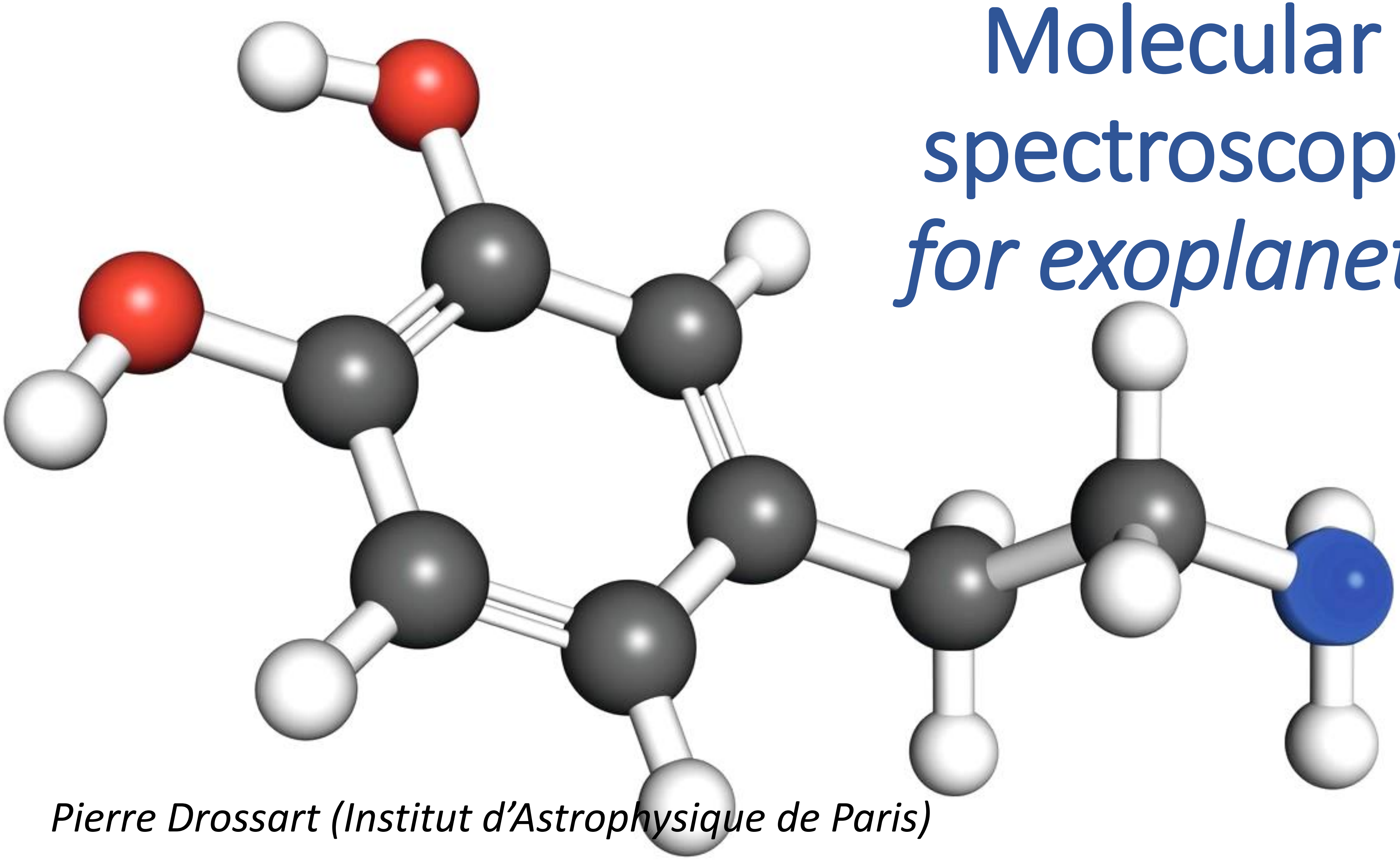

Molecular spectroscopy *for exoplanets*

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& Isabelle Kleiner (LISA, Univ. Créteil)

Credits

- Isabelle Kleiner, Les Houches course (Ariel school 2022)
- Herzberg : Infrared and Raman spectra of polyatomic molecules
- Spectral line shapes course : Professor Ronald K. Hanson https://cefrc.princeton.edu/sites/g/files/toruqf1071/files/documents/Lecture%20Notes%20-%20Hanson.pdf
- Exomol : Tennyson et al, JQSRT 2020 (The 2020 release of the ExoMol database: Molecular line lists for exoplanet and other hot atmospheres)
- The spectroscopic community : I. Kleiner, M. Rey, V. Boudon, J. Tennyson, V. Tyuterev,… – *(Paris, Reims, Dijon, Rennes, London, Omsk)*

Topics in Molecular spectroscopy

1. **Concepts : spectroscopy and the rotation and vibration of moleculess**
2. **Diatomic molecules**
   1. **The rigid rotator in quantum mechanics**
   2. **The harmonic oscillator in quantum mechanics**
3. **Polyatomic molecules :**
   1. **Linear molecules : CO2**
   2. **Spherical tops : CH4**
   3. **Symmetric tops : NH3**
   4. **Asymmetric tops : H2O**
4. **Thermodynamics**
   1. **Population of vibro-rotational levels**
   2. **Partition functions**
5. **Line widths and absorption coefficients**
   1. **Lorentz shape**
   2. **Doppler shape**
   3. **Voigt shape**
6. **Some special effects**
   1. **Far wings**
   2. **Collision induced absorption**
7. **Data bases**

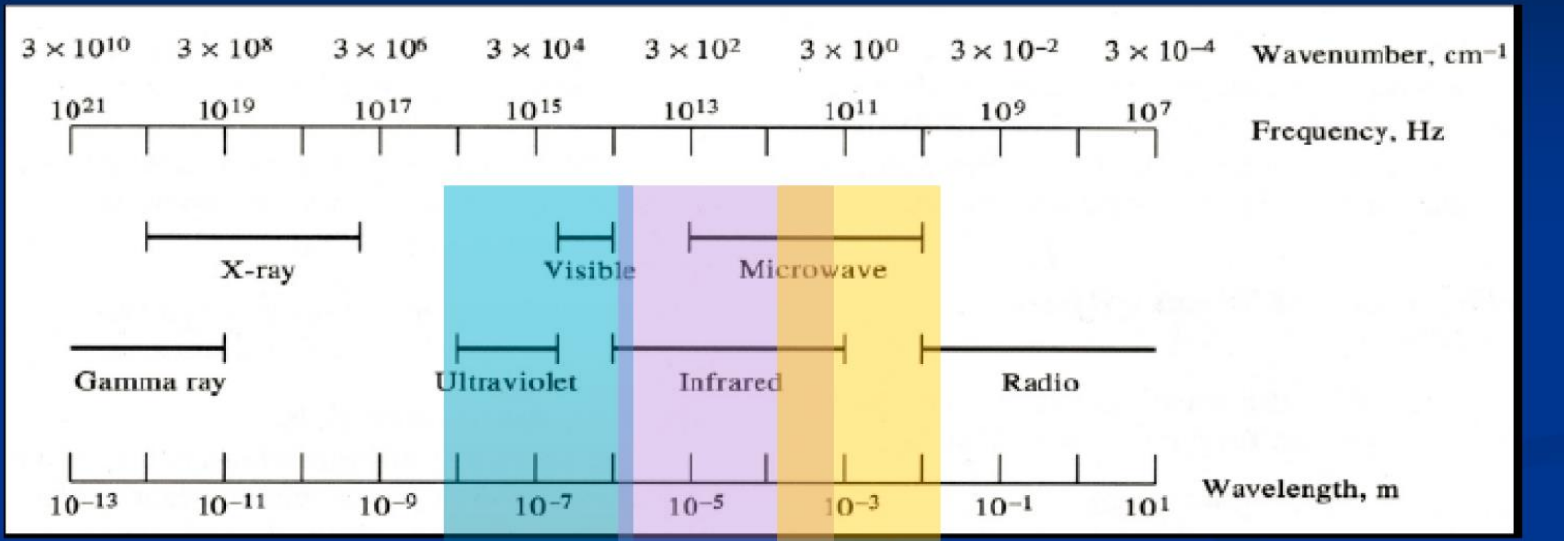
Matter – radiation models for exoplanets

A large part of astrophysics models rely on matter – radiation interaction. In planetary atmospheres, one encounters various phenomena:

- Scattering phenomena (molecular => Rayleigh or particulate => Mie or similar model)
- Molecule-photon interaction in thermal emission or stellar radiation transfer

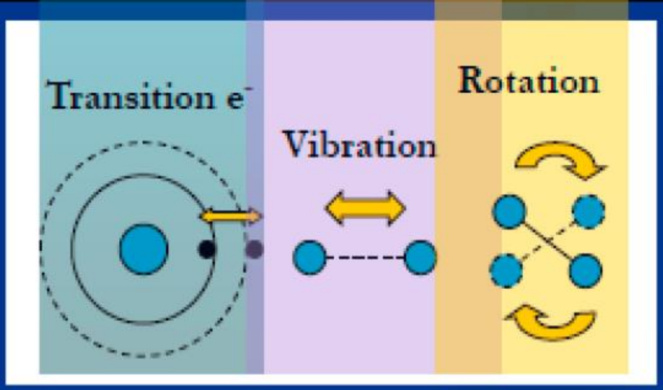
Here, we explore the molecular models : quantum mechanics is at the base of the description of molecule states. For radiation/molecule model, radiative transfer approximation will treat the light in a classical matter – full quantum radiation/molecule models are usually not necessary => Quantum mechanics is usually limited to the matter domain.

Spectral range and molecular motions



Interaction

Rayonnement-Matière



The Born-Oppenheimer approximation

Due to the large difference in the masses of the nuclei and of the electron, the Born-Oppenheimer approximation stipules that the electronic part of the wave function can be decoupled from the nucleus part with q_i the electronic and Q_i the nuclear coordinates

$$\Psi(q_i, Q_i) = \Psi_{el}(q_i; Q_i)\Psi_N(Q_i)$$

The total energy of the molecule is the sum of

- An electronic part
- A vibrational part
- A rotational part

Which are solved independently

Electronic structure is solved by “ freezing ” the nuclei at fixed positions and by resolving electronic Schrödinger equation :

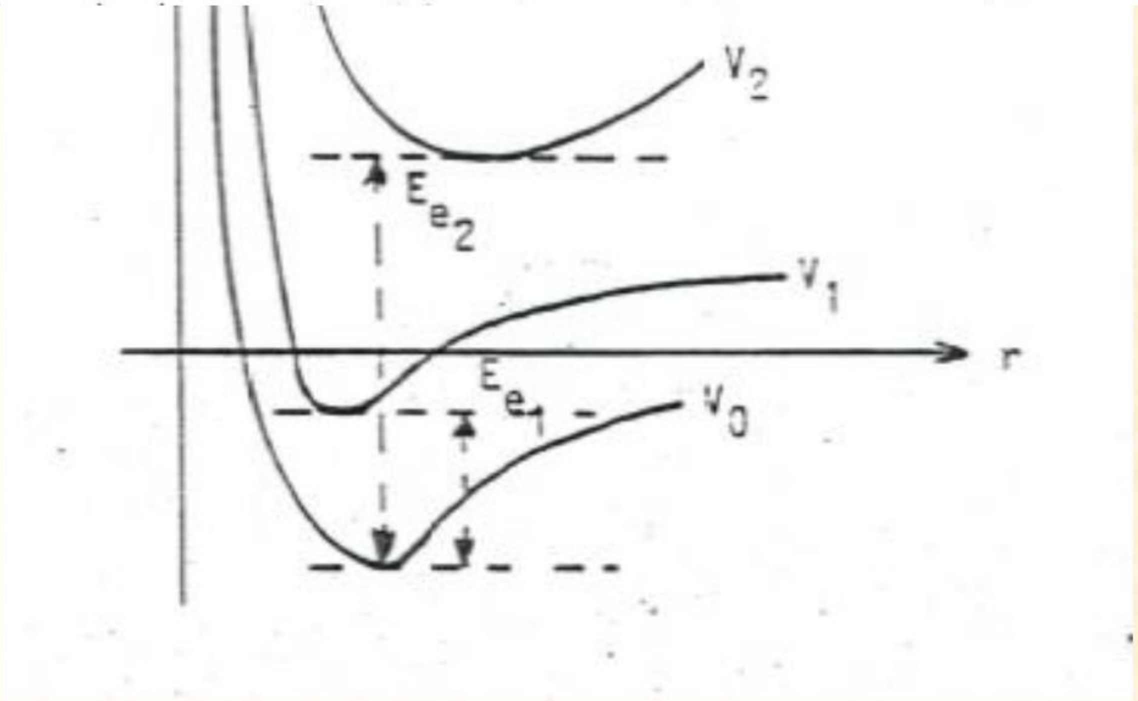
$$H_{el}\,\Psi_{el} = E_{el}\,\Psi_{el}$$

In which $H_{el} = T_e + V_{ee} + V_{ne}$

If all nuclei are fixed in space, then the coulomb energy associated with the repulsion of two nuclei (V_{nn}) is only a number which can be added to the electronic energy

$$U = E_{el} + V_{nn} \tag{7}$$

$$E^{el} = E^{el}(\underbrace{\vec{R}_1, \vec{R}_2, \dots}_{\text{géométrie nucléaire}})$$



For a diatomic molecule

Credit : I. Kleiner, Les Houches 2022

If the potential energy curves are well separated

$E \sim E_e + E_v + E_r$

Electron Motions

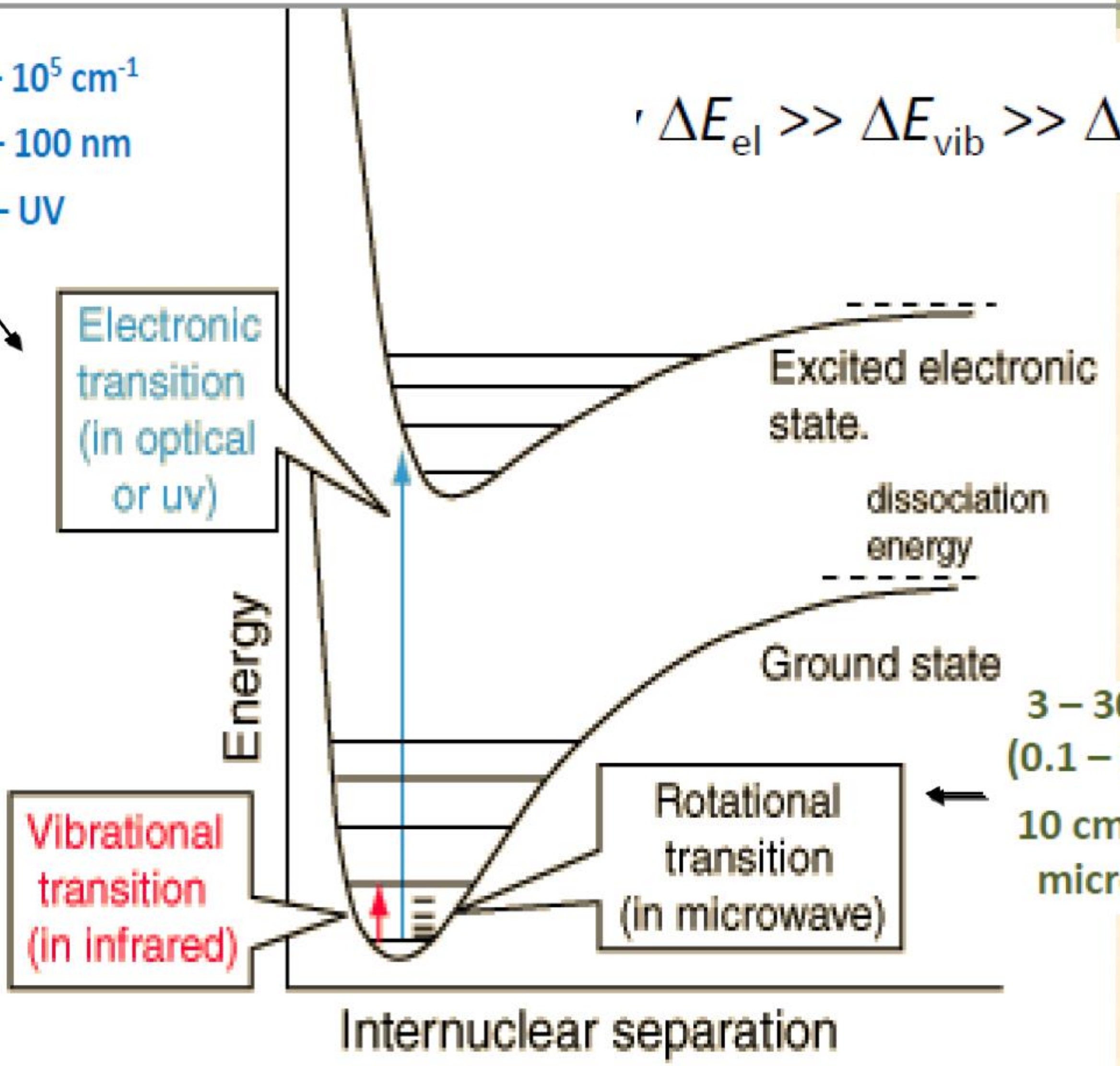
Nuclei motions

$\Delta E \approx 2 \times 10^4 - 10^5\ \text{cm}^{-1}$

Transitions at $\lambda \approx$ 500 – 100 nm

Vis – UV

$\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$



$10^2 - 5 \times 10^3\ \text{cm}^{-1}$

100 µm – 2 µm

infrared

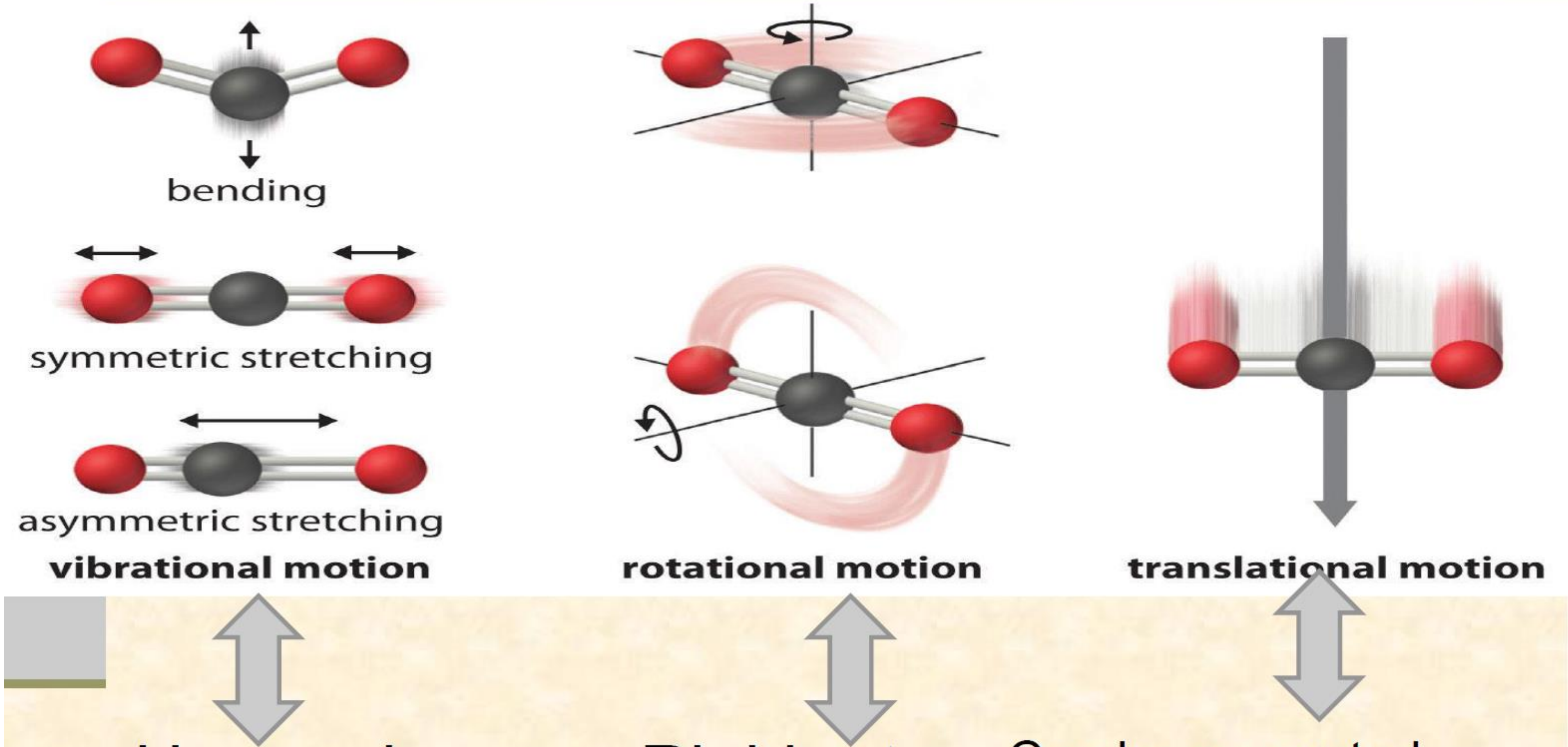
3 – 300 GHz

($0.1 - 10\ \text{cm}^{-1}$)

