Astrofísica de Laboratorio: espectroscopía de iones moleculares

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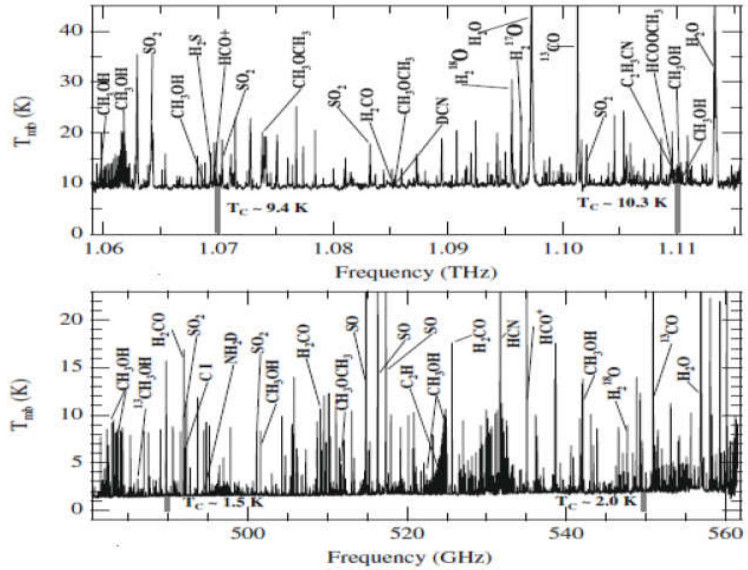
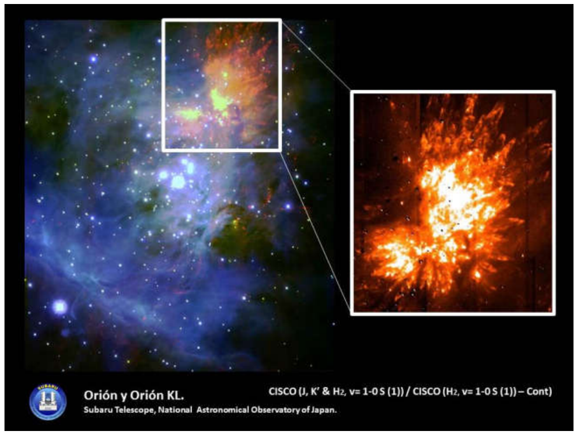
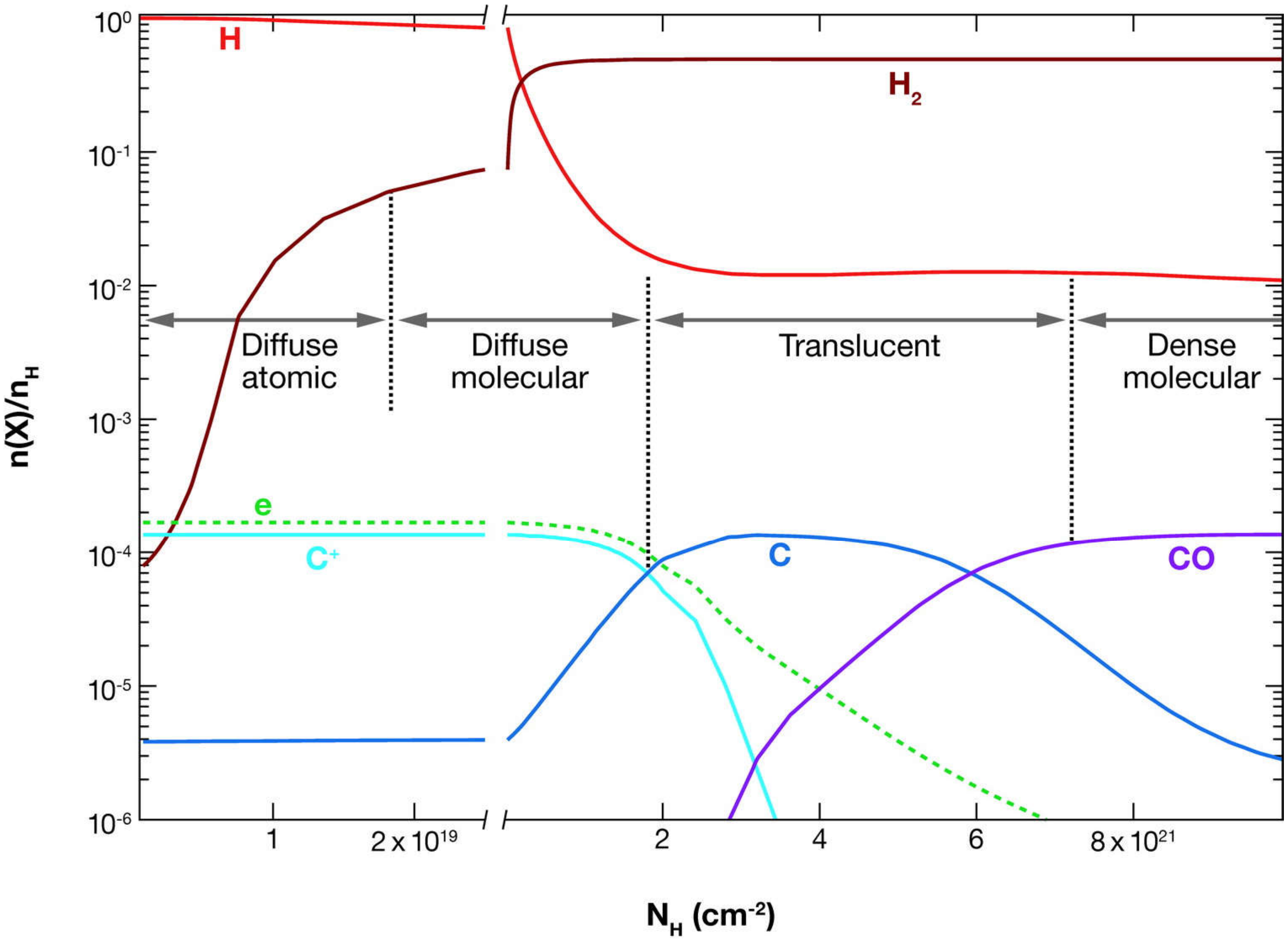
Introducción

- ¿Qué tienen que ver la astrofísica y la espectroscopía molecular?
- ¿Pero hay moléculas en el ISM?
- Nubes moleculares
    - Frías y tenues: v=100 m s^{-1}, $[H_2]\approx10^5$ molec cm^{-3}
    - 1 colisión cada semana
    - ~200 moléculas con hasta 12 átomos (además de C_{60}, C_{70})
    - ~25 cationes y 6 aniones
- Radio (& IR) astronomía



Herschel HIFI spectra of Orion KL [Bergin et al. 2010, A&A, 521, L20]





Snow TP, McCall BJ. 2006.
Annu. Rev. Astron. Astrophys. 44:367–414

MOTIVATION

- The interstellar medium is cold and dilute. How can complex molecules be formed?

- Molecular ions are key intermediates for the formation of molecules in space.
  - ✓ The only reactions occurring in the gas phase are binary (two reactants), exoergic, and no entrance barrier.
  - ✓ Ion–molecule reactions are known to have no entrance barrier.

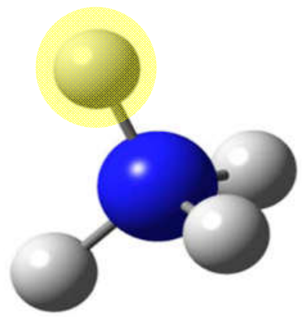
- In space molecular ions are abundant given the long time between collisions and the excitation by UV photons and cosmic rays.

- Laboratory spectroscopy is essential to the interpretation of ISM spectra. But the ion density in laboratory plasmas is really low: ~10^9-10^{10} cm^{-3}

- High sensitivity, accuracy and spectral resolution are necessary in the laboratory.

