Molecules Rotating on Earth and in Space: Laboratory Spectroscopic Strategies

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CONTENT

01 Rotational spectroscopy

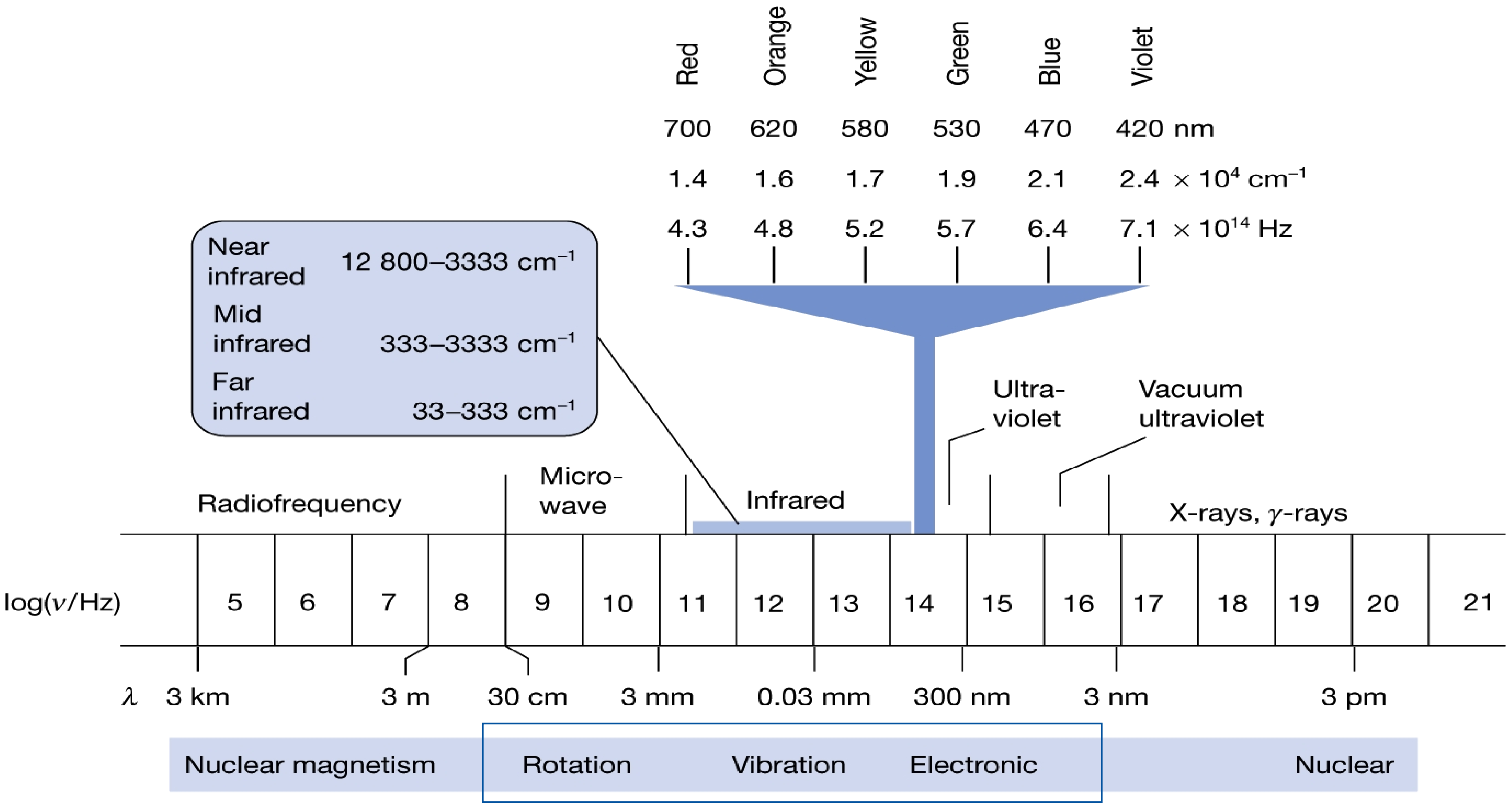
02 Spectroscopic technique

03 Complex organic interstellar molecules

04 Conclusions

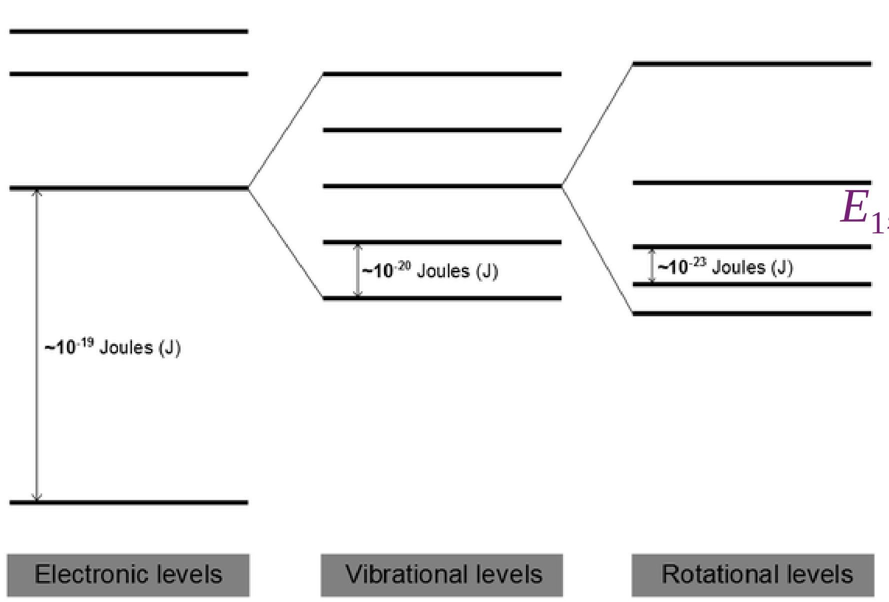
Part 1

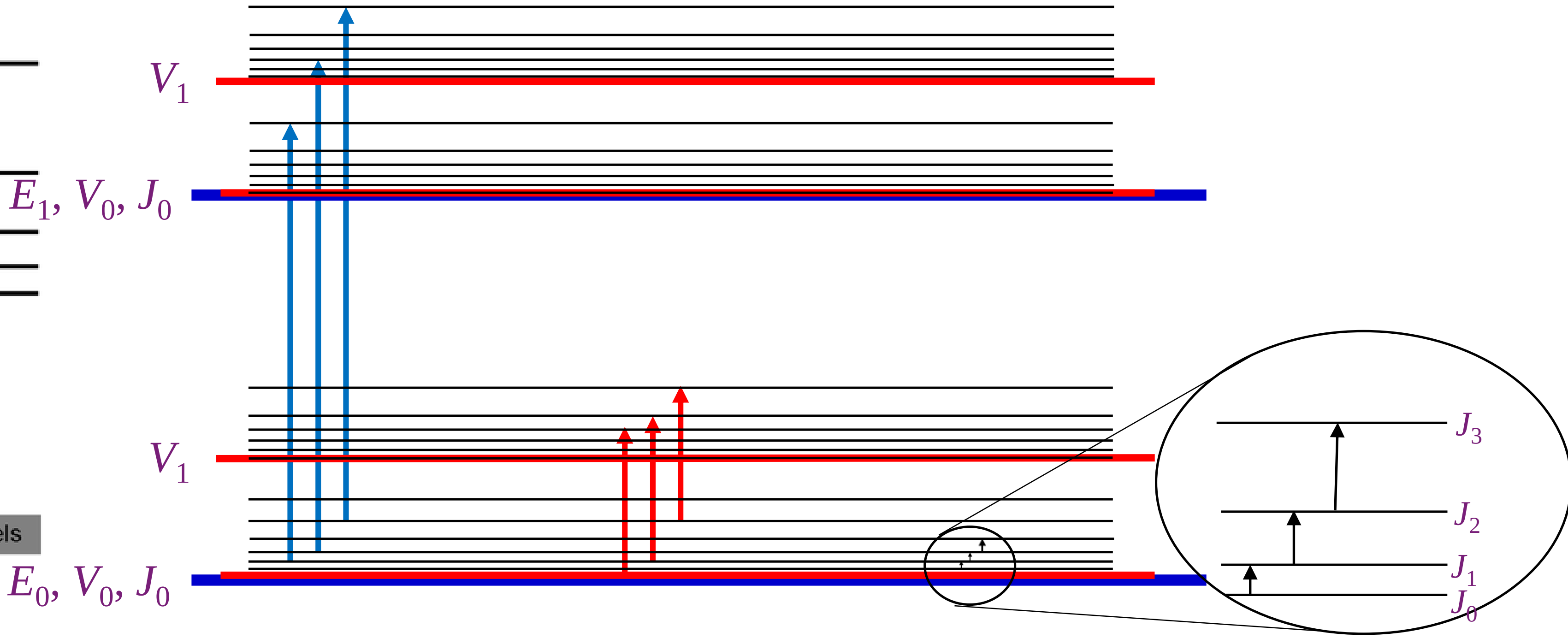
Rotational Spectroscopy

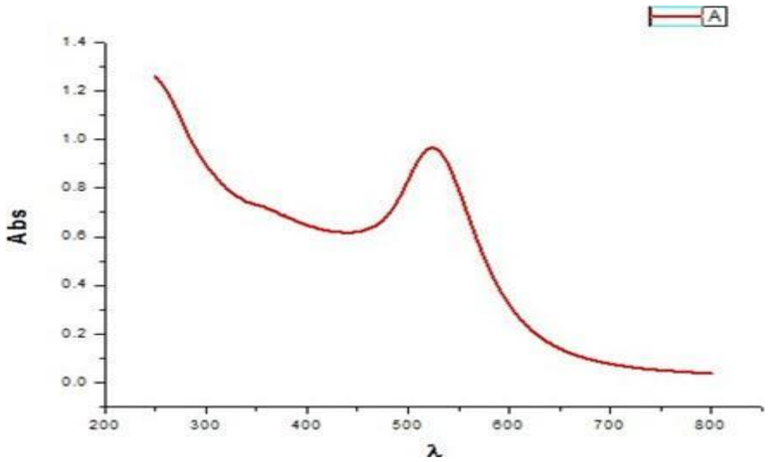


分子光谱（Molecular Spectroscopy）

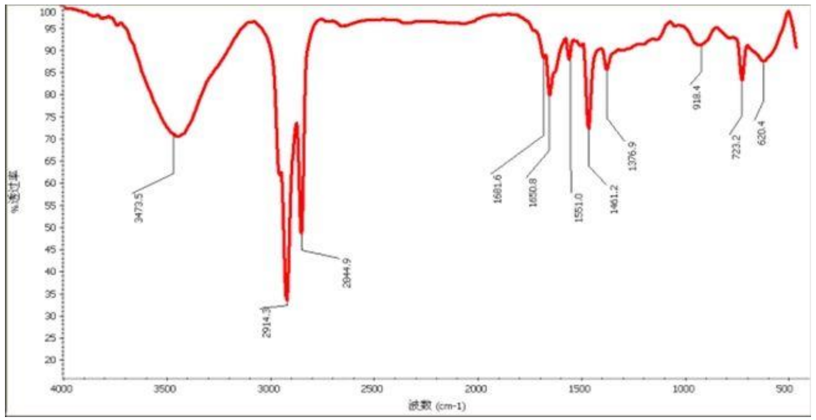
Types of Molecular Transitions and Spectral Features



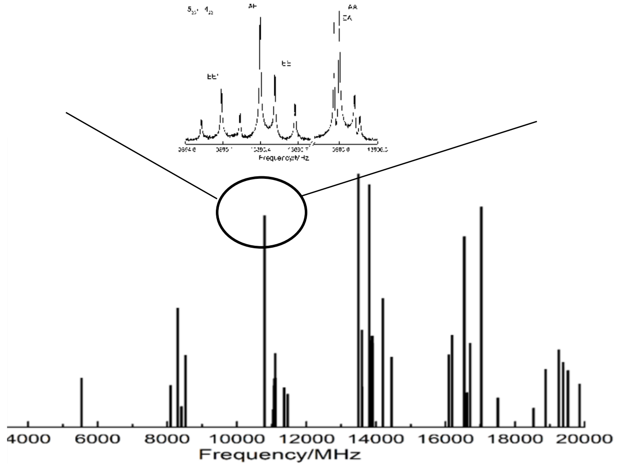




Electronic Transition: UV-Vis



Vibrational Transition: IR

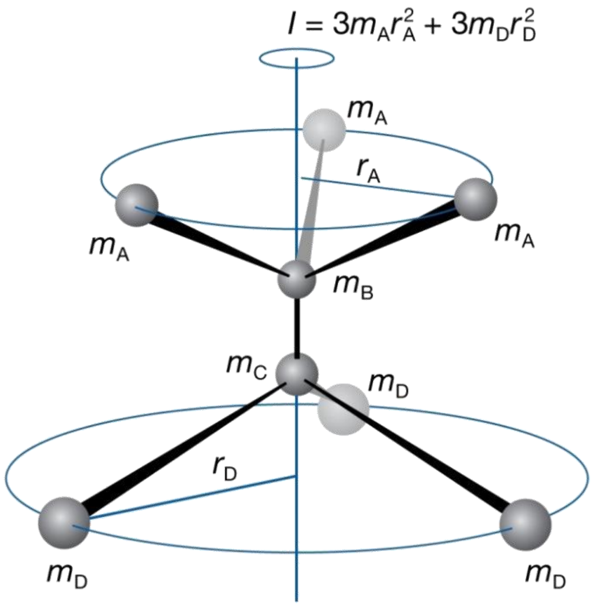


Rotational Transition: MW/MMW

Rotational Spectroscopy

The rotational motion of a molecule can be accurately described when its moment of inertia is known.

The moment of inertia of a system of particle (a molecule) is defined as:



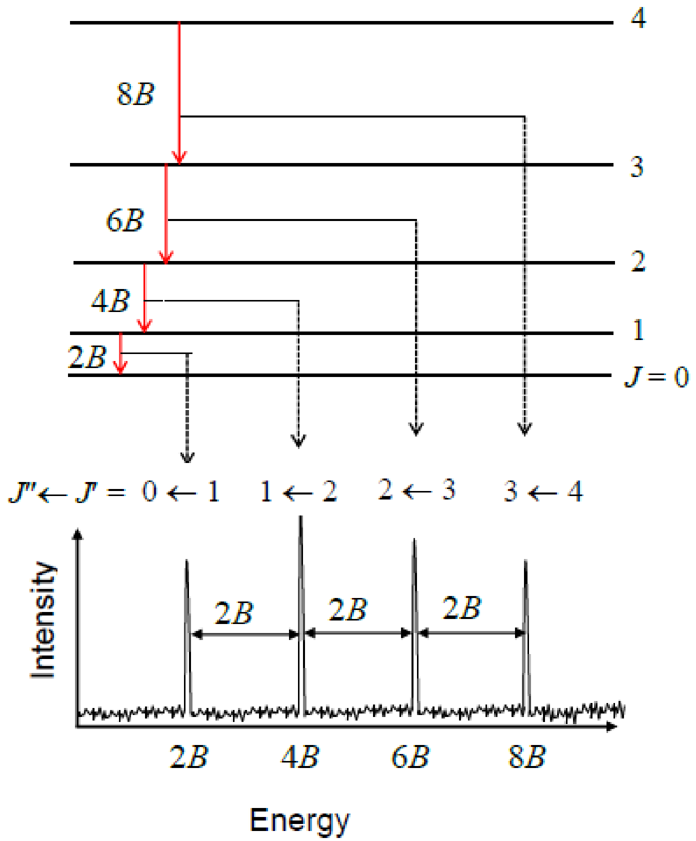
The moment of inertia of a rotor

$$I = \sum_i m_i r_i^2 = \frac{h}{8\pi^2 cB}$$

I is a measure of the inertia of the system to rotational motion. It depends on the mass distribution of the system.

h is the Planck constant

$$B = \frac{h}{8\pi^2 cI}$$: rotational constant (in MHz)



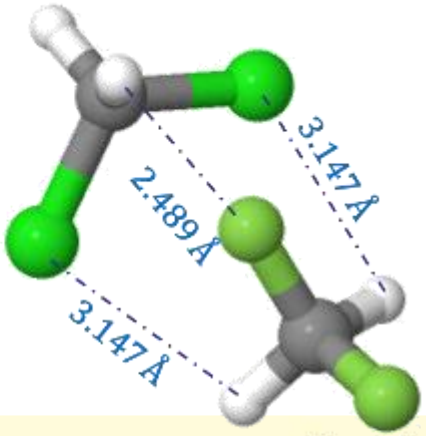
Simplest example: Linear rigid rotor

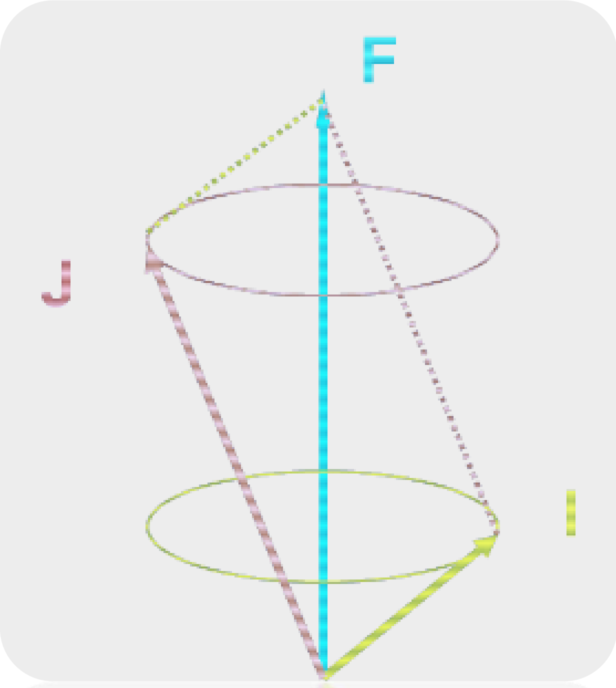
Quadrupole Coupling Effect

Nuclear spin $I > ½$ → Quadrupolar splittings

Quadrupolar hyperfine pattern can be very helpful to assign the spectrum

From quadrupolar coupling constants, the effective orientation can be determined.



