Rudimentary Principles of
Molecular Spectroscopy
for ALMA applications

Content:

Introduction (history,…)

Molecular quantum mechanics

Molecular spectroscopy (basis , types, theory)

Rotational spectroscopy (including hyperfine and structures)

Spectrometers in laboratory and in space

Interstellar spectroscopy

Introduction (history,…)

- The theoretical background of spectroscopy is based on the quantum mechanics (QM)
- Roots of the QM were formed at the beginning of the 20th century. (1900 – Planck, 1905 and 1907 – Einstein, 1912 – Bohr, 1924 – de Broglie, 1925 – Heisenberg, 1926 – Schrödinger) etc.
- 1927 -1970 Molecular quantum mechanics (MQM) was formulated (Born, Oppenheimer, Heitler, London, Slater , Pauling, Hund, Mulliken, Hartree, Fock etc.)
- Quantum Chemistry = an computational application of MQM to molecules. Computers.

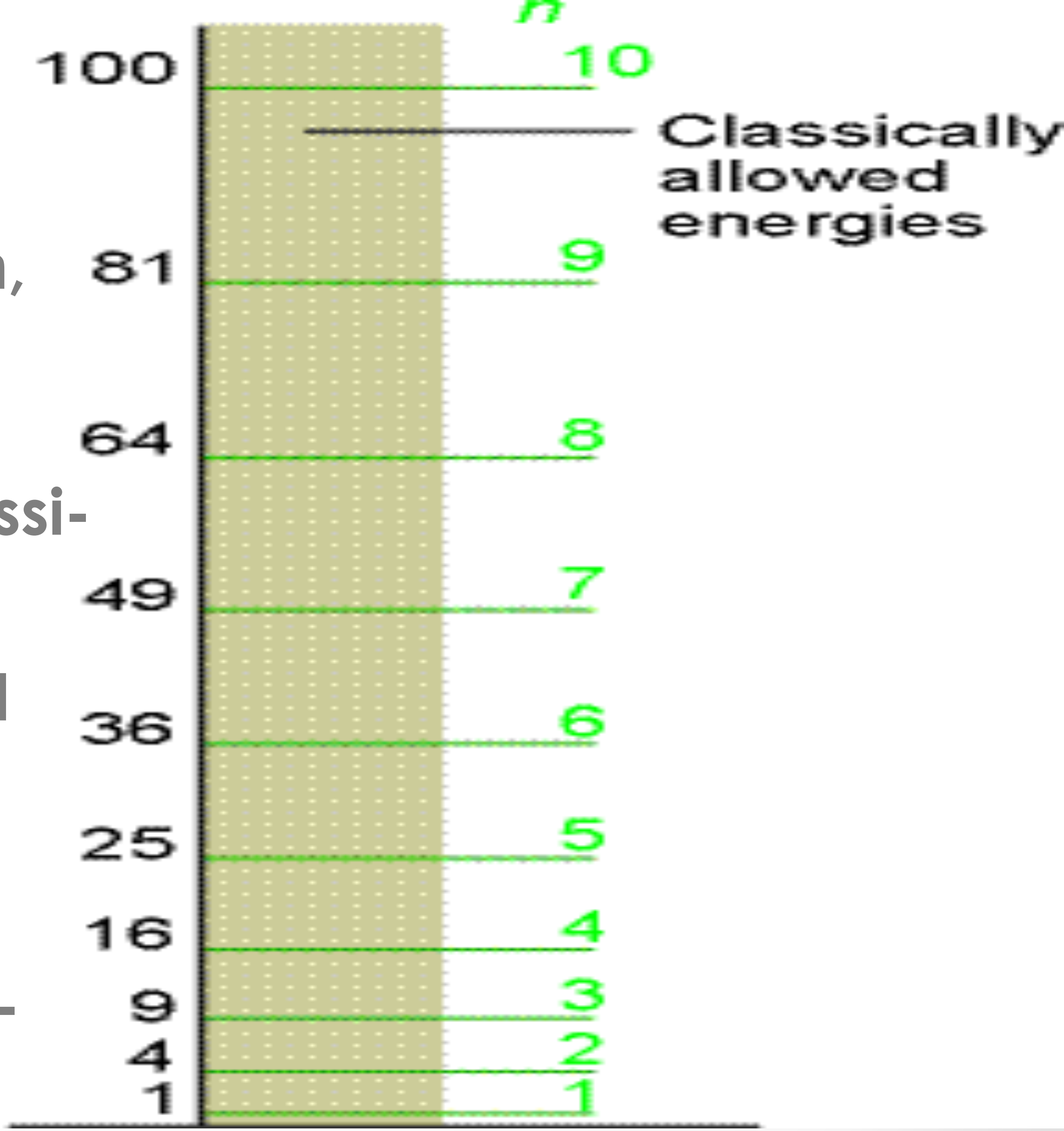
(Molecular) Quantum Mechanics

tells us:

- Materia (mass) is quantized (elementary particles)
- Energy content in matter (molecules) is quantized (energy levels)
- Energy of an electromagnetic radiation is quantized (photons)
- Exchanges of the energie between the radiation and molecules are quantized

Example:

A quantum system, like a **molecule**, cannot have any energy like, it is obvious in the classical mechanics. Energies of these levels are allowed only for certain values which are characteristic for each individual quantum system - **molecule**.



Exchanges of the energie between the radiation and molecules are quantized

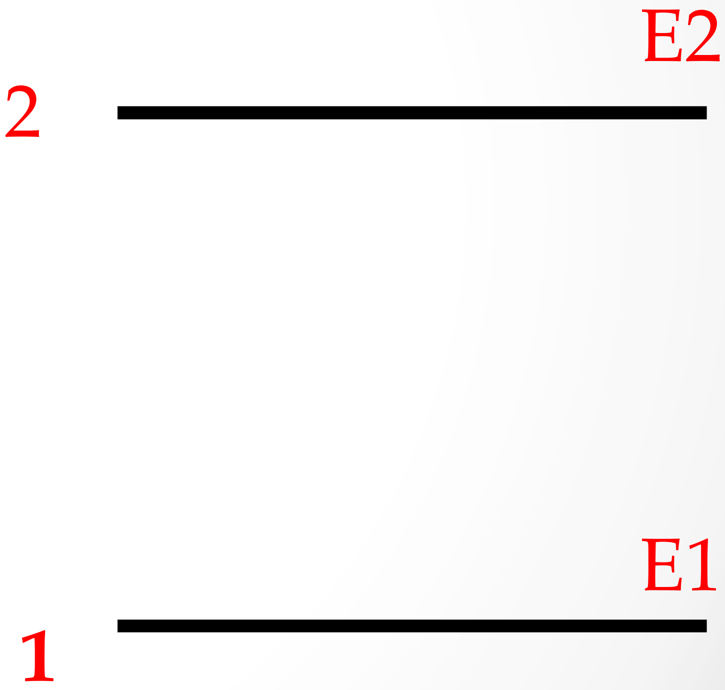
A.Einstein (1906) considered a hypotetical quantum system having only two states:

- **Quantum state 1 with an energy E1**

and

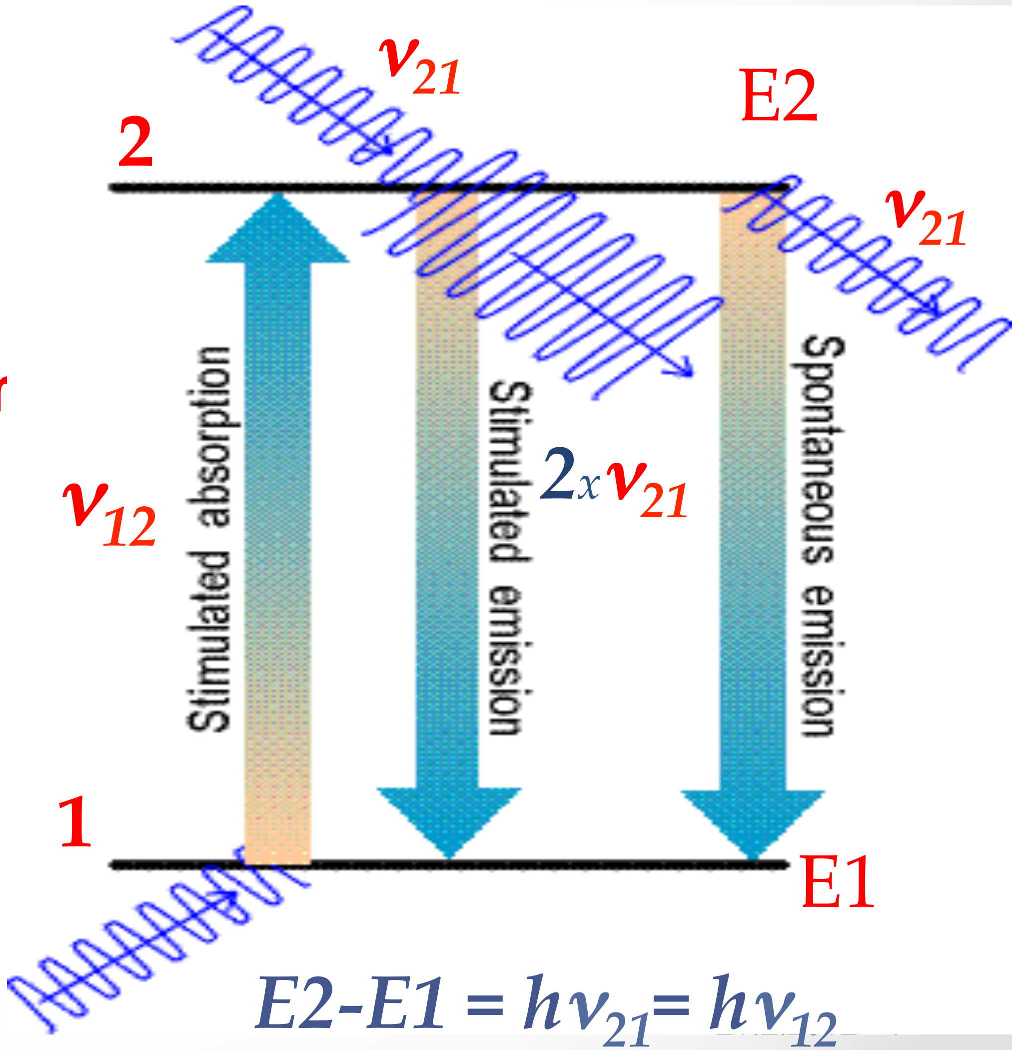
- **Quantum state 2 with an energy E2**

The system is either in the state 1 with the energy **E1** or in the state 2 with the energy **E2**



Exchanges of the energie between the radiation and the quantum system

- If the system is in the **lower state 1**, it can change its state only by receiving the quantum energy **E=E2-E1** .
- If the system is in the **upper state 2** , it can change its state only by emiting the quantum energy **E=E2-E1**.
- There are two radiative mechanisms of the deexcitation for this emission.

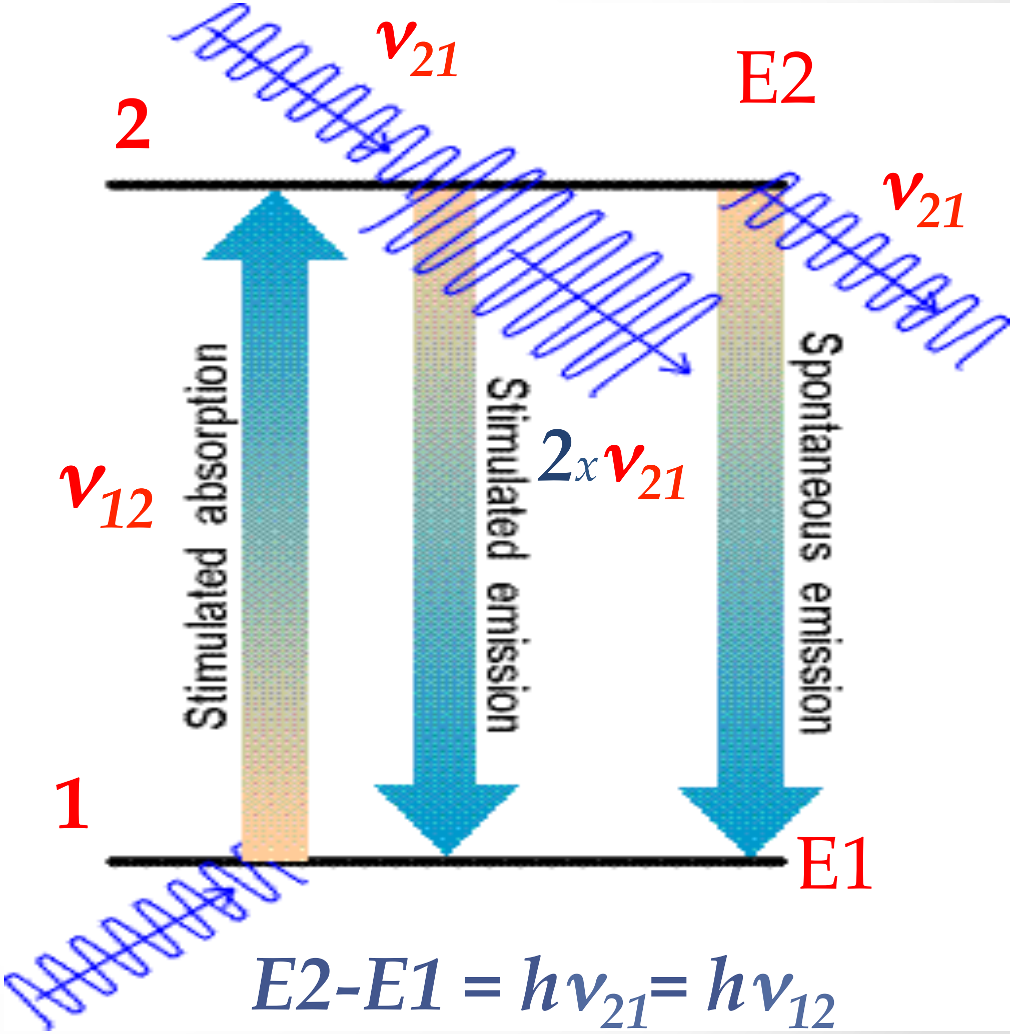


$$E2\text{-}E1 = h\nu_{21} = h\nu_{12}$$

Exchanges of the energie between the radiation and a quantum system

In all the cases, the system is either absorbing or emitting photons with energy satisfying, so called, the Bohr resonance condition :

$$E2-E1 = h\nu_{21} = h\nu_{12}$$

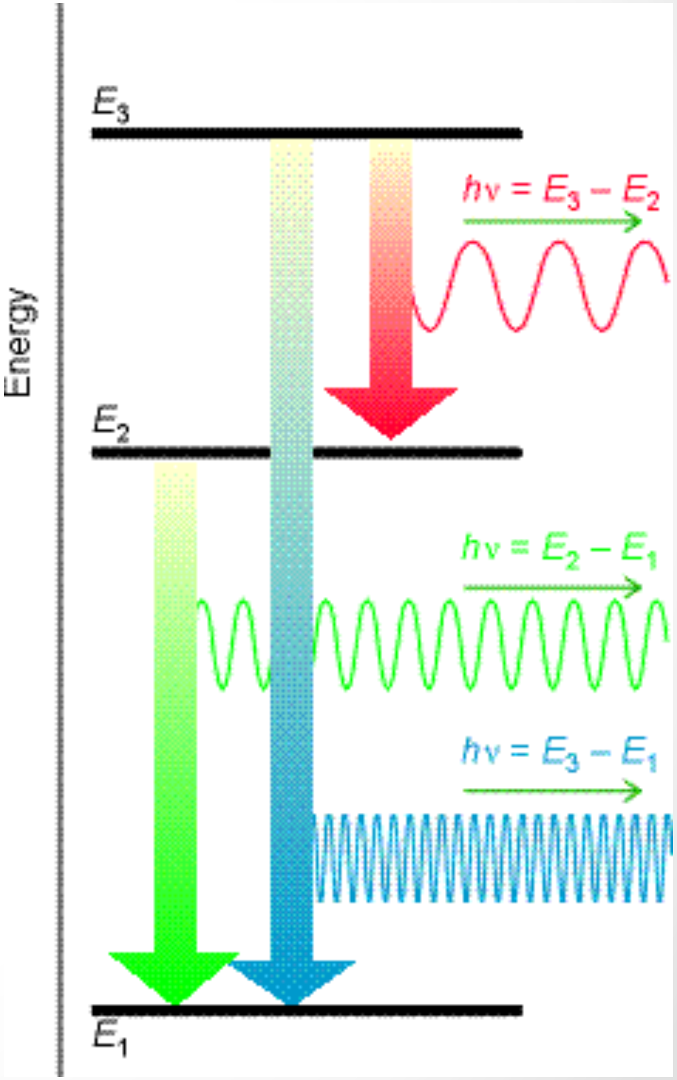


Exchanges of the energie between the radiation and a molecule

- In Molecules, there is a plenty of energy levels as well as a plenty of different photons $h\nu_{xy}$ satisfying the Bohr resonance conditions:

$$Ex\text{-}Ey = h\nu_{xy}$$

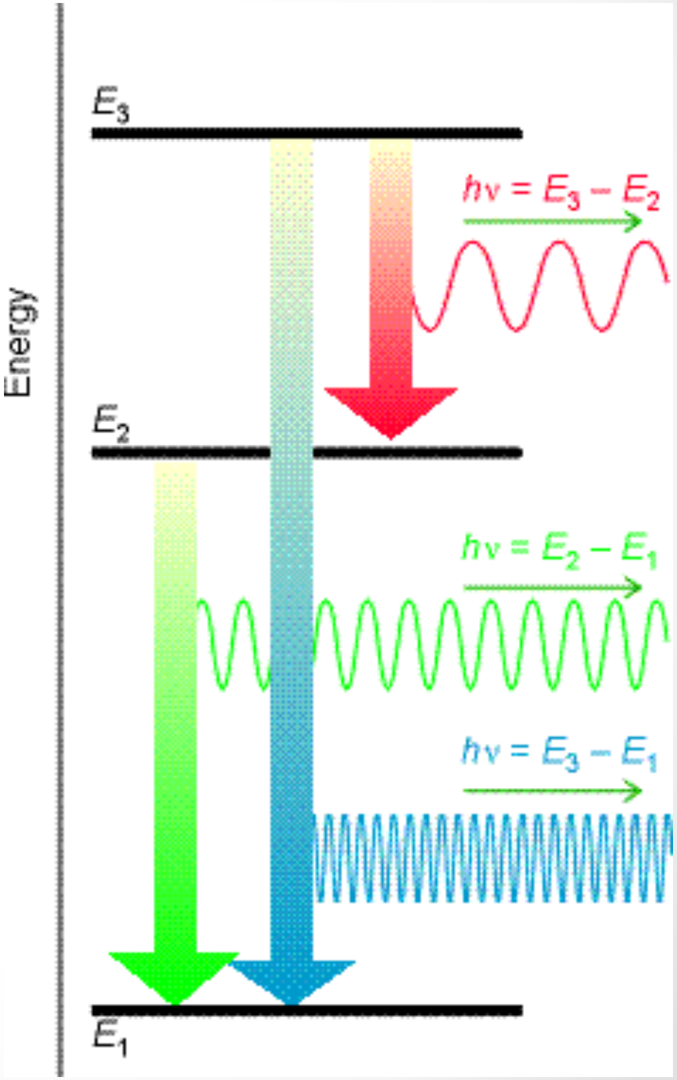
For each molecule, the assembly of energy levels as well as the assembly of the corresponding allowed photons are unique and characteristic.



Molecular Spectroscopy

For each molecule, the assembly of energy levels as well as the assembly of the corresponding allowed photons are unique and characteristic.

Molecular Spectroscopy is a science dealing with molecular energy levels and with **transitions** between them. These transitions are measured by means of the absorption or emission of theresonance photons.

