

Dissociative Recombination of Cold H_3^+ (and its interstellar implications)

Ben McCall

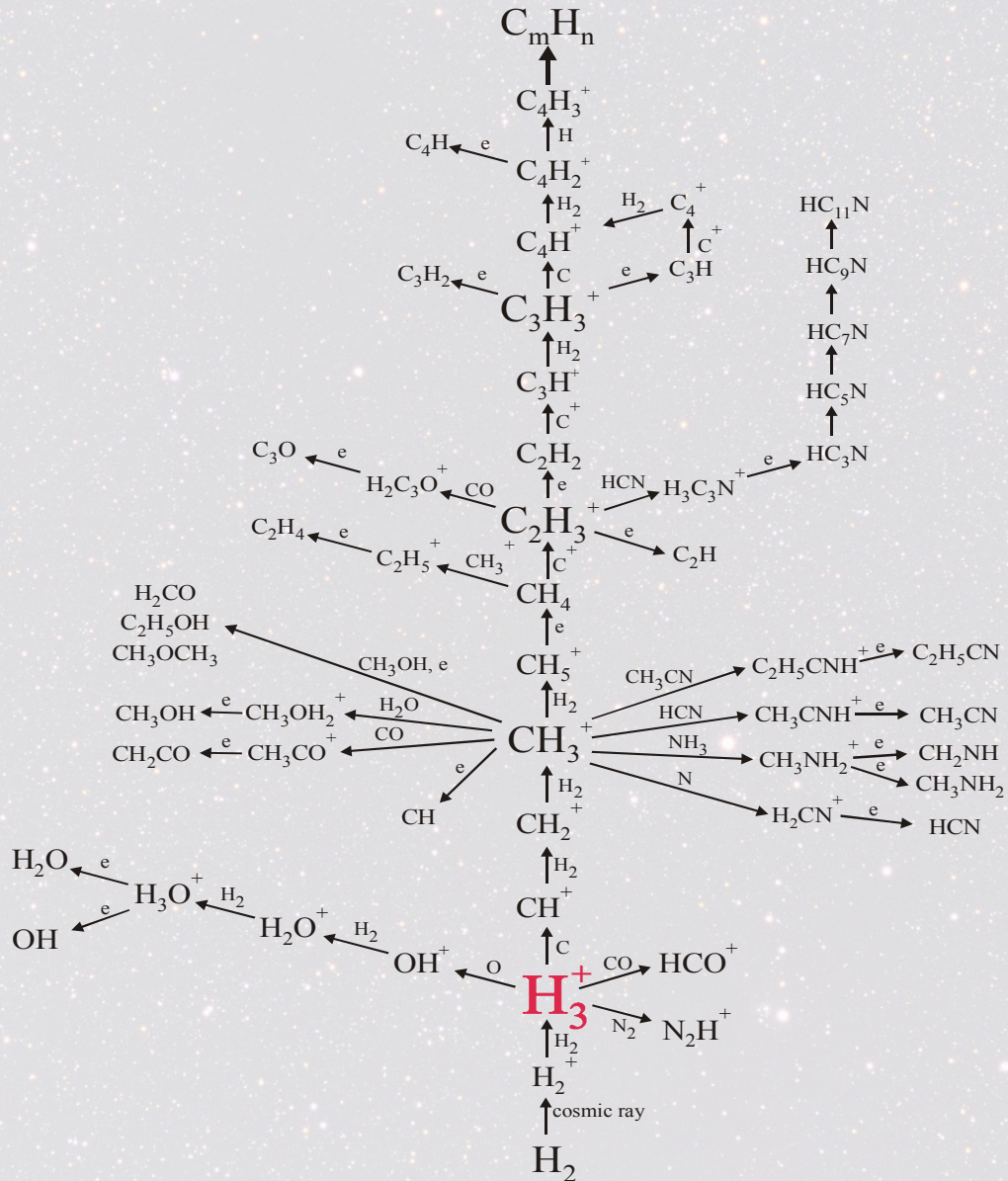
Department of Chemistry

Department of Astronomy

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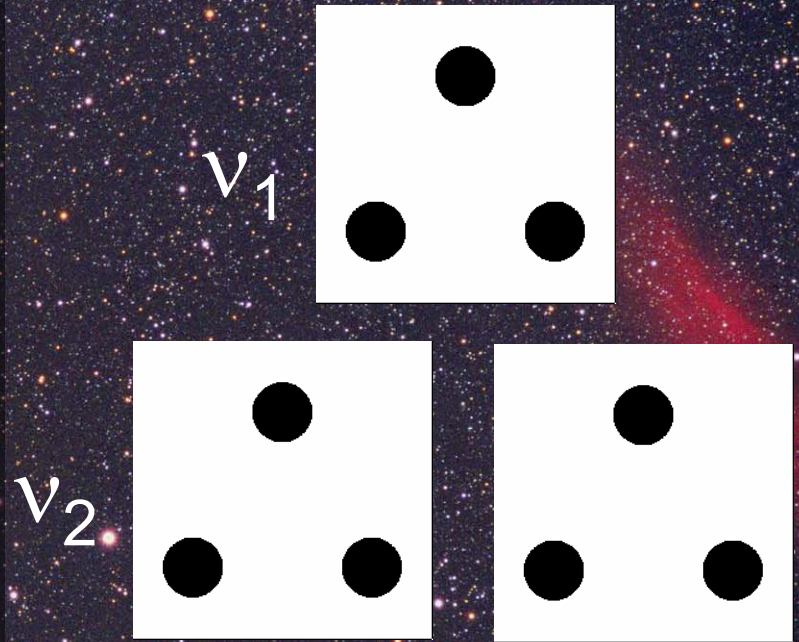
- ★ T. Oka (University of Chicago), T. R. Geballe (Gemini Observatory)
- ★ A. J. Huneycutt, R. J. Saykally (University of California at Berkeley)
- ★ N. Djuric, G. H. Dunn (University of Colorado & NIST)
- ★ J. Semaniak, O. Novotny (Świetokrzyska Academy, Poland)
- ★ A. Paal, F. Österdahl (Manne Siegbahn Laboratory)
- ★ A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, M. Larsson (Stockholm University)

H_3^+ : Cornerstone of Interstellar Chemistry



Observing Interstellar H_3^+

- Equilateral triangle
- “No” rotational spectrum
- “No” electronic spectrum
- Vibrational spectrum is only probe
- Absorption spectroscopy against background or embedded star



Interstellar Cloud Classification*

Dense molecular clouds:

- $\text{H} \rightarrow \text{H}_2$
- $\text{C} \rightarrow \text{CO}$
- $n(\text{H}_2) \sim 10^4 - 10^6 \text{ cm}^{-3}$
- $T \sim 20 \text{ K}$

Diffuse clouds:

- $\text{H} \leftrightarrow \text{H}_2$
- $\text{C} \rightarrow \text{C}^+$
- $n(\text{H}_2) \sim 10^1 - 10^3 \text{ cm}^{-3}$
– [$\sim 10^{-18} \text{ atm}$]
- $T \sim 50 \text{ K}$



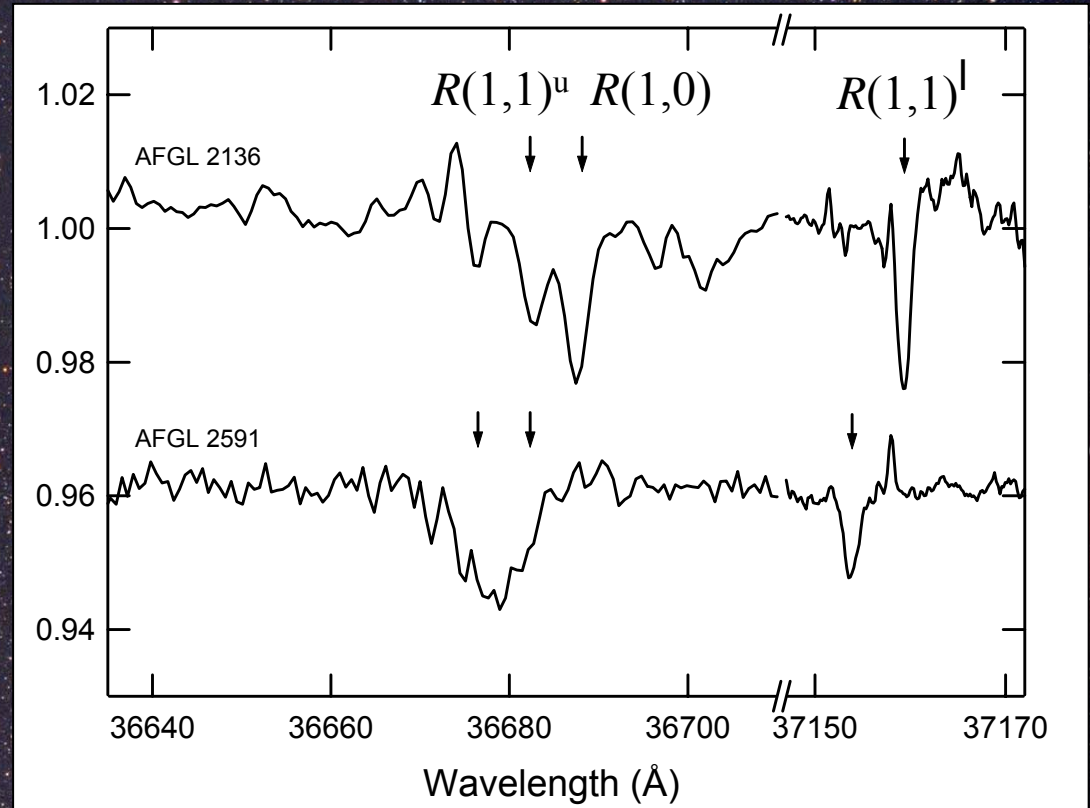
Barnard 68 (courtesy João Alves, ESO)

← ζ Persei

- Diffuse atomic clouds
– $\text{H}_2 \ll 10\%$
- Diffuse molecular clouds
– $\text{H}_2 > 10\%$ (self-shielded)

* Snow & McCall, *ARAA*, 2006 (in press)