NH_3D^+: MOTIVATION

- The Ammonium Ion (NH_4^+) is the starting point to form Ammonia (NH_3) and amine prebiotic molecules in Space

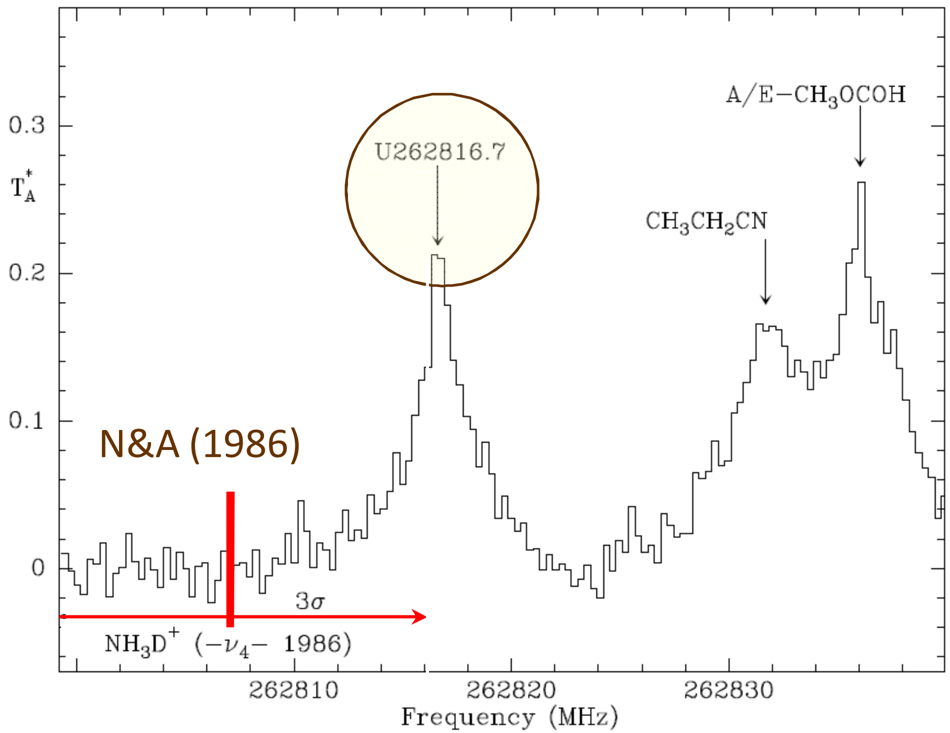


- NH_4^+ has tetrahedral symmetry, hence no permanent electric dipole moment, and no pure rotation spectrum, so it can not be observed with radio-telescopes.

- NH_3D^+ has C_{3v} symmetry and a small dipole electric dipole moment (0.26 D), so it has pure rotational transitions and should be usable as a tracer of NH_4^+ in the insterstellar medium.

- There is (was) no laboratory rotational spectrum (mm-wave) of NH_3D^+

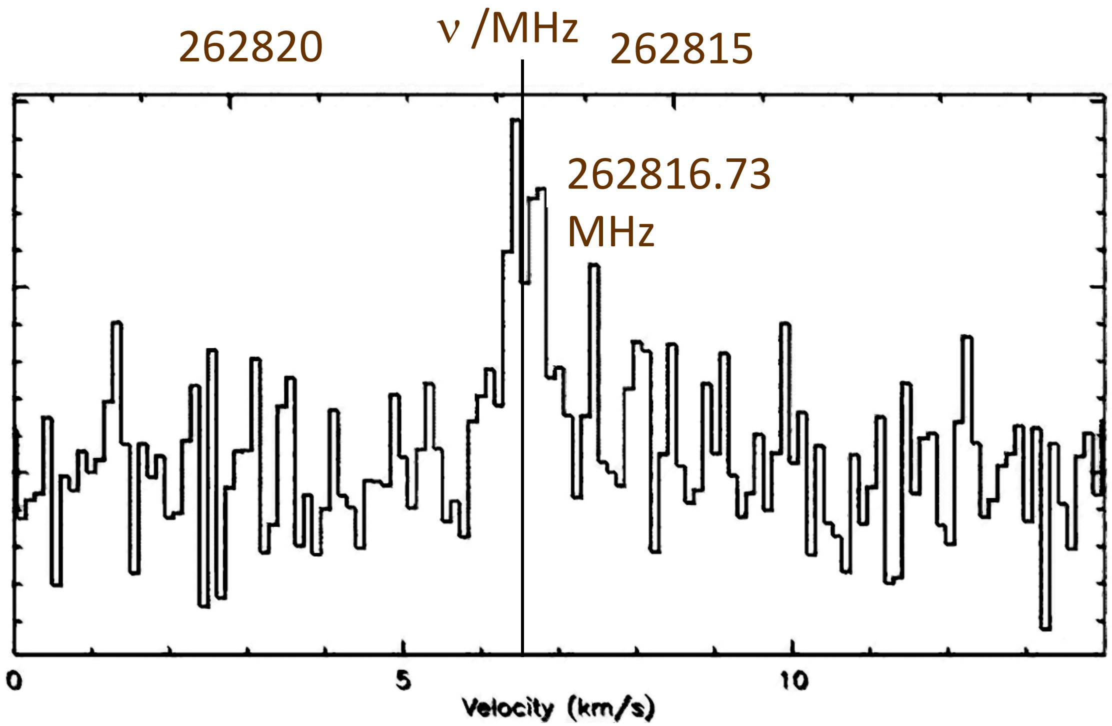
NH_3D^+: MOTIVATION



- A strong unidentified line at 262816.7 MHz in Orion-IRc2 [1]
- From the analysis of the ν_4 infrared band of NH_3D^+, **Nakanaga & Amano[2]** predicted the 1_0-0_0 transition at 262807±9 MHz (±3σ)
- No match with other known species in Orion.
- **Is U262816.7 NH_3D^+ ?**

[1] Tercero, B., Cernicharo, J., Pardo, J. R., & Goicoechea, J. R., 2010, A&A, 517, 96
[2] Nakanaga, T., & Amano, T., 1986, Can. J. Phys., 64, 1356

Observations towards B1-b

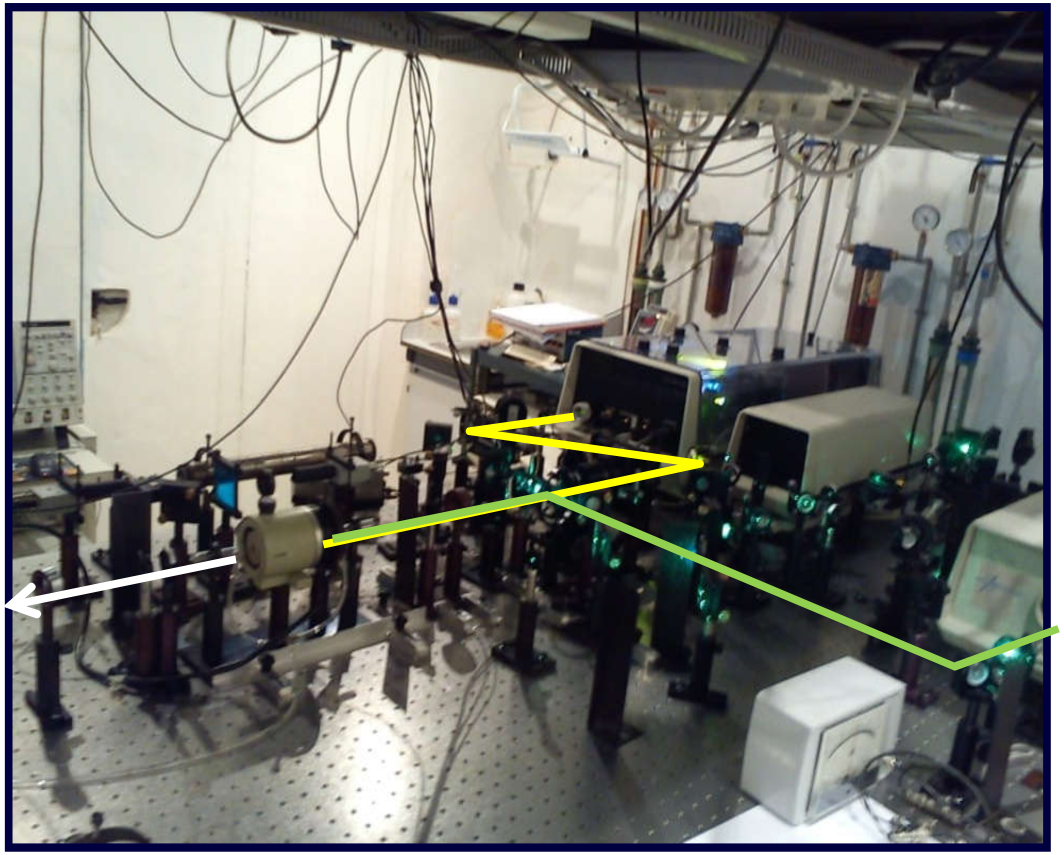


IRAM 30m Pico Veleta

- Narrow and isolated feature (no more lines in 3.8 GHz)
- Kinetic temperature is ~ 12 K, so the carrier has to be a light species
- NH_3, $^{15}NH_3$, NH_2D, $^{15}NH_2D$, ND_2H, ND_3 have been detected in B1-b, plus NNH^+, NND^+, $^{15}NNH+$, $N^{15}NH^+$
- More laboratory data are needed!!

