The ortho:para Ratio of H_3^+ in Laboratory and Astrophysical Plasmas


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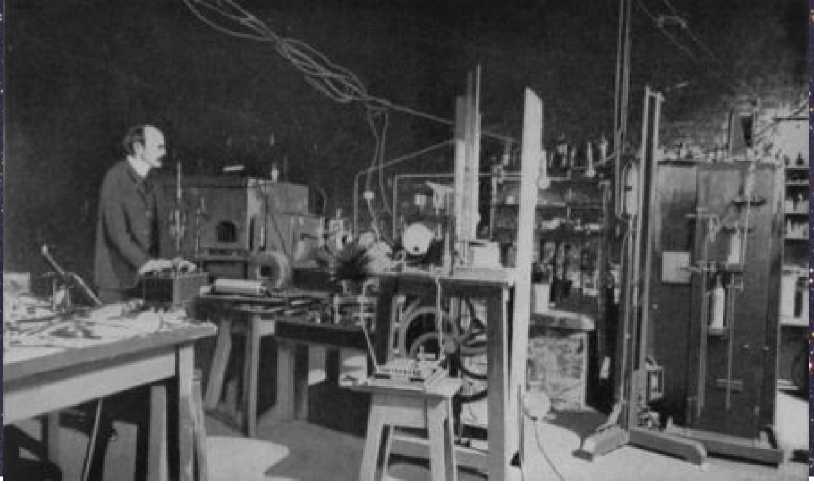
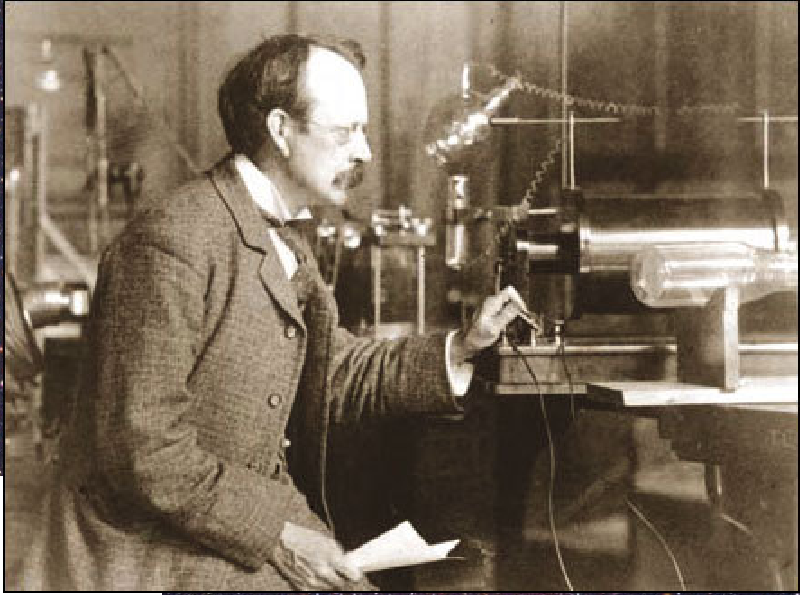
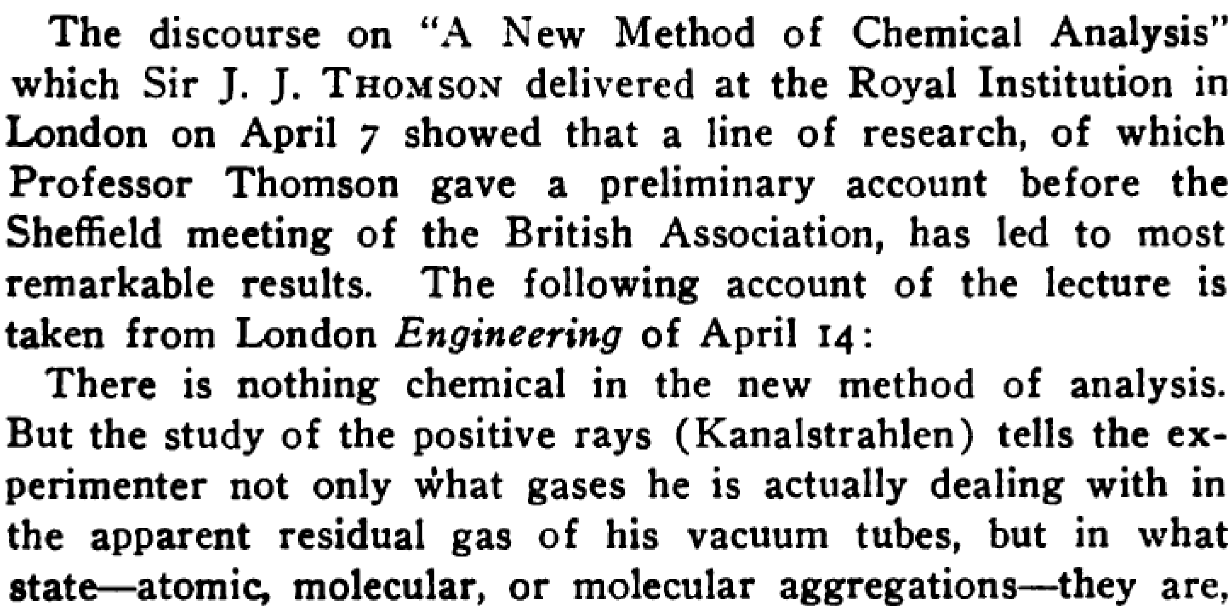


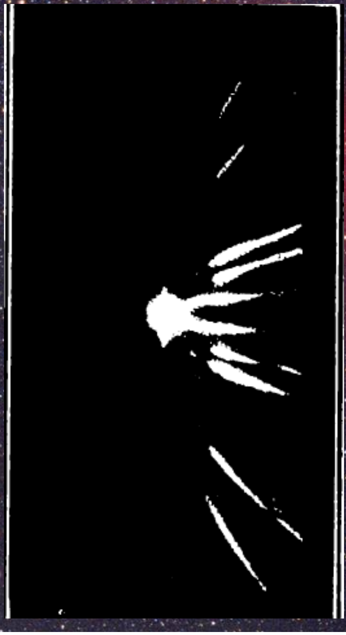


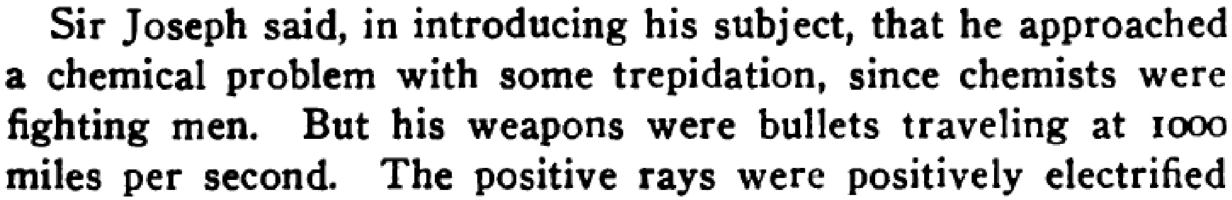
Positive Rays and Chemical Analysis



The discourse on "A New Method of Chemical Analysis" which Sir J. J. THOMSON delivered at the Royal Institution in London on April 7 showed that a line of research, of which Professor Thomson gave a preliminary account before the Sheffield meeting of the British Association, has led to most remarkable results. The following account of the lecture is taken from London *Engineering* of April 14:

There is nothing chemical in the new method of analysis. But the study of the positive rays (Kanalstrahlen) tells the experimenter not only what gases he is actually dealing with in the apparent residual gas of his vacuum tubes, but in what state—atomic, molecular, or molecular aggregations—they are,





Sir Joseph said, in introducing his subject, that he approached a chemical problem with some trepidation, since chemists were fighting men. But his weapons were bullets traveling at 1000 miles per second. The positive rays were positively electrified

Metallurgical and Chemical Engineering
Vol. IX, No. 6, p.298 (1911)

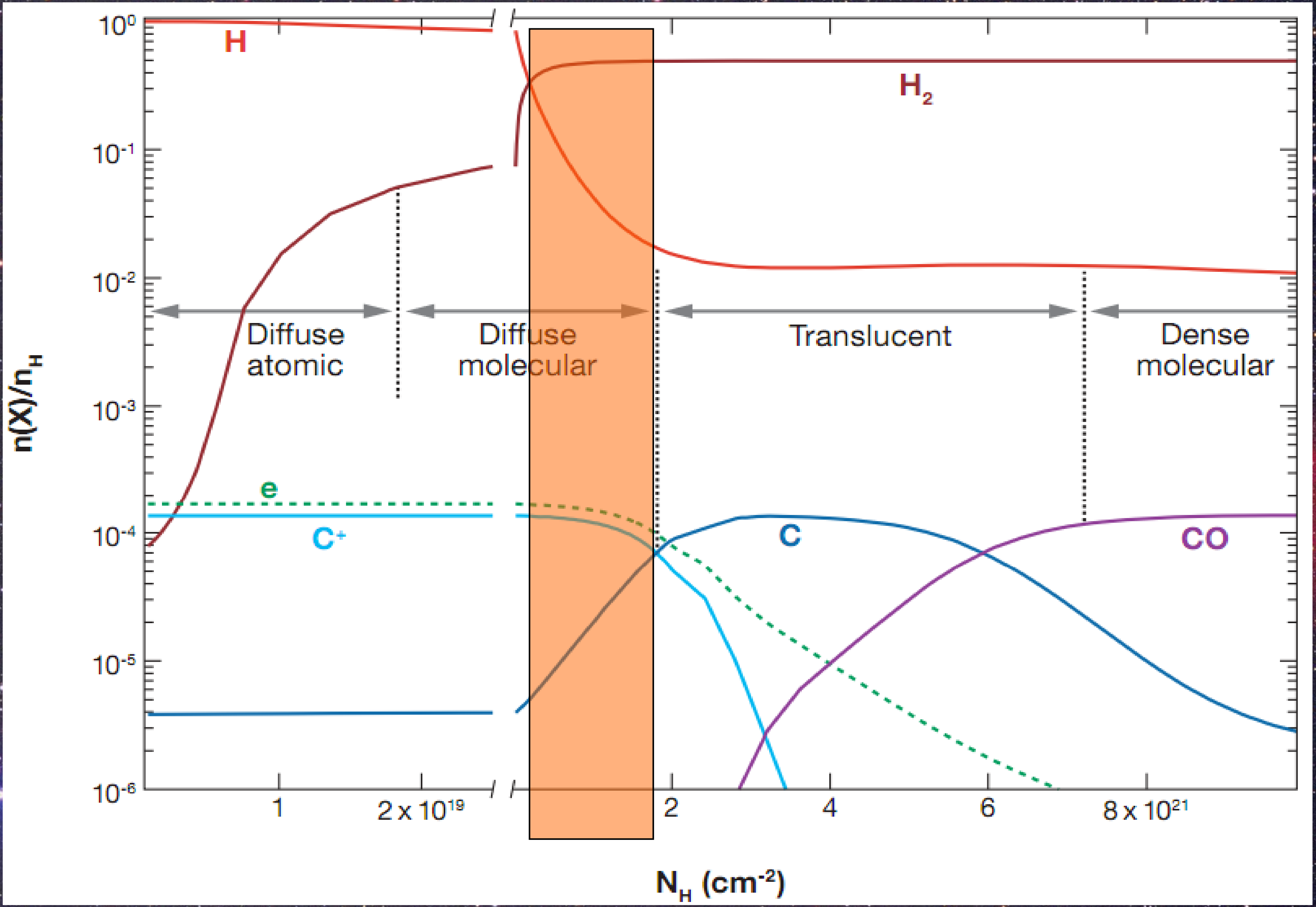
Interstellar gas
~1/6th of mass!

~10^{66} molecules

~half in diffuse
clouds

Richard Payne (Arizona Astrophotography)