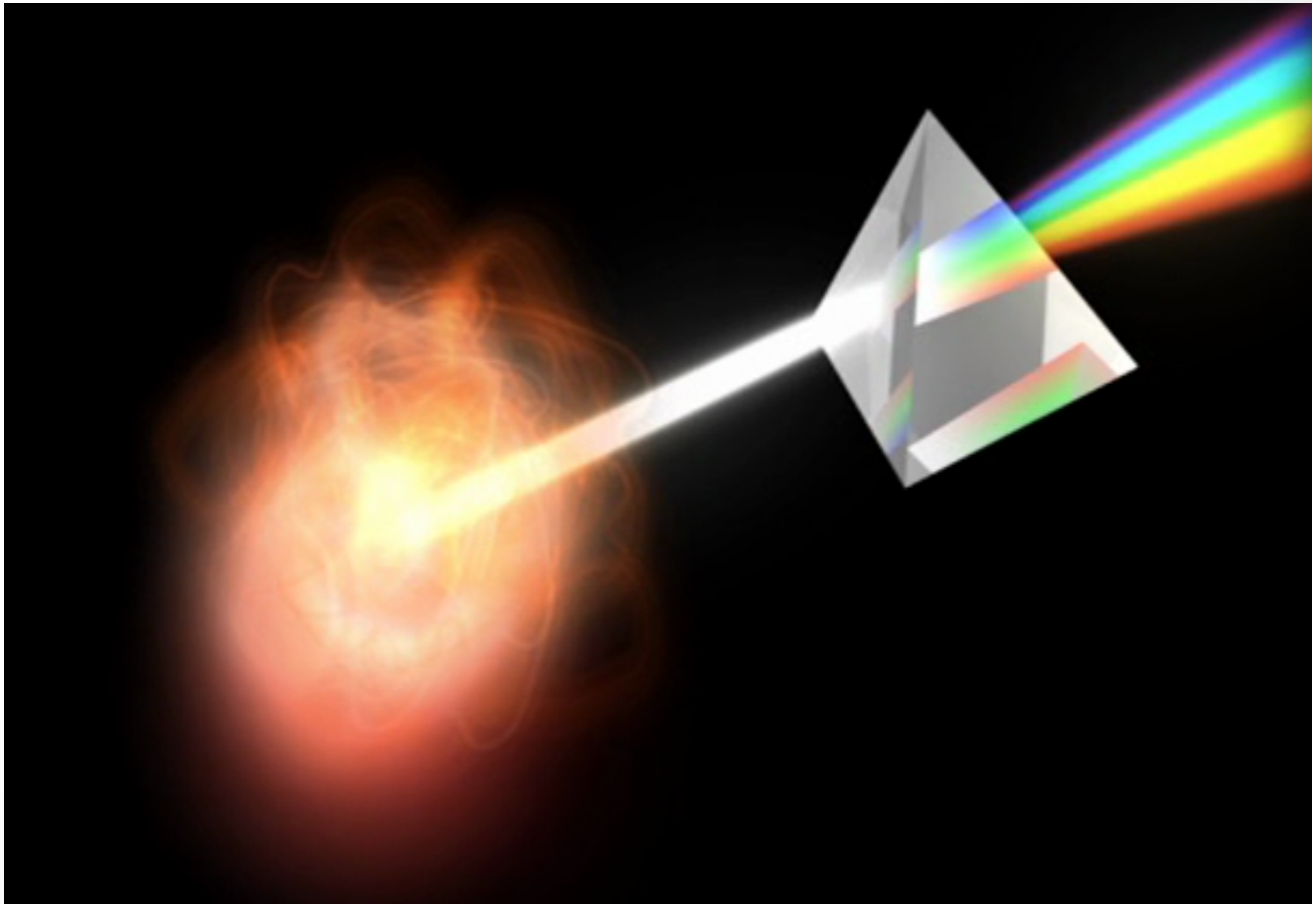


Molecular Spectroscopy

Spectroscopy is classified into **emission** and **absorption**. In the case of the **emission spectroscopy** , the basic source of radiation is a sample which is analysed.

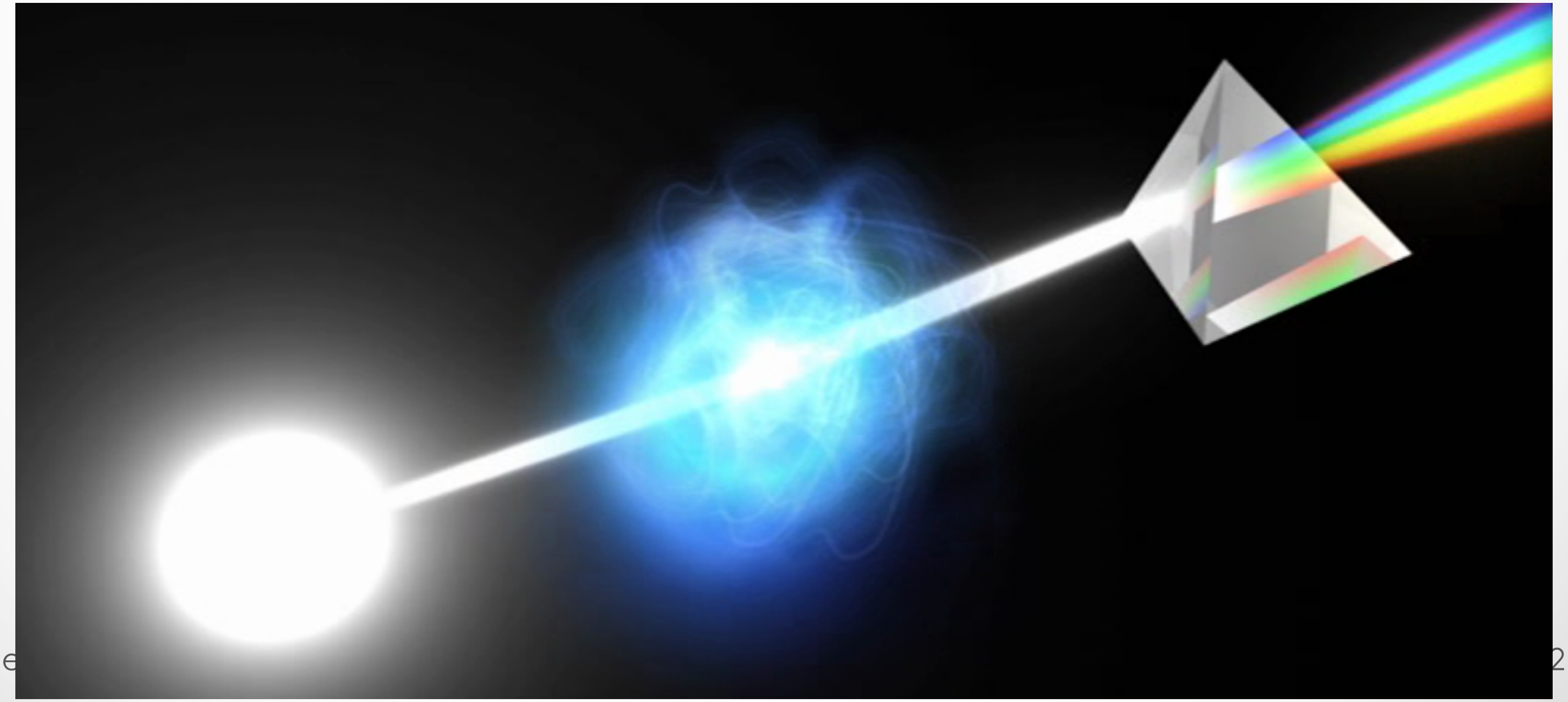
It means, that the radiating molecular system is, at least partly, in an excited state.

Sample can be anywhere (in lab, in space), the spectrometer on satelites, on Earth etc.



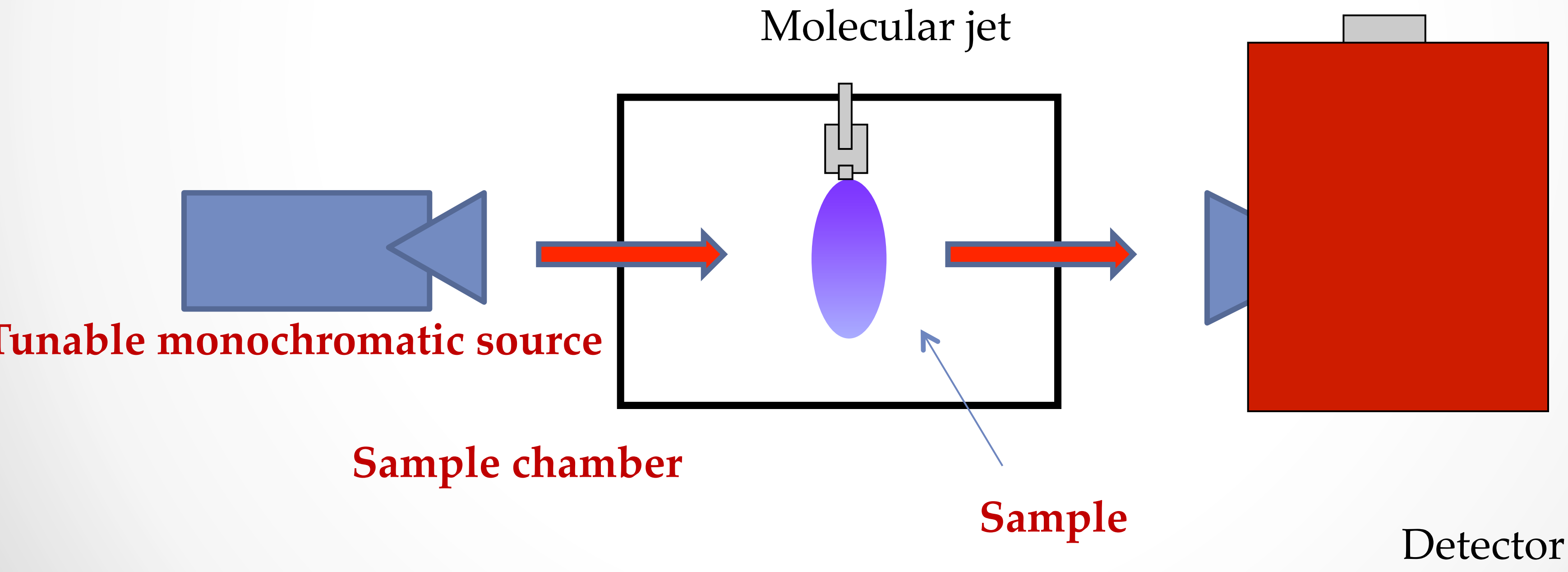
Molecular Spectroscopy

In the case of **absorption sp**ectroscopy, a source of radiation is used. The source is either polychromatic or monochromatic. Setup with the polychromatic radiation source must involve some dispersion system (prisma, interferometer, grating …



Molecular Spectroscopy

On the second hand, the **monochromatic tunable source**s are available only exceptionally, only in the spectral regions, where these high–tech sources are available (tunable lasers, gun diodes, karcinotrons, klystrons …)



Molecular jet

Tunable monochromatic source

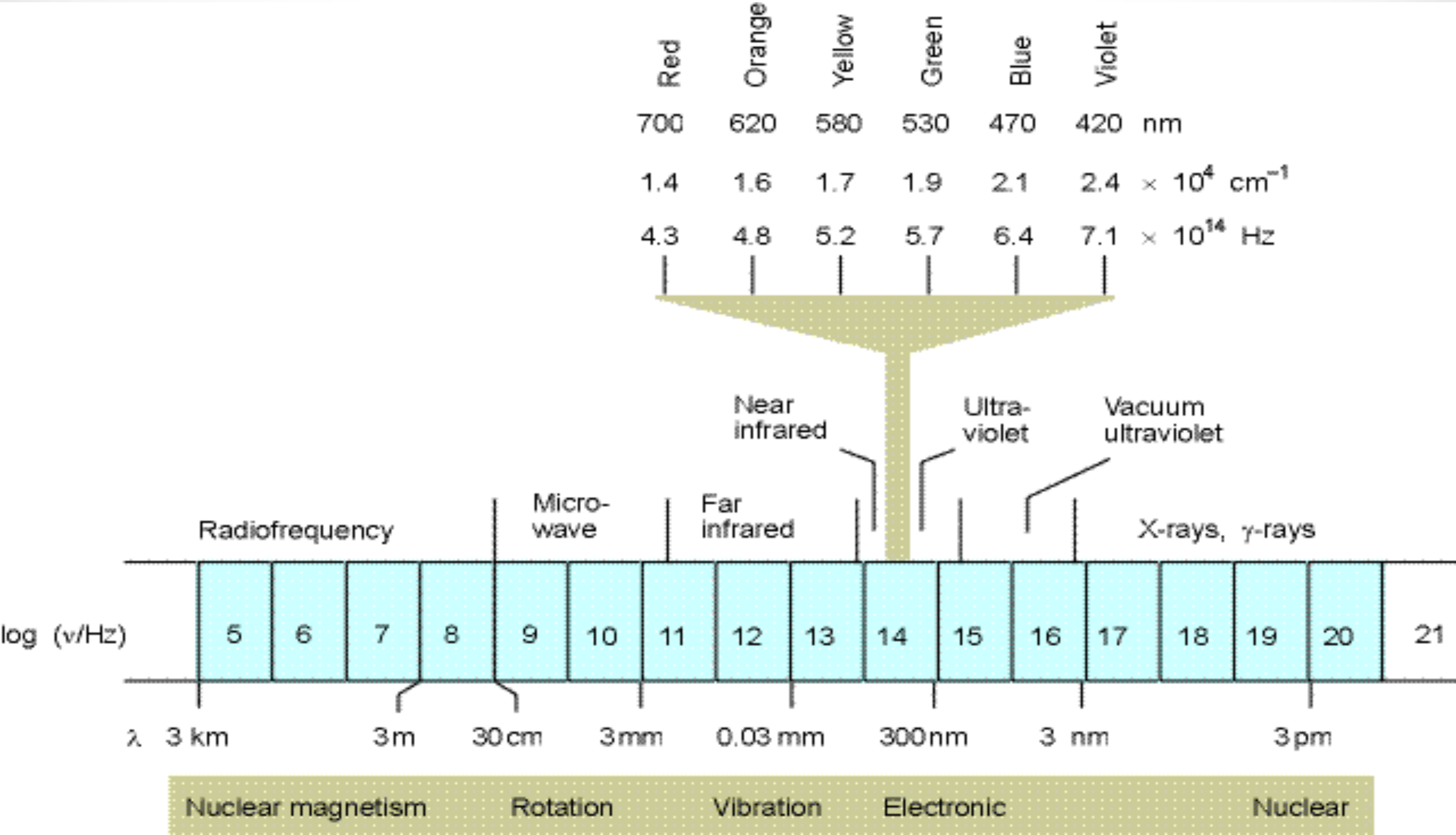
Sample chamber

Sample

Detector

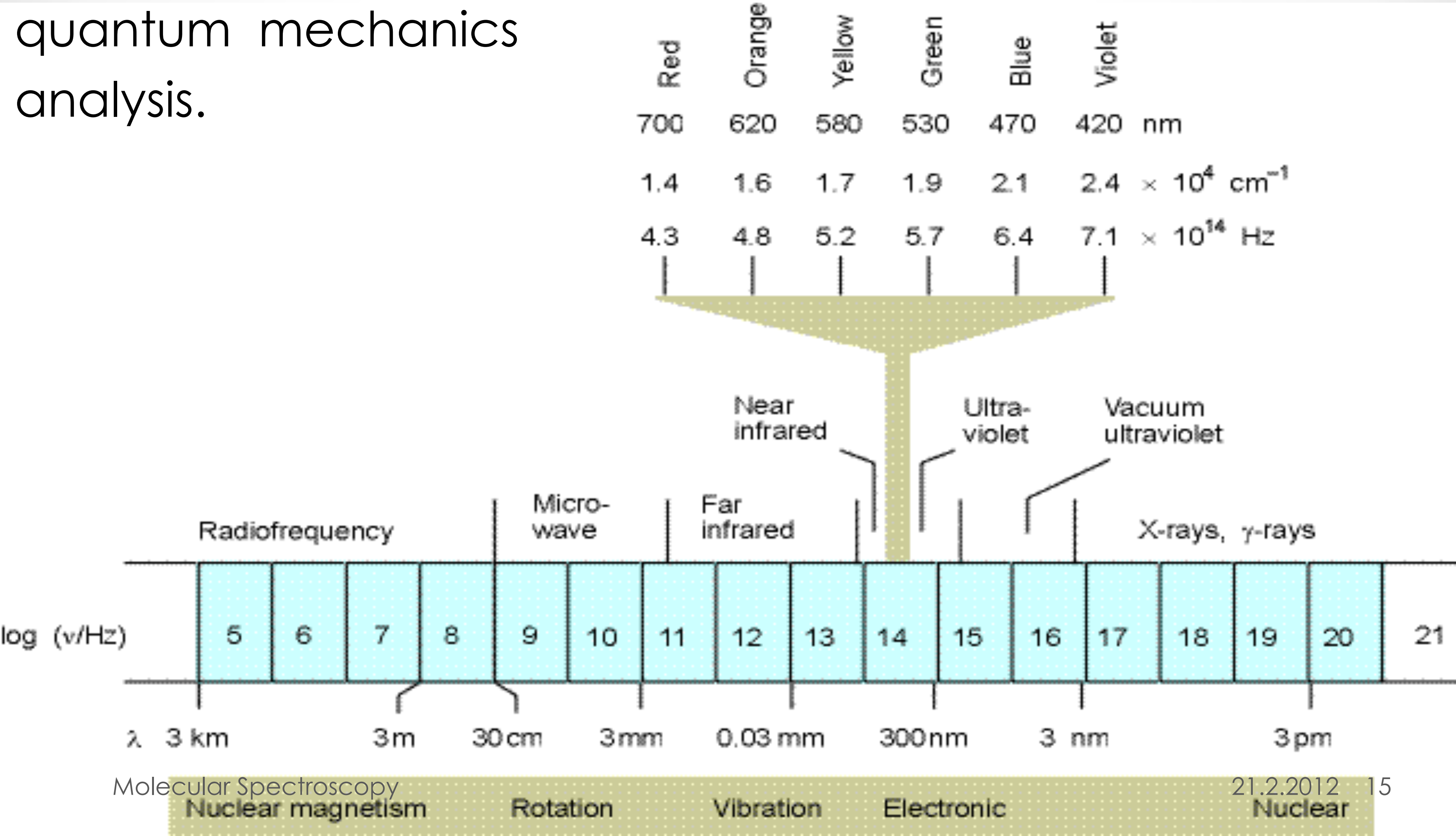
Molecular Spectroscopy

Spectroscopy is also divided according to **frequency regions**



Molecular Spectroscopy

or according to **theoretical model** which is used for the quantum mechanics analysis.

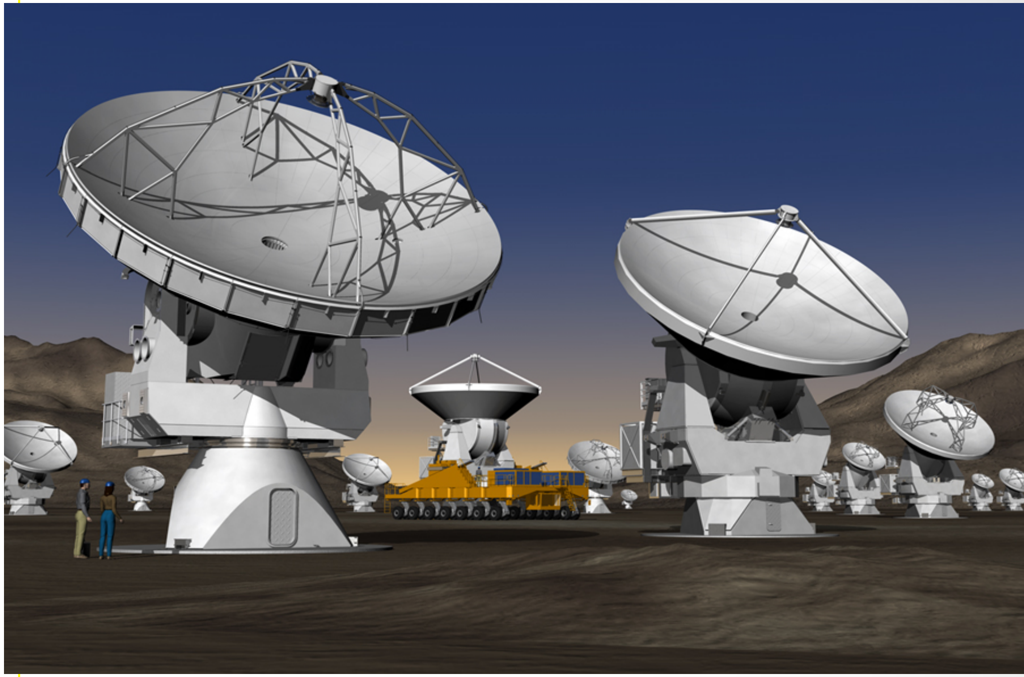


Molecular Spectroscopy

- **Electronic spectroscopy** (visible, ultraviolet, x-rays) observes transitions with a change of the quantum states of electronic molecular orbitals
- **Vibrational spectroscopy** (Infrared, THz) transitions between states with different vibrational quantum numbers (q.n.). These vibrational states have different content of the internal energy of molecular frame.
- **Rotational spectroscopy** (cm, mm, sub-mm, and FIR)observes transitions between the states which have the same vibrational and electronic q.n. but rotational ones are different.

