Rotational Spectroscopy
A Laboratory Perspective

2024 COST / DAN School

Sandra Brünken

FELIX Laboratory, Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Dutch Astrochemistry Network III

EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

NanoSpace

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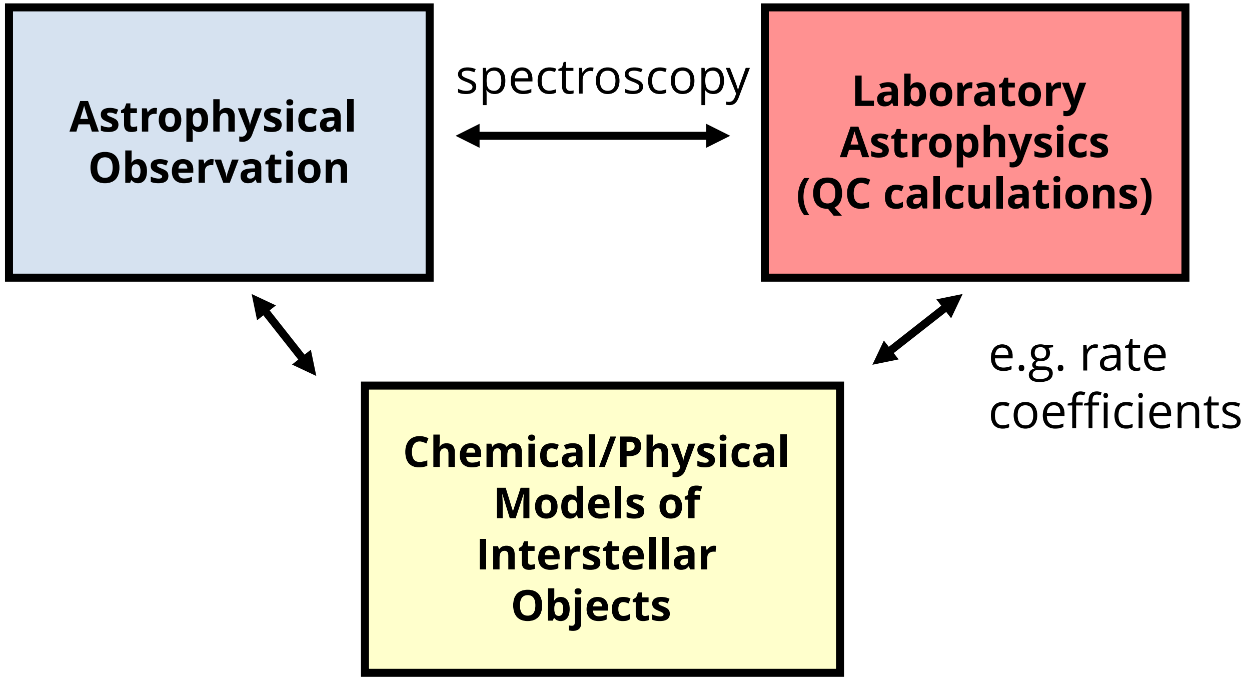
Origins Center

HFML Science in High Magnetic Fields

FELIX Free Electron Lasers for Infrared eXperiments

Radboud University

The Golden Triangle of Astrochemistry



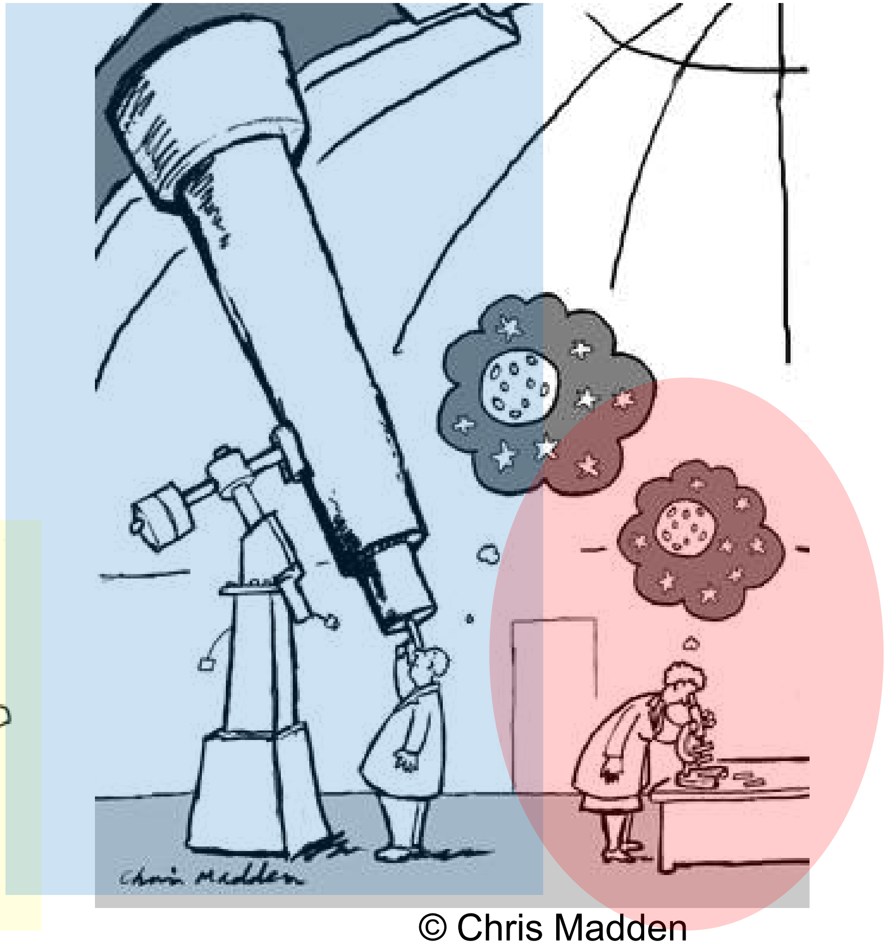
Astrophysical Observation

spectroscopy

Laboratory Astrophysics (QC calculations)

e.g. rate coefficients

Chemical/Physical Models of Interstellar Objects



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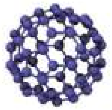
This Lecture – Laboratory Rotational Spectroscopy

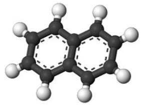
- How do we measure (rotational) molecular spectra in the laboratory?
- How do we analyse these spectra?
- Why do we do this? What do molecules tell us about space?

Molecular Complexity in Space (www.cdms.de)

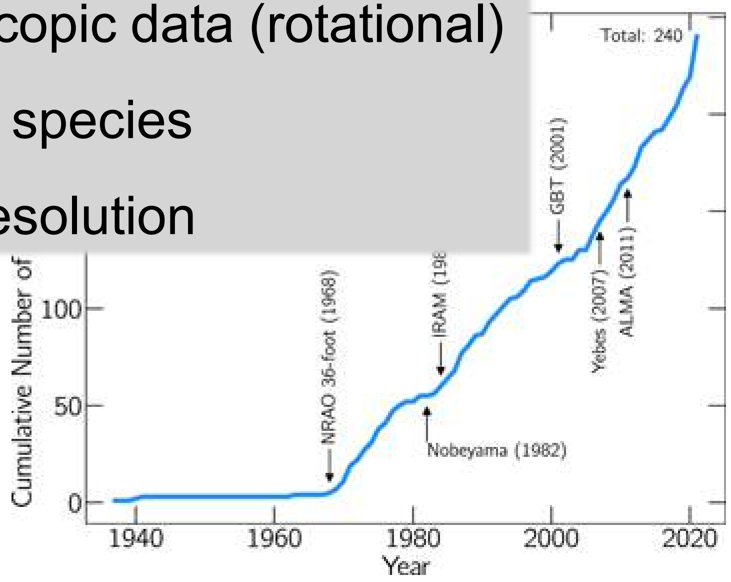
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms
H2	C3 *	c-C3H	C5 *	C5H	C6H	CH3C3N	CH3C4H
AlF	C2H	l-C3H	C4H	l-H2C4	CH2CHCN	HC(O)OCH3	CH3CH2CN
AlCl	C2O	C3N	C4Si	C2H4*	CH3C2H	CH3COOH	(CH3)2O
C2**	C2S	C3O	l-C3H2	CH3CN	HC5N	C7H	CH3CH2OH
NO	MgCN	H2CS	SiH4 *	H2CCNH ?	c-C3HCCH	HC5NH+	H2C3HCCH
NS	MgNC	H3O+	H2COH+	C5N–	l-H2C5	CH2CHCCH	HOCHCHCHO
NaCl	N2H+	c-SiC3	C4H–	HNCHCN	MgC5N	MgC6H	
OH	N2O	CH3 *	HC(O)CN	SiH3CN	CH2C3N	C2H3NH2	
O2	HCP	HONO	H2CsS				
CF+	CCP	MgC2H	C4S				
SiH ?	AlOH	HCCS	HC(O)SH				
PO	H2O+	HNCN	HC(S)CN				
AlO	H2Cl+	H2NC	HCCCO				
OH+	KCN	HCCS+					
CN–	FeCN						
SH+	HO2						
SH	TiO2						
HCl+	C2N						
TiO	Si2C						
ArH+	HS2						
NO+ ?	HCS+						
NS+	HSC						
HeH+	NCO						
PO+	CaNC						

10 atoms	11 atoms	12 atoms	>12 atoms
CH3C5N	HC9N	c-C6H6 *	HC11N
(CH3)2CO	CH3C6H	n-C3H7CN	C60 *
(CH2OH)2	C2H5OCHO	i-C3H7CN	C70 *
CH3CH2CHO	CH3OC(O)CH3	C2H5OCH3	C60+ *
	CH3C(O)CH2OH	1-c-C5H5CN	c-C6H5CN
	c-C5H6	2-c-C5H5CN	HC11N
	HOCH2CH2NH2	CH3C7N	1-C10H7CN
	H2CCCHC4H	n-C3H7OH	2-C10H7CN
		i-C3H7OH	c-C9H8
			1-c-C5H5CCH
			2-c-C5H5CCH
CH3CHCHCN			c-C5H4CCH2
CH3C(CN)CH2			2-C9H7CN
CH2CHCH2CN			





- Molecular transitions probe: chemical composition
  physical conditions
  (temperature, densities, ...)
- Laboratory needs: spectroscopic data (rotational)
  for many species
  at high resolution



Inga Kamp

> 320 total
~ 70 % organic
~ 15 % ions

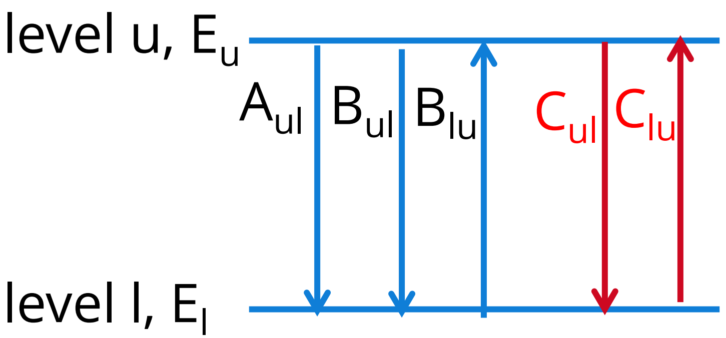
- www.cdms.de
- McGuire, ApJS 259 (2022) 30

Most species detected by their rotational lines!

Why rotational spectroscopy?

- typical kinetic temperatures in molecular clouds: **10 – 150 K**
- often collisions dominate over radiation

critical density n_{crit}: $\frac{C_{ul}}{A_{ul}} = 1$



Boltzmann population:

Probability to be in state i

$$p_i = \frac{e^{-\frac{E_i}{kT}}}{\sum_j e^{-\frac{E_j}{kT}}} = \frac{e^{-\frac{E_i}{kT}}}{U(T)}$$

$$\frac{n_i}{n} = g_i \frac{e^{-\frac{E_i}{kT}}}{U(T)}$$

Relative number density in state i

LTE: local thermal equilibrium

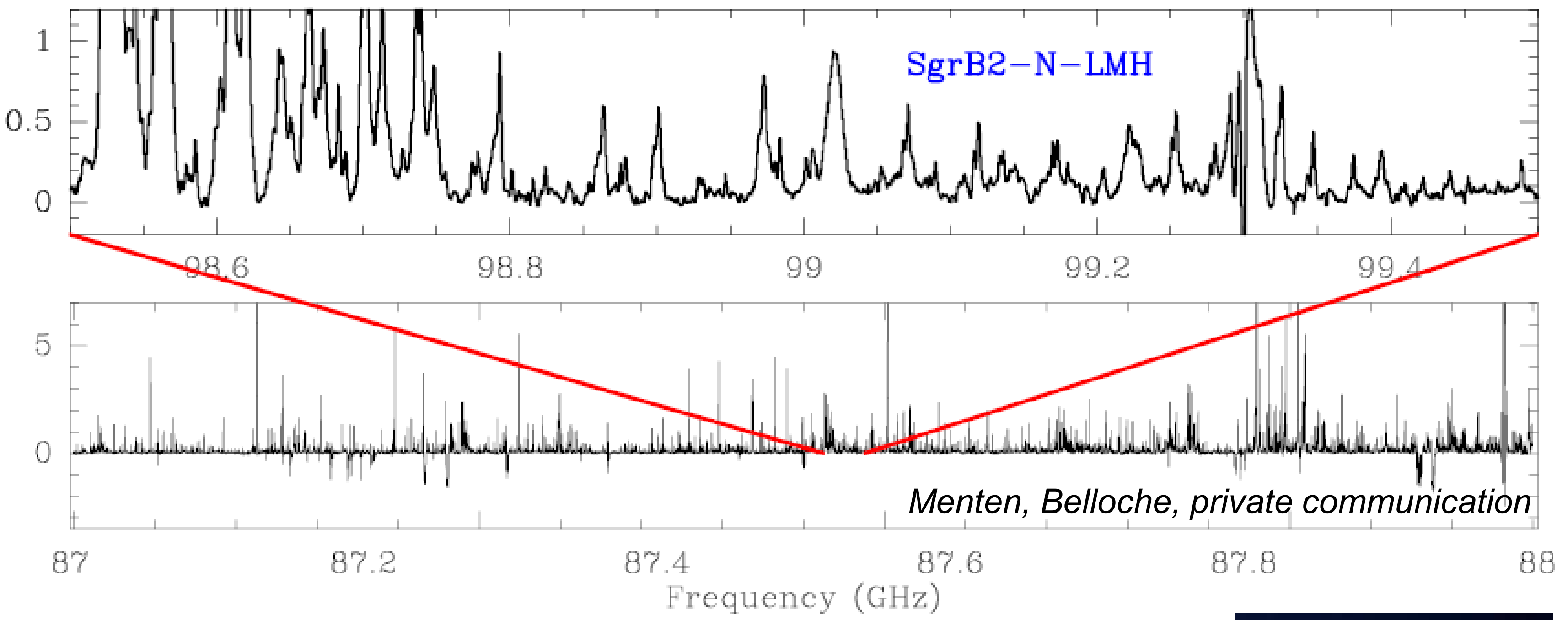
- Typical **rotational** constants: 0.03 – 30 cm^{-1} (1 – 1000 GHz)
  E ≈ **0.05 – 50 K** (via E=kT)

- Typical vibrational energies: 100 – 3000 cm^{-1}
  E ≈ **150 – 5000 K**

Jacques le Bourlot

Why at “high” resolution?

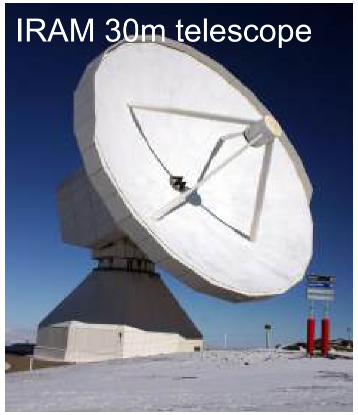
“Large Molecule Heimat”



Menten, Belloche, private communication

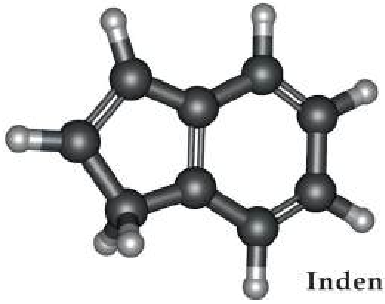
- Line rich sources, often 100 lines per GHz → high chance of wrong assignments

- Observed linewidth $R=\Delta\nu/\nu$ can reach 10^{-6}



IRAM 30m telescope

Recent successes: Detection of hydrocarbon cycles in TMC-1



Indene, c-C_9H_8

- First unambiguous detection of pure polycyclic hydrocarbon (PAHs)
- Found by two groups at the same time!
- Laboratory measurements 1979, 2005, 2021

Alessandra Candian

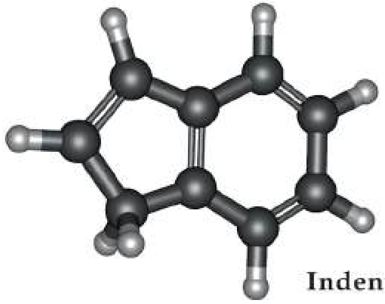
Burkhardt et al., ApJL 2021
https://doi.org/10.3847/2041-8213/abfd3a

100m Green Bank Telescope (USA)

Cernicharo et al., A&A Lett., 2021
https://doi.org/10.1051/0004-6361/202141156

Yebes 40m telescope (Spain)

Recent successes: Detection of hydrocarbon cycles in TMC-1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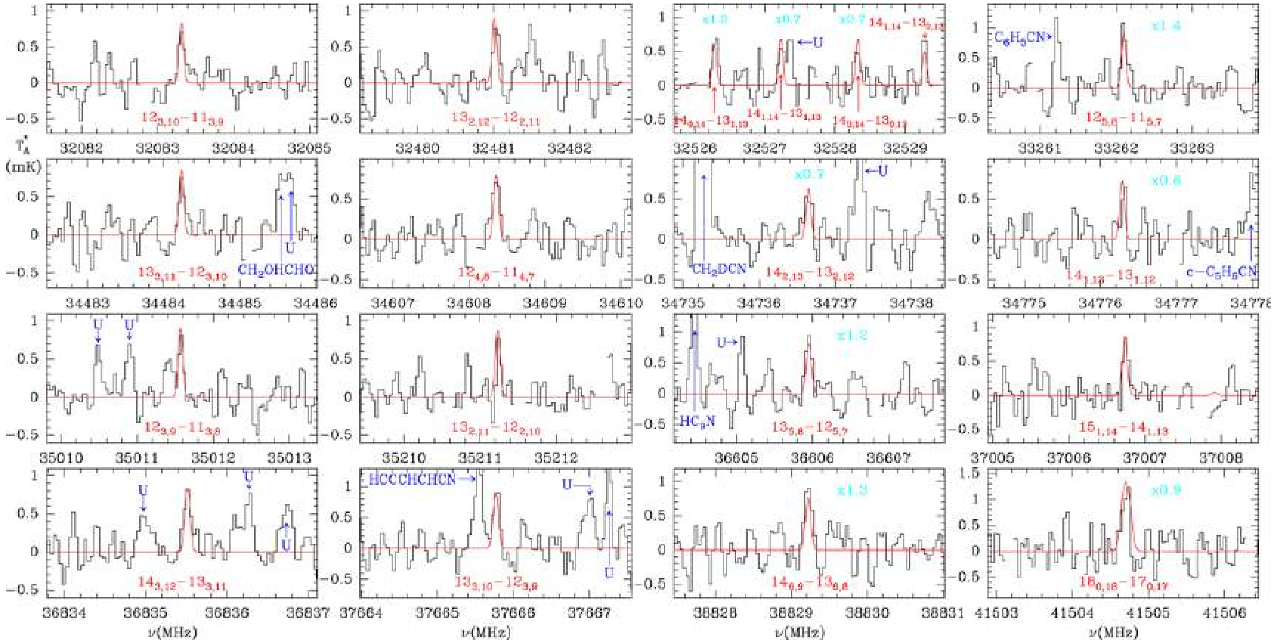
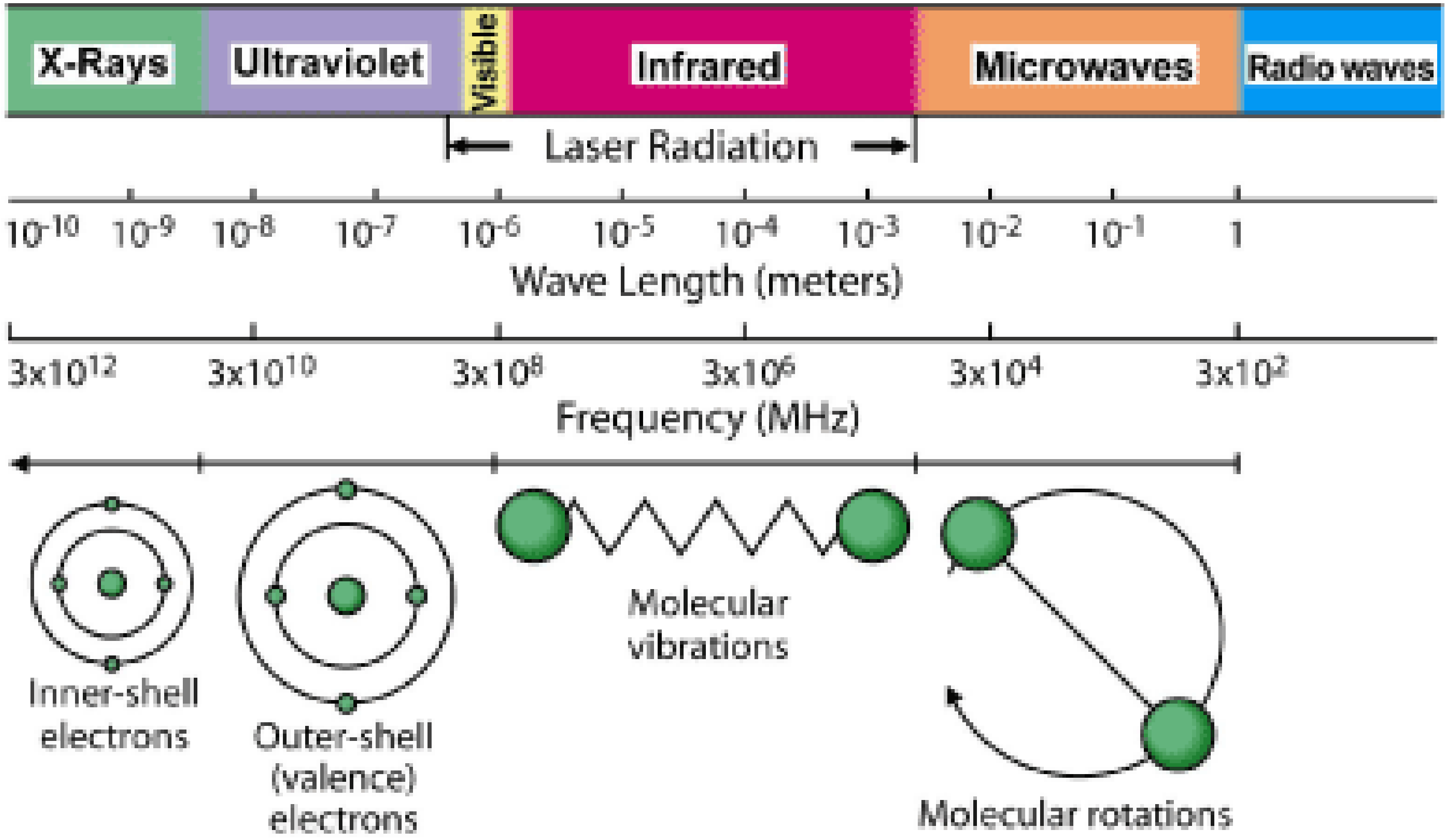


