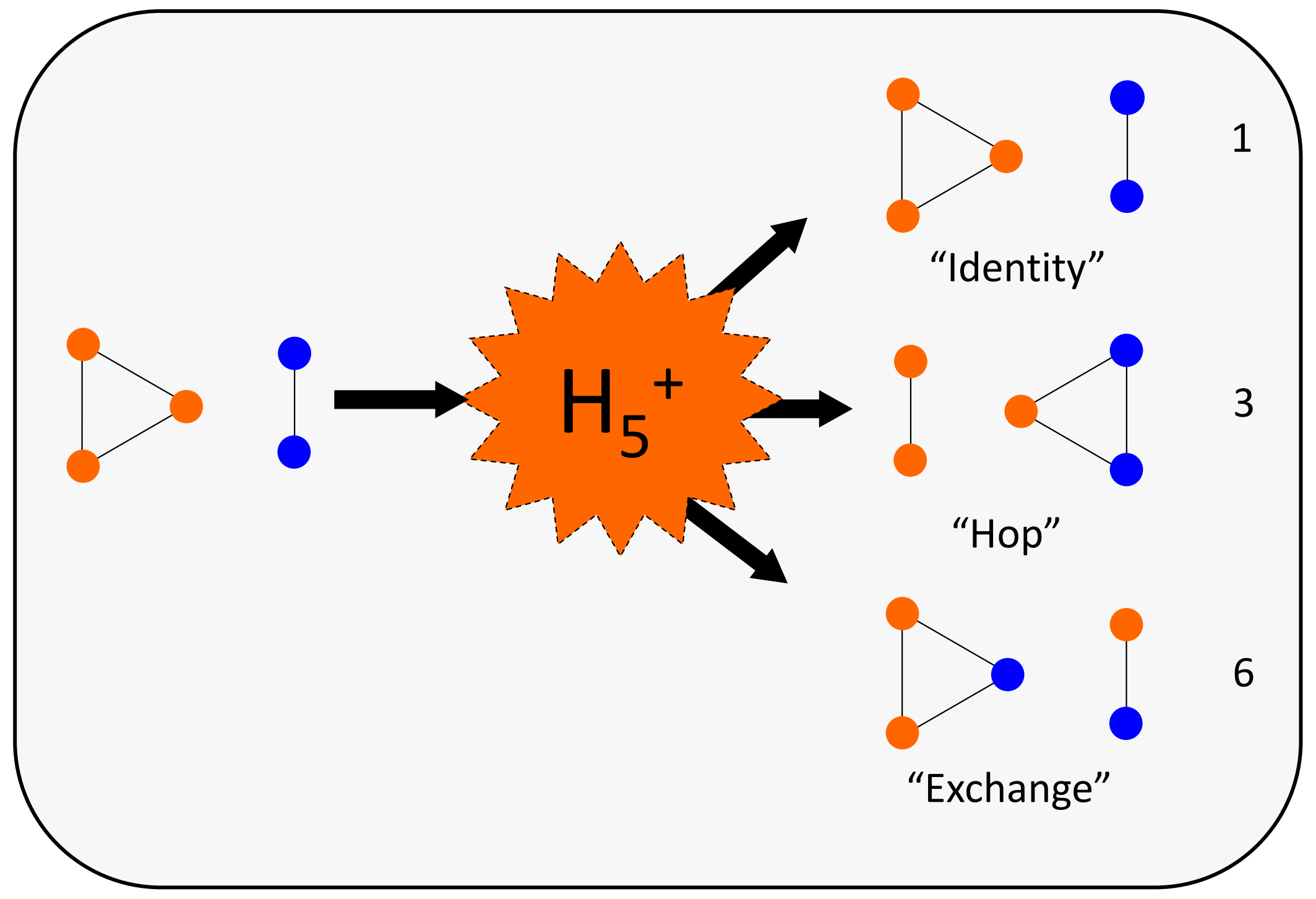
Hydrogen is the most abundant element in the universe. Therfore, it can be stated that hydrogenic species and the reactions (e.g. deuterium fractionation) are arguably the most important reactions occurring in our universe. Due to their simplicity, they are also useful as benchmark species to test *ab initio* calculations and other computational methods. Despite many experimental and theoretical studies, more research is needed to understand these species and their reactions.



