



**MAX PLANCK INSTITUTE**  
FOR EXTRATERRESTRIAL PHYSICS

# MOLECULAR SPECTROSCOPY FOR ASTROCHEMISTRY

## Part I — Context and Theory

Valerio Lattanzi — CAS@MPE

# MAIN REFERENCES AND CREDITS:



- Master in Astrochemistry — Ewine van Dishoeck (University of Leiden, 2010)
  - 2021 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules — Brett McGuire (ApJS 2022)
  - Interstellar Medium: Physics and Chemistry — Javier Goicoechea (IRAM 2021 summer school)
- 
- Microwave Molecular Spectra — W. Gordy and R.L. Cook (John Wiley and Sons, Inc, 1984)
  - Spectra of Atoms and Molecules — P.F. Bernath (Oxford University Press, 2005)
  - Molecular Rotation Spectra — H.W. Kroto (Dover Publications Inc. 1992)



# MENU OF THE DAY



- Molecules in the ISM.
- Why? Where? What?
- How to derive useful information?
- Molecular (rotational) spectroscopy
- A bit of theory...

# MOLECULES ARE EVERYWHERE!

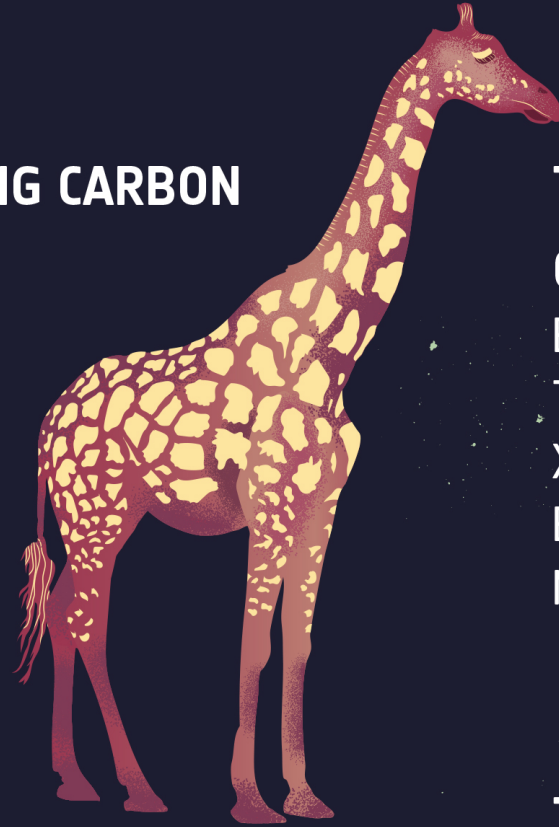


## → THE COMETARY ZOO: GASES DETECTED BY ROSETTA



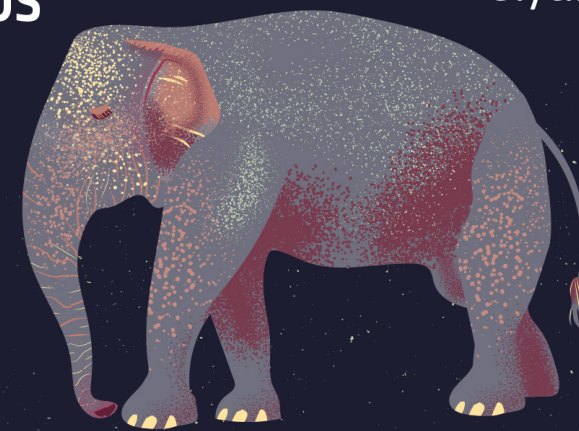
### THE LONG CARBON CHAINS

Methane  
Ethane  
Propane  
Butane  
Pentane  
Hexane  
Heptane



### THE AROMATIC RING COMPOUNDS

Benzene  
Toluene  
Xylene  
Benzoic acid  
Naphtalene



### THE KING OF THE ZOO

Glycine (amino acid)



### THE "MANURE SMELL" MOLECULES

Ammonia  
Methylamine  
Ethylamine



### THE "POISONOUS" MOLECULES

Acetylene  
Hydrogen cyanide  
Acetonitrile  
Formaldehyde



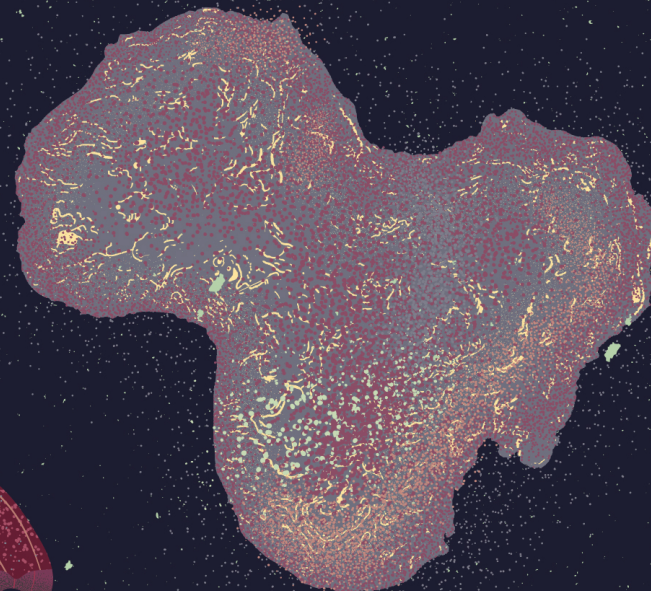
### THE ALCOHOLS

Methanol  
Ethanol  
Propanol  
Butanol  
Pentanol



### THE VOLATILES

Nitrogen  
Oxygen  
Hydrogen peroxide  
Carbon monoxide  
Carbon dioxide



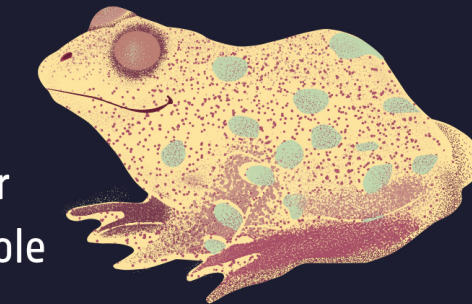
### THE "SMELLY" MOLECULES

Hydrogensulphide  
Carbonylsulphide  
Sulphur monoxide  
Sulphur dioxide  
Carbon disulphide



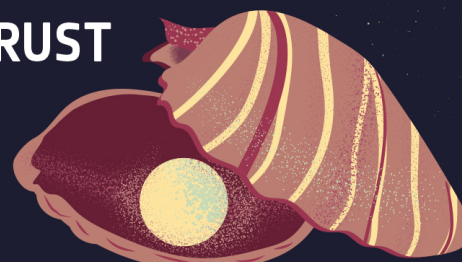
### THE "SMELLY AND COLOURFUL"

Sulphur  
Disulphur  
Trisulphur  
Tetrasulphur  
Methanethiole  
Ethanethiol  
Thioformaldehyde



### THE TREASURES WITH A HARD CRUST

Sodium  
Potassium  
Silicon  
Magnesium



### THE "SALTY" BEASTS

Hydrogen fluoride  
Hydrogen chloride  
Hydrogen bromide  
Phosphorus  
Chloromethane



### THE BEAUTIFUL AND SOLITARY

Argon  
Krypton  
Xenon



### THE "EXOTIC" MOLECULES

Formic acid  
Acetic acid  
Acetaldehyde  
Ethylenglycol  
Propylenglycol  
Butanamide



### THE MOLECULE IN DISGUISE

Cyanogen



www.esa.int

Credits: Based on data from ROSINA

European Space Agency



# A BIT OF PHYSICS



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SLOW chemistry!  
and astrophysicists did not expect many molecules in space...

# SCIENTISTS WERE SKEPTICAL...



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It is difficult to admit the existence of **molecules in** interstellar **space** because when once a molecule becomes dissociated there seems **no** chance of the atoms joining up again.<sup>28</sup>

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## MOLECULAR SPECTRA *and* MOLECULAR STRUCTURE

### I. SPECTRA OF DIATOMIC MOLECULES

BY

GERHARD HERZBERG, F.R.S.  
*National Research Council of Canada*

With the co-operation, in the first edition, of  
J. W. T. SPINKS, F.R.S.C.

The observation that in interstellar space only the very lowest rotational levels of CH, CH<sup>+</sup>, and CN are populated is readily explained by the depopulation of the higher levels by emission of the far infrared rotation spectrum (see p. 4 . ) and by the lack of excitation to these levels by collisions or radiation. The intensity of the rotation spectrum of CN is much smaller than that of CH or CH<sup>+</sup> on account of the smaller dipole moment as well as the smaller frequency [due to the factor  $\nu^4$  in (I, 48)]. That is why lines from the second lowest level ( $K = 1$ ) have been observed for CN. **From the intensity ratio of the lines with  $K = 0$  and  $K = 1$  a rotational temperature of 2.3° K follows, which has of course only a very restricted meaning.**

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In diffuse clouds collisional excitation is negligible

$$T_{rot}(\text{molecules}) \approx T_{bg} \approx T_{CMB}$$



# KNOWN INTERSTELLAR MOLECULES



2 Atoms	3 Atoms	4 Atoms	5 Atoms	6 Atoms	7 Atoms	8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	13+ Atoms
CH CN CH <sup>+</sup> OH CO H <sub>2</sub> SiO CS SO SiS NS C <sub>2</sub> NO HCl NaCl AlCl KCl AlF PN SiC CP	NH SiN SO <sup>+</sup> CO <sup>+</sup> HF N <sub>2</sub> CF <sup>+</sup> PO O <sub>2</sub> AlO CN <sup>-</sup> OH <sup>+</sup> SH <sup>+</sup> HCl <sup>+</sup> SH TiO ArH <sup>+</sup> NS <sup>+</sup> HeH <sup>+</sup> VO PO <sup>+</sup>	H <sub>2</sub> O MgCN HCO <sup>+</sup> H <sub>3</sub> <sup>+</sup> SiCN AlNC SiNC HCP CCP AlOH H <sub>2</sub> O <sup>+</sup> H <sub>2</sub> Cl <sup>+</sup> KCN FeCN HO <sub>2</sub> TiO <sub>2</sub> CCN SiCSi S <sub>2</sub> H HCS HSC NCO CaNC NCS MgNC NH <sub>2</sub> NaCN N <sub>2</sub> O	NH <sub>3</sub> CH <sub>3</sub> C <sub>3</sub> N <sup>-</sup> PH <sub>3</sub> HCNO C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> N HNCS HOCO <sup>+</sup> C <sub>3</sub> O /C <sub>3</sub> H HCNH <sup>+</sup> H <sub>3</sub> O <sup>+</sup> C <sub>3</sub> S c-C <sub>3</sub> H HC <sub>2</sub> N H <sub>2</sub> CN SiC <sub>3</sub>	CH <sub>3</sub> C <sub>3</sub> N <sup>-</sup> PH <sub>3</sub> HCNO C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> N HNCS HOCO <sup>+</sup> C <sub>3</sub> O /C <sub>3</sub> H HCNH <sup>+</sup> H <sub>3</sub> O <sup>+</sup> C <sub>3</sub> S c-C <sub>3</sub> H HC <sub>2</sub> N H <sub>2</sub> CN SiC <sub>3</sub>	HC <sub>3</sub> N CNCHO HNCNH CH <sub>3</sub> O NH <sub>3</sub> D <sup>+</sup> H <sub>2</sub> NCO <sup>+</sup> NCCNH <sup>+</sup> CH <sub>3</sub> Cl MgC <sub>3</sub> N HC <sub>3</sub> O <sup>+</sup> NH <sub>2</sub> OH HC <sub>3</sub> S <sup>+</sup> H <sub>2</sub> CCS C <sub>4</sub> S CHOSH HCSCN HC <sub>3</sub> O C <sub>4</sub> H <sup>-</sup>	CH <sub>3</sub> OH CH <sub>3</sub> CN NH <sub>2</sub> CHO CH <sub>3</sub> SH C <sub>2</sub> H <sub>4</sub> C <sub>5</sub> H CH <sub>3</sub> NC HC <sub>2</sub> CHO H <sub>2</sub> C <sub>4</sub> C <sub>5</sub> S HC <sub>3</sub> NH <sup>+</sup> C <sub>5</sub> N HC <sub>4</sub> H HC <sub>4</sub> N c-H <sub>2</sub> C <sub>3</sub> O CH <sub>2</sub> CNH C <sub>5</sub> N <sup>-</sup> HNCHCN SiH <sub>3</sub> CN MgC <sub>4</sub> H CH <sub>3</sub> CO <sup>+</sup> H <sub>2</sub> CCCS CH <sub>2</sub> CCH HCSCCH C <sub>5</sub> O C <sub>5</sub> H <sup>+</sup> c-C <sub>5</sub> H	CH <sub>3</sub> CHO CH <sub>3</sub> CCH CH <sub>3</sub> NH <sub>2</sub> CH <sub>2</sub> CHCN HC <sub>5</sub> N C <sub>6</sub> H c-C <sub>2</sub> H <sub>4</sub> O CH <sub>2</sub> CHOH C <sub>6</sub> H <sup>-</sup> CH <sub>3</sub> NCO HC <sub>5</sub> O HOCH <sub>2</sub> CN HC <sub>4</sub> NC HC <sub>3</sub> HNH c-C <sub>3</sub> HCCH MgC <sub>5</sub> N CH <sub>2</sub> C <sub>3</sub> N	HCOOCH <sub>3</sub> CH <sub>3</sub> C <sub>3</sub> N C <sub>7</sub> H CH <sub>3</sub> COOH H <sub>2</sub> C <sub>6</sub> CH <sub>2</sub> OHCHO HC <sub>6</sub> H CH <sub>2</sub> CHCHO CH <sub>2</sub> CCHCN NH <sub>2</sub> CH <sub>2</sub> CN CH <sub>3</sub> CHNH CH <sub>3</sub> SiH <sub>3</sub> NH <sub>2</sub> CONH <sub>2</sub> HCCCH <sub>2</sub> CN CH <sub>2</sub> CHCCH MgC <sub>6</sub> H C <sub>2</sub> H <sub>3</sub> NH <sub>2</sub> HOCHCHOH	CH <sub>3</sub> OCH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> OH CH <sub>3</sub> CH <sub>2</sub> CN HC <sub>7</sub> N CH <sub>3</sub> C <sub>4</sub> H C <sub>8</sub> H CH <sub>3</sub> CONH <sub>2</sub> C <sub>8</sub> H <sup>-</sup> CH <sub>3</sub> COCH <sub>3</sub> HOCH <sub>2</sub> CH <sub>2</sub> OH CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> C <sub>5</sub> N CH <sub>3</sub> CHCH <sub>2</sub> O CH <sub>3</sub> OCH <sub>2</sub> OH C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub> NCO HC <sub>7</sub> NH <sup>+</sup> CH <sub>3</sub> CHCHCN CH <sub>2</sub> CCH <sub>3</sub> CN CH <sub>2</sub> CHCH <sub>2</sub> CN	CH <sub>2</sub> CHCH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> SH HC <sub>7</sub> O CH <sub>3</sub> NHCHO H <sub>2</sub> CCCHCCH HCCCHCHCN H <sub>2</sub> CCHC <sub>3</sub> N   <	

267 Molecules

Last Updated: 15 Aug 2022

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- **Identification** => chemical compositions, differentiation, time evolution

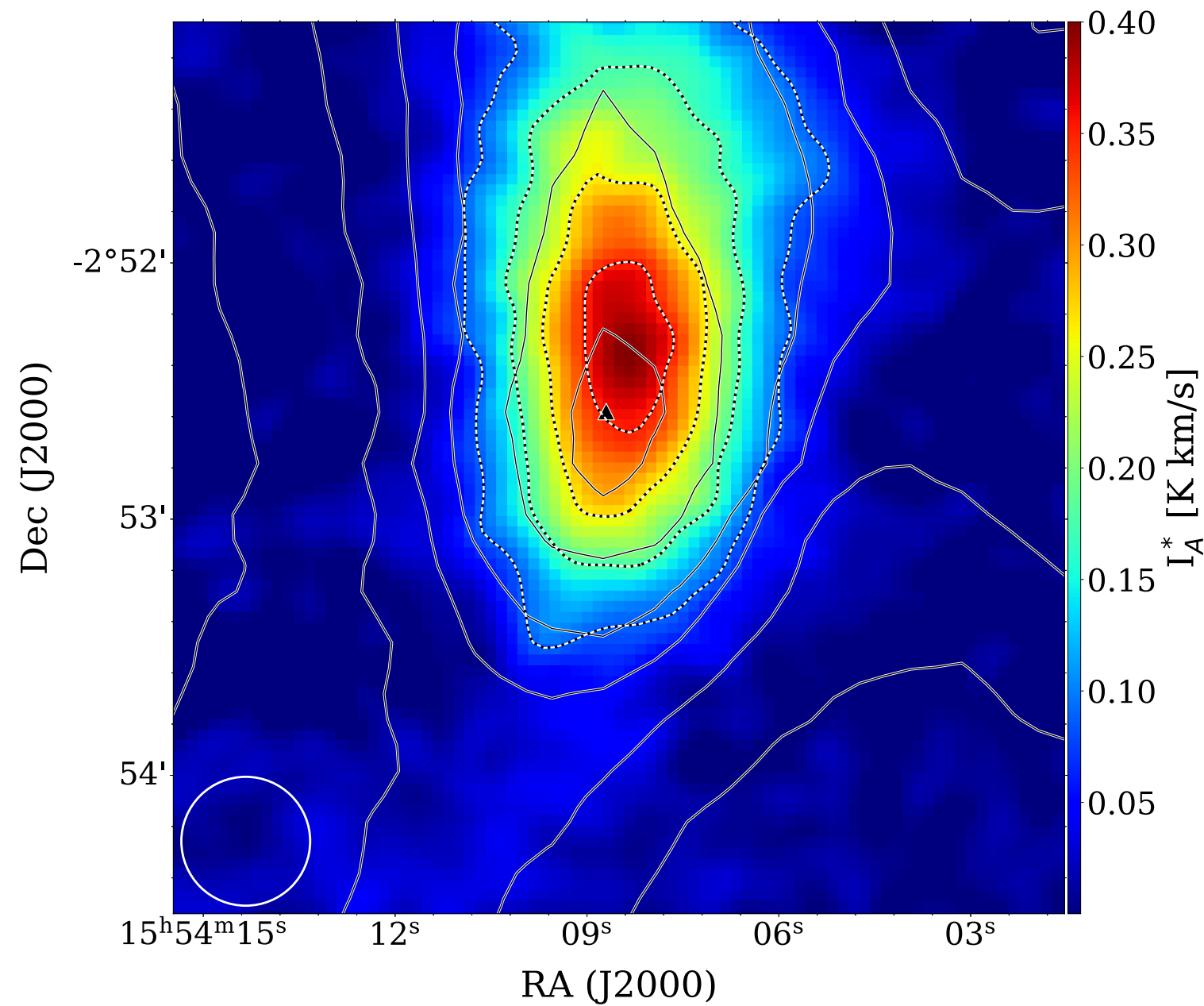
- **Identification** => chemical compositions, differentiation, time evolution
- **Line strengths** => molecular abundances
- **Line ratios** => environment temperatures, densities
- **Line profiles** => kinematical analysis