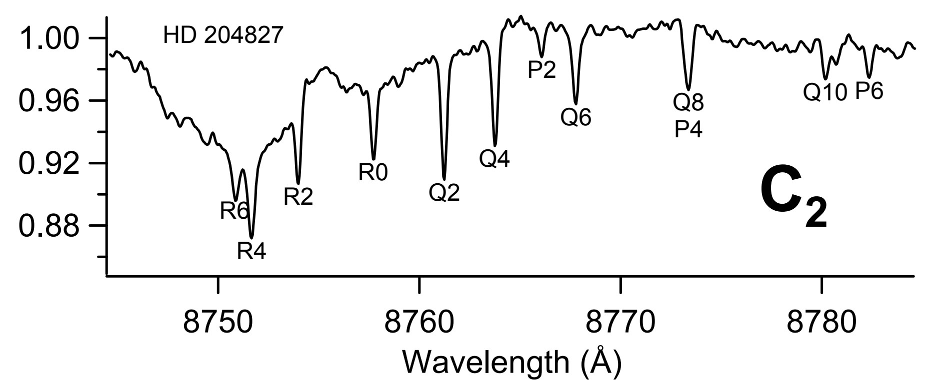
Interstellar Cloud Classification

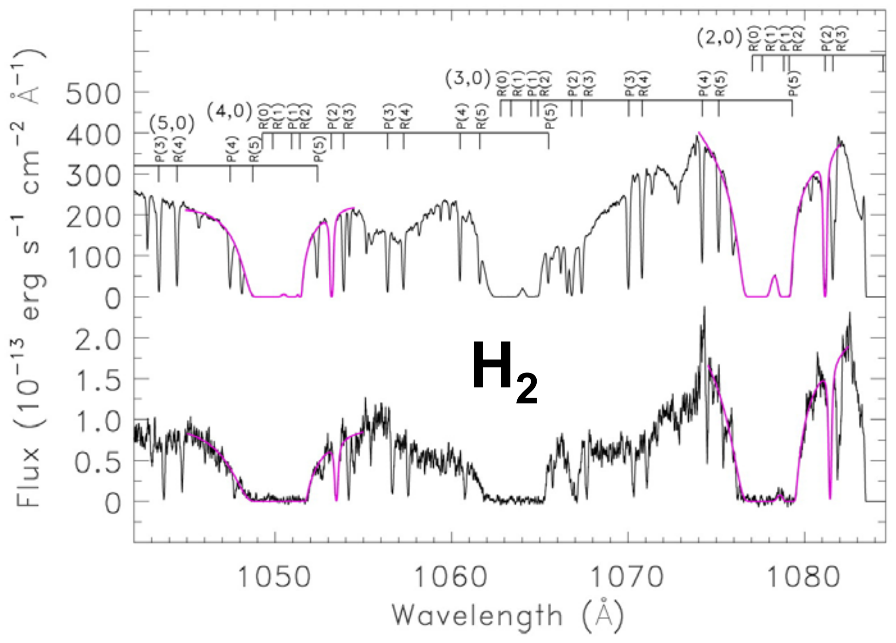


T. P. Snow and B. J. McCall, *Annu. Rev. Astron. Astrophys.* (2006), **44**, 367-414.

Diffuse Molecular Clouds

$n \sim 10^1$–10^3 cm^{-3}
[~10^{-15} Torr]
$T \sim 60$ K





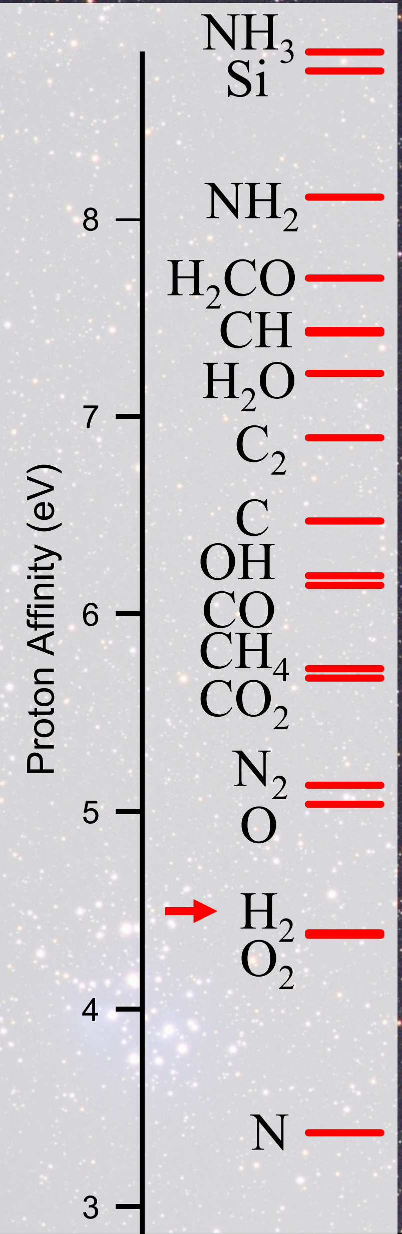
B. L. Rachford et al.,
Astrophys. J. 577, 221 (2002)

← ζ Persei

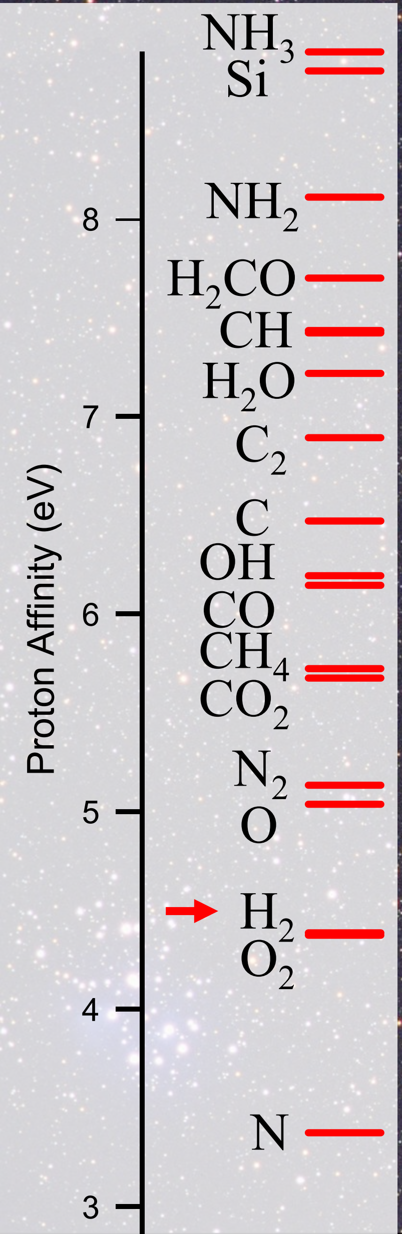
H_2 J=0 (para) & J=1 (ortho)
thermalized by proton swap
$H_2 + H^+ \rightarrow H_2 + H^+$