10 cm – 1 mm

microwave

3 types of nuclear motions

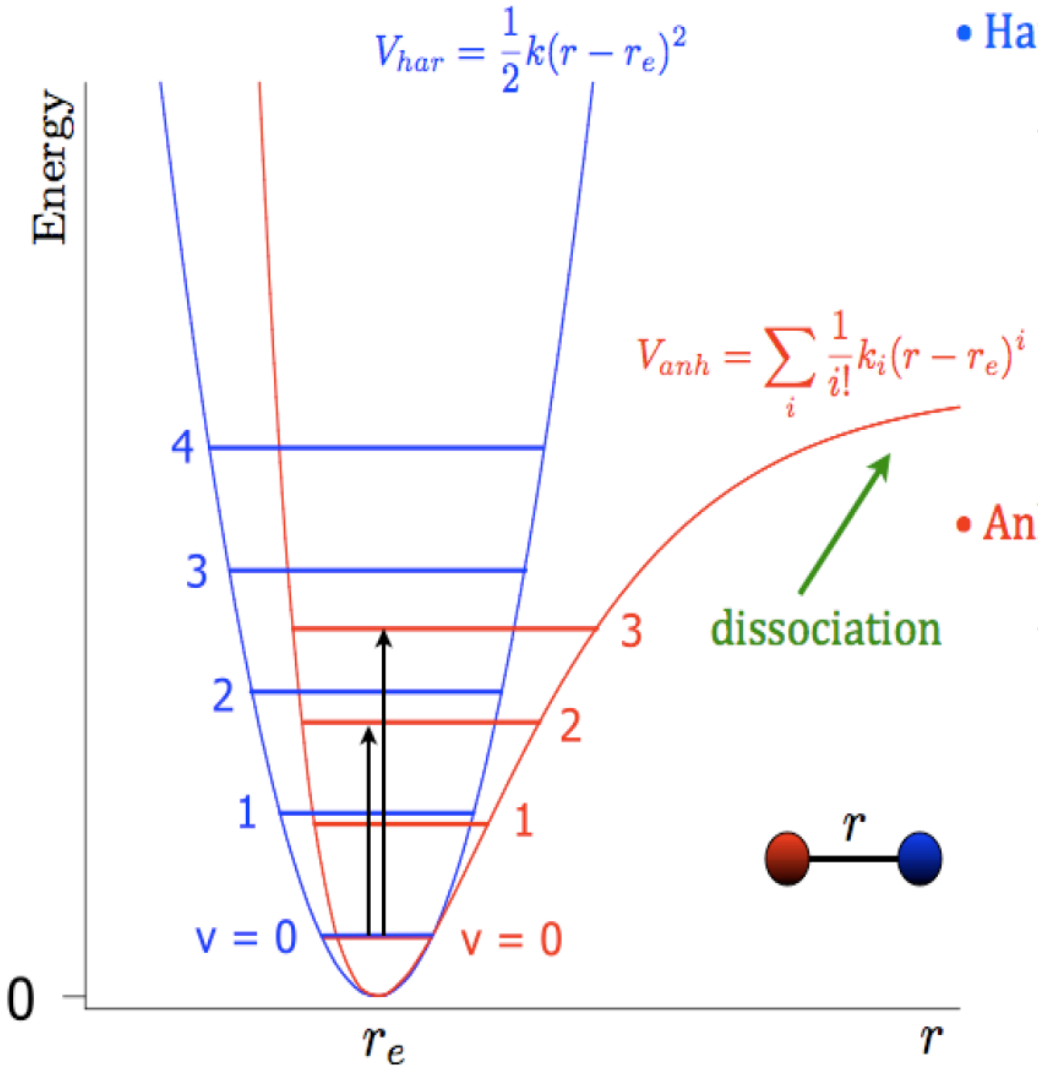


Harmonic Oscillator model

Rigid rotor model

Can be separated
From the other motions
Energy = constante

Vibration: Harmonic and anharmonic oscillators



- **Harmonic oscillator :**

$$E_v = \omega_e(v + 1/2)$$

$$k = \frac{d^2V}{dr^2}$$

$$\omega_e = \frac{1}{2\pi c}\sqrt{k/\mu}$$

Reduced mass : $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

- **Anharmonic oscillator :**

$$E_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots$$

$$\omega_e x_e = -\frac{5\,k_3^2}{48\,\omega_e} + \frac{k_4}{16}$$

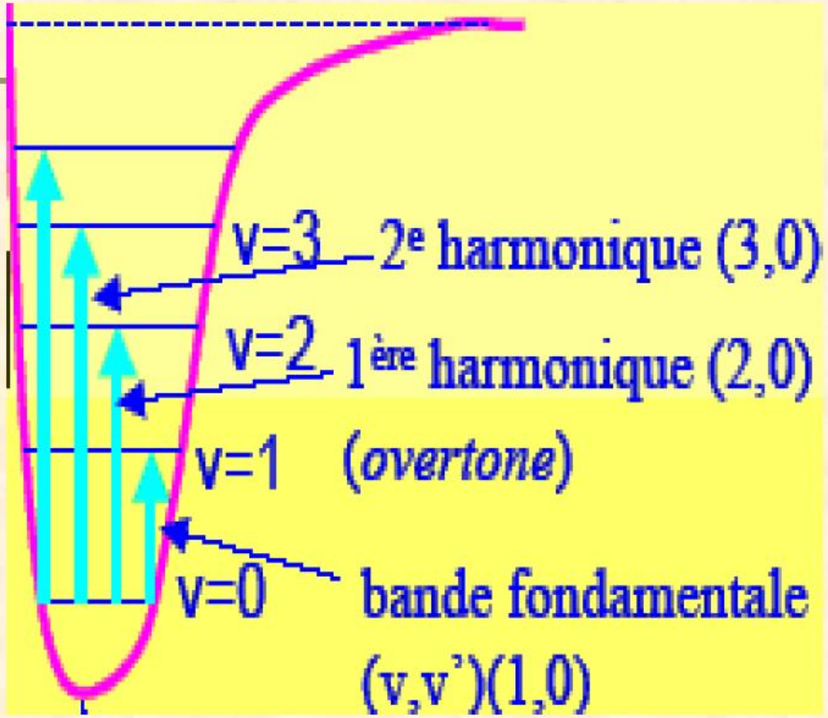
Force constants : $k_n = \frac{d^nV}{dr^n}$

Courtesy of

J. Vander Auwera

On the IR spectrum, weobserve :

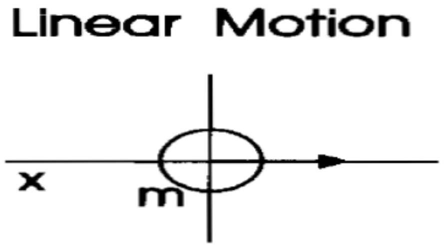
*** Fundamental Bands:**
vibrations v=0→ v=1

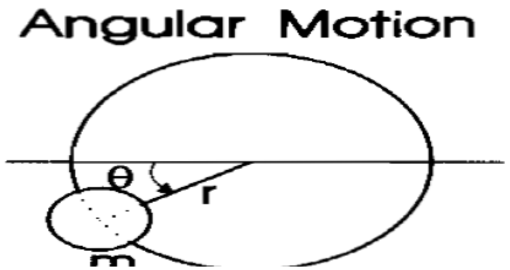


* Overtone bands:
multiples of fundamental bands (Ex. 2v)

- Combination bands ($v_1 + v_2$ for example) : simultaneous excitation of several fundamental vibrations
- Hot bands: initial levels are not v = 0

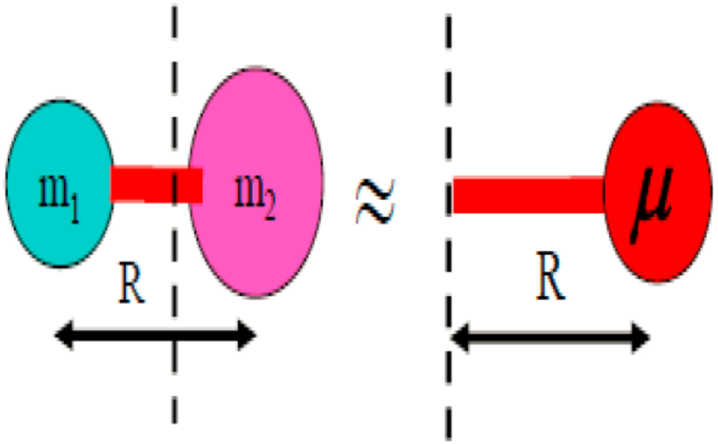
Moments of inertia, rotational angular momentum





Linear Motion		Angular Motion
	Position	
Distance, x		Angle, θ
	Velocity	
Velocity, $v = \dot{x} = dx/dt$		Angular velocity, $\omega = \dot{\theta} = d\theta/dt$
	Mass	
Mass, m		Moment of inertia, $I = mr^2$
	Momentum	
Linear momentum, $p = mv$		Angular momentum, $J = I\omega$
	Kinetic energy	
$E_k = \frac{1}{2}mv^2 = p^2/2m$		$E_k = \frac{1}{2}I\omega^2 = J^2/2I$

Diatomic molecule

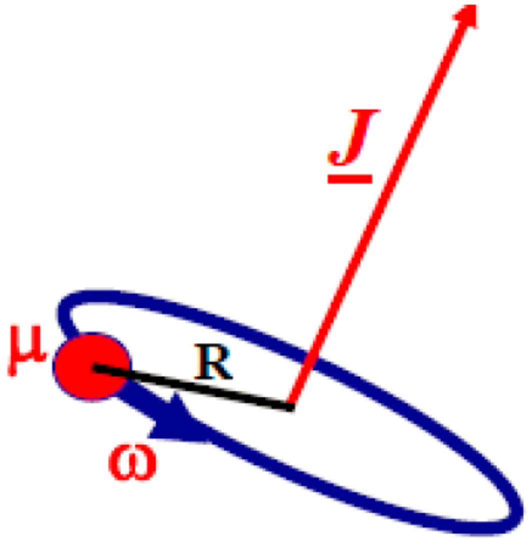


$$I = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 = \mu R^2$$

Where the reduced mass, $\boxed{\mu = \frac{m_1 m_2}{(m_1 + m_2)}}$

Definition: The moment of inertia I of

centre of mass is given by; $\boxed{I = \sum_i m_i r_i^2}$ where m_i is the mass of the ith particle and r_i is its perpendicular distance from the axis



The angular momentum, $\boxed{J = I\omega}$ (c.f. $p = mv$)

The rotational kinetic energy, $\boxed{E = J^2/2I = ½\, I\omega^2}$

(c.f. $E = p^2/2m = ½mv^2$)

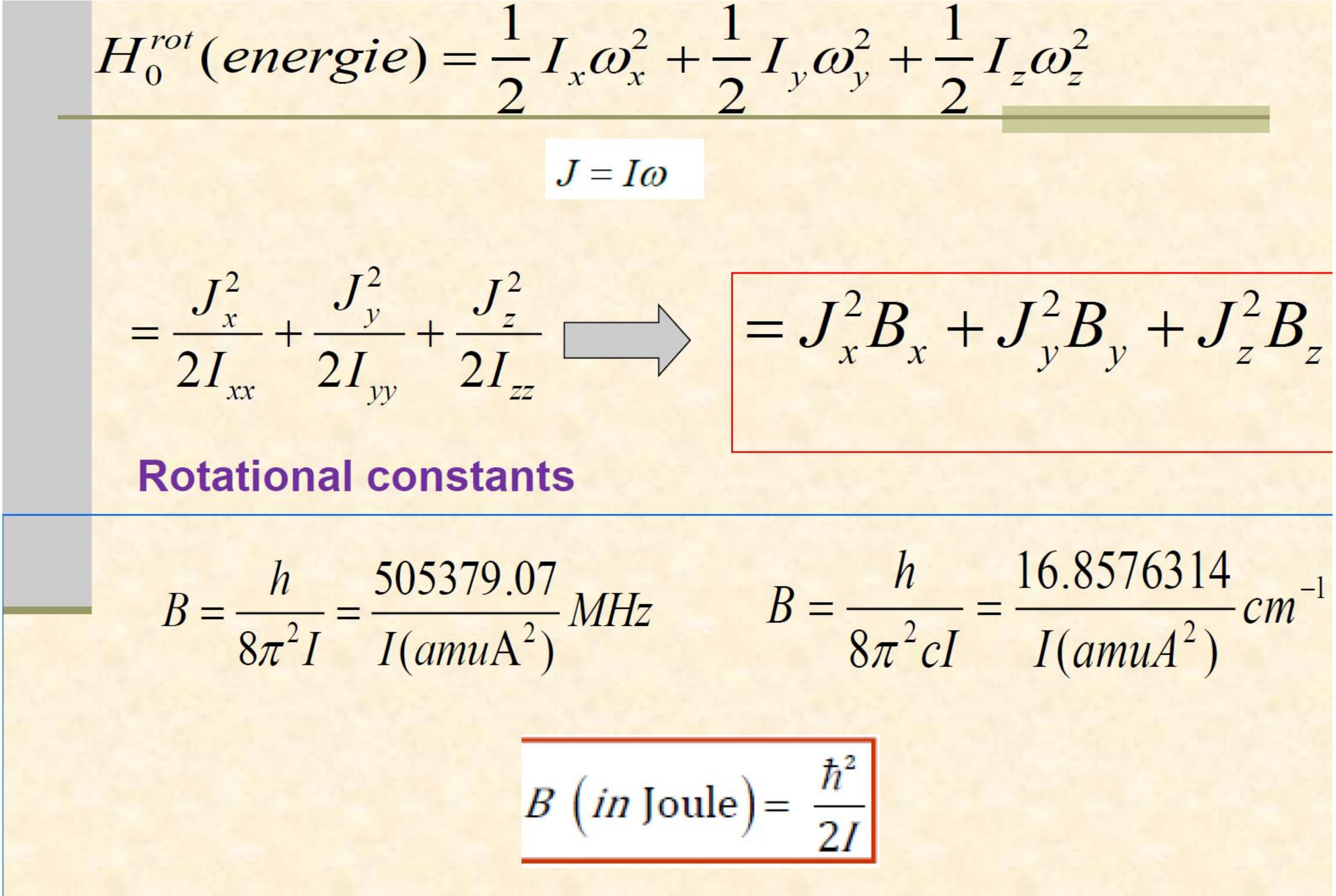
From diatomics to polyatomic molecules

$$E = J^2/2I = \tfrac{1}{2} I \omega^2 \longrightarrow \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

$$J = I\omega$$

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} I_{xx} I_{xy} I_{xz} \\ I_{yx} I_{yy} I_{yz} \\ I_{zx} I_{zy} I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

Rotational energies: how to calculate them ?



$$H_0^{rot}(energie) = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

$$J = I\omega$$

$$= \frac{J_x^2}{2I_{xx}} + \frac{J_y^2}{2I_{yy}} + \frac{J_z^2}{2I_{zz}} \Rightarrow \boxed{= J_x^2 B_x + J_y^2 B_y + J_z^2 B_z}$$

Rotational constants

$$B = \frac{h}{8\pi^2 I} = \frac{505379.07}{I(amu\mathrm{A}^2)} MHz \qquad B = \frac{h}{8\pi^2 cI} = \frac{16.8576314}{I(amuA^2)} cm^{-1}$$

$$\boxed{B\ (in\ \mathrm{Joule}) = \frac{\hbar^2}{2I}}$$

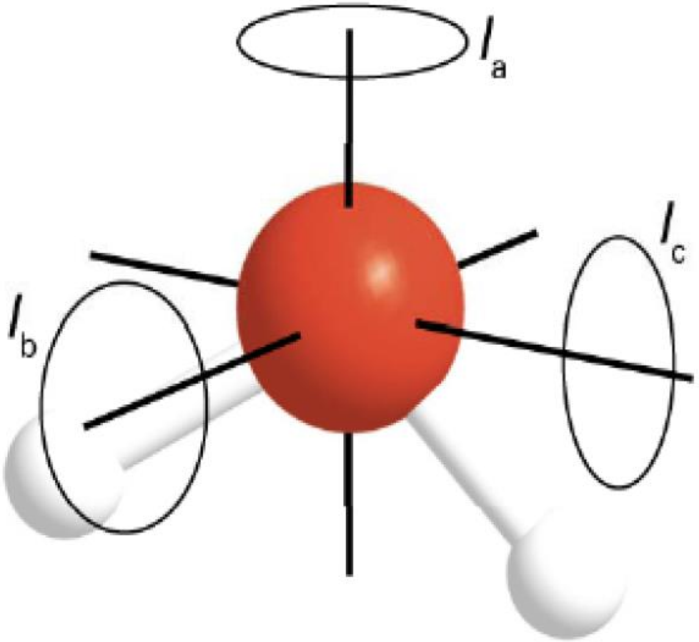
Rotational constants are related to molecular structure

For diatomics we defined a rotational constant $\tilde{B} \propto \frac{1}{I} = \frac{1}{\mu R^2}$

In general we require three such rotational constants:

as wavenumbers: $\boxed{\tilde{A} = \frac{h}{8\pi^2 c I_a}}$ $\boxed{\tilde{B} = \frac{h}{8\pi^2 c I_b}}$ $\boxed{\tilde{C} = \frac{h}{8\pi^2 c I_c}}$

$$\tilde{A} \geq \tilde{B} \geq \tilde{C}$$



H_2O molecule

$\tilde{A} = 27.9 \text{ cm}^{-1}$

$\tilde{B} = 14.5 \text{ cm}^{-1}$

$\tilde{C} = 9.3 \text{ cm}^{-1}$

But, we can no longer relate these constants explicitly to individual bond lengths within the molecule.

