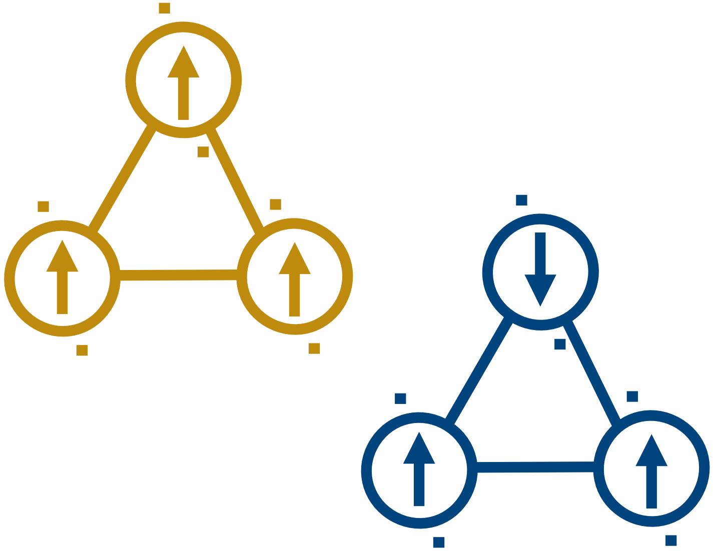
Nuclear Spin Dependent Chemistry of the Trihydrogen Cation in Diffuse Interstellar Clouds

Kyle N. Crabtree, Department of Chemistry, UC Davis



Collaborators

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Holger Kreckel (Max Planck Institute for Nuclear Physics)
Benjamin J. McCall (University of Illinois)
Stephan Schlemmer (University of Cologne)
Dmitry Semenov (Max Planck Institute for Astronomy)
Andreas Wolf (Max Planck Institute for Nuclear Physics)

Photo: APOD Oct 21, 2011

H_3^+ in diffuse clouds

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Detection of H_3^+ in the Diffuse Interstellar Medium Toward Cygnus OB2 No. 12

B. J. McCall,* T. R. Geballe, K. H. Hinkle, T. Oka

The molecular ion H_3^+ is considered the cornerstone of interstellar chemistry because it initiates the reactions responsible for the production of many larger molecules. Recently discovered in dense molecular clouds, H_3^+ has now been observed in the diffuse interstellar medium toward Cygnus OB2 No. 12. Analysis of H_3^+ chemistry suggests that the high H_3^+ column density (3.8×10^{14} per square centimeter) is due not to a high H_3^+ concentration but to a long absorption path. This and other work demonstrate the ubiquity of H_3^+ and its potential as a probe of the physical and chemical conditions in the interstellar medium.

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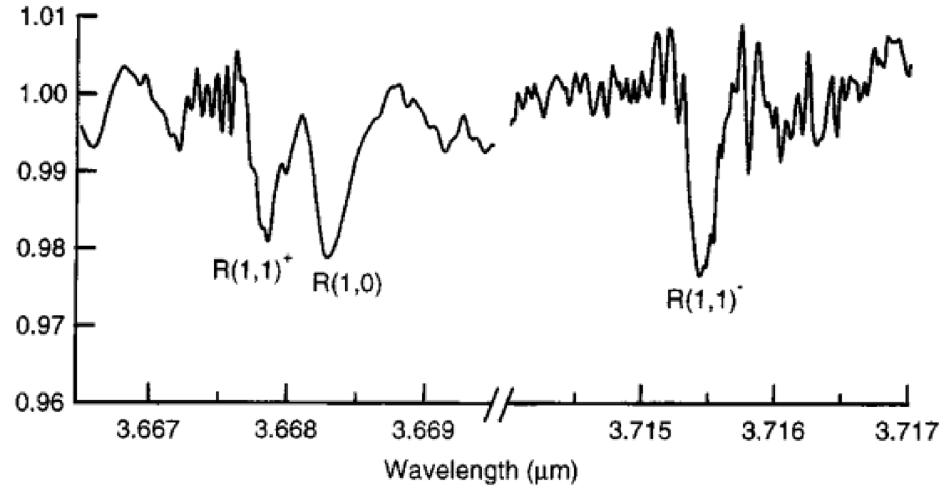


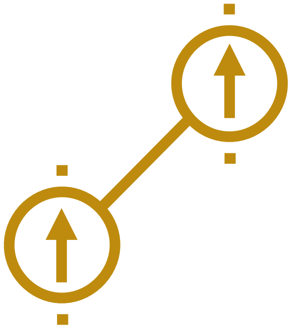
H_3^+ IN DIFFUSE INTERSTELLAR CLOUDS: A TRACER FOR THE COSMIC-RAY IONIZATION RATE

Nick Indriolo,[1] Thomas R. Geballe,[2] Takeshi Oka,[3] and Benjamin J. McCall[1]

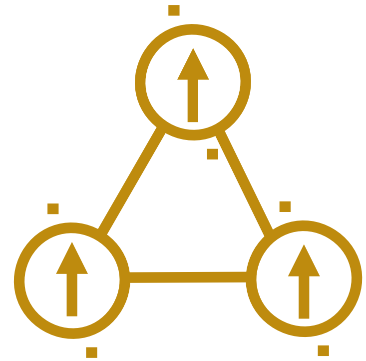
Received 2007 June 6; accepted 2007 September 4

The Astrophysical Journal, 671:1736–1747, 2007 December 20

Spin modifications: H_3^+ and H_2



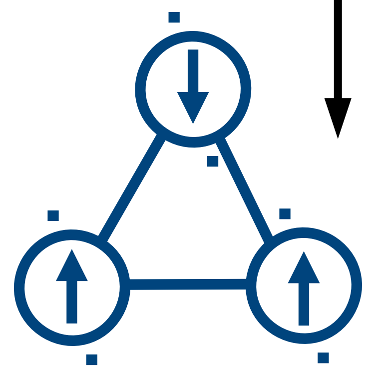
ortho-H_2; $I = 1$



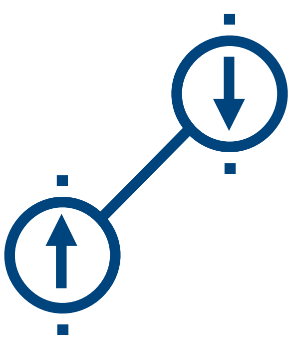
ortho-H_3^+; $I = 3/2$

$\Delta E/k_B = 170$ K

$\Delta E/k_B = 33$ K



para-H_3^+; $I = 1/2$



para-H_2; $I = 0$

Chemical interconversion reactions:

o-H_2 + H^+ → p-H_2 + H^+

o-H_3^+ + p-H_2 → p-H_3^+ + o-H_2

Diffuse molecular clouds

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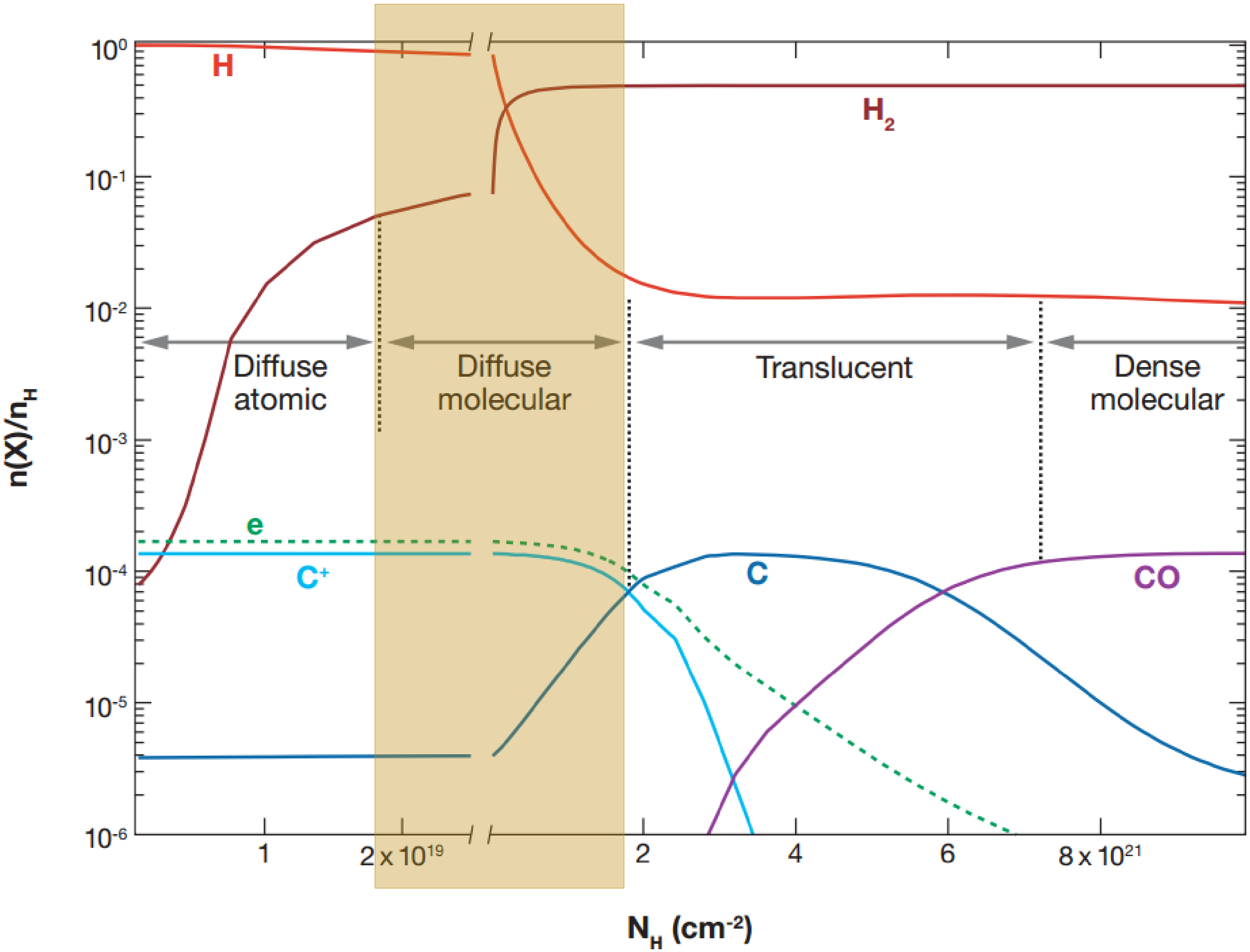
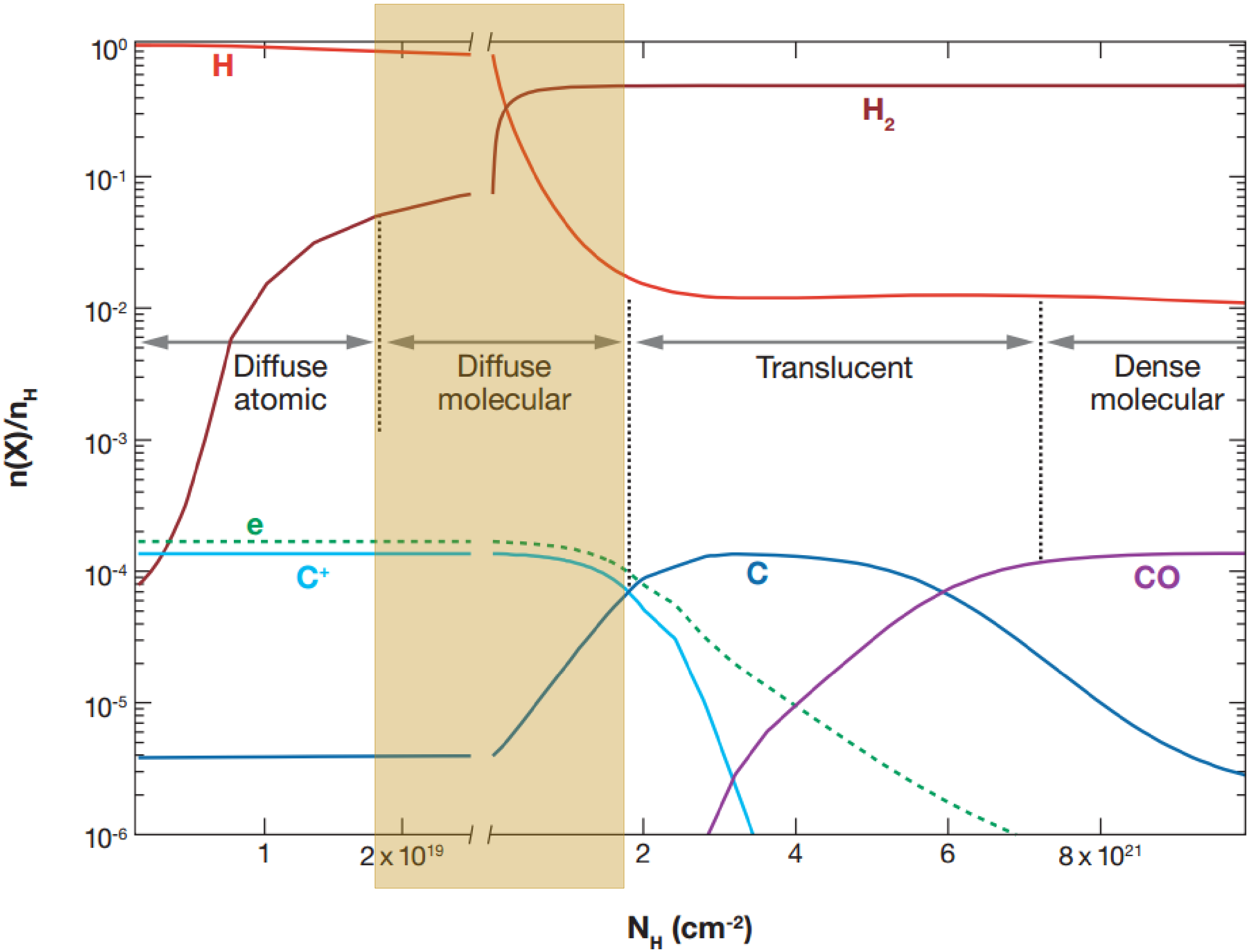


- Typical Conditions:
  - n ~ 10–100 cm^{-3}
  - f_{H2} > 0.1 (typ 0.9)
  - x_e ~ 1.5 x 10^{-4}
  - log[N (cm^{-2})] ~ 21
  - T ~ 50-100 K

T. P. Snow and B. J. McCall, Annu. Rev. Astron. Astrophys. 44, 367 (2006).

Diffuse molecular clouds



- Typical Conditions:
  - n ~ 10–100 cm^{-3}
  - f_{H2} > 0.1 (typ 0.9)
  - x_e ~ 1.5 x 10^{-4}
  - log[N (cm^{-2})] ~ 21
  - T ~ 50-100 K
- 9 sightlines with H_3^+ and H_2 observations:
  - $\langle T_{H2} \rangle$ = 61 K
  - $\langle T_{H3+} \rangle$ = 28 K

T. P. Snow and B. J. McCall, Annu. Rev. Astron. Astrophys. 44, 367 (2006).

Diffuse cloud IR observations

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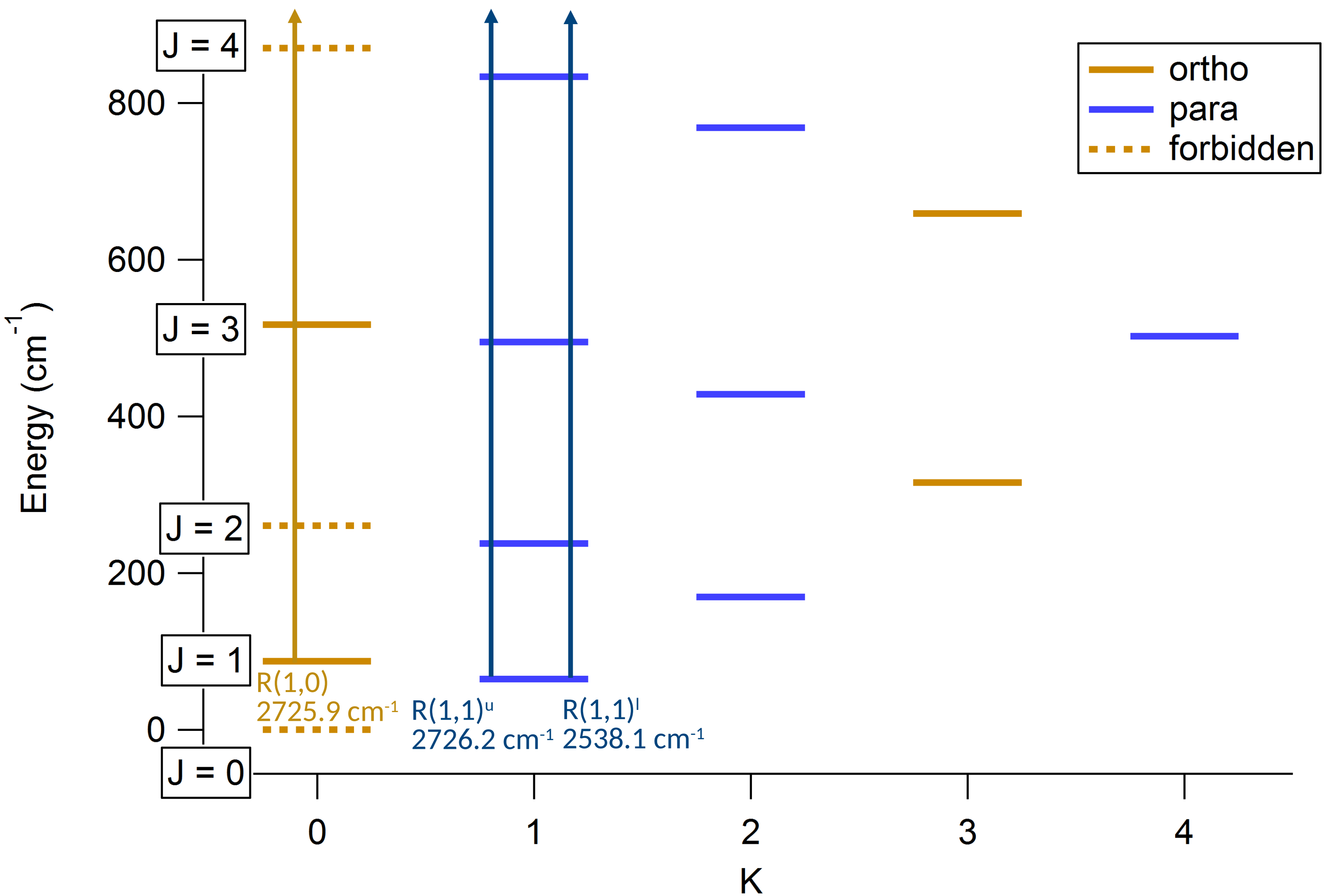
- In diffuse clouds, only (1,0) and (1,1) levels observed



