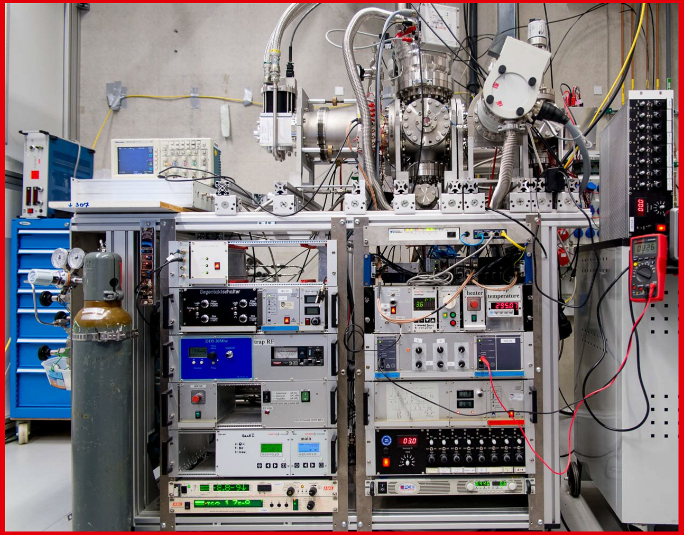
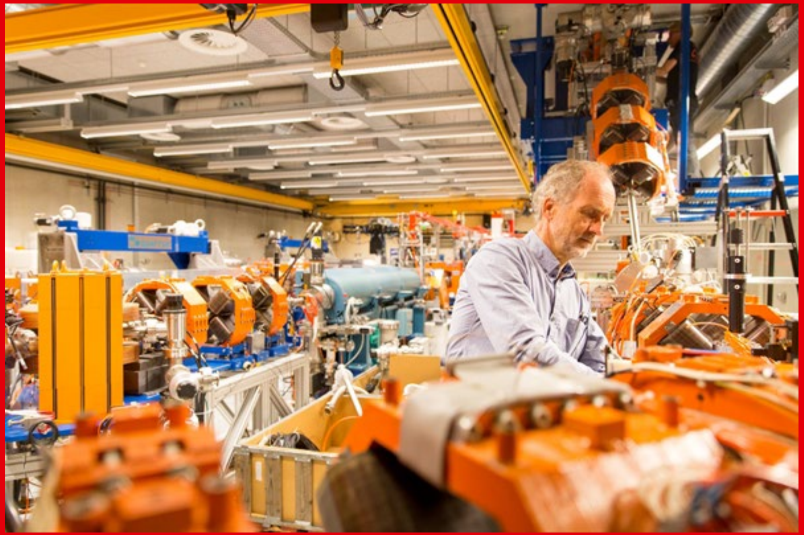
Rotational Spectroscopy
A Laboratory Perspective





2024 COST / DAN School

Sandra Brünken

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

DAN Dutch Astrochemistry Network III

NWO

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

NanoSpace

Funded by the European Union

Origins Center

HFML Science in High Magnetic Fields

FELIX Free Electron Lasers for Infrared eXperiments

Radboud University

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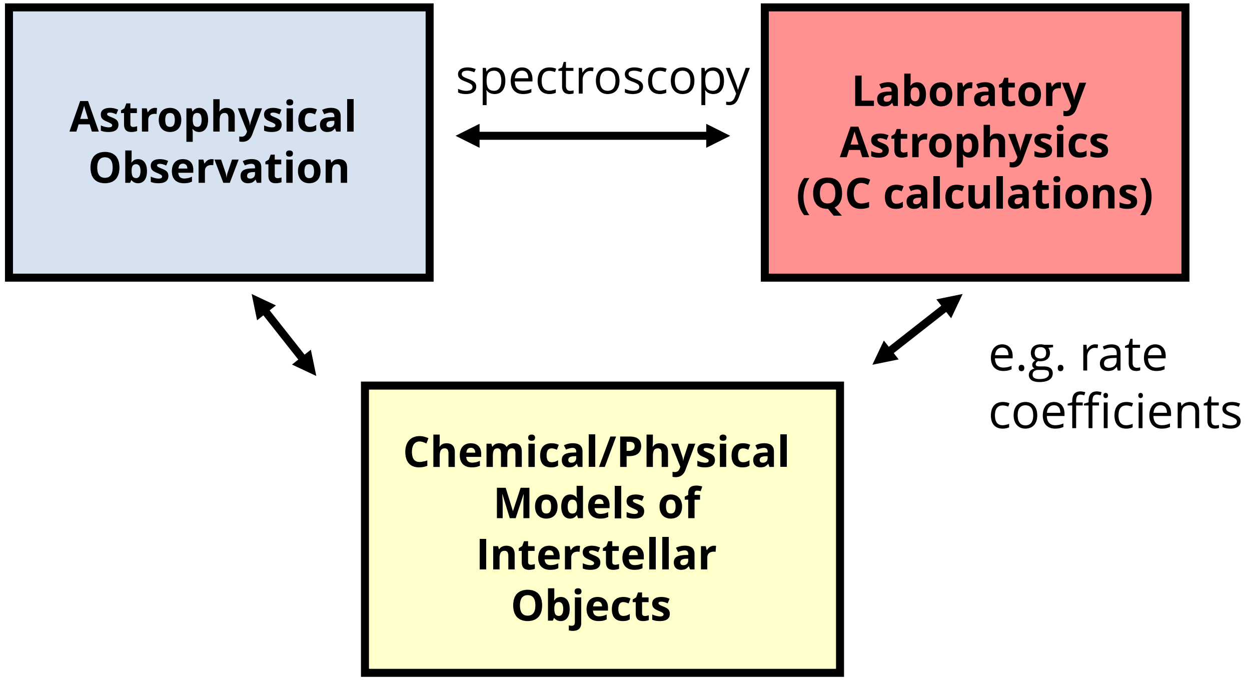
The Golden Triangle of Astrochemistry



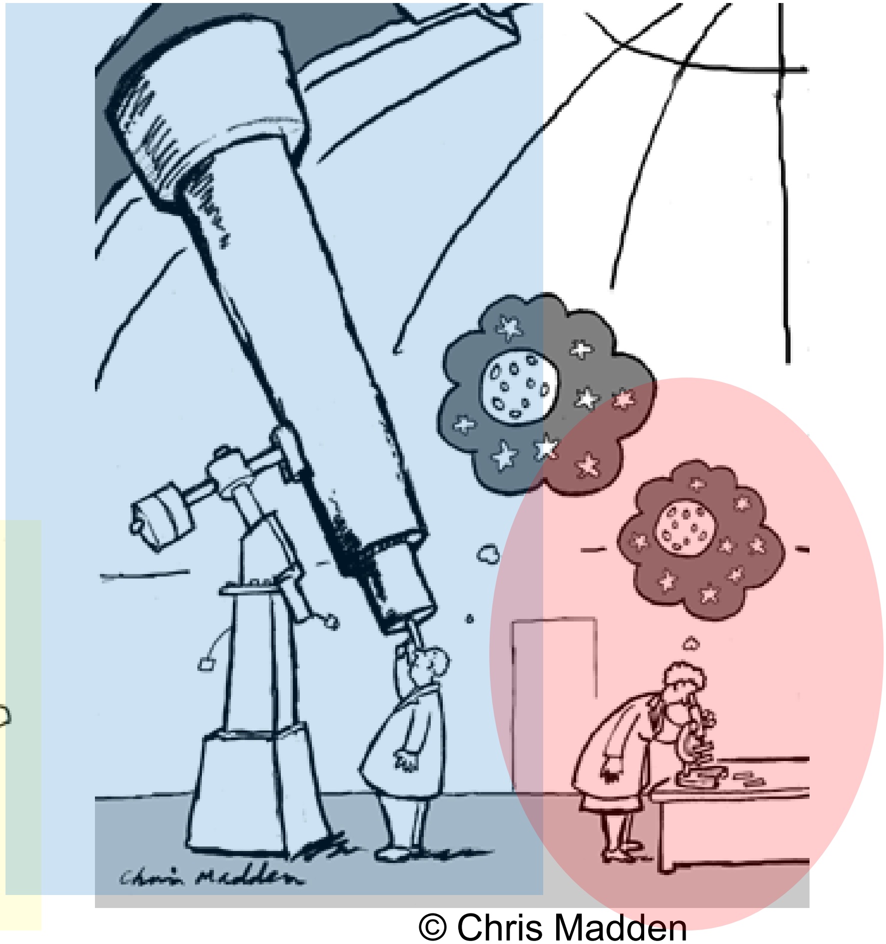
Astrophysical Observation

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

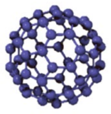
- Molecular transitions probe: chemical composition
  physical conditions
  (temperature, densities, ...)

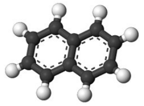
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms
NO	MgCN	H2CS	SiH4 *	H2CCNH ?	c-C3HCCH	HC5NH+	H2C3HCCH
NS	MgNC	H3O+	H2COH+	C5N–	l-H2C5	CH2CHCCH	HOCHCHCHO
NaCl	N2H+	c-SiC3	C4H–	HNCHCN	MgC5N	MgC6H	
OH	N2O	CH3 *	HC(O)CN	SiH3CN	CH2C3N	C2H3NH2	

- Laboratory needs: spectroscopic data (rotational)
  for many species
  at high resolution

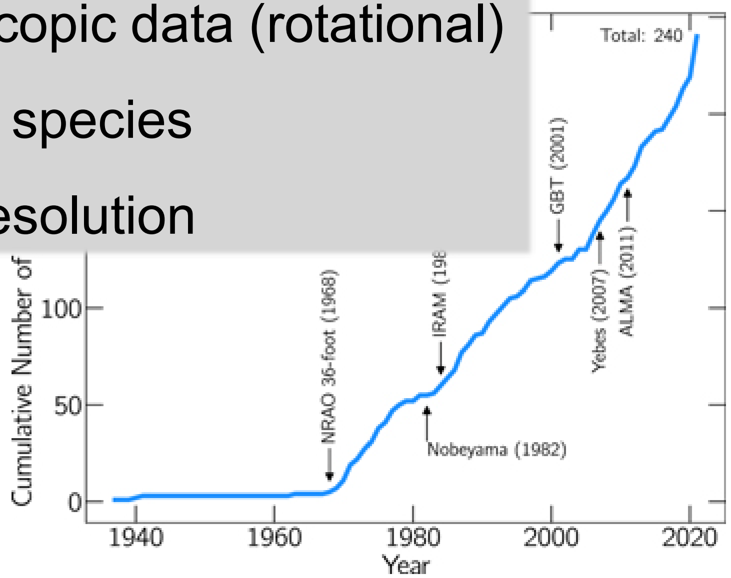
2 atoms	3 atoms	4 atoms	5 atoms
O2	HCP	HONO	H2CsS
CF+	CCP	MgC2H	C4S
SiH ?	AlOH	HCCS	HC(O)SH
PO	H2O+	HNCN	HC(S)CN
AlO	H2Cl+	H2NC	HCCCO
OH+	KCN	HCCS+	
CN–	FeCN		
SH+	HO2		
SH	TiO2		
HCl+	C2N		
TiO	Si2C		
ArH+	HS2		
NO+ ?	HCS+		
NS+	HSC		
HeH+	NCO		
PO+	CaNC		

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			





Inga Kamp



> 320 total
~ 70 % organic
~ 15 % ions

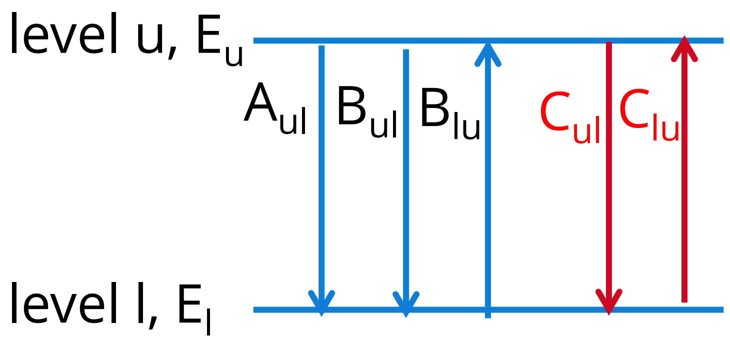
- www.cdms.de
- McGuire, ApJS 259 (2022) 30

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

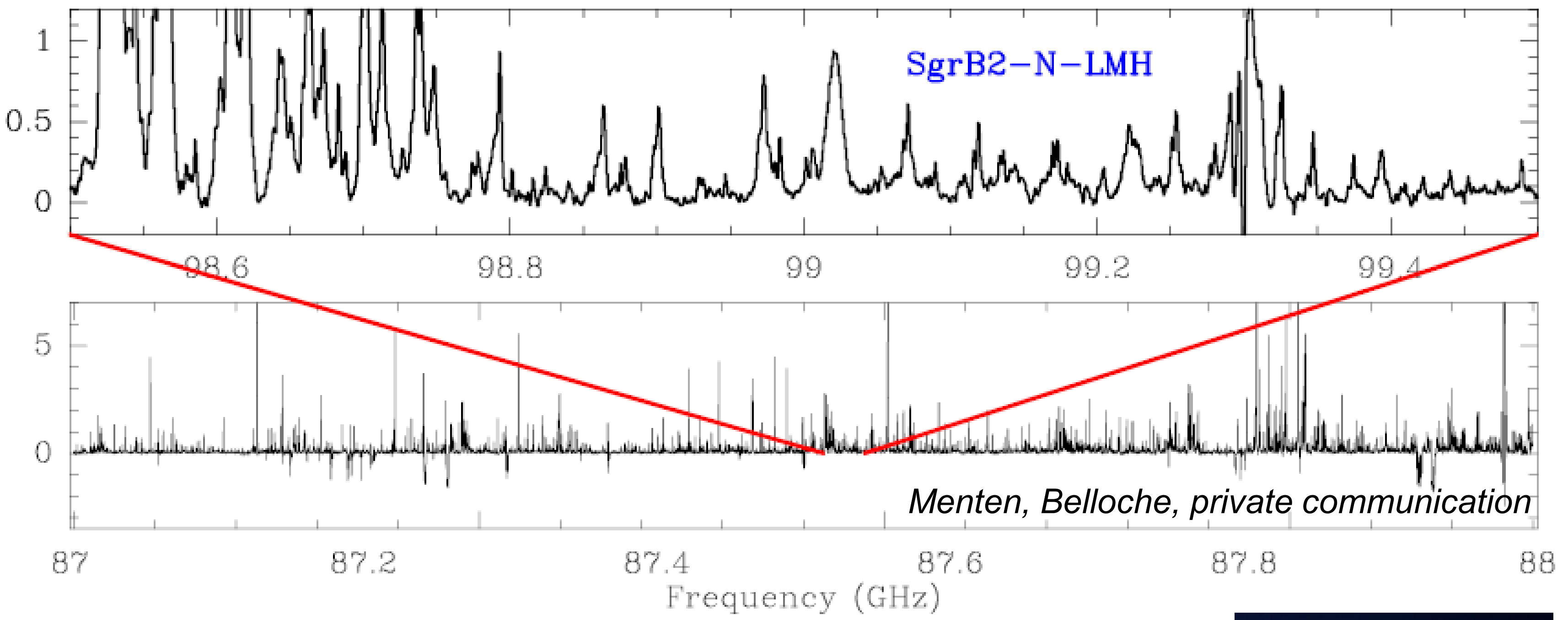
LTE: local thermal equilibrium

- 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?

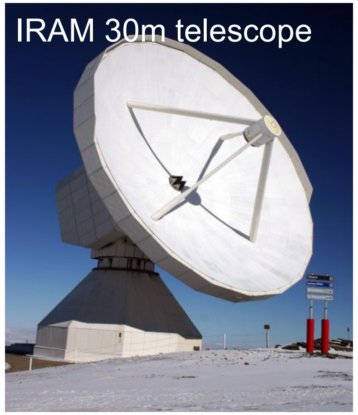


“Large Molecule Heimat”

Menten, Belloche, private communication

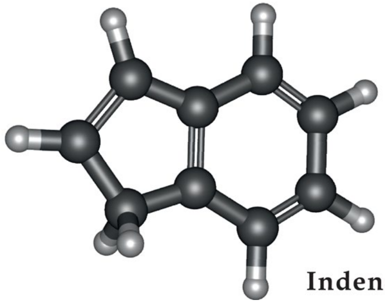
- Line rich sources, often 100 lines per GHz
  → high chance of wrong assignments

- 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

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

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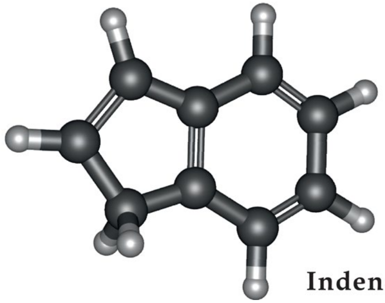

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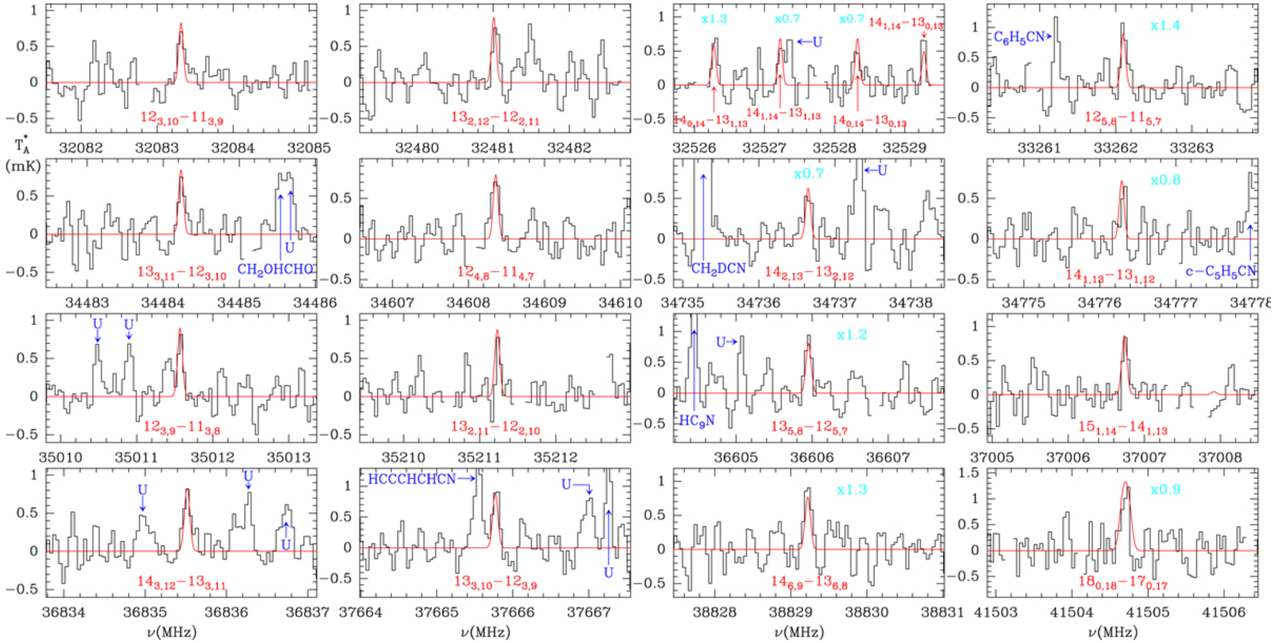
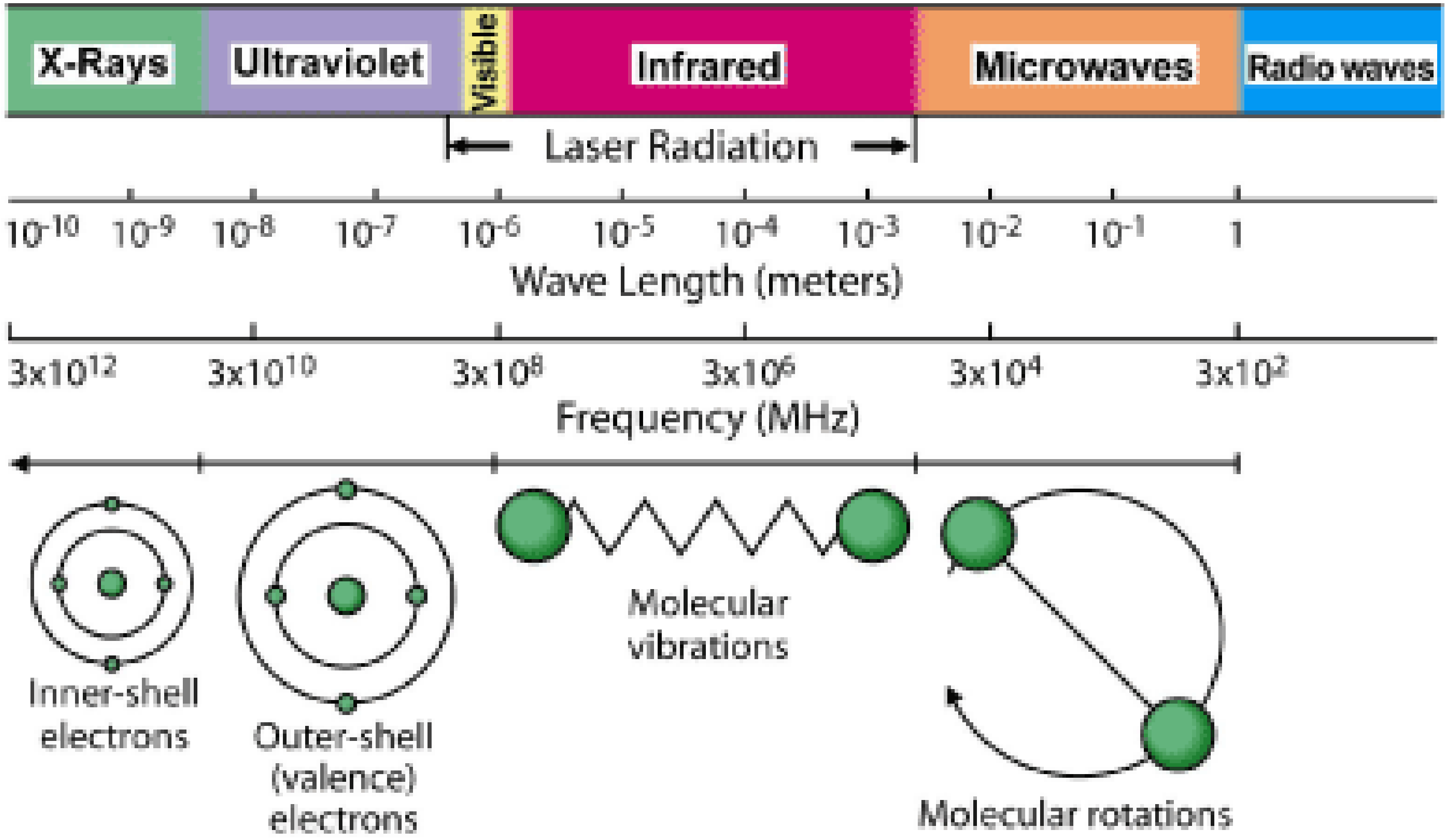


