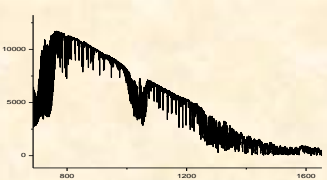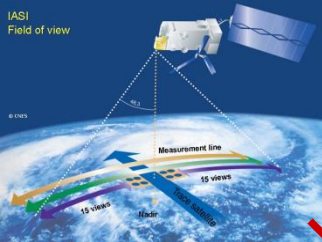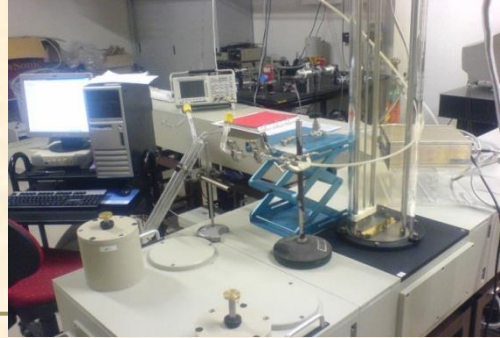# Laboratory spectroscopy and spectral analysis.

Isabelle KLEINER

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS et Université Paris-Est et Université de Paris Cité, Créteil, FRANCE

Exo-atmospheres, Les Houches school of physics, Haute Savoie, France
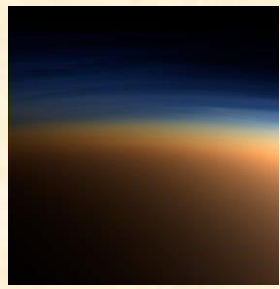
September 12th -23th 2022

Laboratory spectra

Atmospheric or Astrophysical spectra
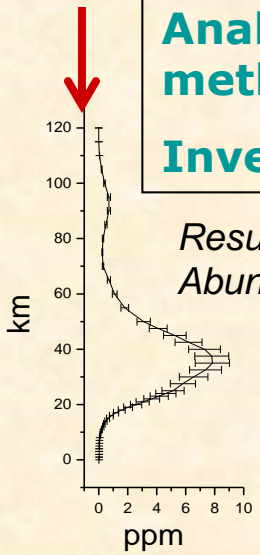
CASSINI SPACECRAFT

Spectroscopic Data: databases
Line positions
Line intensities
Line profiles

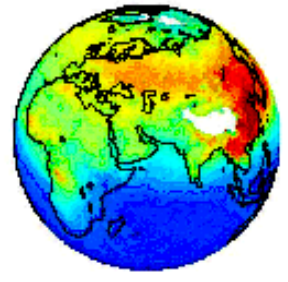**Theoretical Model Spectral analysis**

+

Analysis method/ Inversion

Result: Abundance profile

Chemistry and pollution model

$H\Psi = E\Psi$

Ab initio   Effectif Hamiltonians

2

Molecular spectroscopy and astrophysics

IRAM: Spain

GBT: USA

ESO-VLT: Chili

Very Large Telescope

1 Antenna of 30m
67- 282 GHz ,

Green Bank Telescope
100m, **1.4 , 24, 90, GHz**

IRAM: France

CARMA: USA

CFHT

Canadian French Hawai Telescope

5 antenna of 15m
81-115 GHz

Combined Array for Research in Millimeter-wave Astronomy
23 antenna, **27- 270 GHz**
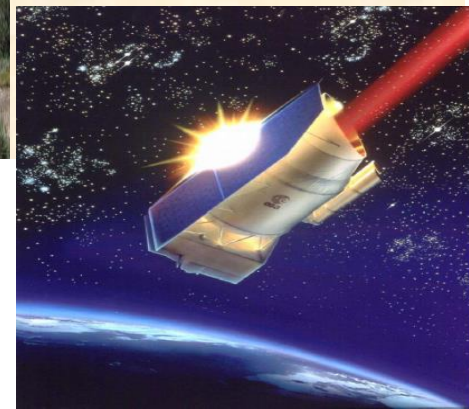
ISO, Infrared Space Laboratory 1995-98

ALMA: The Atacama Large Millimeter/submillimeter Array, Chili

64 antennes of 12m (sur 18.5km)

Molecules in the Interstellar Medium or Circumstellar Shells : 02/2009
CDMS : Cologne Data base http://www.astro.uni-koeln.de/site/vorhersagen/molecules

Molecules in Space

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	13 atoms
H_2	C_3	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	C_6H_6	$HC_{11}N$
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	$CH_3OC_2H_5$	
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$ (?)		$(CH_2OH)_2CO$ (?)	
C_2	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	H_2NCH_2COOH (?)			
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	H_2C_6	HC_7N	CH_3CH_2CHO			
CH^+	HCN	C_2H_2	CH_2CN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4	CH_3SH	c-C_2H_4O	l-HC_6H (?)	CH_3CONH_2				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)					
CO^+	HCS^+	$HNCH^+$	HC_2NC	HC_2CHO		$H_2CCCHCN$					
CP	HOC^+	HNCO	HCOOH	NH_2CHO							
SiC	H_2O	HNCS	H_2CNH	C_5N							
HCl	H_2S	$HOCO^+$	H_2C_2O	l-HC_4H							
KCl	HNC	H_2CO	H_2NCN	l-HC_4N							
NH	HNO	H_2CN	HNC_3	c-H_2C_3O							
NO	MgCN	H_2CS	SiH_4								
NS	MgNC	H_3O^+	H_2COH^+								
NaCl	N_2H^+	c-SiC_3									
OH	N_2O	C_3H									
PN	NaCN										
SO	OCS										

More than 200 detected molecules

Based on intensive laboratory work!

Spatial Observatories

Herschel space telescope, 2009-2013; sub millimeter waves : 55 à 672 µm (Far infrared)
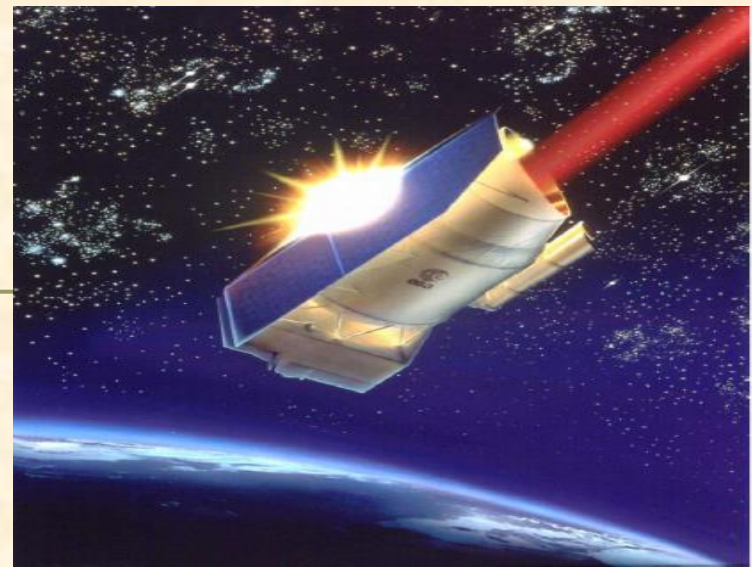
ISO, Infrared Space Observatory 1995-98; LWS: 2,5-45 µm SWS : 45-197µm

James Webb space telescope, 2021
Near infrared: 0,6 à 5,3 µm
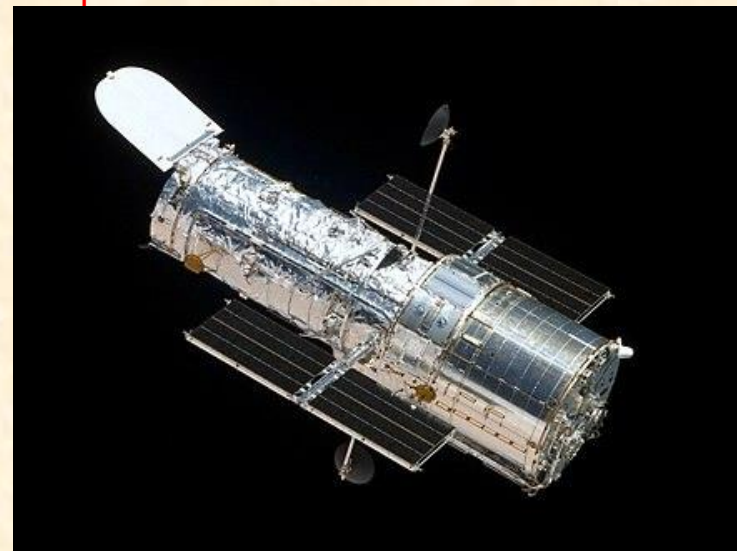
Hubble Space telescope, 1990-
Near UV, VIS, NIR; 115-2500 nm

The James Webb telescope and exoplanets
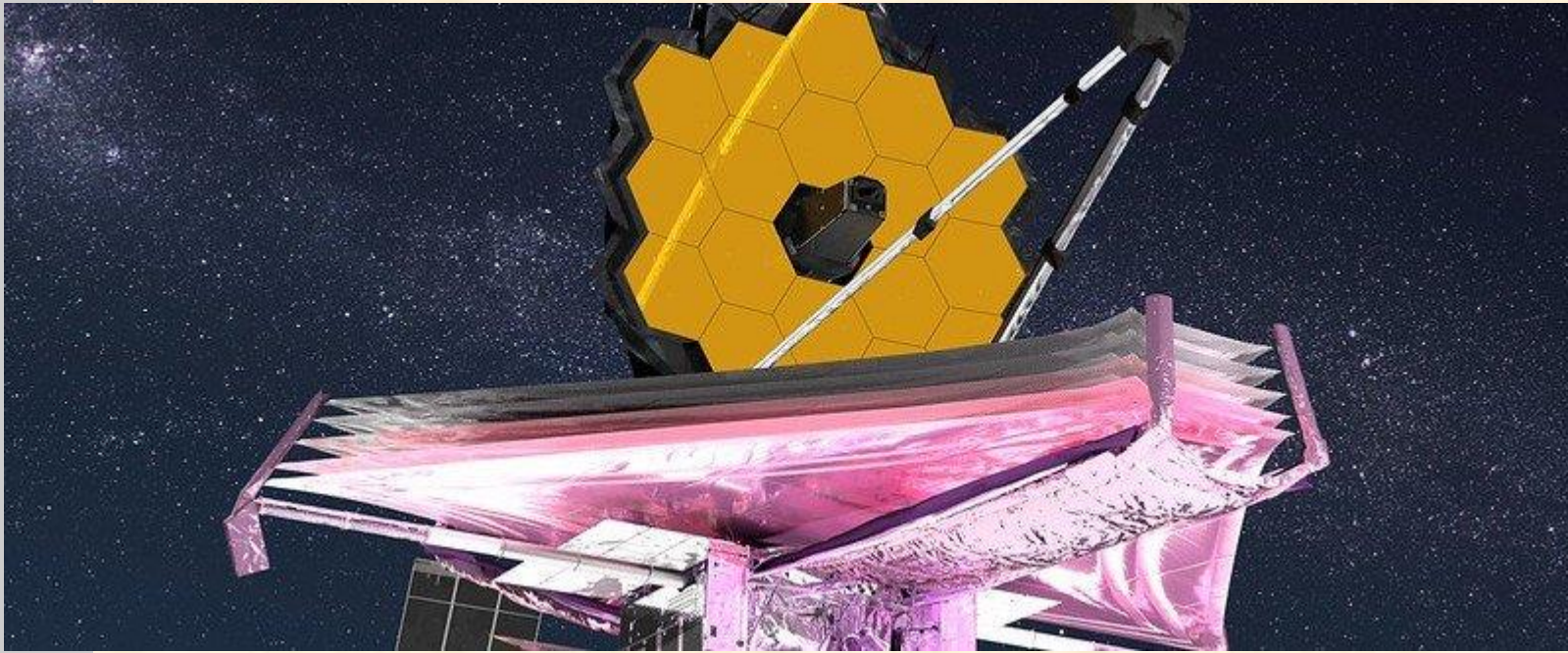
From the visible range (0.6 micron) to middle infrared (28 microns). Le JWST has a 6.6m mirror

Will allow to study the exoplanet atmospheres

Ariel, the Atmospheric Remote-sensing Infrared Exoplanet Large-survey
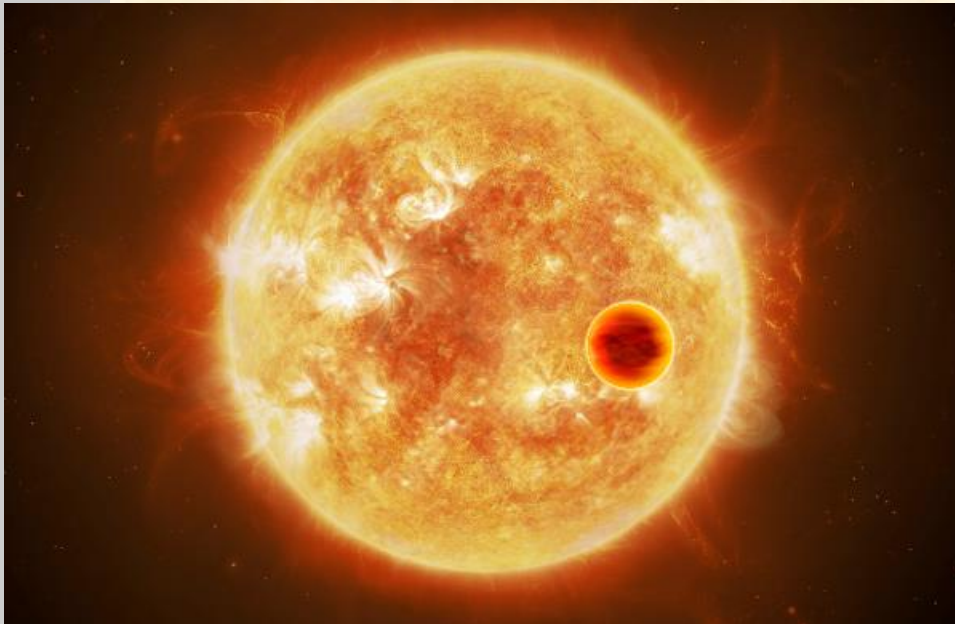
Hot exoplanet. *Credits: ESA/ATG medialab,* [CC BY-SA 3.0 IGO](#)

What are the conditions for planet formation and the emergence of life? Ariel will study what exoplanets are made of, how they formed and how they evolve, by surveying a diverse sample of around 1000 planetary atmospheres simultaneously in visible and infrared wavelengths.