Difference frequency spectrometer

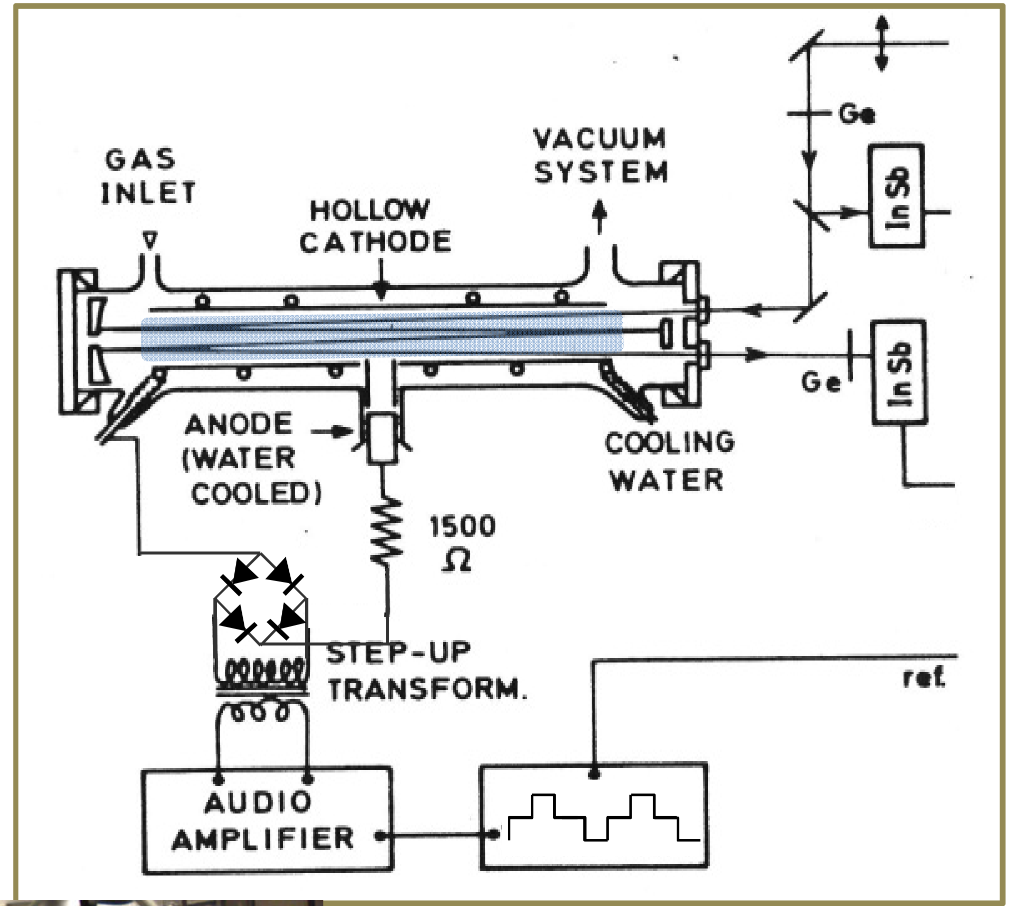
- I_2 locked Ar^+ laser & Ring dye laser
- Mixing in $LiNbO_3$ (DFG)
- Spectral purity: ~1:10^8 (2 MHz)
- Tunability 2.2 – 5 μm (2000-4500 cm^{-1})
- 1.2 cm^{-1} continuous scan
- Sensitivity: ~1:10^4 (in transmission)
- >100 μW vs. 10^{-5} μW NEP of InSb
- First setup: Alan Pine (JOSA1976)
- Accuracy: ~3 MHz (1σ)
- Wavemeter for the dye laser.

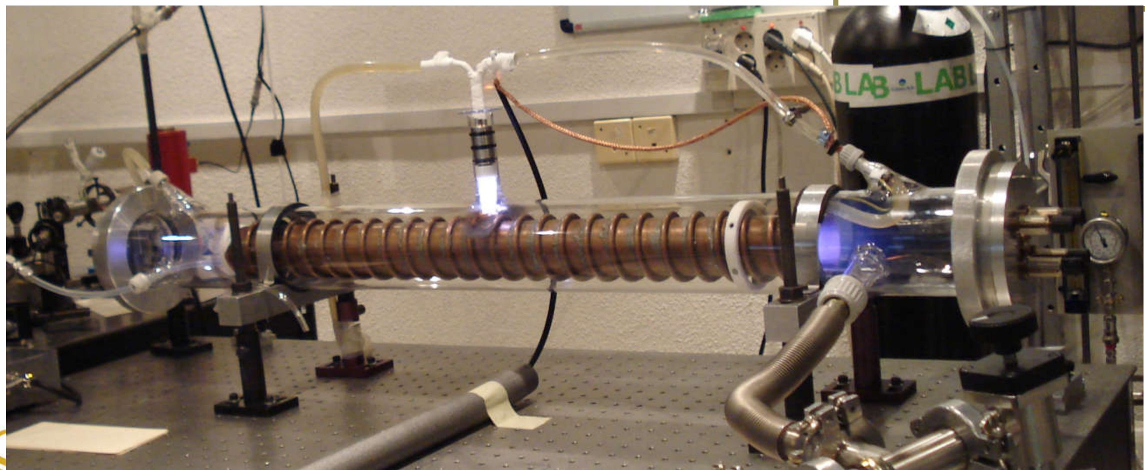


- At each datapoint in the spectrum, we have an 'instantaneous' wavemeter reading. The wavemeter is calibrated with the Ar^+ laser.
- <u>We can average a lot of scans</u>.

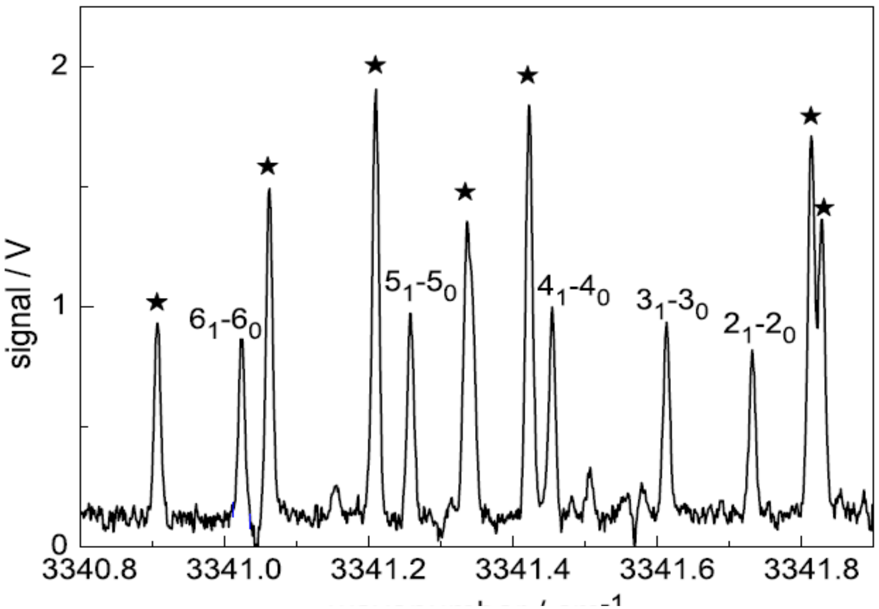
The discharge cell

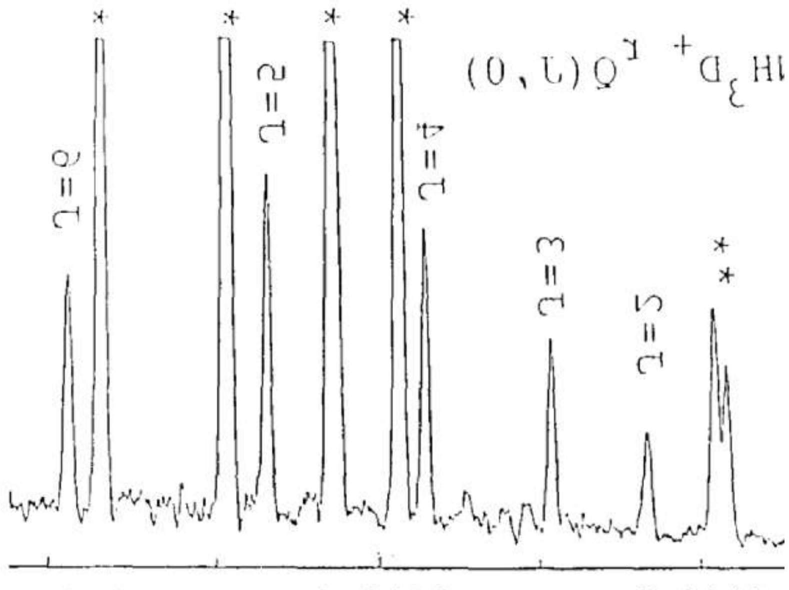
- Hollow-cathode discharge
- 380 V, 200 mA
- White cell ~9 m inside the cathode
- Amplitude modulated at 5.5 kHz
- IR modulated at 14.2 kHz
- Lock-in detection at 19.7 kHz

