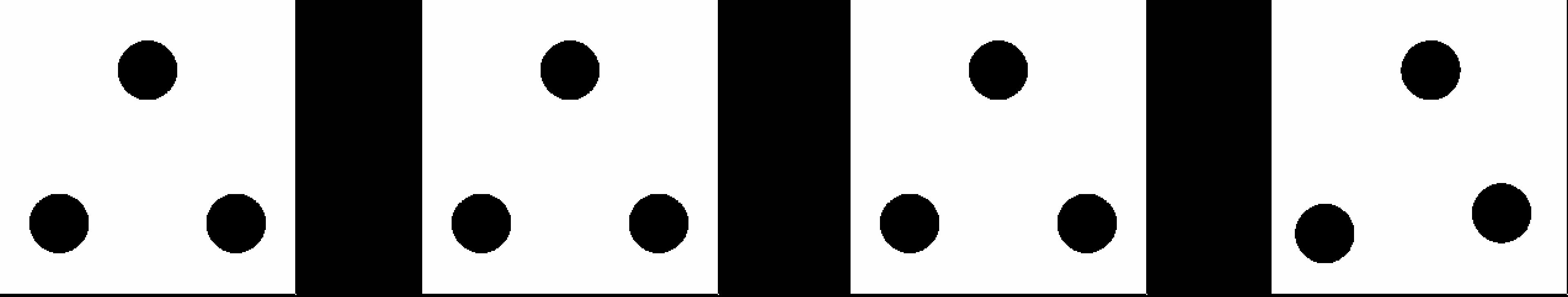
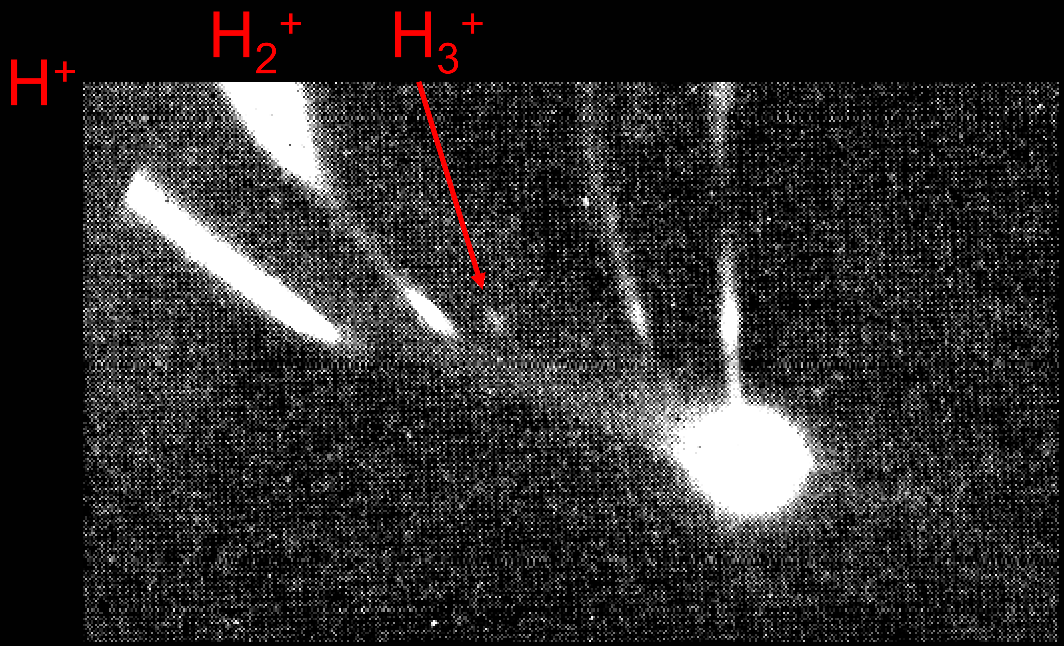


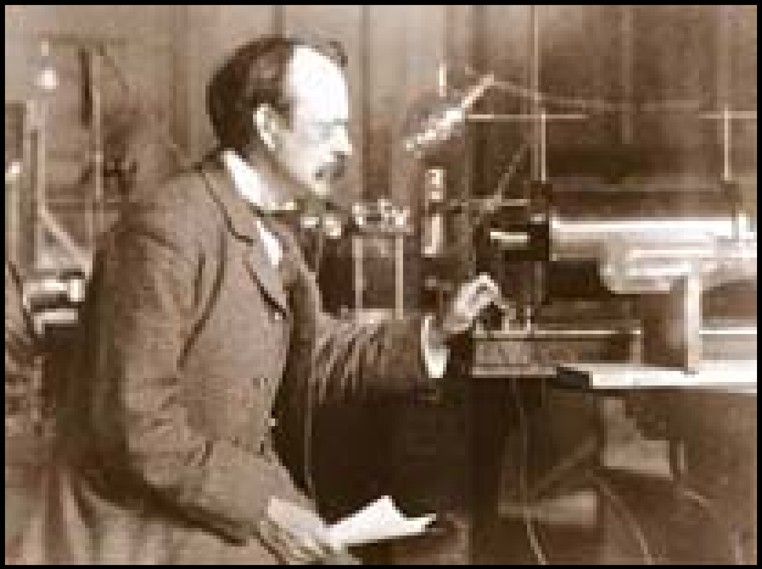
H_3^+: "A Beautiful Jewel of Nature"

Ben McCall
Department of Chemistry
Department of Astronomy
University of California at Berkeley

[Oka Ion Factory™ 1995–2001]

J. J. Thomson

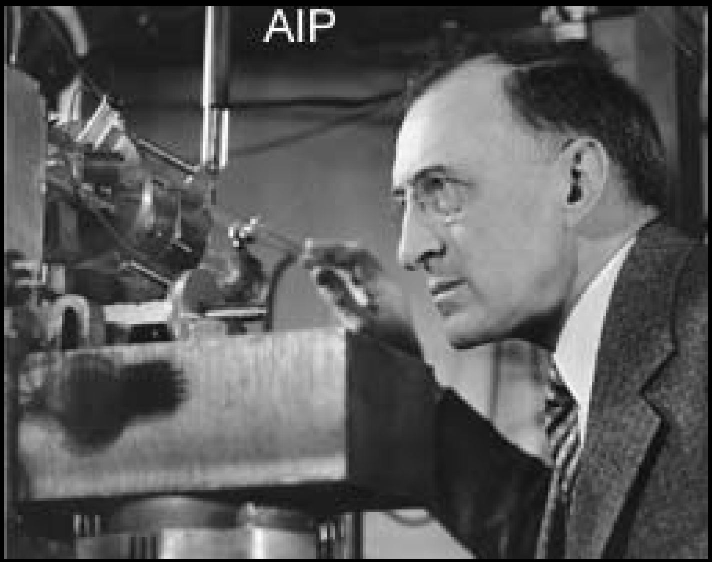


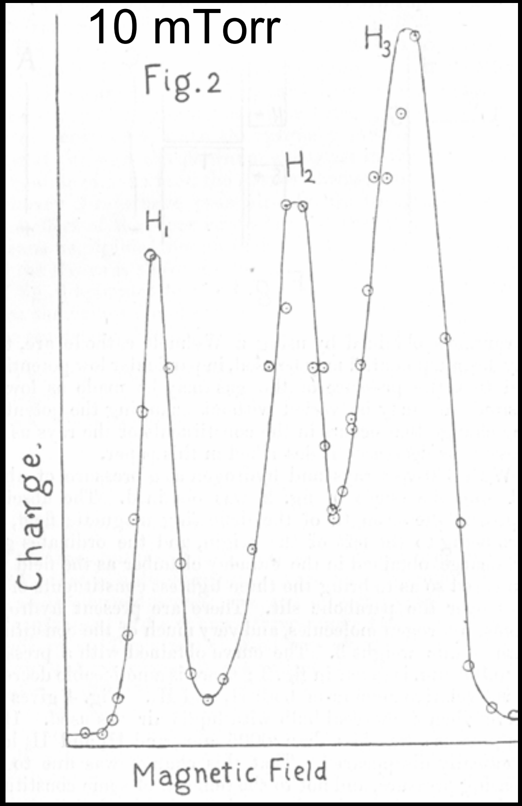


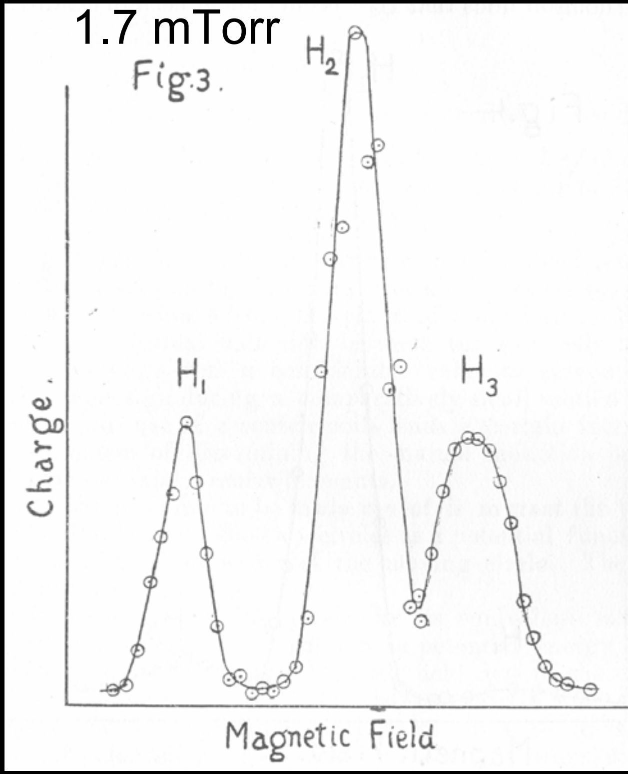
Existence of H_3.—On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which $m/e = 3$ has been detected. There can, I think, be little doubt that this line is due to H_3 The existence of this substance is interesting from a chemical point of view, as it is not possible to reconcile its existence with the ordinary conceptions about valency, if hydrogen is regarded as always monovalent. The polymeric modification of hydrogen seems to require special conditions for its formation, for it cannot be detected on many of the plates taken with hydrogen in the tube.

J. J. Thomson,
Phil. Mag. 24, 209 (1912)

Arthur J. Dempster







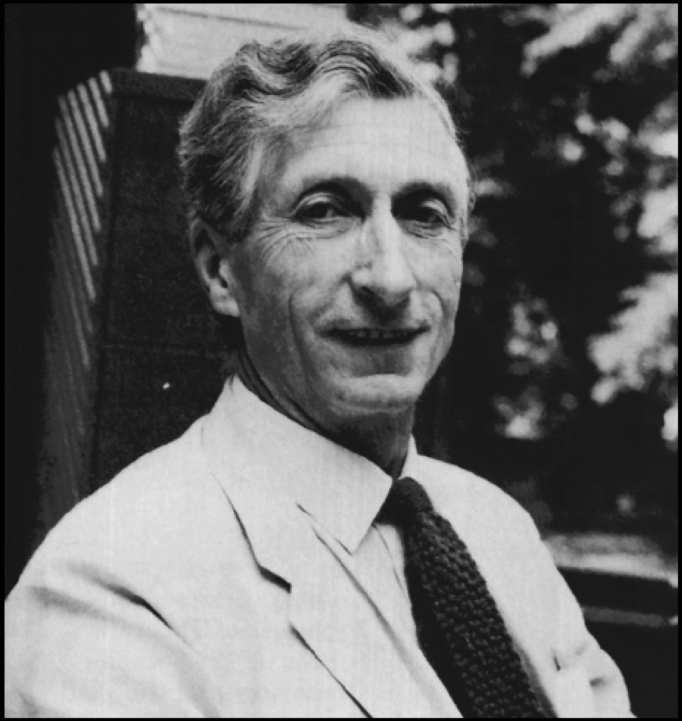
- Discovered ^{235}U
- Physics Prof. at U. Chicago
- Principal American authority on positive rays

$\rightarrow$ H_3^+ formed in secondary reaction

A. J. Dempster,
Phil. Mag. 31, 438 (1916)

Charles A. Coulson

- First Ph.D. student of Lennard-Jones
- First ab initio calculation on a polyatomic molecule
- "It appears that the ion H_3^+ should exist in stable equilateral form with a nuclear distance about 0.85 Å, and that all excited levels are unstable."
- Prediction not accepted by Eyring, Hirschfelder, and others
- With advent of computers, prediction was confirmed (Christoffersen, Hagstrom, & Prosser 1964, Conroy 1964)



C. A. Coulson,
Proc. Camb. Phil. Soc. 31, 244 (1935)

Interstellar H_3^+

ON THE POSSIBLE OCCURRENCE OF H_3^+ IN INTERSTELLAR SPACE

The possibilities for detection of the molecular ion H_2^+ by radio-astronomical techniques have recently received considerable attention, and theoretical predictions of the spectrum have been made by Mizushima (1961) and by Burke (1961). Recent work on ion-molecule reactions indicates that the molecular ion H_3^+ may also be expected in interstellar space. In fact, with the presence of quantities of molecular hydrogen, H_2^+ will react to form H_3^+.

Formation of H_3^+ through the reaction $H_2^+ + H_2 \rightarrow H_3^+$ has been observed independently by Stevenson and Schissler (1958) and by Barnes, Martin, and McDaniel (1961). The cross-section for this reaction has been found to have a remarkably large value of the order of 10^{-14} cm^2 at normal thermal energies. This is much greater than the gas-kinetic cross-section for neutral hydrogen molecules. The cross-section for H_3^+ formation by this reaction varies inversely with the relative velocity of the H_2^+ ion and the hydrogen molecule (Stevenson and Schissler 1958; Lampe and Field 1959). The experimental work of Barnes, Martin, and McDaniel furthermore shows that H_3^+ ions persist over very many subsequent collisions with hydrogen molecules. The H_3^+ ion is stable against spontaneous dissociation. Its binding energy of 4.18 ev (Varney 1960) exceeds that of H_2^+ (2.65 ev), so the formation reaction is exoergic (Hirschfelder, Curtiss, and Bird 1954).

Thus it may be expected that H_2^+ will be converted to H_3^+ upon encounter with a hydrgoen molecule, and the population of H_2^+ will be very strongly influenced by the density of neutral molecular hydrogen. It now appears desirable to consider the possibilities for detecting H_3^+ because this molecular ion may be present under some circumstances to the virtual exclusion of H_2^+.