It is the first mission dedicated to measuring the chemical composition and thermal structures of exoplanets
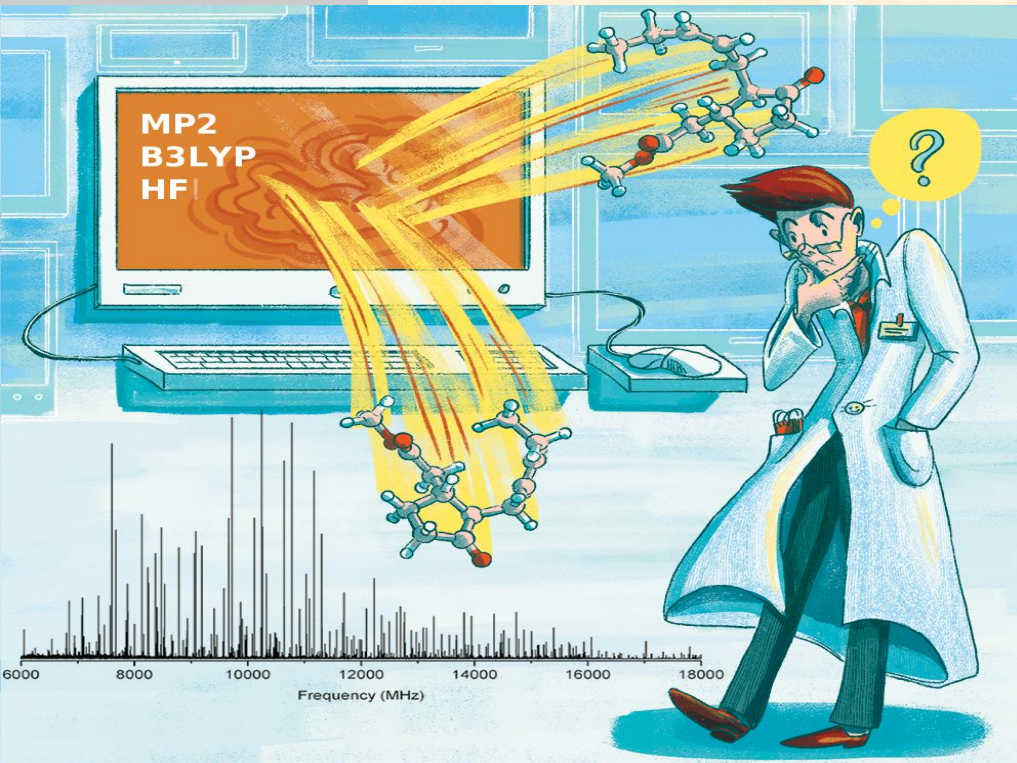
The basics …

Spectral range and molecular motions
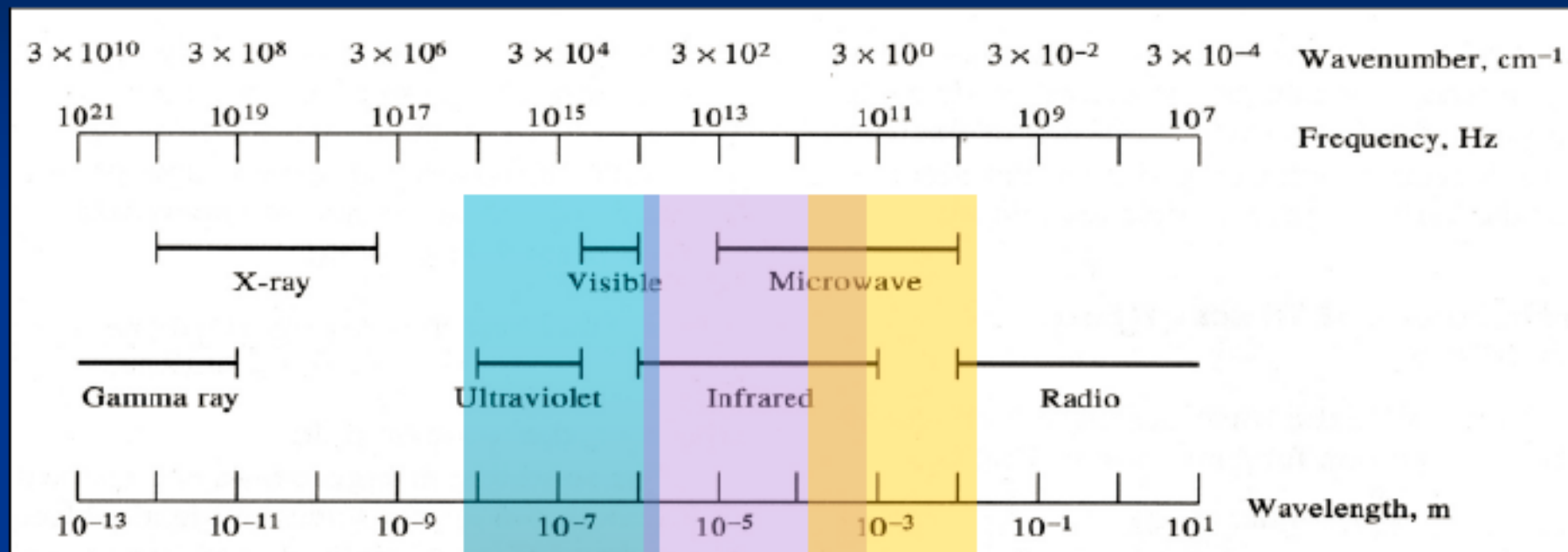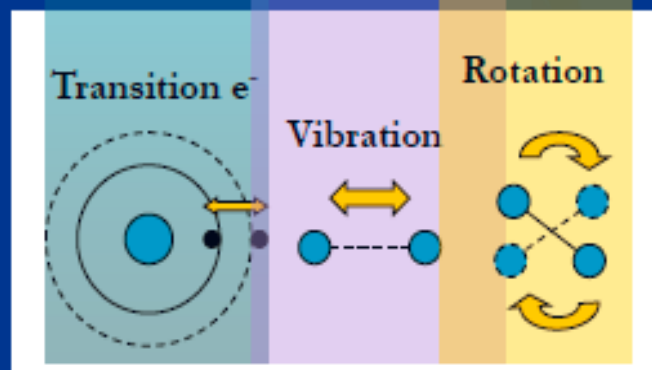
Electronic structure is solved by " freezing " the nuclei at fixed positions and by resolving electronic Schrödinger equation :

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

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

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

$$U = E_{el} + V_{nn} \qquad\qquad (7)$$

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

For a diatomic molecule
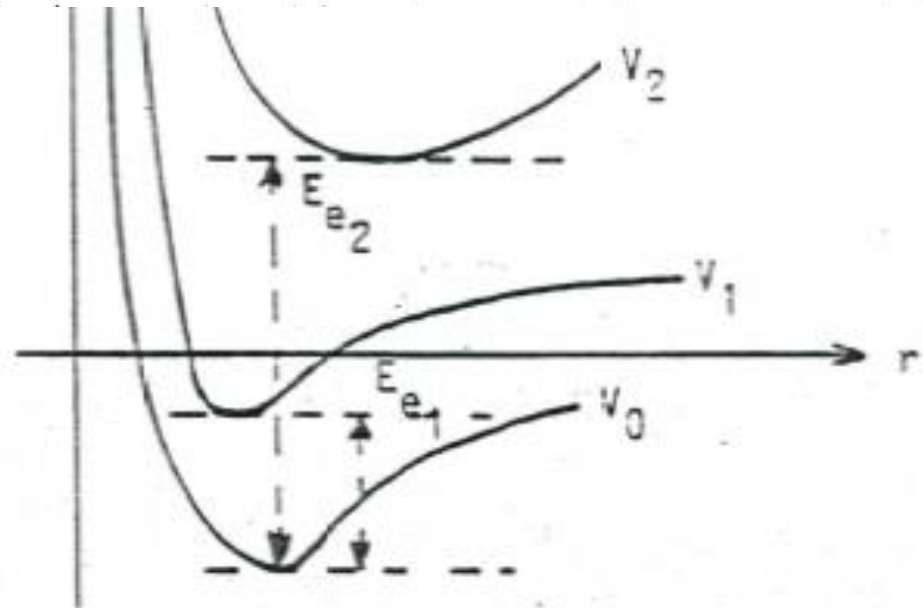
If the potential energy curves are well separated

$$E \sim E_e + E_v + E_r$$

Electron Motions

Nuclei motions

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

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

Vis – UV

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

Electronic transition (in optical or uv)

Excited electronic state.

dissociation energy

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

100 μm – 2 μm

infrared

Ground state

3 – 300 GHz
(0.1 – 10 cm^{-1})

10 cm – 1 mm
microwave

Vibrational transition (in infrared)

Rotational transition (in microwave)

Energy

Internuclear separation
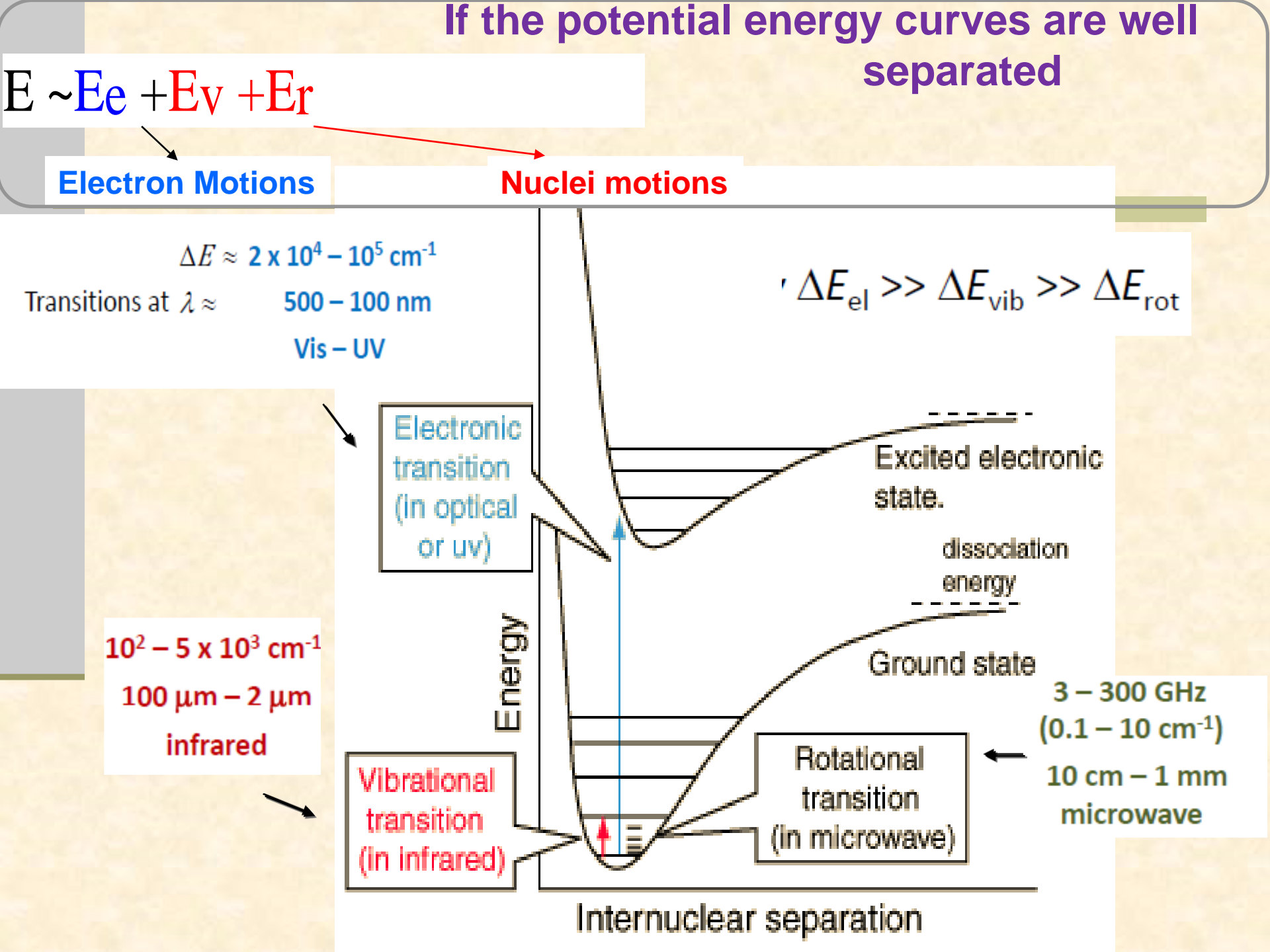
3 types of nuclear motions

bending

symmetric stretching

asymmetric stretching
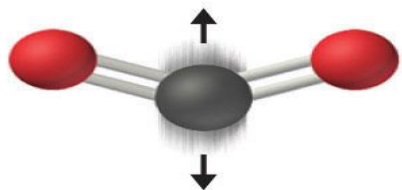
vibrational motion
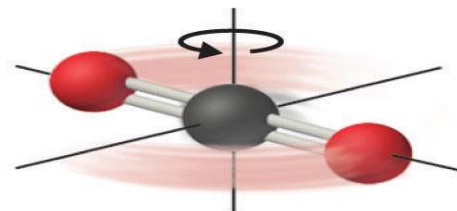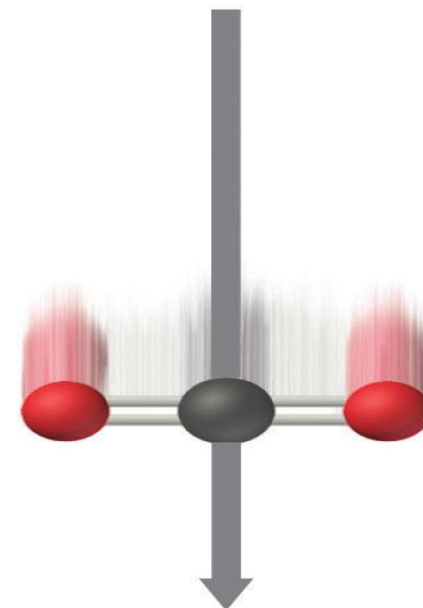
rotational motion