Cernicharo et al., A&A Lett., 2021
https://doi.org/10.1051/0004-6361/202141156

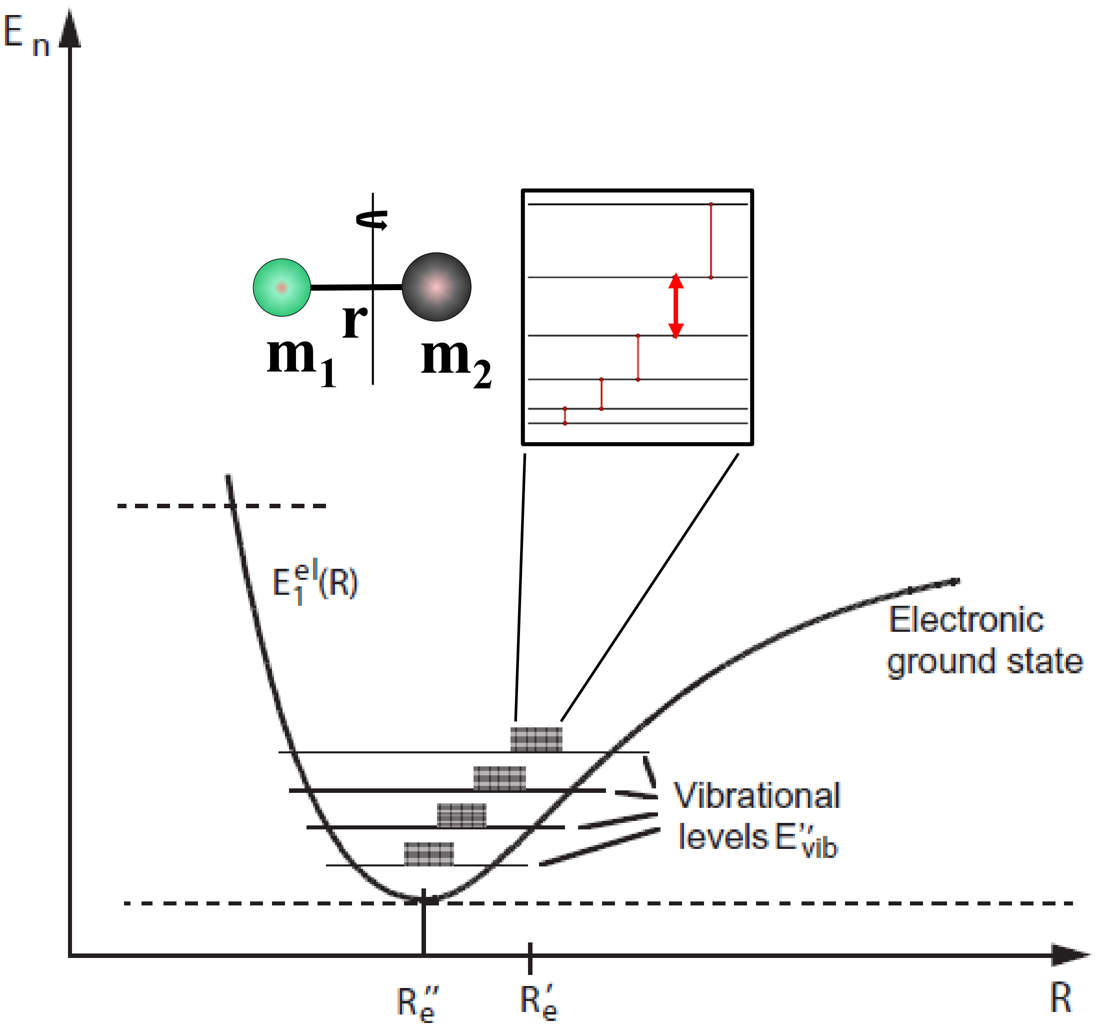
Yebes 40m telescope (Spain)

Spectroscopy is used in all wavelength ranges

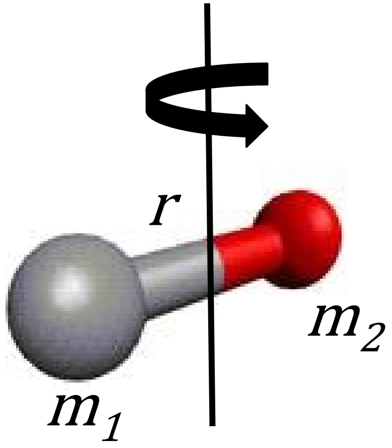


From: https://www.ices-emfsafety.org/electromagnetic-energy/

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: $$\widehat{\boldsymbol{H}}_{rot} \varphi = E_{rot} \varphi$$

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

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

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

Rotational constant
(in Joule)

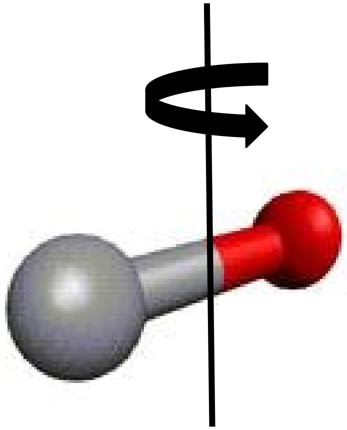
$$\boxed{E = h\nu}$$

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

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

Rotational constant
(in Hz - frequency)

Rotational Spectroscopy - diatomics

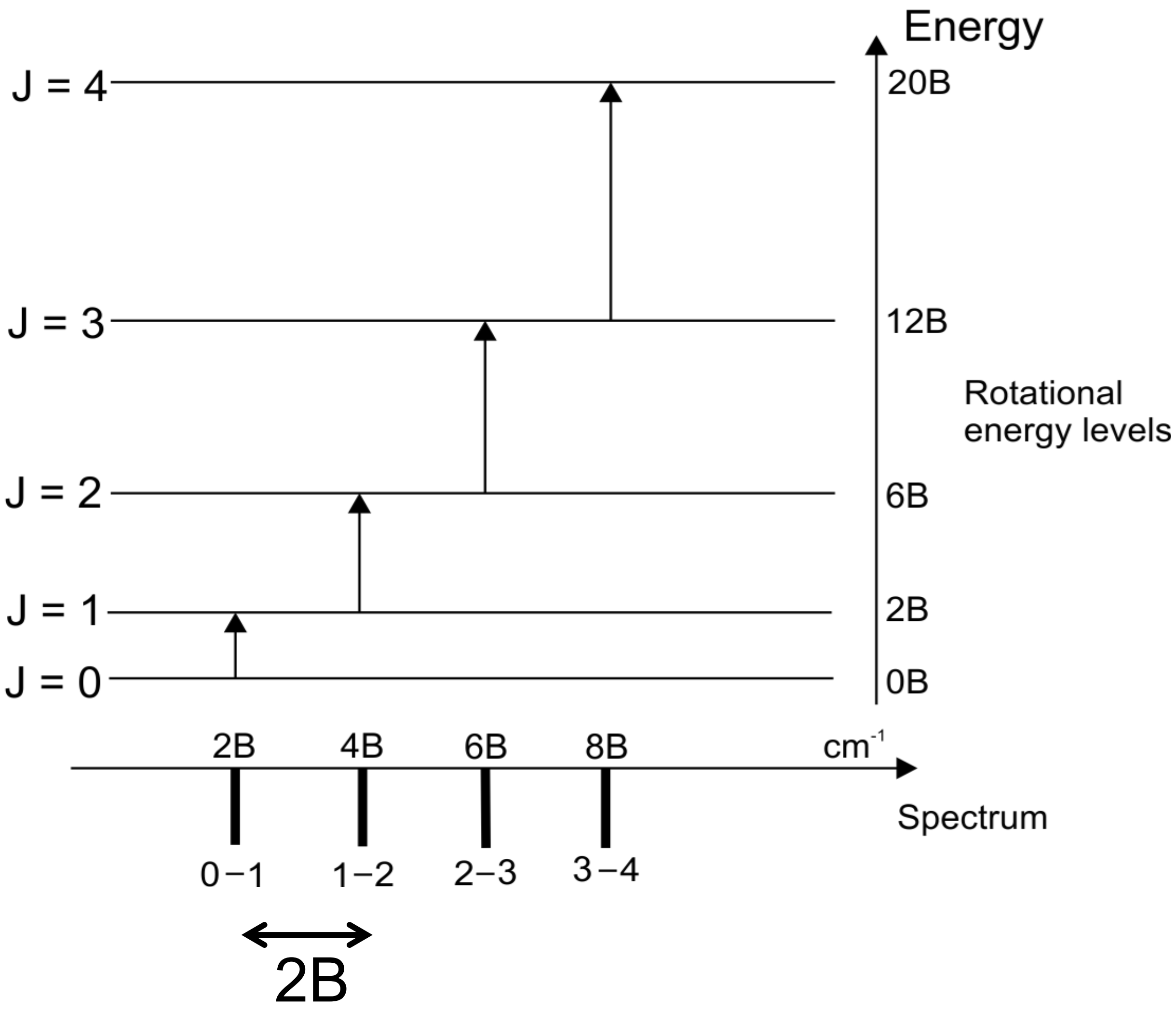


$$E_{\mathrm{rot}} = B \cdot J(J+1)$$

$\Delta J = \pm 1$ selection rule

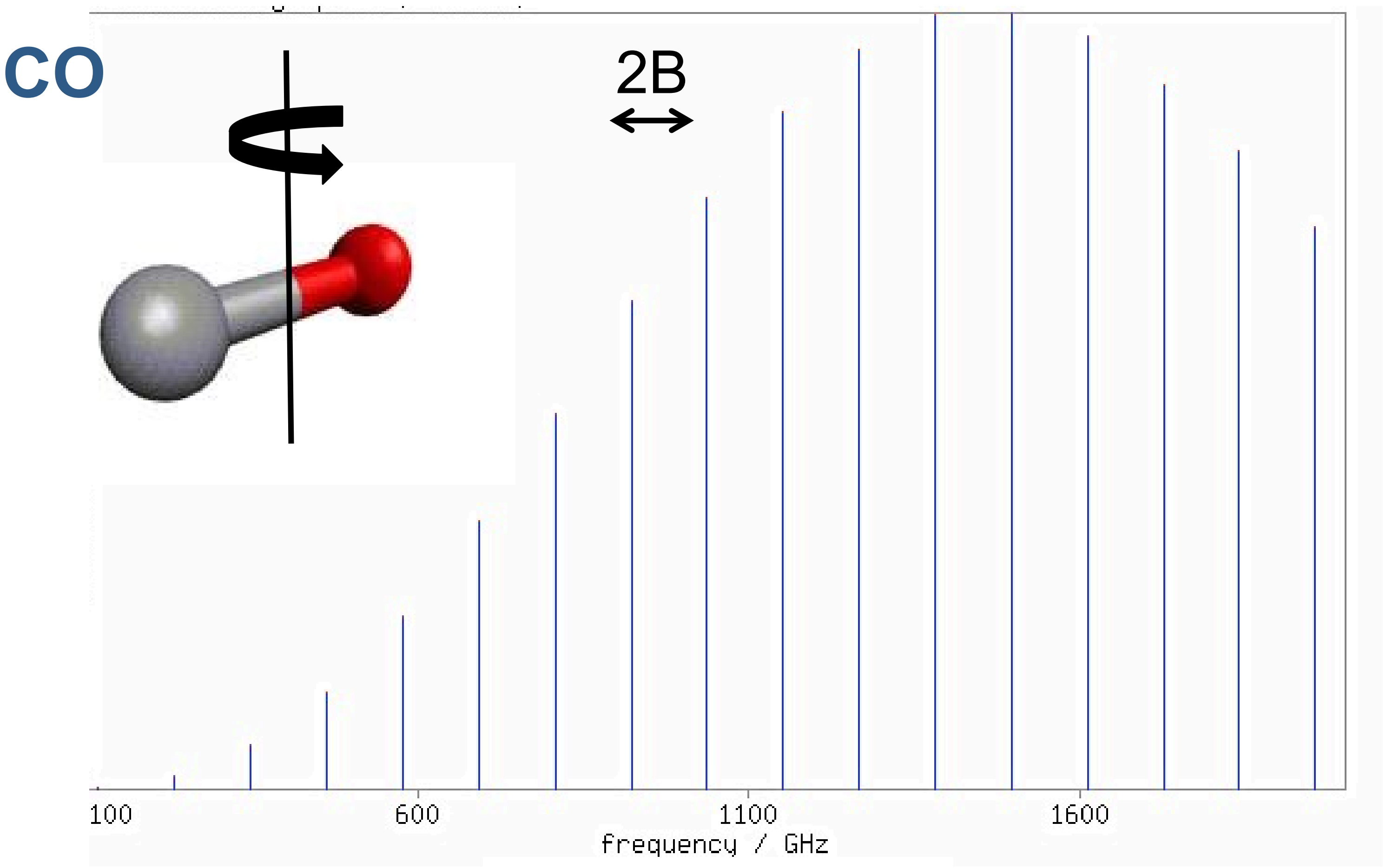
$$\boldsymbol{\Delta E_{\mathrm{rot}} = 2B(J+1) \;= h\nu}$$

rotational transition frequencies



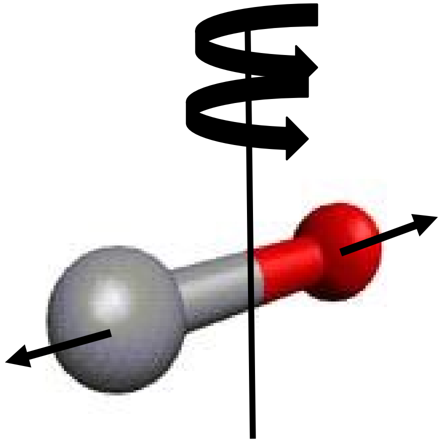
Rotational Spectroscopy - diatomics

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



frequency / GHz

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:

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

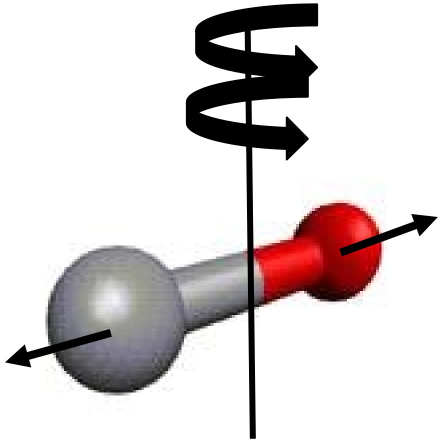
$$E_{rot} = B \cdot J(J+1) - D \cdot J^2\,(J+1)^2 \qquad (+\mathrm{H} \cdot J^3\,(J+1)^3 + \cdots)$$

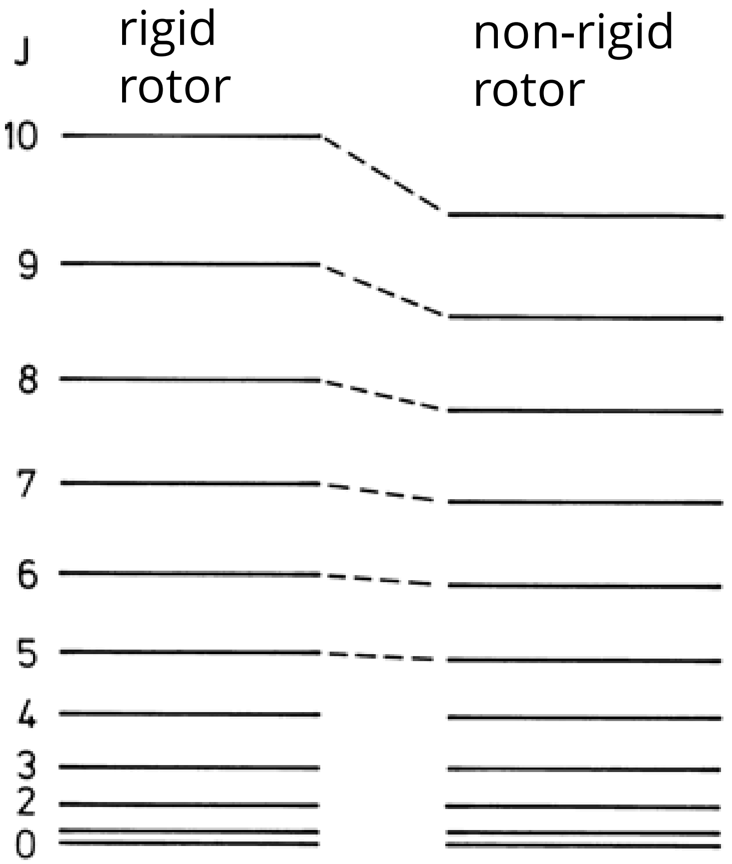
centrifugal distortion constant

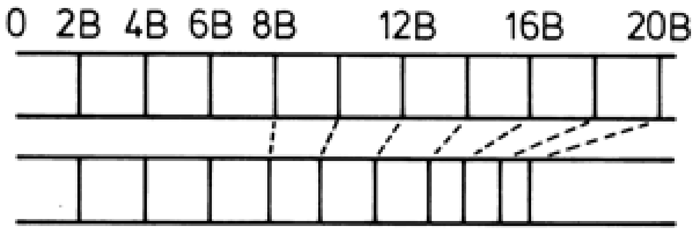
“effective Hamiltonian”