Cernicharo et al., A&A Lett., 2021
https://doi.org/10.1051/0004-6361/202141156

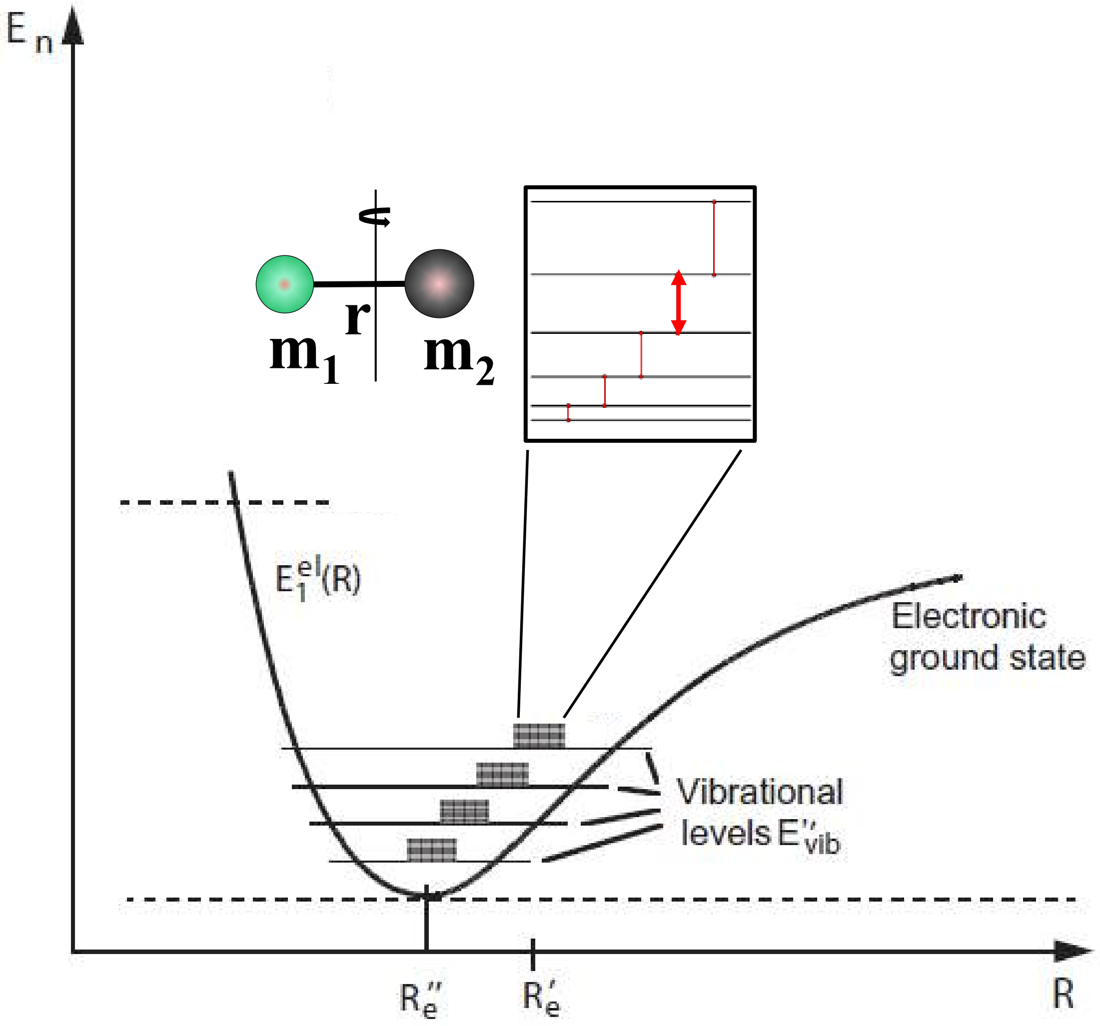

Yebes 40m telescope (Spain)

Spectroscopy is used in all wavelength ranges

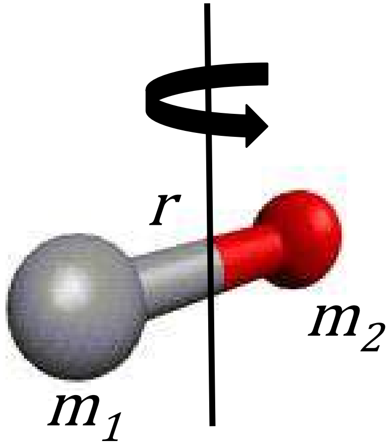


From: https://www.ices-emfsafety.org/electromagnetic-energy/

Rotational Spectroscopy



Rotational Spectroscopy - diatomics



Classical: $$E_{rot} = \frac{1}{2} I\omega^2 = \frac{P^2}{2I}$$

With $$I = \mu r^2 = \frac{m_1 \cdot m_2}{m_1 + m_2} r^2$$ moment of inertia

ω angular velocity around axis
P angular momentum (also called L or J)

Quantum mechanics: $$\hat{\boldsymbol{H}}_{rot}\varphi = E_{rot}\varphi$$

With $$\hat{\boldsymbol{H}}_{rot} = \frac{\hat{\boldsymbol{P}}^2}{2I}$$ rotational Hamiltonian and φ wavefunction (Legendre polynomials)

Solutions $$\boldsymbol{E_{rot}} = \boldsymbol{B} \cdot \boldsymbol{J(J+1)}$$

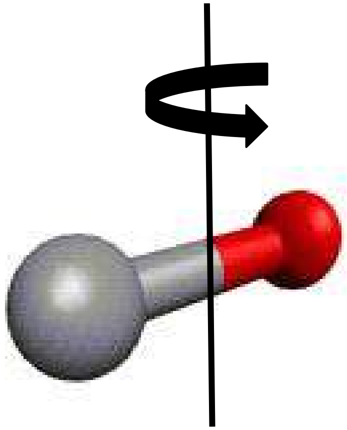
J =0, 1, 2, …
rotational quantum number

$$B = \frac{h^2}{8\pi^2 I}$$ Rotational constant
(in Joule)

↓ $$\boxed{E = h\nu}$$

$$B = \frac{h}{8\pi^2 I}$$ Rotational constant
(in Hz - frequency)

Rotational Spectroscopy - diatomics

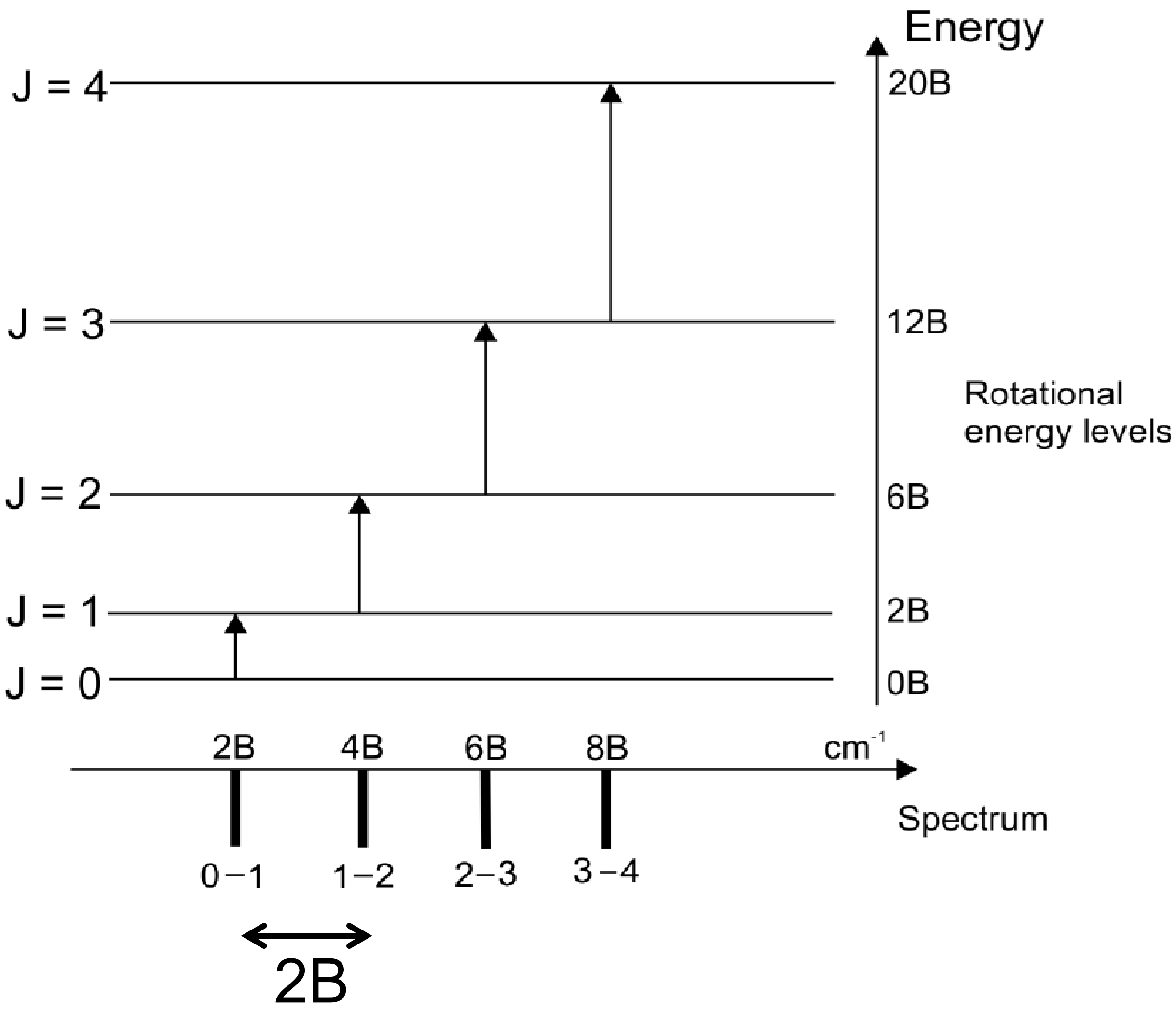


$$E_{\mathrm{rot}} = B \cdot J(J+1)$$

$\Delta J = \pm 1$ selection rule

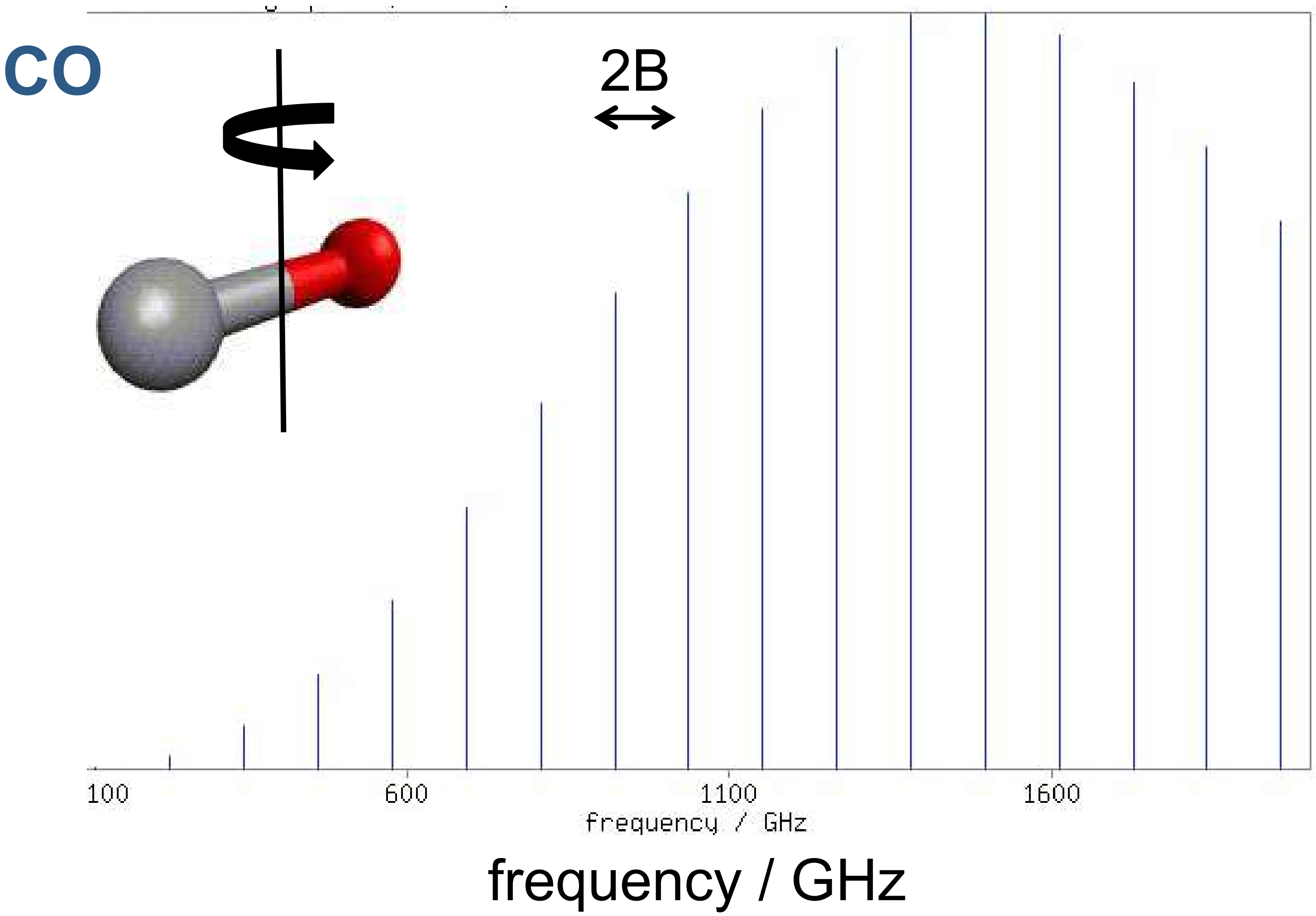
$$\boldsymbol{\Delta E_{\mathrm{rot}} = 2B(J+1) = h\nu}$$

rotational transition frequencies

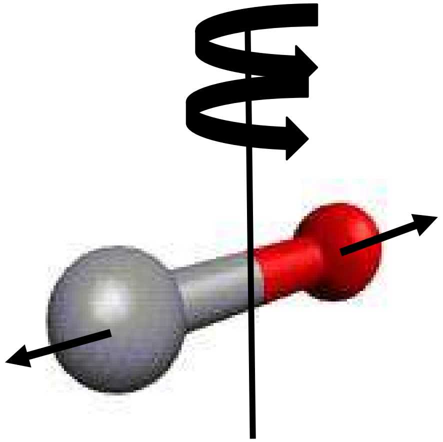


Rotational Spectroscopy - diatomics

<u>Rotation:</u> frequency $\nu = \Delta E / h$ [GHz, THz]



Rotational Spectroscopy – non-rigid rotor



Centrifugal distortion: a molecule in a high rotational quantum state is "stretched"

Q: What consequence does this have on the rotational transitions?

→ $\boldsymbol{r}$ **and** $\boldsymbol{I}$ **change!**

Quantum mechanical non-rigid rotor:

$$\widehat{\boldsymbol{H}}_{rot} = \frac{\widehat{\boldsymbol{P}}^2}{2I} + O(\widehat{\boldsymbol{P}}^n)$$

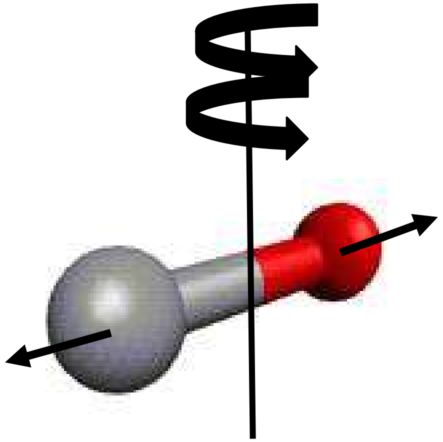
$$E_{rot} = B \cdot J(J+1) - D \cdot J^2\,(J+1)^2 \qquad (+\mathrm{H} \cdot J^3\,(J+1)^3 + \cdots)$$

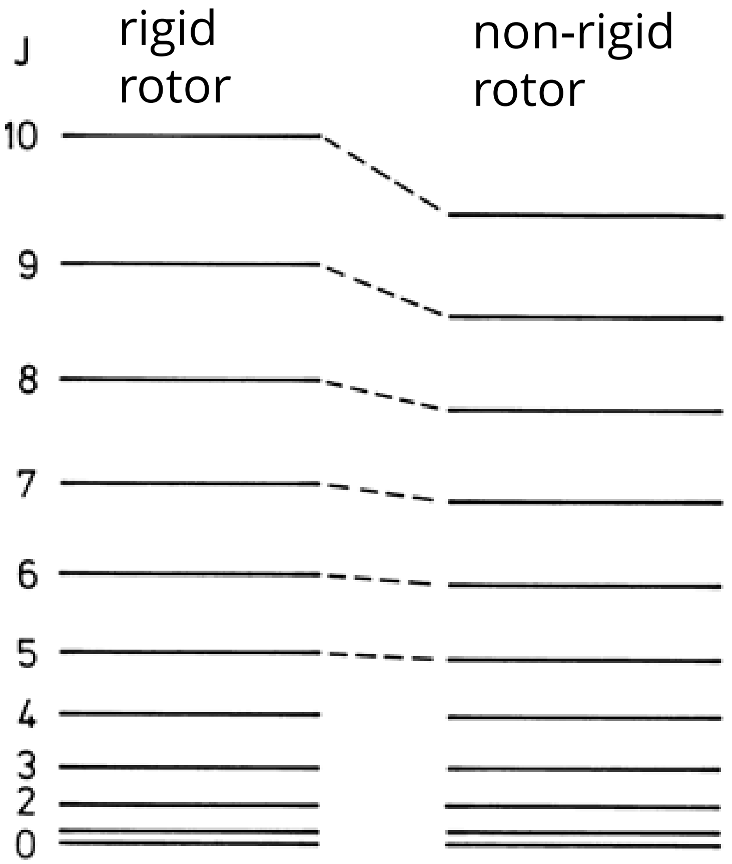
centrifugal distortion constant

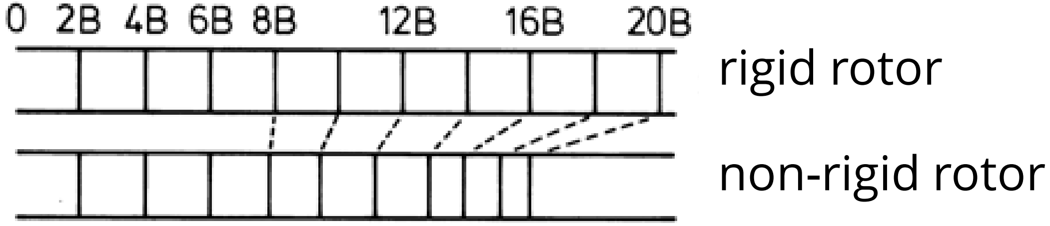
"effective Hamiltonian"

also to deal with asymmetry, fine-structure, hyperfine structure

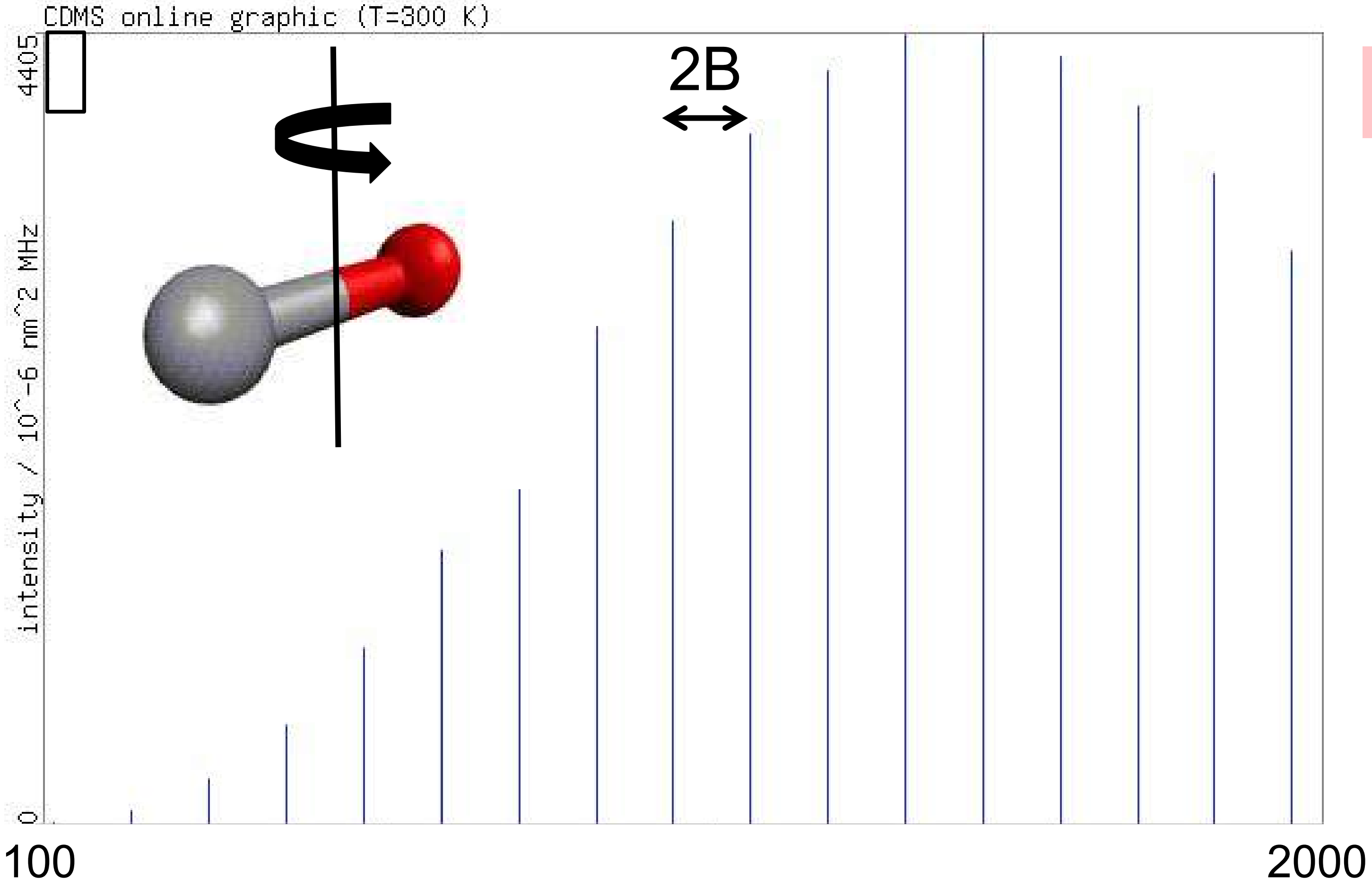
Rotational Spectroscopy – non-rigid rotor