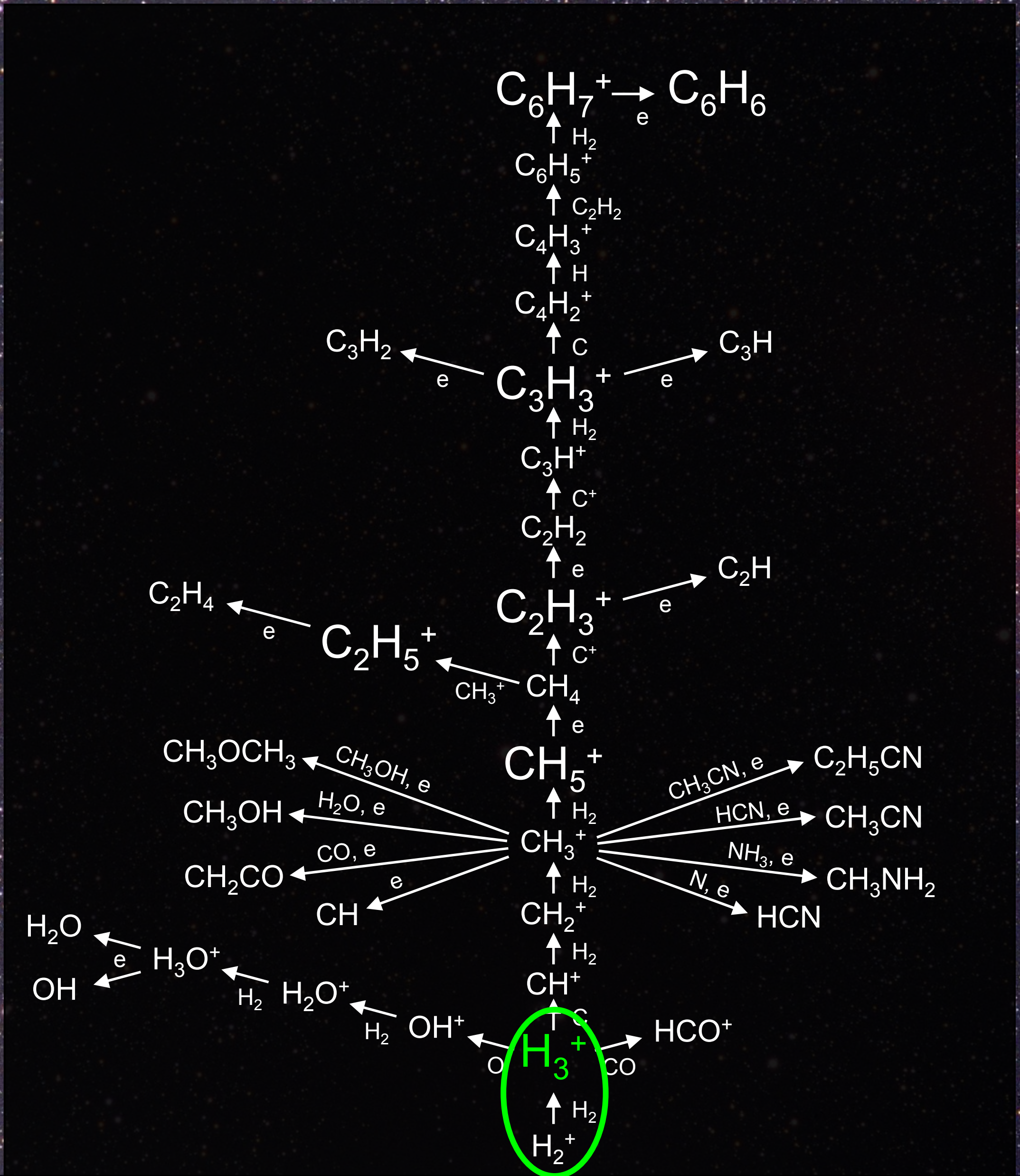
Photo: Jose Fernandez Garcia

Importance of H_2 & H_3^+

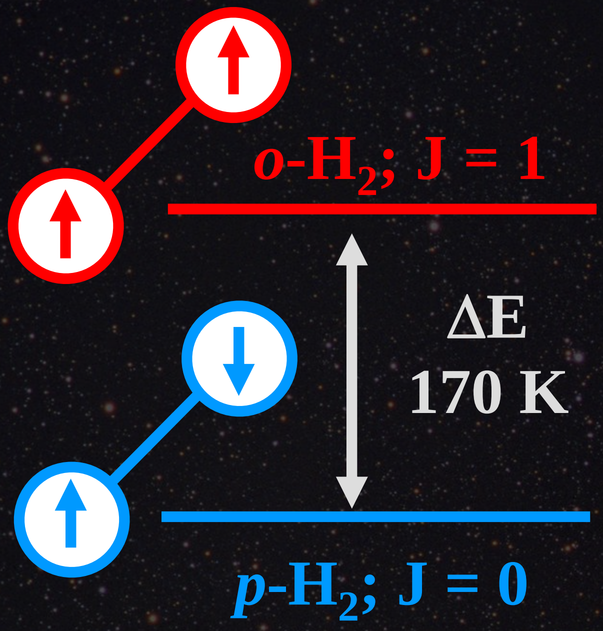


H_3^+: Cornerstone of Interstellar Chemistry





H_2 Temperature

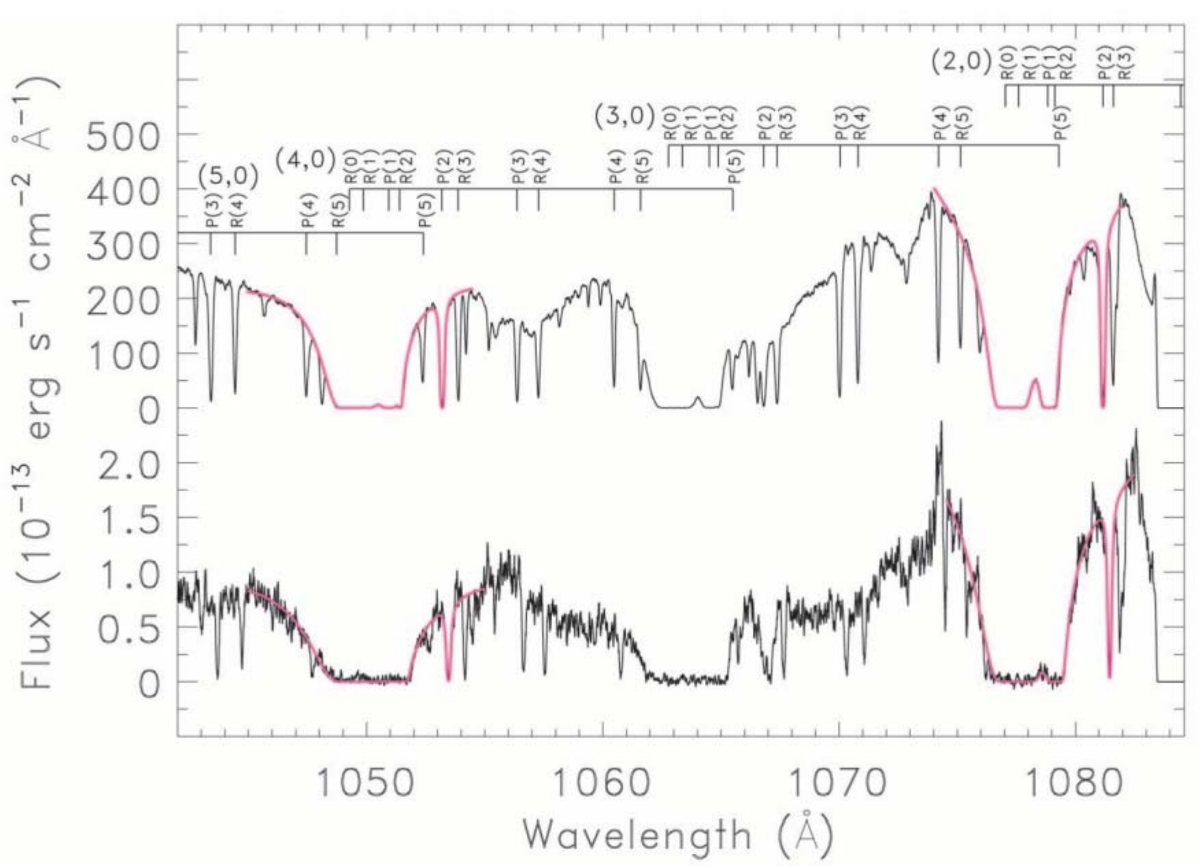


o-H_2; J = 1

ΔE

170 K

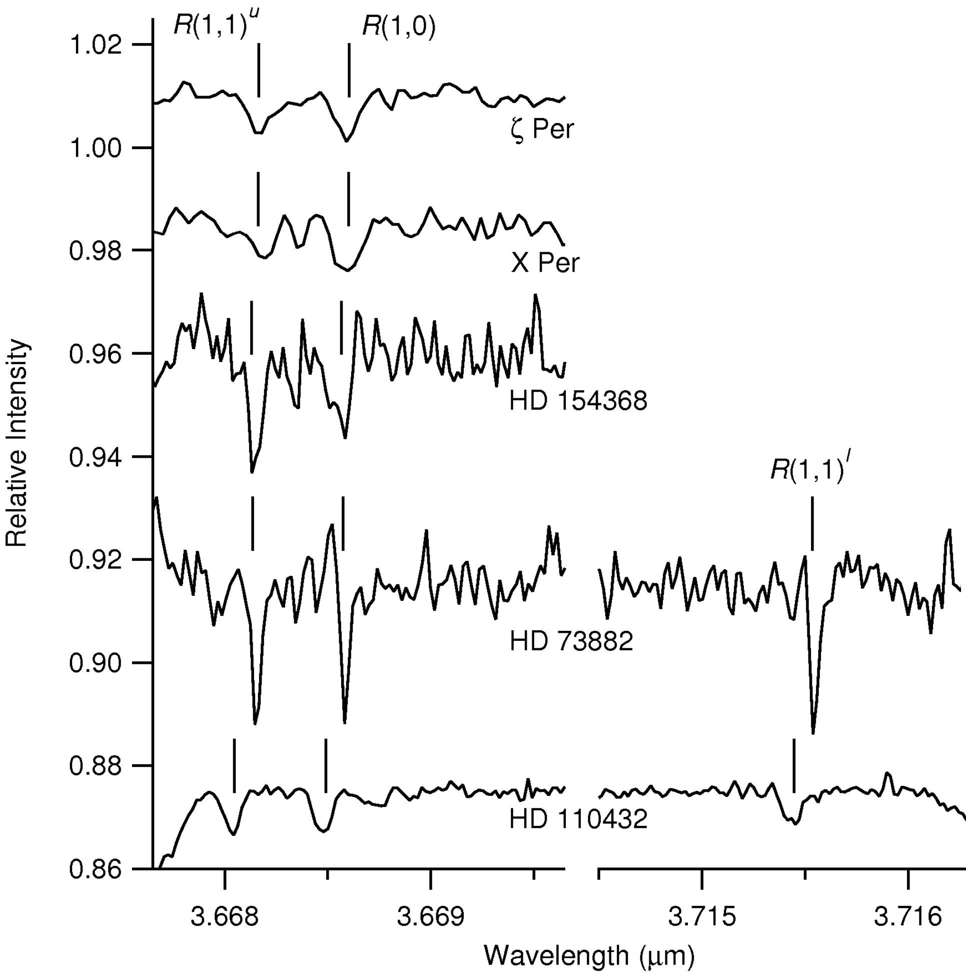
p-H_2; J = 0

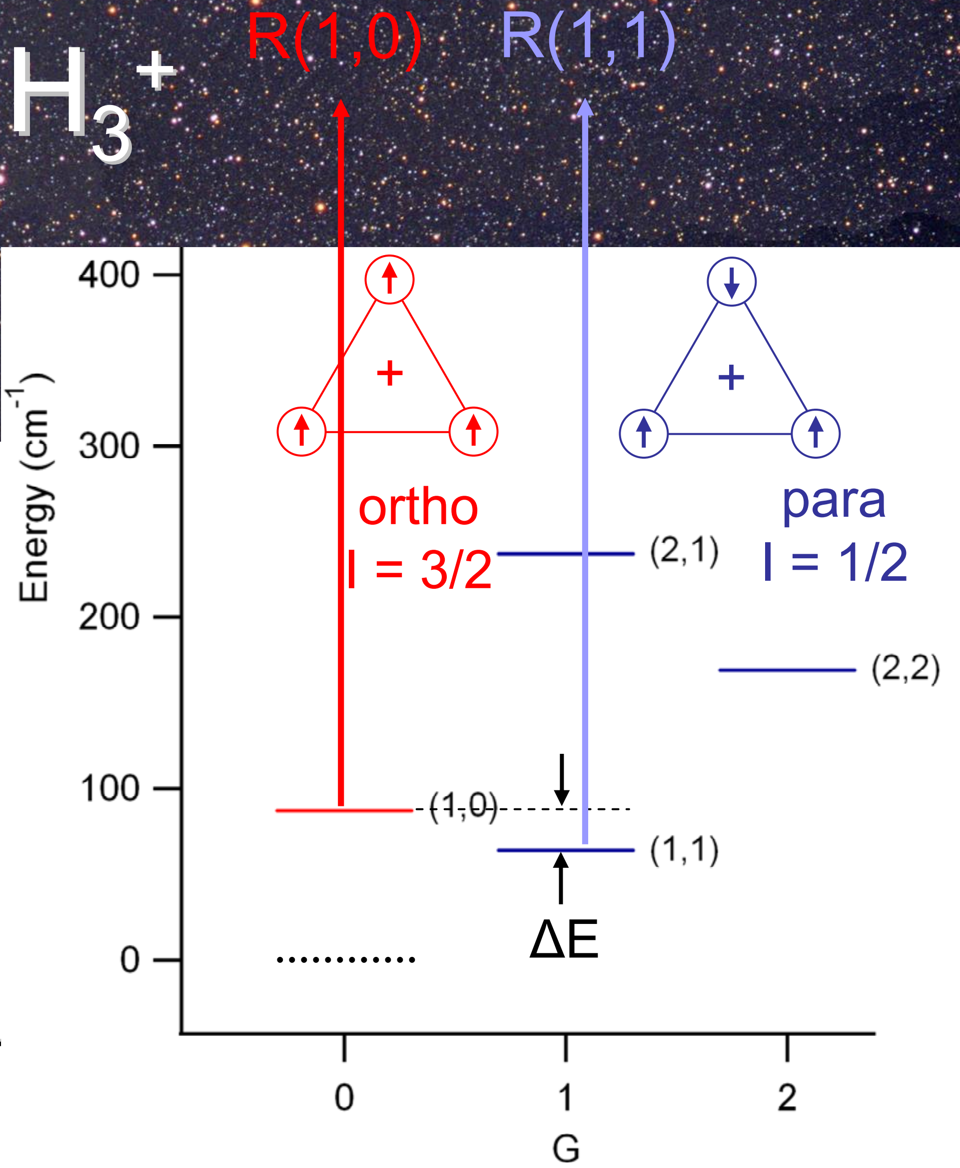


- UV measurements of H_2 absorption
- 99% of H_2 in J=0 (para) and J=1 (ortho) levels
- Profile fitting gives accurate column densities for N(0) and N(1) → T_{01}

B. L. Rachford et al., *ApJ* (2002), **577**, 221-244.

ortho and para H_3^+





$$\frac{N_o}{N_p} = \frac{g_o}{g_p} e^{-\Delta E/kT(H_3^+)}$$

Temperature Discrepancy

- Average T_{01} in diffuse molecular clouds: 70 K (N = 66)
- Average $T(H_3^+)$ in diffuse molecular clouds: 30 K (N = 18)
- Only 2 sight lines in common
- Recent observations expand this number to 6

Target	**Obs.**	**p_3**	**p_2**	**$T(H_3^+)$**	**T_{01}**	**ΔT**
ζ Per	UKIRT	0.65(4)	0.68(6)	25(3)	58(6)	**33**
X Per	UKIRT	0.66(5)	0.69(4)	24(4)	57(4)	**33**
HD 154368	Gem. S.	0.69(6)	0.76(7)	22(4)	51(8)	**29**
HD 73882	VLT	0.67(4)	0.76(5)	23(3)	51(6)	**28**
HD 110432	VLT	0.60(2)	0.57(3)	30(2)	68(5)	**38**
λ Cep	UKIRT/ Keck	0.57(7)	0.54(3)	34(10)	73(4)	**39**

para-H_3^+ Fraction on Formation

Formation

$$H_2 \xrightarrow{\text{cosmic ray}} H_2^+ + e^- \qquad \text{Rate} = \zeta\,[H_2]$$

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

	H_2	H_2^+	ortho-H_3^+	para-H_3^+
$(1-p_2)^2$	ortho	ortho	2/3	1/3 $(1-p_2)^2$
$(1-p_2)p_2$	ortho	para	1/3	+ 2/3 $(1-p_2)p_2$
$p_2(1-p_2)$	para	ortho	1/3	+ 2/3 $p_2(1-p_2)$
p_2^2	para	para	0	+ 1 p_2^2

Observed
para-H_3^+ fraction
$p_3 \sim 0.62$

$(1/3 + 2/3\, p_2) = p_3 = 0.79$ $(p_2 = 0.68)$

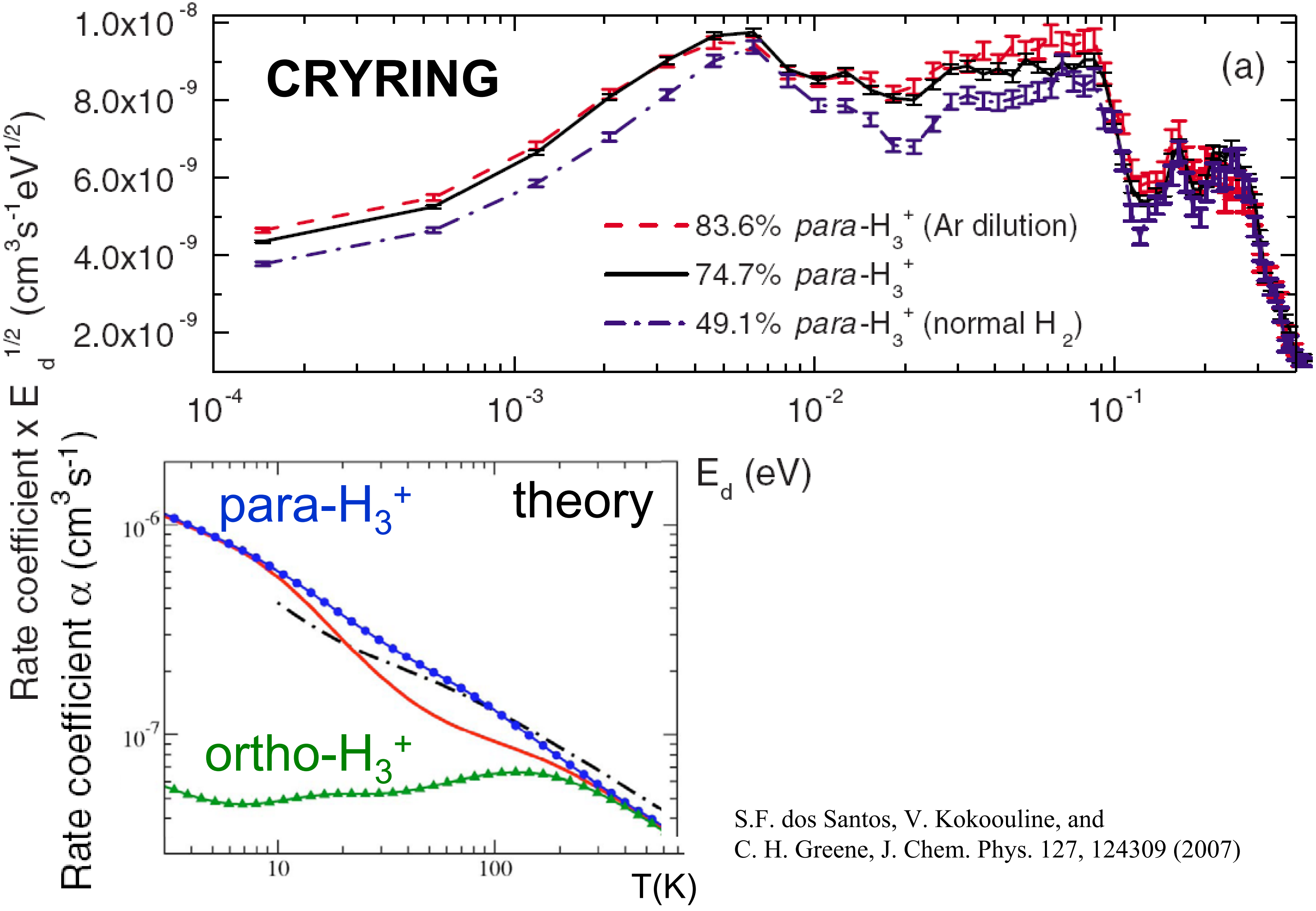
Destruction

$$H_3^+ + e^- \rightarrow H + H_2 \text{ or } 3H \qquad \text{Rate} = k_e\,[H_3^+]\,[e^-]$$

?

M. Quack, Mol. Phys. 34, 477 (1977)
T. Oka, JMS 228, 635 (2004)

para-H_3^+ + e^- vs. ortho-H_3^+ + e^-



S.F. dos Santos, V. Kokoouline, and
C. H. Greene, J. Chem. Phys. 127, 124309 (2007)

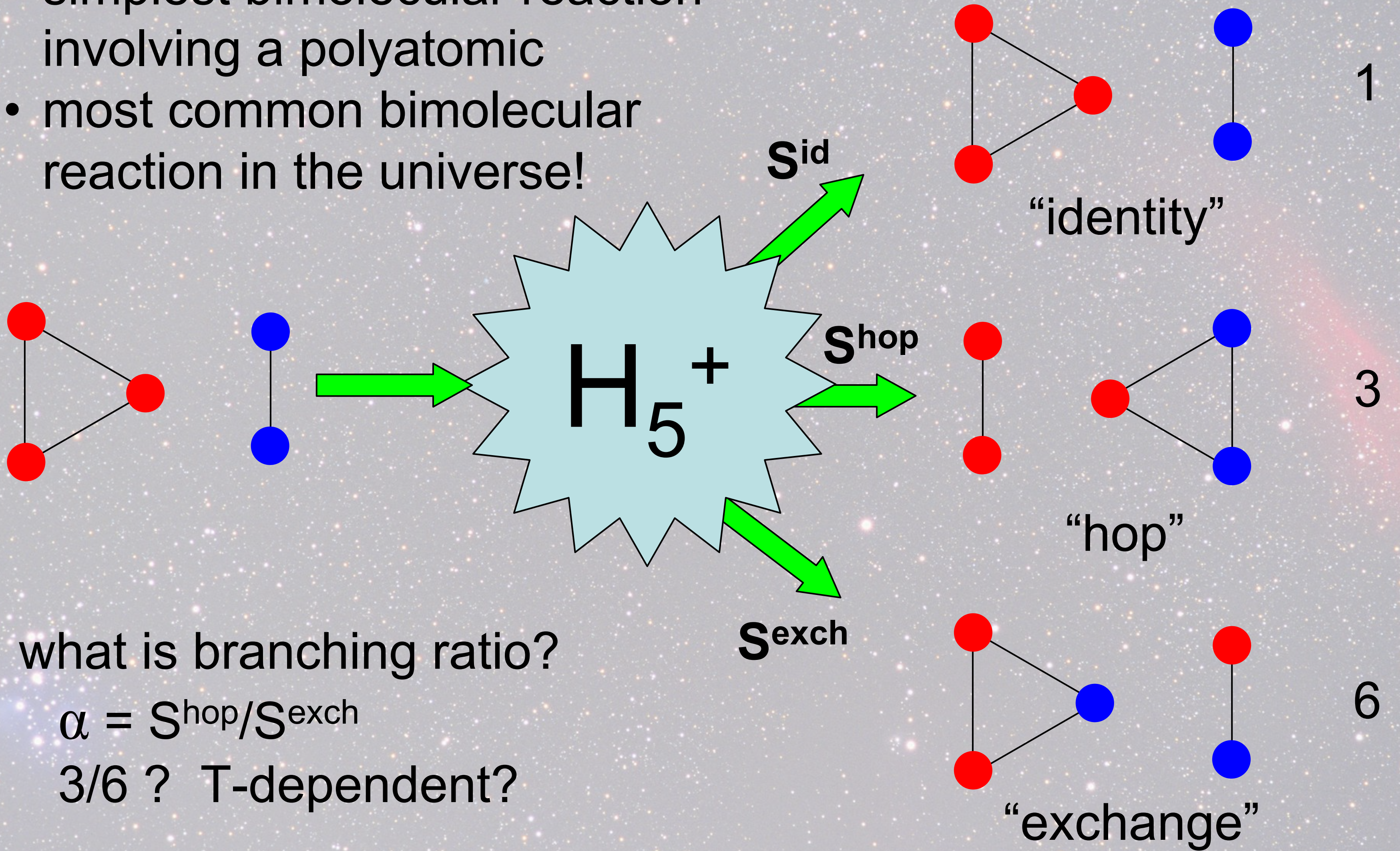
B. A. Tom, V. Zhaunerchyk, M. B.Wiczer, …, M. Larsson, R. D. Thomas, & B. J. McCall, J. Chem. Phys. 130, 031101 (2009)