“All” H_3^+ relaxes to (1,0) and (1,1) states

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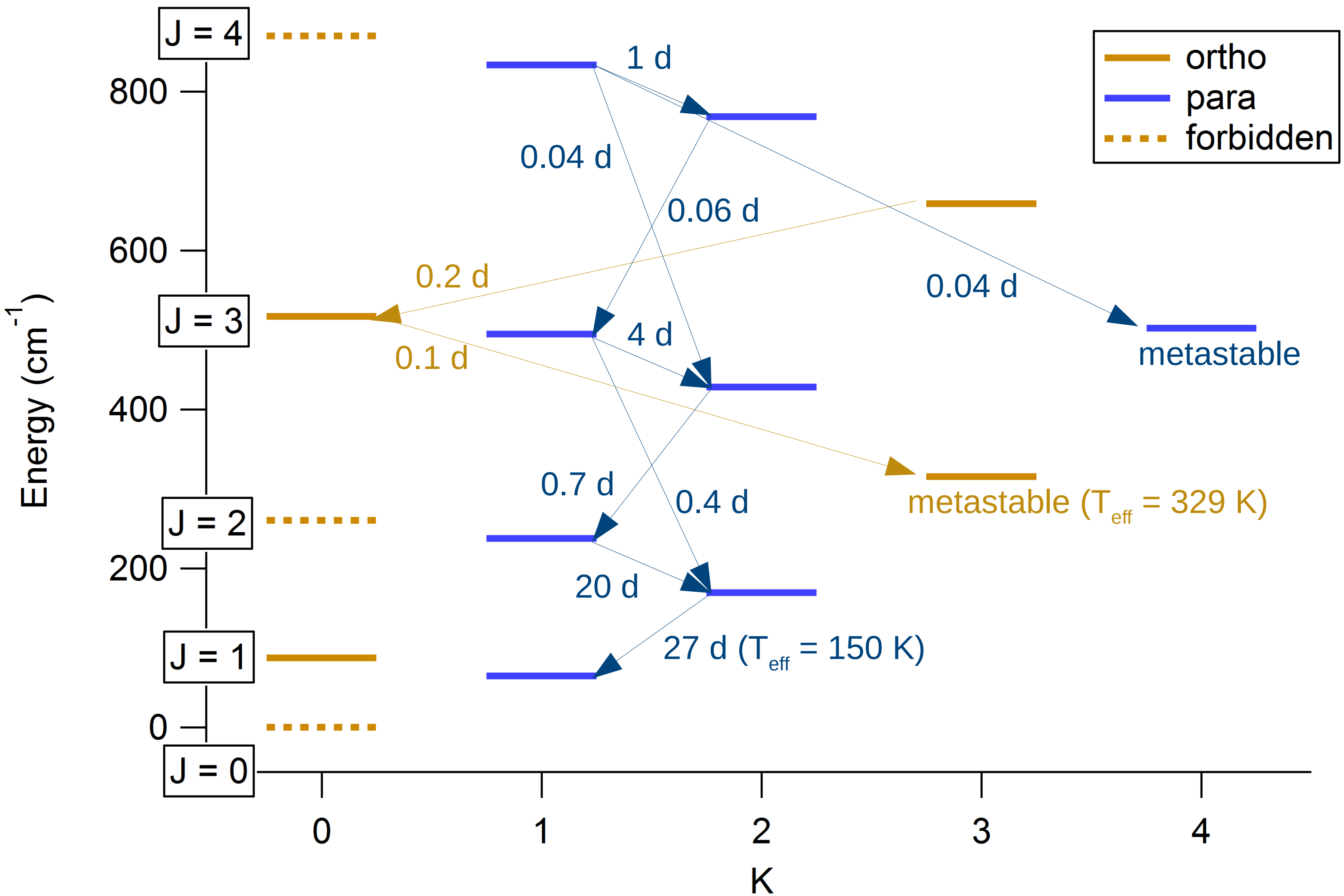
- Collision timescale > 60 days
- H_3^+ ion experiences 10–100 collisions w/ H_2 during lifetime



T. Oka and E. Epp, ApJ 613, 349 (2004).

Observations of H_3^+ → para-H_3^+ fraction

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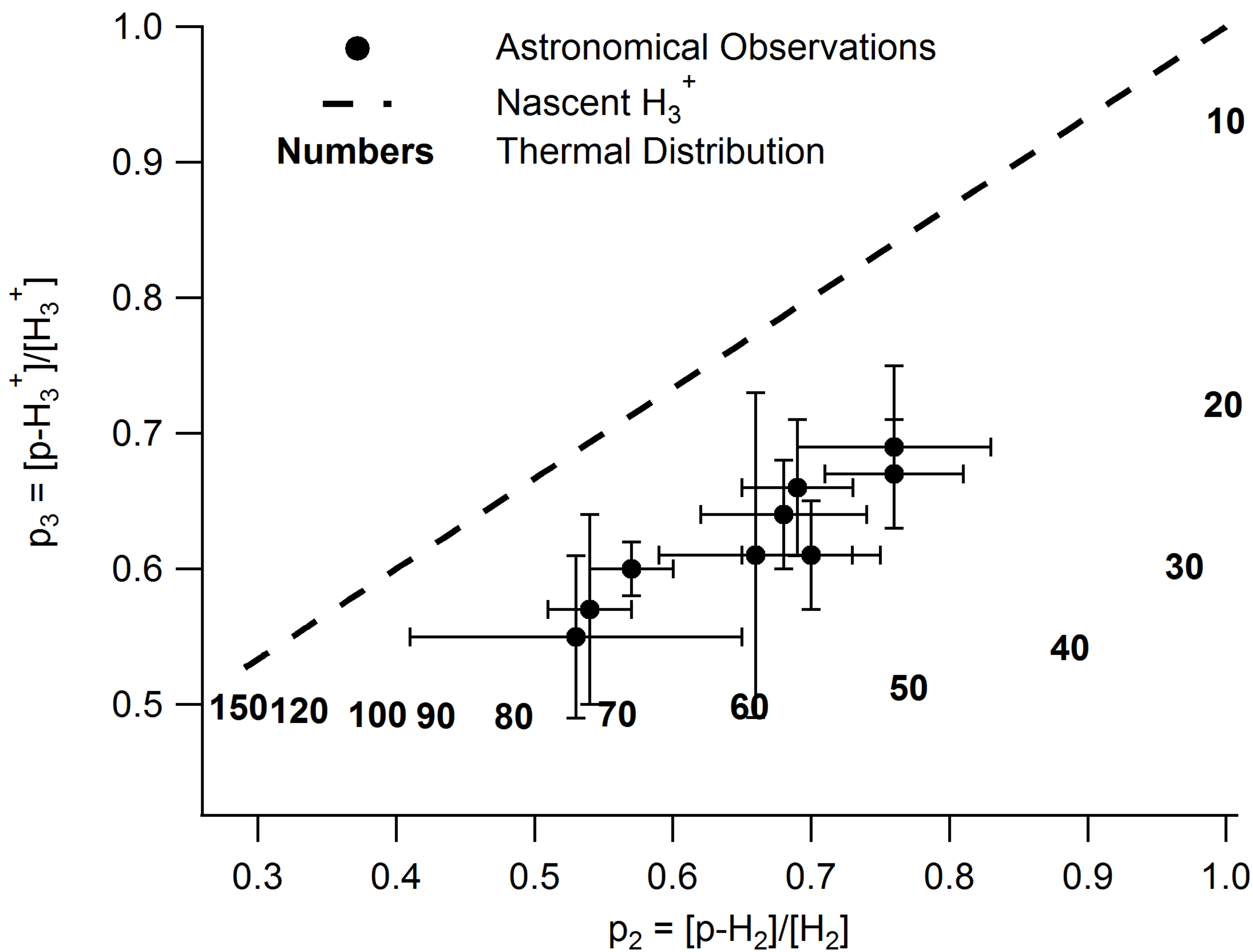

Observations of H_3^+ and H_2 in diffuse clouds

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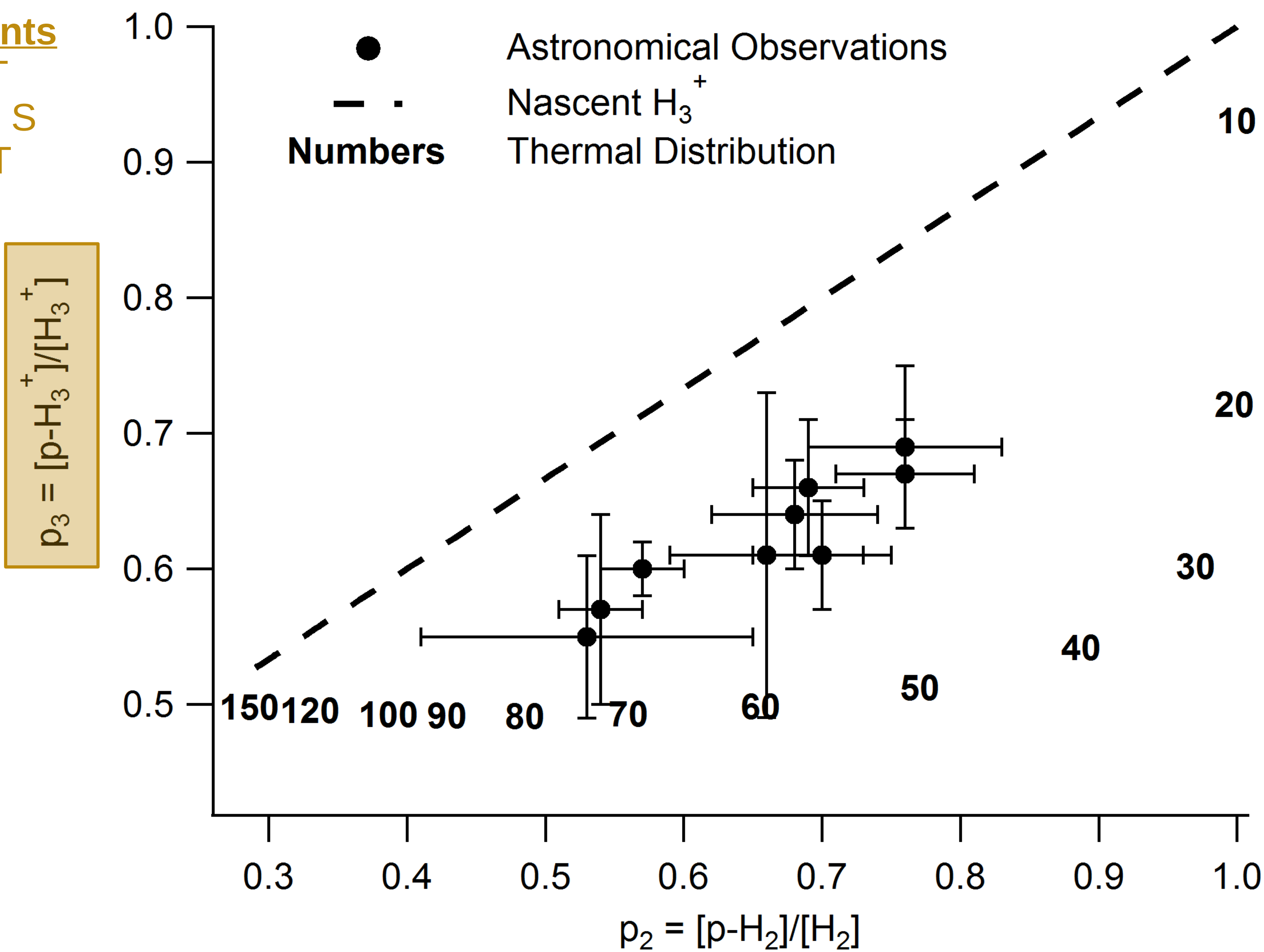
IR measurements
CRIRES/VLT
Phoenix/Gem. S
CGS4/UKIRT



K. N. Crabtree et al. ApJ 729, 15 (2011); T. Albertsson et al. ApJ 787, 44 (2014).

Observations of H_3^+ and H_2 in diffuse clouds

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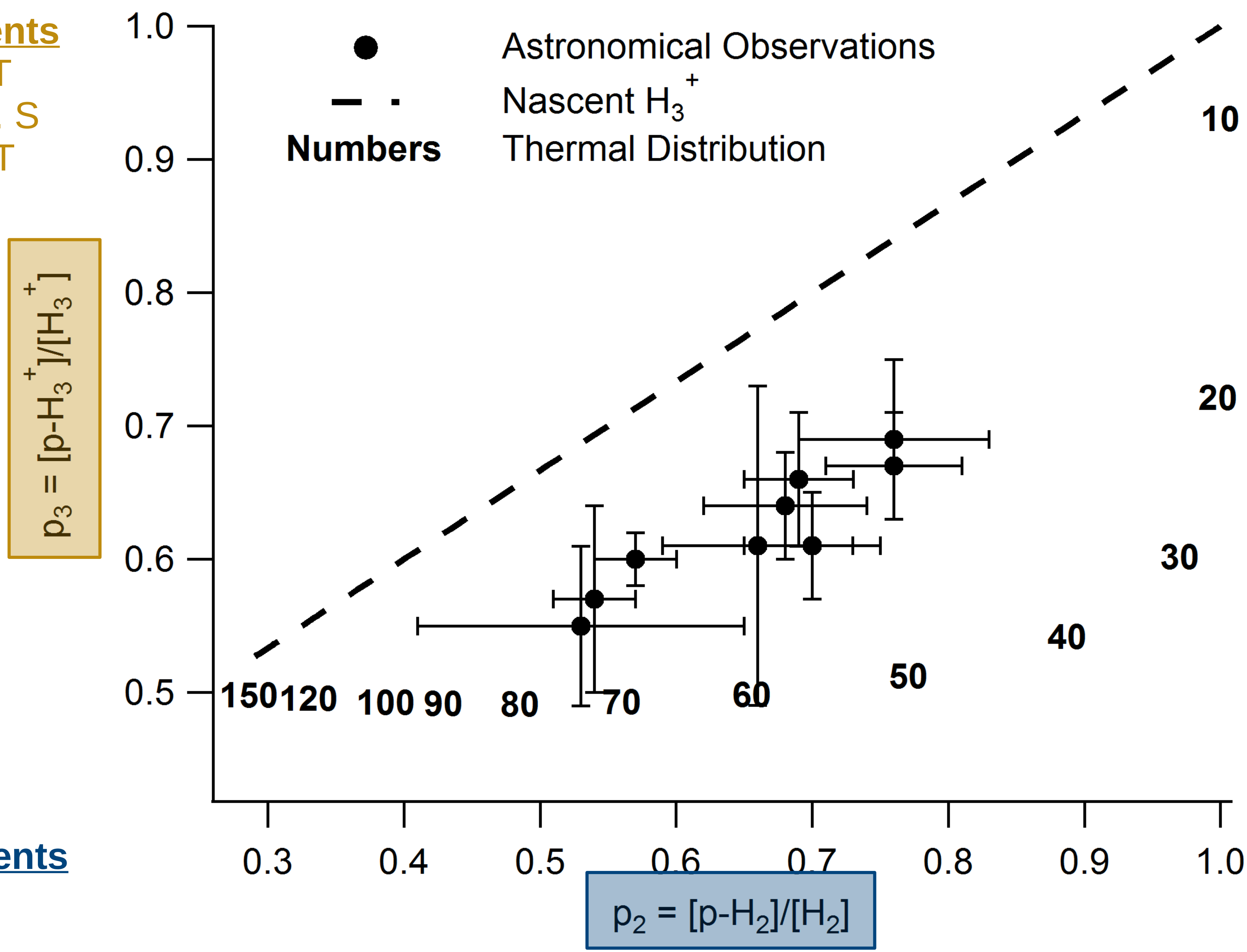

UV measurements
Copernicus
FUSE

K. N. Crabtree et al. ApJ 729, 15 (2011); T. Albertsson et al. ApJ 787, 44 (2014).
B. L. Rachford et al. ApJ 577, 221-244 (2002); B. L. Rachford et al. ApJS 180, 125-137 (2009).

Observations of H_3^+ and H_2 in diffuse clouds

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IR measurements
CRIRES/VLT
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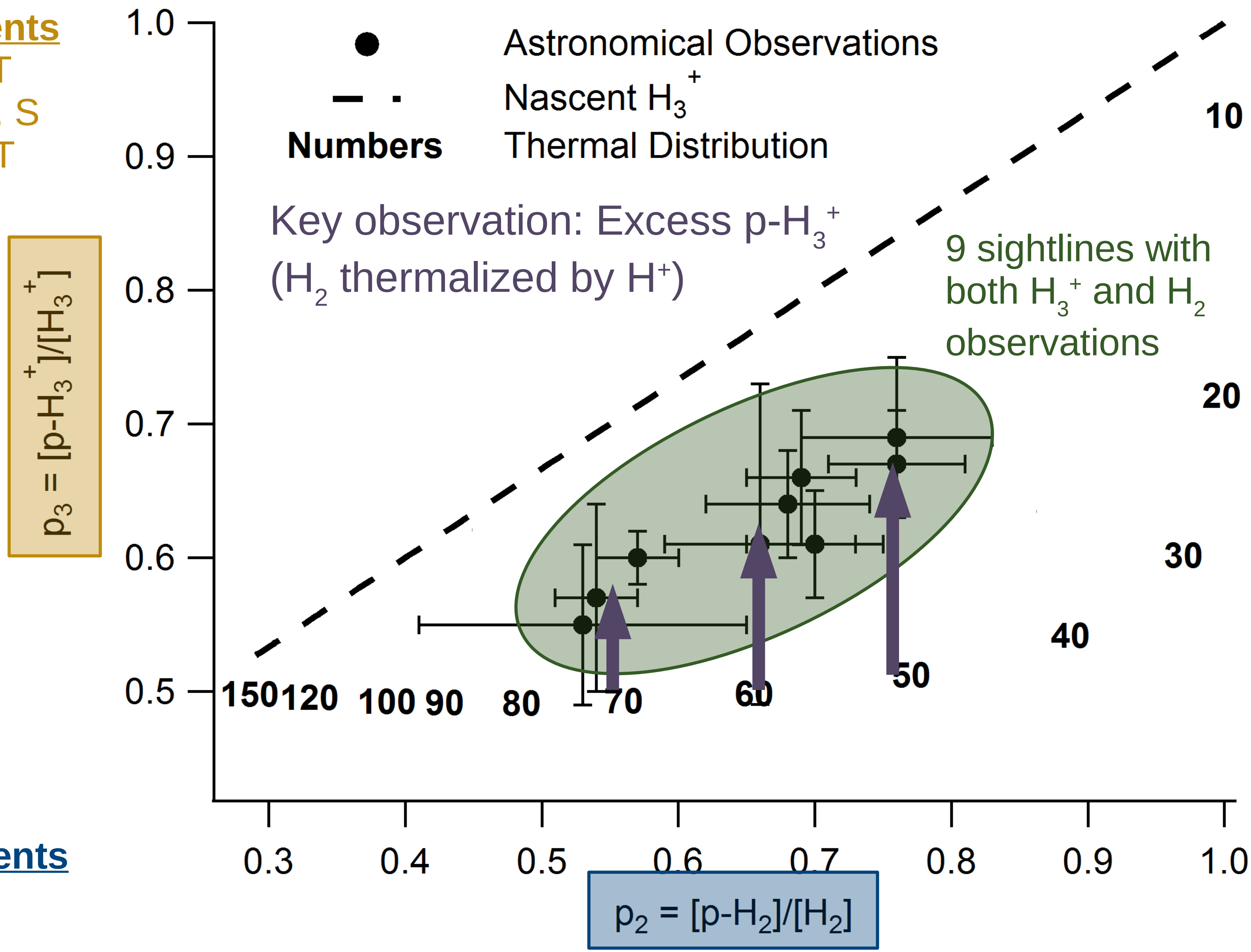

UV measurements
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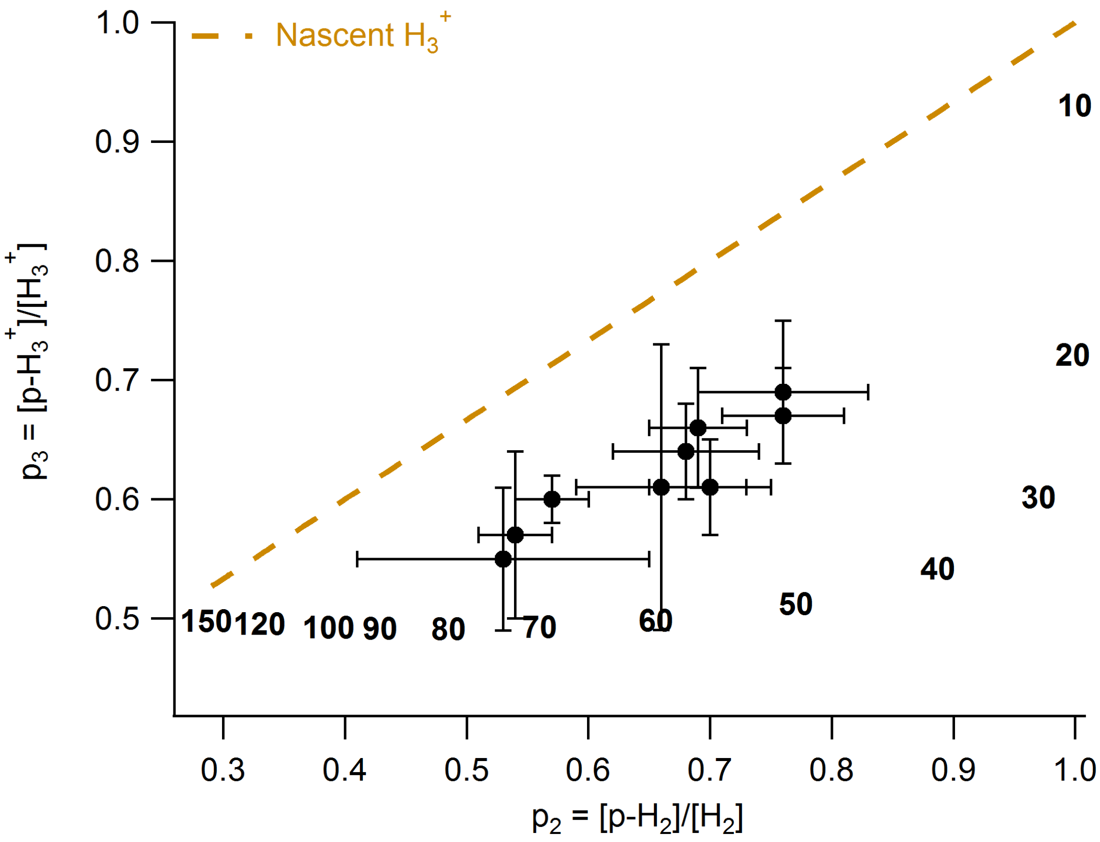
K. N. Crabtree et al. ApJ 729, 15 (2011); T. Albertsson et al. ApJ 787, 44 (2014).
B. L. Rachford et al. ApJ 577, 221-244 (2002); B. L. Rachford et al. ApJS 180, 125-137 (2009).