# MOLECULES AS TOOL FOR CHEMICAL DIFFERENTIATION

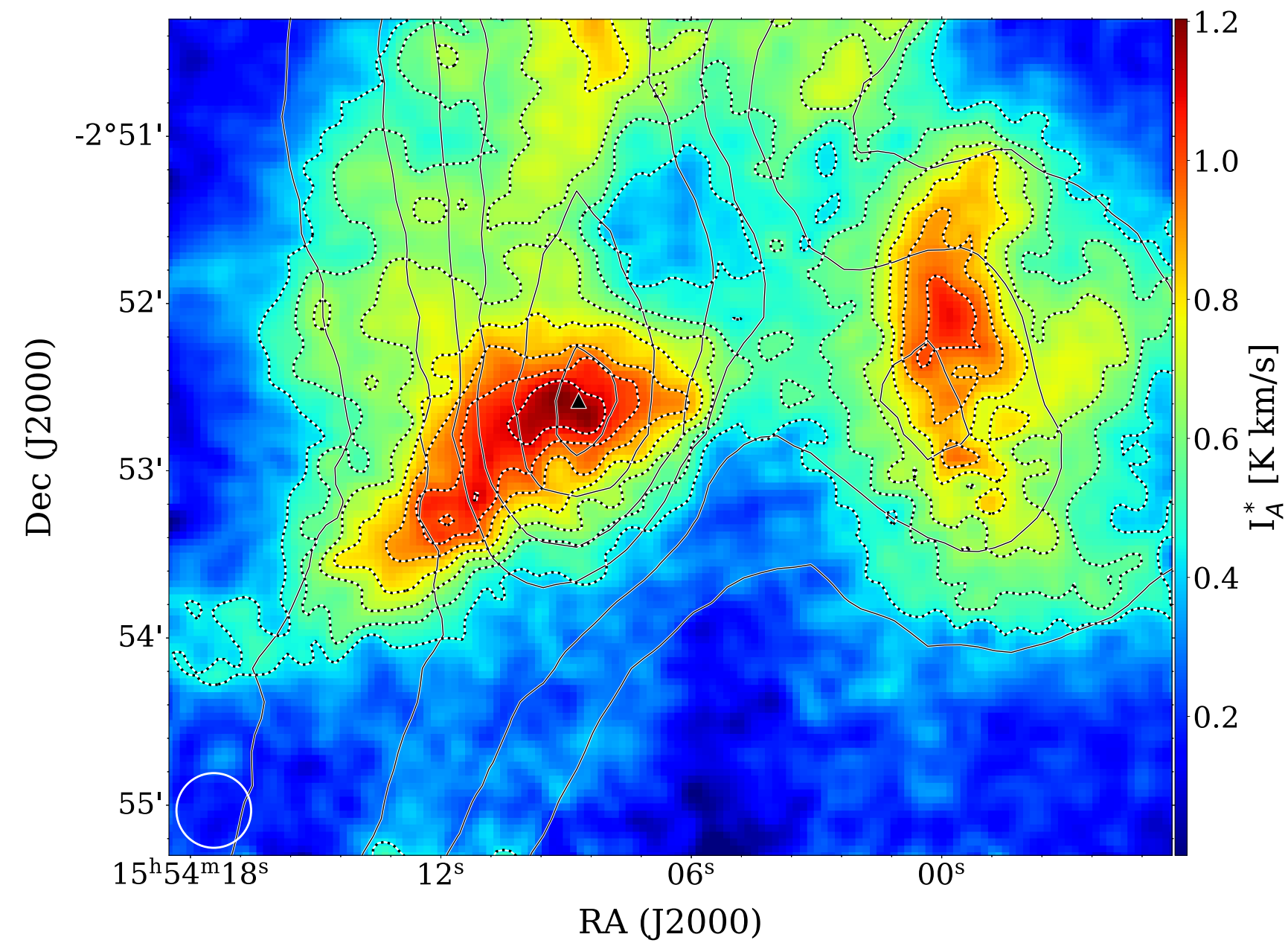


## IRAM 30m view of L183 (prestellar core)

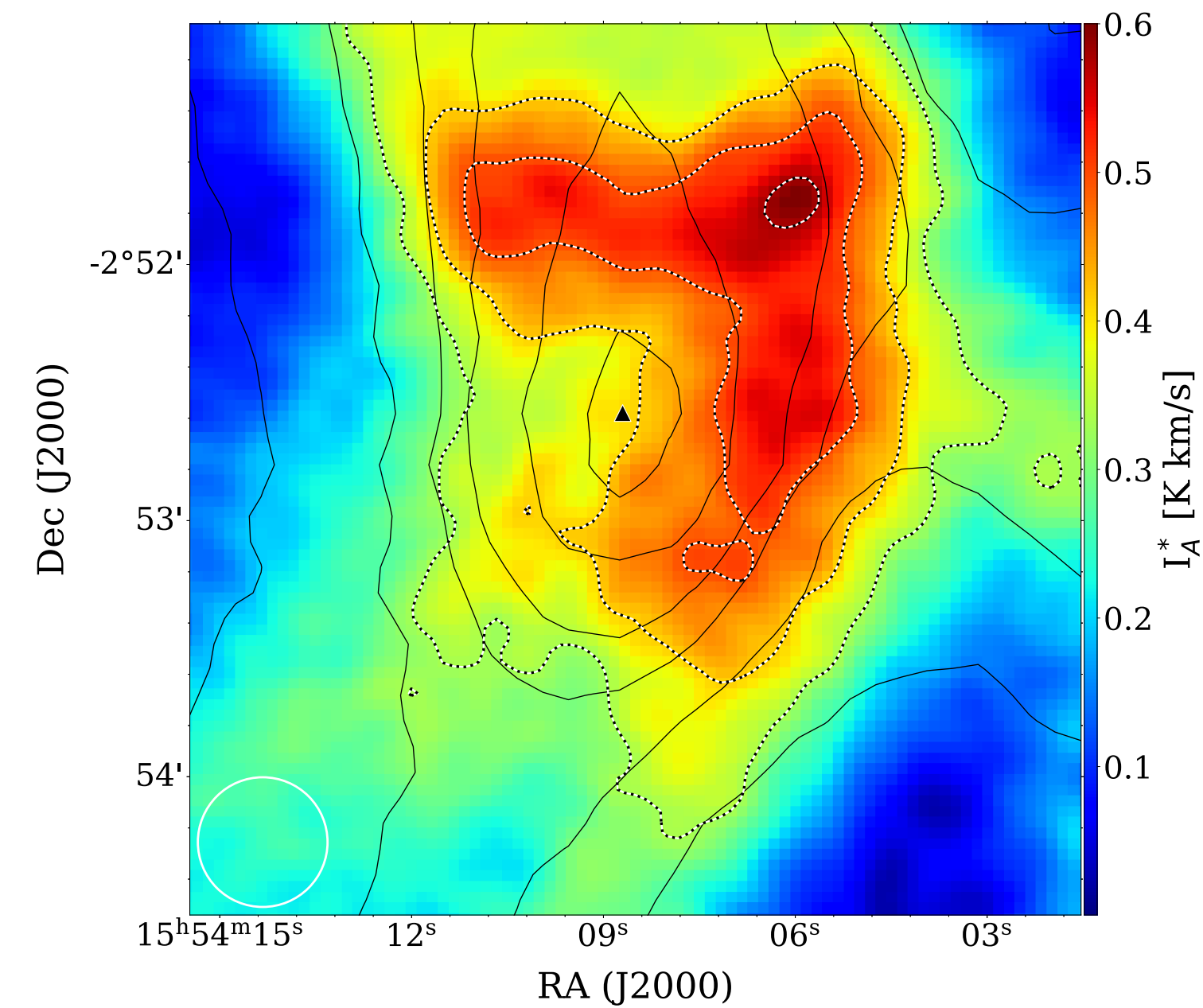
$\text{NH}_2\text{D}$  ( $1_{1,1} - 1_{0,1}$ ,  $F_1 = 0 - 1$ ,  $F=0 - 1$ )



$\text{CH}_3\text{OH}$  ( $2_{0,2} - 1_{0,1}$  ( $A^+$ ))



$\text{c-C}_3\text{H}_2$  ( $2_{1,2} - 1_{0,1}$ )



Continuum in black/white contour

*Lattanzi+ in prep.*



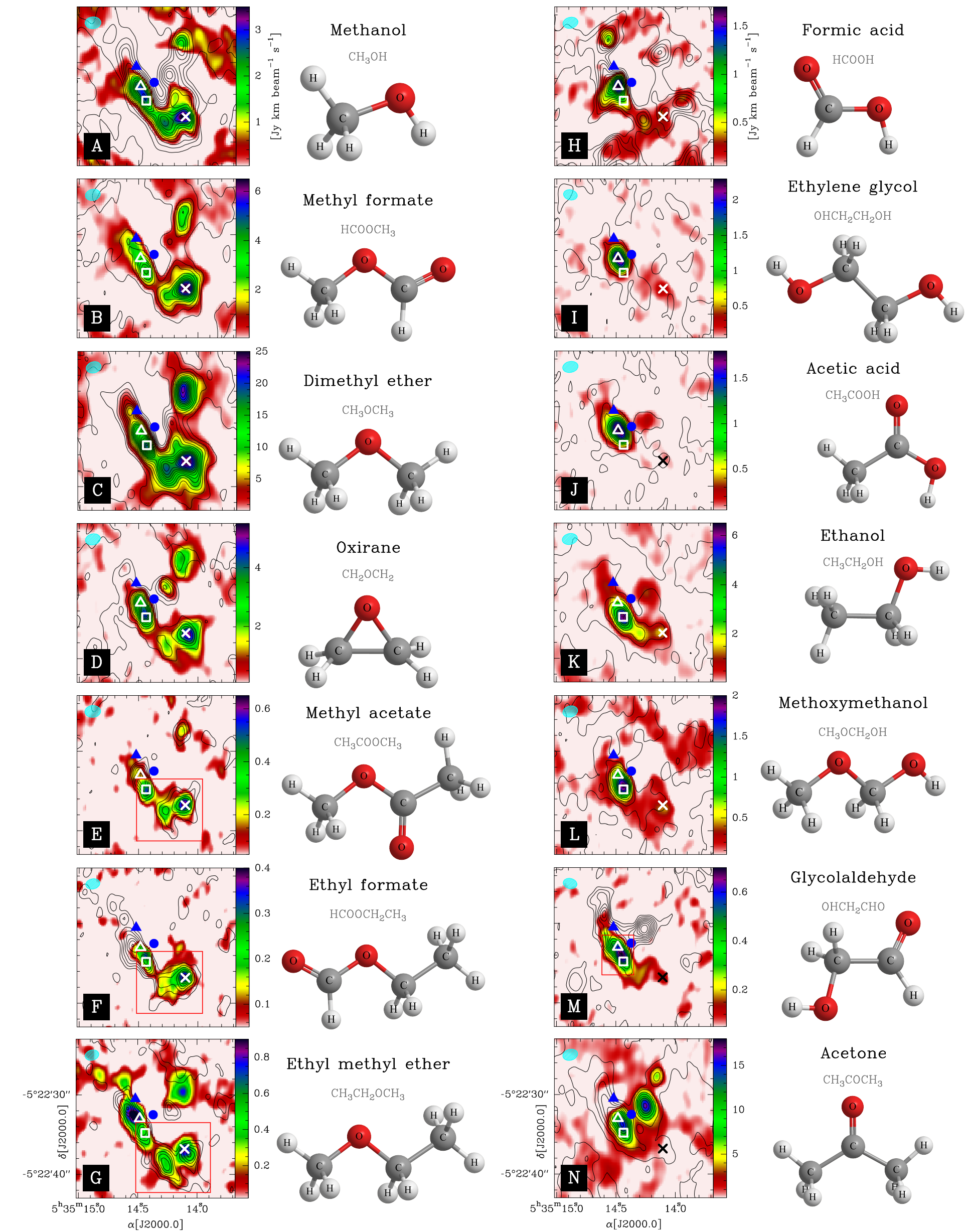
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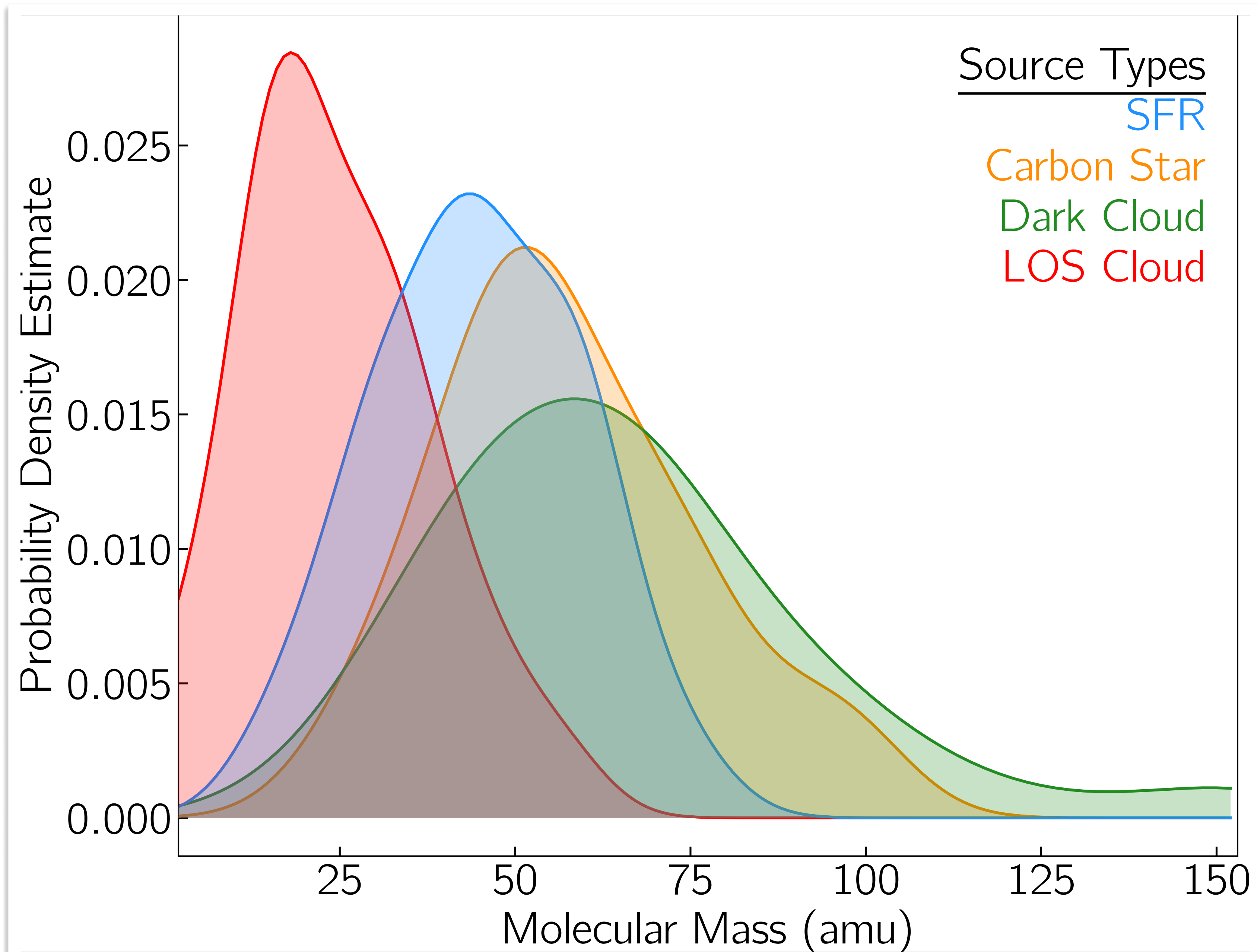