The Life of an H_3^+

- Birth rate: $\zeta\ n(H_2) \sim 3\times10^{-14}\ cm^{-3}\ s^{-1}$
  - in 1 mL, birth once every million years
  - once per second in cube ~300m on a side
  - demographics: 79% para, 21% ortho
- Collision rate with H_2: $k\ n(H_2) \sim 1\times10^{-7}\ s^{-1}$
  - once every ~100 days
  - happens $10^{52}\ s^{-1}$ in our galaxy!
  - influence on ortho:para ????
- Lifetime: $1/[k_e\ n(e)] \sim 5\times10^{8}$ s ~ 16 years

$H_3^+ + H_2 \rightarrow (H_5^+)^* \rightarrow H_2 + H_3^+$

- simplest bimolecular reaction involving a polyatomic
- most common bimolecular reaction in the universe!

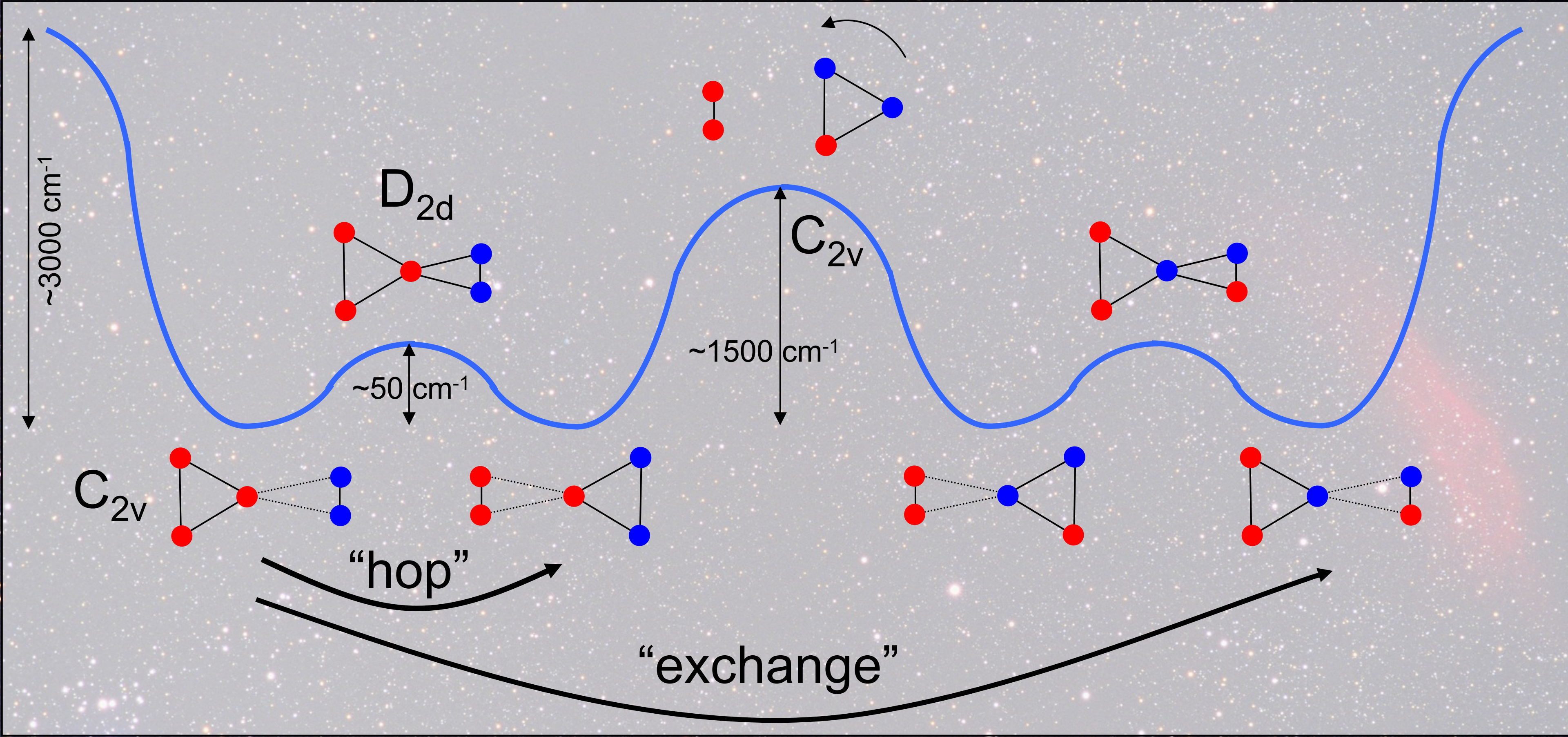


what is branching ratio?

$\alpha = S^{hop}/S^{exch}$

3/6 ? T-dependent?

Dynamics of Reaction



Not obvious that "statistical" hop/exchange = 0.5 is valid!

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

High-T Statistical Model (Oka)

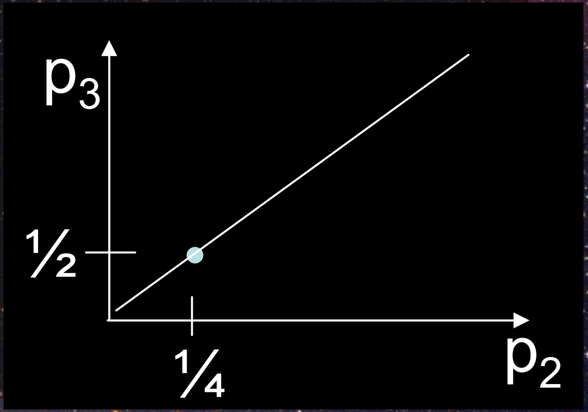
- Adopt constant α (ignore PES)
- Ortho & para as two species (ignore J,K)
- Assume all pathways energetically possible
- Use "nuclear spin branching ratios" as k's

H_3^+	H_2	proton hop		hydrogen exchange	
		ortho-H_3^+	para-H_3^+	ortho-H_3^+	para-H_3^+
ortho	ortho	2/3	1/3	2/3	1/3
ortho	para	0	1	2/3	1/3
para	ortho	2/3	1/3	1/3	2/3
para	para	0	1	1/3	2/3

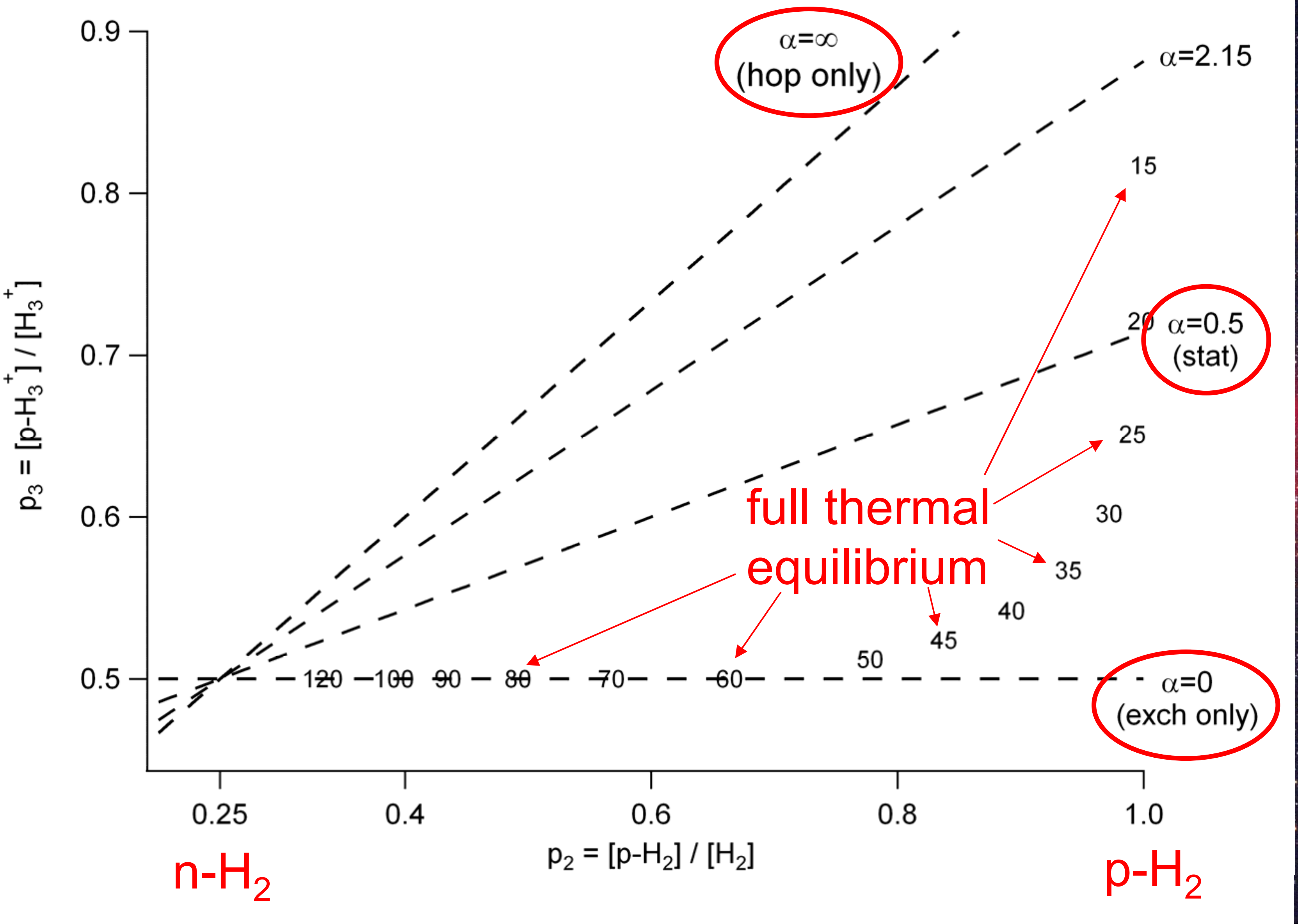
Cordonnier et al., J. Chem. Phys. 113, 3181 (2000)

Our High-T Model

- Assumptions:
  - – Gas has constant $p_2 \equiv [p\text{-}H_2]/[H_2]$
    - Laboratory: p_2 established by preparation
    - Diffuse clouds: p_2 fixed by reaction with H^+
  - – Steady state (reached in a few collisions)
    - Results independent of H_3^+ formation, destruction
- Results:
  - – $p_3 \equiv [p\text{-}H_3^+]/[H_3^+] = \dfrac{\alpha+1+2\alpha p_2}{3\alpha+2}$
  - – If $p_2 = ¼$, $p_3 = ½$ for all α
    - $n\text{-}H_2 \rightarrow n\text{-}H_3^+$