Schrödinger equation rigid rotors

$$\hat{H}\psi_r = E_r\psi_r$$

Rotational operators

$$J^2 \,|\Psi_r> = J(J+1)\,|\Psi_r>$$

$$J_z \,|\,\Psi_r> = K\,|\,\Psi_r>$$

***J* and *K* are the quantum numbers for rotation**

$$(J = 0 \rightarrow \infty)$$

$$J = 0, 1, 2, \ldots$$

repérer la molécule dans le système d'axes

Rotational energies for diatomic or linear molecules

$$\boxed{E_J = BJ\left(J+1\right)}$$

- J is the rotation quantum
- number = 0, 1, 2, …
- B is the rotational constant

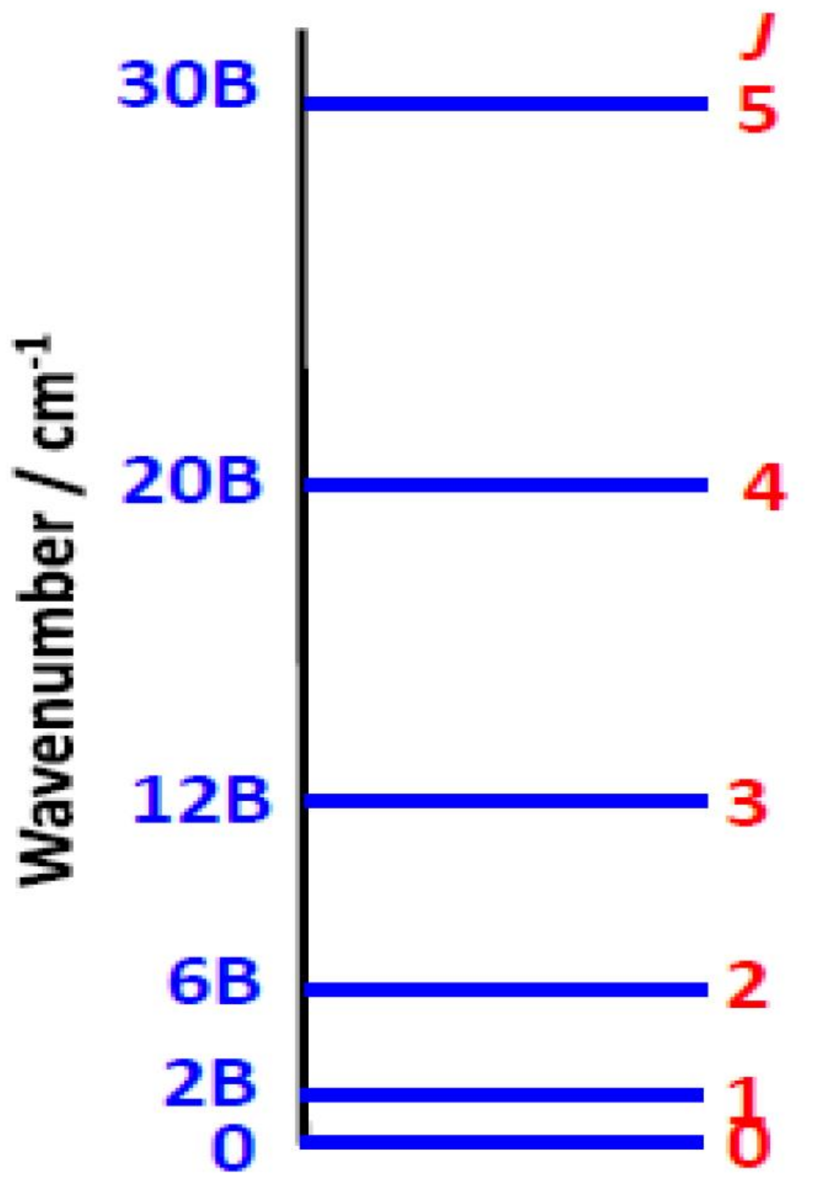
$$\boxed{B\ \left(in\ \text{Joule}\right) = \frac{\hbar^2}{2I}}$$

We can also give the B in cm^{-1}

$$\boxed{F_J = \frac{E_J}{hc} = \tilde{B}J\left(J+1\right)}$$

$$\boxed{\tilde{B} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R^2}}$$

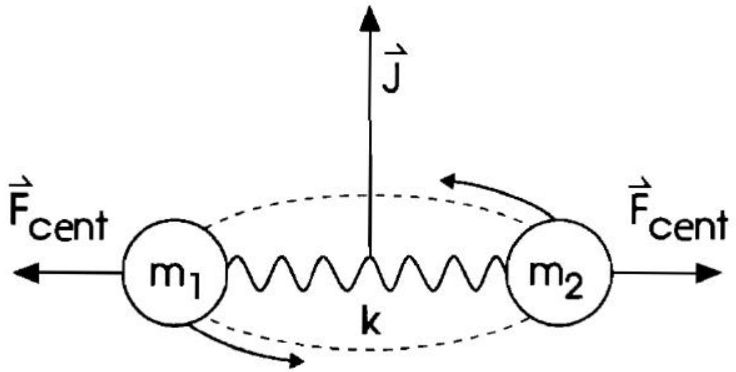
	$\tilde{B}$
H_2	60.85 cm^{-1}
CO	1.93 cm^{-1}
HCl	10.59 cm^{-1}



Centrifugal distortion

The bonds between the atoms are not really rigid, the centrifugal force imposed to the atoms is susceptible to increase the bond length.

if *J* increases, the molecule turns faster, the centrifugal force increases, which increases the bond length, *r*, and thus the moment of inertia increases, since $I = m r^2$.



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

This increase of *I* implies a decrease of *B*

Centrifugal distortion

$$E\,(\mathrm{v}, J) = hc\,[G\,(\mathrm{v}) + F\,(J)]$$

The energy of the vibrating-rotating molecule is :

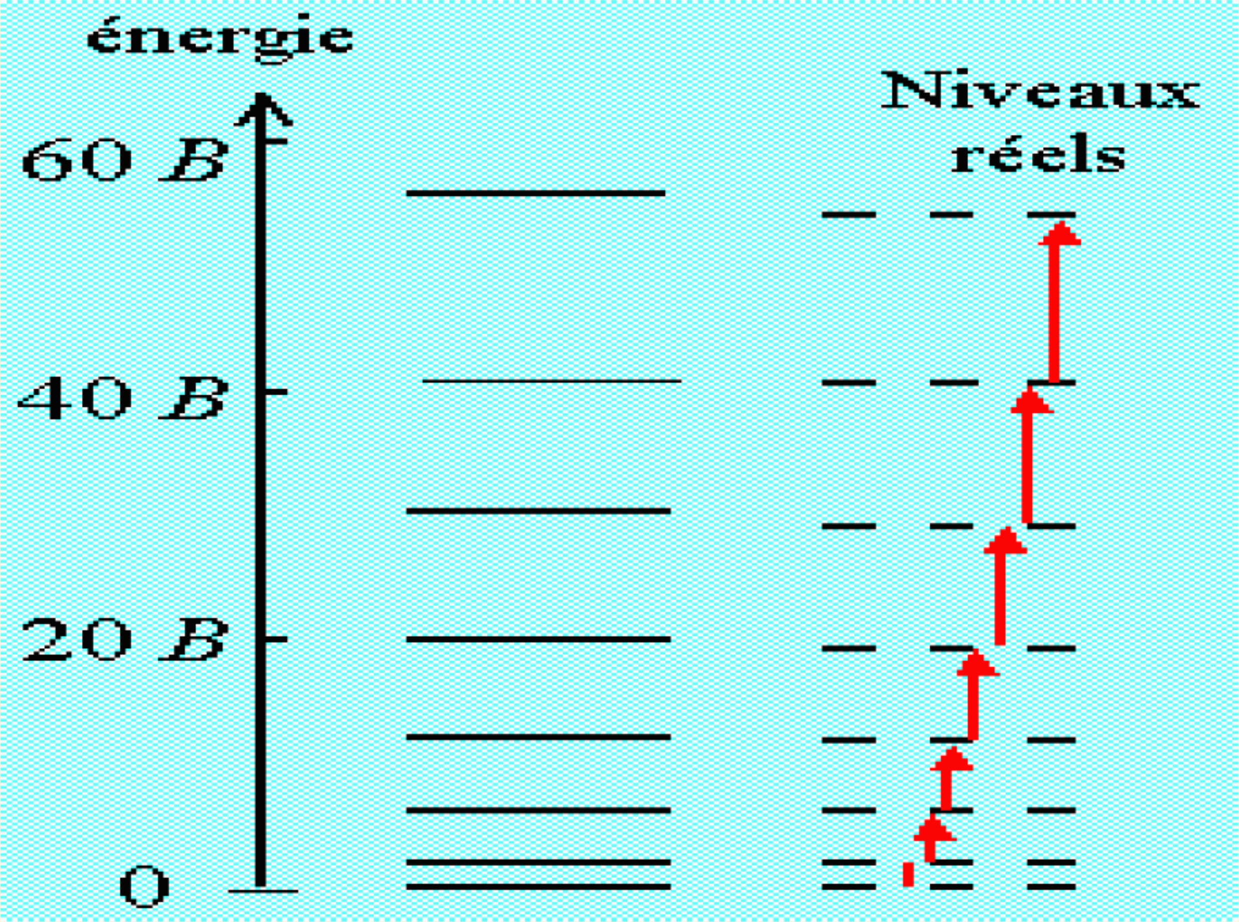
$$G\,(\mathrm{v}) + F\,(J) = \omega_e\,(\mathrm{v} + 1/2) - \omega_e x_e\,(\mathrm{v} + 1/2)^2$$
$$+ B\,J\,(J + 1)$$
$$-DJ^{2}\,(J + 1)^2 - \ldots$$

The *D* parameter is centrifugal **distortion**

Whereas $\omega_e x_e$ *is*

related to the anharmoncity of the vibration

Centrifugal distortion effect on the energy levels



Diatomic molecules

J → J'=J-1 : P **Branch**

J=0 →J'=0 : Q branch

« forbidden » transition

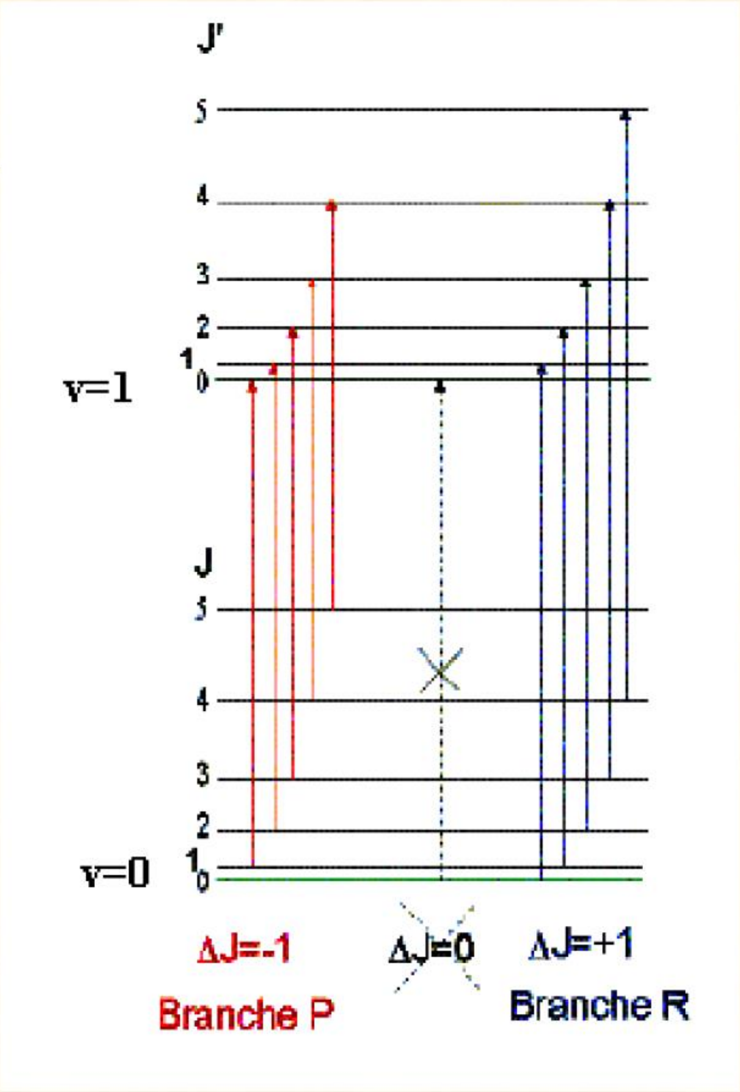
J → J'=J+1 : R Branch

a) Δv = 0 ; ΔJ = ±1: pure rotation spectrum (microwave).

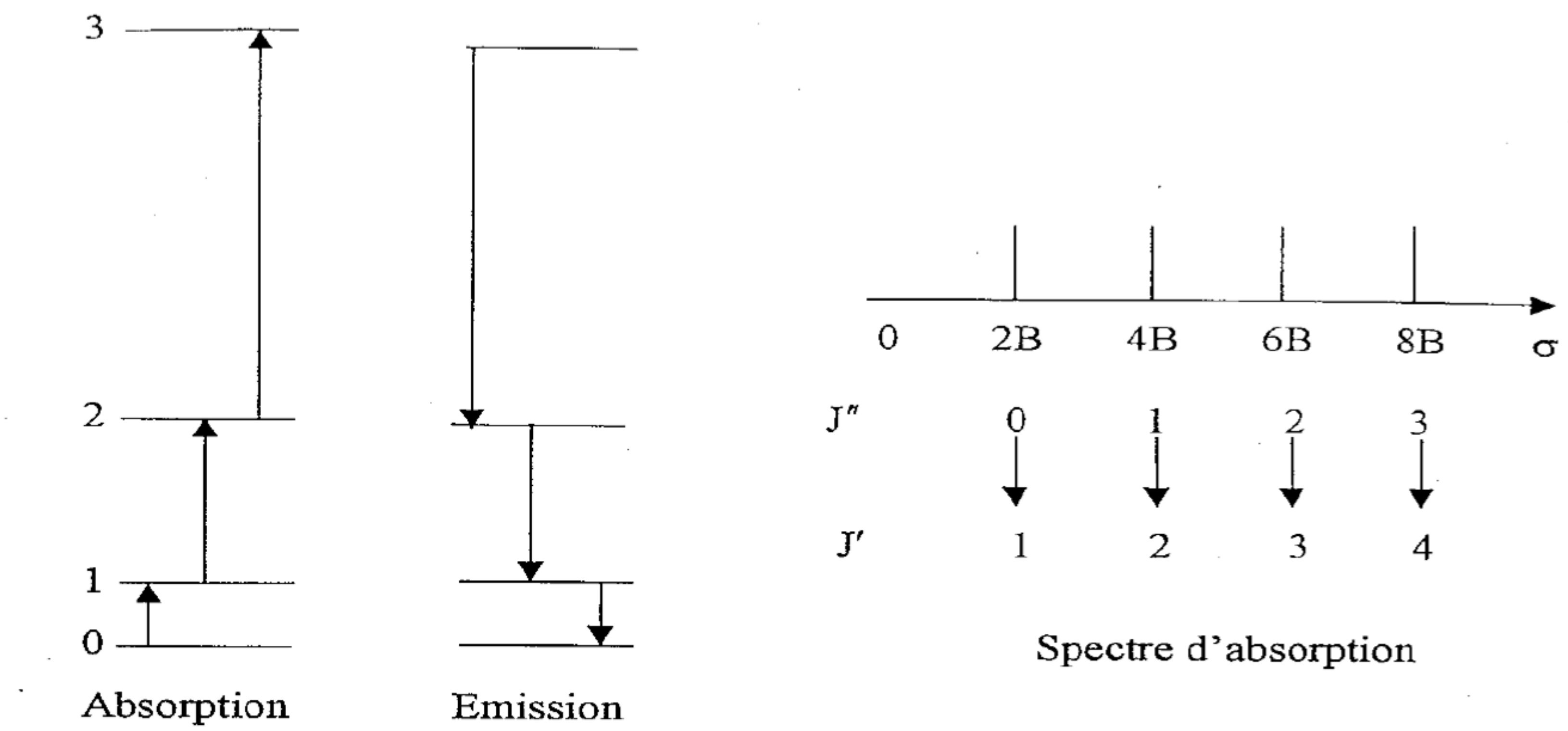
The molecule must have a permanent dipolar moment

b) Δv = ±1; ΔJ = ±1: vibration-torsion (infrared)

The dipole moment must change during the vibration



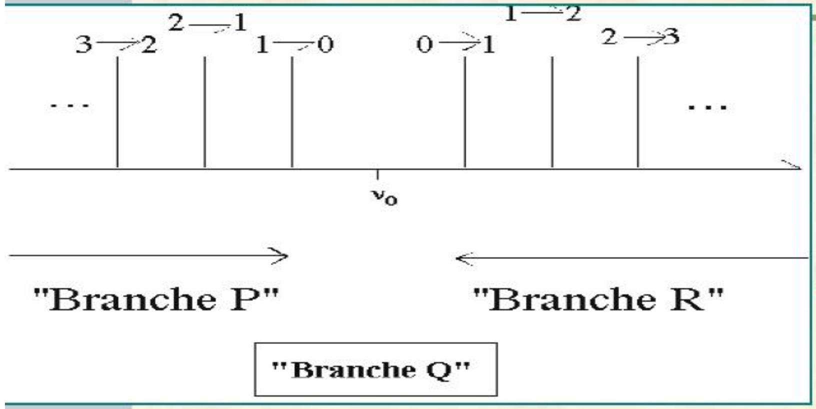
Pure rotation spectrum (microwave) for a diatomic molecule



The heavier the molecule is , the closer the lines are

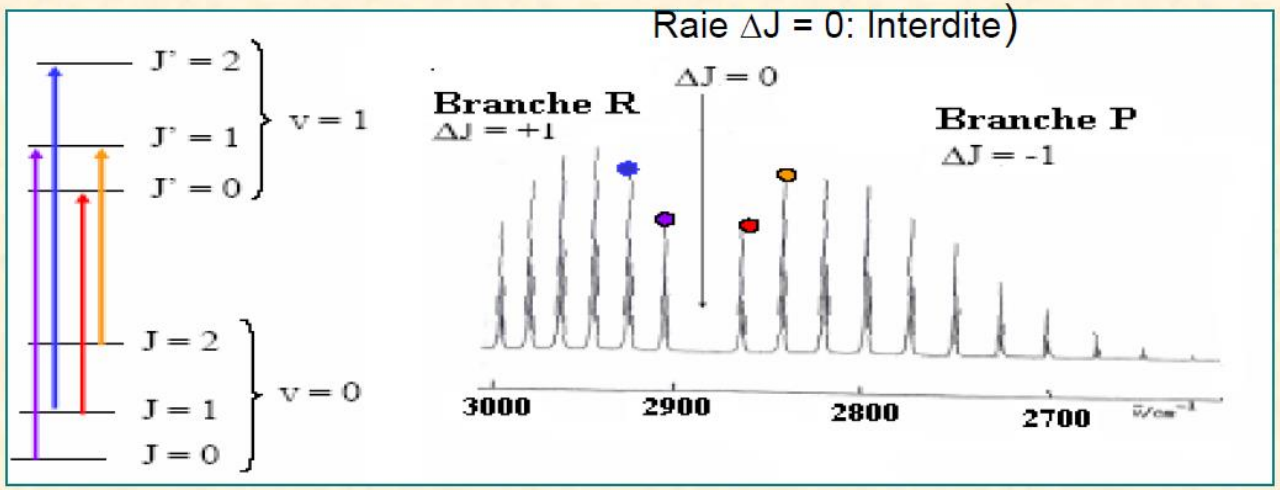
B) rotation-vibration spectrum

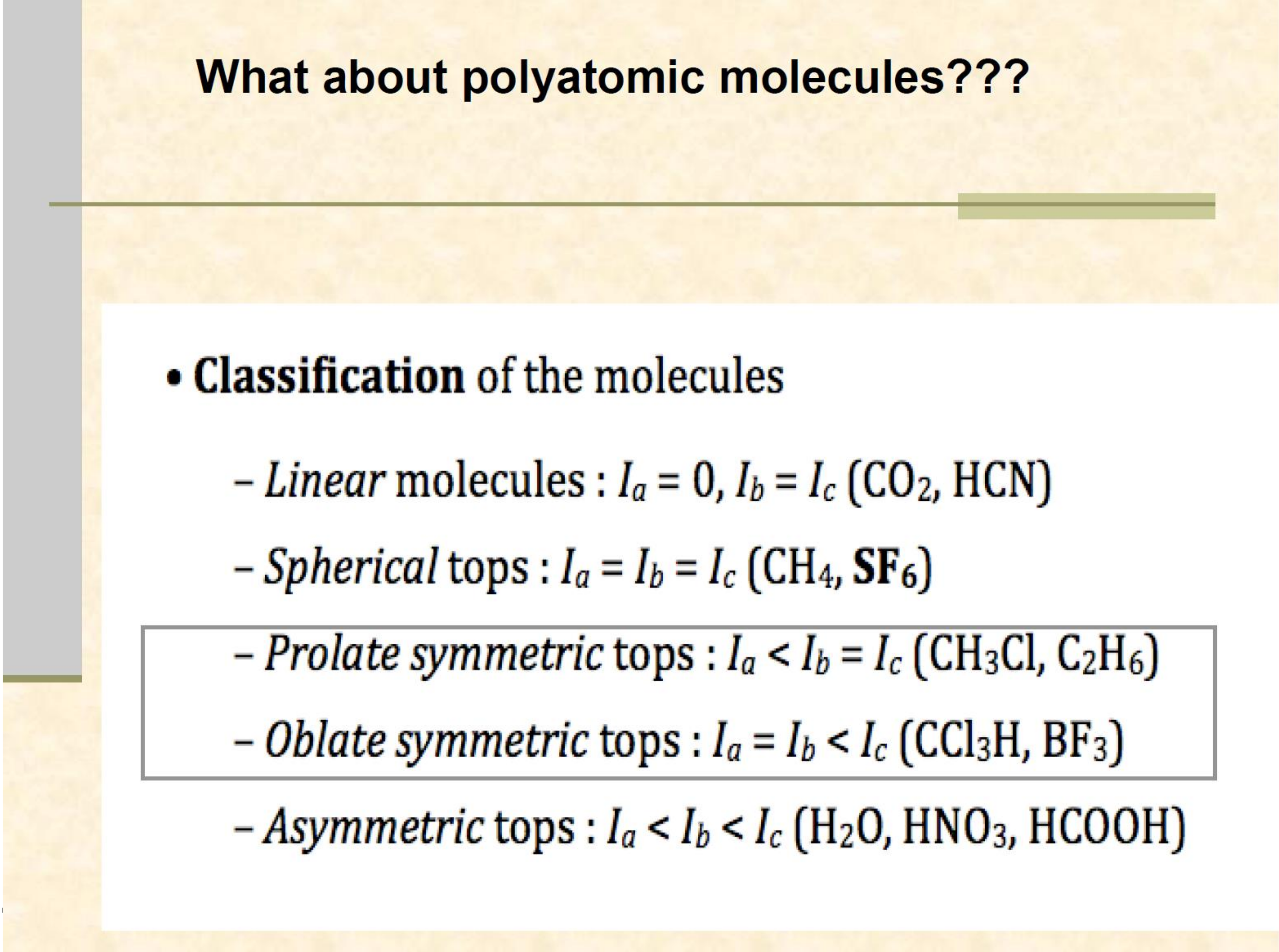
- Vibration-rotation transitions lead to a series of lines



R Branch : at higher frequencies ν relative to the band center ν_0

- Like for pure rotation spectra, intensities depend on the level population (function of J)





What about polyatomic molecules???