Molecular Spectroscopy

From point of view of molecular spectroscopy, the ALMA facilities represent an emission high resolution spectrometer in the region of wave-lengthes cca 0.3 -10 mm.



ALMA spectrometer, therefore, makes measurements of high resolution **rotational** spectra in interstellar and circumstellar environments possible. The ALMA spectrometer array can provide the spectra with the highest sensitivity and space resolution.

Rotational spectrocopy

- From the clasical point of view, rotational spectroscopy studies changes of angular momenta of the **molecular frame rotation.**
- Quantum mechanics (QM) of angular momentum makes a detailed description of rotation spectra possible.
- QM Hamiltonian (operator for Schrödinger equation) for nuclear parts (without ellectrons) of a molecule:

$$\hat{H} = -\frac{\hbar^2}{2M_{\text{tot}}}\sum_{\alpha=1}^{3}\frac{\partial^2}{\partial X_\alpha^2}+\frac{1}{2}\sum_{\alpha,\beta=1}^{3}\mu_{\alpha\beta}(\mathcal{P}_\alpha-\Pi_\alpha)(\mathcal{P}_\beta-\Pi_\beta)+U-\frac{\hbar^2}{2}\sum_{s=1}^{3N-6}\frac{\partial^2}{\partial q_s^2}+V.$$

Rotational spectrocopy

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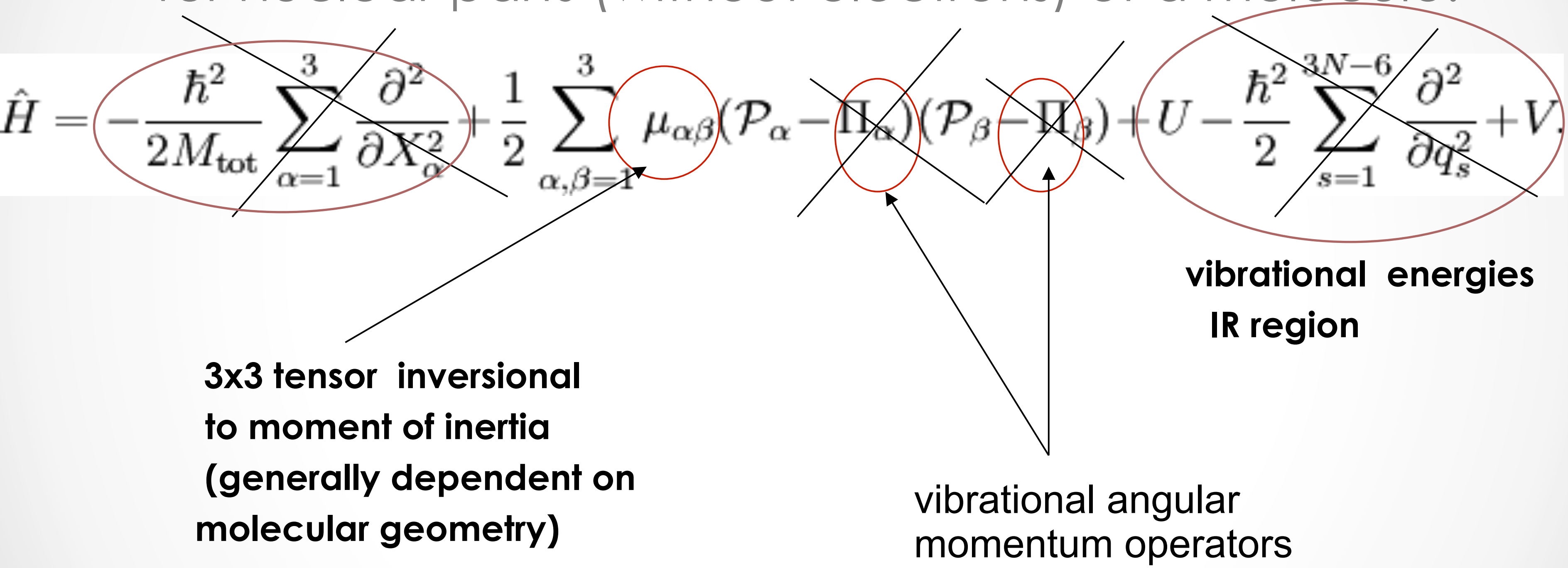
Movement of centre of gravity

Rotational spectrocopy

- QM Hamiltonian (operator for Schrödinger equation) for nuclear parts (without electrons) of a molecule:



$$\hat H = \xcancel{-\frac{\hbar^2}{2M_{\text{tot}}}\sum_{\alpha=1}^{3}\frac{\partial^2}{\partial X_\alpha^2}} + \frac{1}{2}\sum_{\alpha,\beta=1}^{3}\mu_{\alpha\beta}(\mathcal{P}_\alpha \xcancel{-\Pi_\alpha})(\mathcal{P}_\beta \xcancel{-\Pi_\beta}) + U \xcancel{-\frac{\hbar^2}{2}\sum_{s=1}^{3N-6}\frac{\partial^2}{\partial q_s^2} + V}$$

vibrational energies
IR region

3x3 tensor inversional
to moment of inertia
(generally dependent on
molecular geometry)

vibrational angular
momentum operators

Rotational spectrocopy

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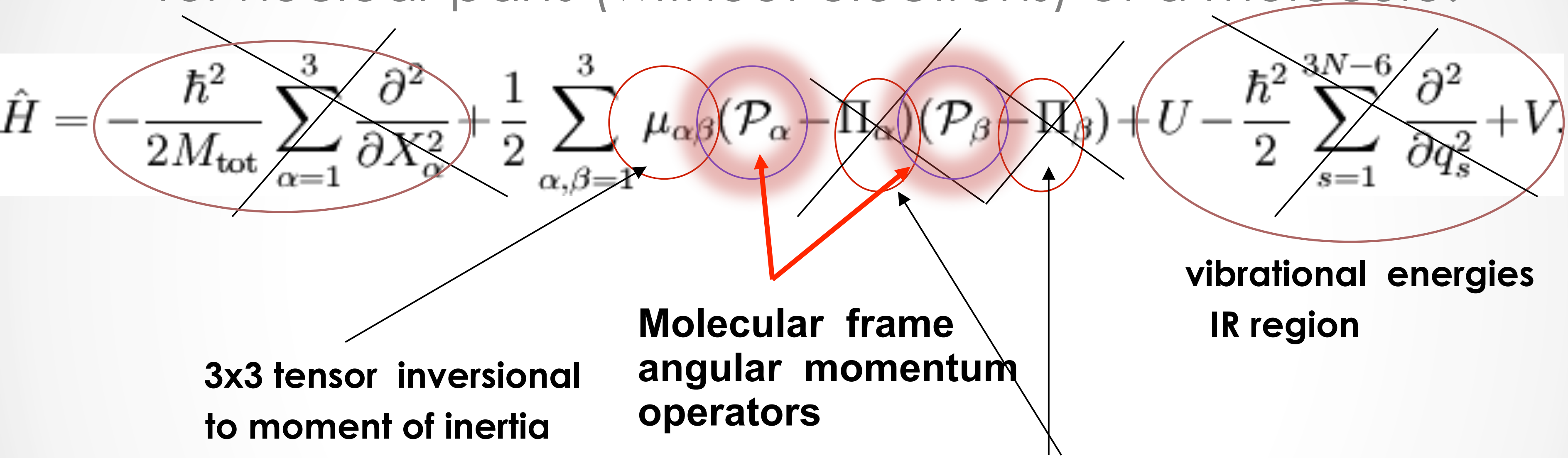


vibrational energies IR region

Molecular frame angular momentum operators

3x3 tensor inversional to moment of inertia (generally dependent on vib. coordinates)

vibrational angular momentum operators

dependence on vib. coordinates neglected → **choice of coordinate system to be the 3x3 tensor diagonal**

Rotational spectrocopy

$$\hat{H} = \cancel{-\frac{\hbar^2}{2M_{\text{tot}}}\sum_{\alpha=1}^{3}\frac{\partial^2}{\partial X_\alpha^2}} + \frac{1}{2}\sum_{\alpha,\beta=1}^{3}\mu_{\alpha\beta}(\mathcal{P}_\alpha - \cancel{\Pi_\alpha})(\mathcal{P}_\beta \cancel{- \Pi_\beta}) + U \cancel{- \frac{\hbar^2}{2}\sum_{s=1}^{3N-6}\frac{\partial^2}{\partial q_s^2} + V}$$

$$\downarrow$$

$$\longrightarrow \tfrac{1}{2}\{J_x^{\,2}/I_{xx} + J_y^{\,2}/I_{yy} + J_z^{\,2}/I_{zz}\}\,\psi_r = E_r\,\psi_r$$

Rotational spectrocopy

Schrödinger equation of the **rigid rotor**

$$\tfrac{1}{2}\{J_x^2/I_{xx} + J_y^2/I_{yy} + J_z^2/I_{zz}\}\,\psi_r = E_r\,\psi_r$$

substitution of J_x *and* I_{xx} *by* J_a *and* I_a *etc. so* $I_a \leq I_b \leq I_c$

$$\tfrac{1}{2}\{J_a^2/I_a + J_b^2/I_b + J_c^2/I_c\}\,\psi_r =$$

$$= \hbar^{-2}\,\{AJ_a^2 + BJ_b^2 + CJ_c^2\}\psi_r = E_r\,\psi_r$$

- where A, B, and C are, so called, **rotational constants**

Rotational spectrocopy

$$\hbar^{-2}\{AJ_a^2 + BJ_b^2 + CJ_c^2\}\psi_r = E_r\,\psi_r$$

where A, B, and C are, so called, **rotational constants**

Rotational constants are interconected with molecular geometry (through the moment inertia) as well as with molecular symmetry.

Schrödinger Equation is for the rigid rotor solvable either analytically or numerically (asymetric top).

$$A = \frac{h^2}{8\pi^2 I_a}$$

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

$$C = \frac{h^2}{8\pi^2 I_c}$$

Rotational spectrocopy

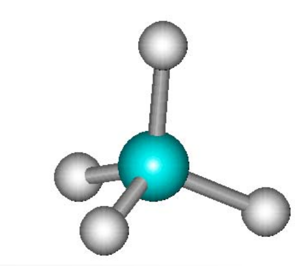
Spherical top (rotational constants

$$I_a = I_b = I_c$$
$$A = B = C$$

$$\hbar^{-2}\{BJ_a^2 + BJ_b^2 + BJ_c^2\}\psi_r = \hbar^{-2} B\{J_a^2 + J_b^2 + J_c^2\}\psi_r = \hbar^{-2} B J^2 = E_r\,\psi_r$$

Rotational energy ${}^{r}E_{J,k,m} = B\,J(J+1)$

Transition frequency (J+1←J) $\nu(J) = 2B(J+1) - 2D_j\,(J+1)^2(J+2)$ …..



In the spherical top case, the spectrum provides app. equidistant lines with spacing 2B

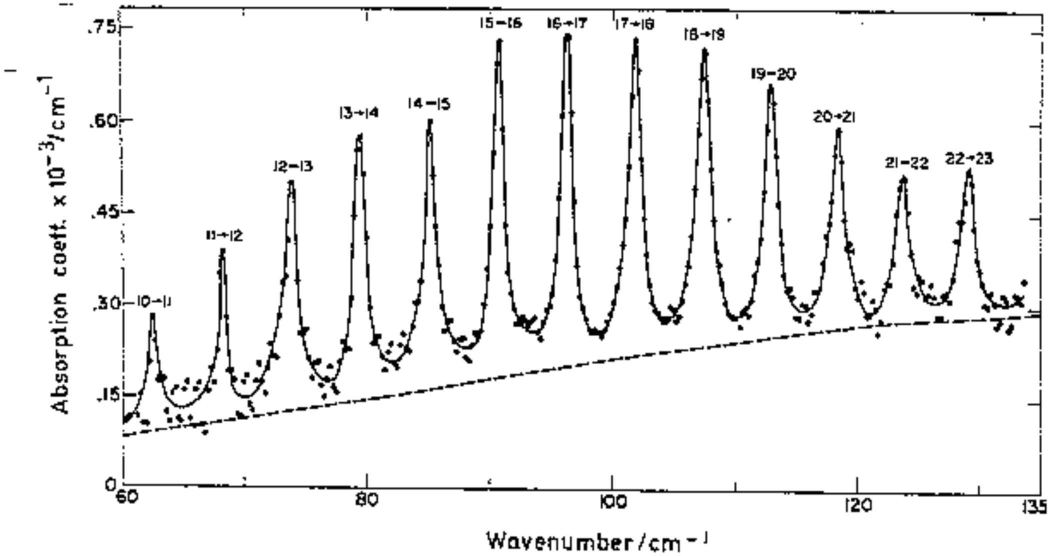
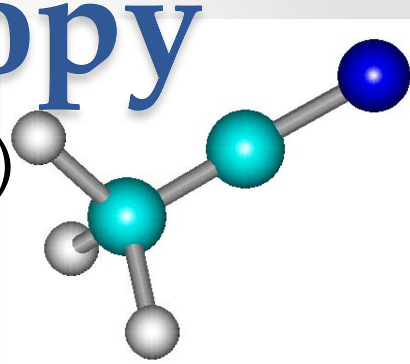


Figure 4.28 The far infrared pure rotational spectrum of the SiH_4 molecule obtained with a Miche interferometer [Reproduced, with permission, from Rosenberg, A. and Ozier, I. (1974). *Can. J. Phys*., **52**,

Rotational spectrocopy

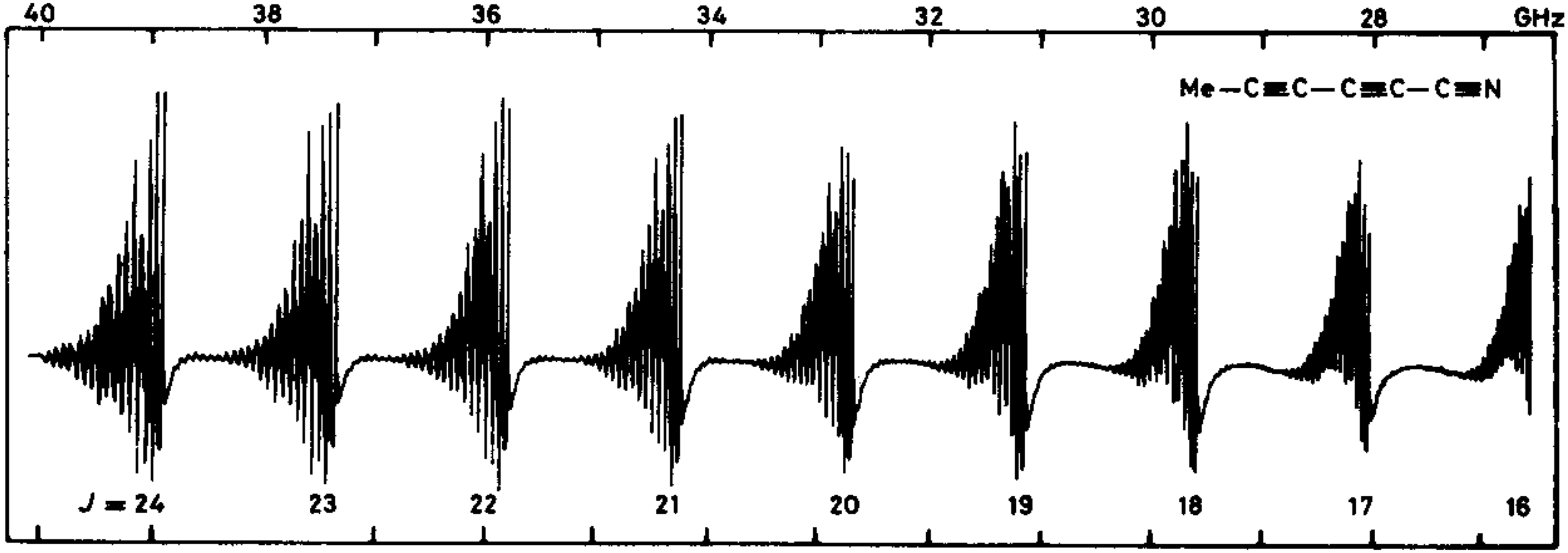


Prolate symmetric top (rot. constants A>B=C)

Oblate symmetric top (rot. constants A=B>C)

Rot. en. ${}^{r}E_{J,k} = B\,J(J+1)+(A-B)k^2$ +. or ${}^{r}E_{J,k} = B\,J(J+1) + (C-B)k^2$+.

Trans.fr.(J+1,k←J,K) $\nu(J) = 2B(J+1)-2D_j\,(J+1)^2(J+2)-2D_{jk}\,(J+1)^2k^2$



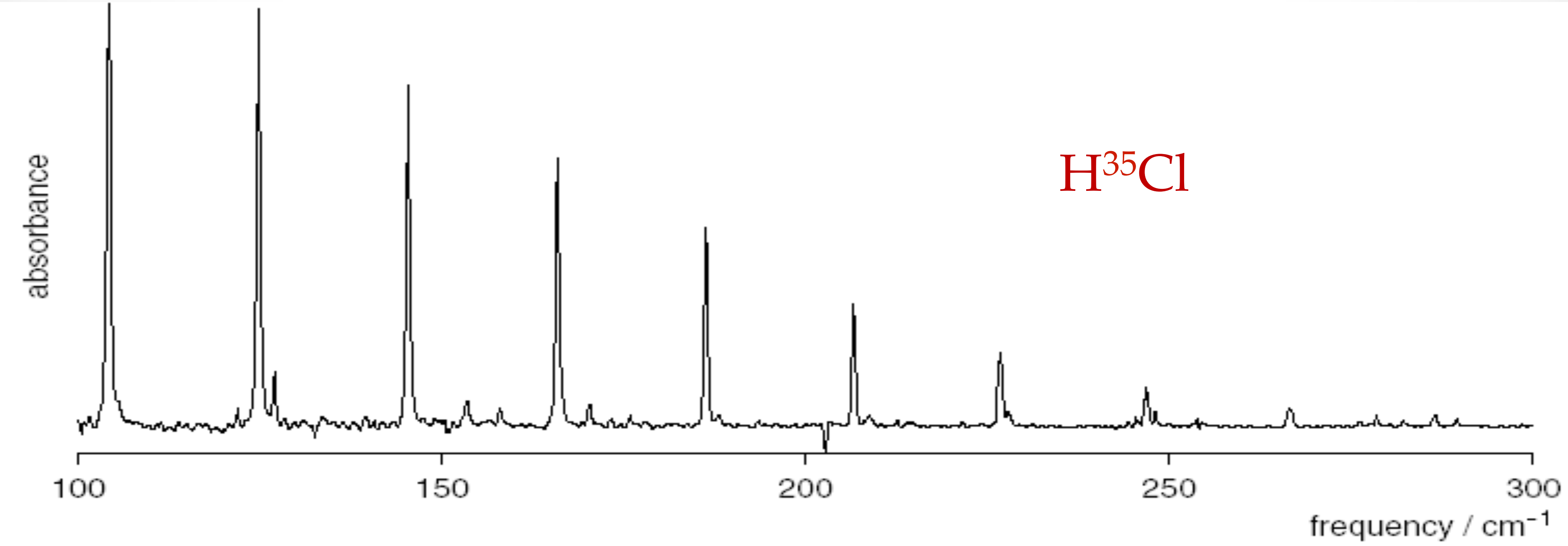
Rotational spectrocopy

Linear molecules are a special case of the prolate **symmetric top** with extremely big rotational constant