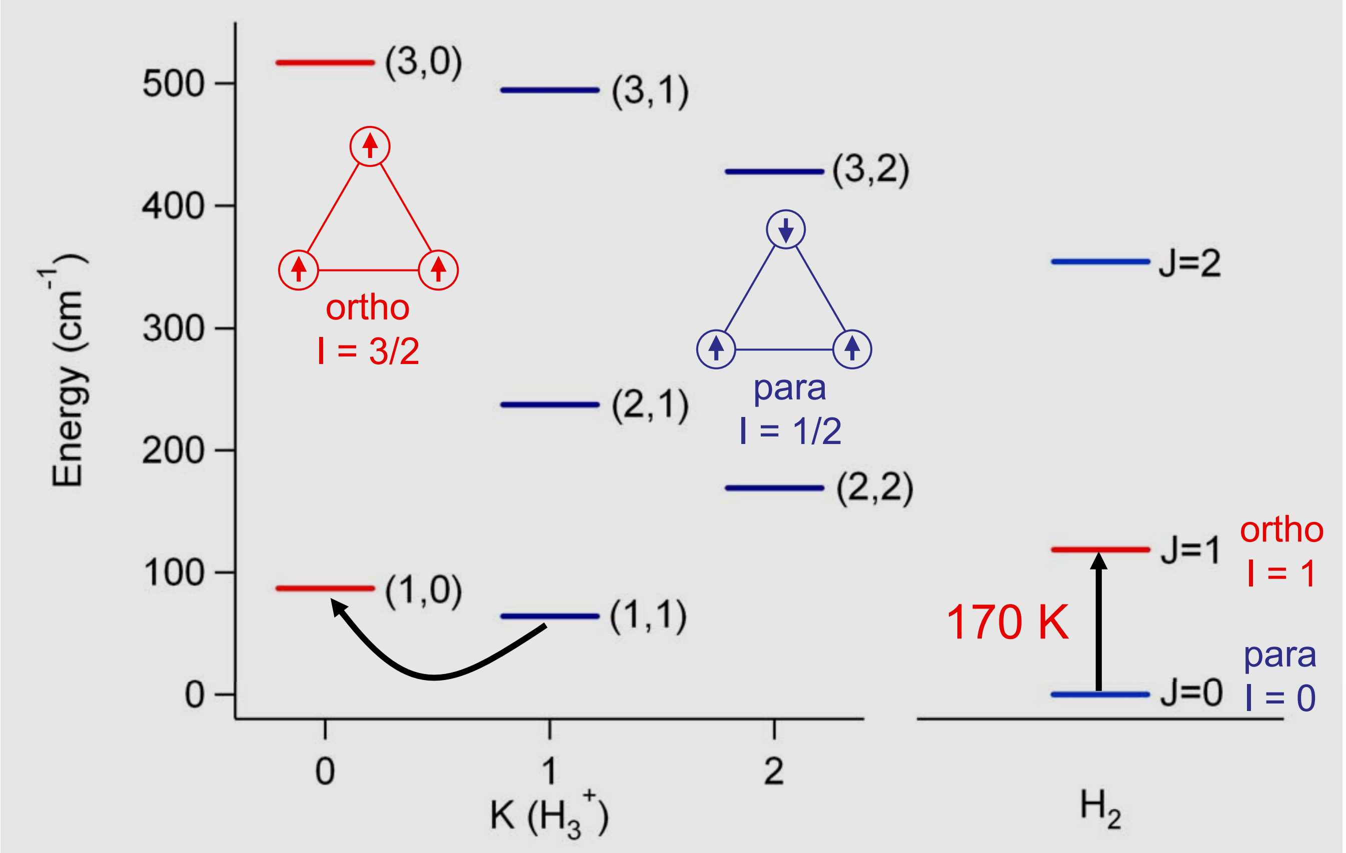
High-T Model Predictions



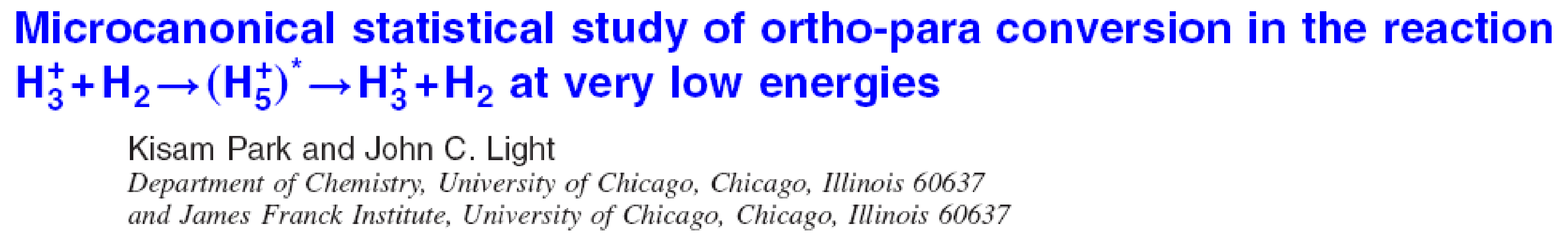
Low Temperature Effects

- Angular momentum restrictions
  - $p\text{-}H_3^+ + p\text{-}H_2 \not\rightarrow o\text{-}H_3^+ + p\text{-}H_2$
  - $p\text{-}H_3^+ + p\text{-}H_2 \rightarrow o\text{-}H_3^+ + o\text{-}H_2$
- At low T in enriched $p\text{-}H_2$, slower $p\text{-}H_3^+ \rightarrow o\text{-}H_3^+$

$1/2 \otimes 0 \not\leftrightarrow 3/2 \otimes 0$



Low Temperature Statistical Model



Microcanonical statistical study of ortho-para conversion in the reaction $H_3^+ + H_2 \rightarrow (H_5^+)^* \rightarrow H_3^+ + H_2$ at very low energies

Kisam Park and John C. Light
Department of Chemistry, University of Chicago, Chicago, Illinois 60637
and James Franck Institute, University of Chicago, Chicago, Illinois 60637

- Still requires α as input parameter (no PES)
- Does consider rotational states & energies
- Rate constants from ground state reactants

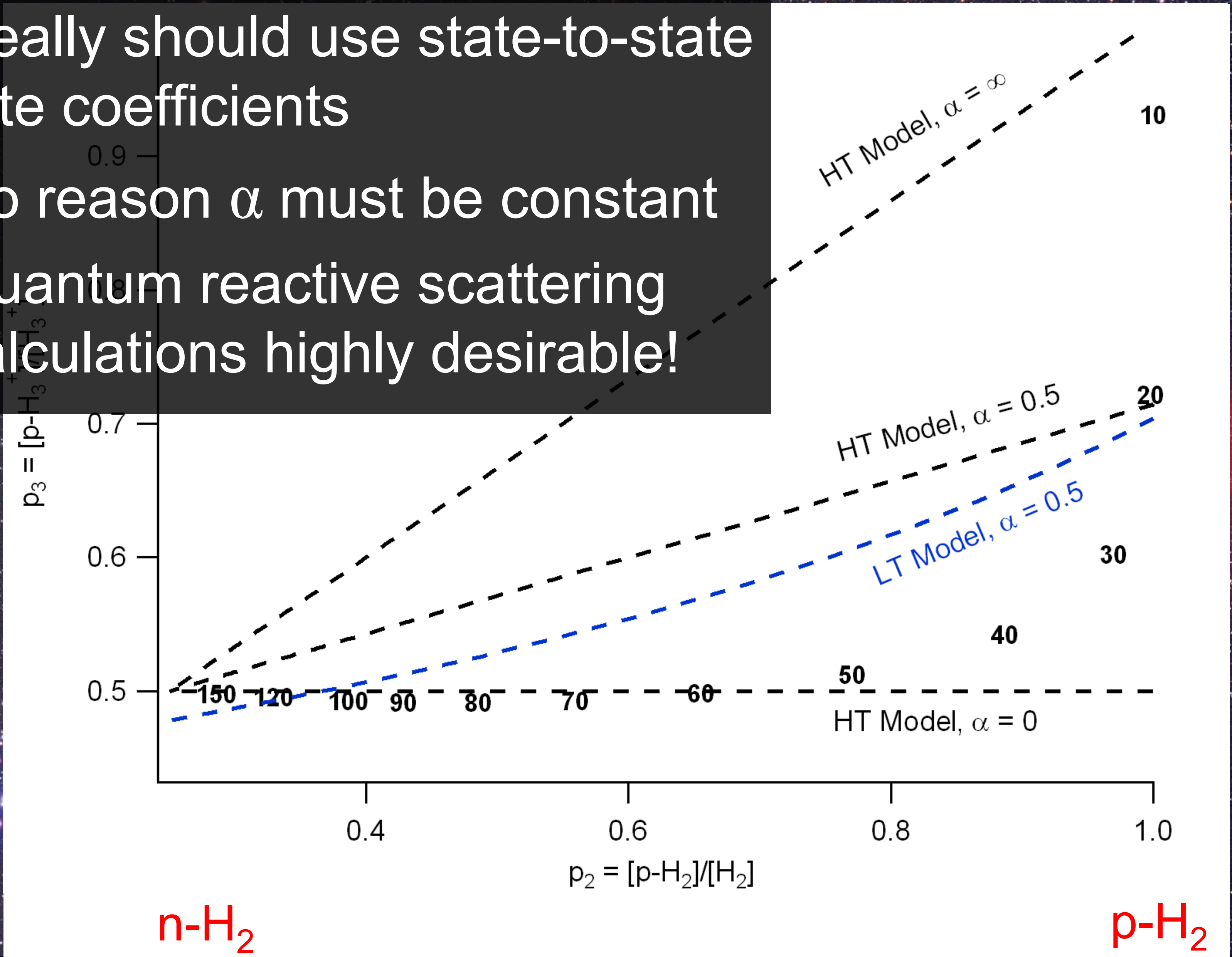
e.g. $k_{oppo}(T_{rot}, T_{kin}) \equiv k(o\text{-}H_3^+ + p\text{-}H_2 \rightarrow p\text{-}H_3^+ + o\text{-}H_2)$

$$\frac{\mathrm{d}}{\mathrm{d}t}[p\text{-H}_3^+] = \{(k_{oopo} + k_{oopp})[o\text{-H}_2] + (k_{oppo} + k_{oppp})[p\text{-H}_2]\}[o\text{-H}_3^+] - \{(k_{pooo} + k_{poop})[o\text{-H}_2] + (k_{ppoo} + k_{ppop})[p\text{-H}_2]\}[p\text{-H}_3^+].$$

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

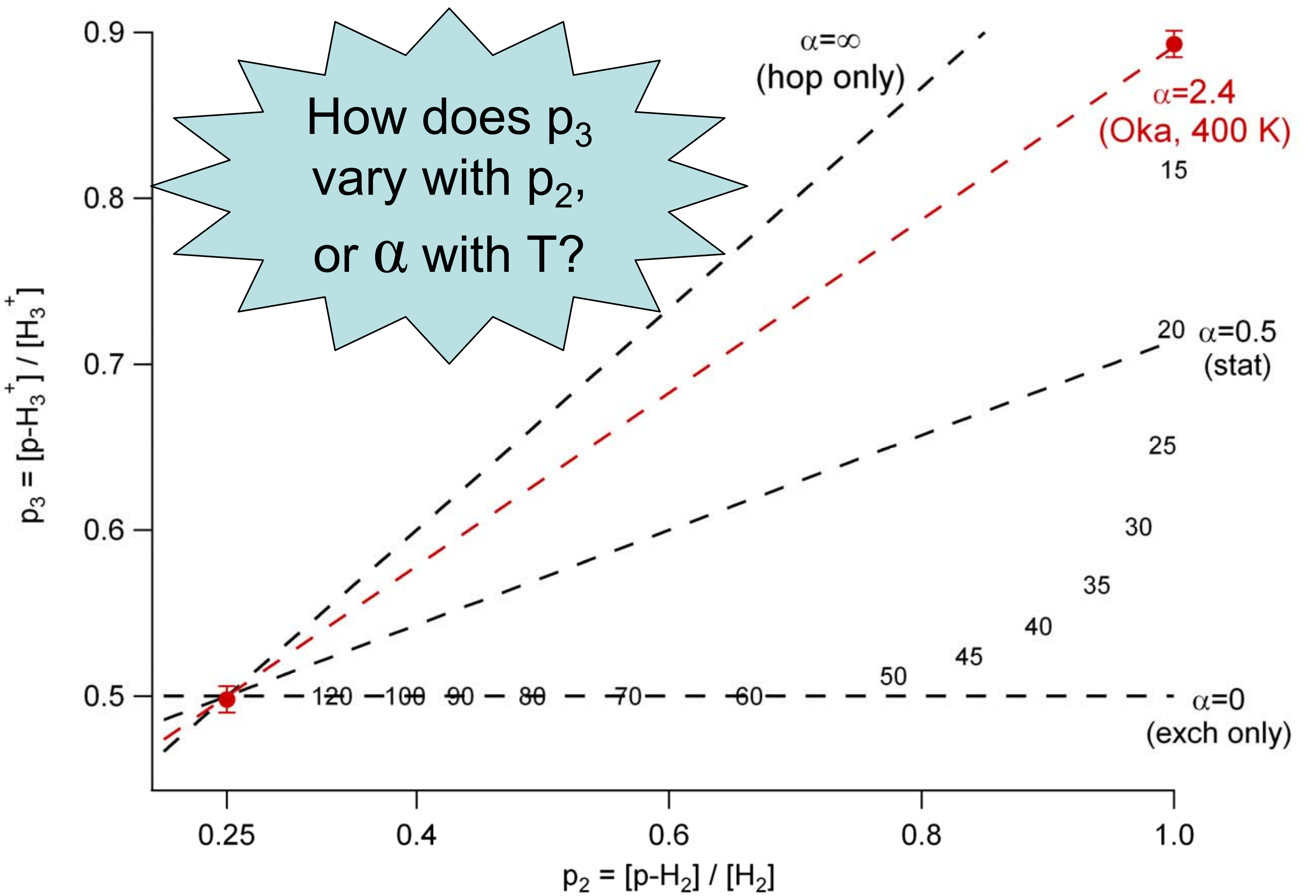
Steady-State Model Predictions

- Really should use state-to-state rate coefficients
- No reason α must be constant
- Quantum reactive scattering calculations highly desirable!



Cordonnier et al. JCP 113, 3181 (2000)

Oka Group Experiments

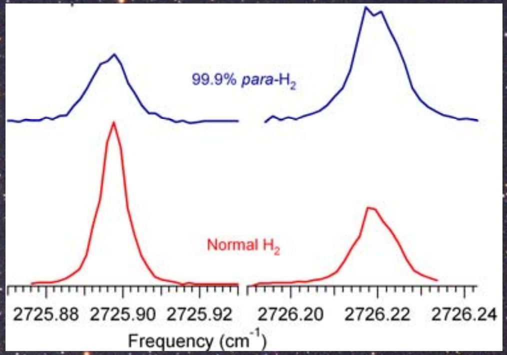


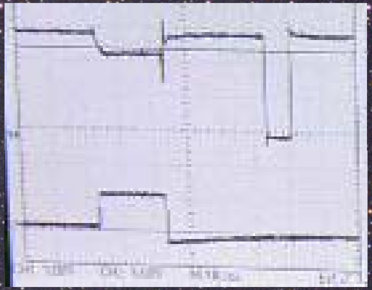
How does p_3 vary with p_2, or α with T?