translational motion

Harmonic
Oscillator
model

Rigid rotor
model

Can be separated
From the other motions
Energy = constante

Vibration: Harmonic and anharmonic oscillators

$$V_{har} = \frac{1}{2}k(r - r_e)^2$$

Energy

$$V_{anh} = \sum_i \frac{1}{i!} k_i (r - r_e)^i$$

dissociation

4

3

2

1

3

2

1

v = 0   v = 0

r

r_e r

0
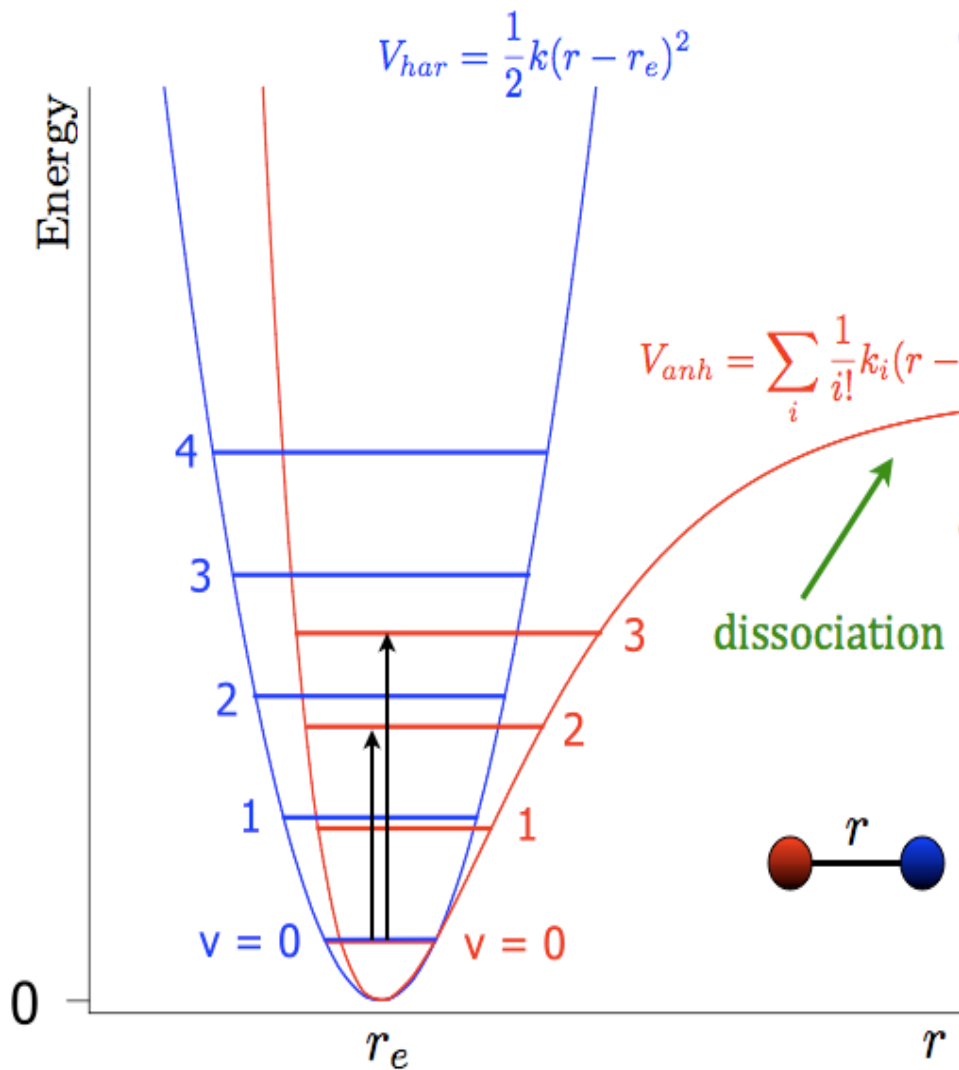
- Harmonic oscillator :

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

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

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

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

On the IR spectrum, weobserve :

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

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

$v=3$ — 2e harmonique $(3,0)$

$v=2$ — $1^{ère}$ harmonique $(2,0)$

$v=1$ (overtone)

$v=0$ — bande fondamentale $(v,v')(1,0)$
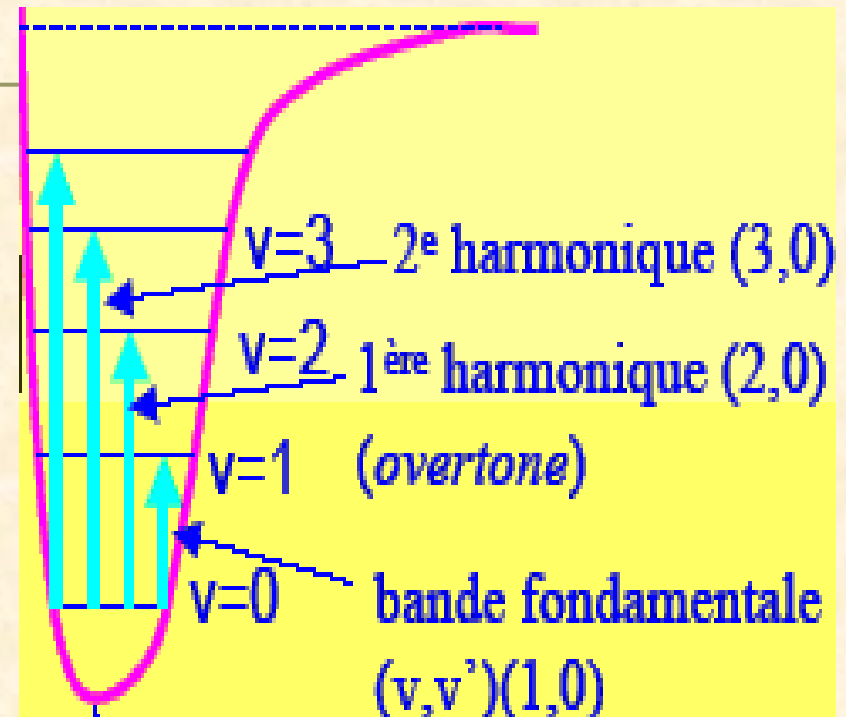
- Combination bands ($v_1 + v_2$ for example) : simultaneous excitation of several fundamental vibrations

- Hot bands: initial levels are not $v = 0$

What about the rotational motion in molecules?

The Trappists: a Belgian tradition…« *Westvleteren, Westmalle, Orval, Chimay...*
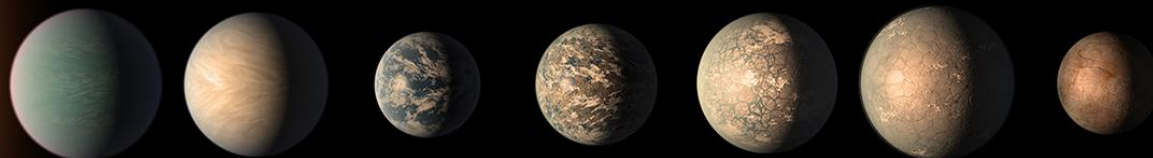
Moments of inertia, rotational angular momentum

Linear Motion

x   m
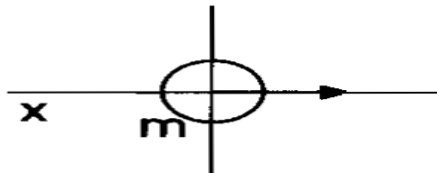
Linear Motion

Angular Motion

θ   r

m
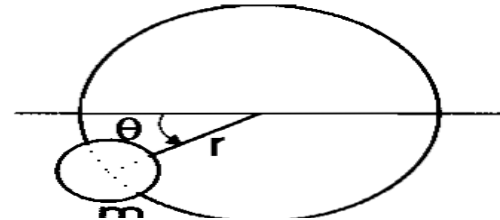
Angular Motion

Linear Motion	Position	Angular Motion
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	
$E_k = \dfrac{1}{2}mv^2 = p^2/2m$		$E_k = \dfrac{1}{2}I\omega^2 = J^2/2I$

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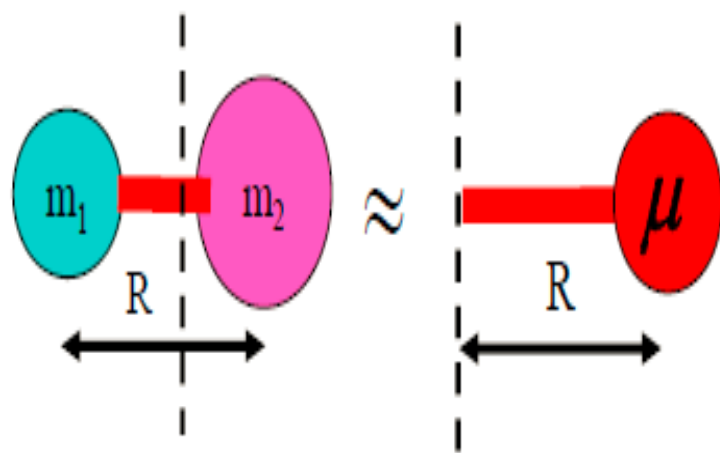
$$I = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 = \mu R^2$$

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

Definition: The moment of inertia I of centre of mass is given by;
$$I = \sum_i m_i r_i^2$$
where m_i is the mass of the ith particle and r_i is its perpendicular distance from the axis
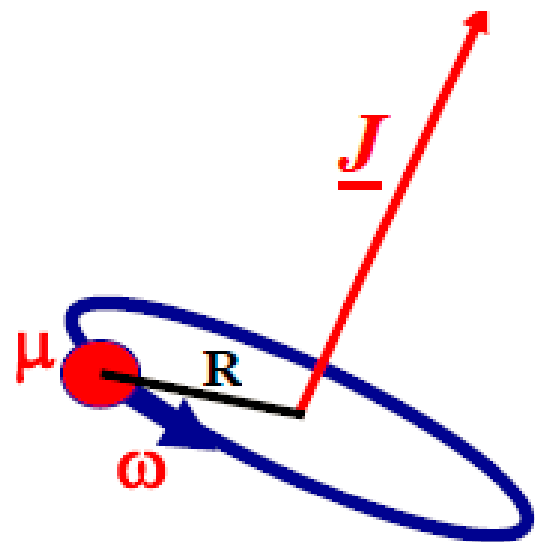
The angular momentum, $J = I\omega$ (c.f. $p = mv$)

The rotational kinetic energy, $E = J^2/2I = \frac{1}{2} I \omega^2$

(c.f. $E = p^2/2m = \frac{1}{2}mv^2$)

From diatomics   to   polyatomic molecules

$$E = J^2/2I = \tfrac{1}{2} I \omega^2$$

$$\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$$

$$J = I\omega$$

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

Rotational energies: how to calculate them ?

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

$$J = I\omega$$

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

Rotational constants

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

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

Molecules classification

- **Classification** of the molecules

  - *Linear* molecules : $I_a = 0$, $I_b = I_c$ (CO_2, HCN) **+CO, HF**)

  - *Spherical* tops : $I_a = I_b = I_c$ (CH_4, **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)

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

In general we require three such rotational constants:

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

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

I_a

I_c

I_b
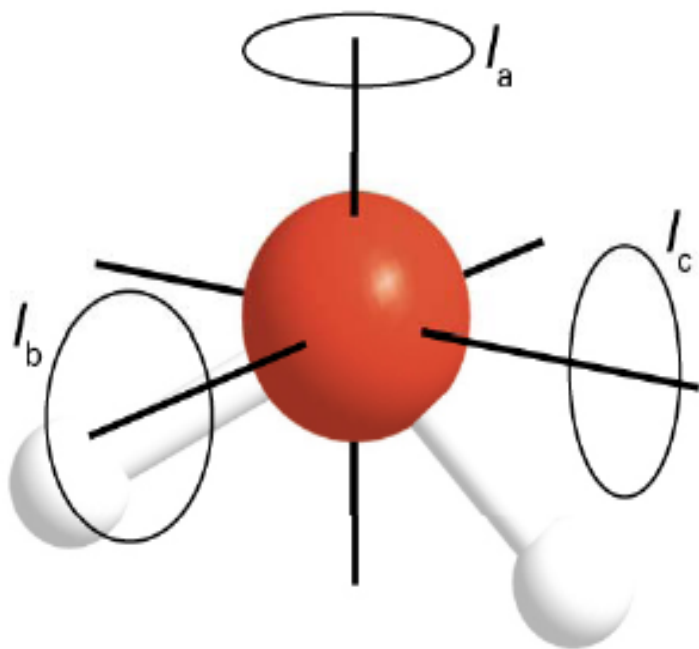
H_2O molecule

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

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

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

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

$$\mathbf{J^2} \, |\Psi_r> = \mathbf{\textcolor{red}{J}(\textcolor{red}{J}+1)} \, |\Psi_r>$$

$$\mathbf{J_z} \, |\Psi_r> = \mathbf{\textcolor{red}{K}} \, |\Psi_r>$$

$\textcolor{red}{J}$ and $\textcolor{red}{K}$ are the quantum numbers for rotation