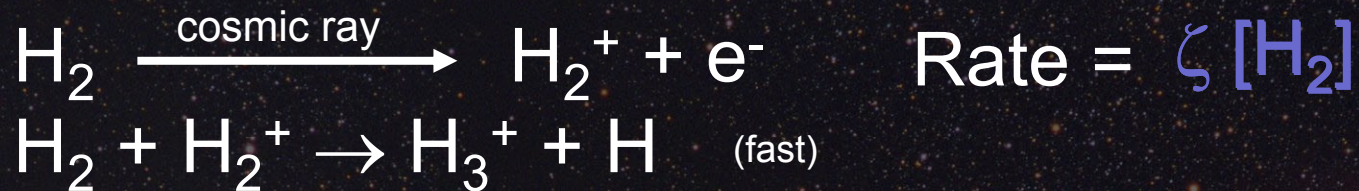
H₃⁺ in Dense Clouds



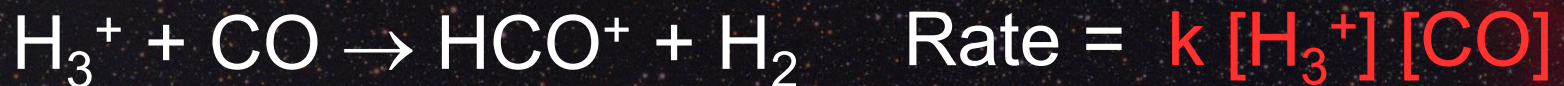
$$N(\text{H}_3^+) = 1-5 \times 10^{14} \text{ cm}^{-2}$$

Dense Cloud H_3^+ Chemistry

Formation



Destruction



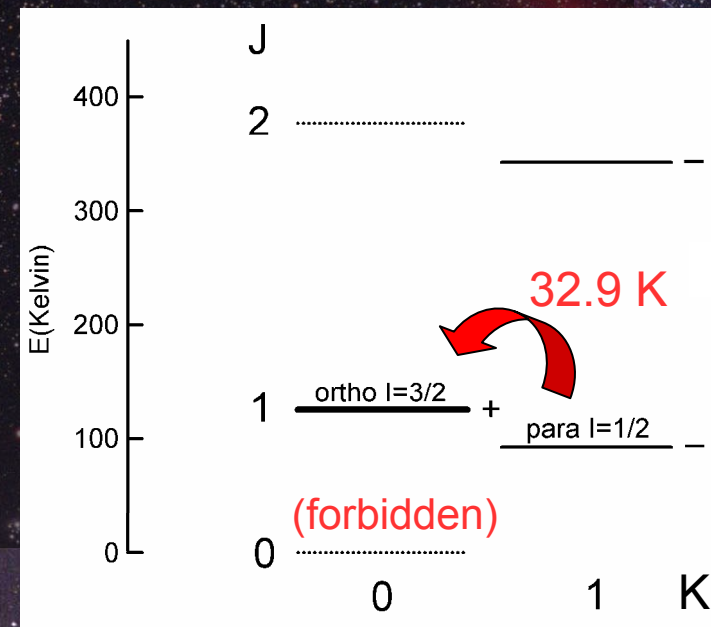
Steady State

$$= \frac{(3 \times 10^{-17} \text{ s}^{-1})}{(2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1})} \times (6700)$$
$$= 10^{-4} \text{ cm}^{-3}$$

Density Independent!

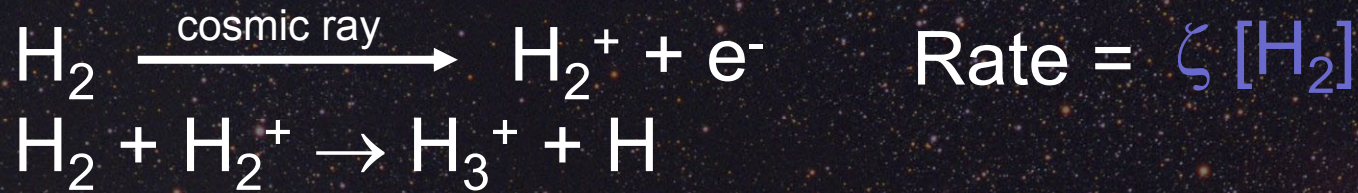
H_3^+ as a Probe of Dense Clouds

- Given $n(\text{H}_3^+)$ from model, and $N(\text{H}_3^+)$ from infrared observations:
 - path length $L = N/n \sim 3 \times 10^{18} \text{ cm} \sim 1 \text{ pc}$
 - density $\langle n(\text{H}_2) \rangle = N(\text{H}_2)/L \sim 6 \times 10^4 \text{ cm}^{-3}$
 - temperature $T \sim 30 \text{ K}$
- Unique probe of clouds
- Consistent with expectations
 - confirms dense cloud chemistry



Diffuse Molecular Cloud H_3^+ Chemistry

Formation



Destruction



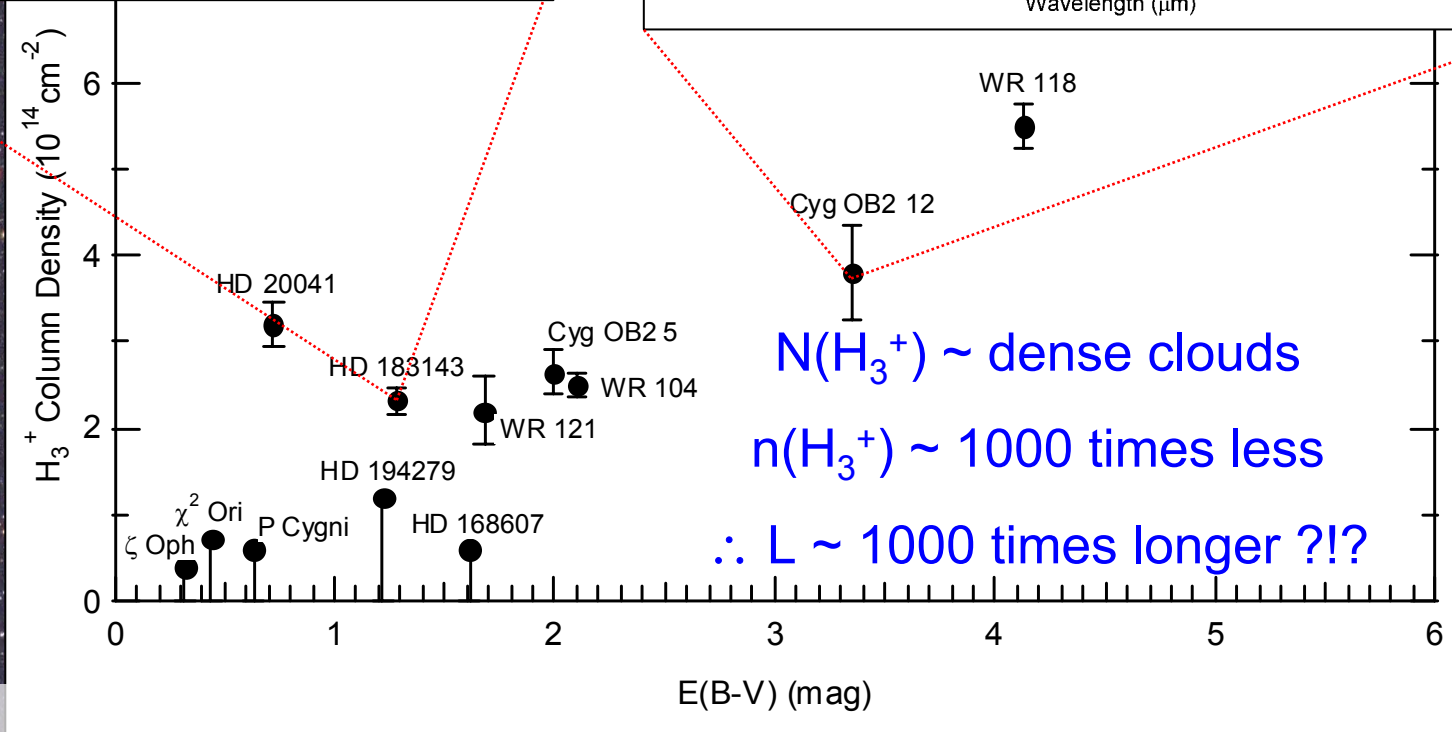
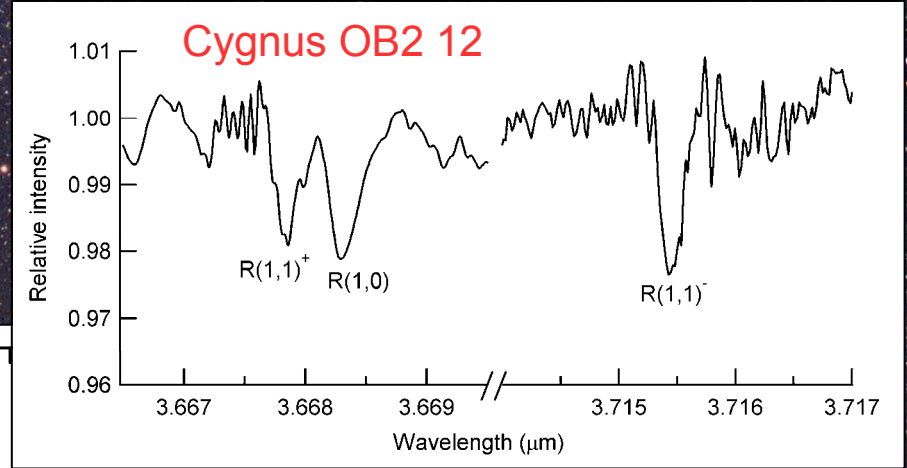
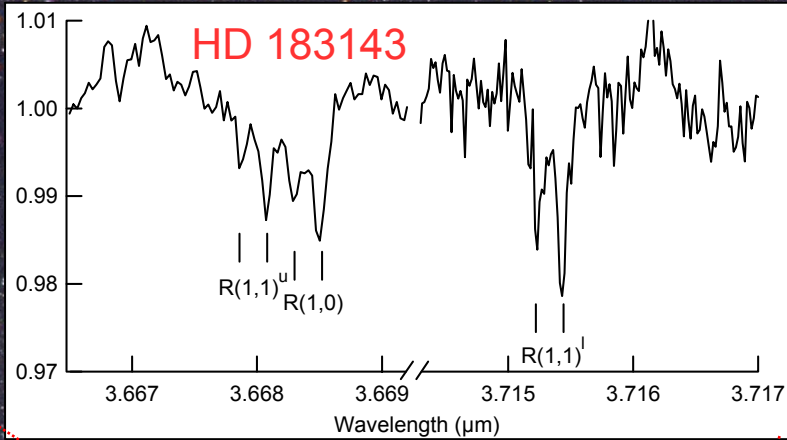
Steady State

$$[\text{H}_3^+] = \frac{\zeta [\text{H}_2]}{k_e [\text{e}^-]} = \frac{(3 \times 10^{-17} \text{ s}^{-1})}{(5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1})} \times (2400)$$

Density Independent!

