Interstellar Molecules: From Hydrogen to Amino Acids

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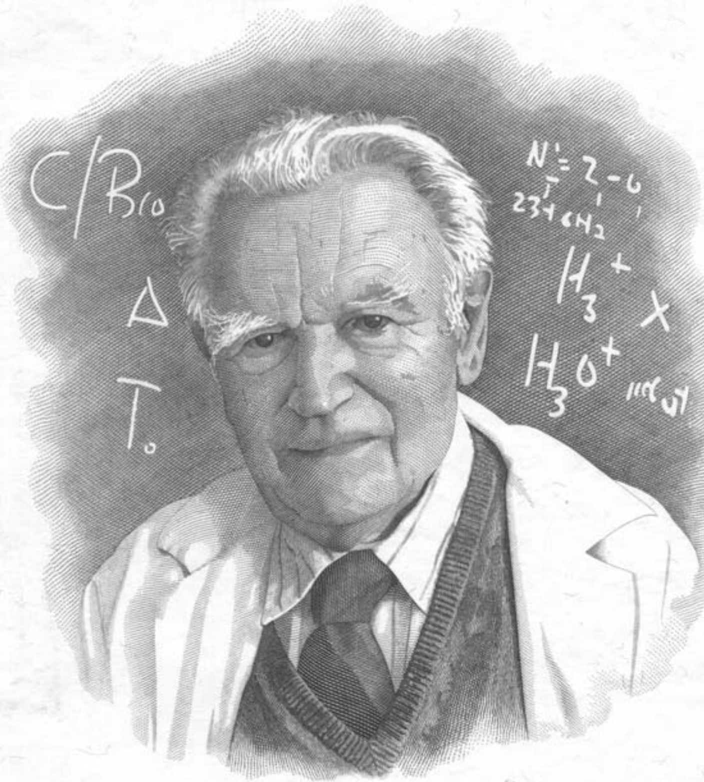
"Hydrogen is the most important constituent of the Universe."

G. Herzberg



Gerhard Herzberg

Gerhard Herzberg

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In this talk・・・・・・・・

- Overview of Interstellar Space and Interstellar Molecules

  (ex) H_3^+ and HCO^+

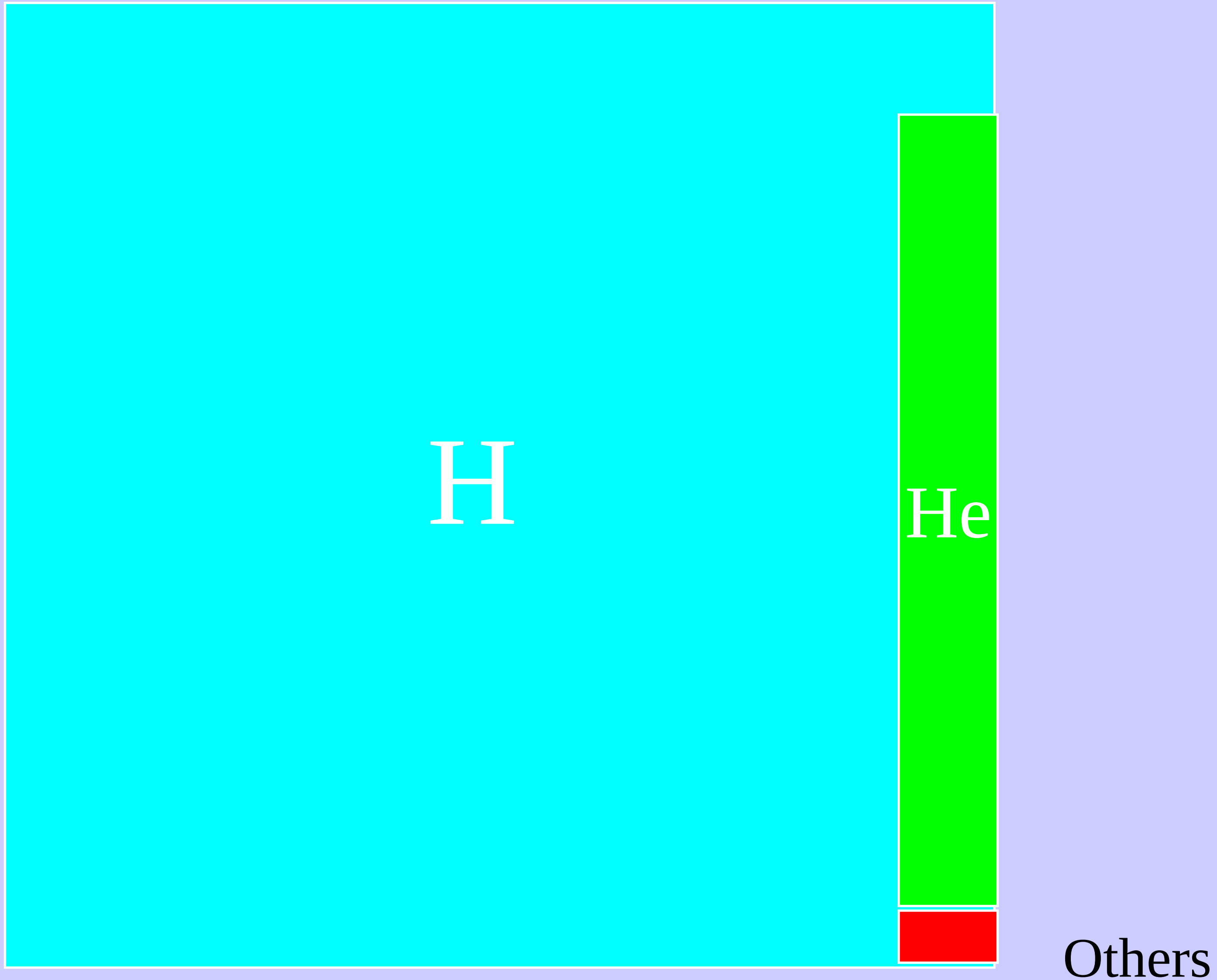
- Submillimeter-wave Spectroscopy and New Initiatives in Submillimeter Astronomy

  Multiply deuterated species in space

  Anions in the lab and in space

  Biological molecules in space

Cosmic Abundance



21cm-Line of Hydrogen Atom

- van de Hulst (Leiden Observatory)

  1944 pointed out possibility of H 21cm line.
- Ewen, Purcell (Harvard University)

  Oort, Muller (Leiden Observatory)

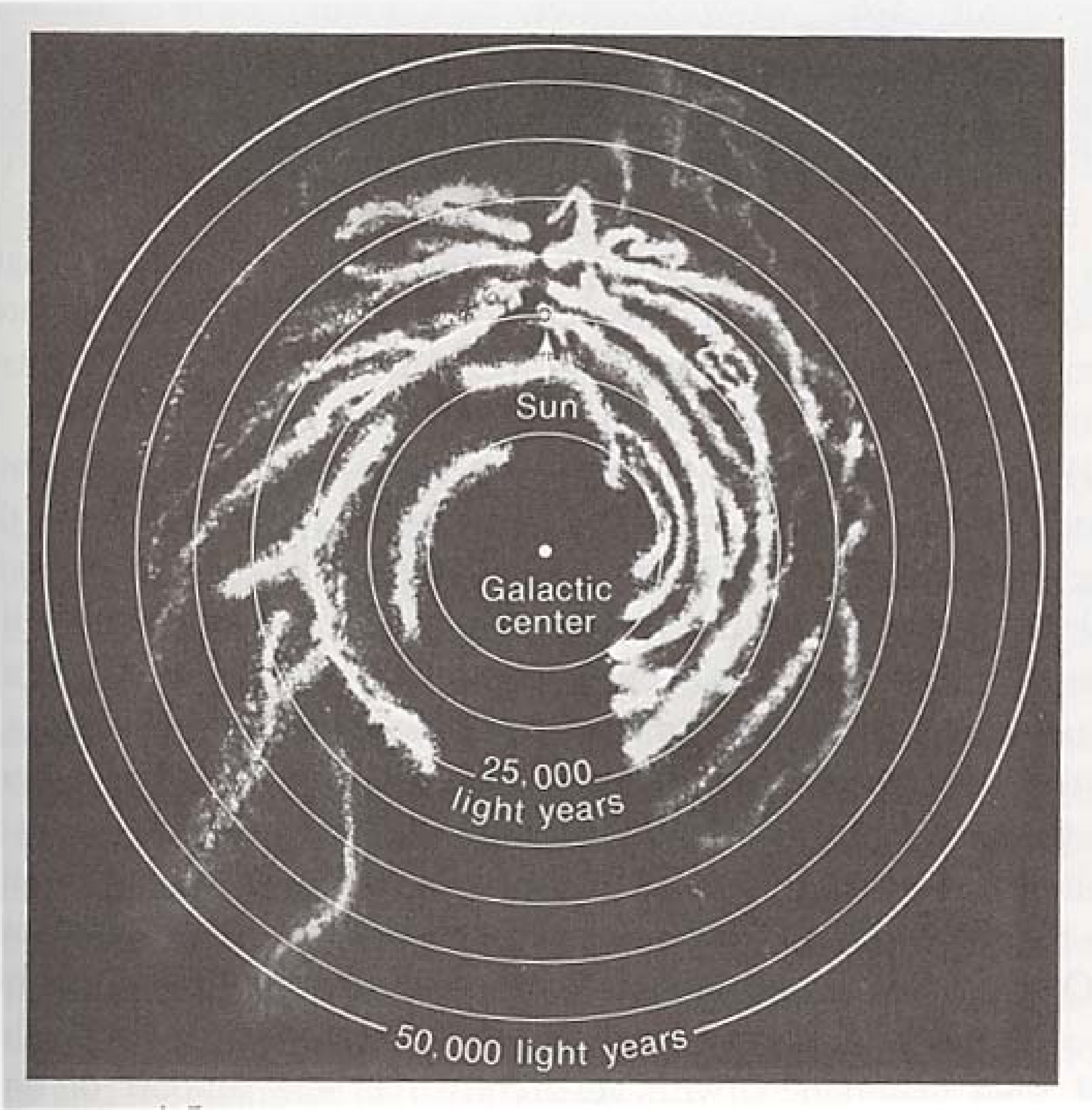
  1951 detection of the line

  Christiansen, Hindman (Australia, AAO)

- Hydrogen Maser (N. F. Ramsey)

  1 420 405 751.786Hz

  21.10611405 cm


Sun
Galactic
center
25,000
light years
50,000 light years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Discovery of Interstellar Molecules

- 1814 Fraunhofer lines
- 1904 Absorption lines of Ca,K against bright stars
- 1934 Discovery of 4 Diffuse Interstellar Bands (DIBS) Still remain unidentified.
- 1937-1941 Discovery of CH^+,CH,CN 4230-4300 Å
- 1951 Bates, Spitzer : skeptical about interstellar molecules.
- 1955~ Townes, Shklovsky: Pointed out possibility of observing molecules with radio telescopes.

OH, NH_3, HCN, CO……………

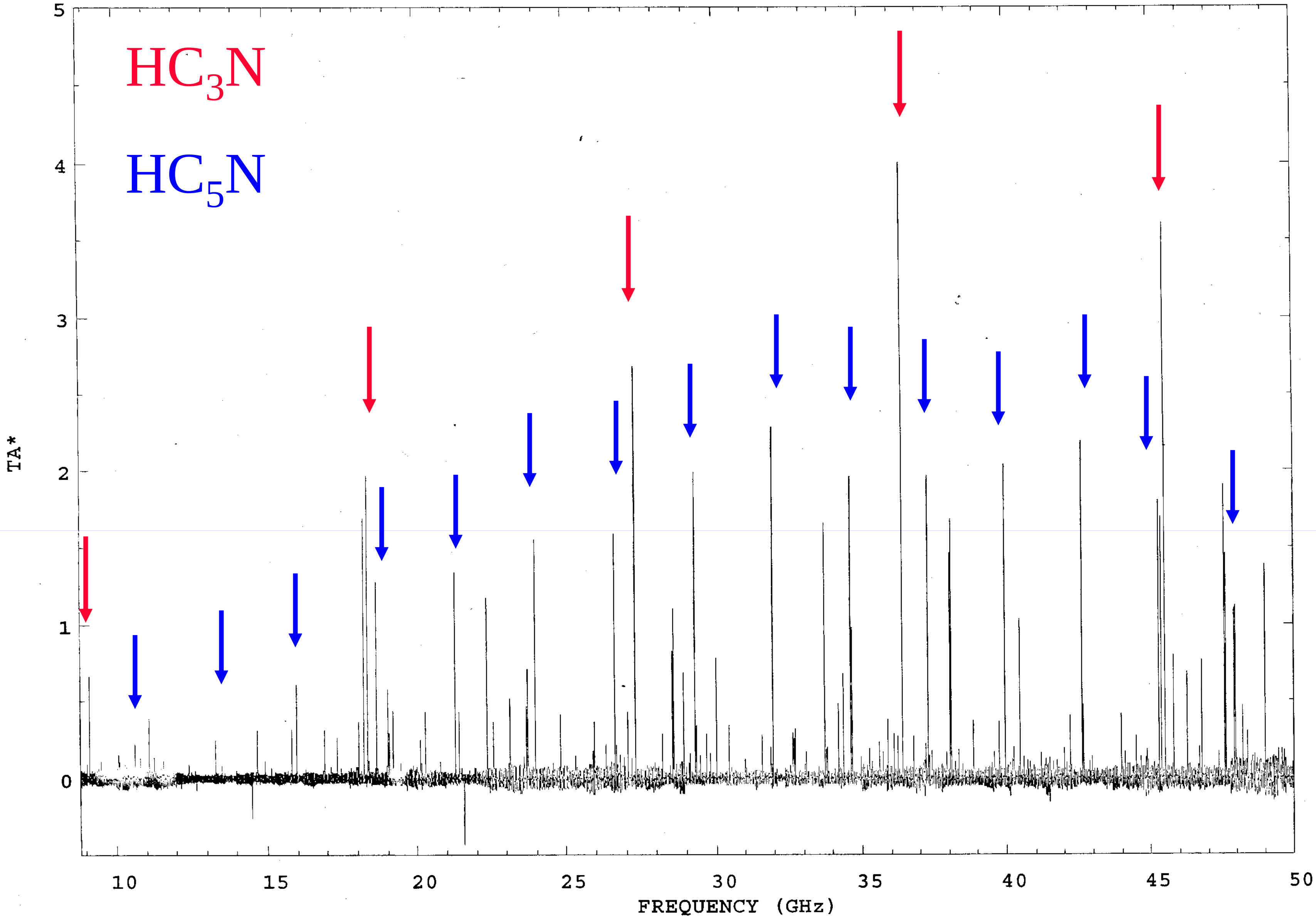
Table 4.1: List of Interstellar Molecules Identified(as of May, 2004).

Simple hydrides, oxides, sulfides, halogenated compounds				
H_2(IR)	CO	NH_3	CS	$NaC\ell^*$
HF	SiO	SiH_4^*(IR)	SiS	$AlC\ell^*$
$HC\ell$	SO_2	C_2(IR)	H_2S	$KC\ell^*$
H_2O	OCS	CH_4^*(IR)	PN	AlF^*
N_2O	CO_2			
Nitryles, Acetylene derivatives				
C_3^*(IR)	HCN	CH_3CN	HNC	$C_2H_4^*$(IR)
C_5^*(IR)	HC_3N	CH_3C_3N	HNCO	C2H2*(IR)
C_3O	HC_5N	CH_3C_5N?	HNCS	HC_4H^*(IR)
C_3S	HC_7N	CH_3C_2H	HNCCC	HC_6H^*(IR)
C_4Si^*	HC_9N	CH_3C_4H	CH_3NC	
	$HC_{11}N$	CH_3CH_2CN	HCCNC	
	HC_2CHO	CH_2CHCN		
Aldehydes, Alcohols, Ethers, Ketones, Amides				
H_2CO	CH_3OH	HCOOH	CH_2NH	H_2C_3
H_2CS	CH_3CH_2OH	$HCOOCH_3$	CH_3NH_2	H_2C_4
CH_3CHO	CH_3SH	CH_3COOH	NH_2CN	H_2C_6
NH_2CHO	$(CH_3)_2O$	CH_2OHCHO		
H_2CCO	$(CH_3)_2CO$	CH_2CHOH		
Cyclic molecules				
c-C_3H_2	c-SiC_2	c-SiC_3^*	c-C_3H	c-C_2H_4O
$C_6H_6^*$(IR)	c-C_2H_4S?			
Molecular Ions				
CH^+(Opt)	HCO^+	$HCNH^+$	H_3O^+	HN_2^+
HCS^+	$HOCO^+$	HC_3NH^+	HOC^+	H_3^+(IR)
CO^+	H_2COH^+	SO^+		H_2D^+
				D_2H^+
Free Radicals				
OH	C_2H	CN	C_2O	C_2S
CH	C_3H	C_3N	NO	NS
CH_2	C_4H	C_5N?	SO	SiC^*
CH_3(IR)	C_5H	$HCCN^*$	HCO	SiN^*
NH(UV)	C_6H	CH_2CN	MgNC	CP^*
NH_2	C_7H	CH_2N	MgCN	$SiCN^*$
SH(IR)	C_8H	HNO	NaCN	FeO?
			AlNC	

Molecules identified other than radio are specified individually.
IR: Infrared, Opt: Visible, and UV: Ultraviolet.
* Indicates molecules observed only in Red Giants.
? Reported, however, not yet confirmed.