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

J = 0, 1, 2, …

repérer la molécule dans le système d'axes

Rotational energies for diatomic or linear molecules

$$E_J = BJ(J+1)$$

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

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

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

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

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

	$\tilde{B}$
H$_2$	60.85 cm^{-1}
CO	1.93 cm^{-1}
HCl	10.59 cm^{-1}

Wavenumber / cm^{-1}

Energy	J
30B	5
20B	4
12B	3
6B	2
2B	1
0	0
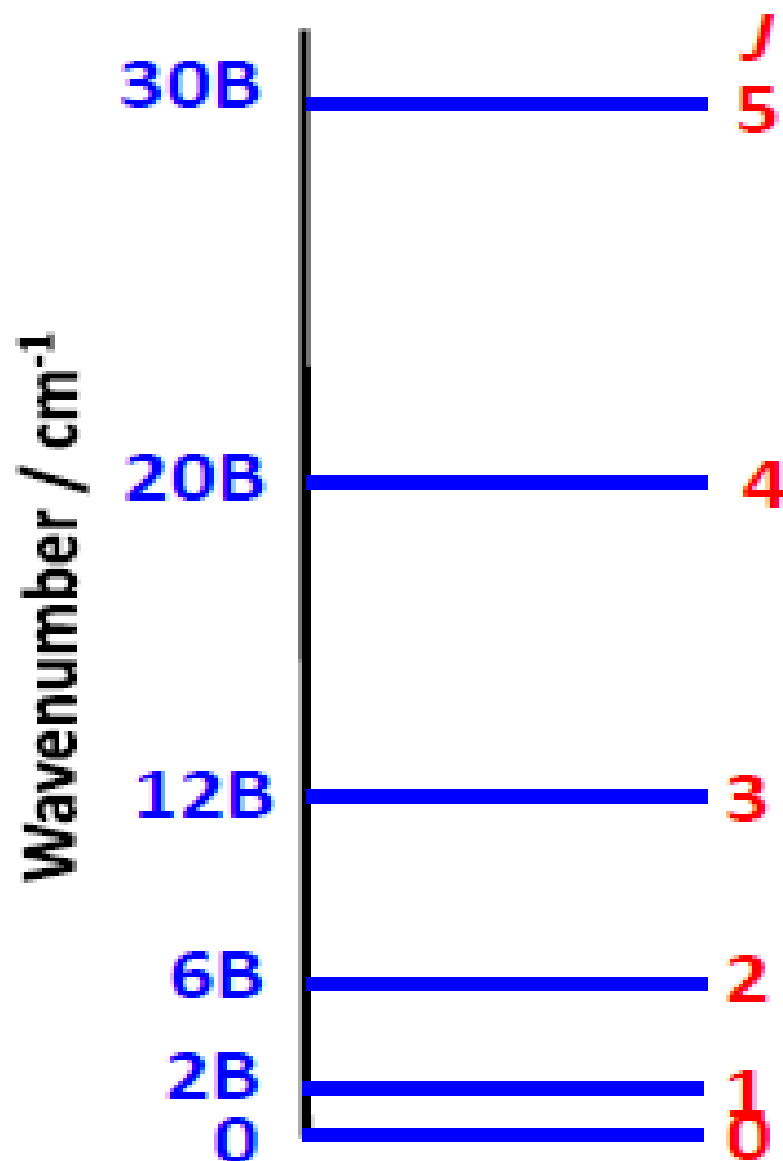
Centrifugal distortion

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 $I = m r^2$.
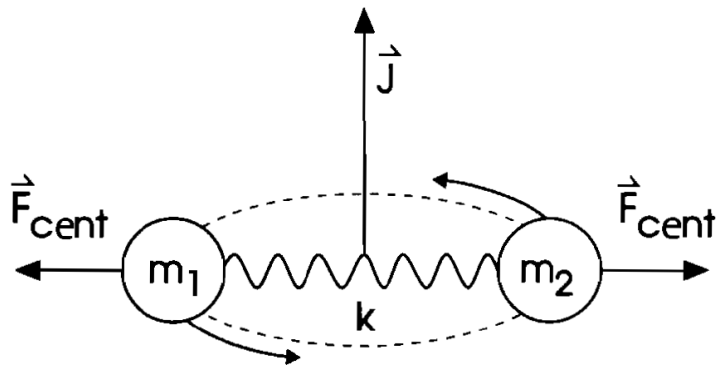
$$B = \frac{h}{8\pi^2 cI}$$

This increase of I implies a decrease of B

Centrifugal distortion

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

The energy of the vibrating-rotating molecule is :

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

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
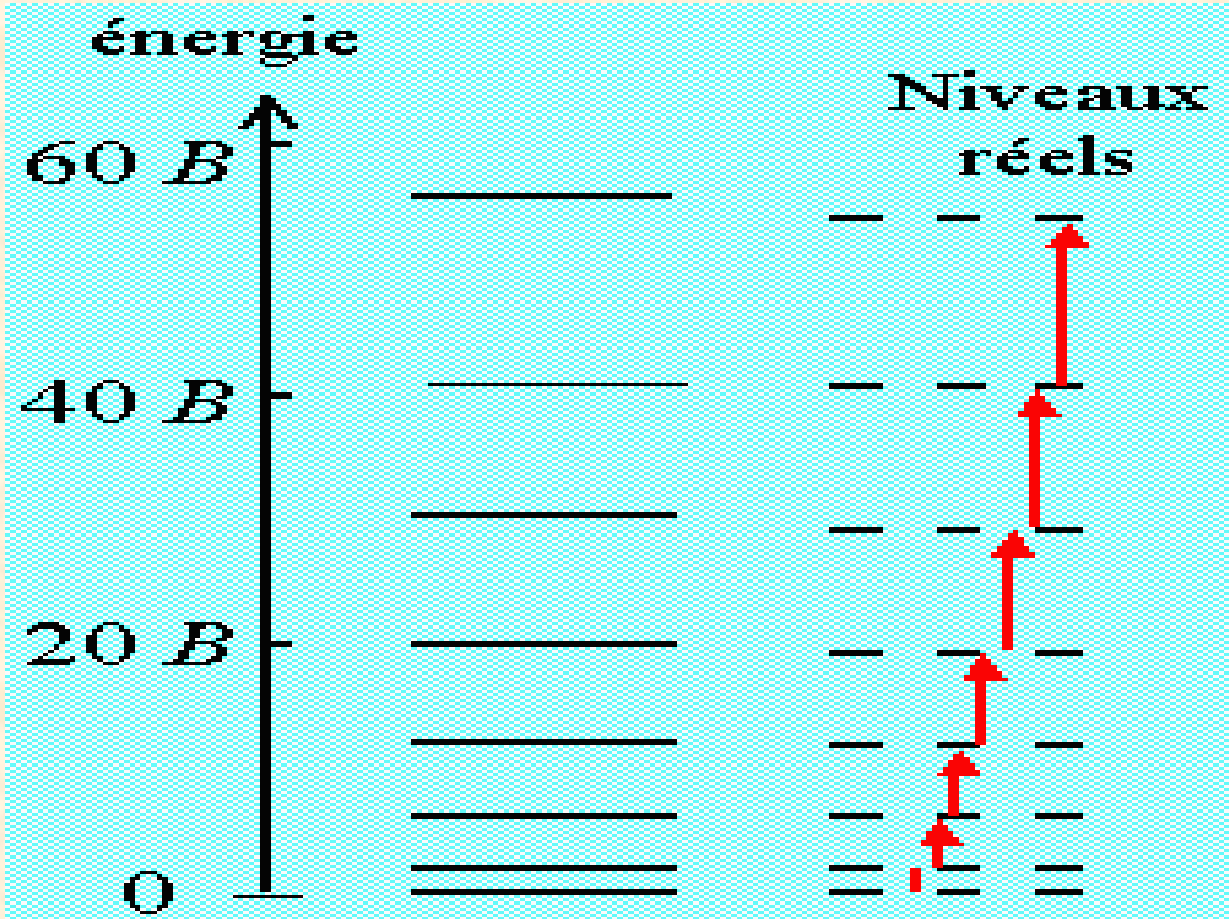
Diatomic molecules

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
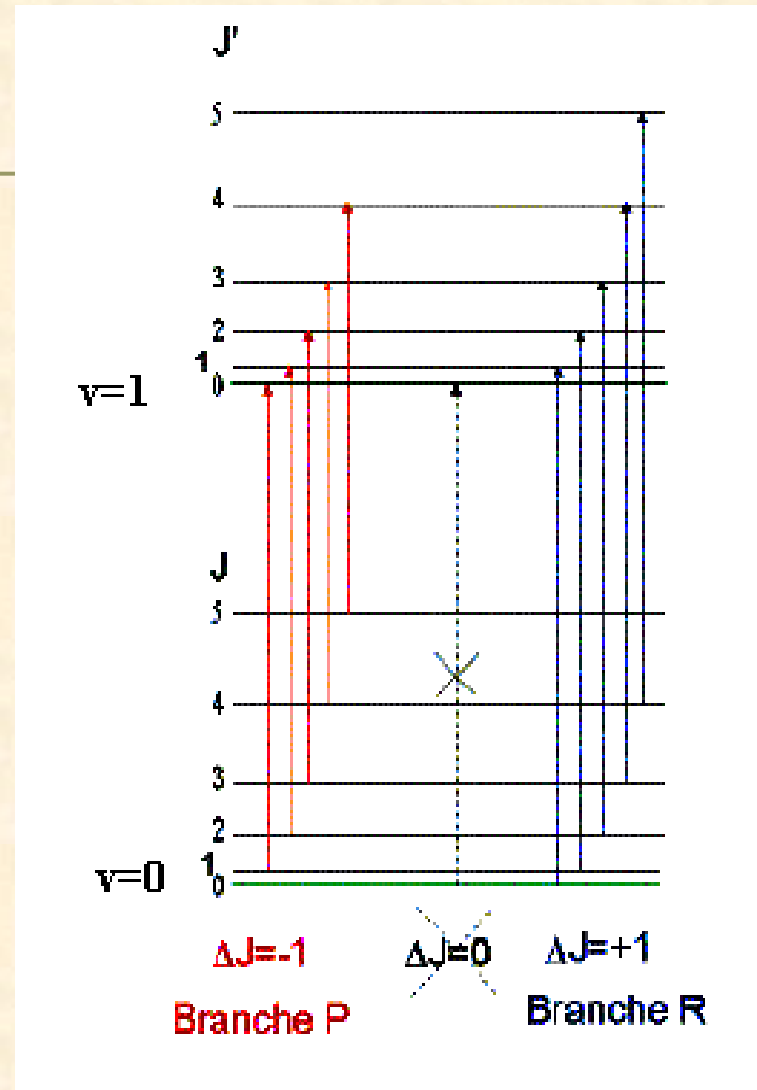
Pure rotation spectrum (microwave) for a diatomic molecule

Absorption   Emission

| 0 | 2B | 4B | 6B | 8B | σ |

| J″ | 0 | 1 | 2 | 3 |
| J′ | 1 | 2 | 3 | 4 |
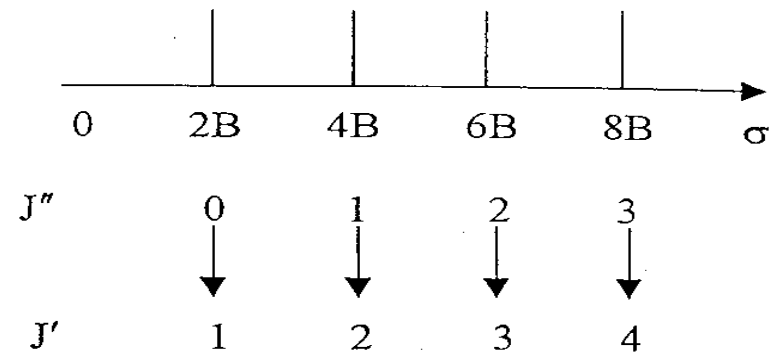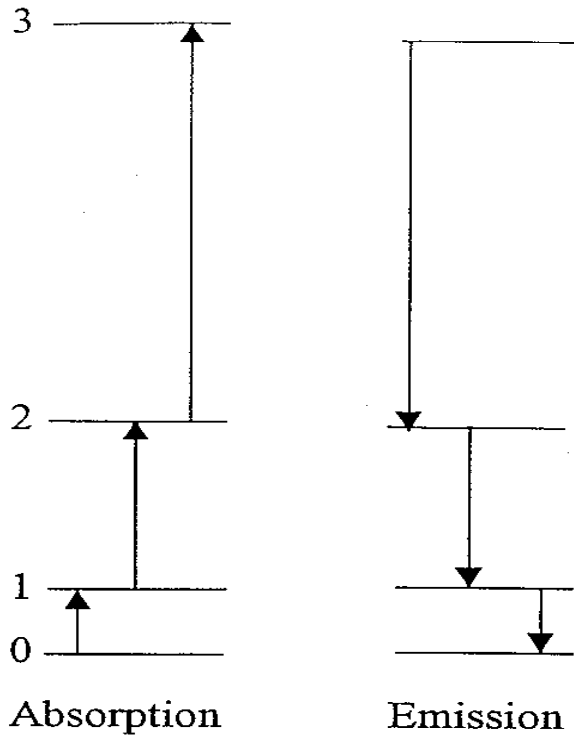
Spectre d'absorption

The heavier the molecule is , the closer the lines are

Line intensities for a diatomic molecule:

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)}I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right)S_{ji}$$