- Formation:
  1) $H_2 + CR \rightarrow H_2^+ + e^- + CR'$
  2) $H_2^+ + H_2 \rightarrow H_3^+ + H$



Spin-dependent H_3^+ chemistry

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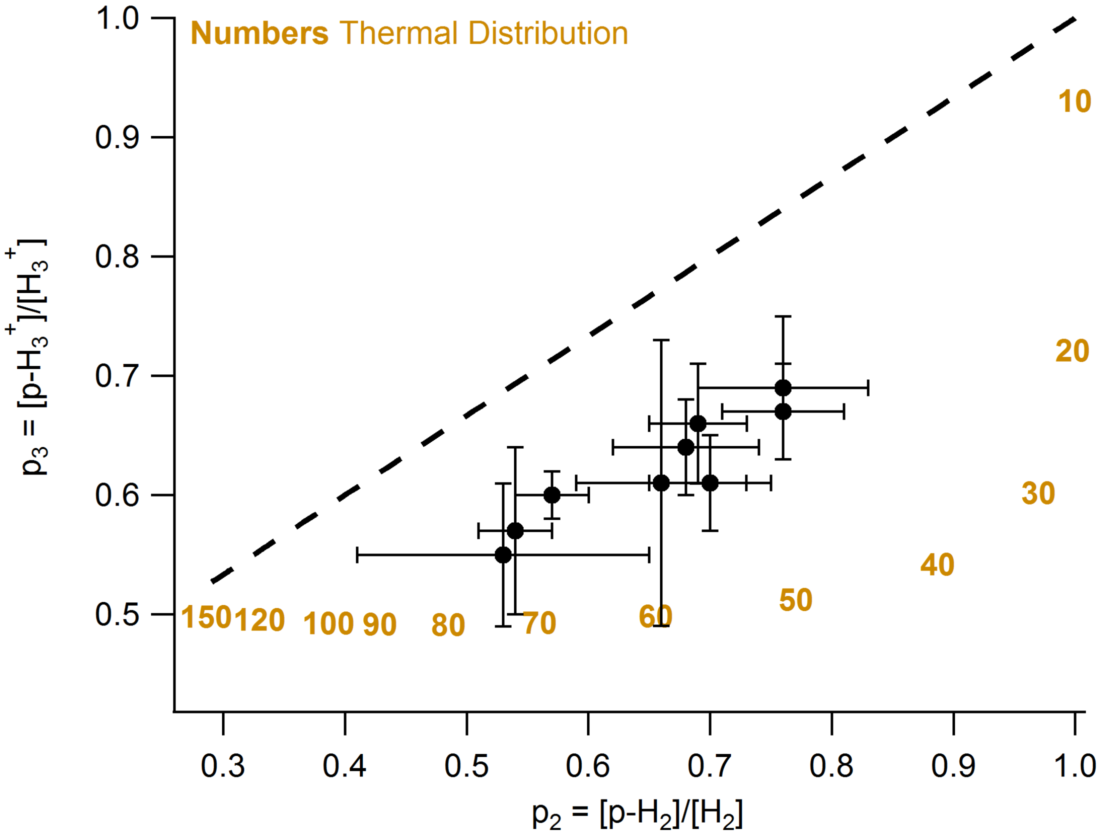
- Formation:
  1) $H_2 + CR \rightarrow H_2^+ + e^- + CR'$
  2) $H_2^+ + H_2 \rightarrow H_3^+ + H$

- Thermalization:
  - $H_3^+ + H_2 \rightarrow H_2 + H_3^+$

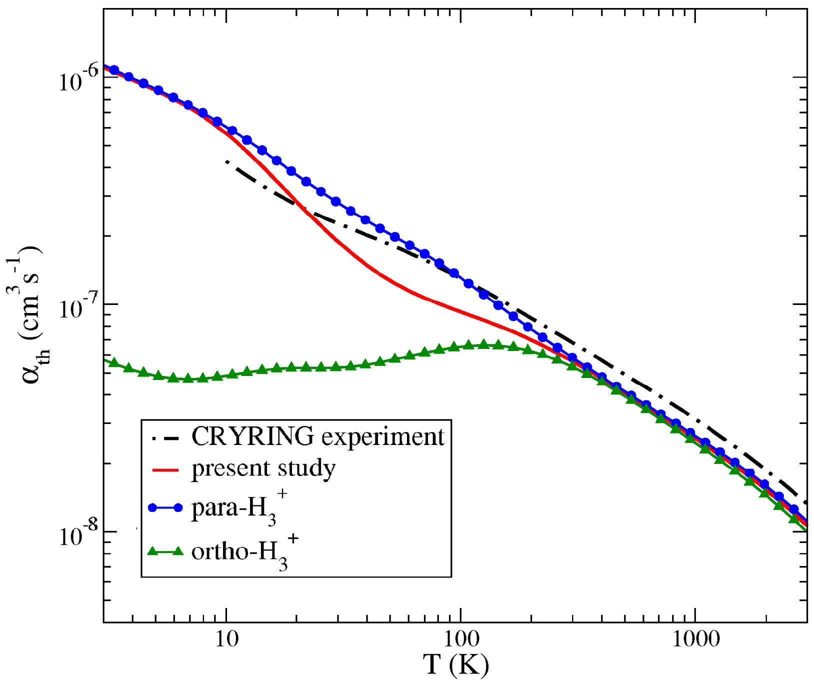


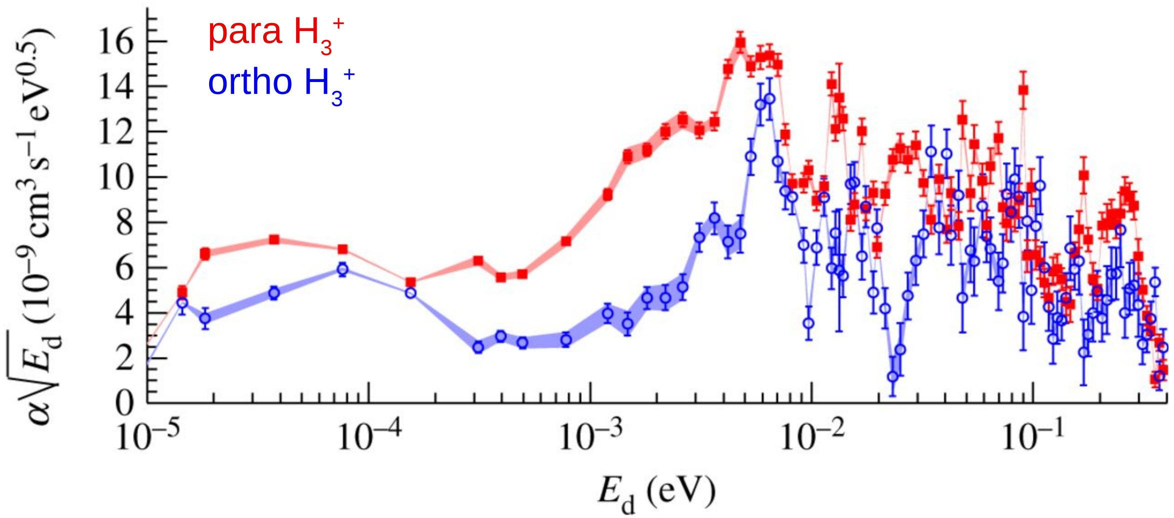
Spin-dependent H_3^+ chemistry

- **Formation:**
  1) H_2 + CR → H_2^+ + e^- + CR'
  2) H_2^+ + H_2 → H_3^+ + H

- **Thermalization:**
  - H_3^+ + H_2 → H_2 + H_3^+

- **Destruction (DR):**
  - H_3^+ + e^- → [H_2 + H] or [3H]





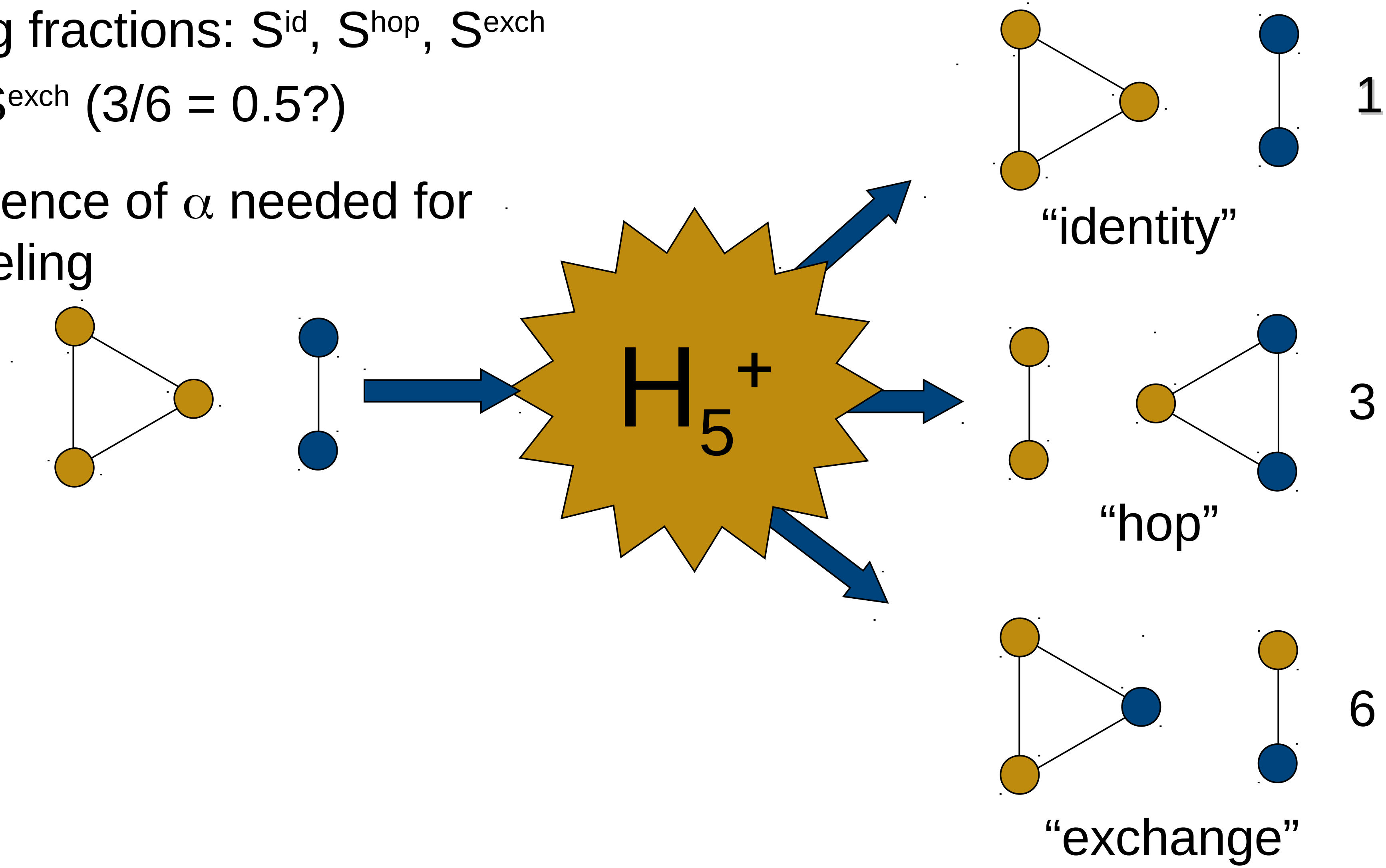
F. S. dos Santos et al. J. Chem. Phys. 127, 124309 (2007).
H. Kreckel et al. Phys. Rev. A 82, 042715 (2010).

Nuclear spin effects in the $H_3^+ + H_2$ reaction

Branching fractions: S^{id}, S^{hop}, S^{exch}

$\alpha = S^{hop}/S^{exch}$ (3/6 = 0.5?)

T-dependence of α needed for modeling



Nuclear spin effects in the $H_3^+ + H_2$ reaction

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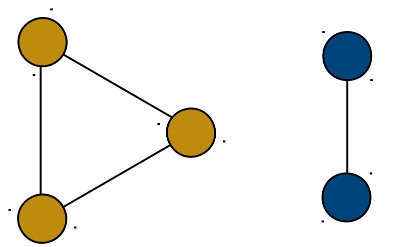
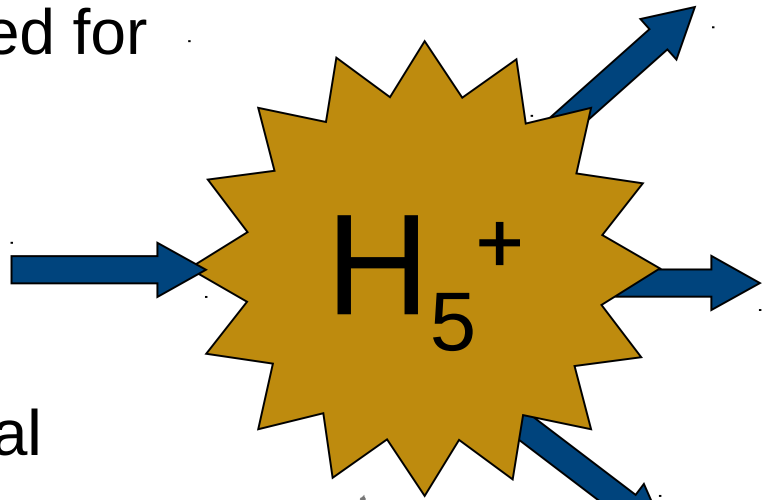
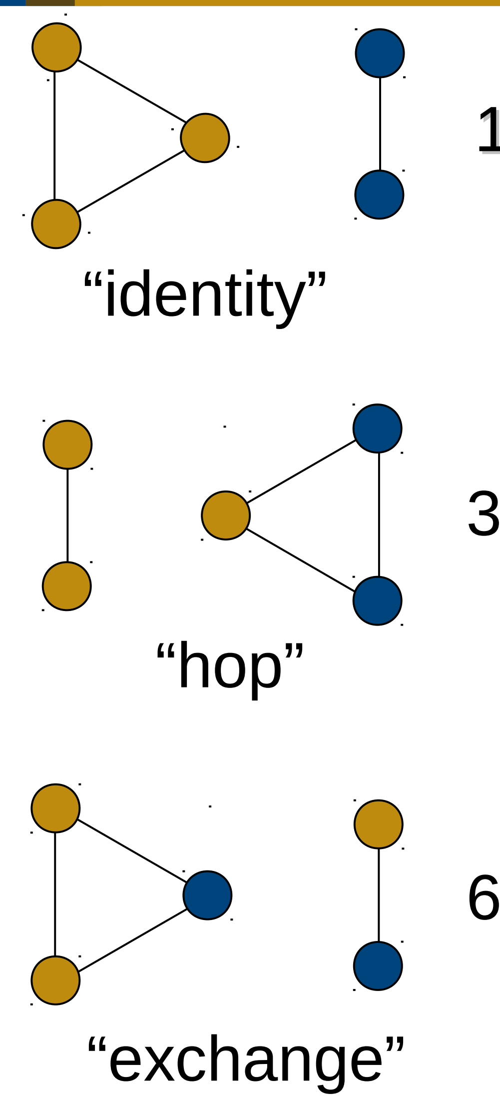


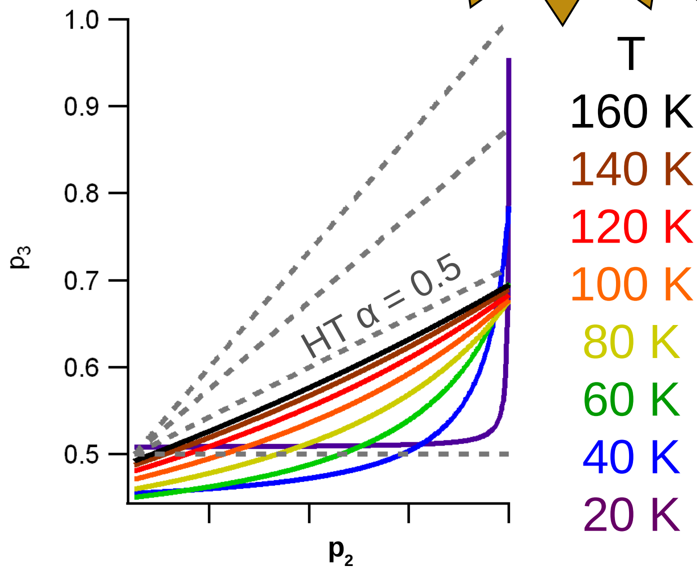




- Microcanonical statistical model: $k(T,\alpha)$:

k_{oooo}	k_{ooop}	k_{oopo}	k_{oopp}
k_{opoo}	k_{opop}	k_{oppo}	k_{oppp}
k_{pooo}	k_{poop}	k_{popo}	k_{popp}
k_{ppoo}	k_{ppop}	k_{pppo}	k_{pppp}