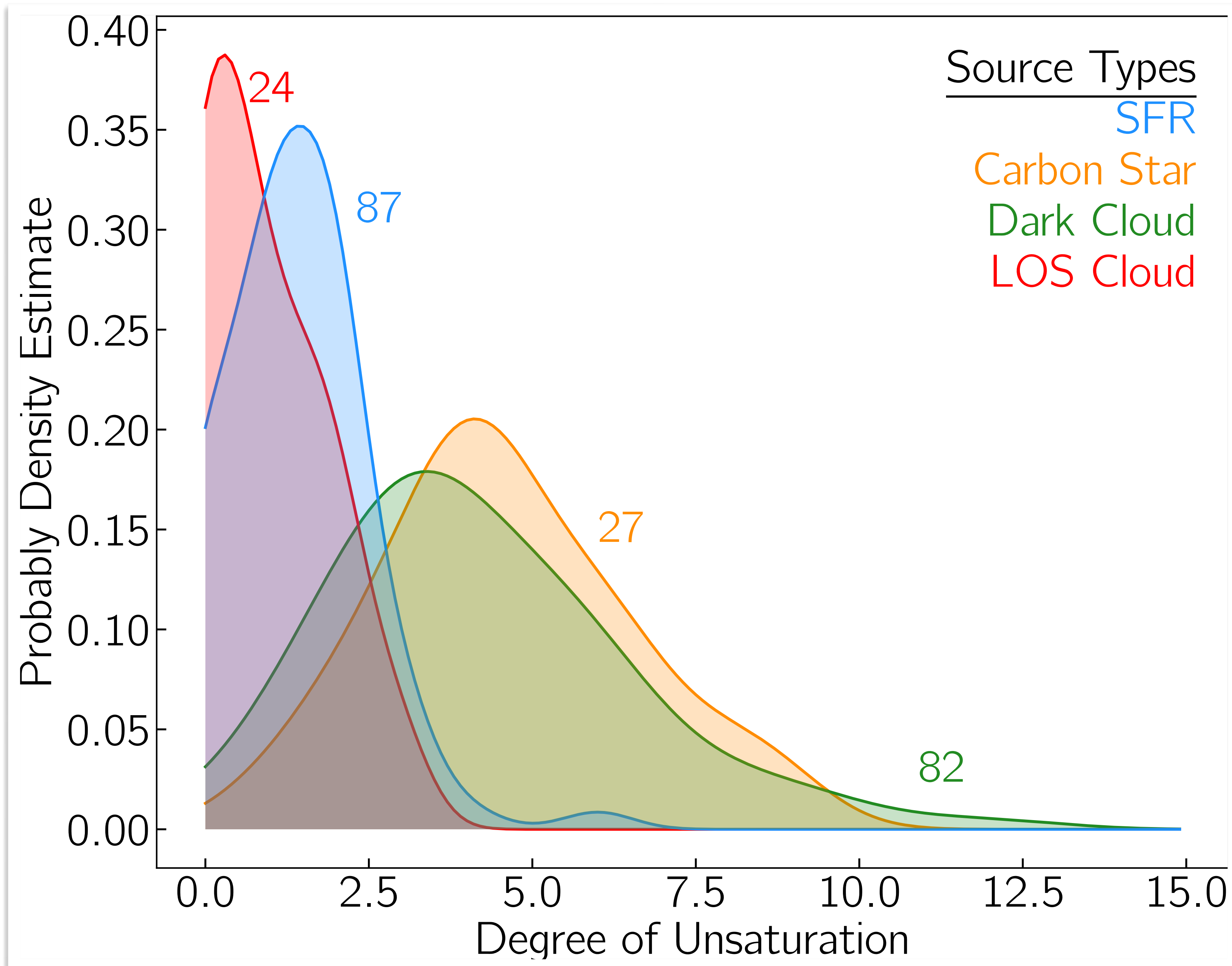
ALMA SV view ORION KL (high-mass SFR)

Colour and contours represent two different transitions

*Tercero+ 2018*





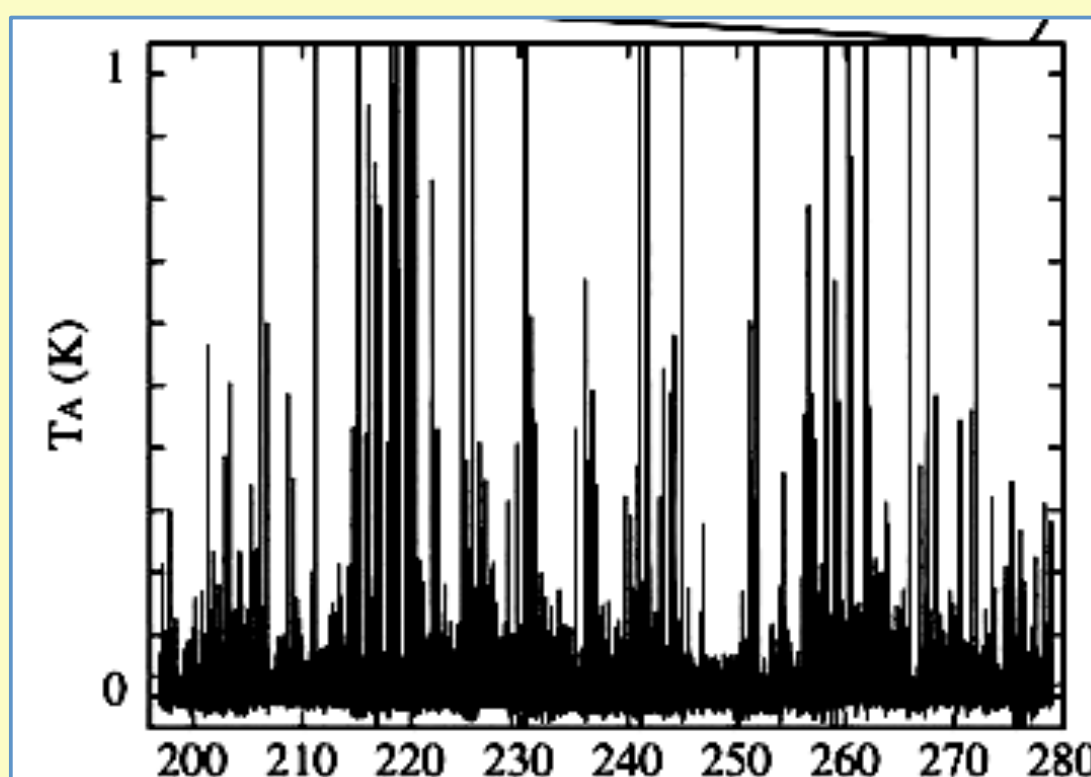




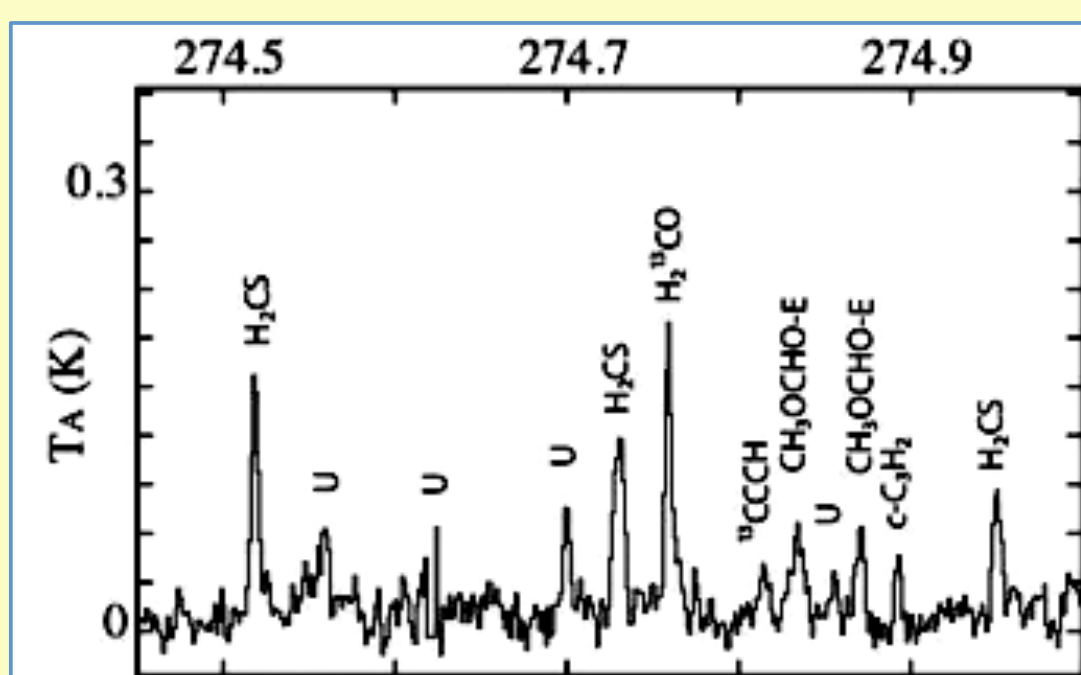
# All very nice, but first...

**All very nice, but first...**

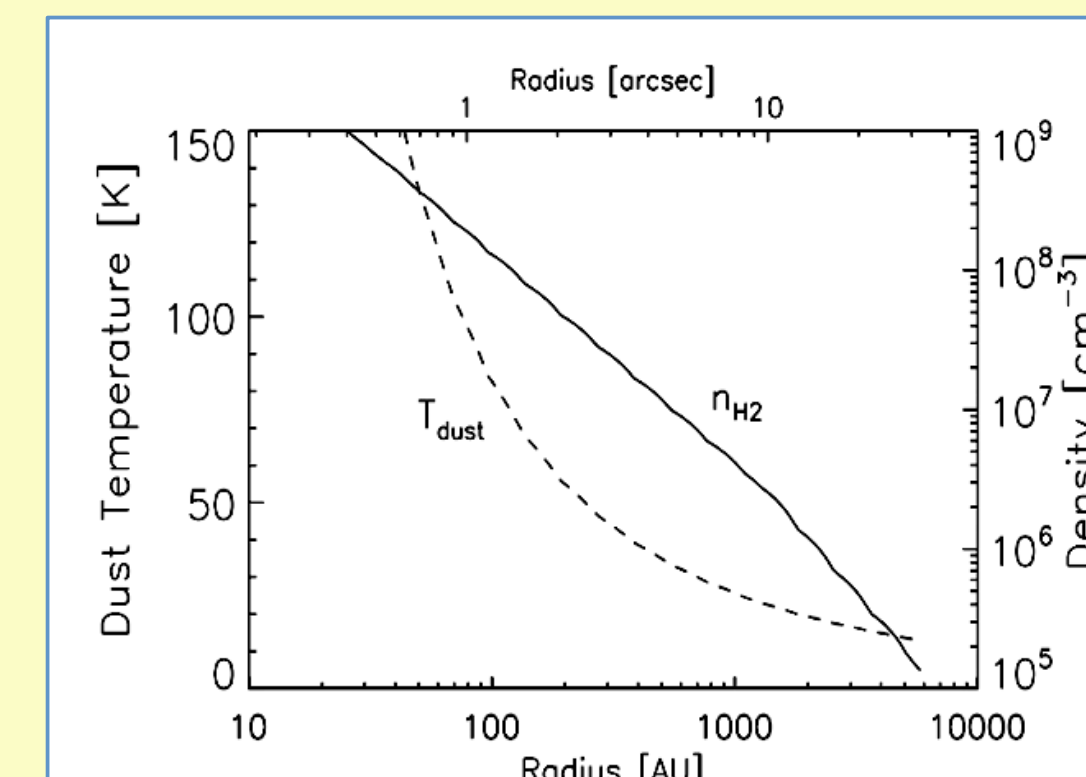
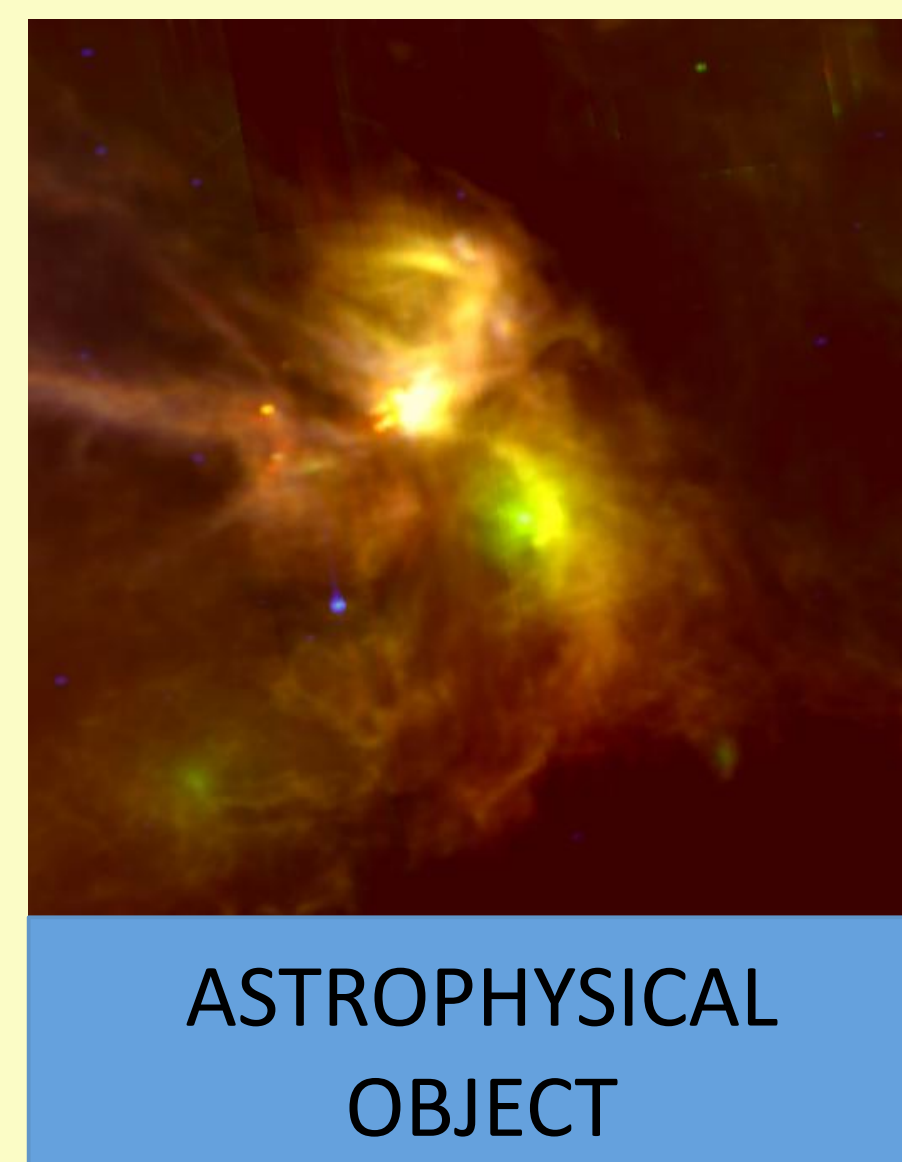
**LINE IDENTIFICATION!**



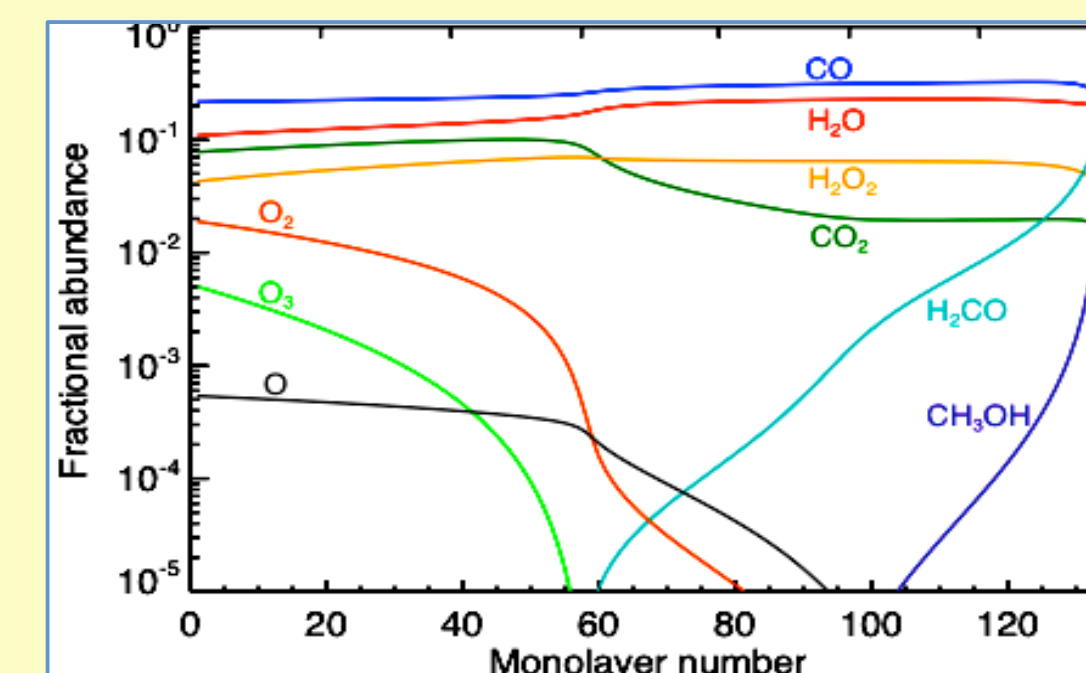
**STEP 1:** Observe the spectrum of the source.  
**Tool:** telescope