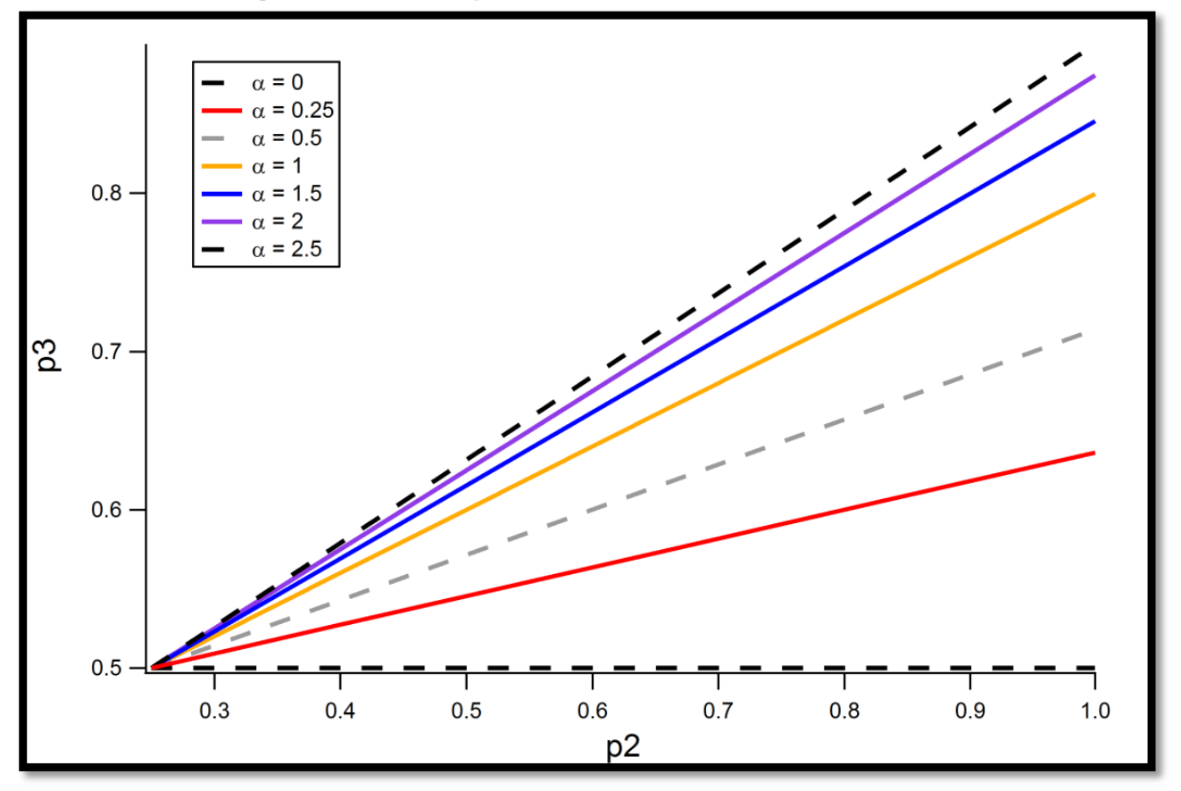
$H_3^+ + H_2$ Reaction

$H_3^+ + H_2$ is the simplest bimolecular reaction involving a polyatomic in the universe (occurring 10^{52} s^{-1} in the Milky Way alone!). Both H_3^+ and H_2 exist in two nuclear spin configurations, *ortho* and *para*. They are unique species and can only interconvert through a chemical reaction. The reaction between these species is the dominant means by which the nuclear spin of H_3^+ is converted.

- •Reaction is governed by conservation of nuclear spin[1,2]
- •Branching fractions: S^{id}, S^{hop}, & S^{exch}
- •α = hop/exchange ratio
- •Statistical α = 0.5
- •Previous measurement by Cordonnier[3] and coworkers at T= 400 yielded α = 2.4
- •What is temperature dependence of α?