Levels of complexity: isotopic species



frequency / GHz

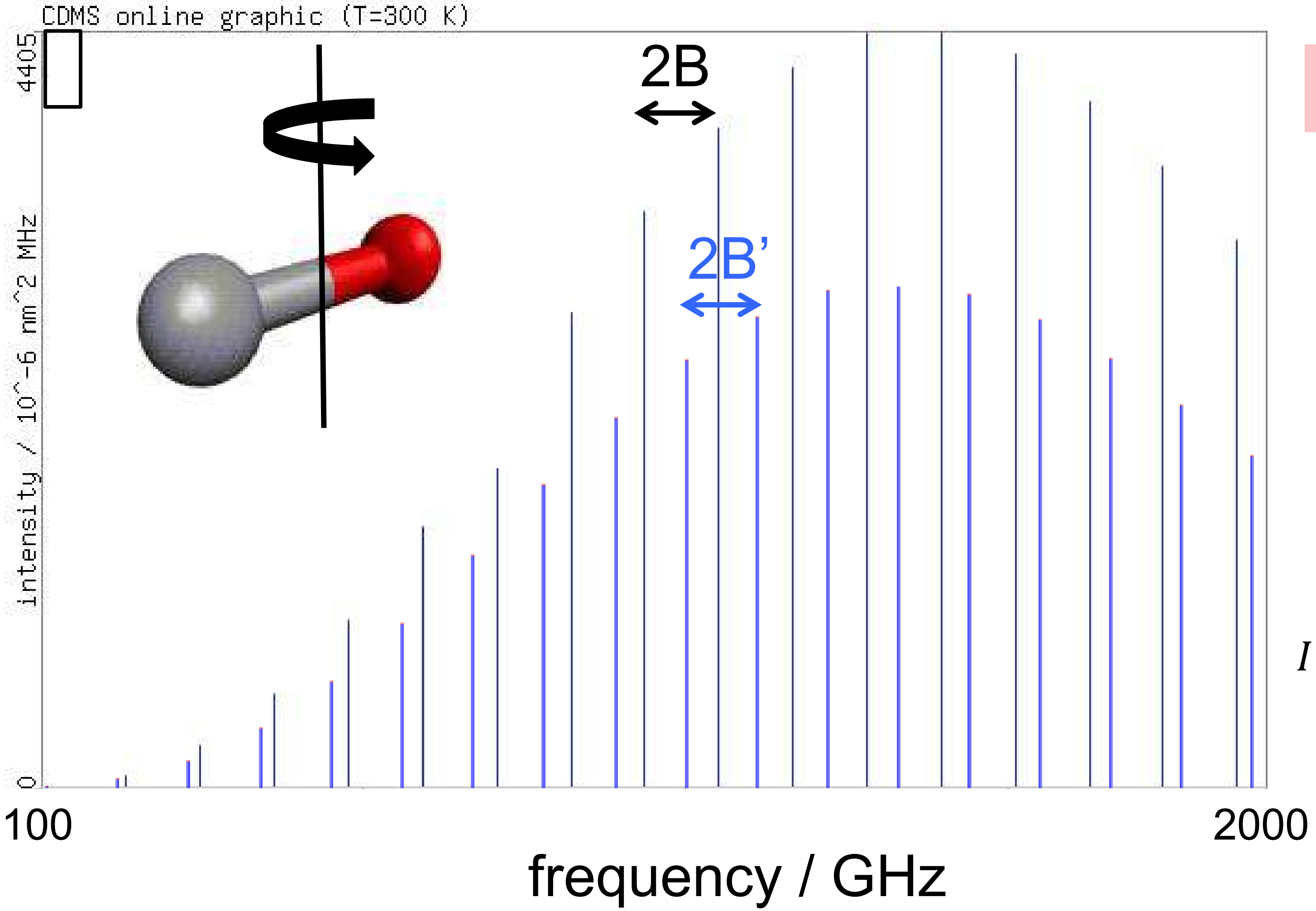
CO & ^{13}CO ??

$$E_{rot} \approx BJ(J+1)$$

$$B = \frac{h}{8\pi^2 I}$$

Levels of complexity: isotopic species

And what if the molecule vibrates?



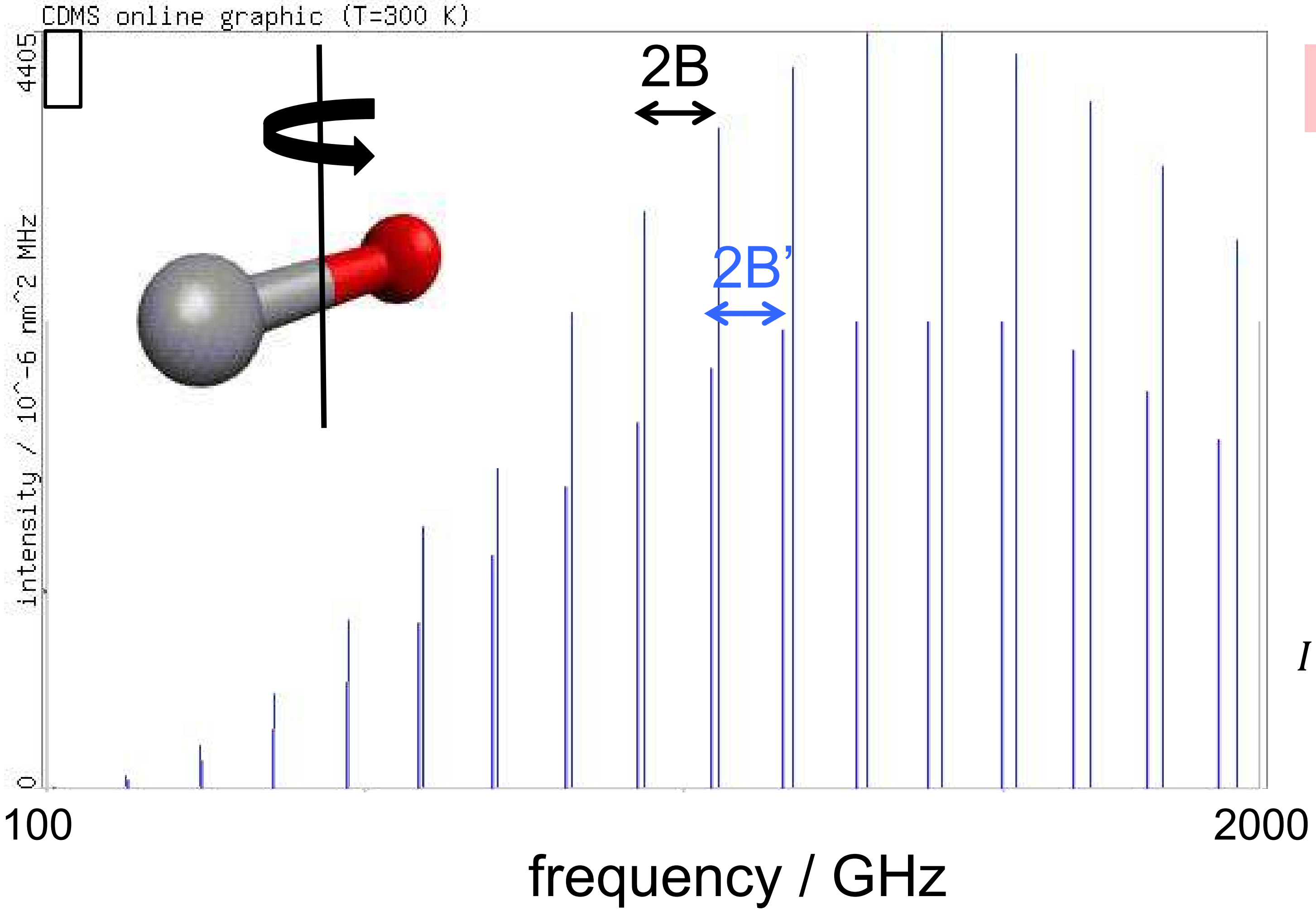
CO & ^{13}CO

$$E_{rot} \approx BJ(J+1)$$

$$B = \frac{h}{8\pi^2 I}$$

$$I = \mu r^2 = \frac{m_1 \cdot m_2}{m_1 + m_2} r^2$$

Levels of Complexity: vibrational excitation



CO & CO vib

$$E_{rot} \approx BJ(J+1)$$

$$B = \frac{h}{8\pi^2 I}$$

$$I = \mu r^2 = \frac{m_1 \cdot m_2}{m_1 + m_2} \boldsymbol{r}^2$$

So what to do with this?

If you know B (and D) you can calculate the rotational spectrum!

Tutorial!

or

If you know a rotational frequency (and the corresponding $J \rightarrow J+1$)

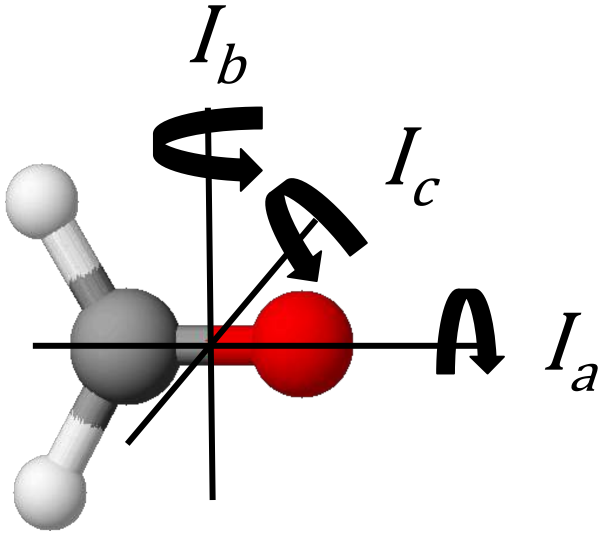
you can calculate B (and D)
and then the full rotational spectrum!

But not all molecules are diatomics (or linear)!

General case rotating molecule

$$E_{rot} = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

Principal axes *a, b, c*
with $I_a \leq I_b \leq I_c$ (convention)



- Linear molecule: $I_a = 0, I_b = I_c$ (same as diatomic)
- Symmetric top: $I_a = I_b < I_c$ (oblate)
  $I_a < I_b = I_c$ (prolate)
- Spherical top: $I_a = I_b = I_c$
- Asymmetric top: $I_a < I_b < I_c$

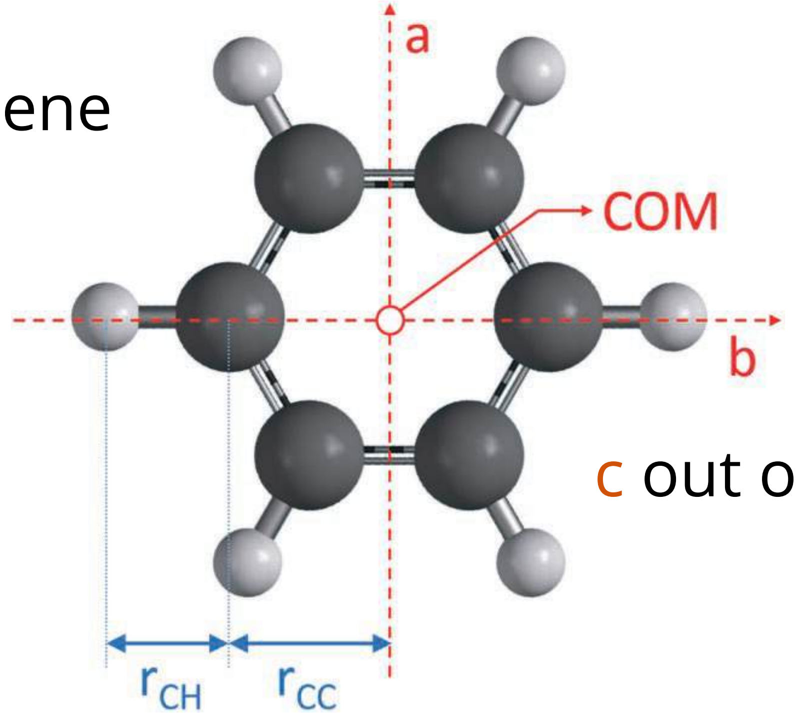
More difficult to calculate rotational spectra!

Symmetric Rotors

- Symmetric top: $I_a < I_b = I_c$ prolate
  $I_a = I_b < I_c$ oblate

Which one is a prolate, which one an oblate rotor?

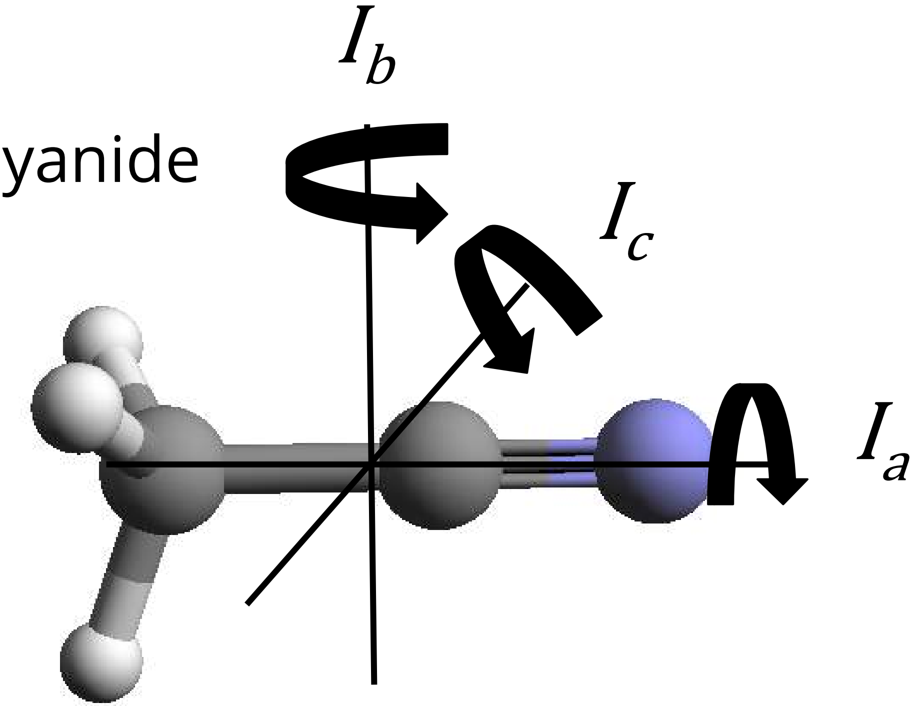
benzene



c out of plane

oblate

methyl cyanide



prolate

Symmetric Rotors

- Symmetric top: $I_a < I_b = I_c$ prolate, e.g., CH_3CN
  $I_a = I_b < I_c$ oblate, e.g., NH_3, benzene

$$\widehat{\boldsymbol{H}}_{rot} = \frac{\widehat{\boldsymbol{P}}_a^2}{2I_a} + \frac{\widehat{\boldsymbol{P}}_b^2}{2I_b} + \frac{\widehat{\boldsymbol{P}}_c^2}{2I_c}$$

Prolate case (oblate analogue): $\widehat{\boldsymbol{H}}_{rot} = \frac{1}{2I_a}\widehat{\boldsymbol{P}}^2 + (\frac{1}{2I_a} - \frac{1}{2I_b})\widehat{\boldsymbol{P}}_a^2$ (prolate, a (z) symmetry axis)

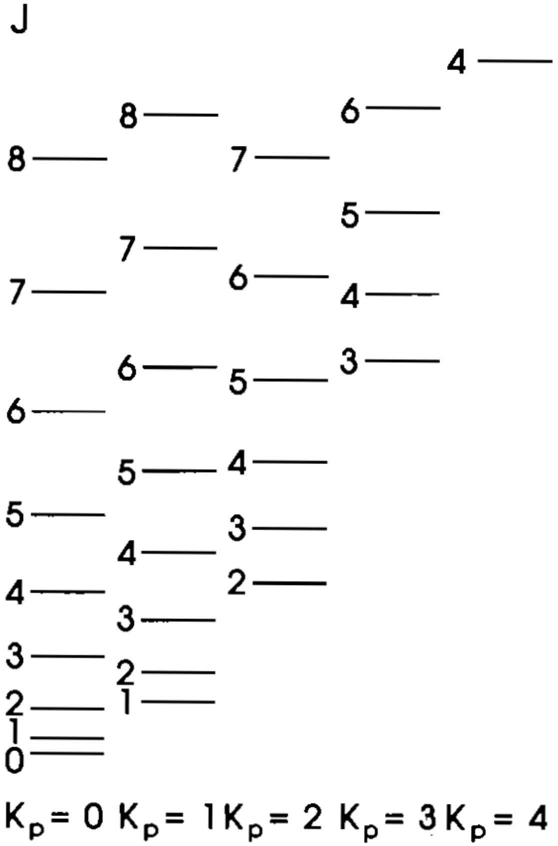
Solutions: $E_{JK} = BJ(J+1) + (A-B)K^2$ $A = \frac{h^2}{8\pi^2 I_a}$ $B = \frac{h^2}{8\pi^2 I_b}$ $C = \frac{h^2}{8\pi^2 I_c}$

$+ \textit{centrigual distortion terms in } J \textit{ and } K\ (D_J, D_K, D_{JK}\ \ldots)$

With $J = 0, 1, 2, \ldots$ total angular momentum quantum number
$K = -J, -J+1, \ldots 0, \ldots J-1,\ J$ $(2J+1)$ values
projection of angular momentum on symmetry axis

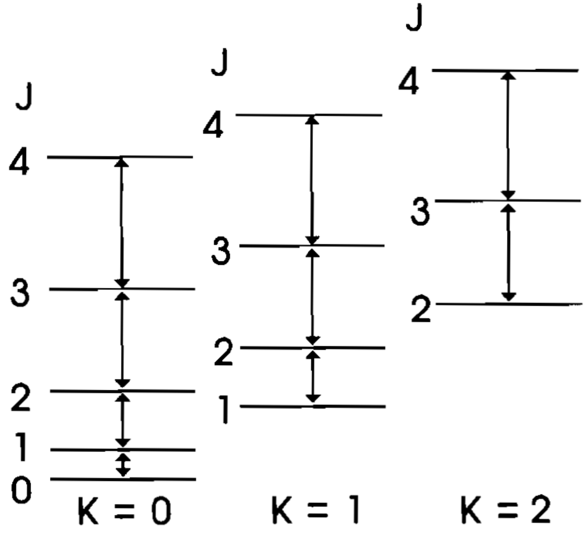
Symmetric Rotors

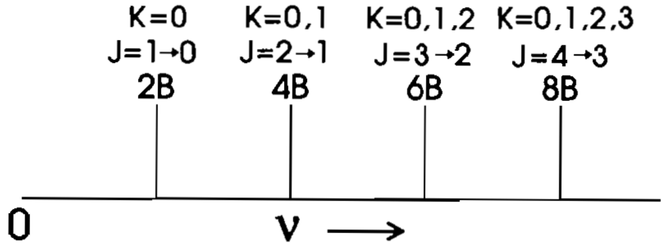
$$E_{JK} = BJ(J+1) + (A-B)K^2 \quad + \textit{centrigual distortion terms in } J \textit{ and } K$$



prolate symmetric top

Allowed transitions (prolate):





$$\Delta J = 1, \Delta K = 0$$

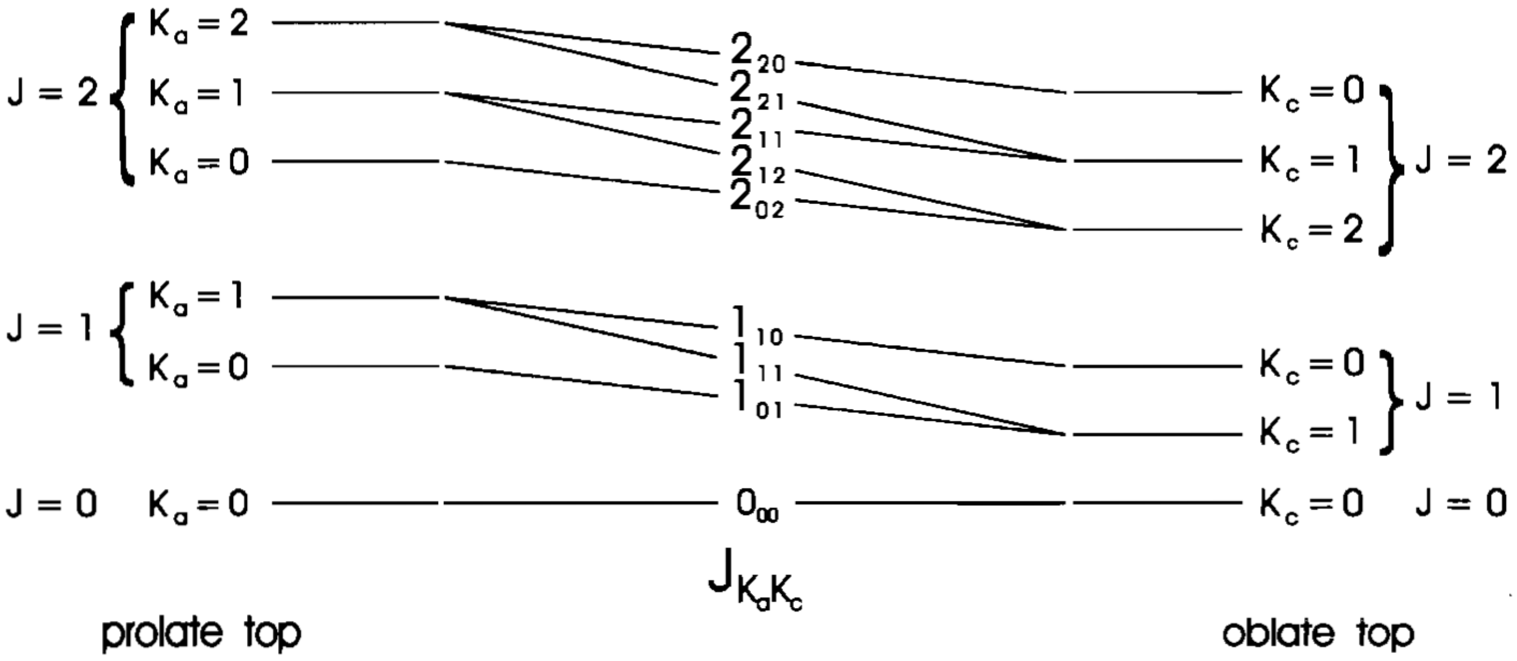
Without centrifugal distortion the spectrum looks as that of a linear molecule!