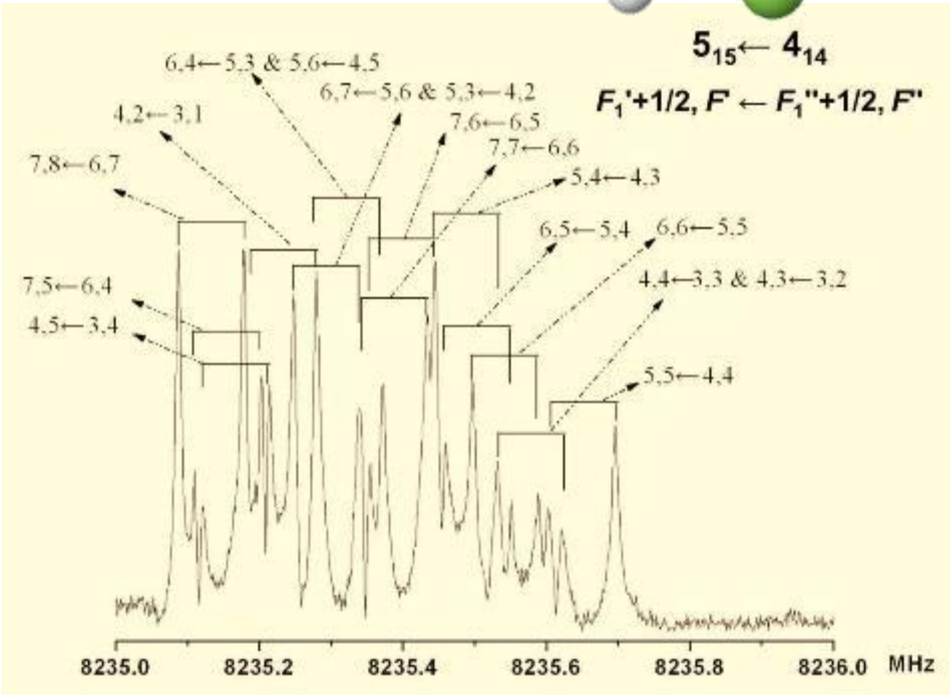


Hyperfine spectral structure！

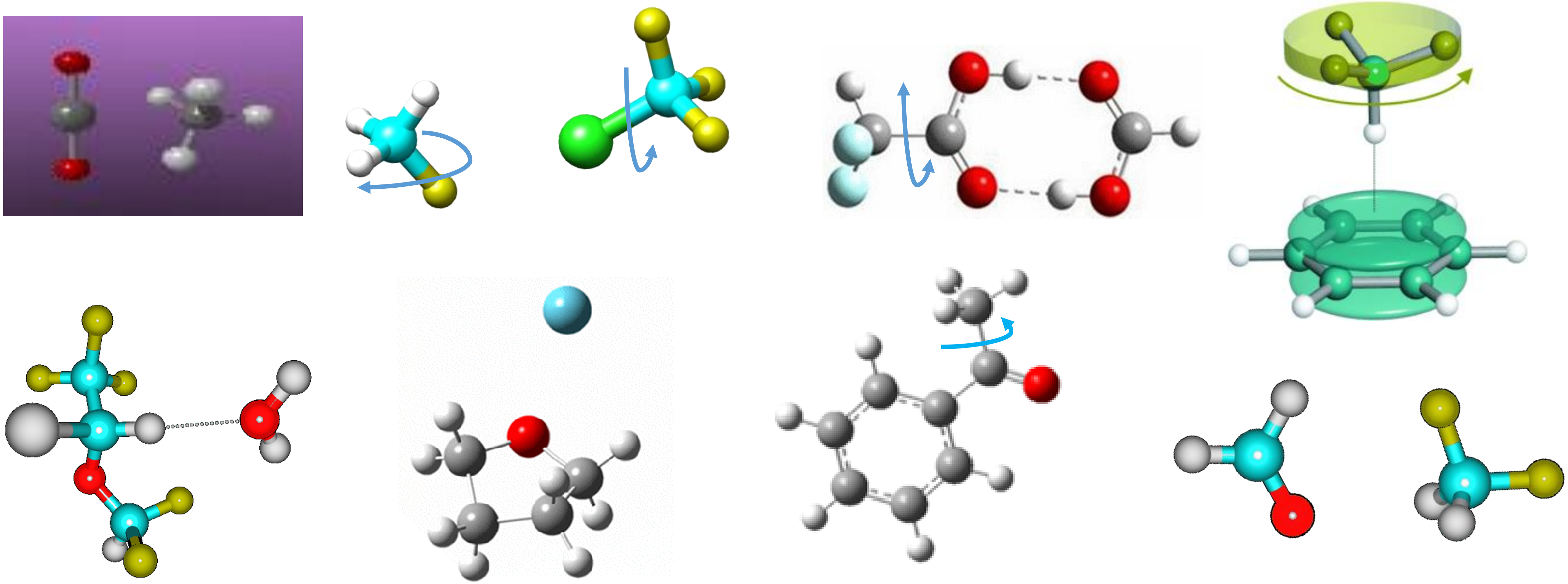
I (^{35}Cl)=3/2

I (^{37}Cl)=3/2

I (^{14}N)= 1



Large amplitude motions

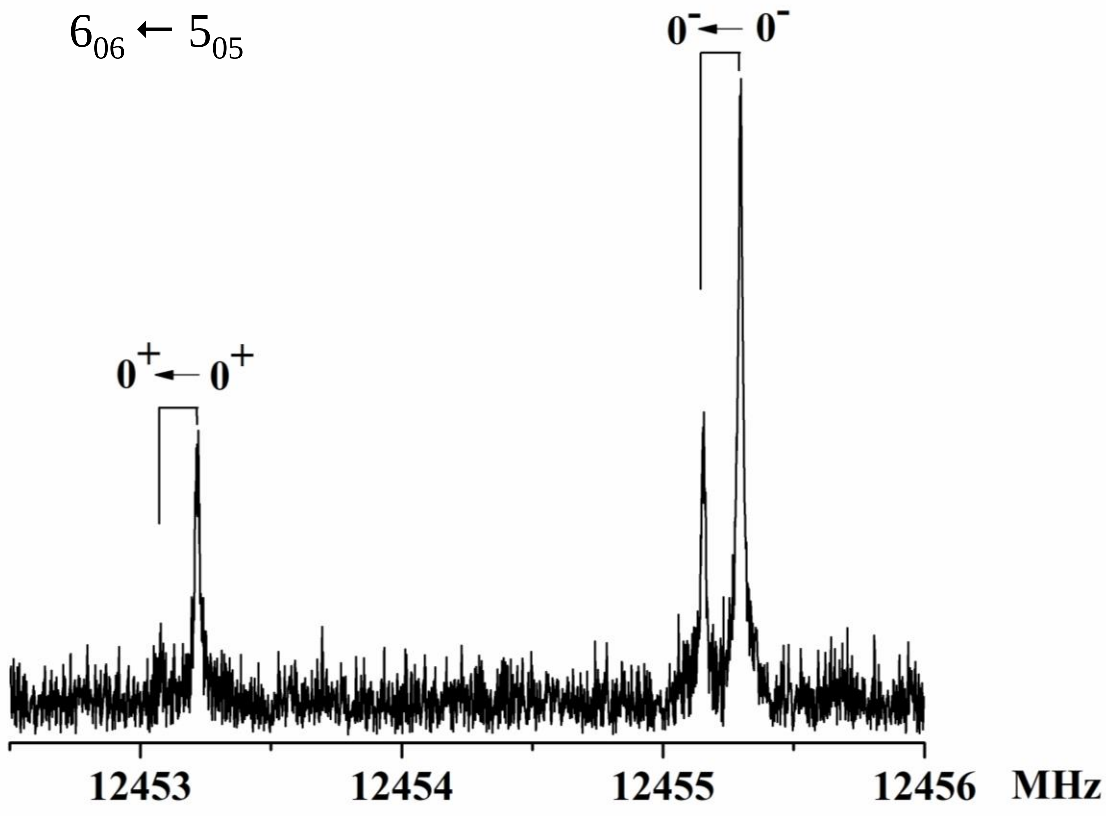


Flexibility of a molecule is one of the important factors in chemical reaction

The large-amplitude motion is greatly affected by the chemical environment

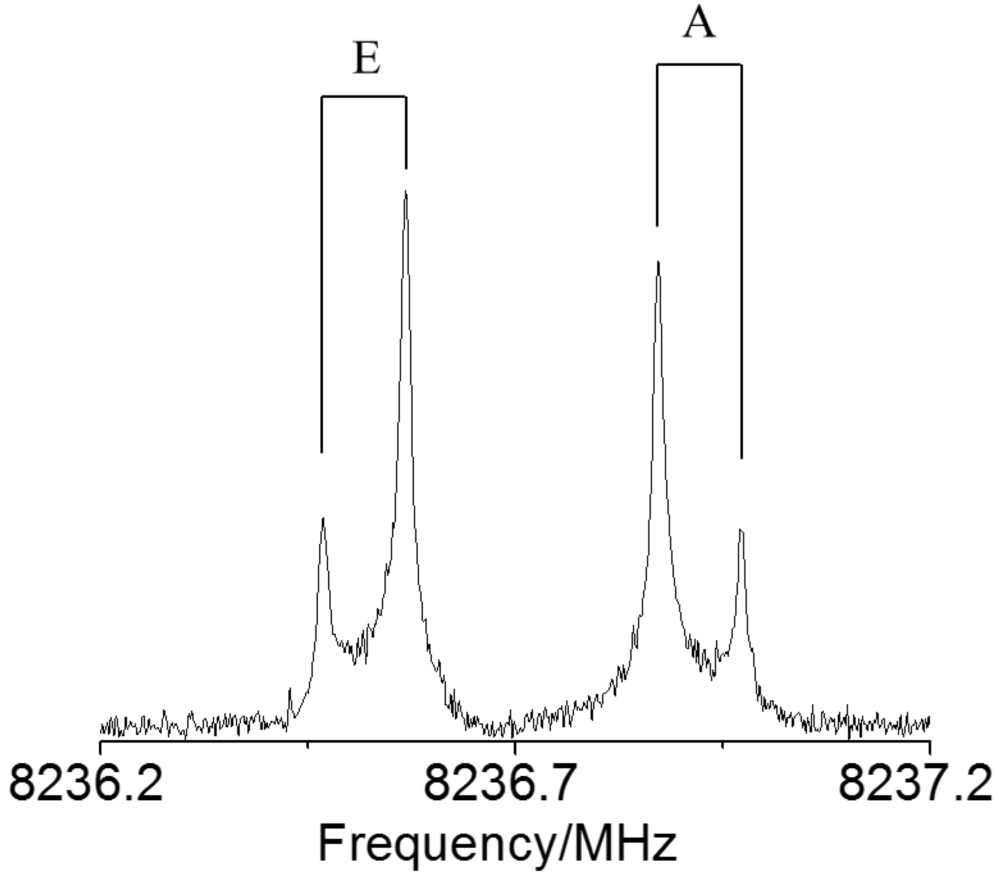
Effects of Internal Dynamics

Asymmetric tunneling splittings



Relative ratio of intensities of the two components: ~1/3

Symmetric tunneling splittings



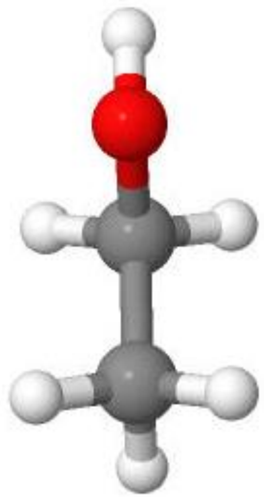
Interchange of two fermions (H) → Statistical weight: $0^+ : 0^- = 1:3$

Internal Rotation of a V_3 top ($-CH_3$)

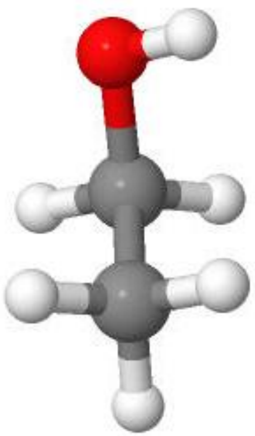
Rotational Spectroscopy

Ethanol

CH_3CH_2OH



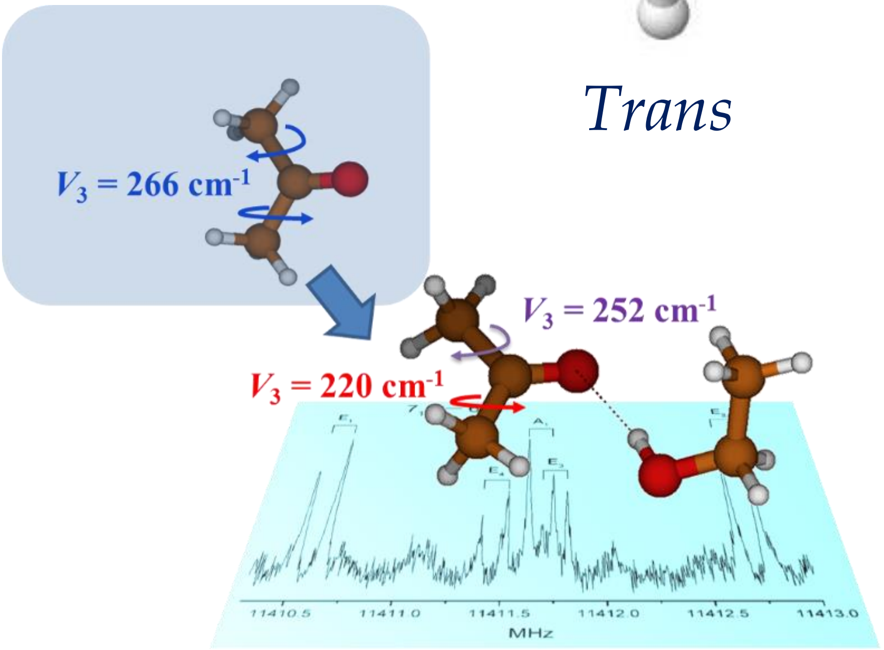
Trans



Gauche

Accurate molecular geometries:

Bond lengths, angles, dihedral angles



One cannot find two identical rotational spectra from two different molecules in the world.

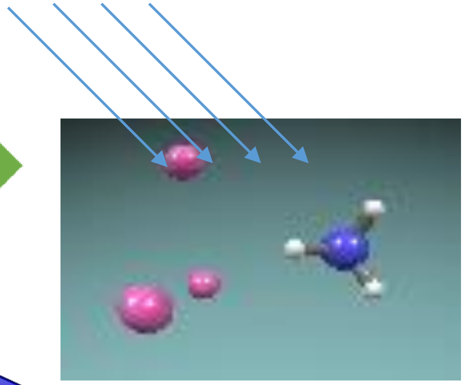
Rotational Spectroscopy

We may not know much, but what we know we really do know – a lot about very little – things. I was to learn later that such levels of satisfying certainty of knowledge are a rarity in many other branches of science and in almost all areas of life in general.

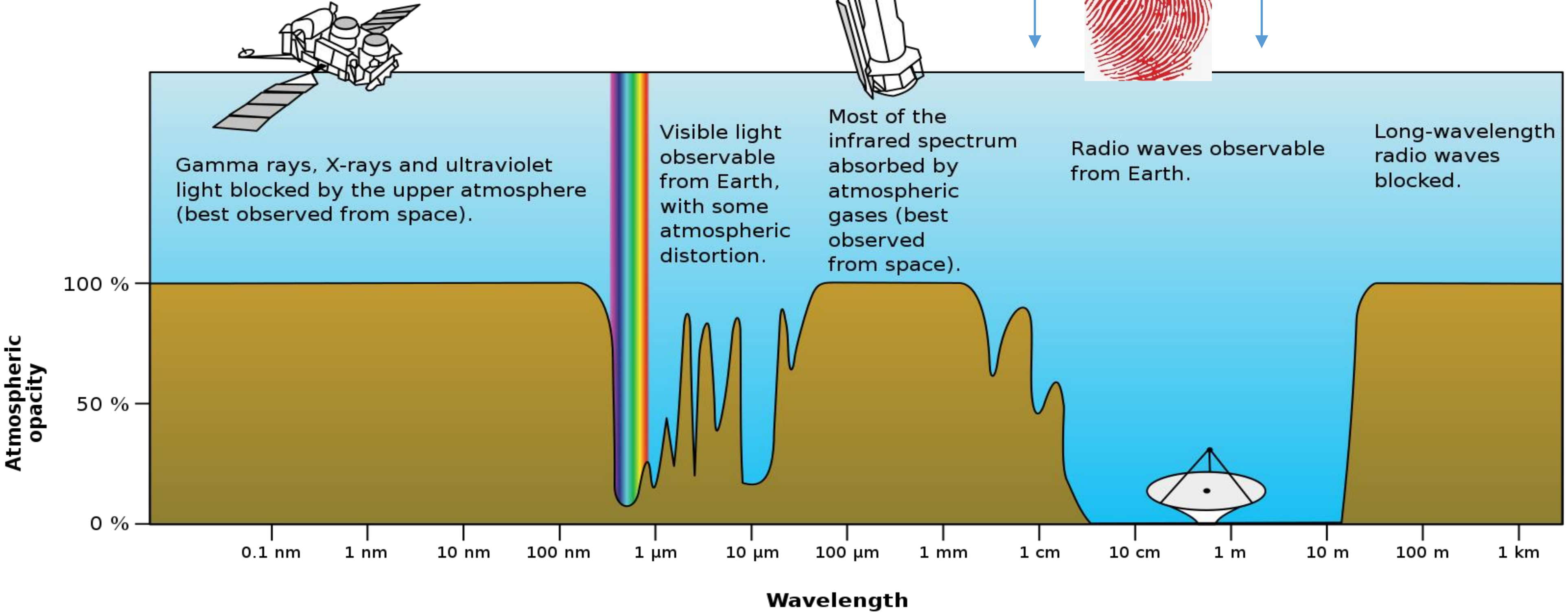
Harold Kroto (1939-2016)

Shared 1996 Nobel Prize in Chemistry with Robert Curl and Richard Smalley for their discovery of fullerenes

Rotational Constants → Inertial moments → Mass Distribution → Bond Lengths and Angles

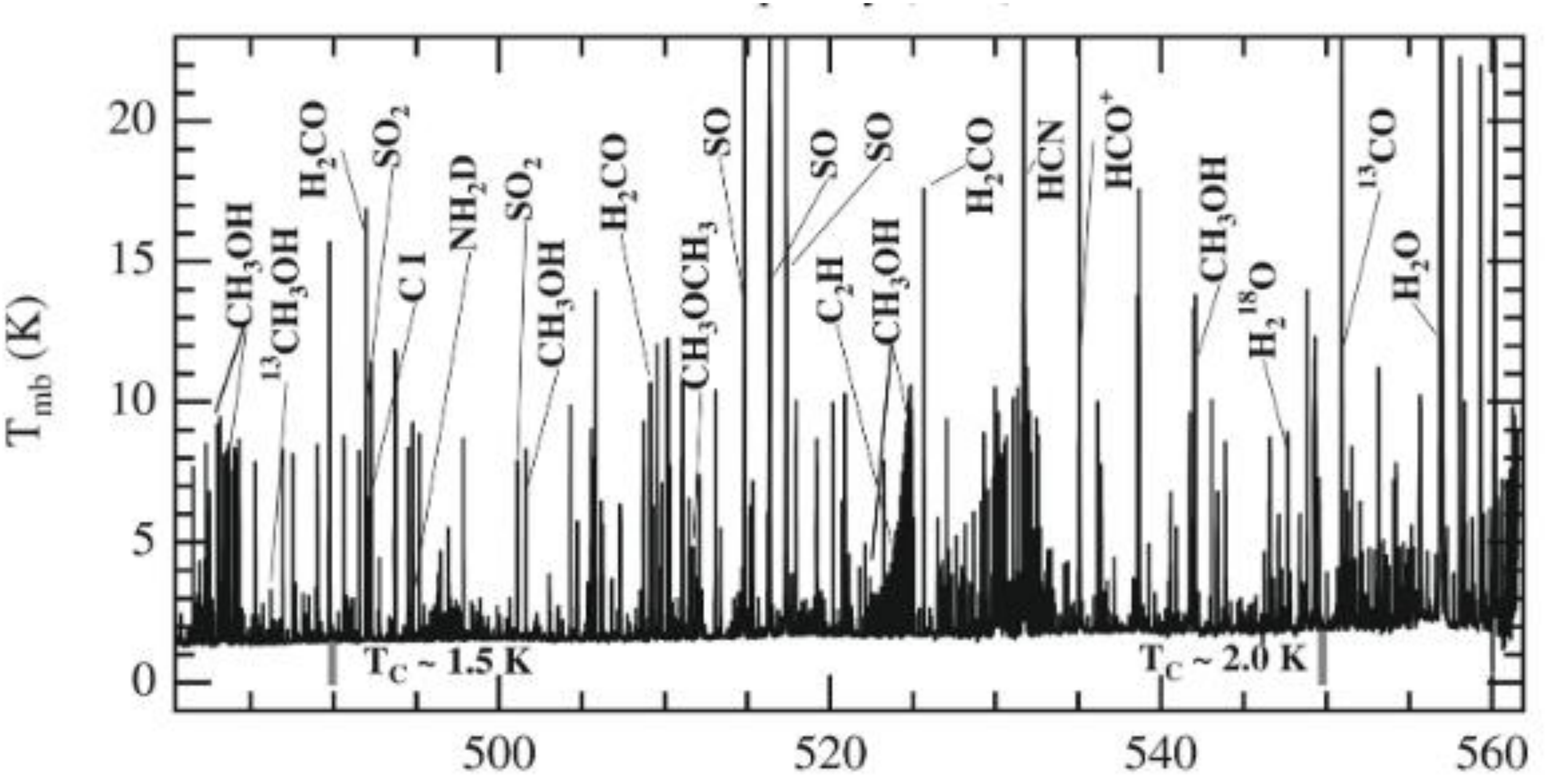


Rotational transitions



Electromagnetic transmittance, or opacity, of the Earth's atmosphere

Observation with Radio telescopes



ALMA Line Survey

Part 2

Spectroscopic technique

Line Intensity

The transition intensity is proportional to the square of the transition moment

$$\boldsymbol{R}_r = \int \psi_r'^{*} \boldsymbol{\mu} \psi_r'' \, \mathrm{d}\tau$$

1. The molecule must have a permanent dipole moment

2. $\Delta J = 0, \pm 1$

- $\Delta J = 0$: *Q*-branch;
- $\Delta J = 1$: *R*-branch;
- $\Delta J = -1$: *P*-branch.