D. W. Martin
E. W. McDaniel
M. L. Meeks

June 13, 1961
Georgia Institute of Technology
Atlanta, Georgia

Martin, McDaniel, & Meeks,
Astrophys. J. 134, 1012 (1961)

Interstellar Chemistry

Another important subclass of reactions are those involving H_3^+. This ion is produced by the well-studied reaction

$$4. \quad H_2 + H_2^+ \rightarrow H_3^+ + H,$$

and then reacts with many neutral species according to the general formula

$$H_3^+ + X \rightarrow XH^+ + H_2, \qquad (4)$$

where X = CO, N_2, H_2O, NH_3, etc. These reactions have been studied by Burt *et al.*

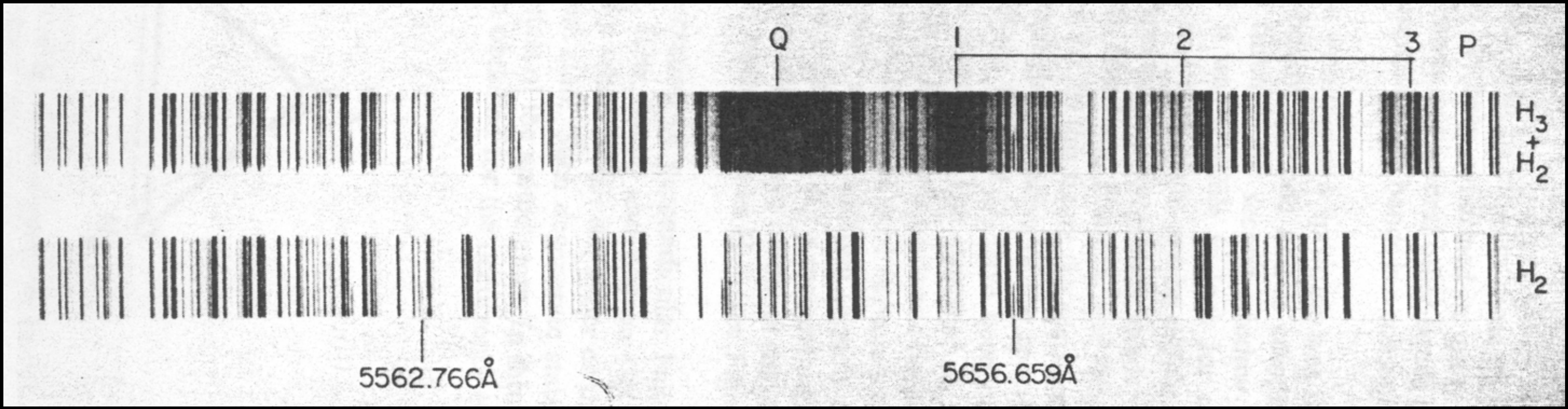
E. Herbst & W. Klemperer, Astrophys. J. 185, 505 (1973)

also: W. D. Watson Astrophys. J. 183, L17 (1973)

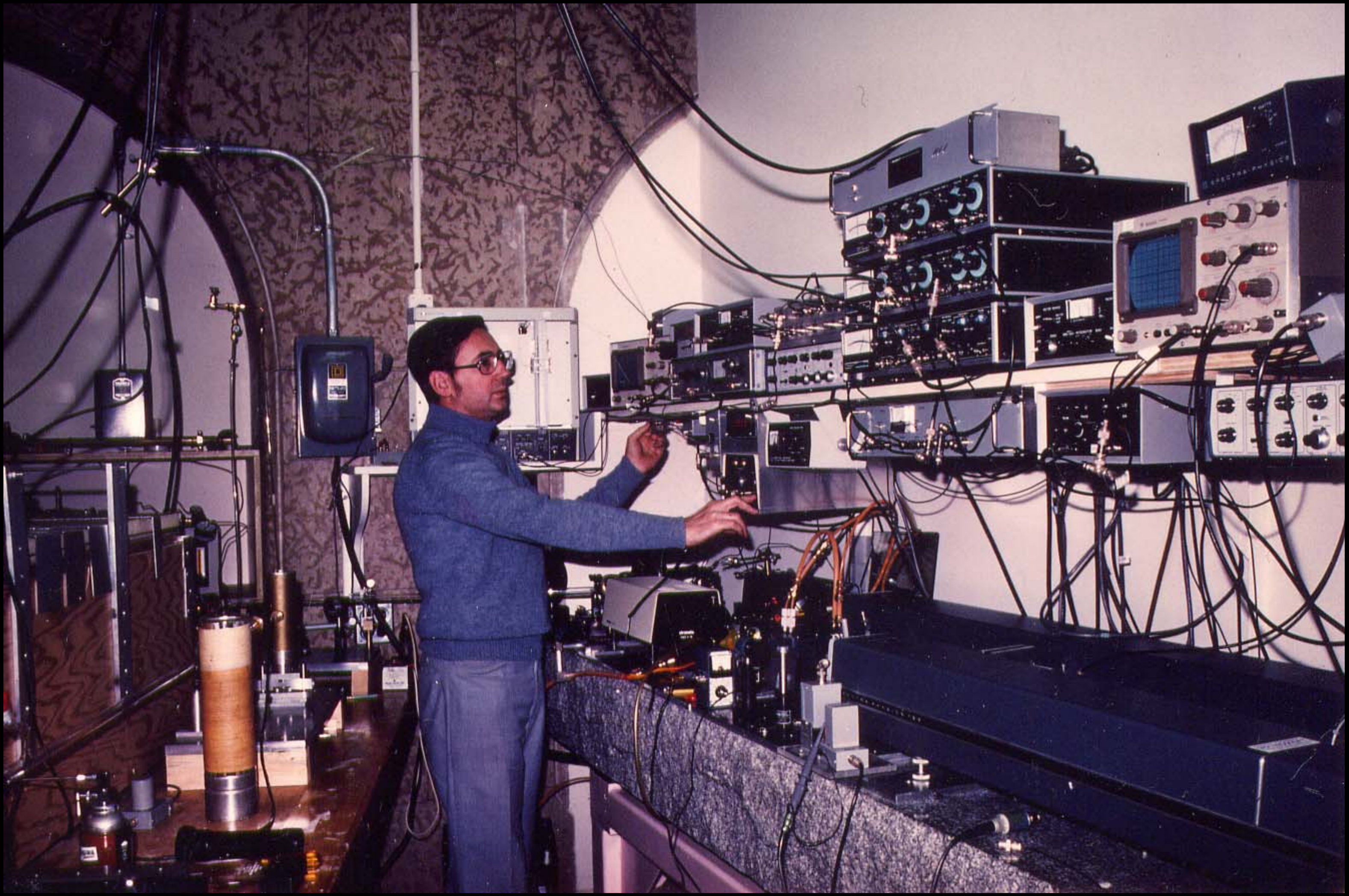
- H_3^+ "universal protonator"
  - $H_3^+ + O \rightarrow H_2 + OH^+$
  - $OH^+ + H_2 \rightarrow H + H_2O^+$
  - $H_2O^+ + H_2 \rightarrow H + H_3O^+$
  - $H_3O^+ + e^- \rightarrow H_2O + H$
- Origin of Earth's water (?)

Herzberg's Search for H_3^+

- 1967: with J. W. C. Johns, searched for emission in IR spectrum of discharge
- Looked for electronic transitions in VUV, found high rotational lines of Lyman bands
- Working in visible, stumbled onto H_3

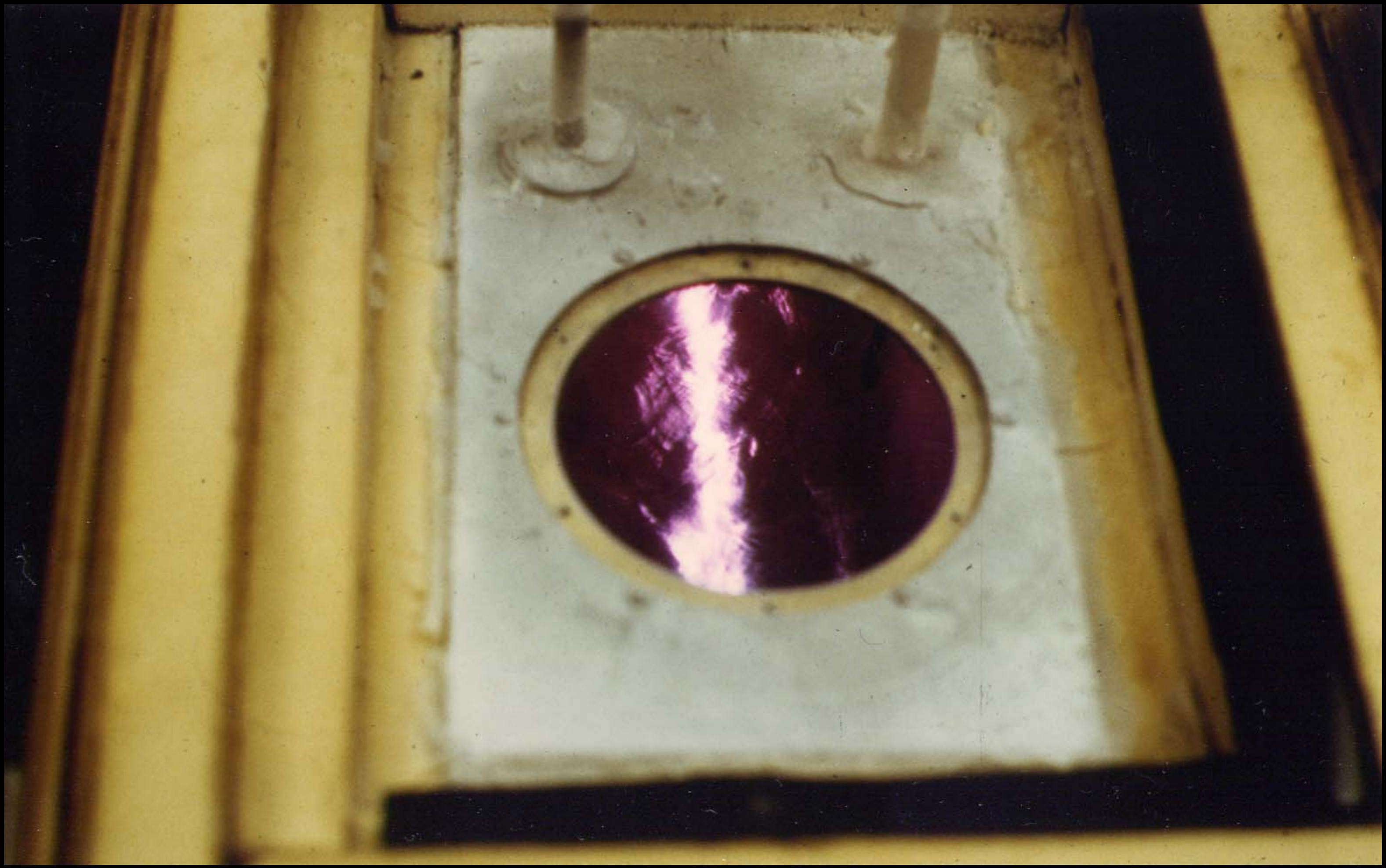


Oka's Search for H_3^+



Allen Karabonik

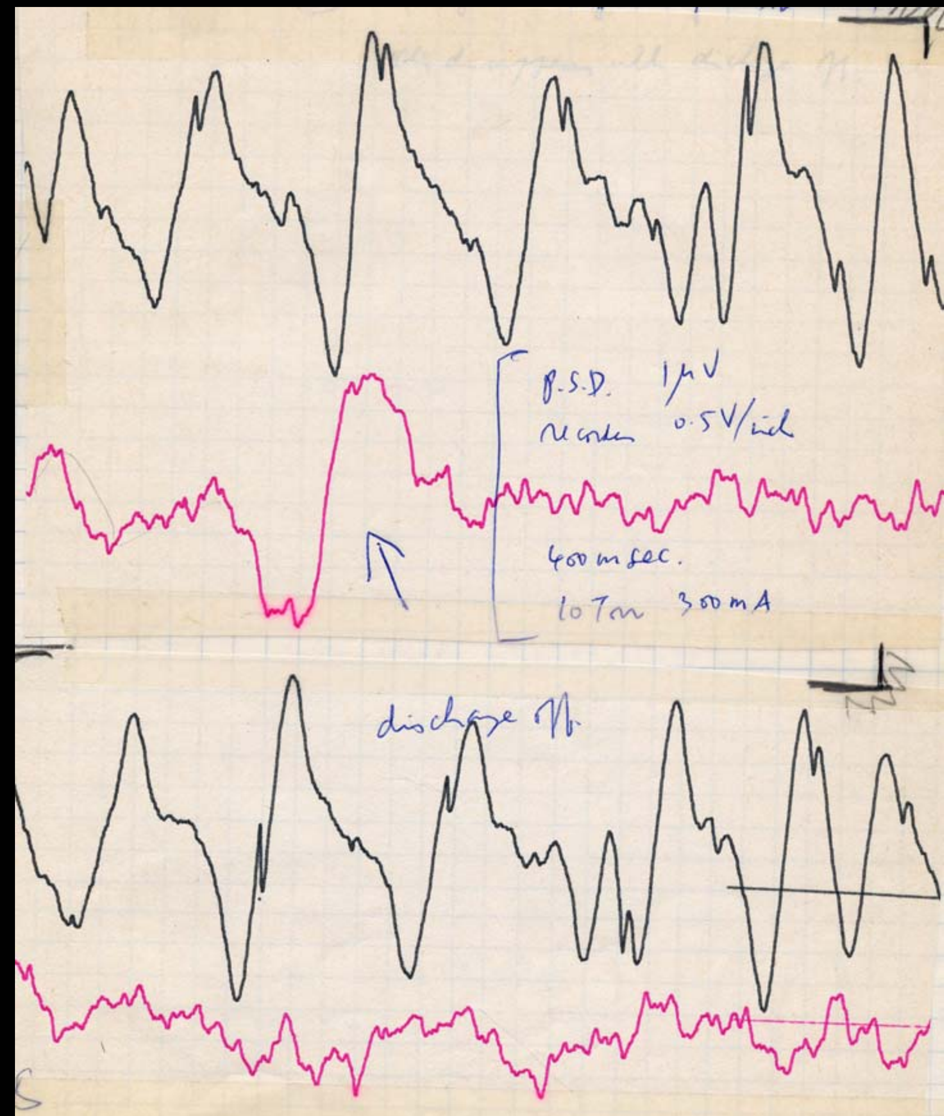
Positive Column Discharge



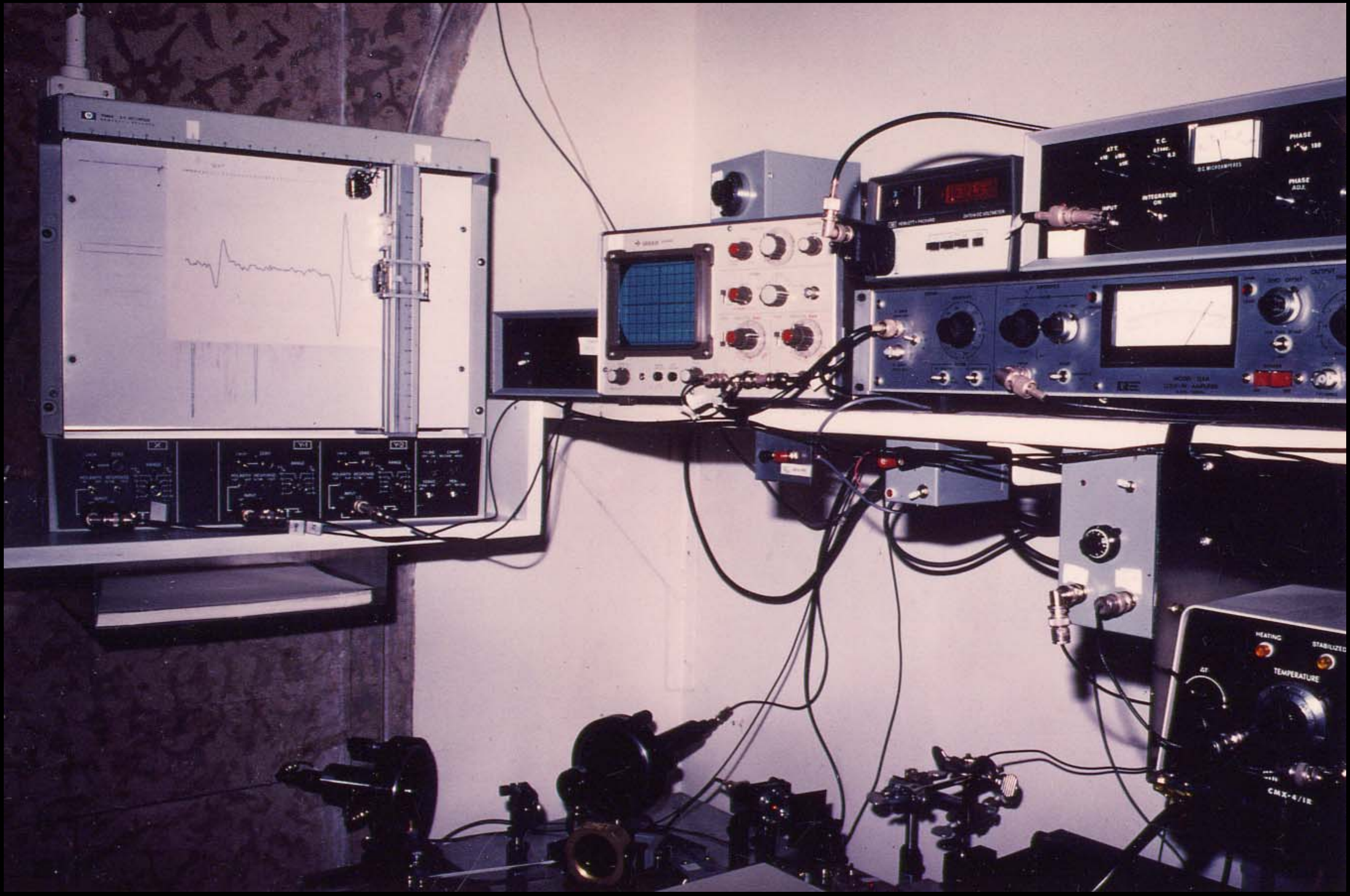
Every morning, he transferred six 50 liter cans of liquid nitrogen to the laboratory!