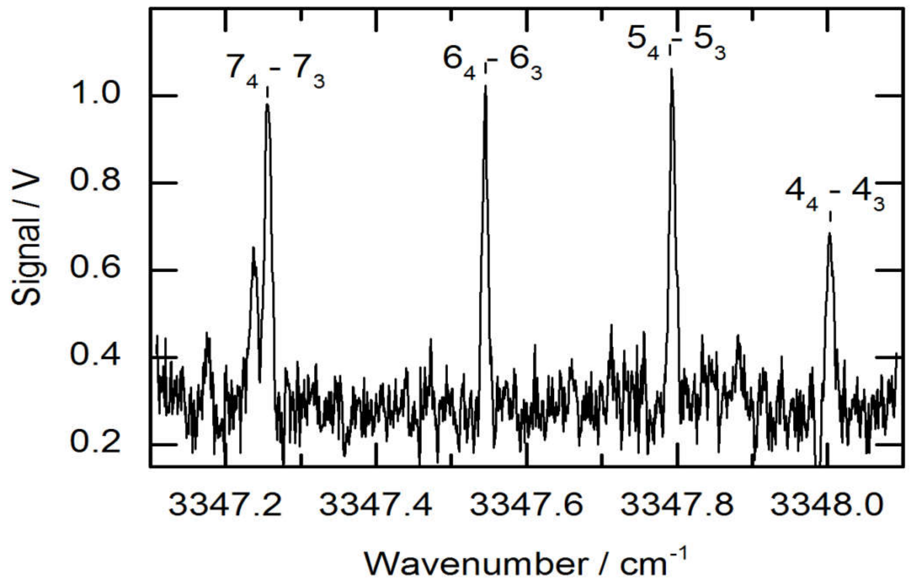


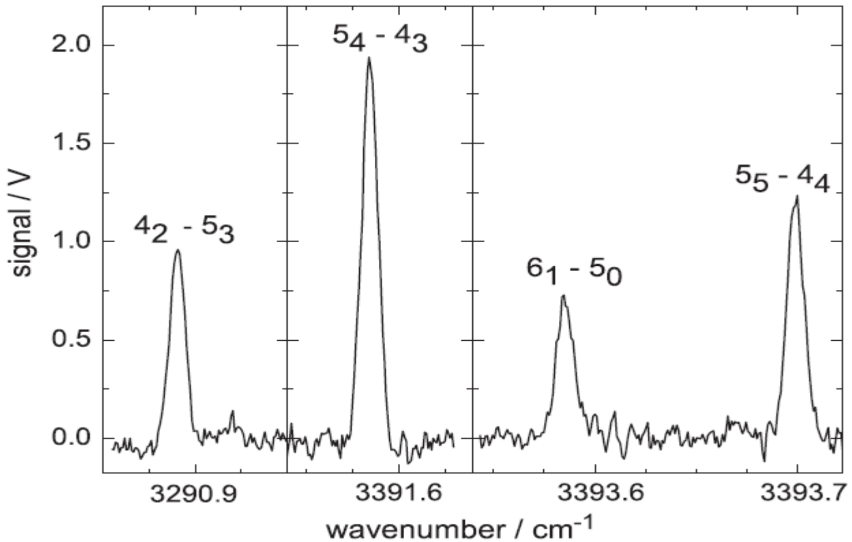


Precursors:
NH_3, D_2, 2:3
Total pressure 0.34 mbar



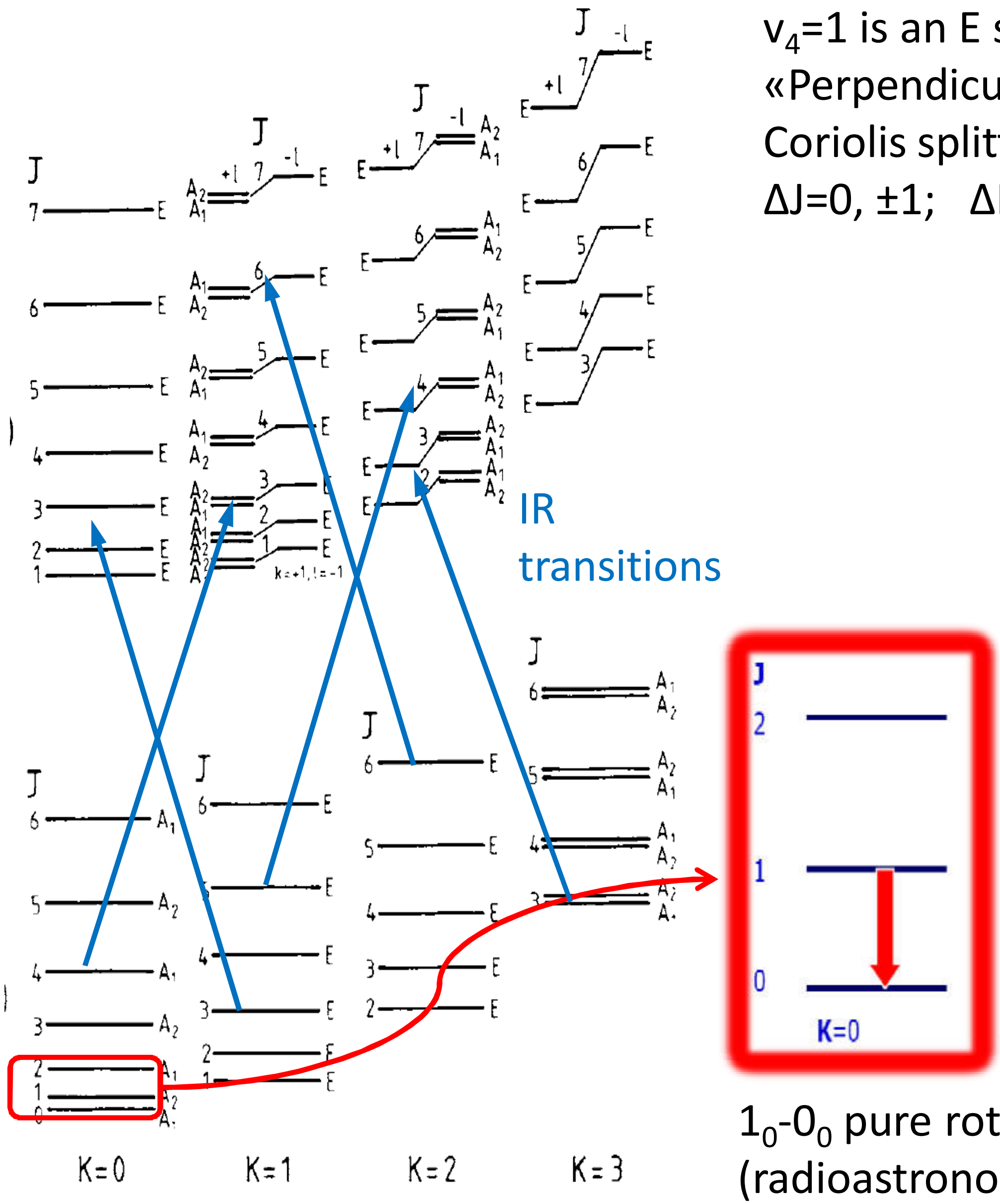






Ion concentration ~10^{10} cm^{-3} ~10^{-9} bar

v_4=1 is an E state (asymmetric N-H stretch)
«Perpendicular» type band of a prolate rotor
Coriolis splitting and k-type doubling
ΔJ=0, ±1;   ΔK= ±1



$$E''(J,K) = B''J(J+1) + (A''-B'')K^2 - D''_J J^2(J+1)^2 - D''_{JK}J(J+1)K^2 - D''_K K^4 + \text{higher order centrifugal distortion terms,} \quad (1)$$