- Free radicals, ions.
- Carbon chains
- Cyclic molecules

H−C≡C−C≡C−C≡C−C≡C−C≡C−C≡N



HC$_3$N
HC$_5$N
TA*
5
4
3
2
1
0
10
15
20
25
30
35
40
45
50
FREQUENCY (GHz)

Formation of molecules in interstellar space

- Ion-molecule reactions

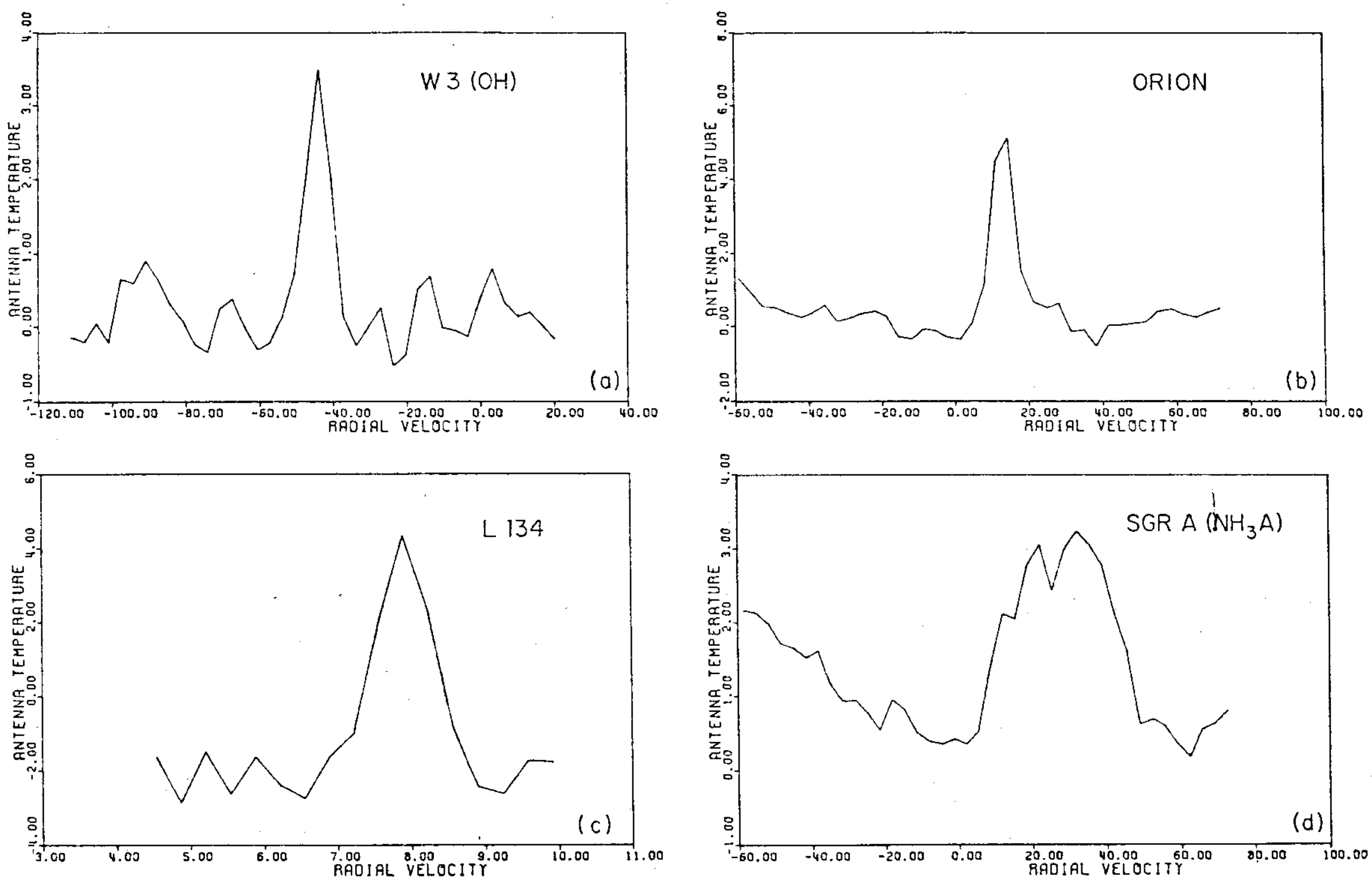
H_3^+ HCO^+

- Neutral molecule reactions

$$CN + C_2H_2 \longrightarrow HC_3N + H$$

- Surface reactions on dust grains

H_2, CO, CO_2, H_2CO, CH_3OH……….



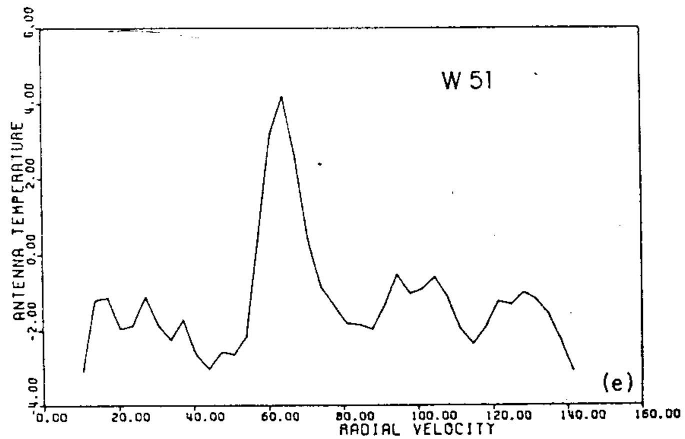


Fig. 1. X-ogen spectra observed for: *a*, W3 (OH); *b*, Orion; *c*, L134; *d*, Sgr A (NH_3A); and *e*, W51. Antenna temperature is in degrees Kelvin uncorrected for antenna efficiency (and dome attenuation in the case of Orion). Radial velocity is in km s^{-1} corrected to the local standard of rest. Spectrum for L134 taken with 100 kHz filter spacing.

Ion-molecule reaction

$$H_2 \longrightarrow H_2^+ + \mathbf{e^-}$$

$$H_2^+ + H_2 \longrightarrow \mathbf{H_3^+} + \mathbf{H}$$

$$H_3^+ + CO \longrightarrow HCO^+ + H_2$$

$$H_3^+ + X \longrightarrow HX^+ + H_2$$

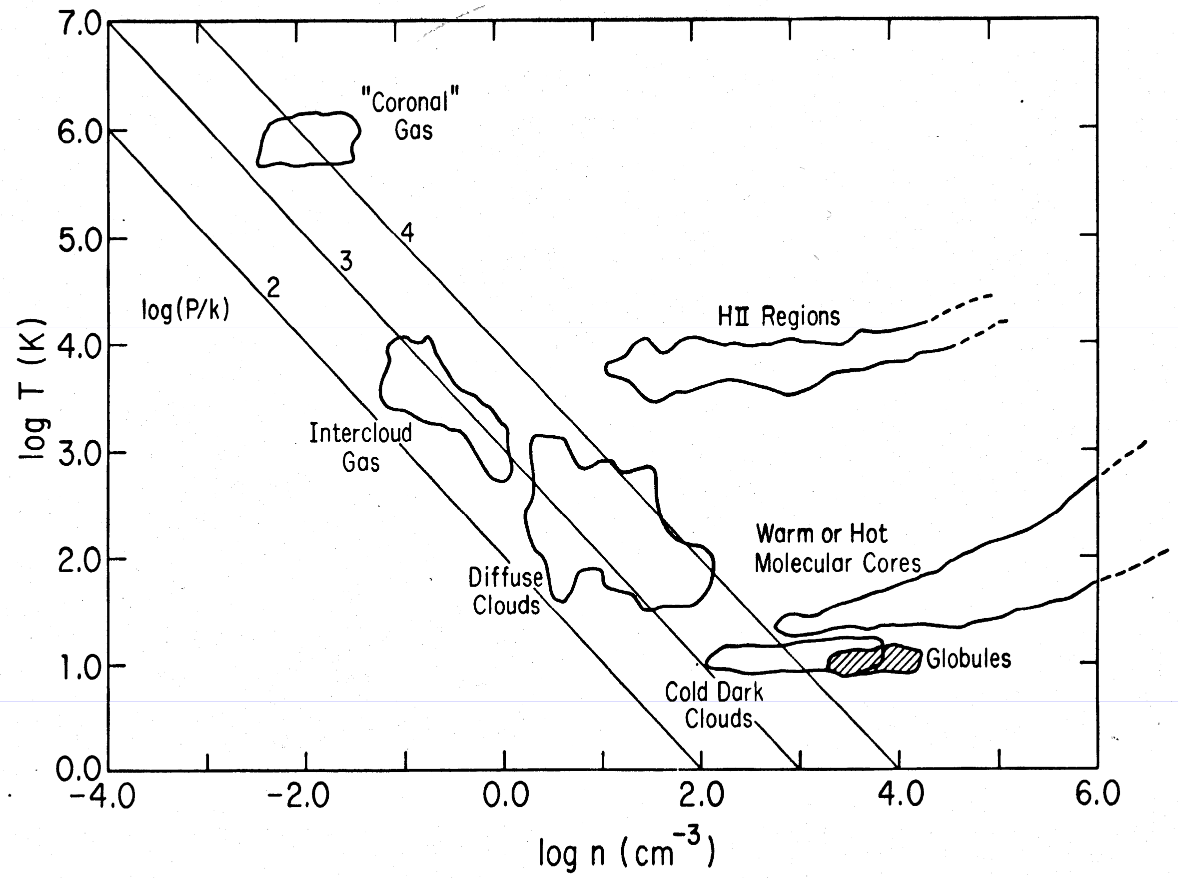


Fig. 4.1. The physical regimes of the interstellar medium, as currently observed.

From B. E. Turner

Particle density of standard atmosphere

3×10^{19} /cm^3

Collision interval

~10^{-9} sec

Molecular Clouds

10 /cm^3

Collision interval

~100 years

H_3^+

- H_3^+ in the laboratories
- H_3^+ in Jupiter
- H_3^+ in Dark clouds
- H_3^+ in Diffuse clouds
- Dissociative recombination of H_3^+ with electrons

Discovery of H_3^+ spectra

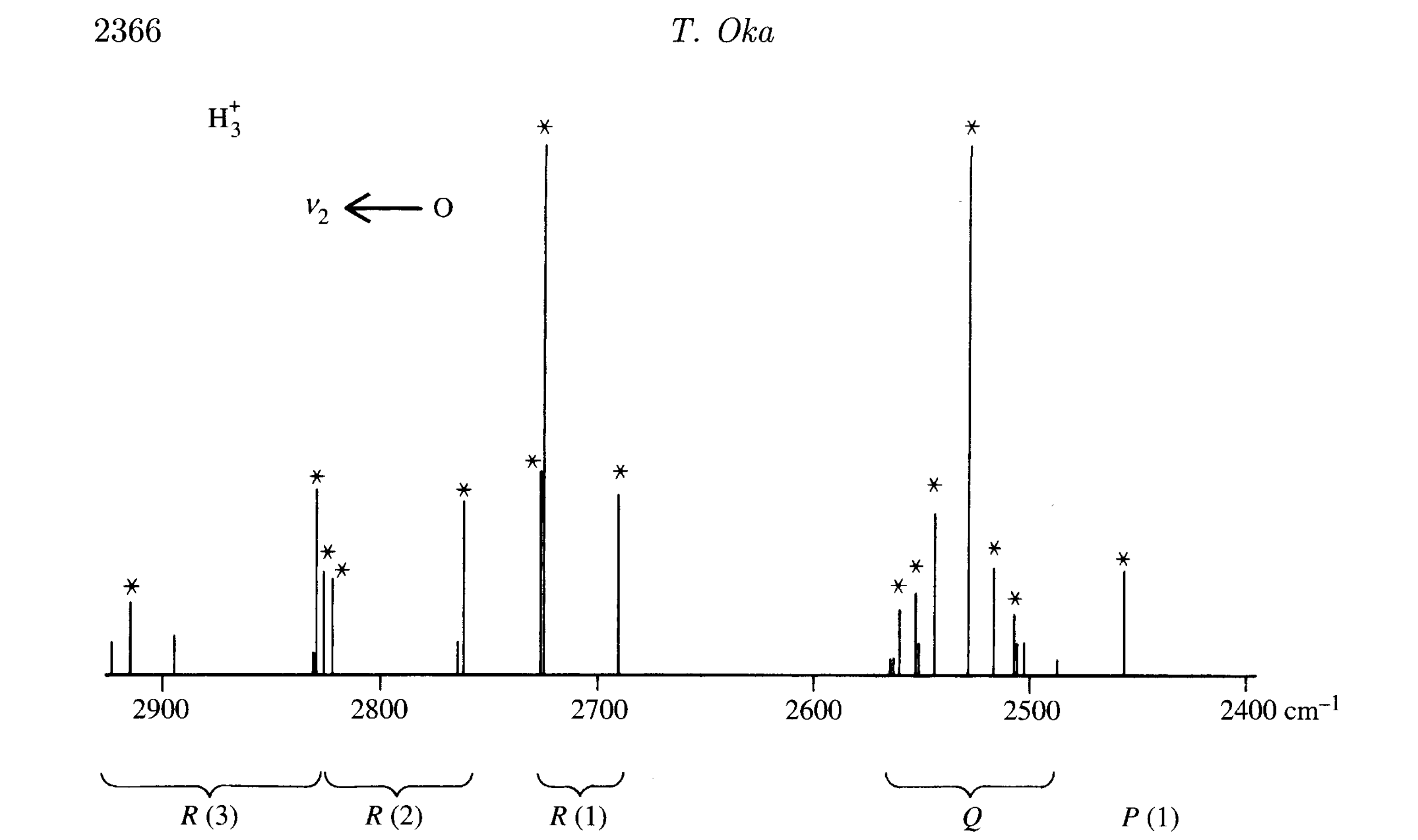


Figure 2. The spectral pattern for the ν_2 band of H_3^+ calculated by Watson for the rotational temperature of 200 K. Observed transitions are marked with asterisks (Oka 1980).