The Long Search

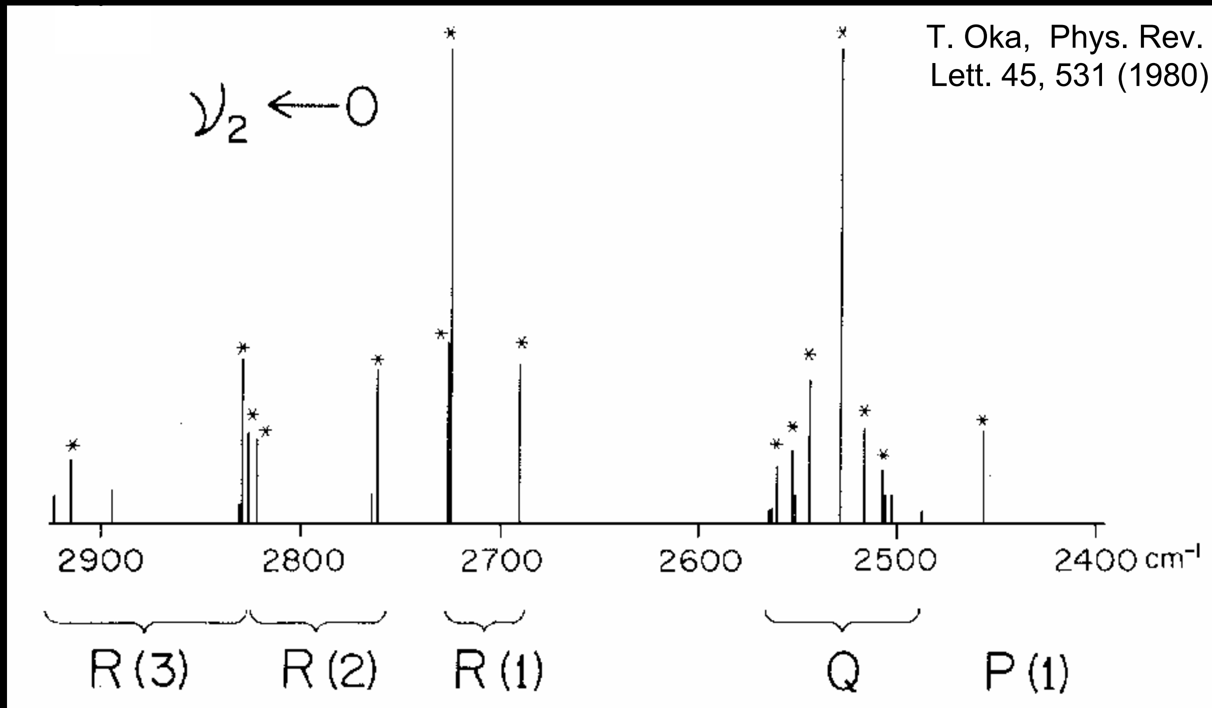
- Four and a half years. Much of it assembling the DF system and discharge cell.
- Scanned from:
  - 6/12-8/3 (1978)
  - 12/18-1/26 (1978-79)
  - 4/24-12/18 (1980)
- R(1,0) April 25, 1980.
  - Oka and Allen Karabonik in lab
  - Keiko came in at 10 pm
- Watson assigned it overnight

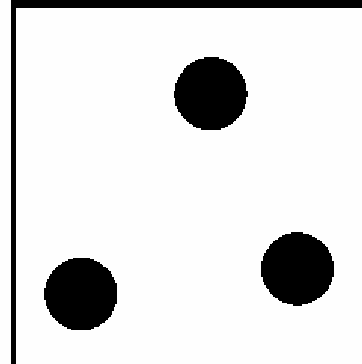


The final spectrum



A Beautiful Jewel of Nature





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

The Search Was On

Phil. Trans. R. Soc. Lond. A **303**, 543–549 (1981) **543**
Printed in Great Britain

A search for interstellar H_3^+

BY T. OKA†
Herzberg Institute of Astrophysics National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

Based on the results of recent laboratory observation of the infrared ν_2 fundamental band of the H_3^+ molecular ion, the possibility of observing this important ion in interstellar space is discussed. An observation of this spectrum has been attempted with the aid of the high-resolution Fourier transform spectrometer on the 4 m Mayall telescope of the Kitt Peak National Observatory.

4. OBSERVATION

Observation was made for 2 days on 1981 March 23–25, with the coudé Fourier transform spectrometer with high resolution (*ca.* 0.041 cm^{-1}) on the 4 m Mayall telescope of the Kitt Peak National Observatory. A liquid He cooled narrow band filter with the centre wavenumber of

Less than one year after first line was seen in laboratory!!!

Tom Geballe & IRTF

15 June, 1981

Dr. T. Geballe,
Mount Wilson and Las Campanas Observatories,
813 Santa Barbara Street,
Pasadena, CA 91101,
U.S.A.

Dear Dr. Geballe:

I enclose a copy of my preprint on an astronomical search for H_3^+ and my paper on laboratory spectra.

This is a very interesting species and I am extremely eager to search for this ion. I hope that you will read my preprint and find such an attempt worthwhile.

You said on the phone that you are in the process of moving. So am I. After the middle of July, my address will be in Chicago as specified on my preprint.

Looking forward very much to our collaboration,

Sincerely yours,

Takeshi Oka

TO:mpt
Encs:

Tom

Observing Period: December 1982 APPENDIX D.

IRTF Use Only:

Proposal No.:
Date Received:

IRTF TIME APPLICATION FORM

1. Investigator(s): Institution Address:

Investigator	Institution Address
* Takeshi Oka	Dept. of Astronomy and Astrophysics, Dept. of Chemistry, The University of Chicago, 5735 S. Ellis Ave., Chicago, IL 60637
S. E. Persson	Mt. Wilson and Las Campanas Observatories 813 Santa Barbara St., Pasadena, CA 91101
T. R. Geballe	United Kingdom Infrared Telescope 900 Leilani St., Hilo, HI 96720

*First person listed is assumed to be the correspondent. Indicate clearly which investigator is requesting the $100 deductible travel support.

2. Others in the observing party: Institution Address:

Carol Lonsdale Astronomy Dept., UCLA, Los Angeles, CA 90024

3. Descriptive Title (less than 12 words):

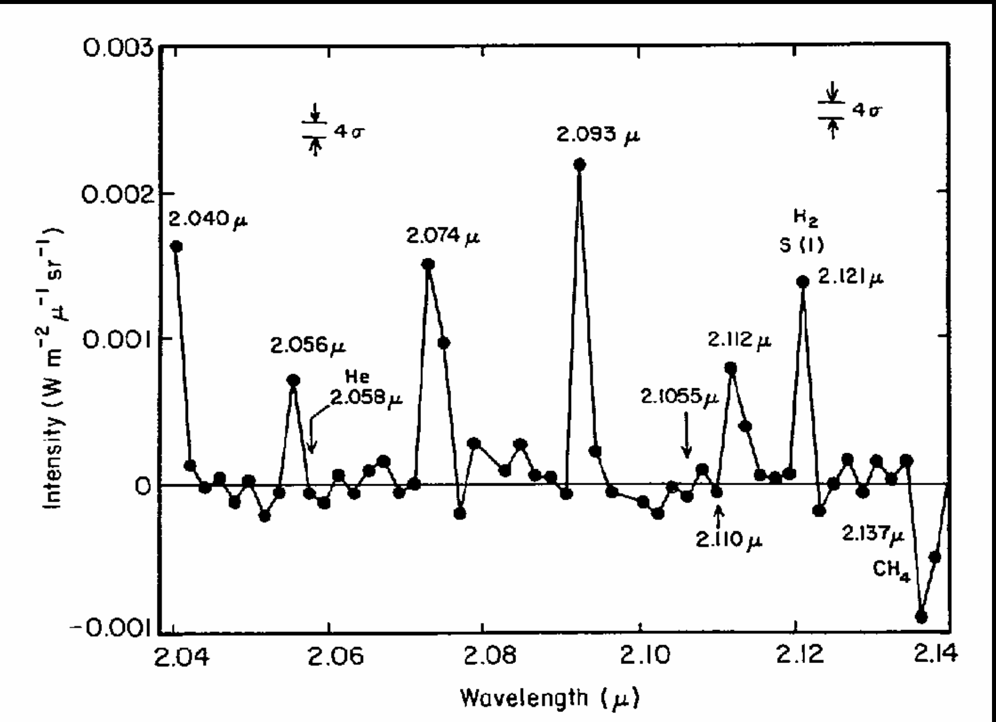
Detection of Interstellar H_3^+ Molecular Ion.

Dear Professor Becklin:

It was nice to have seen you in Mauna Kea last month. This letter is to report our result briefly.

Our search (Eric Persson, Tom Geballe and I) for the IR spectrum of H_3^+ was done on the night of December 6-7. Unfortunately, neither the infrared spectrometer nor the weather was on our side on that night and we ended up with very inconclusive results.

H_3^+ on Jupiter!



- McDonald Observatory 2.7-m
- September 1987 – November 1989
- Study of H_2

After a month's work J. K. G. Watson, who had earlier analyzed the first laboratory H_3^+ spectrum, came to the understanding of the Jovian spectrum as due to the $2\nu_2(2)\rightarrow 0$ band of H_3^+. Crucial to his solution were the laboratory data of the $2\nu(2)\rightarrow\nu_2$ hot band provided by Bawendi *et al.* (1990), the analysis of which is based on the theoretical calculations of Miller and Tennyson (1989). The initial guesses, uncertainties, heated discussions, and the sudden final solution are vividly recorded in extensive E-mail correspondences between Paris (J.-P. Maillard), Ottawa (P. A. Feldman and J. K. G. Watson), and London (S. Miller), with recurring references to Bawendi, Dabrowski, Drossart, Herzberg, Majewski, Oka, Tarrago, and Vervloet. The close collaboration of astronomers, laboratory spectroscopists, and theorists is characteristic of this field.

Trafton, Lester, & Thompson, Astrophys. J. 343, L73 (1989)

T. Oka, Rev. Mod. Phys. 64, 1141 (1992)

H_3^+ Fundamental Band

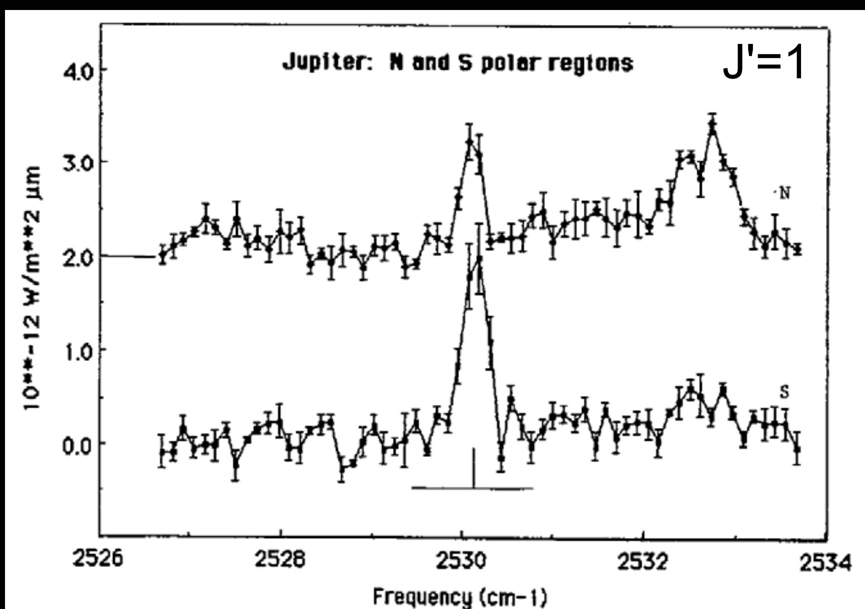
OBSERVATIONS OF THE 4 MICRON FUNDAMENTAL BAND OF H_3^+ IN JUPITER

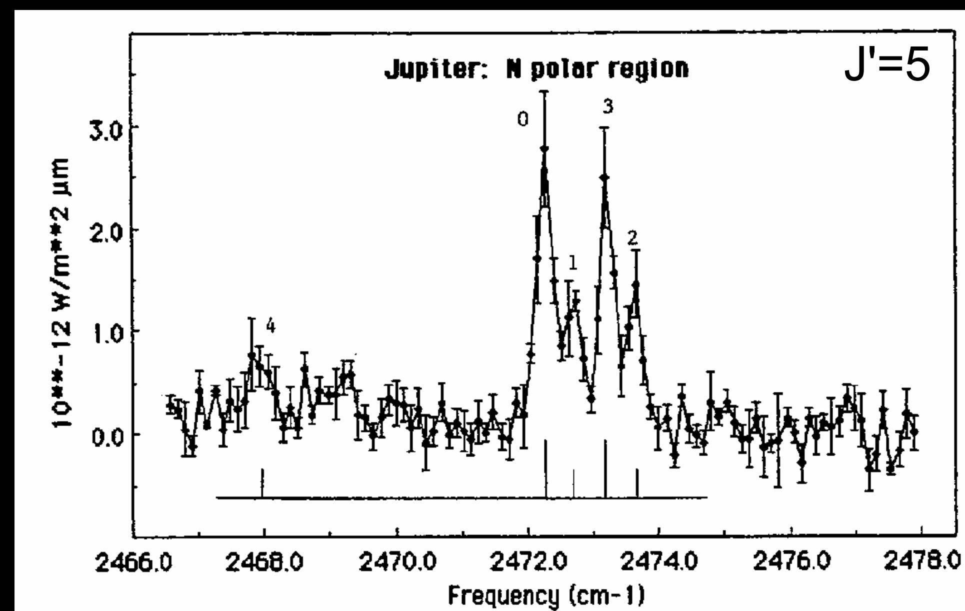
T. Oka
Department of Astronomy and Astrophysics and Department of Chemistry, University of Chicago