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

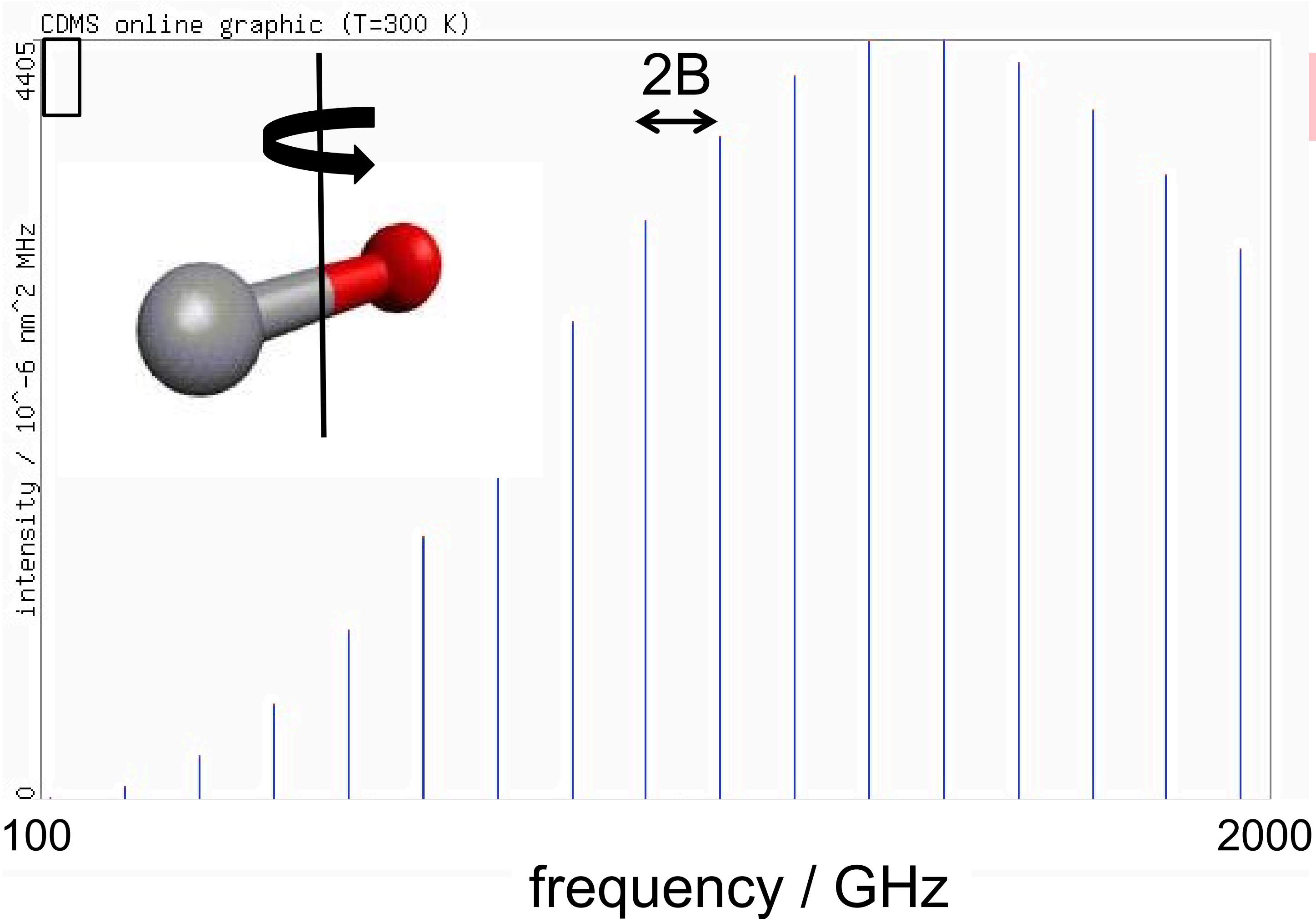
Rotational Spectroscopy – non-rigid rotor







Levels of complexity: isotopic species



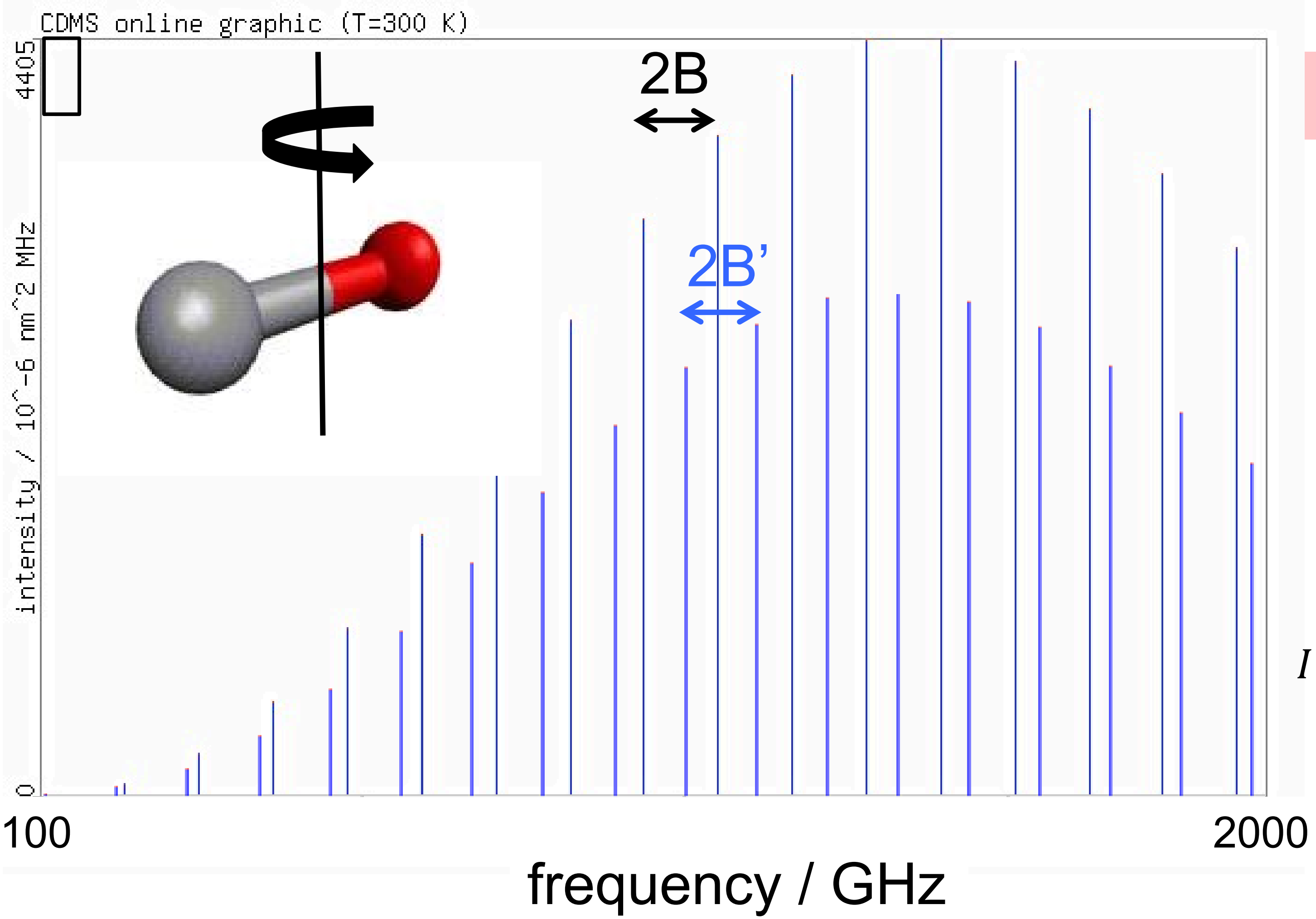
CO & ^{13}CO ??

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

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

Levels of complexity: isotopic species

And what if the molecule vibrates?



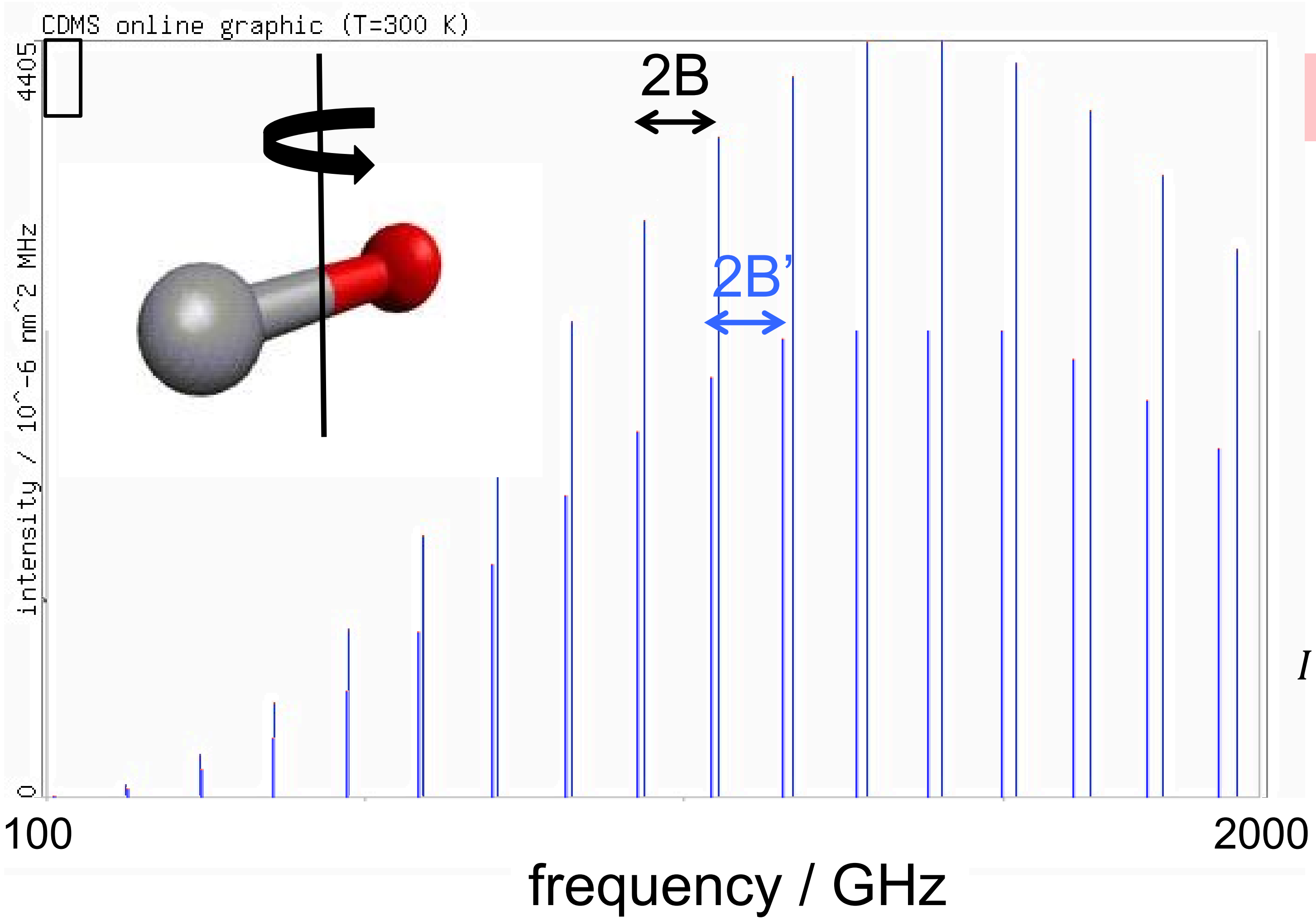
CO & ^{13}CO

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

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

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

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

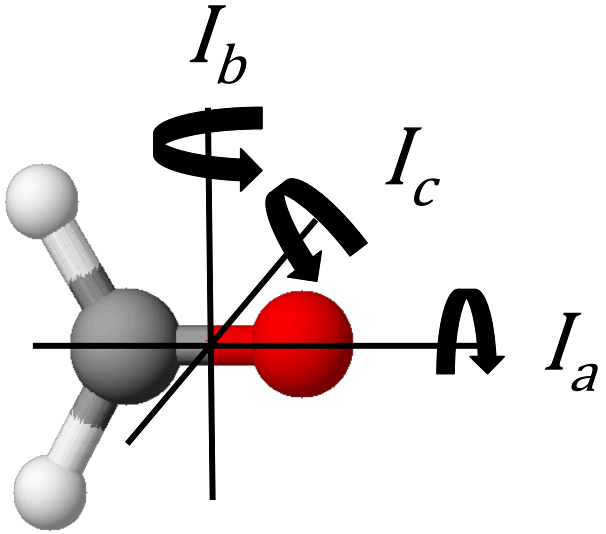
If you know a rotational frequency (and the corresponding $J \rightarrow J + 1$)
you can calculate B (and D)
and then the full rotational spectrum!

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: $I_a < I_b < I_c$

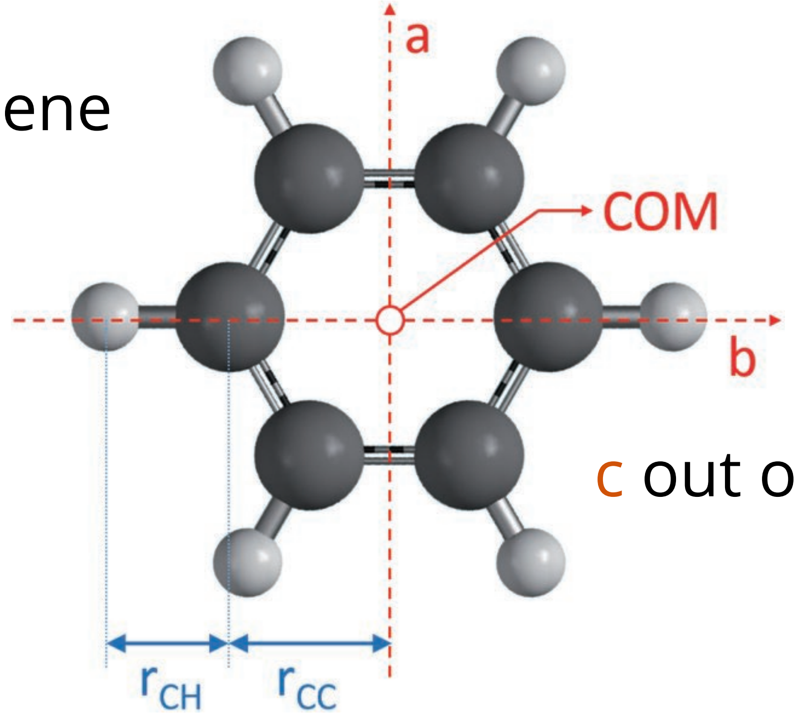
More difficult to calculate rotational spectra!

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?

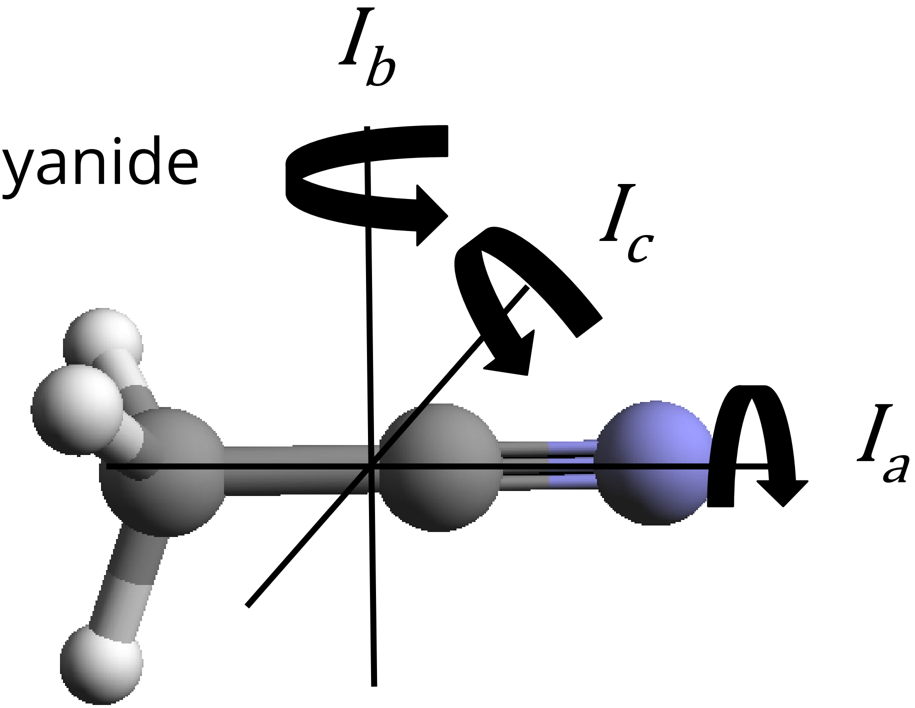
benzene



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

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

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

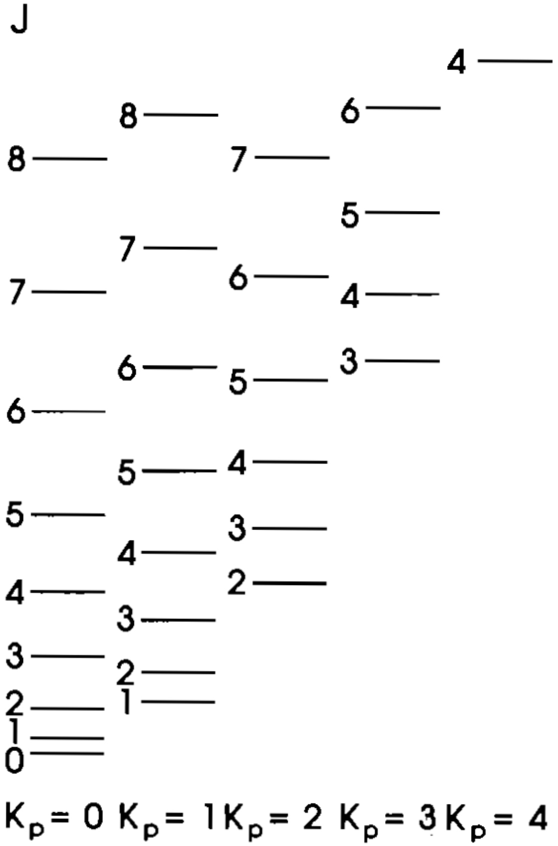
Solutions: $E_{JK} = BJ(J+1) + (A-B)K^2$ $A = \frac{h^2}{8\pi^2 I_a}$ $B = \frac{h^2}{8\pi^2 I_b}$ $C = \frac{h^2}{8\pi^2 I_c}$

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

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

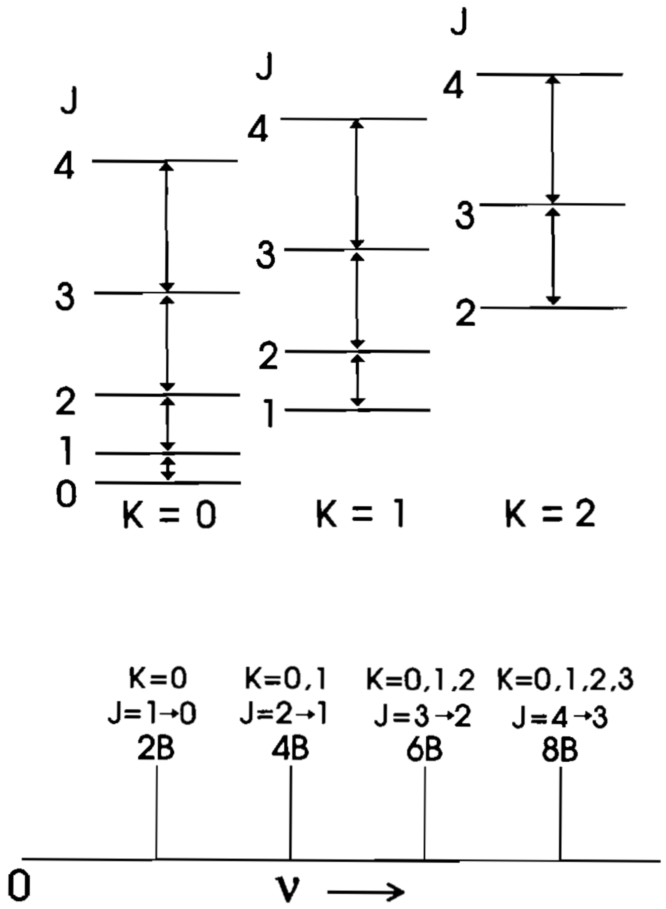
Symmetric Rotors

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



prolate symmetric top

Allowed transitions (prolate):