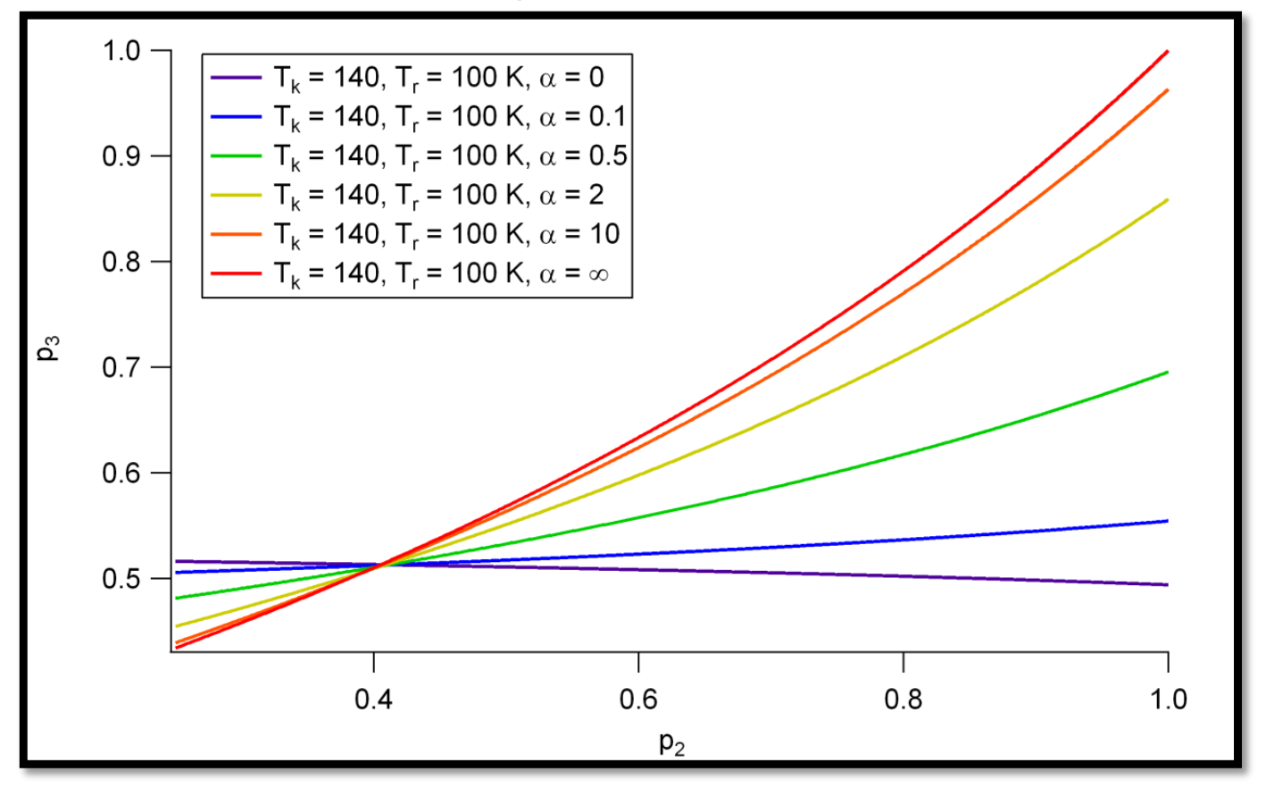
High Temperature Model



$p_3 = \frac{2\propto p_2 + \propto + 1}{2+3\propto}$, where p_2 is *para*-H_2 fraction and p_3 is *para*-H_3^+ fraction

- Reactions constrained by conservation of nuclear spin
- Assumed that there is a sufficient amount of energy to access a large number of excited states for each spin modification