AND

T. R. Geballe
Joint Astronomy Centre, Hilo

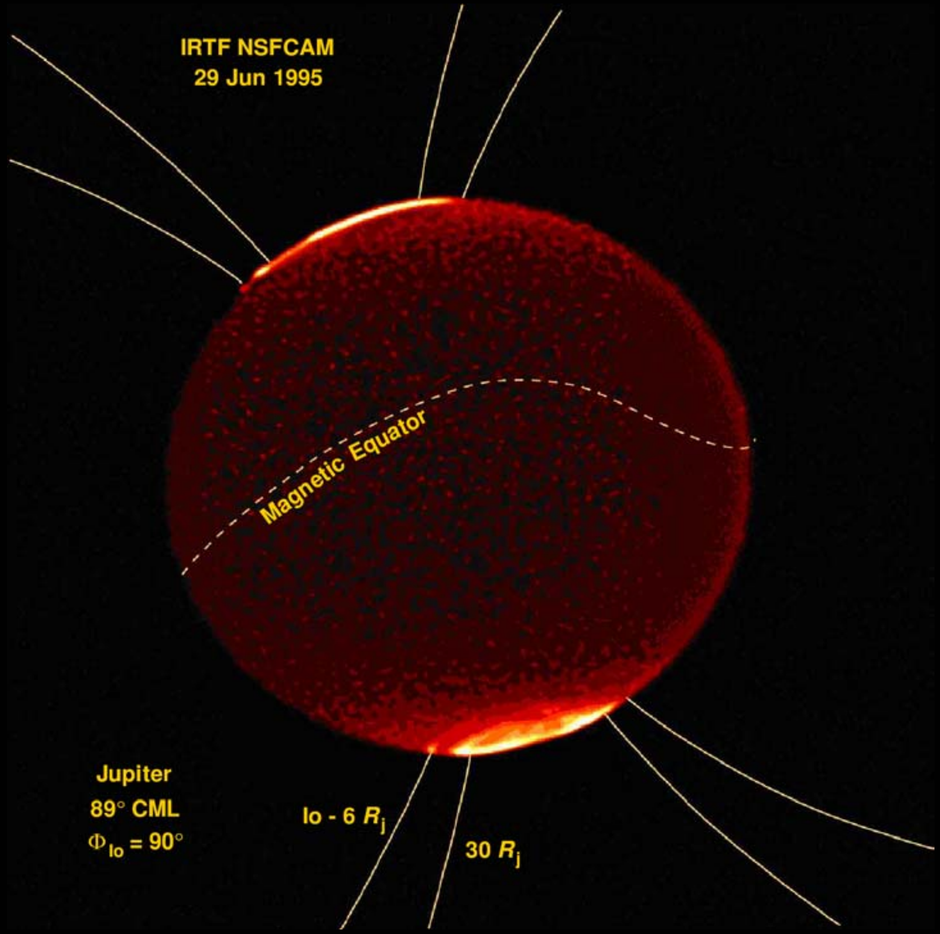
Received 1989 October 24; accepted 1989 December 14



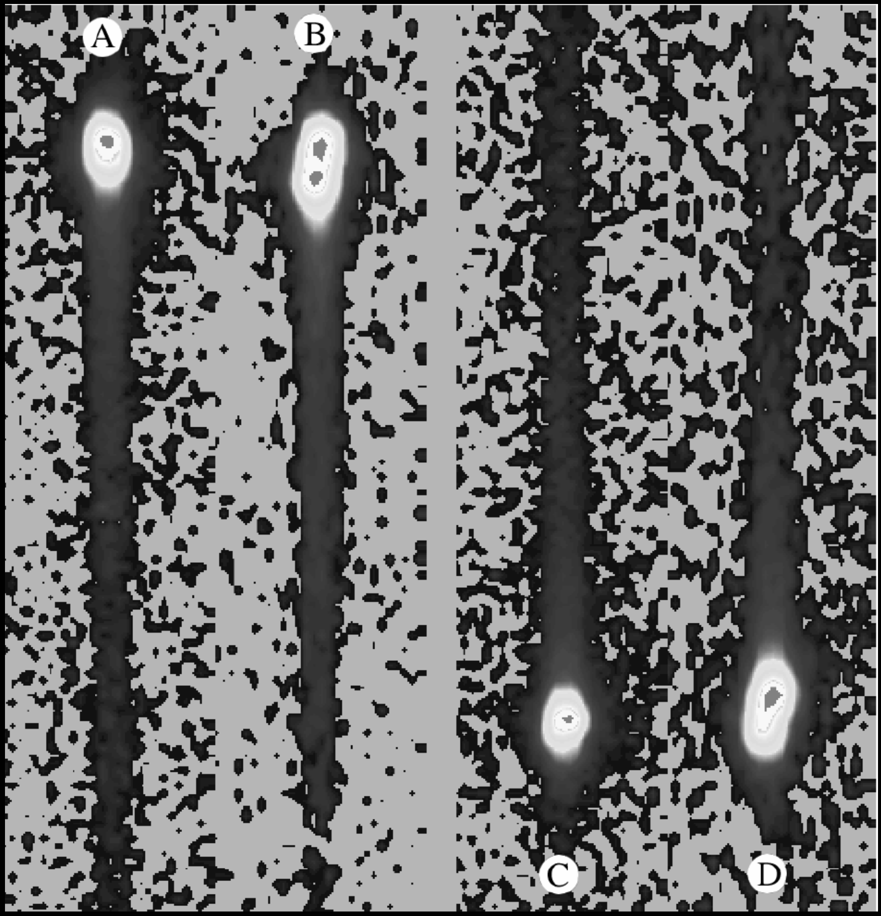


T. Oka and T. R. Geballe,
Astrophys. J. 351, L53 (1990)

H_3^+ as a Diagnostic

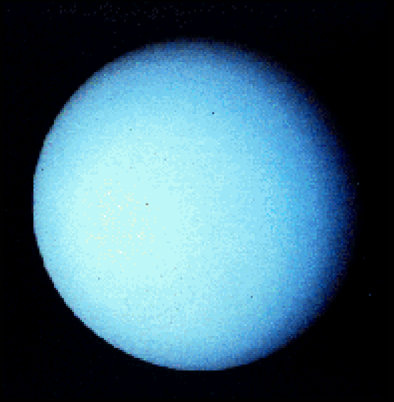


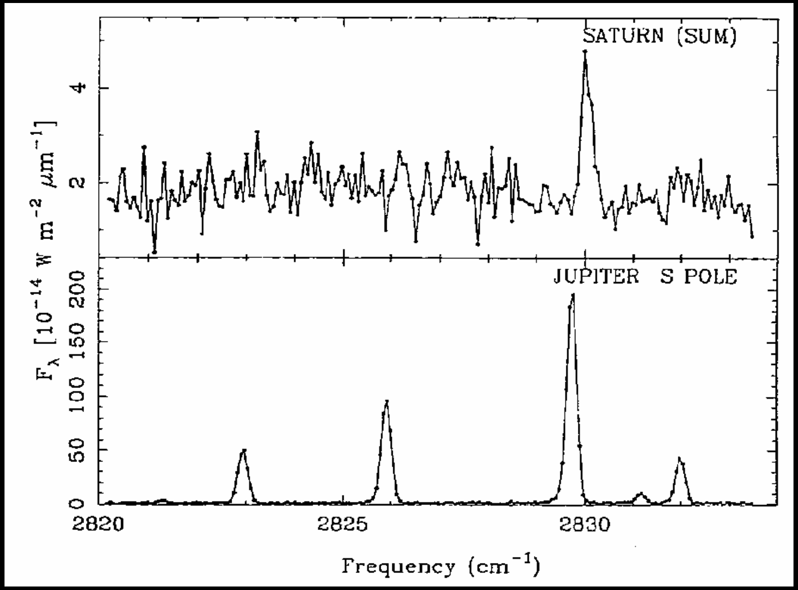
J.E.P. Connerney and T. Satoh,
Phil. Trans. R. Soc. Lond. A358, 2471 (2000)

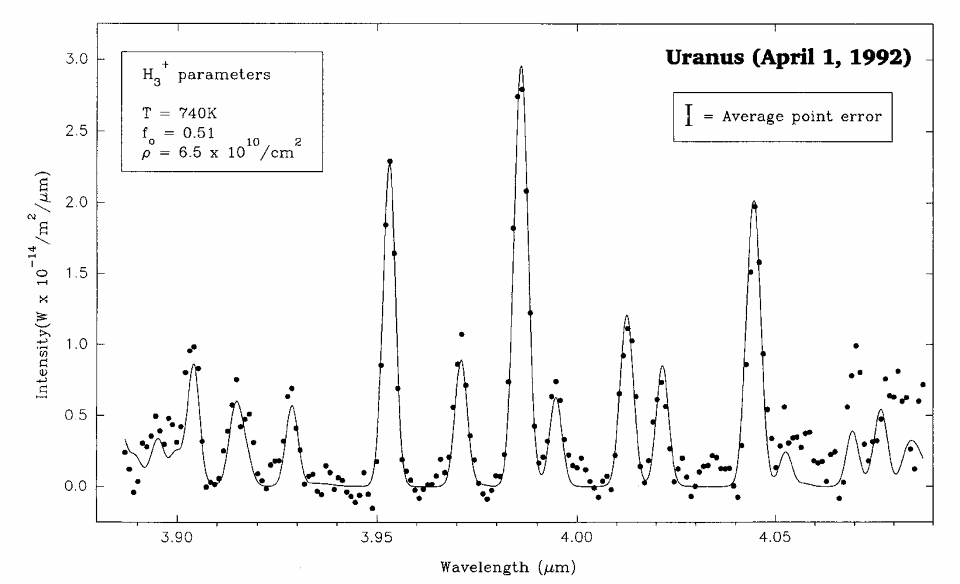


S. Miller, et al.,
Phil. Trans. R. Soc. Lond. A358, 2485 (2000)

Saturn and Uranus





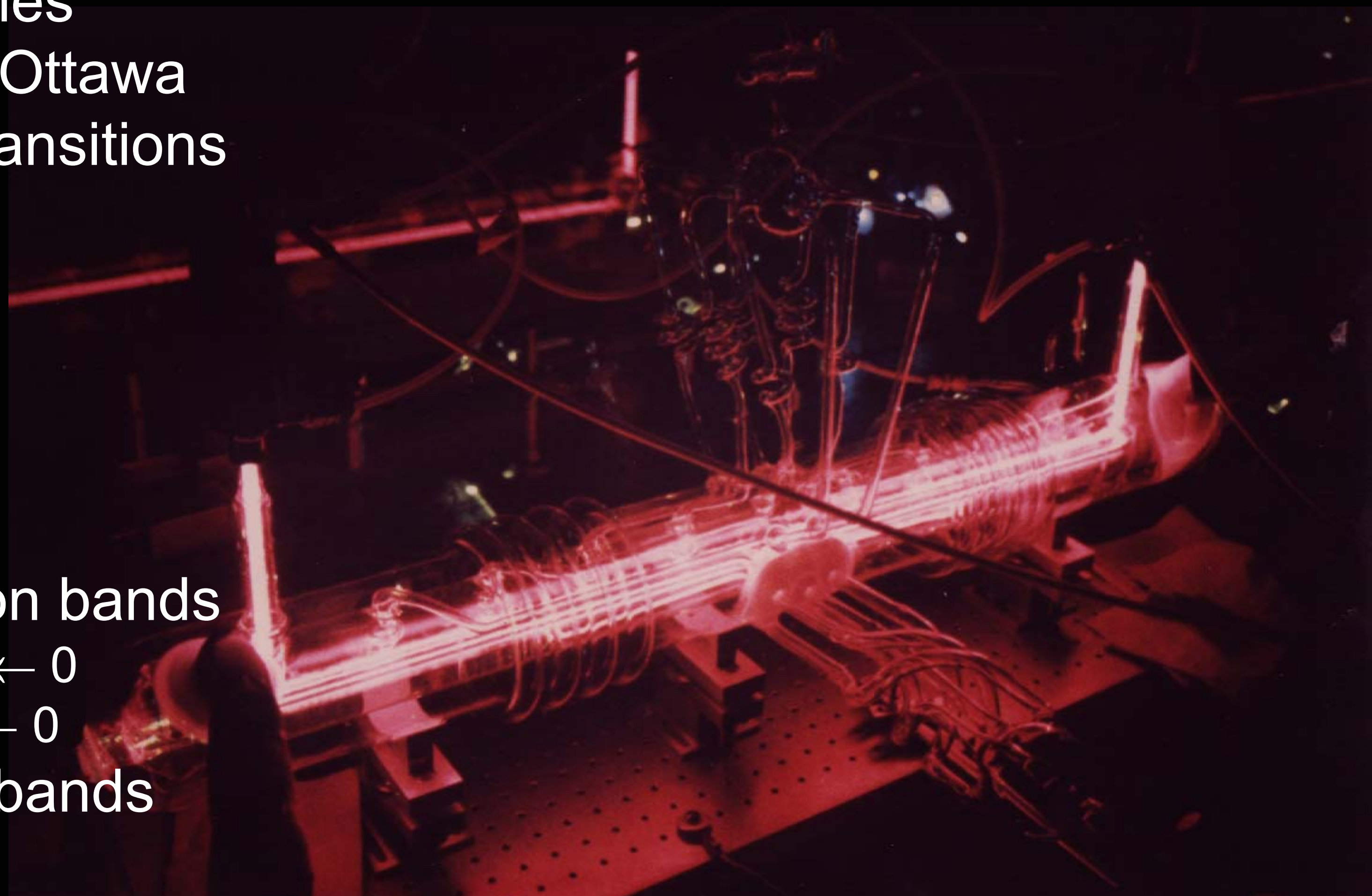


T. R. Geballe, M.-F. Jagod, & T. Oka, Astrophys. J. 408, L109 (1993)

L. M. Trafton, et al., Astrophys. J. 405, 761 (1993)

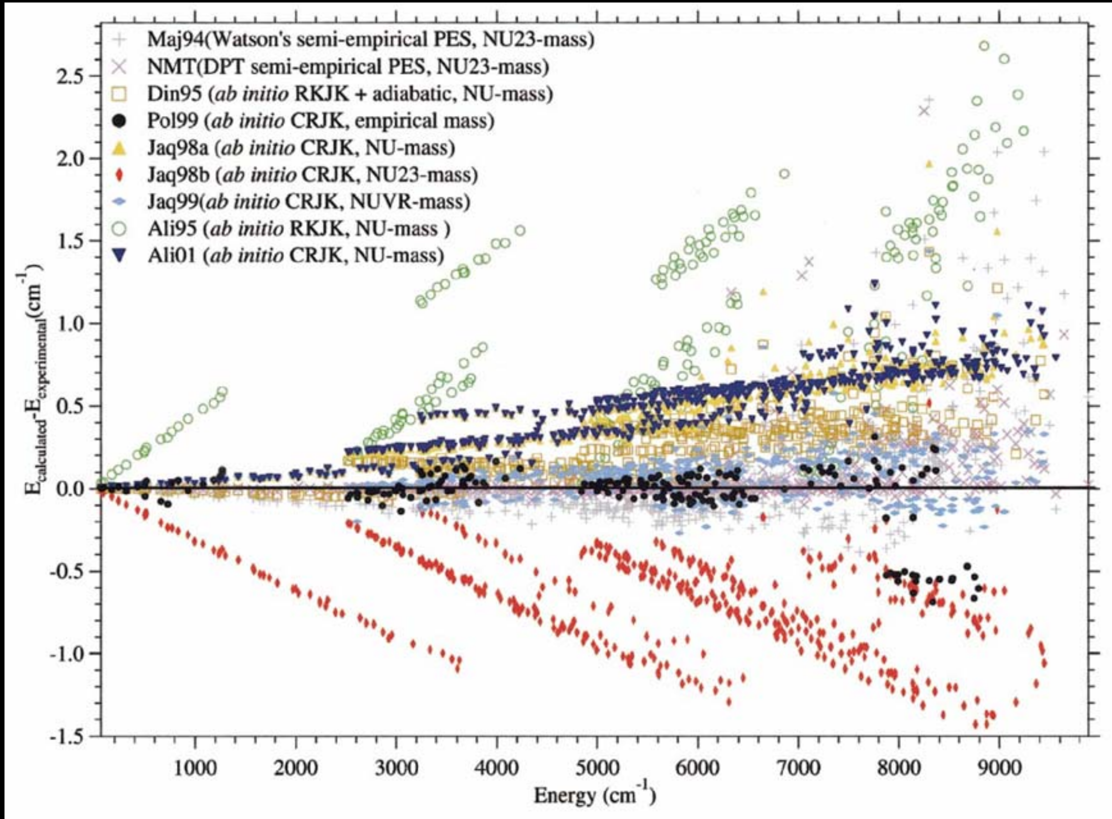
Continued Laboratory Work

- 17 lab studies
- Chicago & Ottawa
- over 800 transitions
- Overtones
  - $2\nu_2 \leftarrow 0$
  - $3\nu_2 \leftarrow 0$
- Hot bands
  - $2\nu_2^2 \leftarrow \nu_2$
  - $2\nu_2^0 \leftarrow \nu_2$
- Combination bands
  - $\nu_1 + 2\nu_2^2 \leftarrow 0$
  - $2\nu_1 + \nu_2 \leftarrow 0$
- Forbidden bands
  - $\nu_1 \leftarrow 0$
  - $\nu_1 + \nu_2 \leftarrow \nu_2$