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

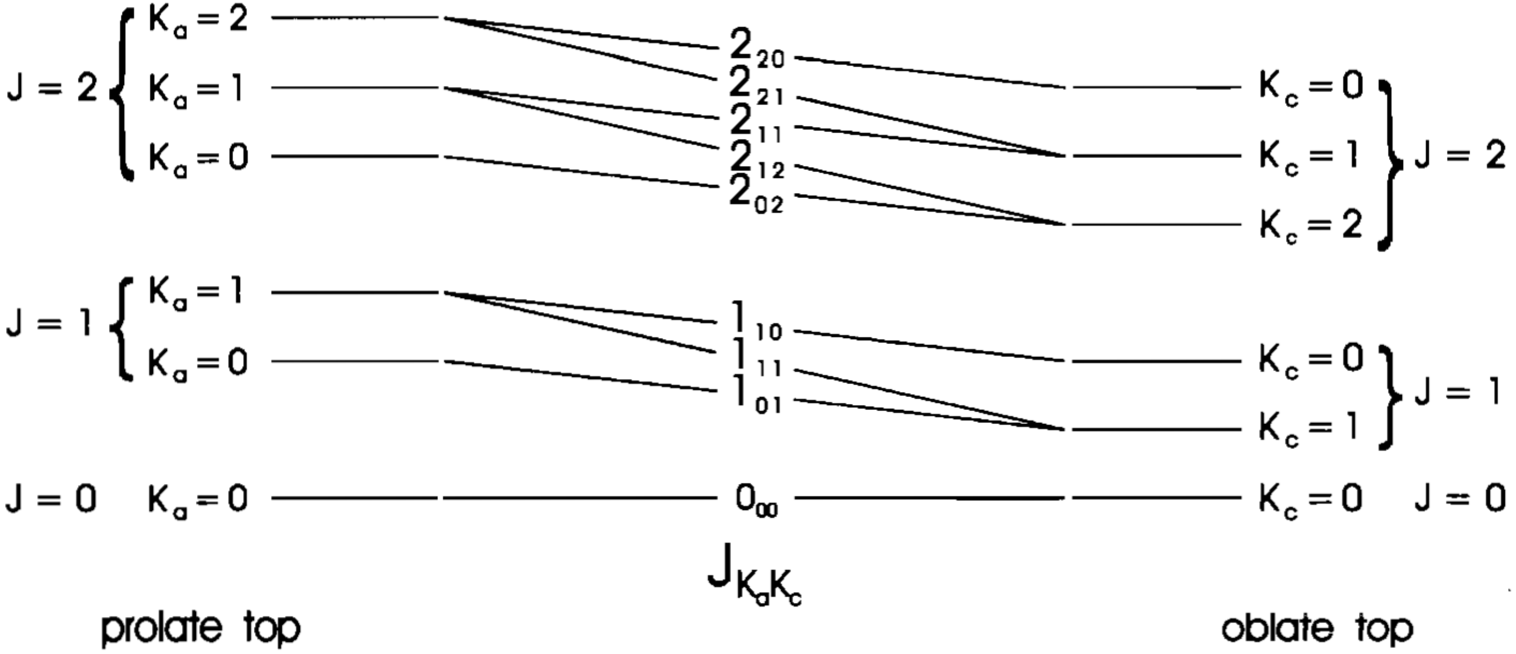
Without centrifugal distortion the spectrum looks as that of a linear molecule!

Reality:
Bonus Tutorial

© P. Bernath, Spectra of Atoms and Molecules

Asymmetric Rotors (brief)

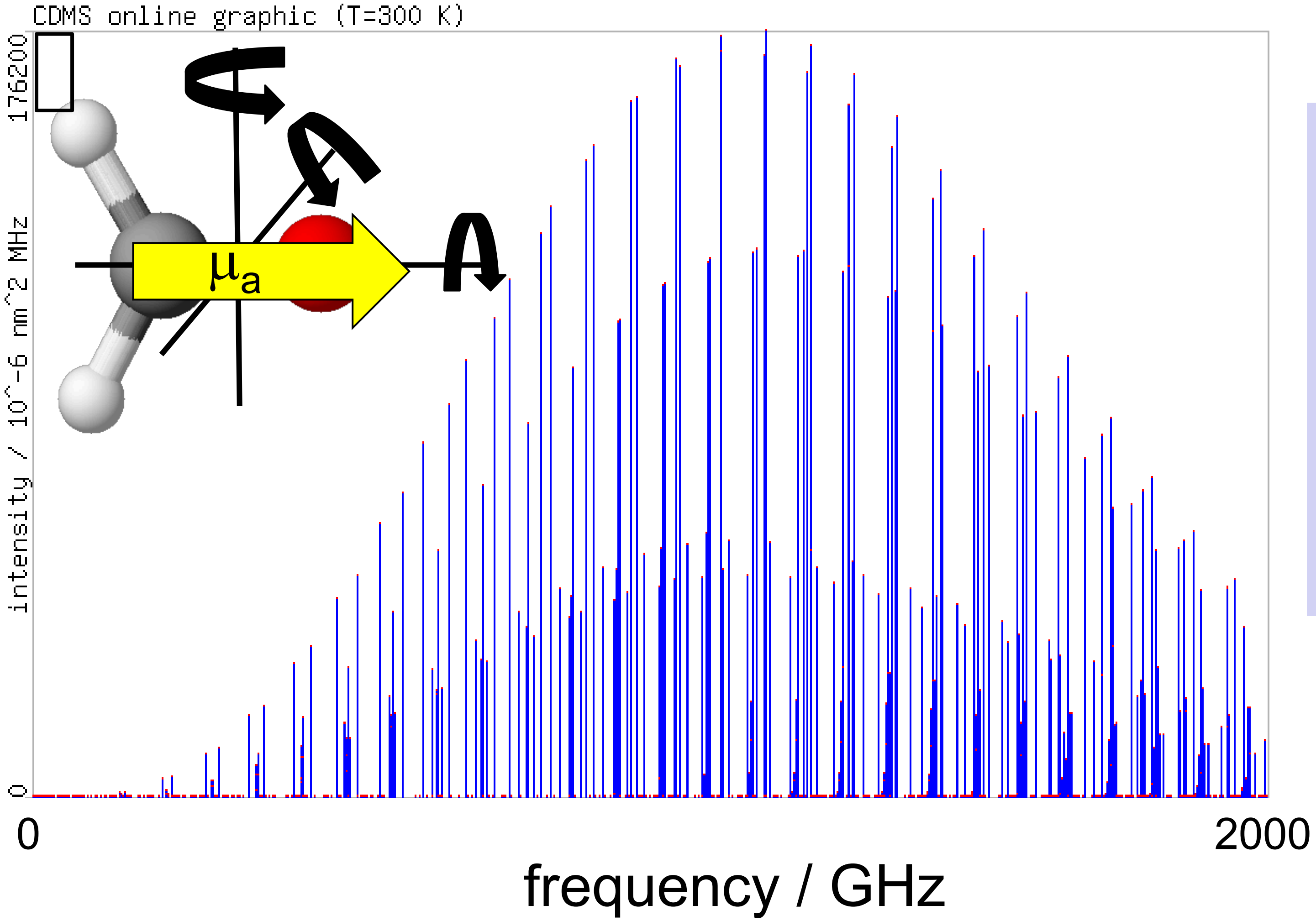
- Asymmetric top: $I_a < I_b < I_c$ $\hat{\boldsymbol{H}}_{rot} = \frac{\hat{\boldsymbol{P}}_a^2}{2I_a} + \frac{\hat{\boldsymbol{P}}_b^2}{2I_b} + \frac{\hat{\boldsymbol{P}}_c^2}{2I_c}$
- No analytical solutions, needs to be solved numerically, using symmetric wavefunctions as basis set.
- Two additional “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 $\mu_a \neq 0$: $\Delta K_a = 0$
    $\Delta K_c = \pm 1\ (\pm 3, \dots)$
  - b-type transitions with $\mu_b \neq 0$: $\Delta K_a = \pm 1\ (\pm 3, \dots)$
    $\Delta K_c = \pm 1\ (\pm 3, \dots)$
  - c-type transitions with $\mu_c \neq 0$: $\Delta K_a = \pm 1\ (\pm 3, \dots)$
    $\Delta K_c = 0$
- All can be allowed!

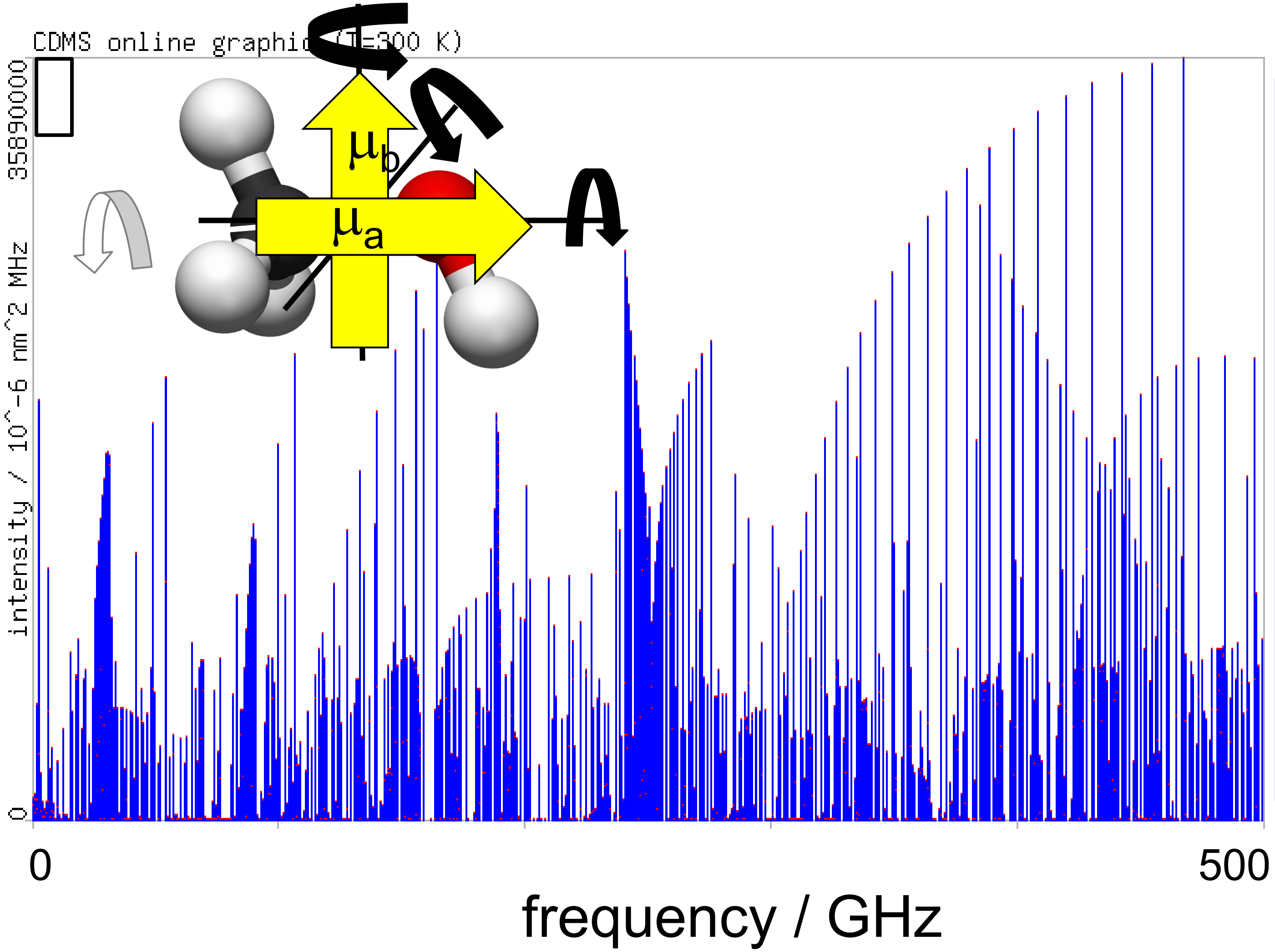
Levels of Complexity: asymmetry



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

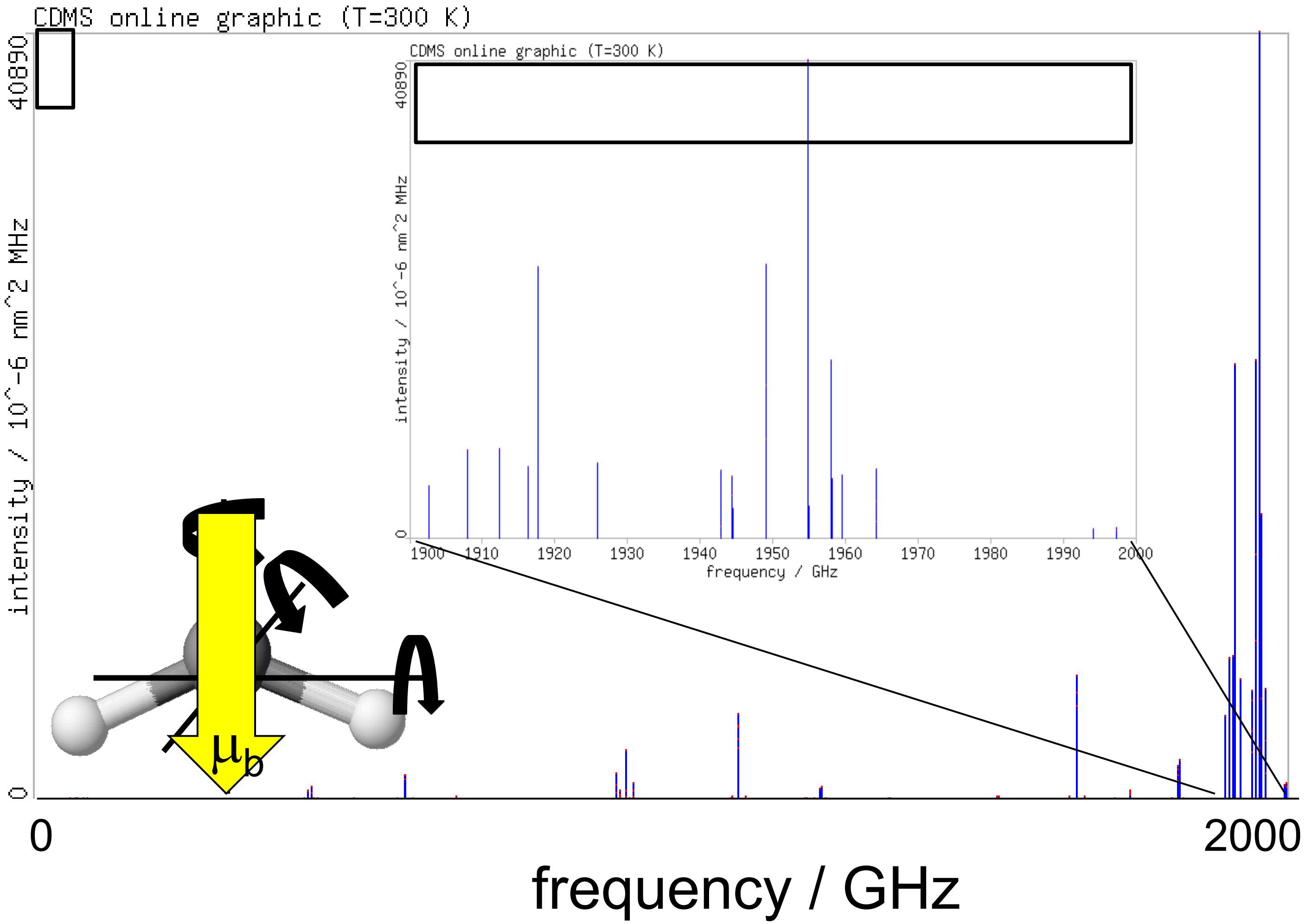
Additional „Complicatons“

- 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

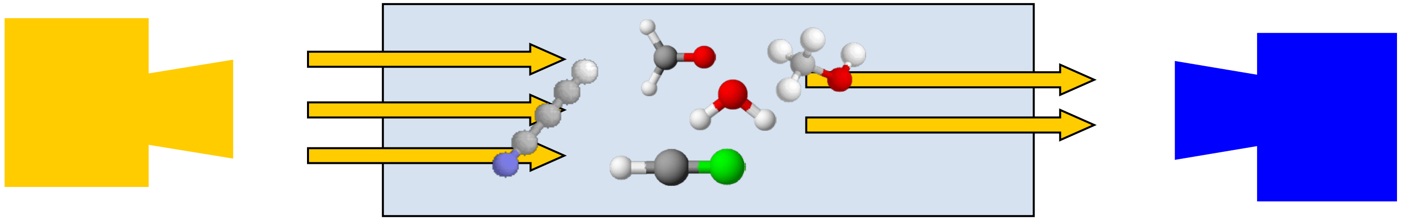
- Finding an efficient way to produce the molecule

- 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

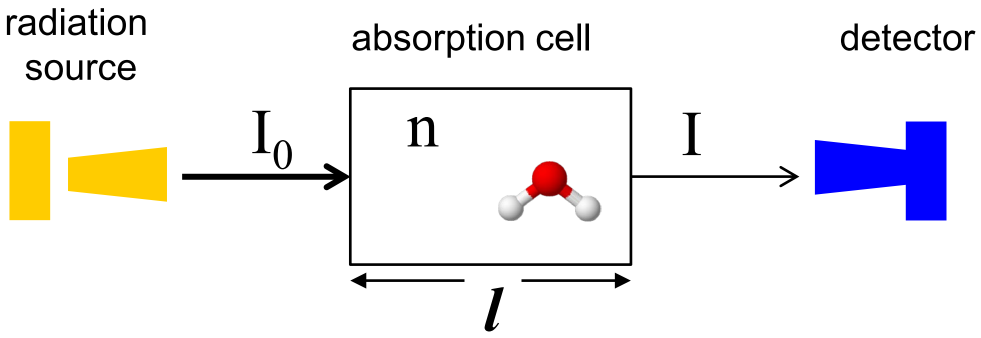


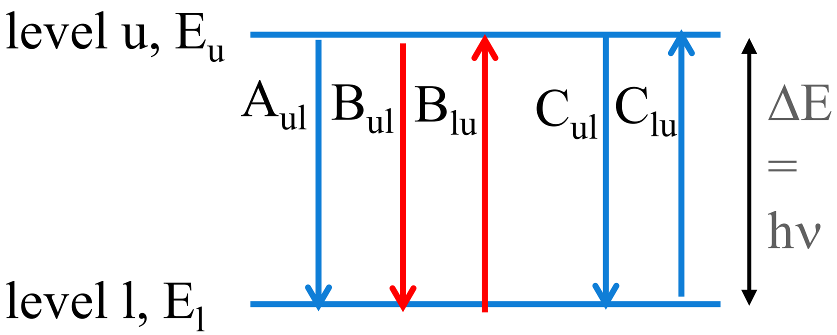
tunable, monochromatic radiation source

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

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

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

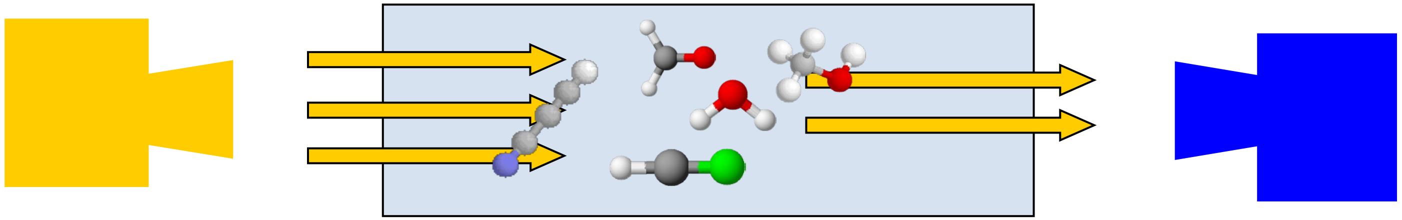
Simplified for $\frac{\mathrm{h}v}{kT} \ll 1$: $\Delta T_B = (T - T_b)\left[1 - e^{-\tau_v}\right]$