Experimental Approach

Takayoshi Amano

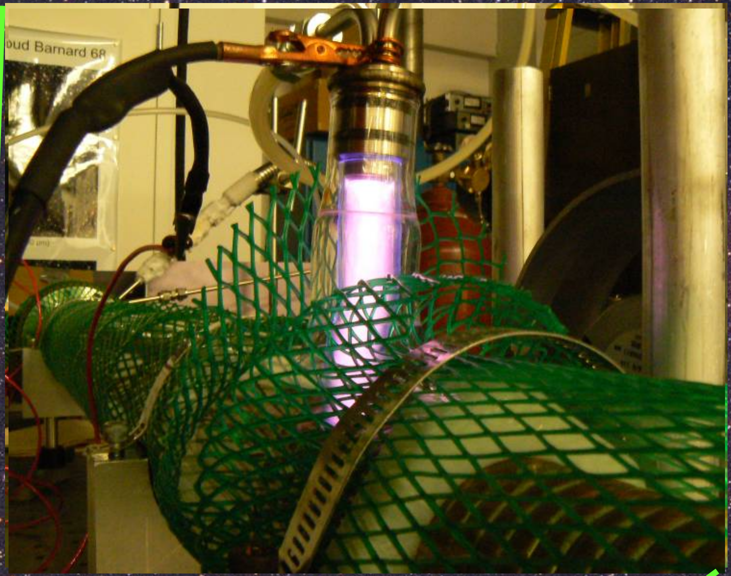
ortho-H_3^+ para-H_3^+

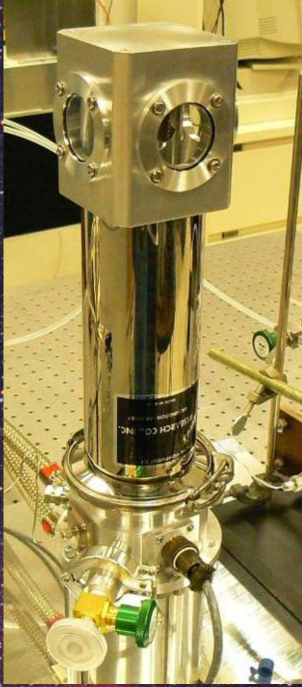




measure steady state

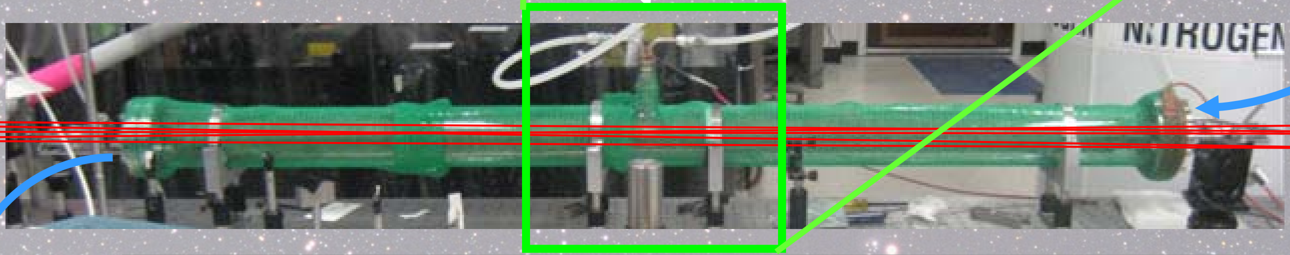
$p_3 \equiv [p\text{-}H_3^+]/[H_3^+]$ vs p_2





(p_2) p-H_2 +

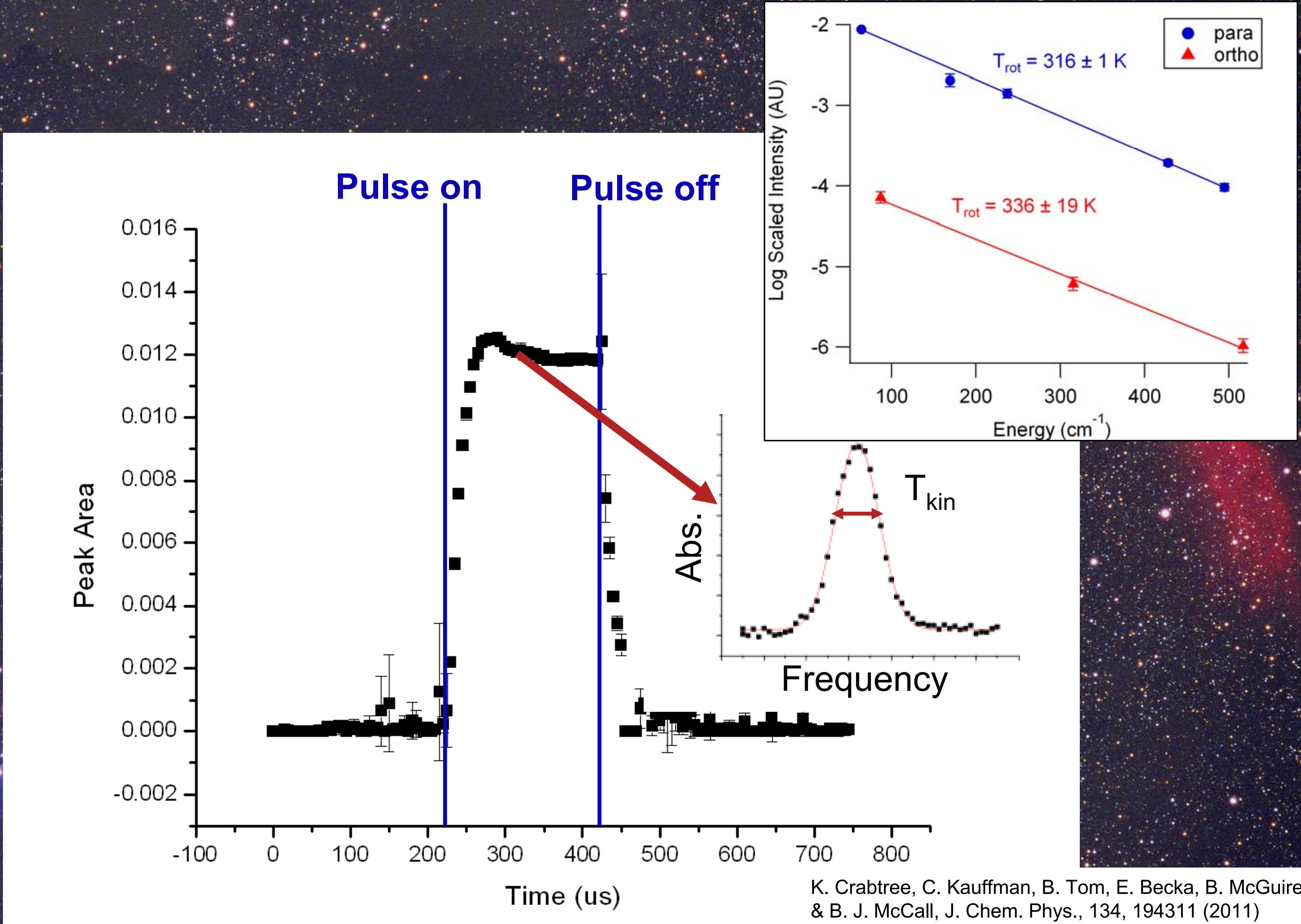
($1-p_2$) o-H_2



pump

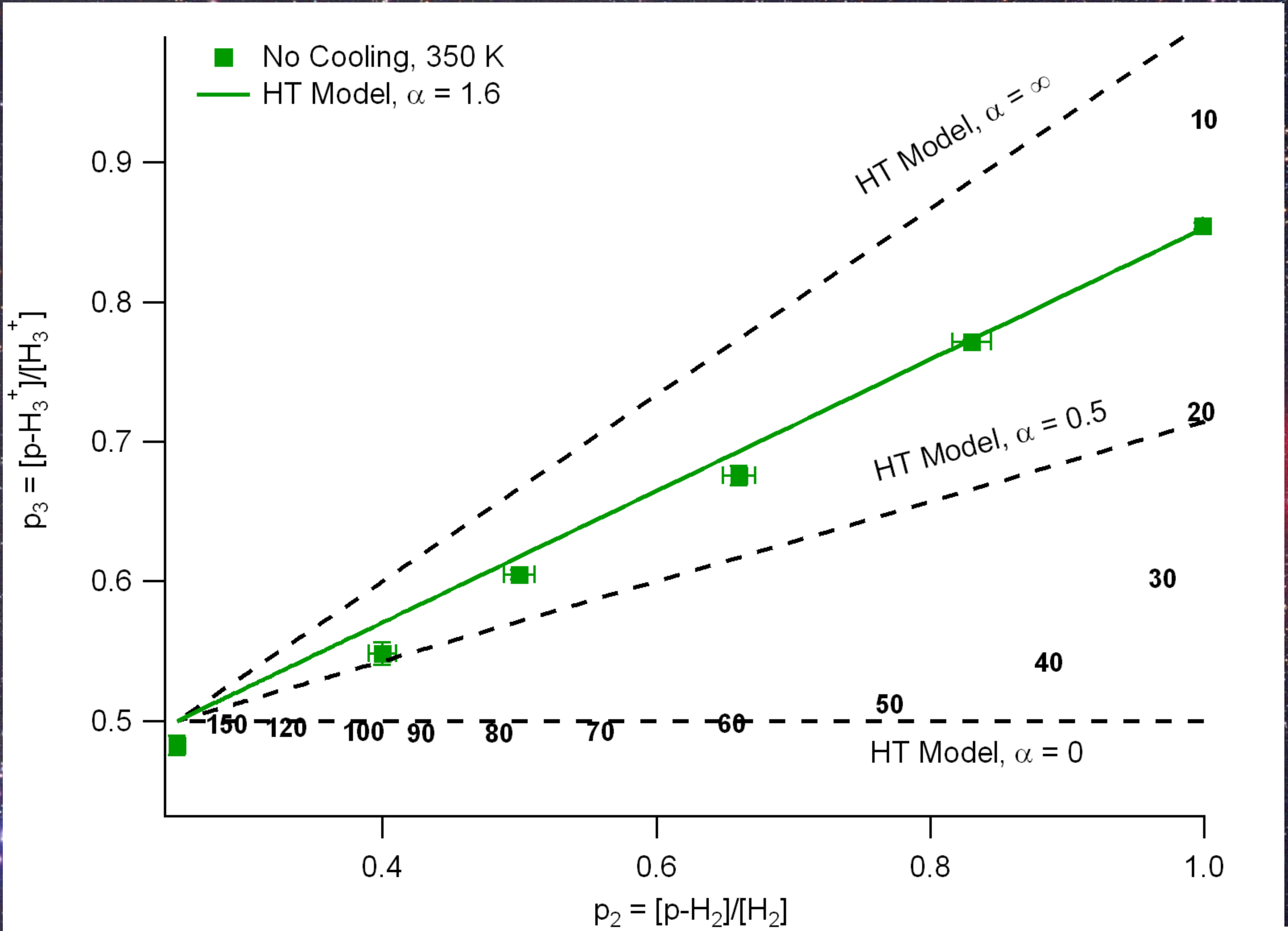
Liquid-nitrogen cooled hollow cathode

Experimental Results



K. Crabtree, C. Kauffman, B. Tom, E. Becka, B. McGuire, & B. J. McCall, J. Chem. Phys., 134, 194311 (2011)

o/p-H_3^+ vs. o/p-H_2



K. Crabtree, C. Kauffman, B. Tom, E. Becka, B. McGuire, & B. J. McCall, J. Chem. Phys., 134, 194311 (2011)

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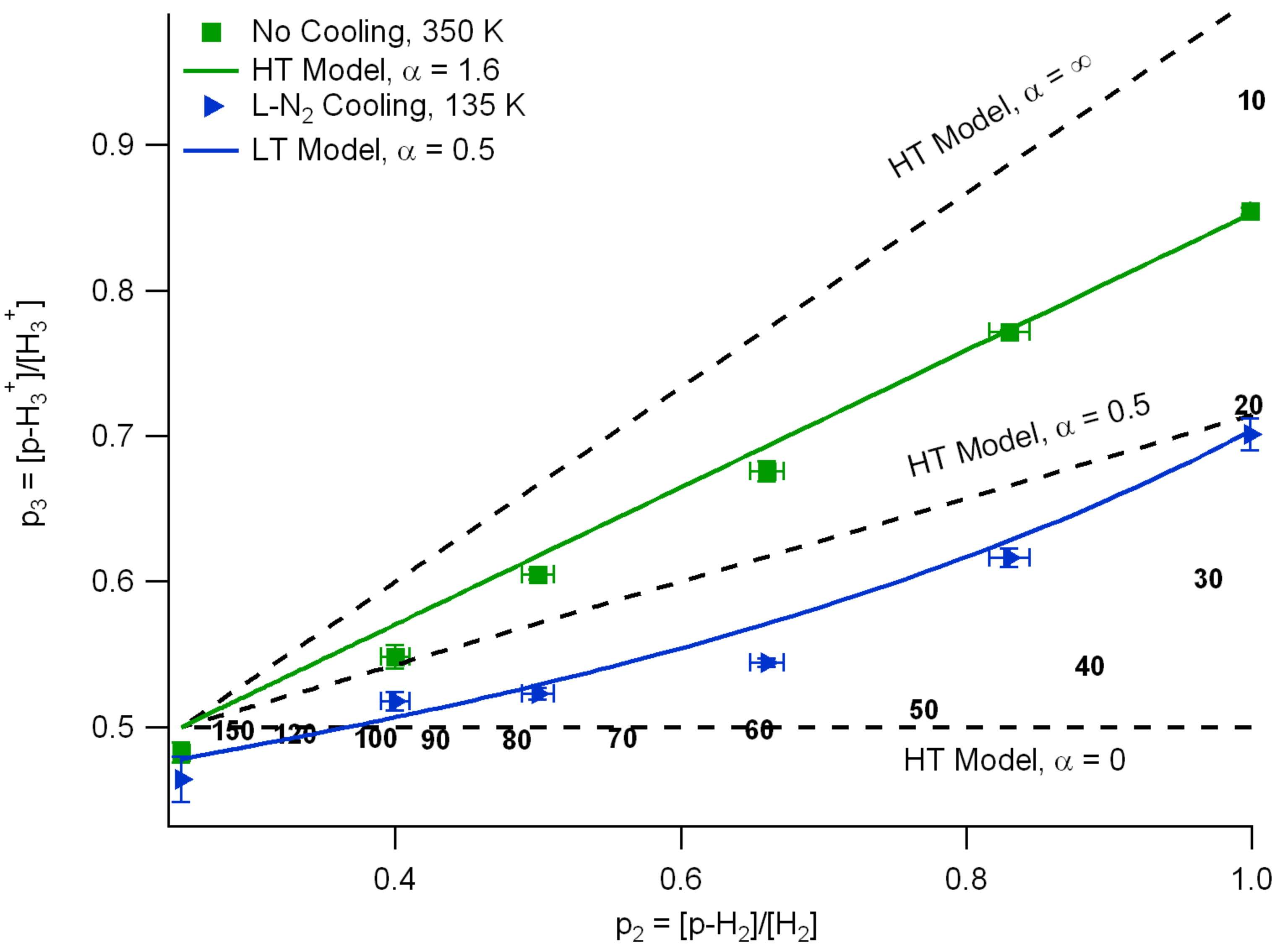