T. Oka, *Phys. Rev. Lett.* 45, 531-534(1980)

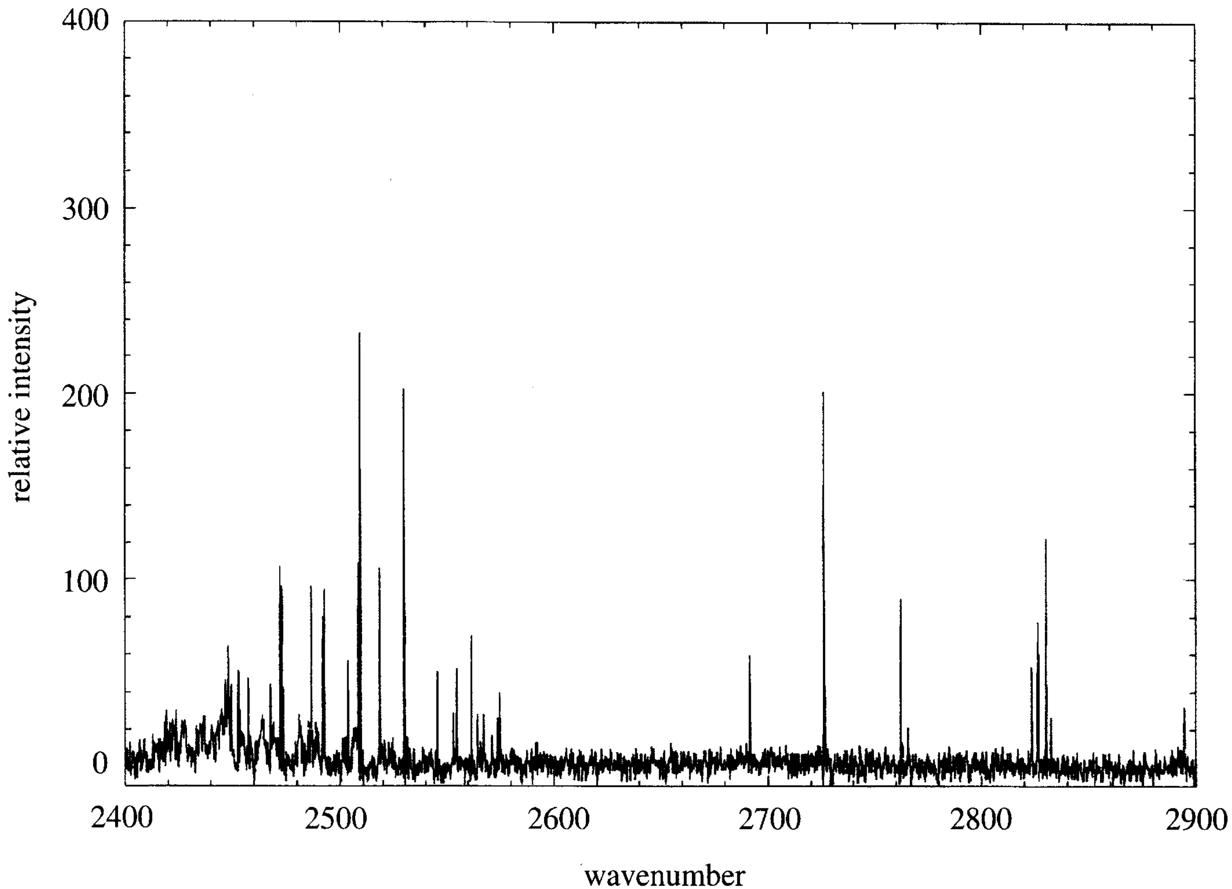
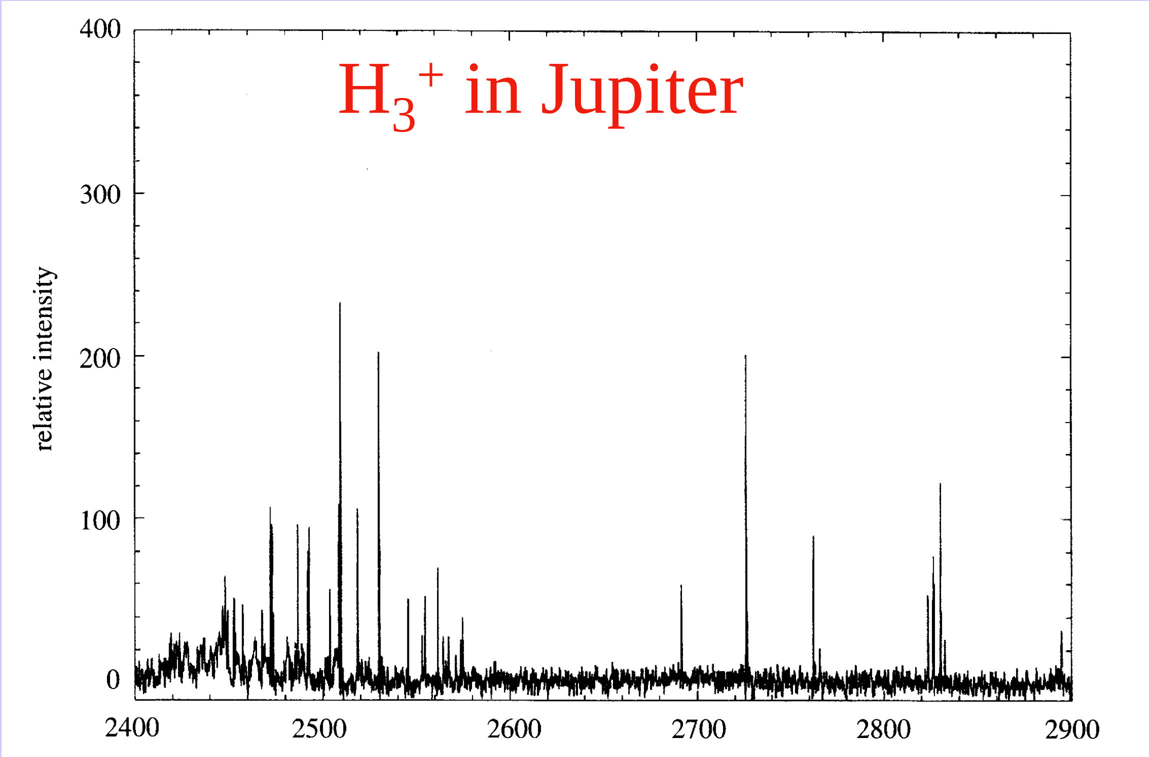
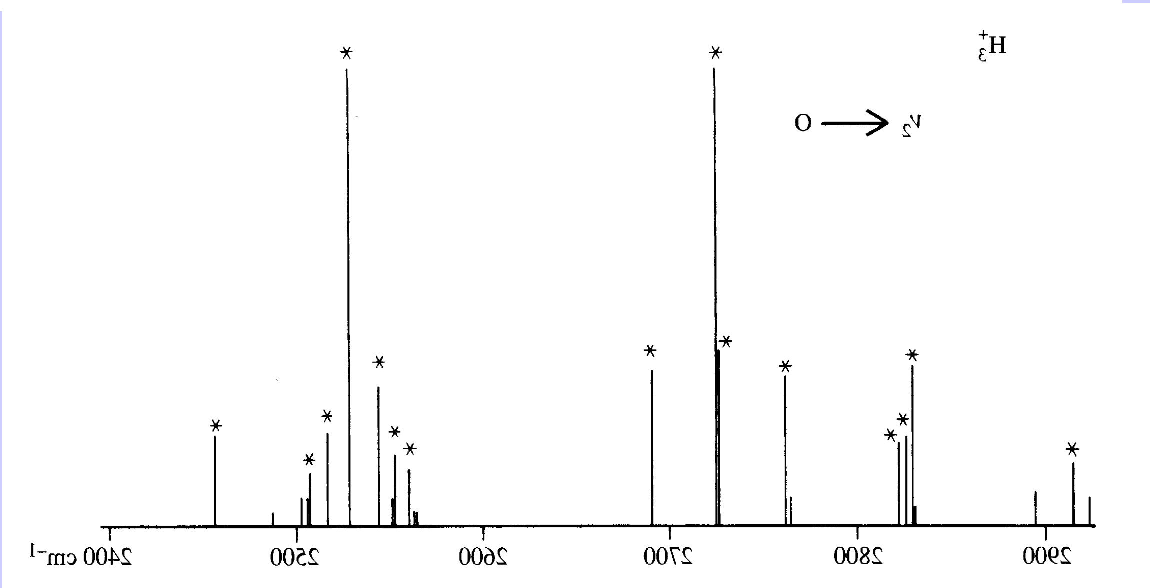


Figure 3. The intense and pure H_3^+ emission spectrum recorded on the southern hemisphere of Jupiter at 60° latitude and mean longitude 40° (Maillard *et al.* 1990).

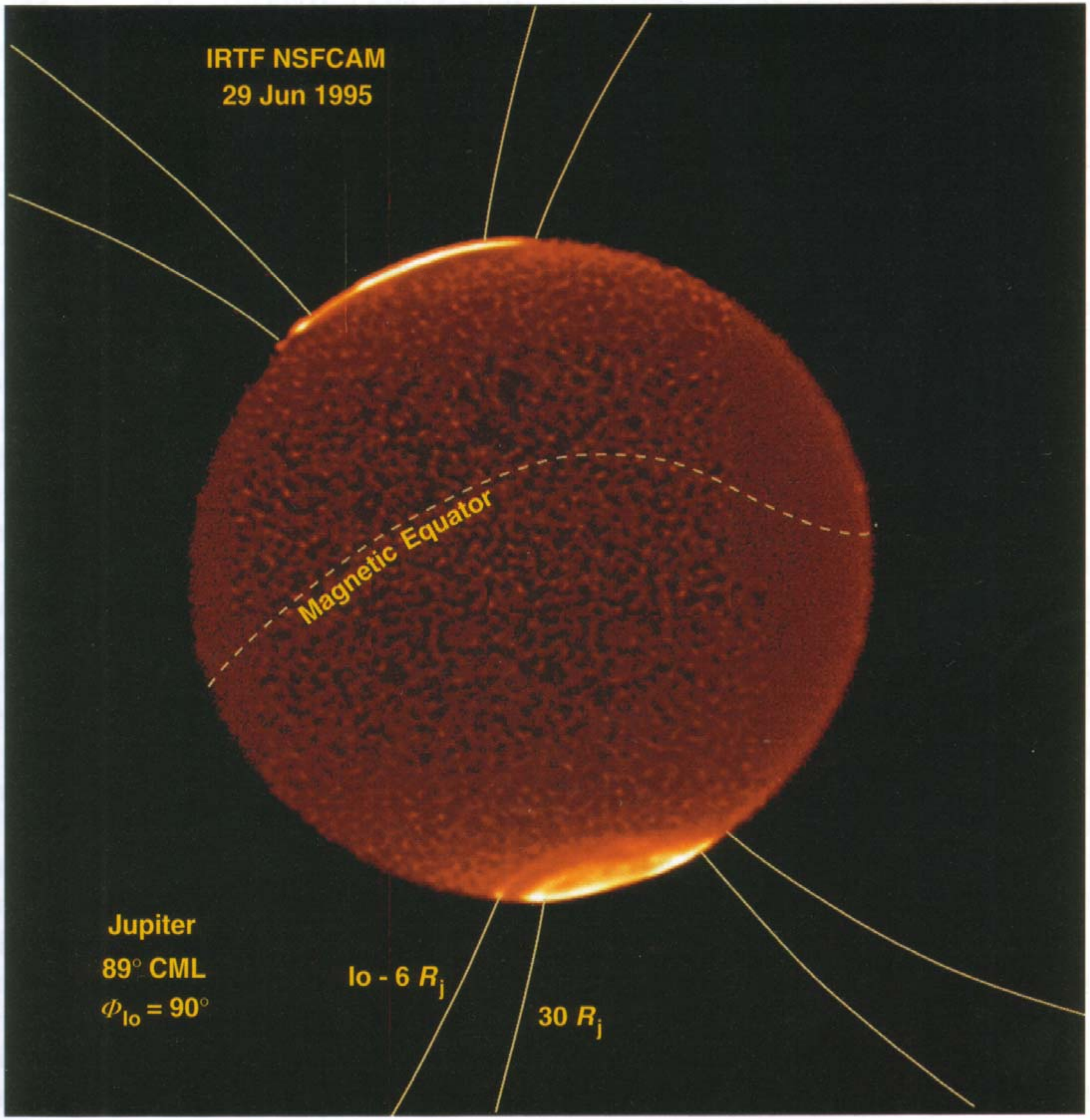
J.P. Maillard *et al*, Astrophys. J. **363**, L37(1990)



H_3^+ in Jupiter
relative intensity
400
300
200
100
0
2400
2500
2600
2700
2800
2900



H_3^+
O → ν_2
2400 cm^{-1}
2500
2600
2700
2800
2900


IRTF NSFCAM
29 Jun 1995
Magnetic Equator
Jupiter
89° CML
$\Phi_{Io} = 90°$
Io - 6 R_j
30 R_j

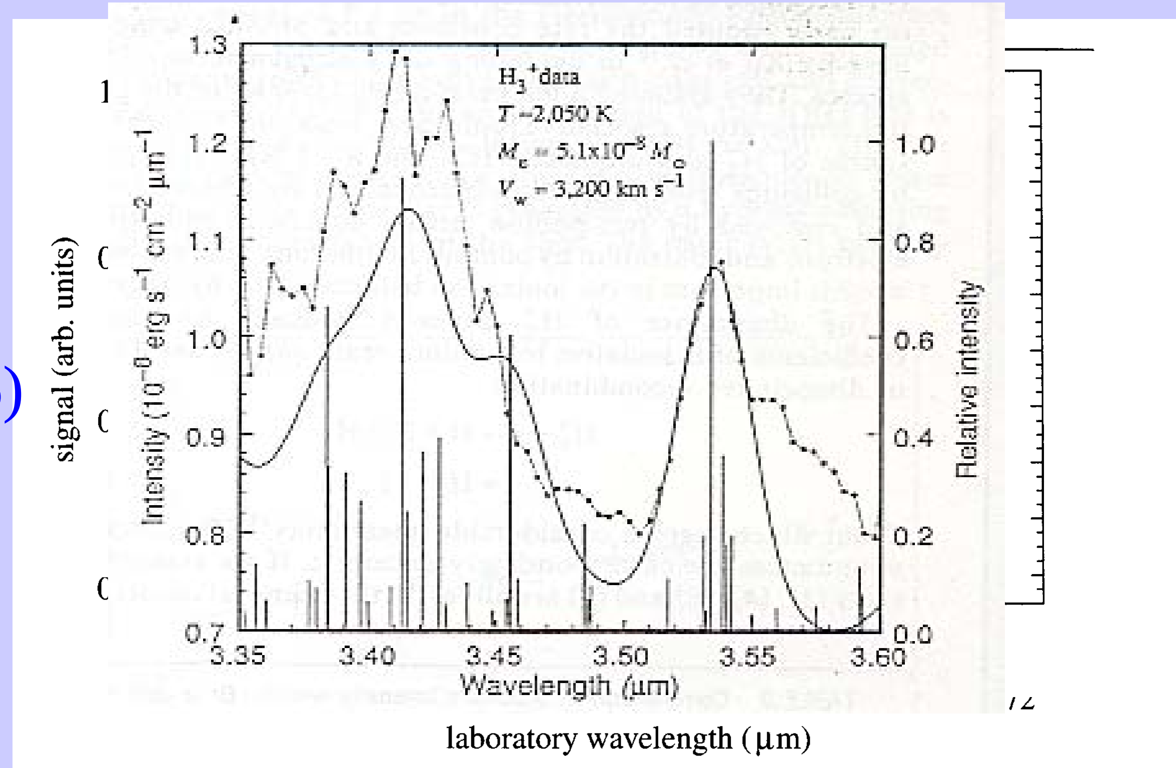
Detection of Interstellar H_3^+

SN1987A Miller, Tennyson, Lepp, and Dalgarno(1992)

Dark cloud

Geballe and Oka(1996)

Diffuse cloud



Geballe, McCall, Hinkle, and Oka(1999)

Formation and destruction of H_3^+

$$H_2 \rightarrow H_2^+ \qquad : \zeta \sim 10^{-17} s^{-1}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad : k_1$$

In dark cloud

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \qquad : k_2$$

$$[H_3^+] \sim \zeta [H_2]/ k_2 [CO]$$

In diffuse cloud

$$H_3^+ + e^- \rightarrow 3H,\ H_2 + H \qquad : k_d$$

$$[H_3^+] \sim \zeta [H_2]/ k_d [e^-]$$

In dark clouds

$[H_3^+] \sim \zeta\,[H_2]/\,k_2\,[CO]$

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

$k_2 = 1.8\times10^{-9}\ cm^3 s^{-1}$

$[CO]/[H_2] = 1.5\times10^{-4}$

$[H_3^+] = 1.1\times10^{-4}\ cm^{-3}$

Observed Column densities

$[H_3^+]L = 6\times10^{14}\ cm^{-2}$ W33

$= 4\times10^{14}\ cm^{-2}$ GL2136 $\Rightarrow$ L=1~2 pc

In diffuse clouds

$[H_3^+] \sim \zeta [H_2]/ k_d [e^-]$

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

$k_d=1.8\times10^{-7}$ cm^{3}s^{-1} (4.6×10^{-7})

$[e^-]/[H_2]=5.6\times10^{-4}$

$[H_3^+]=1.1\times10^{-7}$ cm^{-3}

Observed Column density

$[H_3^+]L=3.8\times10^{14}$ cm^{-2} Cyg OB2 No.12

$\Rightarrow$ L=400~1200 pc

High-resolution Spectroscopy of Negative ions

- OH^- (OD^-)

  IR, FIR

- SH^- (SD^-)

  IR, sub-mm

- FHF^-, $ClHCl^-$, NH_2^-, NCO^-, NCS^-, N_3^-

  IR

Mystery of “B1377”

- Kawaguchi et al (1995)

  Detected a series of emission lines toward IRC+10216. Linear molecule of the rotational constant of

  1376.86868 MHz.
- Aoki (2000)

  “Carrier of B1377 is very likely to be C_6H^-.”
- McCarthy et al (2006)