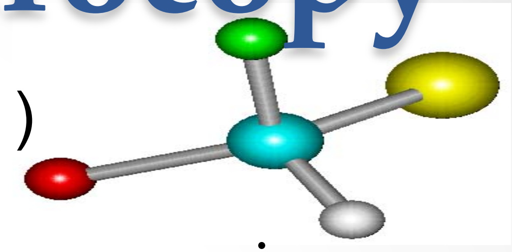
A >>>B=C

Rot. en. $^{r}E_{J,0} = B\,J(J+1)\,\cancel{+(A-B)}k^2 \; - D_j\,J^2(J+1)^2 + ...$

Trans.fr.(J+1,k=0←J, 0) $\nu(J) = 2B(J+1) - 2D_j\,(J+1)^2(J+2)$



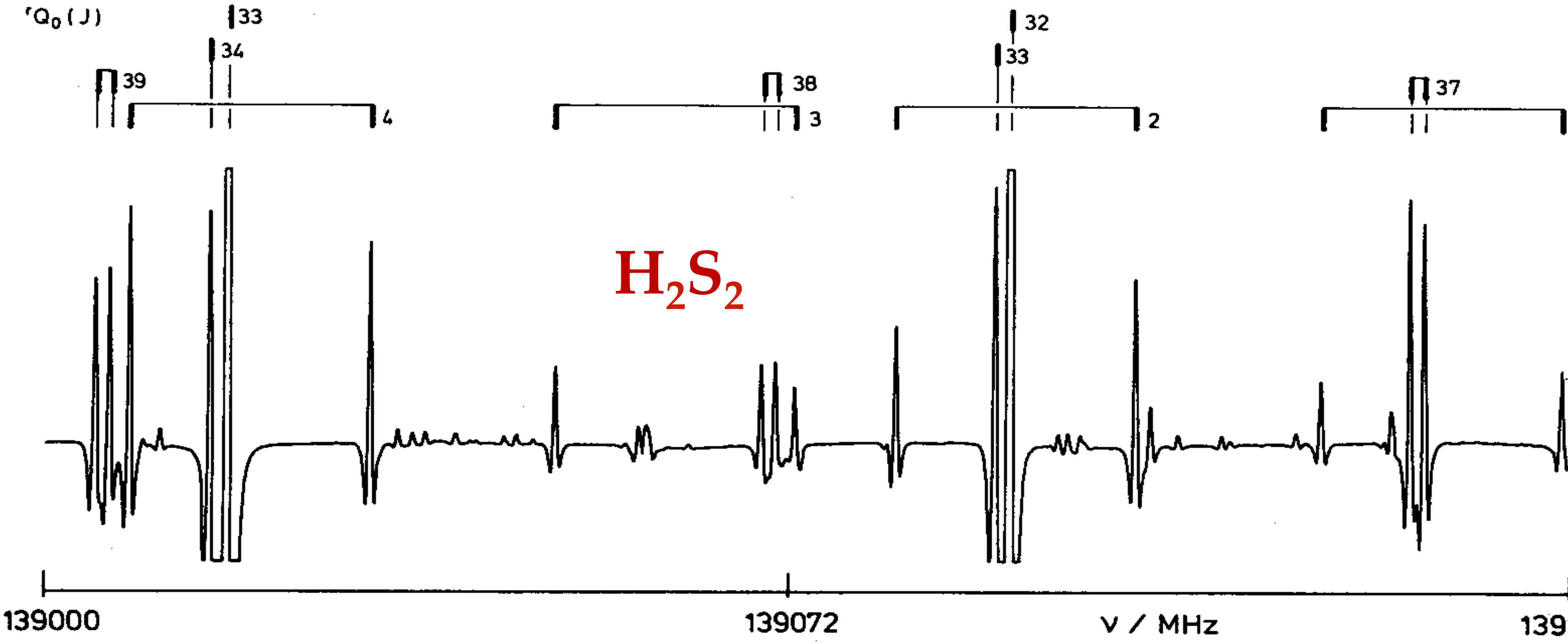
Rotational spectrocopy



Asymmetric top (rot. constants A>B>C)

There is no simple analytical expression for energies.

The energies are calculated from Hamiltonian matrices that are constructed in the basis of symmetric top wavefunctions



Hyperfine and Fine Structures of Rotational Energy Levels

Some nuclei have a **nuclear spin** – inner angular momentum. Since nucleus has an electric charge, it is accompanied with a magnetic moment and, in cases of higher spin S>0.5, the nuclei have also electric quadrupole moment.

Since the possible orientations of the spin moments are quantized, there are also quantized **weak interactions** of the nuclear spin magnetic and electric quadrupole moments with the internal electromagnetic field of molecules.

These weak interactions of nuclear spins with the internal electromagnetic field **generate hyperfine structures** of rotational levels.

Hyperfine and Fine Structures of Rotational Energy Levels

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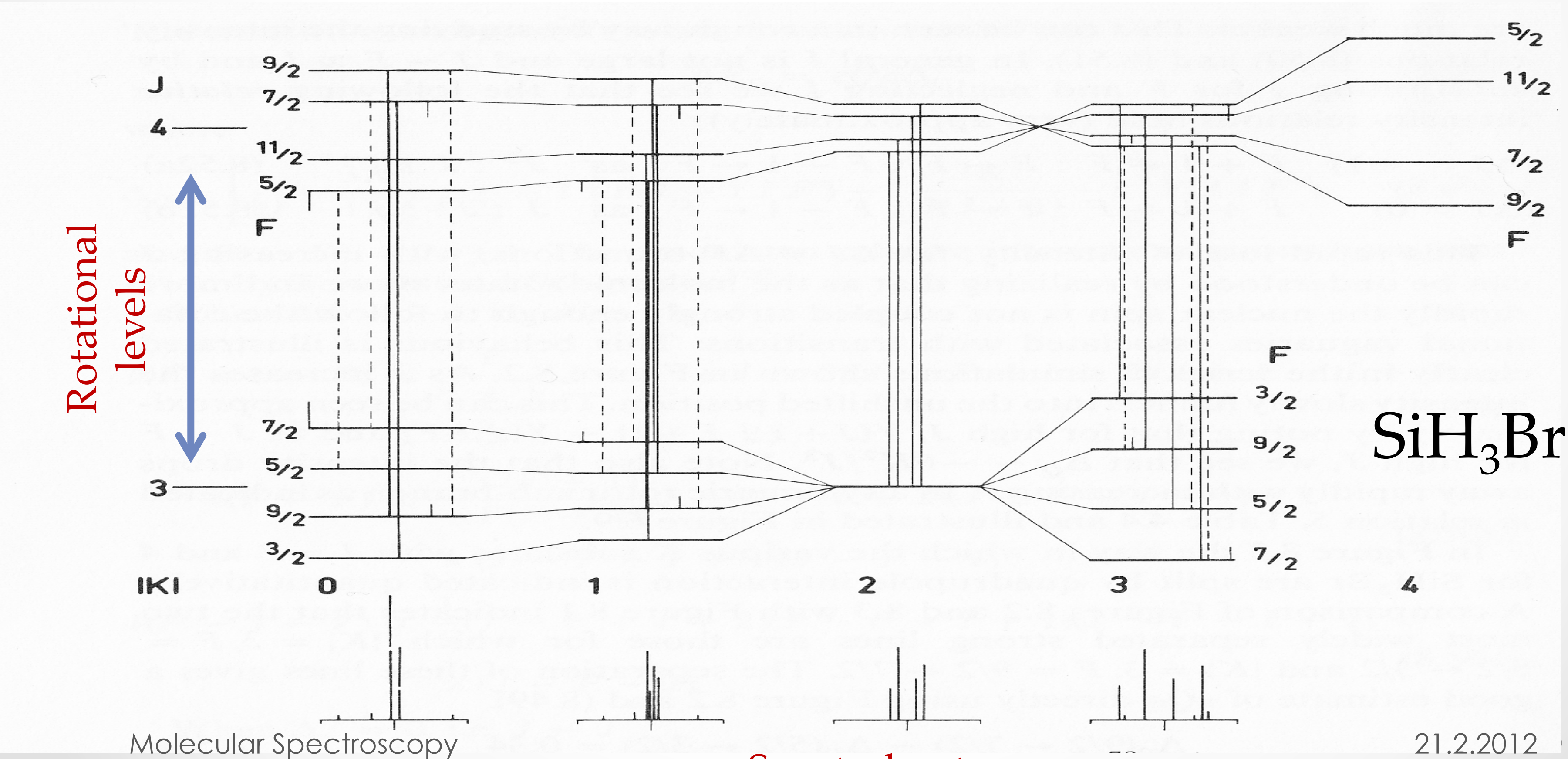


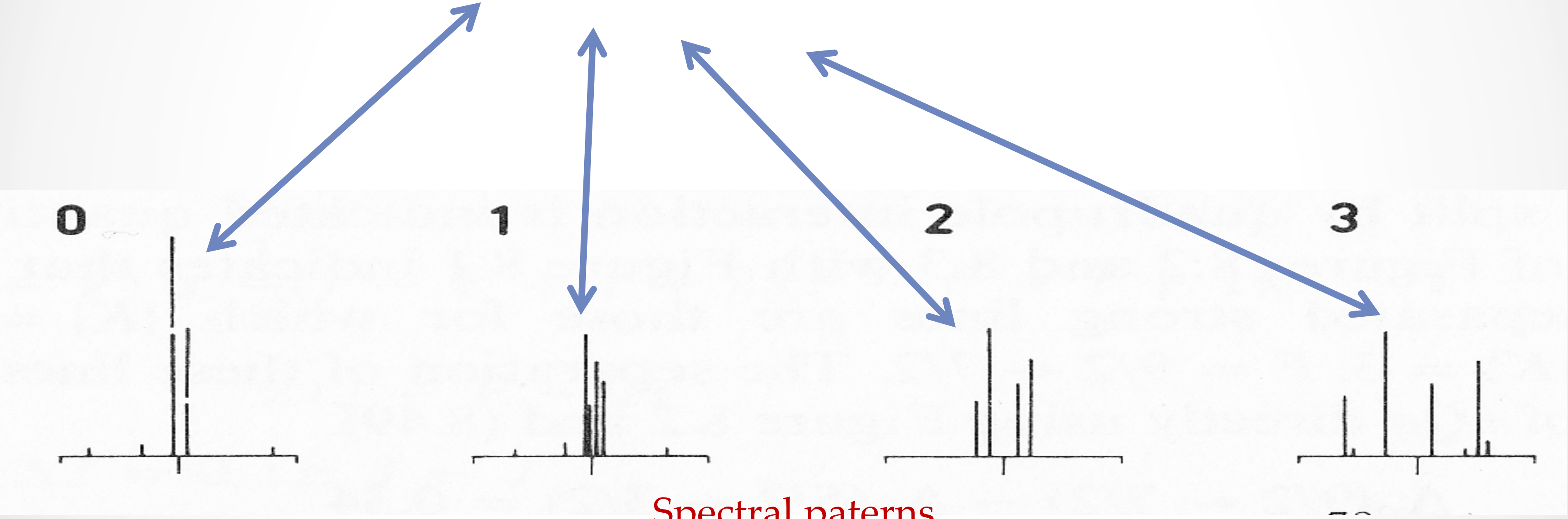
Rotational levels

SiH_3Br (79)

Spectral paterns

Hyperfine and Fine Structures of Rotational Energy Levels

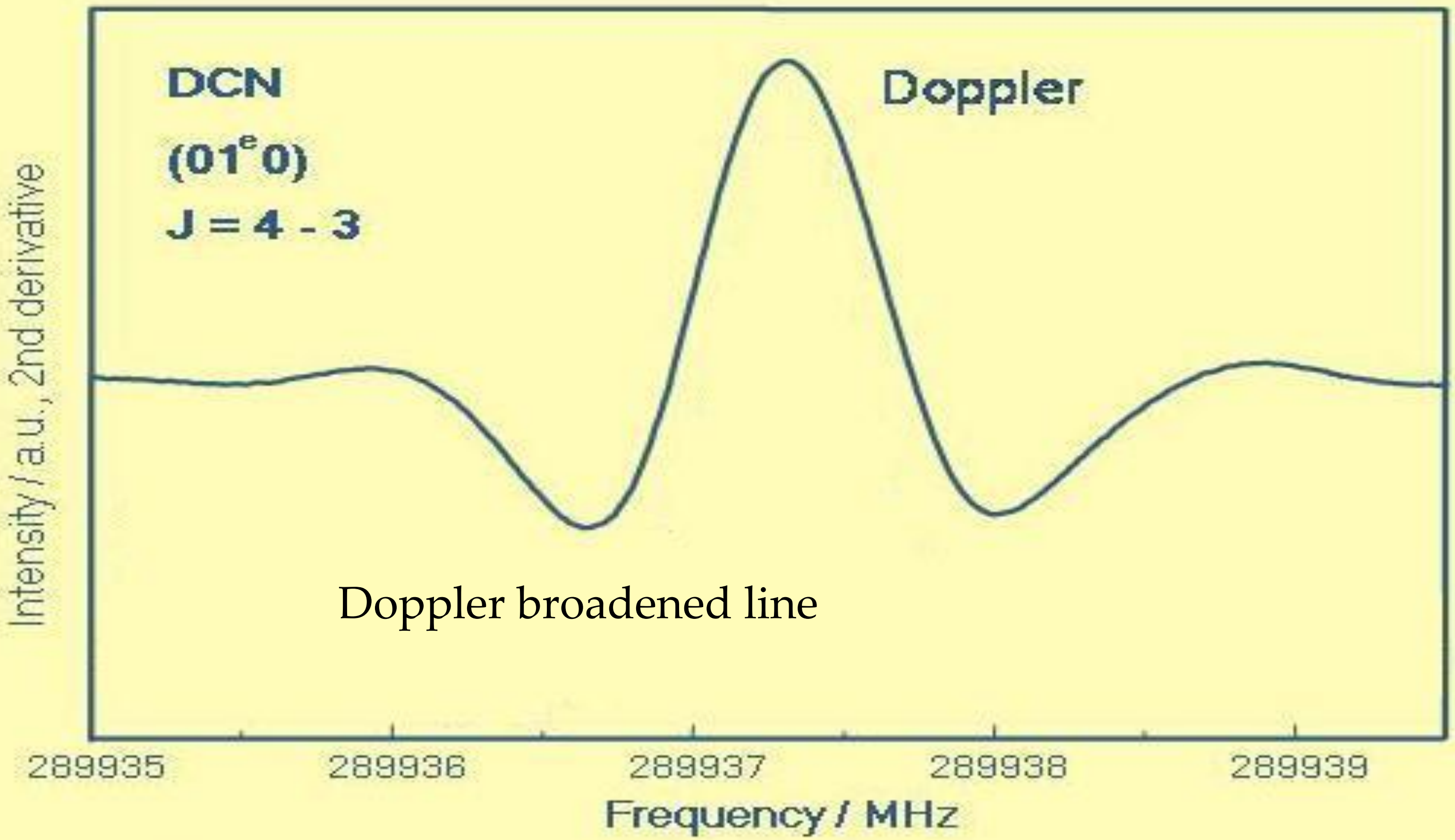
These **hyperfine splittings** of rotational levels are often too fine to be resolved and they are hidden broadened lines.



Spectral paterns

The **collision broadening** of lines can be removed by very low sample pressure when the **Doppler broadening** of remains. The Doppler can be suppressed by special experiments.

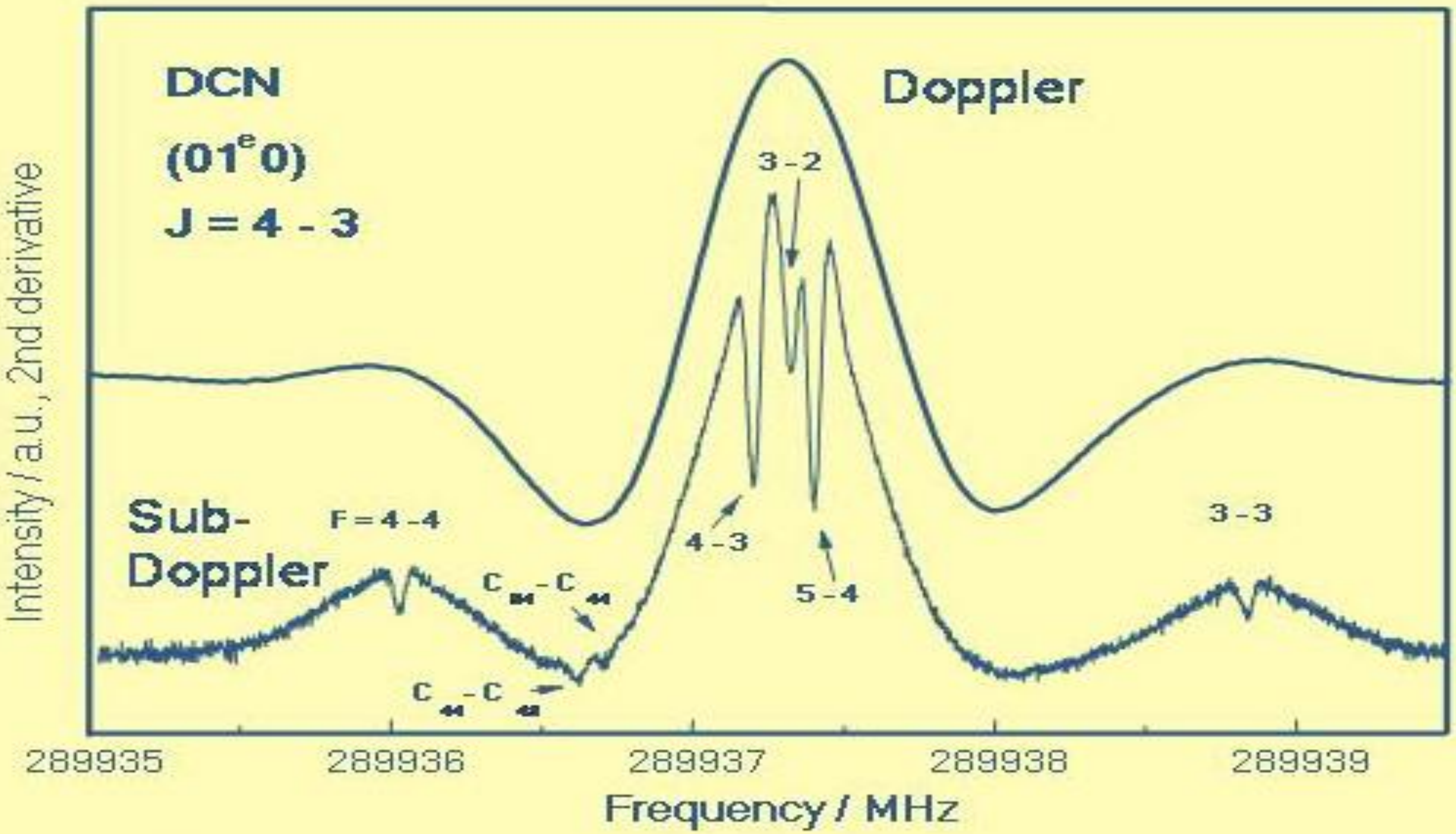
Hyperfine and Fine Structures of Rotational Energy Levels



Doppler broadened line

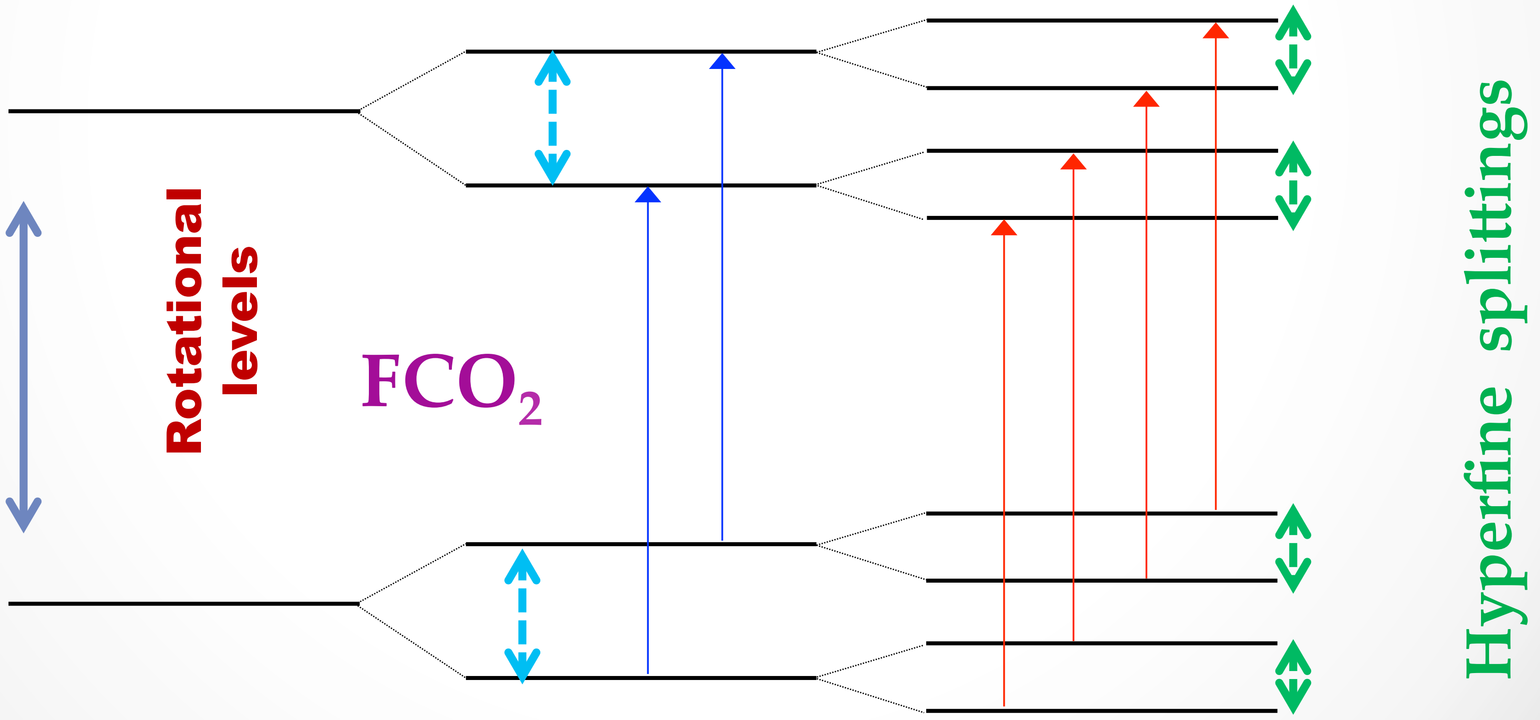
Hyperfine Structures of Rotational Energy

The same line measured by the saturation Lamb dip technique. These sub-doppler measurements uncover hyperfine structures. The natural broadening remains.