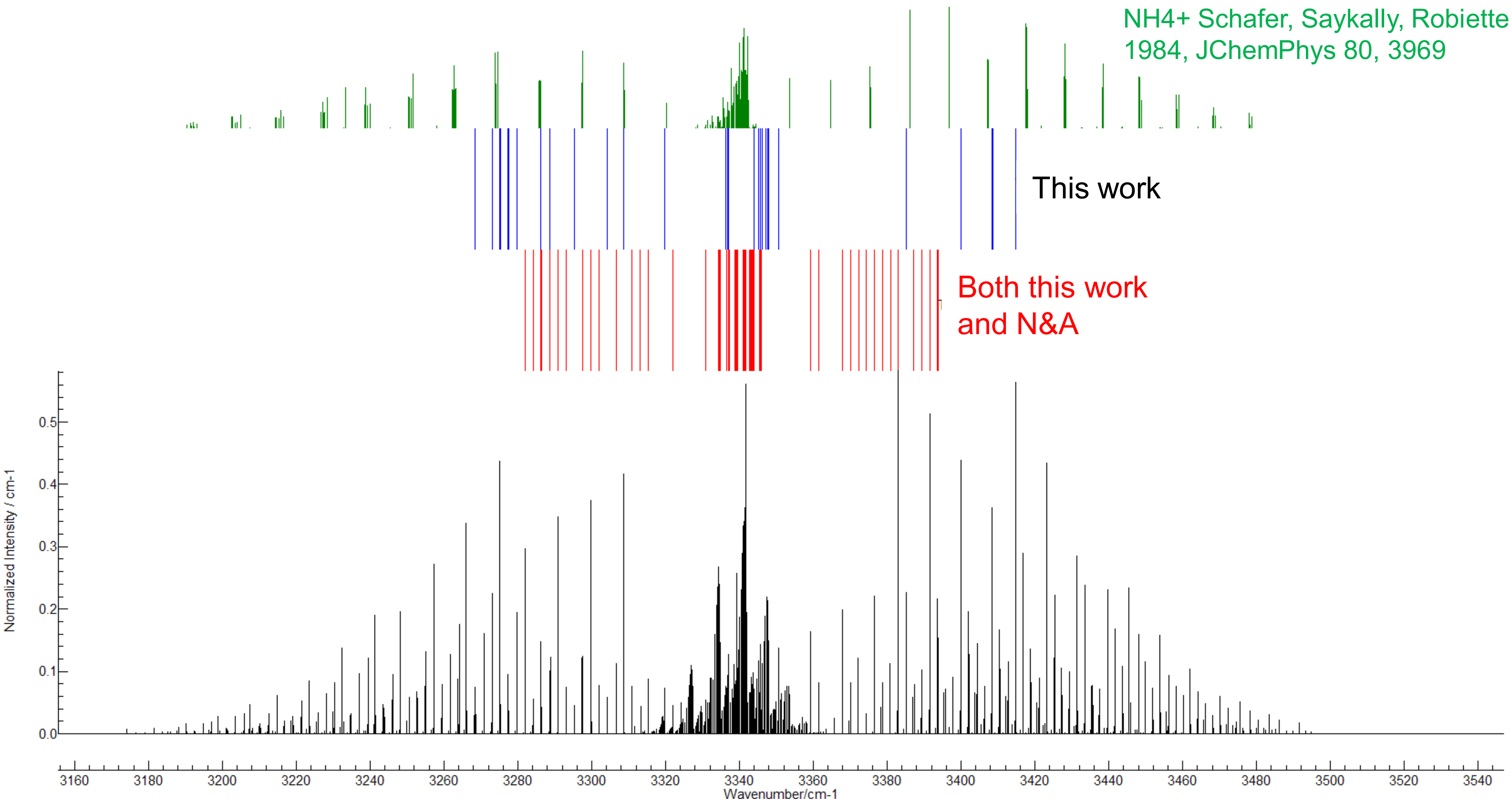
and for the degenerate $v_4 = 1$ state,

$$E'(J,k) = \nu_0 + B'J(J+1) + (A'-B')k^2 + (-2A'\zeta + \eta_J J^2 + \eta_K k^2)lk - D'_J J^2(J+1)^2 - D'_{JK}J(J+1)k^2 - D_K k^4 + \text{higher order centrifugal distortion terms,} \quad (2)$$

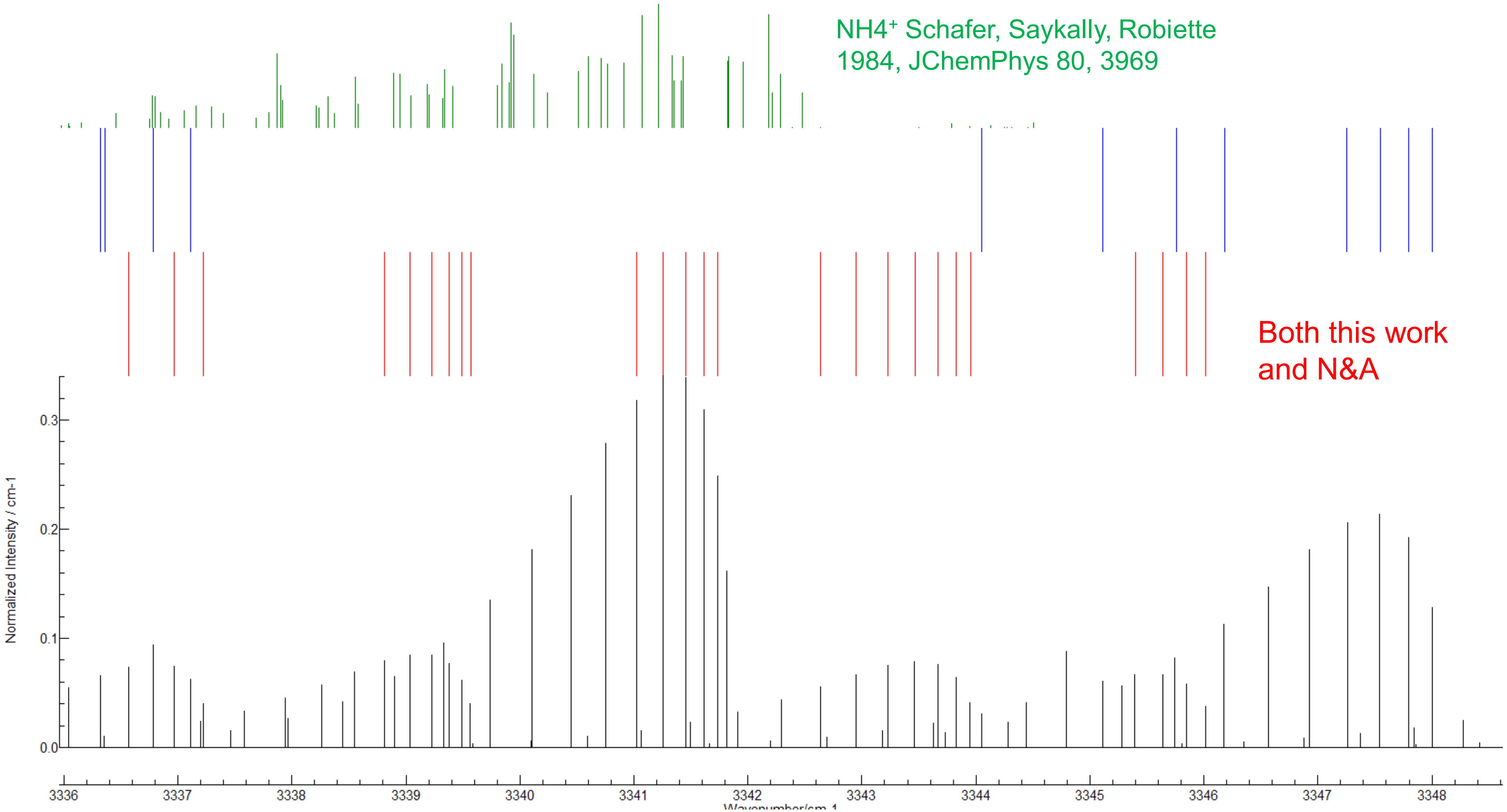
with the off-diagonal matrix elements, responsible for the rotational l-doubling,

$$\langle J, k+2, l+1|H|J, k, l-1\rangle = \frac{1}{2}q_+[(J(J+1) - k(k-1))(J(J+1) - k(k+1))]^{1/2}, \quad (3)$$

1_0-0_0 pure rotation transition
(radioastronomy observation)



Simulations and fits have been done with PGOPHER . (Colin Western, University of Bristol, http://pgopher.chm.bris.ac.uk)