CO

$\sigma(\tilde{\nu})$
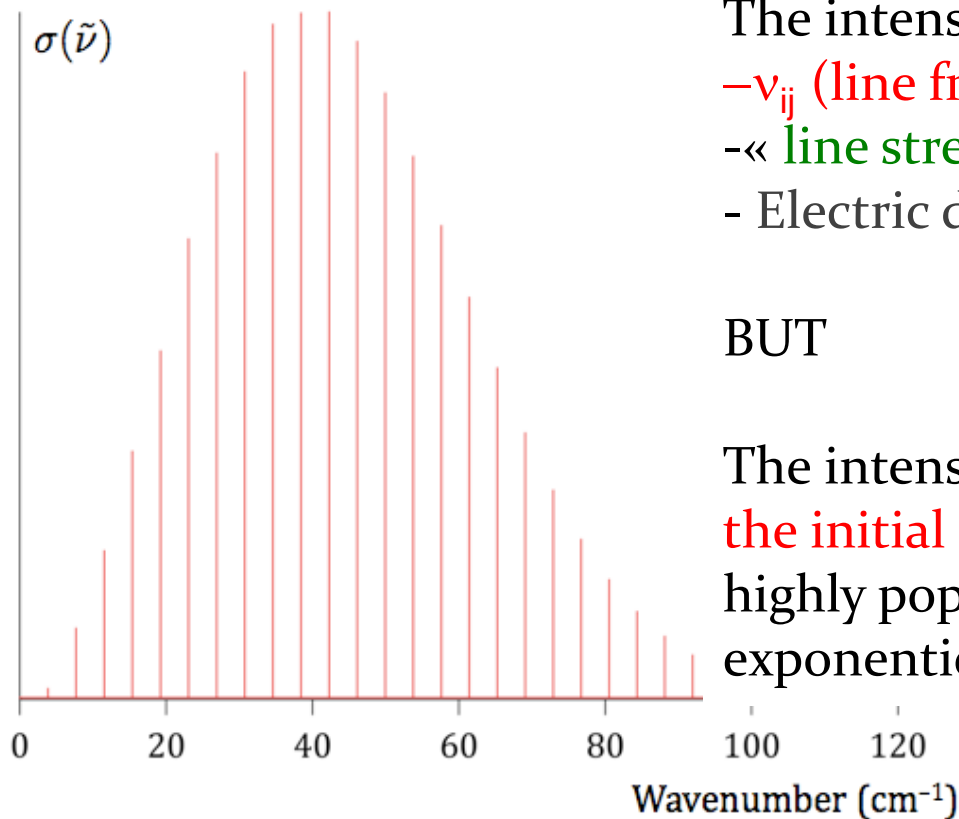
The intensity increases with:
$-\nu_{ij}$ (line frequency)
- « line strength » S_{ji} (proportionnel to $(J+1)$)
- Electric dipole moment of the molecule $|\mu_z|^2$

BUT

The intensity also depends on the population of the initial level i : at low J values, levels are highly populated but this population decreases exponentiely due to the Boltzmann factor)

Permanent dipole

$\mu_z = 1.098$ D

Wavenumber (cm^{-1})

B) rotation-vibration spectrum

➢ **Vibration-rotation transitions lead to a series of lines**
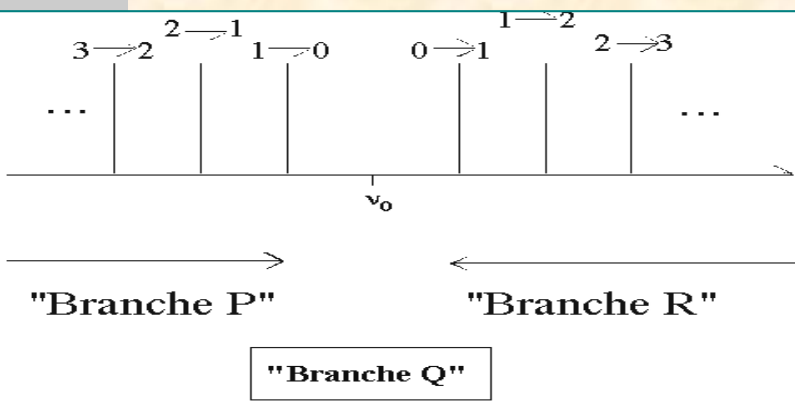
R Branch : at higher frequencies ν relative to the band center ν_0

➢ **Like for pure rotation spectra, intensities depend on the level population (function of J)**
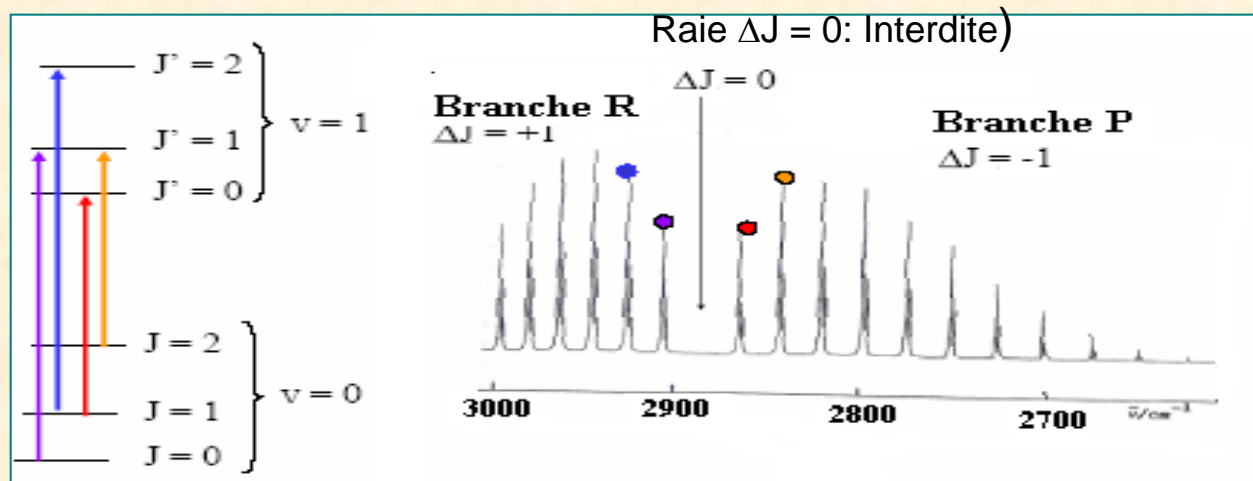
What about polyatomic molecules???

- **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, **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)

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)**

$$A = B_z, \; B = B_x = B_y$$
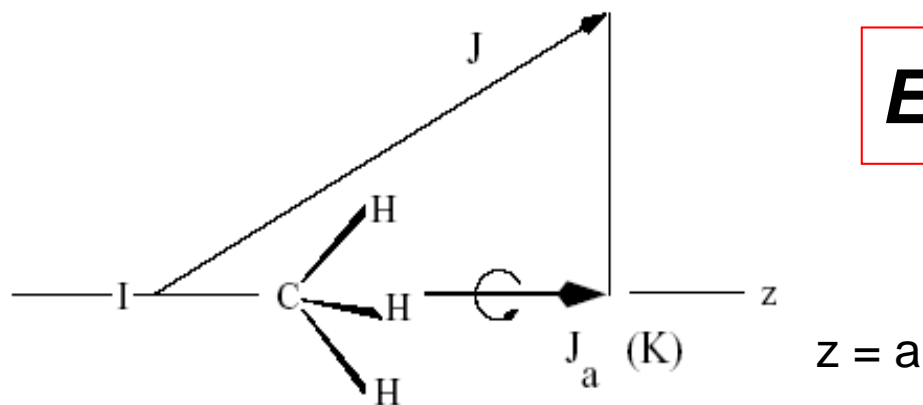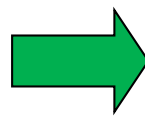
$$E_0^{rot} = B \, J(J+1) + (A-B) \, K^2$$

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)

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

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

K is called K_c for oblate tops
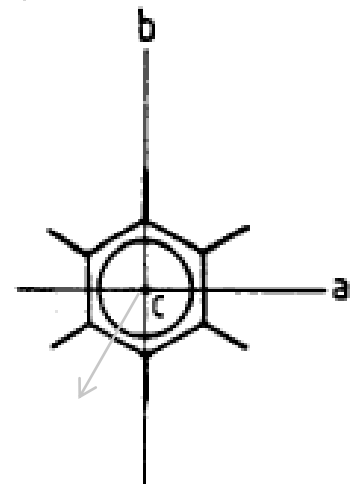
Rotation energies for symmetric tops

$$A \geq B \geq C$$

Prolate

Oblate

K_a

K_c

$K_p = 0$ $K_p = 1$ $K_p = 2$ $K_p = 3$ $K_p = 4$

$K_o = 0$ $K_o = 1$ $K_o = 2$ $K_o = 3$ $K_o = 4$
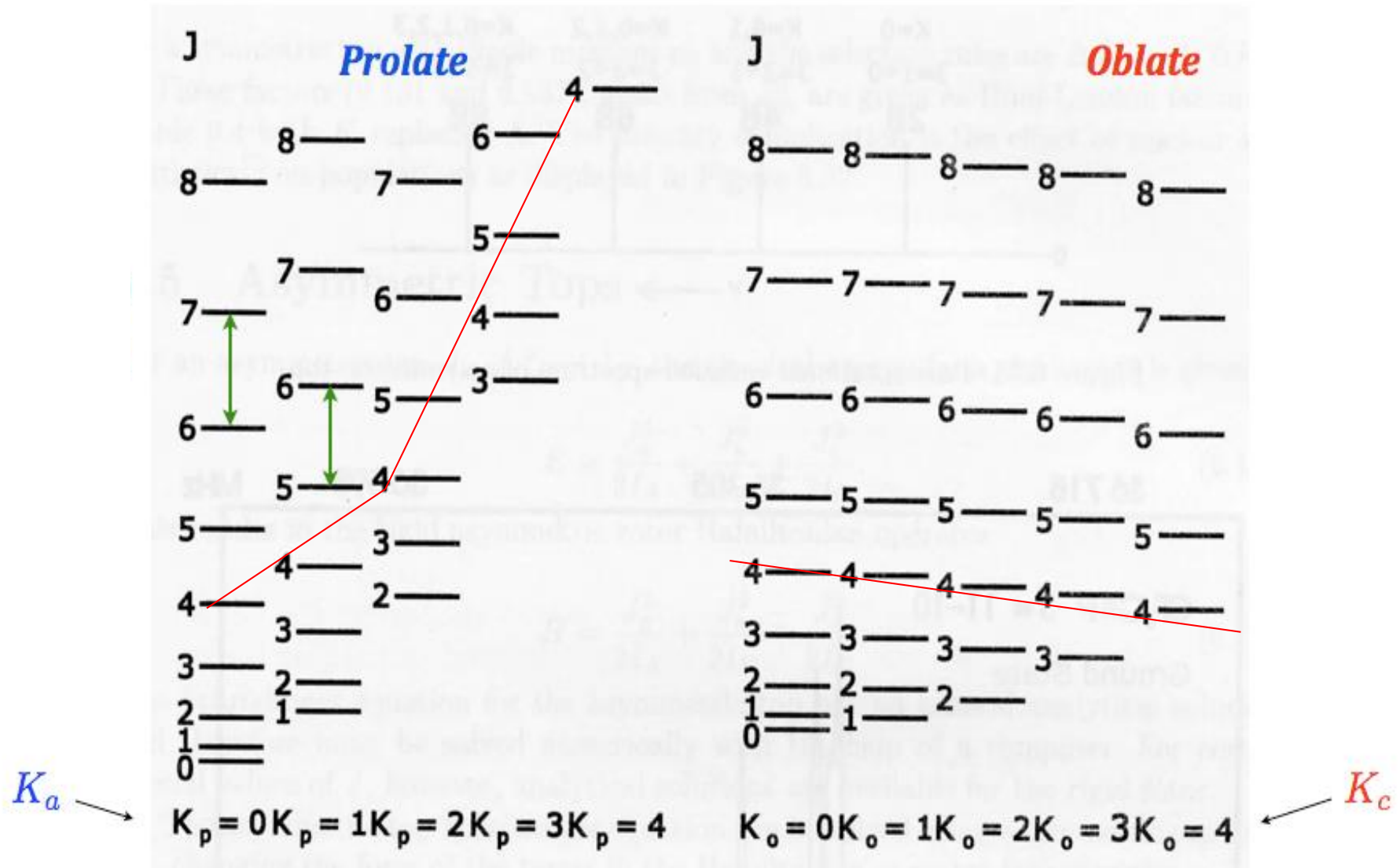
$$E_r(J,K) = BJ(J+1) + \underline{(A-B)K^2} \atop >0$$

$$E_r(J,K) = BJ(J+1) + \underline{(C-B)K^2} \atop <0$$

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 ΔJ=0, ±1 et ΔK= 0
- si K=0 ΔJ= ±1   et ΔK= 0

Perpendicular Band (induced by μ_x, μ_y)

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

ΔJ=0, ±1 et ΔK= ± 1

$\nu_1(A_1)$ symmetric stretch $\nu_2(A_1)$ symmetric bend $\nu_{3a}(E)$ $\nu_{4a}(E)$
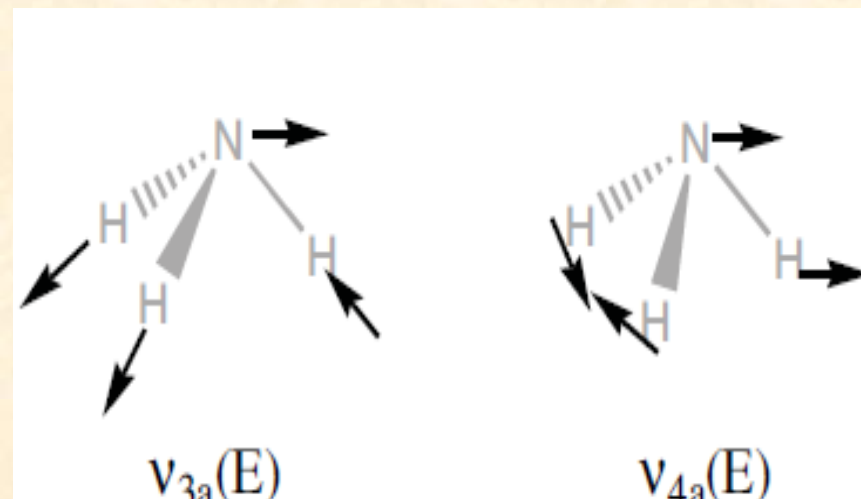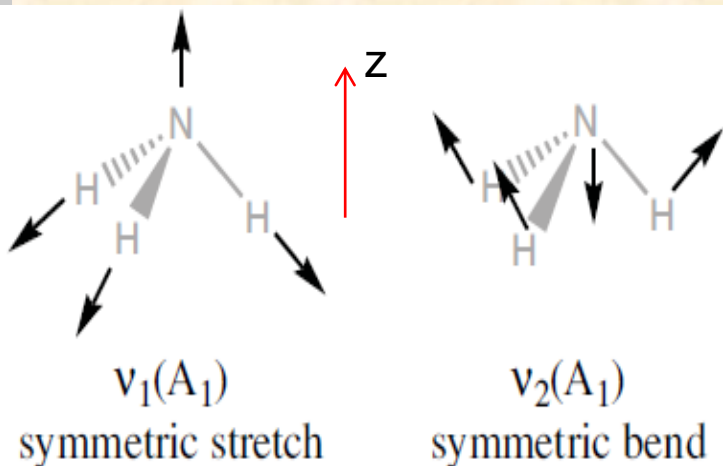
What is hapening in so-called « degenerate » modes?
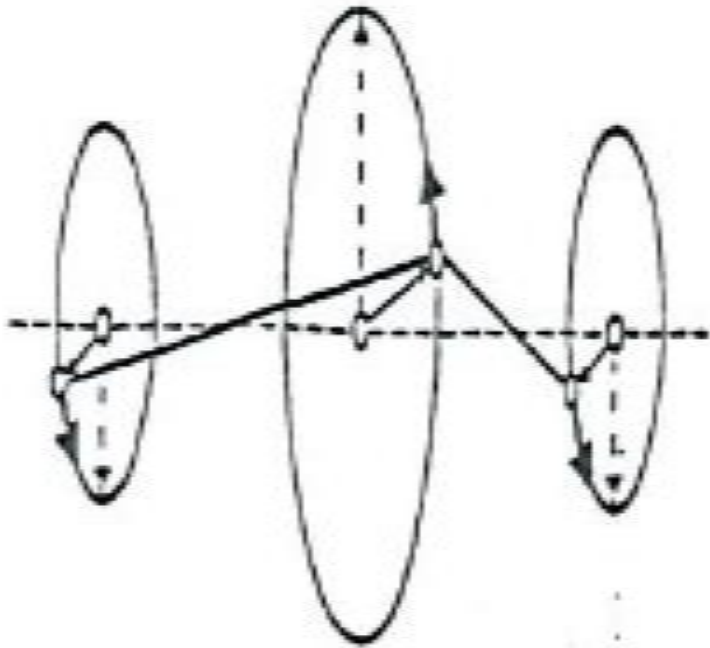
Linear molecule (CO_2)