3. $\Delta M_J = 0, \pm 1$, a rule which is important only if the molecule is in electric or magnetic filed

Transition Intensity

- Dipole moment (which varies relative little with J)
- Population of the lower state of a transition

Line Intensity

Boltzmann's distribution

$$N_J = N\,(2J+1)\,\frac{e^{-BJ(J+1)/kT}}{q_r}$$

$$q_r = \sum_J (2J+1)e^{-BJ(J+1)/kT} \approx \frac{kT}{\sigma B}$$

By setting $\frac{dN_J}{d_J} = 0$

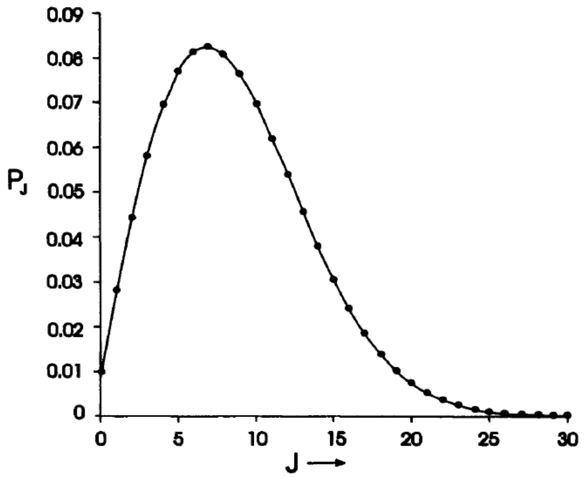
$$J_{max} = \left(\frac{kT}{2B}\right)^{1/2} - \frac{1}{2}$$

- For certain molecules,

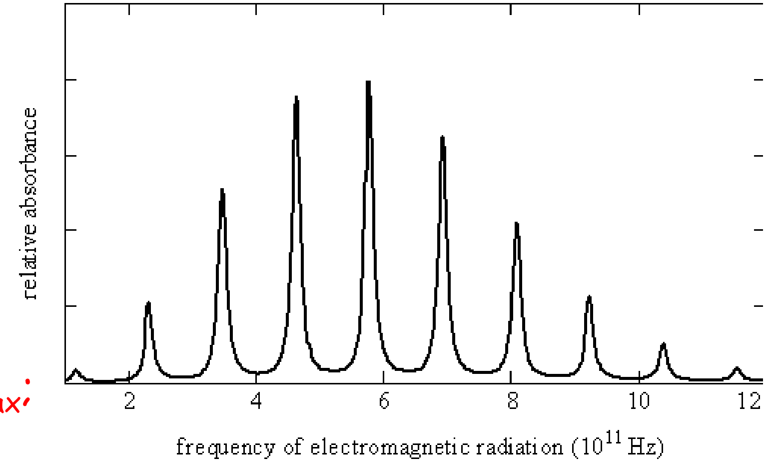
the higher the temperature, the bigger the J_{max};

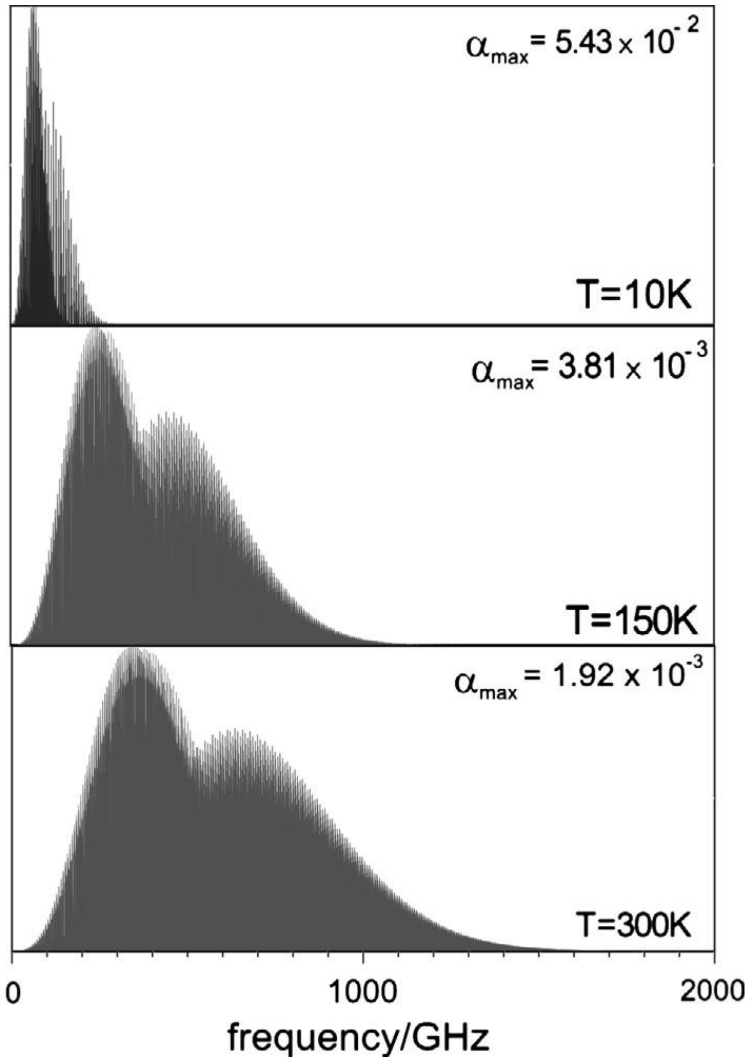
- At certain temperature,

the bigger the molecule, the bigger the J_{max}.

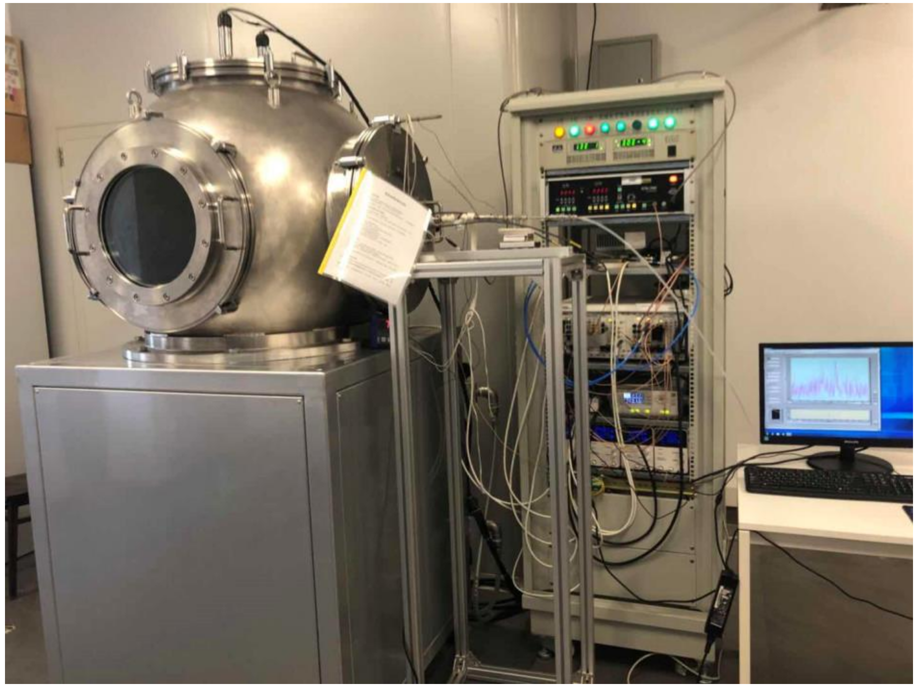


Distribution of population among rotational states of CO at room temperature.





Microwave Spectrometers @ CQU



$\sim 10^{-5}$ *Pa*

< *10 K*

Supersonic pulsed jet-Fourier transform microwave spectrometer

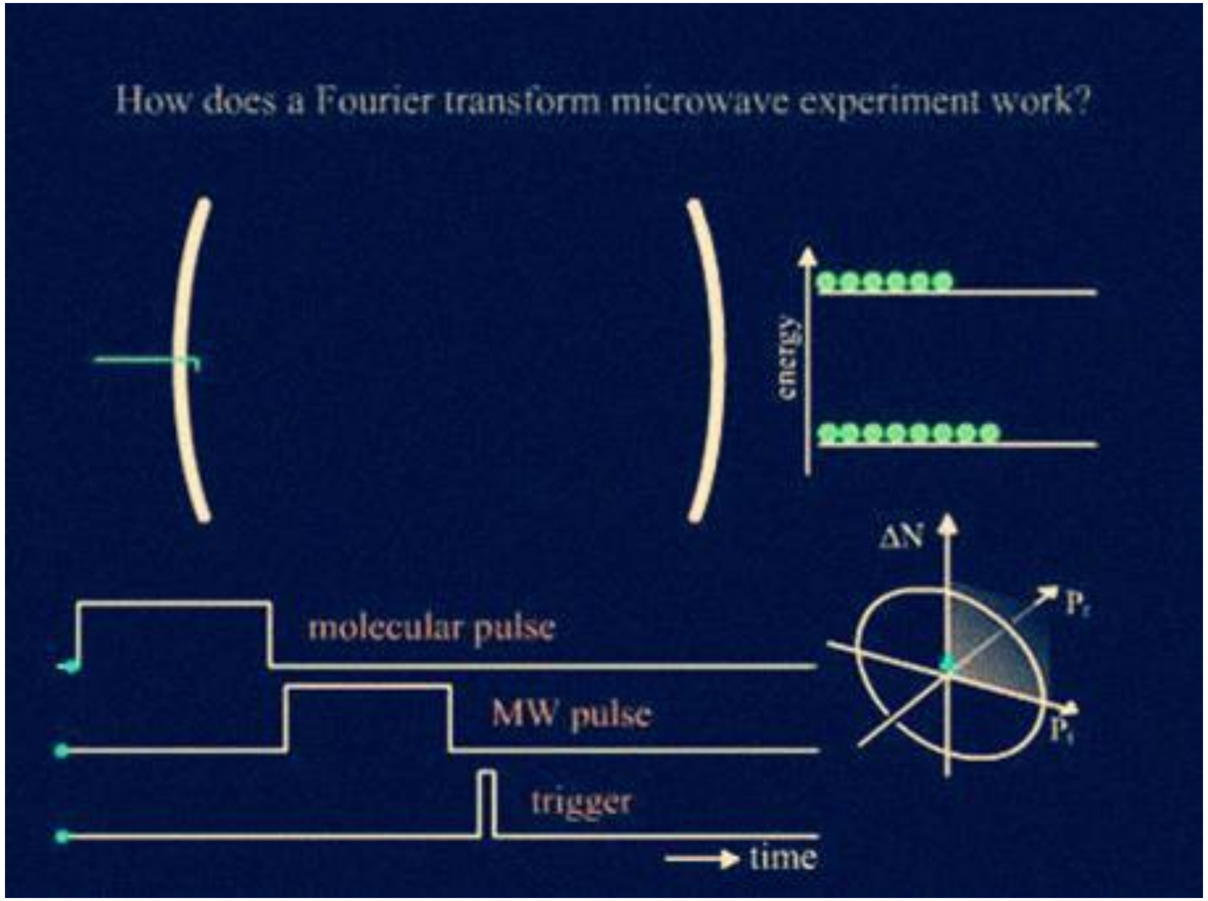
1. High Resolution： <5 kHz

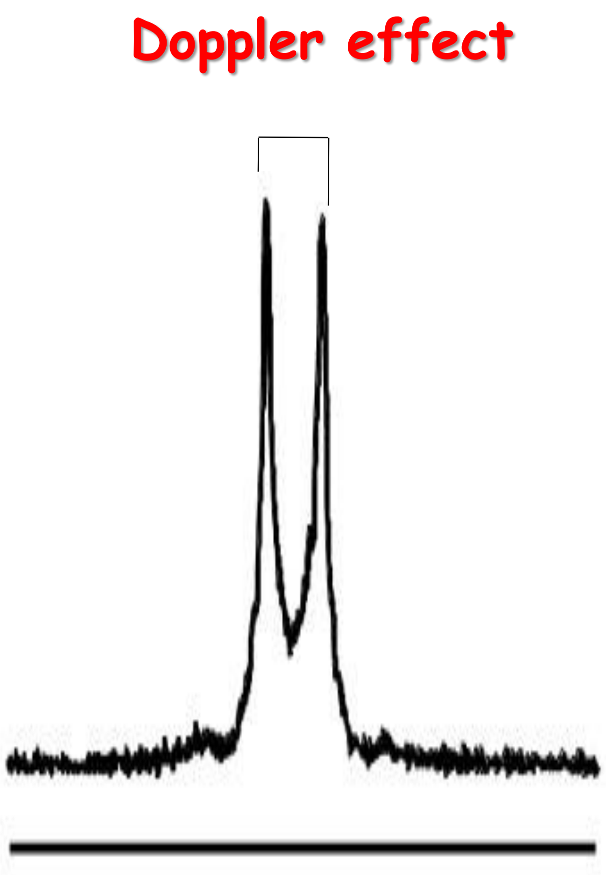
2. High Accuracy： ~1 kHz

3. Frequency Covering : 2 − 20 GHz (extendable up to 20 − 40 GHz)

4. Highly integrated

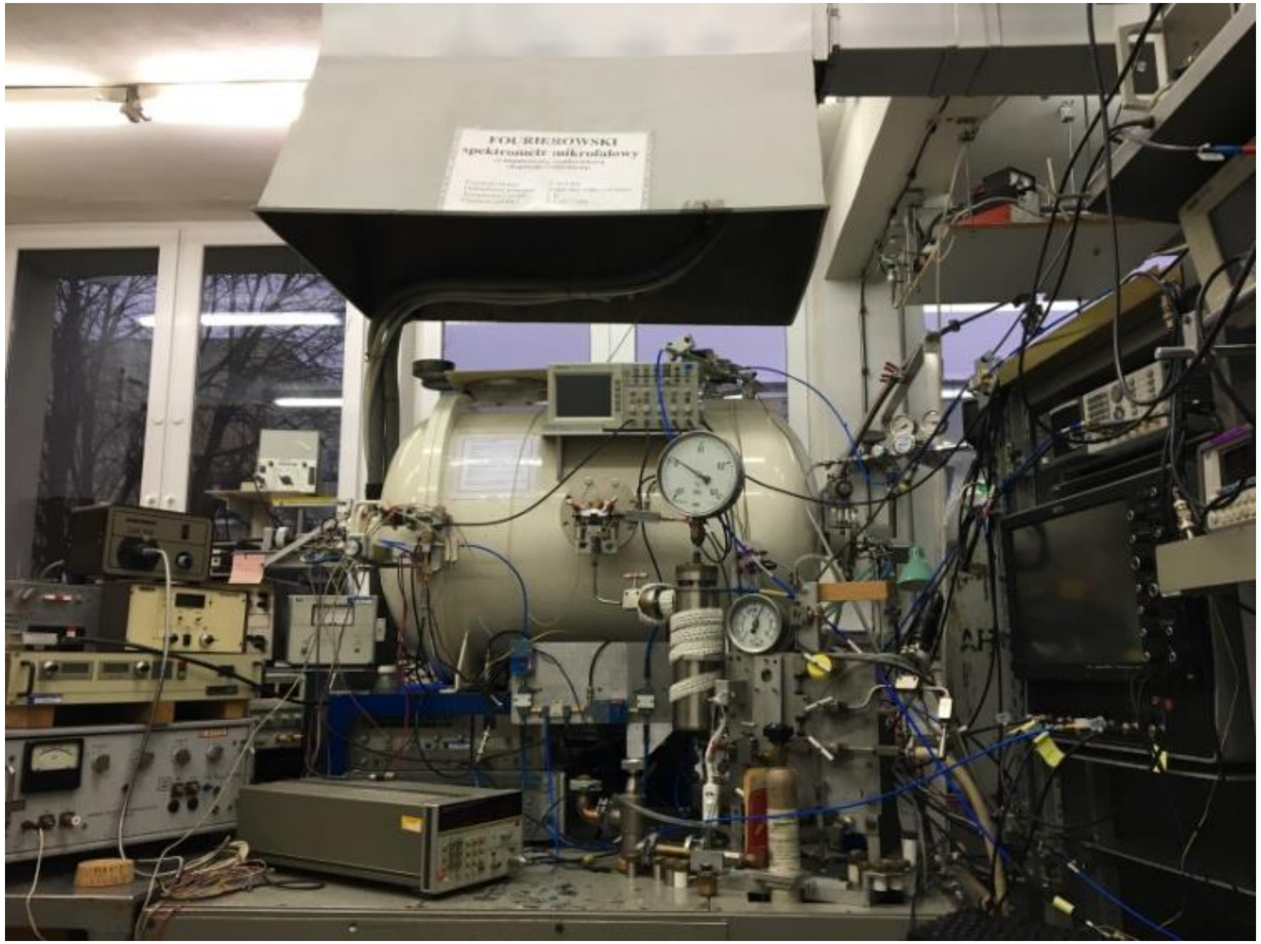
Microwave Spectrometers @ CQU



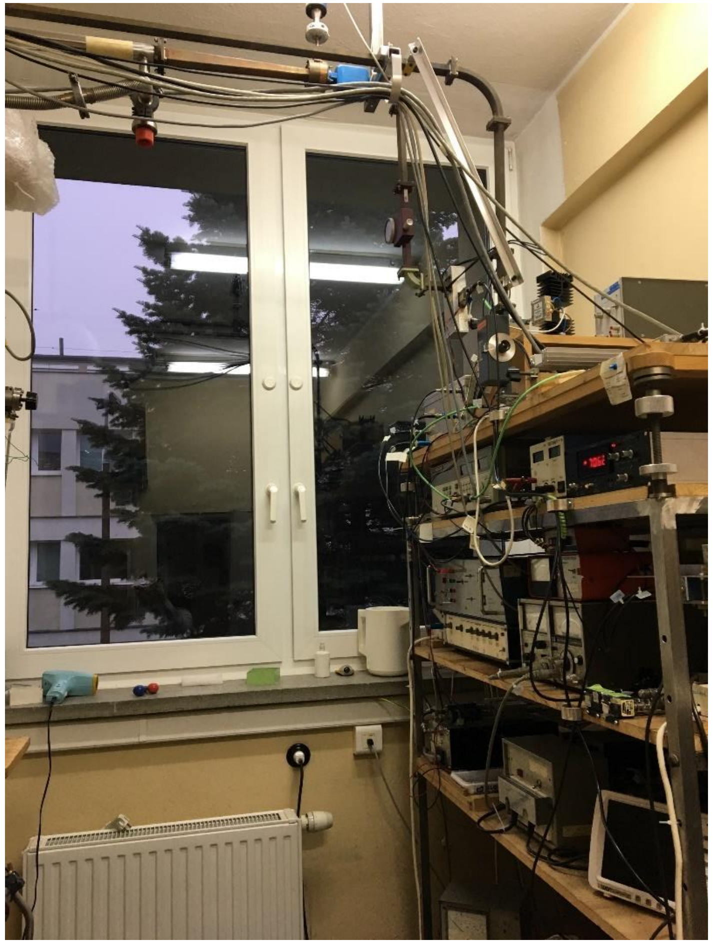


1. A pulse of noble gas carrying the sample
2. A microwave pulse to produce a macroscopic polarization
3. Molecular relaxation gives rise to a transient emission signal (free induction decay)
4. Fourier transformation