NH4+ Schafer, Saykally, Robiette
1984, JChemPhys 80, 3969
Both this work
and N&A
Normalized Intensity / cm-1
0.3
0.2
0.1
0.0
3336
3337
3338
3339
3340
3341
3342
3343
3344
3345
3346
3347
3348

We have recorded 114 transitions between 3268.4 and 3414.7 cm^{-1}
Finally 76 have been included in the fit (vs. 61 in N&A)
Lines not included: J,K >8; or show interference from NH_4^+, NH_3; or are too broad

Constants Derived from the Fit

Constants (cm^{-1})	This Work	N&A (1986)
A''	5.852[a]	5.852[a]
B''	4.3834351(294)	4.38327(5)
D''_J	$6.1363(373) \times 10^{-5}$	$5.87(9) \times 10^{-5}$
D''_{JK}	$1.4689(293) \times 10^{-4}$	$1.52(6) \times 10^{-4}$
D''_K	0.0[a]	0.0[a]
ν_0	3341.07498(17)	3341.0764(3)
A'	5.818834(37)	5.81871(9)
B'	4.3640729(278)	4.36391(5)
D'_J	$5.4024(339) \times 10^{-5}$	$5.13(10) \times 10^{-5}$
D'_{JK}	$9.705(296) \times 10^{-5}$	$1.02(7) \times 10^{-4}$
D'_K	$3.801(91) \times 10^{-5}$	$3.1(3) \times 10^{-5}$
ζ	0.0582020(76)	0.058191(14)[b]
η_J	$-4.2581(686) \times 10^{-4}$	$-4.23(13) \times 10^{-4}$
η_K	$1.744(74) \times 10^{-4}$	$1.76(18) \times 10^{-4}$
q_+	$-3.393(98) \times 10^{-4}$[c]	$2.93(19) \times 10^{-4}$

Notes. Numbers in parentheses are one standard deviation in units of the last quoted digit, as derived from the fit. For this work we give all the significant digits necessary to reproduce the calculated line frequency values.
[a] Constrained in the fit.
[b] Calculated from the values of A' and $A'\zeta$ given in N&A (1986).
[c] Sign convention is opposite to that of N&A (1986).

A', A'', D_K', D_K'', ζ
Cannot be determined independently.
Constraining A'', D_K''
affects ν_0, ζ, A', D_K'

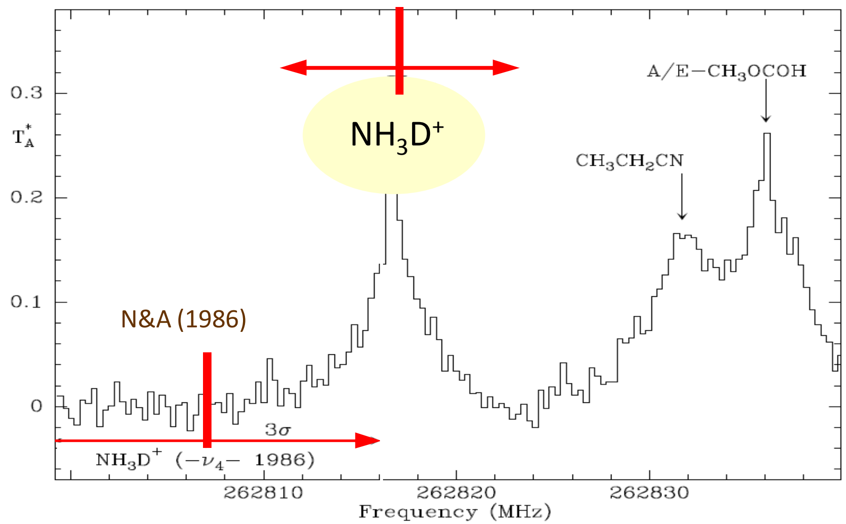
s.d. of the fit 5×10^{-4} cm^{-1}

$\nu(1_0 - 0_0)$ = 2B''-4D''
= **262816.8** MHz; $\sigma = 1.8$ MHz
vs **262816.73** MHz in the radio astronomy observations

- Our frequencies are good to 10 MHz (3σ)
- Our Ar^+ laser is locked to an I_2 line known with 0.1 MHz accuracy
- We have measured more lines than in N&A work
- All statistical parameters are better

- We propose 262817±6 (±3σ) as the frequency of the 1_0-0_0 rotational transition of NH_3D^+, supporting the assignment of emissions in Orion IRc2 and B1b to NH_3D^+

- Published in Astrophysical Journal Letters; Cernicharo et al. 771 L10 (2013). and Doménech et al. 771 L11 (2013).