$\alpha = 0.5$



K. Park and J. C. Light, J. Chem Phys. 127, 224101 (2007).
E. Hugo, et al., J. Chem. Phys. 130, 164302 (2009).

Plasma experiments and semiclassical theory

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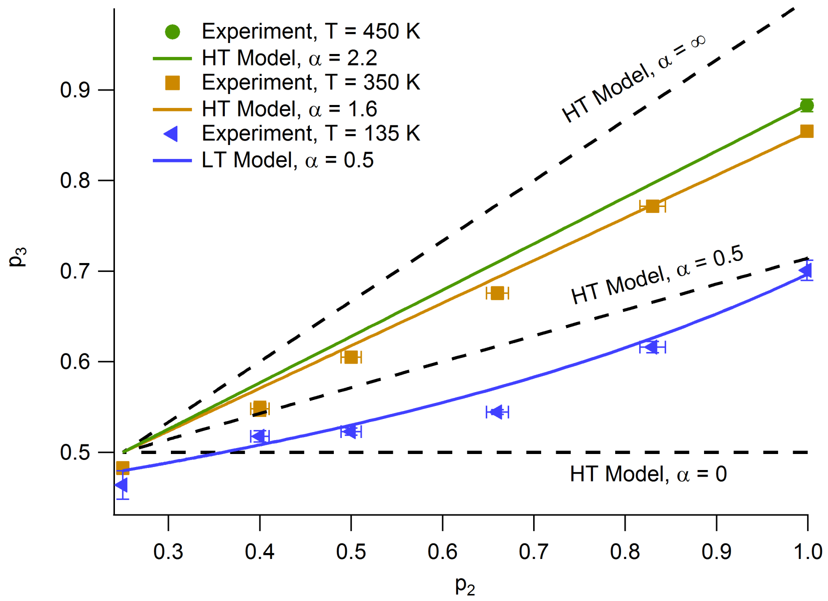
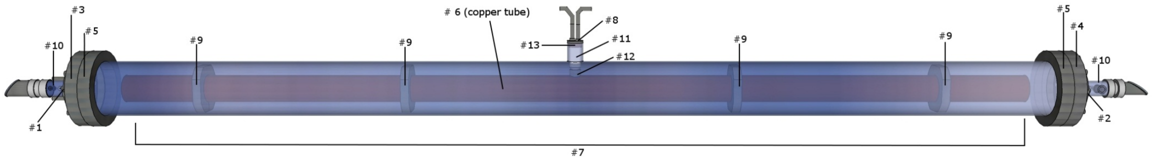
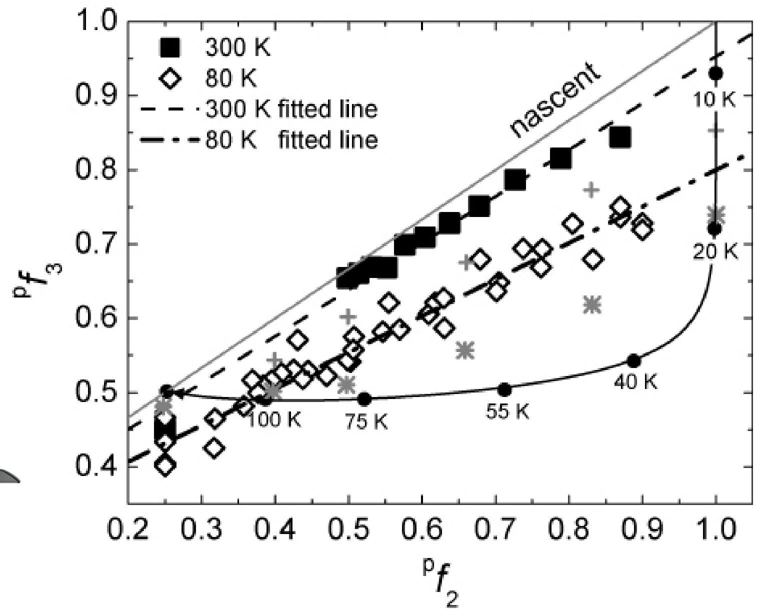
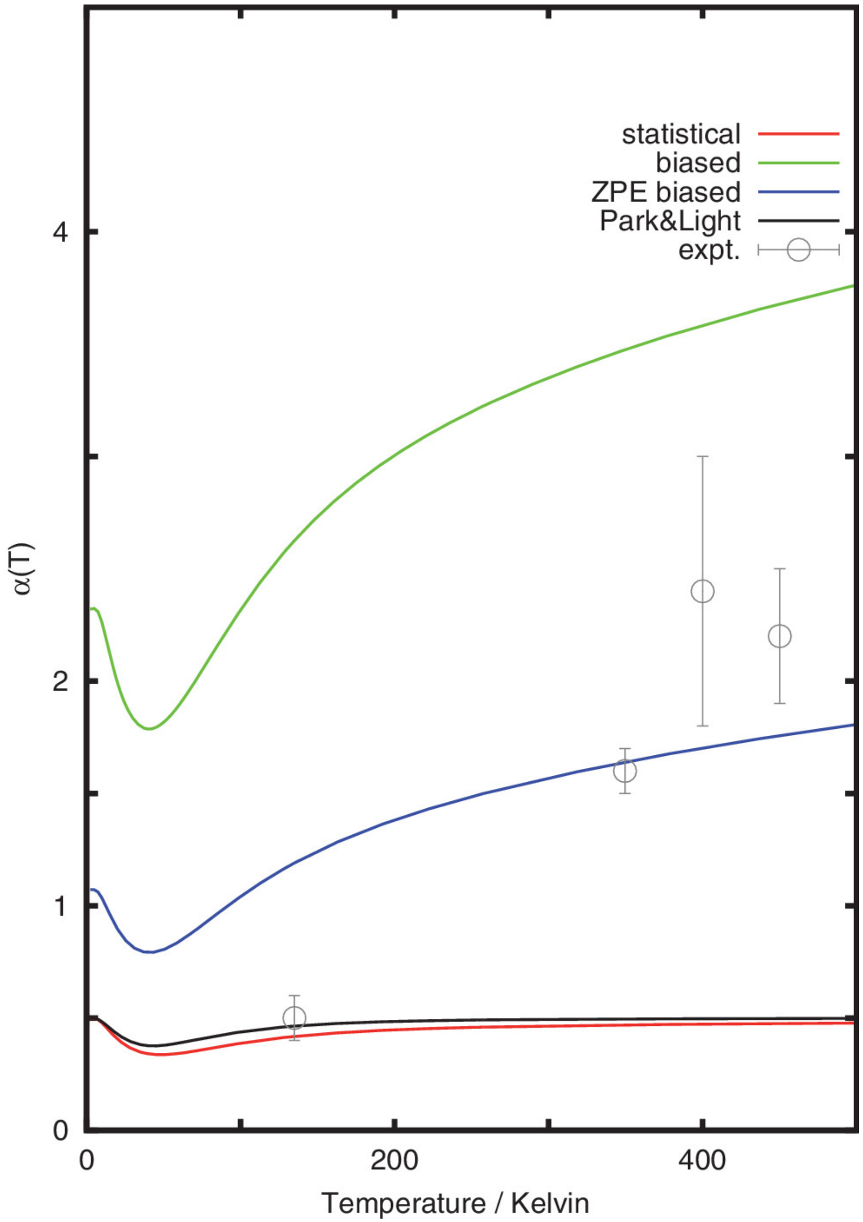


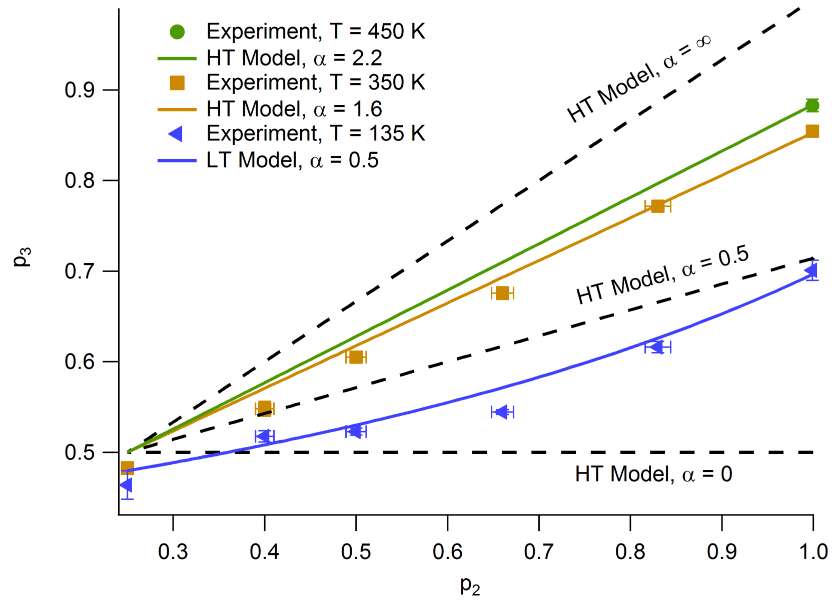


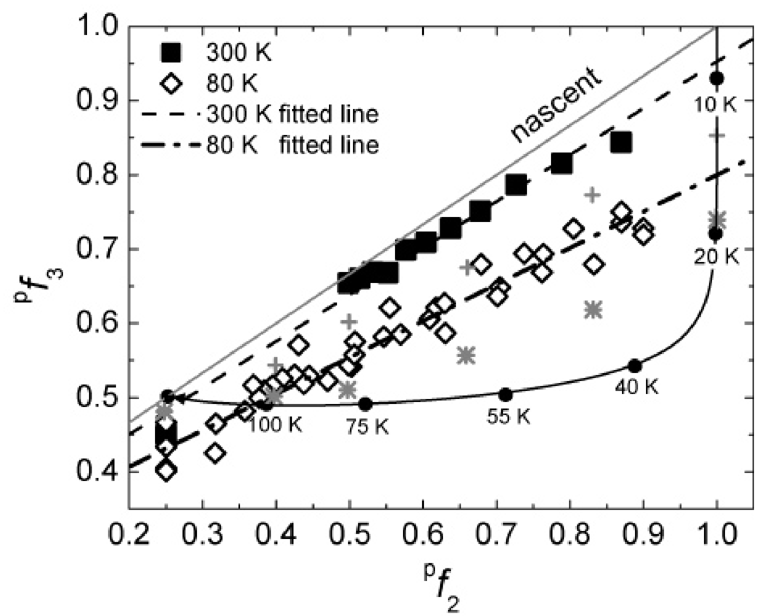


M. Cordonnier et al., J. Chem. Phys. 113, 3181 (2000); K. N. Crabtree et al., J. Chem. Phys. 134, 194311 (2011); M. Hejduk et al., Plasma Sources Sci. Tech. 21, 024002 (2012); S. Gomez-Carrasco et al., J. Chem. Phys. 137, 094303 (2012).

Plasma experiments and semiclassical theory







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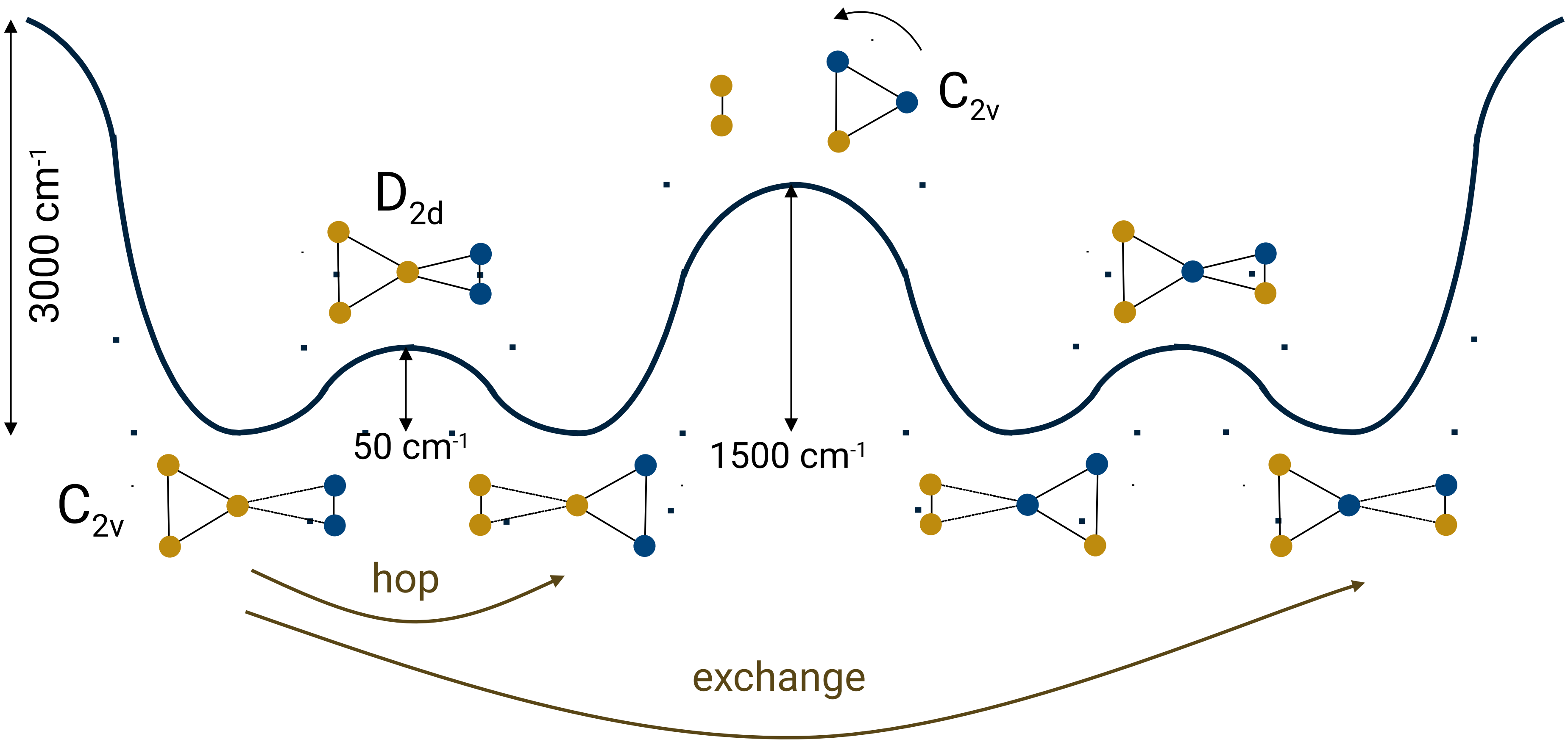
Dynamic bias at high temperature

- Exchange requires 2 hops + internal rotation (at minimum)



- Long complex lifetime → statistical outcome (α = 0.5)

PES: Z. Xie, B. J. Braams, & J. M. Bowman J. Chem. Phys. 122, 224307 (2005).

Ion trap experiment: simulate diffuse clouds

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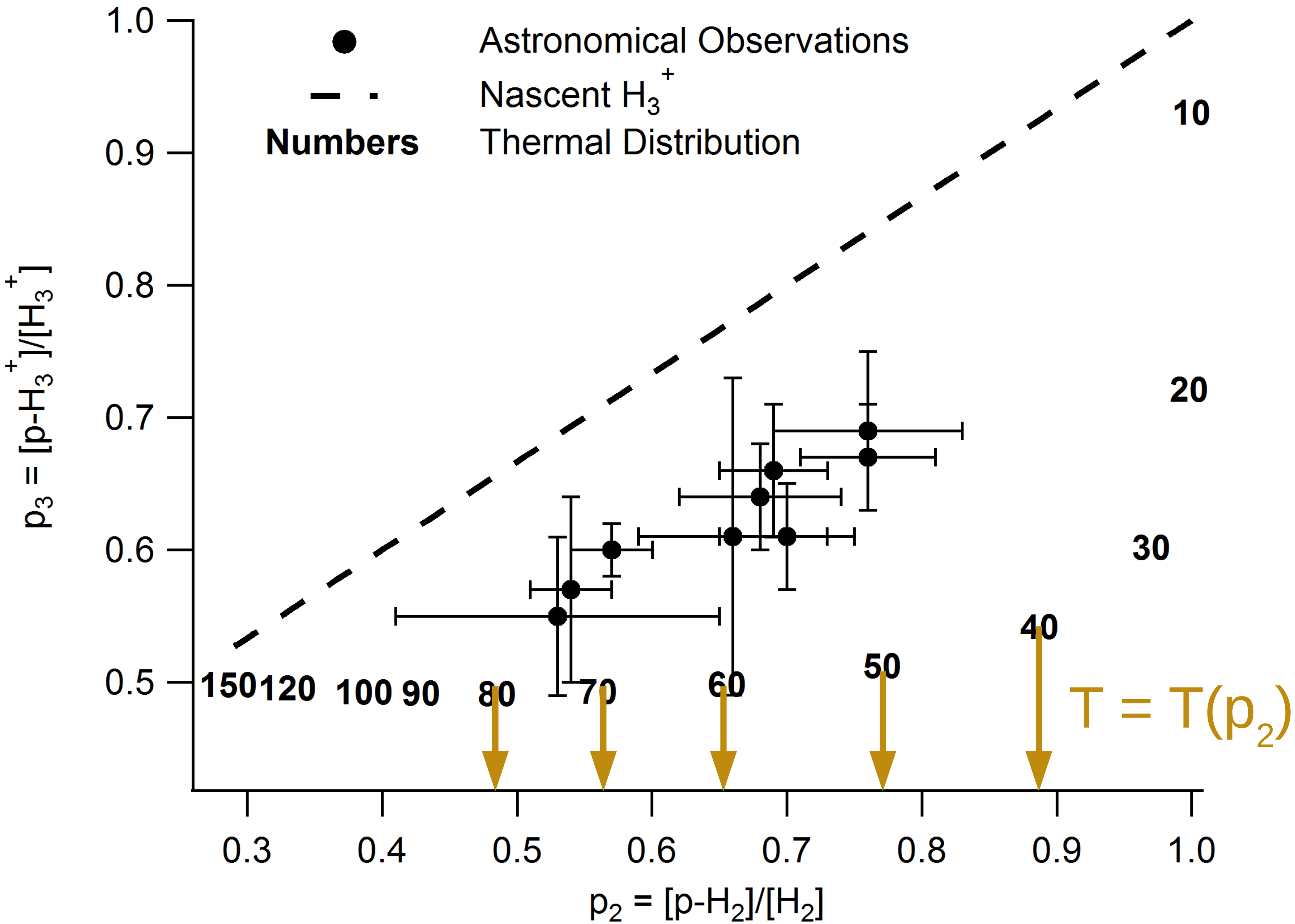

Ion trap LIR measurements

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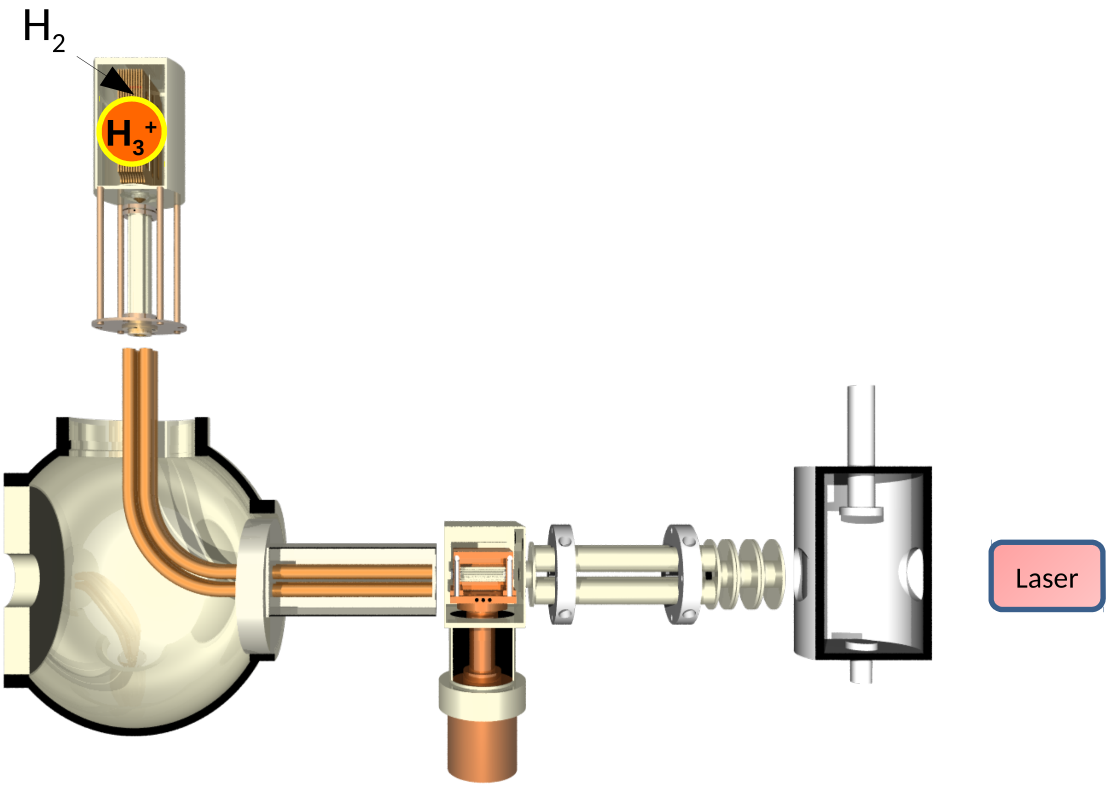