- **Classification** of the molecules
  - *Linear* molecules : $I_a = 0$, $I_b = I_c$ (CO_2, HCN)
  - *Spherical* tops : $I_a = I_b = I_c$ (CH_4, $\mathbf{SF_6}$)
  - *Prolate symmetric* tops : $I_a < I_b = I_c$ (CH_3Cl, C_2H_6)
  - *Oblate symmetric* tops : $I_a = I_b < I_c$ (CCl_3H, BF_3)
  - *Asymmetric* tops : $I_a < I_b < I_c$ (H_2O, HNO_3, HCOOH)

Concept of normal vibrations - fundamentals

Polyatomic molecules : N atoms => 3N motions

Suppressing the motions equivalent to translations => 3N-5 or 6 vibrations

Matrix of motions transformed to eigenvalues => fundamental vibrations

Number of fundamentals < 3N-5 as degenerate vibrations related to the symmetry of the molecule

Symmetries

- Symmetry elements and operations
  - Plane of symmetry (σ)
  - Center of symmetry (i)
  - P-fold axis of symmetry C_p with p=1,2,3…
  - P-flod rotation-reflection axis S_p (rotation C_P + symmetry)
- Point groups

  The combination of the symmetry elements (+ identity) forms a group structure and characterize the molecular structure relevant to the vibrational fundamentals

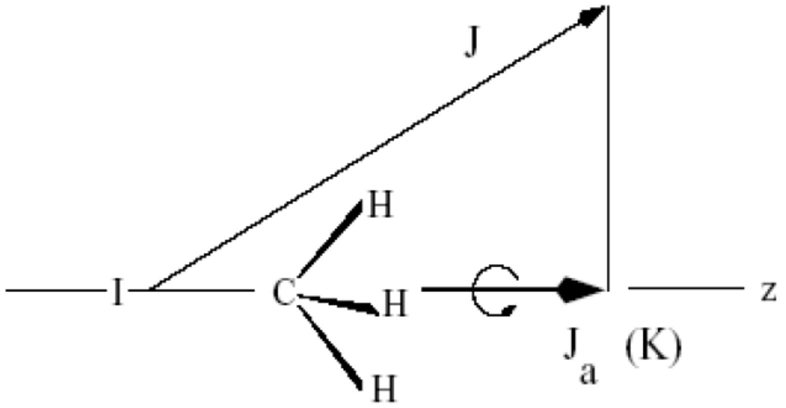
There are two types of symmetric rotors:
1) $B_x = B_y \neq B_z$

- *A) Prolate symmetric rotors* ("cigar" molecules)

- I_{zz} is defined as the smallest inertia moment and corresponds to the « A » rotational constant (which is always the bigest)

$$A = B_z,\ B = B_x = B_y$$

$$\boxed{E_0^{rot} = B\,J(J+1) + (A-B)\,K^2}$$



z = a

K is called K_a for prolate tops

Second type of symmetric tops

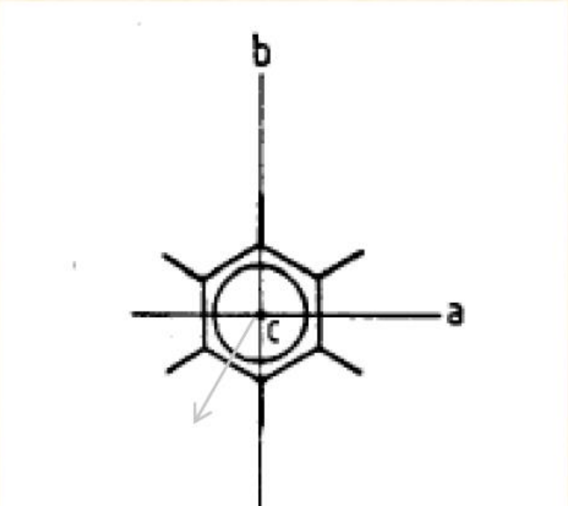
2) $B_x = B_y \neq B_z$

-B) *Oblate symmetric tops* ("plate" molecule)":

I_{zz} is defined for those oblate tops as the bigest moment of inertia and corrspond to the C rotational constant (which is the smallest constant)

$$B_x = B_y = B,\ C = B_z$$

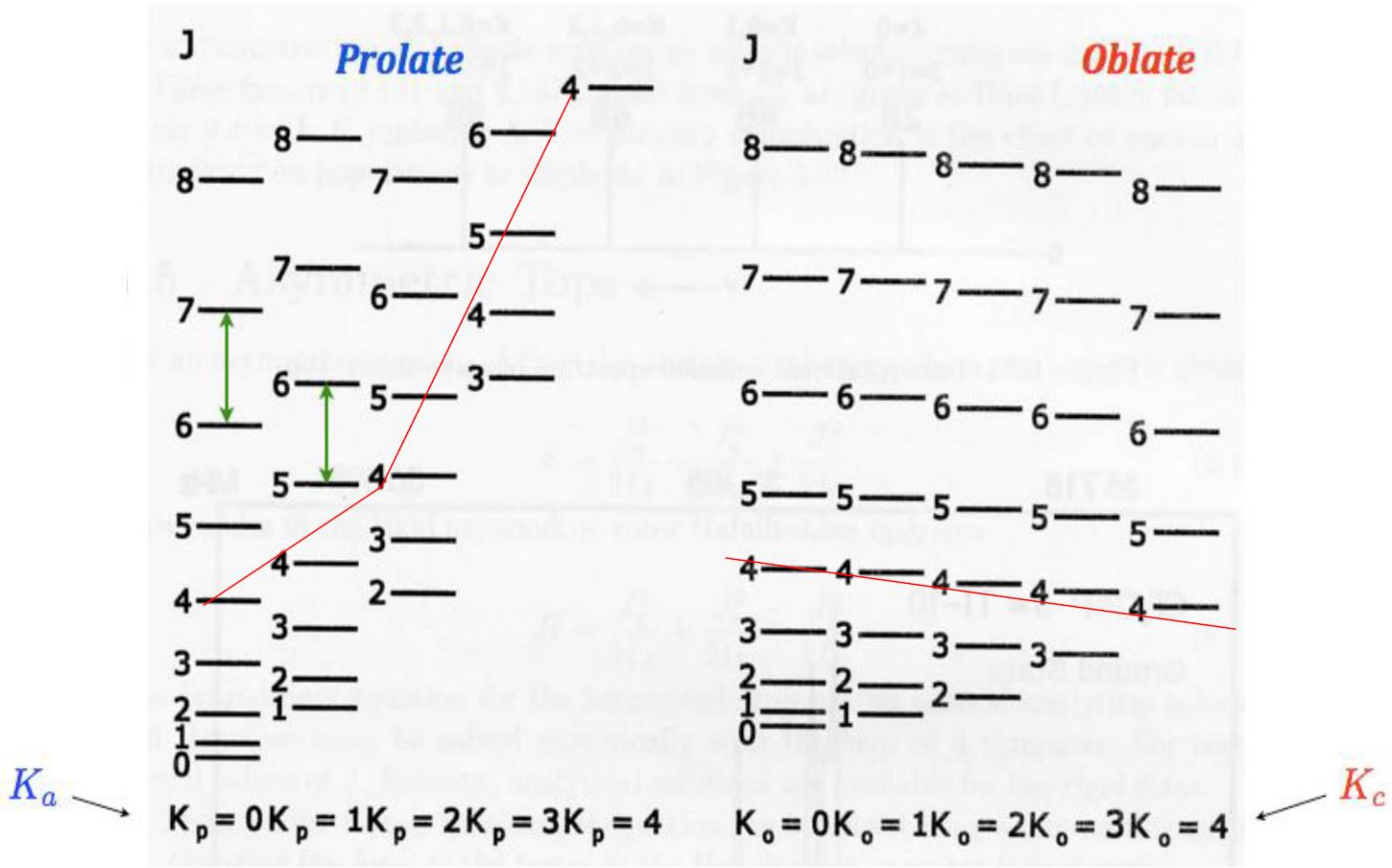
$$\boxed{E_0^{rot} = BJ(J+1) + (C-B)K^2}$$



K is called K_c for oblate tops

Rotation energies for symmetric tops

$$A \geq B \geq C$$



$$E_r(J,K) = BJ(J+1) + \underbrace{(A-B)}_{>0}K^2 \qquad E_r(J,K) = BJ(J+1) + \underbrace{(C-B)}_{<0}K^2$$

Molécules toupies symétriques

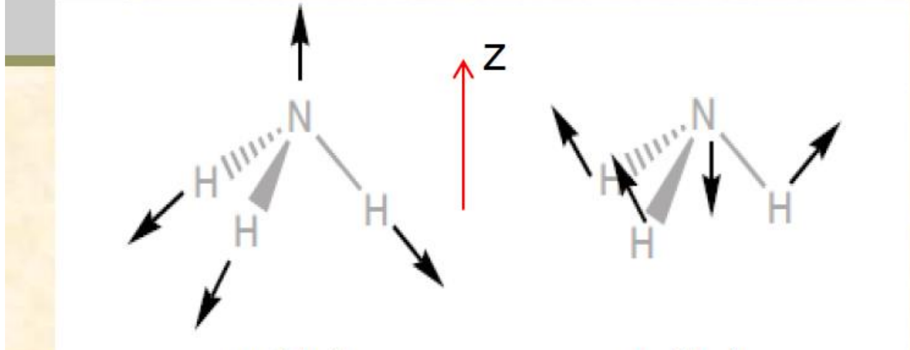
Rotation-vibration: transitions are induced by the variations of the z component of dipole moment parallel to the symmetry axis or by the x et y components perpendicular to this axis.

2 types of selection rules and 2 types of bands

- Parallel Band (induced by the variations de μ_z)

$$\Delta\ell = 0$$

- si K≠0 $\Delta J=0, \pm 1$ et $\Delta K= 0$
- si K=0 $\Delta J= \pm 1$ et $\Delta K= 0$



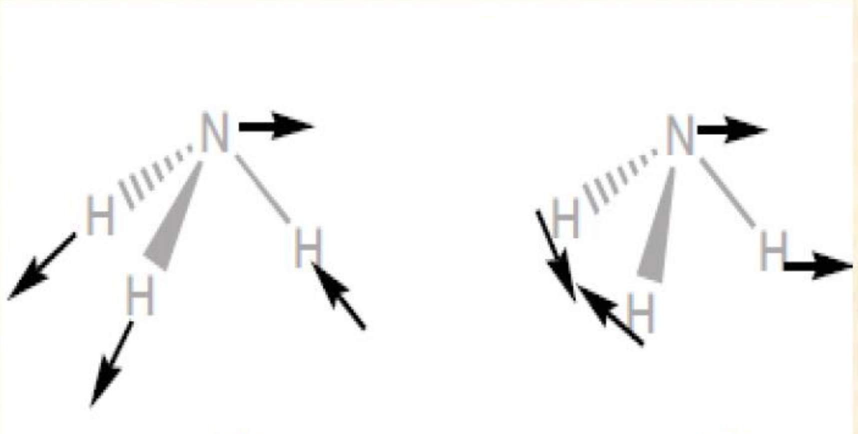
$\nu_1(A_1)$
symmetric stretch

$\nu_2(A_1)$
symmetric bend

- **Perpendicular Band (induced by μ_x, μ_y)**

$$\Delta\ell = \pm 1$$

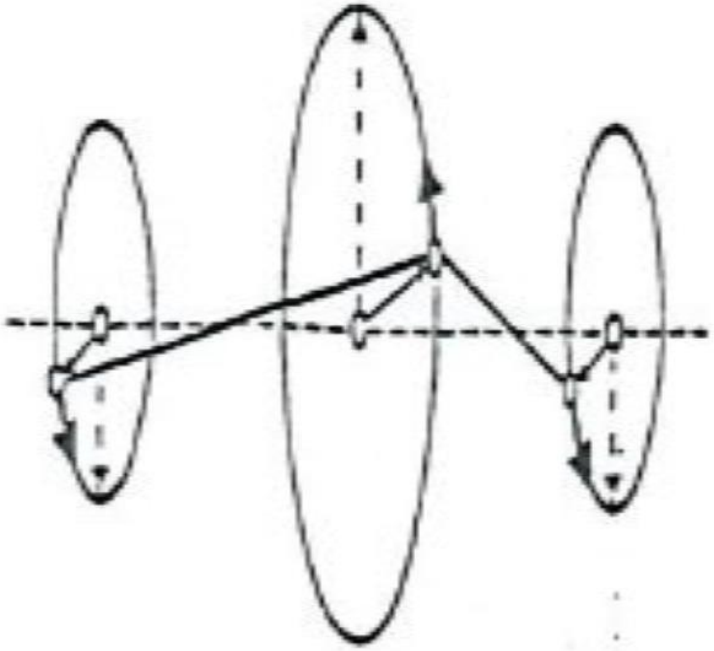
$\Delta J=0, \pm 1$ et $\Delta K= \pm 1$



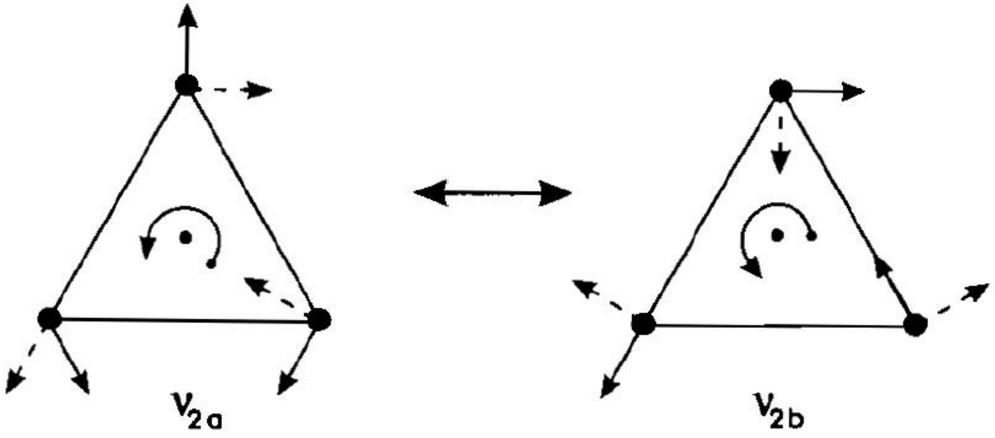
$\nu_{3a}(E)$

$\nu_{4a}(E)$

What is hapening in so-called « degenerate » modes?



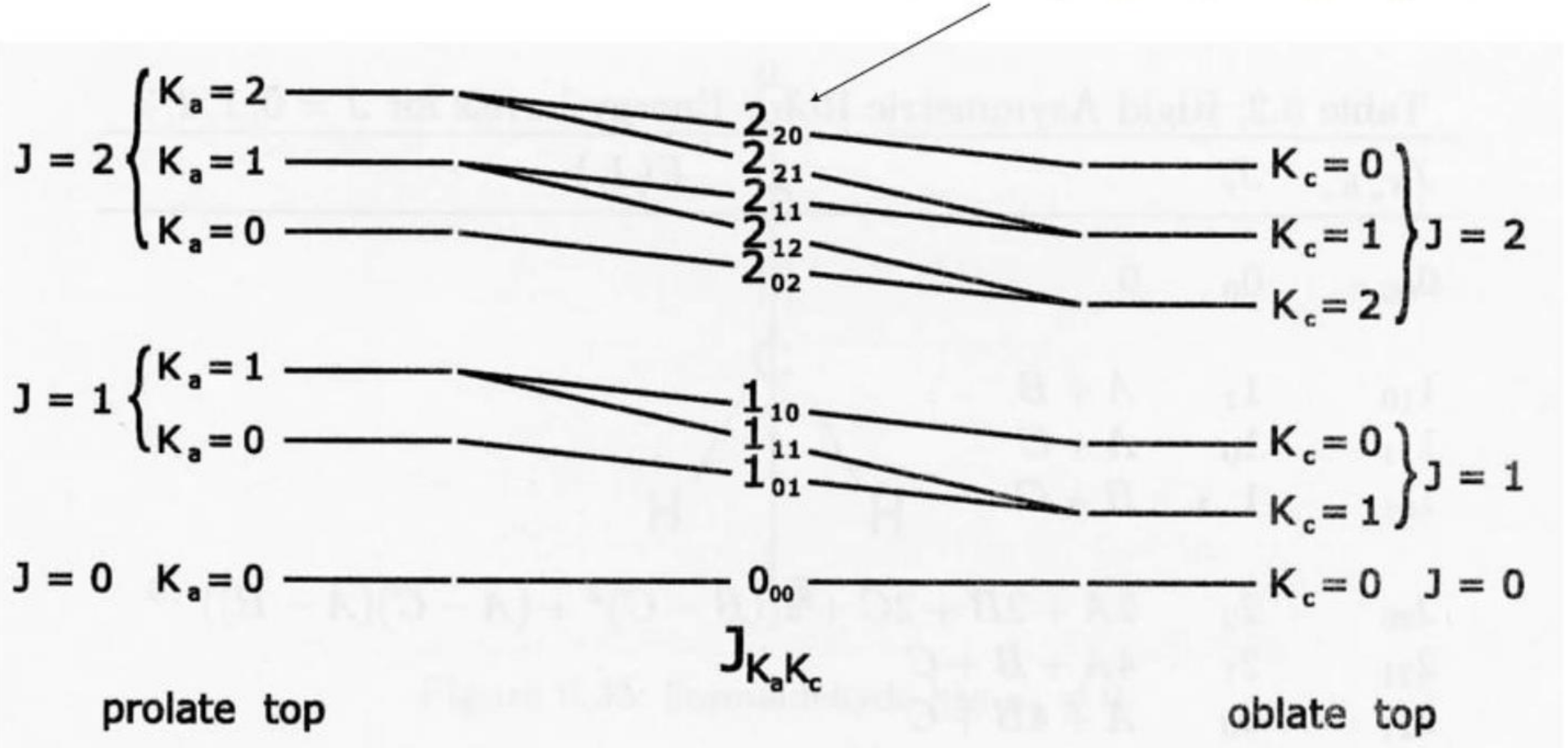
Linear molecule (CO_2)



Symmetric top (H_3^+)

Asymmetric top: energy levels: J K_a K_c

$K_a, K_c =$ pseudo-quantum numbers



$\kappa = -1$

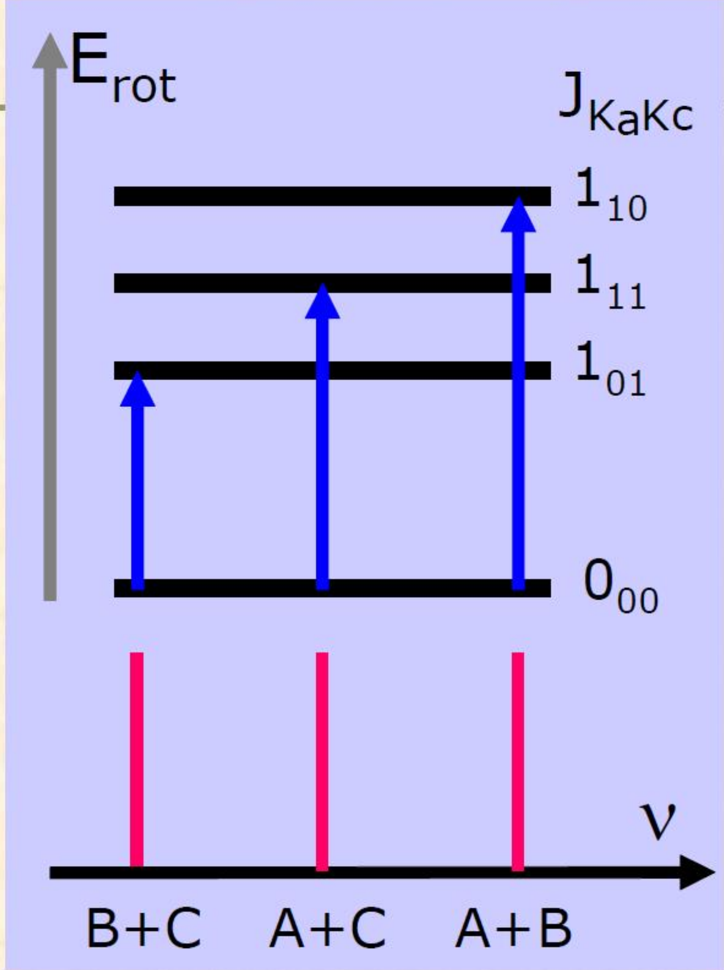
$$\kappa = \frac{2B - A - C}{A - C}$$

$\kappa = +1$

Rotational energy levels and transitions

Rigid rotor (zero order energy)