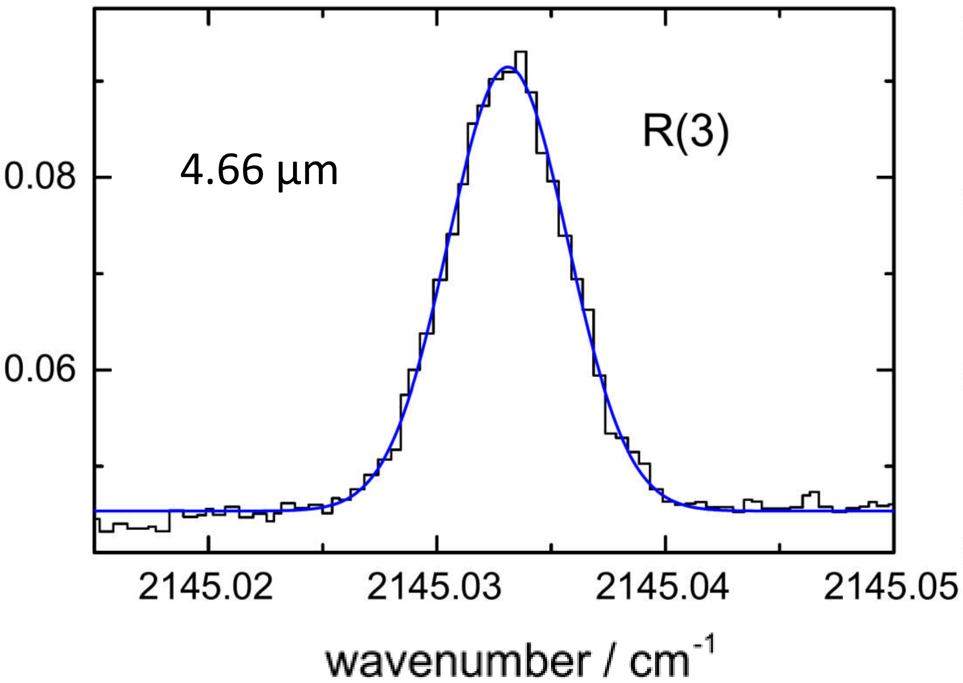


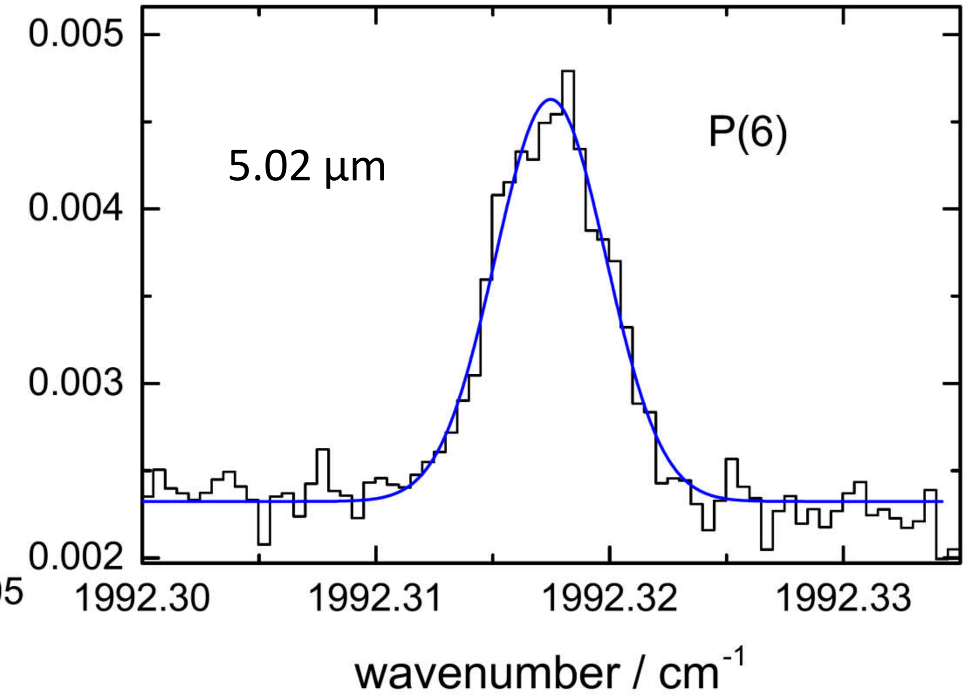
SiH^+: MOTIVATION

- Silicon bearing molecules account for ~10 of the 200 identified molecules in ISM. SiO, SiS, SiC, SiN, SiC_2, SiCN, SiNC, SiC_3, **SiH_4**, SiC_4 .
- SiH_4 in IRC+10126. SiH and SiH^+ have been identified in the solar spectrum. (SiH in some cold stars, and tentatively in Orion KL (Schilke 2001), SiH_3CN tentative (Agúndez 2014)).
- SiH^+ cation (silylidinium) remains undetected in interstellar space. CH^+ is overabundant. Both are $^1\Sigma^+$ in the g.s.
- Formation:
  - $Si^+ + H_2 \longrightarrow SiH^+ + H$ endothermic (~15000 K); exothermic if H_2 v≥3
  - $C^+ + H_2 \longrightarrow CH^+ + H$; $S^+ + H_2 \rightarrow SH^+ + H$ are endothernic (4200, 9800 K)
  - $Si + H_3^+ \longrightarrow SiH^+ + H_2$ is exothermic.
- Destruction:
  - SiH^+ PD rate is higher than that of CH^+. Besides, Si is depleted.
  - Reaction with C, O, N, S, grains, e^-. NO reaction with H_2.

⇒Low expected abundances, ***BUT ∄ NO LAB ROTATIONAL FREQUENCIES!***

SiH^+ experimental results



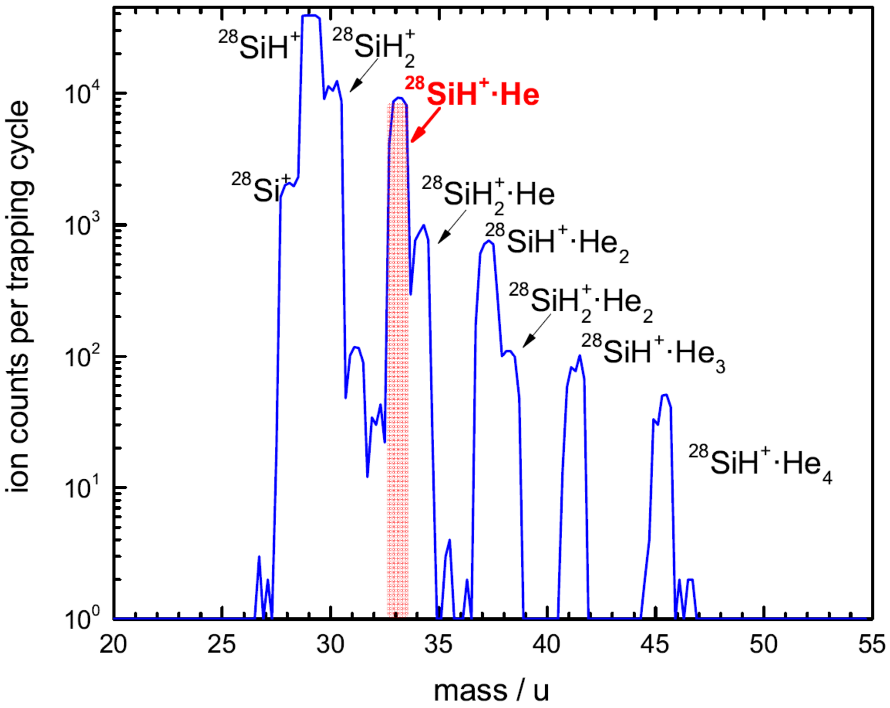


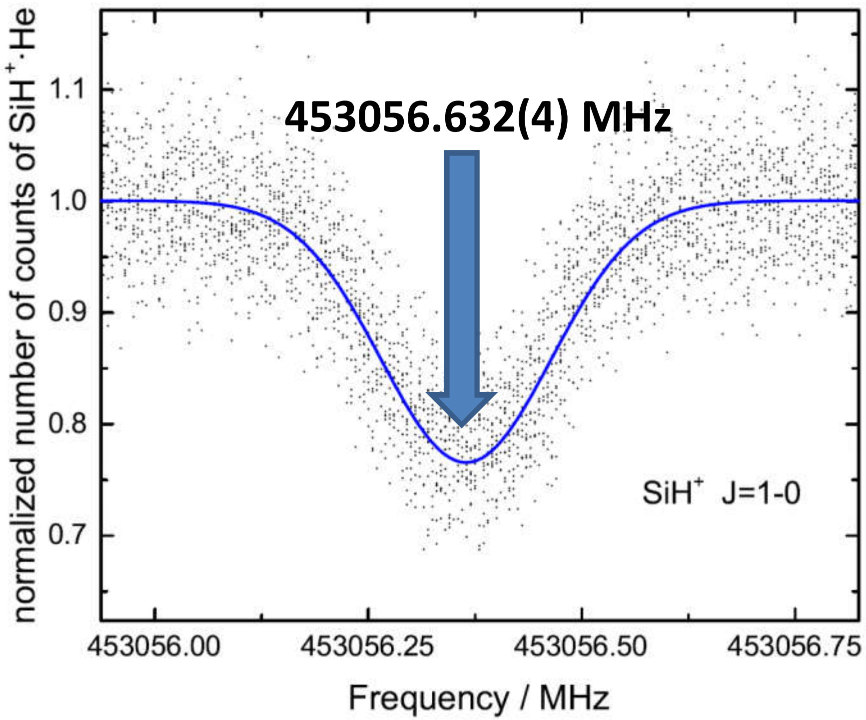
(v′, J′)	←	(v″, J″)	this work
(1,10)	←	(0,11)	1902.42994(25)
(1,9)	←	(0,10)	1921.04096(16)
(1,8)	←	(0,9)	1939.34400(11)
(1,7)	←	(0,8)	1957.33110(14)
(1,6)	←	(0,7)	1974.99216(12)
(1,5)	←	(0,6)	1992.31748(11)
(1,4)	←	(0,5)	2009.29756(10)
(1,3)	←	(0,4)	2025.92322(10)
(1,2)	←	(0,3)	2042.18438(10)
(1,1)	←	(0,2)	2058.07203(11)
(1,0)	←	(0,1)	2073.57690(10)
(1,1)	←	(0,0)	2103.40022(11)
(1,2)	←	(0,1)	2117.70038(10)
(1,3)	←	(0,2)	2131.58102(11)
(1,4)	←	(0,3)	2145.03311(11)
(1,5)	←	(0,4)	2158.04819(10)
(1,6)	←	(0,5)	2170.61766(11)
(1,7)	←	(0,6)	2182.73306(12)
(1,8)	←	(0,7)	2194.38565(11)
(1,9)	←	(0,8)	2205.56783(11)
(1,10)	←	(0,9)	2216.27186(11)
(1,11)	←	(0,10)	2226.48921(25)
(1,12)	←	(0,11)	2236.21237(61)

23 lines between 1902-2236 cm^{-1} (5.258 - 4.472 µm), P(12)-R(12)
S/N ratio 10-100 (500-100 averages for each line)