Fine Structures of Rotational Levels

In the case of the **open shell molecules** (so called radicals) that have unpaired electron(s), the **fine structure** of rotational levels can be observed. This splitting is a consequence of the **magnetic interaction of unpaired electrons with internal magnetic fields** in the molecule .



Fine splitting

Fine Structures of Rotational Levels

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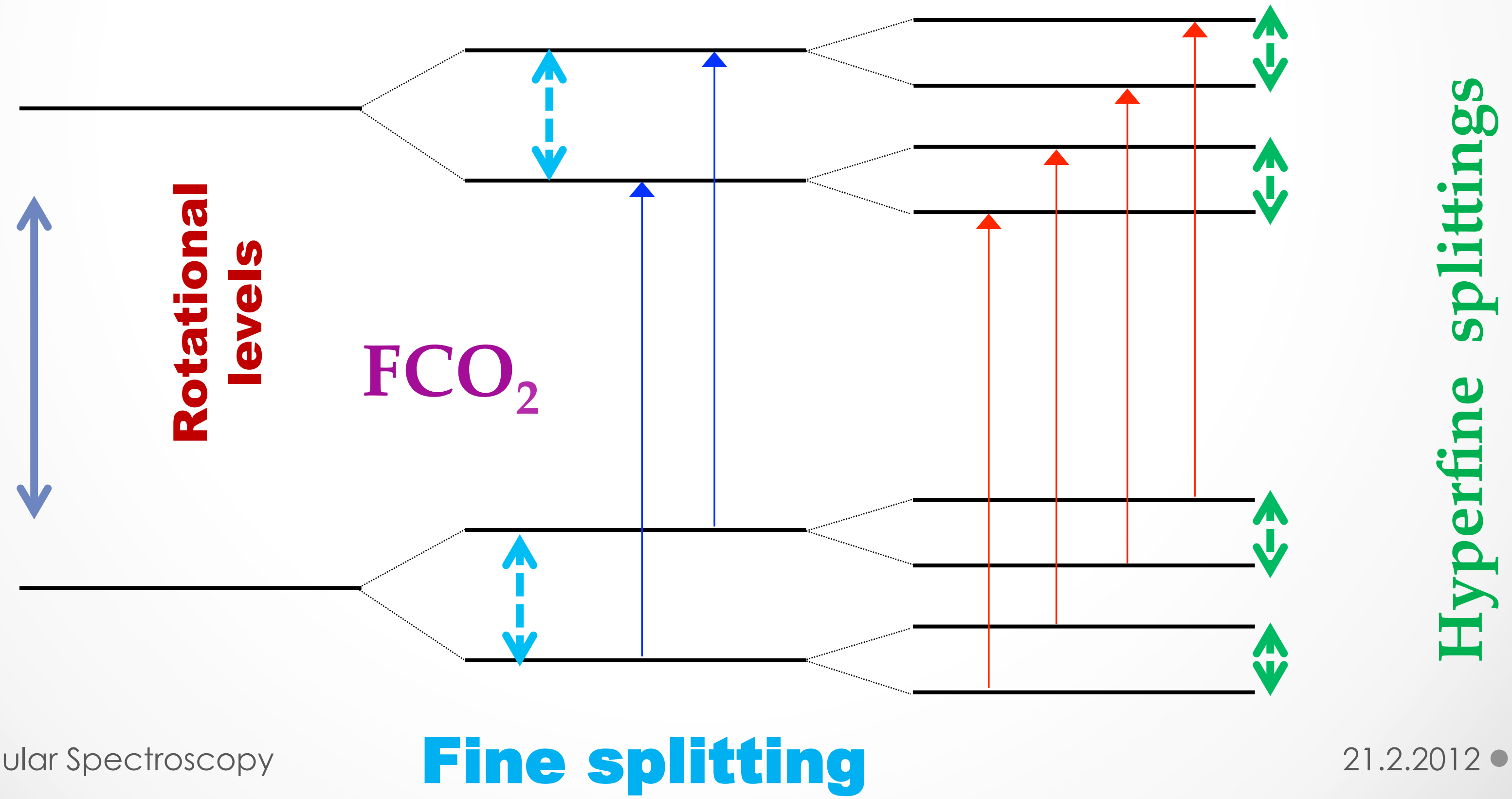

Fine Structures of Rotational Levels

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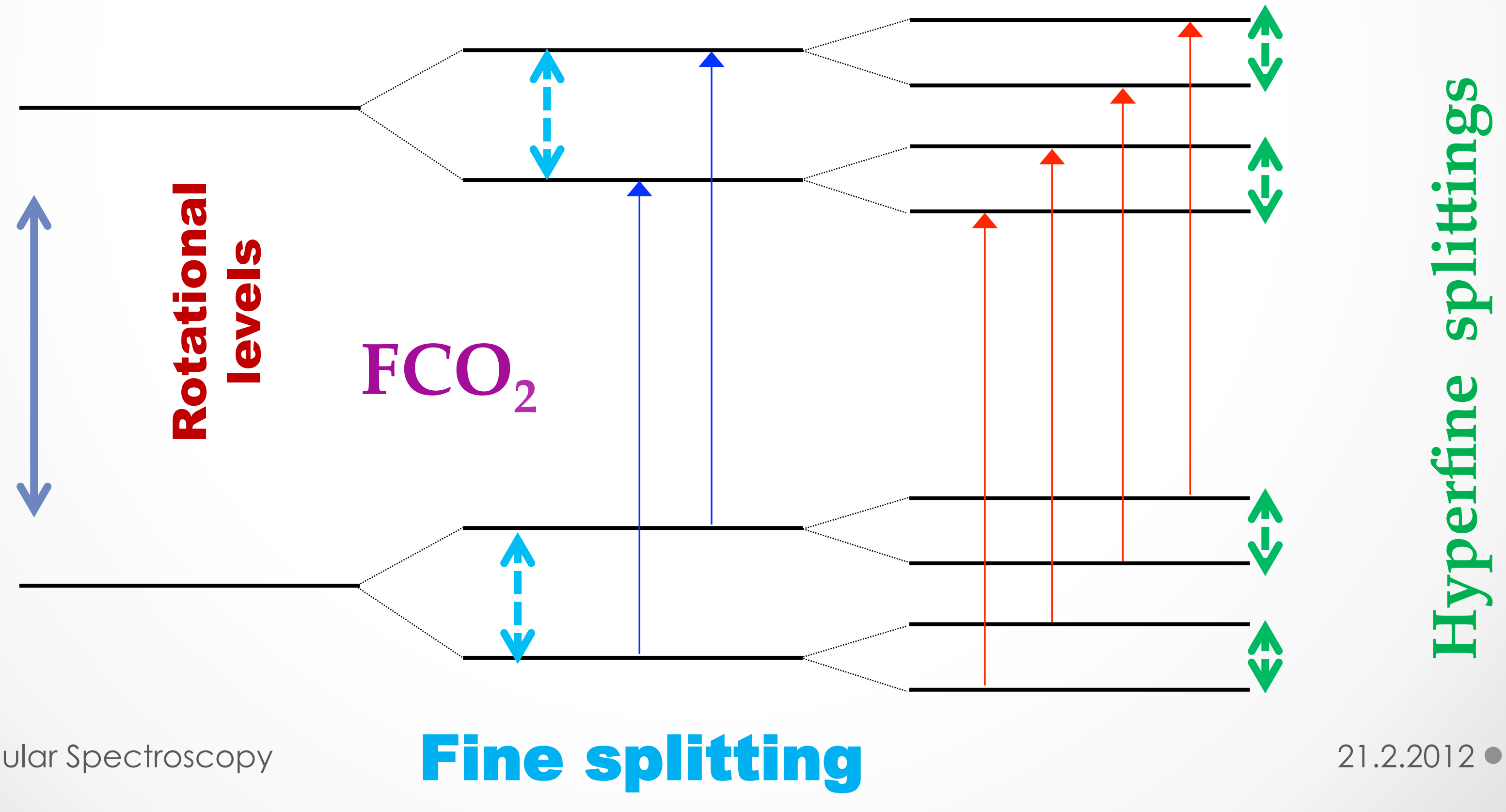
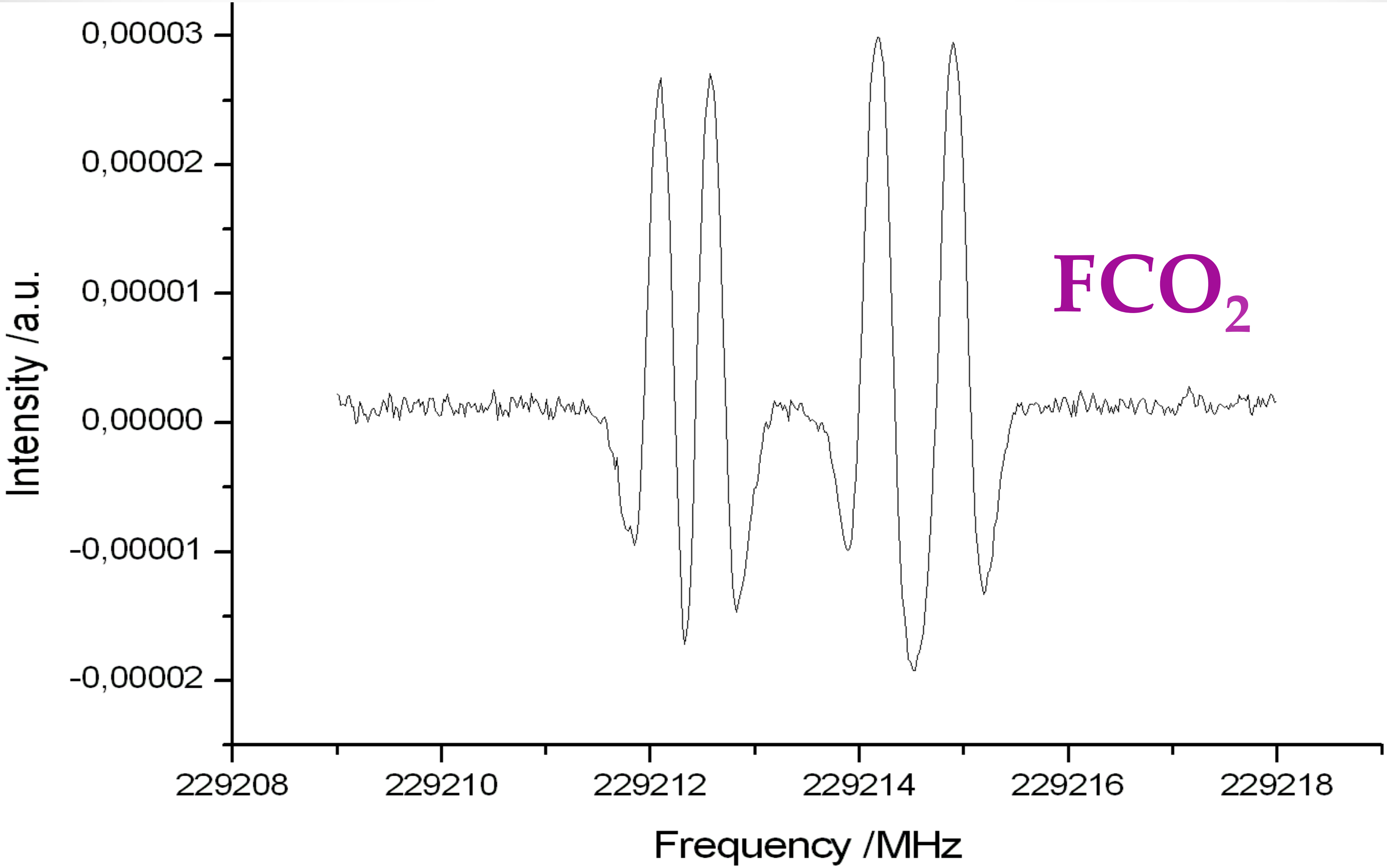


Fine and Hyperfine Splittings



FCO_2

Summary of Rotational Theory

The rotational constants of all molecules and their isotopologues are **unique**

There are **no two molecules with the same rotational constants and with the same rotational spectrum**.

With respect to outstanding accuracy of microwave spectroscopy, the absolutely **certain identification** of an molecule, can be based on observation of several lines (e.g. **hyperfine multiplet**). In the cases, when the speed of the object movements is known, one or two lines are sufficient for the molecule identification.

Summary of Rotational Theory

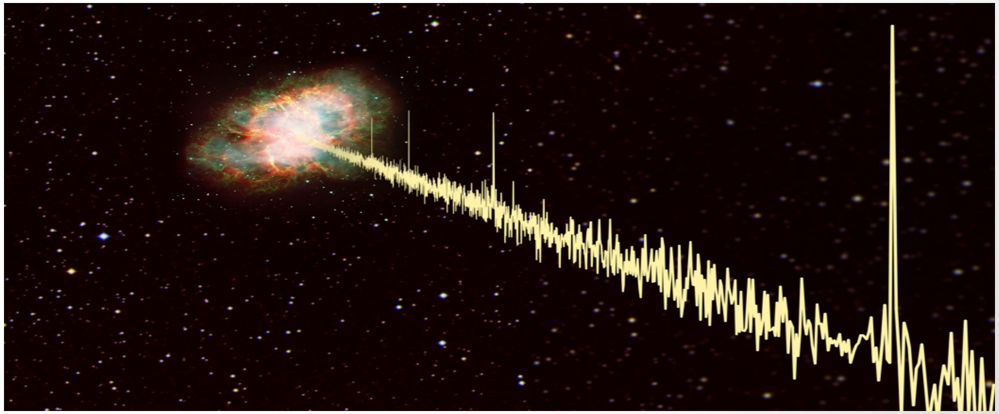
With respect to outstanding accuracy of microwave spectroscopy, the absolutely **certain identification** of an molecule, can be based on observation of several lines (e.g. **hyperfine multiplet**). In the cases, when the speed of the object movements is known, one or two lines are sufficient for the molecule identification.

The identification of molecules is always based on **transition frequencies derived from the laboratory experiment**.

The analysis of experim. data allows evaluation of the **sample temperature** and **ralative speed** to observer.