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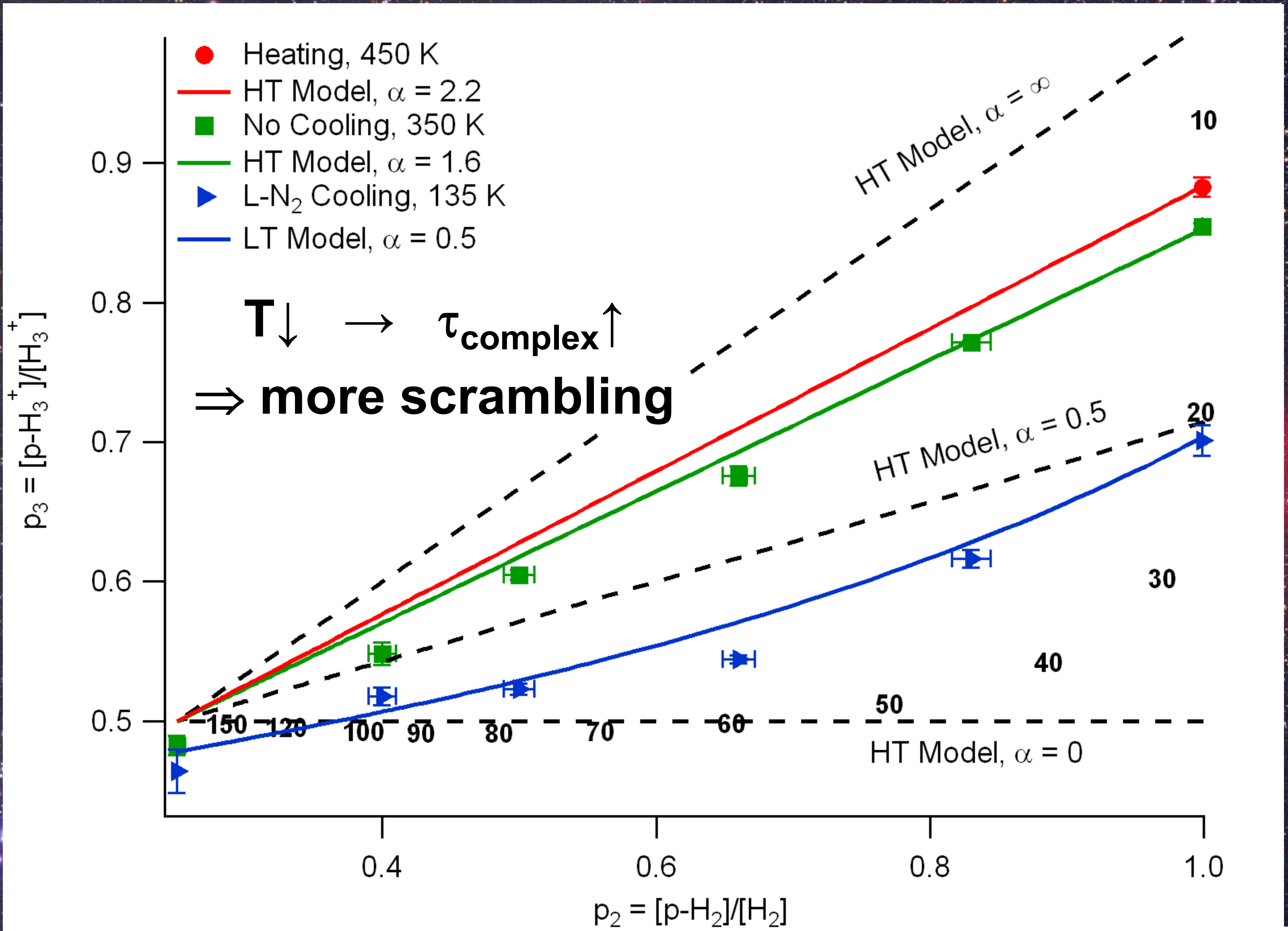


T↓ → $\tau_{complex}$↑

⇒ more scrambling

K. Crabtree, C. Kauffman, B. Tom, E. Becka, B. McGuire, & B. J. McCall, J. Chem. Phys., 134, 194311 (2011)

Isotopically Substituted System

$$D_3^+ + H_2 \xrightarrow{\text{hop}} H_2D^+ + D_2$$

$$D_3^+ + H_2 \xrightarrow[\text{exch.}]{} HD_2^+ + HD$$

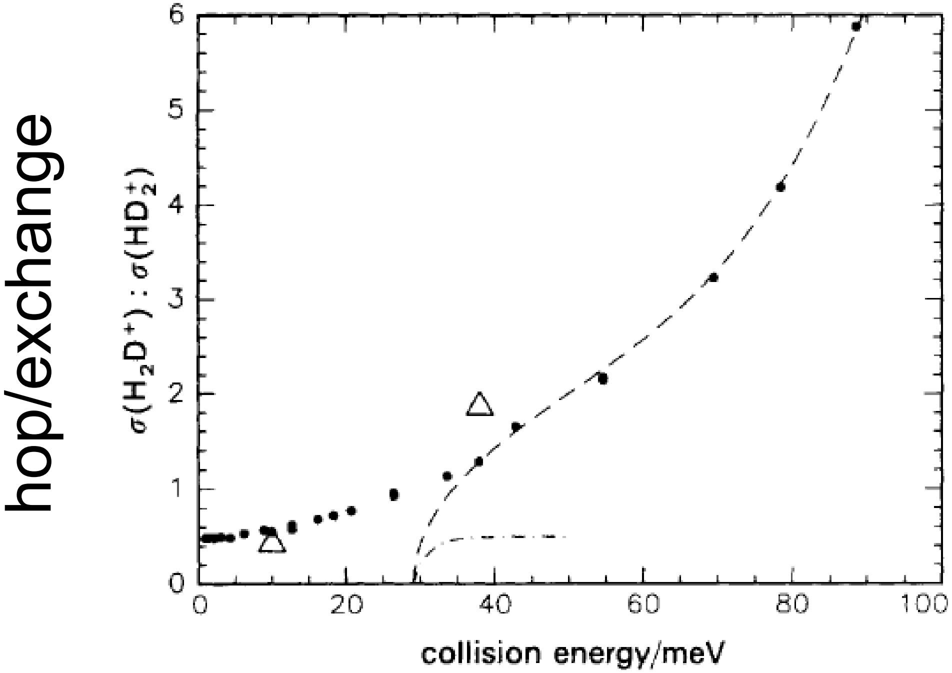
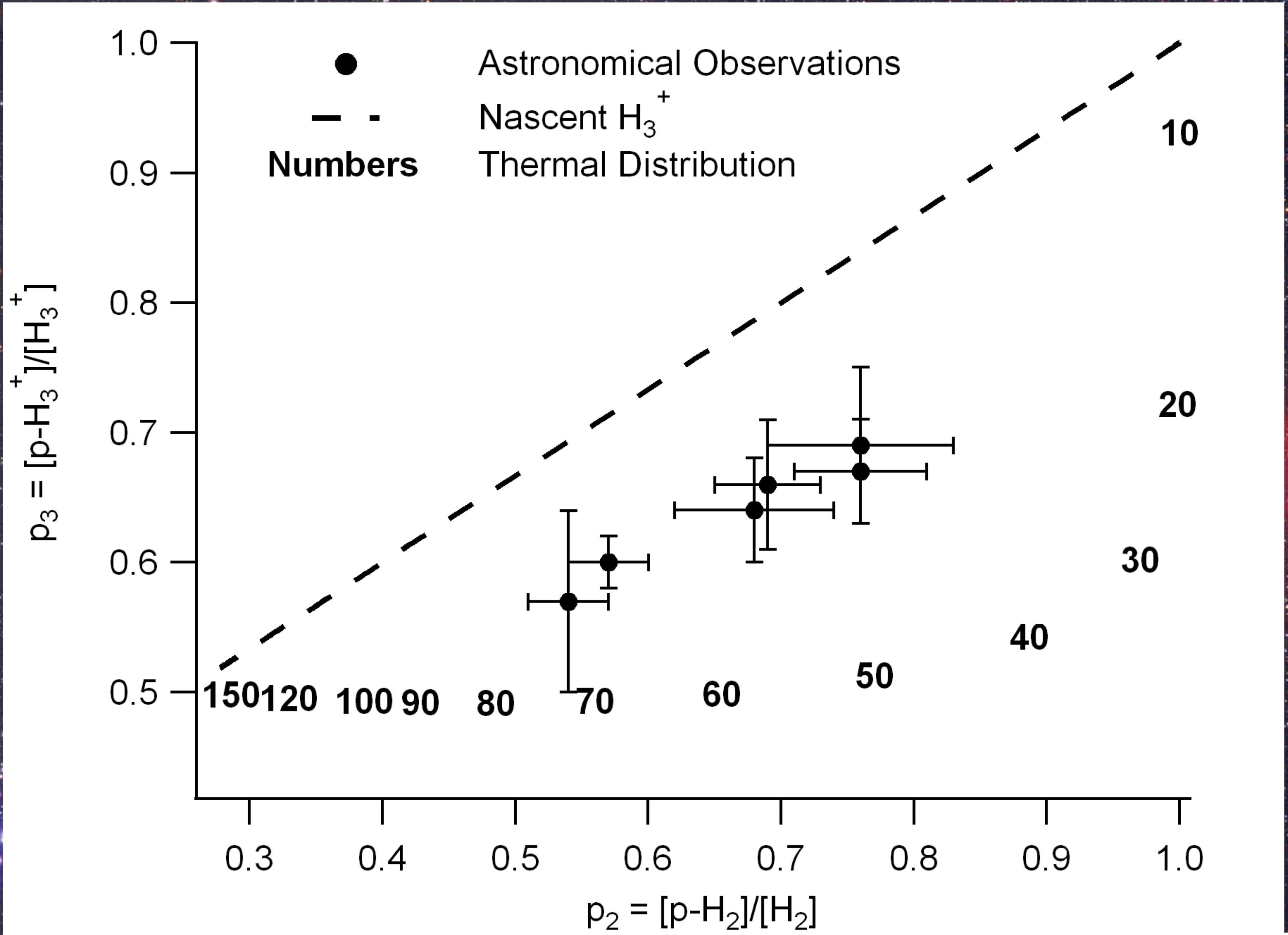


Fig. 10 Branching ratio $\sigma(H_2D^+) : \sigma(HD_2^+)$ for the two channels of the $D_3^+ + H_2$ reaction as a function of the collision energy measured with the merged beam apparatus with cold D_3^+ and an n-H_2 beam.

- Higher energy → hop dominant
- Lower energy → more statistical
- Endothermic!

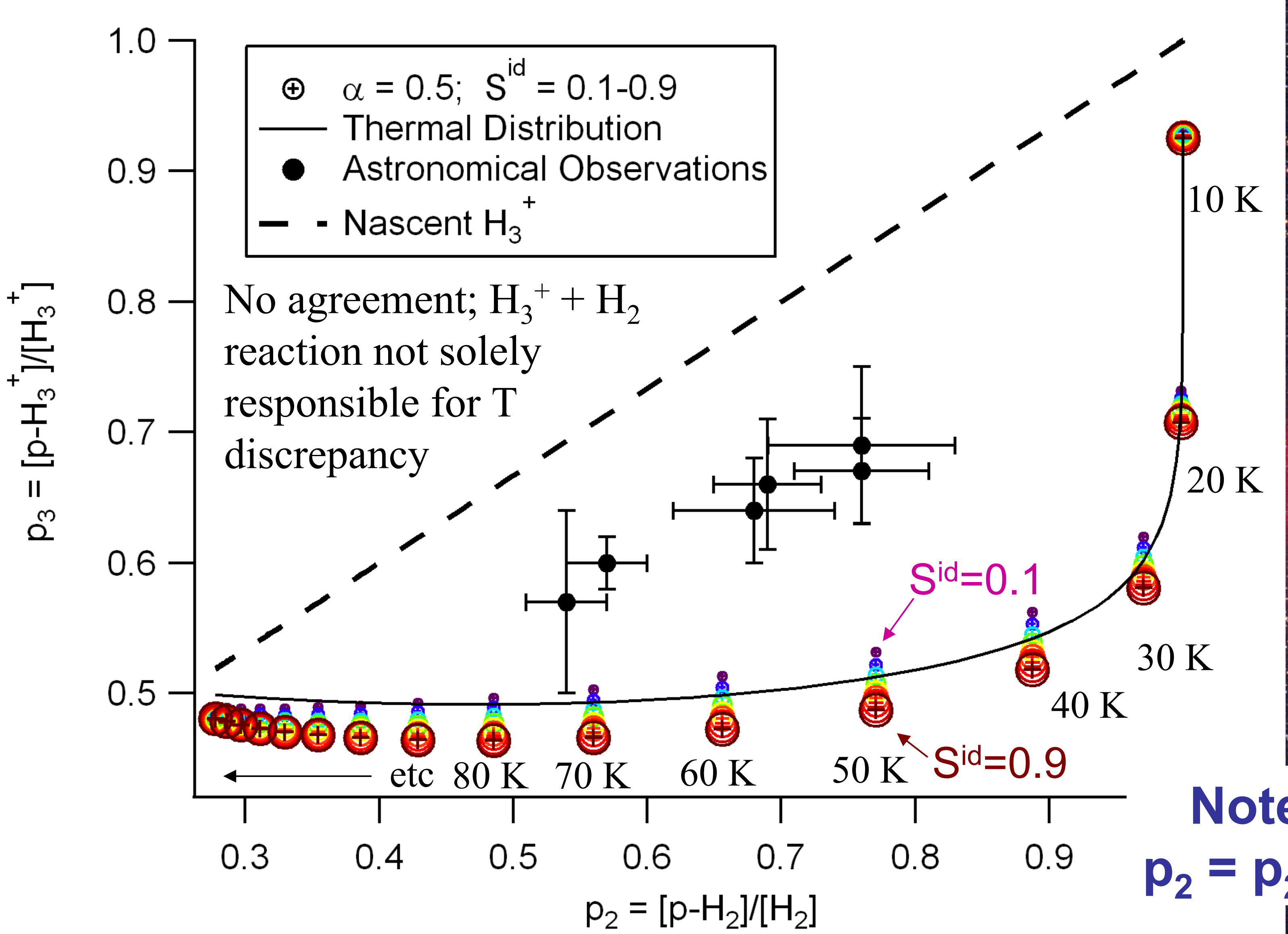
Dieter Gerlich,
J. Chem. Soc. Farad. Trans. 89, 2199 (1993)