10^3 times smaller than dense clouds!

Lots of H_3^+ in Diffuse Clouds!



Big Problem with the Chemistry!

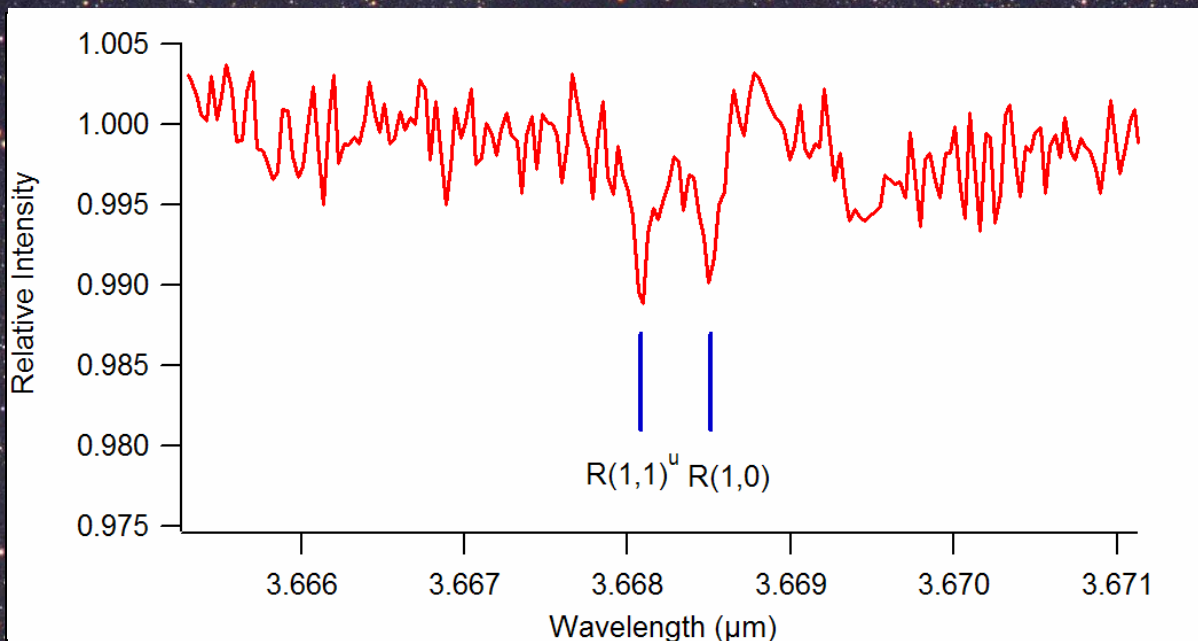
★ ~2 orders of magnitude!!

$$\text{Steady State: } [H_3^+] = \frac{\zeta}{k_e} \frac{[H_2]}{[e^-]}$$

To increase the value of $[H_3^+]$, we need:

- Smaller electron fraction $[e^-]/[H_2]$
- Smaller recombination rate constant k_e
- Higher ionization rate ζ

H₃⁺ toward ζ Persei



McCall, et al. Nature 422, 500 (2003)

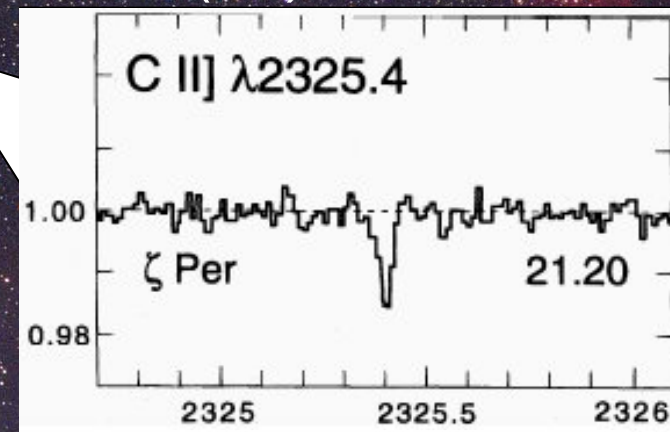
[e⁻]/[H₂]
not to blame

N(H₂) from Copernicus

ID	NAME	<i>l</i> ^{II}	<i>b</i> ^{II}	S. T.	E(B-V) mag.	<i>r</i> [pc]	log N(H ₂) [cm ⁻²]	log N(HI) [cm ⁻²]	log N(HI + H ₂) [cm ⁻²]
24398	ε Per	162	-17	B1 Ib	.33	394	20.67	20.81	21.20
24760	ε Per	157	-10	B0.5 III	.09	308	19.53	20.40	20.50
24912	ζ Per	160	-13	O7.5 IIIuf	.33	538	20.53	21.11	21.30
28497		209	-37	B1.5 Ve	.02	466	14.82	20.20	20.20
30614	α Cam	144	14	O9.5 Ia	.32	1164	20.34	20.90	21.09

Savage et al. ApJ 216, 291 (1977)

N(C⁺) from HST



Cardelli et al. ApJ 467, 334 (1996)

Big Problem with the Chemistry!

Steady State: $[H_3^+] = \frac{\zeta}{k_e} \frac{[H_2]}{[e^-]}$

To increase the value of $[H_3^+]$, we need:

- Smaller electron fraction $[e^-]/[H_2]$
- Smaller recombination rate constant k_e
- Higher ionization rate ζ

H₃⁺ Dissociative Recombination

Table II. Experimental rate constants of dissociative recombination of H₃⁺

k _e (in 10 ⁻⁷ cm ³ s ⁻¹)	Method ^a	Authors	Year
25 ^b	MA	Biondi, Brown ¹⁹	1949
20 ^b	MA	Richardson, Holt ²¹	1951
3.4 ^b	MA	Varnerin ²²	1951
<0.3 ^b	MA	Persson, Brown ²³	1955
2.3	MA/MS	Leu, Biondi, Johnsen ²⁴	1973
2.5	IB	Peart, Dolder ²⁵	1974
2.1	MB	Auerbach et al. ²⁶	1977
1.5	IT	Mathur, Khan, Hasted ²⁷	1978
4.2	MB	McGowan et al. ²⁸	1979
1.6	FA	MacDonald, Biondi, Johnsen ²⁹	1984
<0.2	FALP	Adams, Smith, Alge ³⁰	1984
≤0.0001	FALP ^c	Smith, Adams ³¹	1987
0.2	MB	Hus et al. ³²	1988



Low rate widely believed

- Chemical models (van Dishoeck & Black)
- Grain neutralization models

4.2. Observations of H_3^+

The detection of H_3^+ in diffuse gas has had some ironic twists. Chemical models employed in the original discussion of grain neutralization (Lepp & Dalgarno 1988a; Lepp et al. 1988) were poisoned by inclusion of the then-fashionable assumption of a very small low-temperature gas-phase recombination rate for H_3^+ . This led the authors to a gross overprediction of $N(H_3^+)$, which they suggested would be observable; their suggestion seems not to have been acted upon in a timely manner, thus depriving the world of a seeming corroboration of the incorrect recombination rate. Instead, the recombination rate was corrected (Amano 1988; Larsson et al. 1993; Sundstrom et al. 1994), lowering expectations for the presence of H_3^+ , and, by the time it was widely detected, this was considered surprising. With substantial fluctuations, $N(H_3^+)/E_{B-V} \approx$



IS THE DISSOCIATIVE RECOMBINATION OF H_3^+ REALLY SLOW? A NEW SPECTROSCOPIC MEASUREMENT OF THE RATE CONSTANT

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Herzberg Institute of Astrophysics, National Research Council

Received 1987 December 14; accepted 1988 March 14

ABSTRACT

The decay of an infrared absorption signal of H_3^+ was measured as a function of time. The decay curve was analyzed and found to fit very well to the form expected for a recombination decay. The signal decay is attributed to the dissociative recombination with electrons and the rate constant was determined to be $(1.8 \pm 0.2) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, which disagrees with the recent value ($\leq 2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) obtained with the flowing afterglow/Langmuir probe (FALP) technique.

Subject headings: interstellar: molecules — molecular processes

Adams, Smith, and Algel (1984), on the other hand, obtained a much smaller value for the rate constant ($\leq 2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) by using the flowing afterglow/Langmuir probe (FALP) technique, and later they reached the conclusion that the rate is immeasurably small ($\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) (Adams and Smith 1987). A theoretical calculation also suggested a small rate constant (Michels and Hobbs 1984). Also very recently Hus *et al.* (1988) repeated the merged beam experiments and obtained the cross section which is about an order of magnitude smaller than the previous value (Auerbach *et al.* 1977). These authors attributed the faster rate constants previously obtained to vibrationally excited H_3^+ . Considering the astrophysical impact of these low values, we have carried out direct measurements of the decay of the infrared absorption signals of H_3^+ , which can monitor the ion abundance in a particular vibration-rotation state without ambiguity.