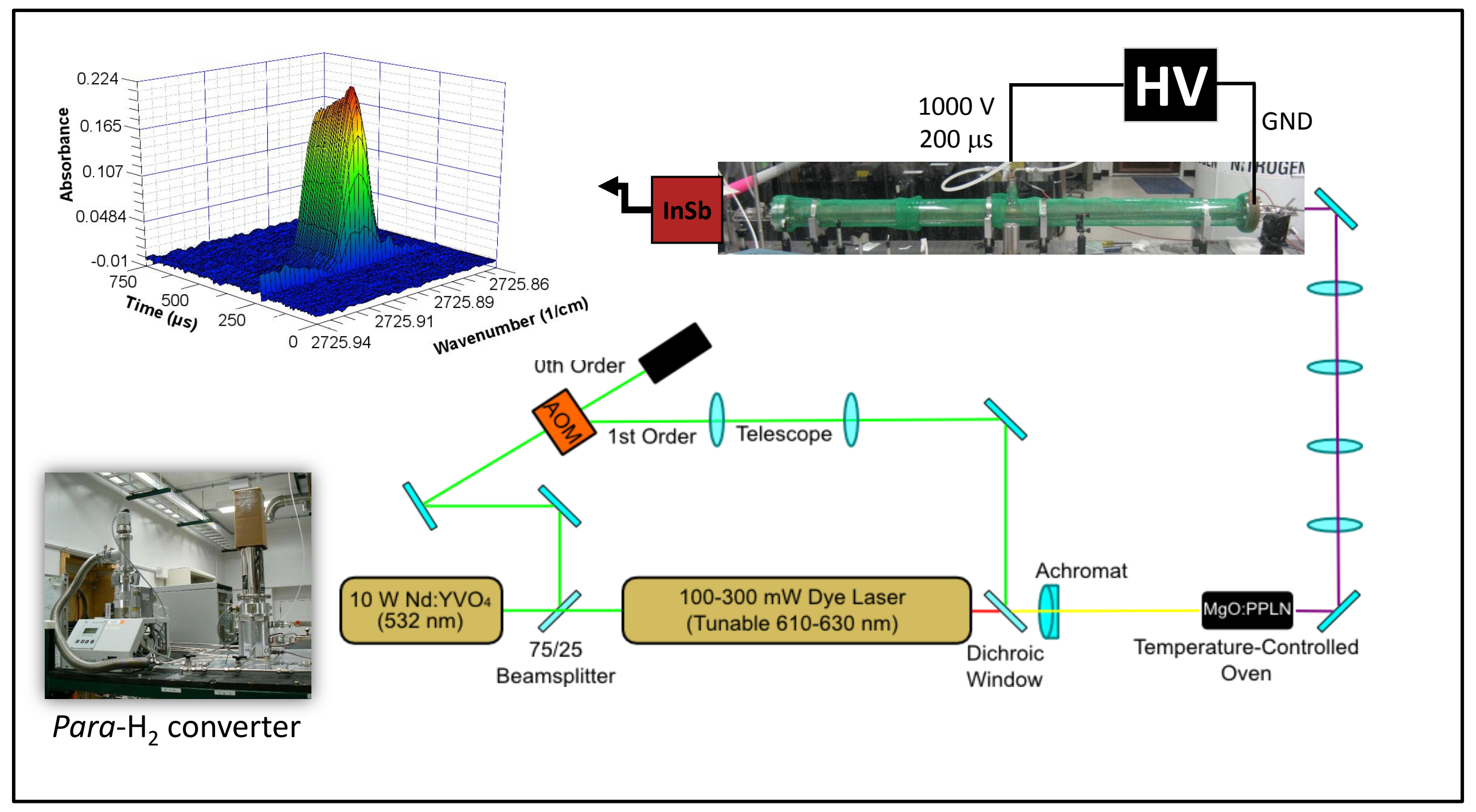
Low Temperature Model



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

- Steady state chemical model based on nuclear spin-dependent proton scrambling in the $H_3^+ + H_2$ system
- Rate coefficients are calculated using the micro-canonical statistical model of Park and Light[4]
- Rate coefficients are dependent on temperature and branching fractions