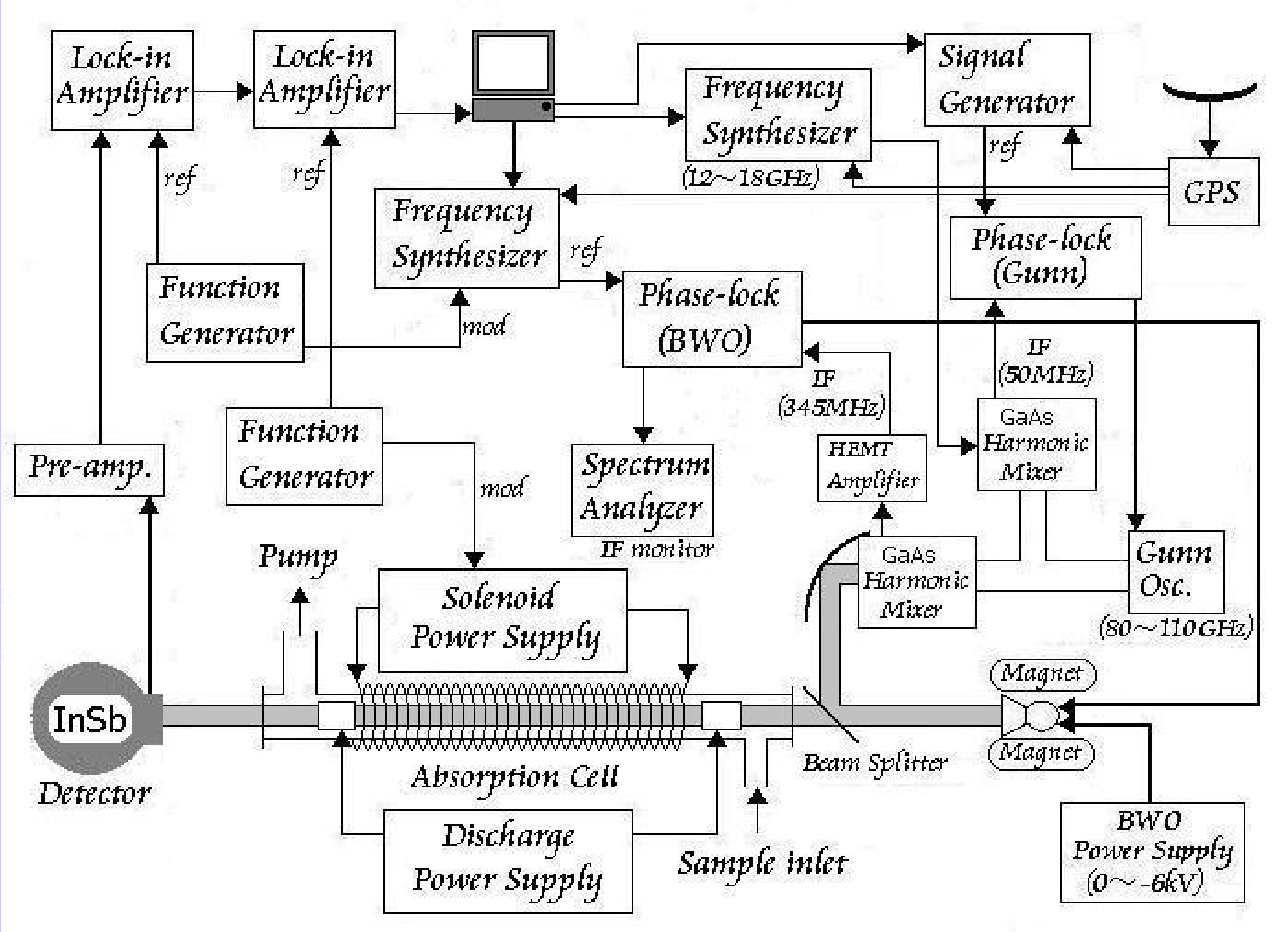
  Succeeded in the laboratory detection of B1377, and in astronomical detection in TMC-1.

  C_5N^- (Cernicharo *et al*, 2008)

Waterloo sub-mm system

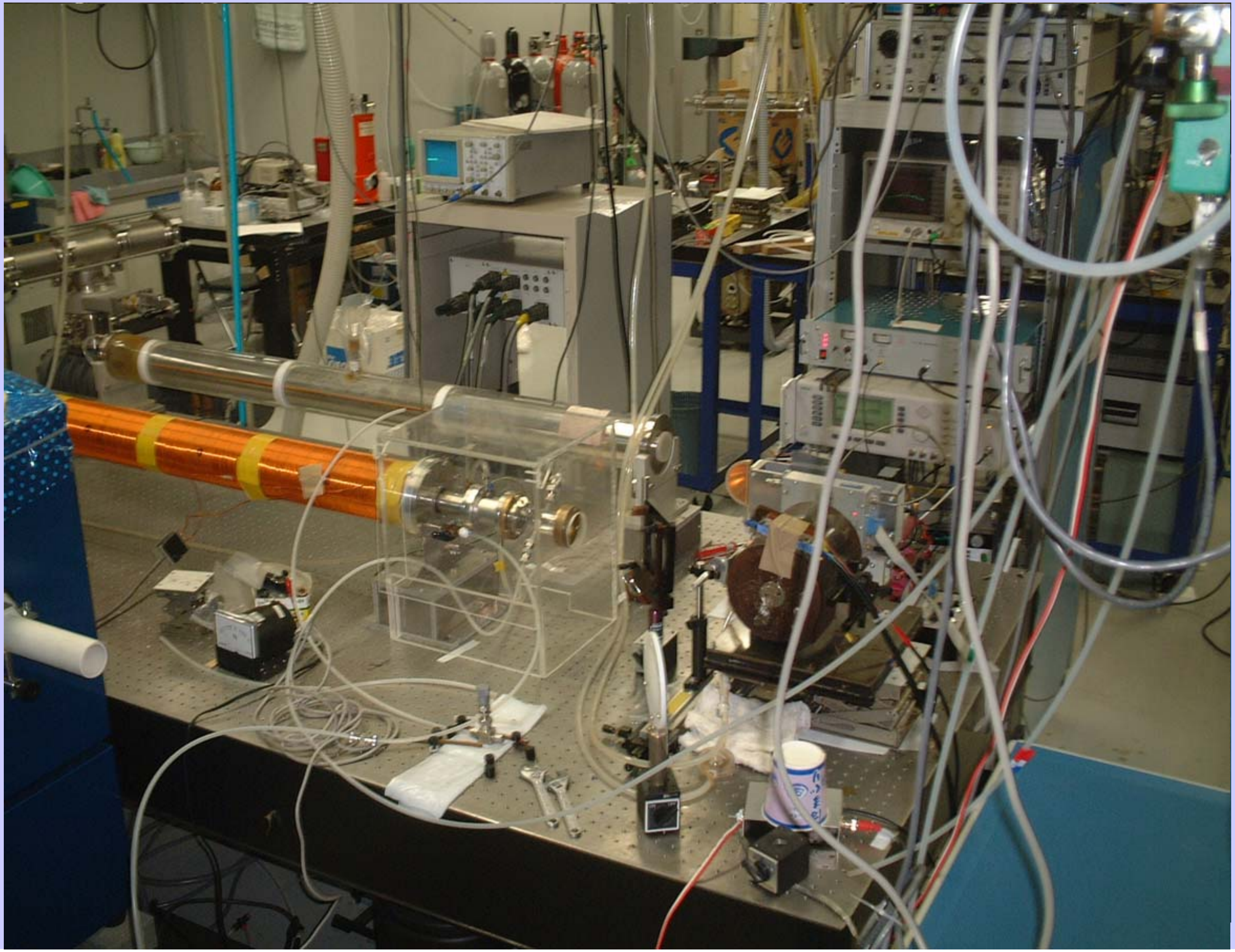
- The frequency range of 270-890 GHz is covered with four BWOs (Backward-wave oscillator) with ~1 mW power.
- The absorption cell is designed to detect positive ions.
- Mostly operated in extended negative glow discharge mode with longitudinal magnetic field of ~250 Gauss.