Asymmetric top, rotation characterized by the quantum numbers : J, K_a, K_c



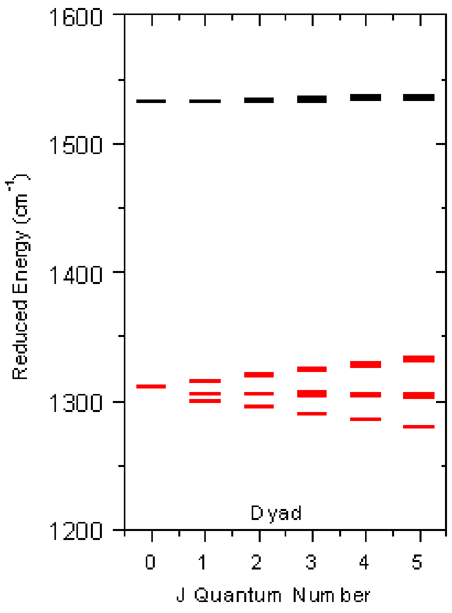
Limitation of the size of the molecule measured by most of Fourier-Transform spectrometers (2-20 GHz) : 250-300 uma

Line Intensities : Depend on the Electric dipole moment

μ (μ_a, μ_b, μ_c)

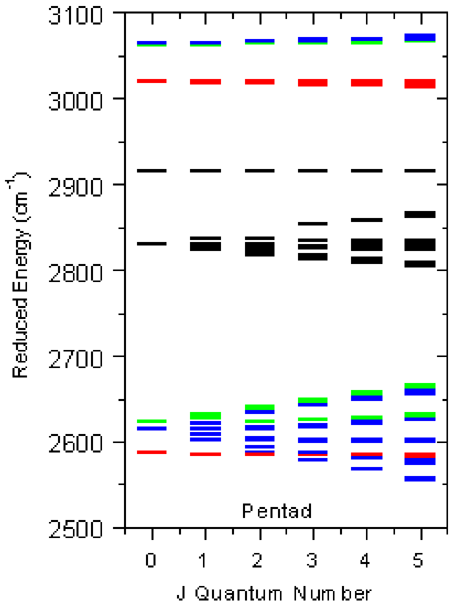
CH_4 : vibration/rotation bands

7.8 µm



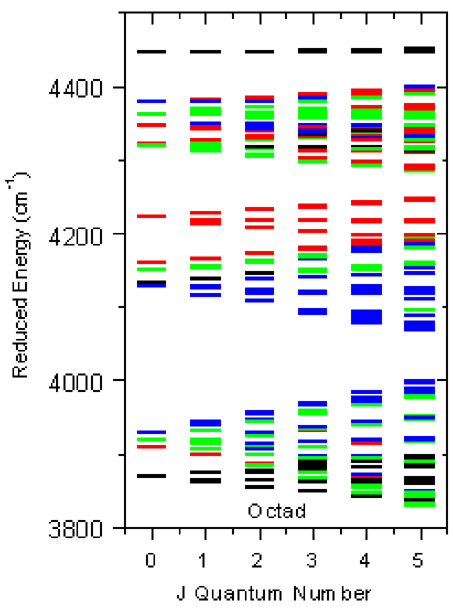
Dyad
2 vibrational states
2 sublevels

3.3 µm



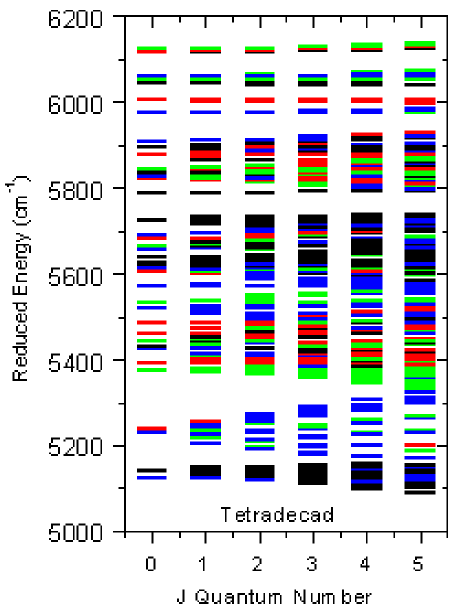
Pentad
5 vibrational states
9 sublevels

2.3 µm



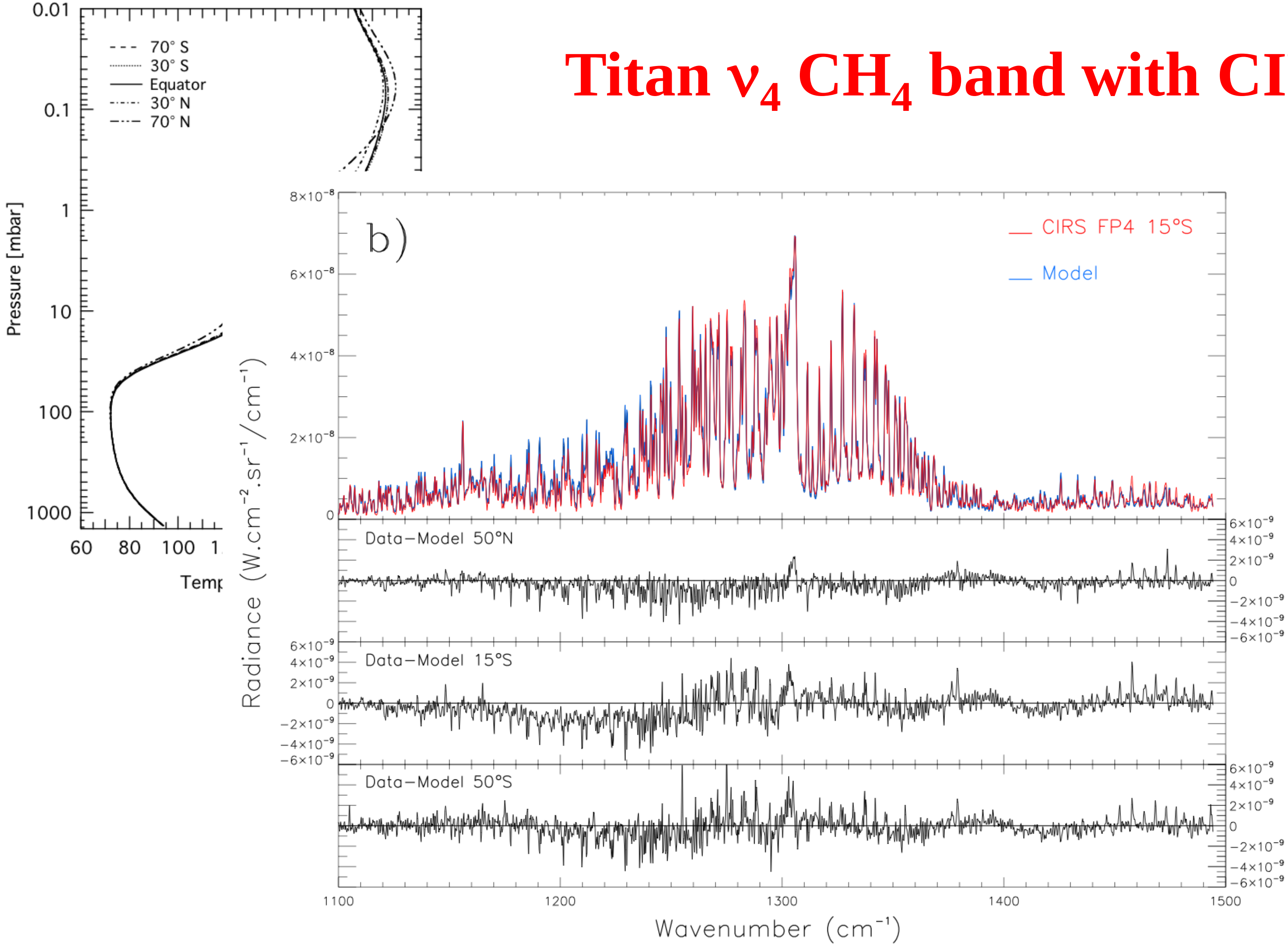
Octad
8 vibrational states
20 sublevels

1.8 µm

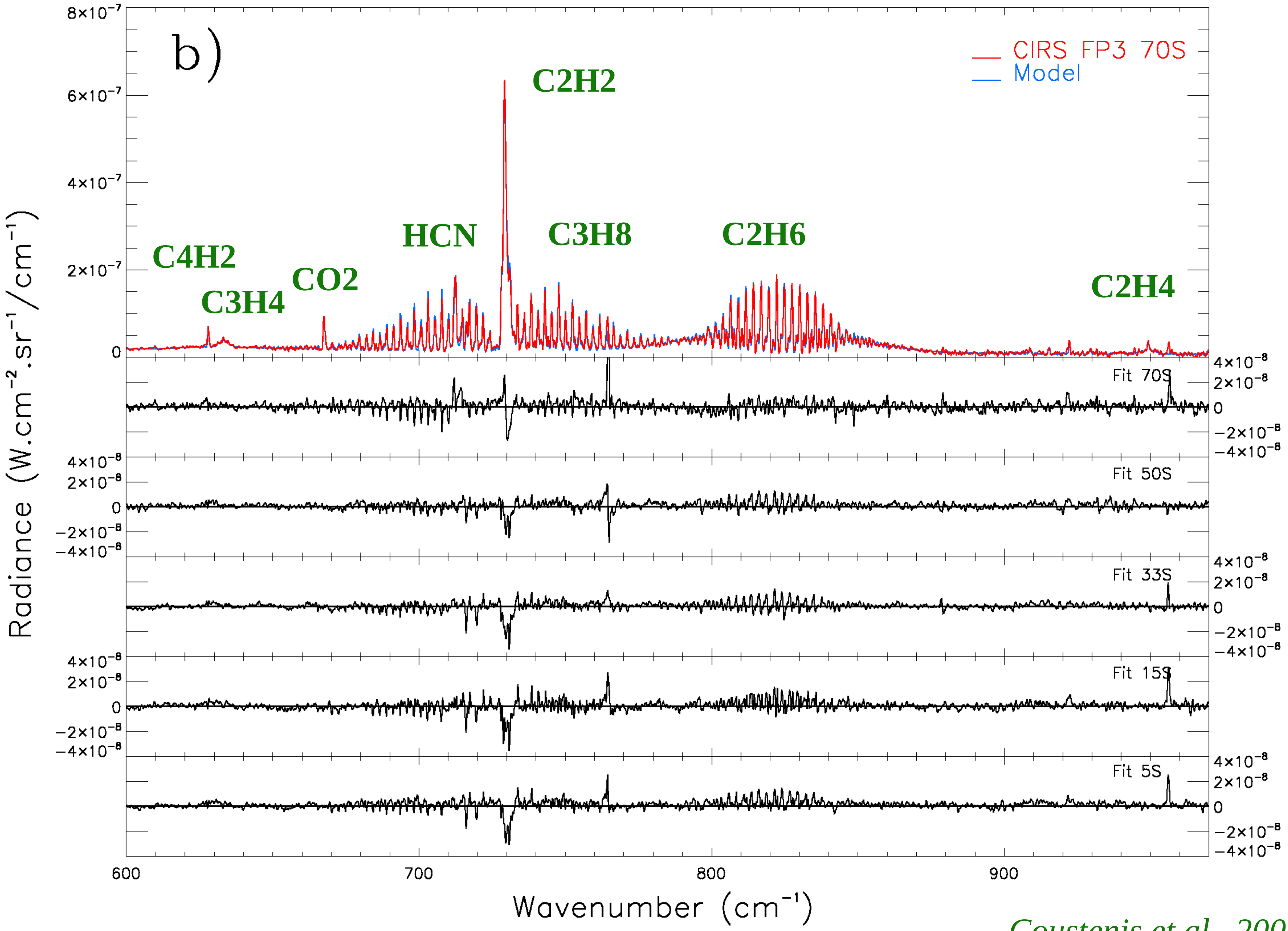


Tetradecad
14 vibrational states
60 sublevels

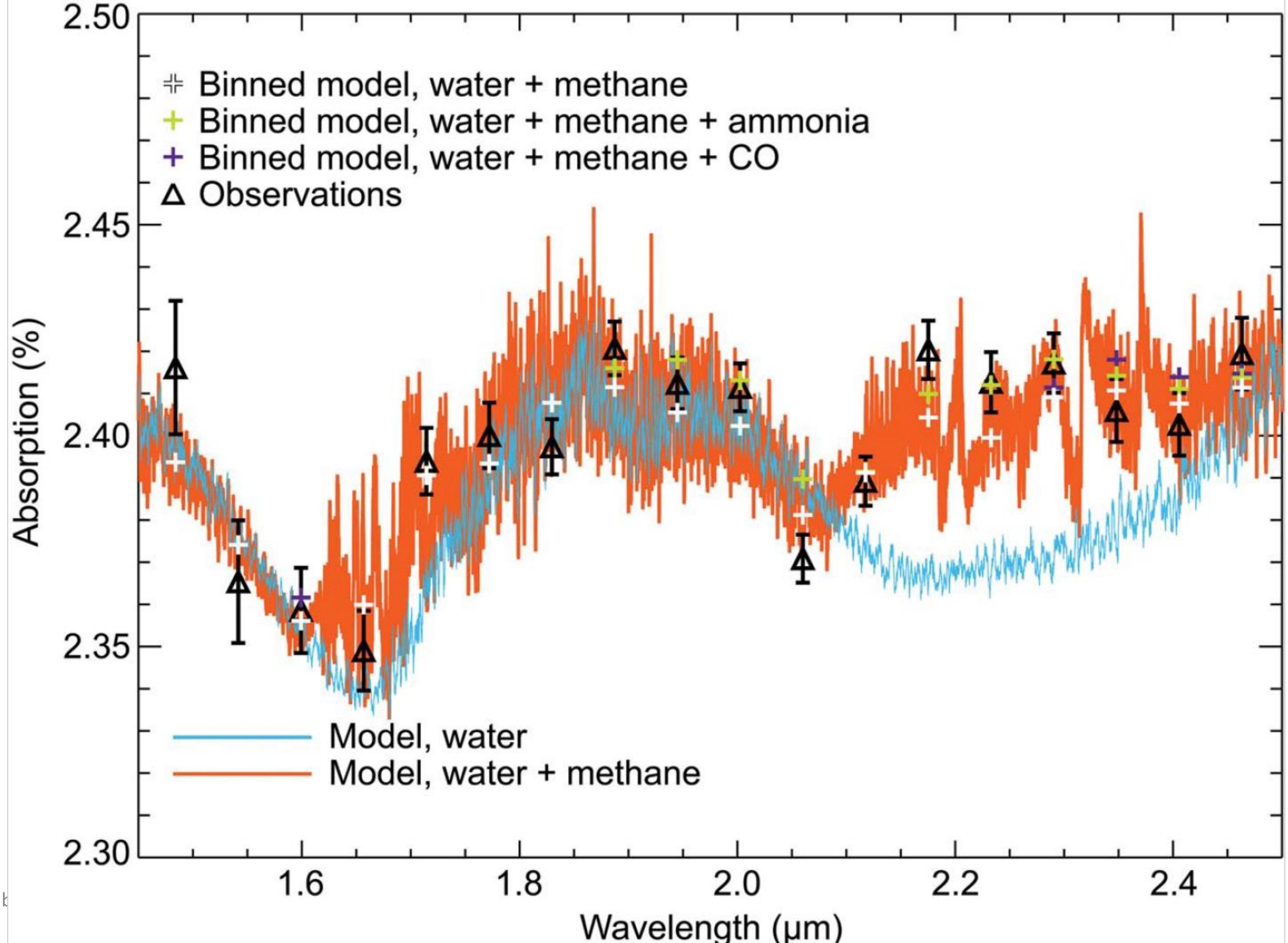
Titan ν_4 CH_4 band with CIRS



Coustenis et al., 2007



Coustenis et al., 2009


Binned model, water + methane
Binned model, water + methane + ammonia
Binned model, water + methane + CO
Observations
Model, water
Model, water + methane
Absorption (%)
Wavelength (µm)
2.50
2.45
2.40
2.35
2.30
1.6
1.8
2.0
2.2
2.4

Additional complexities : internal motions

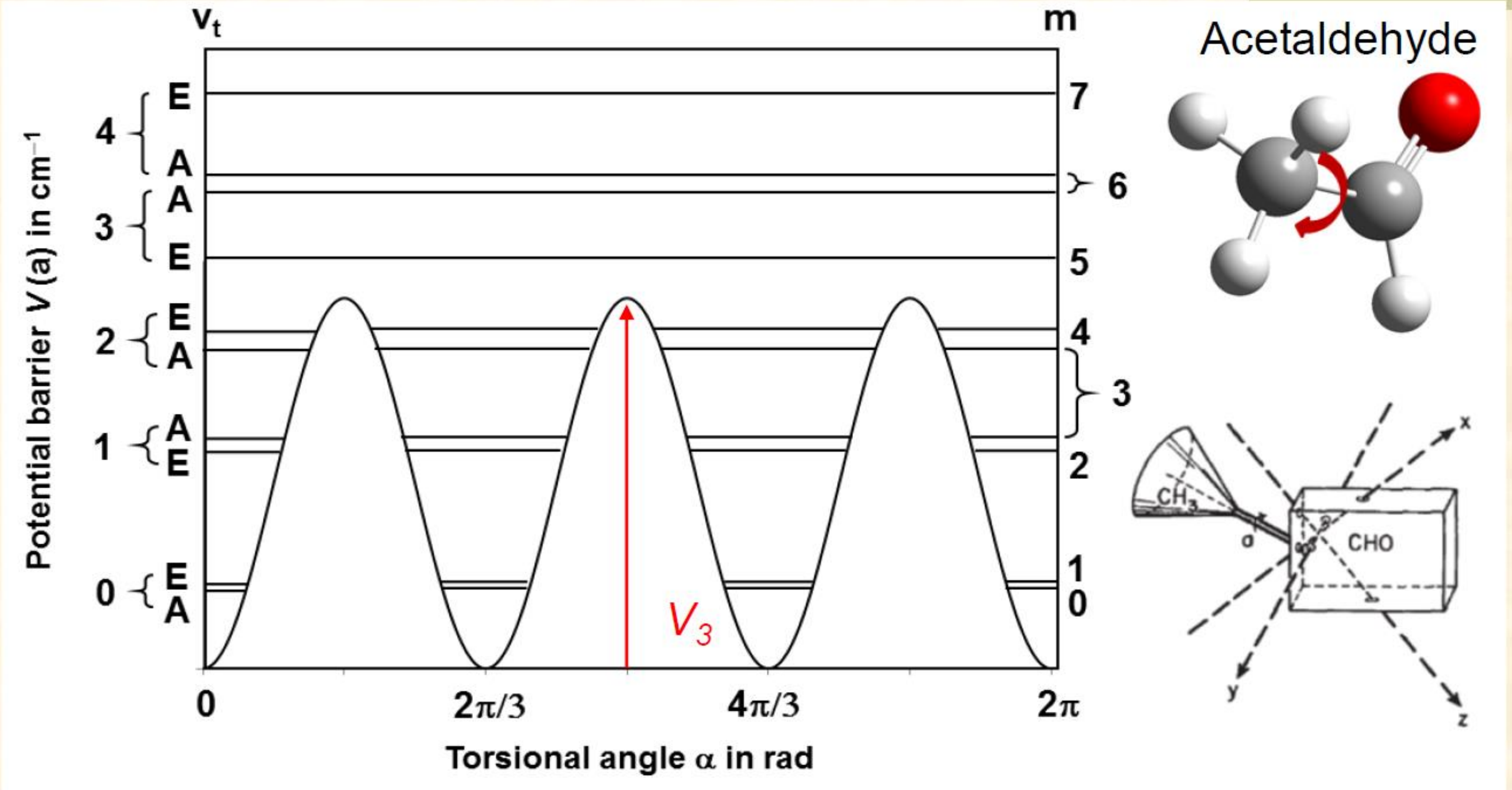
Internal motions in some molecules greatly complexify the spectroscopy.