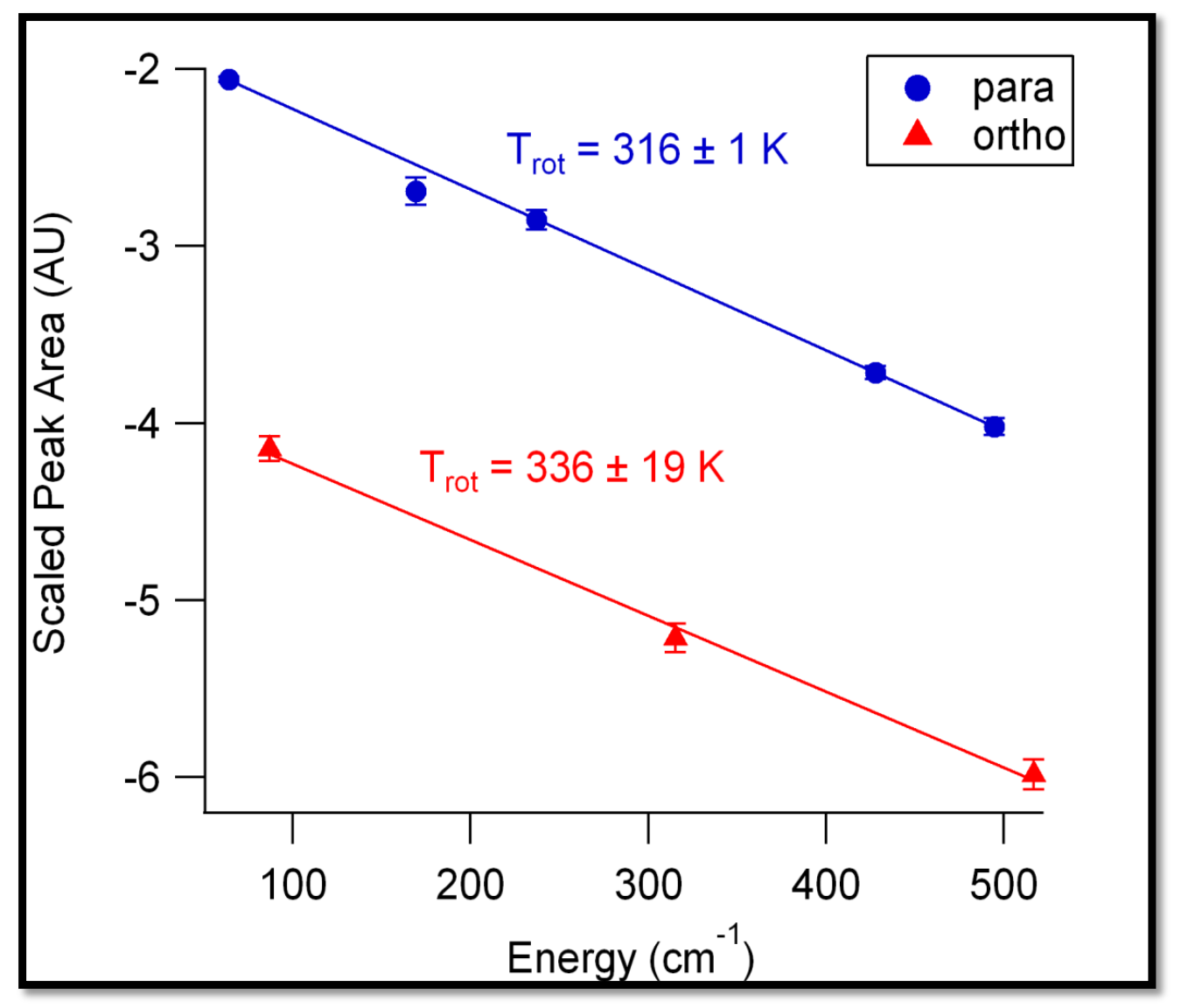
Experimental Set-up



Para-H_2 converter

To monitor the $H_3^+ + H_2$ reaction, we have constructed a hollow cathode cell to produce hydrogenic plasmas of varying *ortho*:*para* ratio. To monitor the *ortho*:*para* ratio, rotational temperature, and kinetic temperature of the various plasmas, we perform direct multi-pass absorption spectroscopy on the ν_2 fundamental band of H_3^+. The temperature of the plasma can be varied by flowing different coolants through a coil surrounding the cathode. We have operated the hollow cathode using liquid nitrogen (T_{kin}~130 K), no cooling (T_{kin} ~ 330 K), and plan to heat the hollow cathode using heated gas.