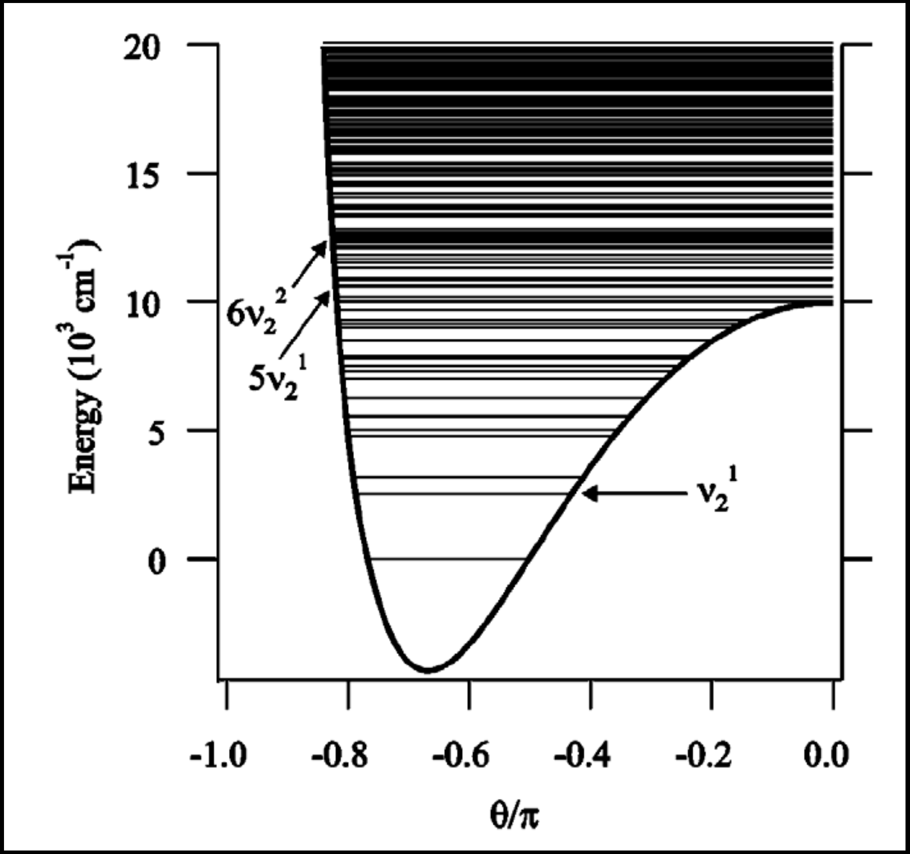
Compilation Work

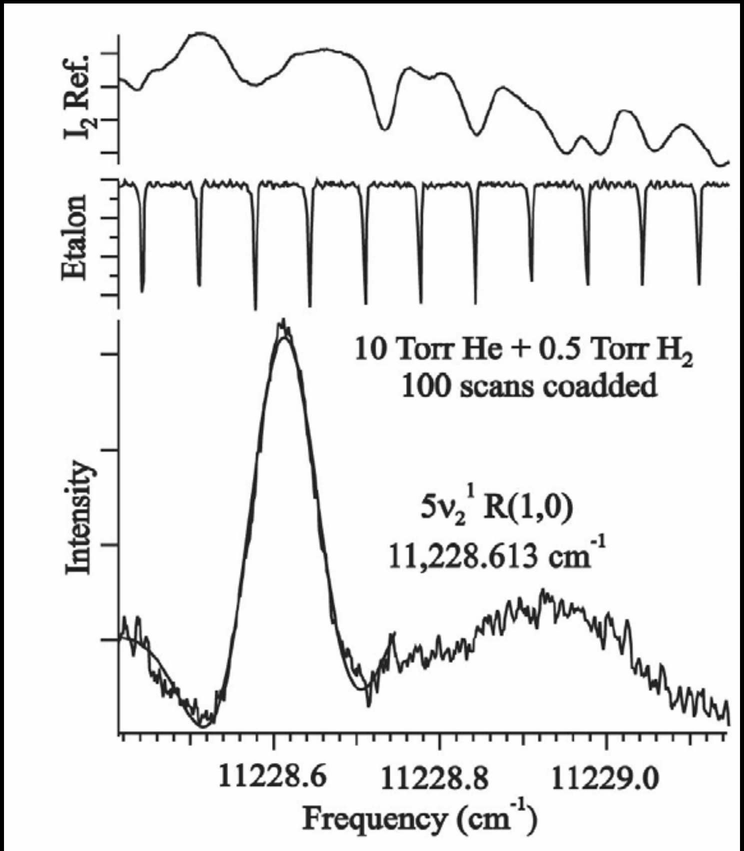
- Reassignment of all observed transitions
- Experimentally determined energy levels
  - utilize variety of band types observed
  - independent of theory
  - 526 energy levels
- Test for theory
- Reliable linelist

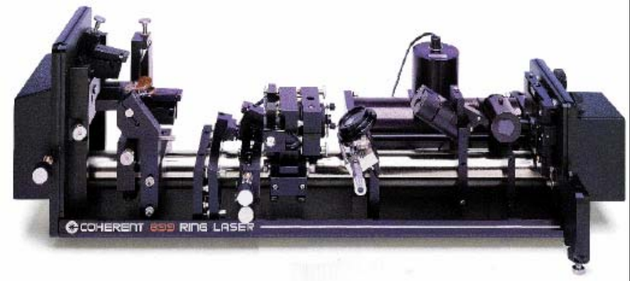


C. M. Lindsay & B. J. McCall,
J. Mol. Spectrosc. 210, 60 (2001)

H_3^+ Above the Linearity Barrier



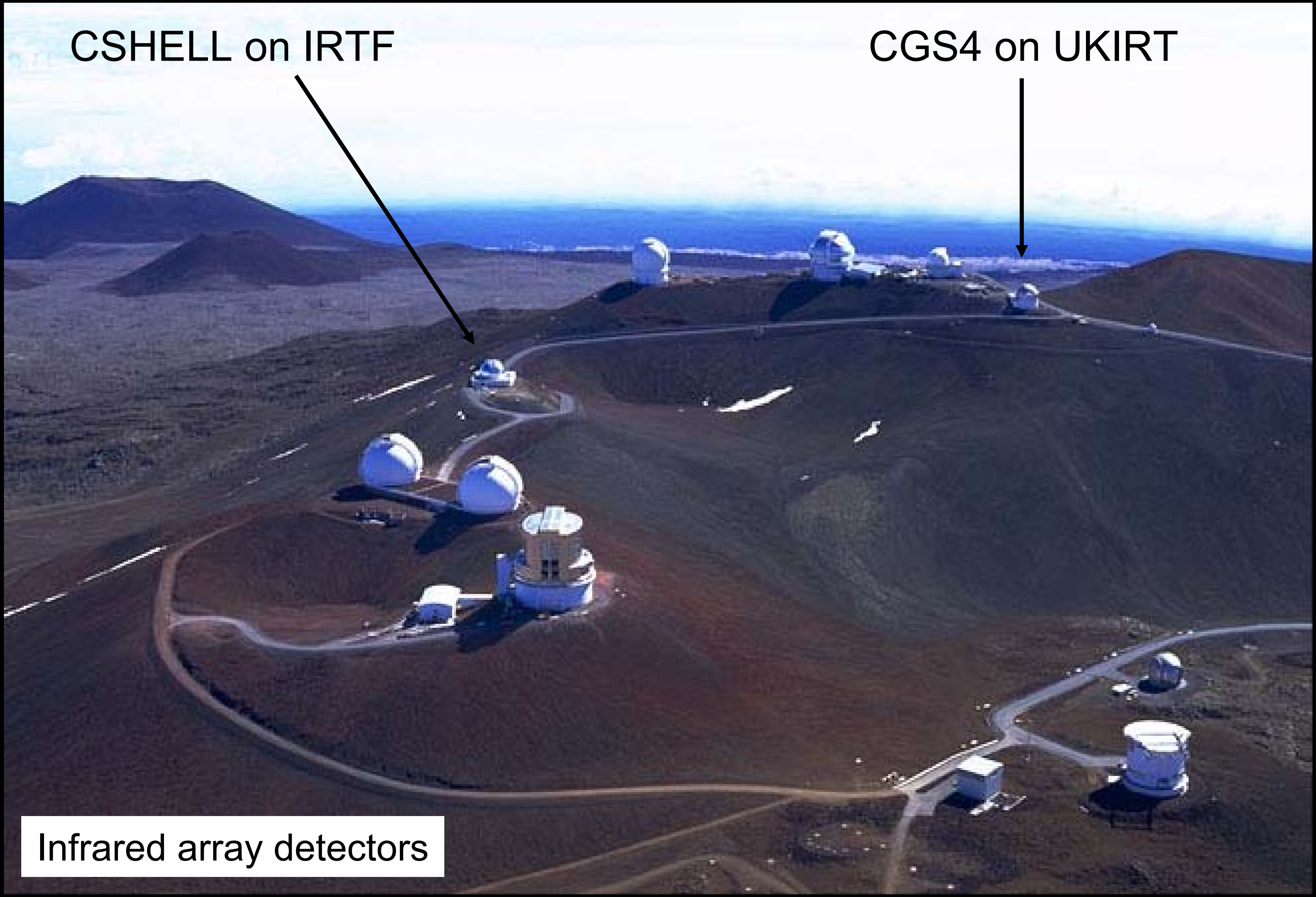




J. L. Gottfried, B. J. McCall, & T. Oka, J. Chem. Phys. 118, 10890 (2003)

poster: Jennifer Gottfried

Back to the Interstellar Search



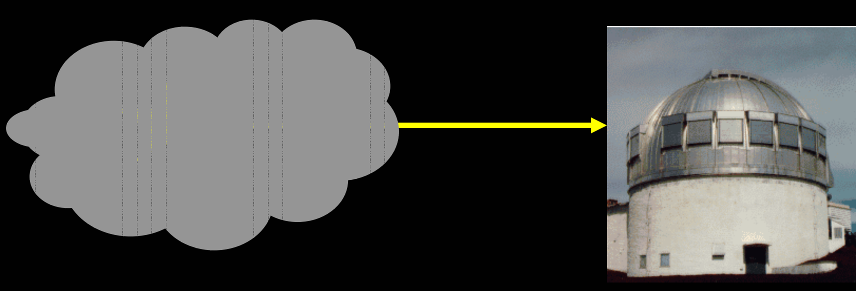
First detection!