Spectrometer @ Warsaw



Pulsed supersonic expansion Fourier transform cavity spectrometer
(2-18.5 GHz)



Waveguide adsorption microwave spectrometer
(2-18 GHz)

Spectrometer @ Bologna

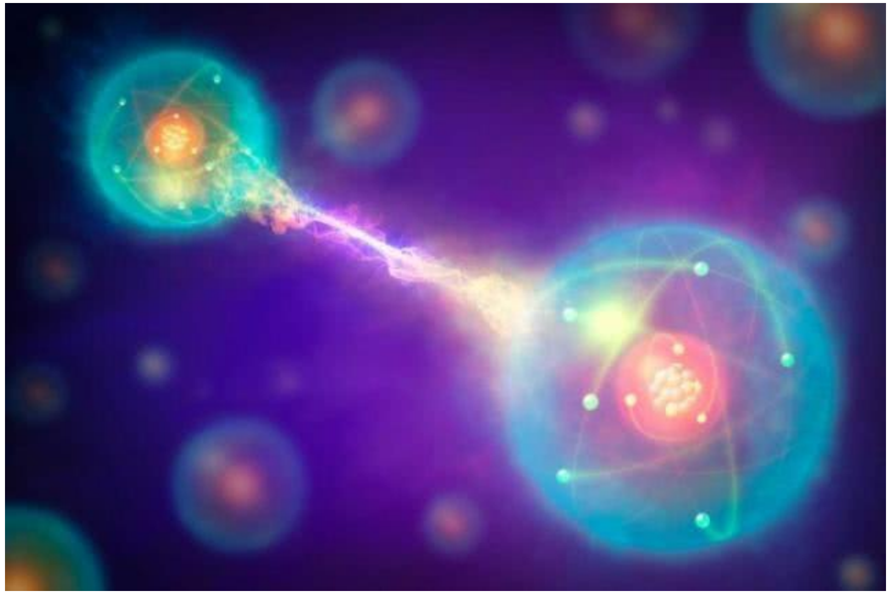
Sub-millimeter Spectrometer

75 – 1600 GHz

Part 3

Complex organic interstellar molecules

Interstellar Molecules



- How many molecules are there on Earth?
- ~ 10^{50} molecules*
- How many molecules are there in the "Milky Way Galaxy"?
- ~ 10^{66} molecules*
- * Courtesy: Prof. B. J. McCall, University of Illinois, Urbana, IL.

~ 200 molecules detected in space

What molecules exactly exist in space?

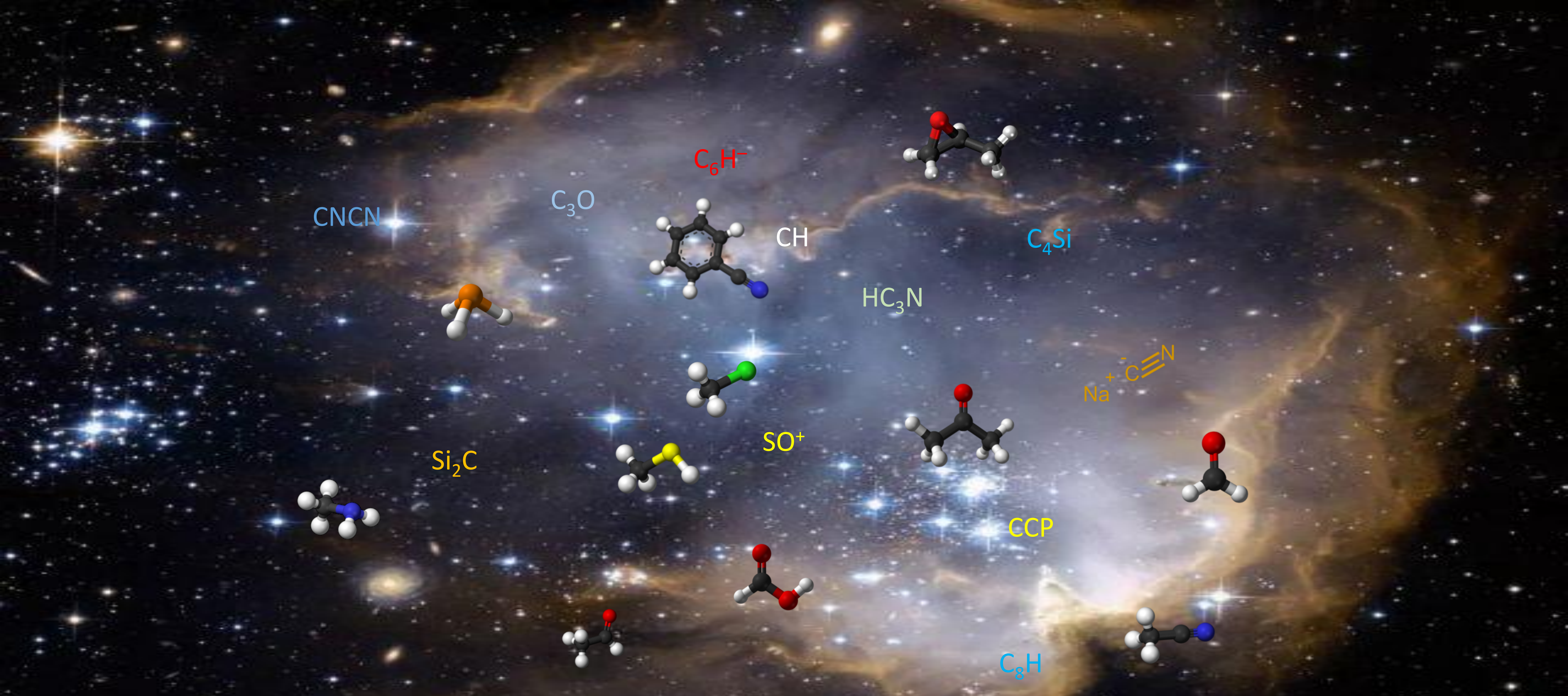
Astrochemistry?

Astrophysics?

$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{D}$$

↑

Low temperature, low pressure, low molecular density, cosmic ray …



The origin of life?

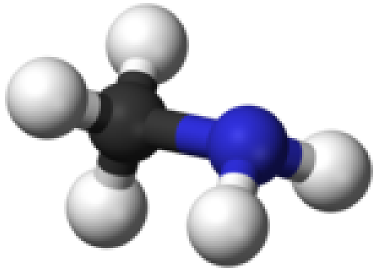
> 6 atoms

Complex organic molecules

Less abundance, less intense

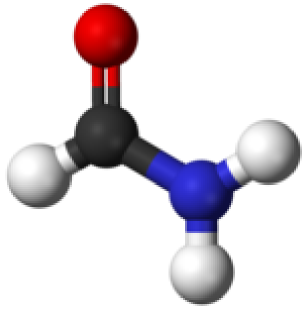
More flexible, more complex rotational spectra

I. Amines



PKS 1830-211

Astron. Astrophys. **535**, (2011)



Sgr A

Astrophys. J. **182**, 699–710 (1973)

Solar-type Protostar

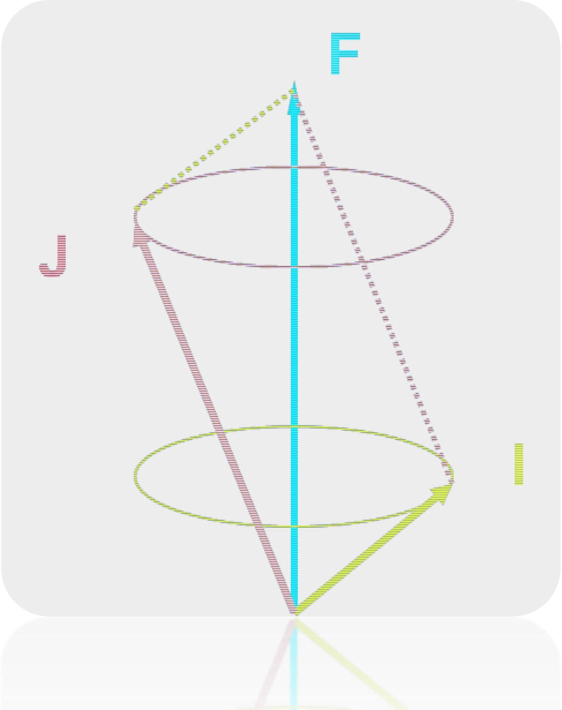
Astrophys. J. **763,** L38 (2013)

Orion KL

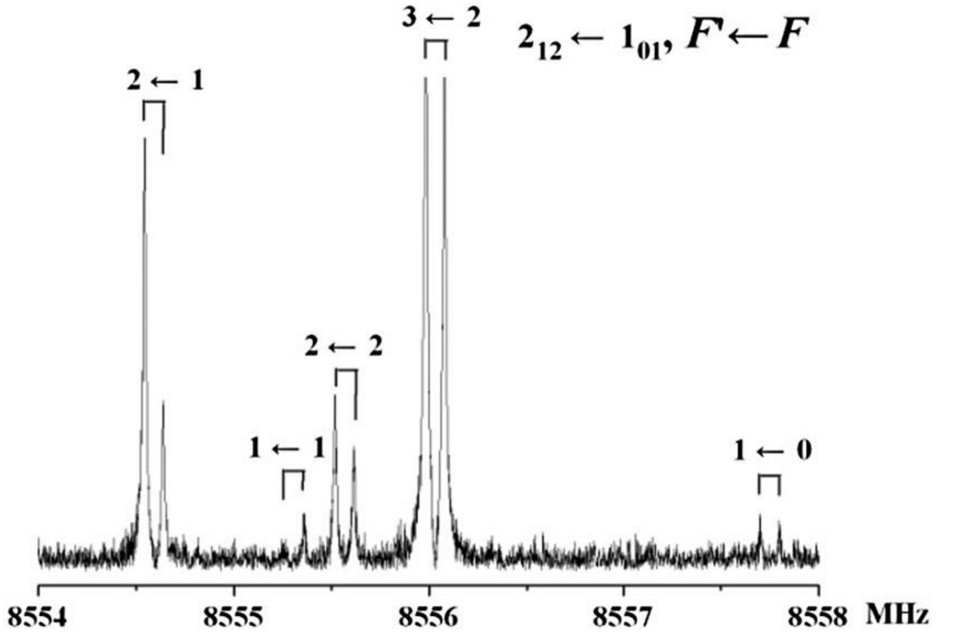
Astron. Astrophys. **590**, L6 (2016)

Sgr B2

Astron. Astrophys. **605,** L6 (2017)



I (^{14}N) = 1

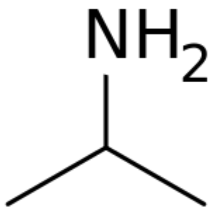


Nuclear quadrupole hyperfine structure

Prebiotic molecules

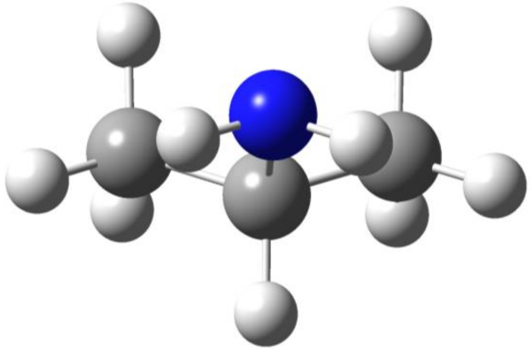
Large electric dipole moments

Intense transition lines



Isopropylamine

Trans

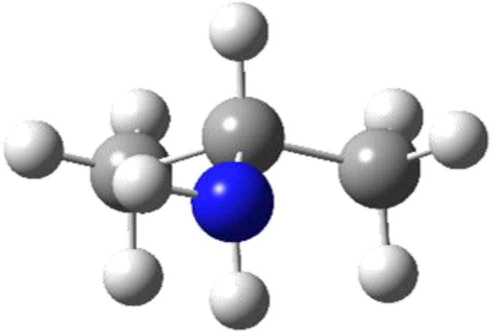


A = 8331.9029(2) MHz

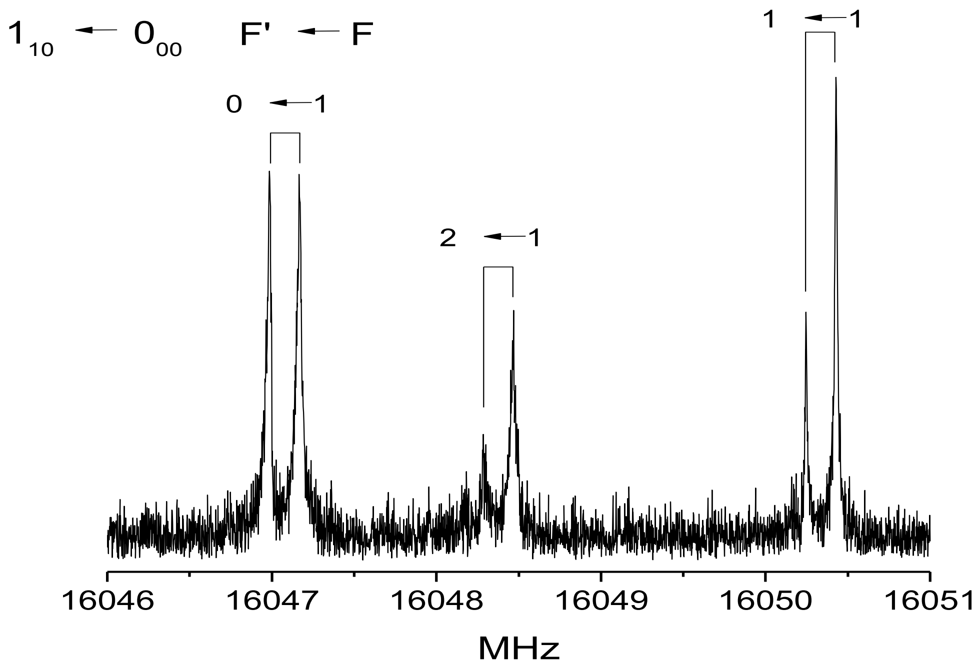
B = 7977.3357(2) MHz

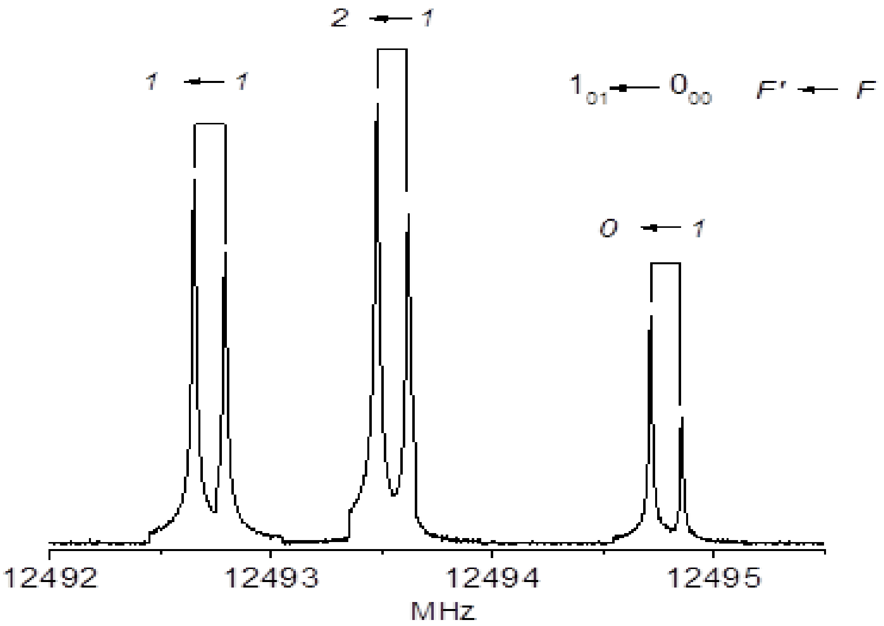
C = 4656.9147(6) MHz

Gauche



Tunneling of $-NH_2$





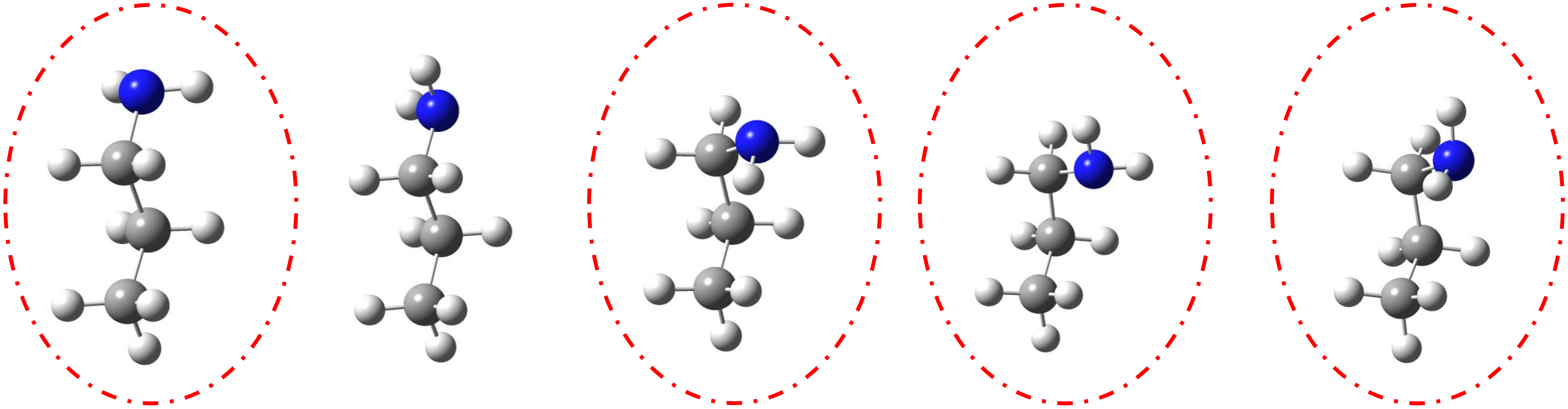
CQU+UNBO+NSP+MPIfR

Sgr B2 1-50 GHz; 90-110 GHz

J. Phys. Chem. A **2020**, *124*, 1372-1381.

n-Propylamine

Four conformers observed in the pulsed jet.