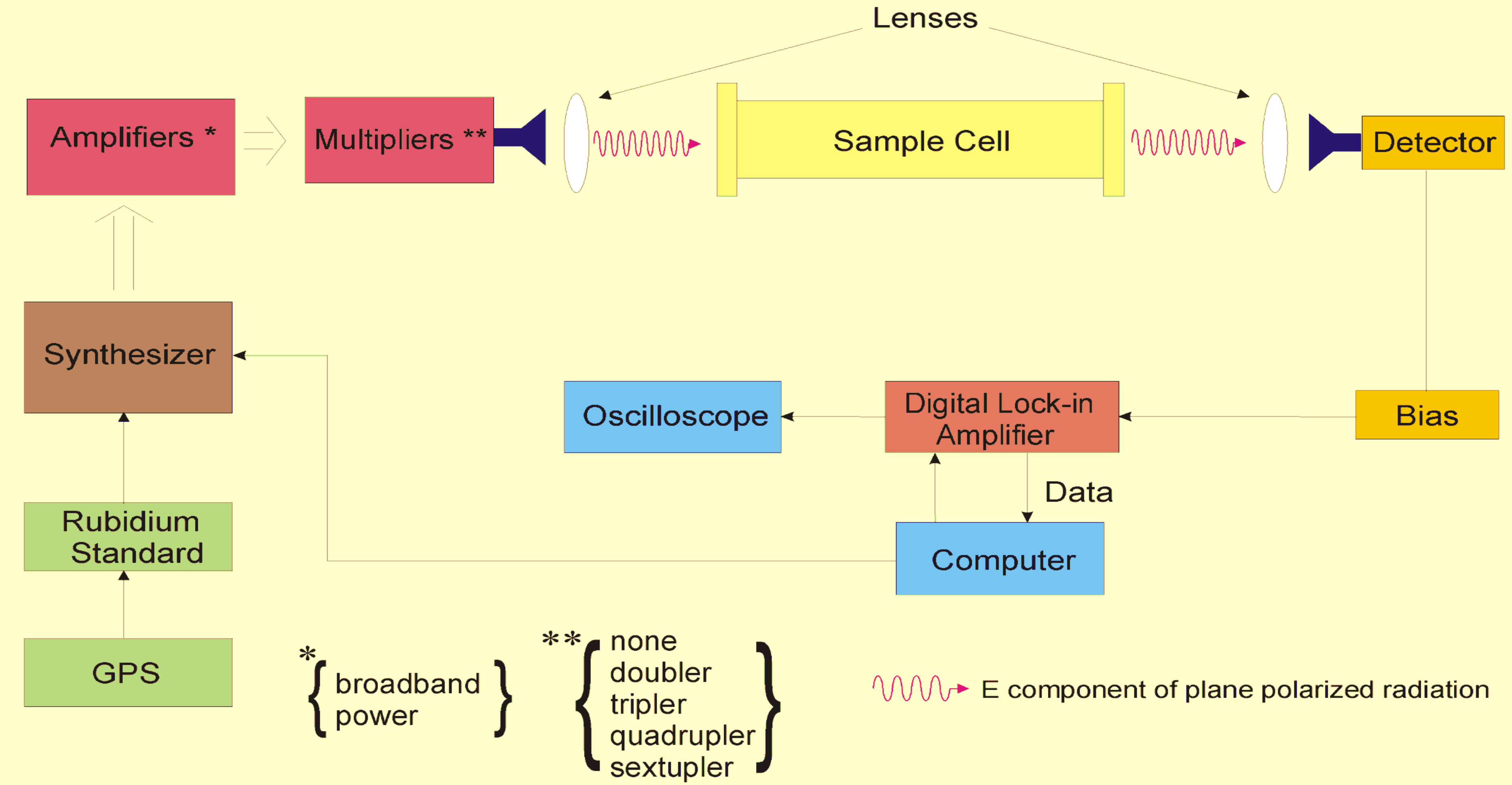
Notes to MW and THz Experiment

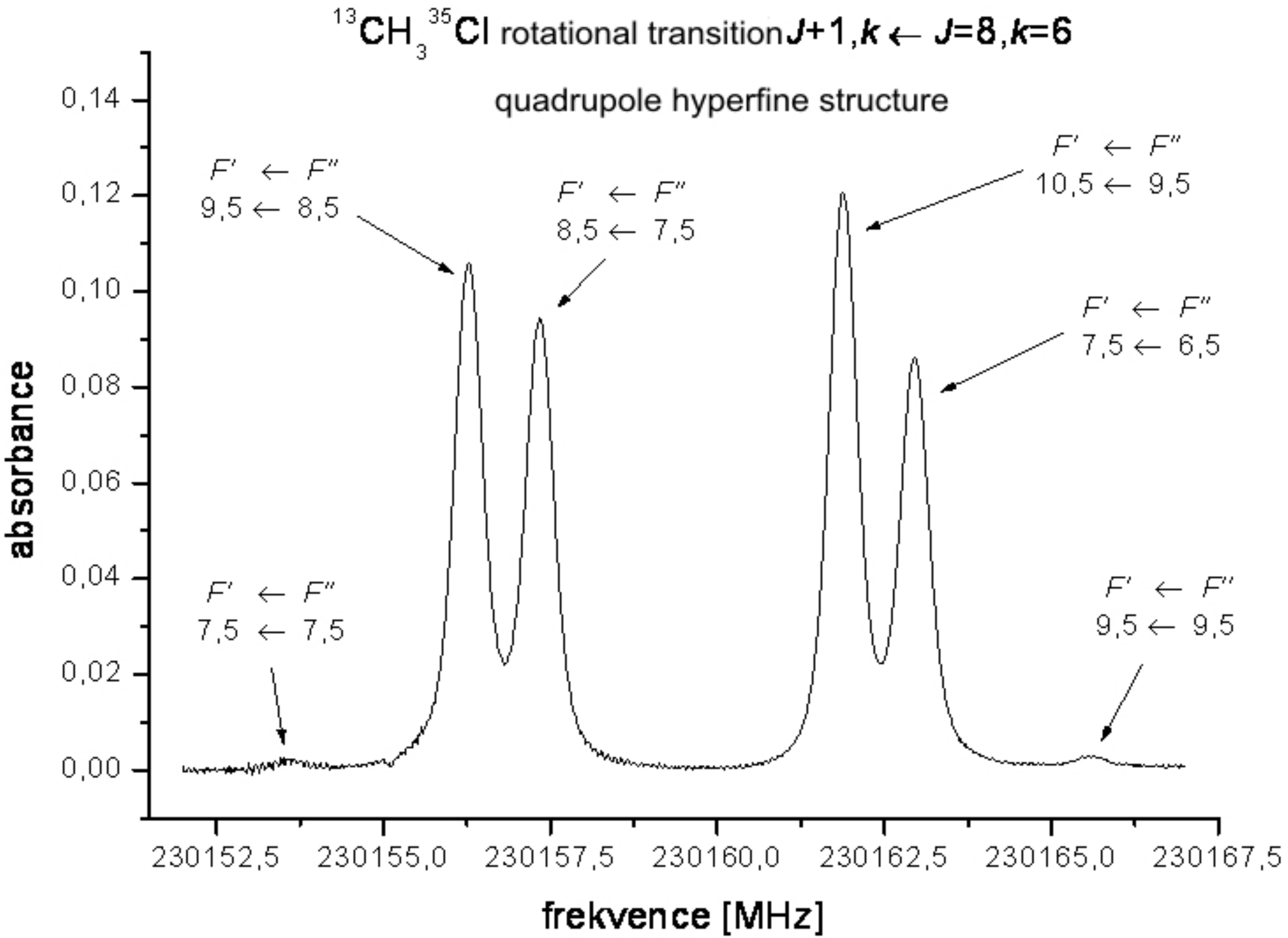
- Present-day advanced microwave and THz spectroscopy uses tunable monochromatic sources of radiation for both, the absorption as well as emission setups.
- These sources are usually online or offline linked to an atomic clock with **extremely high accuracy**.
- Labratory experiments use both the absorption as well as emission arrangemets.
- Spectra from space are always received like emission spectra by telescope

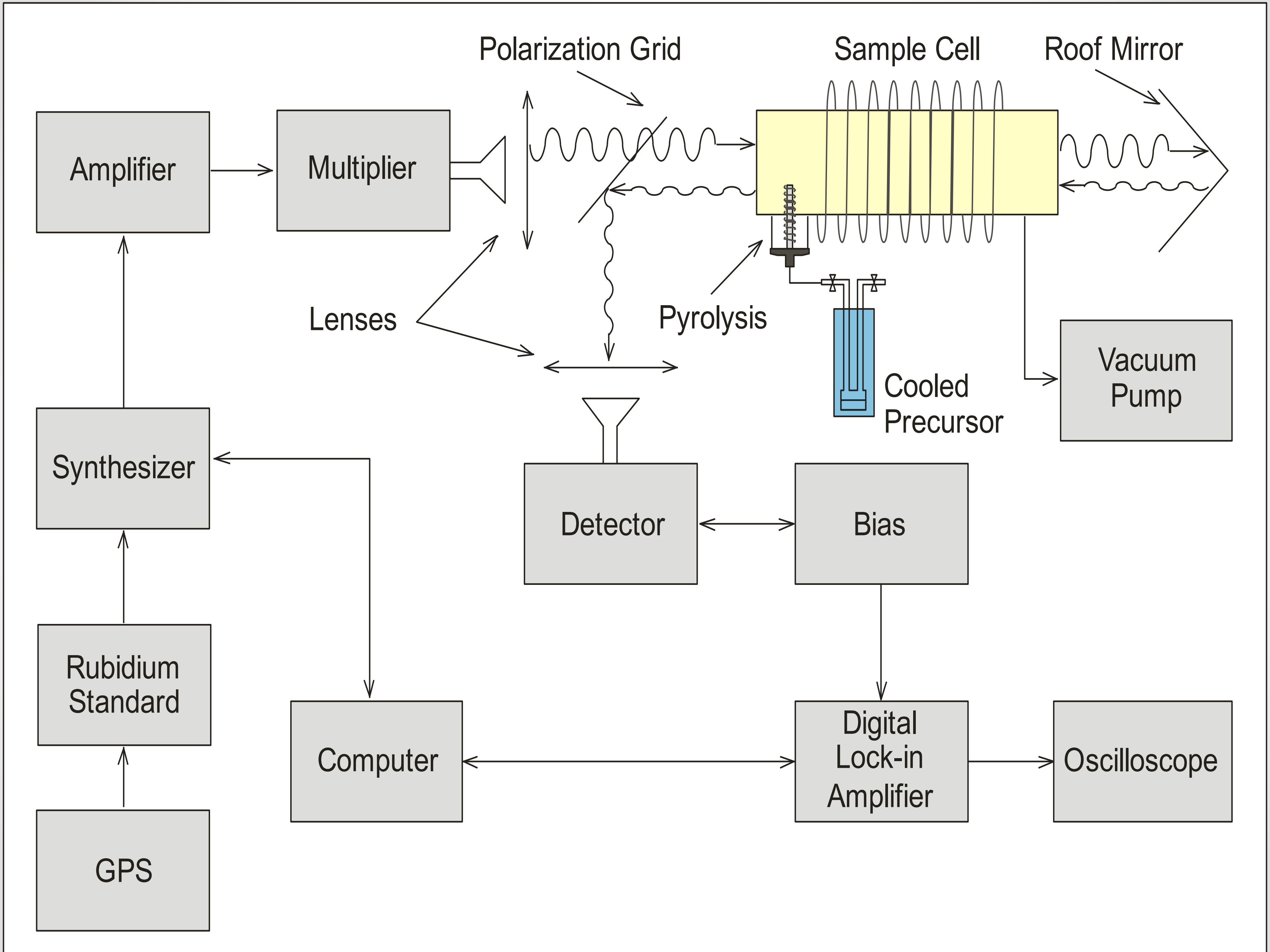


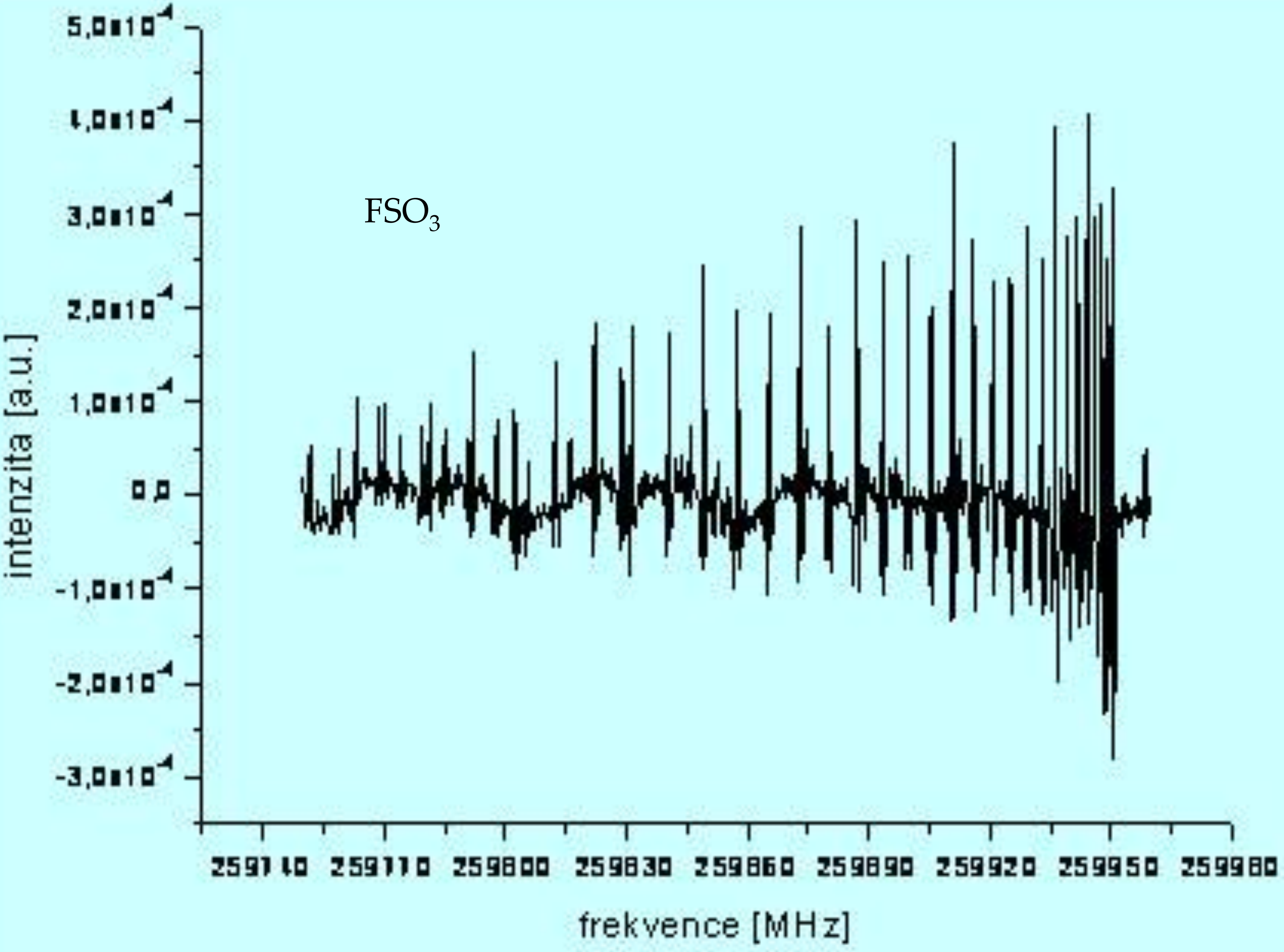
Notes to MW and THz Experiment

Scheme of the Prague Millimeter Wave High Resolution Spectrometer

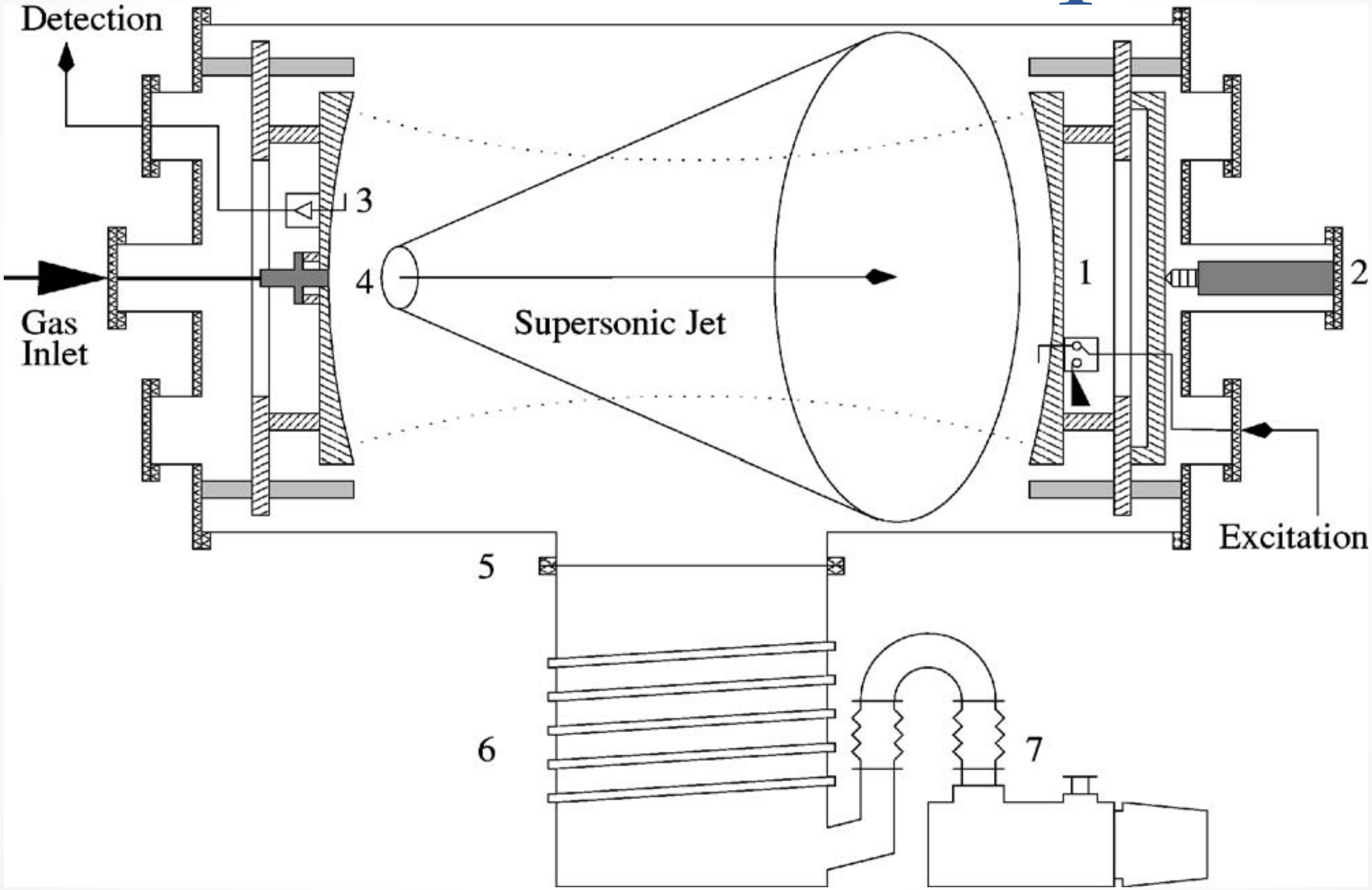



$^{13}CH_3{}^{35}Cl$ rotational transition $J+1,k \leftarrow J=8,k=6$
quadrupole hyperfine structure
F' ← F''
9,5 ← 8,5
F' ← F''
8,5 ← 7,5
F' ← F''
10,5 ← 9,5
F' ← F''
7,5 ← 6,5
F' ← F''
7,5 ← 7,5
F' ← F''
9,5 ← 9,5
absorbance
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
230152,5
230155,0
230157,5
230160,0
230162,5
230165,0
230167,5
frekvence [MHz]

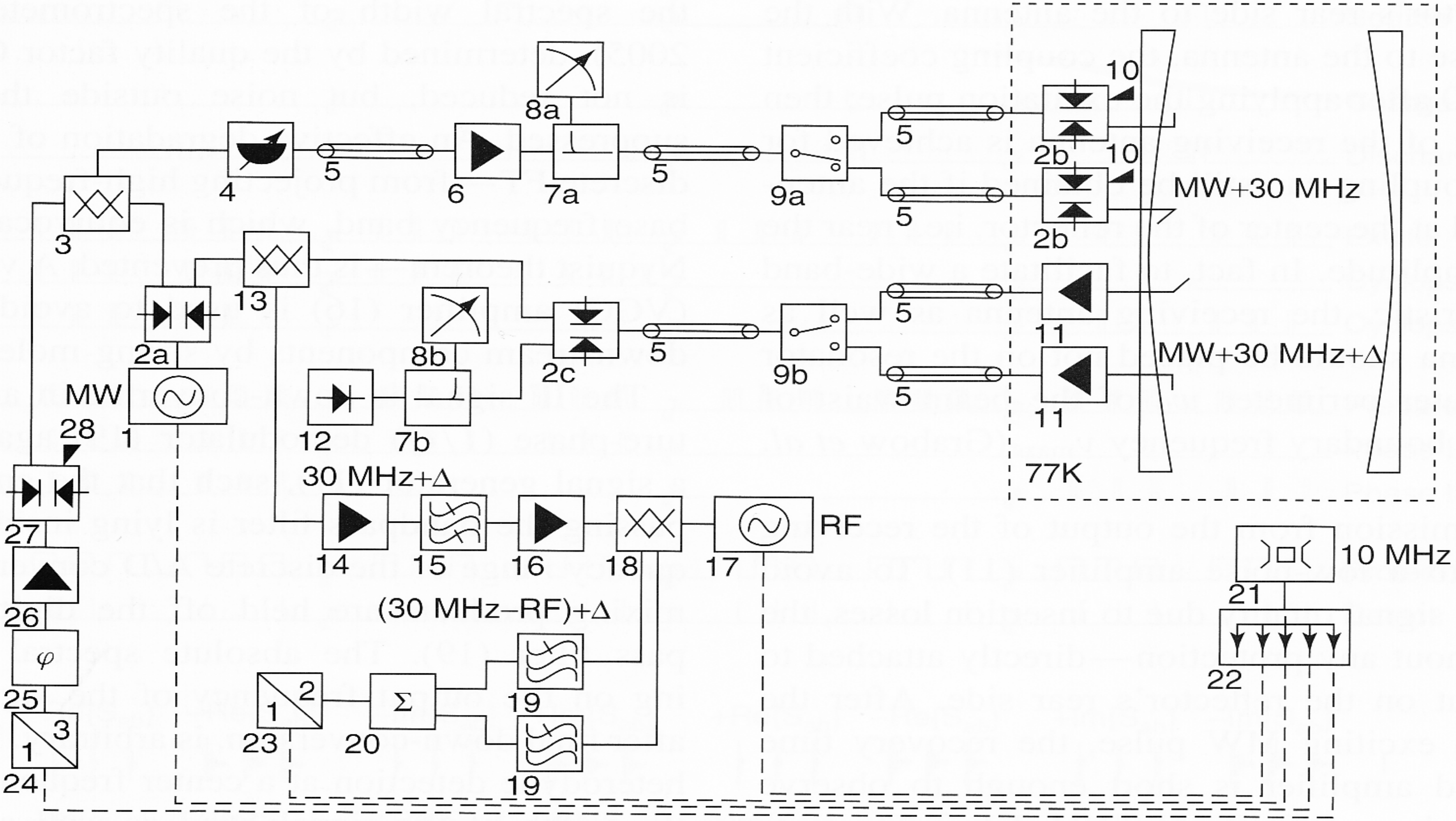

Polarization Grid
Sample Cell
Roof Mirror
Amplifier
Multiplier
Lenses
Pyrolysis
Cooled Precursor
Vacuum Pump
Synthesizer
Detector
Bias
Rubidium Standard
Computer
Digital Lock-in Amplifier
Oscilloscope
GPS