ν_{2a} ⟷ ν_{2b}
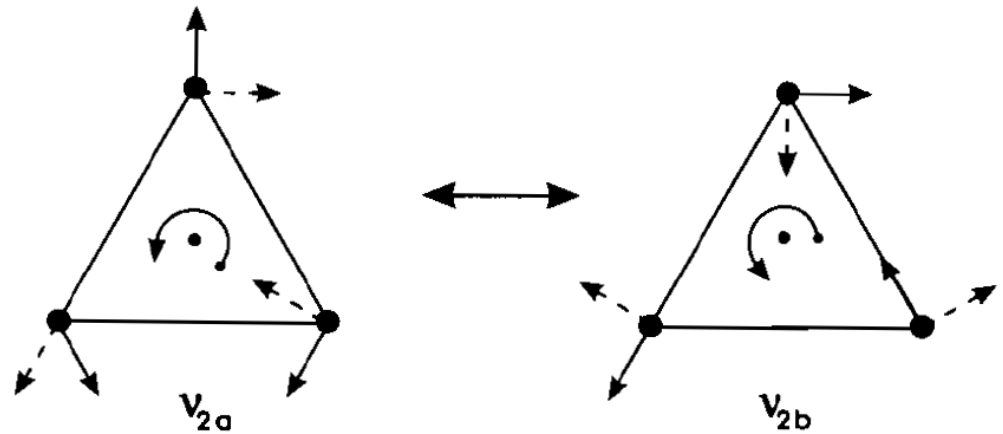
Symmetric top (H_3^+)

For polyatomic, we can have a coupling between rotation and vibrational angular momentum in « degenerate » modes
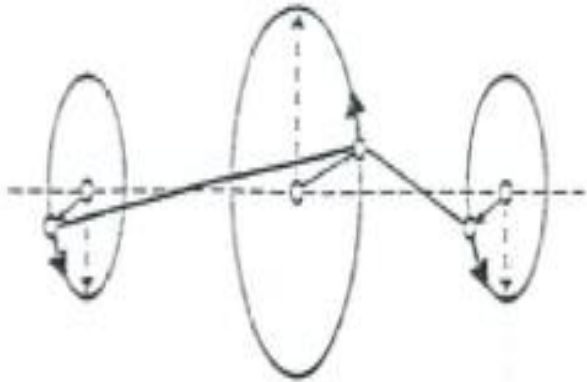
CO$_2$ bending mode ν_2

$$\ell_2 = v_2, \ v_2-2, ..., \ 1 \text{ or } 0$$

Vibrational angular momentum

$$P_s \Psi_{v\ell} = \pm \ell_s \hbar \Psi_{v\ell}$$

Vibrational quantum number

$(\mathscr{P}_s = \hbar \ell_s)$
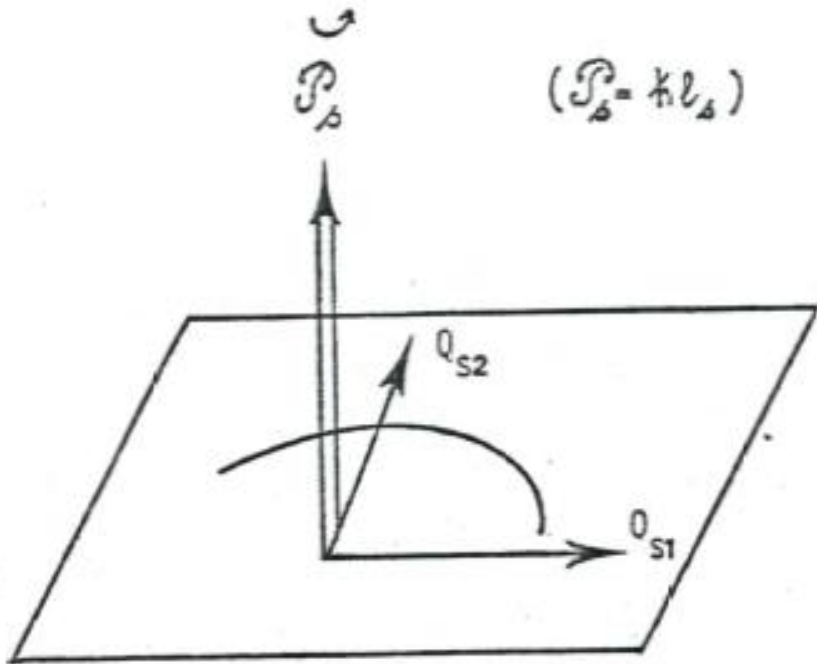
Spectre du mode ν_3 de CH_3Br
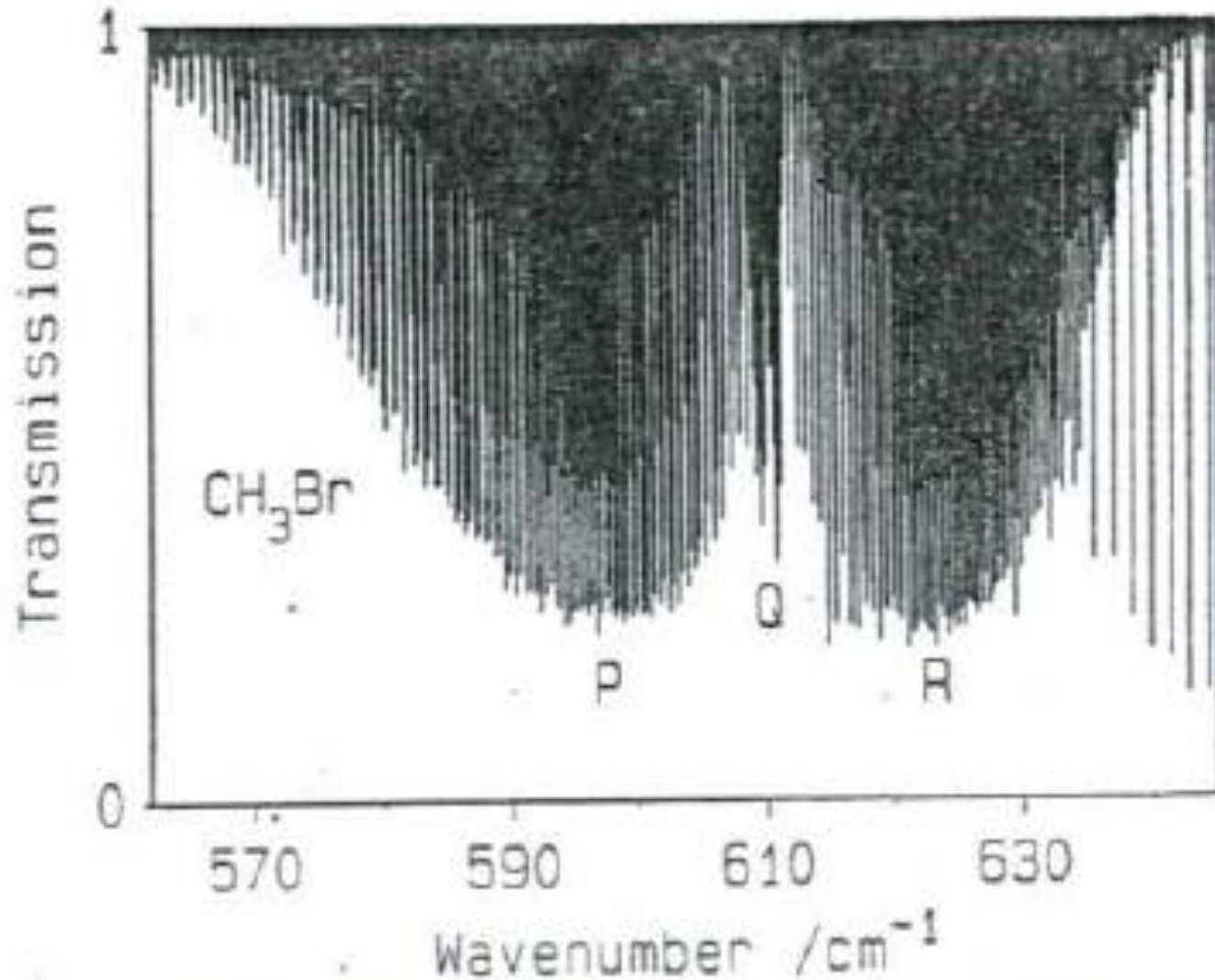
Spectre infrarouge du mode ν_3 de CH_3Br. Notez la présence des 2 branches Q ($\Delta J=0$), l'une due à l'isotope $CH_3{}^{79}Br$ et l'autre due à $CH_3{}^{81}Br$

Asymmetric top: energy levels: J K_a K_c

$K_a, K_c =$ pseudo-quantum numbers

prolate top

oblate top
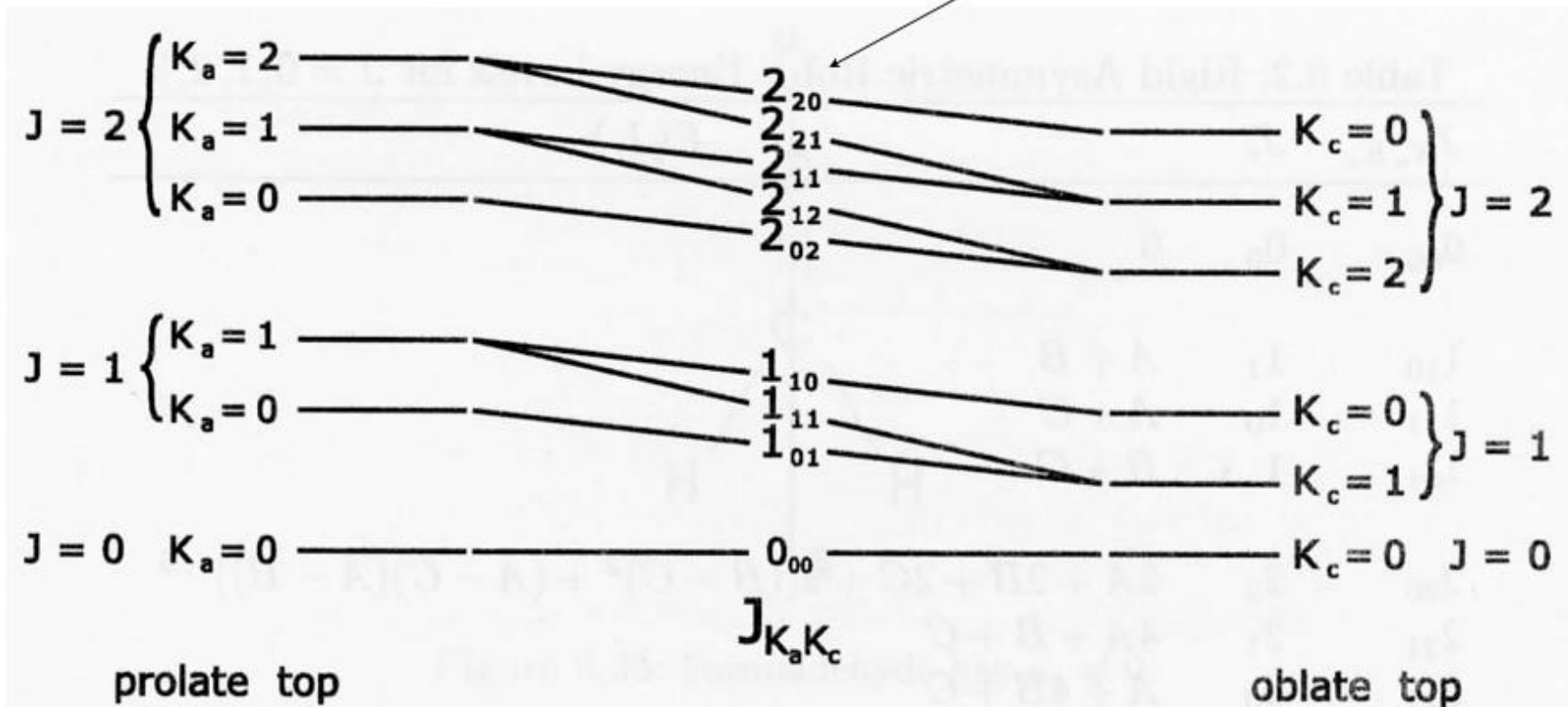
$\kappa = -1$

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

$\kappa = +1$

Rotational energy levels and transitions

Rigid rotor (zero order energy)

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

Line Intensities : Depend on the Electric dipole moment
μ (μ_a, μ_b, μ_c)