F. Grussie et al. ApJ 759, 21 (2012).

Ion trap LIR measurements

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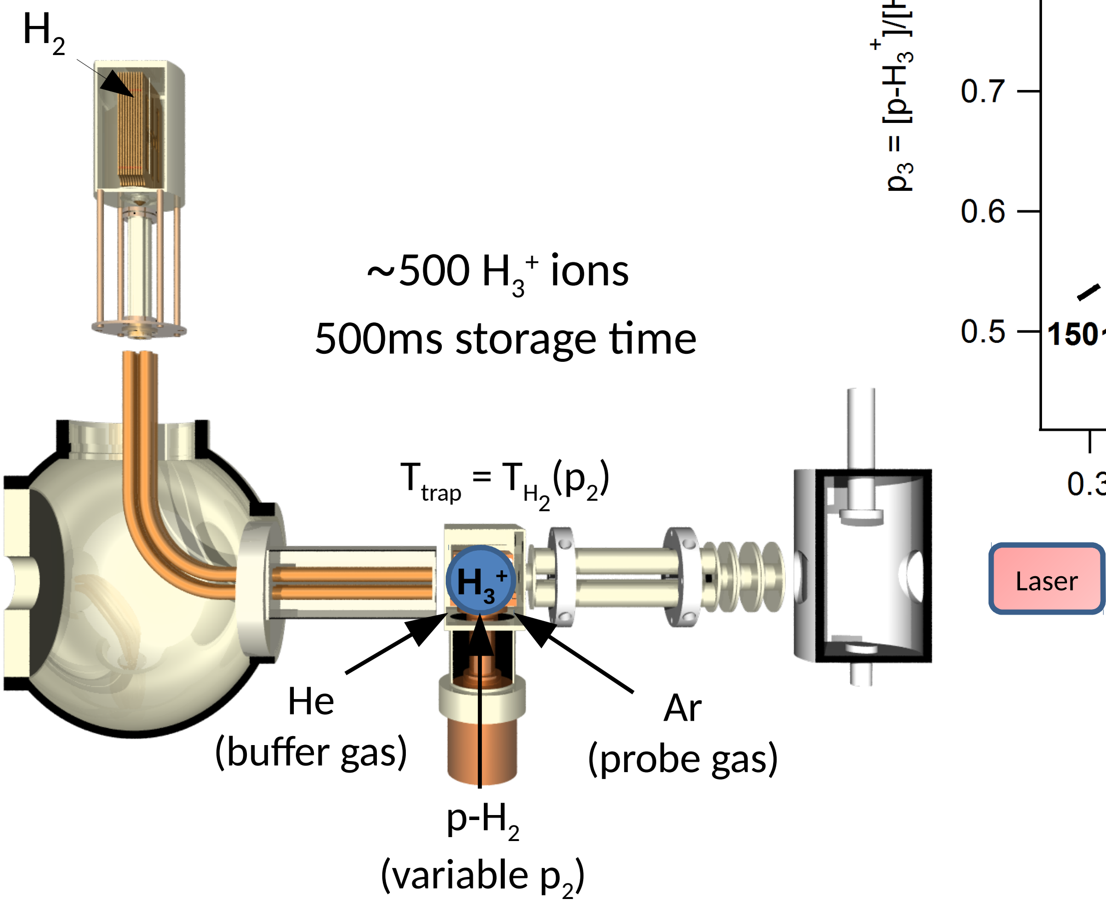
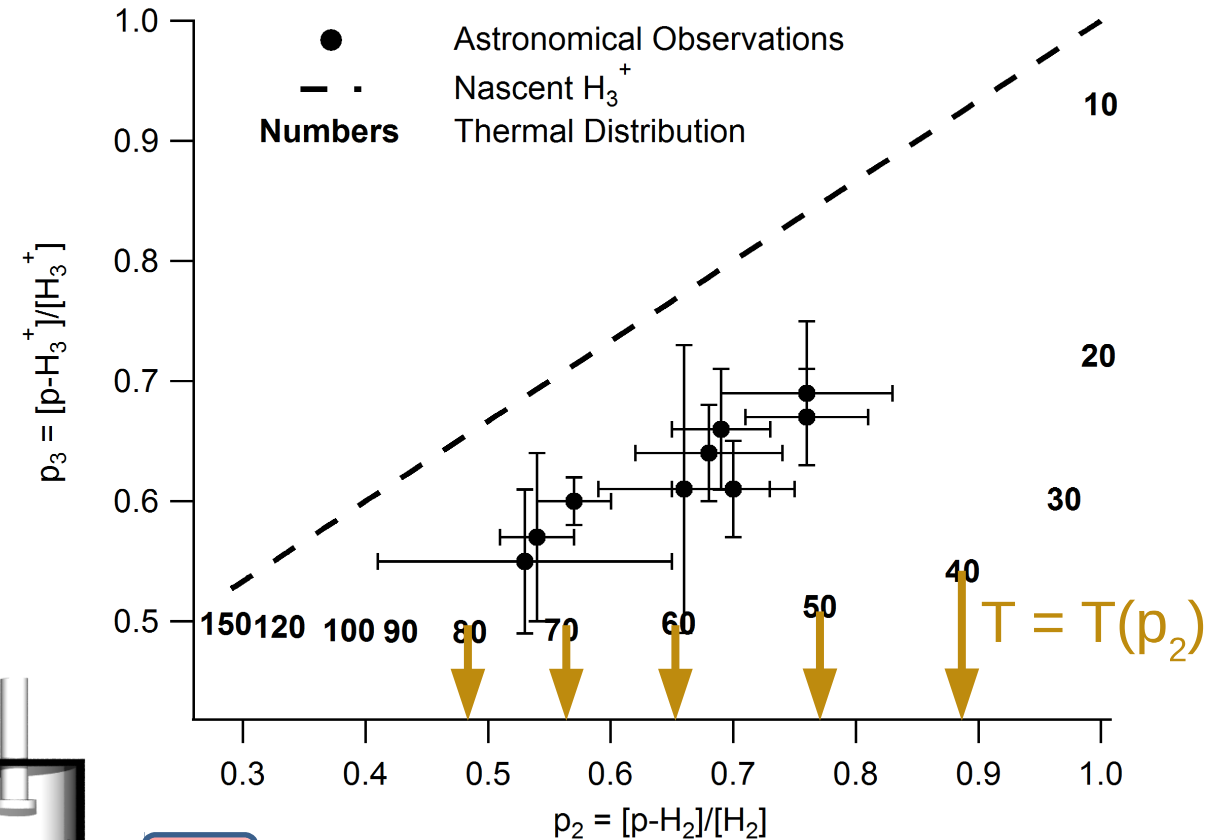
~500 H_3^+ ions
500ms storage time





Ion trap LIR measurements

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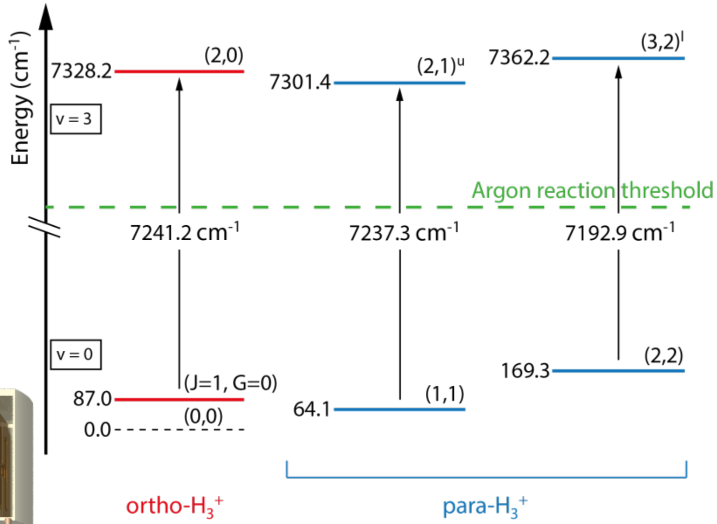
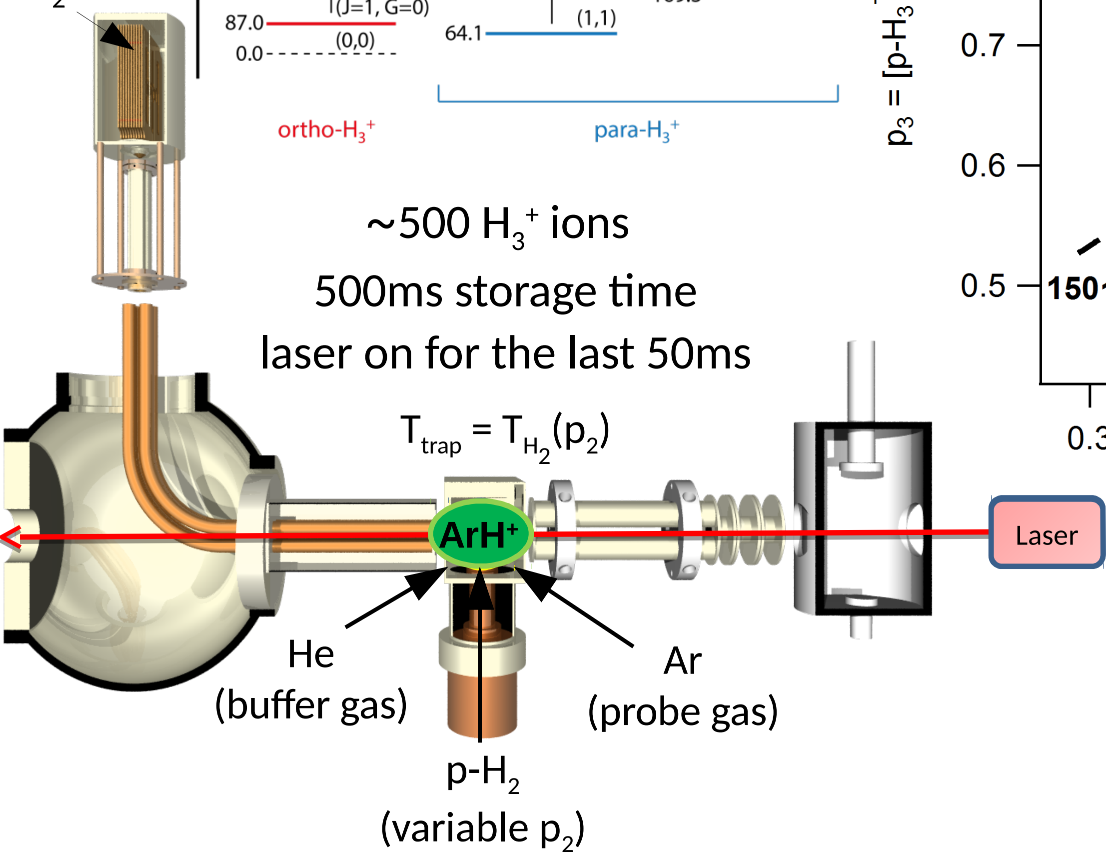
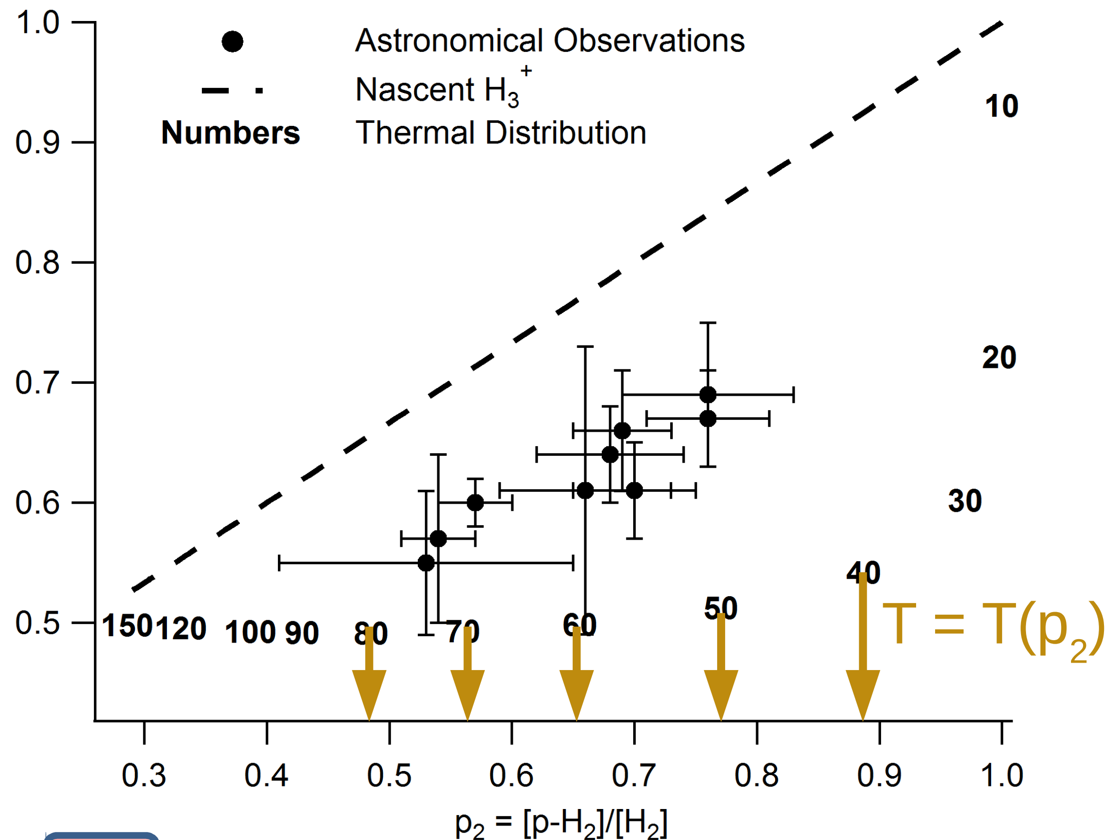