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

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

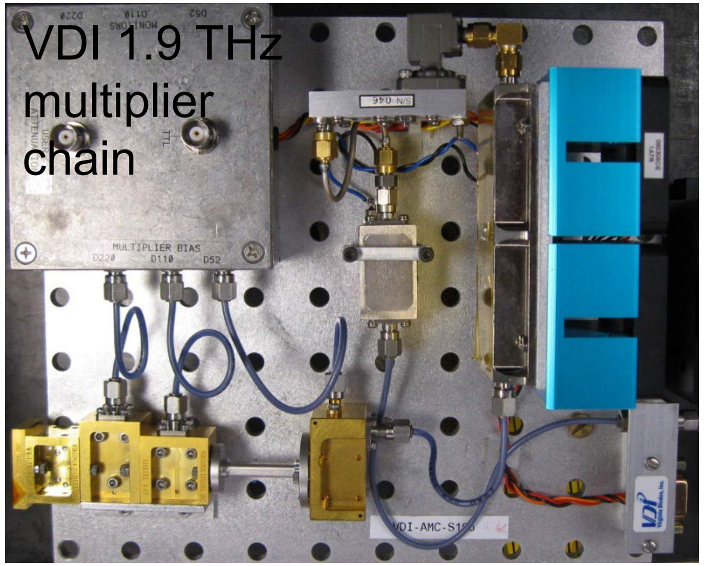


tunable, monochromatic radiation source

absorption cell

broadband photon detector

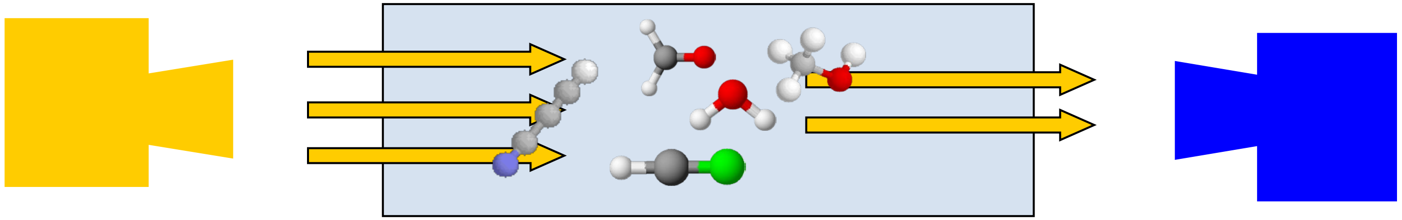
- Infrared: lasers (QCLs, OPOs, diodes)
- mm-, THz radiation sources
    - synthesizer, Gunn diodes
    - **solid state multiplier chains (up-conversion)**
    - FIR laser
    - Photomixing (down-conversion)…



VDI 1.9 THz multiplier chain

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

“Conventional” Absorption Spectroscopy



tunable, monochromatic radiation source

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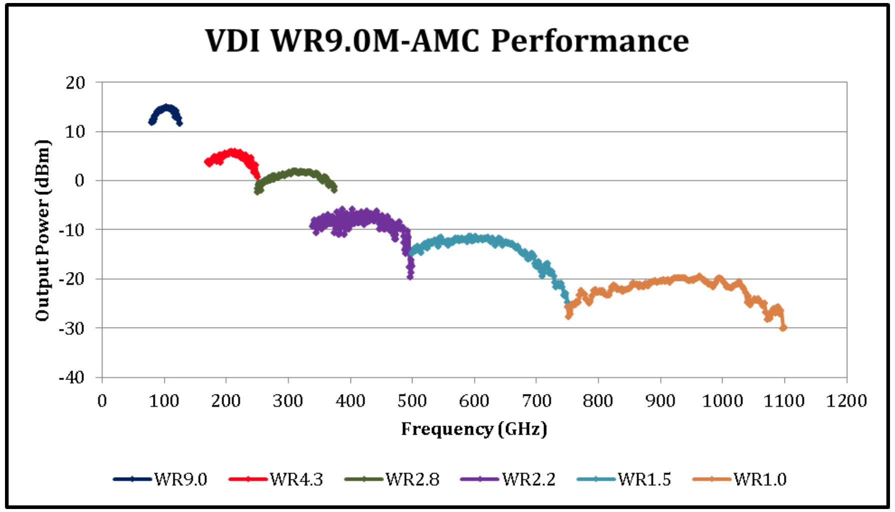
broadband photon detector

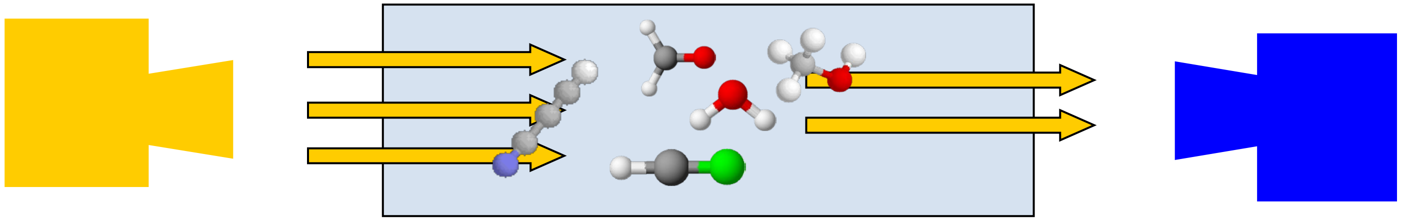
Virginia Diodes, Inc.



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%

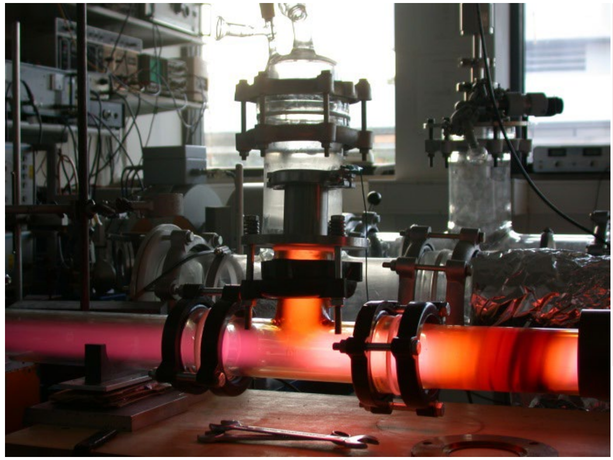
“Conventional” Absorption Spectroscopy



tunable, monochromatic radiation source

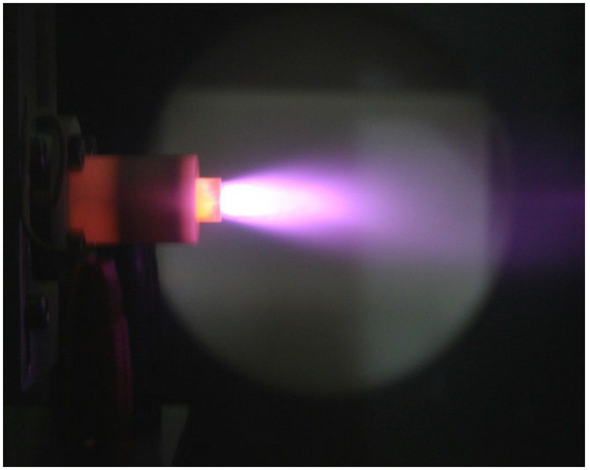
absorption cell

broadband photon detector:



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

  laser ablation



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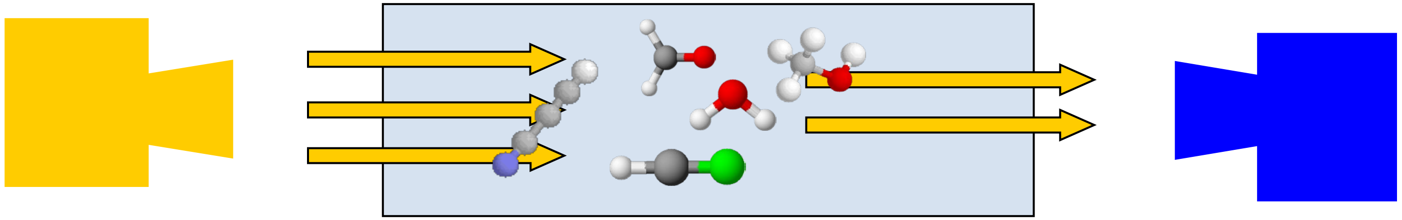

tunable, monochromatic radiation source

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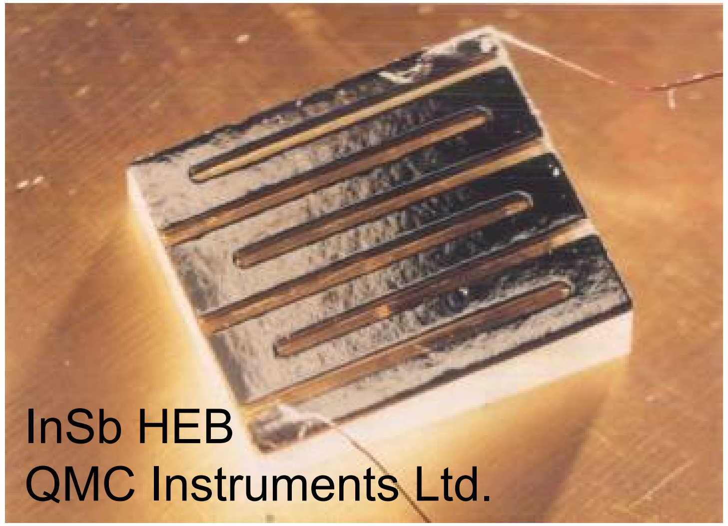


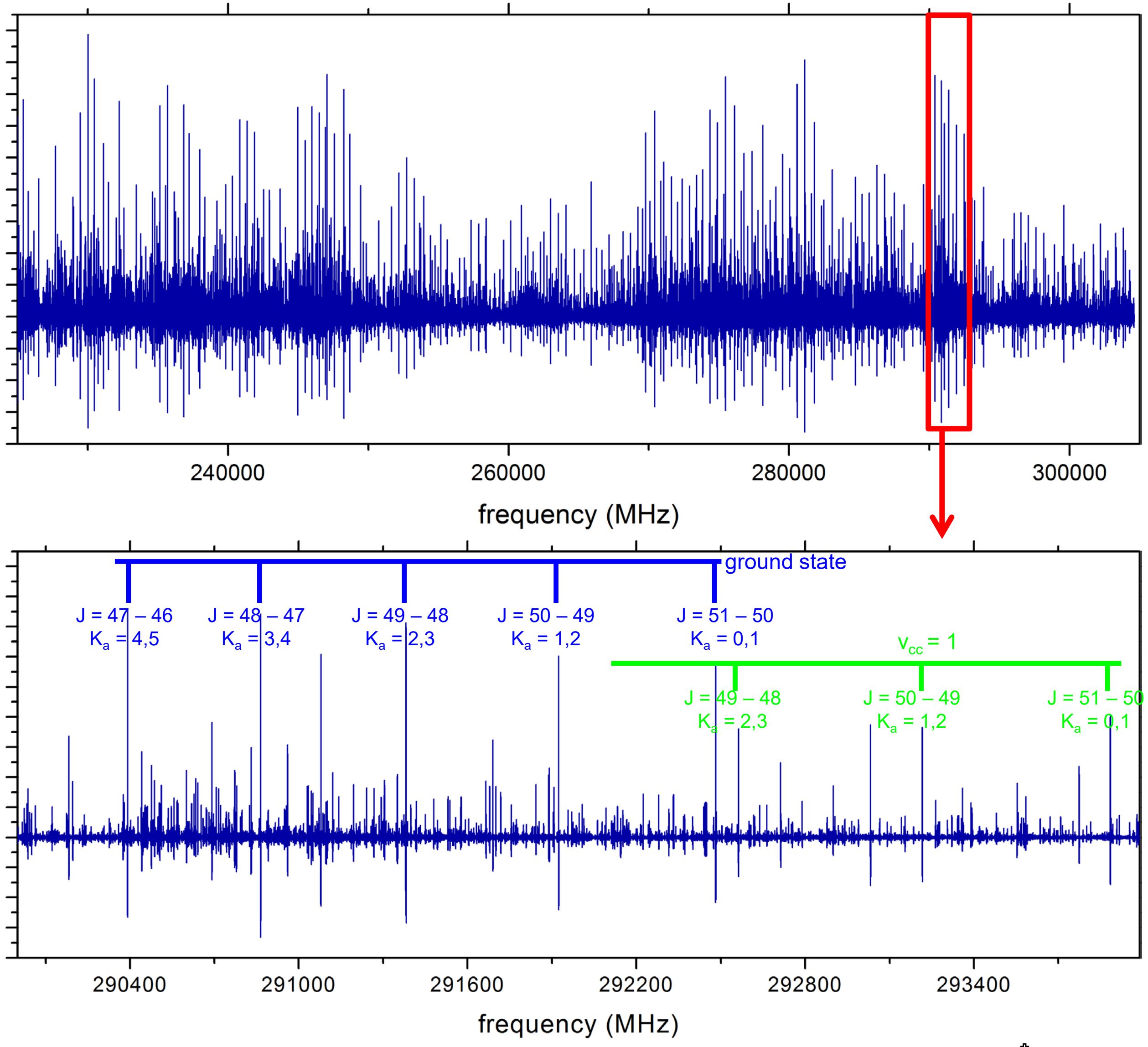
InSb HEB
QMC Instruments Ltd.

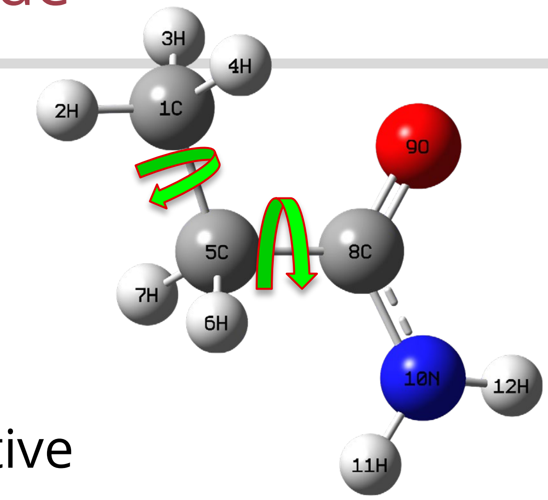
Thermal:
- (hot electron) bolometer
- pyroelectric

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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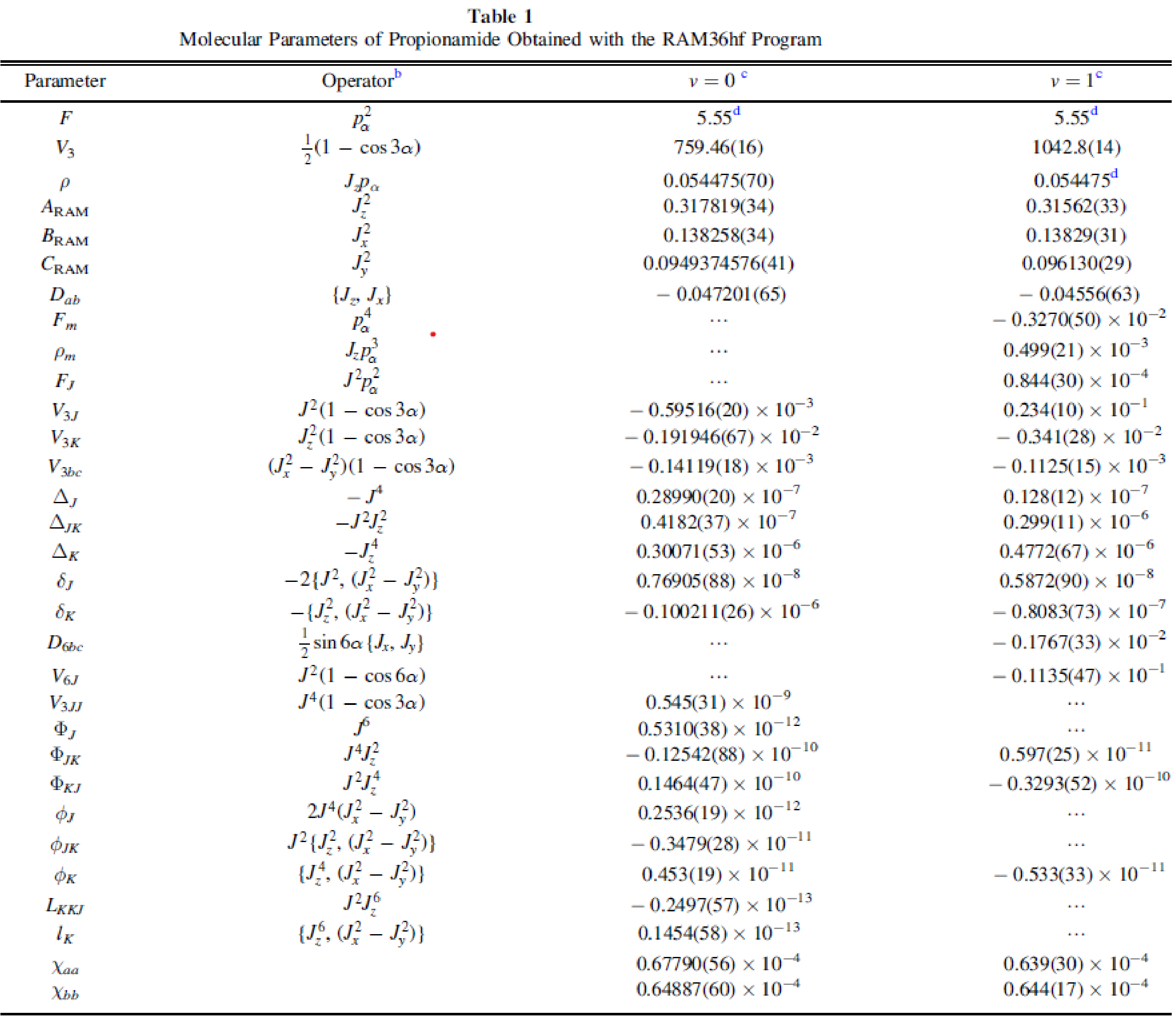
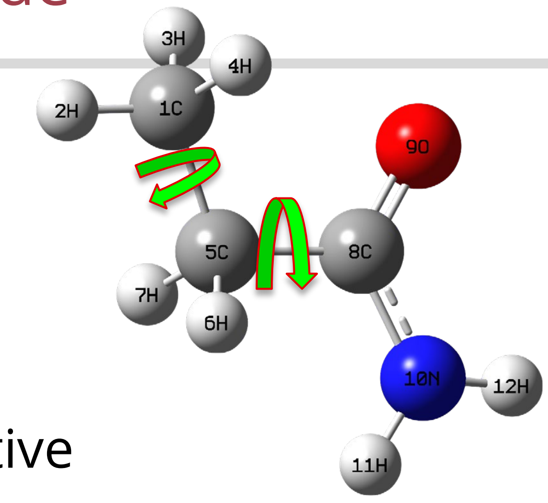


Table 1
Molecular Parameters of Propionamide Obtained with the RAM36hf Program

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	…	$-0.3270(50) \times 10^{-2}$
ρ_m	$J_z p_\alpha^3$	…	$0.499(21) \times 10^{-3}$
F_J	$J^2 p_\alpha^2$	…	$0.844(30) \times 10^{-4}$
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}	$\frac{1}{2}\sin 6\alpha \{J_x, J_y\}$	…	$-0.1767(33) \times 10^{-2}$
V_{6J}	$J^2(1 - \cos 6\alpha)$	…	$-0.1135(47) \times 10^{-1}$
V_{3JJ}	$J^4(1 - \cos 3\alpha)$	$0.545(31) \times 10^{-9}$	…
Φ_J	J^6	$0.5310(38) \times 10^{-12}$	…
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	$2J^4(J_x^2 - J_y^2)$	$0.2536(19) \times 10^{-12}$	…
ϕ_{JK}	$J^2\{J_z^2, (J_x^2 - J_y^2)\}$	$-0.3479(28) \times 10^{-11}$	…
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}	$J^2 J_z^6$	$-0.2497(57) \times 10^{-13}$	…
l_K	$\{J_z^6, (J_x^2 - J_y^2)\}$	$0.1454(58) \times 10^{-13}$	…
χ_{aa}		$0.67790(56) \times 10^{-4}$	$0.639(30) \times 10^{-4}$
χ_{bb}		$0.64887(60) \times 10^{-4}$	$0.644(17) \times 10^{-4}$