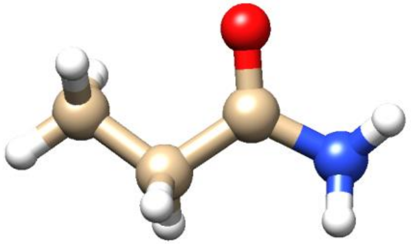
tt 0 cm^{-1} **tg** 37 cm^{-1} **gt** 114 cm^{-1} **ggs** 114 cm^{-1} **ggd** 145 cm^{-1}

Conformational relaxation might take place.

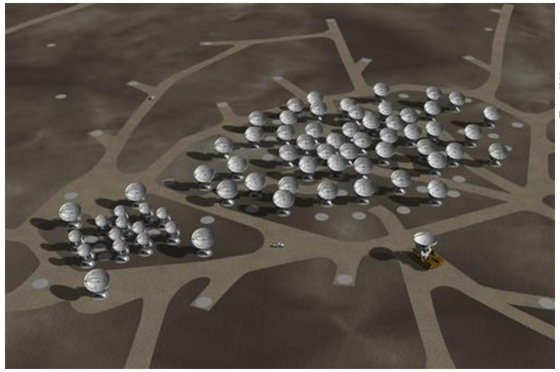
CCSD(T)/PVTZ calculations

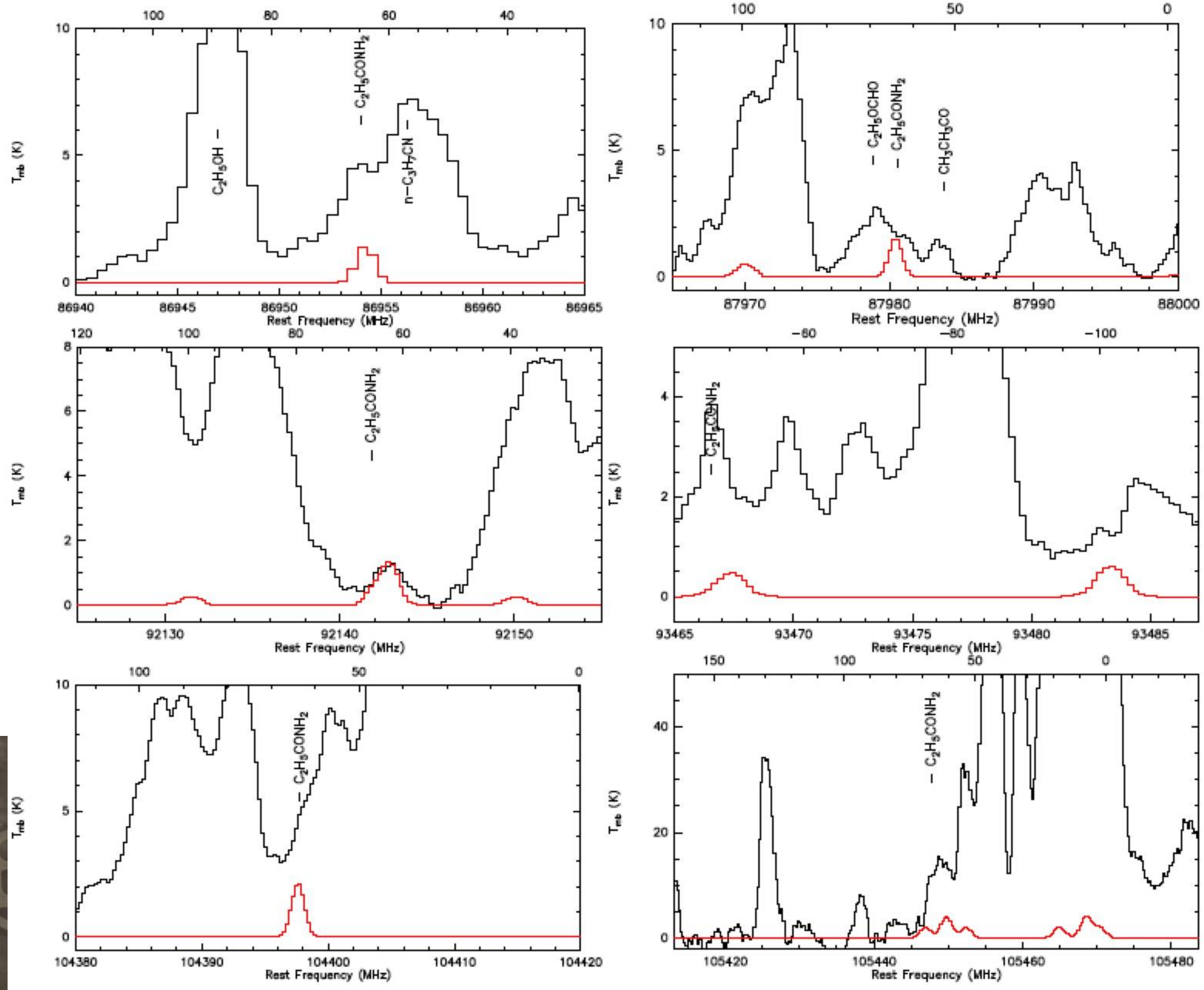
CQU+UNBO+NSP+MPIfR+SHAO

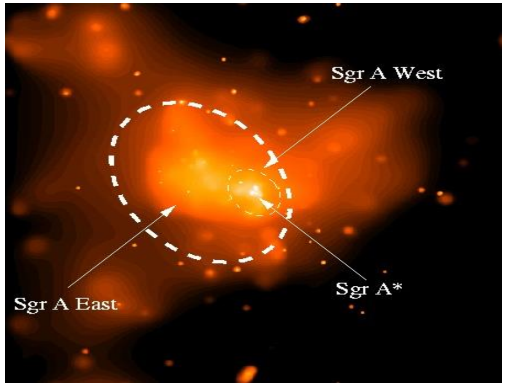
J. Phys. Chem. A **2020**, *124*, 1372-1381.

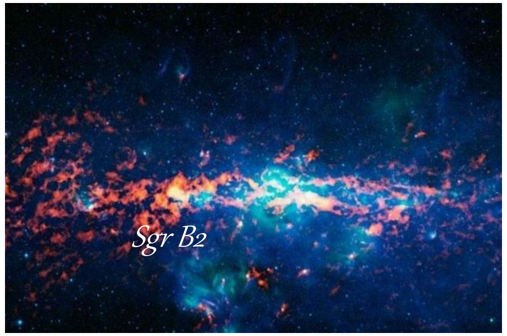


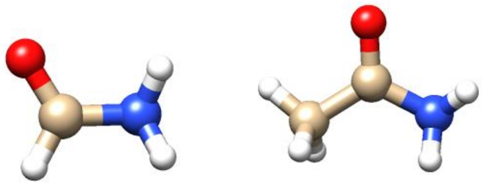
Propanamide











Astrophys. J. **169**, L39–L43 (1971)

Astron. Astrophys. **590**, Art. No. L6 (2016).

Astrophys. J. **763**, Art. No. L38 (2013).

Astrophys. J. **743**, Art. No. 60 (2011)

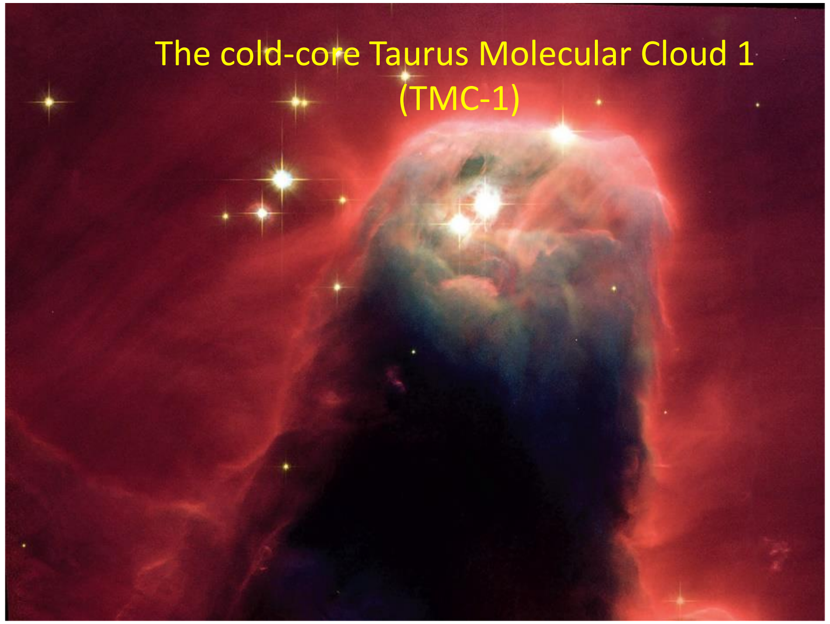
ALMA data, J. Li, J. Wang, et.al. APJL, submitted

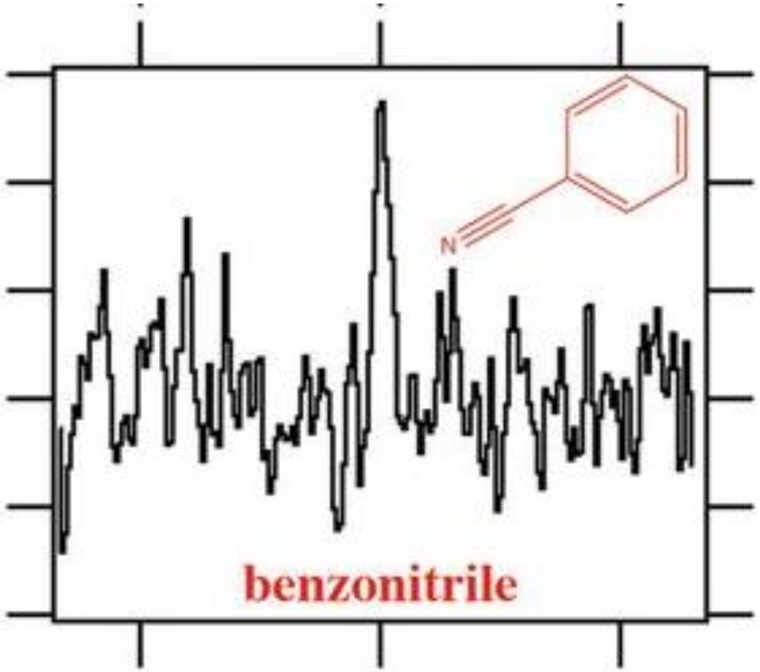
II. Derivatives of Benzonitrile

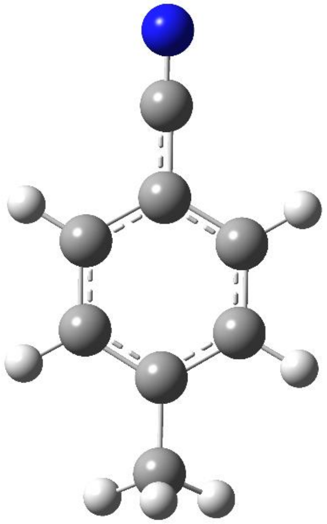
Detection of the aromatic molecule benzonitrile (*c*-C_6H_5CN) in the interstellar medium

Brett A. McGuire[1,2,*], Andrew M. Burkhardt[3], Sergei Kalenskii[4], Christopher N. Shingledecker[5], Anthony J. Remijan[1], Eric H...
+ See all authors and affiliations

Science 12 Jan 2018:
Vol. 359, Issue 6372, pp. 202-205
DOI: 10.1126/science.aao4890





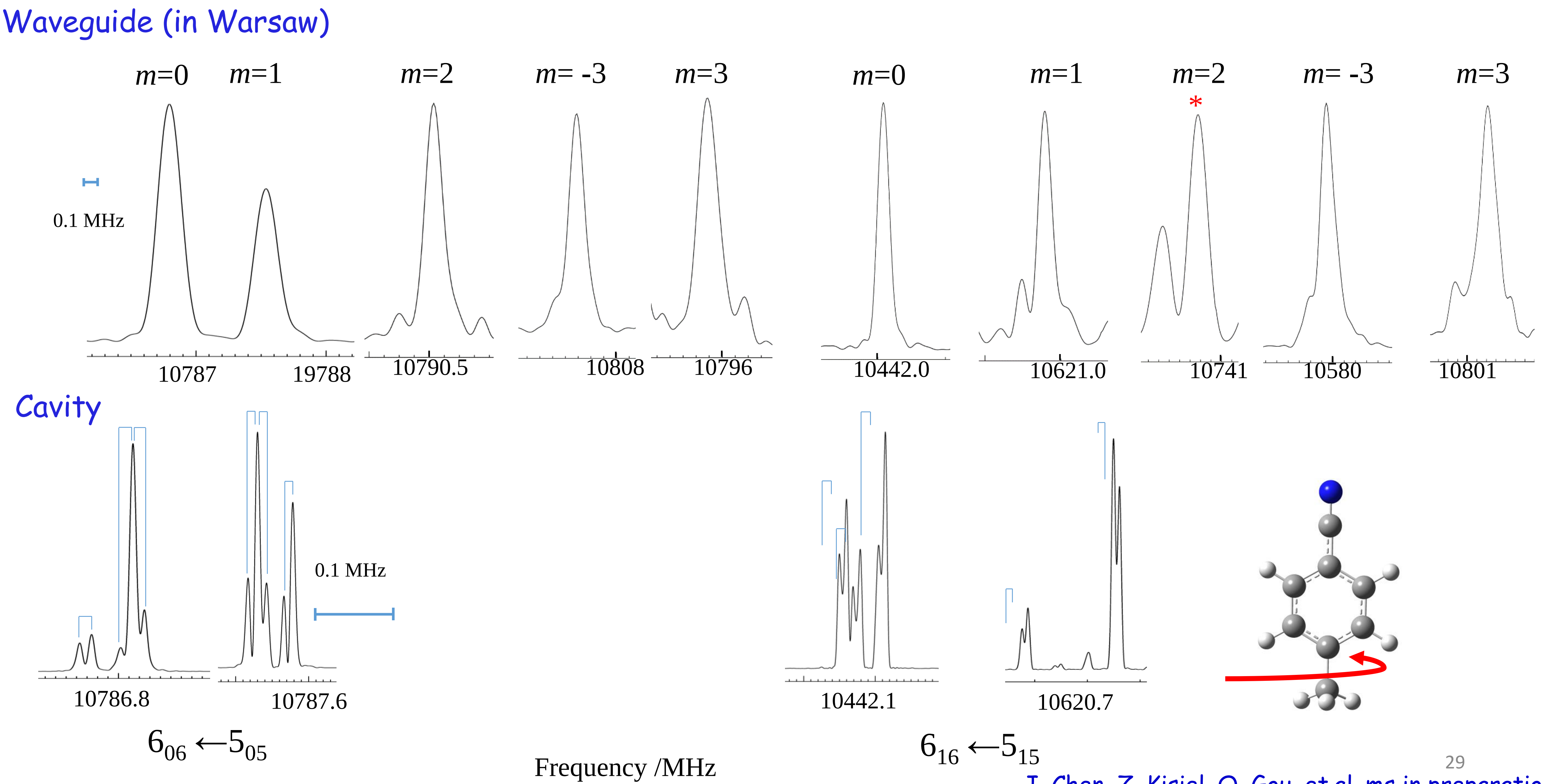


possess a rich chemistry dominated by unsaturated carbon-chain molecules

100-m Green Bank Telescope

4-methylbenzonitrile
$CH_3C_6H_4CN$

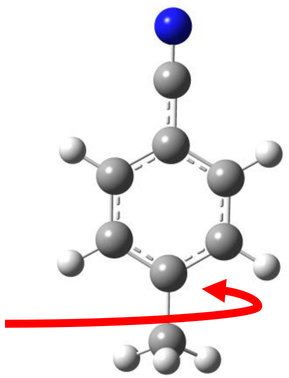
Derivatives of Benzonitrile



J. Chen, Z. Kisiel, Q. Gou, et.al. ms in preparation

II. Derivatives of Benzonitrile

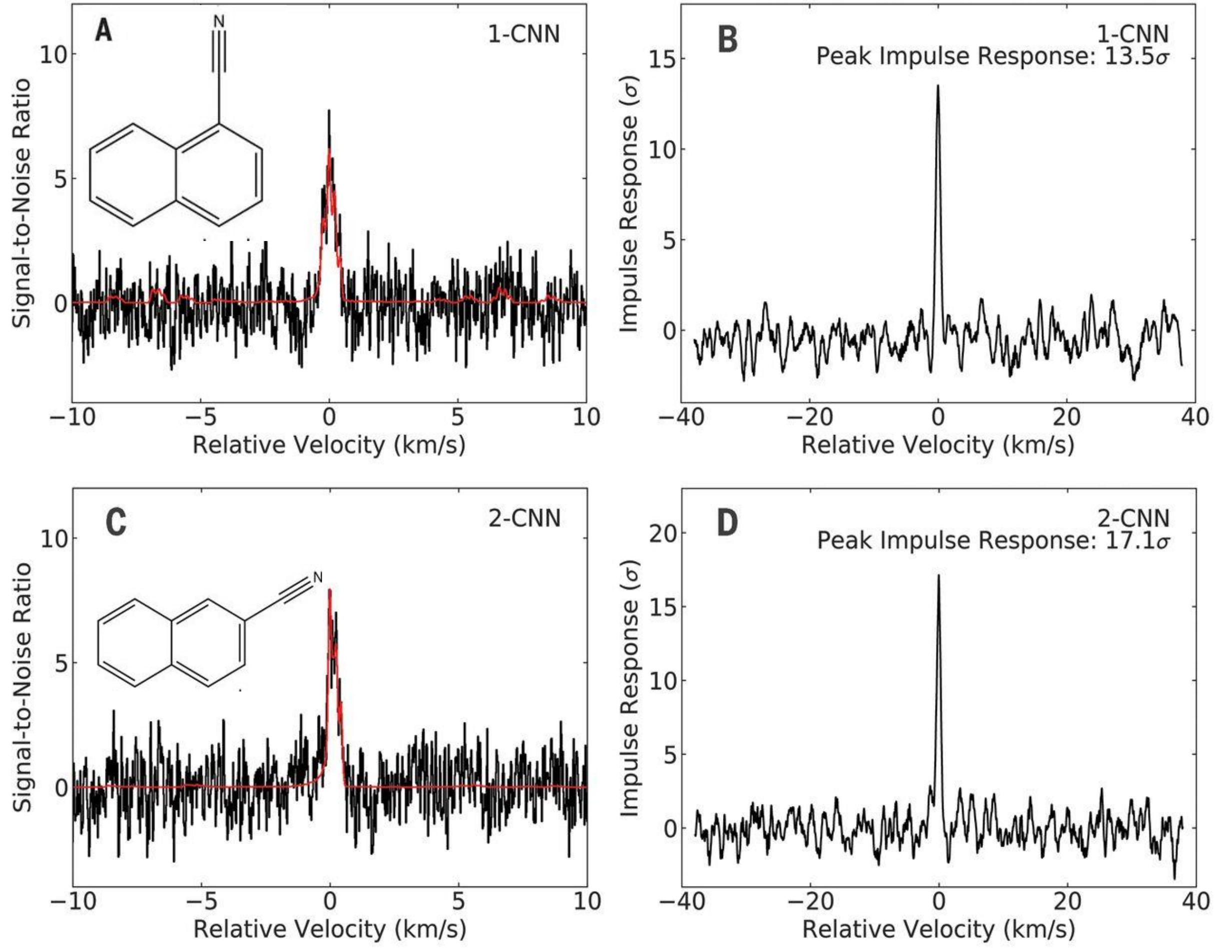
Parameters	Values (MHz)	Parameters	Values (MHz)
F	[163895.215474094]*	ρ_{m}	2.43(13)
$0.5V_6$	71926.(36)	ρ_{J}	0.000069(39)
A-0.5(B+C)	4785.78(14)	ρ_{3c}	[-256.430941437492]
0.5(B+C)	908.25437(40)	ρ_{mm}	0.4437(84)
0.5(B-C)	71.9638(24)	ρ_{bc}	0.0041(21)
$2\rho F$	11303.42(35)	F_{mK}	[-0.005540836582067]
D_J	0.0000681(73)	ρ_{K}	0.112(36)
D_{JK}	-0.000456(42)	ρ_{mK}	[0.000988347465579]
D_K	[0.00348059043738]	V_{6J}	-0.0736(11)
$2D_J$	0.0000828(98)	F_{KK}	[-0.000031072168699]
$2D_K$	0.0003(17)	F_{mJ}	[0.000059424191133]
F_J	-0.002350(30)	F_{JK}	[0.000003729236021]
F_K	[-0.10769406127102]	D_{6bc}	0.320(53)
		D_{3ab}	26.43(70)
		ρ_{mmK}	[-0.000058973526854]