Amano's Results

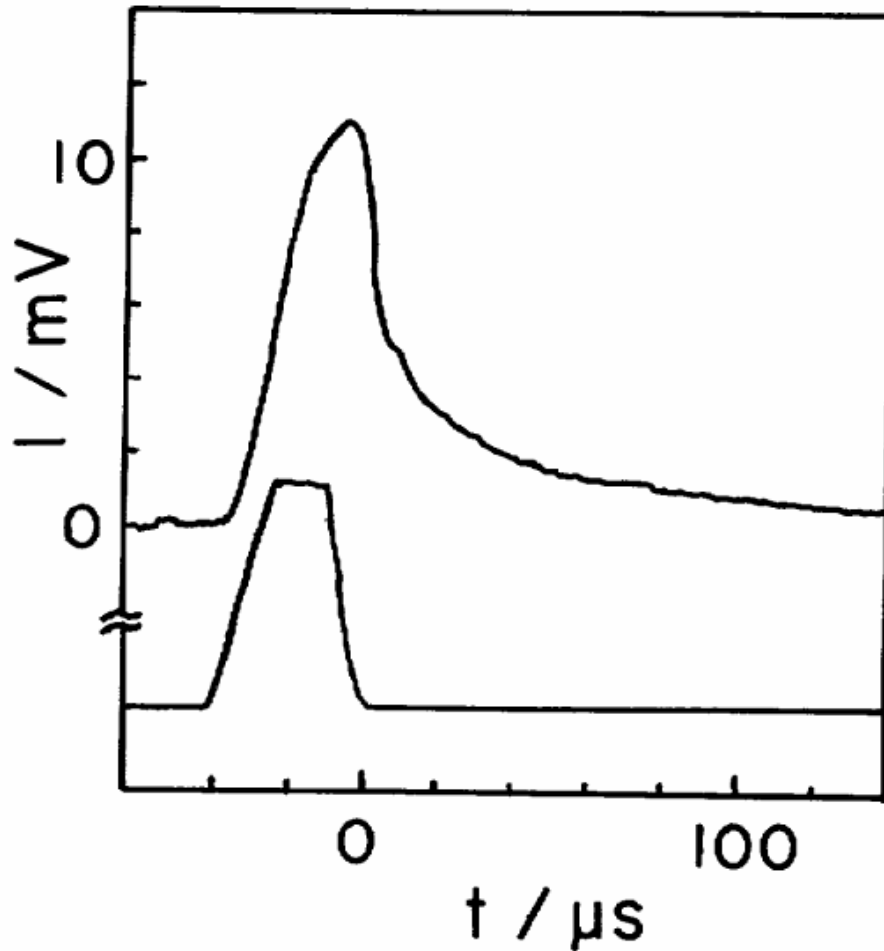


FIG. 2.—The transient absorption signal of the $R_3(3)$ line of H_3^+ (top trace) and the discharge current (bottom trace). The hydrogen pressure was 500 mtorr.

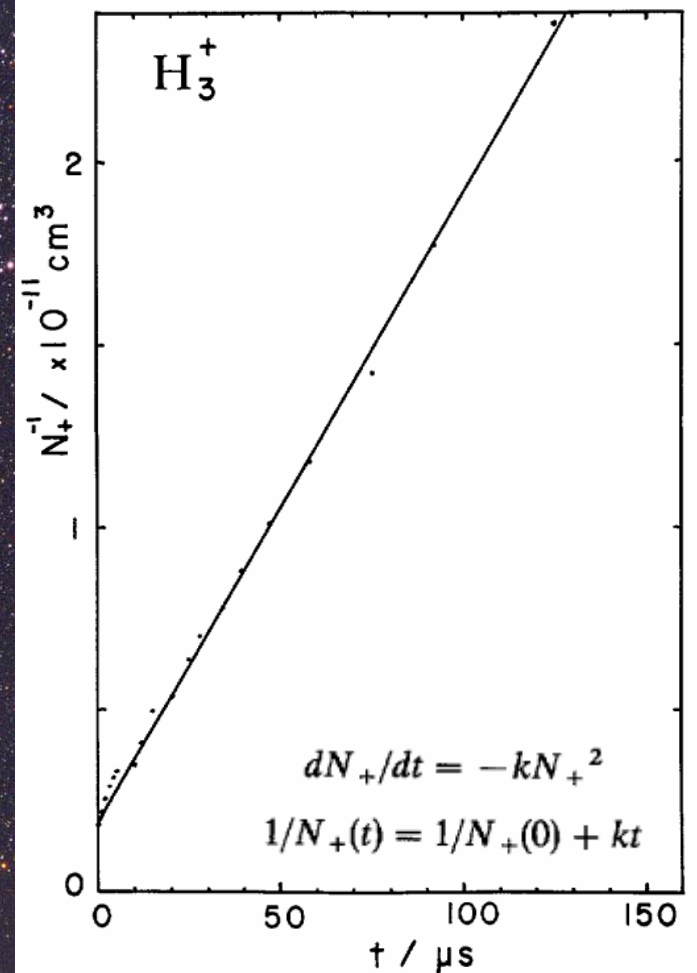


FIG. 3.—The $1/N_+(t)$ vs. t plot of a decay signal of H_3^+ . The origin of the time is taken at the point where the current falls to zero completely, as shown in Fig. 2. The ion concentration at $t = 0$ is measured to be $3 \times 10^{12} \text{ cm}^{-3}$ in this example. The peak concentration is larger than that at $t = 0$ by about 30%, as seen from Fig. 2.

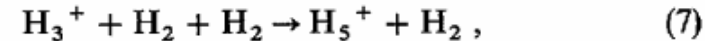
Amano's Analysis

IV. DISCUSSION

The rate constant was found to be unchanged in cathodes with different diameters, indicating that the ambipolar diffusion process is not a dominant depletion process. Our tech-

Since the dissociative recombination rate constant for H_3^+ obtained in the present experiment was very different from that obtained by Smith and his co-workers (Adams, Smith, and Alge 1984; Smith and Adams 1984; Adams and Smith 1987), we carefully checked whether any serious impurity (N_2 is the most serious one) might cause the decay of H_3^+ faster than the dissociative recombination with electrons. This possibility was ruled out for two reasons. First, by monitoring the signal of HN_2^+ in a "pure" hydrogen discharge, we concluded that the abundances of N_2 was $2 \times 10^{11} \text{ cm}^{-3}$ at most and was negligibly small. Second, the decay curves fit very well to the recombination decay curve given by equation (3). If constant leak or back diffusion causes the depletion of H_3^+ , the decay should be exponential. Also if the hydrogen gas contains noncondensable impurities like CH_4 which react with H_3^+ , the decay rate should show a linear dependence on the hydrogen pressure.

The dissociative recombination of H_5^+ is known to be rapid ($k_e = 3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$) (Leu, Biondi, and Johnsen 1973). Small amount of H_5^+ may exist, although the spectroscopic detection of this species has never been successful under our experimental conditions. The dominant formation process of H_5^+ is



and the rate constant of this reaction was measured to be $9 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$ (Hiraoka and Kebarle 1973), which gives the rate for the reaction (7) to be about $1 \times 10^4 \text{ s}^{-1}$ at the hydrogen pressure of 1 torr. This rate is too slow to explain the decay observed in this investigation. Also if this process (7) is dominant, then the decay rate should have the hydrogen pressure dependence.

Smith and co-workers (Adams, Smith, and Alge 1984; Smith and Adams 1984) argued that the H_3^+ in the ground vibrational state does not react with electrons and the fast decay obtained previously might have been caused by vibrationally excited H_3^+ . Our spectroscopic measurements are state specific. The absorption signal measured in the present experiment monitored the population decay of the $J = 3, K = 3$ rotational level in the ground vibrational state. In the pressure range of our experiments, the rotational equilibration is completed in a few microseconds after the discharge is terminated. Also the vibrational temperature is low and the population of the first excited vibrational state ($v_2 = 1$) is estimated not to exceed 1% and therefore the effect of the vibrational relaxation is negligible. We plan further measurements of the rate constant of H_3^+ and other ions at lower temperatures.

Amano 1990

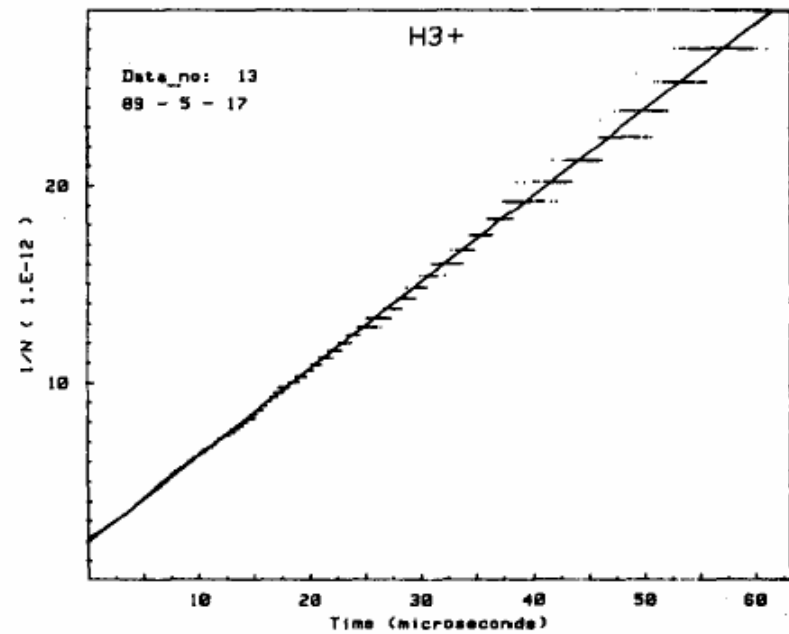
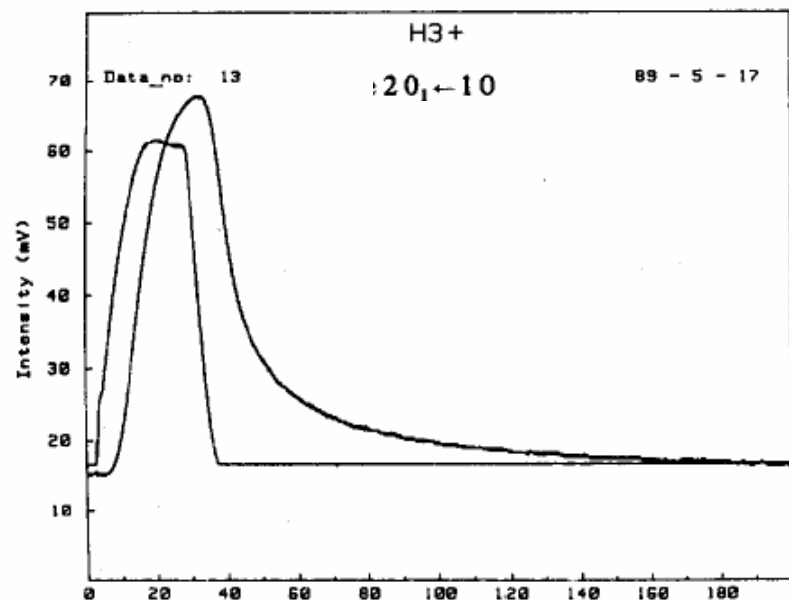


TABLE I. The dissociative recombination rate coefficients of H_3^+ in the ground vibrational state (in units of $10^{-7} \text{ cm}^3 \text{ s}^{-1}$).