Reality:
Bonus Tutorial

© P. Bernath, Spectra of Atoms and Molecules

Asymmetric Rotors (brief)

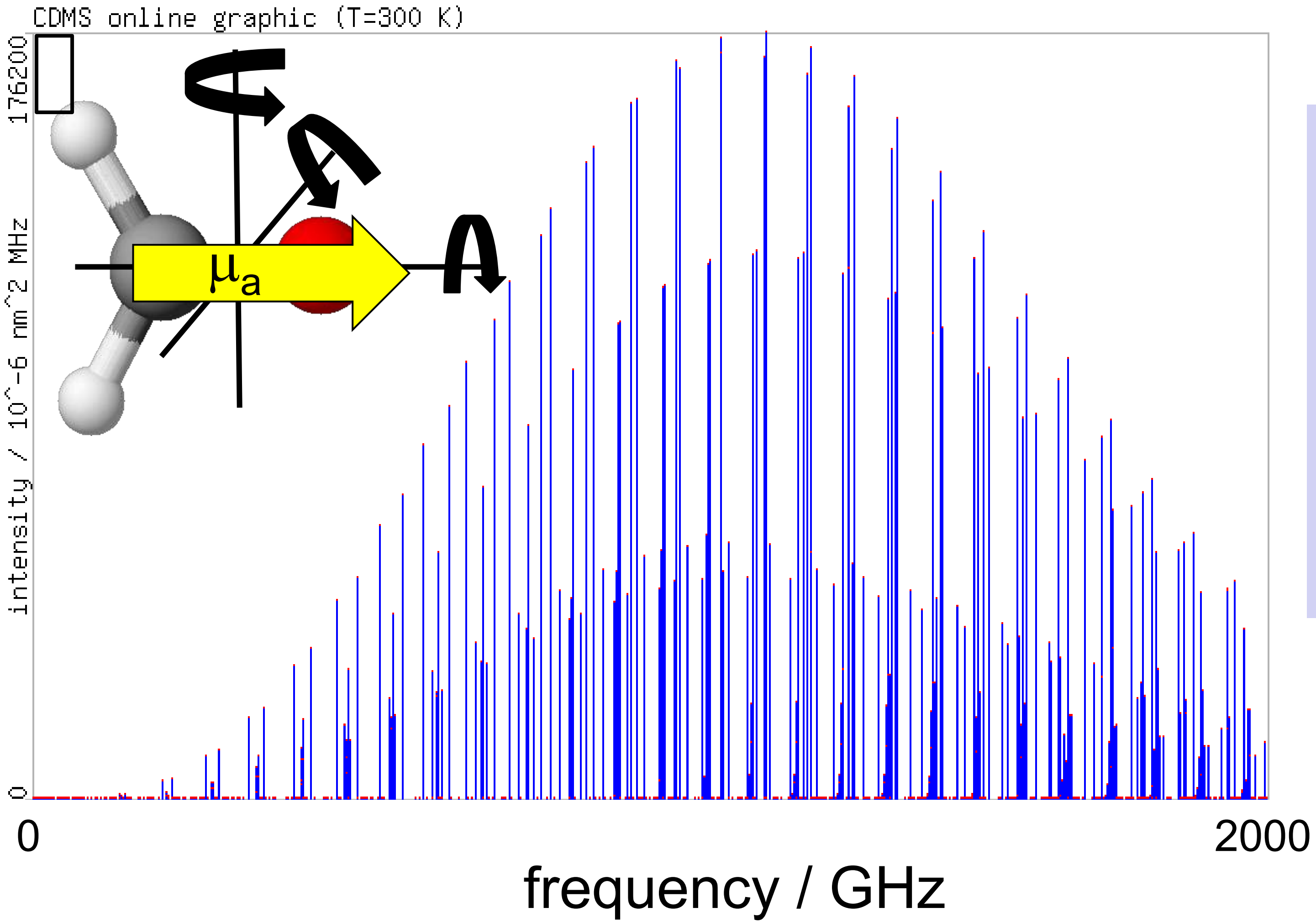
- Asymmetric top: $I_a < I_b < I_c$ $\hat{\boldsymbol{H}}_{rot} = \frac{\hat{\boldsymbol{P}}_a^2}{2I_a} + \frac{\hat{\boldsymbol{P}}_b^2}{2I_b} + \frac{\hat{\boldsymbol{P}}_c^2}{2I_c}$
- No analytical solutions, needs to be solved numerically, using symmetric wavefunctions as basis set.
- Two additional “labels”are used, but no good quantum numbers: K_a, K_c



Asymmetric Rotors (brief)

- Asymmetric top: $I_a < I_b < I_c$ $\hat{\boldsymbol{H}}_{rot} = \frac{\hat{\boldsymbol{P}}_a^2}{2I_a} + \frac{\hat{\boldsymbol{P}}_b^2}{2I_b} + \frac{\hat{\boldsymbol{P}}_c^2}{2I_c}$
- No analytical solutions, needs to be solved numerically, using symmetric wavefunctions as basis set.
- Two additional "labels"are used, but no good quantum numbers: K_a, K_c
- Selection rules depend on the orientation of the dipole moment in the molecule
  - a-type transitions with $\mu_a \neq 0$: $\Delta K_a = 0$
    $\Delta K_c = \pm 1\ (\pm 3, \ldots)$
  - b-type transitions with $\mu_b \neq 0$: $\Delta K_a = \pm 1\ (\pm 3, \ldots)$
    $\Delta K_c = \pm 1\ (\pm 3, \ldots)$
  - c-type transitions with $\mu_c \neq 0$: $\Delta K_a = \pm 1\ (\pm 3, \ldots)$
    $\Delta K_c = 0$
- All can be allowed!

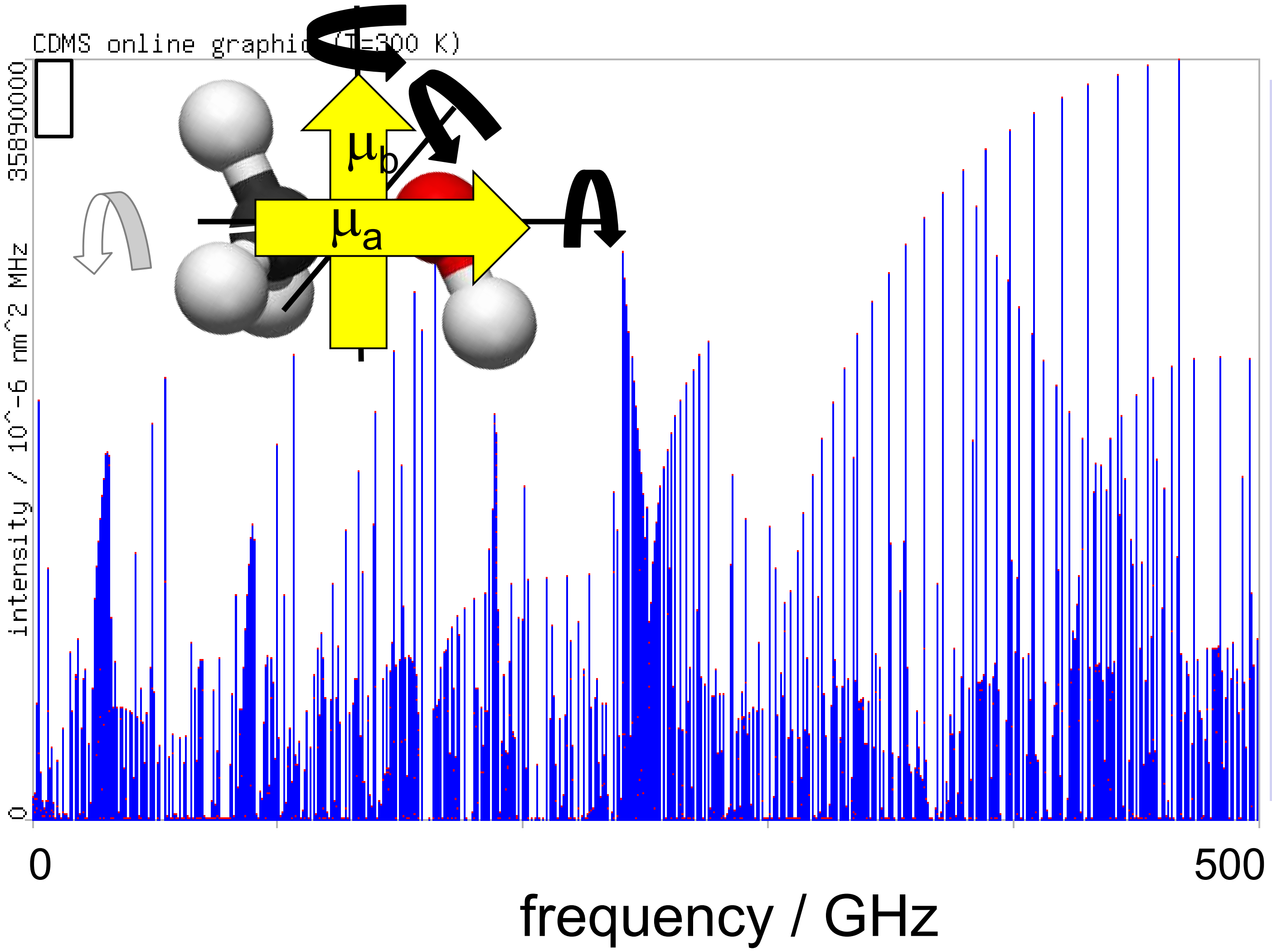
Levels of Complexity: asymmetry



H_2CO

- asymmetric top
- closed shell
- rigid

Levels of Complexity: asymmetric rotor + internal rotation



CH_3OH

- asymmetric top
- a- and b-type
- closed shell
- internal rotor

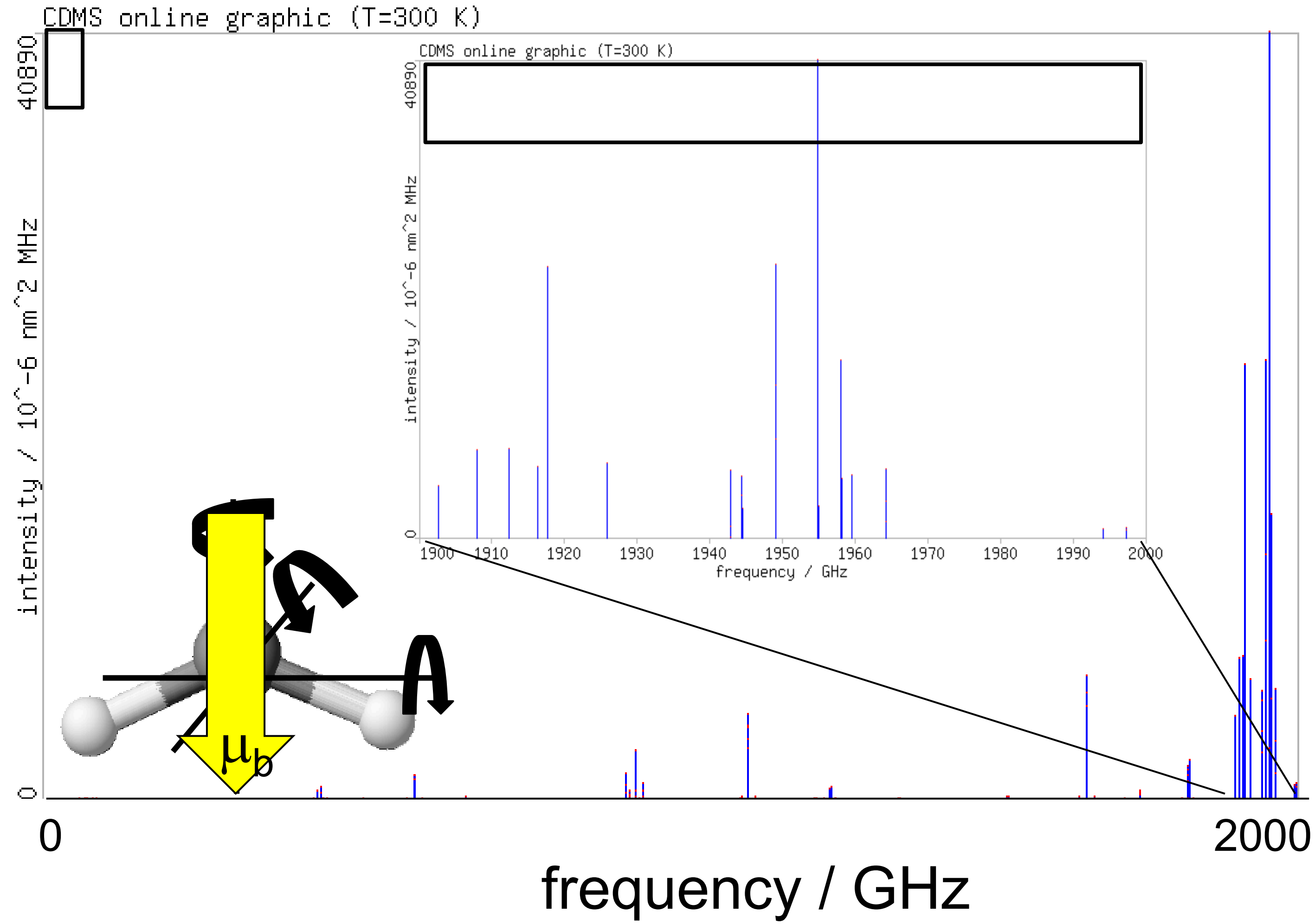
Additional „Complicatons“

- Internal rotors (methanol), inversion (ammonia)

- Radical species

  Open shell molecules, finestructure due to electronic angular momentum / spin & coupling with rotation

Levels of Complexity: electronic interaction



CH_2

- asymmetric top
- light & “floppy”
- radical $^3B_2$ spin-rotation interaction + hyperfine structure

Additional „Complicatons“

- Internal rotors (methanol), inversion (ammonia)

- Radical species
  Open shell molecules, finestructure due to electronic angular momentum / spin & coupling with rotation

- Hyperfine structure
  Interactions of rotation with nuclear spin of atoms
  interactions of electronic angular momentum / spin with nuclear spin

Most of this well understood, but needs to be measured / fitted for each individual molecule (and all ist isotopologies, vibrational excited states, ...)

Tools

Tools for analysis of experimental spectra and prediction of rotational spectra
Based on effective Hamiltonian approaches

- spfit / spcat: https://spec.jpl.nasa.gov (basis of jpl and cdms catalogues)
- Pgopher: https://pgopher.chm.bris.ac.uk/ (see tutorial!)
- PROSPE: http://info.ifpan.edu.pl/~kisiel/prospe.htm

The spectroscopist's To Do list

- Quantum chemical *ab initio calculations* to get an idea of the structure, ground state and rotational constants

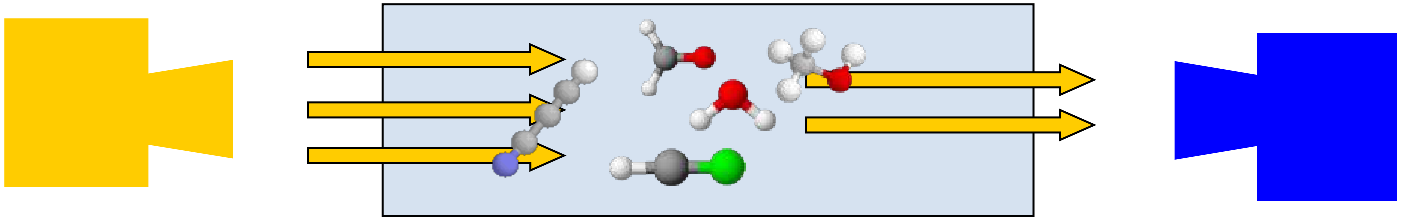
- Finding an efficient way to produce the molecule

- High resolution measurements over a broad range of the spectrum

- "Understand your molecule":

  Fitting the observed lines to an effective rotational Hamiltonian to predict its full spectrum and intensities

“Conventional” Absorption Spectroscopy

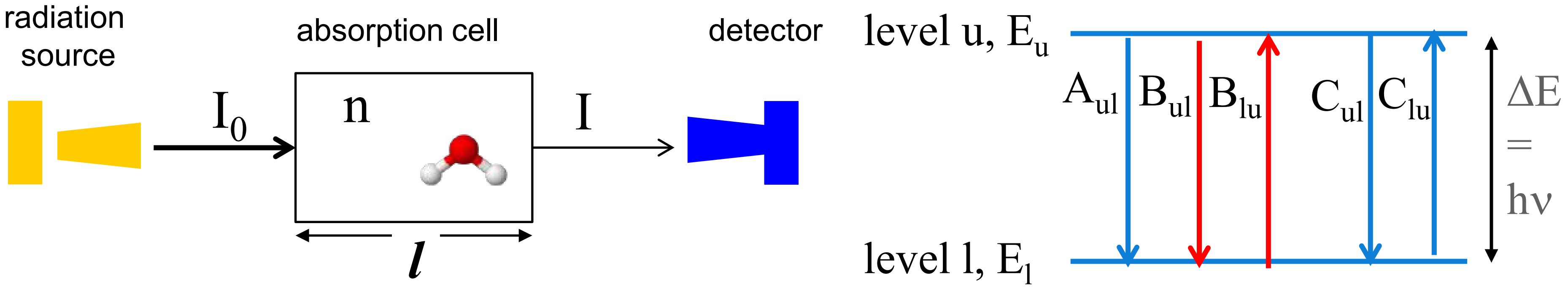


tunable, monochromatic radiation source

absorption cell

broadband photon detector

Line Intensities – Typical Absorption Experiment



Photons absorbed: $dI = -I \cdot \alpha \cdot dz$

Integrate → Beer's Law: $I = I_0 \cdot e^{-\alpha l}$

Same as radiative transfer but neglect self-emission!

Absorption coefficient α depends on number density n, line width Δv, Boltzmann distribution at temperature T, and transition properties (frequency, Einstein coefficients, upper energy, statistical weights)

$$\alpha = n \frac{g_u c^2 A_{ul}}{8\pi v^2 \Delta v \, U(T)} e^{-\frac{E_u}{kT}} \left(e^{\frac{hv}{kT}} - 1 \right)$$

And partition function $U(T) = \sum g_i e^{-\frac{E_i}{kT}}$

Intermezzo: Calculation of astronomical intensities

Remember optical depth $\tau_v = \int_0^L \alpha_v dx = \alpha_n L$

So this means for molecular line: $\tau_v = N \frac{g_u c^3 A_{ul}}{8\pi v^3 \Delta \text{v}\, U(T)} e^{-\frac{E_u}{kT}} \left(e^{\frac{hv}{kT}} - 1\right)$

(use $N = nL$ and $\Delta \text{v} = \frac{\Delta v}{v} c$)

And for the brightness temperature: $\Delta T_B = \frac{hv}{k} \left[\frac{1}{e^{\frac{hv}{kT}} - 1} - \frac{1}{e^{\frac{hv}{kT_b}} - 1}\right] [1 - e^{-\tau_v}]$

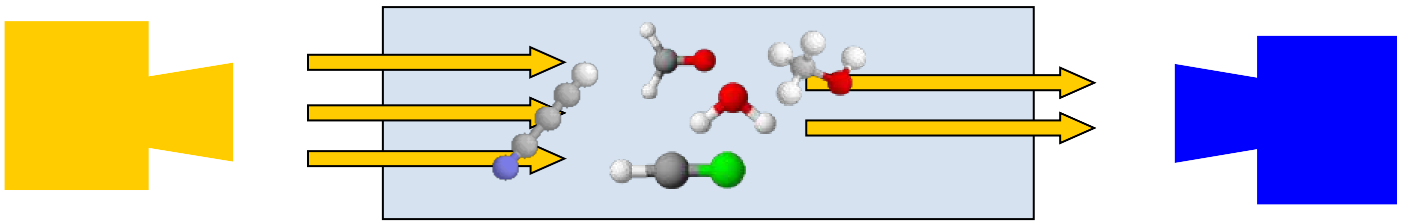
Simplified for $\frac{\text{h}v}{kT} \ll 1$: $\Delta T_B = (T - T_b)[1 - e^{-\tau_v}]$

Simplified for $T_b = 0,$ using τ_v: $\Delta T_B = N \frac{g_u c^3 h A_{ul}}{8k\pi v^2 \Delta \text{v}\, U(T)} e^{-\frac{E_u}{kT}}$

So if you know your molecule & astronomical source, you can

- Calculate brightness temperature (needs modelled abundance)
- Calculate abundance and temperature from observations!