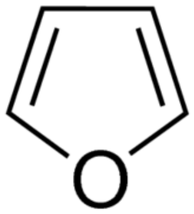


J. Chen, Z. Kisiel, Q. Gou, et.al. ms in preparation

III. furanitriles

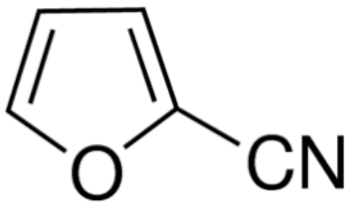
-CN group can introduce large permanent dipole moment





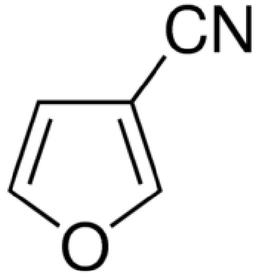
Furan

Dipole moment: 0.7 Debye



2-furanitrile

Dipole moment: 4.9 Debye



3-furanitrile

Dipole moment: 3.7 Debye

Brett A. McGuire et al. Science 2021;371:1265-1269

CQU: High resolution rotational spectra (2- 20 GHz)

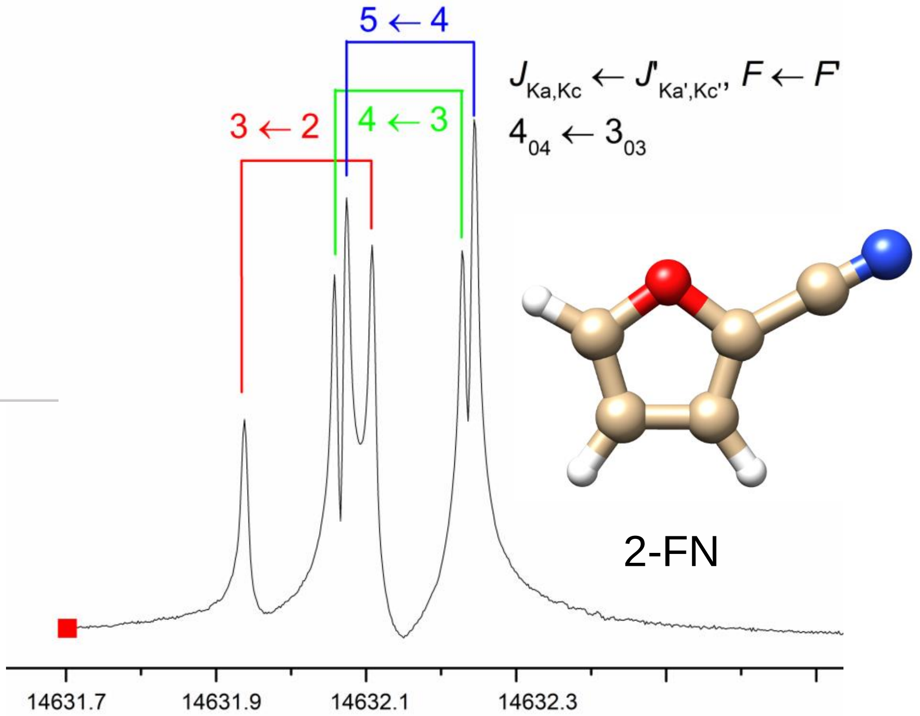
UniBo: Millimeter spectra (> 75 GHz)

Harvard: Astronomical search in TMC-1 with GBT

III. furonitriles

```
Maximum Dimension for Hamiltonian = 18
                                          EXP.FREQ.  -  CALC.FREQ. -    DIFF.   - EXP.ERR
   1:   2  0  2  3  1  0  1  2          7370.25800   7370.25686   0.00114
   2:   2  0  2  2  1  0  1  1          7370.17570   7370.17429   0.00141
   3:   2  0  2  1  1  0  1  0          7369.08510   7369.08638  -0.00128
   4:   2  0  2  2  1  0  1  2          7368.88610   7368.88636  -0.00026
   5:   2  0  2  1  1  0  1  1          7372.30670   7372.30654   0.00016
   6:   2  1  2  3  1  1  1  2          7017.44060   7017.43958   0.00102
   7:   2  1  2  2  1  1  1  1          7016.11860   7016.11677   0.00183
   8:   2  1  2  1  1  1  1  0          7018.92910   7018.92866   0.00044
   9:   2  1  2  2  1  1  1  2          7016.91410   7016.91462  -0.00052
  10:   2  1  2  1  1  1  1  1          7016.93460   7016.93404   0.00056
  11:   2  1  1  3  1  1  0  2          7750.72120   7750.72174  -0.00054
  12:   2  1  1  2  1  1  0  1          7749.37750   7749.37701   0.00049
  13:   2  1  1  1  1  1  0  0          7751.93150   7751.93209  -0.00059
```

	Experimental spectroscopic parameters
A, B, C /MHz	9220.2508(7), 2029.2736(2), 1662.6430(2)
X_{aa}, $(X_{bb}$-$X_{cc})$ /MHZ	-4.294(4), 1.026(4)
D_J /kHz	0.057(3)
D_{JK} /kHz	2.90(1)
D_k /kHz	0.35(6)
d_1 /kHz	-0.016(6)
d_2 /kHz	-0.0112(8)



2-furonitrile

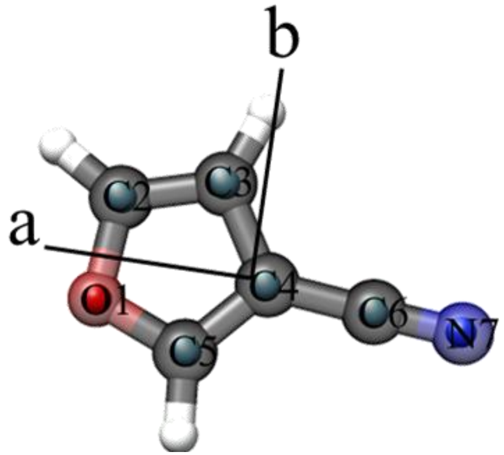
III. furonitriles

Table. 1. Experimental spectroscopic parameters of 3-Furonitrile

	A/MHz	*B*/MHz	*C*/MHz	*N*	*σ*/kHz
Normal	9296.5468(2)	1940.26644(2)	1604.63185(2)	659	5.9
O1	9149.70(4)	1894.4776(1)	1568.9246(1)	58	5.8
C2	9218.015(1)	1916.7287(1)	1586.1899(1)	77	2.4
C3	9068.0379(8)	1938.24136(9)	1596.29796(9)	77	1.9
C4	9296.87(2)	1939.55597(7)	1604.16062(7)	66	1.4
C5	9106.2281(9)	1938.5122(1)	1597.6641(1)	77	2.1
C6	9296.504(1)	1917.8573(1)	1589.2754(1)	77	2.4
N7	9296.5601(9)	1880.0222(1)	1563.1955(1)	18	1.1

Quadrupole hyperfine structure

Fig. 2. The experimental r_s position of the isotopically substituted atoms is included for comparison with the MP2/ 6-311++G(d,p) calculated structure (background).



3-furonitrile

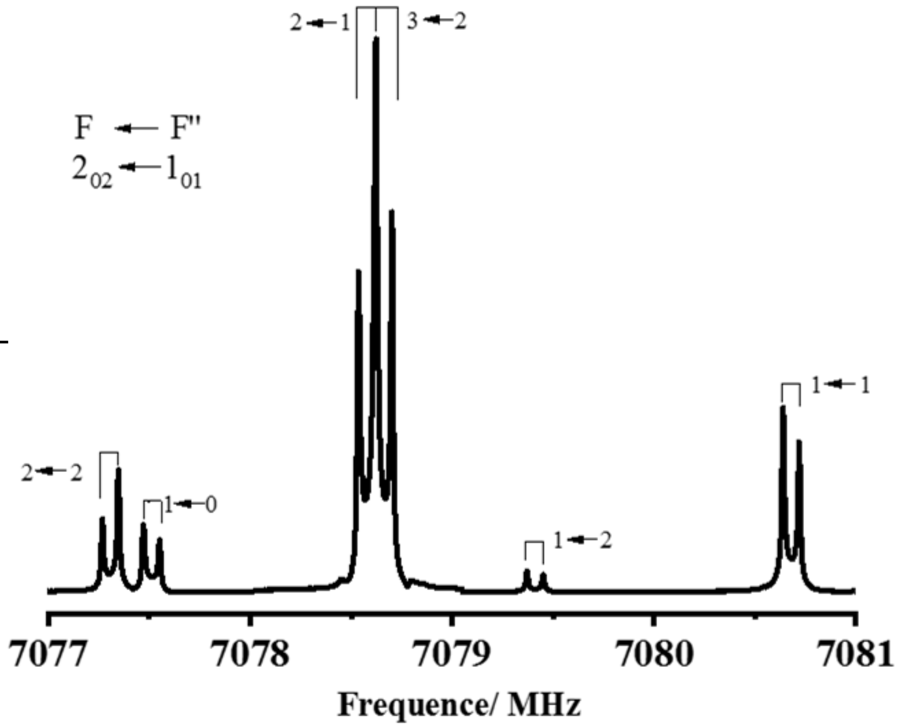
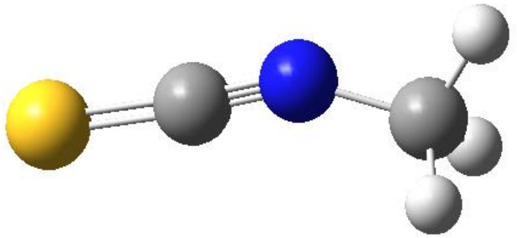


Fig. 3. Rotational spectra recorded with Helium (0.1 MPa) as the carrier gas

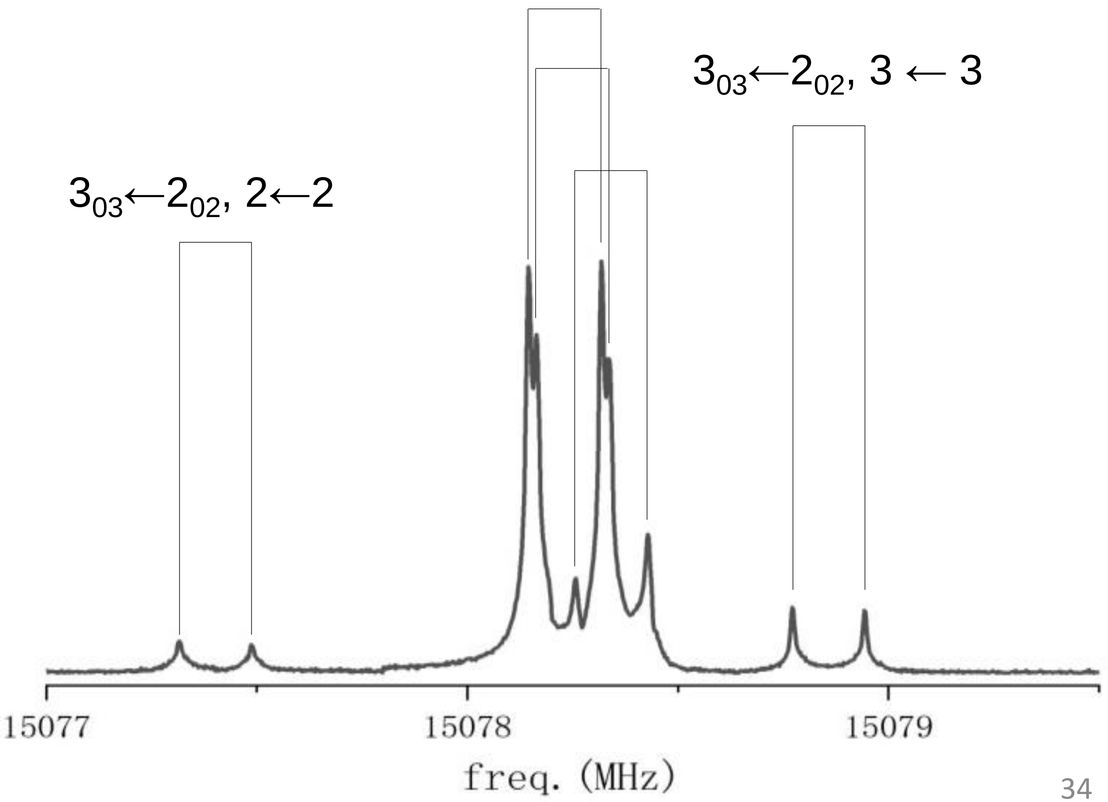
IV. CH_3NCS



A, *B*, *C*: 102100, 2500, 2479 MHz

μ_a, $\mu_{b,}$, μ_c: 3.5,0.6, 0.0 D

Parameter	SPFIT	XIAM
A/MHz	[102100.14]	81071.1931(25)
B/MHz	2532.4445(25)	2532.337(11)
C/MHz	2493.6644(31)	2505.7488(98)
D_J/kHz	0.328(73)	4.113(90)
D_{JK}/kHz	-3899.2(14)	-141.2(17)
Δ_J/kHz	-	1.34(30)
V3/MHz	-	4028.1949(24)
Dpi2J/MHz	-	0.001359(39)



Part 3

Conclusion

Conclusions

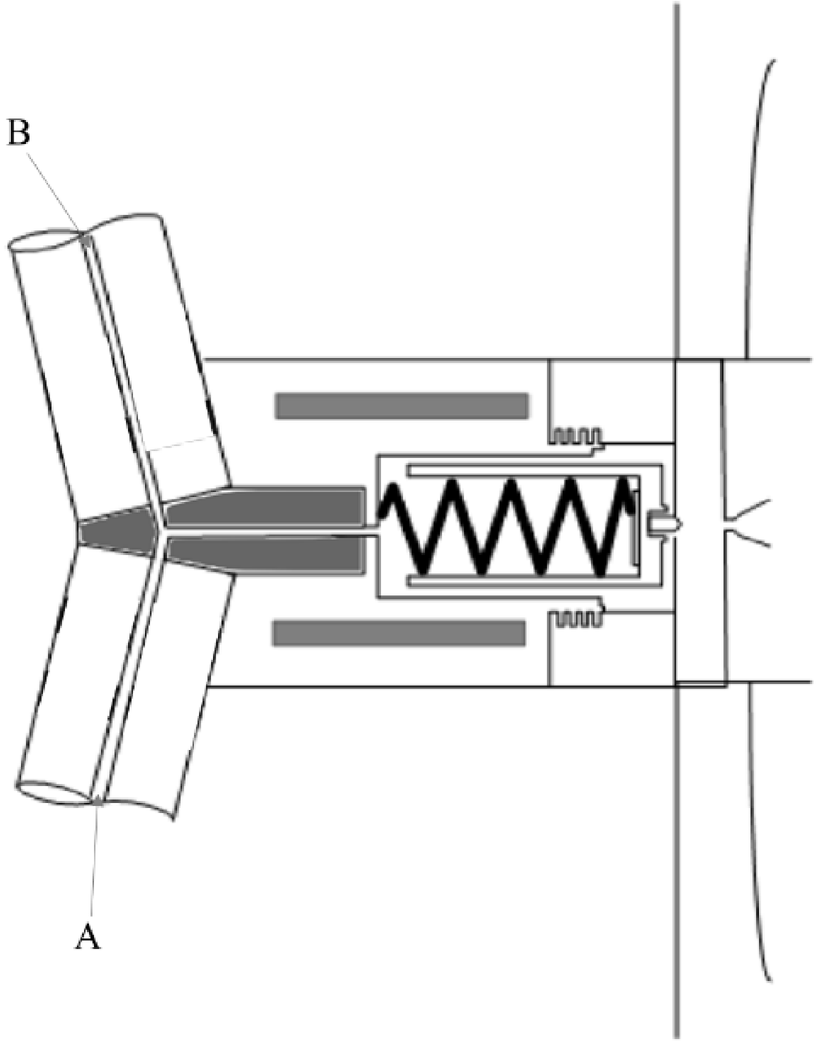
Rotational spectroscopy

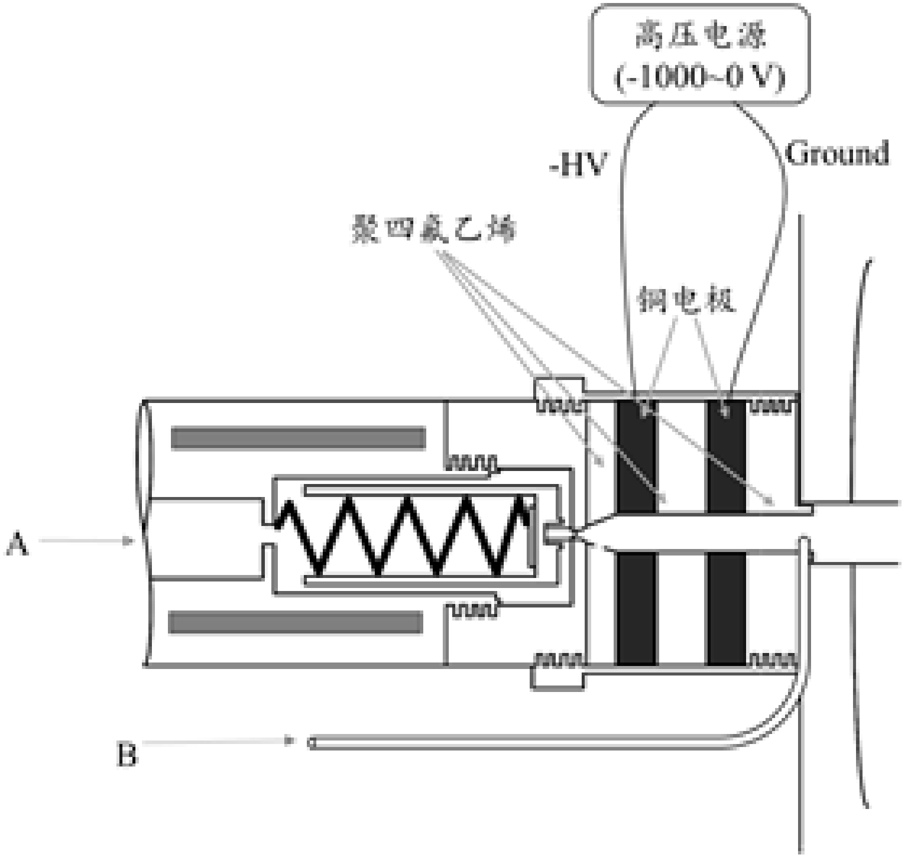
- Sensitive to molecular mass distribution
- Powerful tool to identify molecules in ISM
- Laboratory rotational data is required for detection of new molecules and for identification of new lines of detected molecules