Double modulation sub-mm system at Waterloo



Submillimeter-wave system in Ibaraki

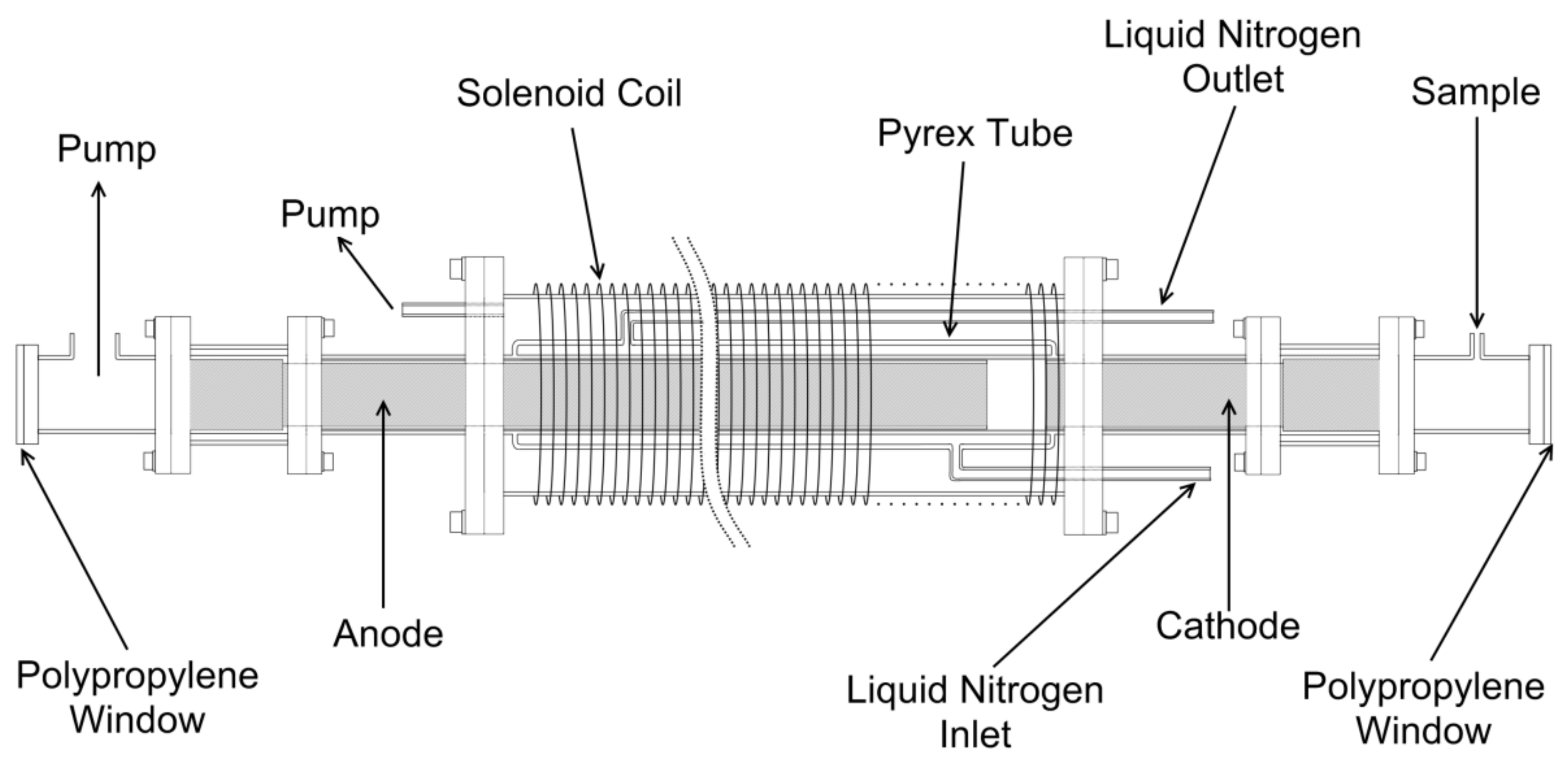
Now moved to Waterloo



Three types of discharges are tried for detection of anions

- Glow discharge
- Hollow anode discharge
- Extended negative glow discharge

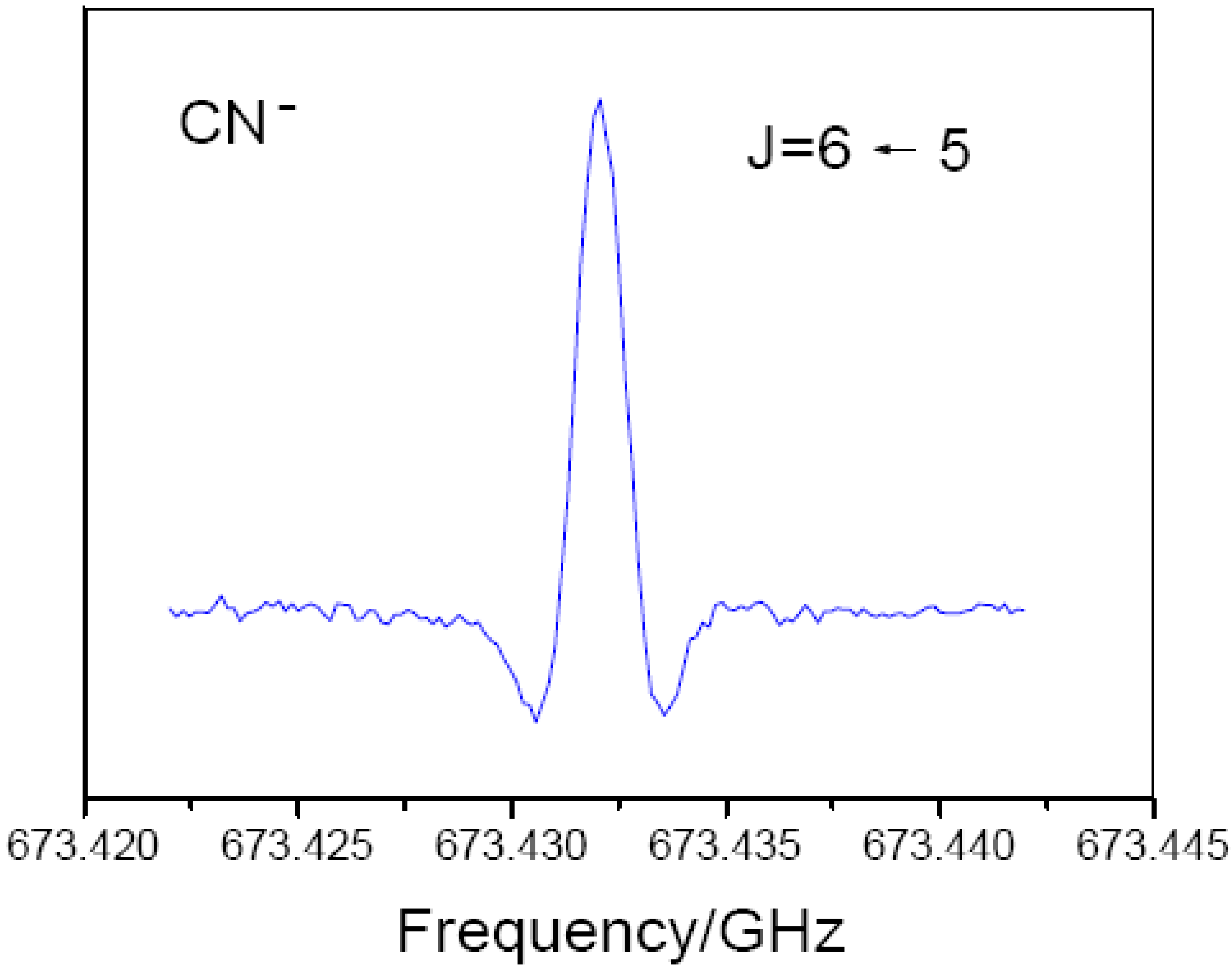
Hollow-anode cell



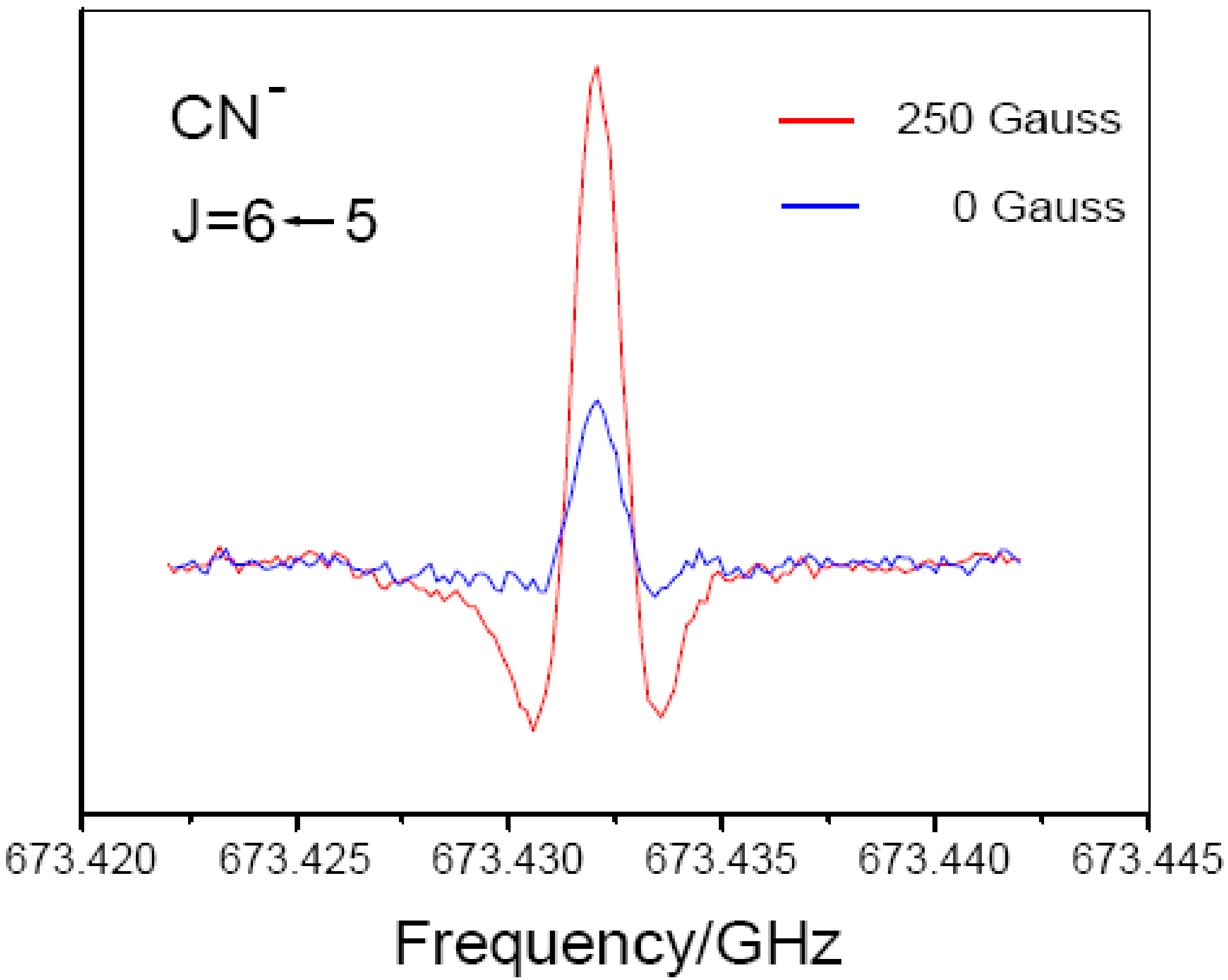
7 cm

1.6 m

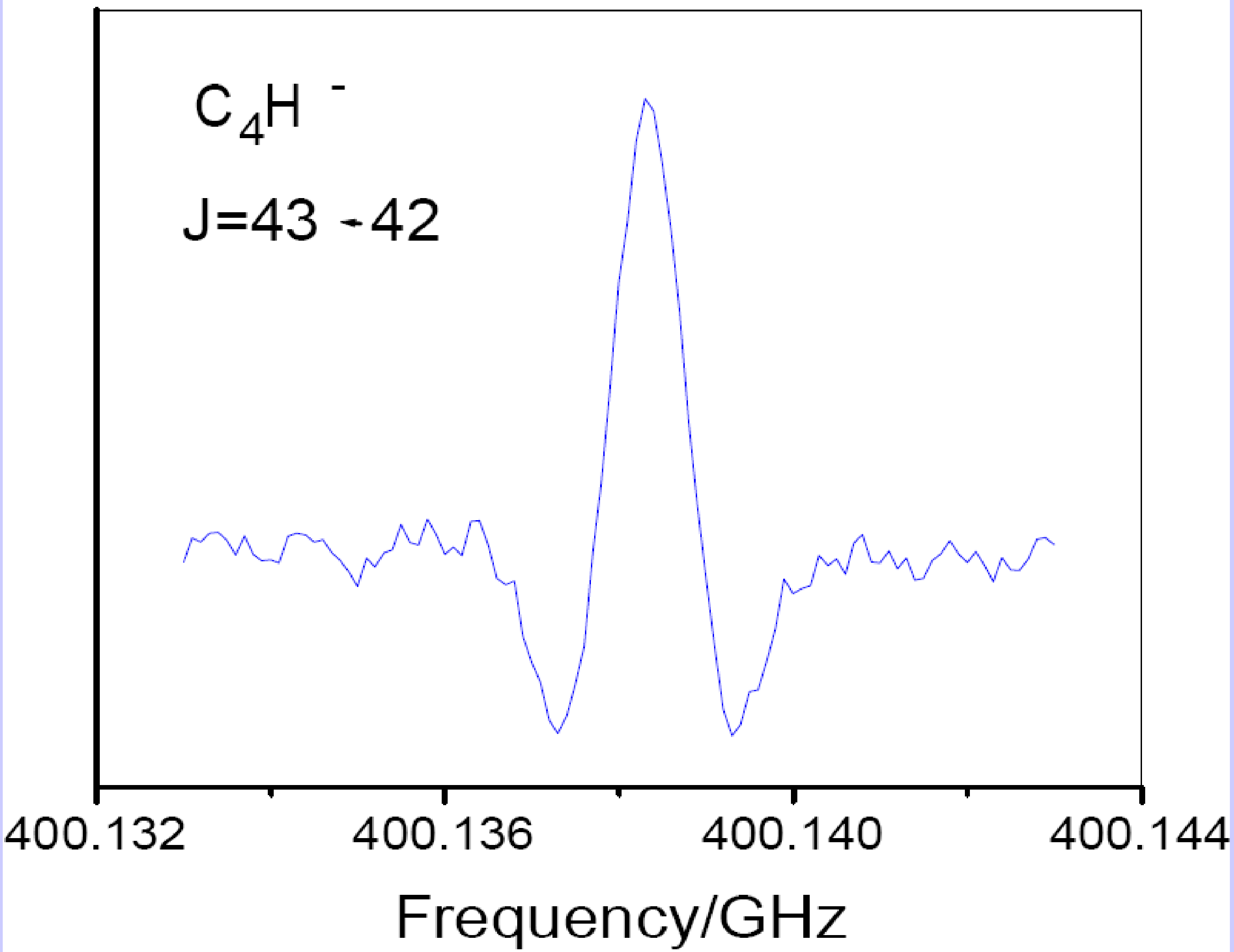
1.8 m


CN⁻
J=6 ← 5
673.420
673.425
673.430
673.435
673.440
673.445
Frequency/GHz

CN^- in "hollow anode" discharge



C_4H^- in extended negative glow discharge



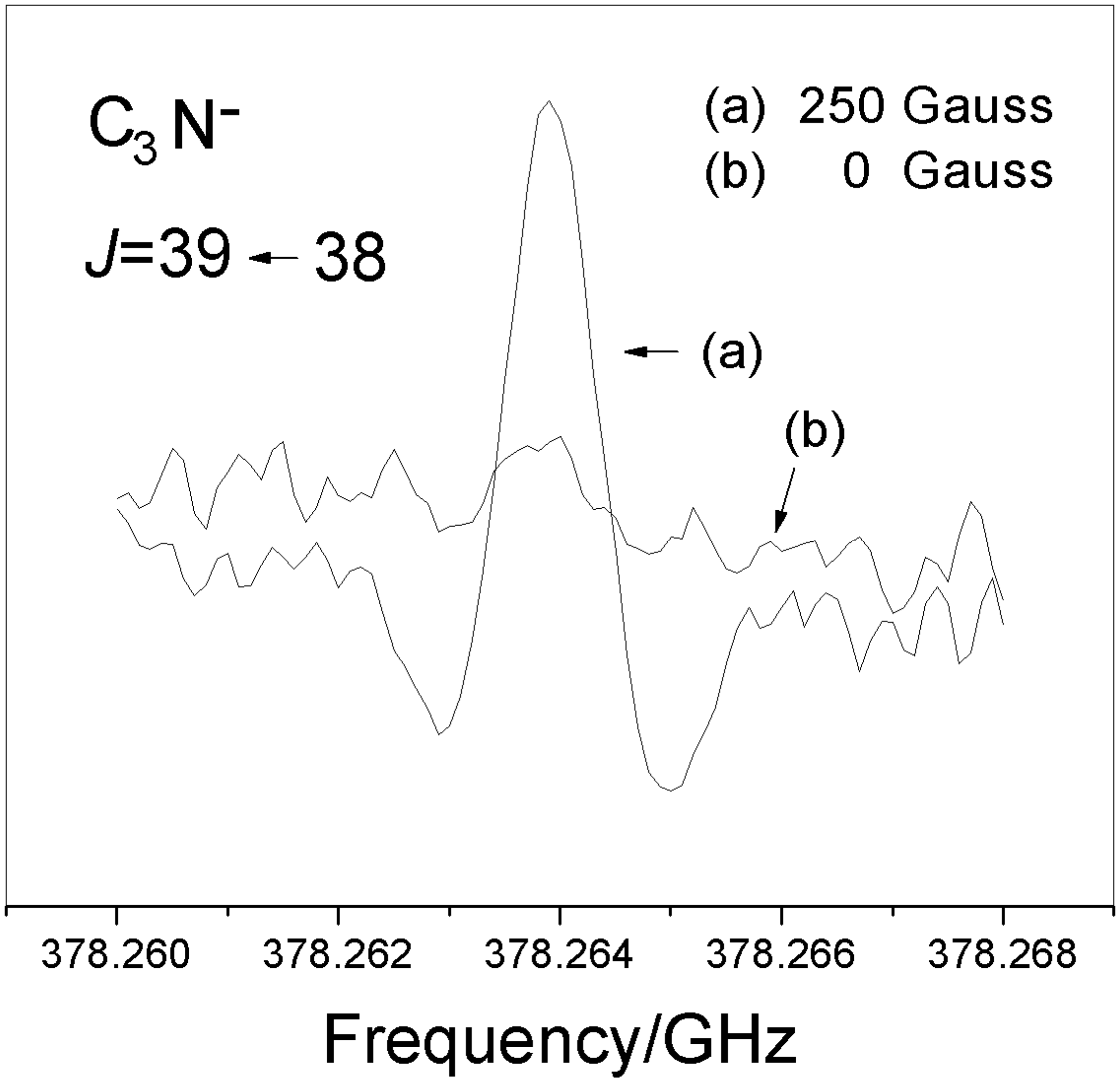
Sub-mm observations of C_3N^-

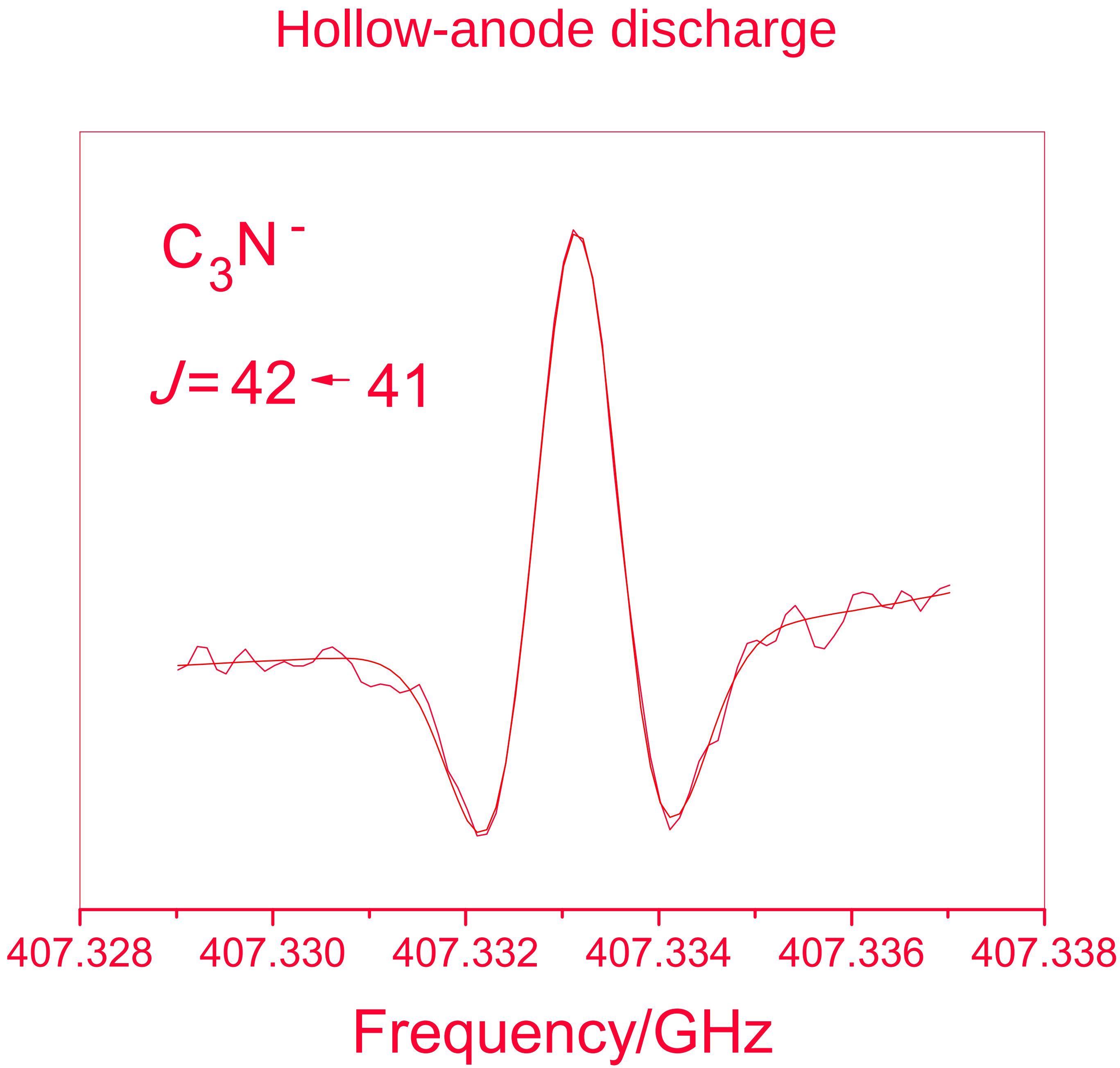
- Production ;

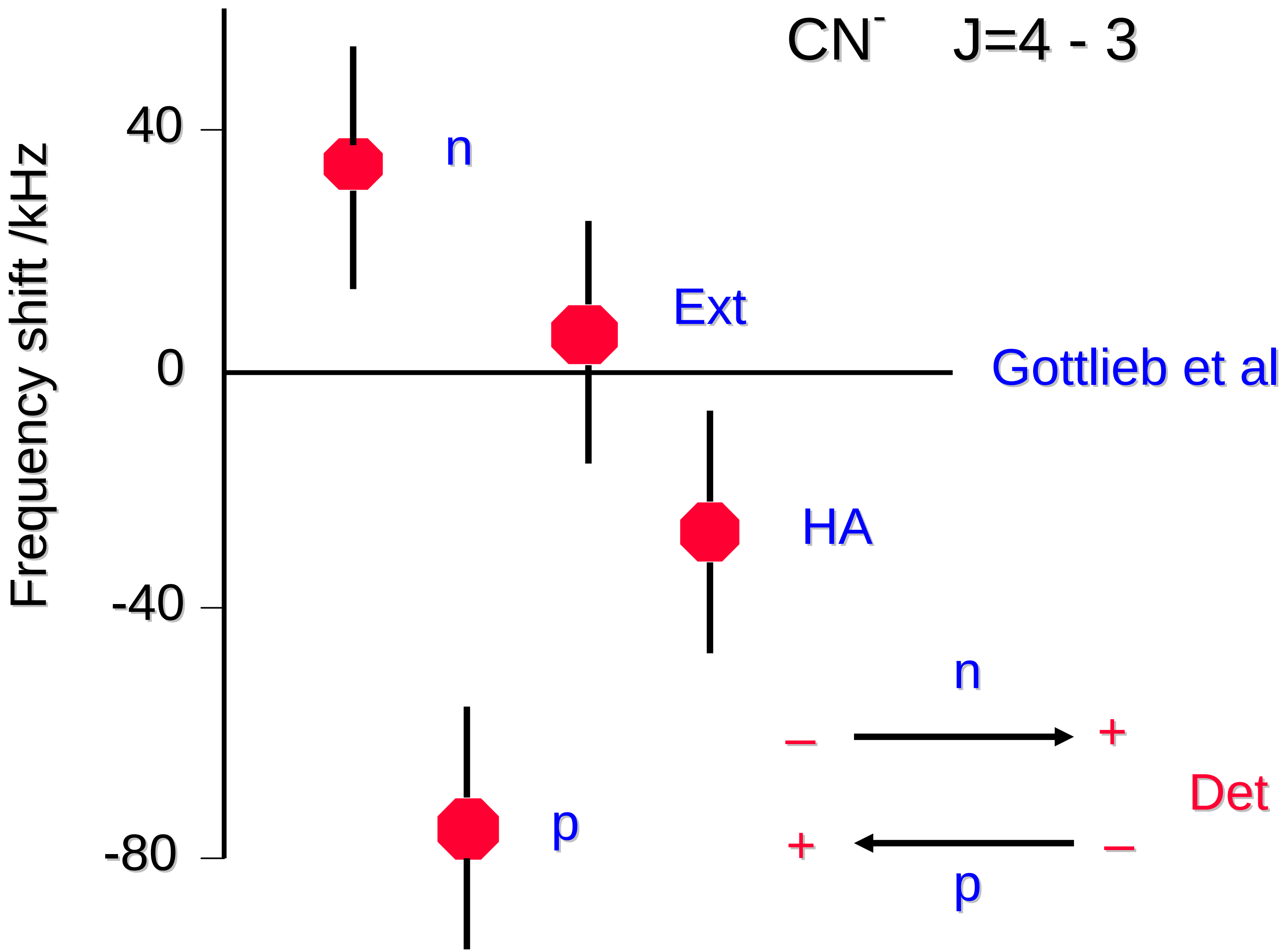
  C_2N_2 ≤1 mTorr + C_2H_2 ~2 mTorr + Ar 12 mTorr
  in either
  "hollow anode discharge" or
  extended negative glow discharge
  of 4~10 mA, cooled to 210 K.
  Freq. range ~ 504 GHz

Thaddeus et al, HC_3N (20 %) + Ar (80 %) ~15 mTorr
dc discharge current of 20 mA at 200 K.