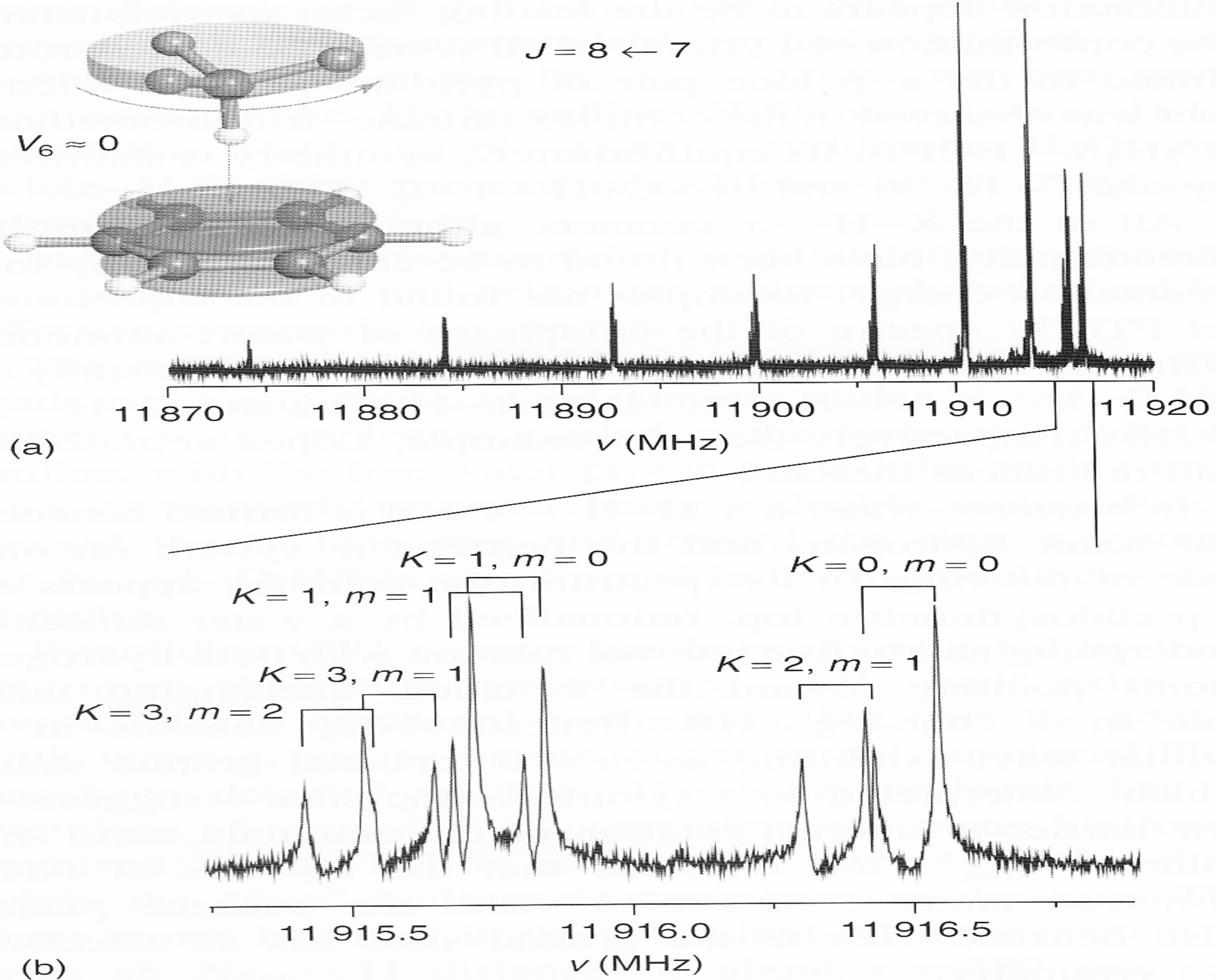

FSO_3
$5{,}0\times10^{-4}$
$4{,}0\times10^{-4}$
$3{,}0\times10^{-4}$
$2{,}0\times10^{-4}$
$1{,}0\times10^{-4}$
0,0
$-1{,}0\times10^{-4}$
$-2{,}0\times10^{-4}$
$-3{,}0\times10^{-4}$
intenzita [a.u.]
259740
259770
259800
259830
259860
259890
259920
259950
259980
frekvence [MHz]

Emission setup



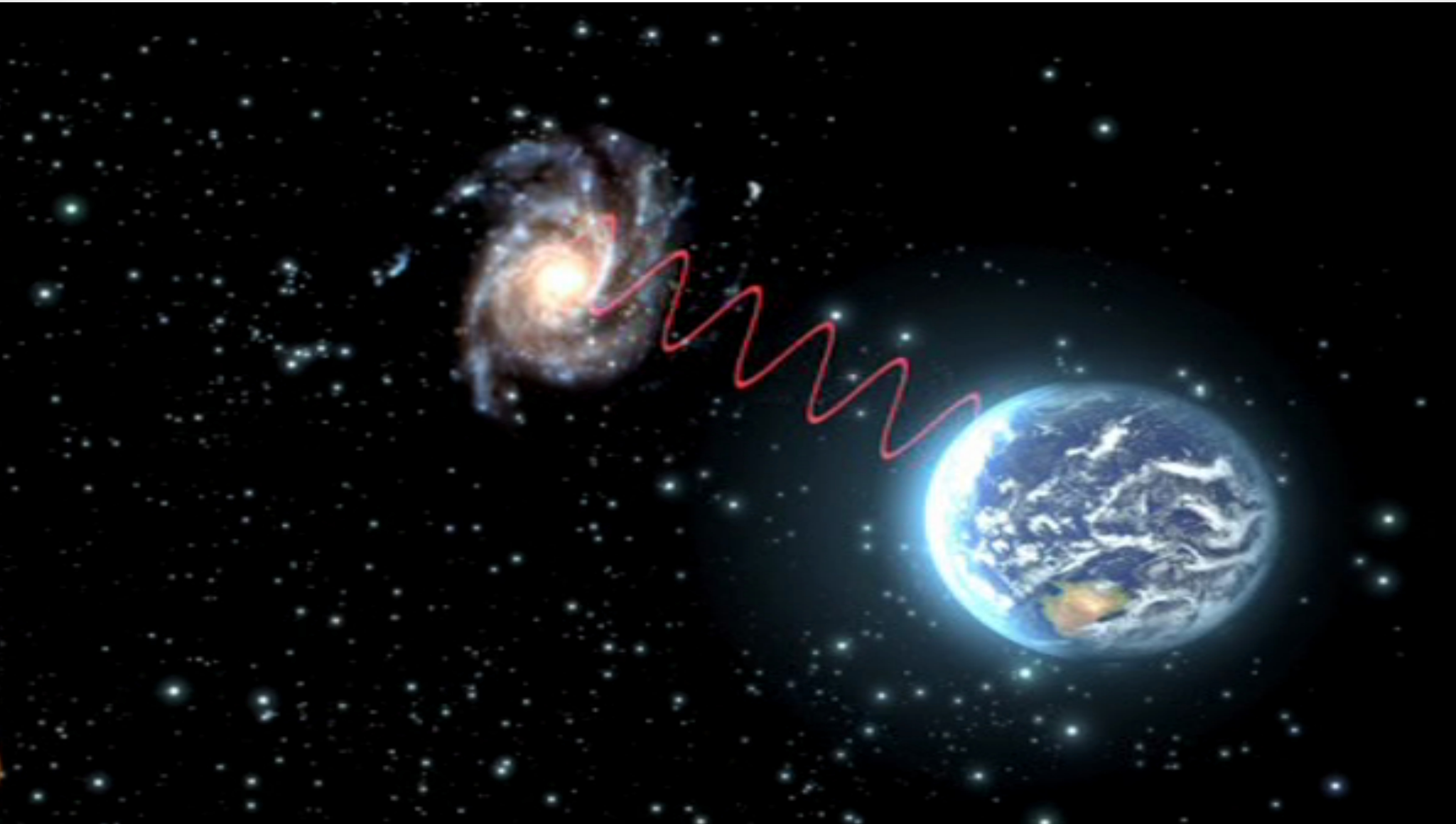
Emission setup

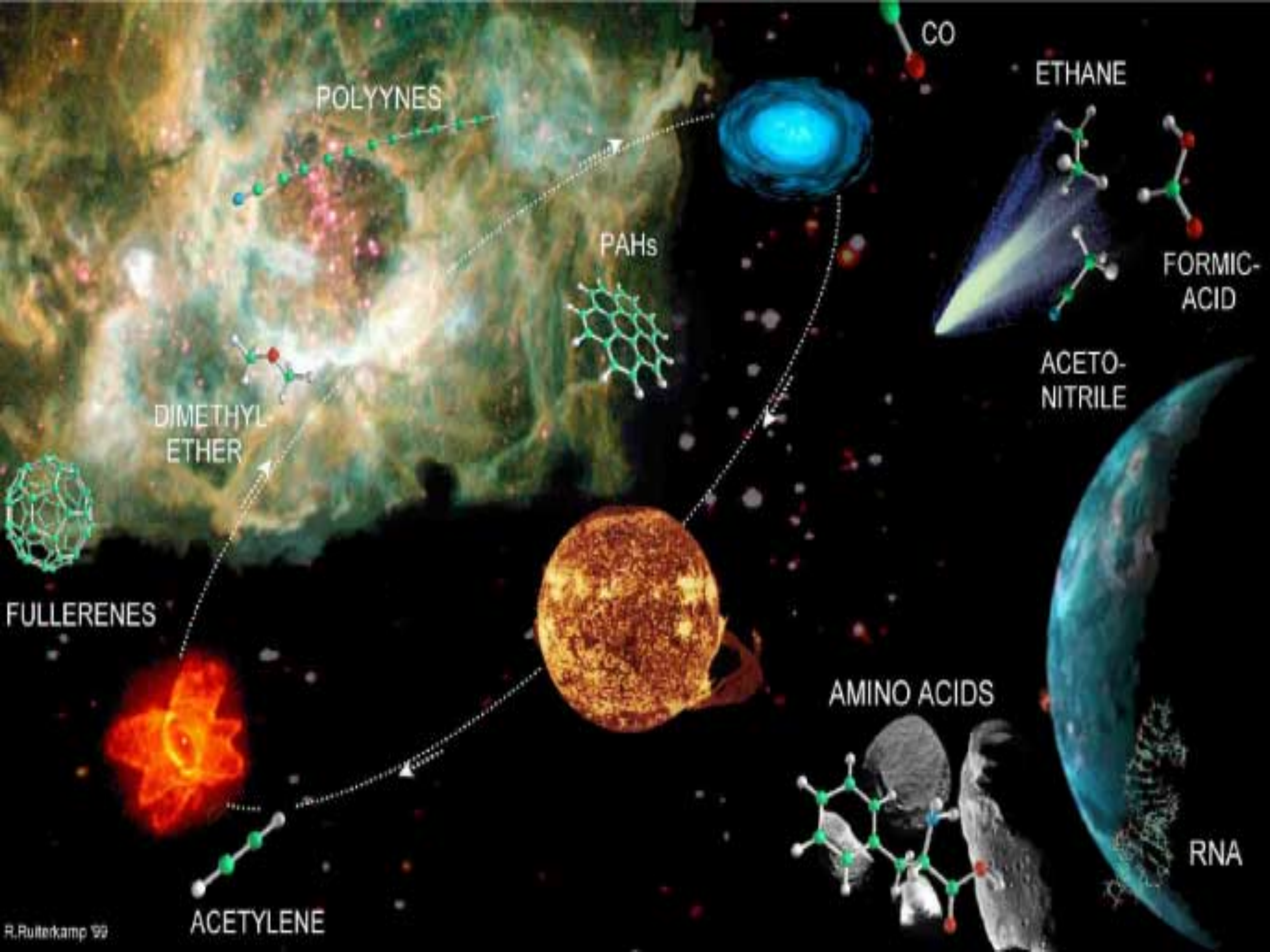




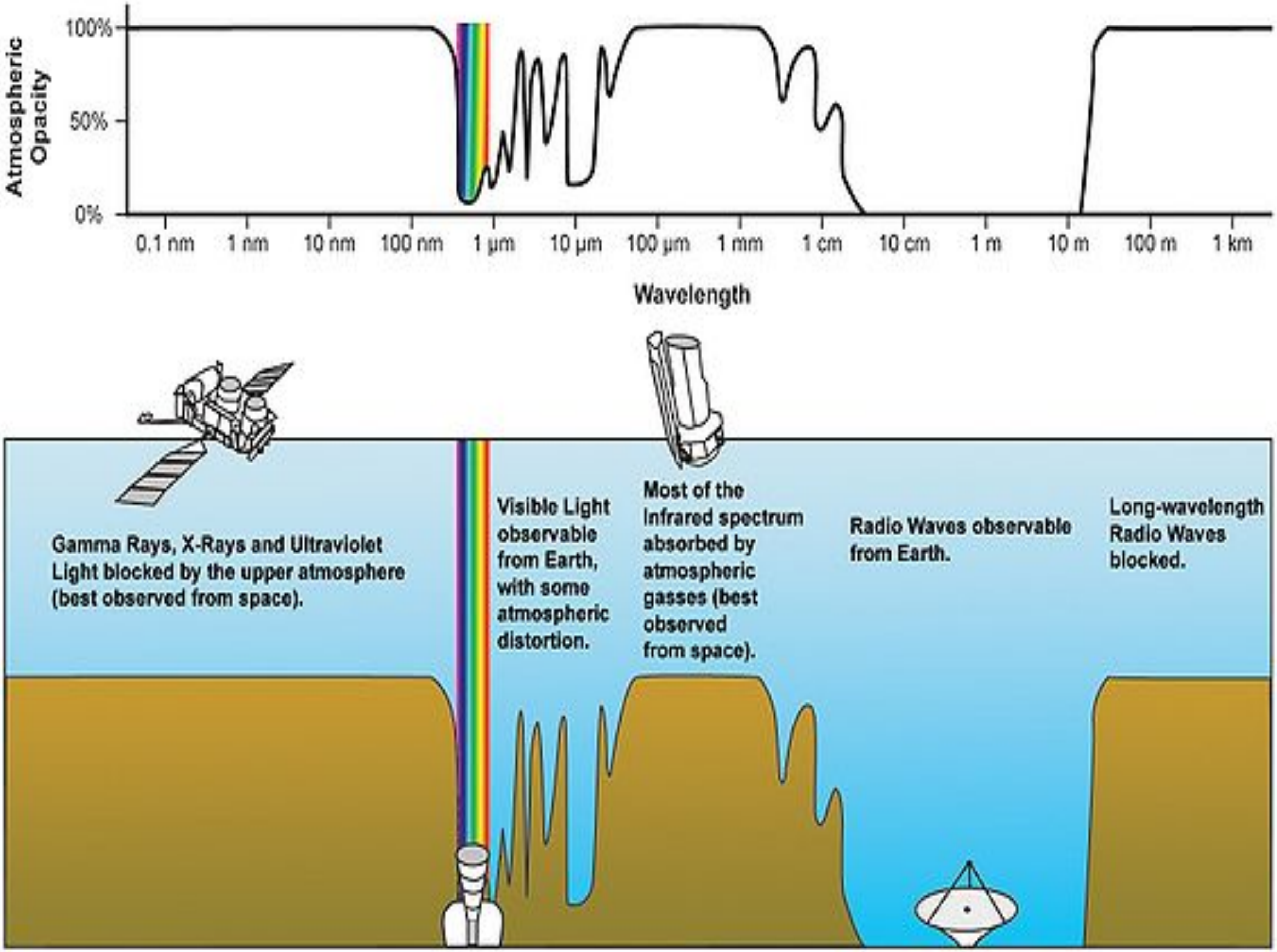
$J = 8 \leftarrow 7$
$V_6 \approx 0$
11870
11880
11890
11900
11910
11920
(a)
ν (MHz)
$K = 1, m = 0$
$K = 1, m = 1$
$K = 0, m = 0$
$K = 3, m = 1$
$K = 2, m = 1$
$K = 3, m = 2$
11 915.5
11 916.0
11 916.5
(b)
ν (MHz)

From Lab to Space





R.Ruiterkamp '99



Gamma Rays, X-Rays and Ultraviolet Light blocked by the upper atmosphere (best observed from space).

Visible Light observable from Earth, with some atmospheric distortion.

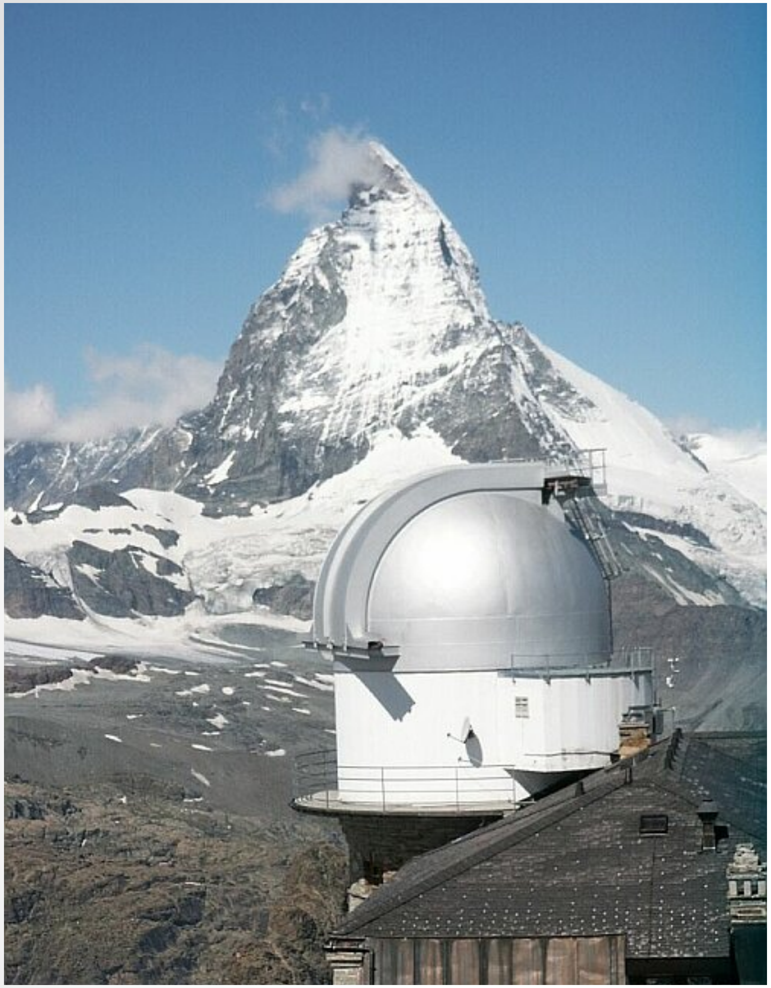
Most of the infrared spectrum absorbed by atmospheric gasses (best observed from space).

Radio Waves observable from Earth.