➢ Ongoing Project

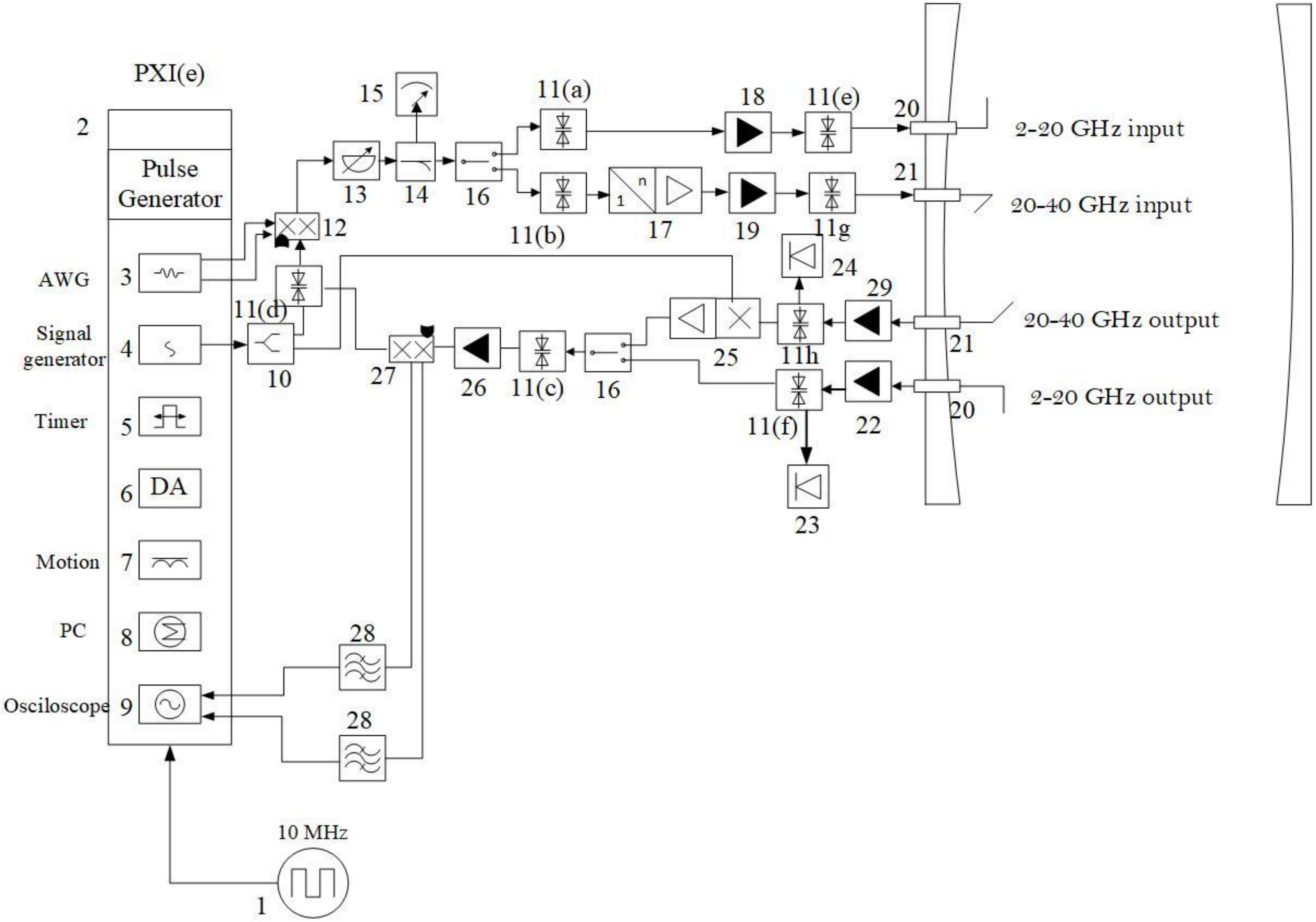
- Electronic discharge nozzle (transient species)
- PJ-FTMW spectrometer (frequency extension up to 40 GHz)
- Room temperature millimeter waveguide cell spectrometer (30-240 GHz)

Update @ DC-discharge

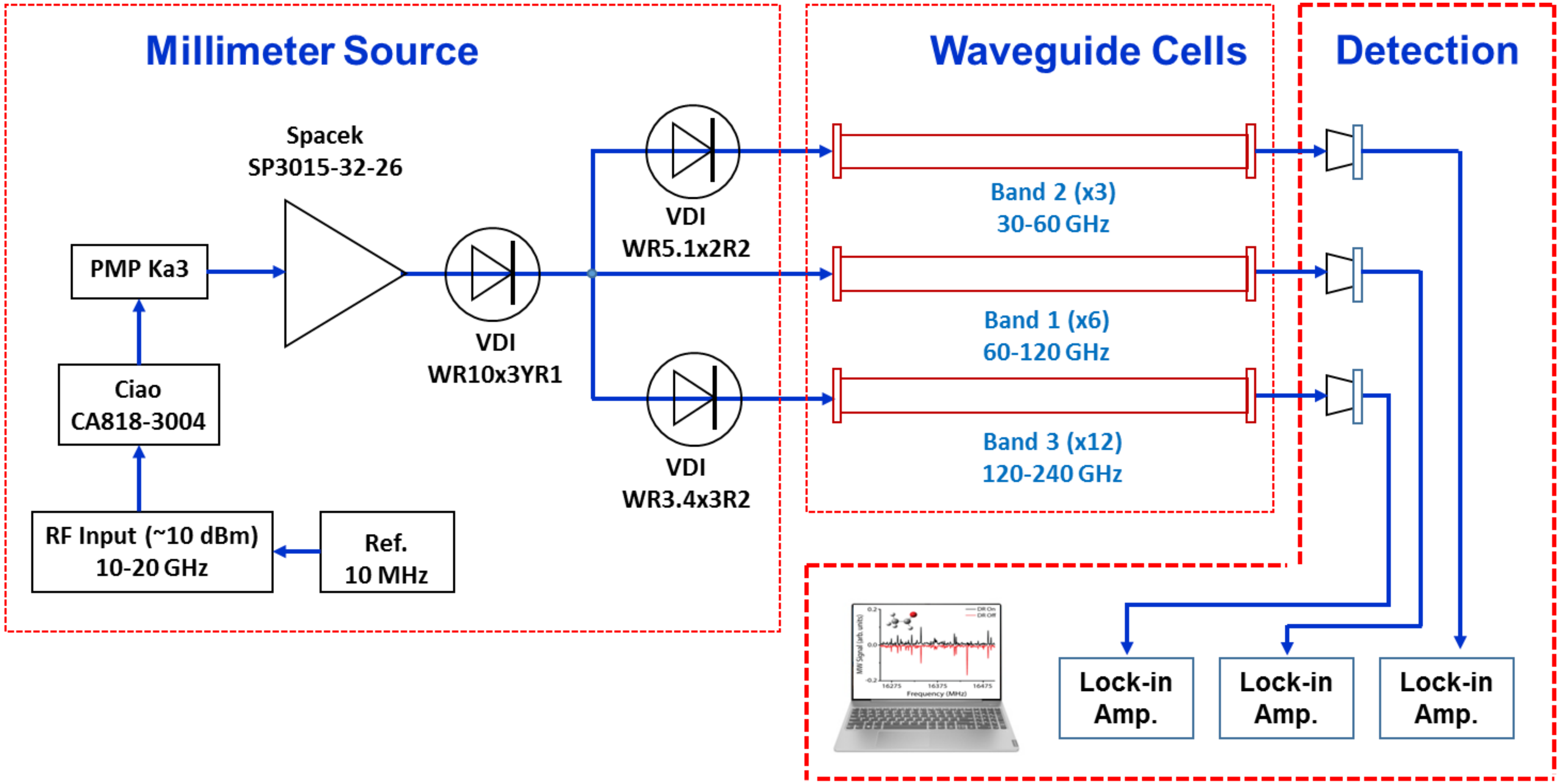




Update@ 20-40 GHz



Update @ Millimeter Spectrometers



Room temperature waveguide cell absorption spectrometer

1. Frequency Covering : 30 – 240 GHz
2. Vibrational exited states
3. High sensitivity

Acknowledgement

- Gottfried-Wilhelm-Leibniz-Universtät, Hannover, Germany
  Prof. J.-U. Grabow
- University of Bologna, Italy
  Prof. W. Caminati, C. Puzzarini
- Scuola Normale Superiore di Pisa, Italy
  Prof. V. Barone, J. Bloino
- Polish Academy of Sciences, Poland
  Prof. Z. Kisiel

NSFC
National Natural Science Foundation of China

CSTC
Chongqing Science and Technology Commission

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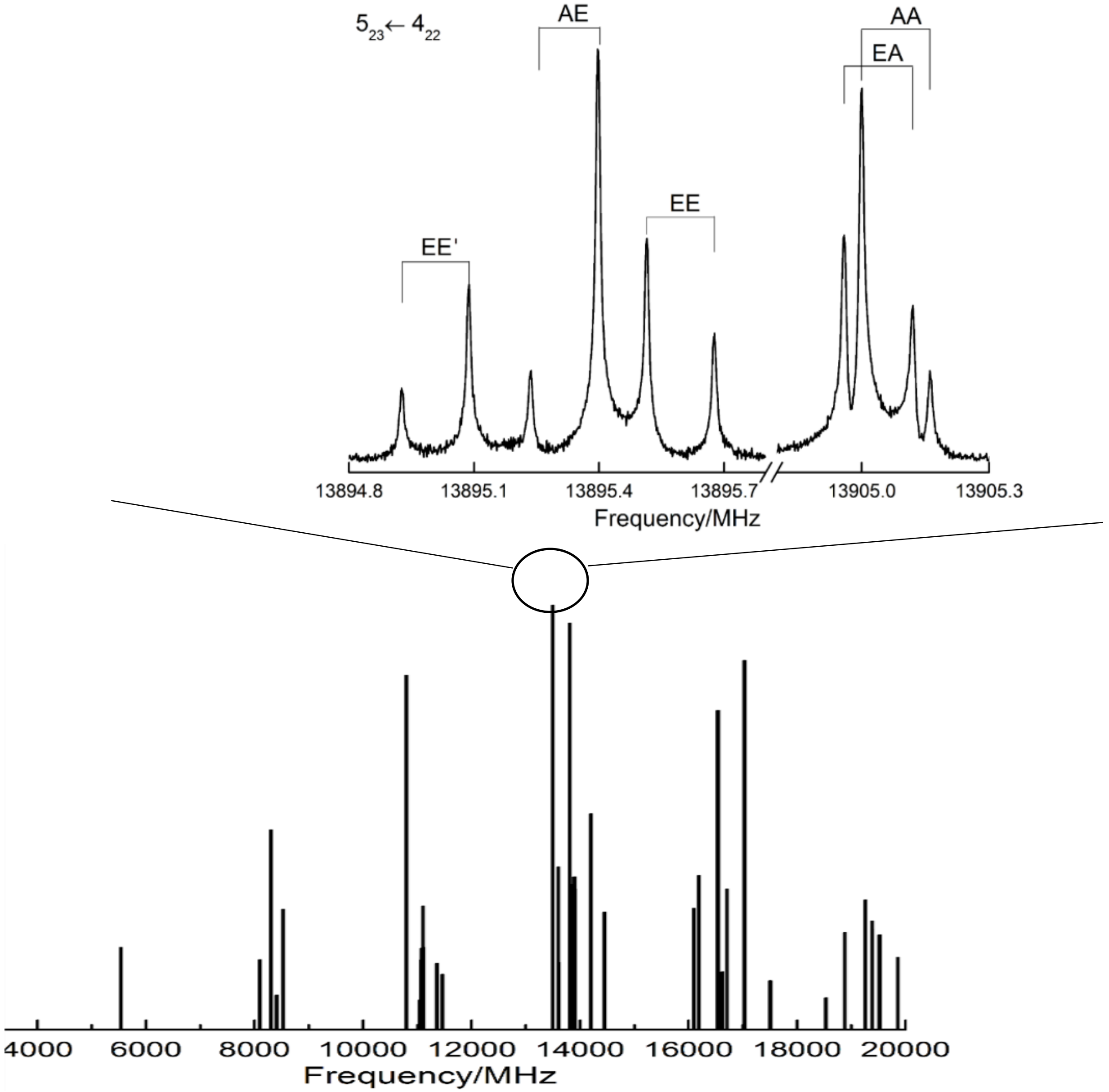
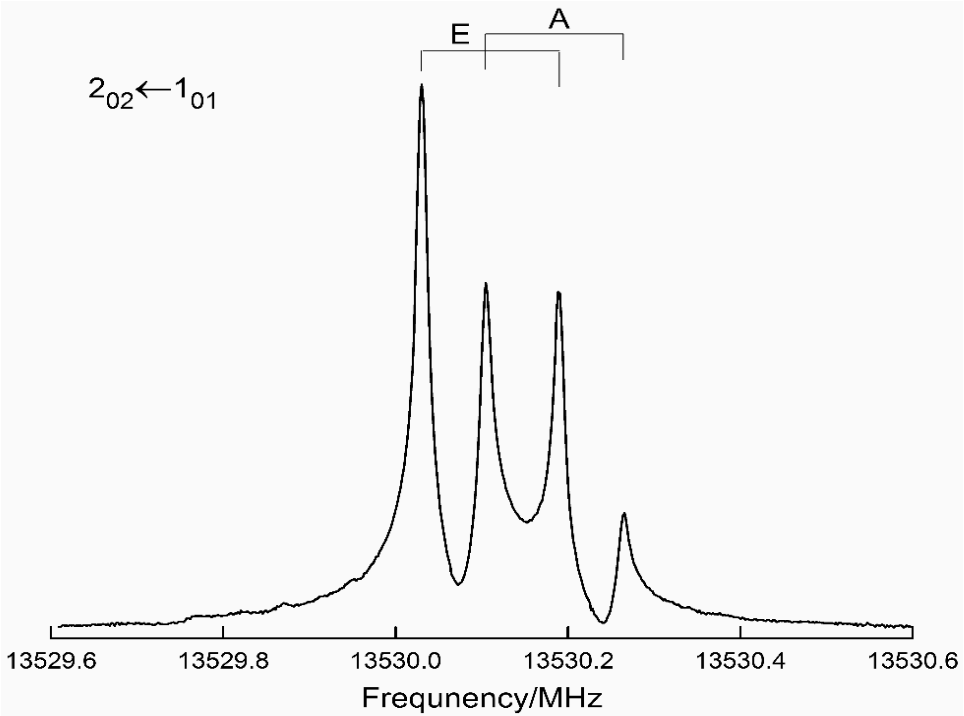
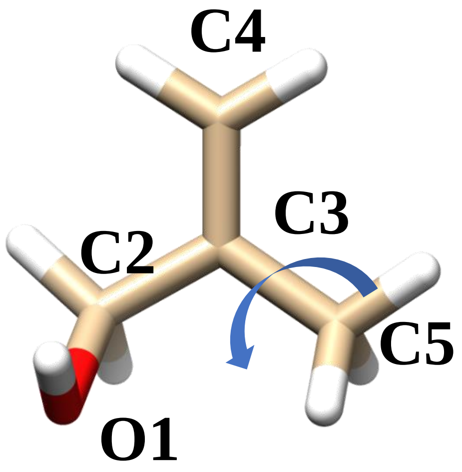
1929

Thank you for your attention!


$5_{23} \leftarrow 4_{22}$
AE
AA
EA
EE
EE'
13894.8
13895.1
13895.4
13895.7
13905.0
13905.3
Frequency/MHz
4000
6000
8000
10000
12000
14000
16000
18000
20000
Frequency/MHz

Methacryl alcohol





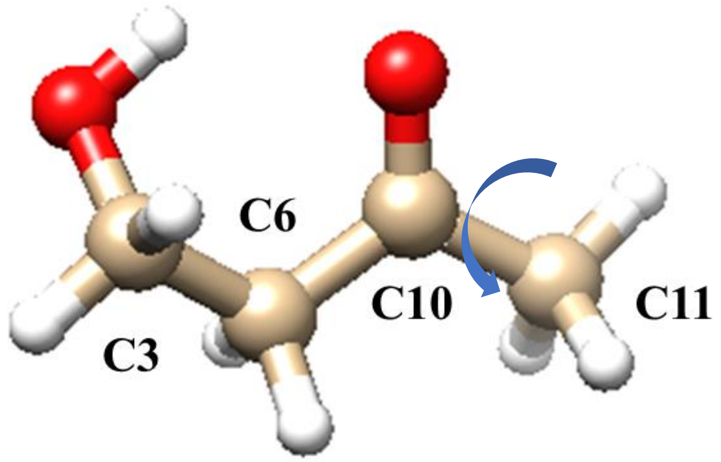
Parent Species

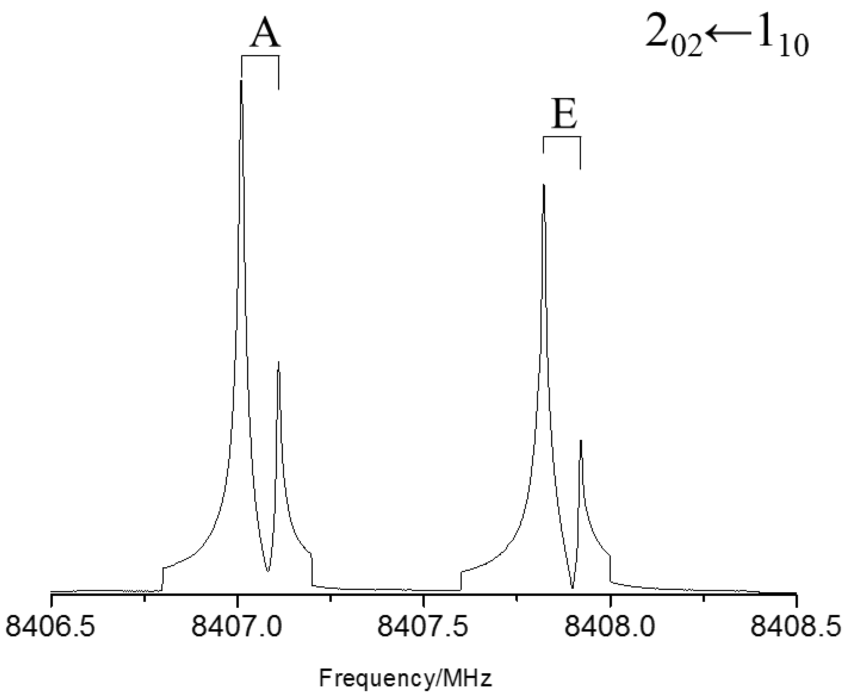
Over rotation		Internal rotation	
A/MHz	7482.831(2)	V_3/cm^{-1}	598(2)
B/MHz	3925.724(2)	*Delta*/rad	1.76(1)
C/MHz	2930.0209(9)	∠(i,a)/ °	100.9(6)
D_J/kHz	0.85(8)	∠(i,b)/ °	11.4(6)
D_{JK}/kHz	13.4(4)	∠(i,c)/ °	86.594(8)
D_K/kHz	-7.2(4)	N	38
d_1/kHz	-0.13(8)	σ/kHz	4.3