“Conventional” Absorption Spectroscopy

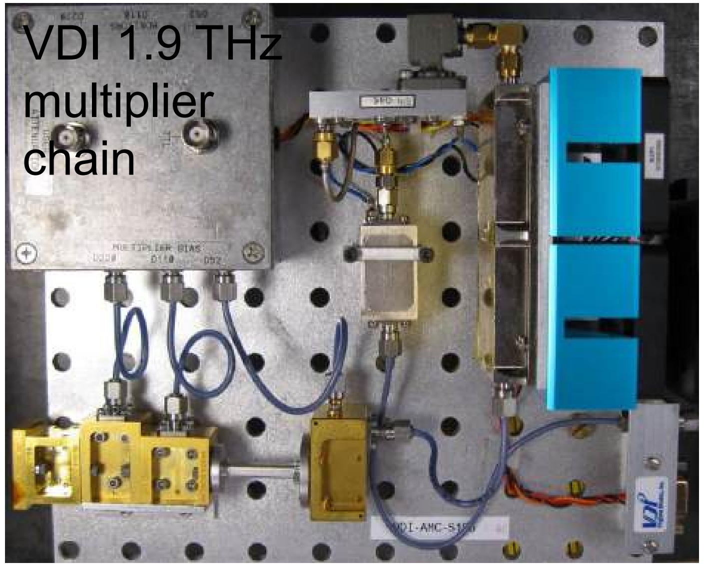


tunable, monochromatic radiation source

absorption cell

broadband photon detector

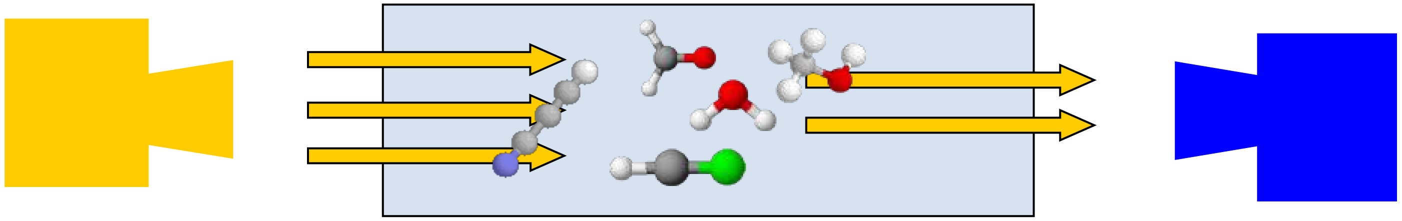
- Infrared: lasers (QCLs, OPOs, diodes)
- mm-, THz radiation sources
  - synthesizer, Gunn diodes
  - **solid state multiplier chains (up-conversion)**
  - FIR laser
  - Photomixing (down-conversion)…



VDI 1.9 THz multiplier chain

frequency accuracy, linewidth, stability, tunability, power, calibration...

“Conventional” Absorption Spectroscopy

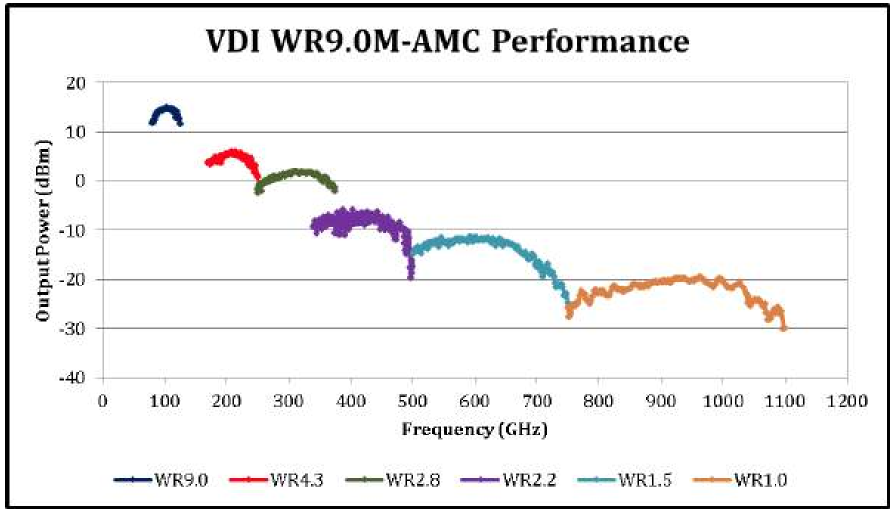


tunable, monochromatic radiation source

absorption cell

broadband photon detector

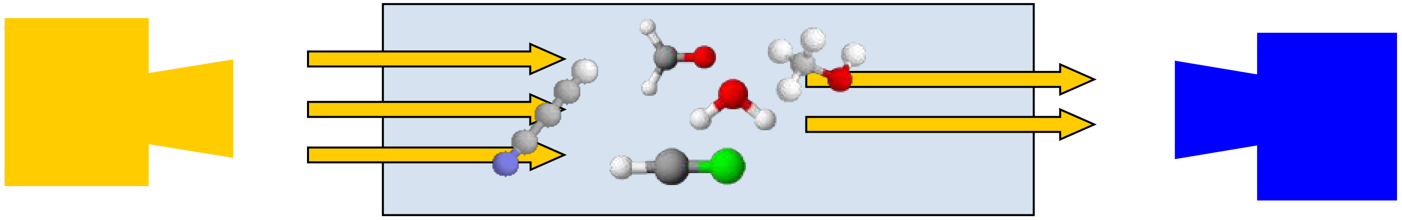
Virginia Diodes, Inc.



Technology mainly driven by heterodyne receiver development!

- automated rapid scanning with fast electronics
- intrinsic linewidth & accuracy << kHz up to 1 THz
- Wide tuning range of 30%

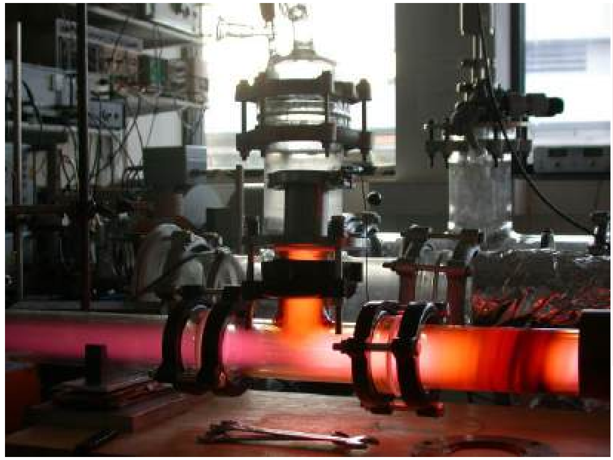
“Conventional” Absorption Spectroscopy



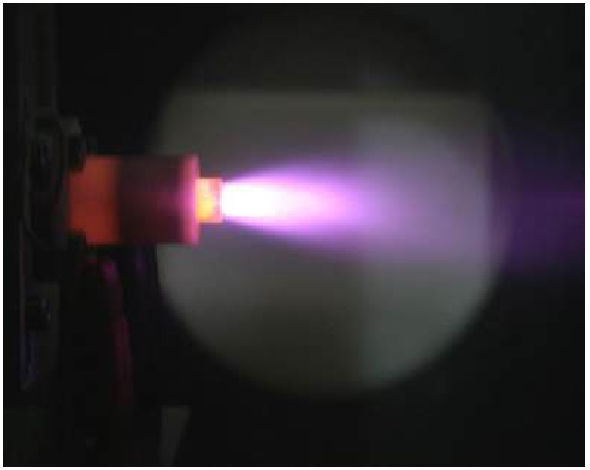
tunable, monochromatic radiation source

absorption cell

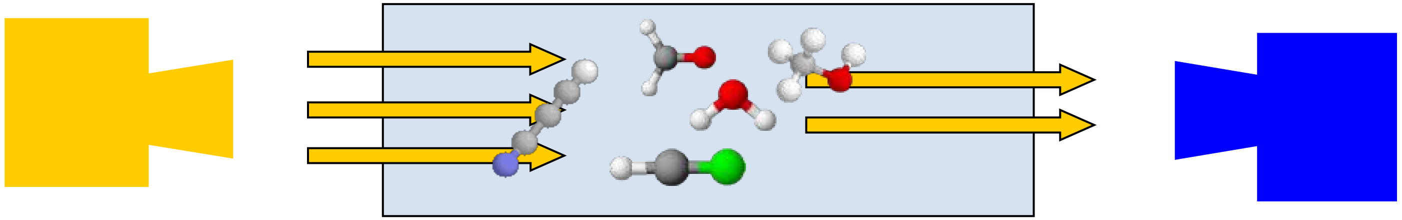
broadband photon detector:



- Stable (bottled) gases
- Radicals & ions: discharges (RF, DC, AC)
- Refractory molecules: pyrolysis & laser ablation



“Conventional” Absorption Spectroscopy



tunable, monochromatic radiation source

absorption cell

broadband photon detector:

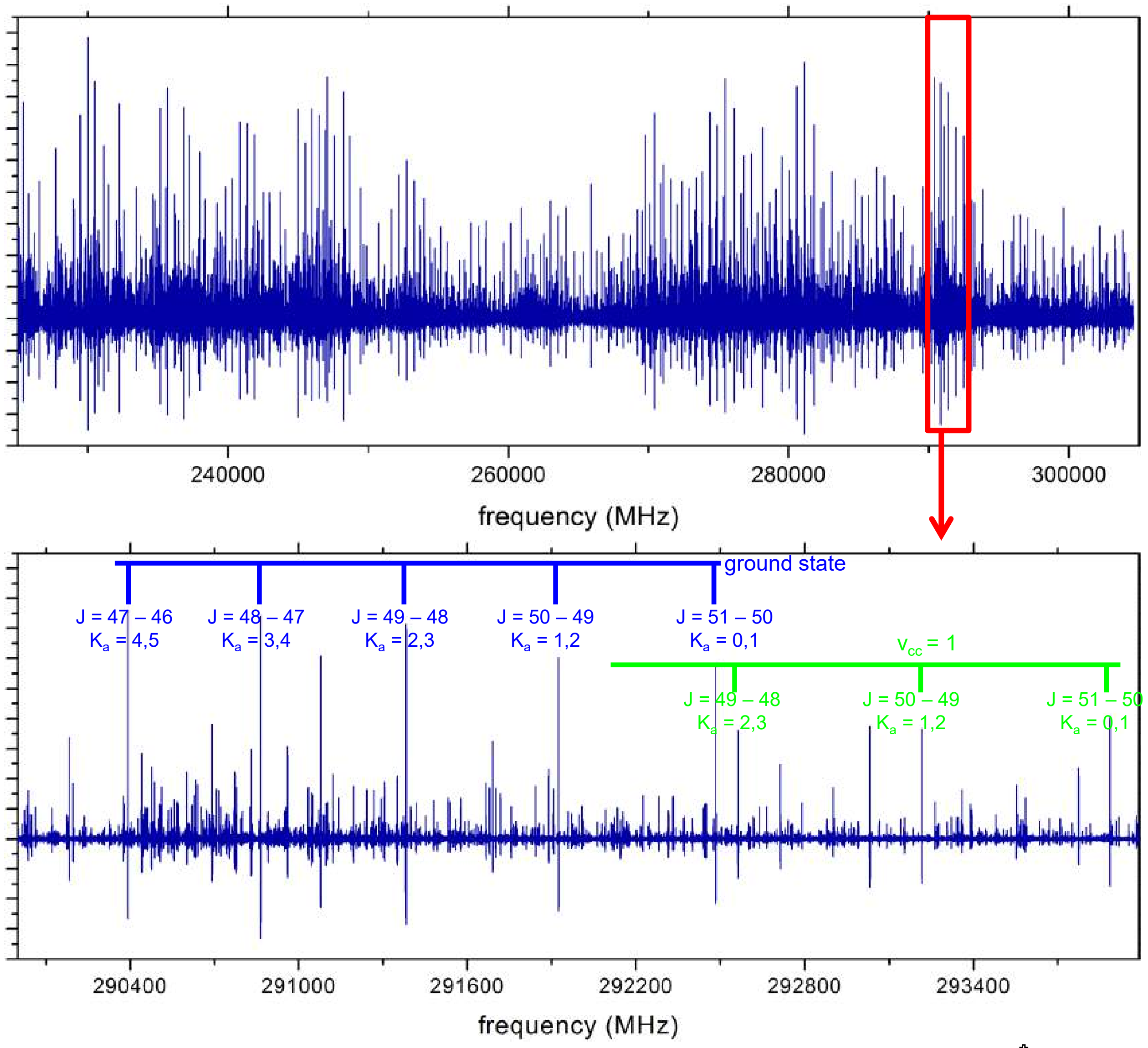

InSb HEB
QMC Instruments Ltd.

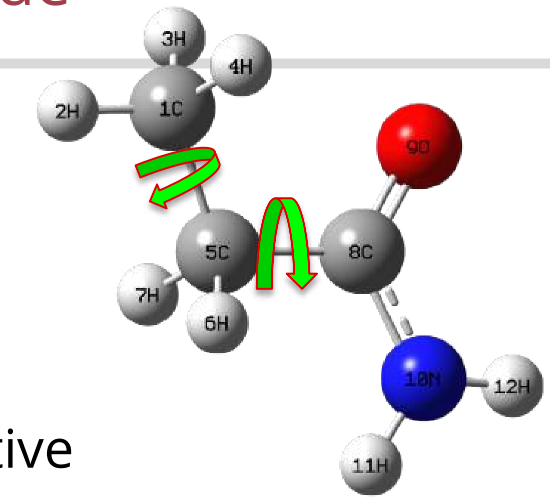
Thermal:
- (hot electron) bolometer
- pyroelectric

Photonic:
- photoconductive
- photovoltaic (photodiodes)
- photoemissive (photo-multiplier)

Sensitivity, noise, spectral coverage, speed, ...

Typical Data of Complex Molecules: Propionamide





Peptide bond motive

Formamide ($HCONH_2$) &
Acetamide (CH_3CONH_2)
were detected in SgrB2(N)

9 – 462 (630) GHz coverage
Analysis challenging
Finally 5495 transitions assigned

Lab: L. Margulés et al. PhLam Lille 69th ISMS (2014)
Astro: J. Li et al., ApJ 919 (2021) 4

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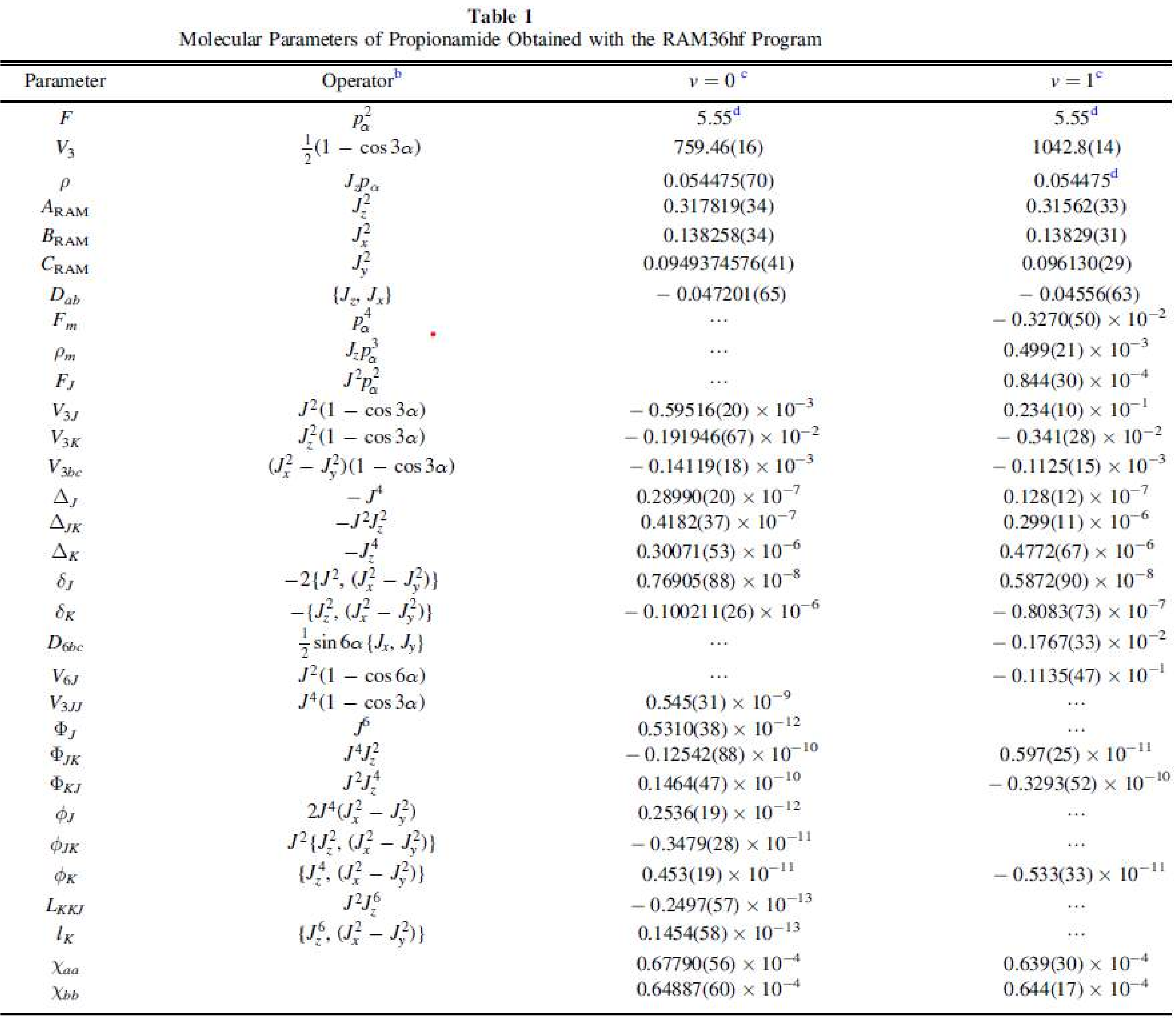
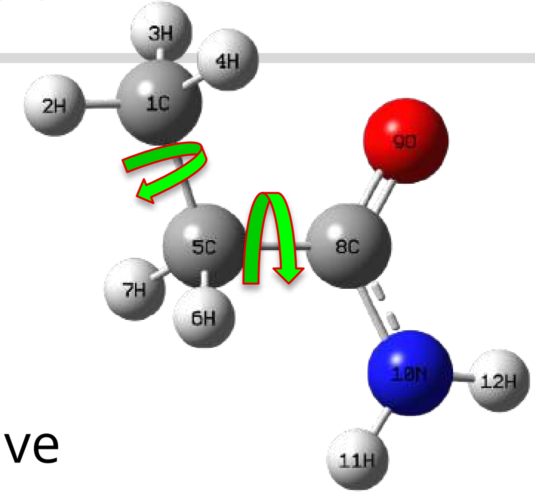


Table 1
Molecular Parameters of Propionamide Obtained with the RAM36hf Program

Parameter	Operator[b]	$v = 0$ [c]	$v = 1$[c]
F	p_α^2	5.55[d]	5.55[d]
V_3	$\frac{1}{2}(1 - \cos 3\alpha)$	759.46(16)	1042.8(14)
ρ	$J_z p_\alpha$	0.054475(70)	0.054475[d]
A_{RAM}	J_z^2	0.317819(34)	0.31562(33)
B_{RAM}	J_x^2	0.138258(34)	0.13829(31)
C_{RAM}	J_y^2	0.0949374576(41)	0.096130(29)
D_{ab}	$\{J_z, J_x\}$	$-0.047201(65)$	$-0.04556(63)$
F_m	p_α^4	$\cdots$	$-0.3270(50) \times 10^{-2}$
ρ_m	$J_z p_\alpha^3$	$\cdots$	$0.499(21) \times 10^{-3}$
F_J	$J^2 p_\alpha^2$	$\cdots$	$0.844(30) \times 10^{-4}$
V_{3J}	$J^2(1 - \cos 3\alpha)$	$-0.59516(20) \times 10^{-3}$	$0.234(10) \times 10^{-1}$
V_{3K}	$J_z^2(1 - \cos 3\alpha)$	$-0.191946(67) \times 10^{-2}$	$-0.341(28) \times 10^{-2}$
V_{3bc}	$(J_x^2 - J_y^2)(1 - \cos 3\alpha)$	$-0.14119(18) \times 10^{-3}$	$-0.1125(15) \times 10^{-3}$
Δ_J	$-J^4$	$0.28990(20) \times 10^{-7}$	$0.128(12) \times 10^{-7}$
Δ_{JK}	$-J^2 J_z^2$	$0.4182(37) \times 10^{-7}$	$0.299(11) \times 10^{-6}$
Δ_K	$-J_z^4$	$0.30071(53) \times 10^{-6}$	$0.4772(67) \times 10^{-6}$
δ_J	$-2\{J^2, (J_x^2 - J_y^2)\}$	$0.76905(88) \times 10^{-8}$	$0.5872(90) \times 10^{-8}$
δ_K	$-\{J_z^2, (J_x^2 - J_y^2)\}$	$-0.100211(26) \times 10^{-6}$	$-0.8083(73) \times 10^{-7}$
D_{6bc}	$\frac{1}{2}\sin 6\alpha\,\{J_x, J_y\}$	$\cdots$	$-0.1767(33) \times 10^{-2}$
V_{6J}	$J^2(1 - \cos 6\alpha)$	$\cdots$	$-0.1135(47) \times 10^{-1}$
V_{3JJ}	$J^4(1 - \cos 3\alpha)$	$0.545(31) \times 10^{-9}$	$\cdots$
Φ_J	J^6	$0.5310(38) \times 10^{-12}$	$\cdots$
Φ_{JK}	$J^4 J_z^2$	$-0.12542(88) \times 10^{-10}$	$0.597(25) \times 10^{-11}$
Φ_{KJ}	$J^2 J_z^4$	$0.1464(47) \times 10^{-10}$	$-0.3293(52) \times 10^{-10}$
ϕ_J	$2J^4(J_x^2 - J_y^2)$	$0.2536(19) \times 10^{-12}$	$\cdots$
ϕ_{JK}	$J^2\{J_z^2, (J_x^2 - J_y^2)\}$	$-0.3479(28) \times 10^{-11}$	$\cdots$
ϕ_K	$\{J_z^4, (J_x^2 - J_y^2)\}$	$0.453(19) \times 10^{-11}$	$-0.533(33) \times 10^{-11}$
L_{KKJ}	$J^2 J_z^6$	$-0.2497(57) \times 10^{-13}$	$\cdots$
l_K	$\{J_z^6, (J_x^2 - J_y^2)\}$	$0.1454(58) \times 10^{-13}$	$\cdots$
χ_{aa}		$0.67790(56) \times 10^{-4}$	$0.639(30) \times 10^{-4}$
χ_{bb}		$0.64887(60) \times 10^{-4}$	$0.644(17) \times 10^{-4}$