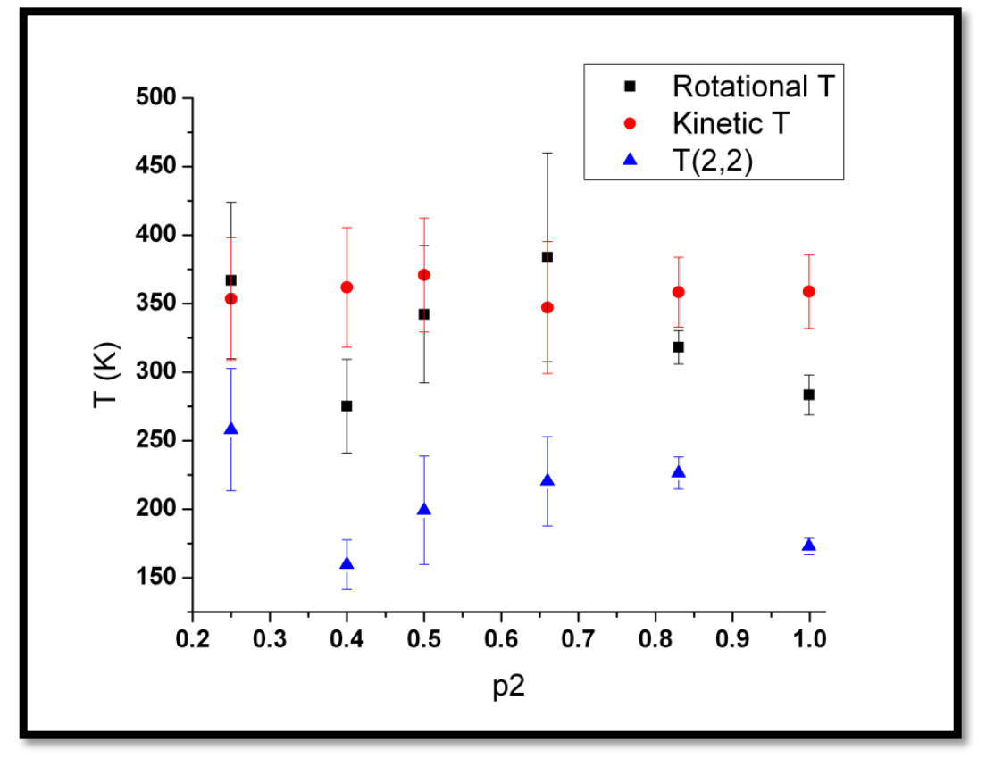
Plasma Temperature



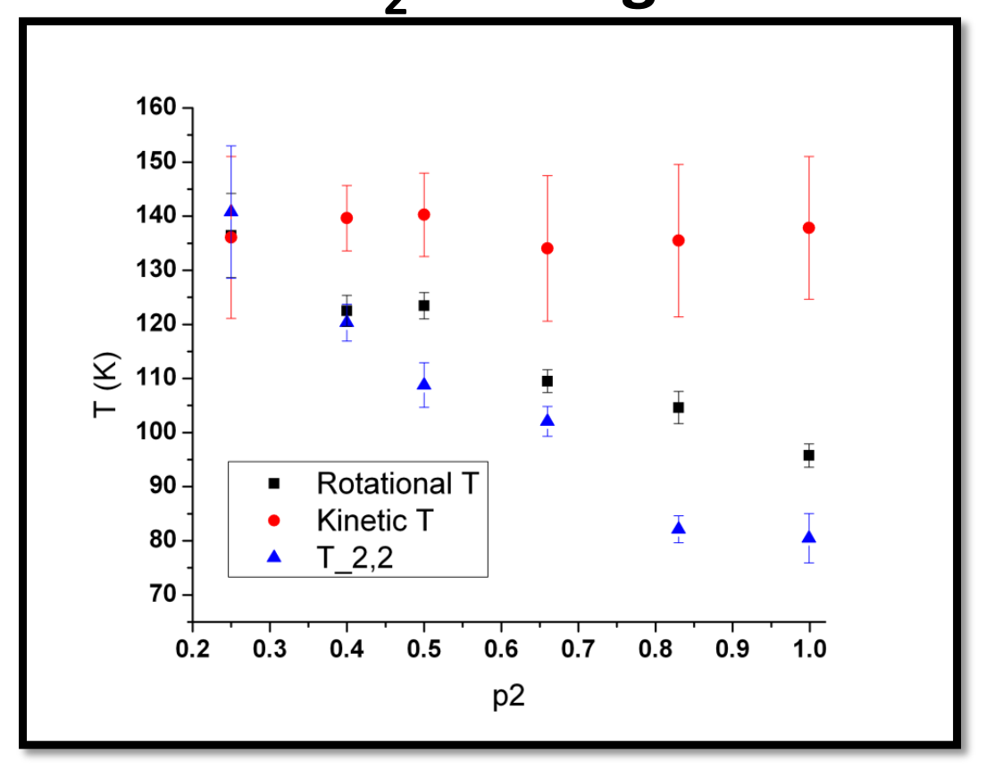
In order accurately characterize the plasma temperature, we verified that the rotational levels of H_3^+ were thermalized by measuring the first eight levels of *o*-H_3^+ and *p*-H_3^+. As demonstrated in the figure, the *ortho* and *para* rotational temperatures agree well. They are also in agreement with the kinetic temperature of the plasma, 319 ± 33K.

One noteworthy feature of this plot is the under-population of (2,2) state relative to the other *para* states. This is consistently present in all data sets.