Examples :

CH3-COH (formaldehyde)

NH3

Internal rotation

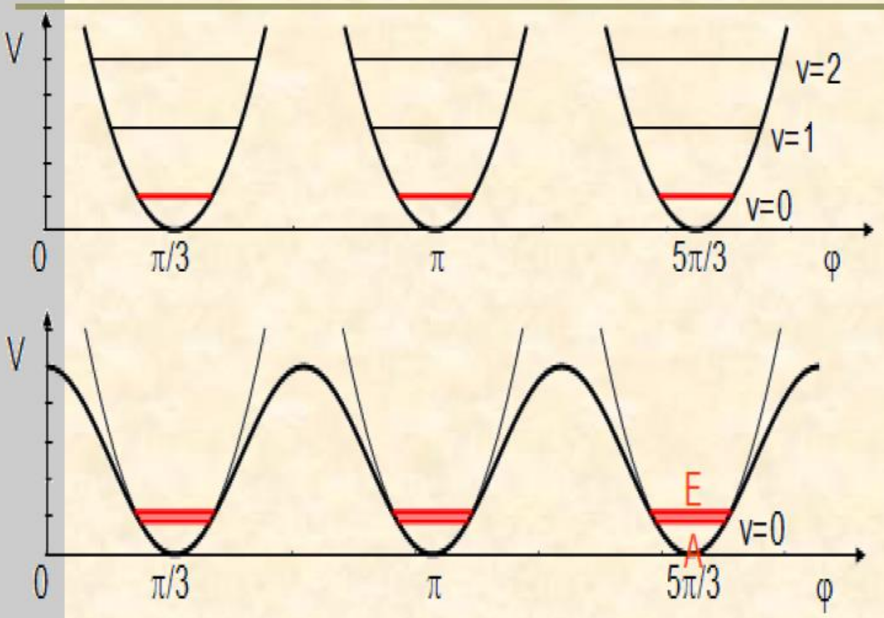


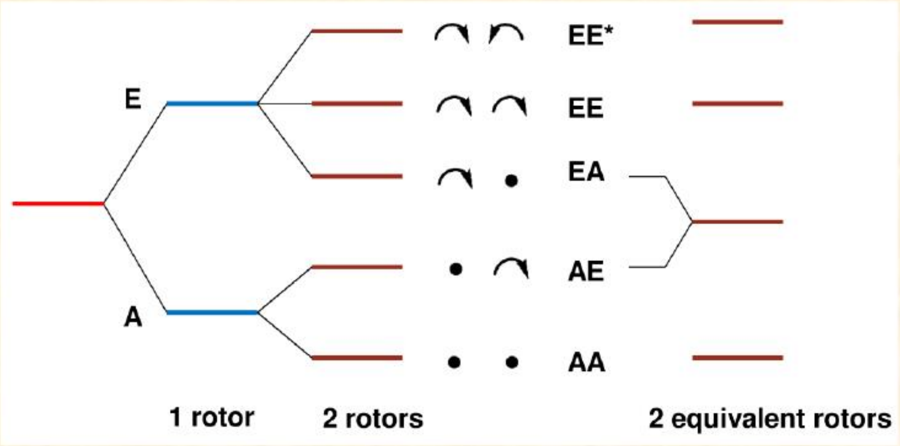
$$V(\alpha)=\frac{V_3}{2}(1-\cos 3\alpha)+\frac{V_6}{2}(1-\cos 6\alpha)+\cdots$$

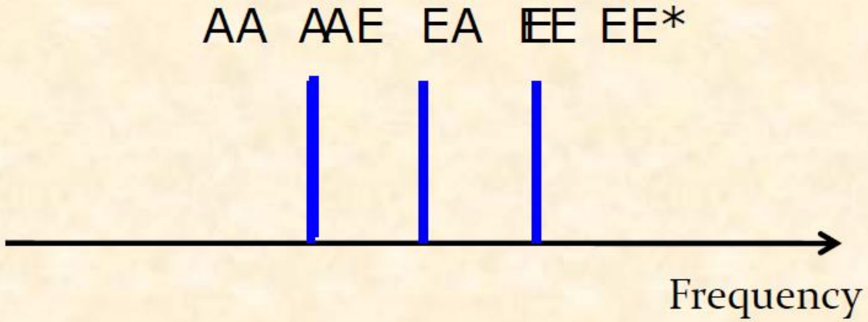
Lin and Swalen Rev. Mod. Phys 1959

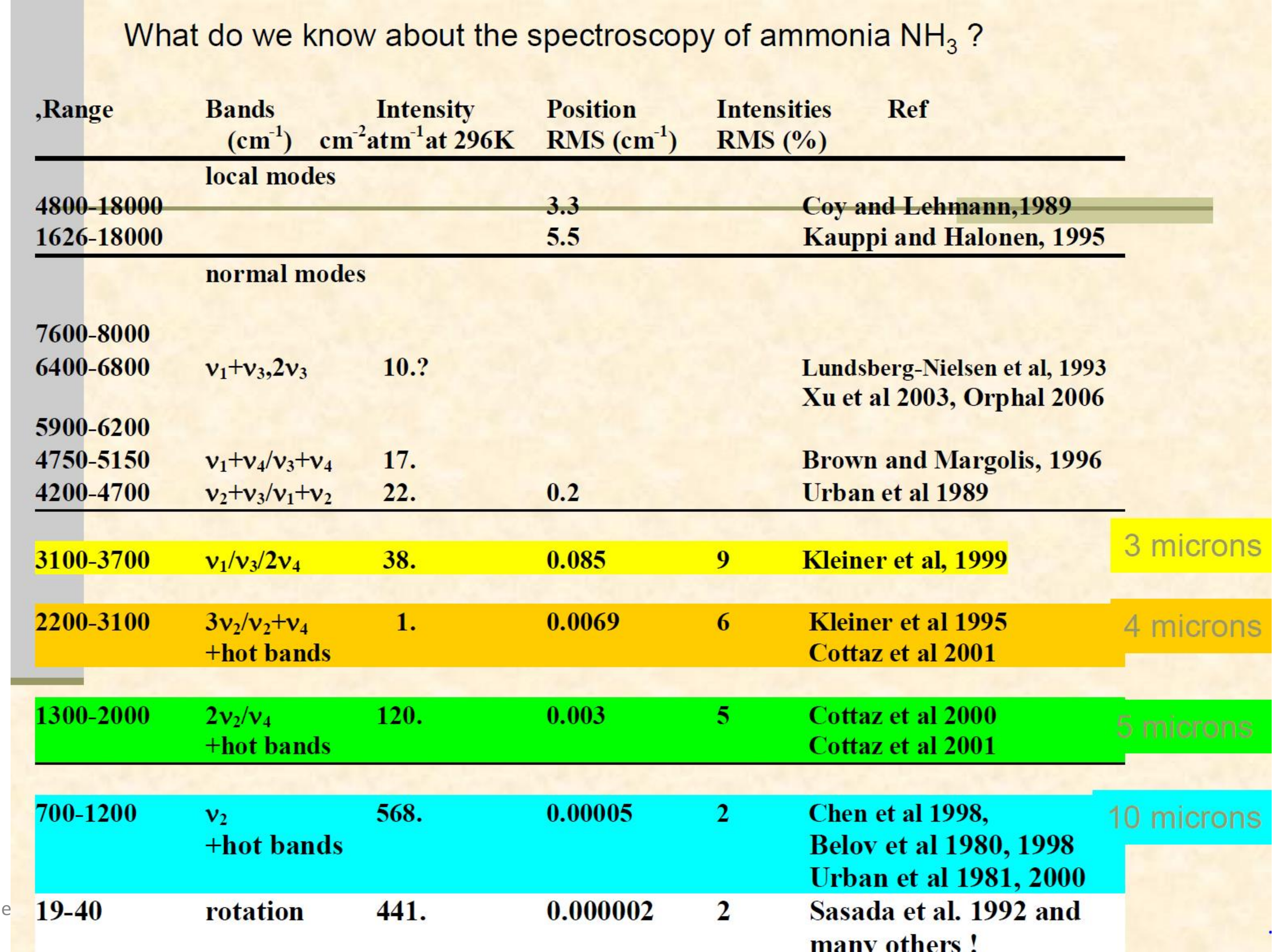
72

Internal rotation







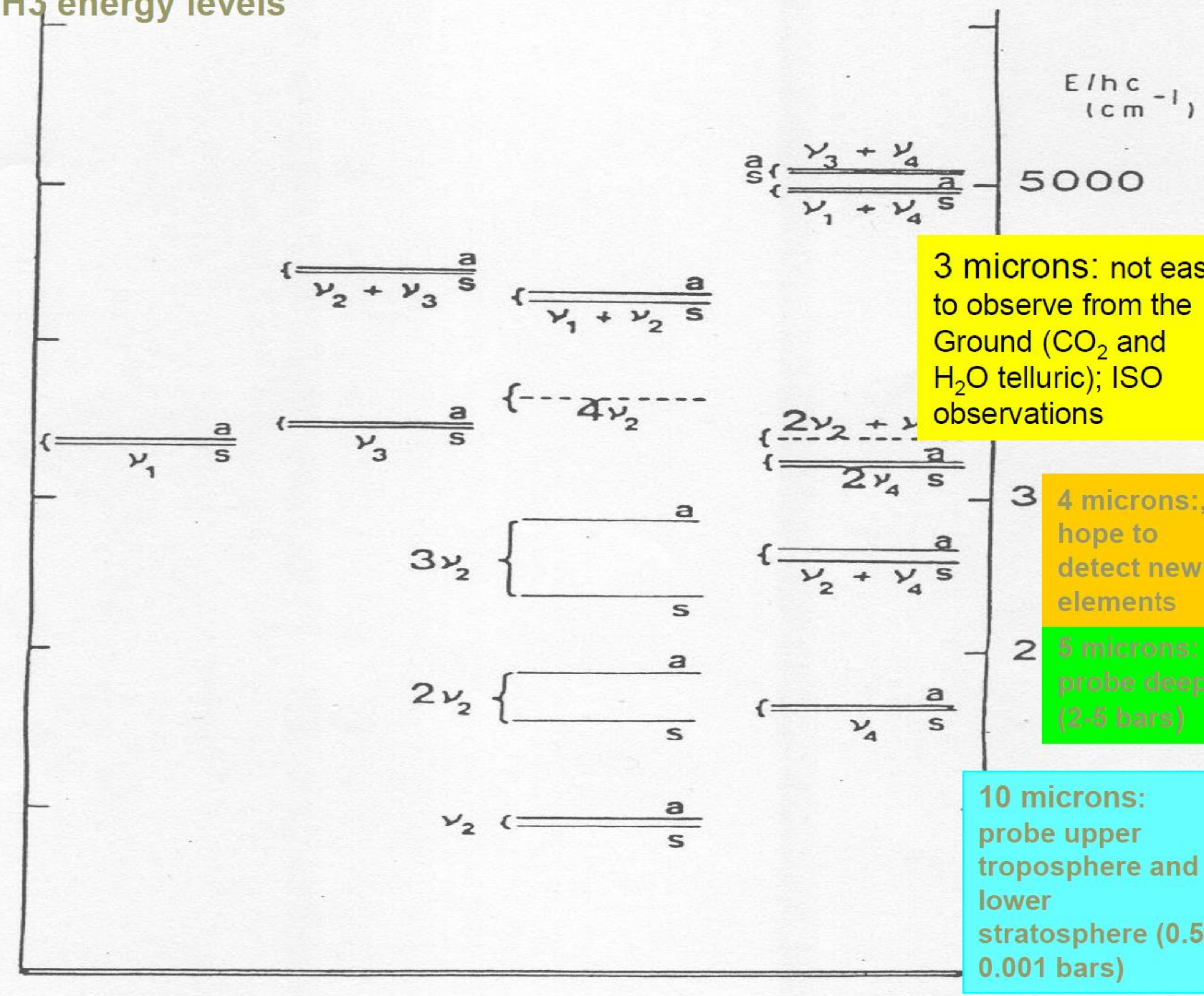


What do we know about the spectroscopy of ammonia NH_3 ?

,Range	Bands (cm^{-1})	Intensity cm^{-2}atm^{-1}at 296K	Position RMS (cm^{-1})	Intensities RMS (%)	Ref	
	local modes					
4800-18000			3.3		Coy and Lehmann,1989	
1626-18000			5.5		Kauppi and Halonen, 1995	
	normal modes					
7600-8000						
6400-6800	$\nu_1+\nu_3,2\nu_3$	10.?			Lundsberg-Nielsen et al, 1993 Xu et al 2003, Orphal 2006	
5900-6200						
4750-5150	$\nu_1+\nu_4/\nu_3+\nu_4$	17.			Brown and Margolis, 1996	
4200-4700	$\nu_2+\nu_3/\nu_1+\nu_2$	22.	0.2		Urban et al 1989	
3100-3700	$\nu_1/\nu_3/2\nu_4$	38.	0.085	9	Kleiner et al, 1999	3 microns
2200-3100	$3\nu_2/\nu_2+\nu_4$ +hot bands	1.	0.0069	6	Kleiner et al 1995 Cottaz et al 2001	4 microns
1300-2000	$2\nu_2/\nu_4$ +hot bands	120.	0.003	5	Cottaz et al 2000 Cottaz et al 2001	5 microns
700-1200	ν_2 +hot bands	568.	0.00005	2	Chen et al 1998, Belov et al 1980, 1998 Urban et al 1981, 2000	10 microns
19-40	rotation	441.	0.000002	2	Sasada et al. 1992 and many others !	

NH3 energy levels

NH$_3$ ENERGY LEVELS



3 microns: not easy to observe from the Ground (CO$_2$ and H$_2$O telluric); ISO observations

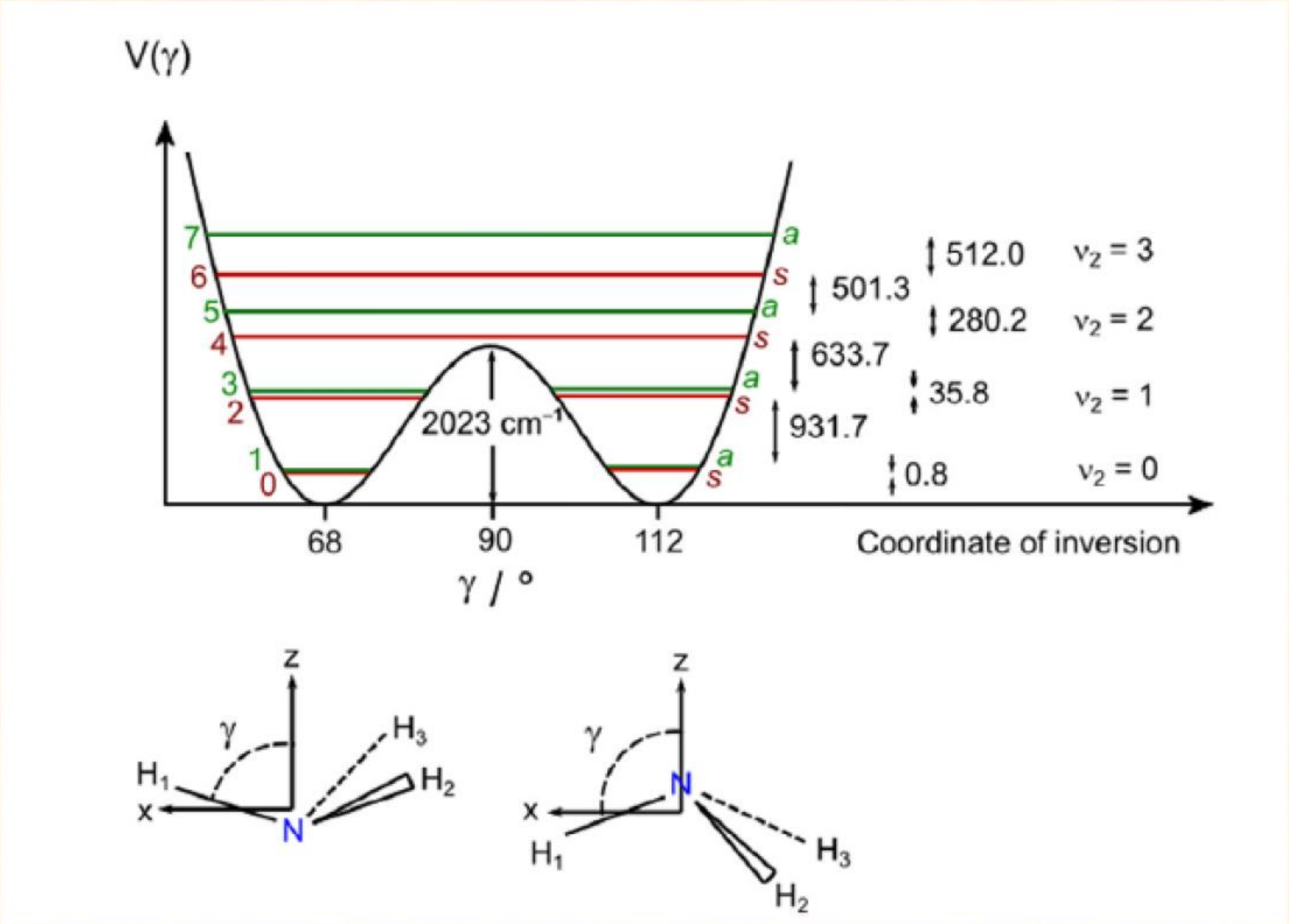
4 microns:, hope to detect new elements

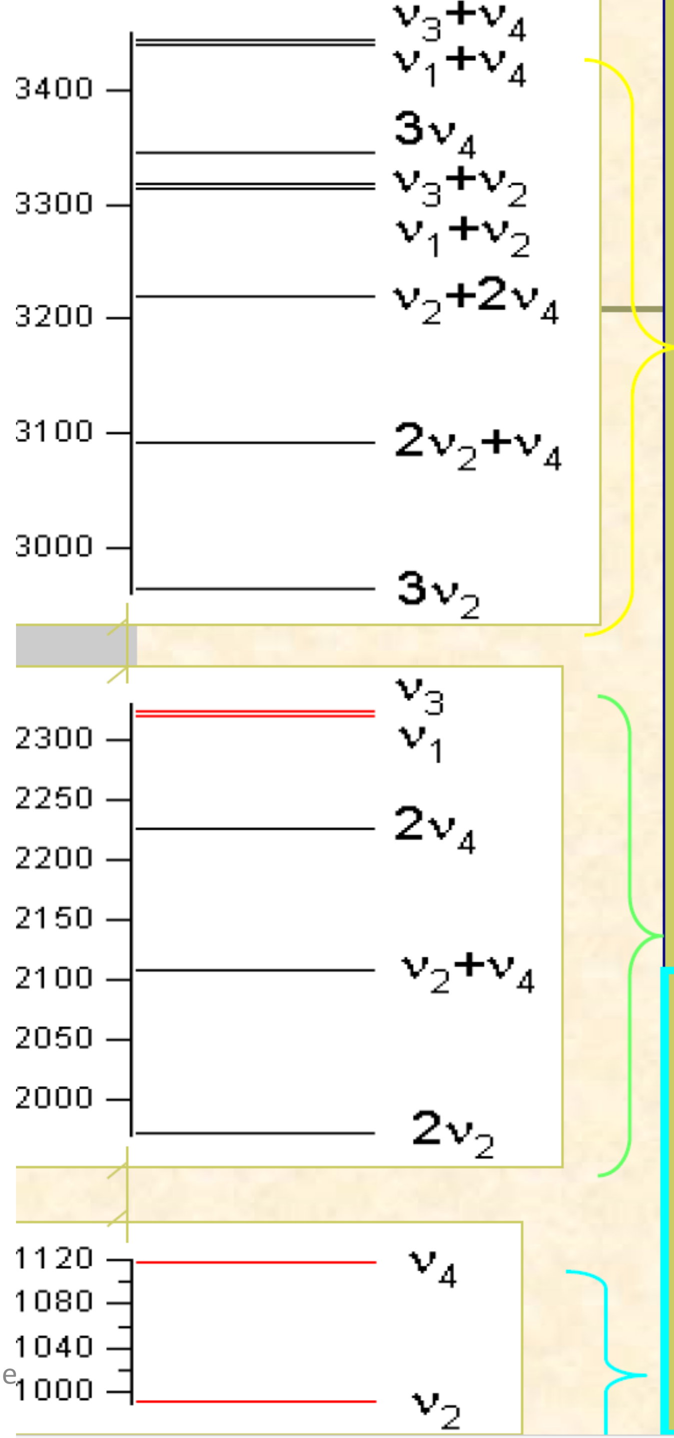
5 microns: probe deep (2-5 bars)

10 microns: probe upper troposphere and lower stratosphere (0.5-0.001 bars)

What makes NH_3 so hard???