J, K	110 K	210 K	273 K
1, 0	4.1(2) ^a	2.5(1)	1.72(5)
1, 1	4.1(1)	2.7(2)	1.77(10)
2, 2	4.6(4)	2.4(2)	1.85(6)
3, 3	4.5(5)	2.6(2)	1.91(7)
4, 4	...	2.2(2)	1.9(4)

^a Standard deviation in units of the last quoted digits

if any. Moreover, because the rotational relaxation is much faster than the recombination decay, only the rotationally averaged rate coefficient is possible to be observed.

CONCLUSION

Our spectroscopic measurements have clearly established that the dissociative recombination rate coefficient of H_3^+ in the ground state is not as small as advocated by Smith and co-workers, being in good agreement with the results obtained with the microwave afterglow and other techniques. Measurements have been extended to HN_2^+ and

H₃⁺ Dissociative Recombination

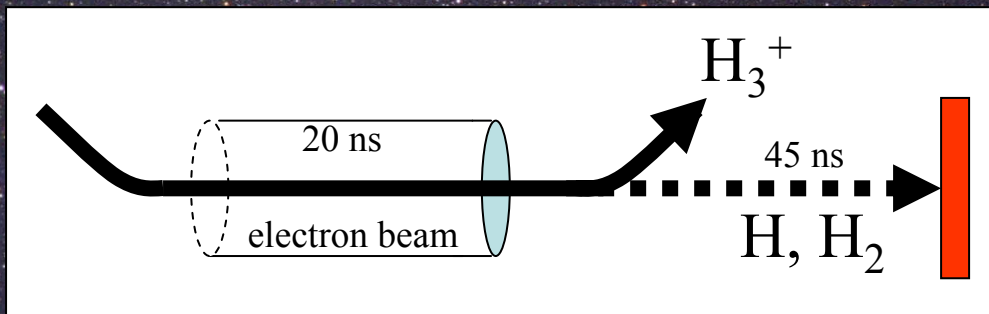
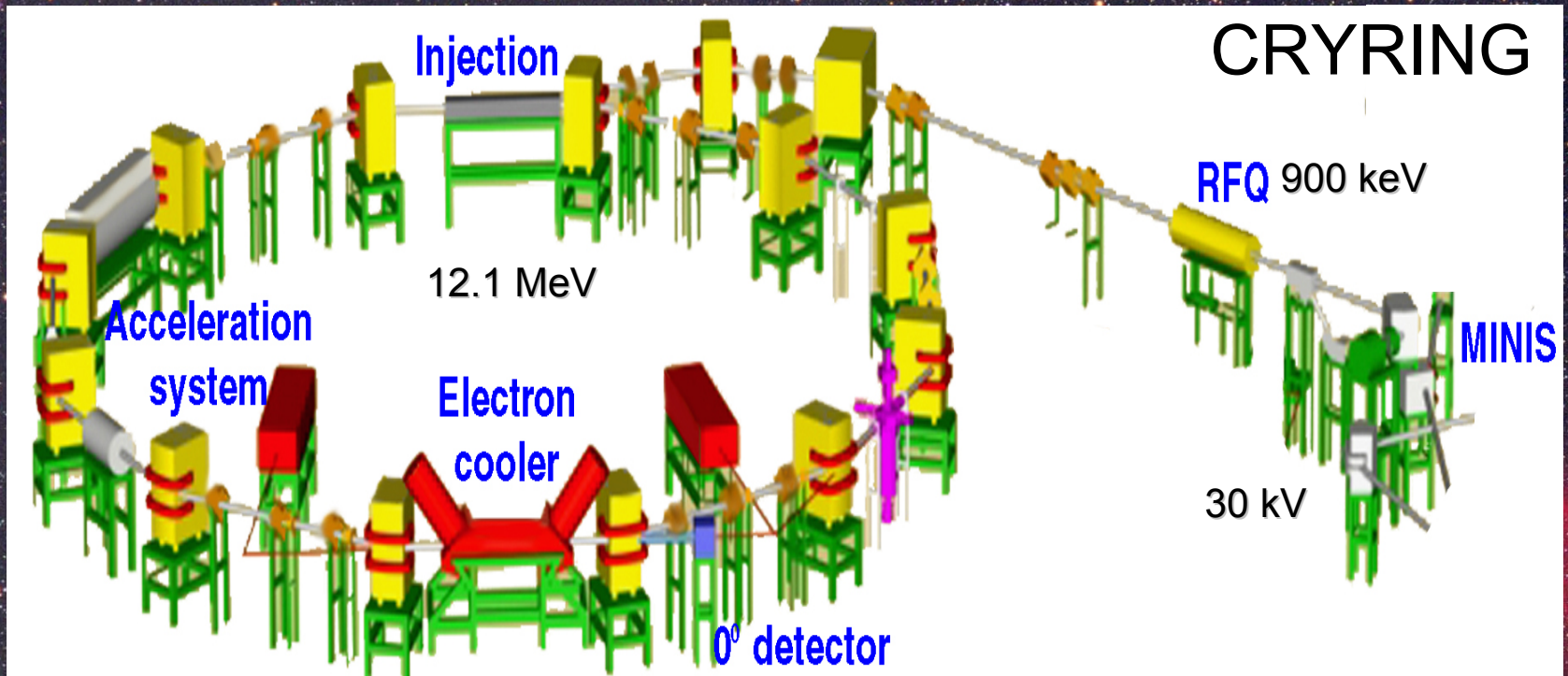
Table II. Experimental rate constants of dissociative recombination of H₃⁺

1.6	FA	MacDonald, Biondi, Johnsen ²⁹	1984
<0.2	FALP	Adams, Smith, Alge ³⁰	1984
≤0.0001	FALP ^c	Smith, Adams ³¹	1987
0.2	MB	Hus et al. ³²	1988
1.8	IR	Amano ³³	1988
≤0.0001	FALP	Adams, Smith ³⁴	1989
≤0.001	FALP	Smith, Adams, Ferguson ³⁵	1990
0.2	MB	Yousif et al. ³⁶	1991
1.5	FALP/MS	Canosa et al. ³⁷	1992
0.1~0.2	FALP	Smith, Španel ³⁸	1993
1.15	SR ^d	Larsson et al. ³⁹	1993
<2	IR/MS	Féher, Rohrbacher, Maier ⁴⁰	1994
	FALP	Gougousi, Johnsen, Golde ⁴¹	1995
0.78	FALP/MS	Laubé et al. ⁴²	1998
<0.13	ISA	Glosík et al. ⁴³	2000
<0.03	ISA	Glosík ⁴⁴	2001

Oka (2003)

- Theory unreliable (until recently)...
- Still not measuring H₃⁺ in ground rotational states