No Cooling



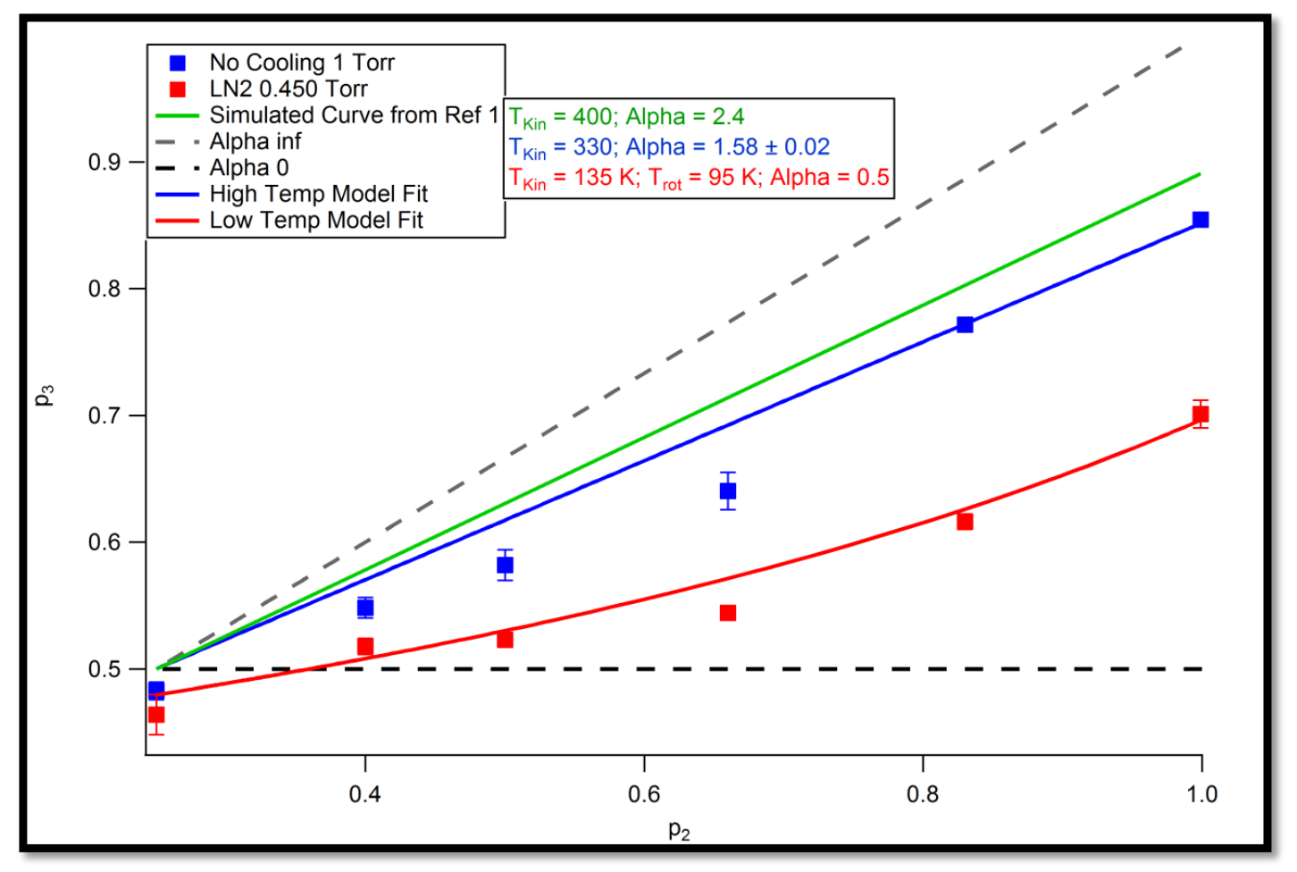
LN_2 Cooling



We also recorded three temperatures as a function of p_2: the rotational temperature that was derived from the $R(1,1)^u$ and $R(2,1)^u$, the kinetic temperature, and T(2,2) that is derived from the $R(1,1)^u$ and $R(2,2)^l$.

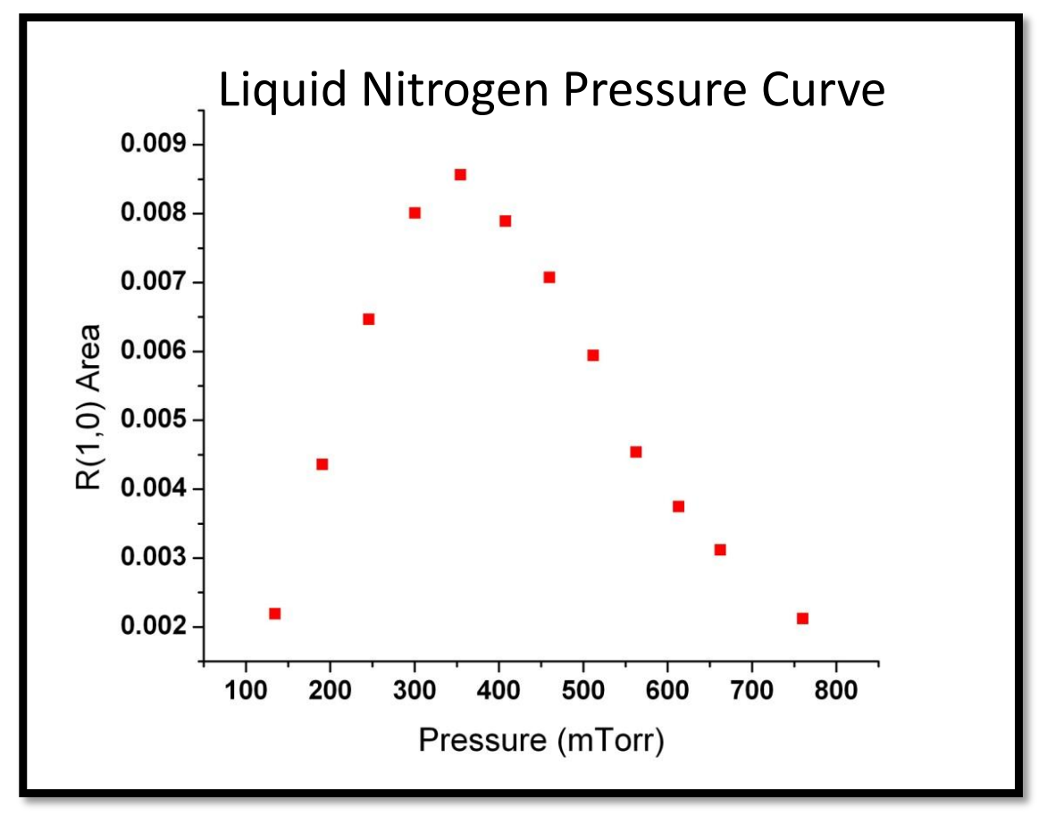
- In the no cooling data set, the rotational temperature, 306 ± 9 K, is approximately 50 K cooler than the observed kinetic temperatures of 359 ± 14 K along p2, and T(2,2) is observed to be even cooler at 184 ± 5 K. The huge discrepancy between T(2,2) and the other derived temperatures is the result of the under-population of the $R(2,2)^l$ state.
- In the LN_2 cooling data set, the average kinetic temperature along p_2 is calculated to be 139 ± 4 K. An interesting feature is found with the rotational temperature and T(2,2); both decrease with an increase of p_2.