**STEP 2:** Identify the lines and species.  
**Tool:** spectroscopic data



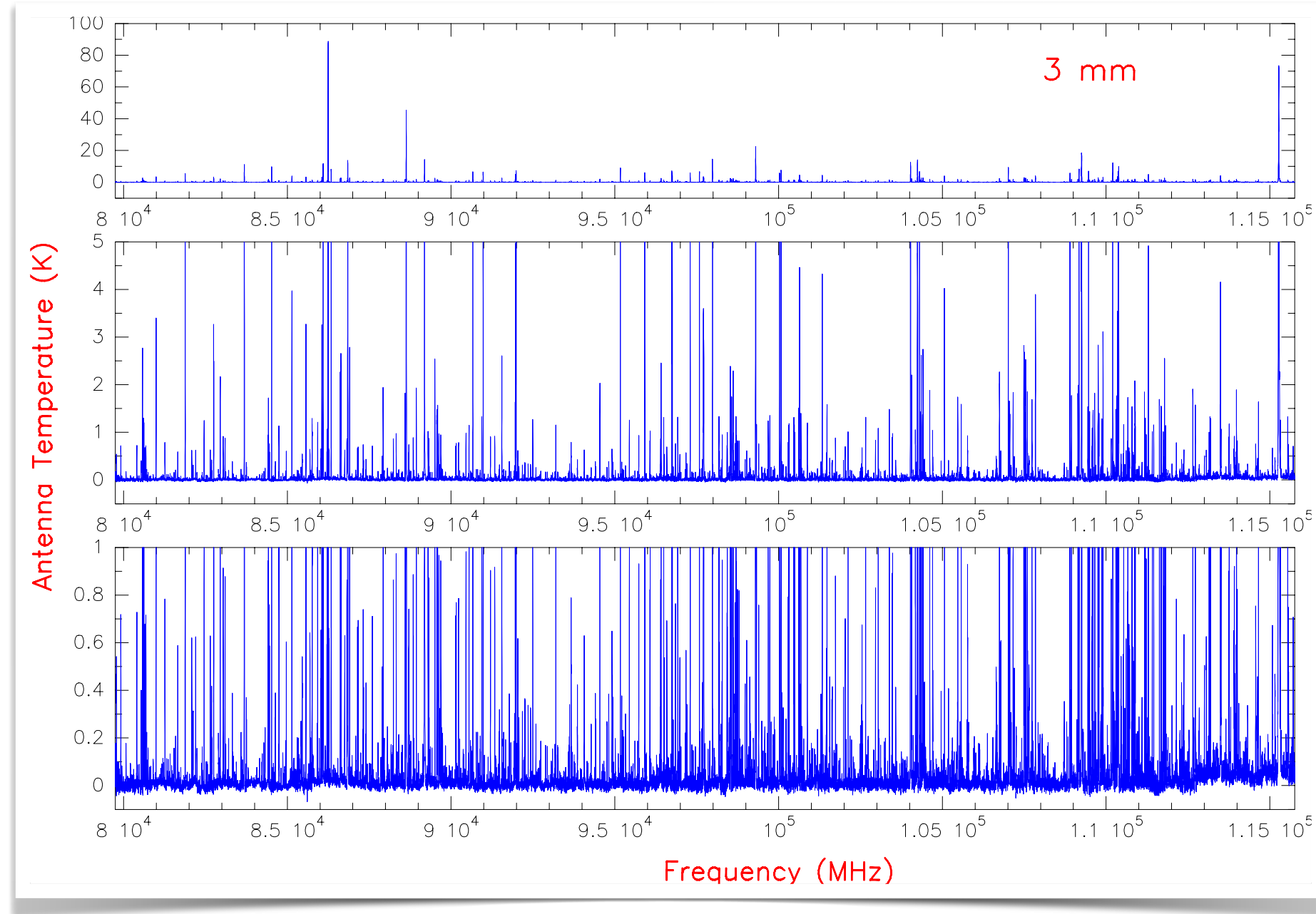
**STEP 3:** Derive the physical and chemical structure.  
**Tool:** collisional coefficients



**STEP 4:** Understand the chemical structure.  
**Tool:** reaction pathways and rate coefficients

Caselli & Ceccarelli 2012

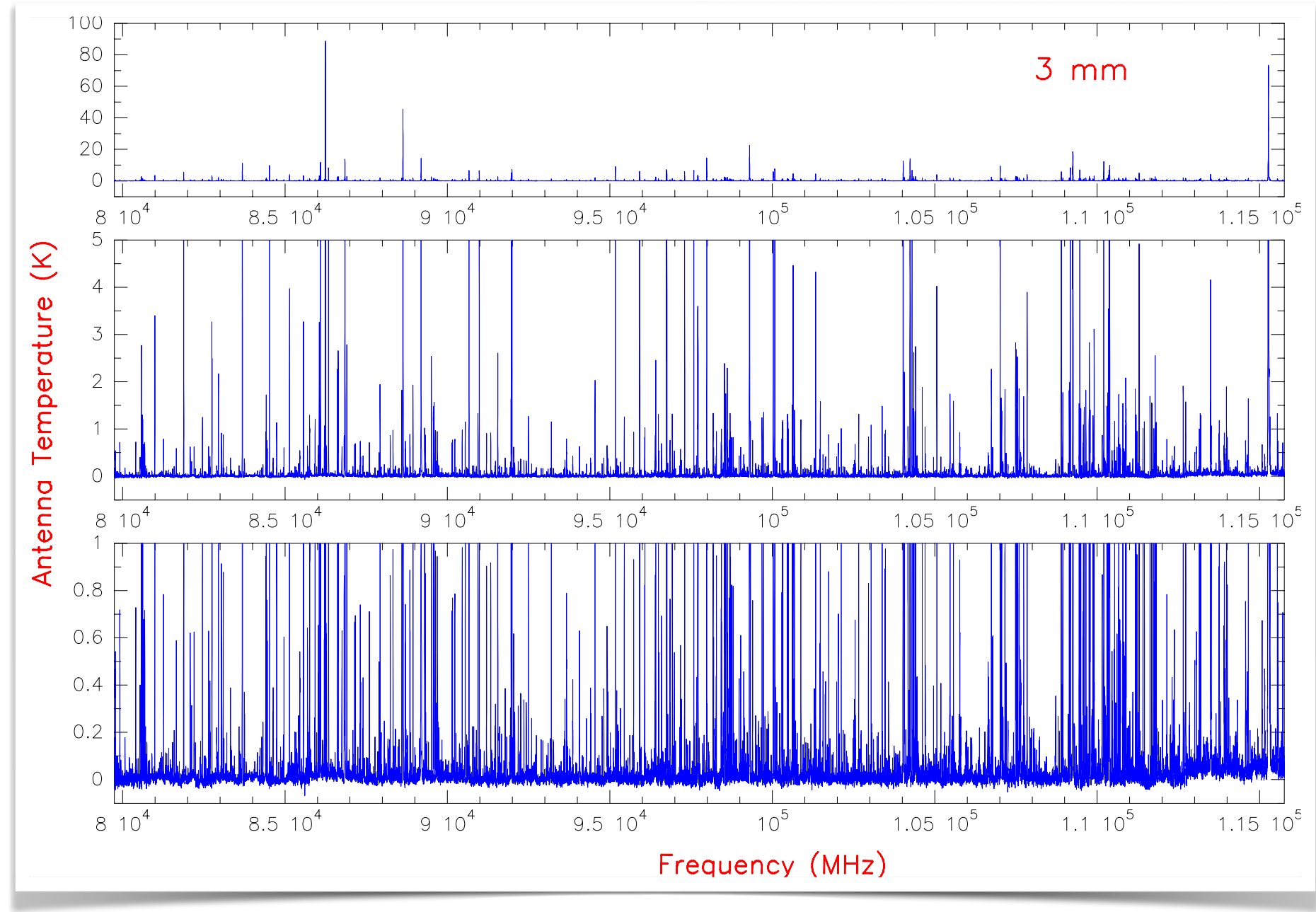
# LINES, LINES, AND MORE LINES



Orion KL with IRAM 30m

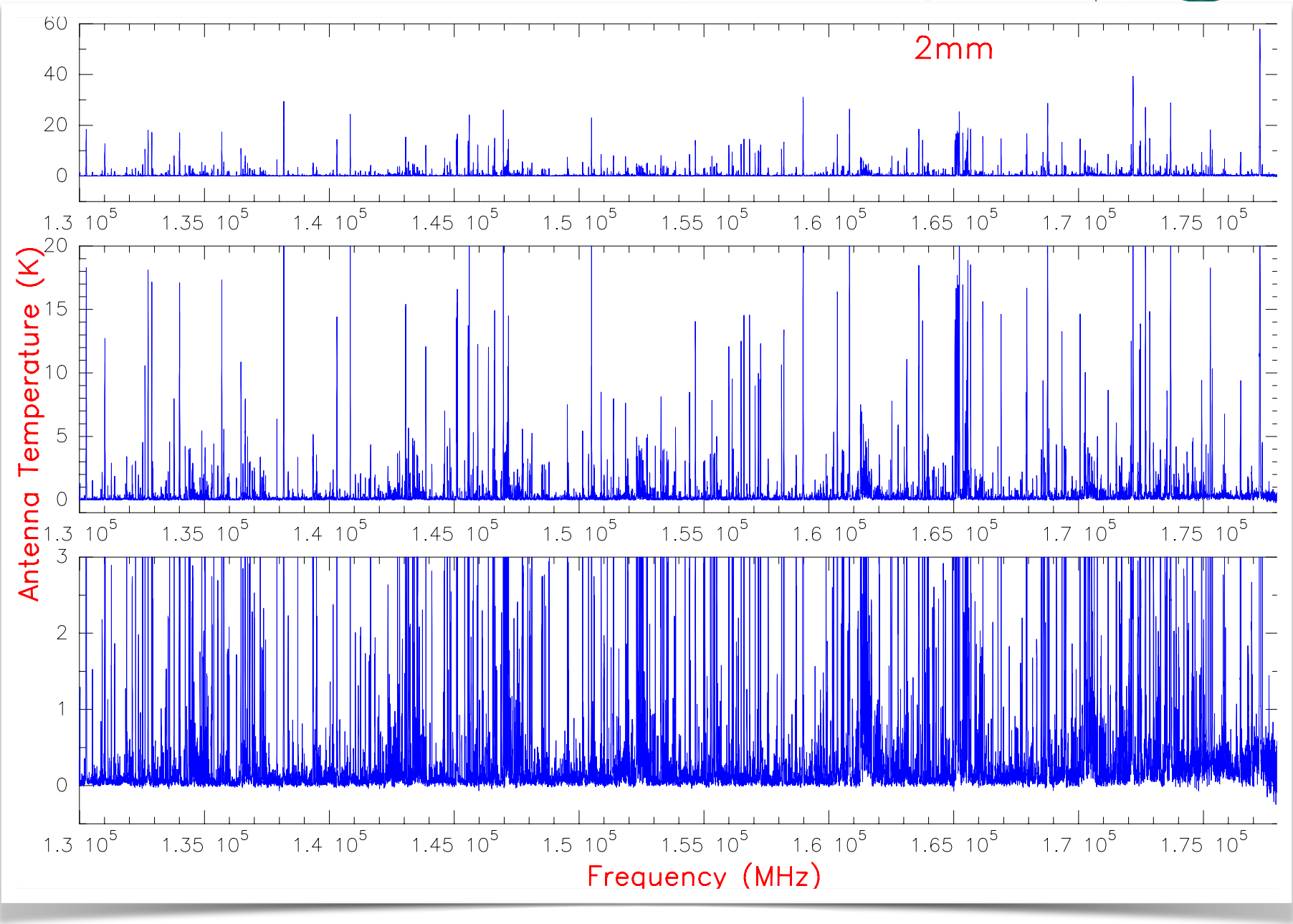
Tercero+ 2010

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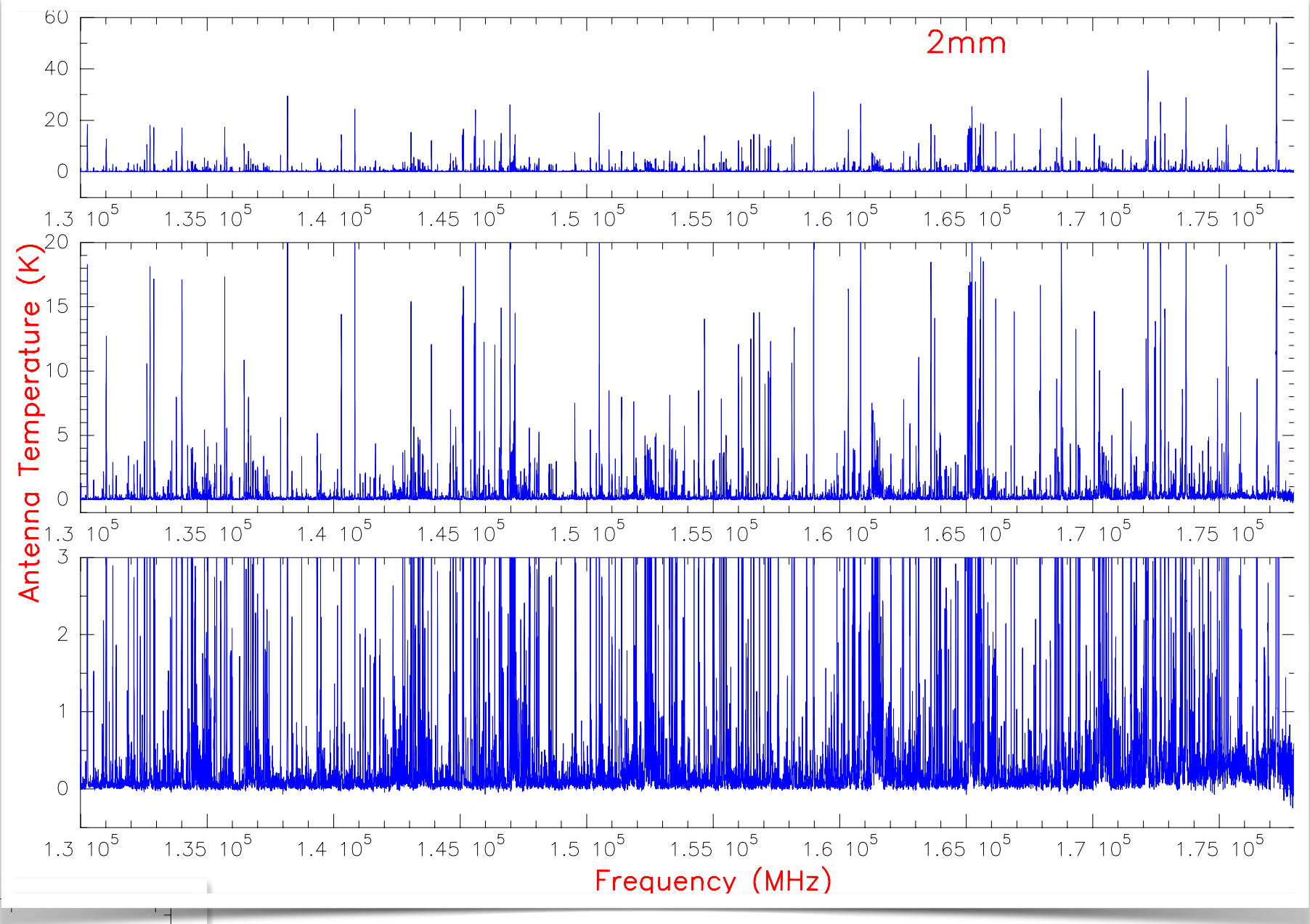
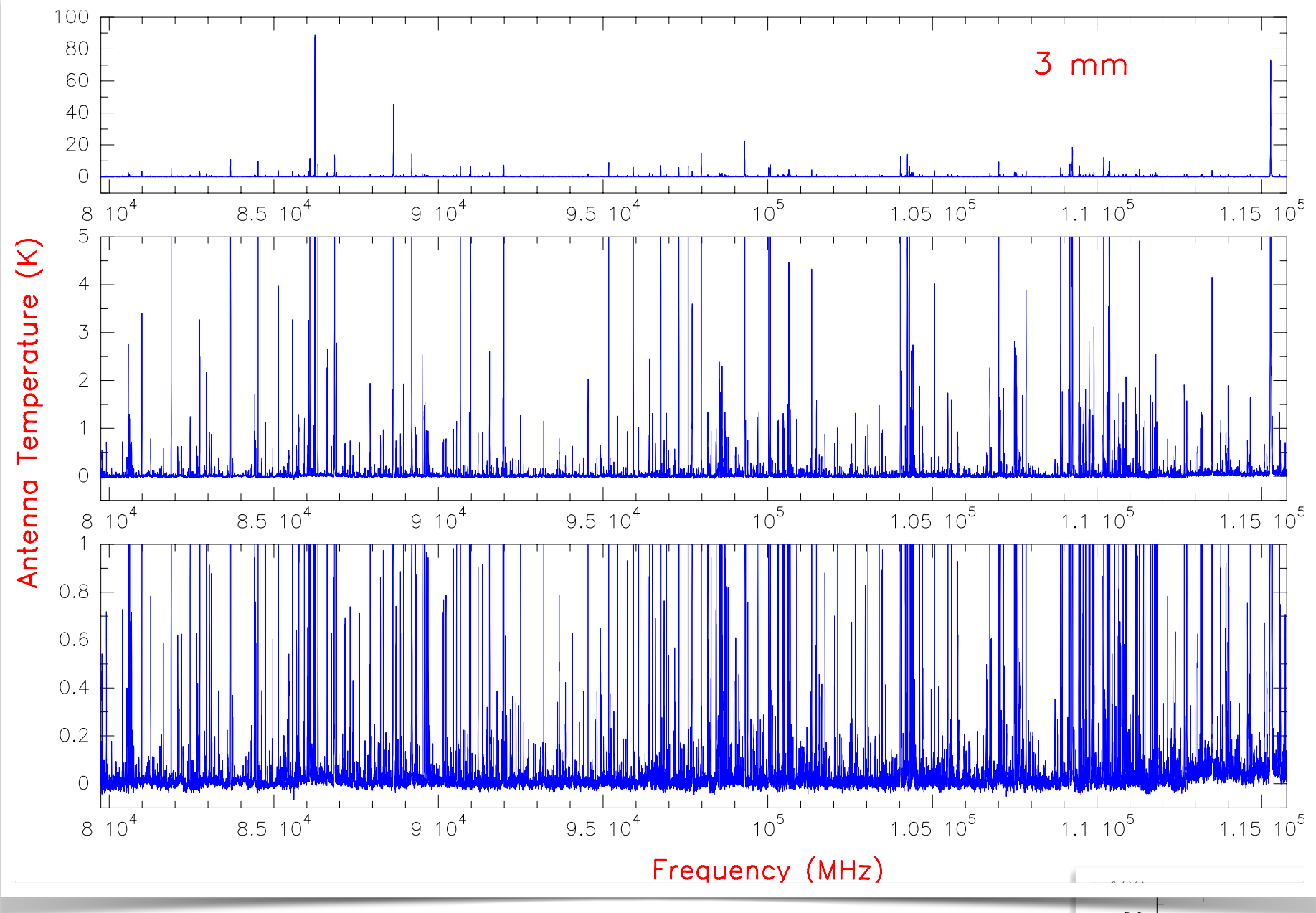