~500 H_3^+ ions

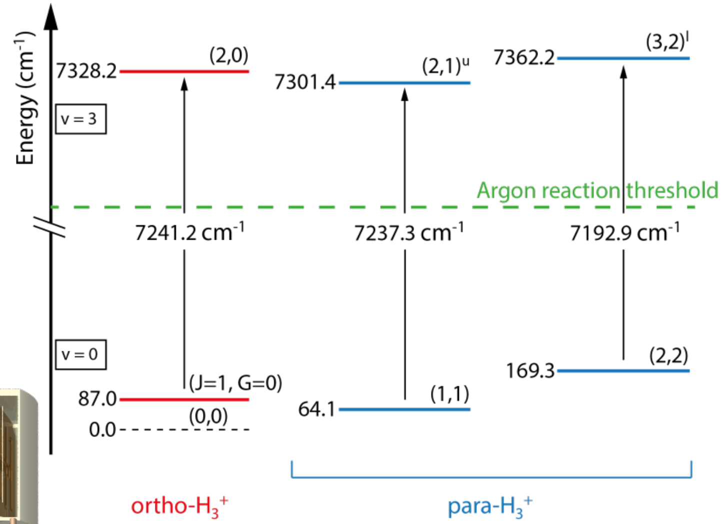
500ms storage time

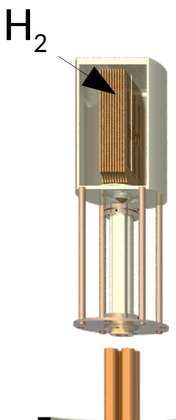
laser on for the last 50ms





Ion trap LIR measurements

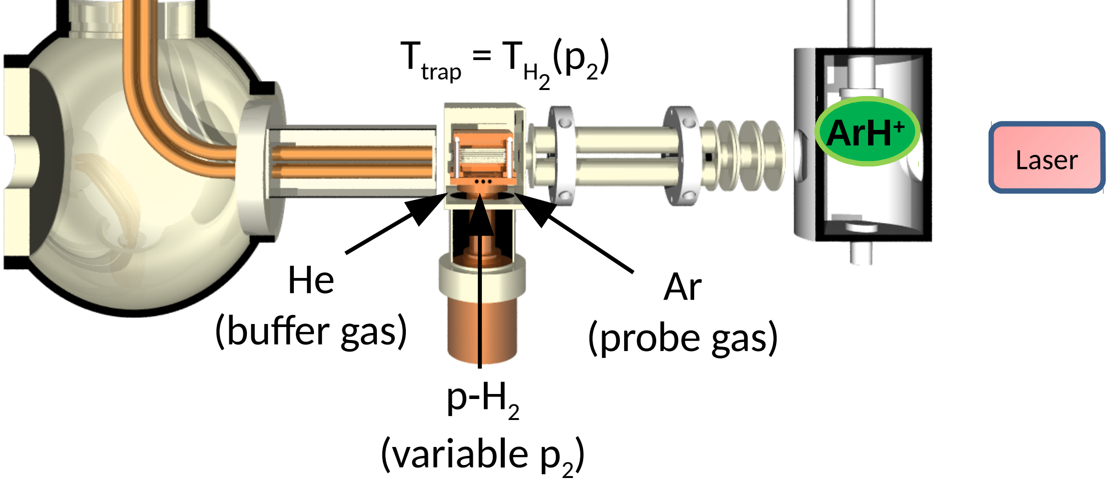


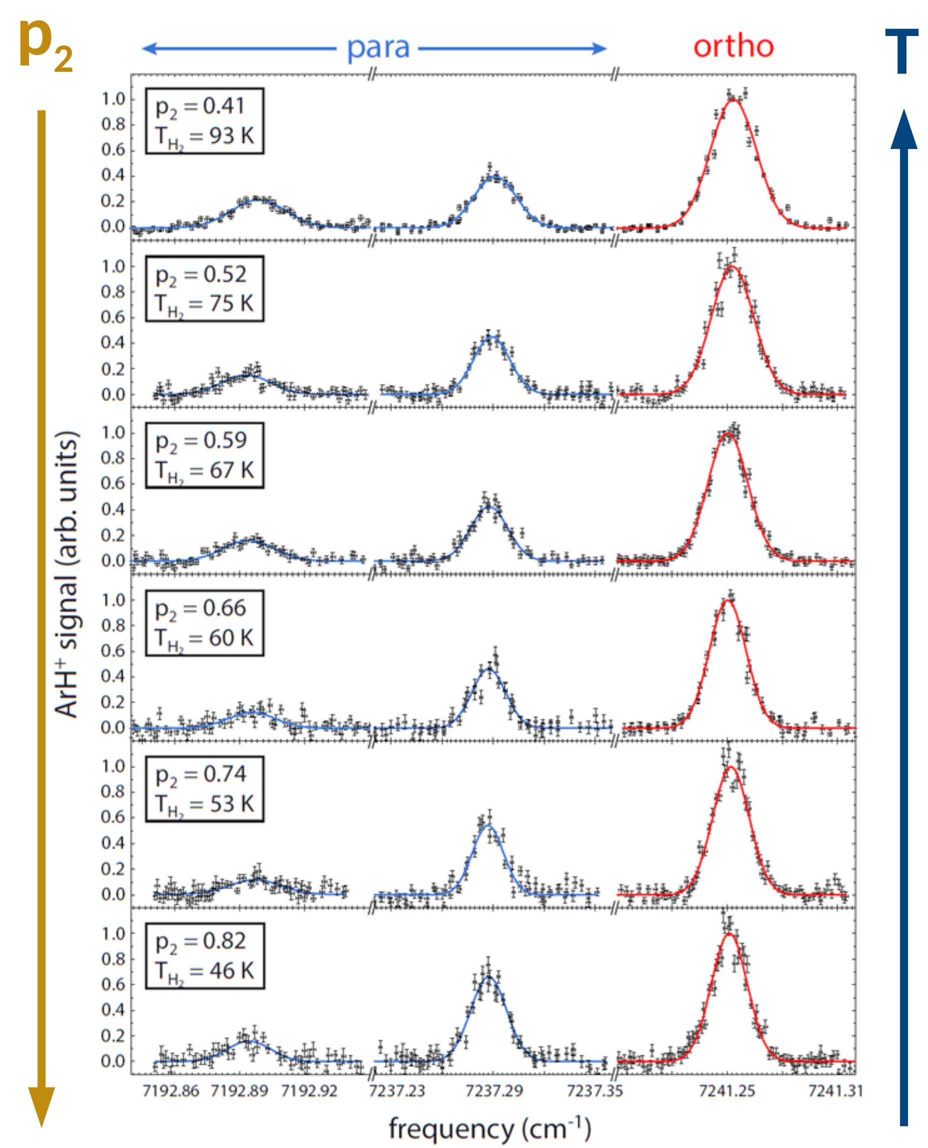


~500 H_3^+ ions

500ms storage time

laser on for the last 50ms





F. Grussie et al. ApJ 759, 21 (2012).

Ion trap LIR results

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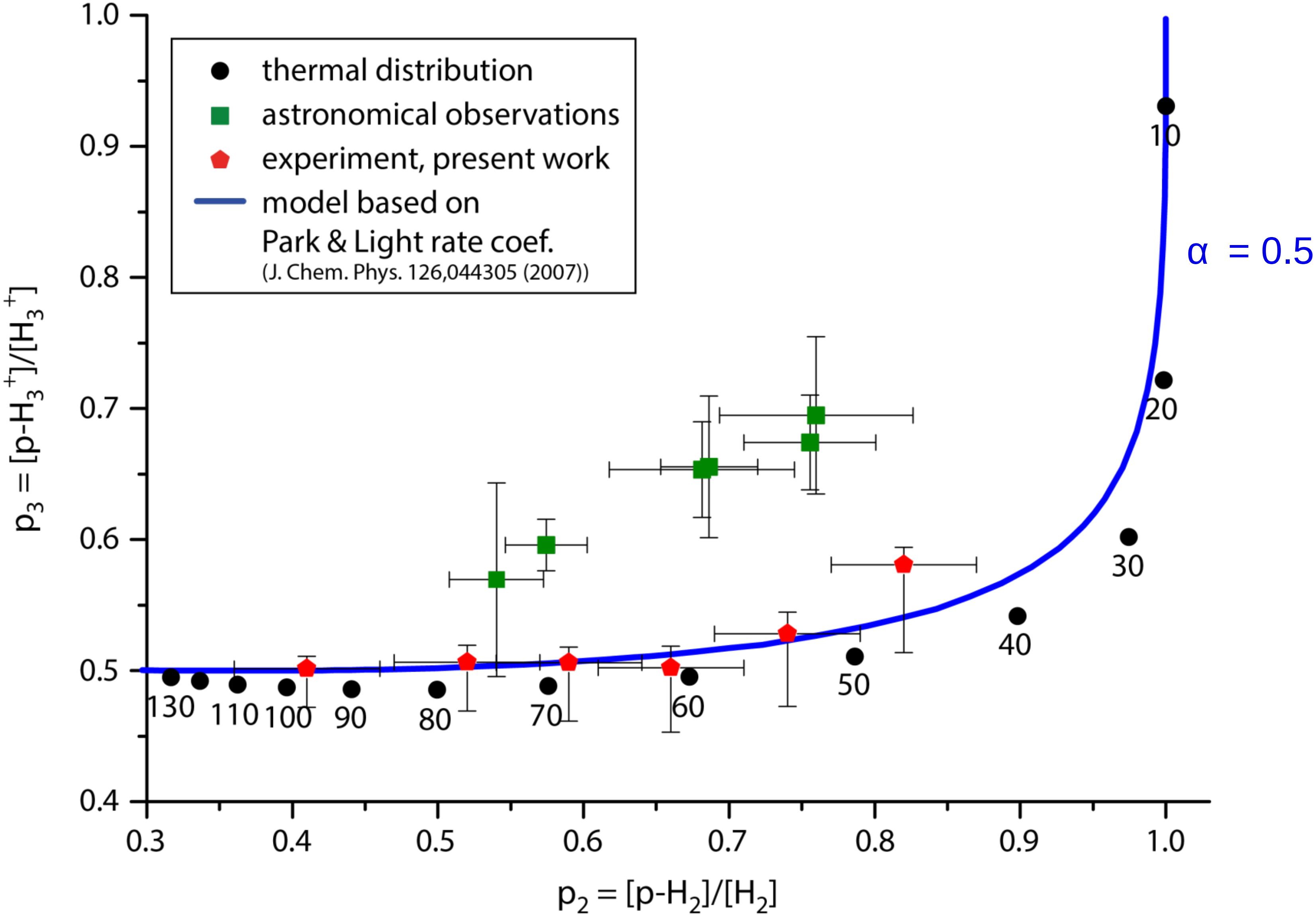

F. Grussie et al. ApJ 759, 21 (2012).

H_3^+ DR: A controversial history

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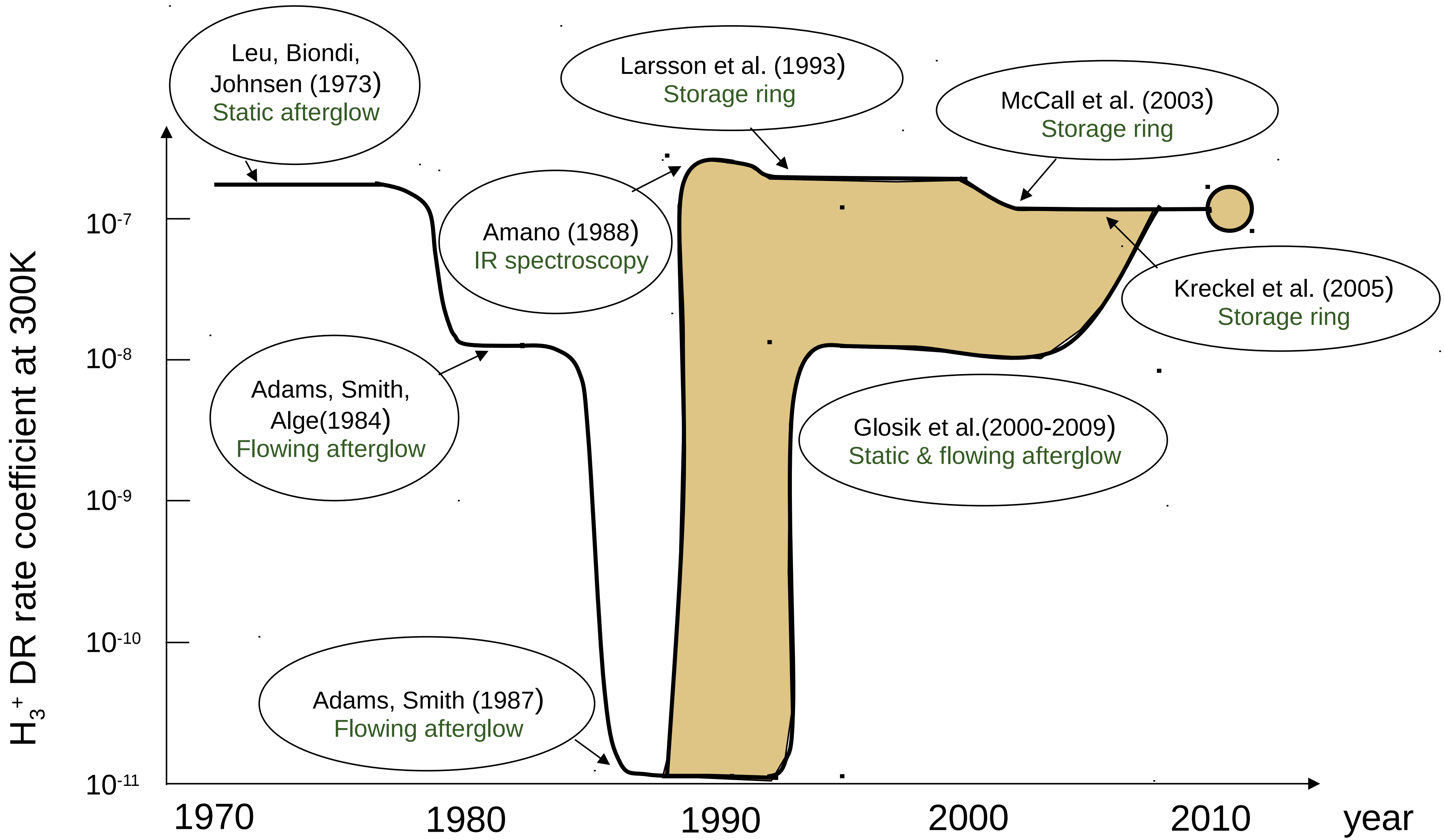
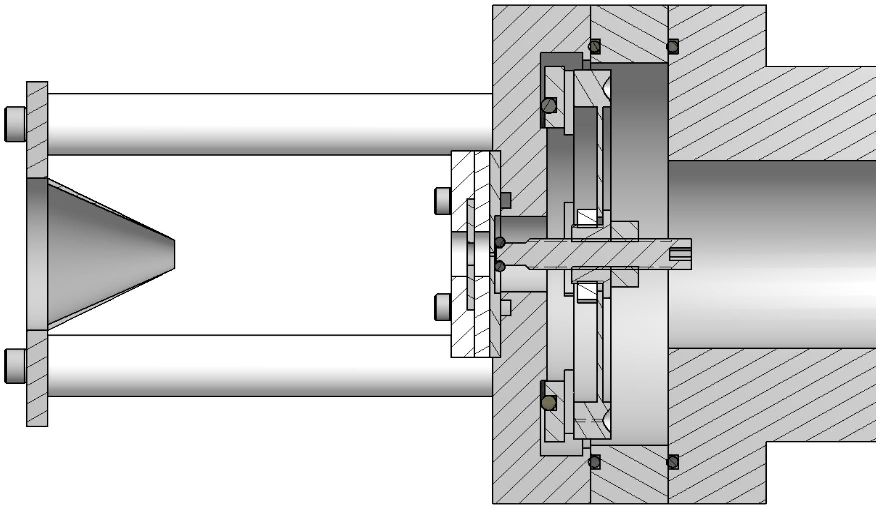


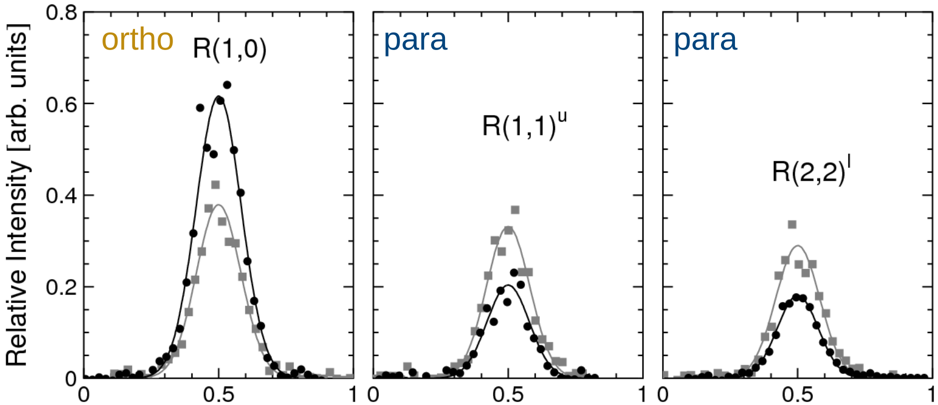
Outstanding question: DR rates for o- and p-H_3^+ in ground rotational states (1,0) and (1,1)?

DR measurement: TSR (MPIK)

Piezo Supersonic Expansion Source



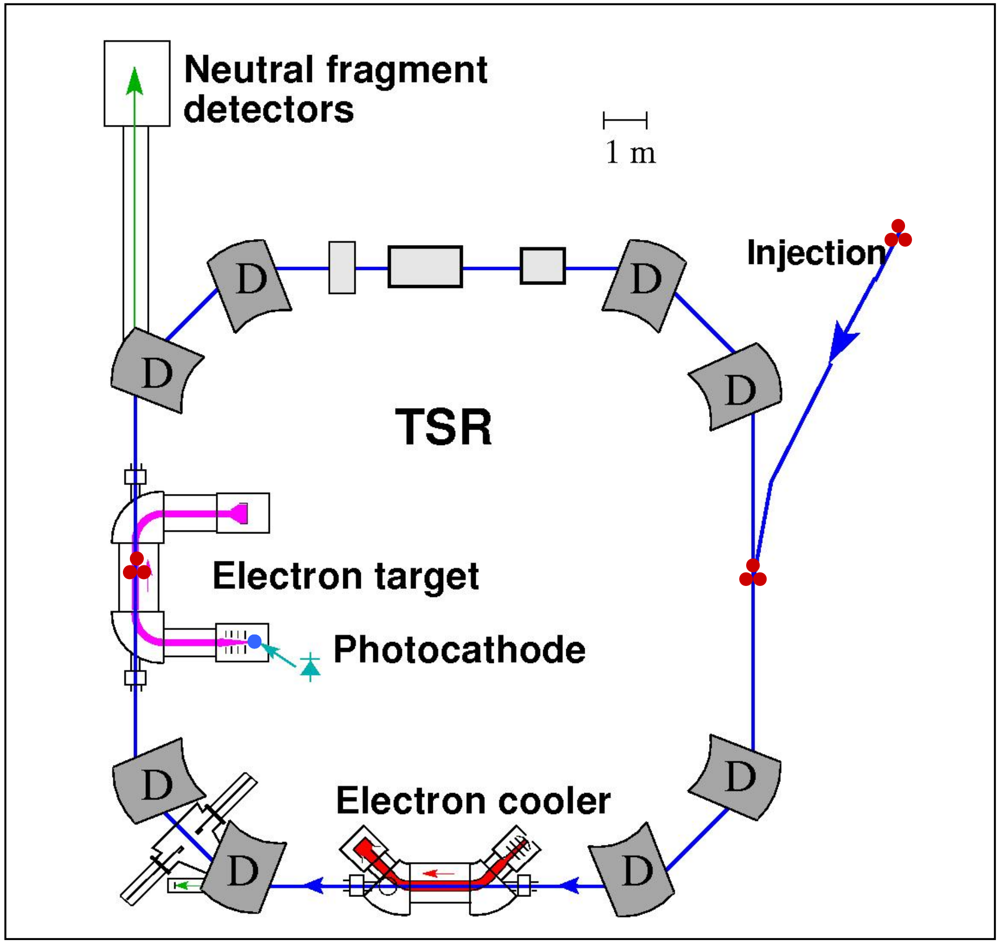
Spectroscopic measurement: T and p-H_3^+ fraction



p_3 = 48%

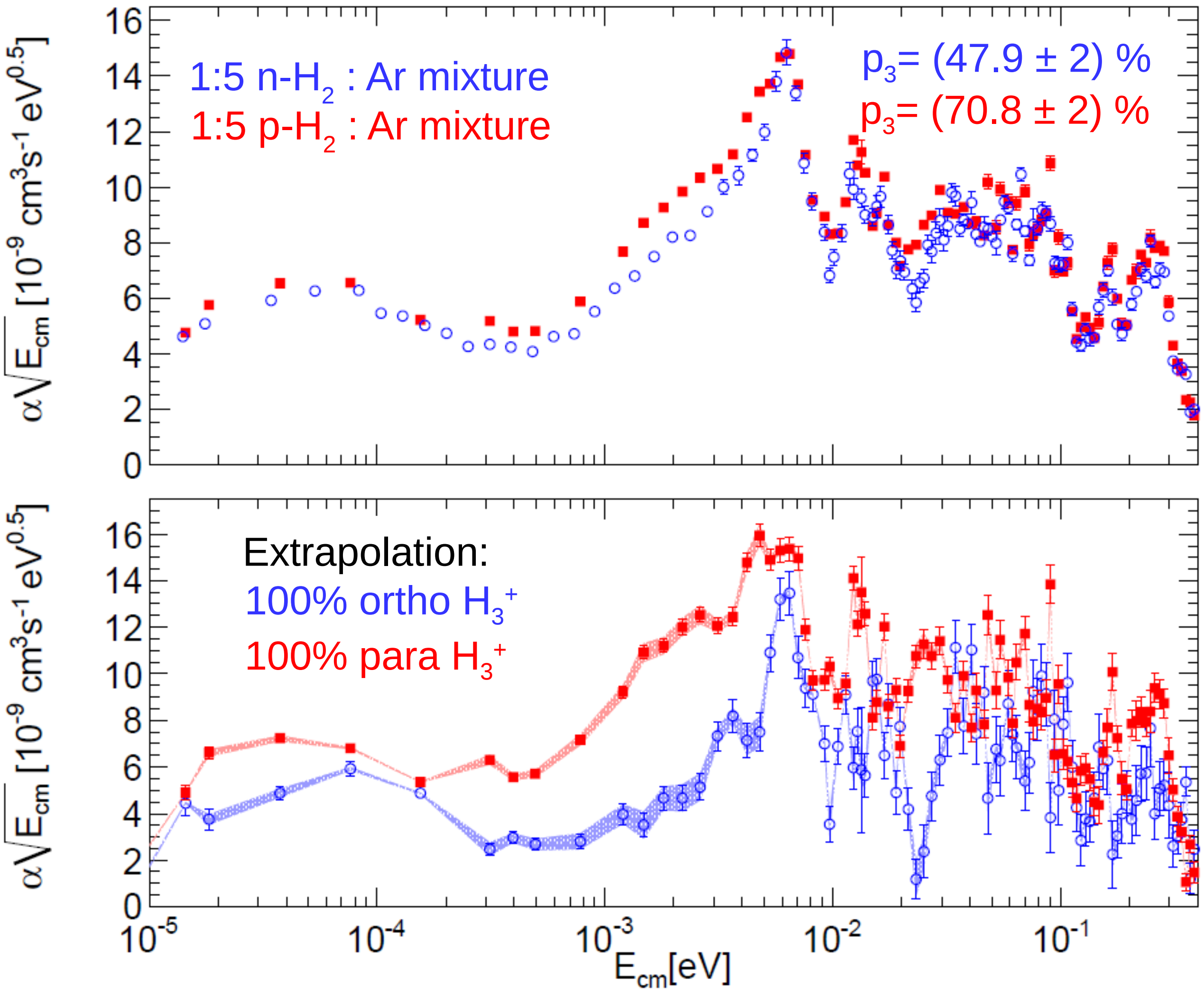
p_3 = 71%

T = 180 K



H. Kreckel et al. Phys. Rev. A 82, 042715 (2010).

Spin-dependent H_3^+ DR

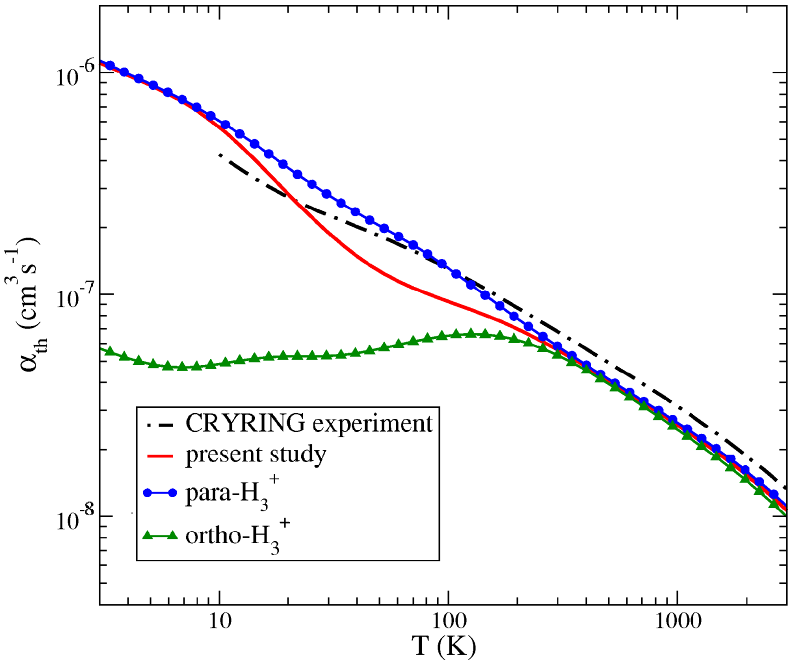


- Overall rate agrees with theory; previous storage ring measurements
- At low collision energies, p-H_3^+ DR is ~2x rate of o-H_3^+ DR
- Complication: fragment imaging shows H_3^+ is rotationally hot (900 K) in ring → acceleration heating
- No state-selective storage ring measurements have been made