Large amplitude motion : inversion





-The band $3\nu_2$:

-Low resolution of line positions (Maki et al. JCP 1973)

- The octad bands:

New line positions and intensities measurements (Butler et al., JMS 2006)

The Global analysis of the Dyad, pentad and octad bands: (Nikitin et al., JMS 2009)

- **The $2\nu_2/\nu_2+\nu_4/2\nu_4/\nu_1/\nu_3$ pentad**:

-Frequencies: rms=**0.009 cm^{-1}** up to J=16

(Tarrago et al. **JMS**, 1992, Ulenikov and al. **JMS**, 2002)

-Intensities: rms= **13%** (Tarrago et al. **JMS**, 1992

- **The ν_2/ν_4 dyad**:

-Frequencies: rms=**0.0004cm^{-1}** up to J=22

(Fusina and al, **J.Mol.Struc.**,2000)

-Intensities: rms=**2%** (Brown and al., **JMS**, 2001)

-Linewidth: self Broadening coefficients

(J. Salem and al, JMS, 2004)

The pentad- 5 micron

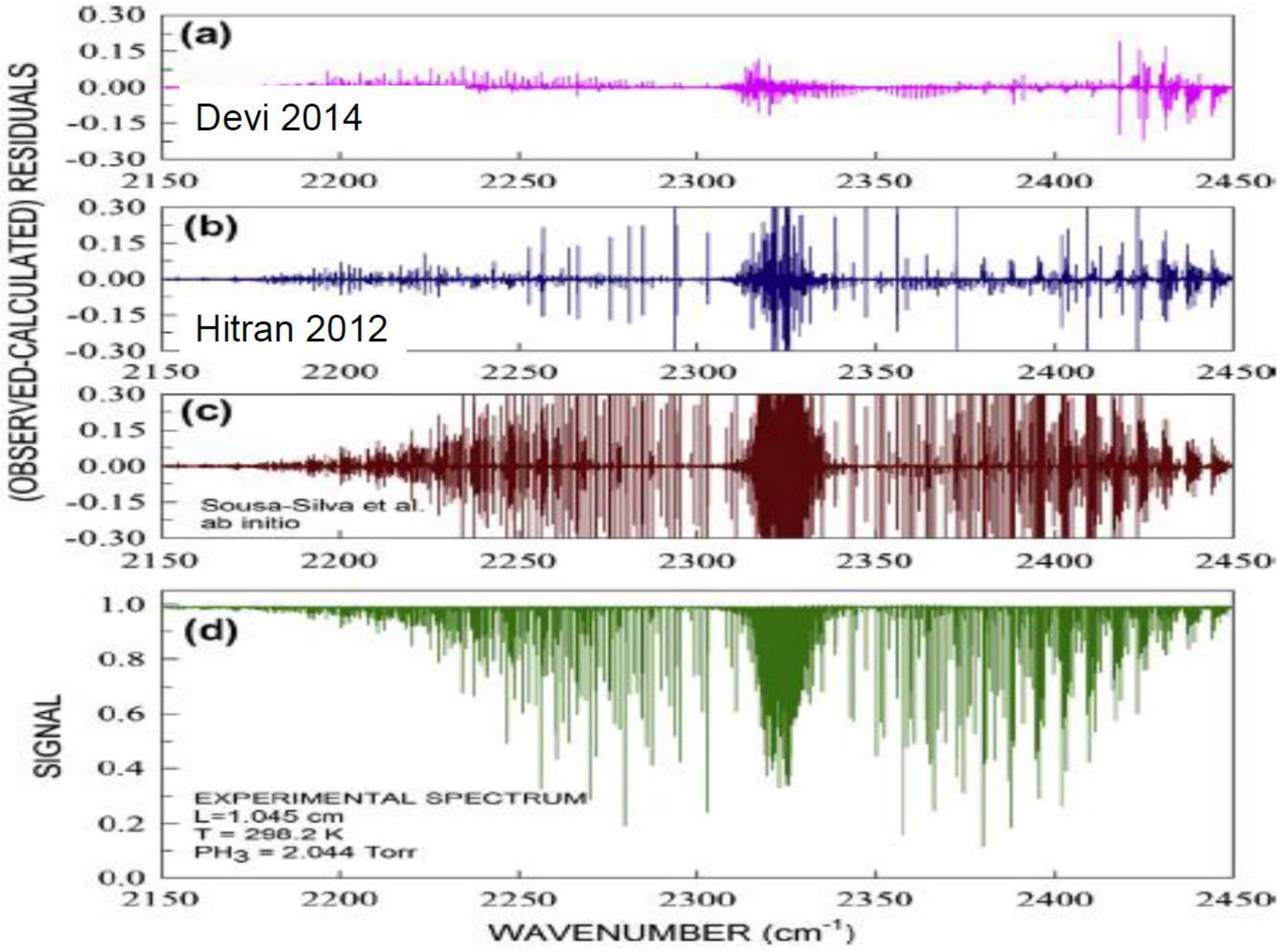
- Over 3400 line positions and 1750 intensities measured and fitted in the pentad bands ($2\nu_2$,$\nu_2+\nu_4$,$2\nu_4$, ν_1 and ν_3 of PH3) by analyzing 9 high-resolution room-temperature spectra recorded with two FTS spectrometers.

5 spectra recorded using the FT spectrometer at PNNL (short path of 1.045 cm) for the band intensities of the strong ν_1 and ν_3 fundamentals. 4 spectra recorded at Kitt Peak for the weak $2\nu_2$ and $\nu_2+\nu_4$ (long path cell of 425 cm).

up to J=14 (rms = 0.00133 cm^{-1}), total line-list consists of 9894 transitions

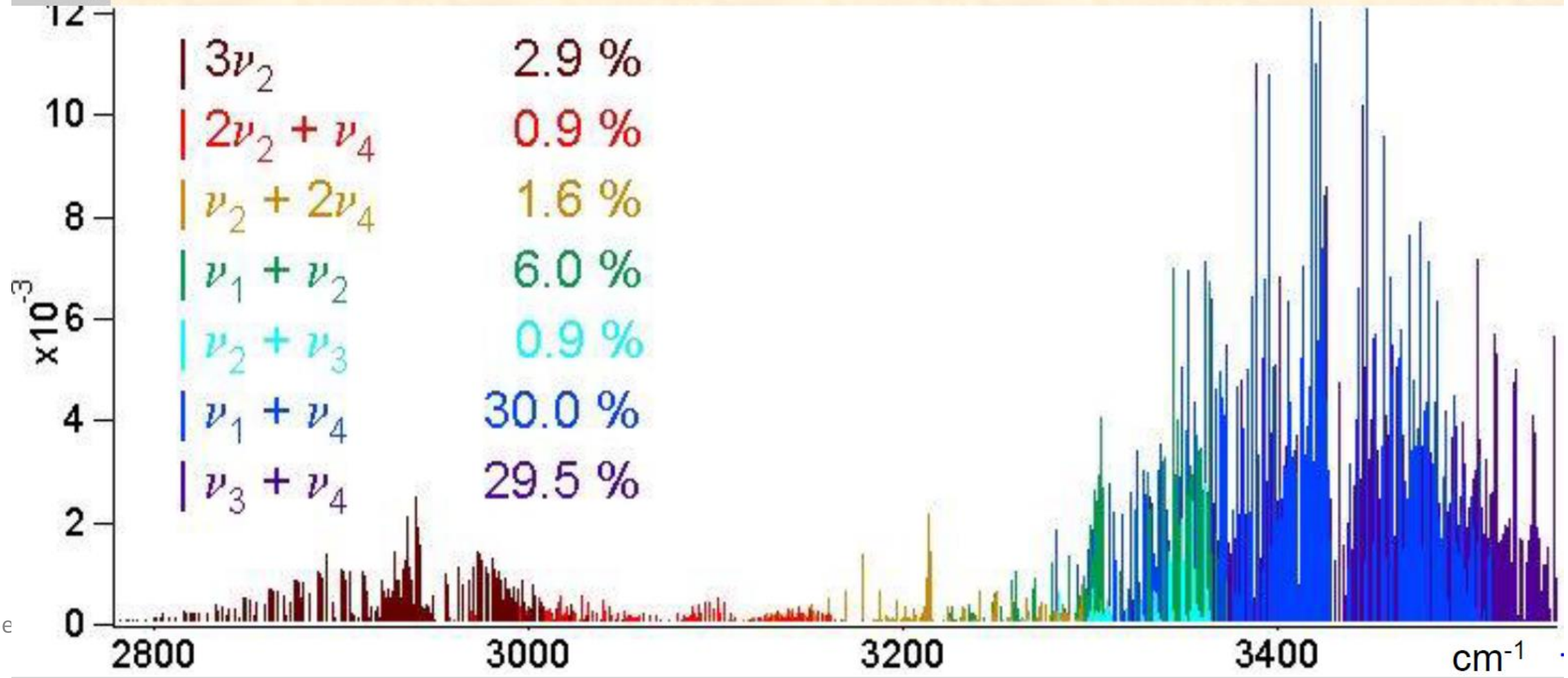
- Our intensity measurements are about 7% higher than previous measurements. This cannot explain the 50% discrepancy observed in the vertical mixing ratios derived by astronomers ! → other effects: aerosol amounts ???

Observed-calculated in the pentad region



ANALYSIS OF THE 3 MICRON REGION :

- Data 2750 - 3600 cm^{-1} : 8075 line positions and intensities obtained by L. R. Brown and R. Butler (Kitt Peak FTS, spectral resolution of 0.0115 cm^{-1}).
- Analysis of spectra: 4095 lines identified.
- 7 vibrational states simultaneously analysed
- 79% of intensity of region accounted for, - Unassigned state is $3\nu_4$



Isotopes

Isotopes can be treated as regular molecular structures : isotopic ratio have no reason to be similar to Solar System values (Warning : terrestrial databases include the « standard » terrestrial ratio)

Special case : some isotopes change the symmetry of the molecule and can therefore have a very different spectroscopy – ex. CH_3D

Partition functions

Statistical physics

From the vibro-rotational calculations we have calculated the energy of upper level of each transition – this energy allows us to calculate the population of every level through Boltzmanna statistics:

$N_i = g_i \, e(-E_i/kT) \, / \, Z$

Where Z is the partition function: Z = summation over all N_i

Emission and absorption coefficients

Calculation of transition probabilities =>

* related to the molecular dipole momentum of the molecule

- Depends on the population of the emitting/absorbing level
- Basis : spontaneous, stimulated and absorption coefficients (Einstein coefficients)
- Emission and radiation : Enstein relations A_{ij}, B_{ij}, B_{ji}

Credit : Hanson, Summer School on Combustion and the Environment, June 19-24, 2022, Princeton, NJ, USA

Definition of line strength and absorption coefficients

See spectral line shapes course : Professor Ronald K. Hanson
https://cefrc.princeton.edu/sites/g/files/toruqf1071/files/documents/Lecture%20Notes%20-%20Hanson.pdf

Lorenz shapes (Collisions OR natural lines)
Gaussian shapes (Doppler thermal motions)

Far wings effects

Very strong lines can dominate the opacity very far from line center: the Lorentz line shape reaches the limit of validity when applied too far from line center

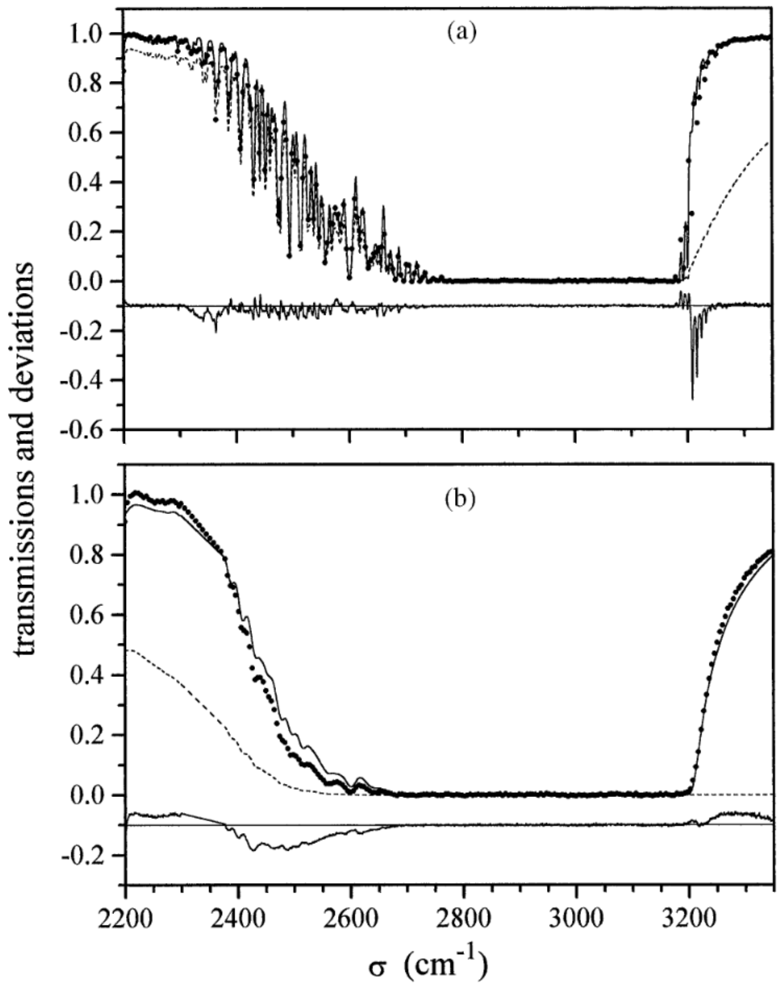
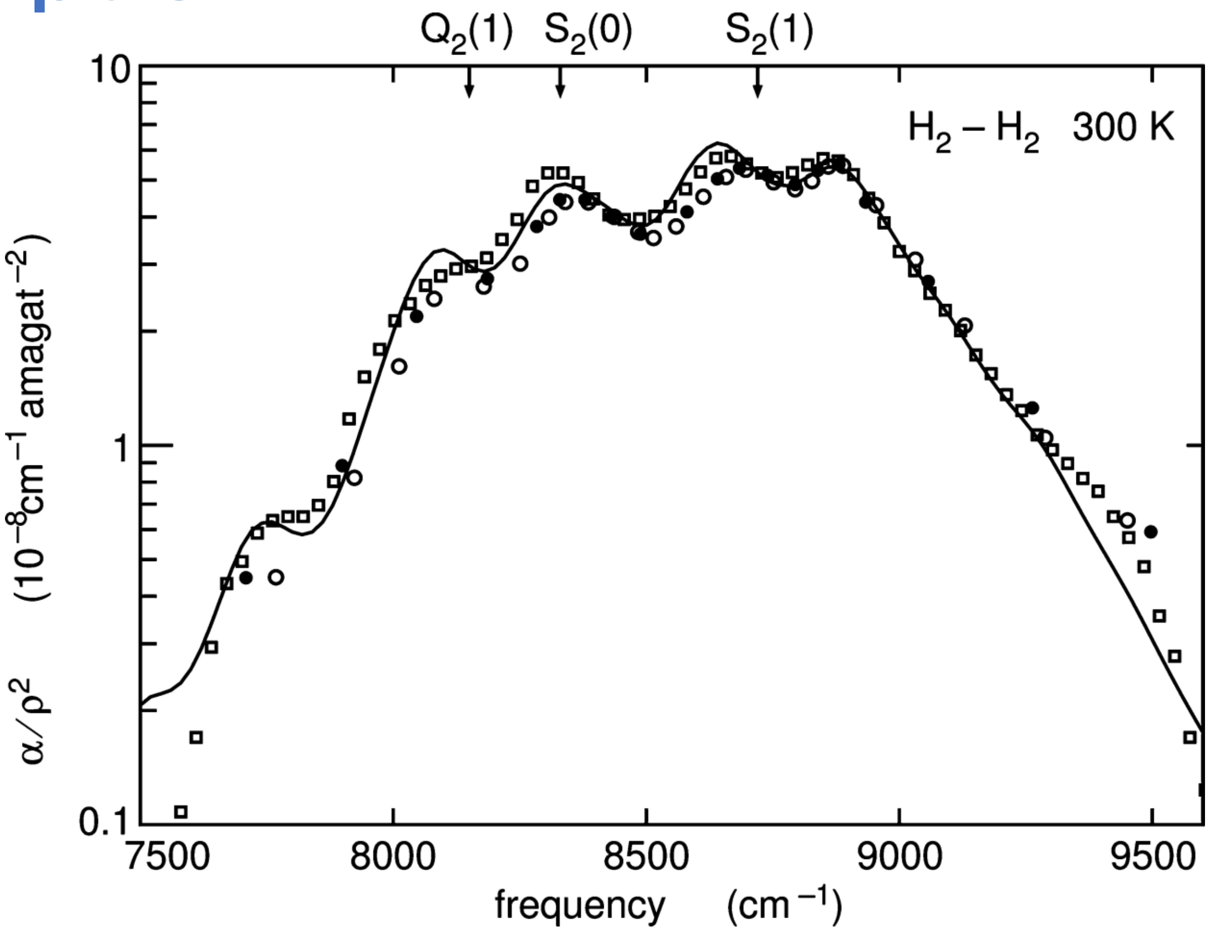


Fig. 1. Transmissions of CH$_4$–H$_2$ mixtures at room temperature (297 K) for a 3 m long path. ● are measured values. —– and - - - - have been calculated with the χ factor of Eq. (2) and purely lorentzian line shapes ($\chi=1$), respectively. (a) $d_{\mathrm{CH_4}}=0.919$ Am, $d_{\mathrm{H_2}}=25.0$ Am. (b) $d_{\mathrm{CH_4}}=1.84$ Am, $d_{\mathrm{H_2}}=163$ Am. Measured-calculated residuals are given below the spectra.

Hartmann et al, 2002

Collision induced absorption

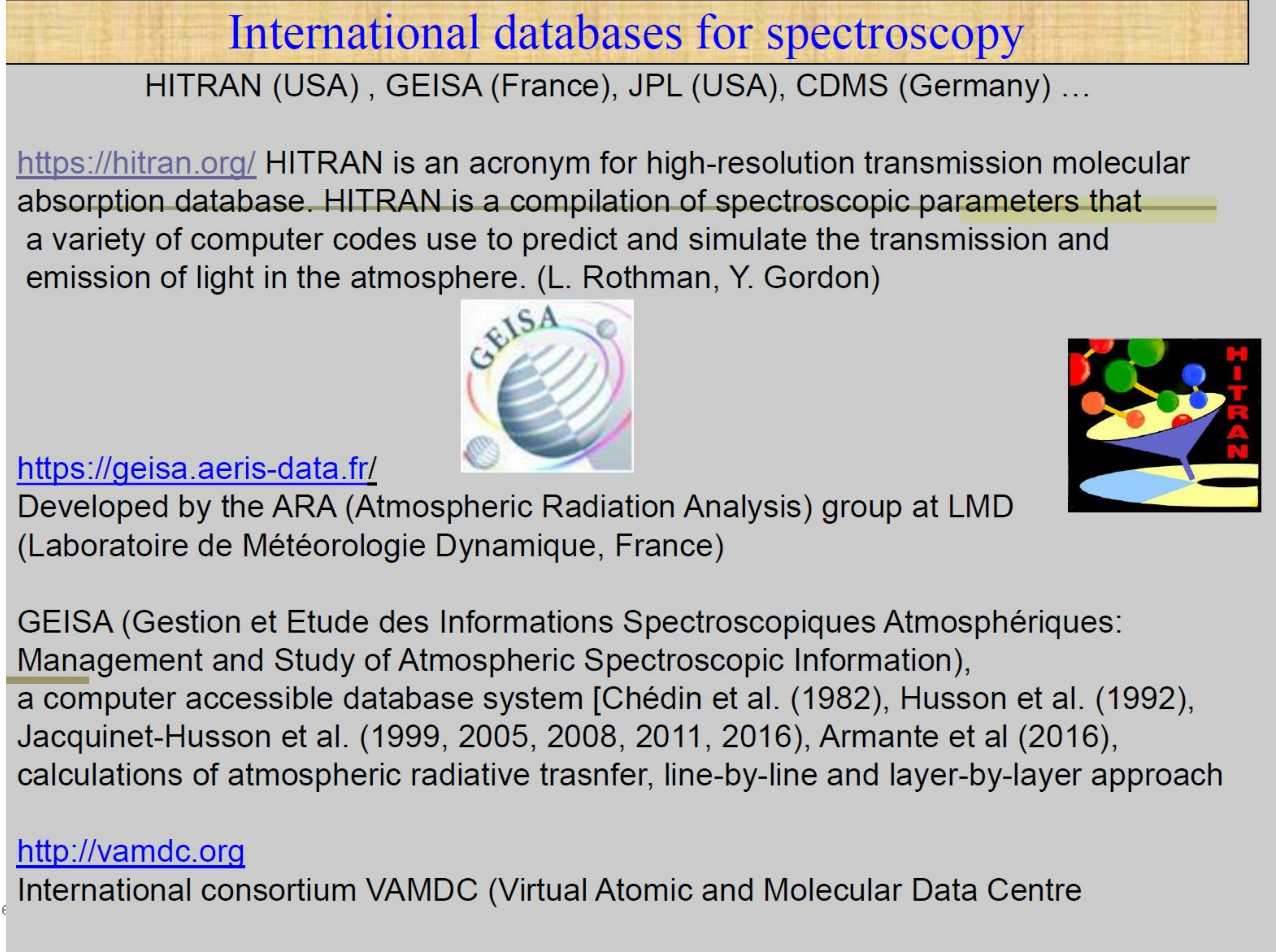
The continuum of atmospheric spectra, outside strong molecular bands, is dominated by quadrupolar effects from homopolar diatomic molecules like N_2 or H_2



Abel et al., J. Phys. Chem. A 2011, 115, 25, 6805–6812

Databases: how to compute a spectroscopic database ?