Orion KL with IRAM 30m

Tercero+ 2010

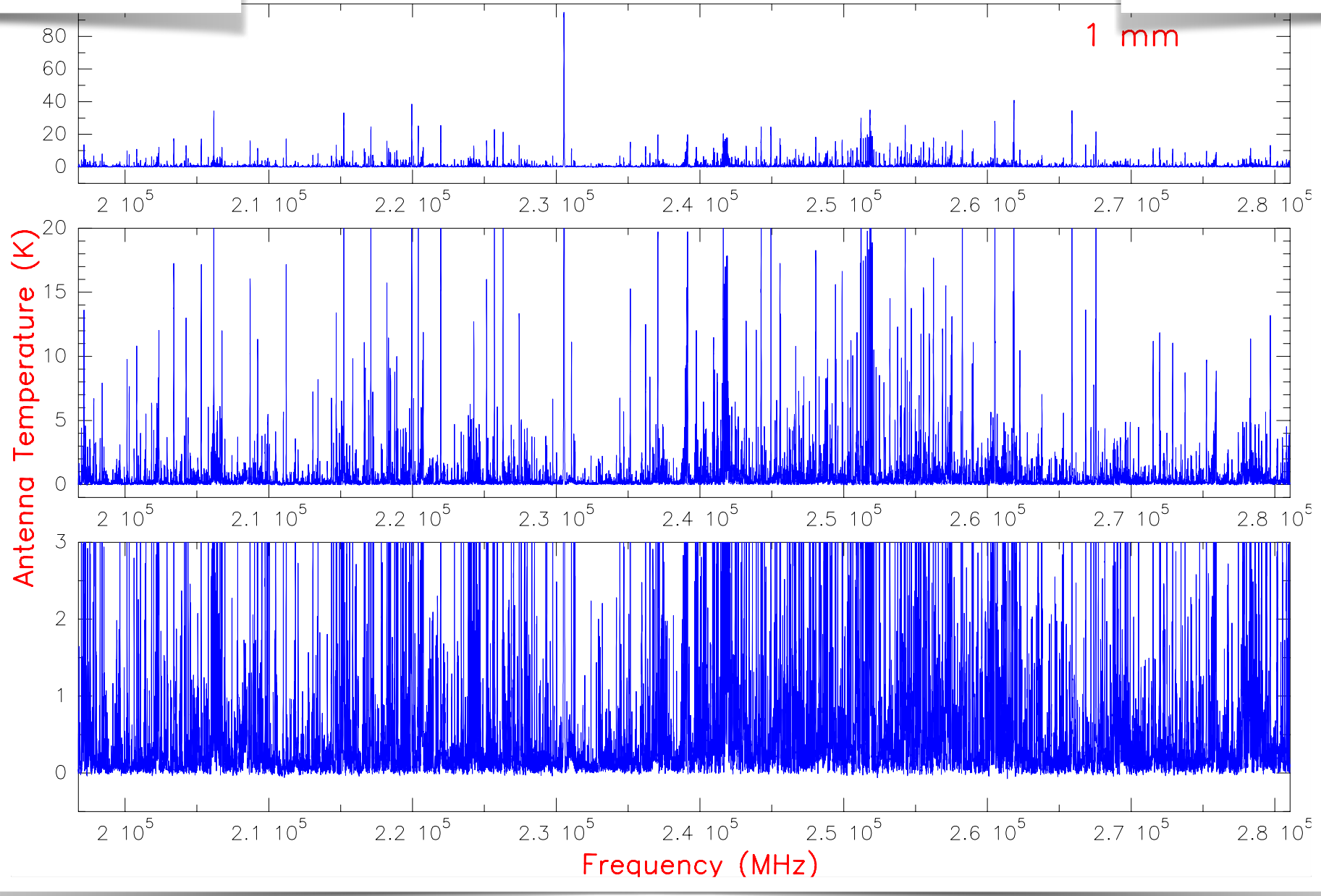


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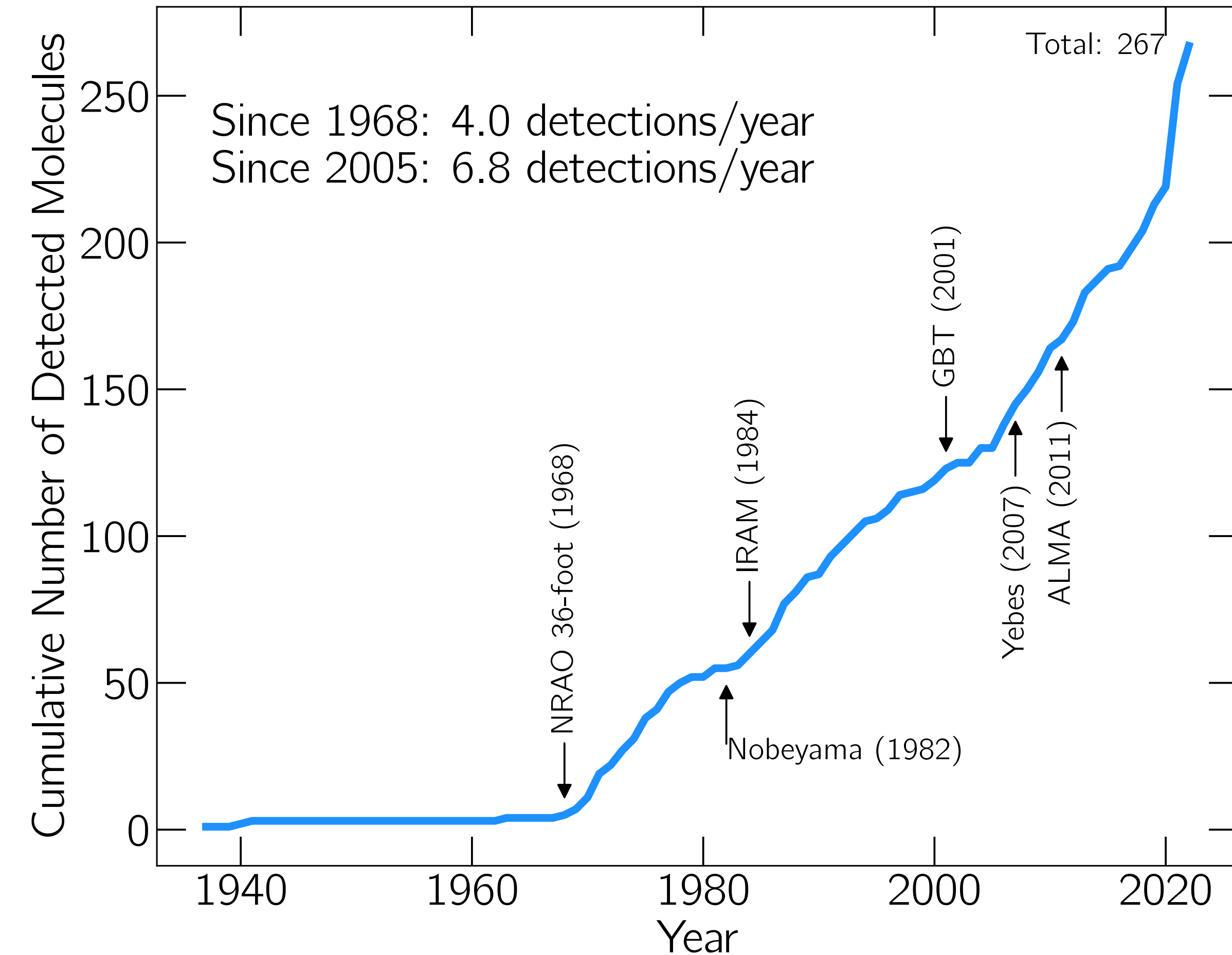
Orion KL with IRAM 30m

Tercero+ 2010





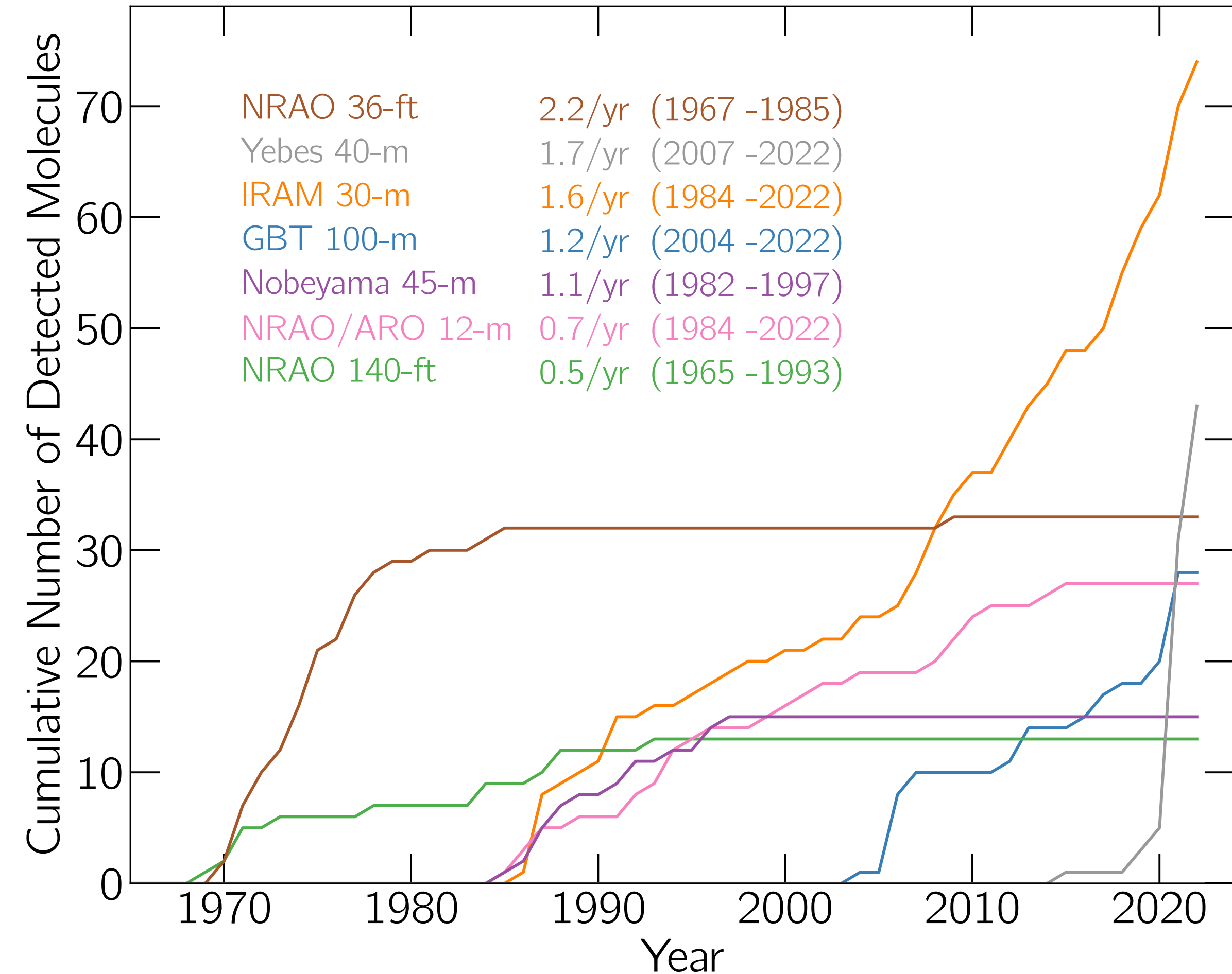
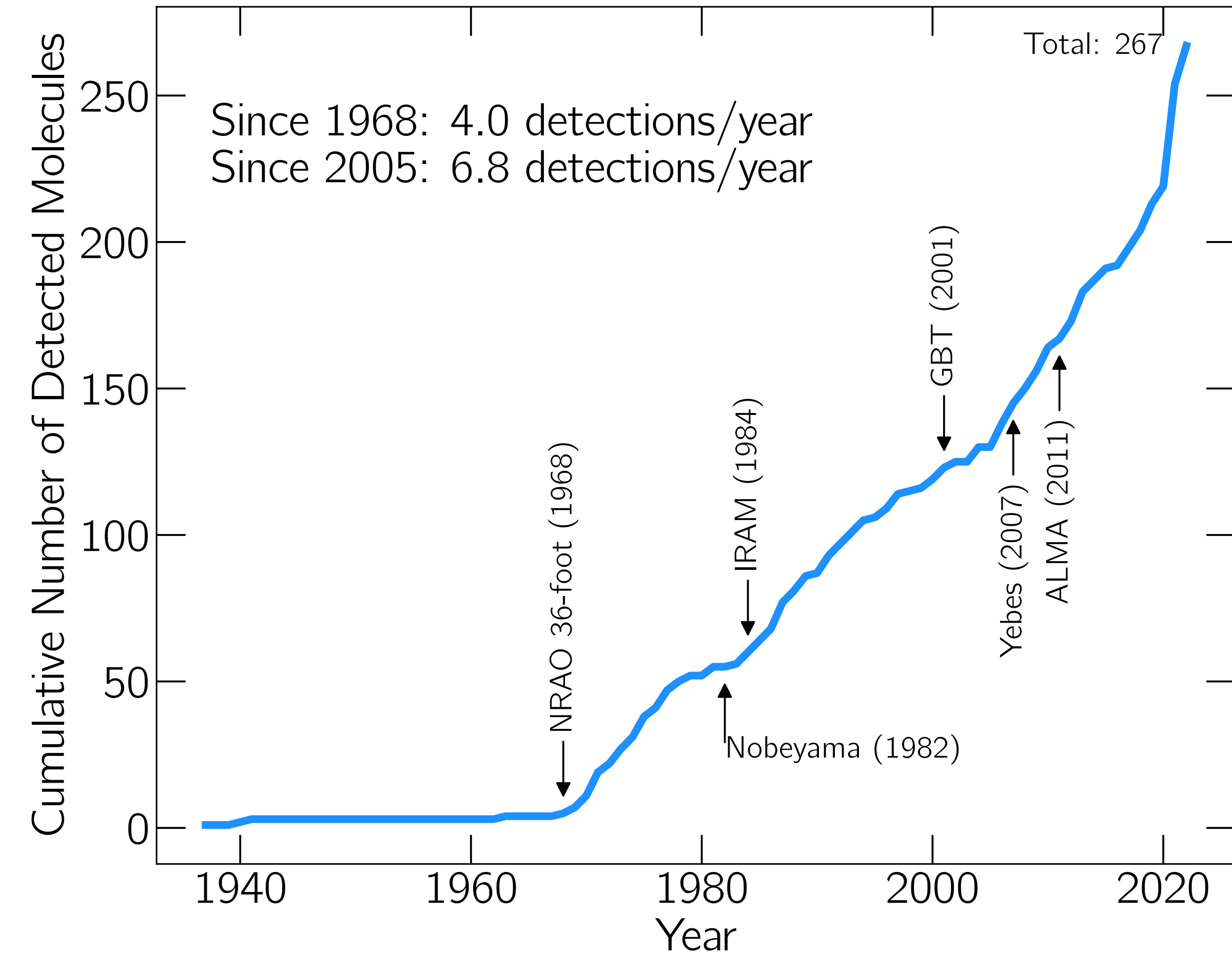
# CUMULATIVE DETECTIONS



Two main surveys recently (both focused on TMC-1):

QUIJOTE (PI: J. Cernicharo) with Yebes 40m / GOTHAM (PI: B. McGuire) with GBT 100m

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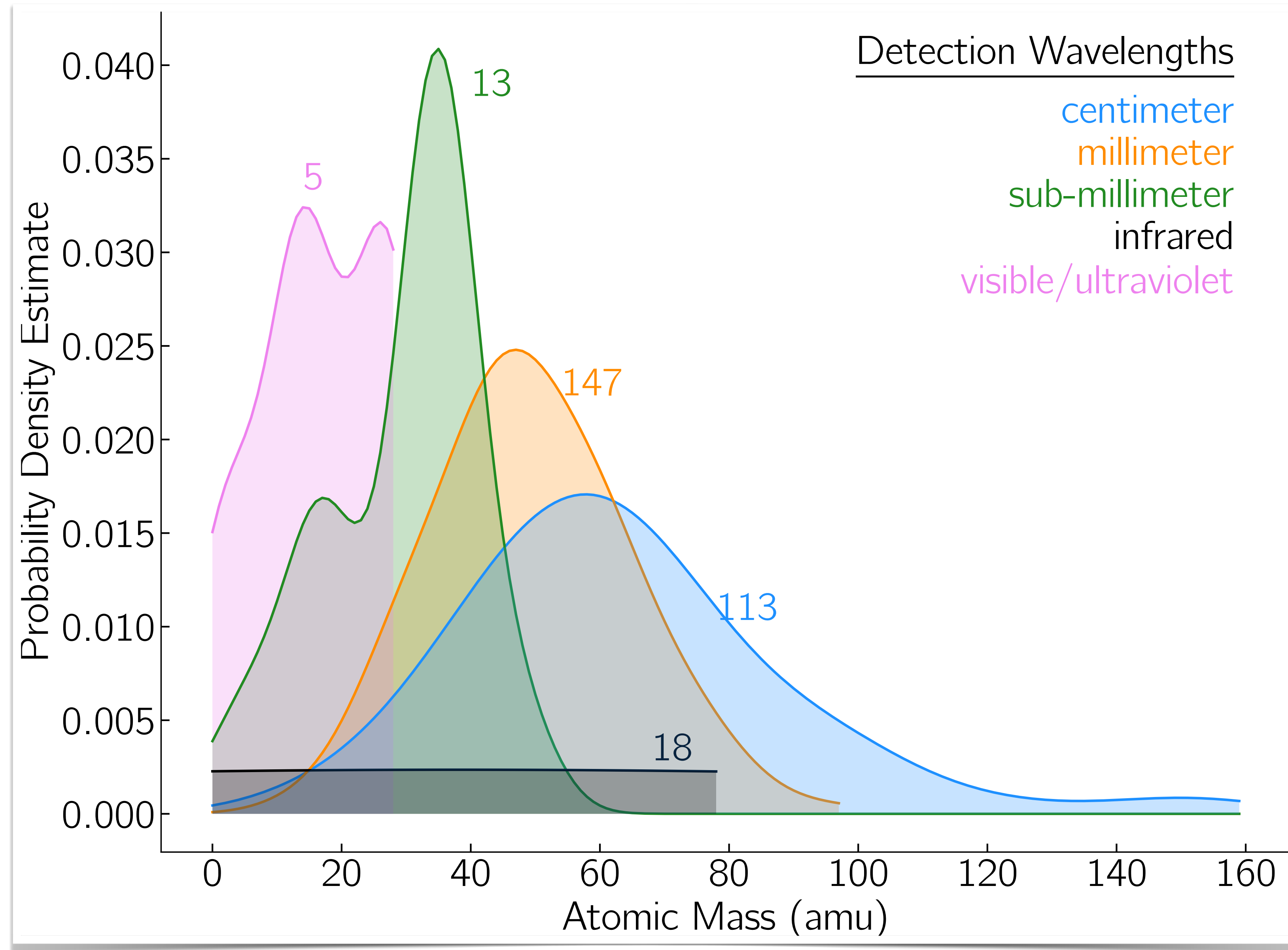