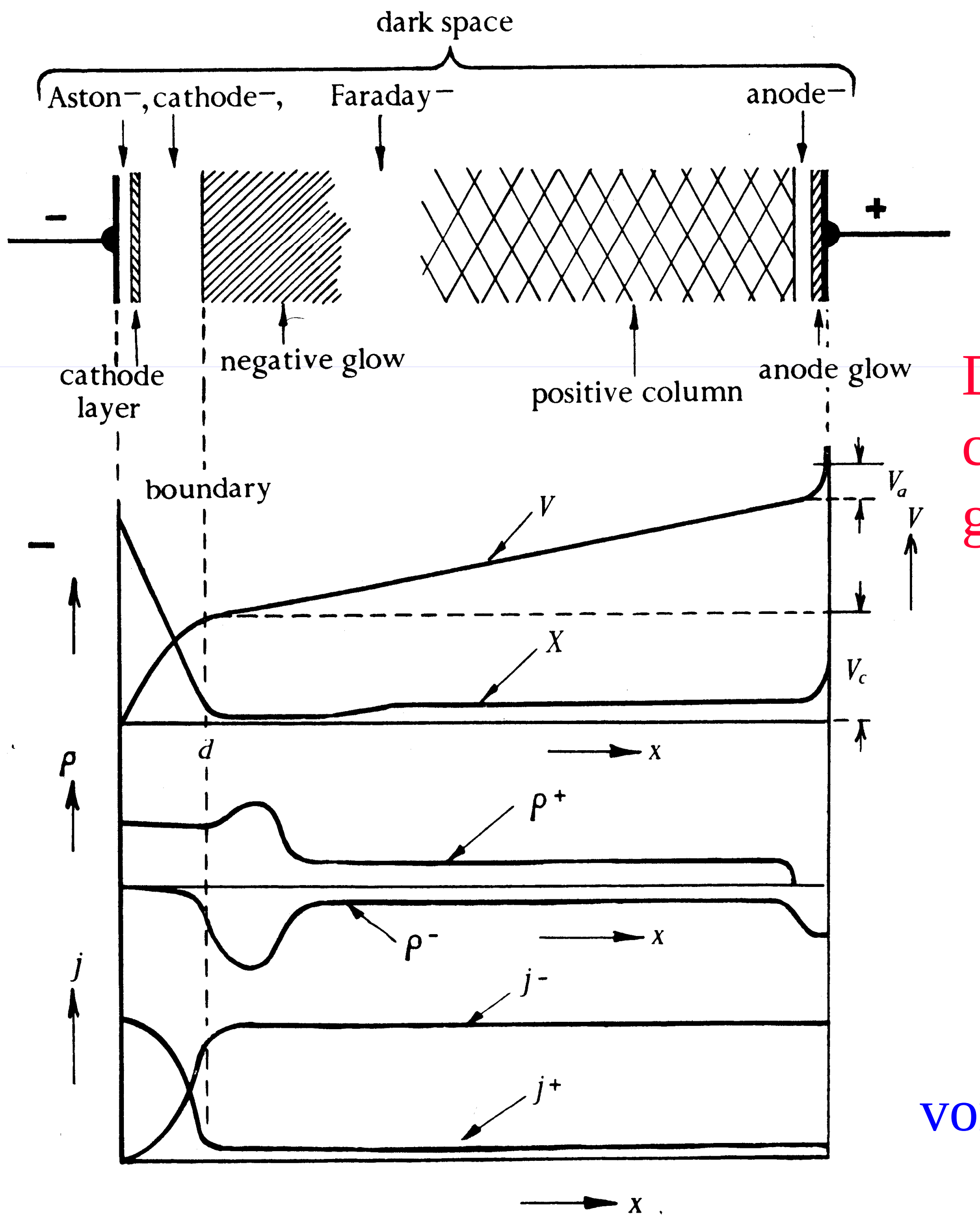
Extended Negative Glow




Hollow-anode discharge
C3N-
J= 42 ← 41
407.328
407.330
407.332
407.334
407.336
407.338
Frequency/GHz



CN⁻ J=4 - 3
Frequency shift /kHz
40
0
-40
-80
n
Ext
Gottlieb et al
HA
p
n
–
+
Det
+
–
p



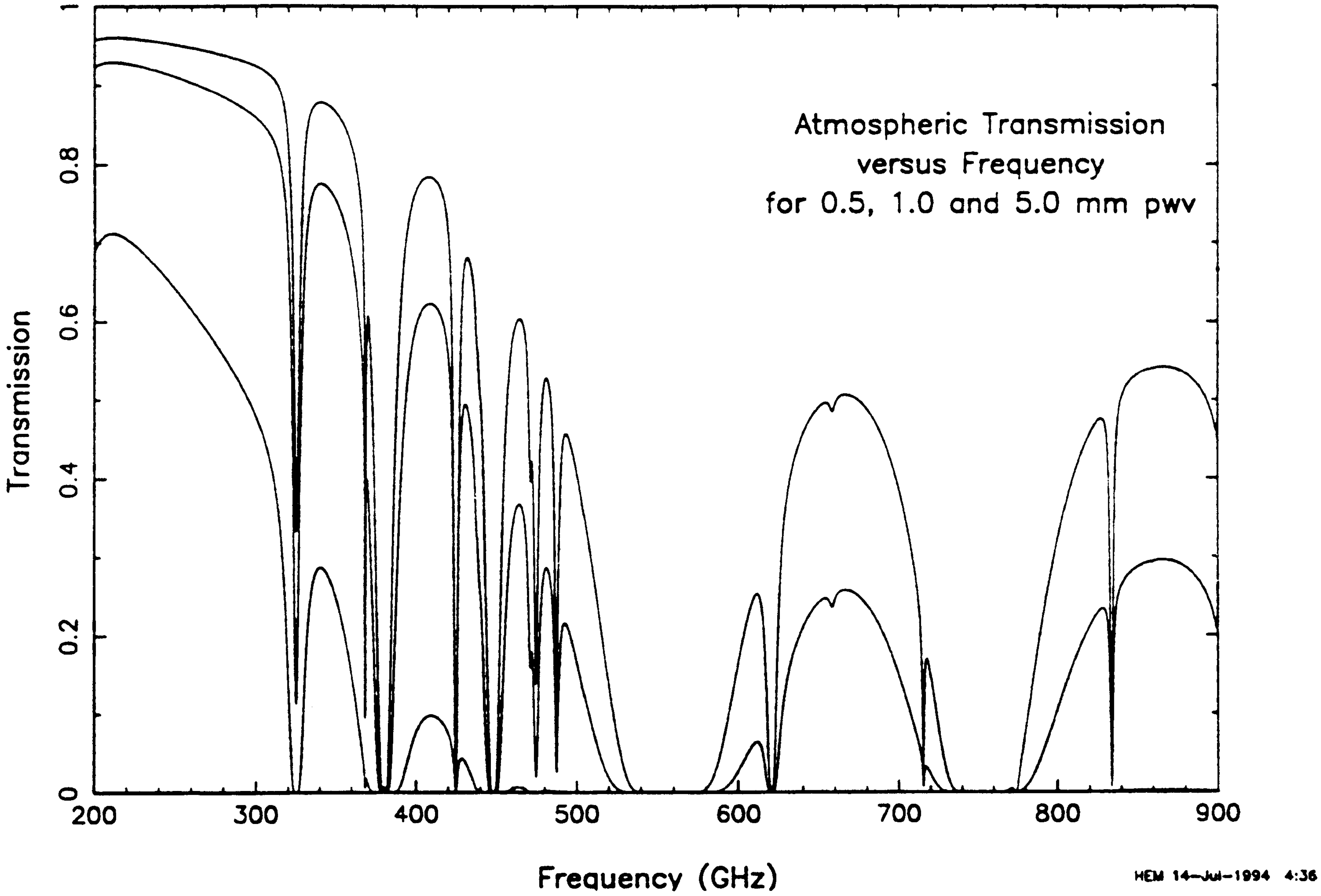
Density of negative charges is high in negative glow and anode glow

von Engel “Ionized Gases”

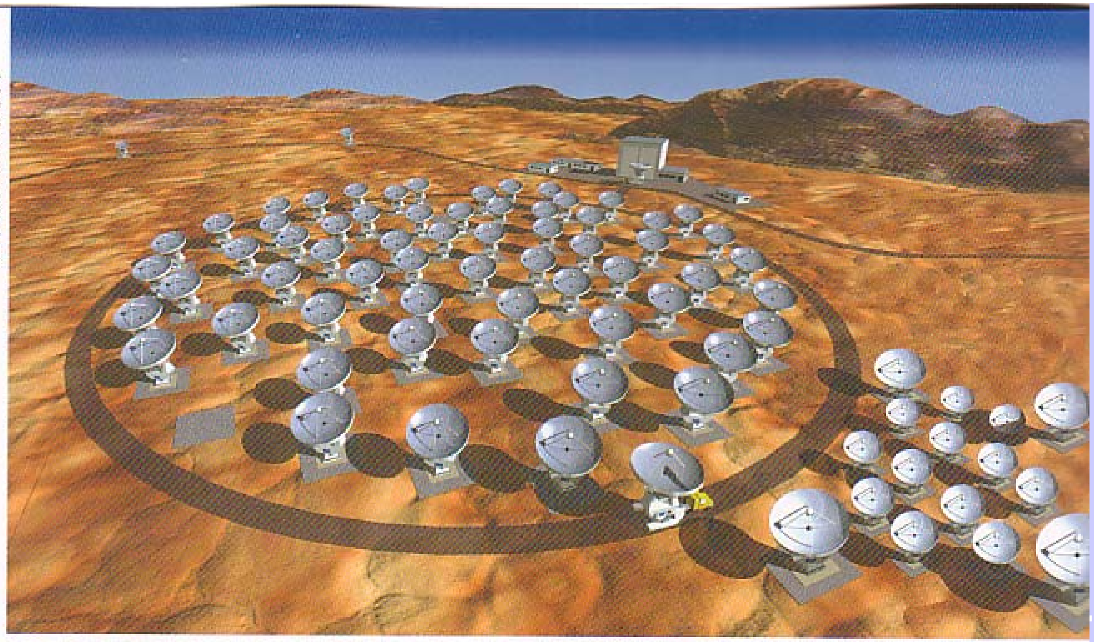
Why sub-mm now?

- Ground- and satellite-based astronomical and/or atmospheric observation platforms.
  - Higher spatial resolution with shorter wavelength.
  - Better sensitivity.
- Easy to use laboratory system.
  - multipliers.
  - BWOs.

Atmospheric Opacity in the submillimeter-wave region



- S
- S 7)
- H
- C
- A

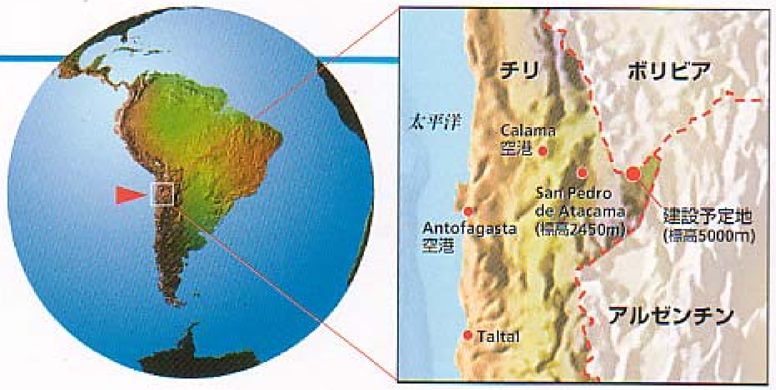


Original CG courtesy of ESO, modified by NAOJ

ALMA（アルマ）は、日本・北アメリカ・ヨーロッパの諸国が協力して、チリ・アンデス山中の標高5000mの高原に建設することを計画している、アタカマ大型ミリ波サブミリ波干渉計（**A**tacama **L**arge **M**illimeter/submillimeter **A**rray）の略称です。直径12mの高精度アンテナ64台と「ACAシステム」と呼ばれる超高精度アンテナ16台からなる、全部で80台のアンテナを干渉計方式で組み合わせ、ひとつの巨大な電波望遠鏡を合成します。電波の中で最も波長が短く、最高の周波数帯である「ミリ波・サブミリ波」を使って、ビッグバン後間もない宇宙初期における銀河の誕生、今も続くさまざまな惑星系の誕生、そして生命につながる物質の進化を解き明かします。

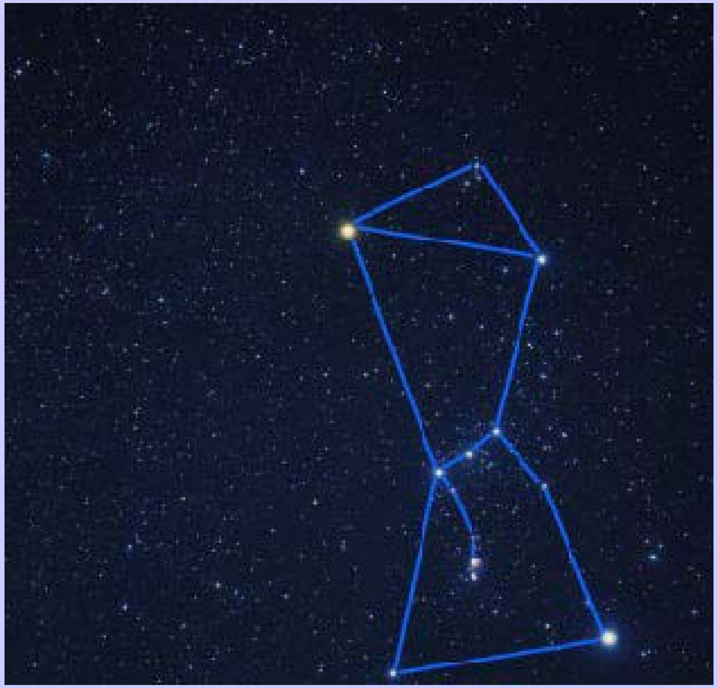
宇宙に一番近い場所

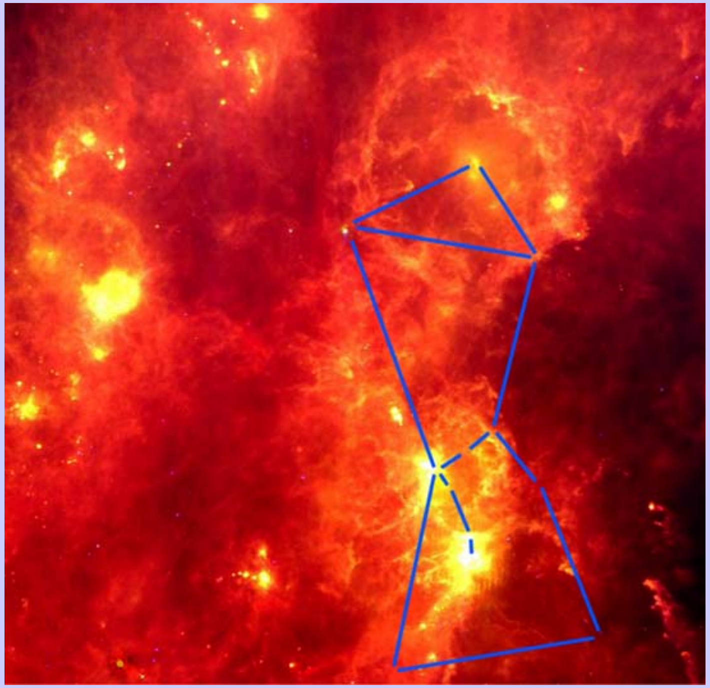
ALMAの設置場所は、チリ共和国北部にあるアタカマ砂漠に近い、アンデス山中の標高約5000mの高原です。世界の候補地を詳しく調査・比較した結果、乾燥した気候、高い標高、平坦な地形、そして安全で容易なアクセスという条件を満たす、この土地が選ばれました。