- Example = Hitran extraction
- How to retrieve the database ?
  - Schrödinger equation in Born-Oppenheimer approximation
  - Calculation of a database ⬄ calculation of the hamiltonian of the molecule
- Practical approaches :
  - combination of prediction/experiments => parametrized hamiltonian
  - Ab initio calculations
  - What is the necessary accuracy for practical use ?



International databases for spectroscopy

HITRAN (USA) , GEISA (France), JPL (USA), CDMS (Germany) …

https://hitran.org/ HITRAN is an acronym for high-resolution transmission molecular absorption database. HITRAN is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere. (L. Rothman, Y. Gordon)

https://geisa.aeris-data.fr/
Developed by the ARA (Atmospheric Radiation Analysis) group at LMD (Laboratoire de Météorologie Dynamique, France)

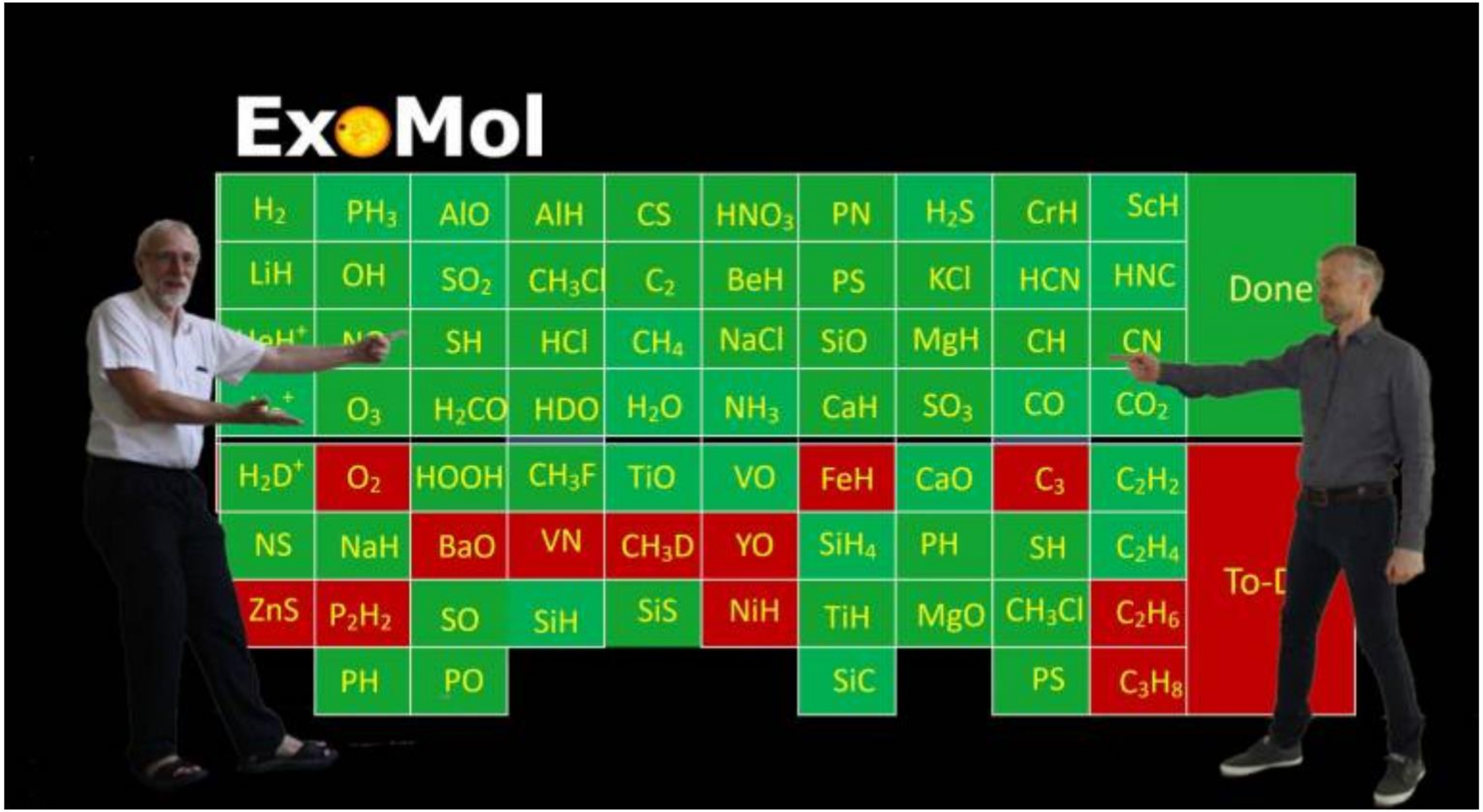
GEISA (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information),
a computer accessible database system [Chédin et al. (1982), Husson et al. (1992), Jacquinet-Husson et al. (1999, 2005, 2008, 2011, 2016), Armante et al (2016), calculations of atmospheric radiative trasnfer, line-by-line and layer-by-layer approach

http://vamdc.org
International consortium VAMDC (Virtual Atomic and Molecular Data Centre

Databases : ExoMol

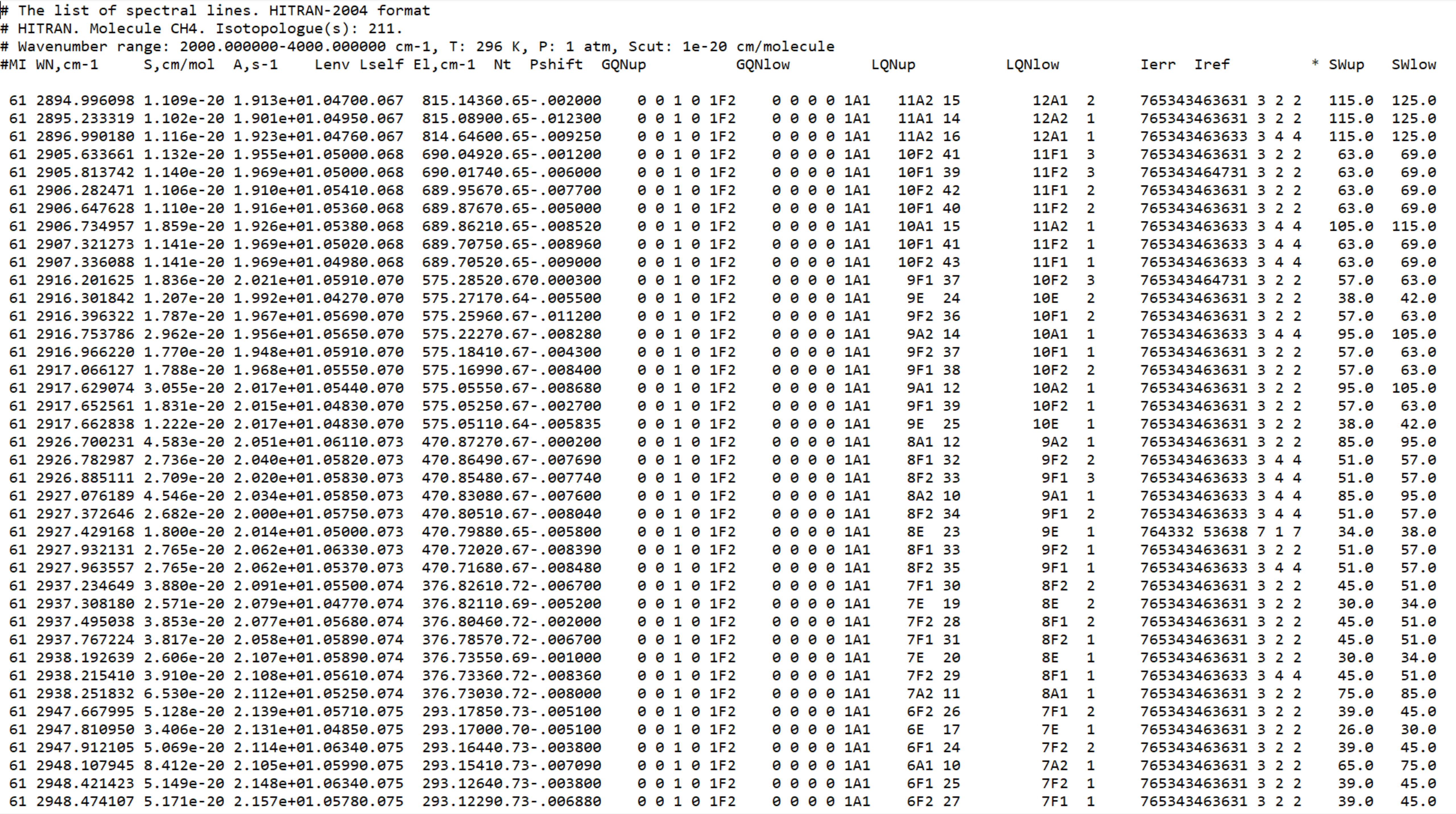
Tennyson et al, JQSRT 2020

Mixture of ab inition calculations and laboratory data



ExoMol

H_2	PH_3	AlO	AlH	CS	HNO_3	PN	H_2S	CrH	ScH	Done
LiH	OH	SO_2	CH_3Cl	C_2	BeH	PS	KCl	HCN	HNC	
HeH^+	NO	SH	HCl	CH_4	NaCl	SiO	MgH	CH	CN	
[illegible]	O_3	H_2CO	HDO	H_2O	NH_3	CaH	SO_3	CO	CO_2	
H_2D^+	O_2	HOOH	CH_3F	TiO	VO	FeH	CaO	C_3	C_2H_2	To-
NS	NaH	BaO	VN	CH_3D	YO	SiH_4	PH	SH	C_2H_4	
ZnS	P_2H_2	SO	SiH	SiS	NiH	TiH	MgO	CH_3Cl	C_2H_6	
	PH	PO				SiC		PS	C_3H_8	



```
# The list of spectral lines. HITRAN-2004 format
# HITRAN. Molecule CH4. Isotopologue(s): 211.
# Wavenumber range: 2000.000000-4000.000000 cm-1, T: 296 K, P: 1 atm, Scut: 1e-20 cm/molecule
#MI WN,cm-1     S,cm/mol  A,s-1    Lenv Lself El,cm-1  Nt  Pshift  GQNup          GQNlow         LQNup         LQNlow        Ierr  Iref        * SWup   SWlow

 61 2894.996098 1.109e-20 1.913e+01.04700.067  815.14360.65-.002000   0 0 1 0 1F2   0 0 0 0 1A1   11A2 15       12A1  2       765343463631 3 2 2  115.0  125.0
 61 2895.233319 1.102e-20 1.901e+01.04950.067  815.08900.65-.012300   0 0 1 0 1F2   0 0 0 0 1A1   11A1 14       12A2  1       765343463631 3 2 2  115.0  125.0
 61 2896.990180 1.116e-20 1.923e+01.04760.067  814.64600.65-.009250   0 0 1 0 1F2   0 0 0 0 1A1   11A2 16       12A1  1       765343463633 3 4 4  115.0  125.0
 61 2905.633661 1.132e-20 1.955e+01.05000.068  690.04920.65-.001200   0 0 1 0 1F2   0 0 0 0 1A1   10F2 41       11F1  3       765343463631 3 2 2   63.0   69.0
 61 2905.813742 1.140e-20 1.969e+01.05000.068  690.01740.65-.006000   0 0 1 0 1F2   0 0 0 0 1A1   10F1 39       11F2  3       765343464731 3 2 2   63.0   69.0
 61 2906.282471 1.106e-20 1.910e+01.05410.068  689.95670.65-.007700   0 0 1 0 1F2   0 0 0 0 1A1   10F2 42       11F1  2       765343463631 3 2 2   63.0   69.0
 61 2906.647628 1.110e-20 1.916e+01.05360.068  689.87670.65-.005000   0 0 1 0 1F2   0 0 0 0 1A1   10F1 40       11F2  2       765343463631 3 2 2   63.0   69.0
 61 2906.734957 1.859e-20 1.926e+01.05380.068  689.86210.65-.008520   0 0 1 0 1F2   0 0 0 0 1A1   10A1 15       11A2  1       765343463633 3 4 4  105.0  115.0
 61 2907.321273 1.141e-20 1.969e+01.05020.068  689.70750.65-.008960   0 0 1 0 1F2   0 0 0 0 1A1   10F1 41       11F2  1       765343463633 3 4 4   63.0   69.0
 61 2907.336088 1.141e-20 1.969e+01.04980.068  689.70520.65-.009000   0 0 1 0 1F2   0 0 0 0 1A1   10F2 43       11F1  1       765343463633 3 4 4   63.0   69.0
 61 2916.201625 1.836e-20 2.021e+01.05910.070  575.28520.670.000300   0 0 1 0 1F2   0 0 0 0 1A1    9F1 37       10F2  3       765343464731 3 2 2   57.0   63.0
 61 2916.301842 1.207e-20 1.992e+01.04270.070  575.27170.64-.005500   0 0 1 0 1F2   0 0 0 0 1A1    9E  24       10E   2       765343463631 3 2 2   38.0   42.0
 61 2916.396322 1.787e-20 1.967e+01.05690.070  575.25960.67-.011200   0 0 1 0 1F2   0 0 0 0 1A1    9F2 36       10F1  2       765343463631 3 2 2   57.0   63.0
 61 2916.753786 2.962e-20 1.956e+01.05650.070  575.22270.67-.008280   0 0 1 0 1F2   0 0 0 0 1A1    9A2 14       10A1  1       765343463633 3 4 4   95.0  105.0
 61 2916.966220 1.770e-20 1.948e+01.05910.070  575.18410.67-.004300   0 0 1 0 1F2   0 0 0 0 1A1    9F2 37       10F1  1       765343463631 3 2 2   57.0   63.0
 61 2917.066127 1.788e-20 1.968e+01.05550.070  575.16990.67-.008400   0 0 1 0 1F2   0 0 0 0 1A1    9F1 38       10F2  2       765343463631 3 2 2   57.0   63.0
 61 2917.629074 3.055e-20 2.017e+01.05440.070  575.05550.67-.008680   0 0 1 0 1F2   0 0 0 0 1A1    9A1 12       10A2  1       765343463631 3 2 2   95.0  105.0
 61 2917.652561 1.831e-20 2.015e+01.04830.070  575.05250.67-.002700   0 0 1 0 1F2   0 0 0 0 1A1    9F1 39       10F2  1       765343463631 3 2 2   57.0   63.0
 61 2917.662838 1.222e-20 2.017e+01.04830.070  575.05110.64-.005835   0 0 1 0 1F2   0 0 0 0 1A1    9E  25       10E   1       765343463631 3 2 2   38.0   42.0
 61 2926.700231 4.583e-20 2.051e+01.06110.073  470.87270.67-.000200   0 0 1 0 1F2   0 0 0 0 1A1    8A1 12        9A2  1       765343463631 3 2 2   85.0   95.0
 61 2926.782987 2.736e-20 2.040e+01.05820.073  470.86490.67-.007690   0 0 1 0 1F2   0 0 0 0 1A1    8F1 32        9F2  2       765343463633 3 4 4   51.0   57.0
 61 2926.885111 2.709e-20 2.020e+01.05830.073  470.85480.67-.007740   0 0 1 0 1F2   0 0 0 0 1A1    8F2 33        9F1  3       765343463633 3 4 4   51.0   57.0
 61 2927.076189 4.546e-20 2.034e+01.05850.073  470.83080.67-.007600   0 0 1 0 1F2   0 0 0 0 1A1    8A2 10        9A1  1       765343463633 3 4 4   85.0   95.0
 61 2927.372646 2.682e-20 2.000e+01.05750.073  470.80510.67-.008040   0 0 1 0 1F2   0 0 0 0 1A1    8F2 34        9F1  2       765343463633 3 4 4   51.0   57.0
 61 2927.429168 1.800e-20 2.014e+01.05000.073  470.79880.65-.005800   0 0 1 0 1F2   0 0 0 0 1A1    8E  23        9E   1       764332 53638 7 1 7   34.0   38.0
 61 2927.932131 2.765e-20 2.062e+01.06330.073  470.72020.67-.008390   0 0 1 0 1F2   0 0 0 0 1A1    8F1 33        9F2  1       765343463631 3 2 2   51.0   57.0
 61 2927.963557 2.765e-20 2.062e+01.05370.073  470.71680.67-.008480   0 0 1 0 1F2   0 0 0 0 1A1    8F2 35        9F1  1       765343463633 3 4 4   51.0   57.0
 61 2937.234649 3.880e-20 2.091e+01.05500.074  376.82610.72-.006700   0 0 1 0 1F2   0 0 0 0 1A1    7F1 30        8F2  2       765343463631 3 2 2   45.0   51.0
 61 2937.308180 2.571e-20 2.079e+01.04770.074  376.82110.69-.005200   0 0 1 0 1F2   0 0 0 0 1A1    7E  19        8E   2       765343463631 3 2 2   30.0   34.0
 61 2937.495038 3.853e-20 2.077e+01.05680.074  376.80460.72-.002000   0 0 1 0 1F2   0 0 0 0 1A1    7F2 28        8F1  2       765343463631 3 2 2   45.0   51.0
 61 2937.767224 3.817e-20 2.058e+01.05890.074  376.78570.72-.006700   0 0 1 0 1F2   0 0 0 0 1A1    7F1 31        8F2  1       765343463631 3 2 2   45.0   51.0
 61 2938.192639 2.606e-20 2.107e+01.05890.074  376.73550.69-.001000   0 0 1 0 1F2   0 0 0 0 1A1    7E  20        8E   1       765343463631 3 2 2   30.0   34.0
 61 2938.215410 3.910e-20 2.108e+01.05610.074  376.73360.72-.008360   0 0 1 0 1F2   0 0 0 0 1A1    7F2 29        8F1  1       765343463633 3 4 4   45.0   51.0
 61 2938.251832 6.530e-20 2.112e+01.05250.074  376.73030.72-.008000   0 0 1 0 1F2   0 0 0 0 1A1    7A2 11        8A1  1       765343463631 3 2 2   75.0   85.0
 61 2947.667995 5.128e-20 2.139e+01.05710.075  293.17850.73-.005100   0 0 1 0 1F2   0 0 0 0 1A1    6F2 26        7F1  2       765343463631 3 2 2   39.0   45.0
 61 2947.810950 3.406e-20 2.131e+01.04850.075  293.17000.70-.005100   0 0 1 0 1F2   0 0 0 0 1A1    6E  17        7E   1       765343463631 3 2 2   26.0   30.0
 61 2947.912105 5.069e-20 2.114e+01.06340.075  293.16440.73-.003800   0 0 1 0 1F2   0 0 0 0 1A1    6F1 24        7F2  2       765343463631 3 2 2   39.0   45.0
 61 2948.107945 8.412e-20 2.105e+01.05990.075  293.15410.73-.007090   0 0 1 0 1F2   0 0 0 0 1A1    6A1 10        7A2  1       765343463631 3 2 2   65.0   75.0
 61 2948.421423 5.149e-20 2.148e+01.06340.075  293.12640.73-.003800   0 0 1 0 1F2   0 0 0 0 1A1    6F1 25        7F2  1       765343463631 3 2 2   39.0   45.0
 61 2948.474107 5.171e-20 2.157e+01.05780.075  293.12290.73-.006880   0 0 1 0 1F2   0 0 0 0 1A1    6F2 27        7F1  1       765343463631 3 2 2   39.0   45.0
```

Application to exoplanets

The spectroscopy of exoplanets collect the most challenging parts for spectroscopy : high temperatures (=> high J, hot vibrational bands), large number of molecules and complex atmospheric structures

Difficulties for high temperature spectra

- Large number of overtones
- Accuracy of the database (missing bands, accuracy of coefficients at high temperatures)

The need for continued research in cooperation with spectroscopic group is mandatory to adapt the needs of exoplanets community with spectroscopic research !