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Finally 5495 transitions assigned

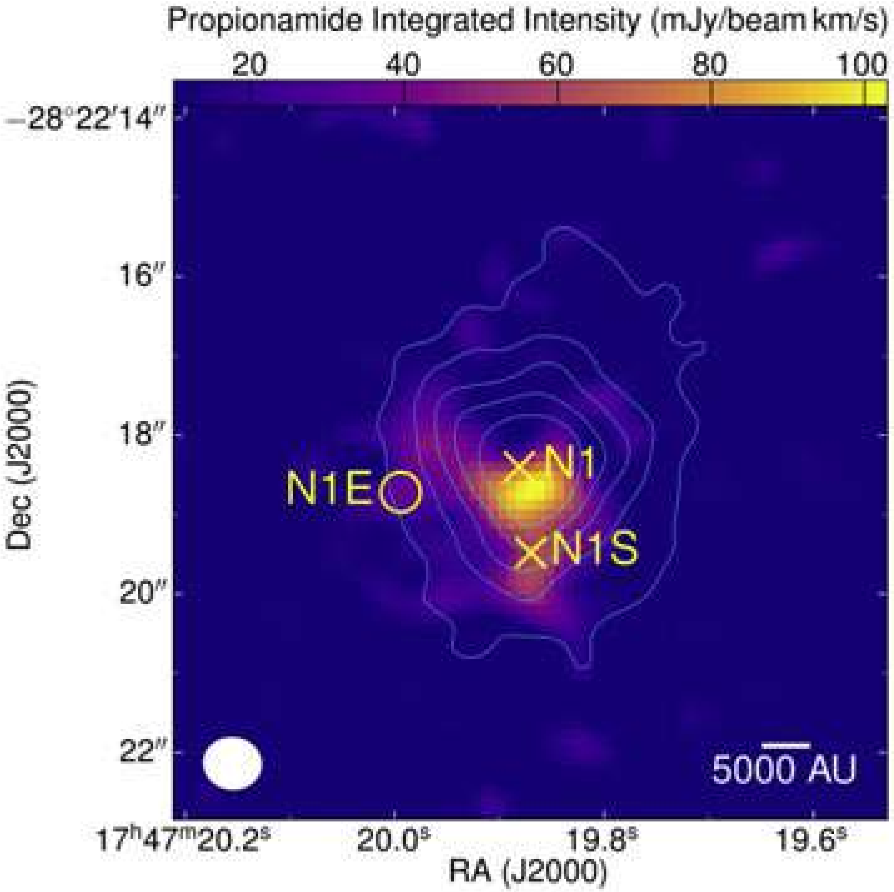
Lab: L. Margulés et al. PhLam Lille 69th ISMS (2014)
Astro: J. Li et al., ApJ 919 (2021) 4

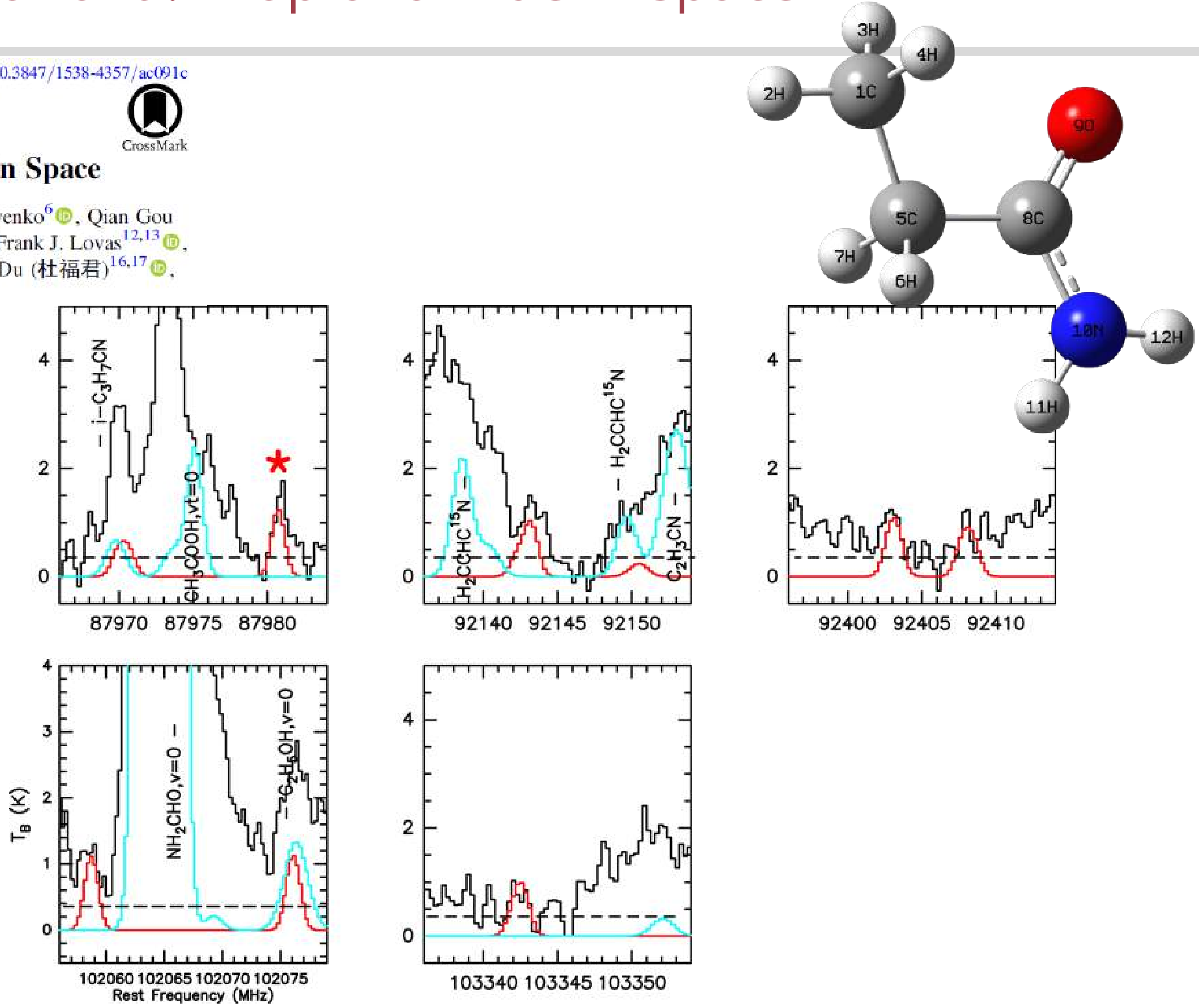
But once you understand it : Propionamide in space

The Astrophysical Journal, 919:4 (18pp), 2021 September 20
https://doi.org/10.3847/1538-4357/ac091c

Propionamide ($C_2H_5CONH_2$): The Largest Peptide-like Molecule in Space

Juan Li (李娟)[1,2], Junzhi Wang (王均智)[1,2], Xing Lu (吕行)[3], Vadim Ilyushin[4,5], Roman A. Motiyenko[6], Qian Gou (勾茜)[7], Eugene A. Alekseev[4,5], Donghui Quan (全冬晖)[8,9], Laurent Margulès[6], Feng Gao (高峰)[10,11], Frank J. Lovas[12,13], Yajun Wu (吴亚军)[1,2], Edwin Bergin[14], Shanghuo Li (李尚活)[15], Zhiqiang Shen (沈志强)[1,2], Fujun Du (杜福君)[16,17], Meng Li (李梦)[7], Siqi Zheng (郑思琪)[1,2,18], and Xingwu Zheng (郑兴武)[19]



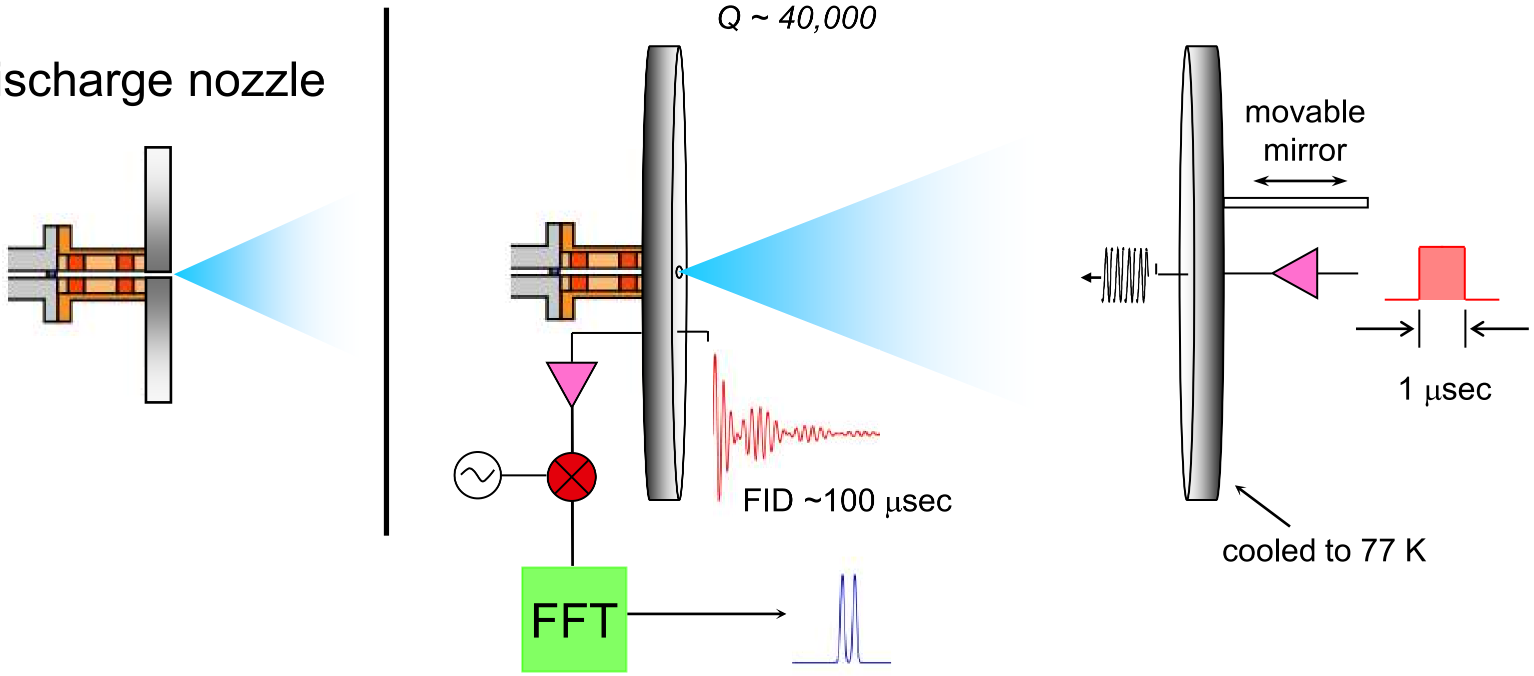


Lab: L. Margulés et al. PhLam Lille 69th ISMS (2014)
Astro: J. Li et al., ApJ 919 (2021) 4

Fourier Transform Microwave Spectroscopy (FTMW)

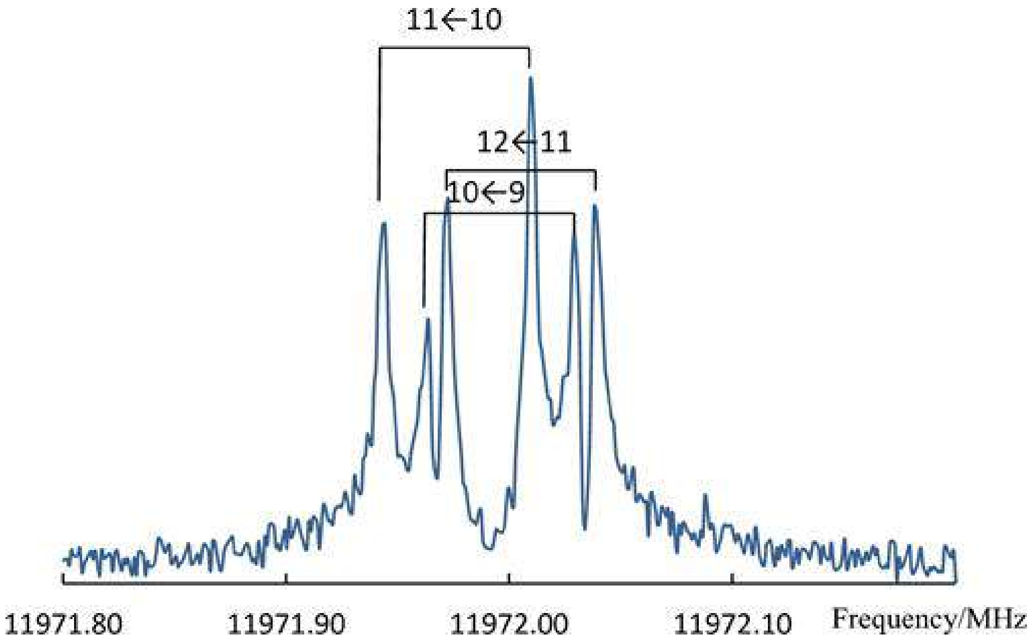
supersonic nozzle coupled to a high-*Q* Fabry-Perot cavity

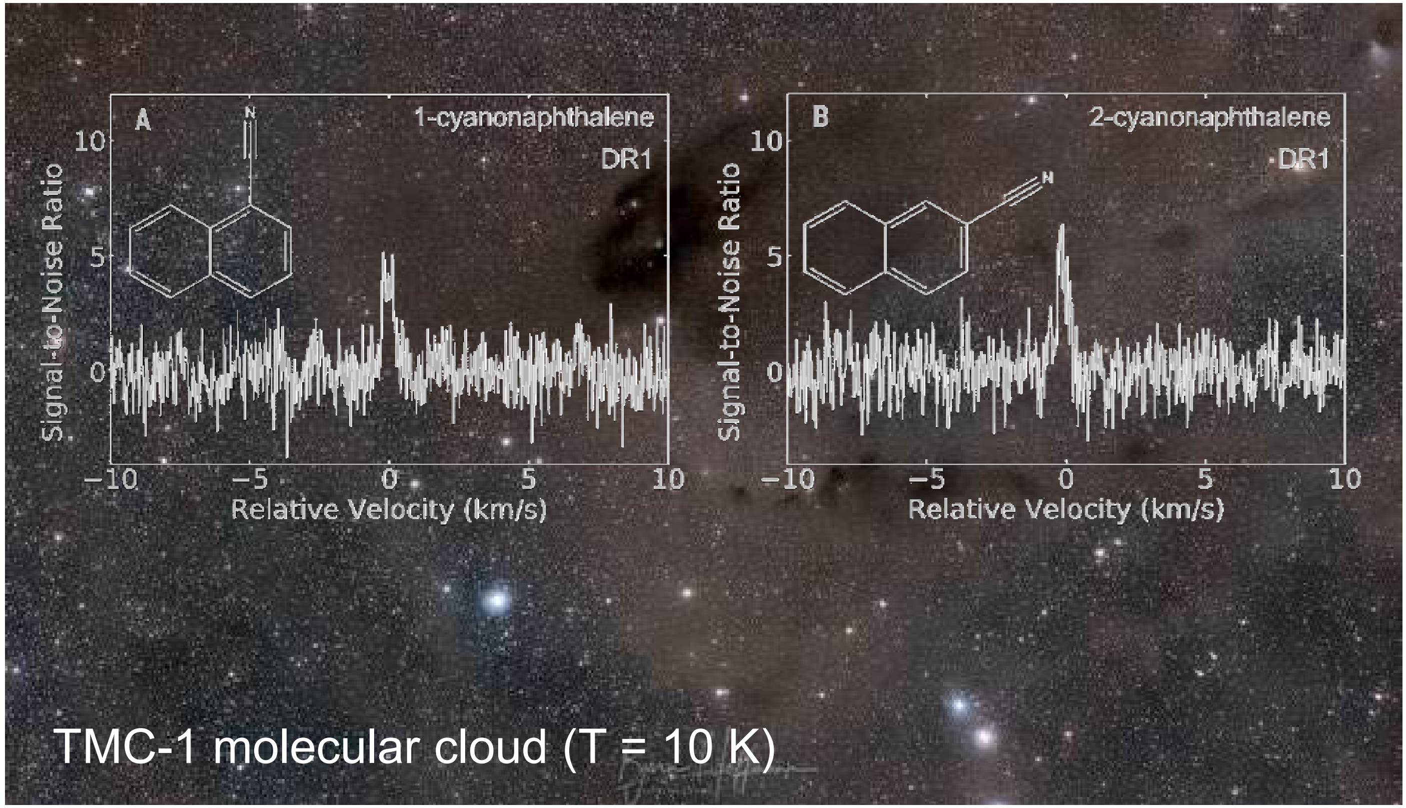
Balle & Flygare,
Rev. Sci. Instrum. 52 (1981) 33



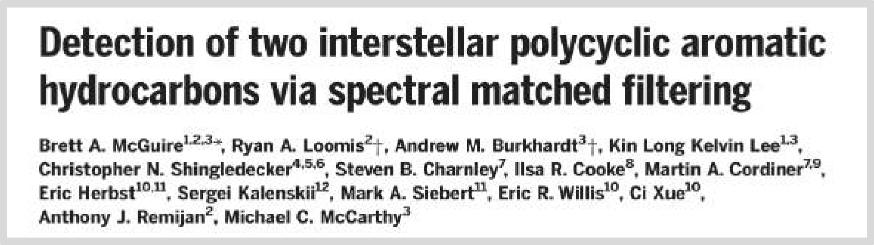
- frequency range: 5 – 42 GHz line width: 20 kHz accuracy: 1-2 kHz bandwidth: 1 MHz
- High Q Fabry-Perot cavity for excitation and detection
- Molecular beam expansion leads to cooling of the molecules to few K (narrow lines, high population in low J states)
- Use discharges or laser ablation to produce molecules in gas phase

FTMW Example I – Detection of cyanonaphtalene





TMC-1 molecular cloud (T = 10 K)

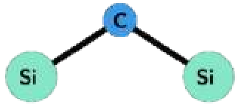


Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering

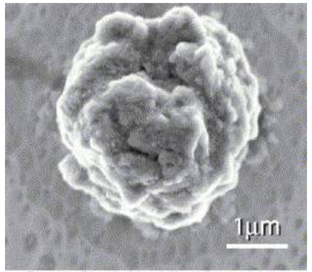
Brett A. McGuire[1,2,3*], Ryan A. Loomis[2†], Andrew M. Burkhardt[3†], Kin Long Kelvin Lee[1,3], Christopher N. Shingledecker[4,5,6], Steven B. Charnley[7], Ilsa R. Cooke[8], Martin A. Cordiner[7,9], Eric Herbst[10,11], Sergei Kalenskii[12], Mark A. Siebert[11], Eric R. Willis[10], Ci Xue[10], Anthony J. Remijan[2], Michael C. McCarthy[3]

Lab: D. McNaughton et al., MNRAS 476 (2018) 5268
Astro: B. McGuire et al., *Science* **371** (2021) 1265

FTMW Example II Laboratory and Astronomical Detection of SiCSi



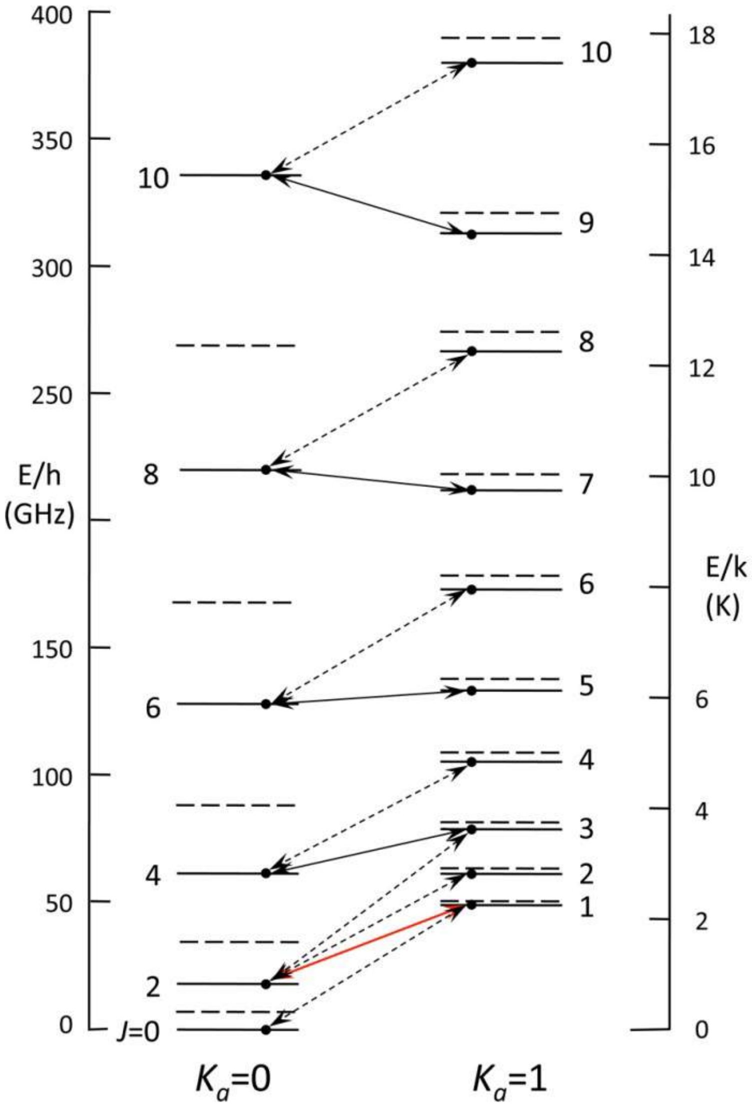
Si_nC_m molecular species act as seeds for carbonaceous dust formation in C-rich AGB stars

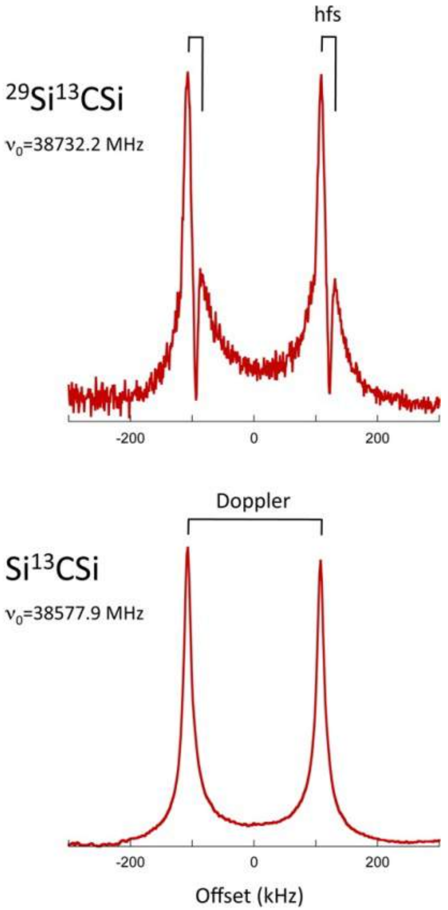


(Photo by Rhonda Stroud, Naval Research Lab.)