^{13}C isotopologues in natural abundance (~1%)

	C2	C3	C4	C5
A/MHz	7430.932(2)	7481.638(2)	7365.901(2)	7281.080(2)
B/MHz	3897.8431(8)	3915.3717(9)	3859.0142(9)	3900.5971(8)
C/MHz	2915.9834(4)	2924.3826(6)	2876.4740(5)	2884.7245(5)
N	16	16	17	18
σ/kHz	3.3	4.2	3.8	3.4
V_3/cm^{-1}	604(2)	601(3)	598(2)	602(2)

4-Hydroxy-2-butanone





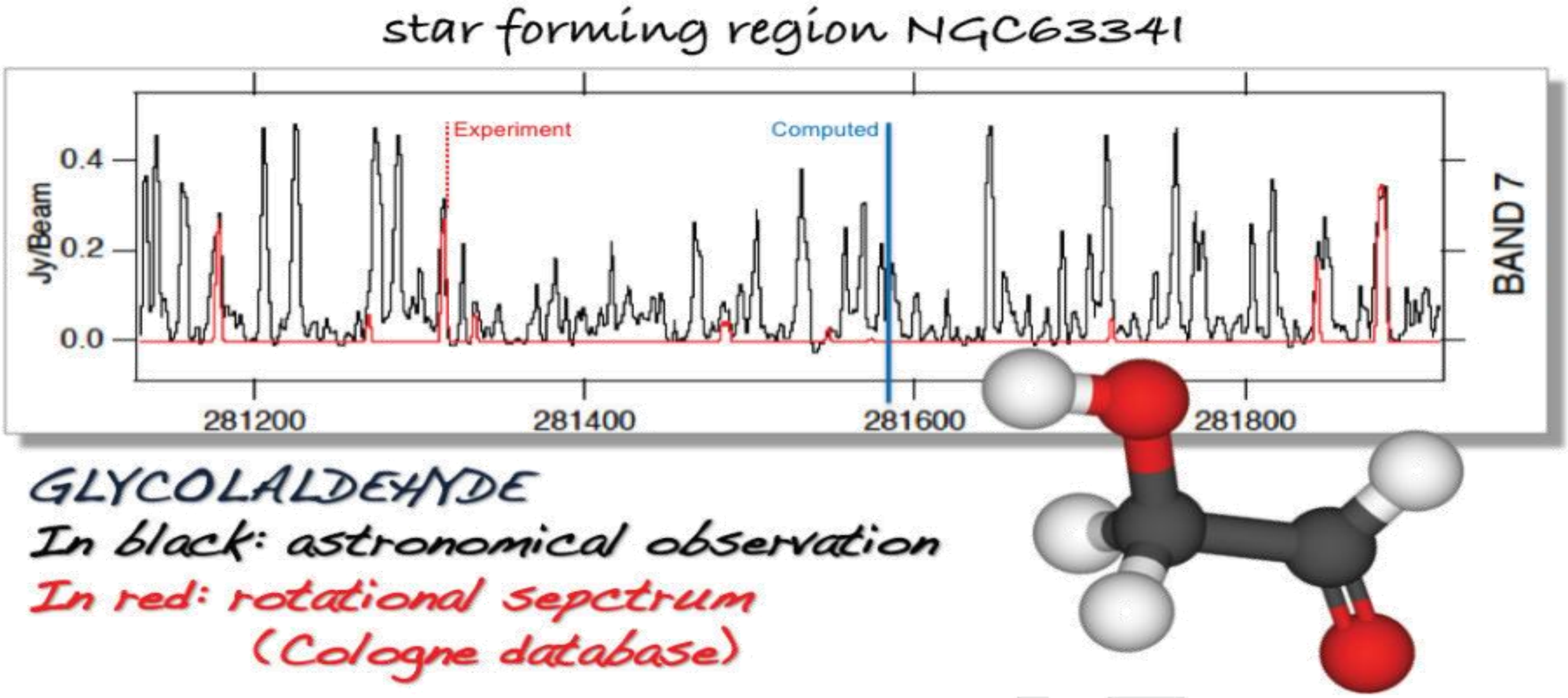
Parent Species

Over rotation		Internal rotation	
A/MHz	7284.365(3)	V_3/cm^{-1}	206.721(1)
B/MHz	2286.331(2)	ε/rad	0.688(5)
C/MHz	1926.799(2)	δ/rad	2.809(1)
D_J/ kHz	0.70(5)	$\angle(i,a)$/°	75.3(1)
N	76	$\angle(i,b)$/°	78.0(1)
		$\angle(i,c)$/°	160.92(6)

^{13}C isotopologues in natural abundance (~1%)

	C3	C6	C10	C11
A/MHz	7236.890(6)	7177.468(3)	7283.889(3)	7267.730(4)
B/MHz	2261.383(1)	2286.2526(7)	2277.805(1)	2230.762(1)
C/MHz	1908.334(1)	1919.2207(6)	1920.7442(9)	1886.941(1)
V_3/cm^{-1}	206.7450(1)	206.54042(7)	206.8607(1)	206.8461(2)
N	16	13	16	17

Laboratory Rotational Spectroscopy

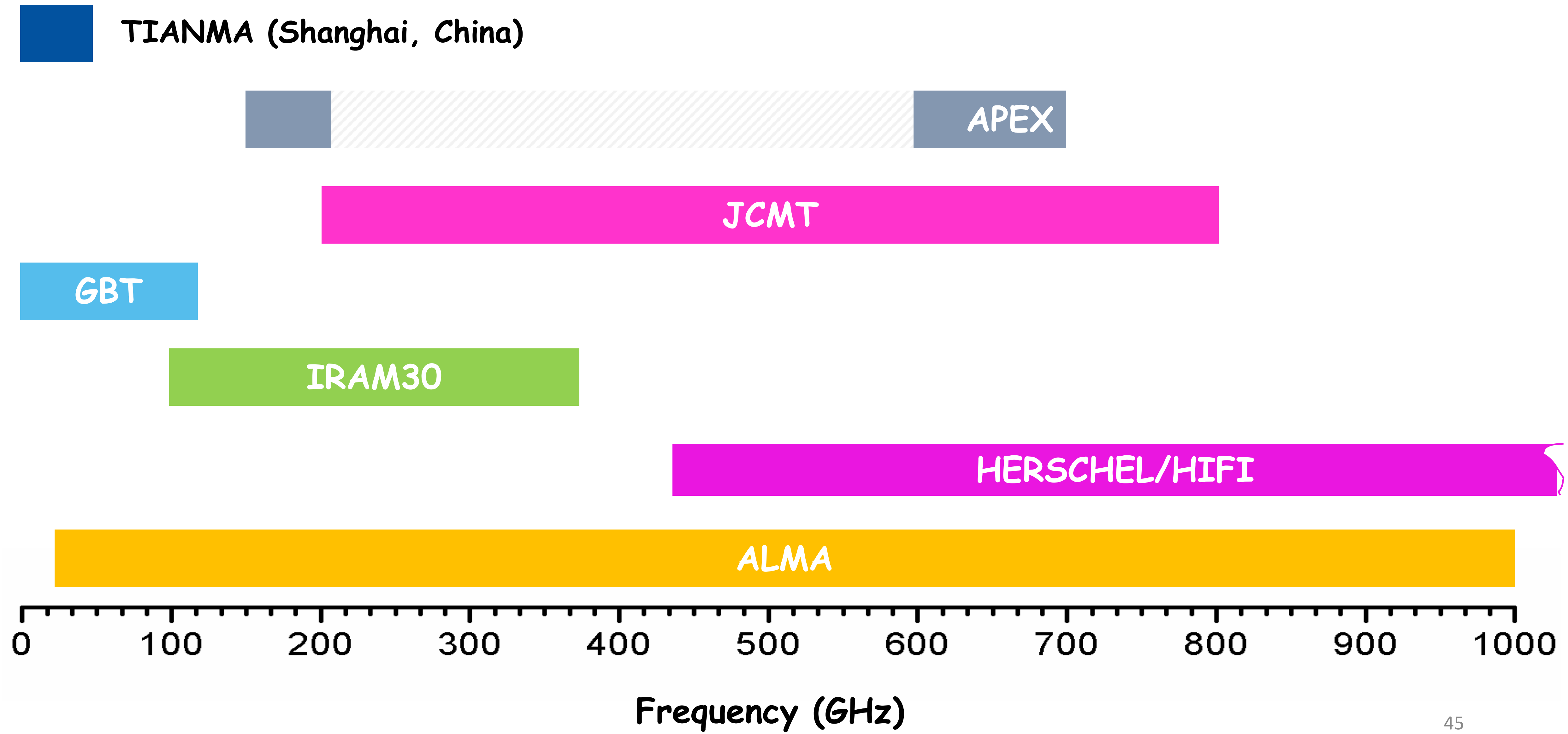


Radiotelescope observation requires the accuracy of transition frequency better than 100 kHz.

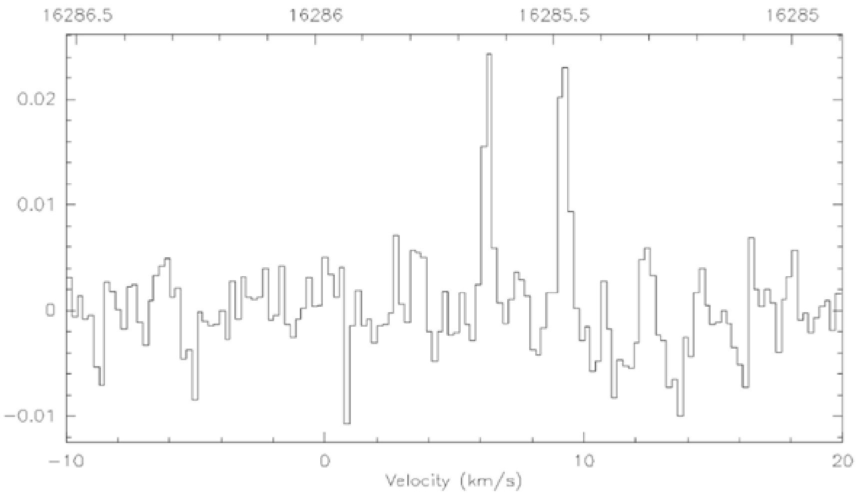
Computational accuracy > MHz (and gets worse with J increasing).

Phys Life Rev 2020, 32， 59-94

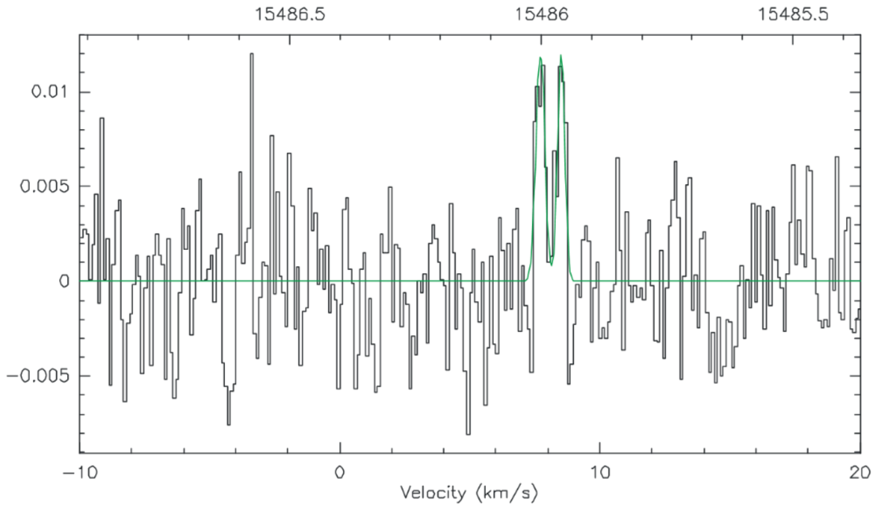
Observation with Radio telescopes



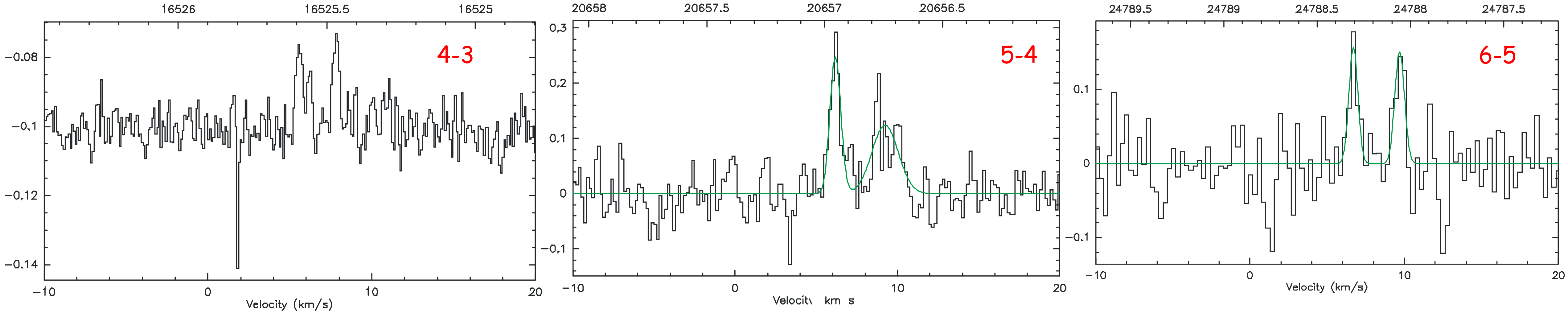
Observation with Radio telescopes



CH_3C_4H



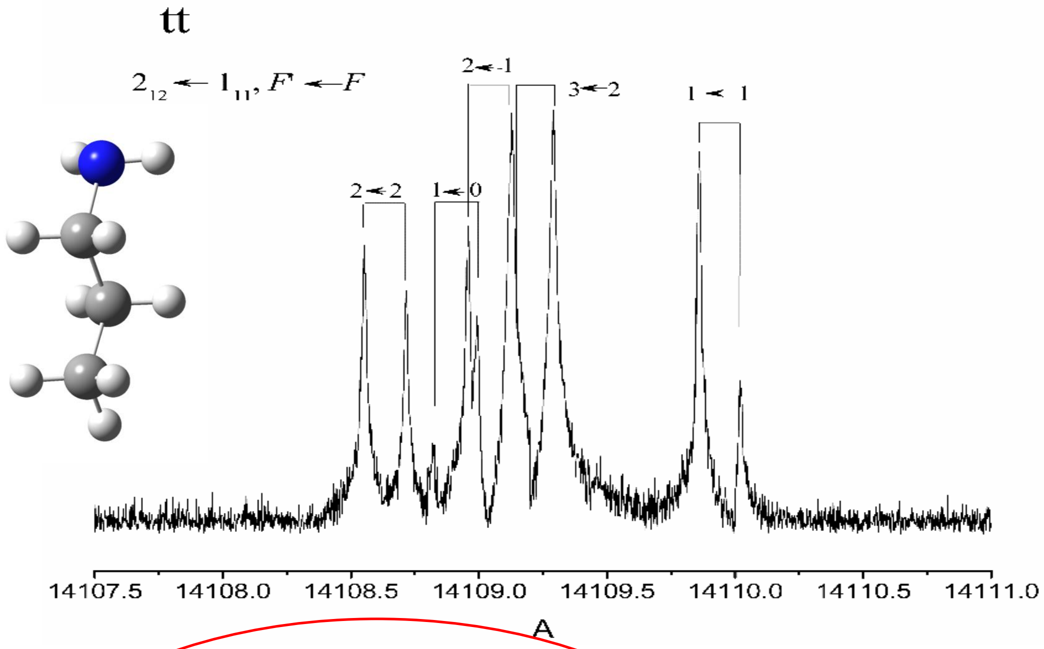
CH_2CCHCN

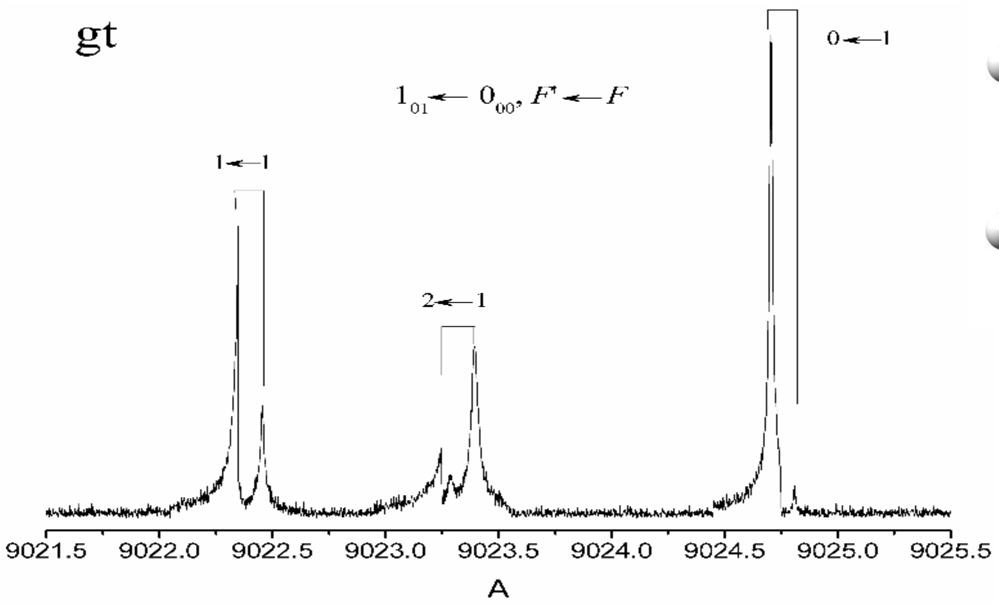


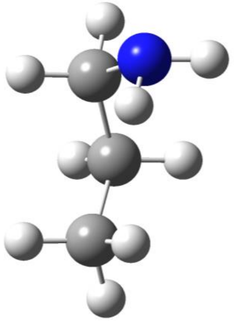
CH_3C_3N

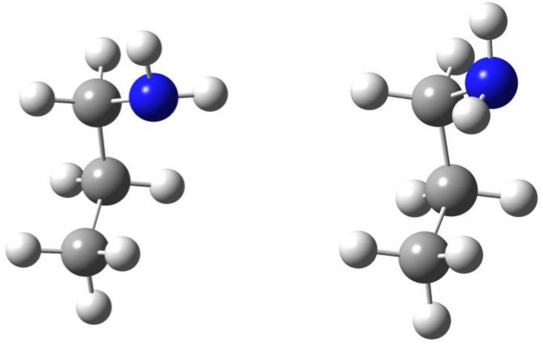
Tianma towards TMC-1

n-Propylamine









ggs 114 cm^{-1} **ggd** 145 cm^{-1}

Parameters	tt	gt
A(MHz)	24546(33)	13760.834(3)
B(MHz)	3687.5373(9)	4873.885(2)
C(MHz)	3473.8709(9)	4149.318(2)
1.5χ_{aa}(MHz)	-0.648(7)	-4.718(7)
0.25(χ_{bb}-χ_{cc}) (MHz)	-0.790(3)	0.376(3)
D_J(kHz)		4.2(1)
D_{JK}(kHz)		17.6(4)
d_1(kHz)		-1.48(9)
σ(kHz)	5.5	2.6
N	19	29

CQU+UNBO+NSP+MPIfR+SHAO

J. Phys. Chem. A **2020**, *124*, 1372-1381.