Peptide bond motive

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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

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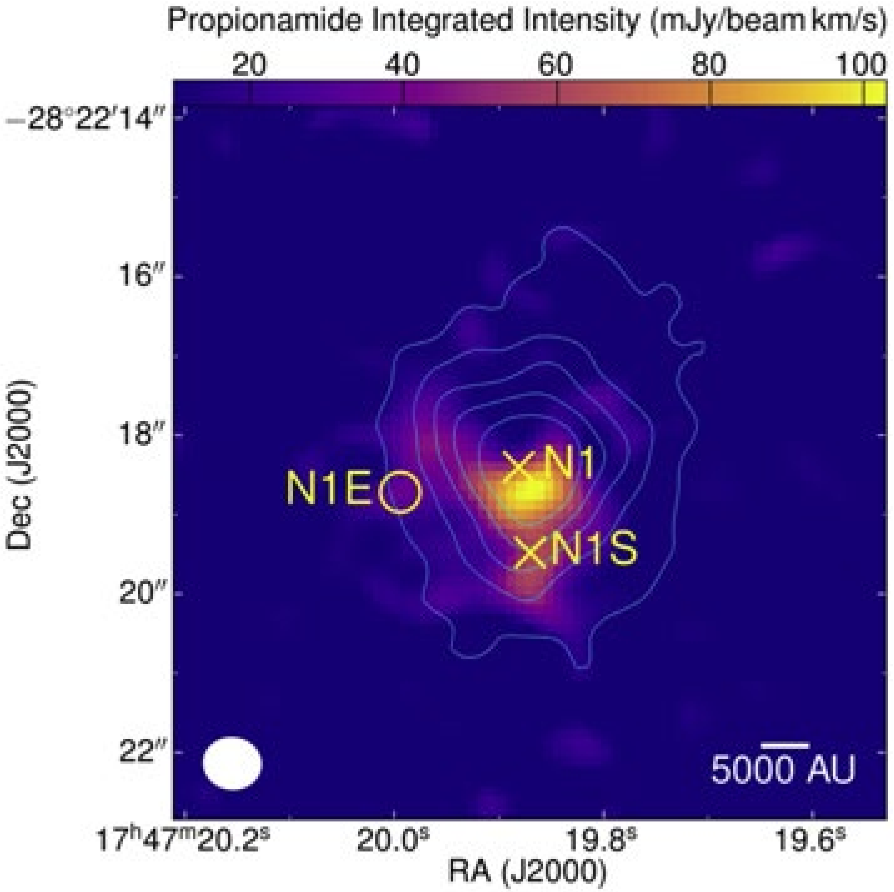
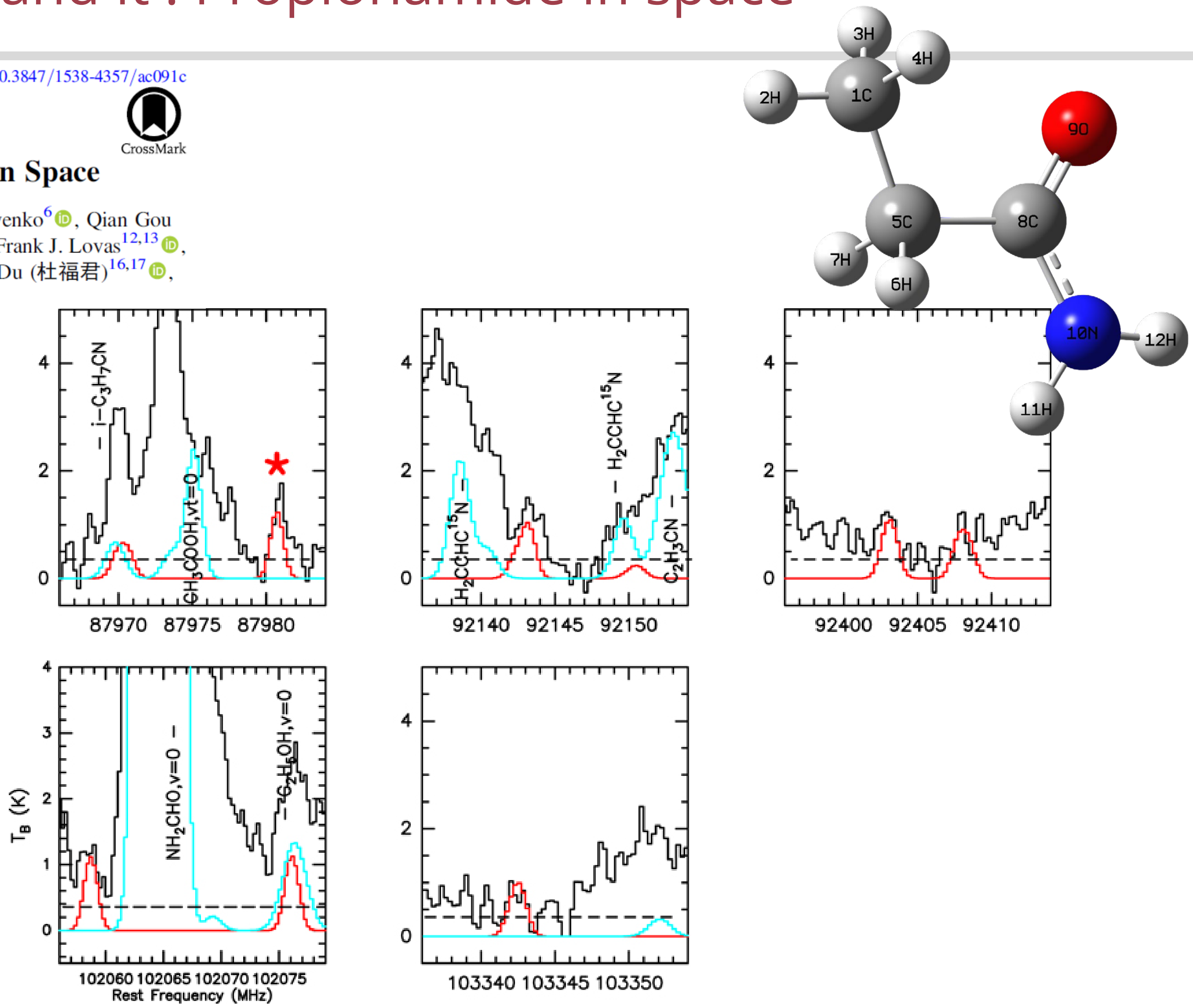
CrossMark

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]



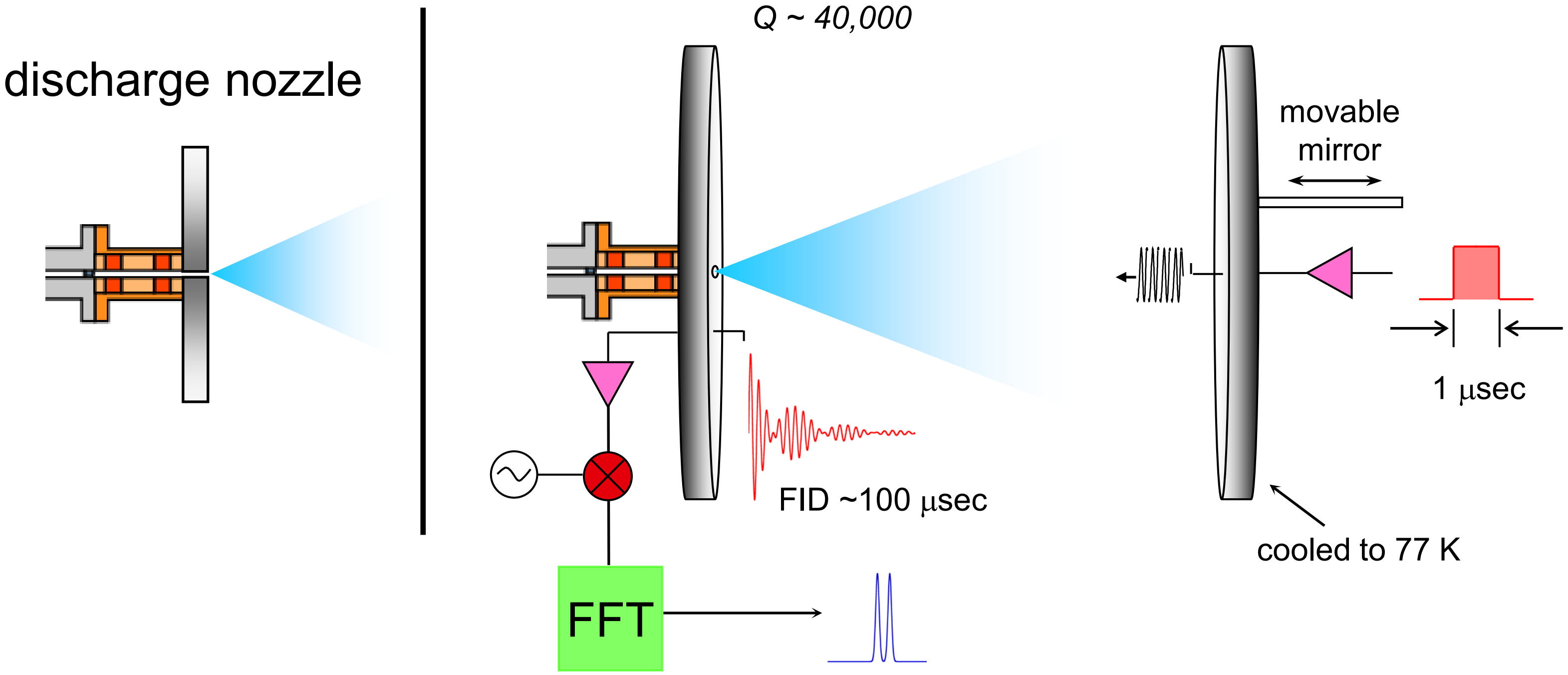


Lab: L. Margulés et al. PhLam Lille 69th ISMS (2014)
Astro: J. Li et al., ApJ 919 (2021) 4

Fourier Transform Microwave Spectroscopy (FTMW)

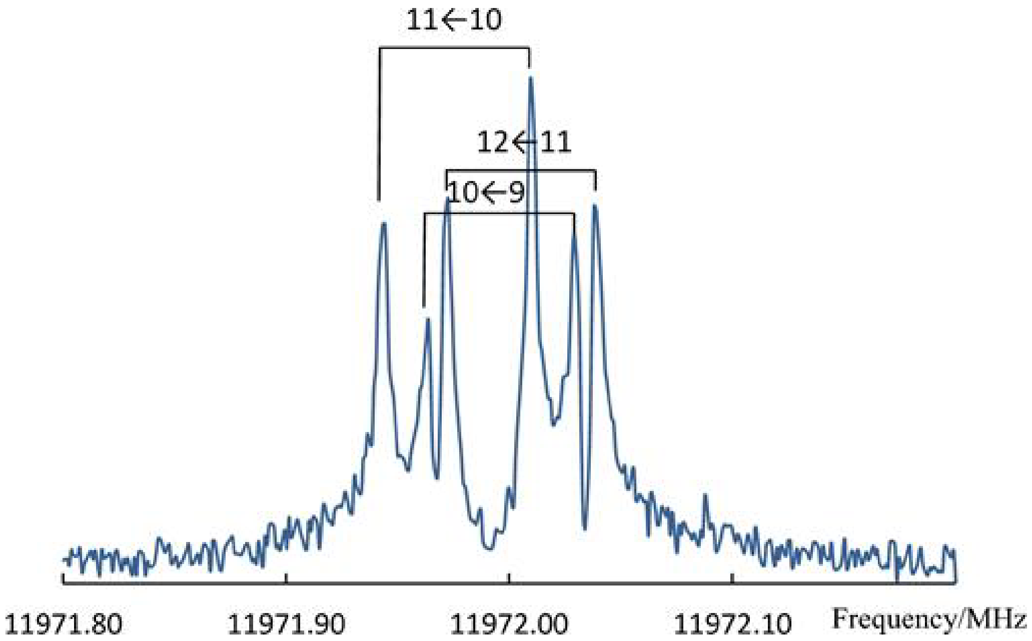
supersonic nozzle coupled to a high-*Q* Fabry-Perot cavity

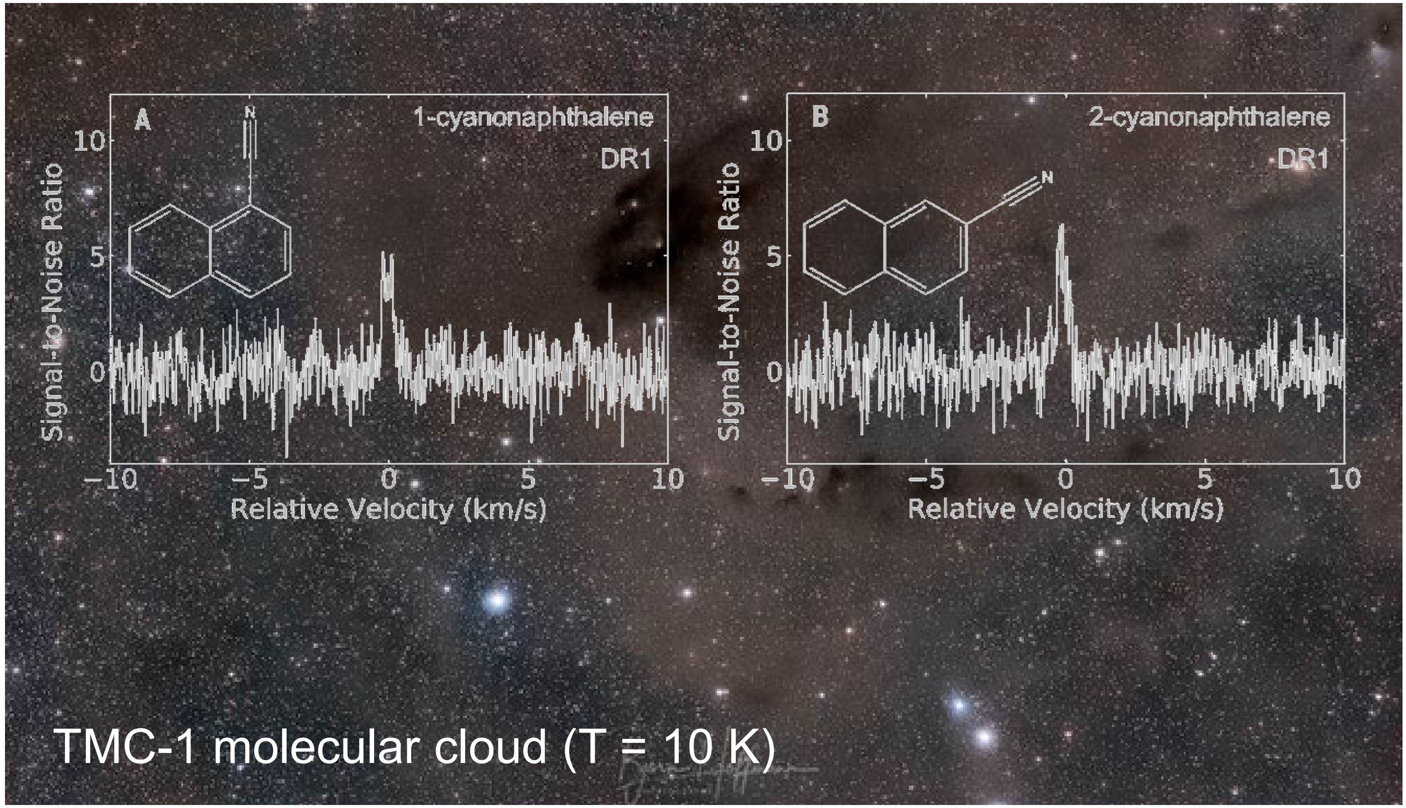
Balle & Flygare,
Rev. Sci. Instrum. 52 (1981) 33



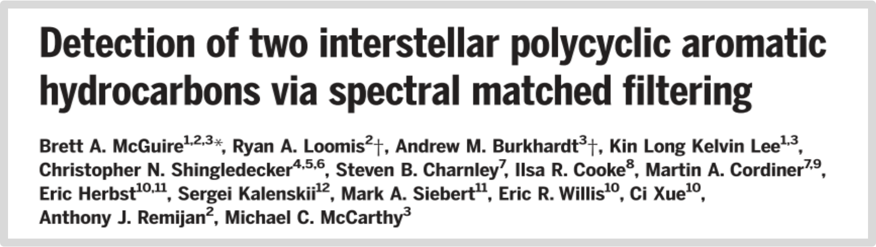
- frequency range: 5 – 42 GHz line width: 20 kHz accuracy: 1-2 kHz bandwidth: 1 MHz
- High Q Fabry-Perot cavity for excitation and detection
- Molecular beam expansion leads to cooling of the molecules to few K (narrow lines, high population in low J states)
- Use discharges or laser ablation to produce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

FTMW Example I – Detection of cyanonaphtalene





TMC-1 molecular cloud (T = 10 K)

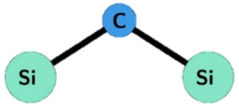


Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering

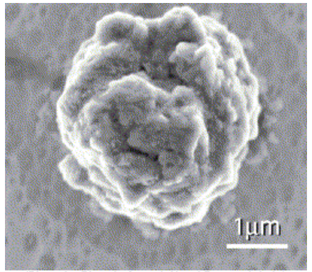
Brett A. McGuire[1,2,3]*, Ryan A. Loomis[2]†, Andrew M. Burkhardt[3]†, Kin Long Kelvin Lee[1,3], Christopher N. Shingledecker[4,5,6], Steven B. Charnley[7], Ilsa R. Cooke[8], Martin A. Cordiner[7,9], Eric Herbst[10,11], Sergei Kalenskii[12], Mark A. Siebert[11], Eric R. Willis[10], Ci Xue[10], Anthony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

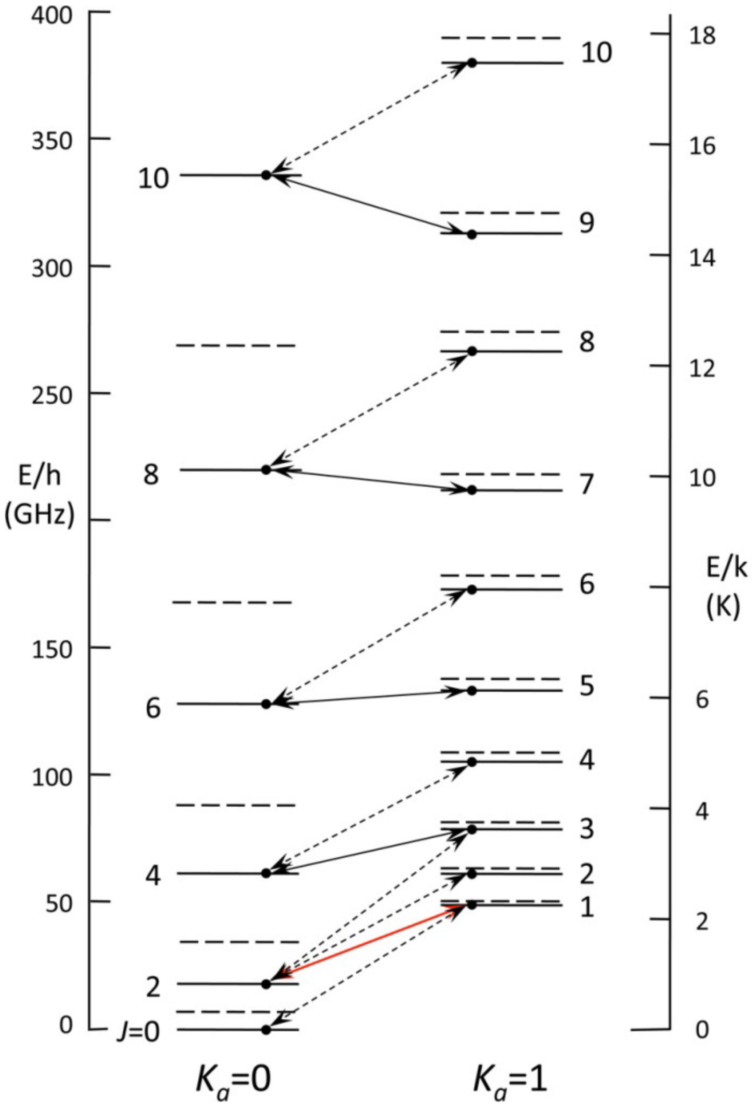


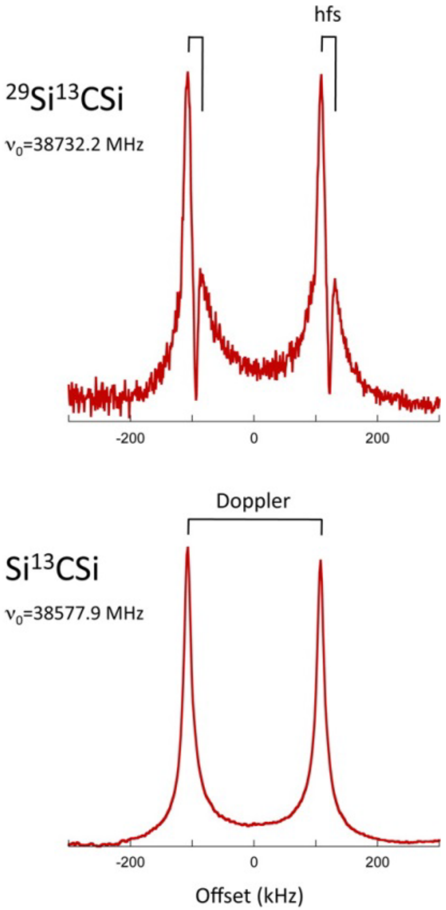
Si_nC_m molecular species act as seeds for carbonaceous dust formation in C-rich AGB stars



(Photo by Rhonda Stroud, Naval Research Lab.)