- discharge of SiH_4 & C_2H_2
- up to 12 lines for several isotopic species
- reliable transition frequencies
- structural analysis
- double-resonance experiments

McCarthy et al., JPC Lett. 6 (2015), 2107





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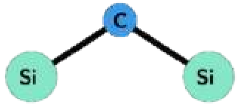
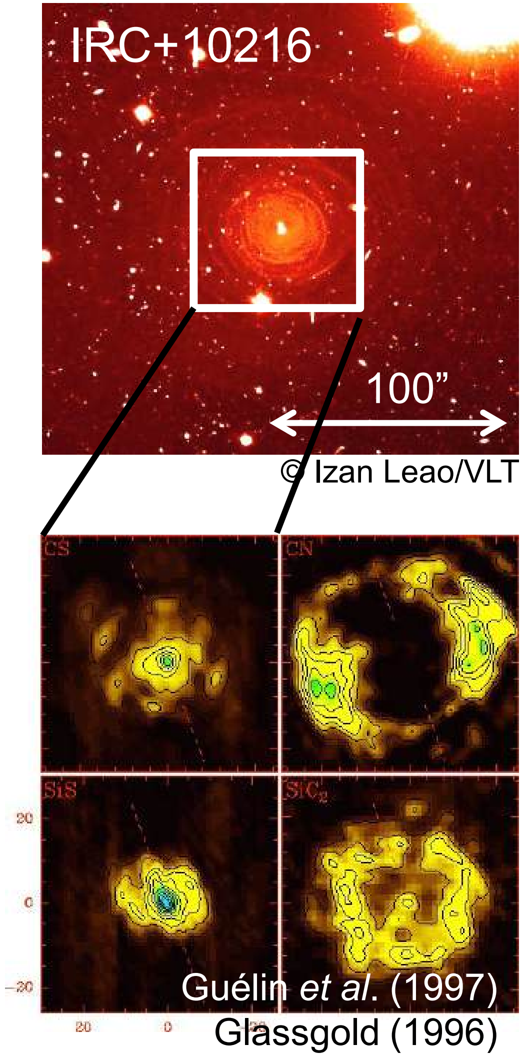


Si_nC_m molecular species act as seeds for carbonaceous dust formation in C-rich AGB stars
SiC & SiC_2 already detected in circumstellar envelope of the carbon-rich AGB star IRC +10216



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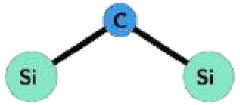
Guélin *et al.* (1997)
Glassgold (1996)

FTMW Example II Laboratory and Astronomical Detection of SiCSi



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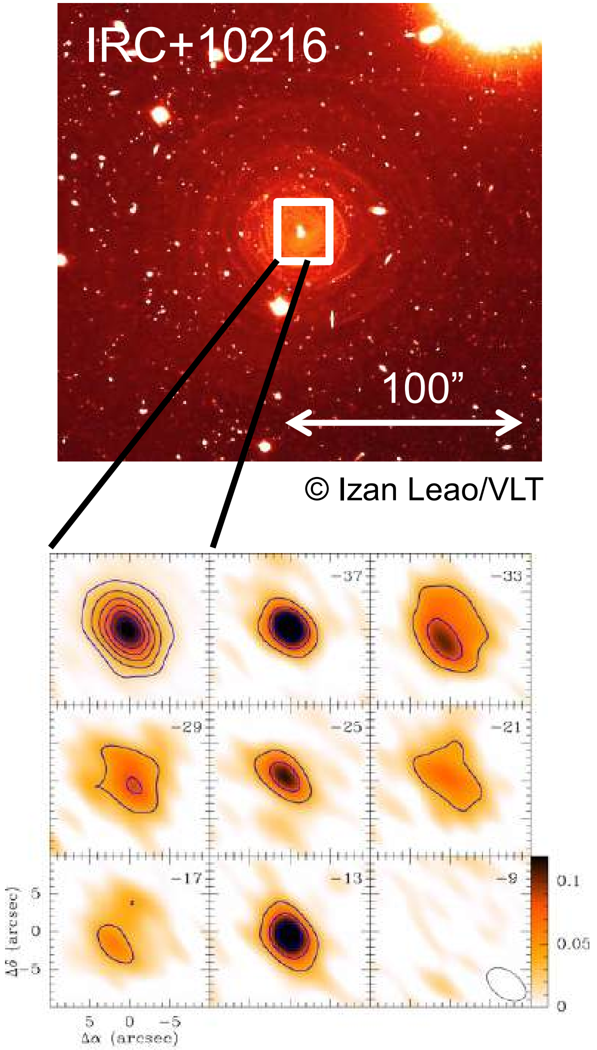

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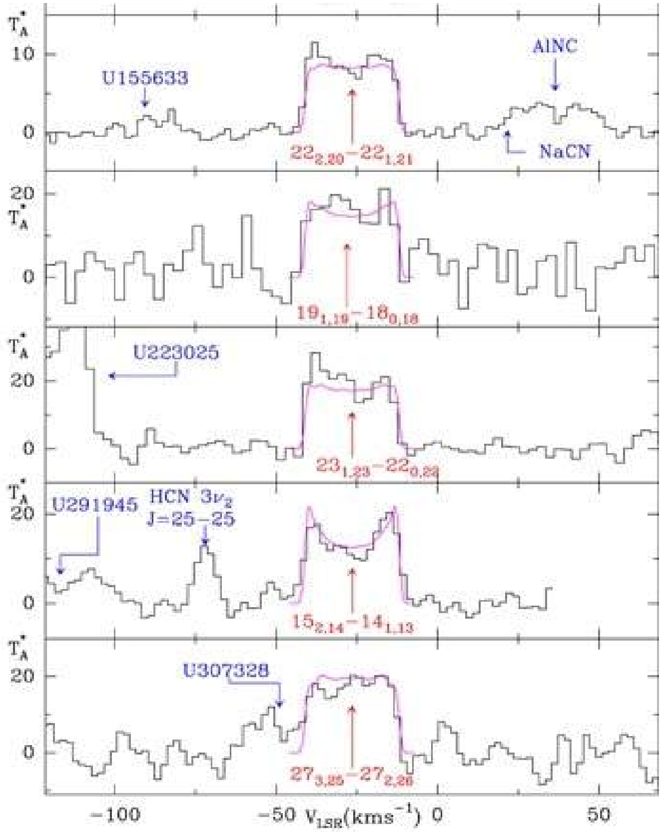
IRAM 30m & SMA: >100 lines
(80-350 GHz)

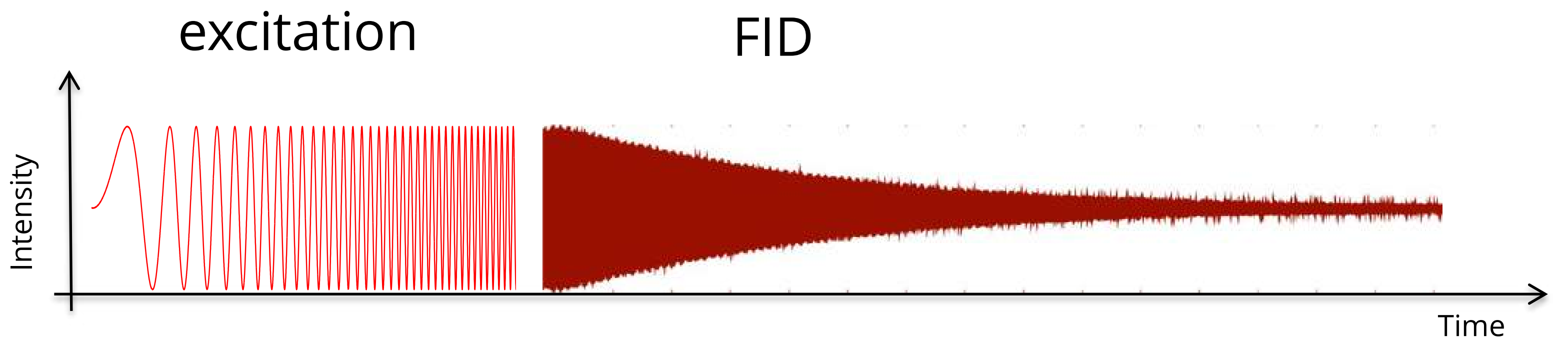


J. Cernicharo et al., ApJ 806(2015) L3

Chirped-Pulse Fourier Transform Microwave (CP-FTMW)

With a cavity FTMW, the excitation bandwidth is limited to ~1 MHz due to the cavity Q!
-> slow stepping through the frequency range

Solution: use a chirped pulse, containing many frequencies & no cavity!



Macroscopic Polarization

$$P \propto \mu^2 \cdot E_{Pulse} \cdot \frac{\Delta N_0}{\sqrt{\alpha}}$$

[G. Barratt Park et. al. 2011]

Dephasing of FID Signal

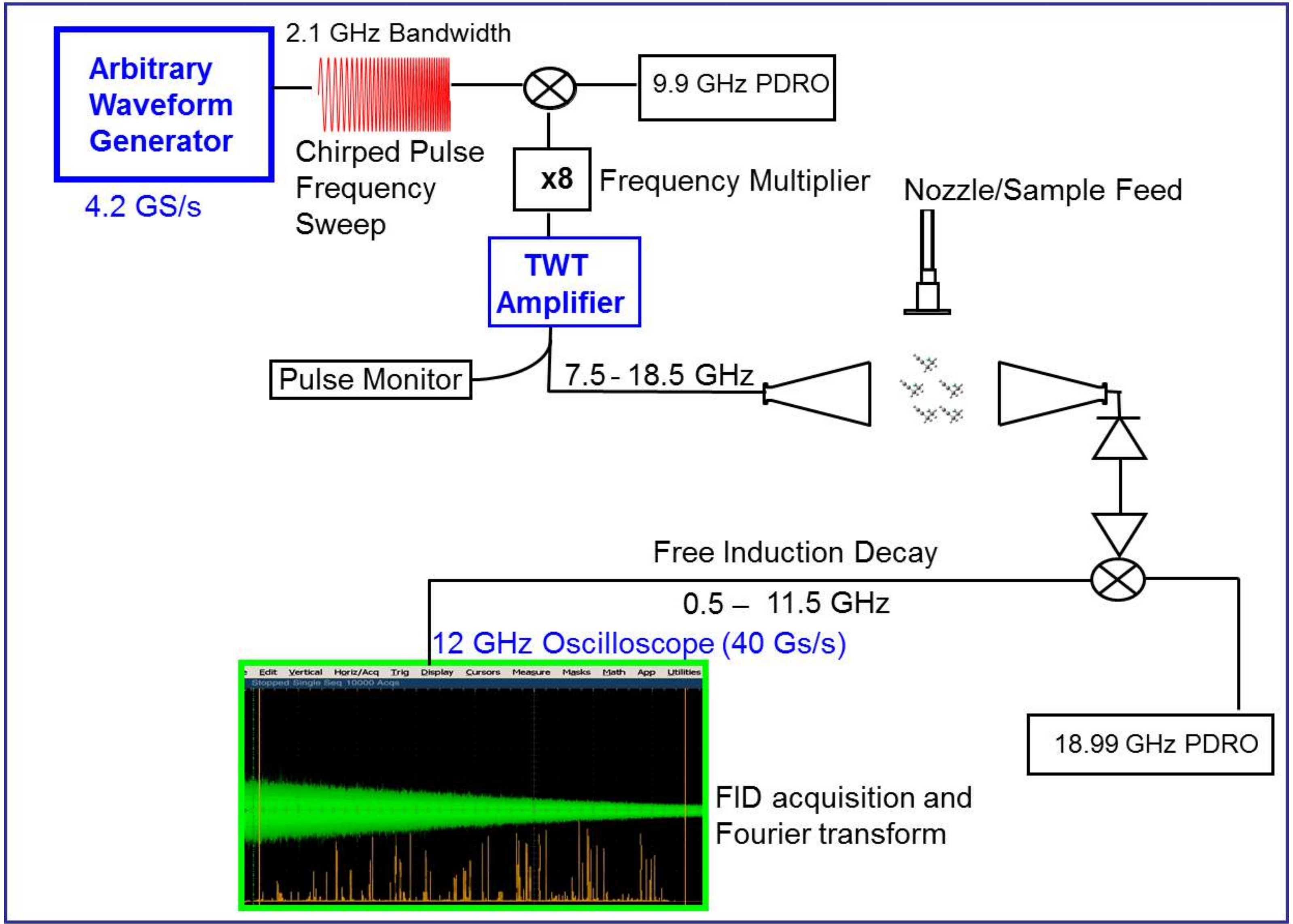
$$S_{FID} \propto \sin(\omega_{10} t) \cdot e^{\frac{-t}{T_1}} \cdot e^{\frac{-t}{T_2}}$$

T_1 : population lifetime
T_2 : coherence lifetime

[R. G. Bird 2011]

α: chirp rate
ΔN_0: original population difference
typically not enough power for $\pi/2$ pulse -> only few percent polarization

Chirped-Pulse Fourier Transform Microwave (CP-FTMW)



Arbitrary Waveform Generator

4.2 GS/s

2.1 GHz Bandwidth

Chirped Pulse Frequency Sweep

9.9 GHz PDRO

x8 Frequency Multiplier

TWT Amplifier

Pulse Monitor

7.5 - 18.5 GHz

Nozzle/Sample Feed

Free Induction Decay

0.5 – 11.5 GHz

12 GHz Oscilloscope (40 Gs/s)

18.99 GHz PDRO

FID acquisition and Fourier transform

G.G. Brown et al., JMS 238 (2006) 200,
Brooks Pate group, University of Virginia

Chirped-Pulse Fourier Transform Microwave (CP-FTMW)

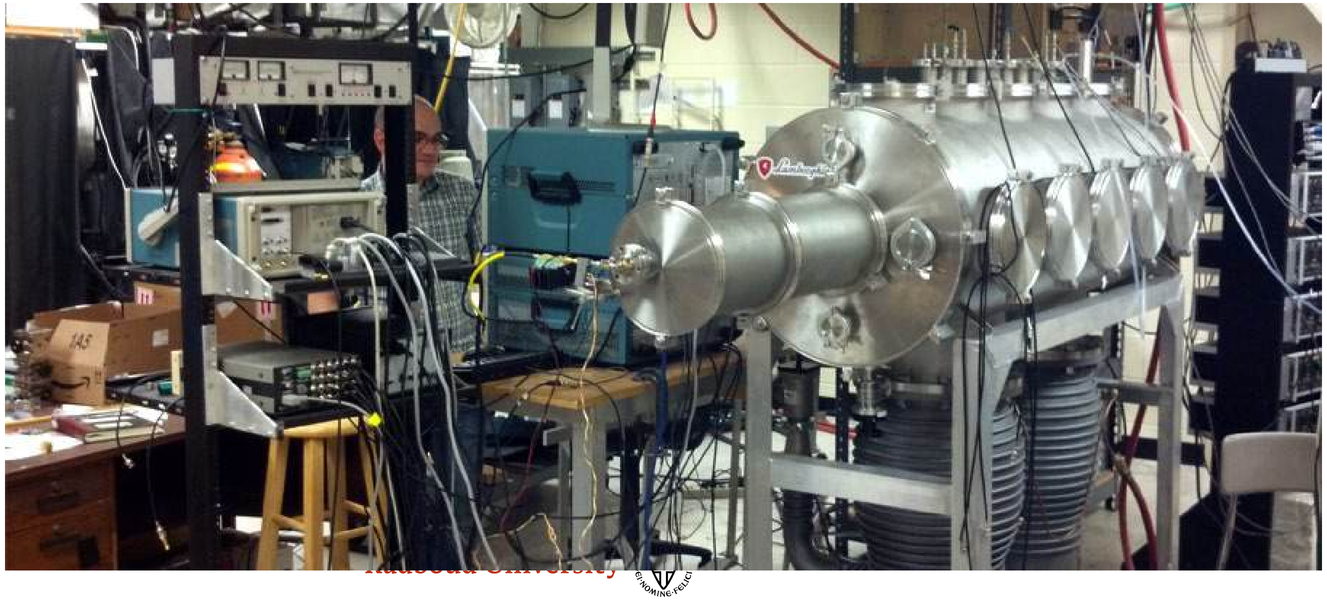
- fast spectrum acquisition: >10 GHz in one go
  high sensitivity due to multiplexing
  accurate relative intensities

→ complex species, search for unstable species, investigating chemistry

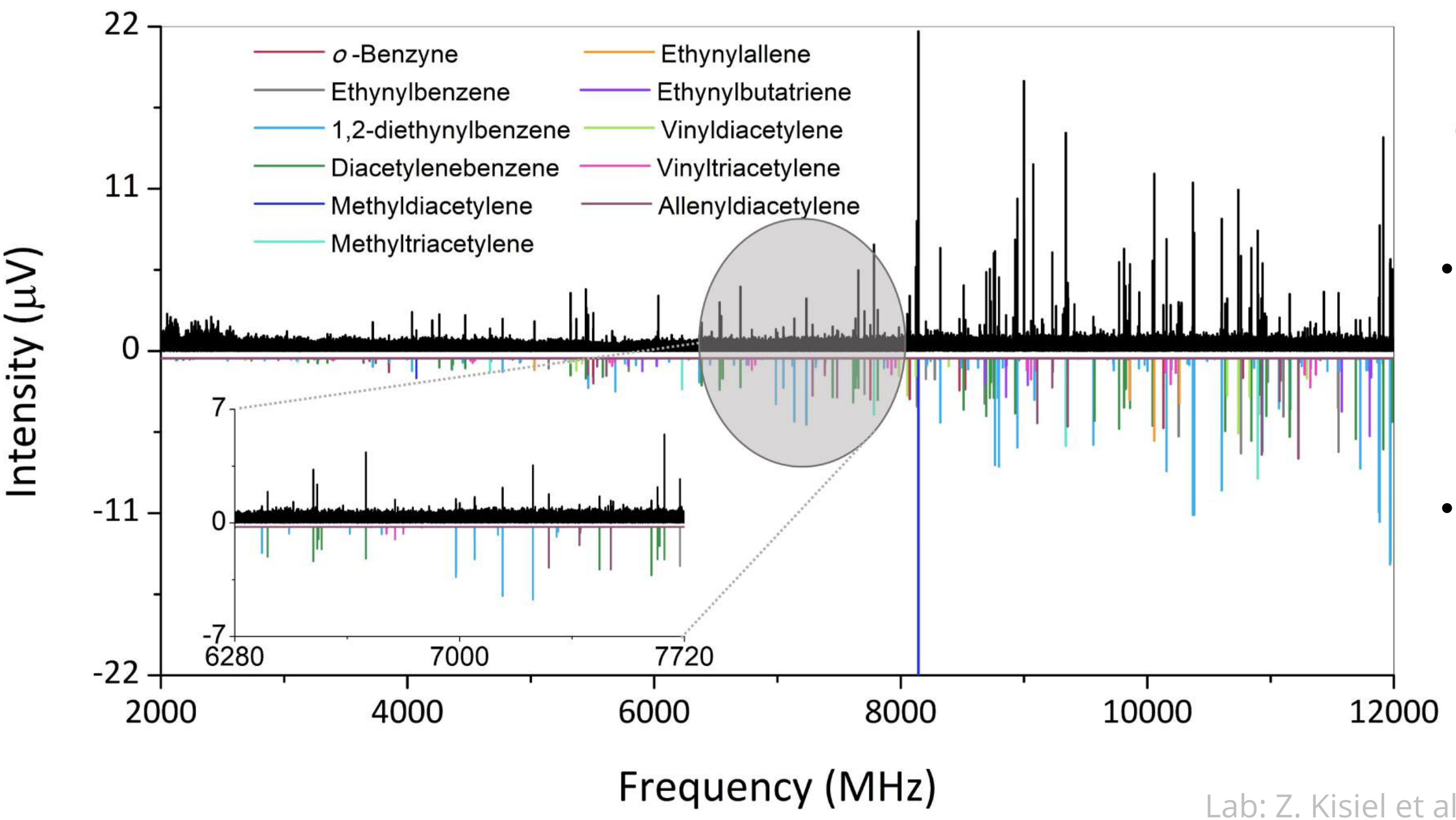
- extension up to the 1mm (300 GHz) region