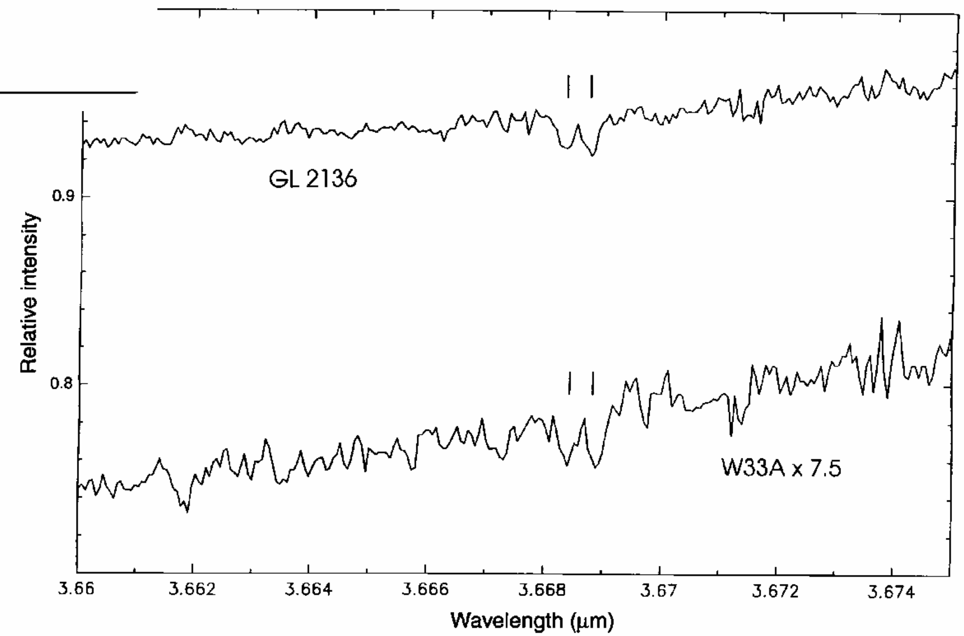
LETTERS TO NATURE

Detection of H_3^+ in interstellar space

T. R. Geballe* & T. Oka†

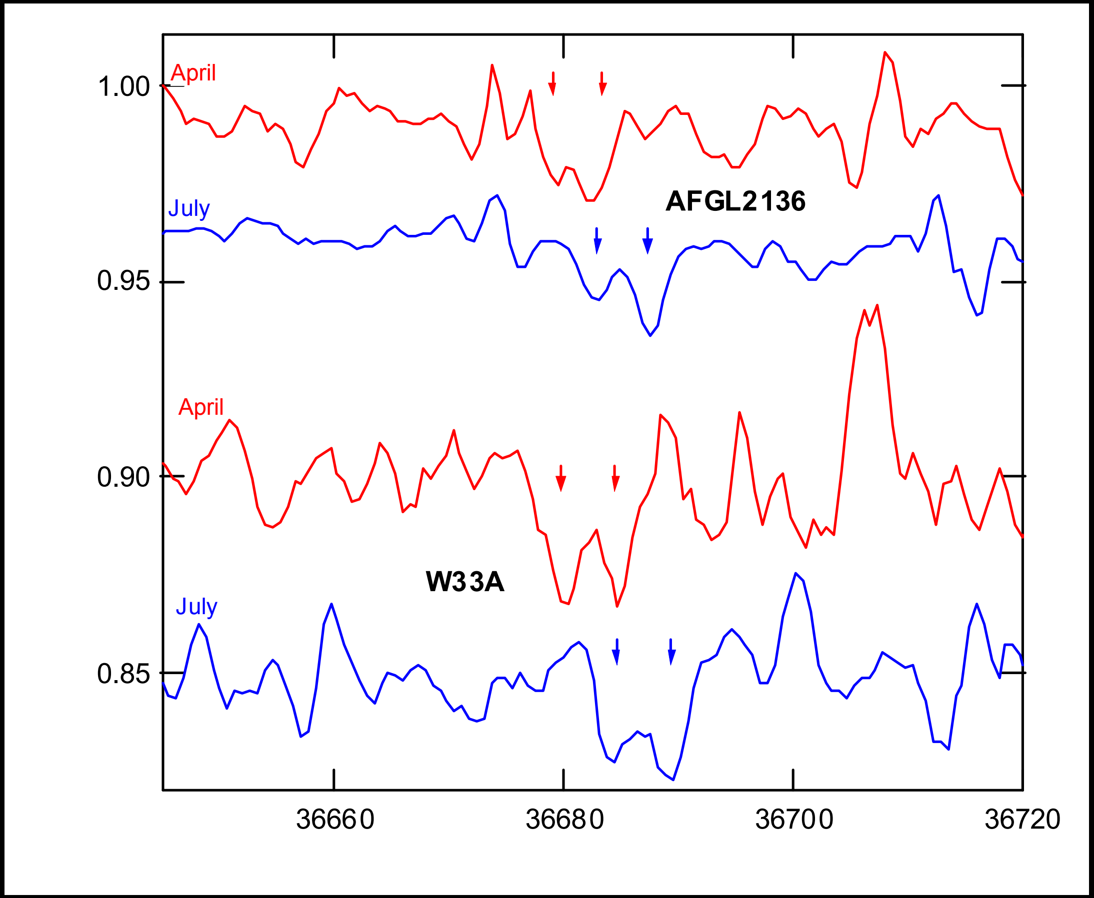
* Joint Astronomy Centre, University Park, Hilo, Hawaii 96720, USA
† Department of Astronomy and Astrophysics, Department of Chemistry and the Enrico Fermi Institute, The University of Chicago, Chicago, Illinois 60637-1403, USA



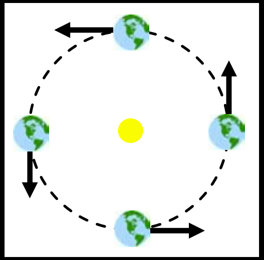


T. R. Geballe & T. Oka, Nature 384, 334 (1996)

Confirmed by Doppler Shift



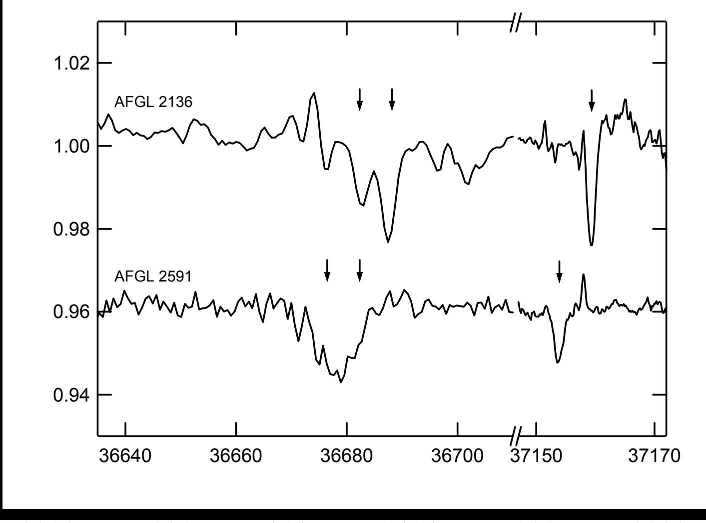
reprocessed
↓
Doppler shift confirms interstellar origin



B. J. McCall, T. R. Geballe, K. H. Hinkle & T. Oka, Astrophys. J. 522, 338 (1999)

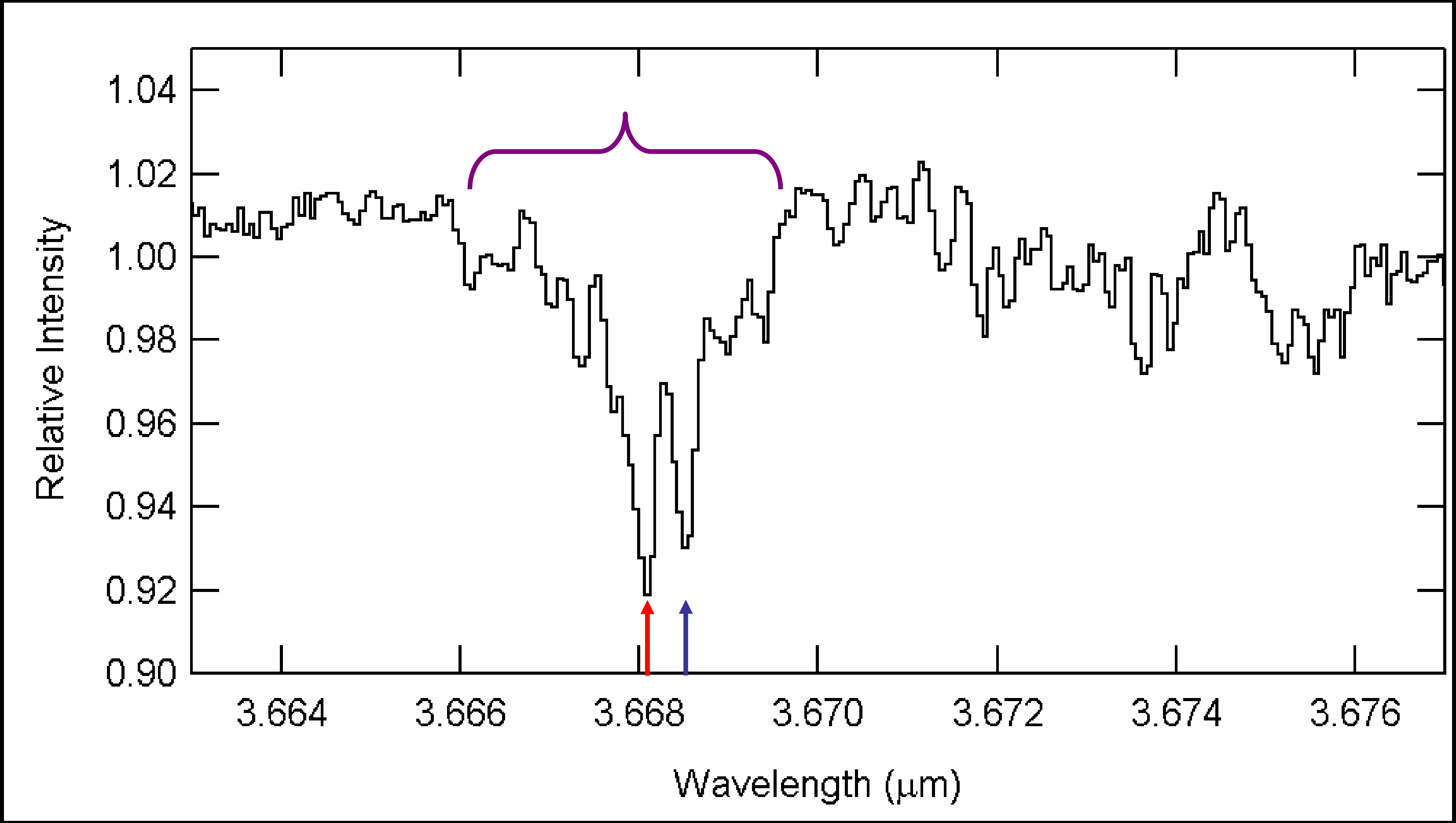
H_3^+ as a Probe of Dense Clouds

- Spectrum gives $N(H_3^+) = 1\text{–}5\times10^{14}$ cm^{-2}
- Given $n(H_3^+)$ from model, and $N(H_3^+)$ from infrared observations:
  - path length $L = N/n \sim 3\times10^{18}$ cm ~ 1 pc
  - density $\langle n(H_2)\rangle = N(H_2)/L \sim 6\times10^{4}$ cm^{-3}
  - temperature $T \sim 30$ K
- Unique probe of clouds
- Consistent with expectations
  - confirms dense cloud chemistry



B. J. McCall, T. R. Geballe, K. H. Hinkle & T. Oka, Astrophys. J. 522, 338 (1999)

The Galactic Center



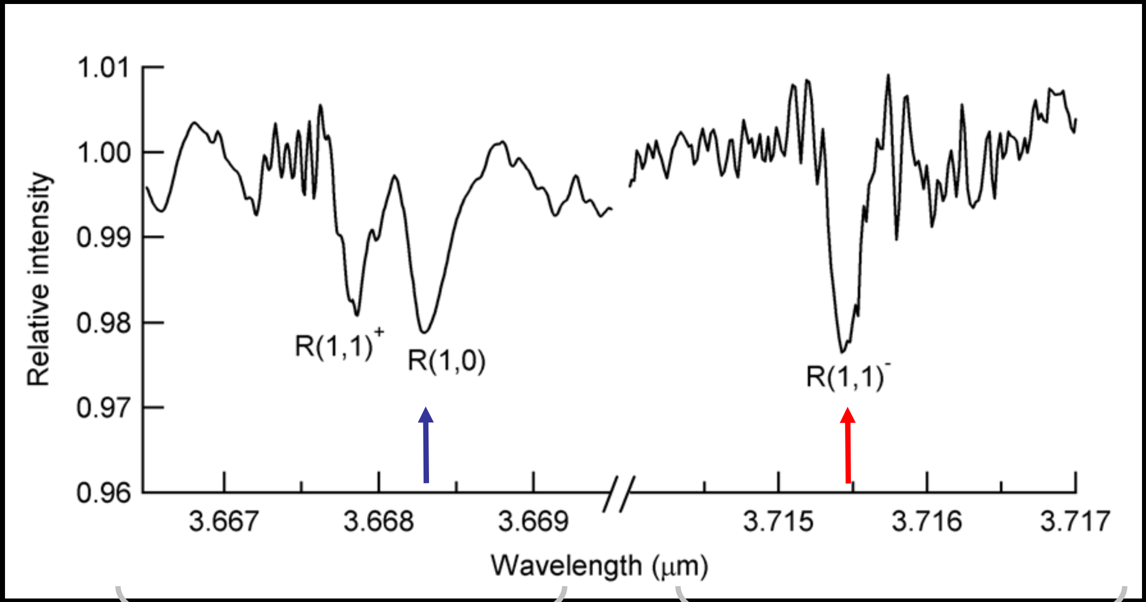
$N_{para} = 5.1(1.7) \times 10^{14}\ cm^{-2}$

$N_{ortho} = 2.4(1.1) \times 10^{14}\ cm^{-2}$

$N_{broad} = 17.5(3.9) \times 10^{14}\ cm^{-2}$

T. R. Geballe, B. J. McCall, K. H. Hinkle & T. Oka, Astrophys. J. 510, 251 (1999)

Cygnus OB2 12



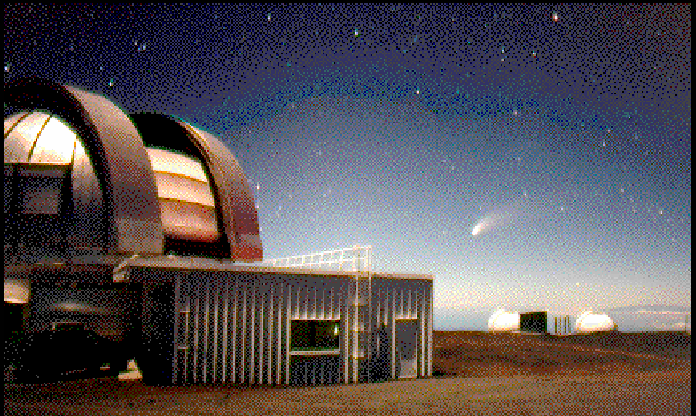
$N_{para} = 2.4(3) \times 10^{14}$ cm^{-2}

$N_{ortho} = 1.4(2) \times 10^{14}$ cm^{-2}

Similar column density to dense clouds!!

observed at UKIRT

observed at Kitt Peak



B. J. McCall, T. R. Geballe, K. H. Hinkle & T. Oka, Science 279, 1910 (1998)

Chemistry & Implications

Formation

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

$$H_2 + H_2^+ \rightarrow H_3^+ + H \quad \text{(fast)}$$

Destruction

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

Steady State

$$= \text{——} \;\; \text{————} = \frac{(3\times10^{-17}\ \text{s}^{-1})}{(5\times10^{-7}\ \text{cm}^3\ \text{s}^{-1})} \times (2400)$$

$$= 10^{-7}\ \text{cm}^{-3}$$

Density Independent!

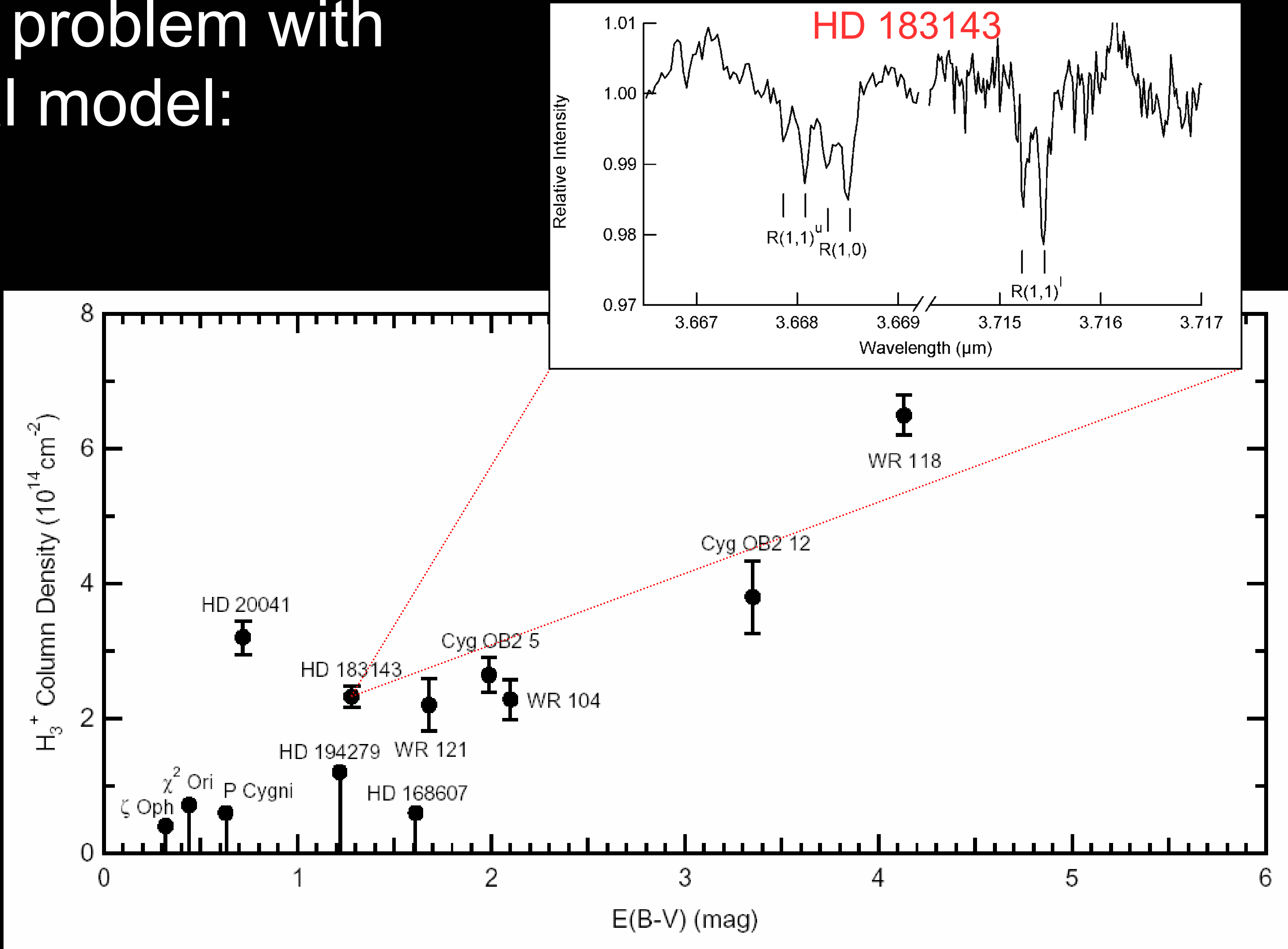
→ path length $L = N/n \sim 1$ kpc

→ density $\langle n(\text{H})\rangle = N(\text{H})/L \sim 20\ \text{cm}^{-3}$

Other Diffuse Clouds, too!