H. Kreckel et al. Phys. Rev. A 82, 042715 (2010).

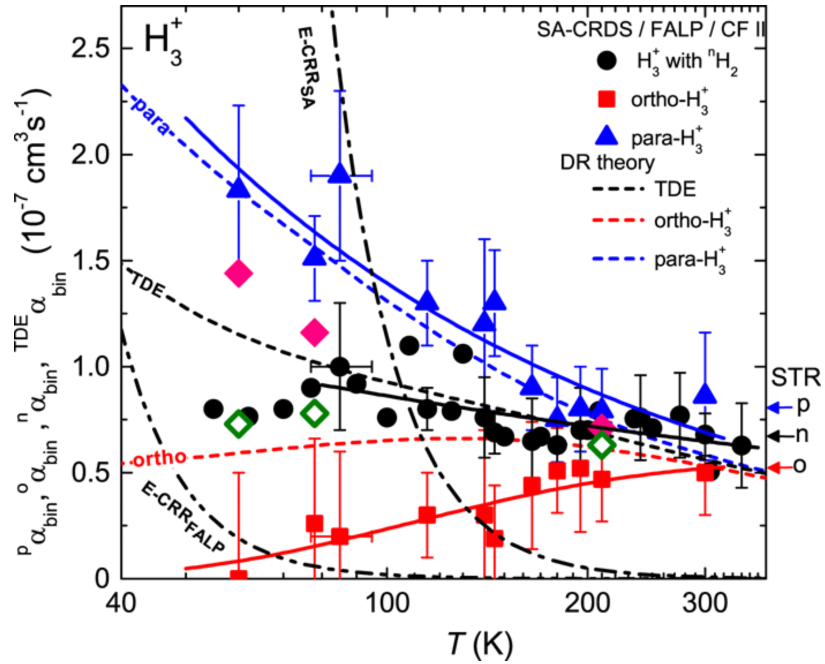
Other studies of H_3^+ DR

- Theory



- $p\text{-}H_3^+$ is ~3-4x rate of $o\text{-}H_3^+$ DR at 50-70 K
- Sensitive to exact H_3 Rydberg resonance energies

- Plasma measurements (60 K)



- $p\text{-}H_3^+$ is at least 3x rate of $o\text{-}H_3^+$ DR at 60 K
- Sensitive to He, Ar, H_2 densities

All evidence suggests $p\text{-}H_3^+$ DR is faster than $o\text{-}H_3^+$ at diffuse cloud temperatures!

Theory: F. S. dos Santos et al. J. Chem. Phys. 127, 124309 (2007).
Plasma experiments: M. Hejduk et al. J. Chem. Phys. 143, 044303 (2015).

Steady state modeling in diffuse clouds

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- Formation:
  1) $H_2 + CR \rightarrow H_2^+ + e^-$ (rate limiting step)
  2) $H_2^+ + H_2 \rightarrow H_3^+ + H$ (fast)

Nuclear spin statistics

- Thermalization:
  - $H_3^+ + H_2 \rightarrow H_2 + H_3^+$

Microcanonical model,
Hollow cathode experiment,
Ion trap LIR experiment

- Destruction (DR):
  - $H_3^+ + e^- \rightarrow [H_2 + H]$ or $[3H]$

Storage ring measurements; theory

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

f = molecular fraction = 0.9
x_e = fractional ionization = 1.5 x 10^{-4}

K. N. Crabtree et al. ApJ 729, 15 (2011).
K. N. Crabtree and B. J. McCall Phil. Trans. A 370, 5055 (2012)

Steady state modeling in diffuse clouds

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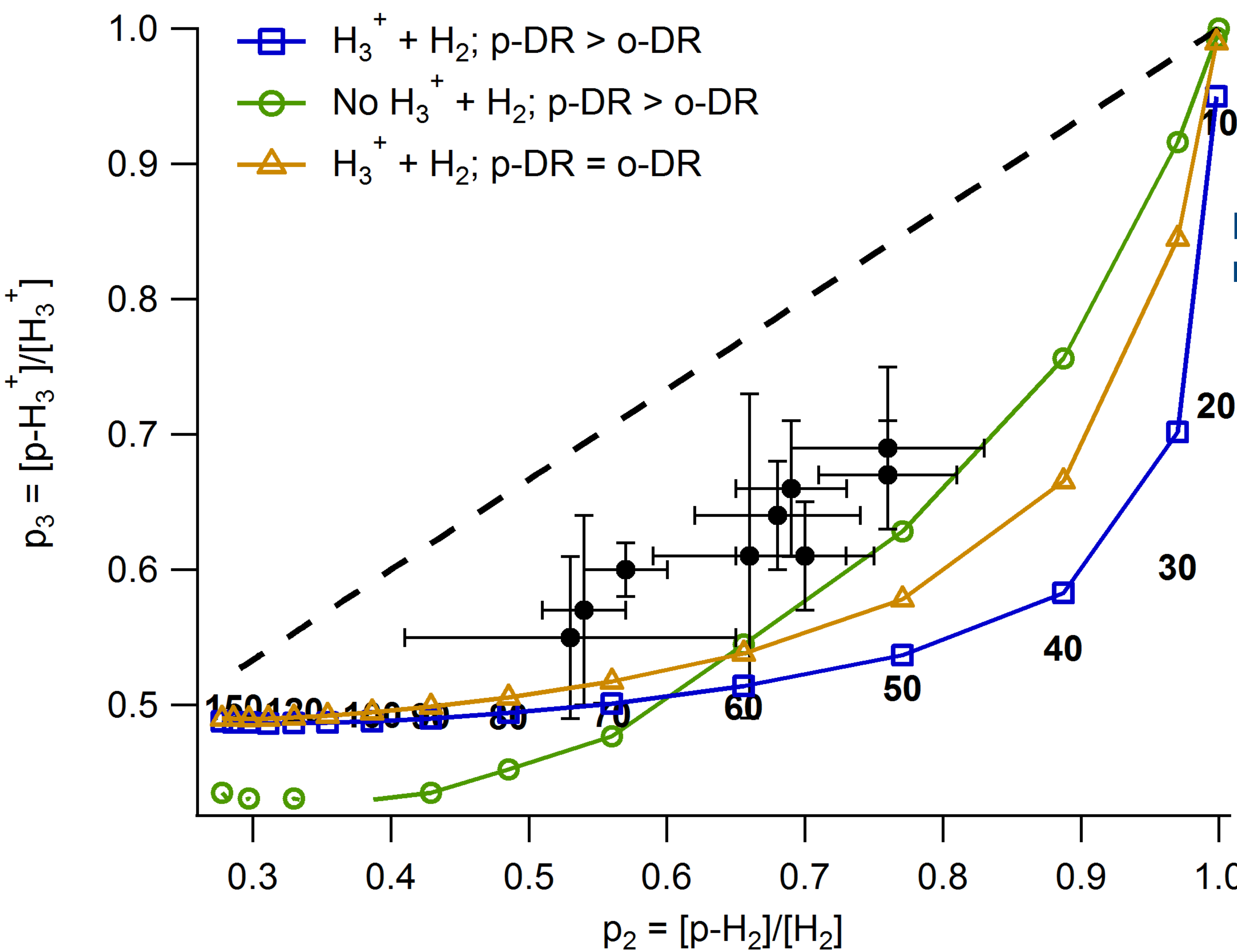

K. N. Crabtree et al. ApJ 729, 15 (2011).
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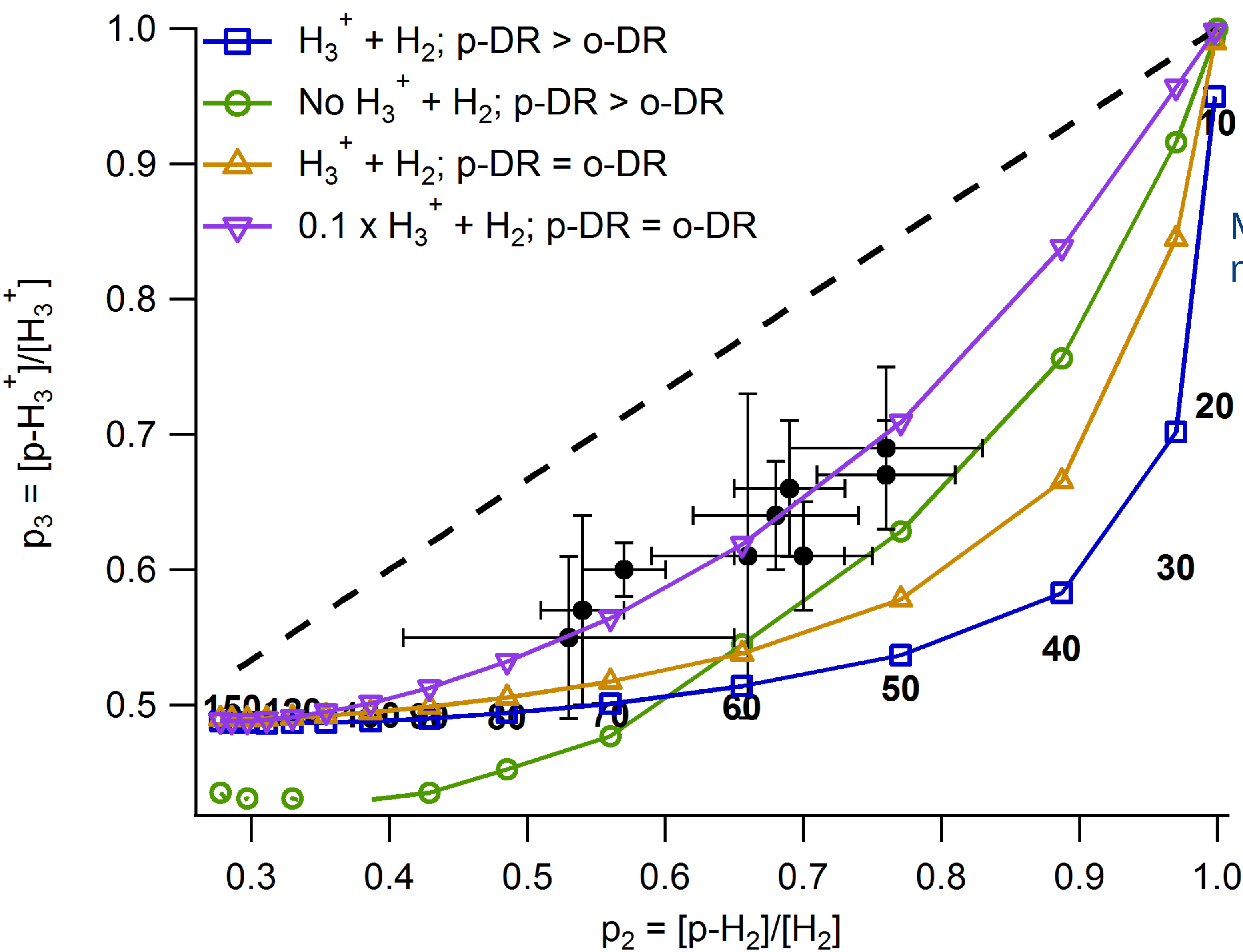
Steady state modeling in diffuse clouds

UCDAVIS DEPARTMENT OF CHEMISTRY

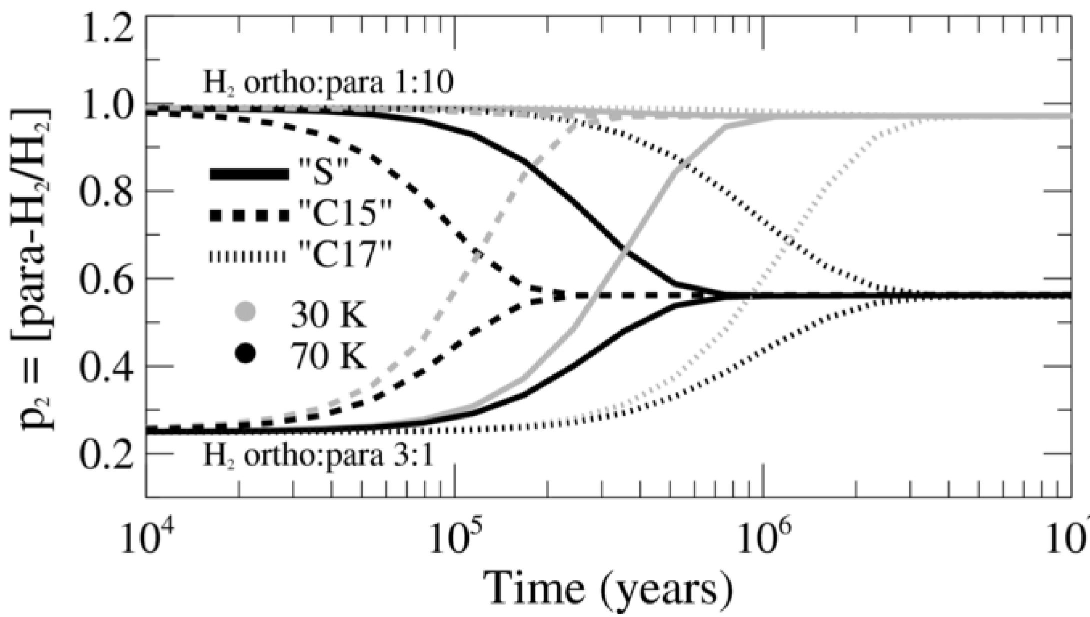


Most realistic model

K. N. Crabtree et al. ApJ 729, 15 (2011).
K. N. Crabtree and B. J. McCall Phil. Trans. A 370, 5055 (2012)

Time-dependent modeling

- Code: ALCHEMIC
  - Deuterium chemistry
  - H_3^+/H_2 spin chemistry
  - 40,000+ reactions
  - 1300 species



Timescale for H_2 thermalization: < 10^6 yr
(n = 10 cm^{-3}, $\zeta > 10^{-16}$ s^{-1})

- Variable parameters:
  - $\zeta = 10^{-15}$ (C15), 10^{-16} (S), 10^{-17} (C17) s^{-1}
  - T = 10 – 90 K
  - n_H = 10 – 1000 cm^{-3}
  - DR rate coefficients:
    - $k_p = k_o$ ("S" McCall et al 2004)
    - $2(k_p = k_o)$ ("2X" McCall et al 2004)
    - $k_p > k_o$ (dos Santos et al 2007)

T. Albertsson et al. ApJ 787, 44 (2014).

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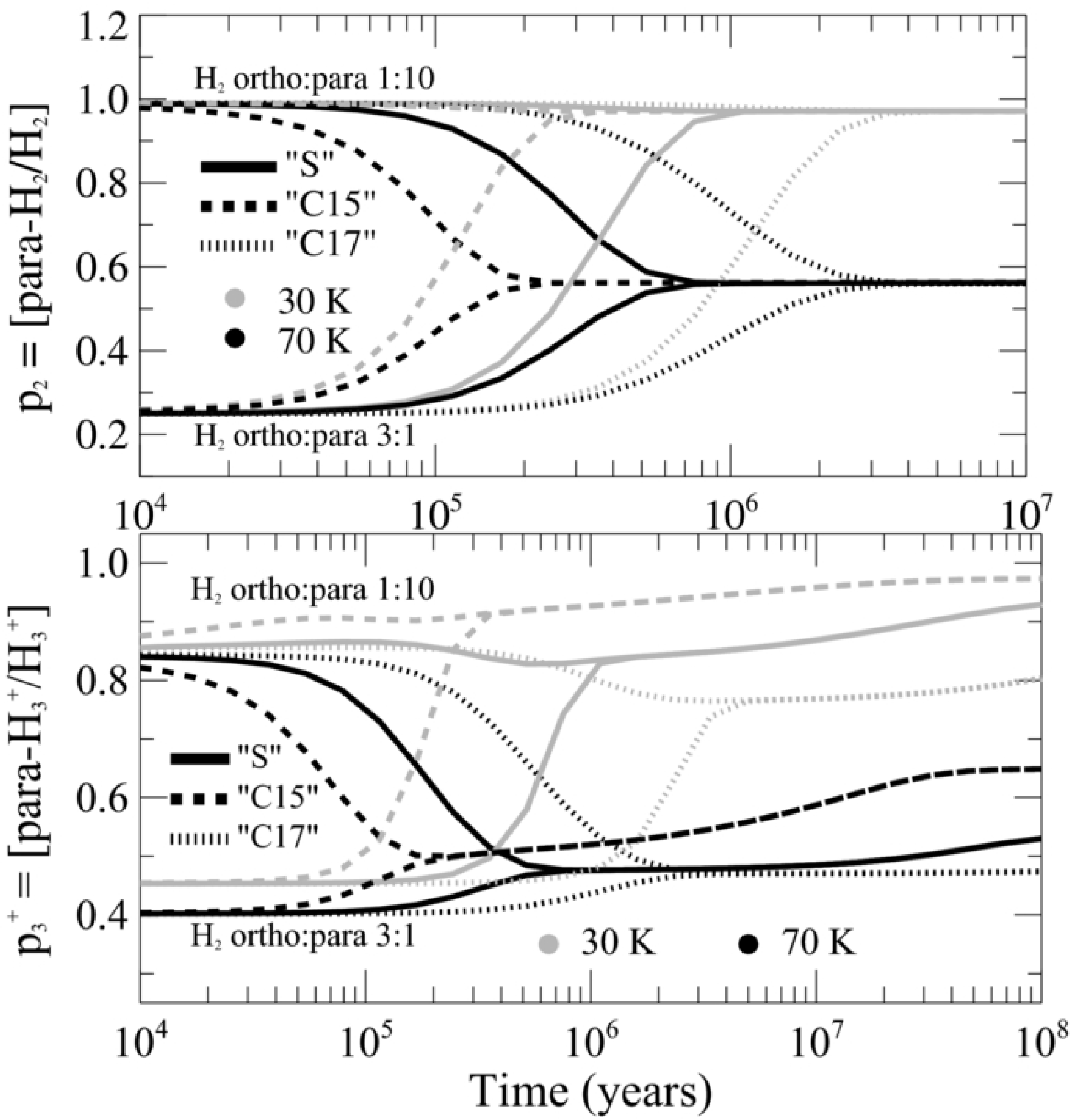