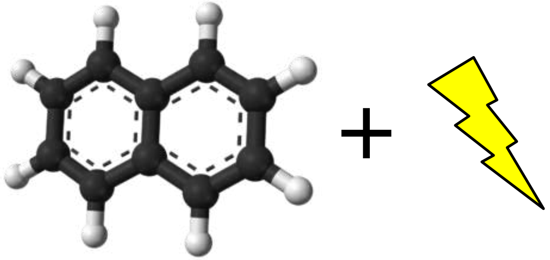
Steber et al., JMS 280 (2012) 3; Park et al. JCP 135, (2011) 024202

- used in many laboratories worldwide



CP-FTMW Example: Naphtalene discharge products





- Rotational lines of all products formed in a discharge of the PAH naphtalene!
- Most assigned and fitted to specific molecules

Lab: Z. Kisiel et al., JMS 262 (2010), 82
Astro: Cernicharo et al., A&A 655 (2021) L1
Lab & Astro: D. Loru et al., A&A 677 (2023) A166

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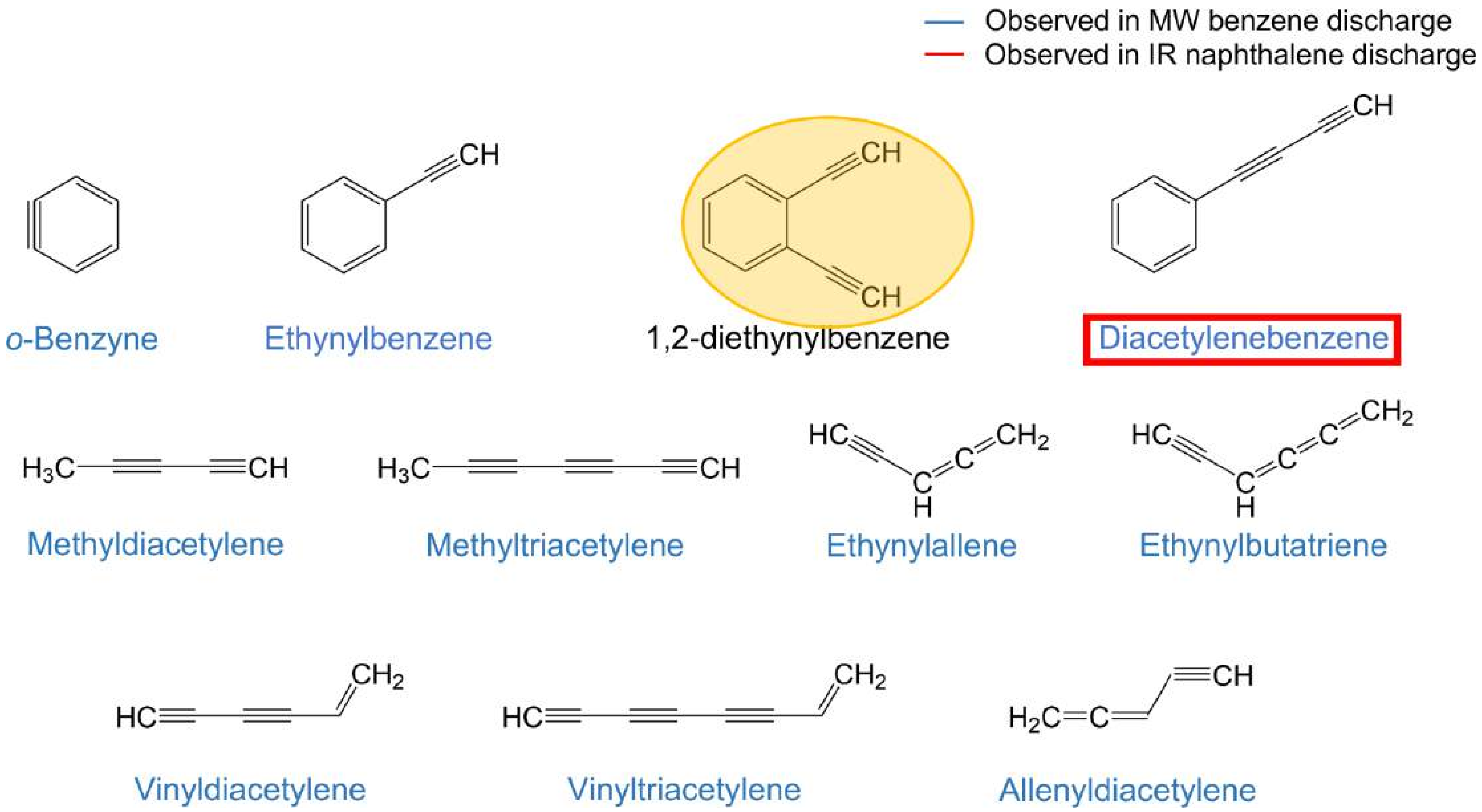

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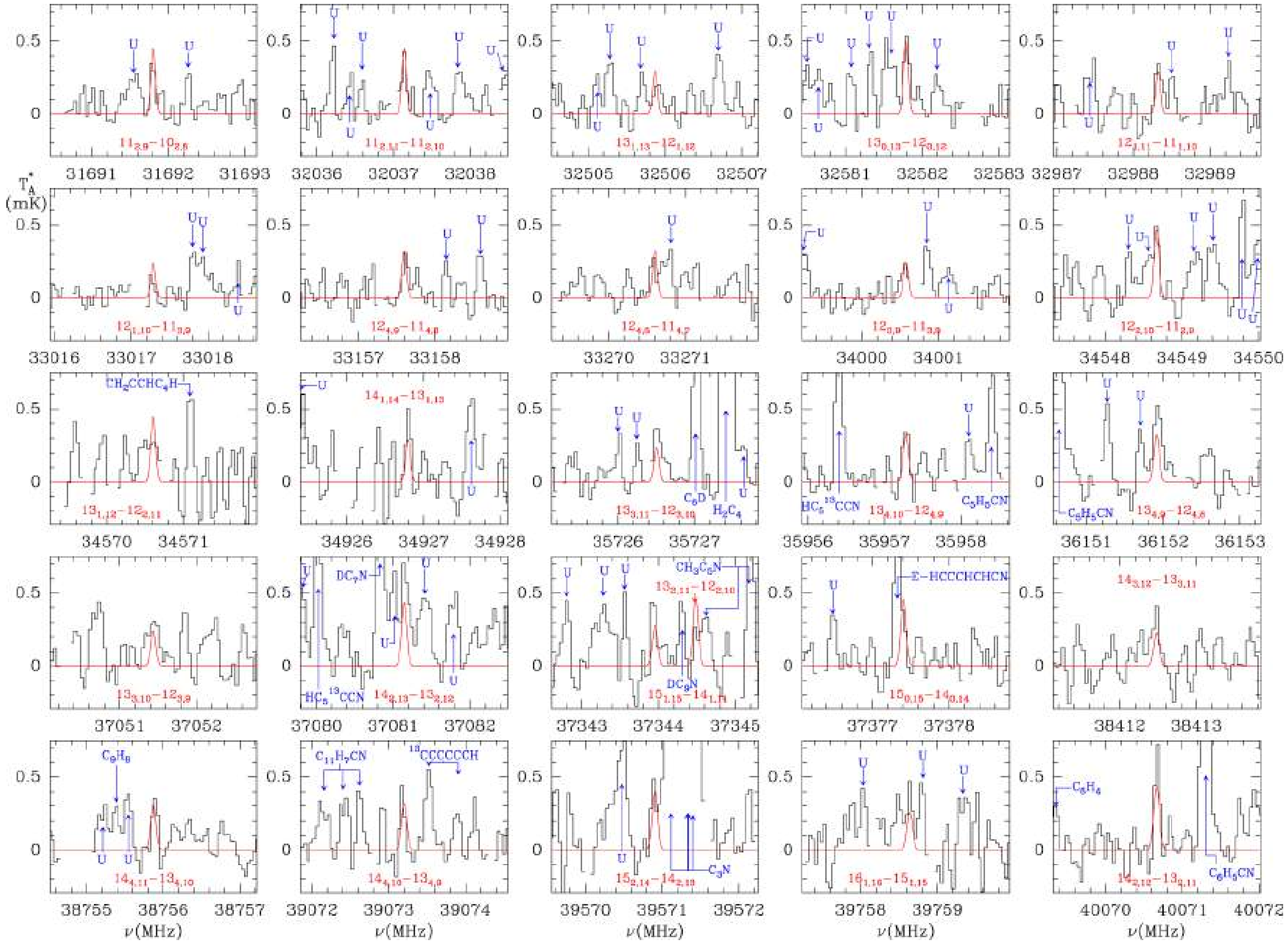
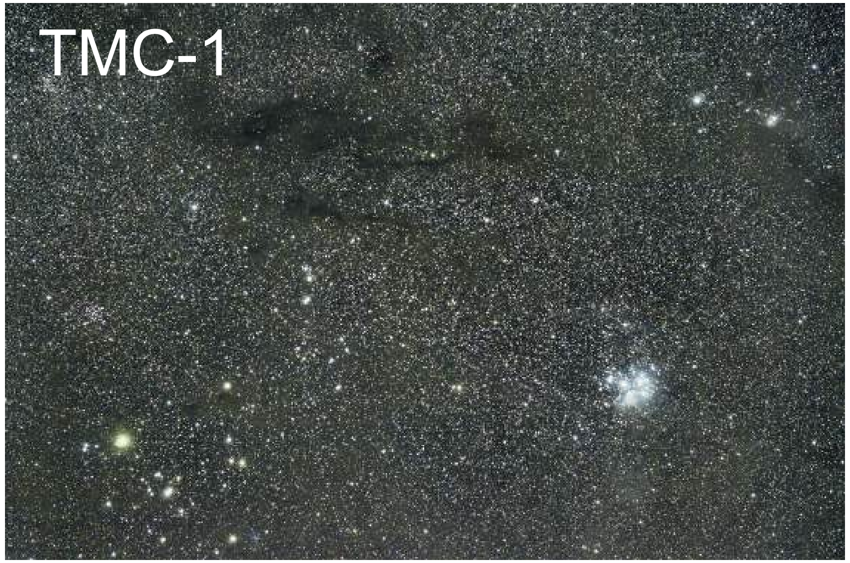
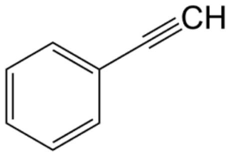
CP-FTMW Example: Naphtalene discharge products

Confirmation of **ethynylbenzene** in TMC-1 (3.0(5) ·10^{12} cm^{-2}) ☺
Diethynyl benzene not detected (<2.0 ·10^{12} cm^{-2}) ☹





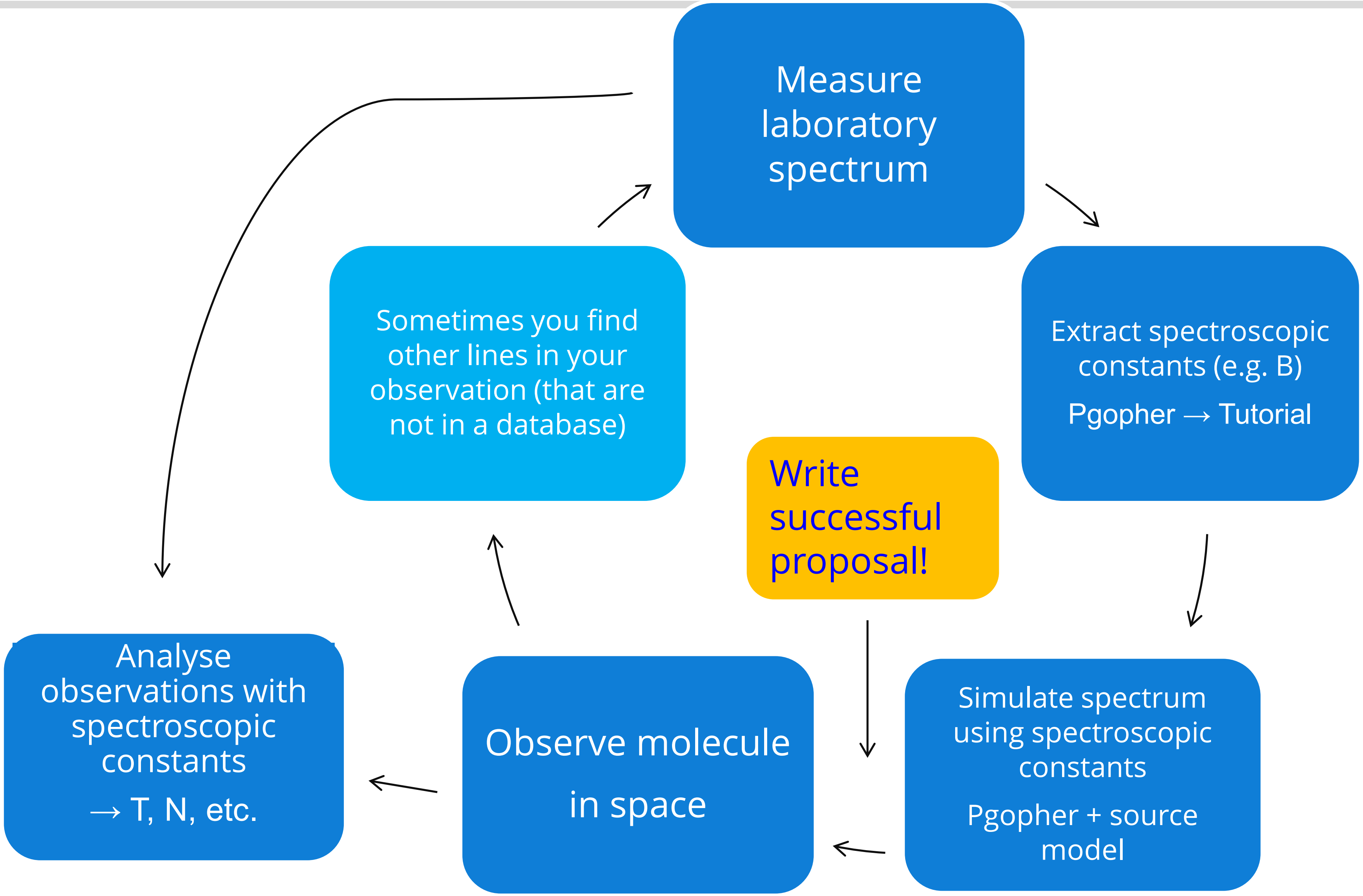


- Main formation via reactions of benzene with CCH

Lab (chemistry): Jones et al., JPCA 114 (2010)
Lab & Astro: D. Loru et al., A&A 677 (2023) A166

Radboud University

How to get from laboratory data to astronomical search



Measure laboratory spectrum

Extract spectroscopic constants (e.g. B)

Pgopher → Tutorial

Simulate spectrum using spectroscopic constants

Pgopher + source model

Observe molecule in space

Analyse observations with spectroscopic constants

→ T, N, etc.

Sometimes you find other lines in your observation (that are not in a database)

Write successful proposal!

Concept Test

Is it „easier“ to observe a molecule like CO or a complex molecule like indene?

(assuming the same source temperature and dipole moment)

Concept Test

Is it „easier“ to observe a molecule like CO or a complex molecule like indene?

(assuming the same source temperature and dipole moment)

Answer: Intensity „dilution“

$$\Delta T_B = N \frac{g_u c^3 h A_{ul}}{8k\pi v^2 \Delta \text{v}\, U(T)} e^{-\frac{E_u}{kT}} \qquad U(T) = \sum g_i e^{-\frac{E_i}{kT}}$$

For a complex molecule with small rotational constant many rotational levels are populated, so the emission intensity is „spread“ over many transitions

Summary

- Molecules can be observed in different regions of the electromagnetic spectrum: from the **optical via the infrared to microwaves** – corresponding to **electronic, vibrational, and rotational transitions** in molecules

- Rotational transitions are well suited to observe **cold** molecular clouds

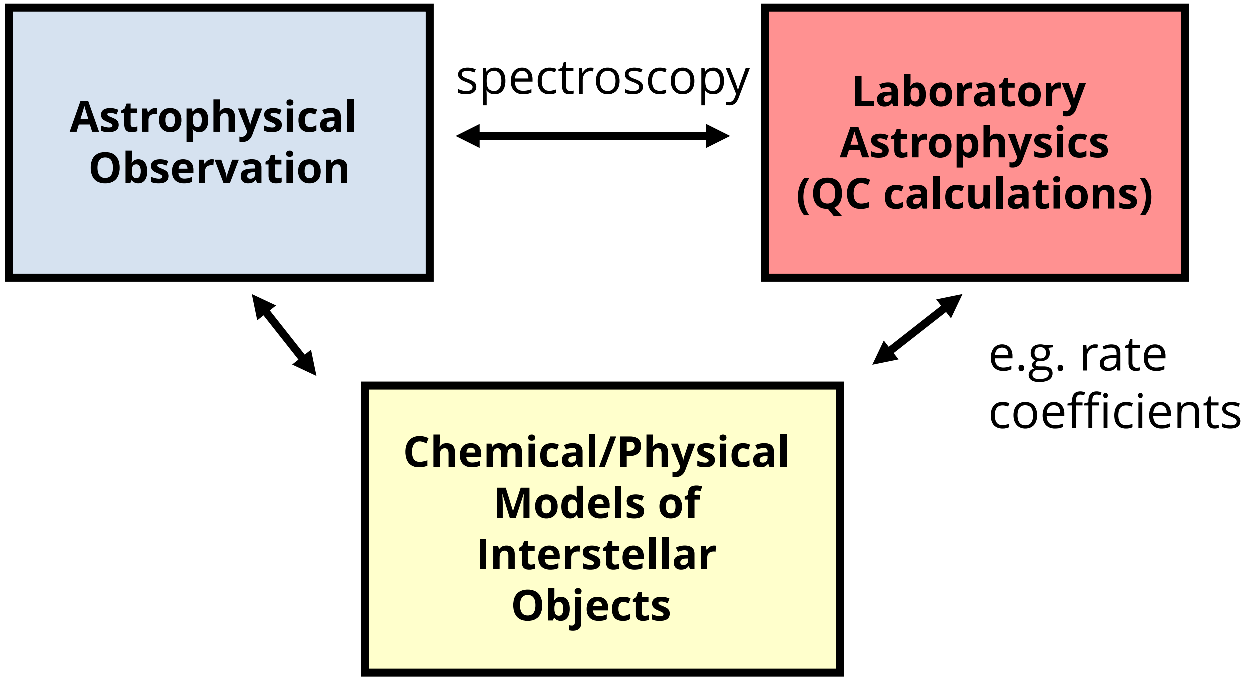
- Spectroscopy in the laboratory provides the **spectral fingerprint** needed to identify molecules in space

- Databases for rotational spectroscopy:
  - https://cdms.astro.uni-koeln.de
  - http://www.vamdc.org/
  - https://spec.jpl.nasa.gov/

Challenges

- Calculations alone often not good enough for an unambiguous identification
- Each and every molecule (+ isotopes, vibrational states) needs to be measured and analysed, often thousands of lines – tedious
- Not all molecules (in particular radicals, ions) are easy to make, much experimental effort for new spectroscopic methods (action spectroscopy!)
- As an astronomer: please cite the laboratory work (not only the databases), so we get funding for this work

Questions?



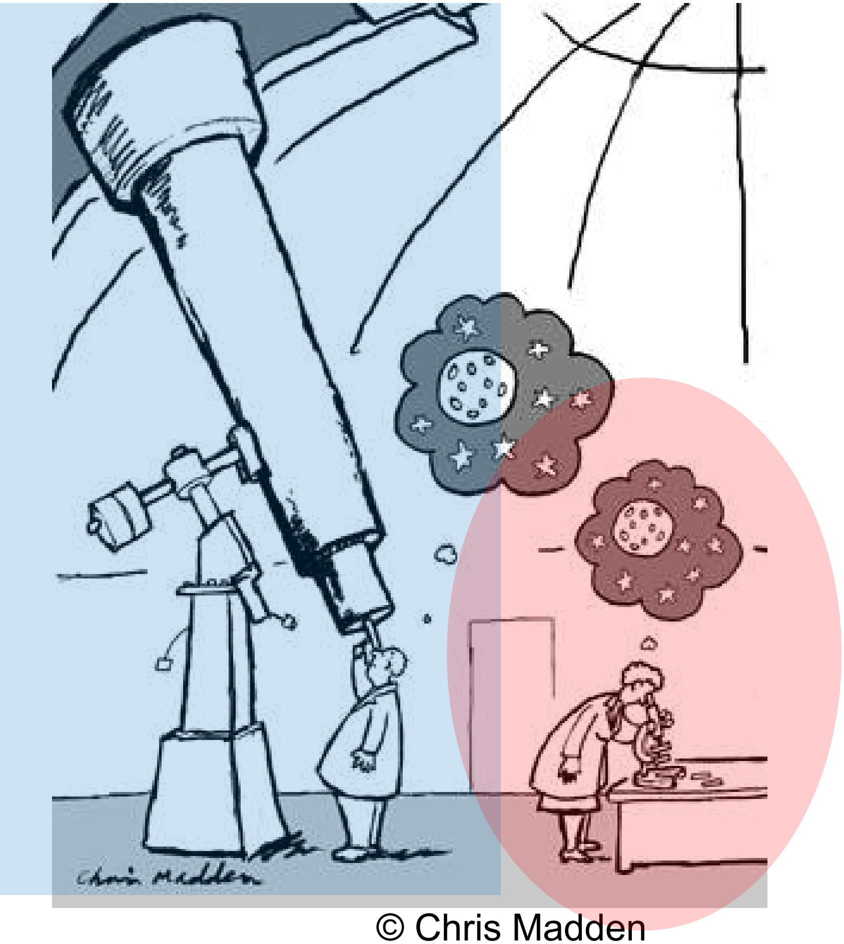
Astrophysical Observation

spectroscopy

Laboratory Astrophysics (QC calculations)

e.g. rate coefficients

Chemical/Physical Models of Interstellar Objects



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