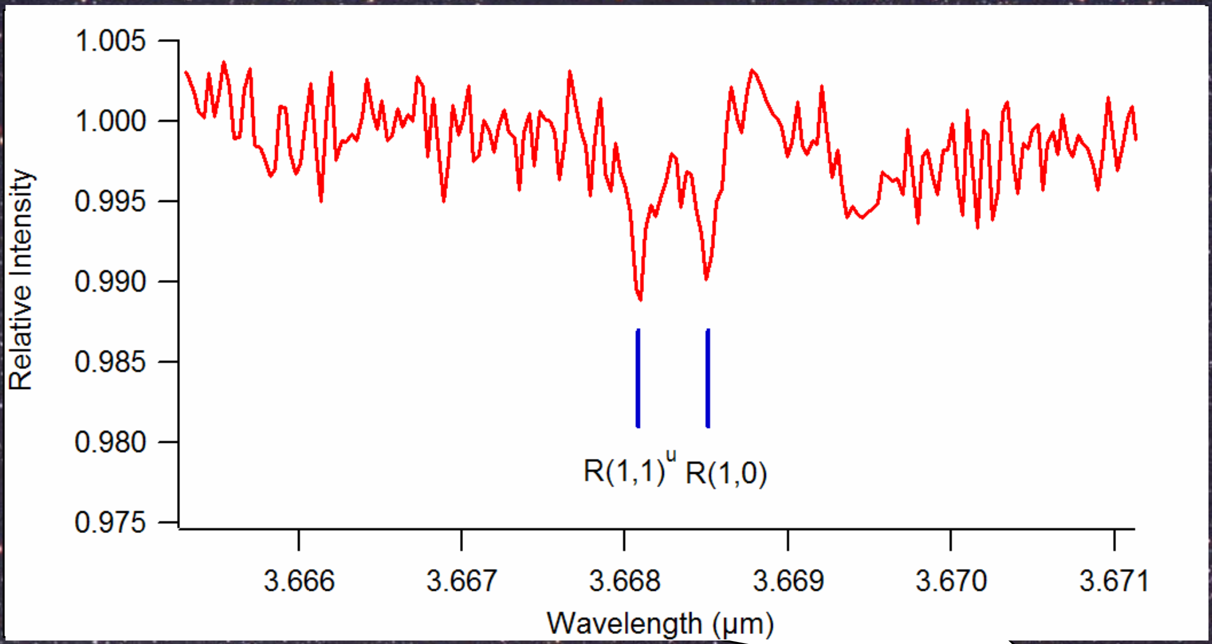
- General problem with chemical model:

- ζ
- k_e
- $[e^-]/[H_2]$



McCall, et al.
Astrophys. J. 567, 391 (2002)

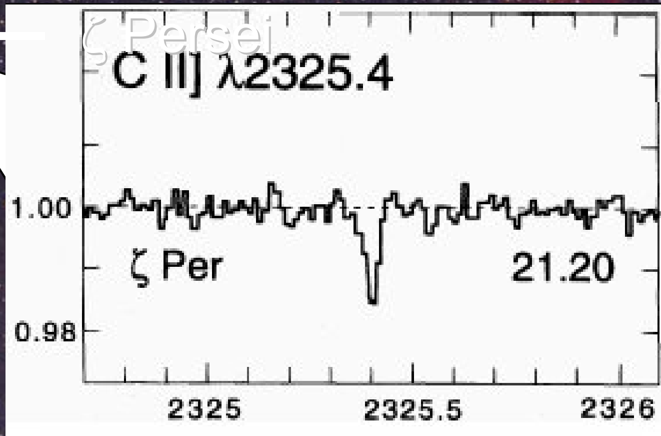
H_3^+ toward ζ Persei



Rules out $[e^-]/[H_2]$

ζ Persei

N(C^+) from HST



Cardelli et al. Astrophys. J. 467, 334 (1996)

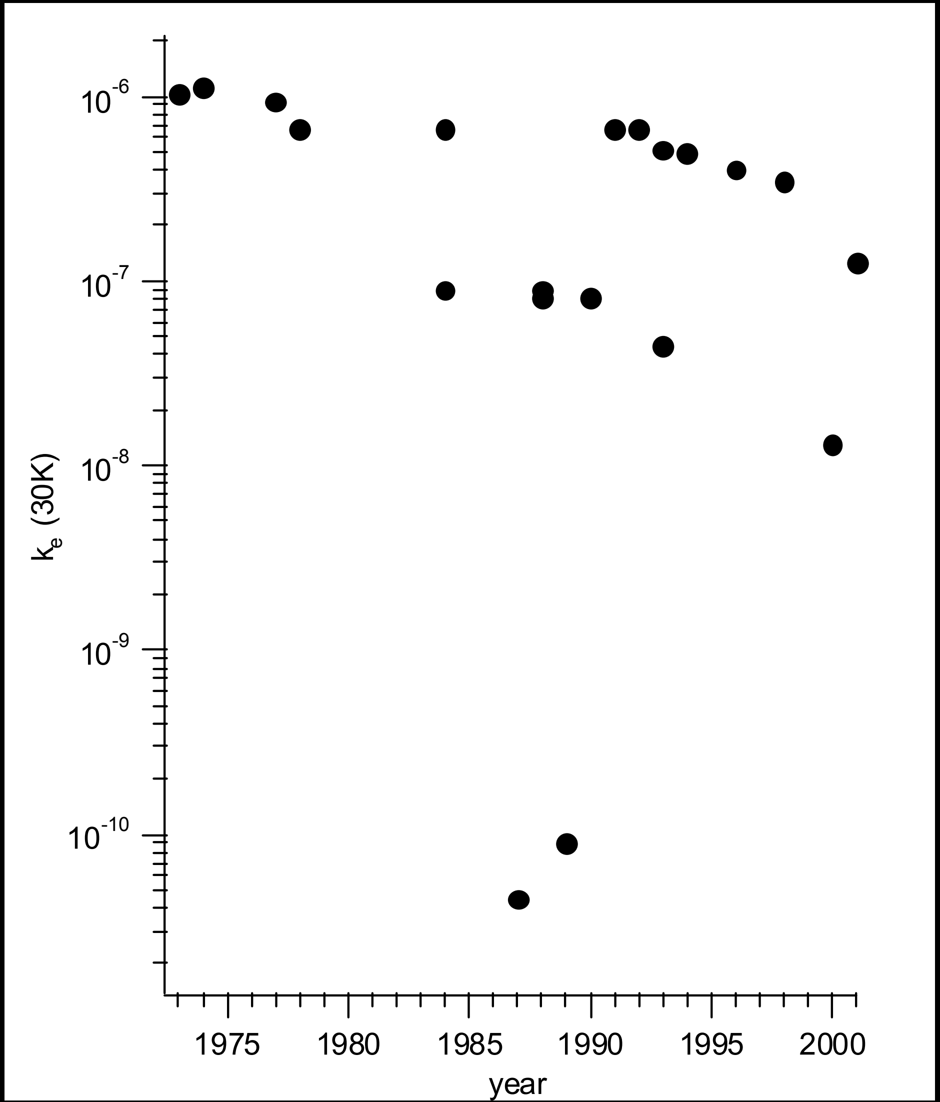
N(H_2) from Copernicus

HD	NAME	ℓ^{II}	b^{II}	S. T.	E(B−V) mag.	r [pc]	log N(H_2) [cm^{-2}]	log N(HI) [cm^{-2}]	log N(HI + H_2) [cm^{-2}]
24398	ζ 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	ξ 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

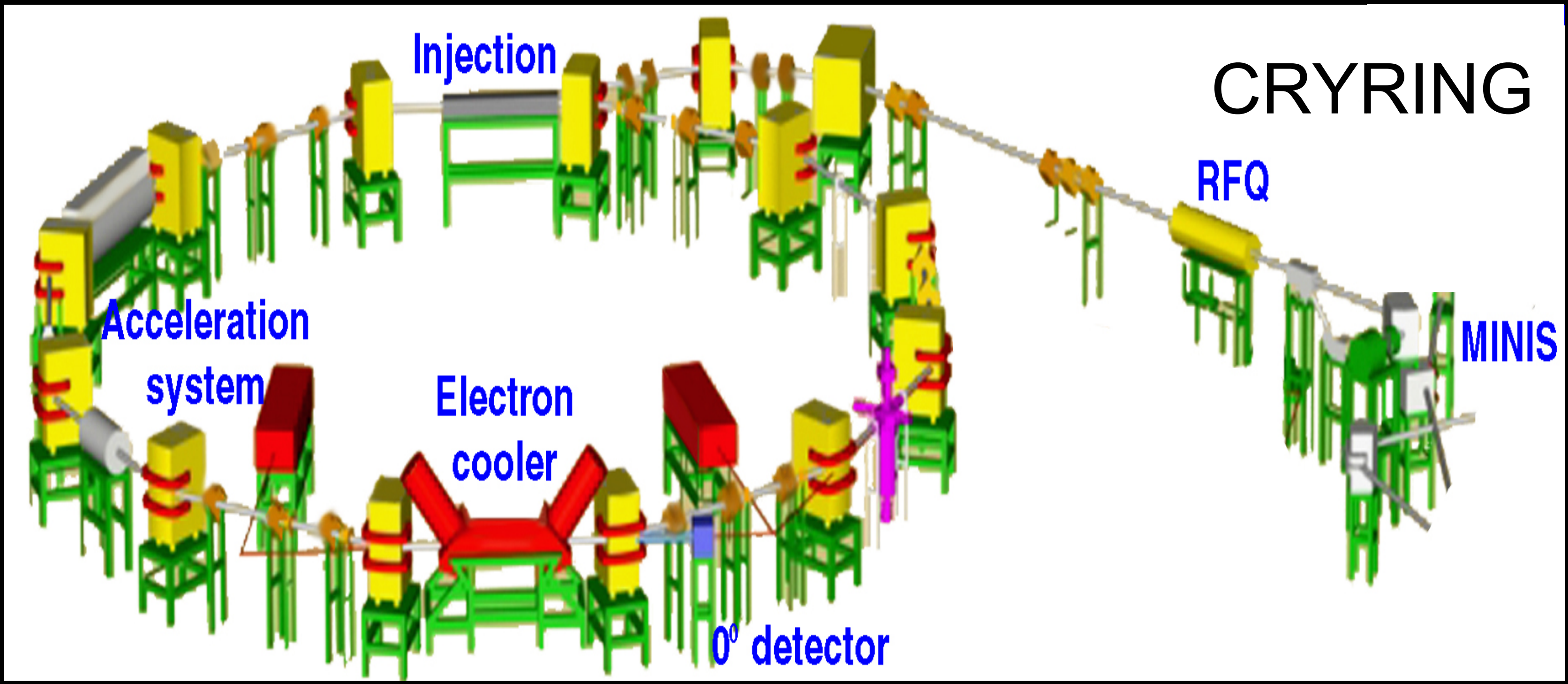
Savage et al. Astrophys. J. 216, 291 (1977)

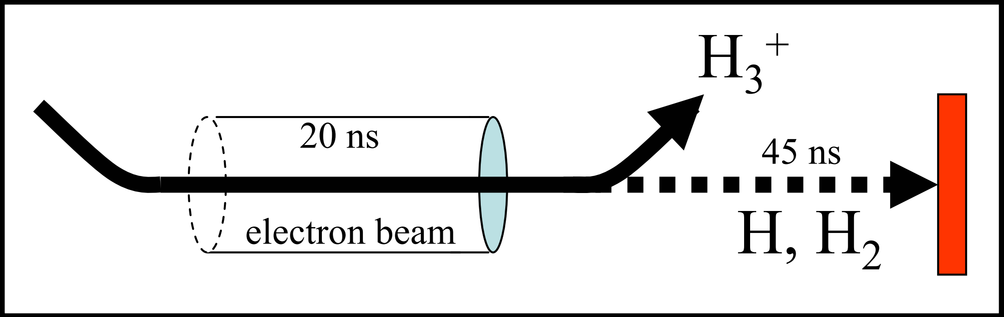
H_3^+ Dissociative Recombination

- Laboratory values of k_e varied by 4 orders of magnitude!
- Even worse: theory in infancy, way off...
- Big problem: not measuring H_3^+ in ground states