New Astronomical Observations



K. Crabtree, N. Indriolo, H, Kreckel, B. A. Tom, & B. J. McCall, Astrophys. J., 729, 15 (2011)

$H_3^+ + H_2$ Reaction Results



No agreement; $H_3^+ + H_2$ reaction not solely responsible for T discrepancy

Note:
$p_2 = p_2(T)$

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Steady State Model Revisited

- Include formation and destruction reactions:

$$\frac{\mathrm{d}}{\mathrm{d}t}[p\text{-H}_3^+] = \boxed{k_1\left([p\text{-H}_2][p\text{-H}_2^+] + \frac{2}{3}[p\text{-H}_2][o\text{-H}_2^+] + \frac{2}{3}[o\text{-H}_2][p\text{-H}_2^+] + \frac{1}{3}[o\text{-H}_2][o\text{-H}_2^+]\right)}$$
$$+ \left\{(k_{oopo} + k_{oopp})[o\text{-H}_2] + (k_{oppo} + k_{oppp})[p\text{-H}_2]\right\}[o\text{-H}_3^+]$$
$$- \left\{(k_{pooo} + k_{poop})[o\text{-H}_2] + (k_{ppoo} + k_{ppop})[p\text{-H}_2]\right\}[p\text{-H}_3^+]$$
$$\boxed{-k_{e,p}[e^-][p\text{-H}_3^+]}$$

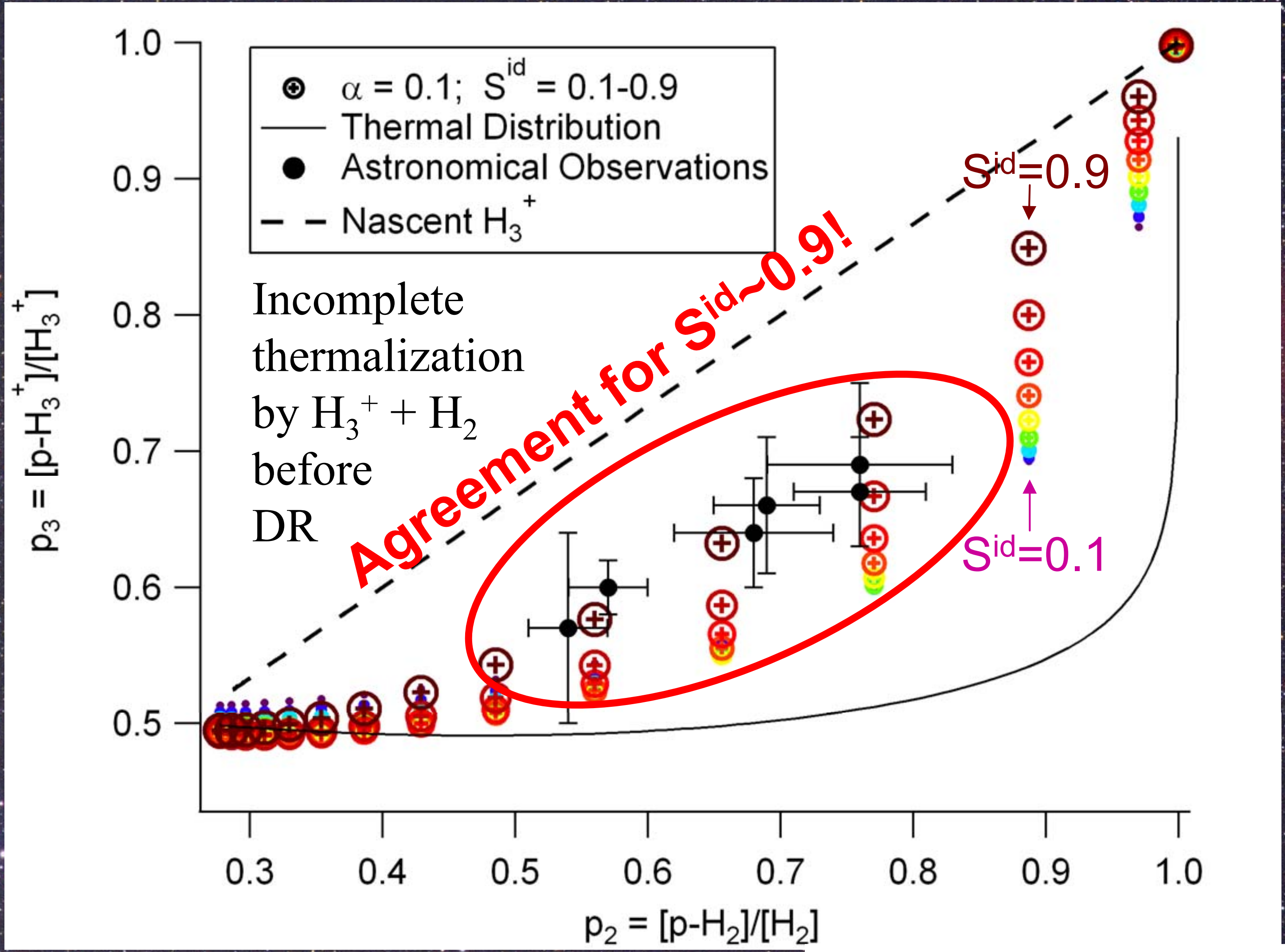
- Assume steady state, simplify:

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

K. Crabtree, N. Indriolo, H, Kreckel, B. A. Tom, & B. J. McCall, Astrophys. J., 729, 15 (2011)

Model Results for $k_{e,p} = k_{e,o}$

Rate Coefficients from McCall *et al.*, PRA 2004, 70, 052716



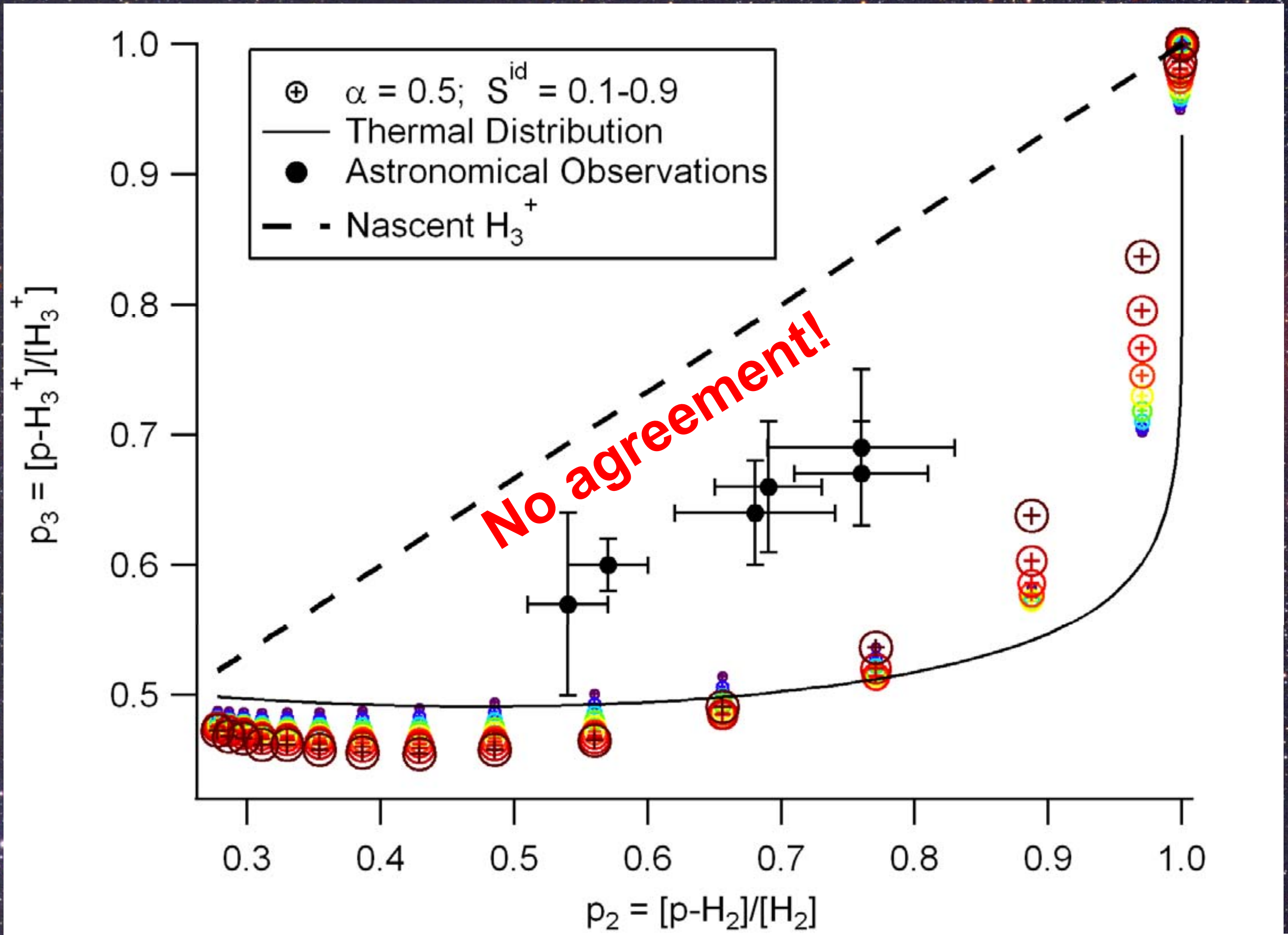
Incomplete thermalization by $H_3^+ + H_2$ before DR

Agreement for S^{id}~0.9!

K. Crabtree, N. Indriolo, H, Kreckel, B. A. Tom, & B. J. McCall, Astrophys. J., 729, 15 (2011)

Model Results for $k_{e,p} > k_{e,o}$

Rate Coefficients from dos Santos *et al.*, JCP 2007, 127, 124309



K. Crabtree, N. Indriolo, H, Kreckel, B. A. Tom, & B. J. McCall, Astrophys. J., 729, 15 (2011)

Future Work

- Experiments
  - – Cold o/p DR in storage ring (CSR?)
  - – $H_3^+ + H_2$ in 22-pole ion trap (MPIK, Cologne)
    - test low temperature model
    - measure S^{id}
- Observations (VLT)
  - – Additional sightlines
- Theory
  - – State-to-state model
  - – Quantum reactive scattering calculations?

Acknowledgments: Part 1

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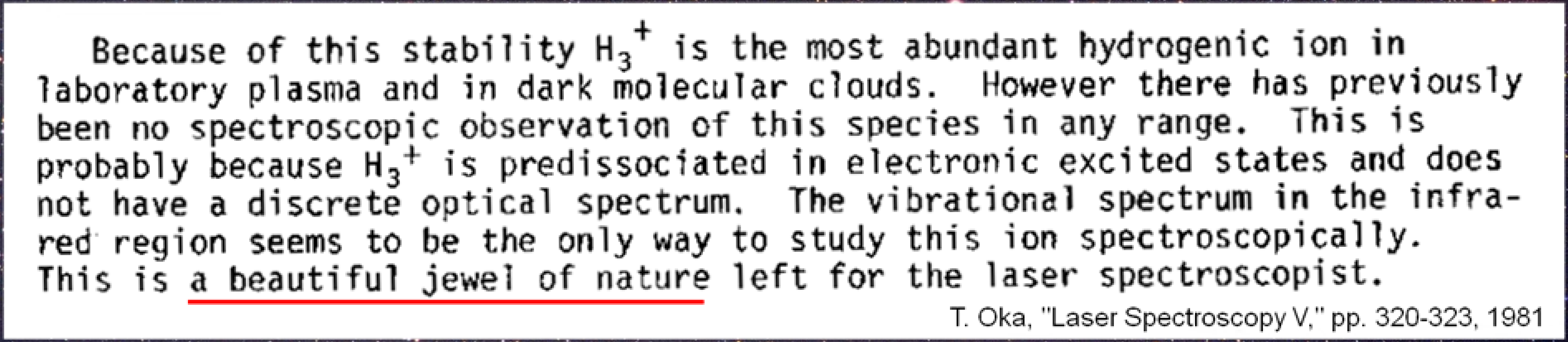
Acknowledgments: Part 2



Because of this stability H_3^+ is the most abundant hydrogenic ion in laboratory plasma and in dark molecular clouds. However there has previously been no spectroscopic observation of this species in any range. This is probably because H_3^+ is predissociated in electronic excited states and does not have a discrete optical spectrum. The vibrational spectrum in the infrared region seems to be the only way to study this ion spectroscopically. This is a beautiful jewel of nature left for the laser spectroscopist.

T. Oka, "Laser Spectroscopy V," pp. 320-323, 1981