E_{rot}

$J_{K_aK_c}$

1_{10}

1_{11}

1_{01}

0_{00}

ν

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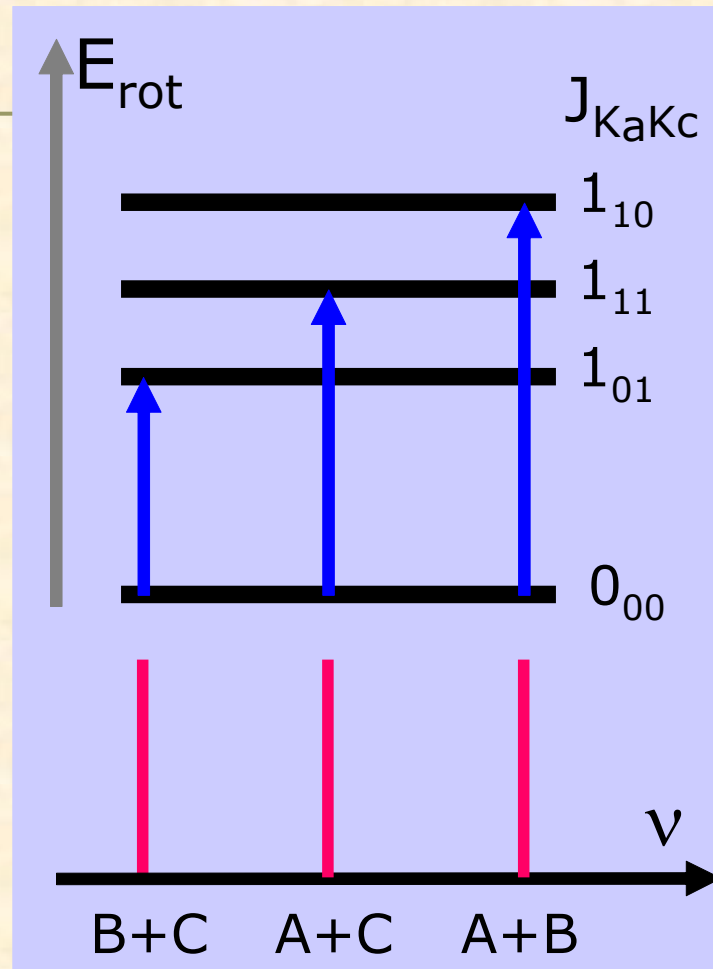
Limitation of the size of the molecule measured by most of Fourier-Transform spectrometers (2-20 GHz) : 250-300 uma

Gas phase studies

« Effectifs Hamiltonians »
operators x parameters :
Development in series

« Quantum chemistry », *ab initio*
Eq. Schrödinger (Born-Oppenheimer)
Interatomic distances, angles

Spectral analysis
Line positions and intensity fits

Spectroscopic parameters related to molecular structure :
rotation constants, Torsion potential function,
electric dipole moments, vibrational parameters …

Fitting the laboratory data to be able to produce a reliable prediction: an (long) iterative procedure

High precision analysis: how to find the right model and code to fit the data ?

Programs for ROtational SPEctroscopy: managed by Z. Kiziel (Poland)
PROSPE - Programs for ROtational SPEctroscopy (ifpan.edu.pl)

MOLECULAR MODELING

Summary of the available programs:

	Analysis of spectra
AABS	The **AABS** package for *Assignment and Analysis of Broadband Spectra*: consists of linked viewers of spectra and predictions, which are integrated with several programs for fitting/prediction. Several other programs for analysis of broadband spectra are also available - you will find a brief comparison and links here

	Asymmetric rotor
ASFIT	To fit rotational transitions in an asymmetric top with various versions of Watson's asymmetric top Hamiltonian, tailored for repetitive online operation
ASROT	Predictive program complementing ASFIT
ASCP	Graphical program to display spectral predictions from ASROT and from Pickett's program SPCAT
PICKETT	The SPFIT/SPCAT program suite written by H.M.Pickett (and available from JPL Molecular Spectroscopy) has become the workhorse of analysis of high resolution rotation and rotation-vibration spectra. This section provides some useful accessories for use with these programs:

	Internal rotation
XIAM XIAM_mod	IAM internal rotation program of Holger Hartwig from the Kiel group for up to three symmetric internal rotors and up to one quadrupolar nucleus. The **XIAM_mod** extension by Sven Herbers allows the use of two additional internal rotation parameters.
ERHAM	Peter Groner's **E**ffective **R**otational **HAM**iltonian program for molecules with up to two-periodic large-amplitude motions
BARRIER	Internal rotation barrier from energy level differences (by Peter Groner)
BELGI	The **BELG**ian **I**nternal Rotor program of Isabelle Kleiner *et al.* for a C_3v rotor attached to a Cs or a C_1 framework
RAM36 RAM36hf	Vadim Ilyushin's **R**ho-**A**xis **M**ethod program for **3** and **6** fold barriers (without and with nuclear quadrupole hyperfine structure)
SPFIT$_{int}$	*Can SPFIT be used to fit internal rotation ?*

	Nuclear quadrupole coupling
NSYM	To predict hyperfine splitting in a linear/symmetric top with one quadrupolar nucleus
ASQ1P	To predict hyperfine splitting in an asymmetric top with one quadrupolar nucleus - first order calculation only but produces handy plots of expected splitting patterns
Q2FIT	To fit rotational transitions for an asymmetric top with up to two quadrupolar nuclei in the *I,F* coupling scheme.
QDIAG	Diagonalization of the inertial quadrupole tensor with errors
QPRINC	Rotation of the quadrupole tensor from its principal to inertial axes

	Electric dipole moment

Infrared spectroscopy of Phosphine for planet's atmospheres

M. REY
  GSMA, *Université de Reims, France*

    I. KLEINER
    LISA, *CNRS/IPSL-Université Paris-Est and Université de Paris, France*

      R. HARGREAVES, I. GORDON
      Harvard-Smithsonian Center for Astrophysics, Cambridge, USA

       V. TYUTEREV
       GSMA*, Université de Reims, France*

         K. SUNG
   *Jet Propulsion Laboratory, Caltech,Pasadena, USA*

           V. Malathy DEVI
           The College of William and Mary, Williamsburg, USA

             A. NIKITIN
I   *Institute of Atmospheric Optics, Tomsk, Russia*

Phosphine is a molecule of astrophysical and astronomical interest and has been observed in both the Jupiter and Saturn atmospheres PH₃ : A non-equilibrium species

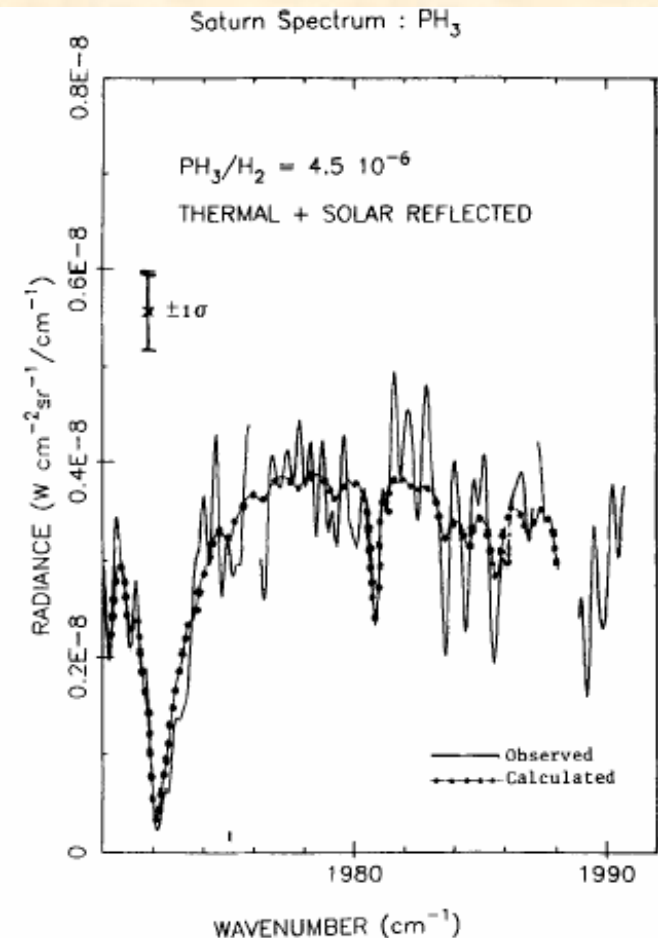Between 800-300 K:

$$4PH_3 + 6H_2O \iff P_4O_6 + 12H_2$$
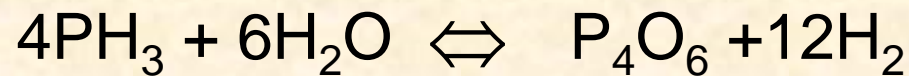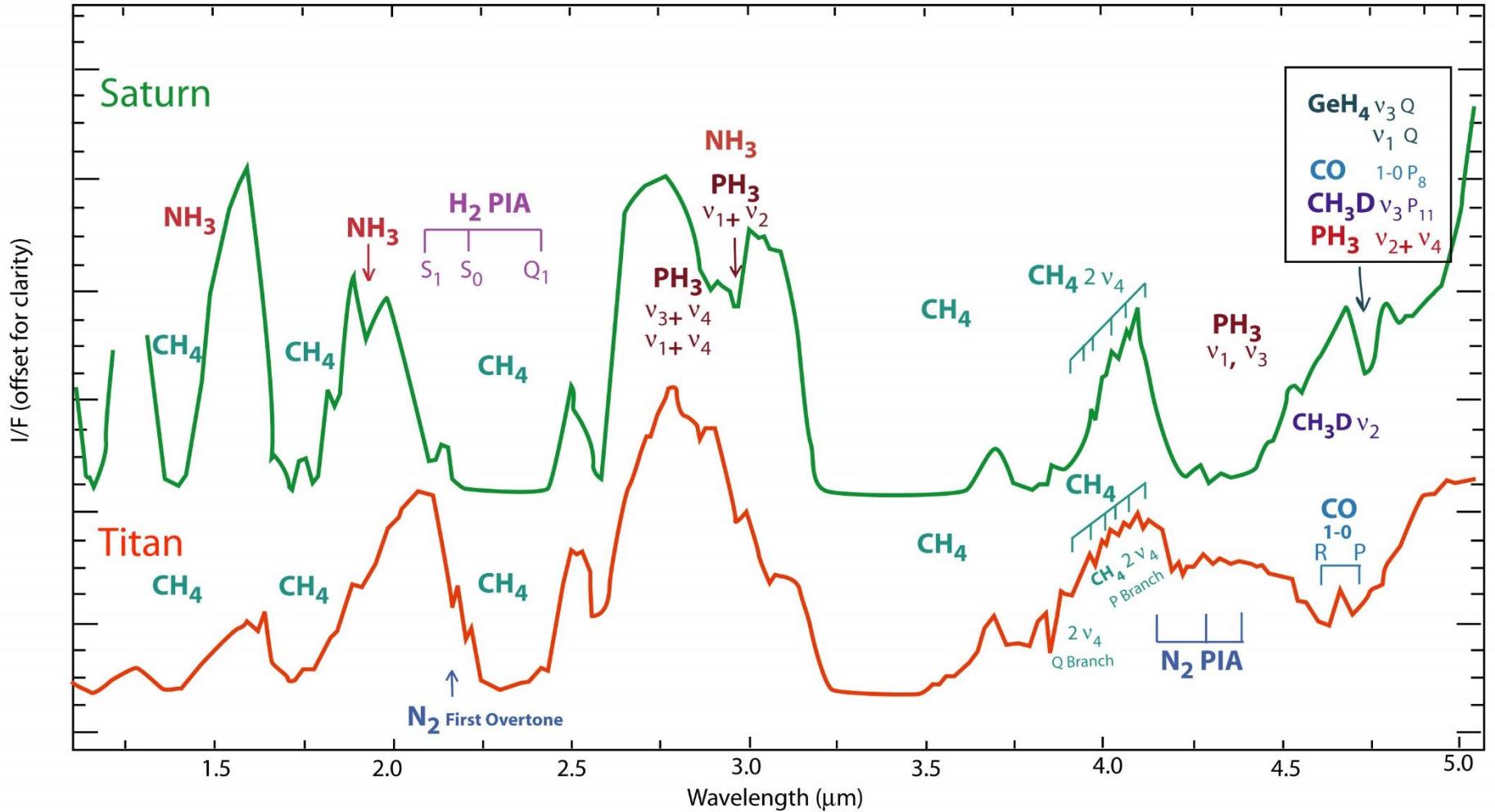
At the cold temperatures of upper troposphere should not be detectable

BUT **vertical mixing transports PH₃ faster than oxidation**.

PH₃ abundance gives information on vertical circulation

Saturn Spectrum : PH₃

$PH_3/H_2 = 4.5 \ 10^{-6}$

THERMAL + SOLAR REFLECTED

$\pm 1\sigma$

RADIANCE (W cm⁻² sr⁻¹/cm⁻¹)

—— Observed
+++++ Calculated

WAVENUMBER (cm⁻¹)

Tarrago et al, JMS 1992
Drossart et al Icarus 1990

Drossart et al. private communication

Phosphine gas in the cloud decks of Venus ?
Greaves et al Nature Astronomy sept 2020

20 November 2020 Editor's Note: The authors have informed the editors of Nature Astronomy about an error in the original processing of the ALMA Observatory data underlying the work in this Article, and that recalibration of the data has had an impact on the conclusions that can be drawn. 20 ppb -→ 1 ppb

Recent detection of phosphine (PH_3) was reported from James Clerk Maxwell Telescope and Atacama Large **Millimetre/submillimeter Array** observations: Based on one line….
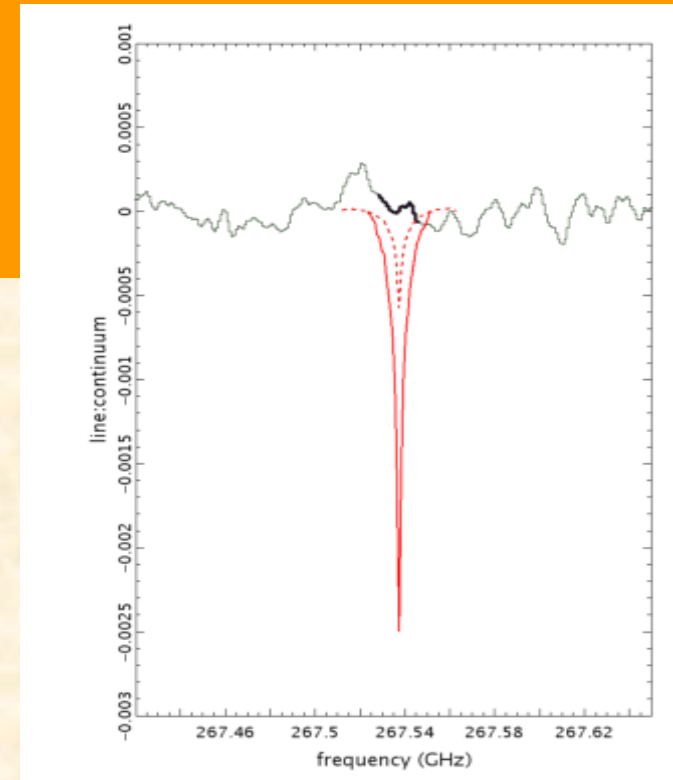
abundance to a 1 ppb global disk average ?