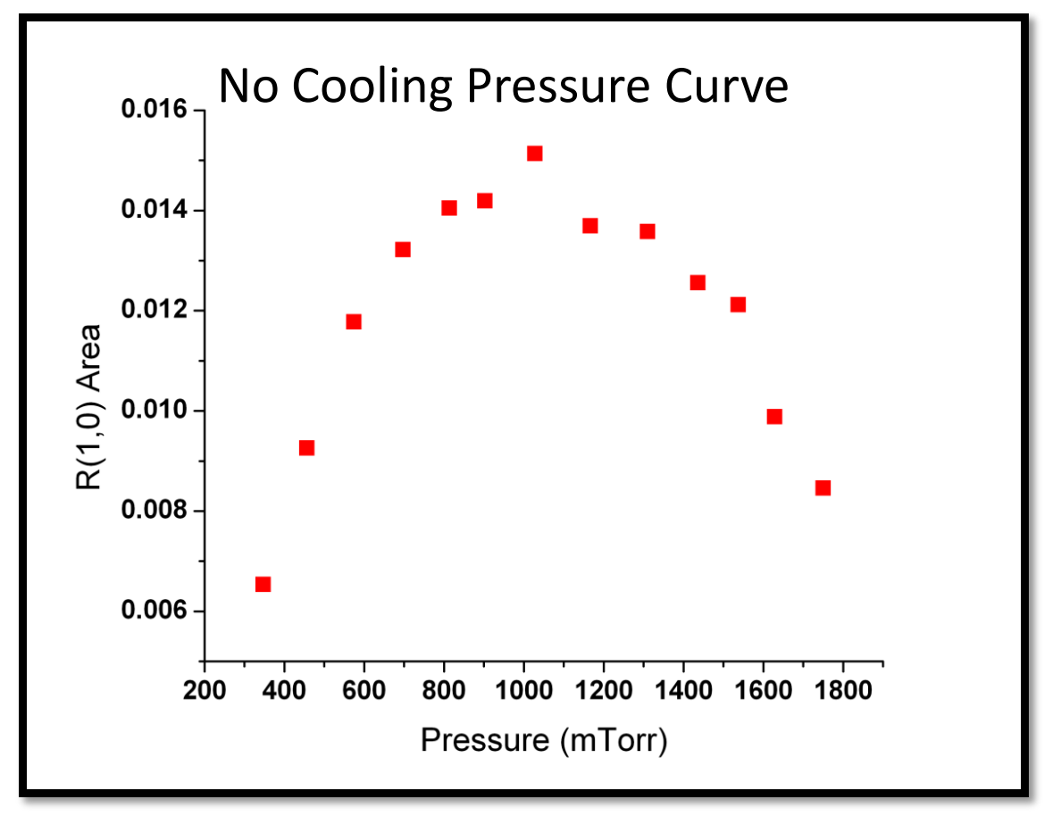
Temperature Dependence



- A fit to the high temperature model yields an α of 1.55
- In the low temperature model, the best fit was with an α of 0.5
- The decrease in α with a decrease in temperature is consistent with pervious studies of the reaction $D_3^+ + H_2$.[5] It also seems to approach the statistical limit of α = 0.5 that is consistent with an increase in the lifetime of the H_5^+ reaction intermediate

Pressure Dependence





In hydrogenic plasmas, it has been shown that an increase in pressure results in formation of the product H_5^+ resulting from the three-body reaction $H_3^+ + 2H_2 \rightarrow H_5^+ + H_2$.[6] We observe this effect when we see a decrease in H_3^+, but the discharge current remains fixed. Since the electron mobility should decrease monotonically with increasing pressure and the ion density should be increasing as well, we believe that H_3^+ must be consumed by this three body process.

Conclusions

- Both derived models, high temperature and low temperature, agree well with the acquired data sets.
- As temperature decreases, a decrease in α is observed. This is consistent with previous studies with deuterium and indicates an increase in the lifetime of H_5^+ reaction intermediate.
- Pressure dependence studies indicate three-body reactions occur, and we are currently assessing how those reactions will influence the α we derive from our models.
- The consistent under-population of $R(2,2)^l$ indicates state-specific chemistry is occurring and highlights the need for quantum reactive scattering calculations.
- Future directions include quantum reactive scattering calculations and ion trap studies to measure this reaction at lower temperatures and densities

Funding & References

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