Storage Ring Measurements

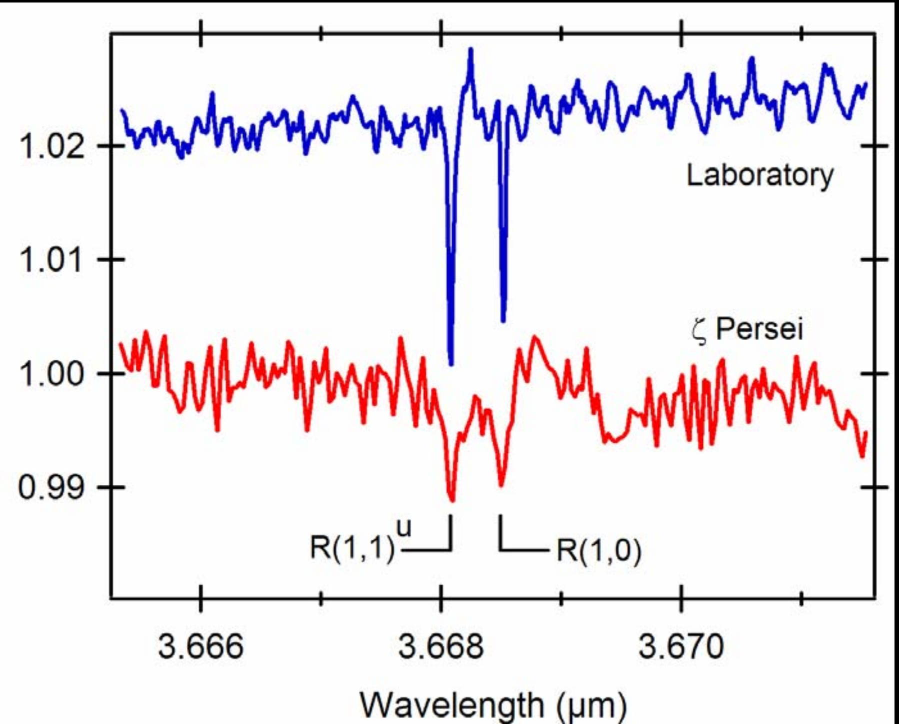


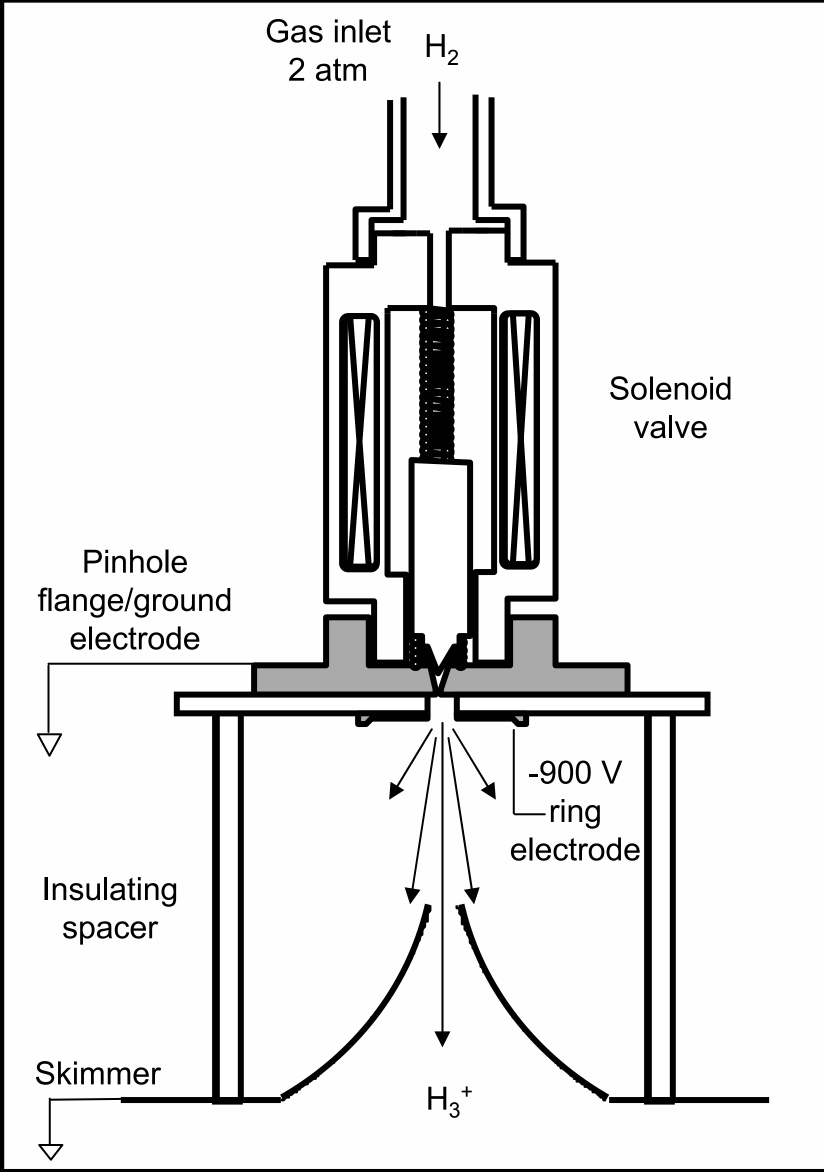


- \+ Complete vibrational relaxation
- \+ Very simple experiment
- \+ Control H_3^+ – e^- impact energy
- \- Rotationally hot ions produced
- \- No rotational cooling in ring

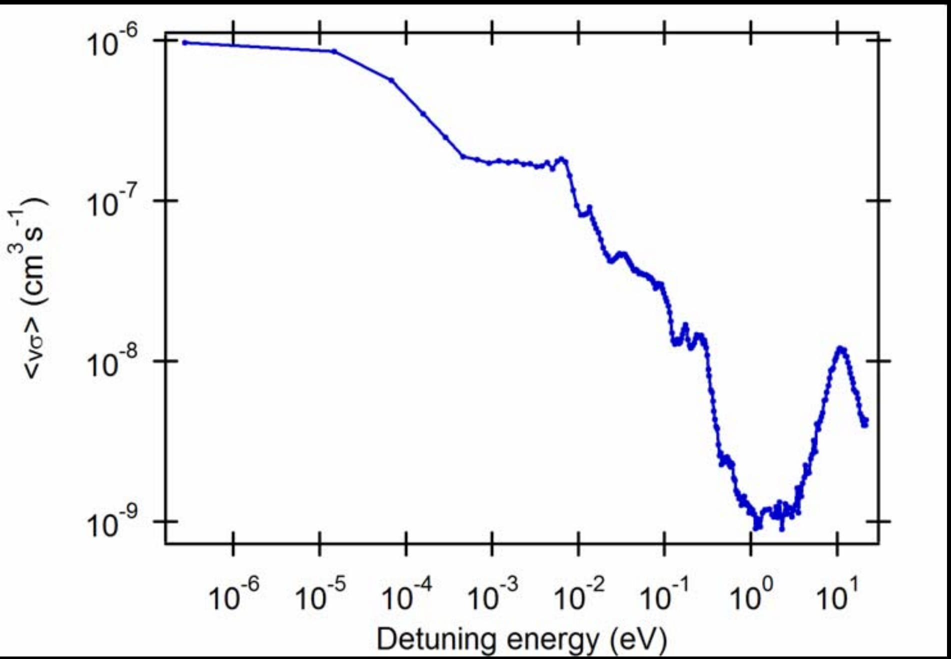
Berkeley Supersonic Ion Source

- Supersonic expansion leads to rapid cooling
- Discharge from ring electrode downstream
- Skimmer to minimize arcing



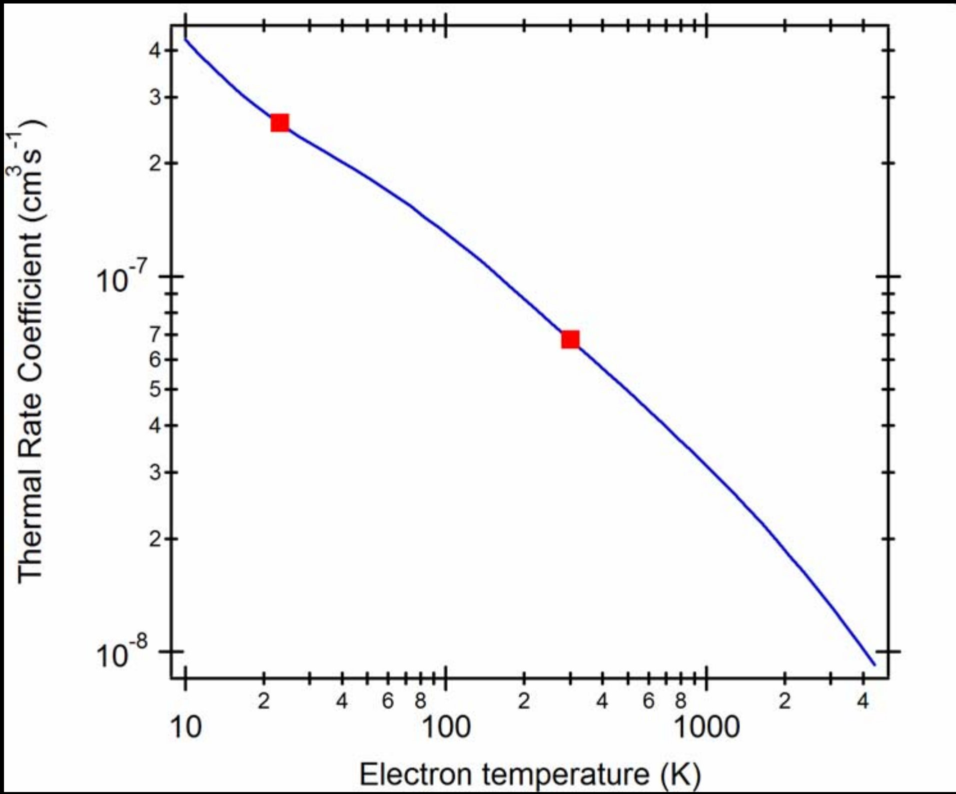


CRYRING Results



Rules out k_e

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



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

Implications for ζ Persei

$$\frac{N(H_3^+)}{L} = [H_3^+] = \frac{\zeta}{k_e} \frac{N(H_2)}{N(e^-)}$$

$$\zeta L = k_e \, N(H_3^+) \, \frac{N(e^-)}{N(H_2)}$$

$(2.6\times10^{-7}\ \mathrm{cm^3\ s^{-1}})$ $(8\times10^{13}\ \mathrm{cm^{-2}})$ (3.8×10^{-4})

$$\zeta L = 8000\ \mathrm{cm\ s^{-1}}$$

Adopt $\zeta = 3\times10^{-17}\ \mathrm{s^{-1}}$

L = 85 pc

$\langle n \rangle = 6\ \mathrm{cm^{-3}}$

Adopt L=2.1 pc

$\zeta = 1.2\times10^{-15}\ \mathrm{s^{-1}}$

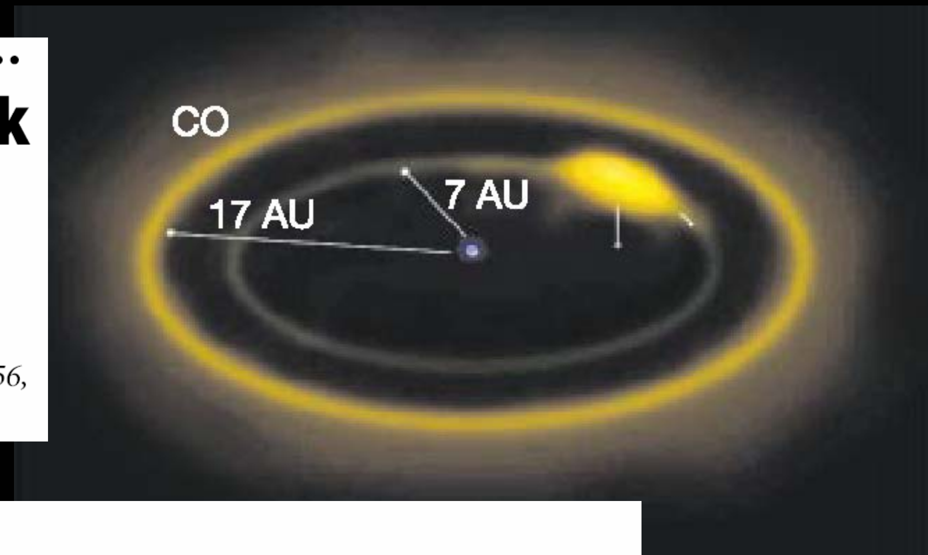
(40x higher!)

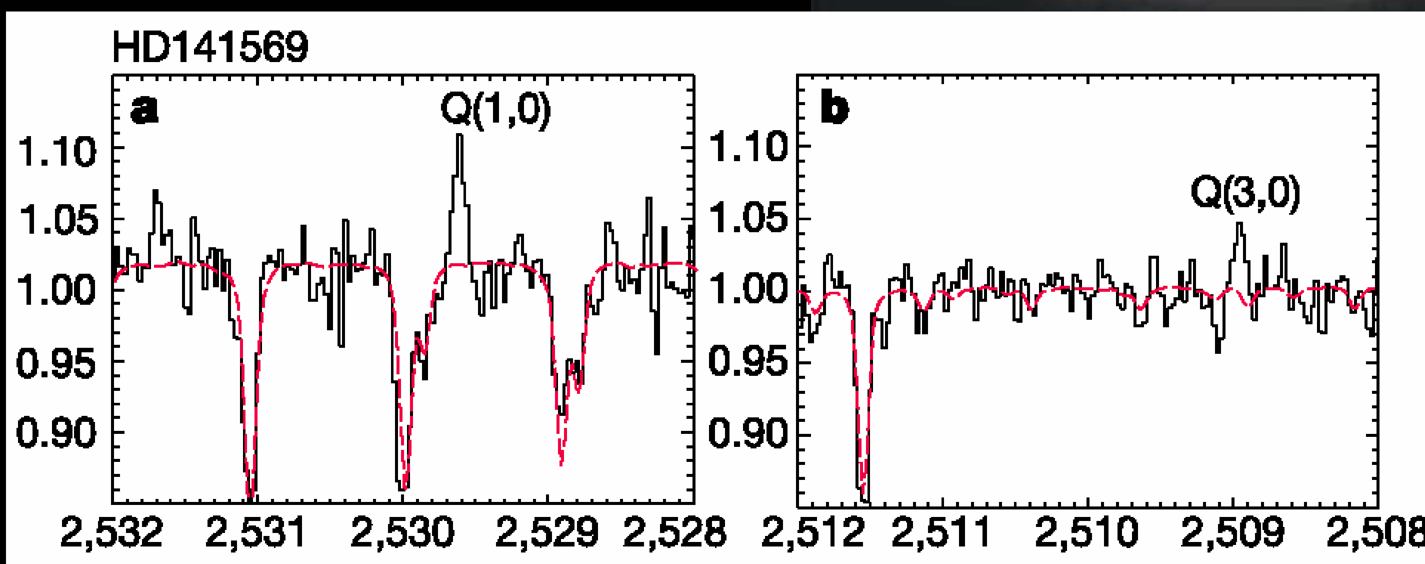
Extrasolar Planetary H_3^+ ?

CO and H_3^+ in the protoplanetary disk around the star HD141569

Sean D. Brittain & Terrence W. Rettig

University of Notre Dame, Center for Astrophysics, Notre Dame, Indiana 46556, USA





S. D. Brittain & T. W. Rettig, Nature 418, 57 (2002)

Schawlow Thinking Disputed about Diatomic Molecules

In his very readable article "Chemistry: Blithe Sibling of Physics" (PHYSICS TODAY, April, page 11), Dudley Herschbach quotes the well-known remark attributed to Art Schawlow, "A diatomic molecule has one atom too many."

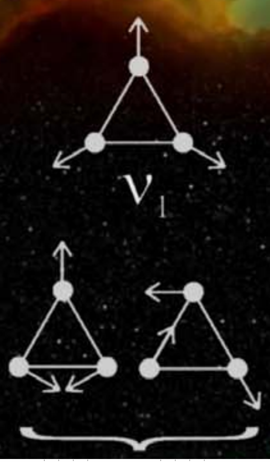
My love affair with H_3+ over many years,[1] has led me to believe that some beautiful subtleties of physics do not appear until one faces a three-particle system. I suspect quantum chromodynamicists agree with this.

As for me, I say that a diatomic molecule has one atom too *few*.

Reference

1. T. Oka, Rev. Mod. Phys. **64**, 1141 (1992).

TAKESHI OKA
(t-oka@uchicago.edu)
University of Chicago
Chicago, Illinois



T. Oka,
Physics Today July 1997