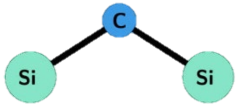
- discharge of SiH_4 & C_2H_2
- up to 12 lines for several isotopic species
- reliable transition frequencies
- structural analysis
- double-resonance experiments



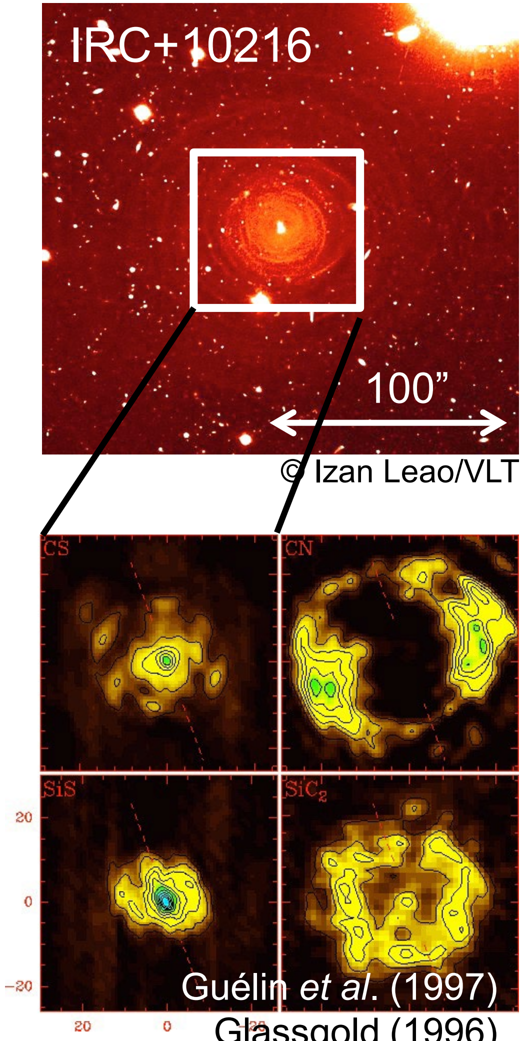


McCarthy et al., JPC Lett. 6 (2015), 2107

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
SiC & SiC_2 already detected in circumstellar envelope of the carbon-rich AGB star IRC +10216



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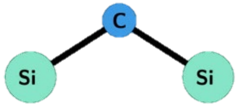
Guélin *et al*. (1997)
Glassgold (1996)

FTMW Example II Laboratory and Astronomical Detection of SiCSi



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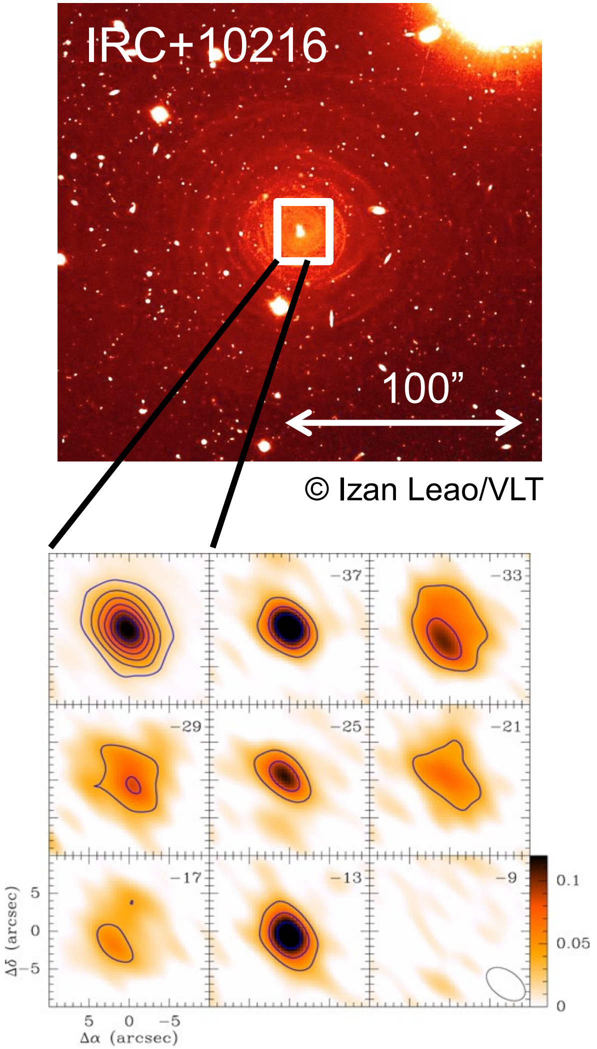

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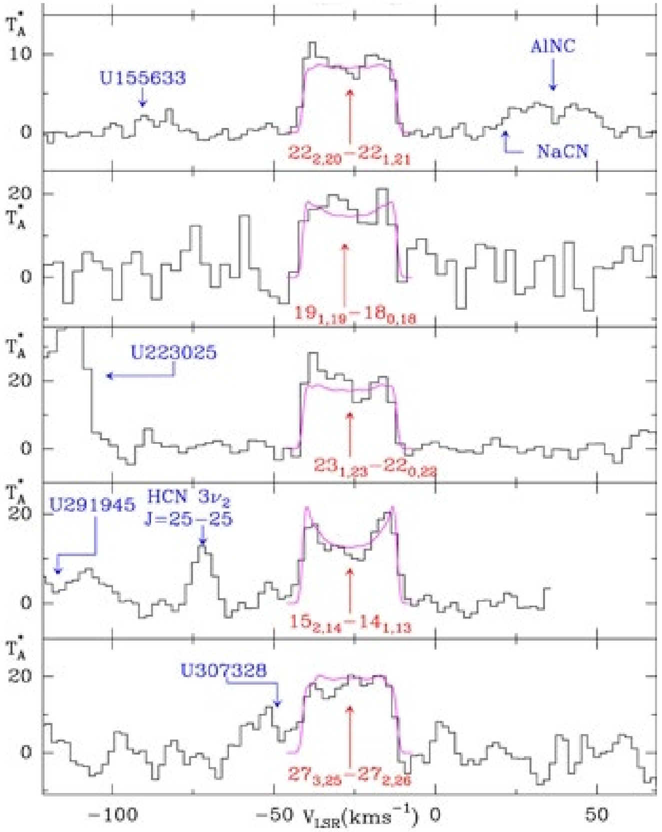
IRAM 30m & SMA: >100 lines
(80-350 GHz)

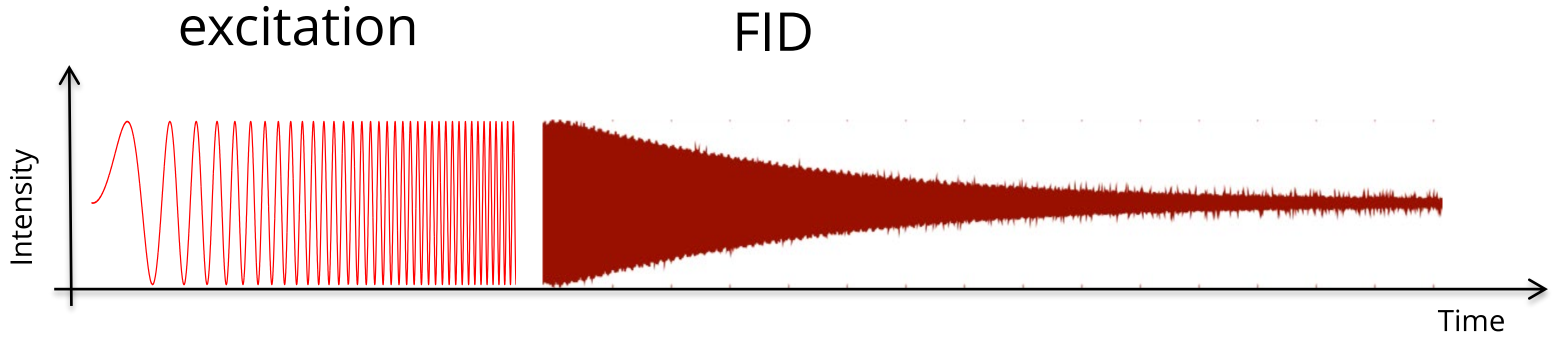


J. Cernicharo et al., ApJ 806(2015) L3

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

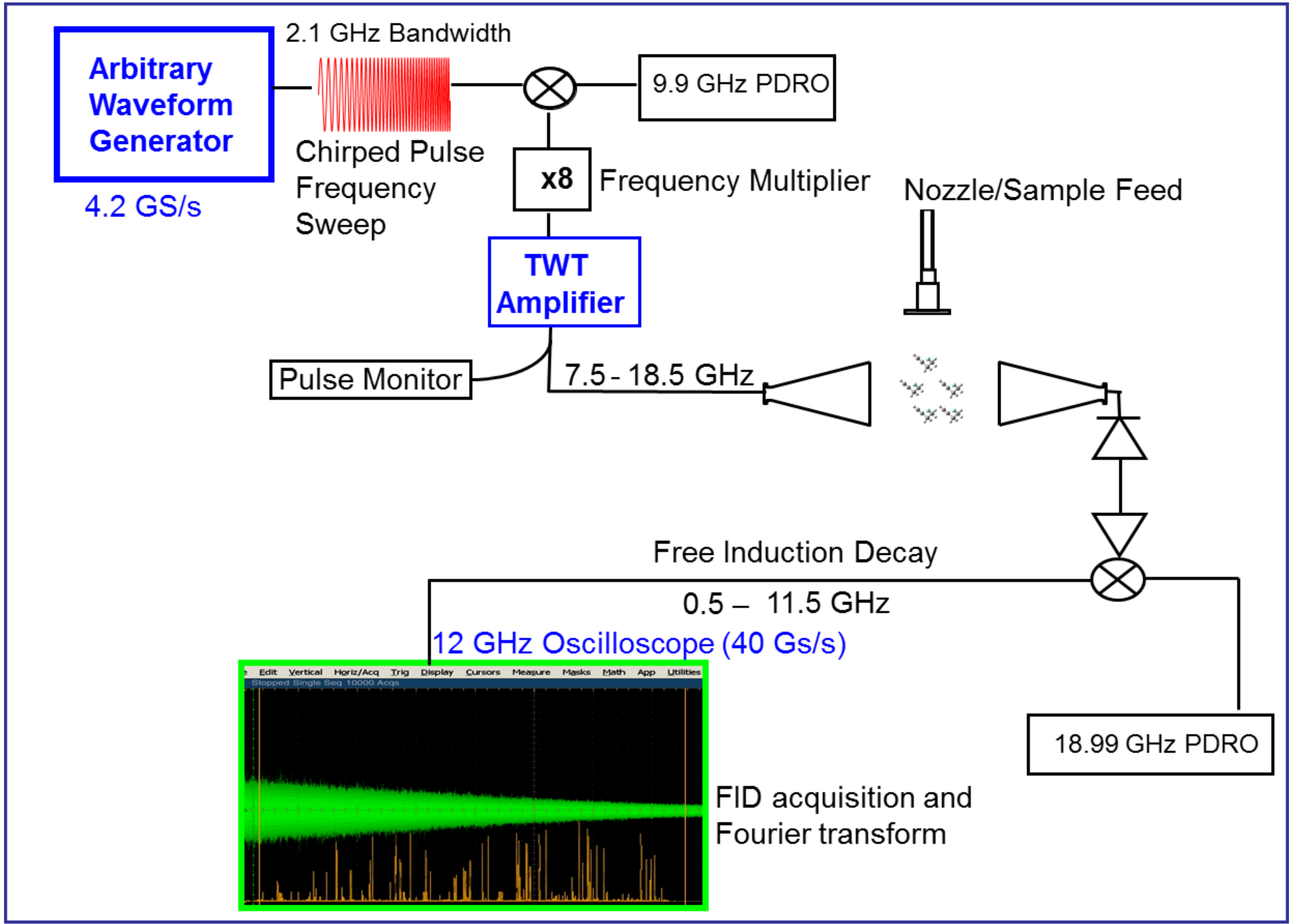
$$S_{FID} \propto \sin(\omega_{10} t) \cdot e^{\frac{-t}{T_1}} \cdot e^{\frac{-t}{T_2}}$$

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)



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

Chirped-Pulse Fourier Transform Microwave (CP-FTMW)

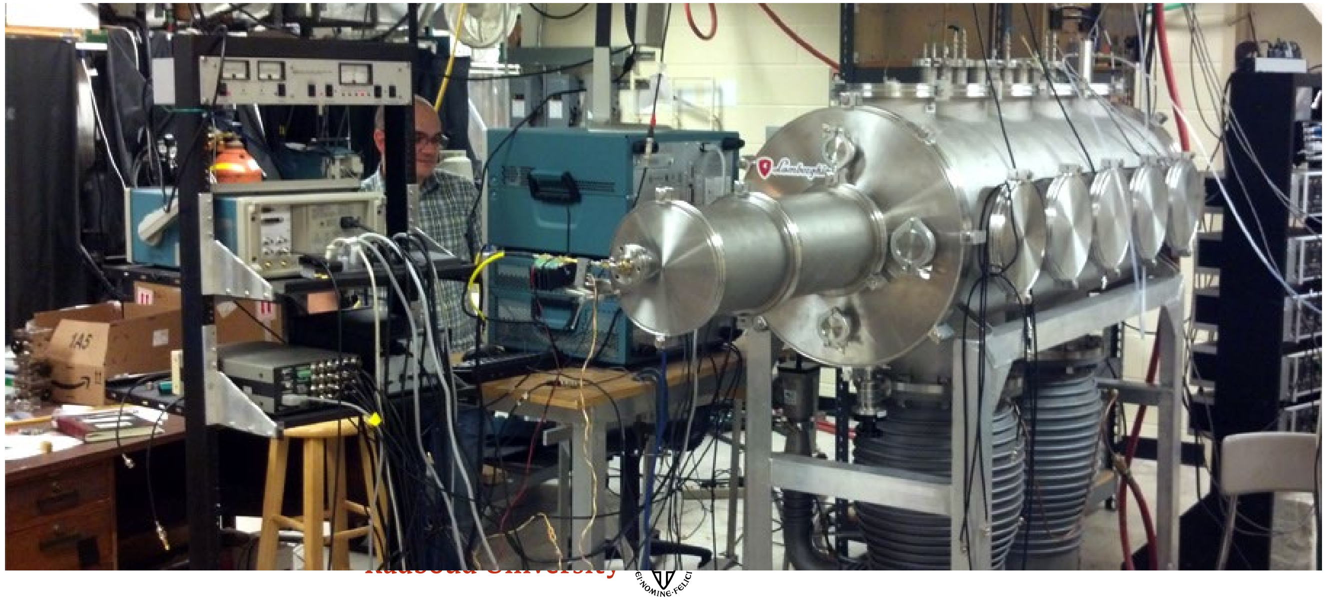
- fast spectrum acquisition: >10 GHz in one go
  high sensitivity due to multiplexing
  accurate relative intensities

→ complex species, search for unstable species, investigating chemistry

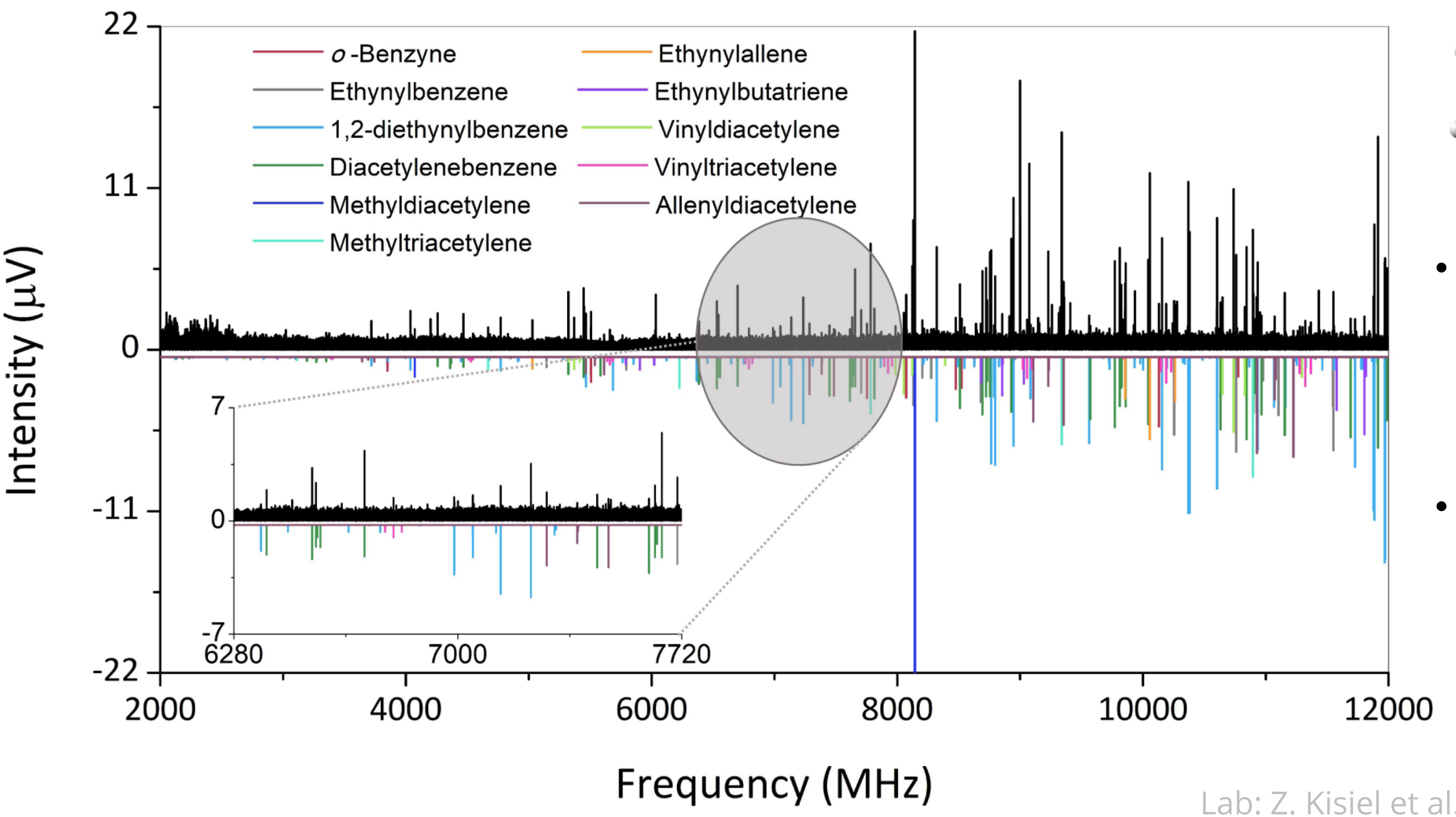
- extension up to the 1mm (300 GHz) region