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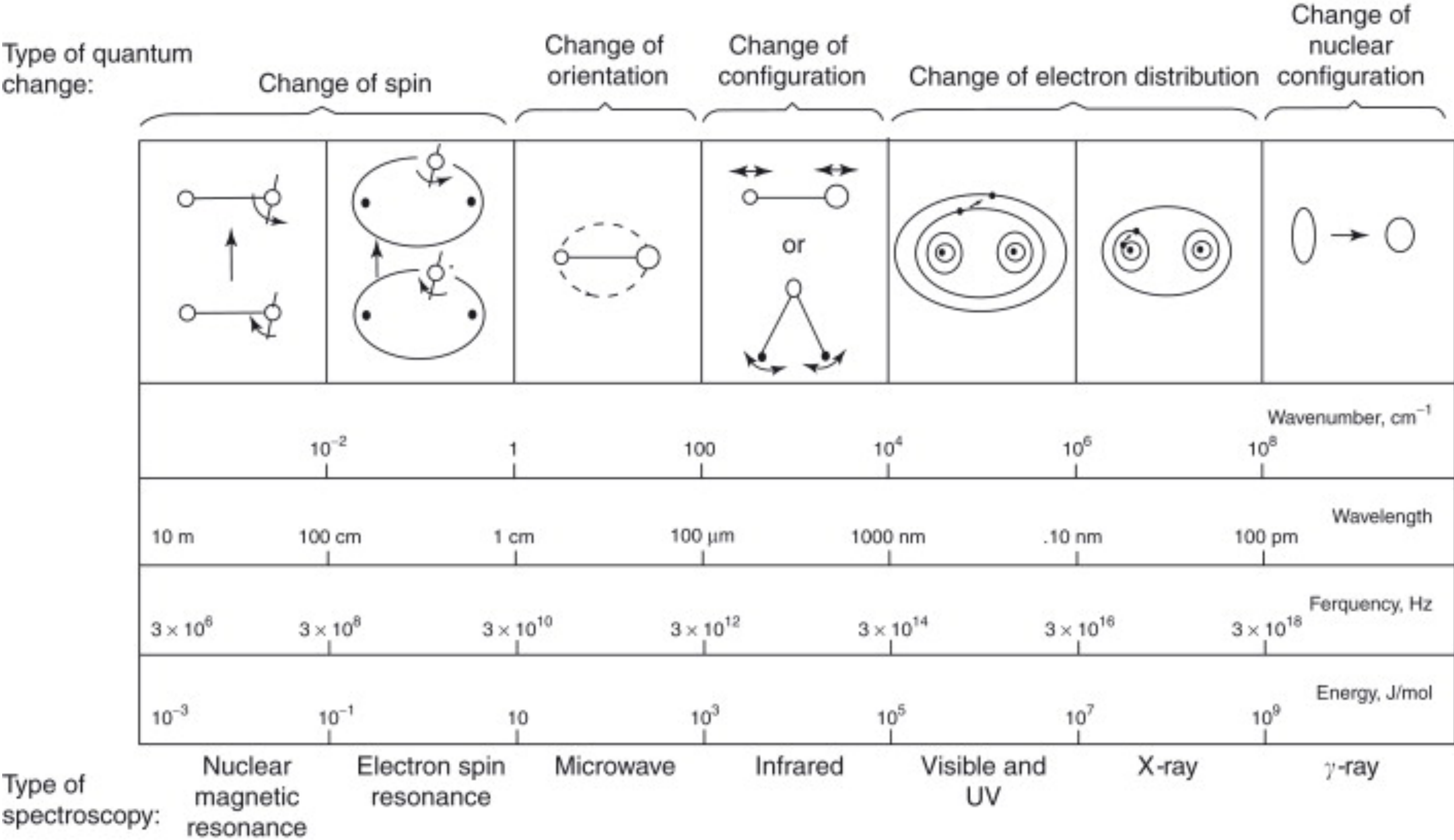


# DETECTIONS AND WAVELENGTHS

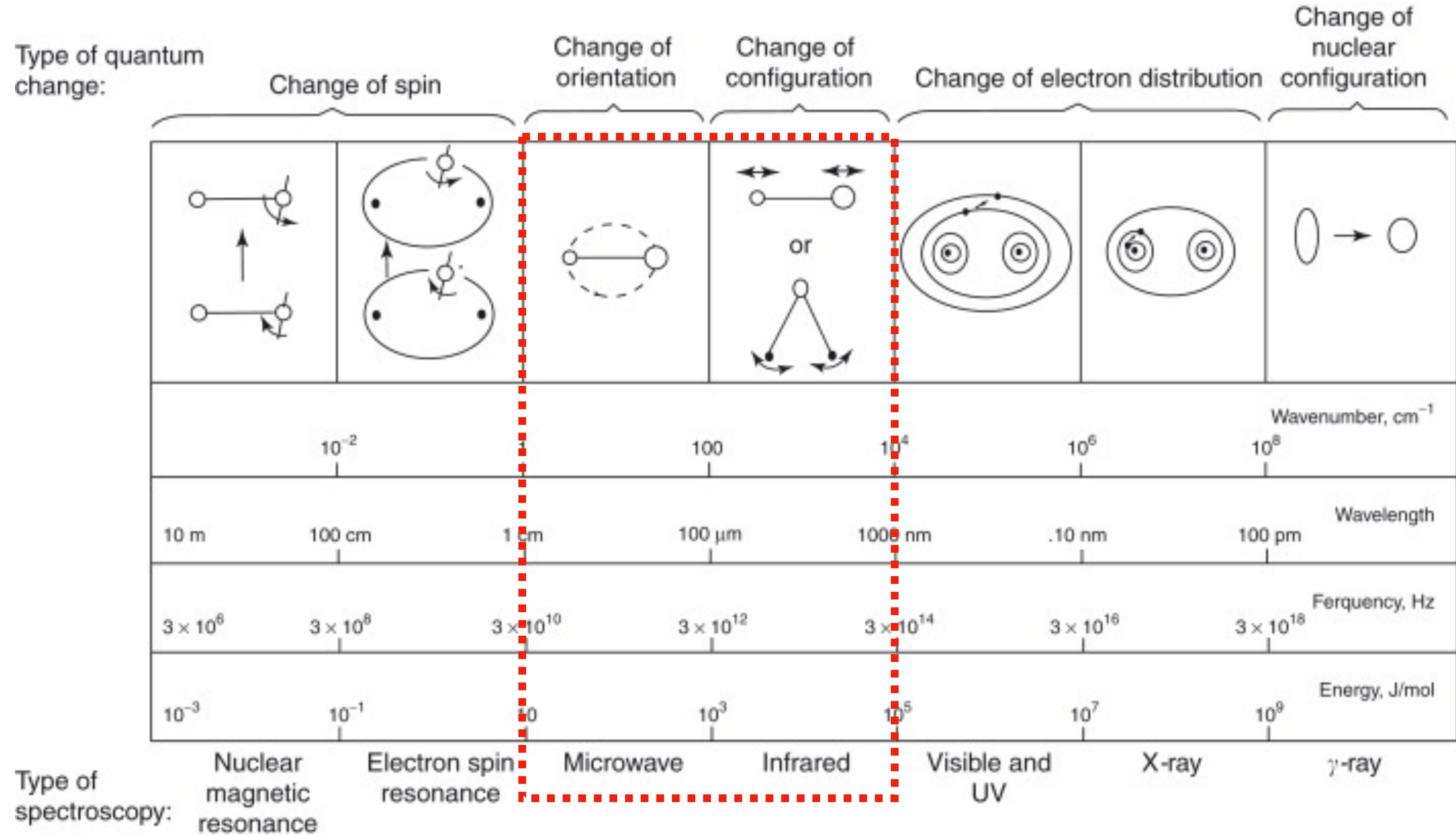


- “Spectroscopy is the general field of study that measures and interprets the electromagnetic spectra that result from the interaction between electromagnetic radiation and matter as a function of the wavelength or frequency of the radiation.” (*Wikipedia*)
- Depending on the frequency and matter we can have different “*kind*” of spectroscopy

# ELECTROMAGNETIC SPECTRUM

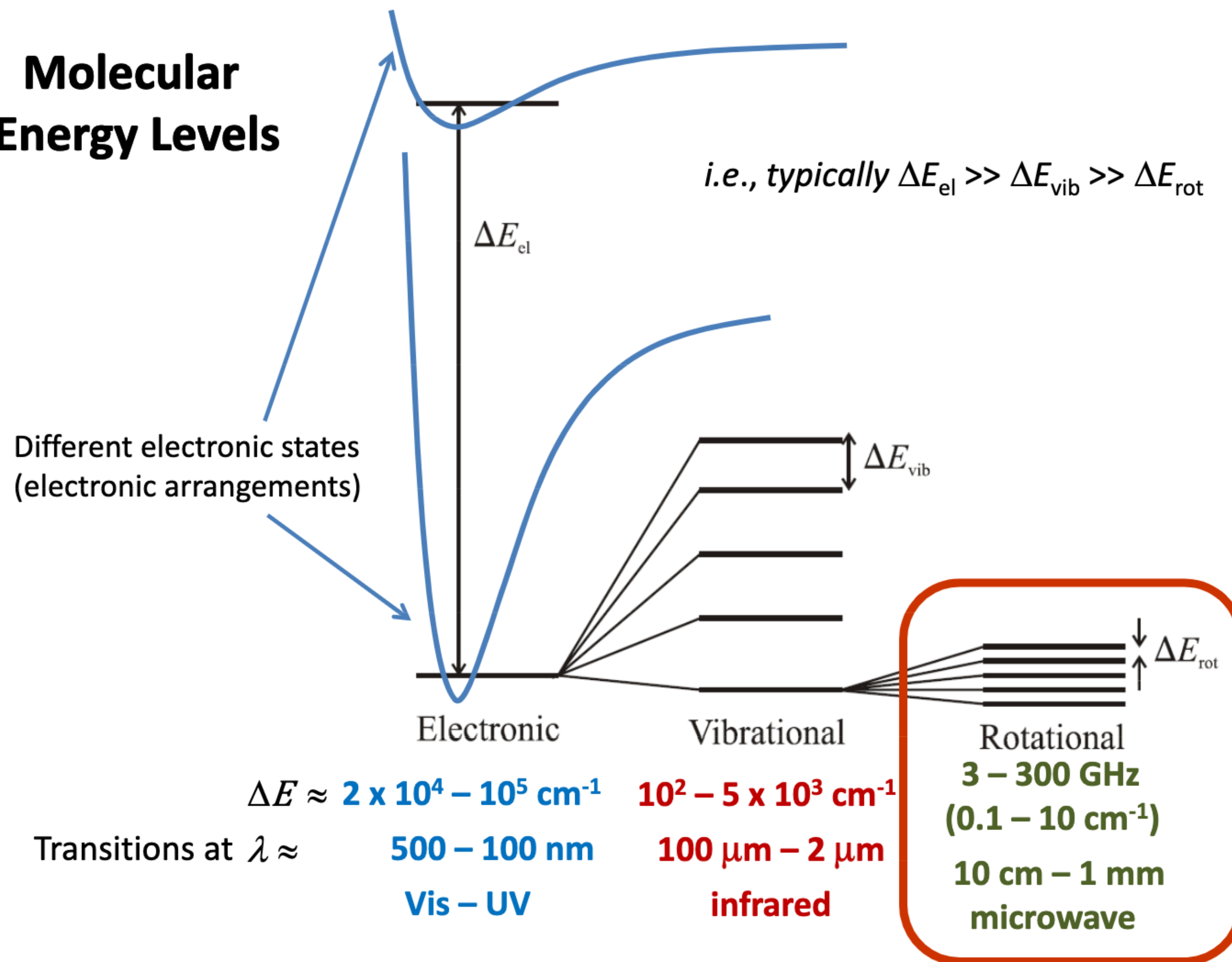


# ELECTROMAGNETIC SPECTRUM





# Molecular Energy Levels





# (SUB)MILLIMETER VS INFRARED



- **(Sub)millimeter:**

- A. Very high spectral resolution ( $R > 10^6$ )
- B. Probing gas-phase w/ very low abundance (down to  $10^{-12}$  w.r.t.  $H_2$ )
- C. Mapping regions

- **Infrared:**

- A. Moderate spectral resolution ( $R \sim 10^3 - 10^4$ )
- B. Gases and solids w/ abundances (down to  $10^{-8}$  w.r.t.  $H_2$ )
- C. Molecules w/o permanent dipole moment ( $C_2H_2$ ,  $CH_4$ ,  $CO_2$ ,...)



# IR REVOLUTION WITH JWST IS HAPPENING!



- Things are going to change very soon thanks to Webb.
- Unprecedented sensitivity.
- => very good for lab!!! => new experiments needed?
- Very likely will revolutionise the gas-grain chemistry as we know it so far.