Getting the WHOLE picture

- An object can look radically different depending on the type of light collected from it:



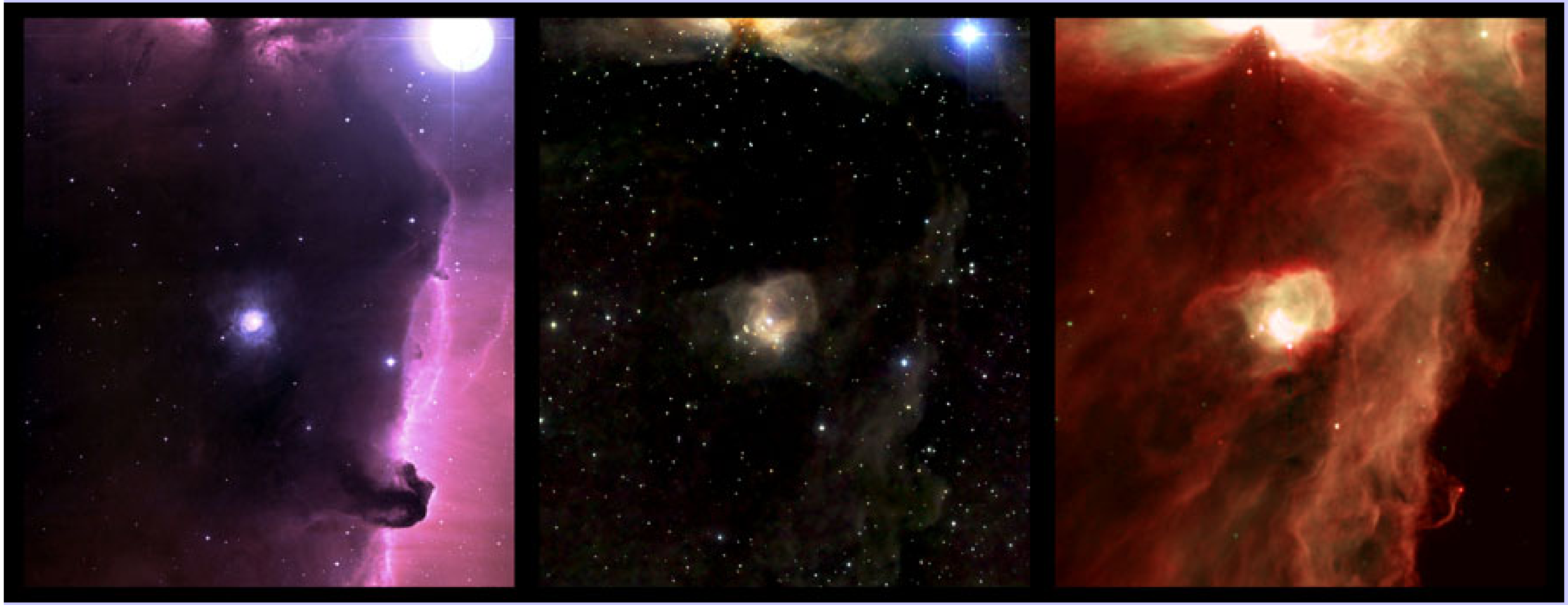


Constellation Orion
left: visual wavelengths
right: far-infrared image

From NASA web page

- Visible: dark nebula, heavily obscured by interstellar dust
- Near-IR: dust is transparent, embedded proto-stars can be observed
- Mid- and far-IR: glow from cold dust is directly observable

From NASA web page



Visible **Near Infrared** **Mid-Infrared**

NASA/DLR

THE ASTROPHYSICAL JOURNAL, 619:914–930, 2005 February 1

A RIGOROUS ATTEMPT TO VERIFY INTERSTELLAR GLYCINE

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ABSTRACT

In 2003, Kuan and coworkers reported the detection of interstellar glycine (NH_2CH_2COOH) based on observations of 27 lines in 19 different spectral bands in one or more of the sources Sgr B2(N-LMH), Orion KL, and W51 e1/e2. They supported their detection report with rotational temperature diagrams for all three sources. In this paper we present essential criteria that can be used in a straightforward analysis technique to confirm the identity of an interstellar asymmetric rotor such as glycine. We use new laboratory measurements of glycine as a basis for applying this analysis technique, both to our previously unpublished 12 m telescope data and to the previously published Swedish-ESO Submillimetre Telescope (SEST) data of Nummelin and colleagues. We conclude that key lines necessary for an interstellar glycine identification have not yet been found. We identify some common molecular candidates that should be examined further as more likely carriers of several of the lines reported as glycine. Finally, we illustrate that a rotational temperature diagram used without the support of correct spectroscopic assignments is not a reliable tool for the identification of interstellar molecules.

Subject headings: ISM: abundances — ISM: clouds —
ISM: individual (Sagittarius B2(N-LMH), Orion Kleinmann-Low, W51 e1/e2) —
ISM: molecules — radio lines: ISM

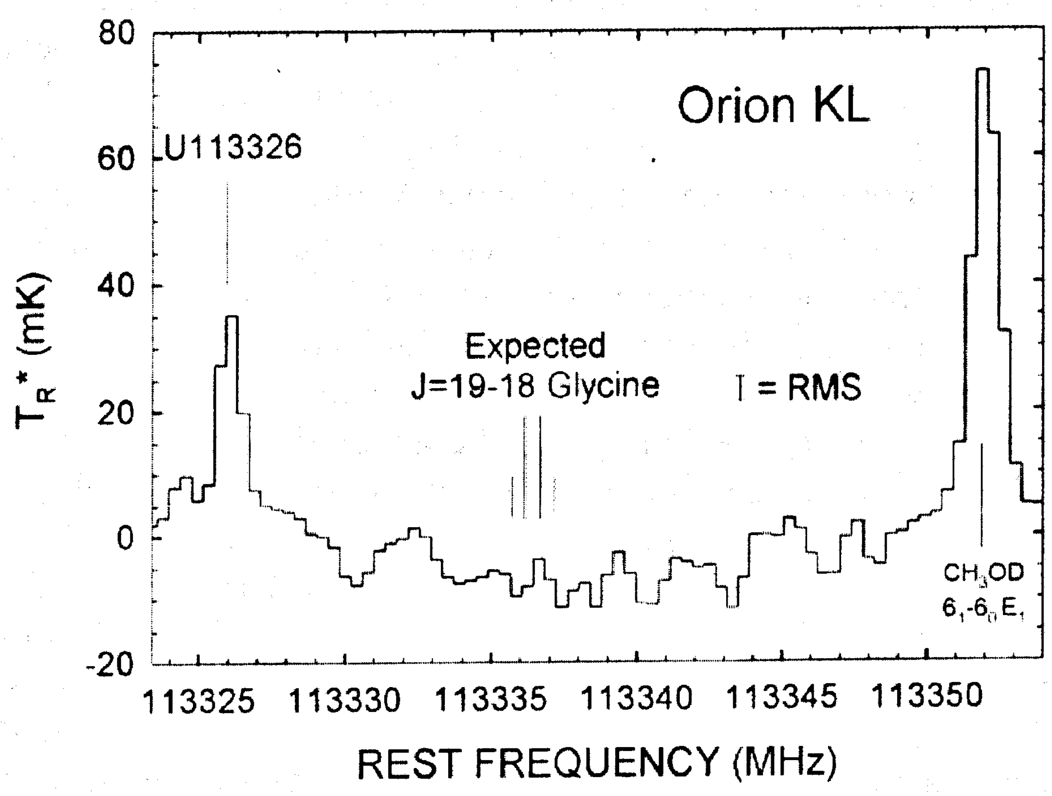
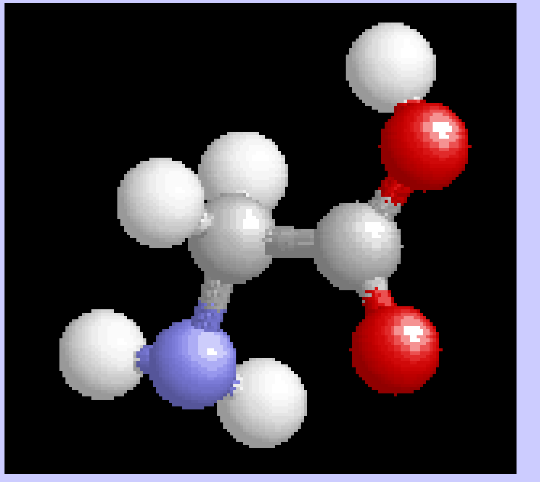


FIG. 1.—Orion KL spectra from 113323 to 113355 MHz (centered at 113339 MHz) observed with the hybrid spectrometer on the NRAO 12 m telescope. The spectral positions of the negative results for the nearly fourfold degenerate $J = 19-18$ glycine lines are marked by the four vertical lines centered at 113336 MHz. U113326 is on the left, and CH_3OD is on the right. The ordinate is in units of mK on the T_R^* scale. The abscissa is rest frequency calculated with respect to $V_{LSR} = 9$ km s^{-1} (for the Orion compact ridge), except for the CH_3OD rest frequency, which is with respect to $V_{LSR} = 5.6$ km s^{-1} (representative of the Orion hot core). The rms noise level for the spectral region between U113326 and CH_3OD is 3.7 mK.



L. E. Snyder et al, *Astrophys. J.* **619**, 914-930(2005)

Glycine in Comet Tail

Glycine has been identified in a dust sample collected by the Stardust Spacecraft from the tail of Comet Wild 2.

http://www.newscientist.com/article/dn17628-found-first-amino-acid-on-a-comet.html

http://scientificinquiry.suite101.com/article.cfm/comet_tail_with_glycine_amino_acid_amazes_all

In future・・・・・・・

- Sub-mm astronomical observations with very high spatial resolution.

ALMA

- In the process of star and planet formation, what kind of molecules can survive and be entrained into the planetary system? Life related molecules?
- Lab. data are essential in such identifications.

"To understand hydrogen is to understand all of physics,

chemistry, and biology."

Victor Weisskopf

Hydrogen, light colorless odorless gas,
which given enough time
turns into human being

氢，轻質量 無色 無味的気体，
如果給它足够的時間
它会逐漸演変成今天的人類

Discovery of multiply deuterated species in space

$[D]/[H] \sim 1.5\times10^{-5}$

D_2CO :	Turner(1990)	Ori-KL	0.3%
	Ceccarelli *et al* (1998)	IRAS 16293-2422	5%
	Loinard *et al* (2001)	16293E	26%

NHD_2 (2000) , ND_3 (2002)

CHD_2OH (2002), CD_3OH (2004)

D_2S (2003)

Formation of Deuterated Species

- H/D exchange reactions of H_3^+ with HD are exothermic.

$$H_3^+ + HD \rightarrow H_2D^+ + H_2 + 230\ K$$
$$H_2D^+ + HD \rightarrow D_2H^+ + H_2 + 180\ K$$
$$D_2H^+ + HD \rightarrow D_3^+ + H_2 + 230\ K$$

- Under liquid-N_2 cooled environment , such reactions become dominant.

Spectroscopy of H_2D^+ and D_2H^+

IR

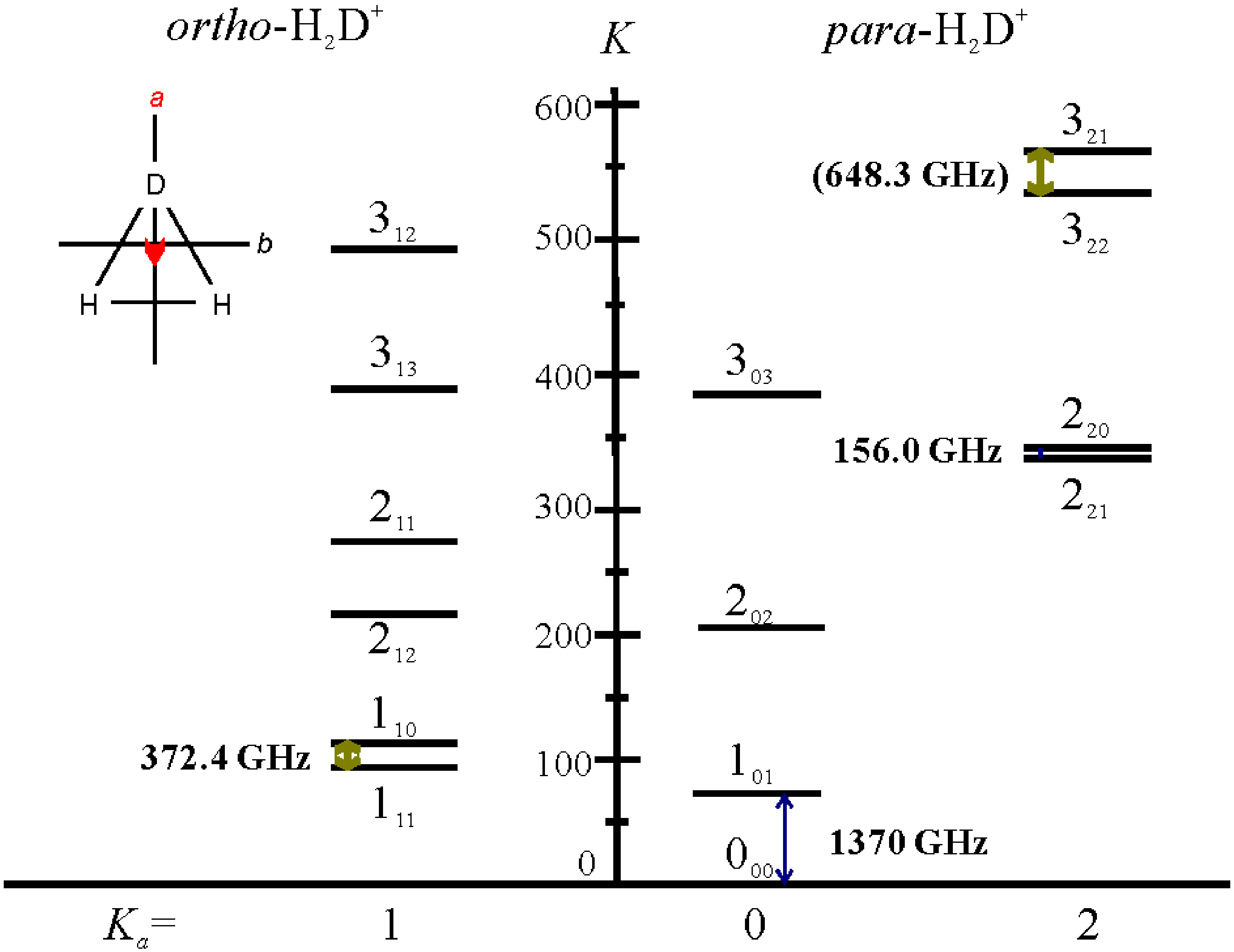
- Shy, Farley, Wing (1981): Ion beam
- Amano & Watson (1984), Amano (1985): ν_1 band (H_2D^+)
- Lubic & Amano (1984): ν_1 band (D_2H^+)
- Foster et al. (1986): ν_2 /ν_3 bands (H_2D^+)
- Foster, McKellar, Watson. (1986): ν_2 /ν_3 bands (D_2H^+)
- Polyansky & McKellar (1990): All available data were fitted together to improve molecular constants. (D_2H^+)
- Fárník et al. (2002):

  Molecular beam experiments of vibrational overtone and combination bands ($2\nu_2$, $2\nu_3$, $\nu_2+\nu_3$).