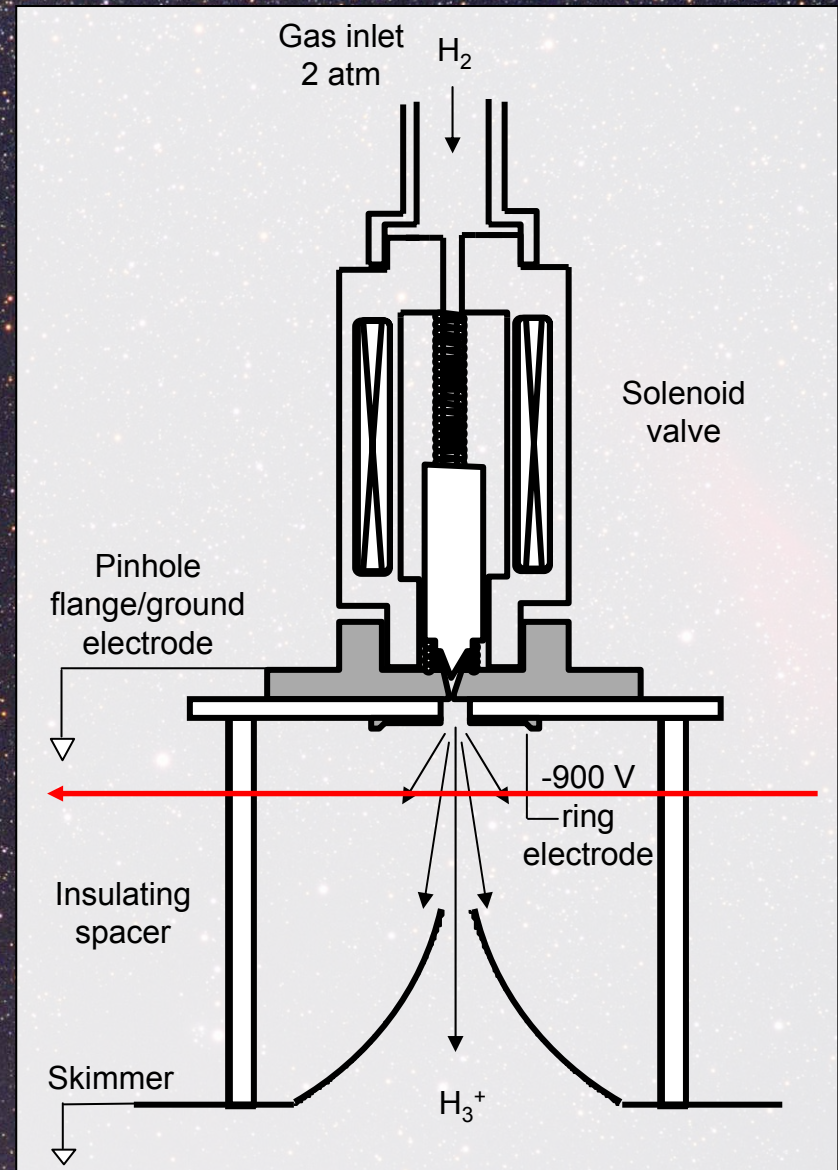
Storage Ring Measurements



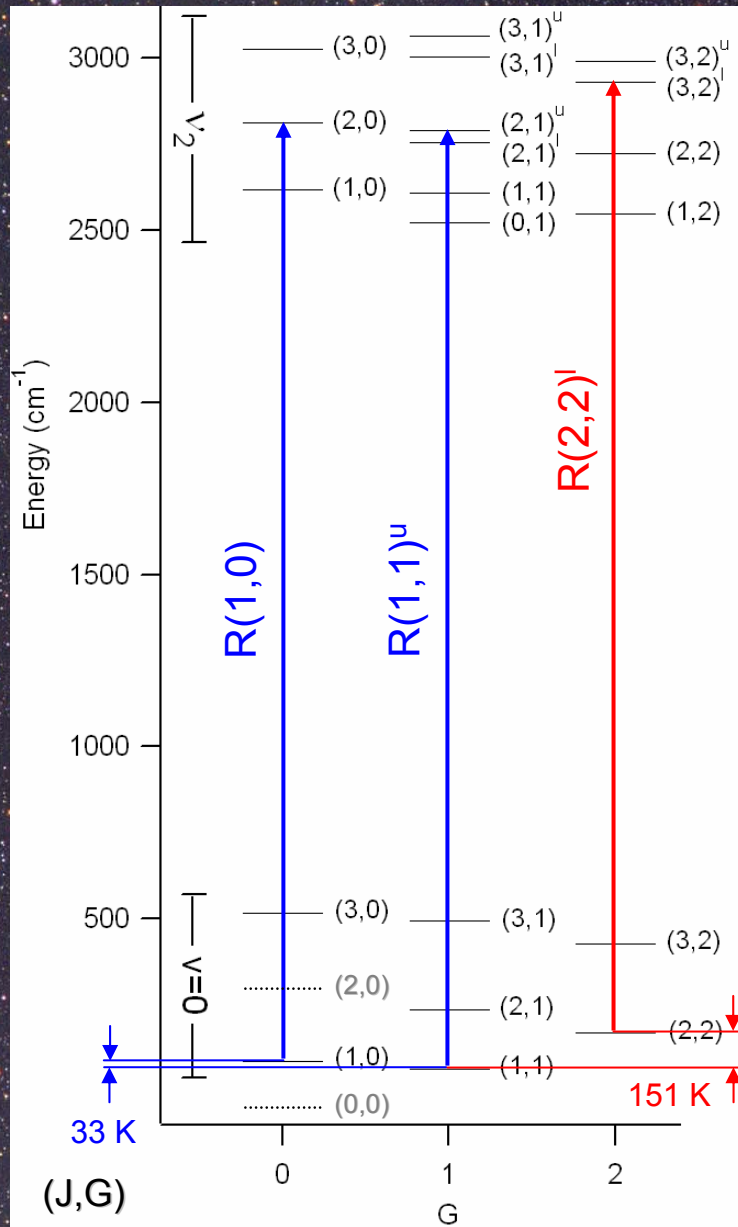
- + Very simple experiment
- + Complete vibrational relaxation
- + Control H₃⁺ – e⁻ impact energy
- Rotationally hot ions produced
- “No” rotational cooling in ring

Supersonic Expansion Ion Source

- Similar to sources for laboratory spectroscopy in many groups
- Pulsed nozzle design
- Supersonic expansion leads to rapid cooling
- Discharge from ring electrode downstream
- Spectroscopy used to characterize ions
- Skimmer employed to minimize arcing to ring



H₃⁺ Energy Level Structure

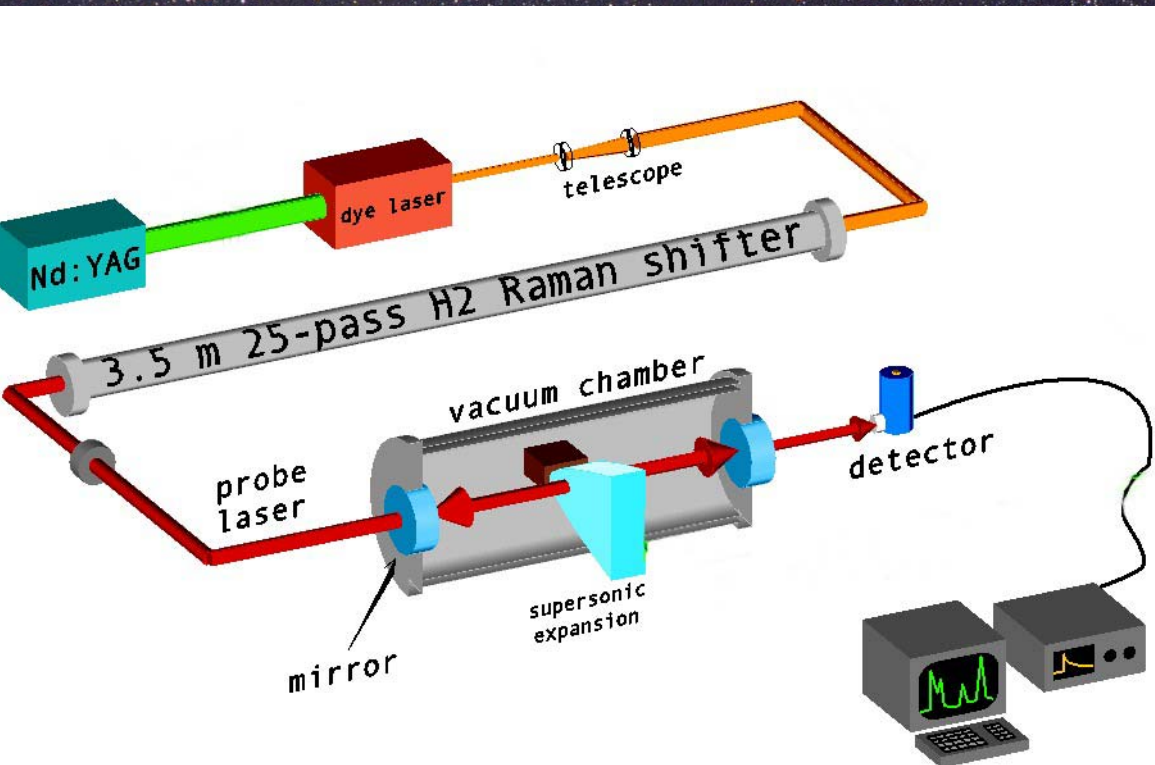


probe of temperature

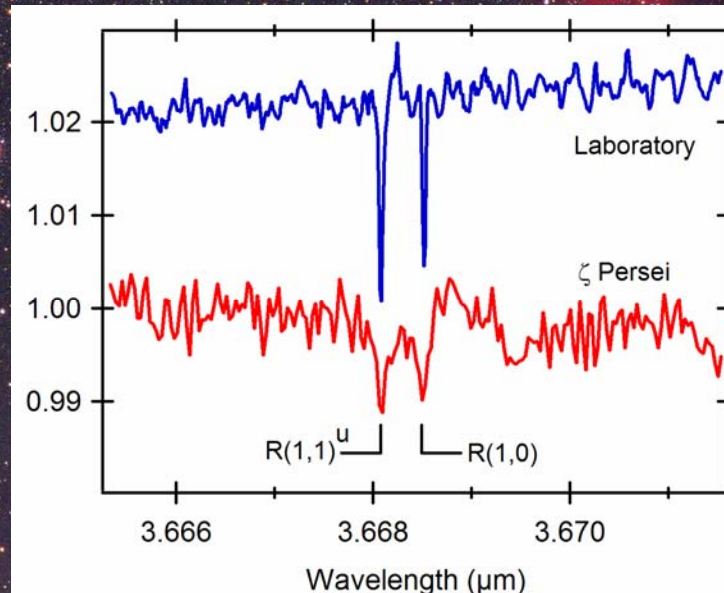
not detected

Spectroscopy of H_3^+ Source

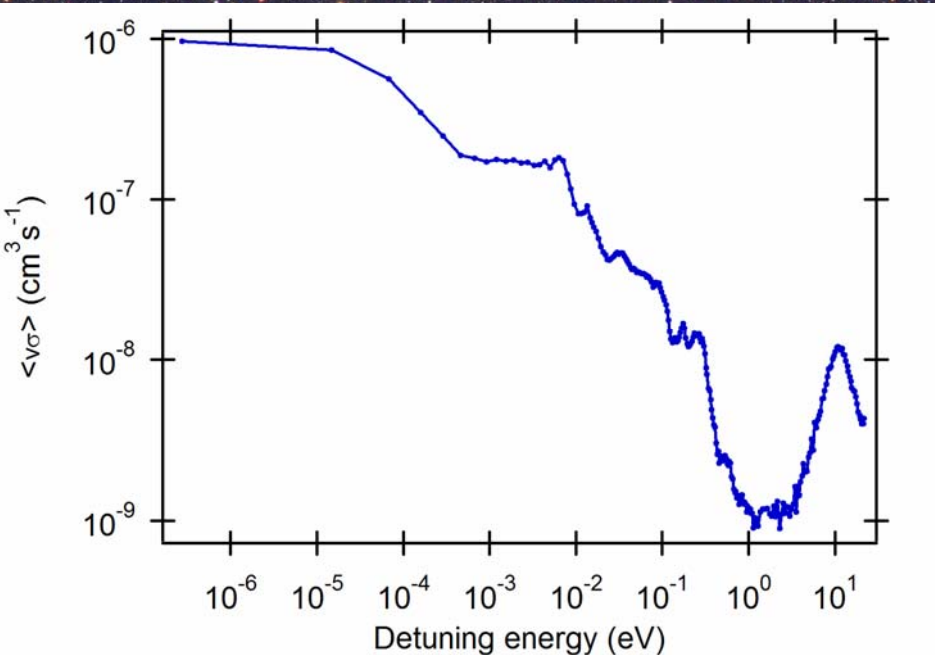
Infrared Cavity Ringdown Laser
Absorption Spectroscopy