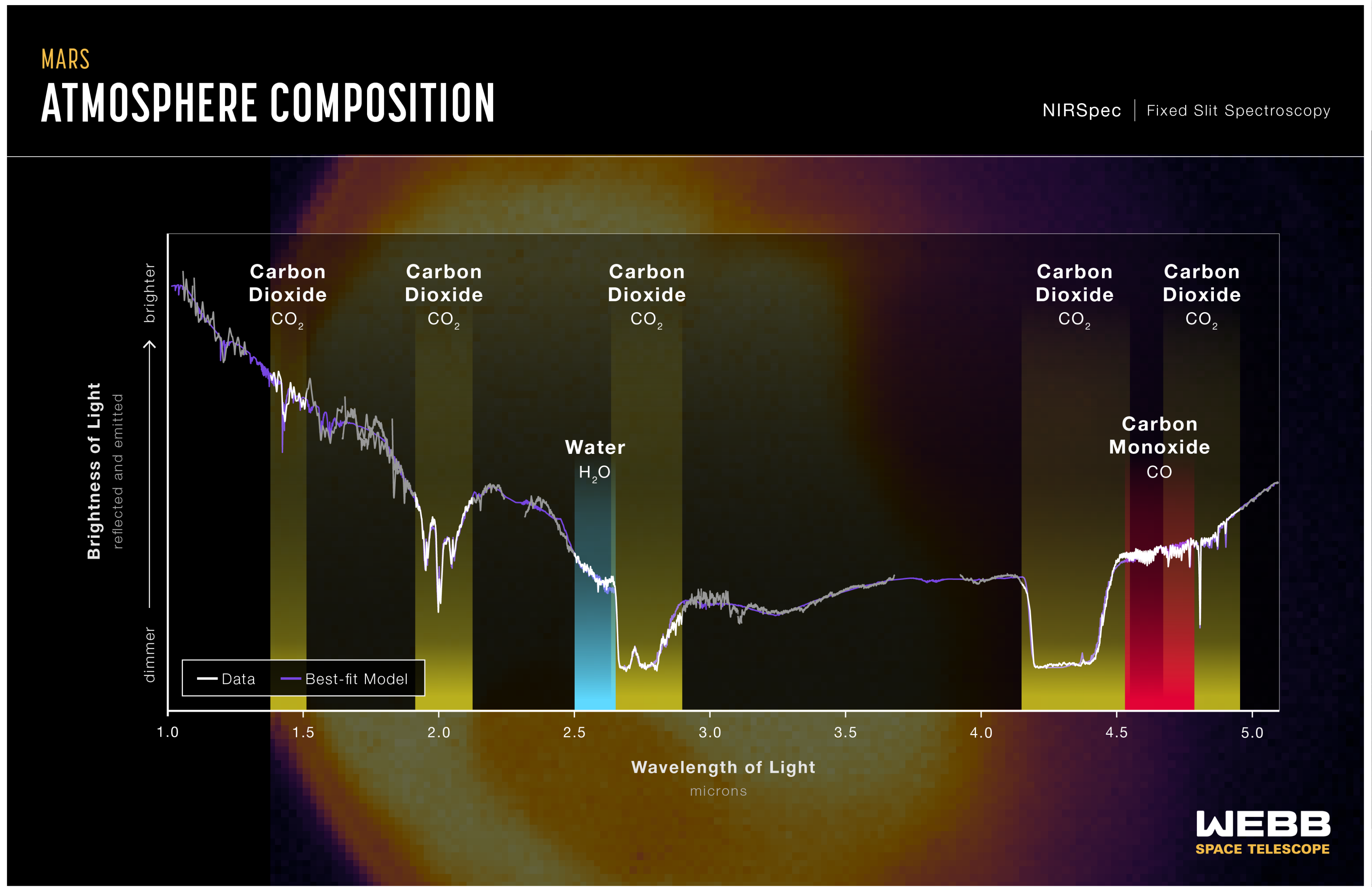




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# Hubble

# JWST







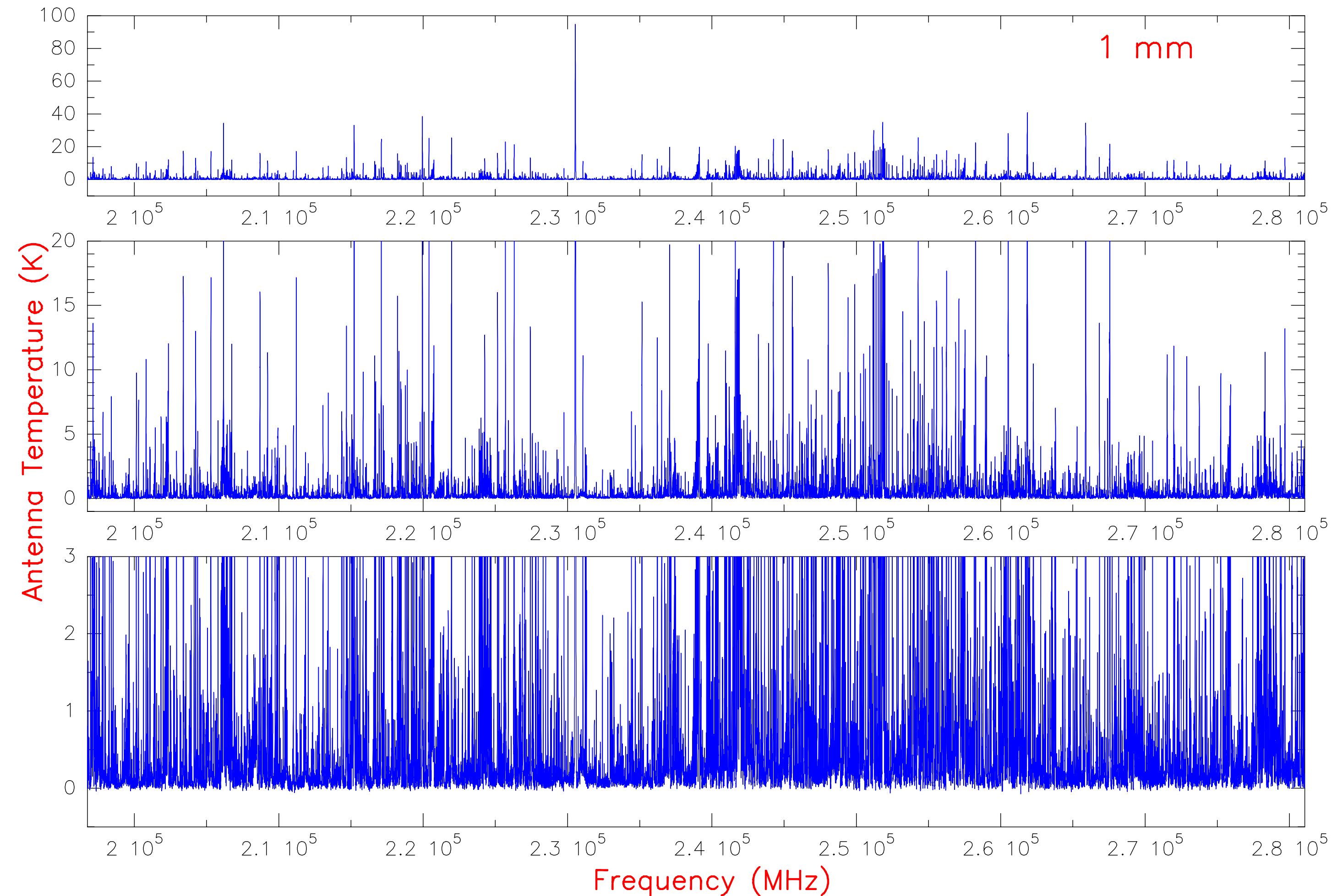
- The protostar within the dark cloud L1527 is embedded within a cloud of material feeding its growth. Ejections from the star have cleared out cavities above and below it, whose boundaries glow orange and blue in this infrared view. The upper central region displays bubble-like shapes due to stellar “burps,” or sporadic ejections. Webb also detects filaments made of molecular hydrogen that has been shocked by past stellar ejections. The edges of the cavities at upper left and lower right appear straight, while the boundaries at upper right and lower left are curved. The region at lower right appears blue, as there’s less dust between it and Webb than the orange regions above it.
- Release date: 16/11/2022



# SO, WE NEED LINE CATALOGUES AND WE NEED HIGH RESOLUTION!



- Modern Radioastronomical facilities have
  - A. **amazing sensitivity** => new species, isotopologues, vibrational excited states
  - B. **unprecedented bandwidth** => more transitions, unbiased survey, more molecules
  - C. **higher velocity/frequency resolution** => high resolution catalogues needed
- Confusion limited!



# ROTATIONAL SPECTROSCOPY

Microwave Molecular Spectra — W. Gordy and R.L. Cook (John Wiley and Sons, Inc, 1984)

Spectra of Atoms and Molecules — P.F. Bernath (Oxford University Press, 2005)

Molecular Rotation Spectra — H.W. Kroto (Dover Publications Inc. 1992)

Symmetry and Spectroscopy — D.C. Harris and M.D. Bertolucci (Dover Publications Inc. 1989)

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- Replacing classic observables with corresponding operator:

$$P_x \rightarrow \hat{J}_x = \sum_n \frac{\hbar}{i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \quad P_y \rightarrow \hat{J}_y = \sum_n \frac{\hbar}{i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \quad P_z \rightarrow \hat{J}_z = \sum_n \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

- The resulting Hamiltonian operator is:  $\hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}$
- The three primary axes defined in body-fixed coordinates  $a, b, c$ , and their corresponding moments of inertia  $I_i$  are found by diagonalising the 3D moment of inertia tensor.
- The **rotational constants**  $A$ ,  $B$ , and  $C$  are defined in terms of these  $I_i$  values as:

$$A = \frac{\hbar^2}{2I_a}, \quad B = \frac{\hbar^2}{2I_b}, \quad C = \frac{\hbar^2}{2I_c}$$

with  $A$ ,  $B$ , and  $C$  in MHz.

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- The resulting Hamiltonian operator is:  $\hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}$
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- Depending on the symmetry and structure of the molecule, different rotor (or “top”):
  1. Spherical Top:  $I_a = I_b = I_c$  (e.g.  $CH_4$ )
  2. Linear Rotor:  $I_a = 0$ ;  $I_b = I_c$  (e.g.  $HCN$ )
  3. Symmetric Oblate Top:  $I_a = I_b < I_c$  (e.g.  $NH_3$ )
  4. Symmetric Prolate Top:  $I_a < I_b = I_c$  (e.g.  $CH_3CN$ )
  5. Asymmetric Top:  $I_a \neq I_b \neq I_c$  (e.g.  $CH_3OH$ )

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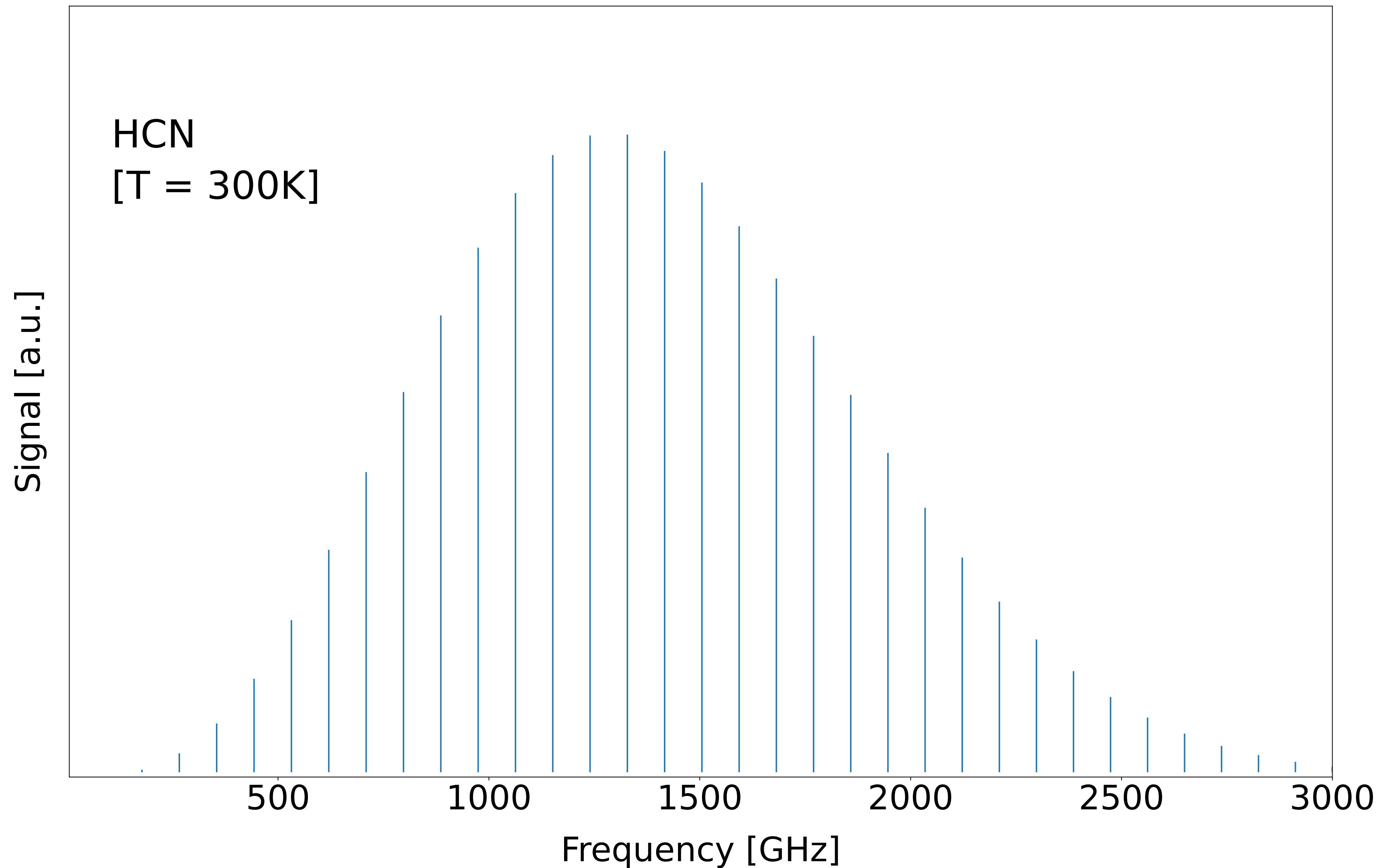
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- Rotational spectrum consists of a harmonic series of lines having frequencies  $\nu = 2B, 4B, 6B, \dots$

# HYDROGEN CYANIDE



- The line intensity is determined by the product of the transition probability  $P_{mn}$  and the population difference  $\Delta p$  between a lower and an upper energy state, where  $P_{mn}$  is:

$$P_{mn} = |\langle \psi_m | \hat{\mu} | \psi_n \rangle|^2$$

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“Larger” the molecule  $\rightarrow$  Smaller rotational constants  $\rightarrow$  Denser the spectrum!

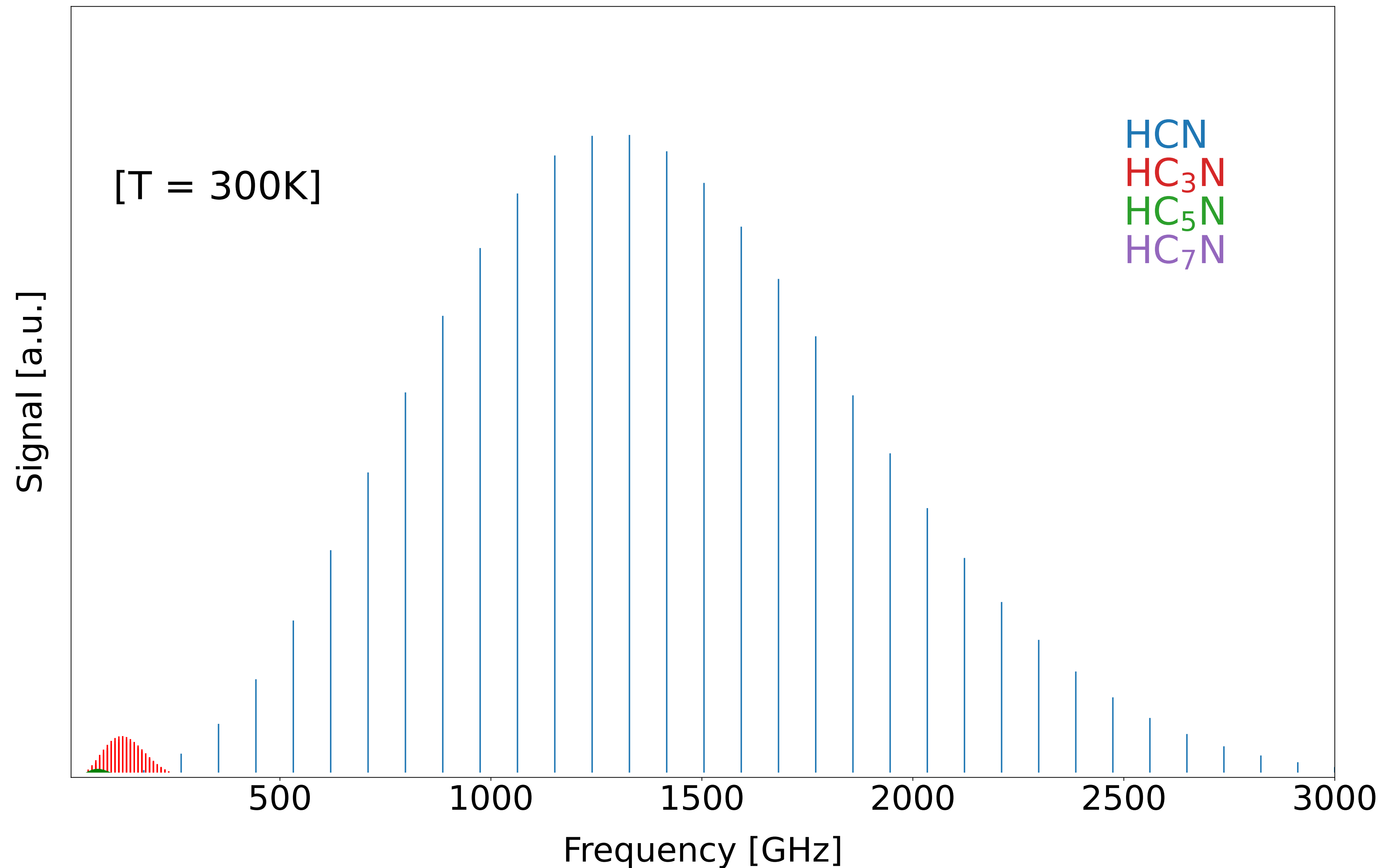




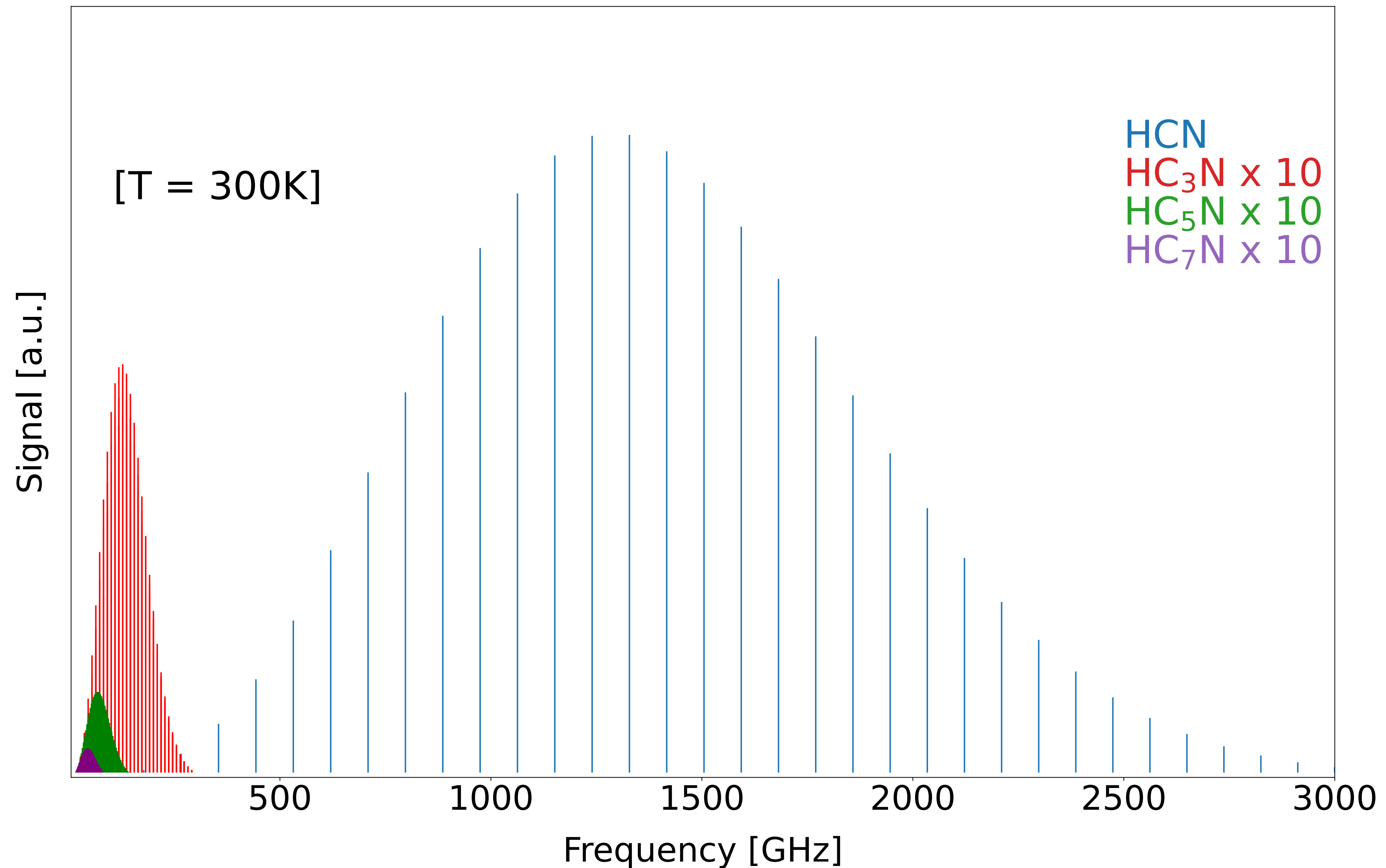
Rotational Constants and Number of Energy Levels below  $kT$  at 150 K for All  $\text{HC}_x\text{N}$  Species Detected in the ISM