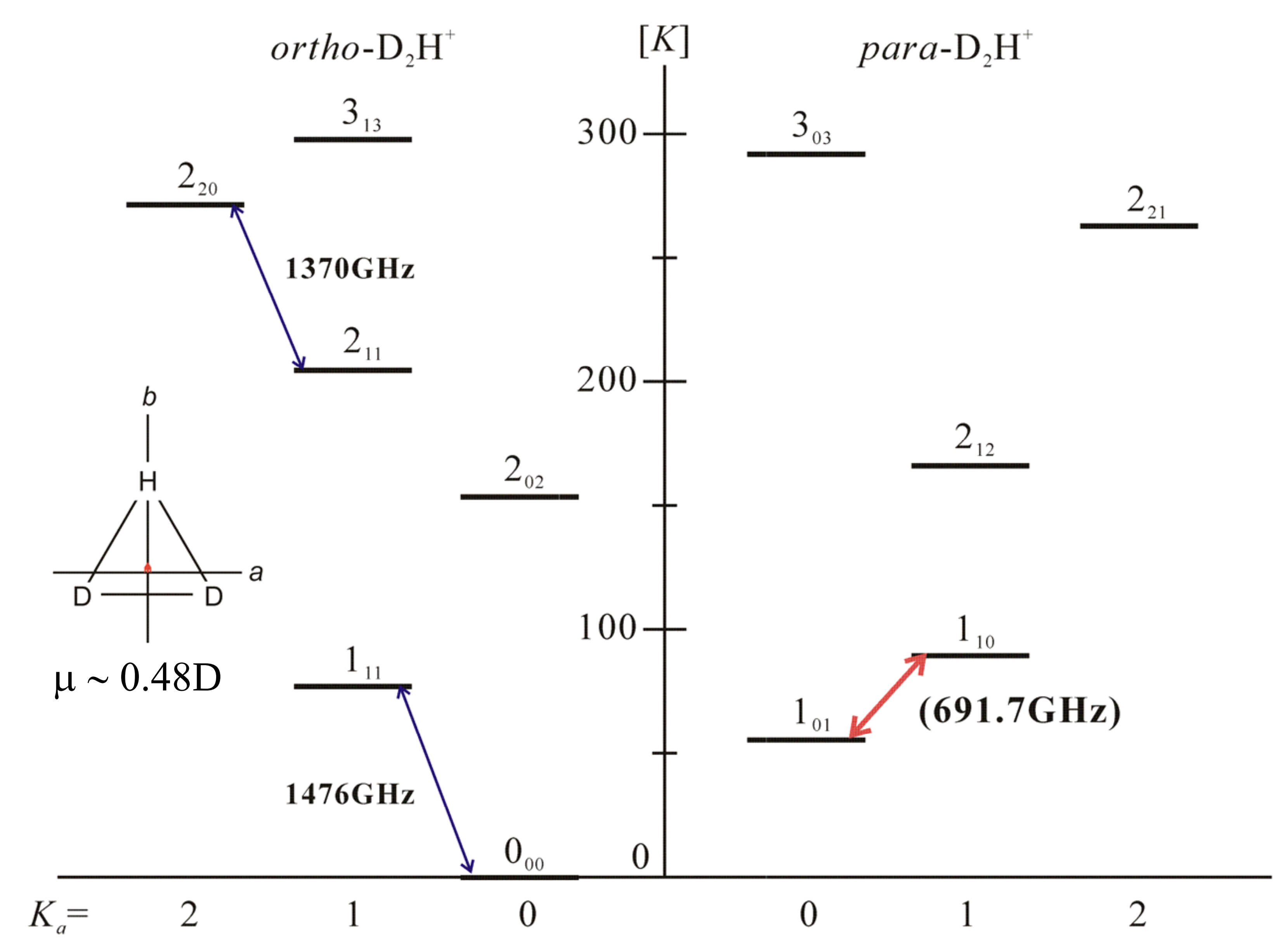
mm-, sub-mm, FIR

- Bogey et al. (1984): 1_{10}-1_{11} H_2D^+ (372.4 GHz)
  Warner et al.(1984):
- Saito, Kawaguchi, Hirota (1985): 2_{20}-2_{21} H_2D^+ (156.0 GHz)
- Jennings, Demuynck, Banek, Evenson (unpublished):
  1_{01}-0_{00} H_2D^+ (1370.1 GHz)
  1_{11}-0_{00} D_2H^+ (1476.6 GHz)
  2_{20}-2_{11} D_2H^+ (1370.1 GHz)
- Hirao & Amano (2003): 1_{10}-1_{01} D_2H^+ (691.7 GHz)
- Amano & Hirao (2005): 3_{21}-3_{22} H_2D^+ (646.4 GHz)

Energy Level Diagram of H_2D^+



Energy Level Diagram of D_2H^+



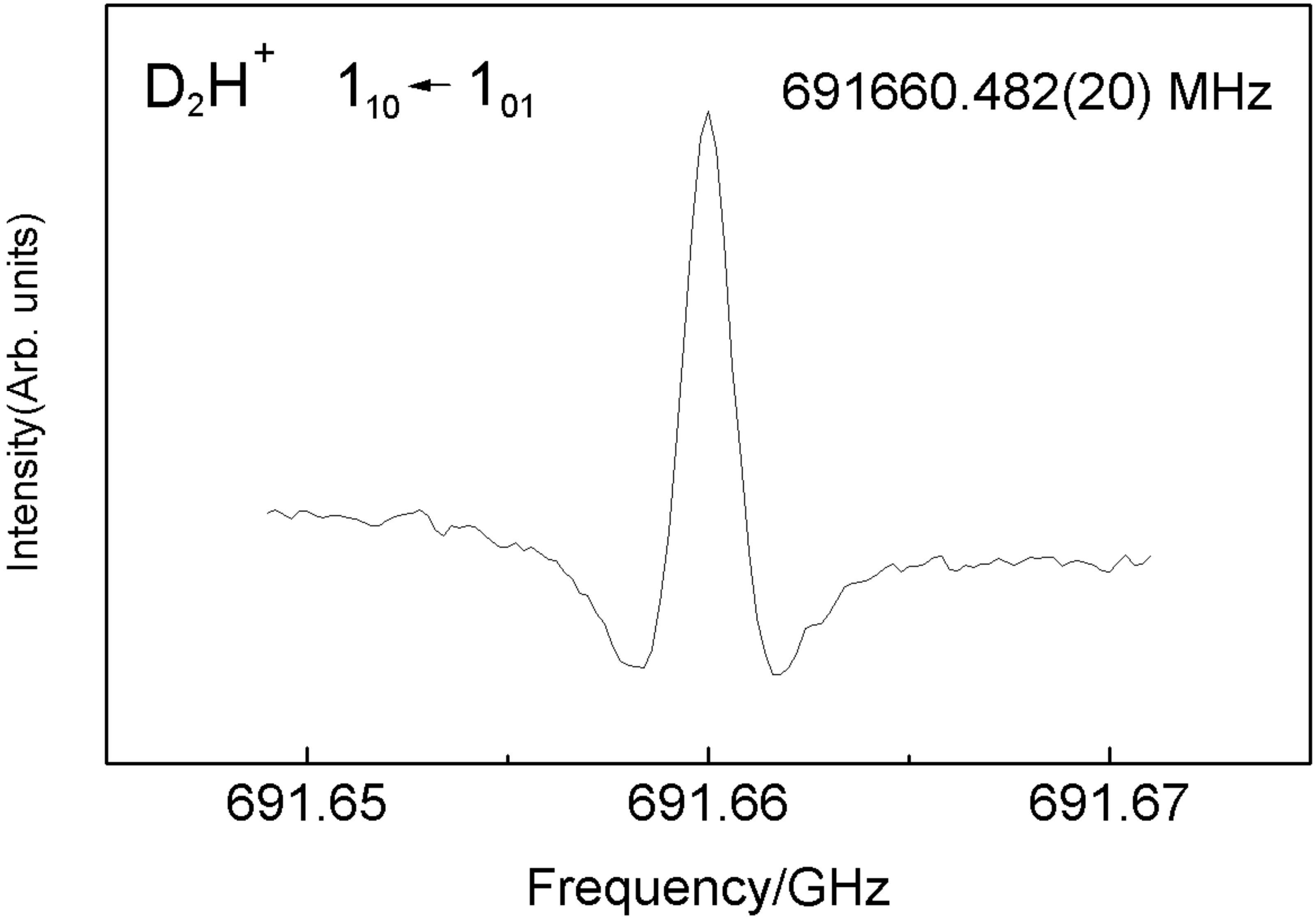
Experimental Details

- Extended negative glow discharge source.
  (Magnetic field: 200G).
- Double modulation.
- $H_2/D_2/Ar$ = 3 /2 /17 mTorr, I = 8 mA,
  T ~ 77 K

↓

Search around 691.705 (90) GHz.

(Polyansky and McKellar)



T. Hirao and T. Amano, Astrophys. J. Lett. ***597****, L85(2003).*

D_2H^+ HAS
IN

C. Vastel, T. G. Ph

Ap. J. Lett. **606**

16293E pre-stellar

$[D_2H^+] \sim [H_2D^+]$

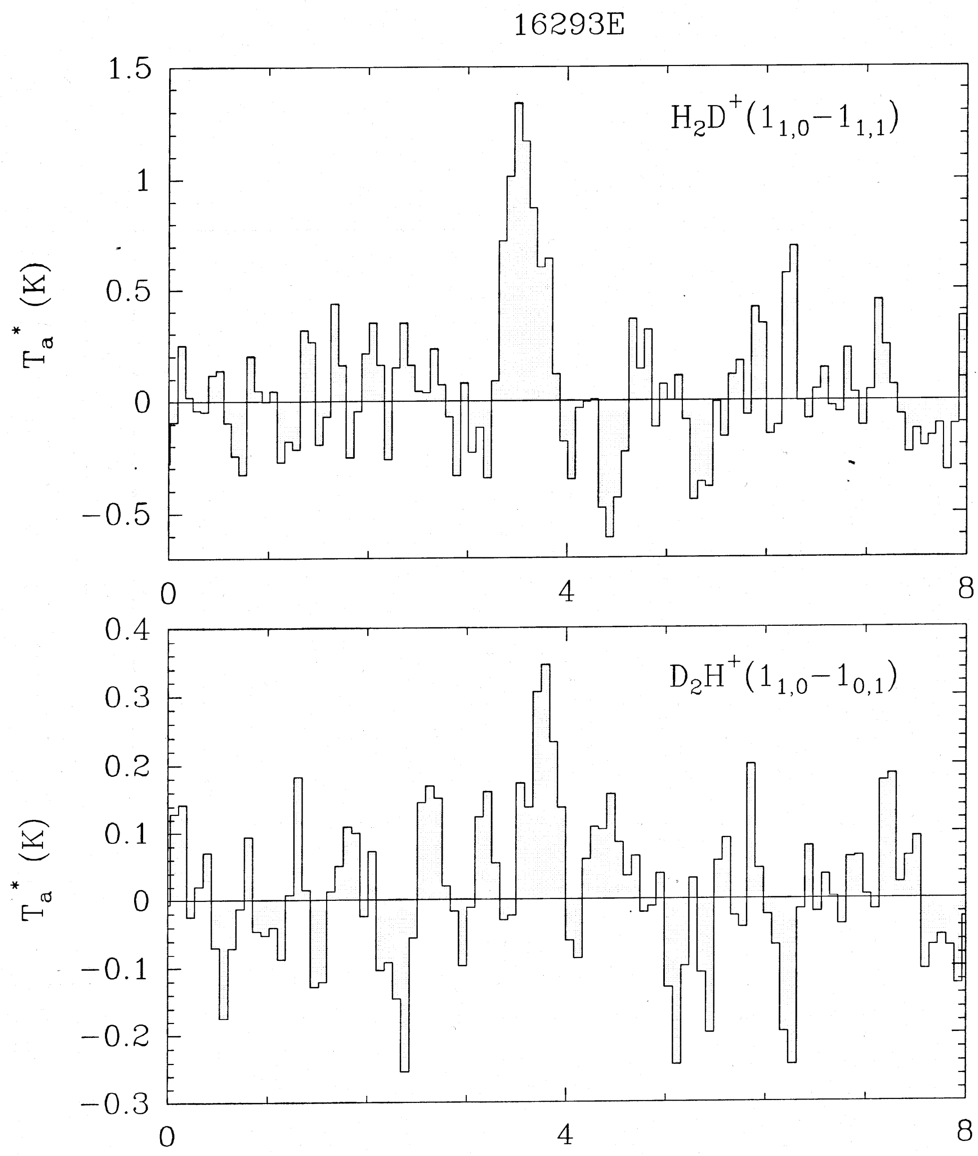


Fig. 3.— Spectra of the ortho-H_2D^+ 1_{10}-1_{11} and para-D_2H^+ 1_{10}-1_{01} transitions towards 16293E.

Table 1. Results of Gaussian fits to the H_2D^+ and D_2H^+ spectra.

Line	ν (GHz)	T_a^* (K)	Δv (km s^{-1})	V_{LSR} (km s^{-1})
H_2D^+ (1_{10}-1_{11})	372.42134(20)[a]	1.31	0.36 ± 0.04	3.55 ± 0.02
D_2H^+ (1_{10}-1_{01})	691.660440(19)[b]	0.34	0.29 ± 0.07	3.76 ± 0.03

[a]Measured frequency by Bogey et al. (1984).

[b]Measured frequency by Hirao and Amano (2003).

⇒ Prompted us to remeasure H_2D^+ line

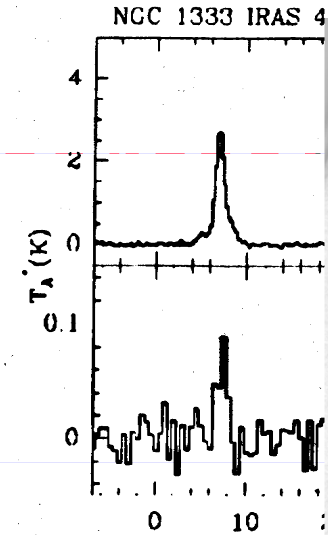


FIG. 1.—Observ
at 372.672 GHz. Tl
spectra have been

Caselli, van d ... 003

P. Caselli et al.: F

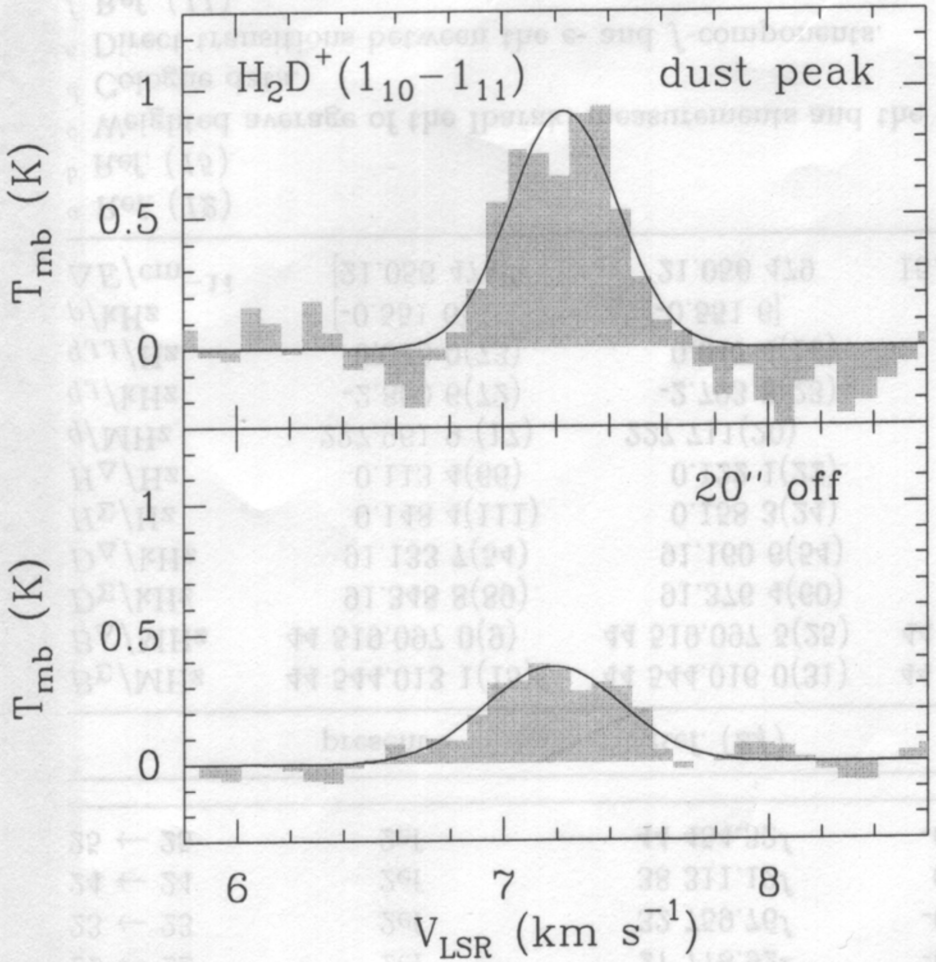


Fig. 1. (*Top*) The $H_2D^+(1_{10}–1_{11})$ line at the dust peak of L1544 (RA(1950) = 05:01:13.1, Dec(1950) = 25:06:35.0). The black curve is the Gaussian fit (see Table 1). (*Bottom*) The $H_2D^+(1_{10}–1_{11})$ spectrum averaged in the four positions 20″ off the dust peak.