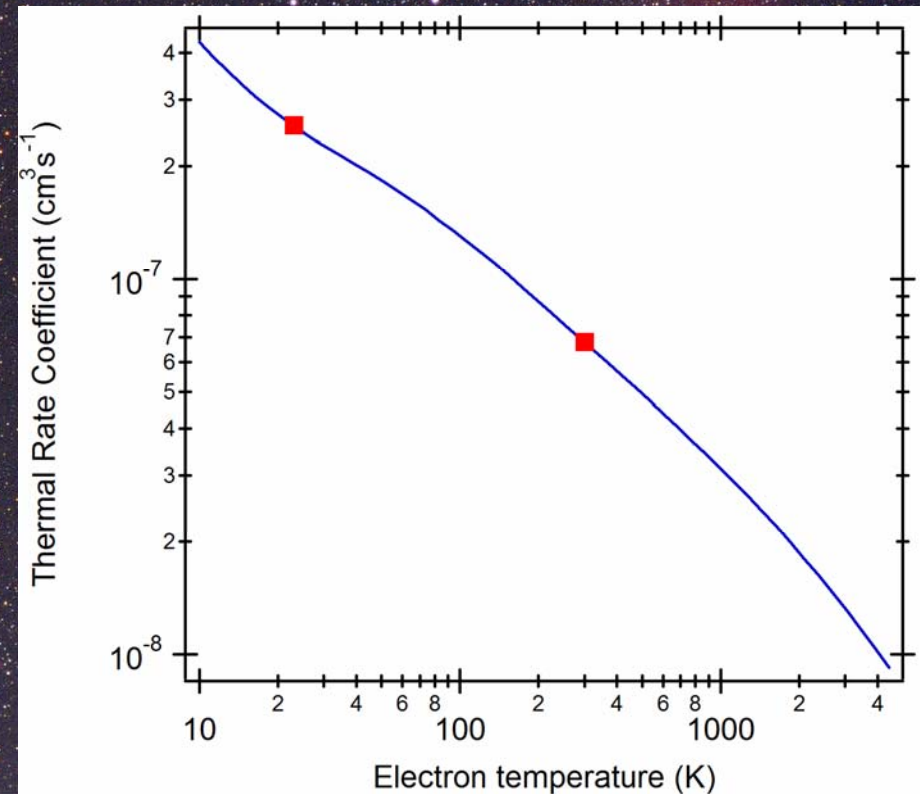
- Confirmed that H_3^+ produced is rotationally cold, as in interstellar medium



CRYRING Results



- Considerable amount of structure (resonances) in the cross-section
- $k_e = 2.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$
- Factor of two smaller



Recent Theoretical Work

VOLUME 90, NUMBER 13

PHYSICAL REVIEW LETTERS

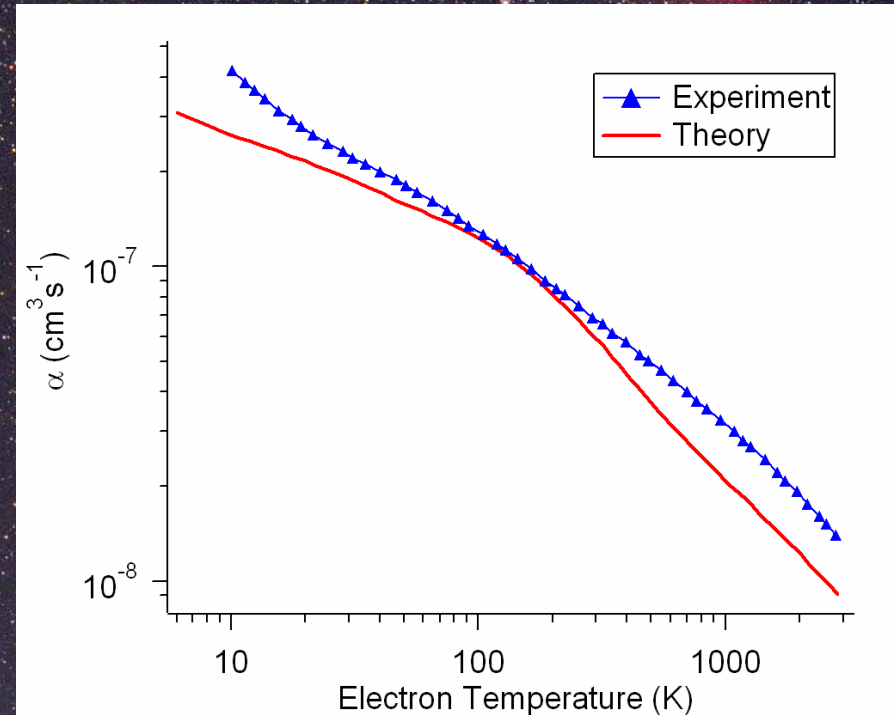
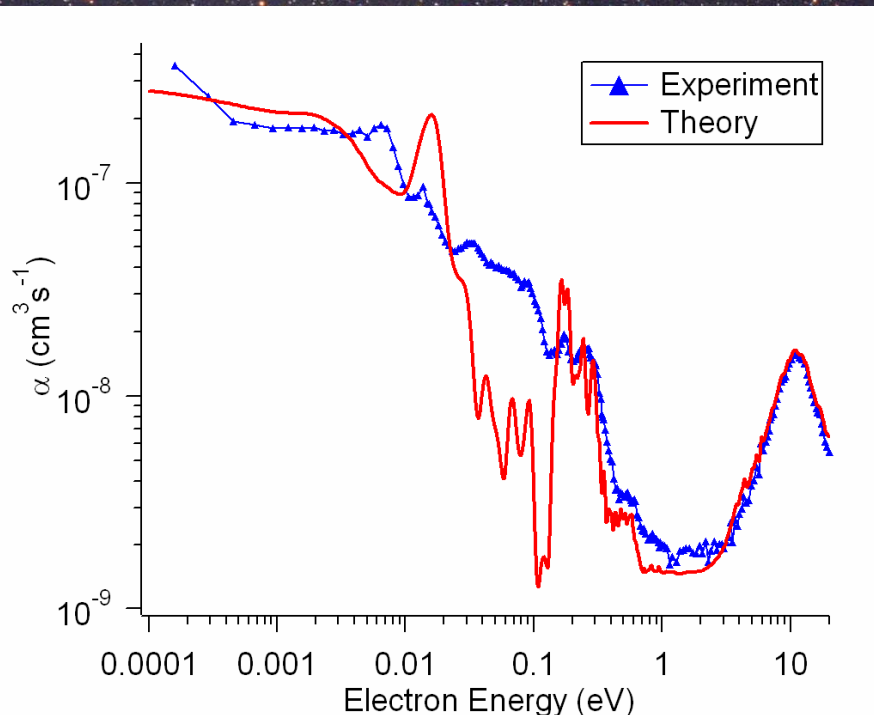
week ending
4 APRIL 2003

Theory of Dissociative Recombination of D_{3h} Triatomic Ions Applied to H_3^+

Viatcheslav Kokoouline and Chris H. Greene

Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440

(Received 3 December 2002; published 3 April 2003)



Recent TSR Results

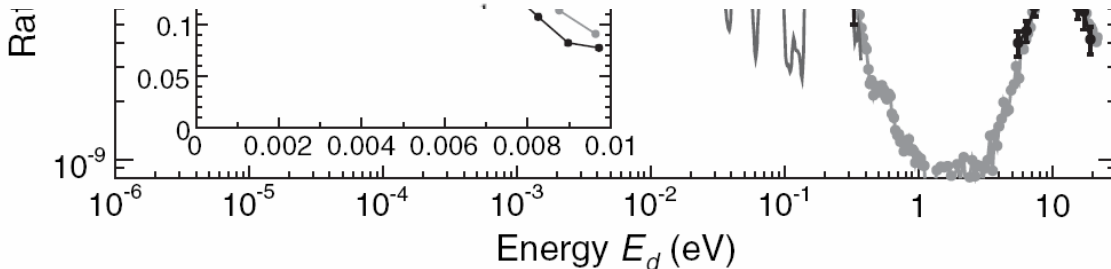
PRL **95**, 263201 (2005)

PHYSICAL REVIEW LETTERS

week ending
31 DECEMBER 2005

High-Resolution Dissociative Recombination of Cold H_3^+ and First Evidence for Nuclear Spin Effects

H. Kreckel,¹ M. Motsch,¹ J. Mikosch,^{1,2} J. Glosík,³ R. Plašil,³ S. Altevogt,¹ V. Andrianarijaona,¹ H. Buhr,¹ J. Hoffmann,¹ L. Lammich,¹ M. Lestinsky,¹ I. Nevo,⁴ S. Novotny,¹ D. A. Orlov,¹ H. B. Pedersen,¹ F. Sprenger,¹ A. S. Terekhov,⁵ J. Toker,⁴ R. Wester,² D. Gerlich,⁶ D. Schwalm,¹ A. Wolf,¹ and D. Zajfman^{1,4}



CRYRING

TSR

Supersonic expansion

RF 22-pole ion trap @ 13 K

Electron target

$kT_{\perp} \sim 2 \text{ meV}$
 $n_e \sim 6.3 \times 10^6 \text{ cm}^{-3}$

$kT_{\perp} \sim 500 \text{ } \mu\text{eV}$
 $n_e \sim 4.5 \times 10^5 \text{ cm}^{-3}$

Electron cooler

(same as target)

$kT_{\perp} \sim 10.5 \text{ meV}$
 $n_e \sim 1.6 \times 10^7 \text{ cm}^{-3}$

Beam energy

12.1 MeV

5.25 MeV

Back to the Interstellar Clouds!

Steady State: $[H_3^+] = \frac{\zeta}{k_e} \frac{[H_2]}{[e^-]}$

To increase the value of $[H_3^+]$, we need:

- Smaller electron fraction $[e^-]$ ~~$[H_2]$~~
- Smaller recombination rate constant ~~k_e~~
- Higher ionization rate ζ

Implications for ζ Persei

$$\frac{N(\text{H}_3^+)}{L} = [\text{H}_3^+] = \frac{\zeta}{k_e} \frac{N(\text{H}_2)}{N(\text{e}^-)}$$

$$\zeta L = (2.6 \times 10^4 \text{ cm}^3 \text{ s}^{-1}) \frac{N(\text{H}_3^+)}{N(\text{H}_2)} \frac{N(\text{e}^-)}{(3.8 \times 10^4)}$$

$$\zeta L = 8000 \text{ cm s}^{-1} \quad (\text{solid})$$

Adopt
 $\zeta = 3 \times 10^{-17} \text{ s}^{-1}$

~~$L = 85 \text{ pc}$
 $\langle n \rangle = 6 \text{ cm}^{-3}$~~

Adopt
 $L = 2.1 \text{ pc}$

$\zeta = 1.2 \times 10^{-15} \text{ s}^{-1}$
 (40x higher!)