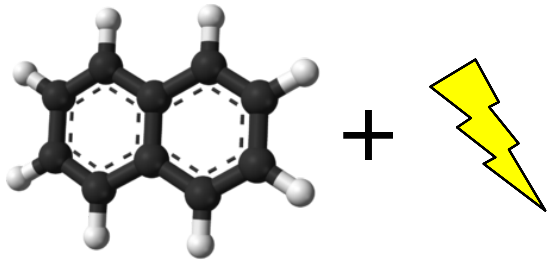
Steber et al., JMS 280 (2012) 3; Park et al. JCP 135, (2011) 024202

- used in many laboratories worldwide



CP-FTMW Example: Naphtalene discharge products

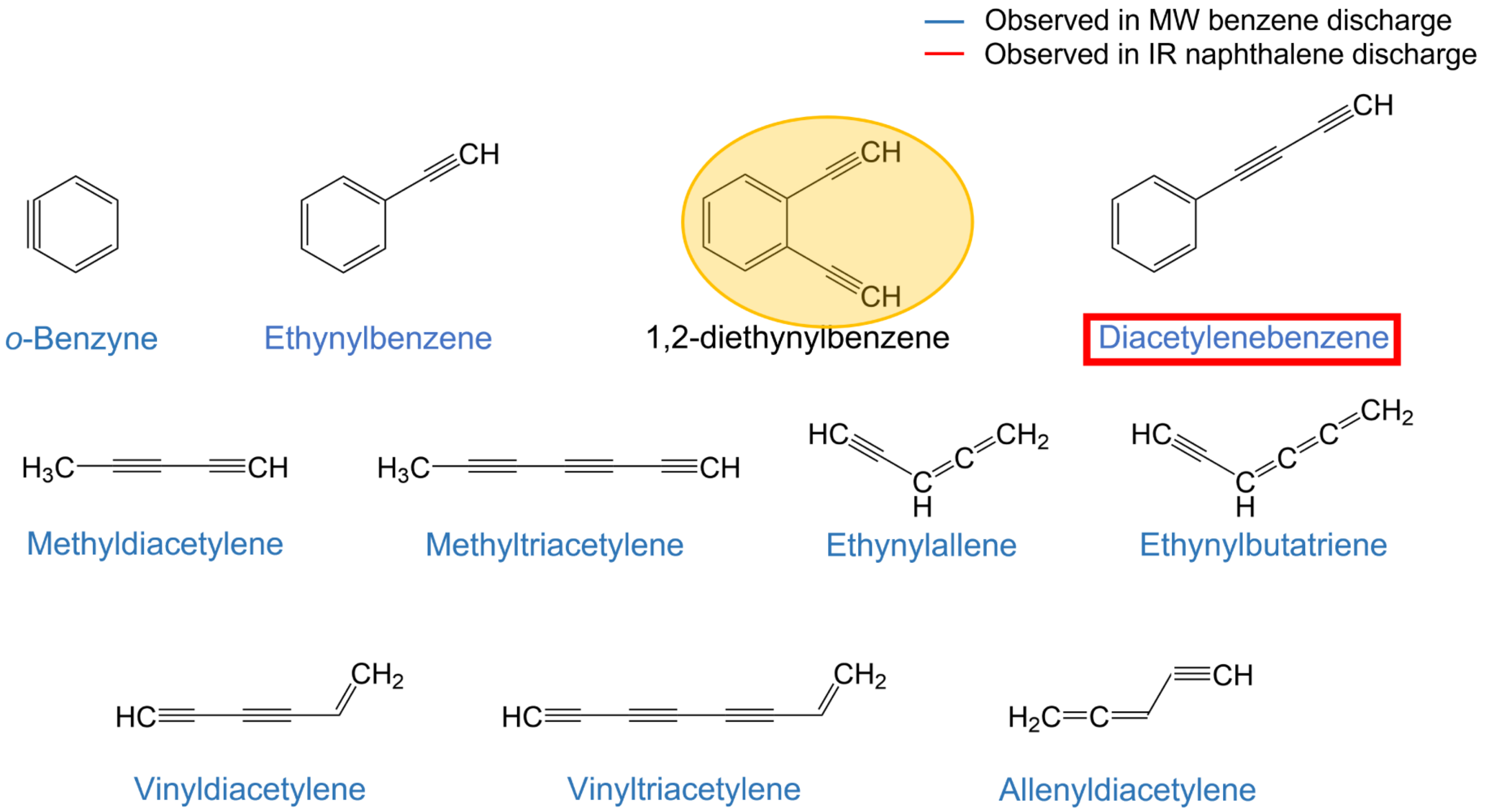




- Rotational lines of all products formed in a discharge of the PAH naphtalene!
- Most assigned and fitted to specific molecules

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

CP-FTMW Example: Naphtalene discharge products

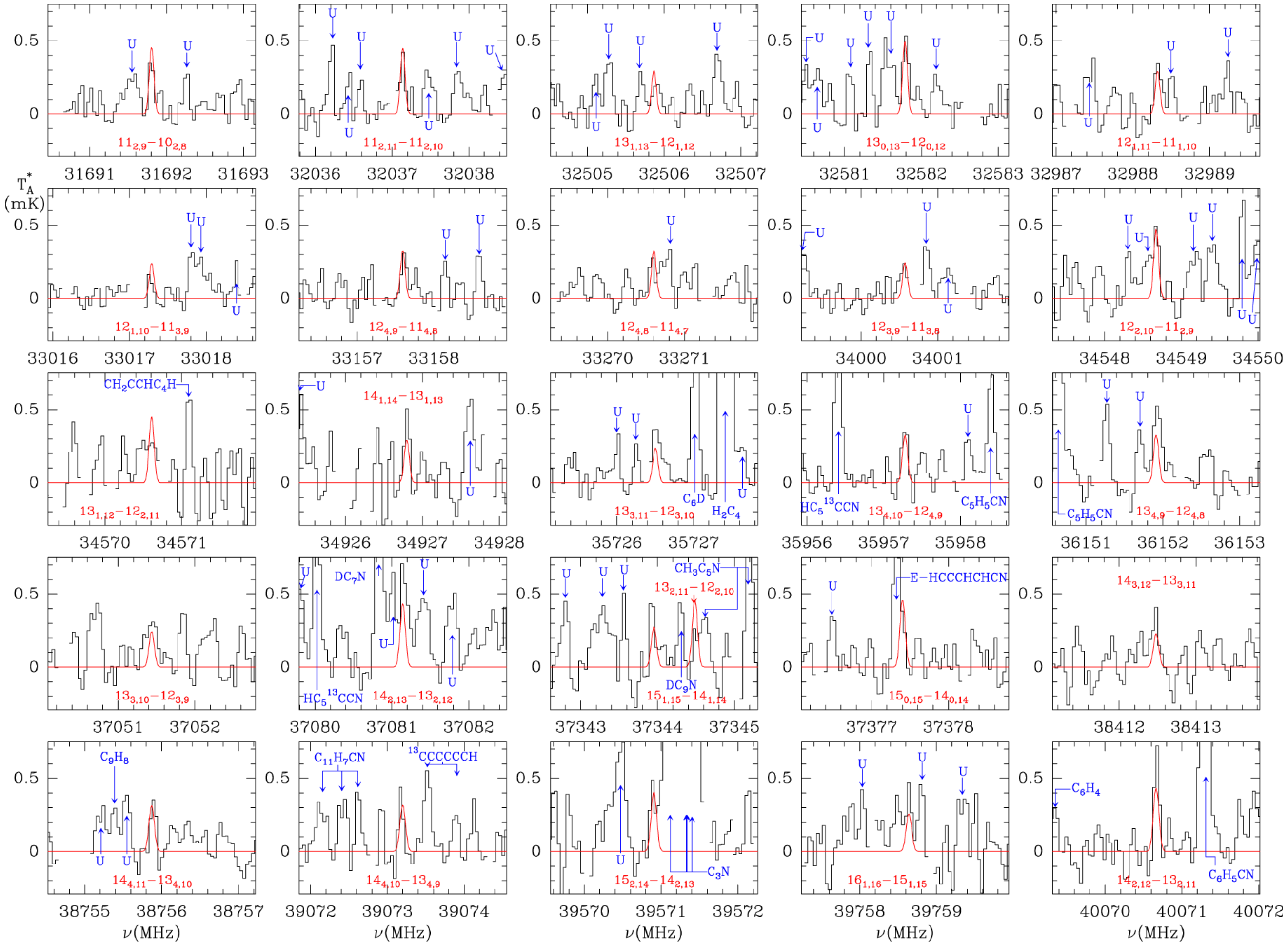


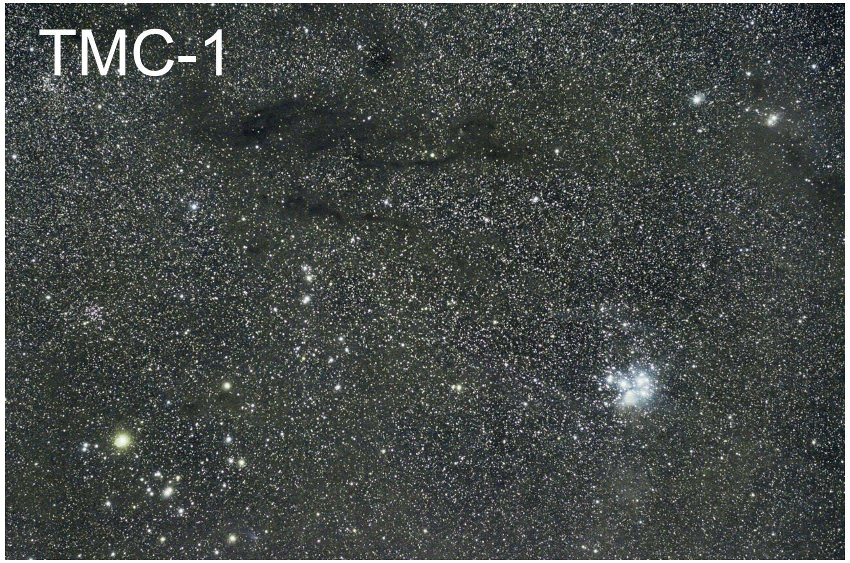
- Rotational lines of all products formed in a discharge of the PAH naphtalene!
- Most assigned and fitted to specific molecules

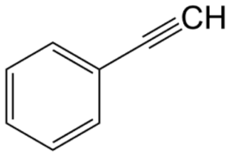
Lab: Z. Kisiel et al., JMS 262 (2010), 82
Astro: Cernicharo et al., A&A 655 (2021) L1
Lab & Astro: D. Loru et al., A&A 677 (2023) A166

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}) ☹



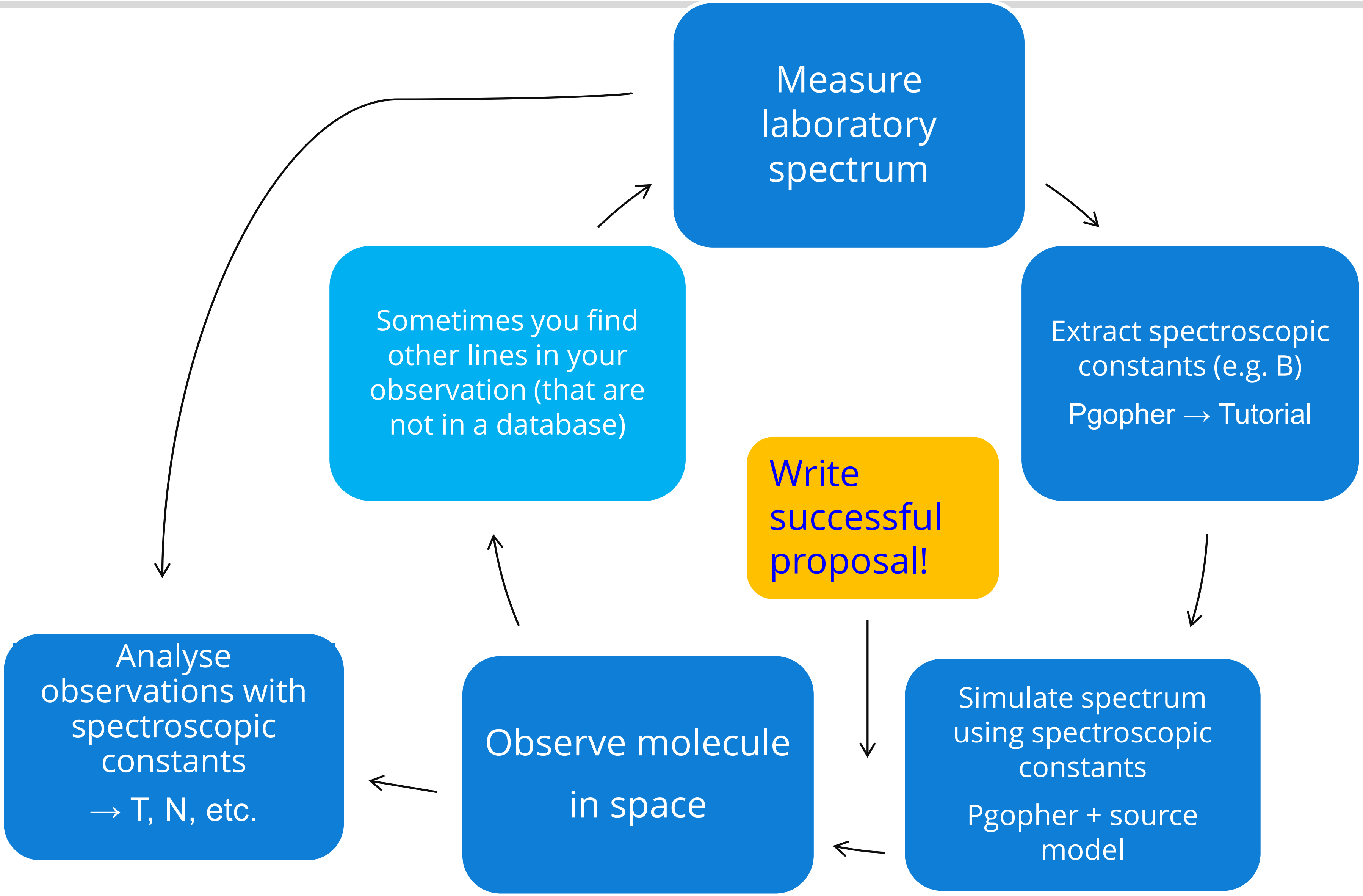




- Main formation via reactions of benzene with CCH

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

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

Write successful proposal!

Observe molecule in space

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

Analyse observations with spectroscopic constants

→ T, N, etc.

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“

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

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

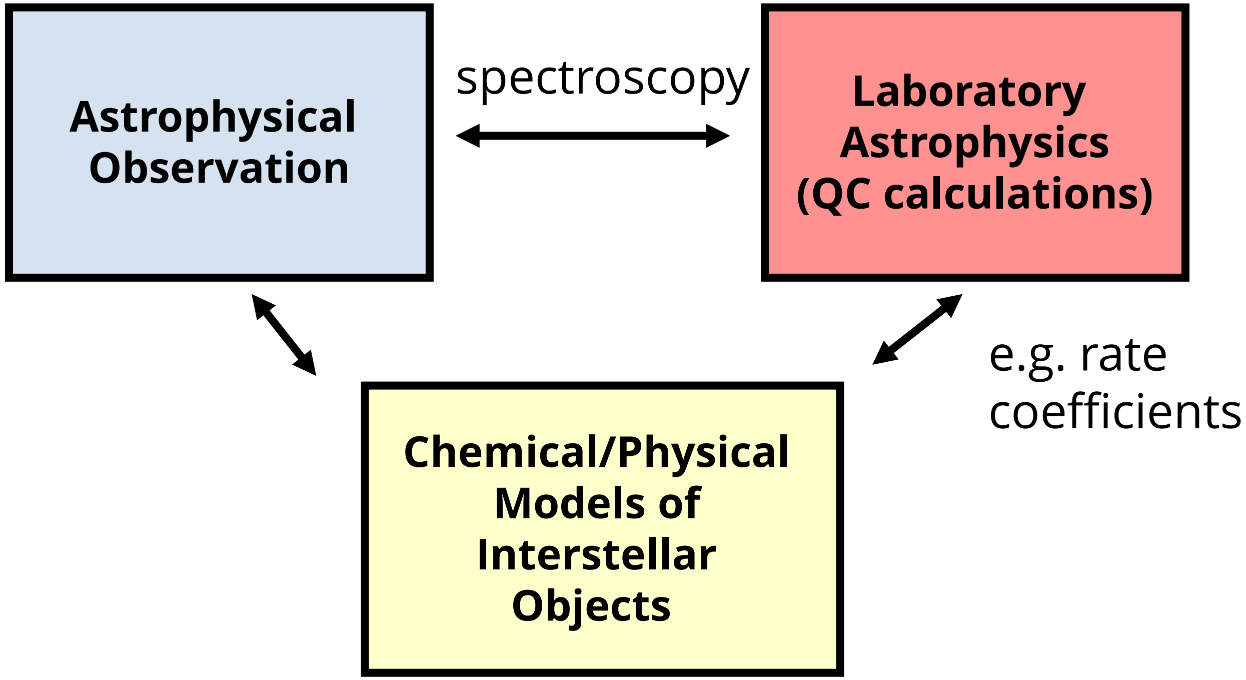
- Spectroscopy in the laboratory provides the **spectral fingerprint** needed to identify molecules in space

- 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?



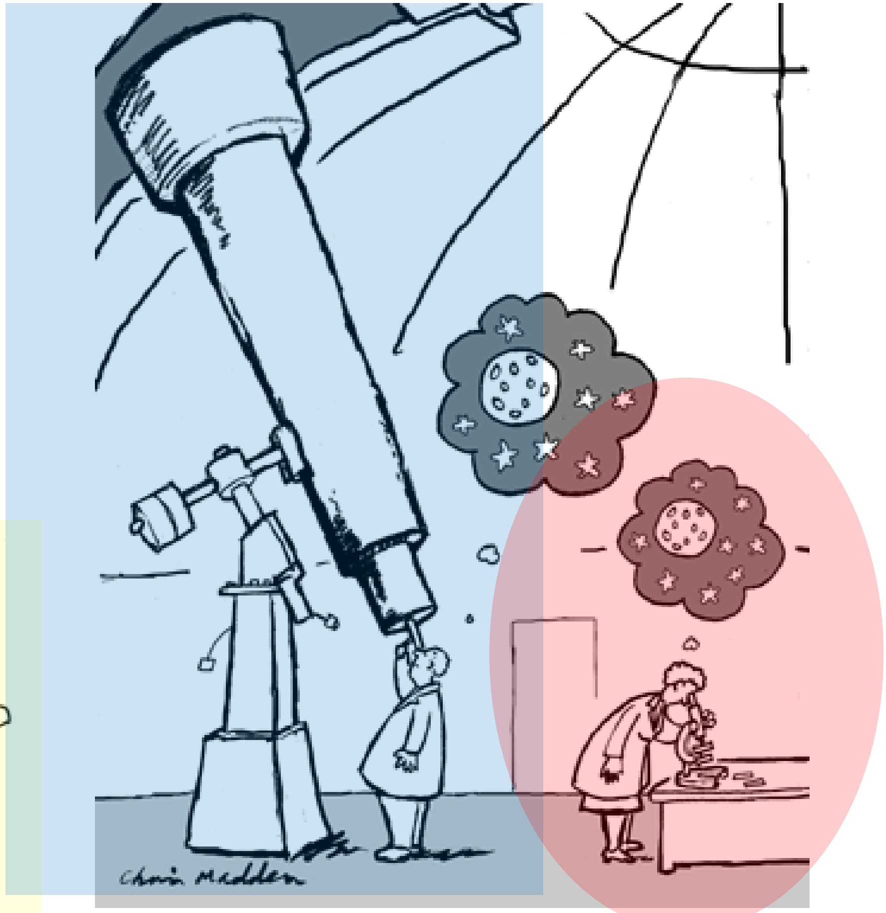
Astrophysical Observation

spectroscopy

Laboratory Astrophysics (QC calculations)

e.g. rate coefficients

Chemical/Physical Models of Interstellar Objects



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