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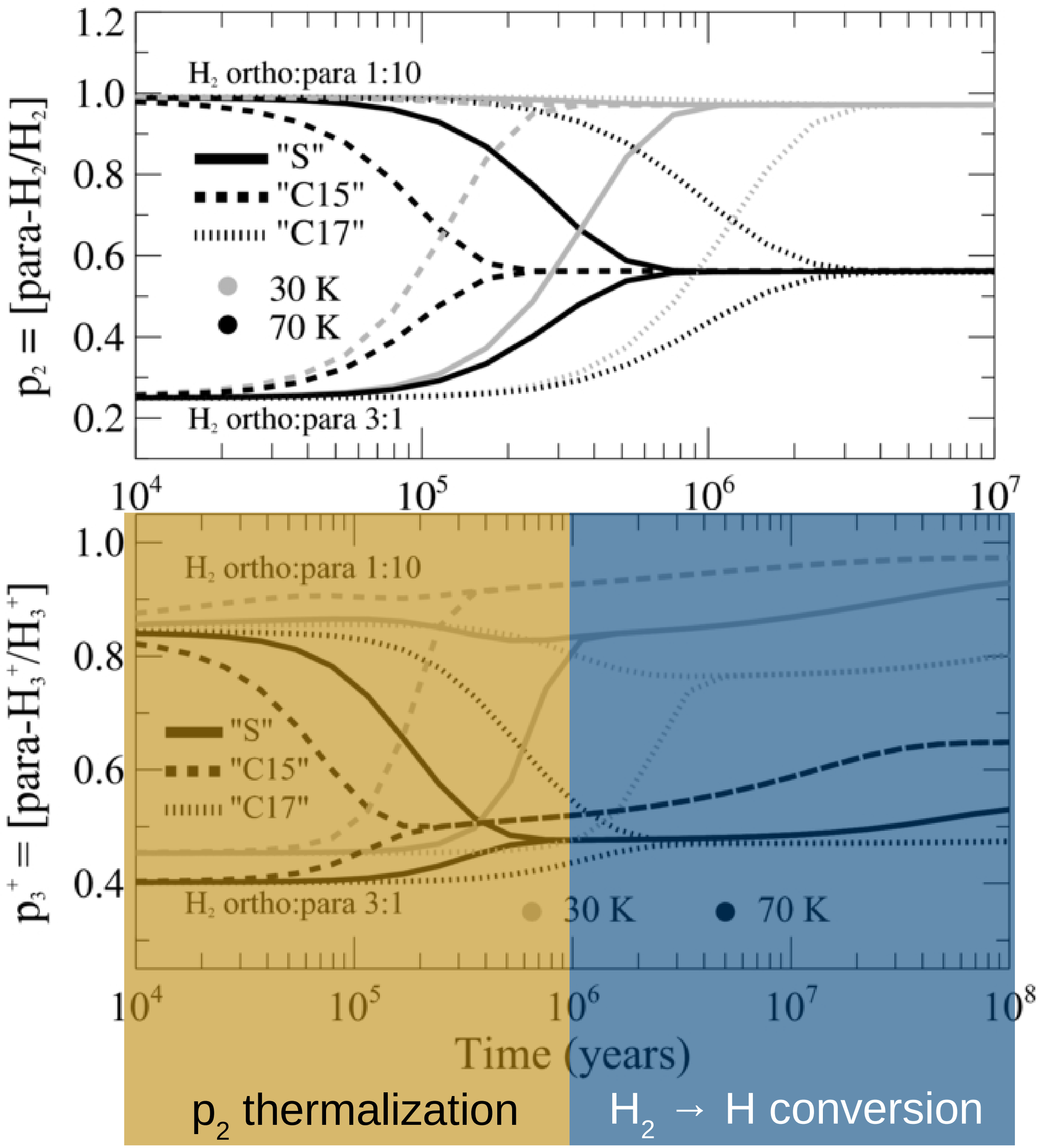
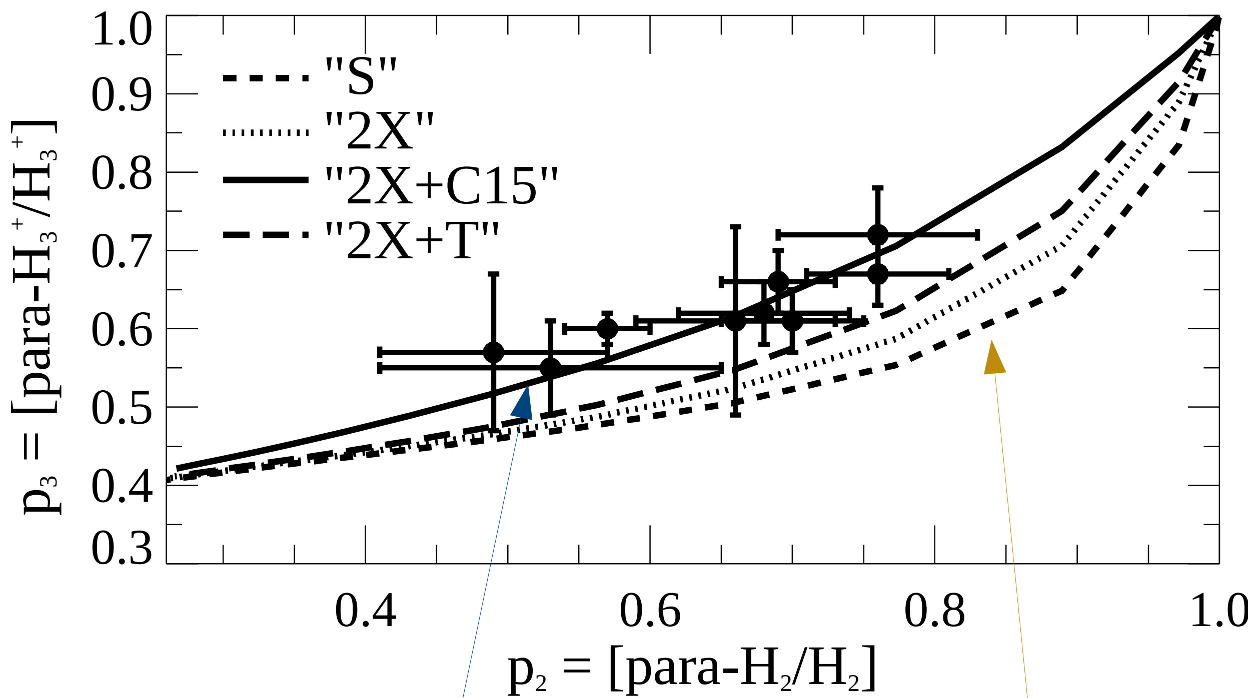


Comparison to observations: 1 MYr

- “Agreement” using inflated DR rates (ortho = para) and elevated ζ.



“Best fit” model
$n_H = 10\ cm^{-3}$
$\zeta = 10^{-15}\ s^{-1}$
(x2) DR: $p\text{-}H_3^+ = o\text{-}H_3^+$

“Standard” model
$n_H = 10\ cm^{-3}$
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- “Agreement” using inflated DR rates (ortho = para) and elevated ζ.
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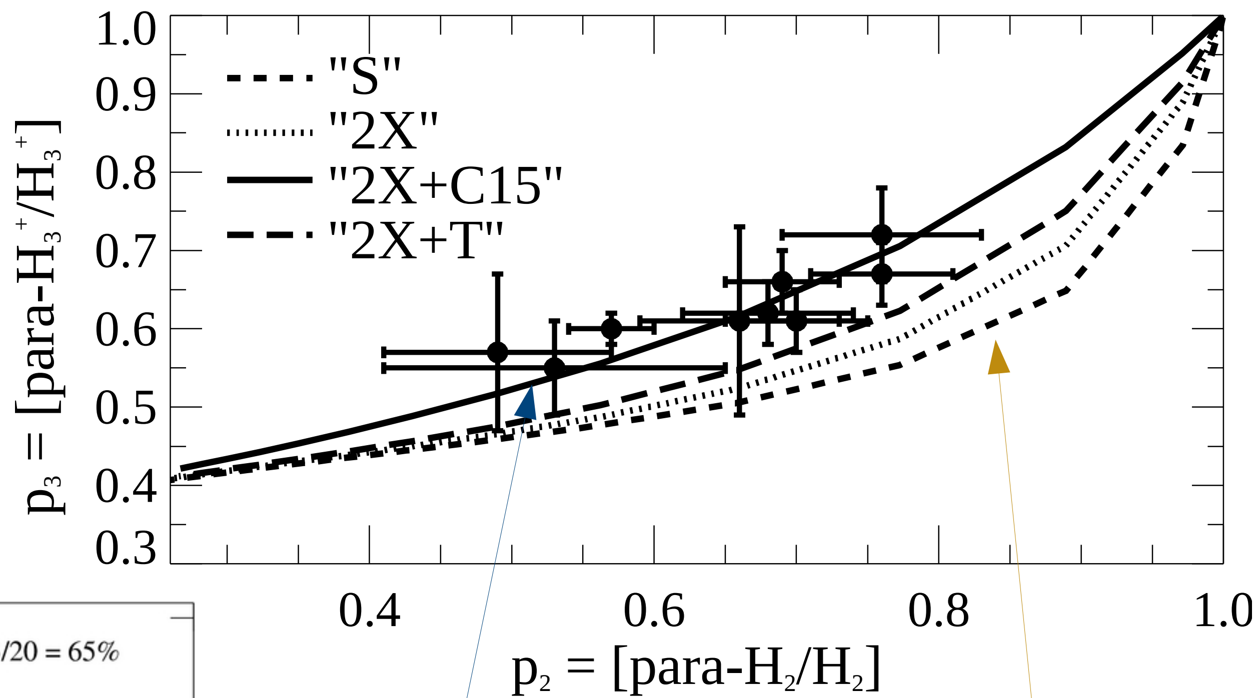

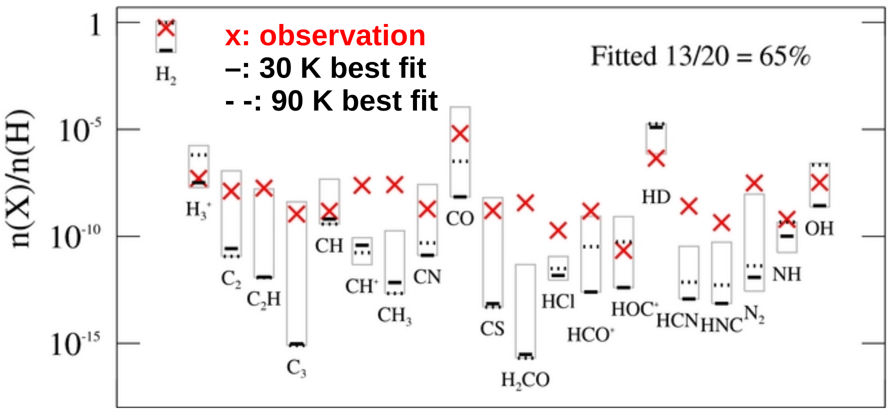

“Best fit” model
n_H = 10 cm^{-3}
ζ = 10^{-15} s^{-1}
(x2) DR: p-H_3^+ = o-H_3^+

“Standard” model
n_H = 10 cm^{-3}
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DR: p-H_3^+ = o-H_3^+

Comparison to observations: 1 MYr

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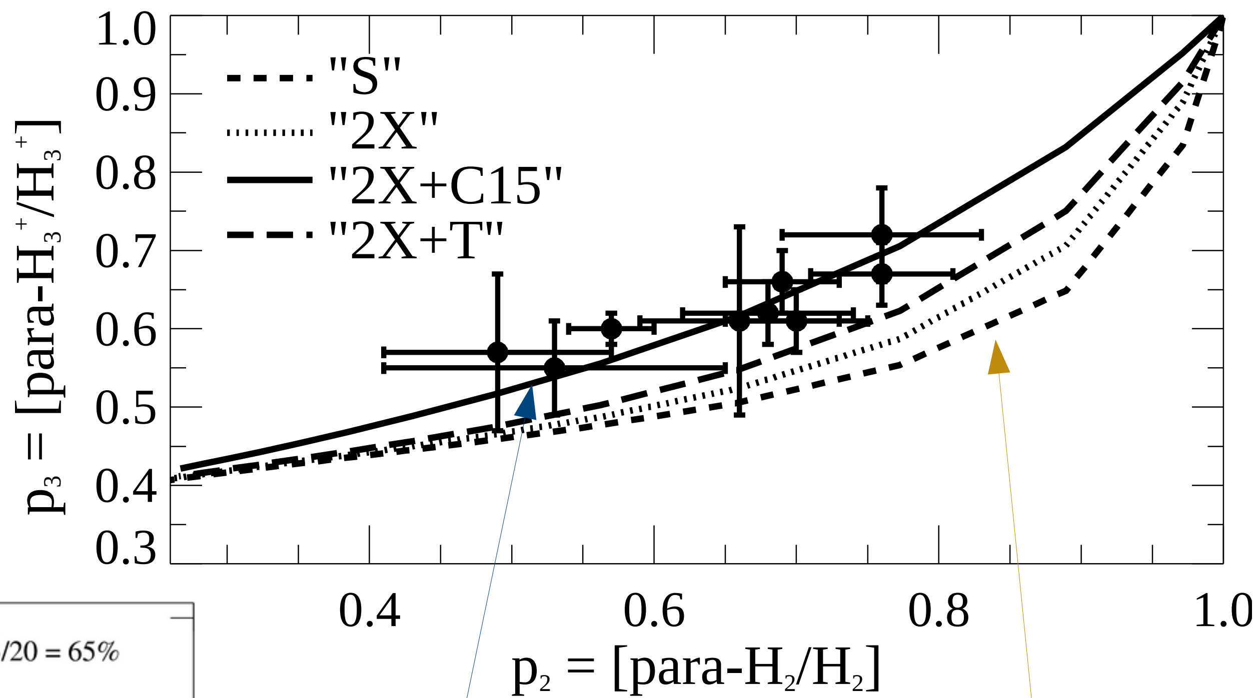
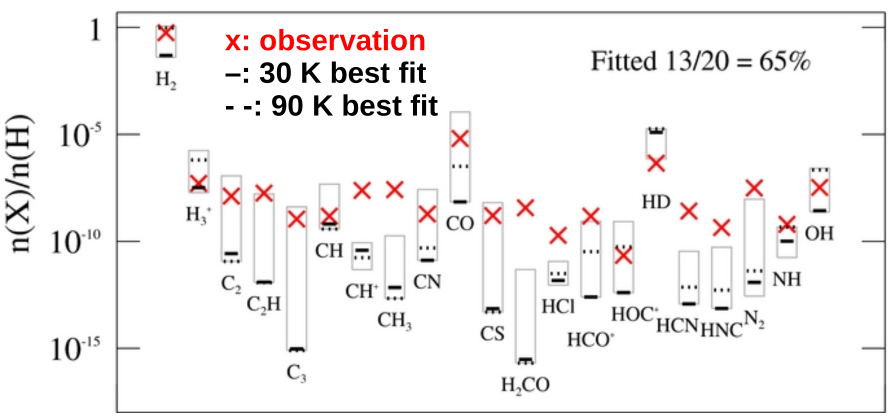
- "Agreement" using inflated DR rates (ortho = para) and elevated ζ.
- Model abundances match observations poorly
- Increases x_e and decreases f, making DR outcompete H_3^+ + H_2 reaction





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Why the excess of p-H_3^+ in diffuse clouds?

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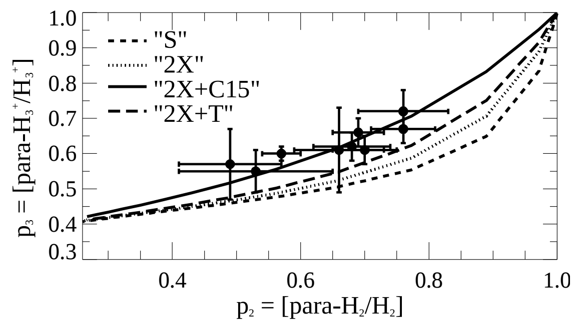
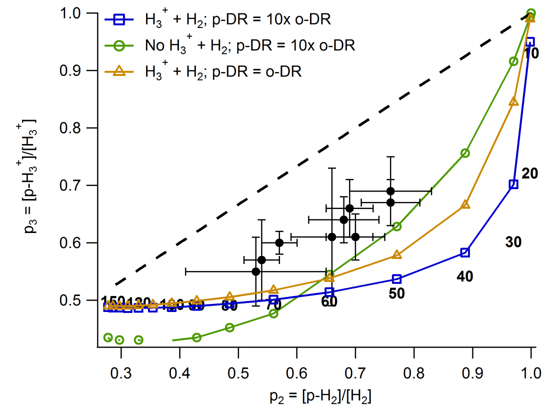
- Excess p-H_3^+ in diffuse molecular clouds not well-explained by latest experiments & models

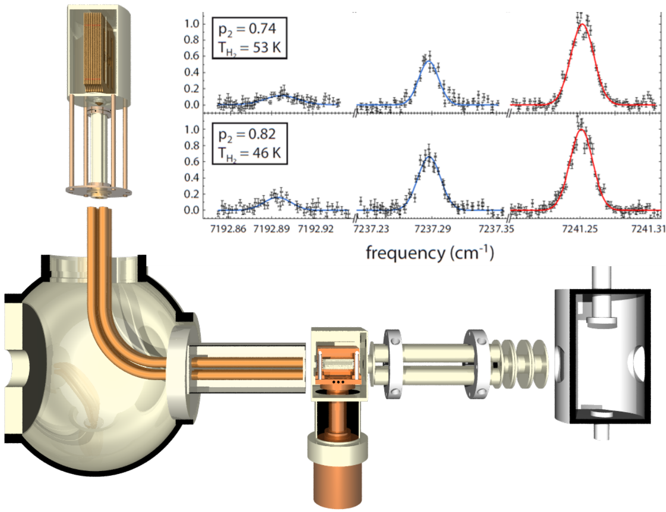
1) Fundamental misinterpretation of relationship between p_2 and T?
2) Total rate coefficient for $H_3^+ + H_2$ collisions too high by ~10x?
3) State specific DR cross sections for (1,0) and (1,1) different from thermally averaged values at 50-70 K?



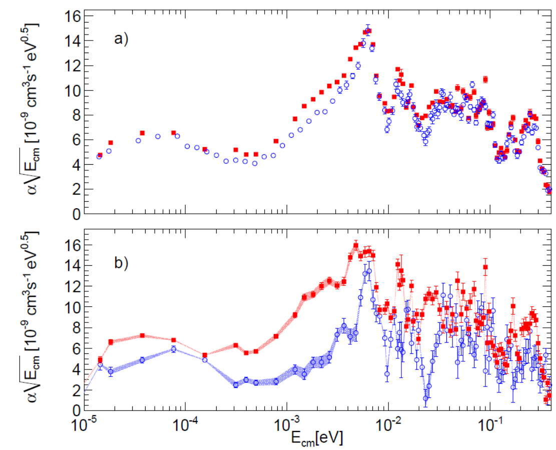
Time-dependent models



Steady state models



$H_3^+ + H_2$ collision experiments



H_3^+ DR measurements

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