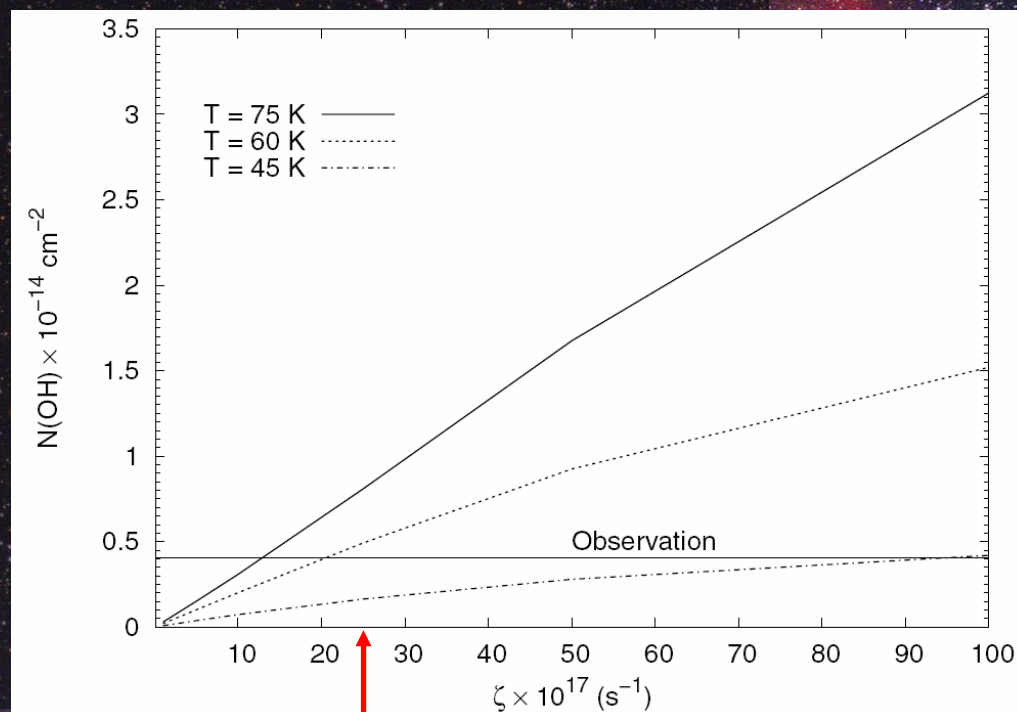
What Does This Mean?

- Enhanced ionization rate in ζ Persei
- Widespread H_3^+ in diffuse clouds
 - perhaps widespread ionization enhancement?
- Dense cloud H_3^+ is "normal"
 - enhanced ionization rate only in diffuse clouds
 - low energy cosmic-ray flux?
 - cosmic-ray self-confinement?
 - no constraints, aside from chemistry!!
- New chemical models necessary
 - Harvey Liszt
 - Franck Le Petit

H_3^+ and other species in the diffuse cloud towards ζ Persei: A new detailed model

F. Le Petit^{1,2}, E. Roueff¹, and E. Herbst³

- Parameters: $n=100 \text{ cm}^{-3}$, $L=4.2 \text{ pc}$, $T=60 \text{ K}$
- Matches all observations within a factor of 3
- $\zeta = 2.5 \times 10^{-16} \text{ s}^{-1}$
 - $10\times$ canonical value
- OH not a problem
 - $\text{H}^+ + \text{O} \rightarrow \text{O}^+ + \text{H}$
endothermic by 227 K
 - OH lowered: $T \rightarrow 60 \text{ K}$
- Still underpredicts H_3^+
 - “Proof of concept”



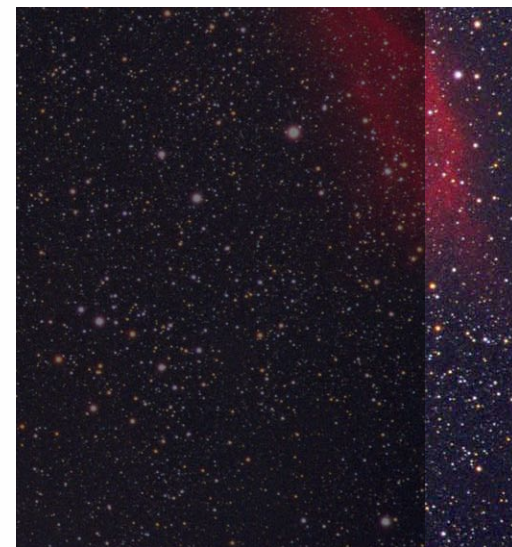
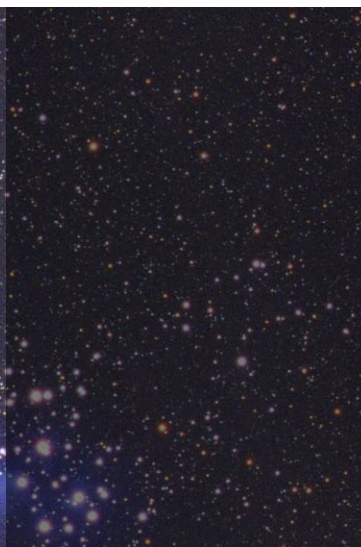
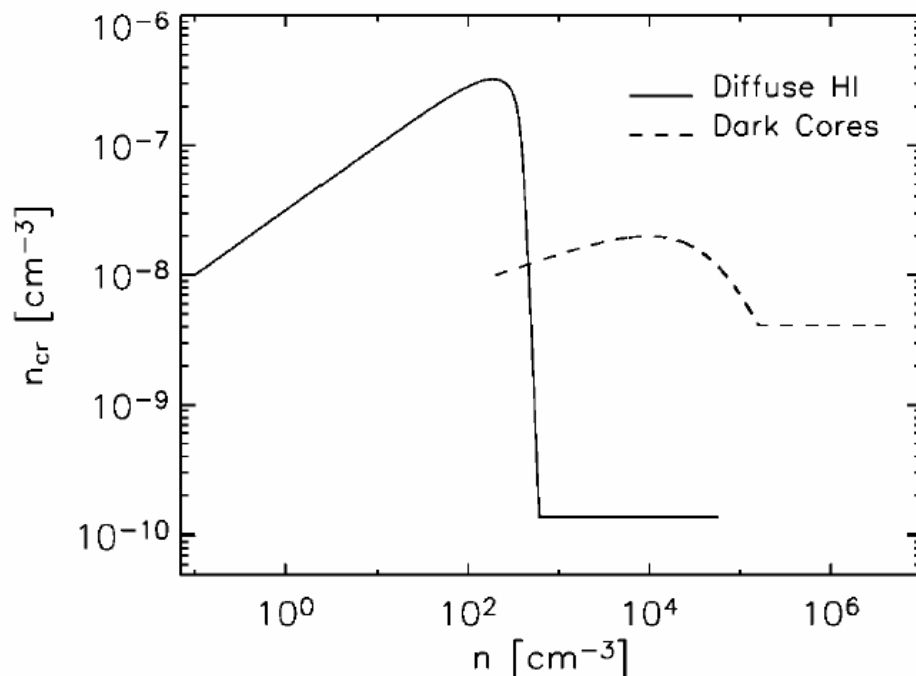
CONFINEMENT-DRIVEN SPATIAL VARIATIONS IN THE COSMIC-RAY FLUX

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ABSTRACT

Low-energy cosmic rays (CRs) are confined by self-generated MHD waves in the mostly neutral interstellar medium. We show that the CR transport equation can be expressed as a continuity equation for the CR number density involving an effective convection velocity. Assuming a balance between wave growth and ion-neutral damping, this equation gives a steady state condition $n_{\text{cr}} \propto n_i^{1/2}$ up to a critical density for free streaming. This relation naturally accounts for the heretofore unexplained difference in CR ionization rates derived for dense diffuse clouds (McCall et al.) and dark clouds, and predicts large spatial variations in the CR heating rate and pressure.



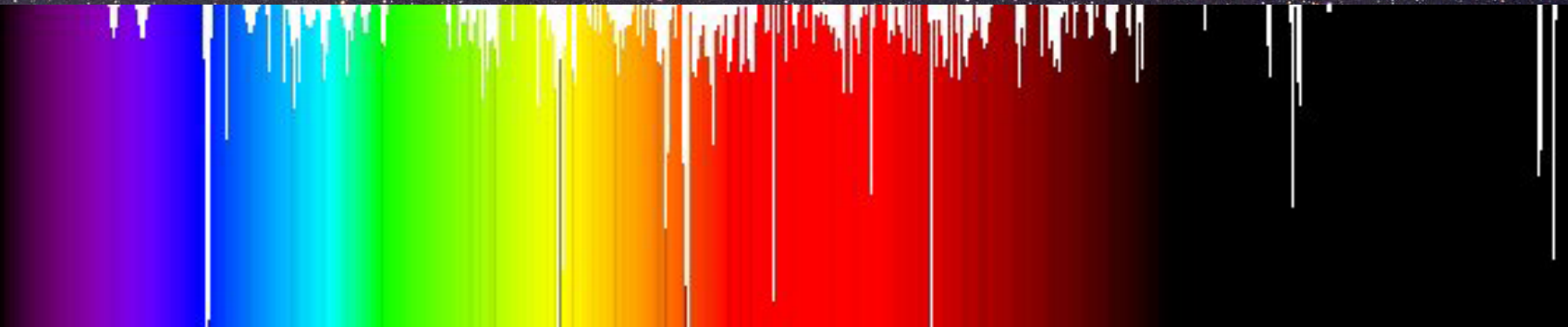
Future Work

- More experiments!
 - Improved spectroscopy of ion source
 - Higher resolution & higher sensitivity
 - Better characterization of ro-vib distribution
 - Testing of new (piezo) ion source
 - Single quantum-state CRYRING measurements
 - produce pure para- H_3^+ using para- H_2
- More observational data!
 - Search for H_3^+ in more diffuse cloud sightlines
 - Confirm generality of result in classical diffuse clouds
 - Observations of H_3^+ in "translucent" sightlines
 - $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$



Rich Diffuse Cloud Chemistry

- From 1930s through the mid-1990s, only diatomic molecules thought to be abundant in diffuse clouds
- Recently, many polyatomics observed:
 - H_3^+ in infrared
 - HCO^+ , C_2H , C_3H_2 , etc. in radio (Lucas & Liszt)
 - C_3 in near-UV (Maier, et al.)
- Diffuse Interstellar Bands!



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