Molecule	$B$ (MHz)	# Levels <sup>a</sup> < $kT$ @ 150 K	Lab Ref.
HCN	44316	18	1
HC <sub>2</sub> N	10986	36	2
HC <sub>3</sub> N	4549	58	3
HC <sub>4</sub> N	2302	80	4
HC <sub>5</sub> N	1331	107	5
HC <sub>7</sub> N	564	166	6
HC <sub>9</sub> N	290	231	7

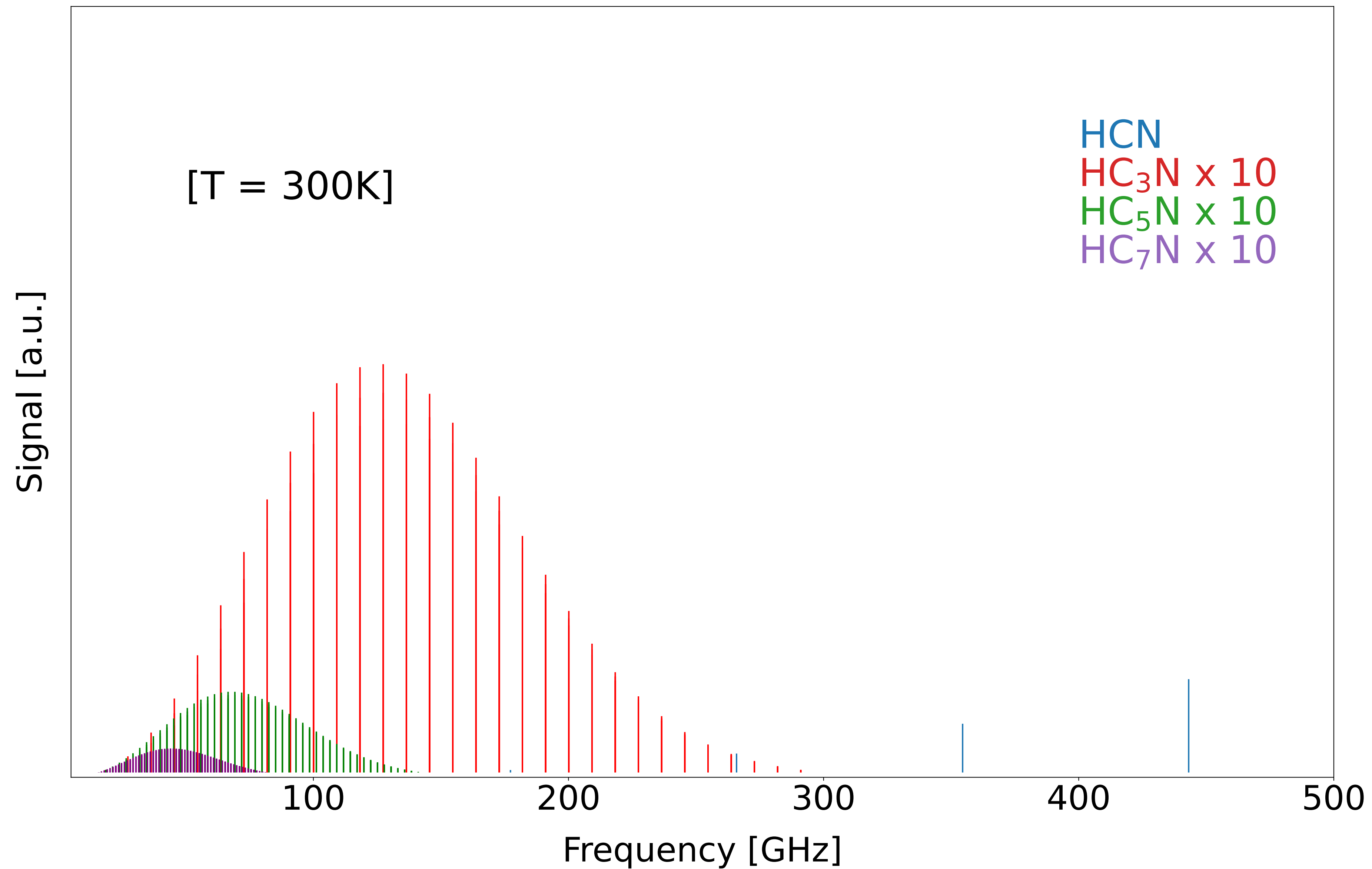
# CYANOPOLYYNES



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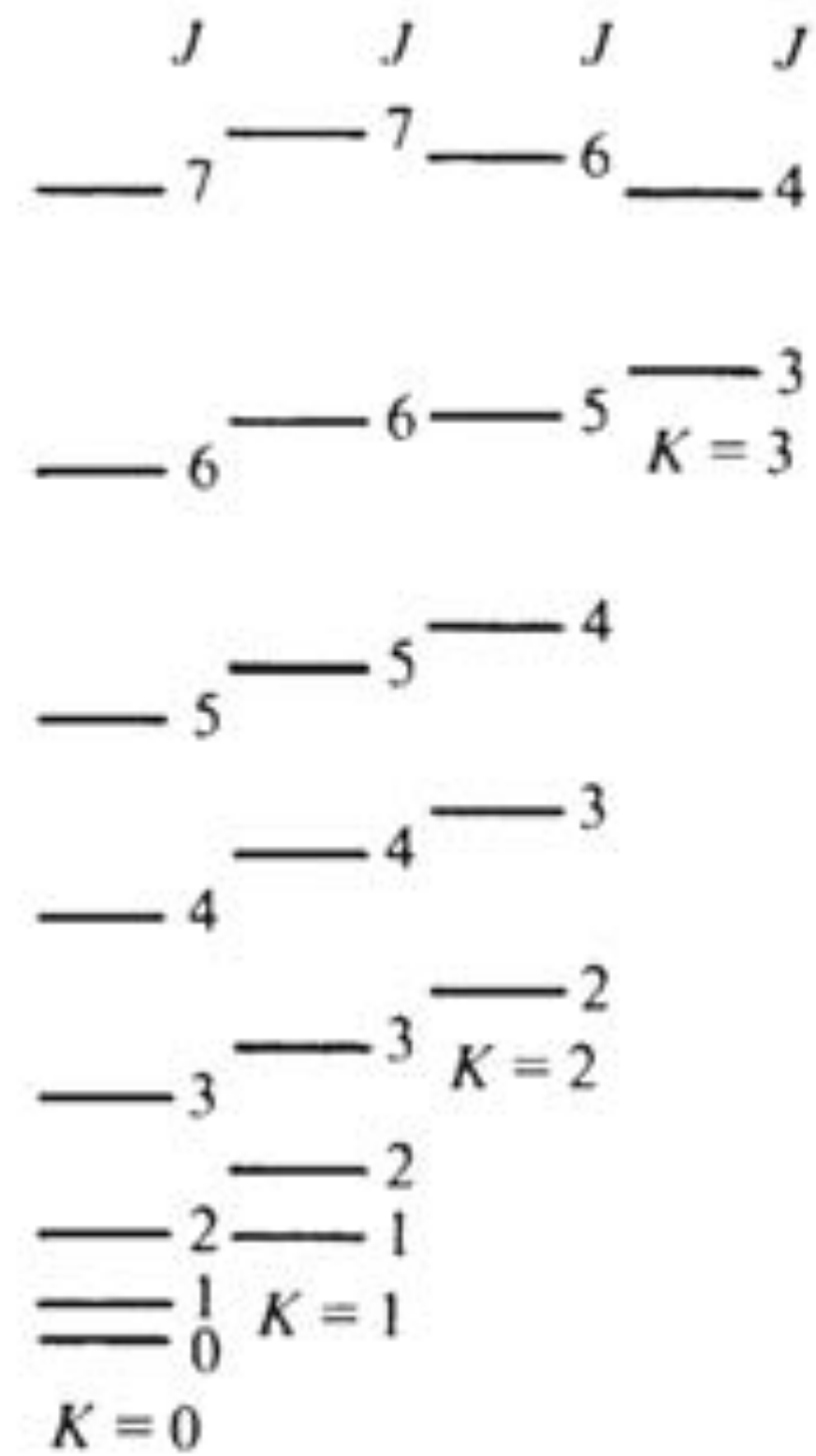
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Prolate

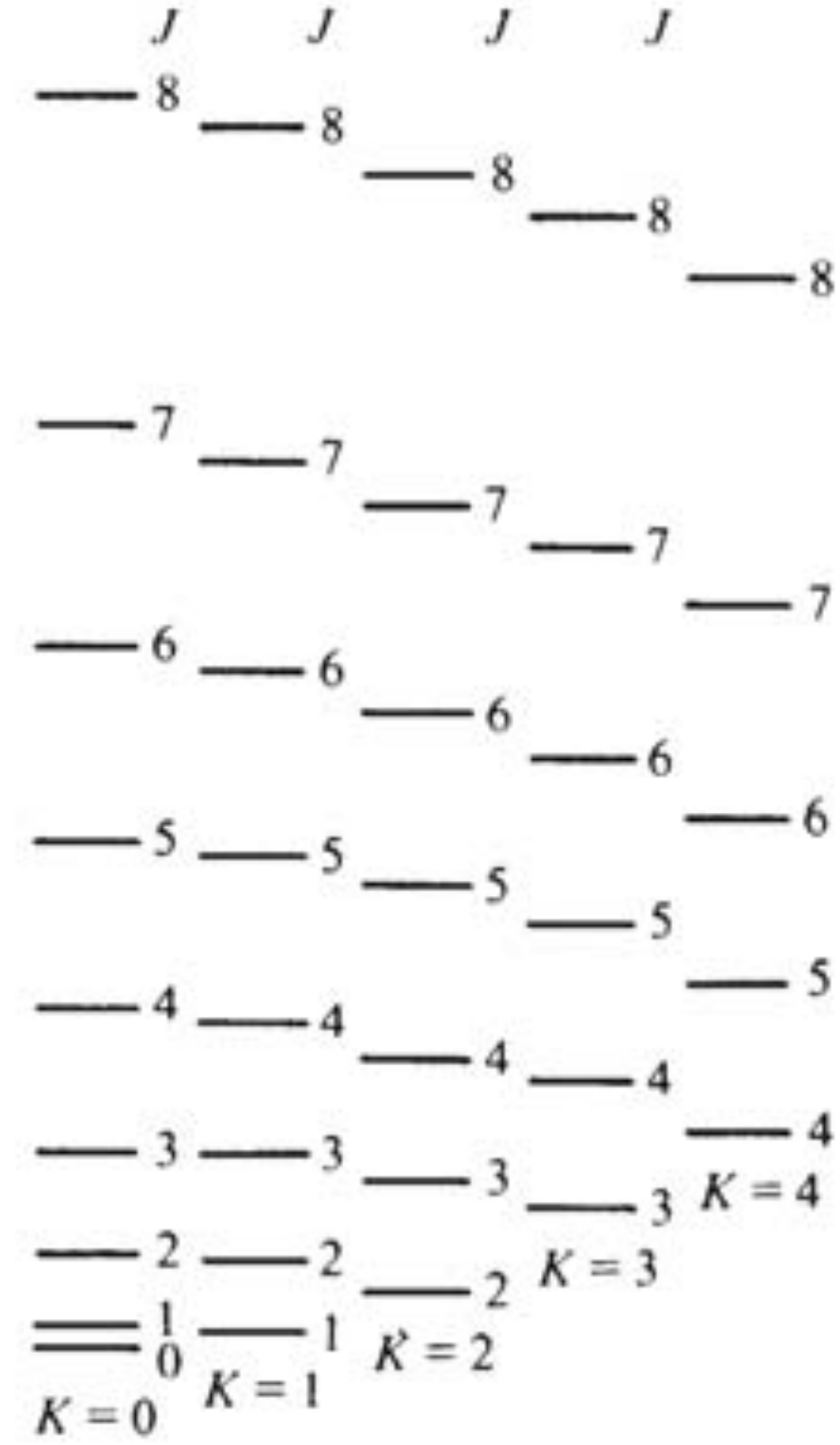
$$E = BJ(J + 1) + (A - B)K^2$$



(a)

Oblate

$$E = BJ(J + 1) + (C - B)K^2$$



(b)

- Now  $I_a \neq I_b \neq I_c$
- The Schrödinger equation has no general analytical solutions!
- It can be solved using a symmetric top basis set and changing the form of the terms on the Hamiltonian operator.
- The degree of asymmetry is quantified by Ray's asymmetry parameter  $\kappa = \frac{2B - A - C}{A - C}$

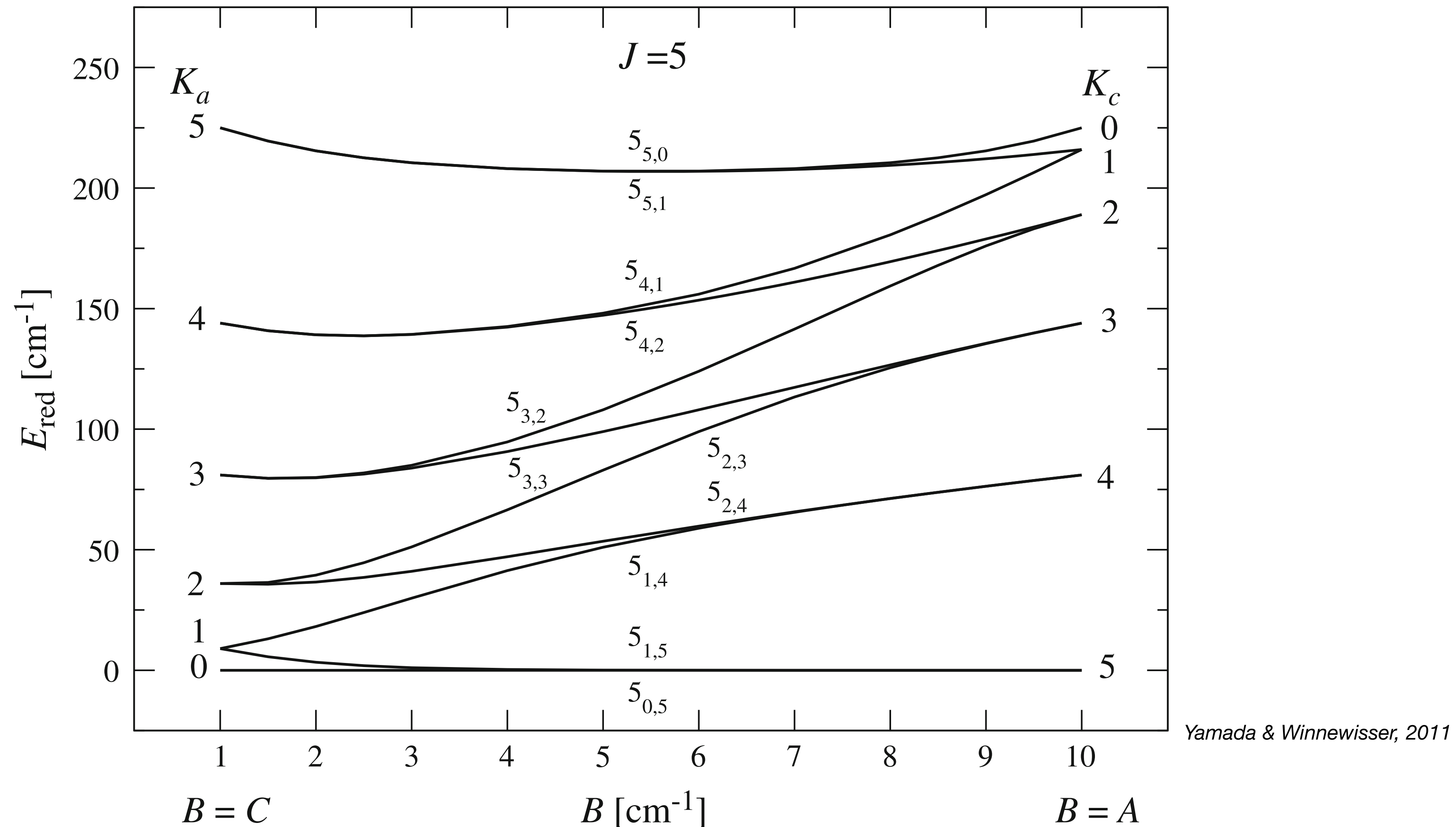
which runs from -1 for a prolate top to +1 for an oblate top.

- Levels are now labelled  $J_{K_a, K_c}$ , where now only  $J$  is a “good” quantum number, while  $K_a$  and  $K_c$  are just for labels (they become good quantum numbers in the prolate and oblate symmetric top limit, respectively).

# ASYMMETRIC TOPS



Scheme of the energy levels of an asymmetric top, plotted for  $J=5$ , with the constant  $B$  varying continuously from  $C$  (prolate limit) to  $A$  (oblate limit).





- In general three non-vanishing dipole moments components  $\mu_a$ ,  $\mu_b$ , and  $\mu_c$ .
- Selection rules are  $\Delta J = -1, 0, +1$  (*P*-branch, *Q*-branch, *R*-branch).

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Transition	Dipole moment component	$\Delta K_a$ <sup>a</sup>	$\Delta K_c$ <sup>a</sup>
<i>a</i> -type	$\mu_a \neq 0$	$0, (\pm 2, \pm 4, \dots)$	$\pm 1, (\pm 3, \pm 5, \dots)$
<i>b</i> -type	$\mu_b \neq 0$	$\pm 1, (\pm 3, \pm 5, \dots)$	$\pm 1, (\pm 3, \pm 5, \dots)$
<i>c</i> -type	$\mu_c \neq 0$	$\pm 1, (\pm 3, \pm 5, \dots)$	$0, (\pm 2, \pm 4, \dots)$

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<sup>a</sup> The transitions in the brackets are much weaker than the main ones.

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- Tomorrow: from Theory to Lab to Observations.
- Some examples.