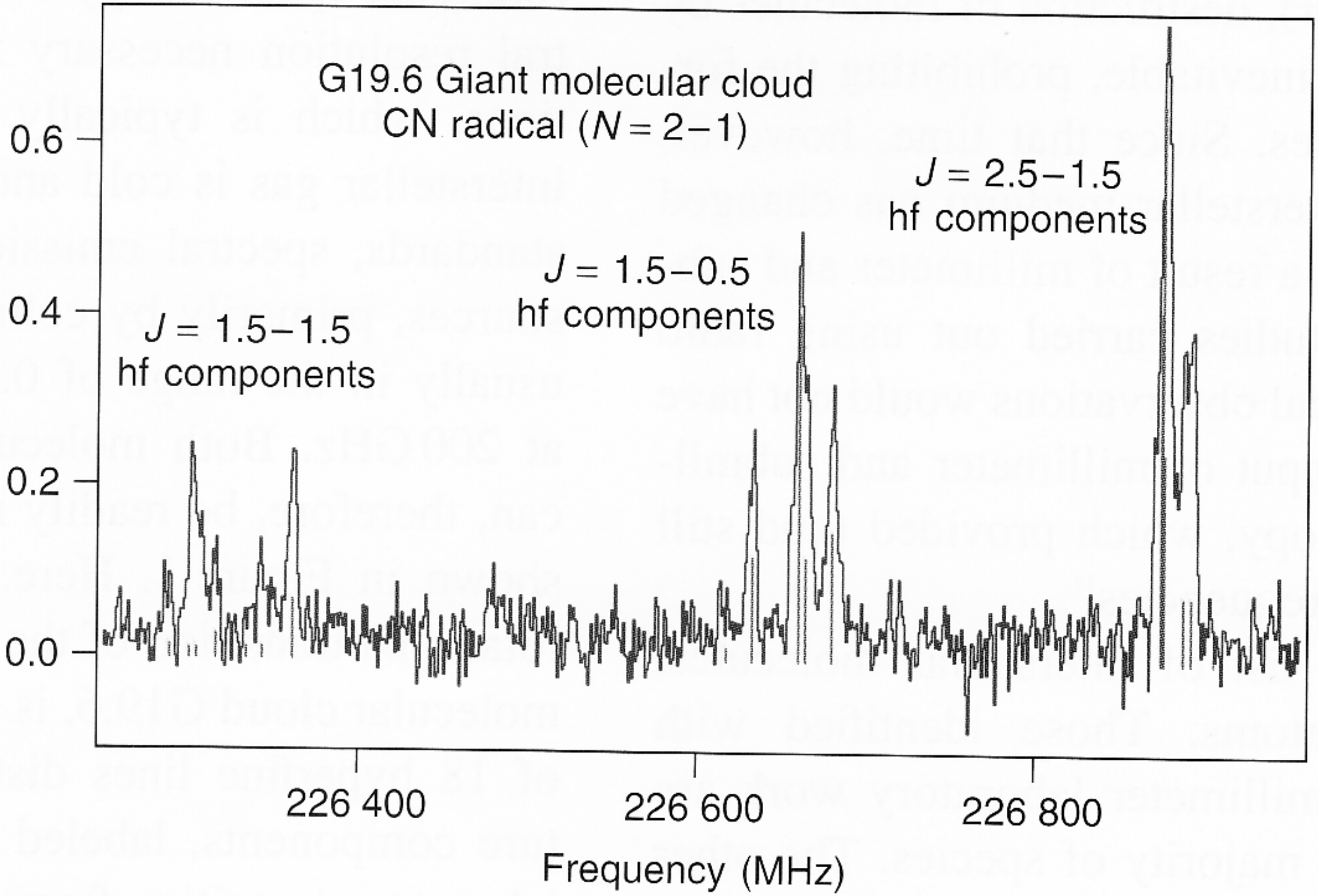
Long-wavelength Radio Waves blocked.

Microwave–radiofrequency 100m telescope -spectrometr, Effelsberg , Bonn, BRD

MW 3m-telescope in Zermatt (Gornergrat 3180m).



IRAM - 30m
Granada


G19.6 Giant molecular cloud
CN radical ($N = 2-1$)
$J = 1.5-1.5$ hf components
$J = 1.5-0.5$ hf components
$J = 2.5-1.5$ hf components
0.6
0.4
0.2
0.0
T_R^* (K)
226 400
226 600
226 800
Frequency (MHz)

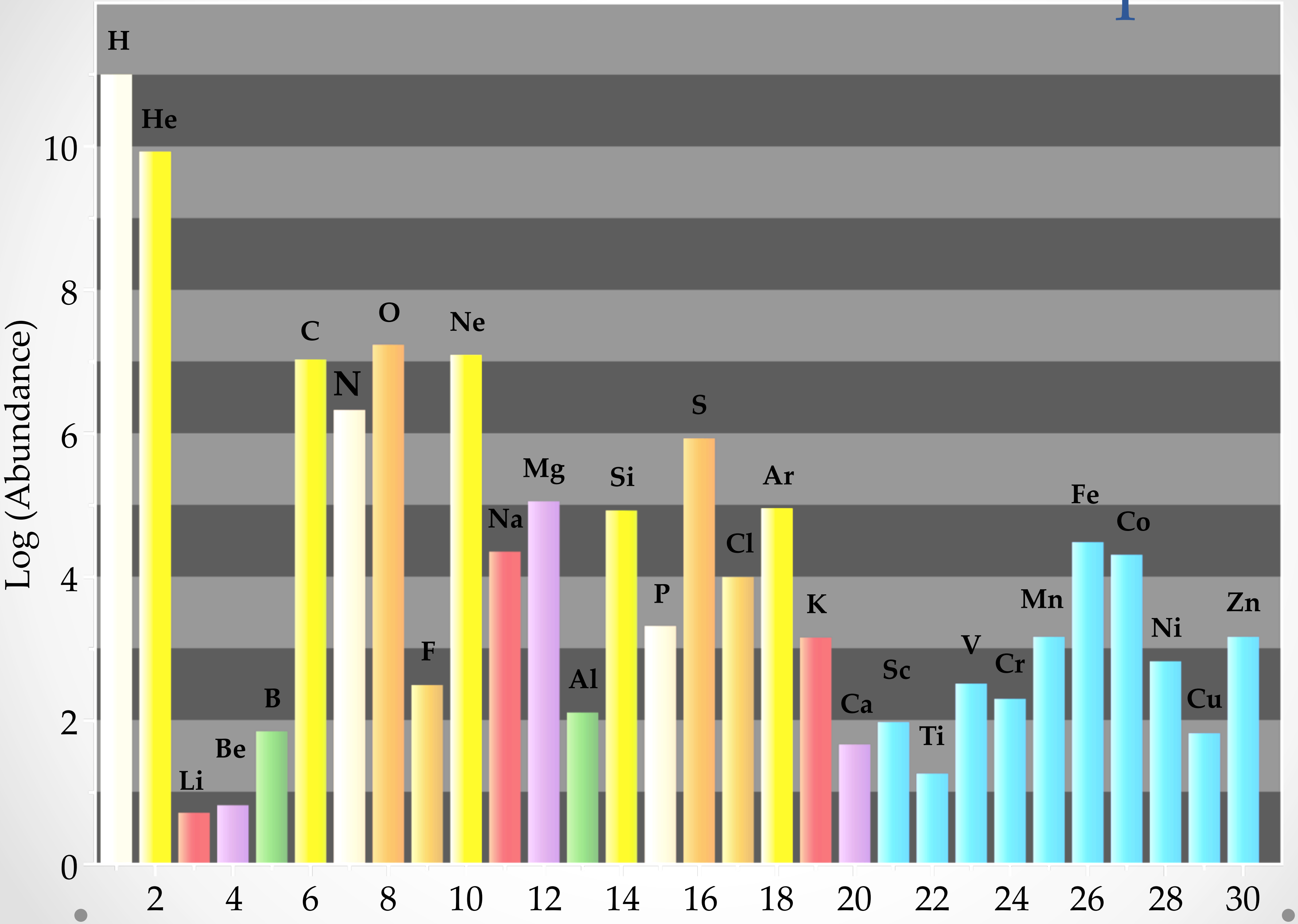
Planck, mw telescope

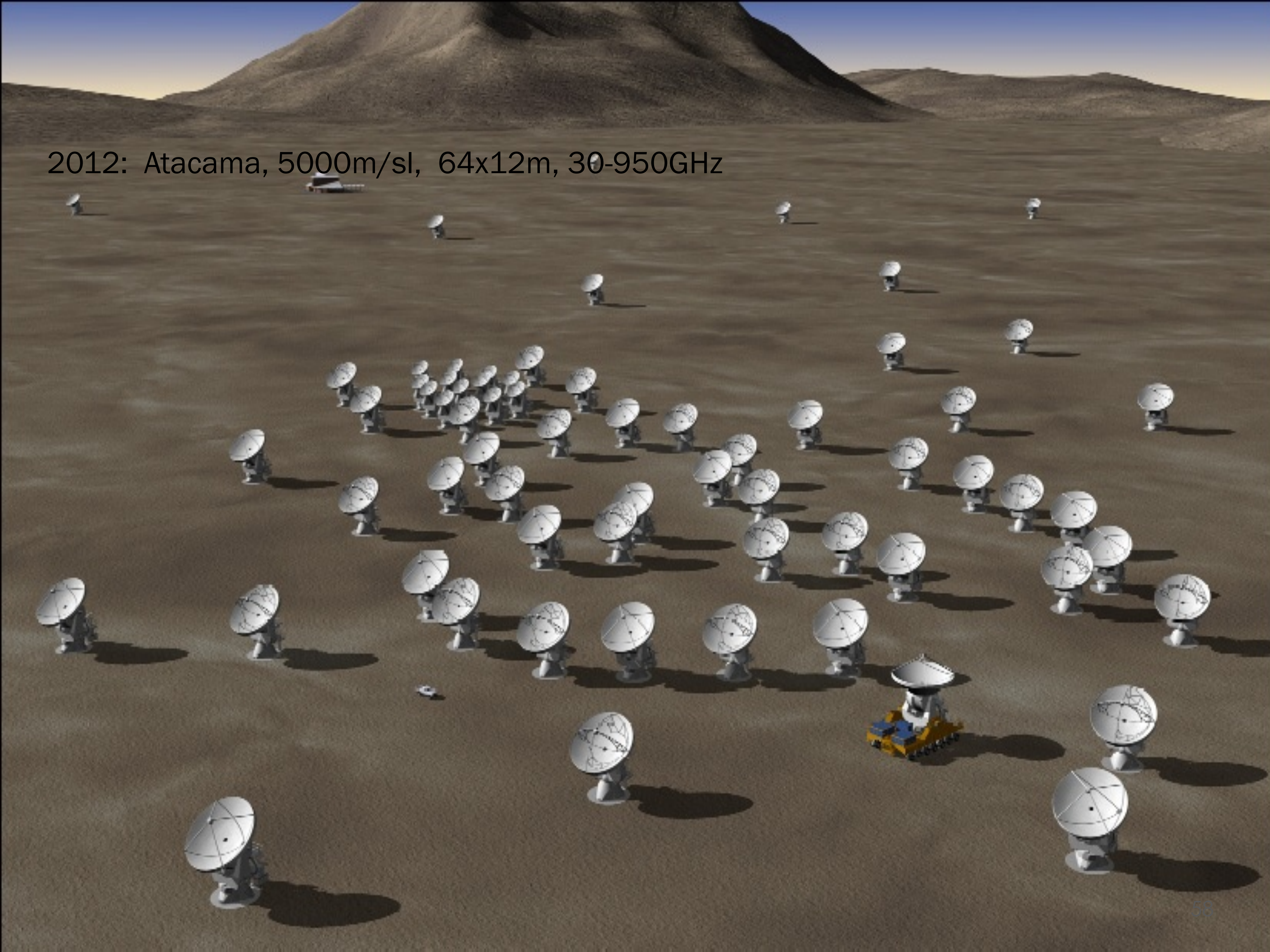
Frequencies: 0.45 – 5 THz, Herschel , mw /ir telescope/spectometer

Molecules in the ISM or Circumstellar Shells

2 Atoms		3 Atoms		4 Atoms	5 Atoms	6 Atoms	7 Atoms	8 Atoms	9 Atoms
H_2	NS	C_3^*	MgNC	c-C_3H	C_4Si	C_5H	C_6H	CH_3C_3N	CH_3C_4H
AlF	NaCl	C_2H	N_2H^+	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN
AlCl	OH	C_2O	N_2O	C_3N	C_4Si	$C_2H_4^*$	CH_3C_2H	CH_3COOH	$(CH_3)_2O$
C_2^{**}	PN	C_2S	NaCN	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH
CH	SO	CH_2	c-SiC_2	C_3S	c-C_3H_2	CH_3NC	$HCOCH_3$	H_2C_6	HC_7N
CH+	SO^+	HCN	SO_2	$C_2H_2^*$	CH_2CN	CH_3OH	NH_2CH_3	CH_2OHCHO	C_8H
CN	SiN	HCO	c-SiC_2	CH_2D^+ ?	CH_4^*	CH_3SH	c-C_2H_4O	l-HC_6H^* (?)	CH_3N
CO	SiO	HCO^+	CO_2^*	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	
CSi	SiS	HCS+	NH_2	$HCNH^+$	HC_2NC	HC_2CHO			
CP	CS	HOC^+	H_3^{+*}	HNCO	HCOOH	NH_2CHO			
CSi	HF	H_2O	H_2D^+	HNCS	H_2CNH	C_5N			
HCl	SH*	H_2S	HD_2^+	$HOCO^+$	H_2C_2O	l-HC_4H (?)			
KCl	HD	HNC	SiCN	H_2CO	H_2NCN	l-HC_4N			
NH	FeO ?	HNO	SiNC	H_2CN	HNC_3	**10 Atoms**	**11 Atoms**	**12 Atoms**	**13 Atoms**
NO	O_2 ?	MgCN	AlNC	H_2CS	SiH_4^*	CH_3C_5N (?)	HC_9N	$C_6H_6^*$ (?)	$HC_{11}N$
CF^+				c-SiC_3	H_2COH^+	$(CH_3)_2CO$	CH_3C_6H	$C_2H_5OCH_3$ (?)	
				NH_3		$(CH_2OH)_2$?			
				c-SiC_3		H_2NCH_2COOH			
				CH_3^*		CH_3CH_2CHO			

Abundance of Elements in Space

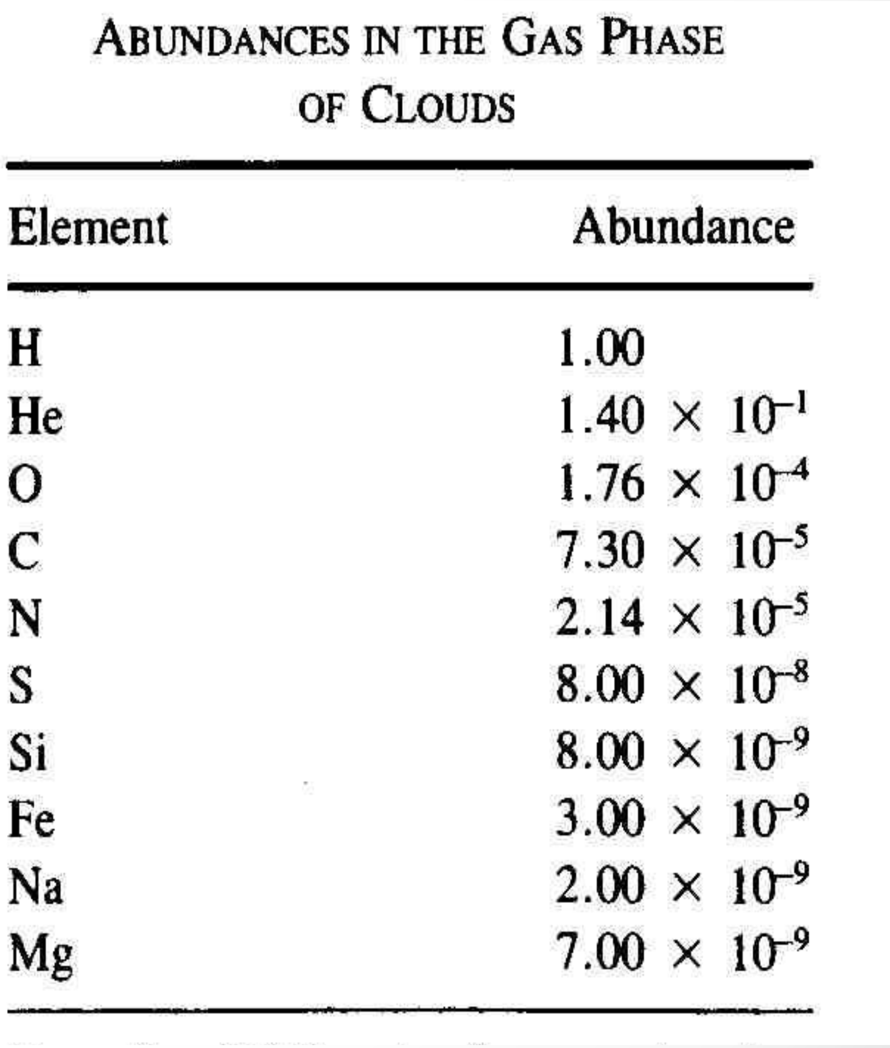




2012: Atacama, 5000m/sl, 64x12m, 30-950GHz

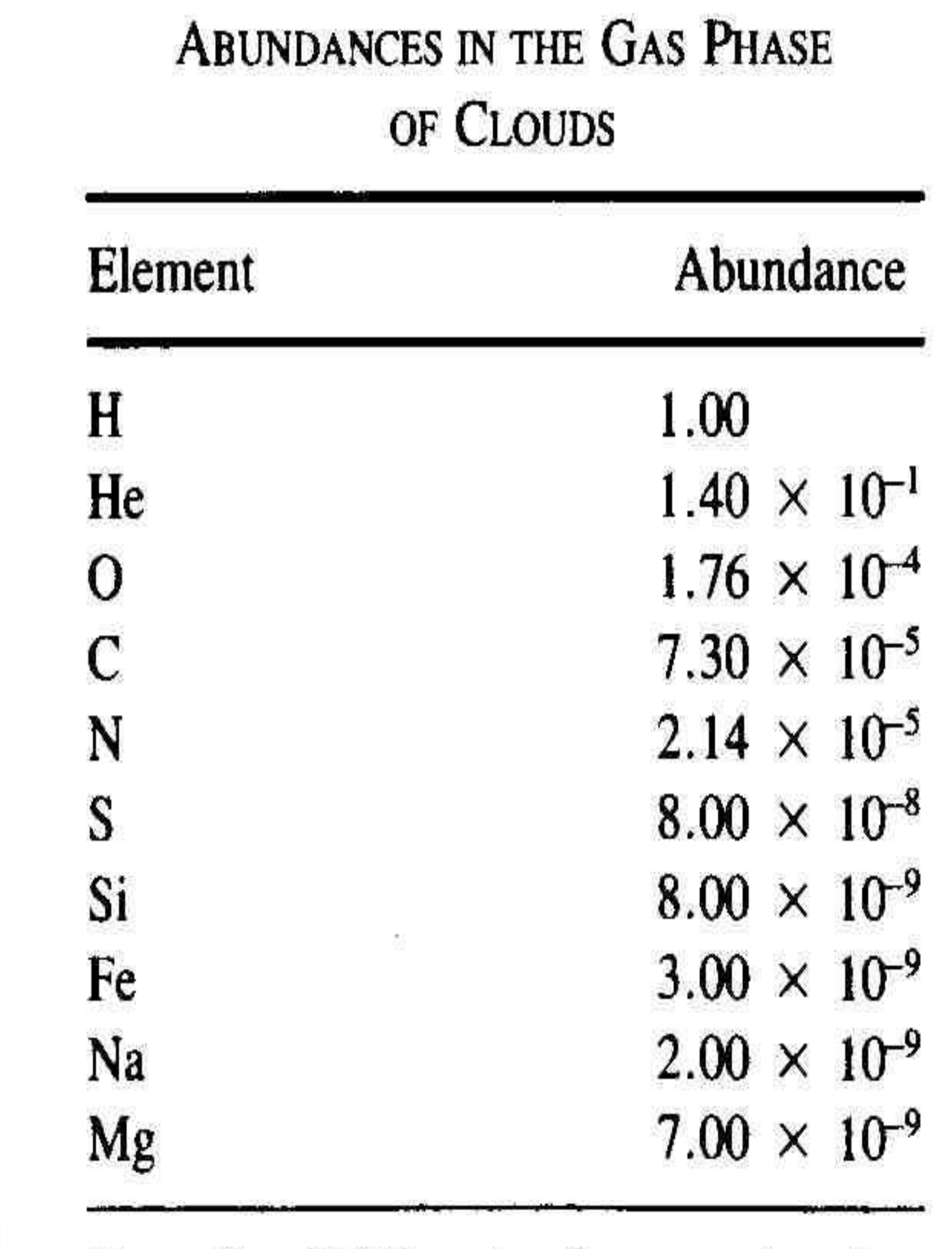
Ions in Space

CH^+	C_4H^-
CO^+	C_6H^-
SO^+	C_8H^-
H_3^+	C_3N^-
HCO^+	
HOC^+	
HN_2^+	
HCS^+	
H_3O^+	
$HCNH^+$	
$HOCO^+$	
HC_3NH^+	



ABUNDANCES IN THE GAS PHASE OF CLOUDS

Element	Abundance
H	1.00
He	1.40×10^{-1}
O	1.76×10^{-4}
C	7.30×10^{-5}
N	2.14×10^{-5}
S	8.00×10^{-8}
Si	8.00×10^{-9}
Fe	3.00×10^{-9}
Na	2.00×10^{-9}
Mg	7.00×10^{-9}



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