SiH^+: Pure rotation transitions

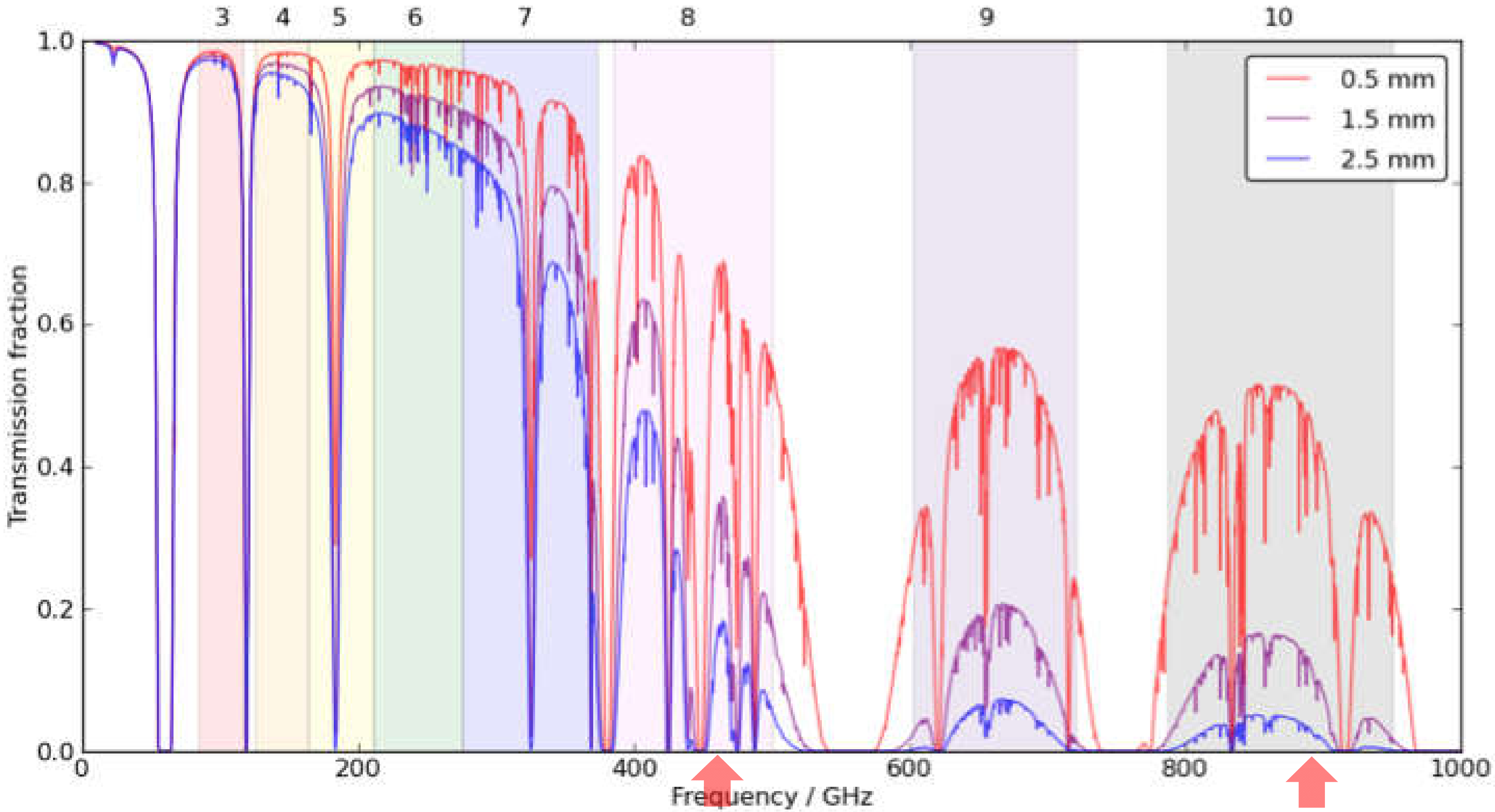
- Cologne ion trap
- Ion source: SiH_4/He. SiH^+ is mass selected
- SiH^+ is trapped in a 22 pole trap with He at 4 K
- He attaches to SiH^+ forming **SiH^+•He**, SiH^+•He_2, SiH^+•He_3, SiH^+•He_4

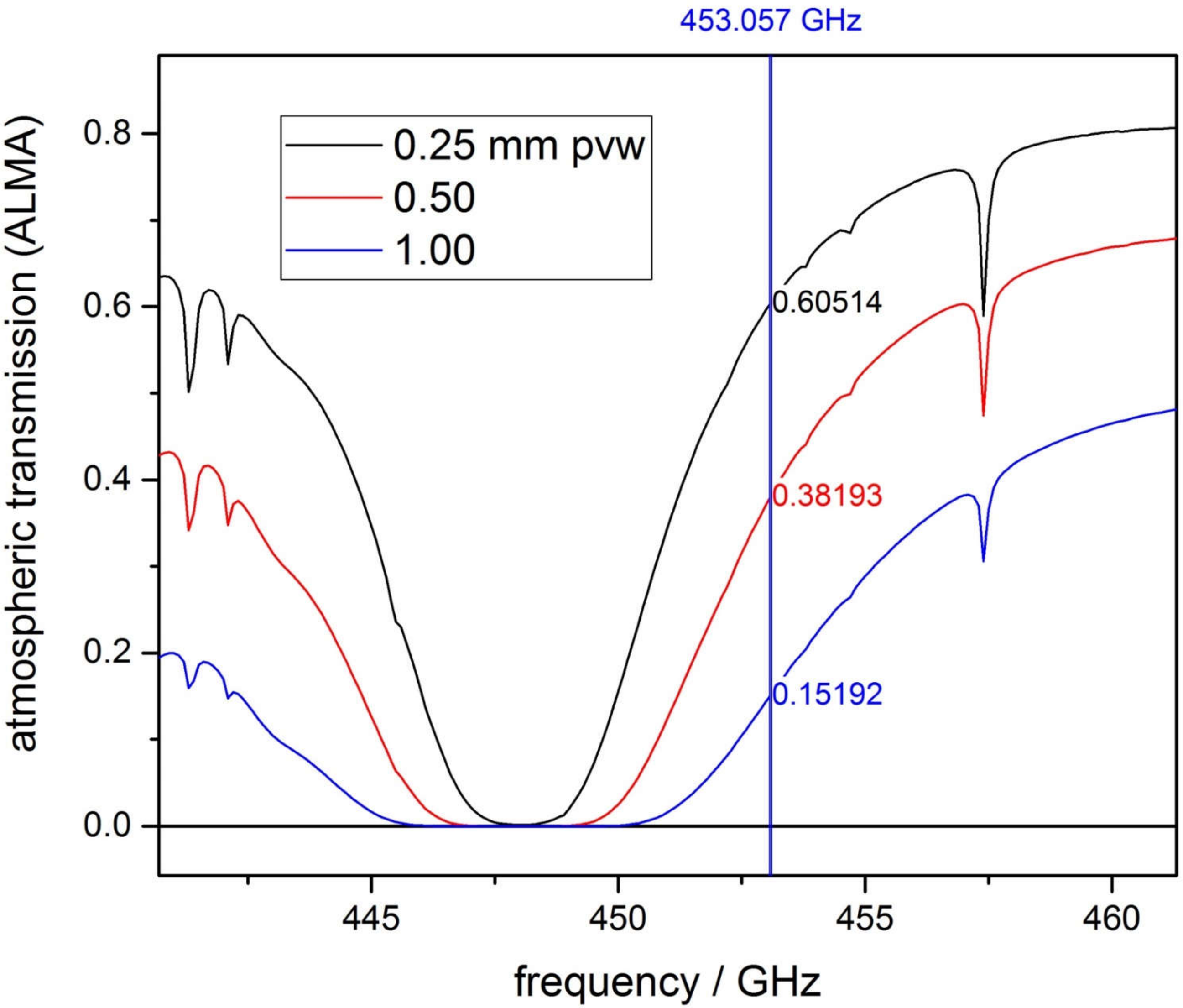




- Ion count at mass **33** as a function of frequency (DDS + VDI multipliers, referenced to a Rb clock)

Atmospheric transmission at ALMA site




453.057 GHz
0.25 mm pvw
0.50
1.00
0.60514
0.38193
0.15192
atmospheric transmission (ALMA)
0.0
0.2
0.4
0.6
0.8
445
450
455
460
frequency / GHz

Conclusions and outlook

- We have measured 23 vibration-rotation transitions of $^{28}SiH^+$ in the ground state with ~3 MHz accuracy (1σ).
- We have measured the pure rotation transition J=1-0 in the ground state with 1:10^9 accuracy.
- These frequencies will help in future searches for this ion in the ISM.
- Absorption by diffuse gas towards bright sources, SN remnants, shocks…
- J=1-0 frequency below HIFI in *Herschel.*
- Possibilities:

  ALMA band 8 J=0-1, band 10 J=1-2
  SOFIA GREAT, J=2-3
  SOFIA EXEs, v=1-0 } IR telescopes
  CRIRES+ VLT v=1-0 } IR telescopes
  iSHELL IRTF v=1-0 } IR telescopes

Conclusions and outlook

High resolution IR spectroscopy can predict rotational transitions with sufficiently high accuracy to guide space and/or laboratory observations.

Observations from Earth with high resolution IR telescopes are another available means to study light hydrides with rotational transitions in the mm- and submm-wave region.

¿Cómo es el trabajo en el *«laboratorio de infrarrojo por diferencia de frecuencias»*?

No se trata de instrumentos comerciales. Aprenderéis:

Láseres, óptica, (lineal y no lineal)
algo de astrofísica, (o mucho gracias a nuestros colegas),
electrónica,
fontanería, bricolaje y chapuzillas en general,

e incluso Física y Espectroscopía Molecular!