On earth PH_3 comes from biogenic sources!
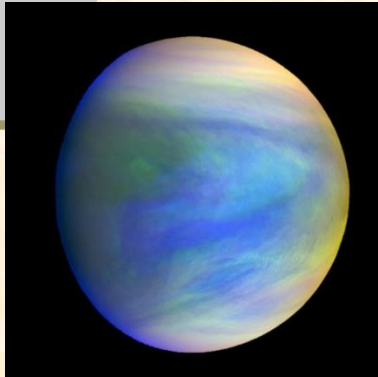
Phosphine as a Biosignature Gas in Exoplanet Atmospheres
Clara Sousa-Silva et al.
Astrobiology 2020
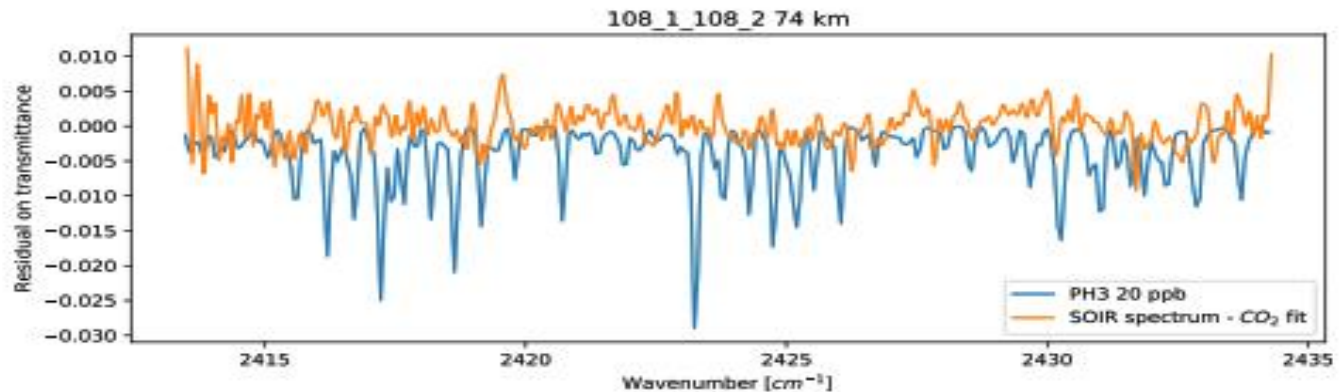
On Earth, PH_3 is associated with anaerobic ecosystems

Infrared instrument on board of ESA Venus Express : 2.2 to 4.3 μm

The SOIR PH$_3$ upper limits are almost two orders of magnitude below the announced detection of 20 ppb
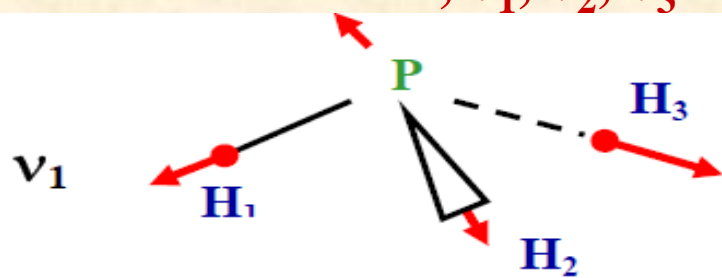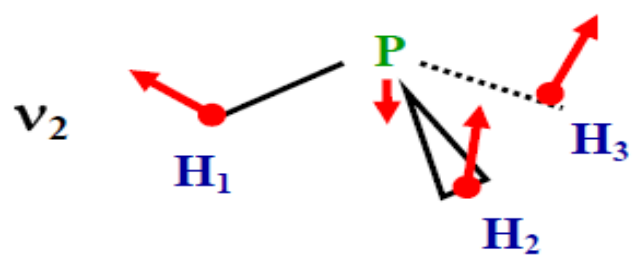
A&A 645, L4 (2021)

Fig. 2. Example of spectrum for orbit 108.1 order 108 bin 2 at a tangent altitude of 74 km. The SOIR spectrum subtracted by the ASIMAT CO_2 fit is plotted in orange. The synthetic spectrum of 20 ppb of PH$_3$ is plotted in blue.
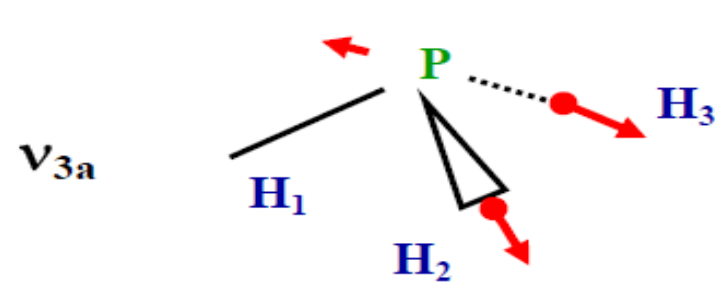
LET US GO BACK TO SPECTROSCOPY!!!

PH$_3$ is a symmetric top molecule belonging to the C$_{3v}$ point group. It has a pyramidal structure and has 4 distinct IR vibrational fundamental bands, ν_1, ν_2, ν_3 and ν_4.
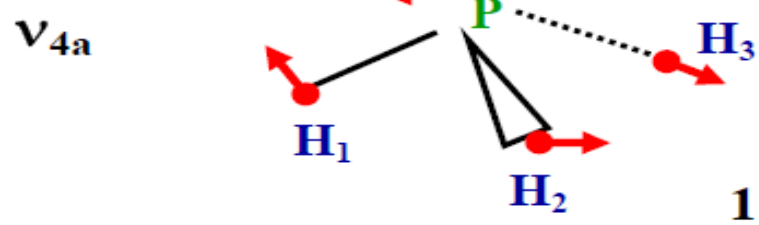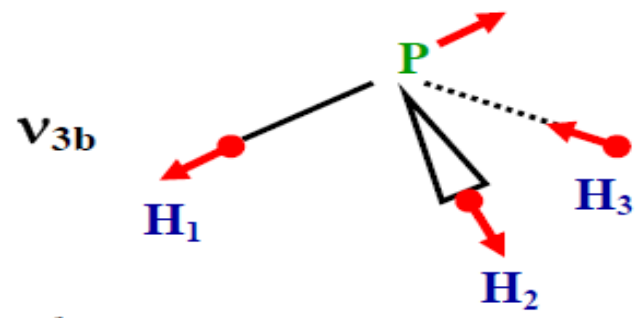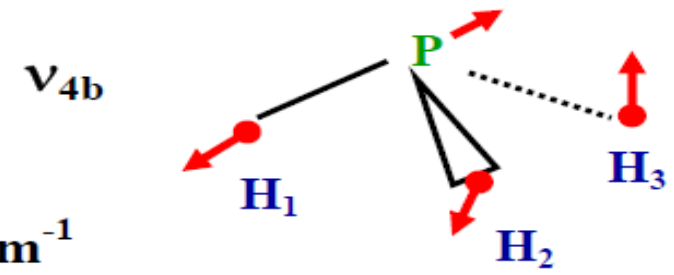

ν_1

2320 cm^{-1}

ν_2

992 cm^{-1}

ν_{3a}

ν_{3b}

2325 cm^{-1}

ν_{4a}

ν_{4b}

1118 cm^{-1}

Energy level diagram (cm⁻¹):

- $\nu_3 + \nu_4$
- $\nu_1 + \nu_4$
- $3\nu_4$
- $\nu_3 + \nu_2$
- $\nu_1 + \nu_2$
- $\nu_2 + 2\nu_4$
- $2\nu_2 + \nu_4$
- $3\nu_2$
- ν_3
- ν_1
- $2\nu_4$
- $\nu_2 + \nu_4$
- $2\nu_2$
- ν_4
- ν_2

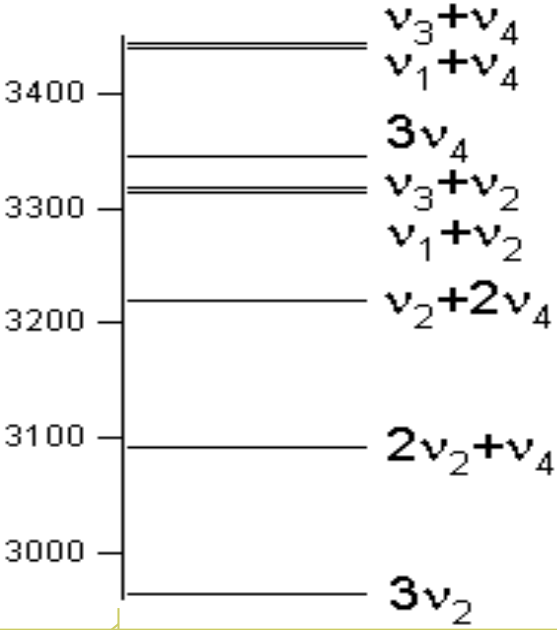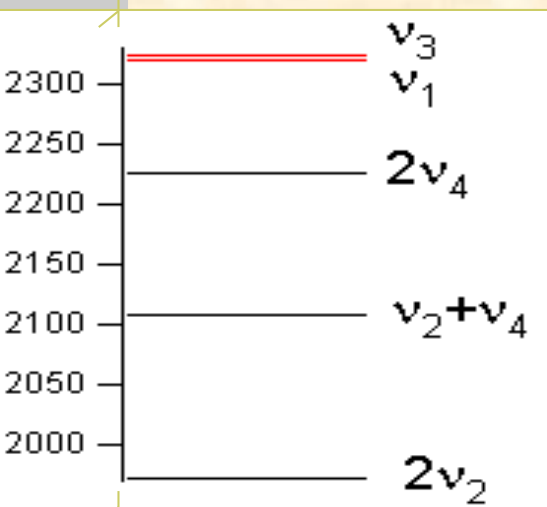**-The band $3\nu_2$:**

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

- The octad bands:

New line positions and intensities measurements (Butler et al., JMS 2006)
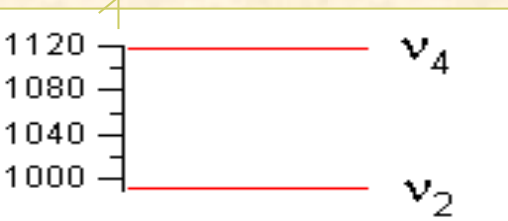**The Global analysis of the Dyad, pentad and octad bands:** (Nikitin et al., JMS 2009)

• 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)

Development of the theoretical model and new programs

	$2\nu_2$	$\nu_2+\nu_4$ l_4	$2\nu_4$ l_4	ν_1	ν_3 l_3
$2\nu_2$	K-type interaction Diag	Coriolis	Coriolis Fermi	Fermi	Coriolis
$\nu_2+\nu_4$		l- type interaction Diag	Coriolis Fermi	Coriolis	Fermi
$2\nu_{42}$			l- type interaction Diag	Coriolis Fermi	Coriolis Fermi
ν_1				K-type Interaction Diag	Coriolis
ν_3					l- type interaction Diag

More recent works on PH$_3$

<u>Theoretical studies</u>:

■ A computed room temperature line list for phosphine, Clara Sousa-Silva, Sergei N. Yurchenko, Jonathan Tennyson, *J. Mol. Spectrosc.* 288 (2013) using the TROVE program: 137 million transitions up to J_{max} =31 and energies up to 8000 cm^{-1}

■ Global calculations using potential energy (Nikitin et al J. Chem. Phys 2009) and dipole moment surfaces (Nikitin et al Chem Phys Lett 2013)/ effective Hamiltonian models (Reims - Tomsk) for vibration-rotation spectroscopy : TheoReTS

Rey et al J Chem Phys 136 (2012) 244106;

Rey et al PCCP 20 (2018) 21008

- Accurate line parameters for PH_3 in the pentad region are important for the correct interpretation of **Jovian** observations by **JUNO** and **ESA's** selected mission **JUICE (Jupiter icy moons explorer)**.

- However astronomers found that the mixing ratio for PH_3 from **Cassini VIMS** and **Cassini CIRS** experiments at 100, 11 and 4.3 μm **give inconsistent results** → poor knowledge of spectroscopic parameters in the pentad ?

- To **improve intensities at 4.3 μm**, we measured over 4000 line positions and intensities for all five bands in the 1930-2440 cm^{-1}

- High resolution, high S/N spectra of >99.5% pure PH_3 were recorded at room temperature with the Bruker FTS at PNNL and the Kitt Peak FTS at the NSO **($2\nu_2$ lines are weak and hence absent in the PNNL data; so Kitt Peak spectra were used)**.

Line positions and intensities: **Devi et al JMS 2014**

+ A few hundred self-broadened half width + self-induced pressure shifts obtained. Line mixing measured for 15 A+/A- pairs of transitions **(Devi et al JMS 2014)**

The 5 micron region of PH$_3$
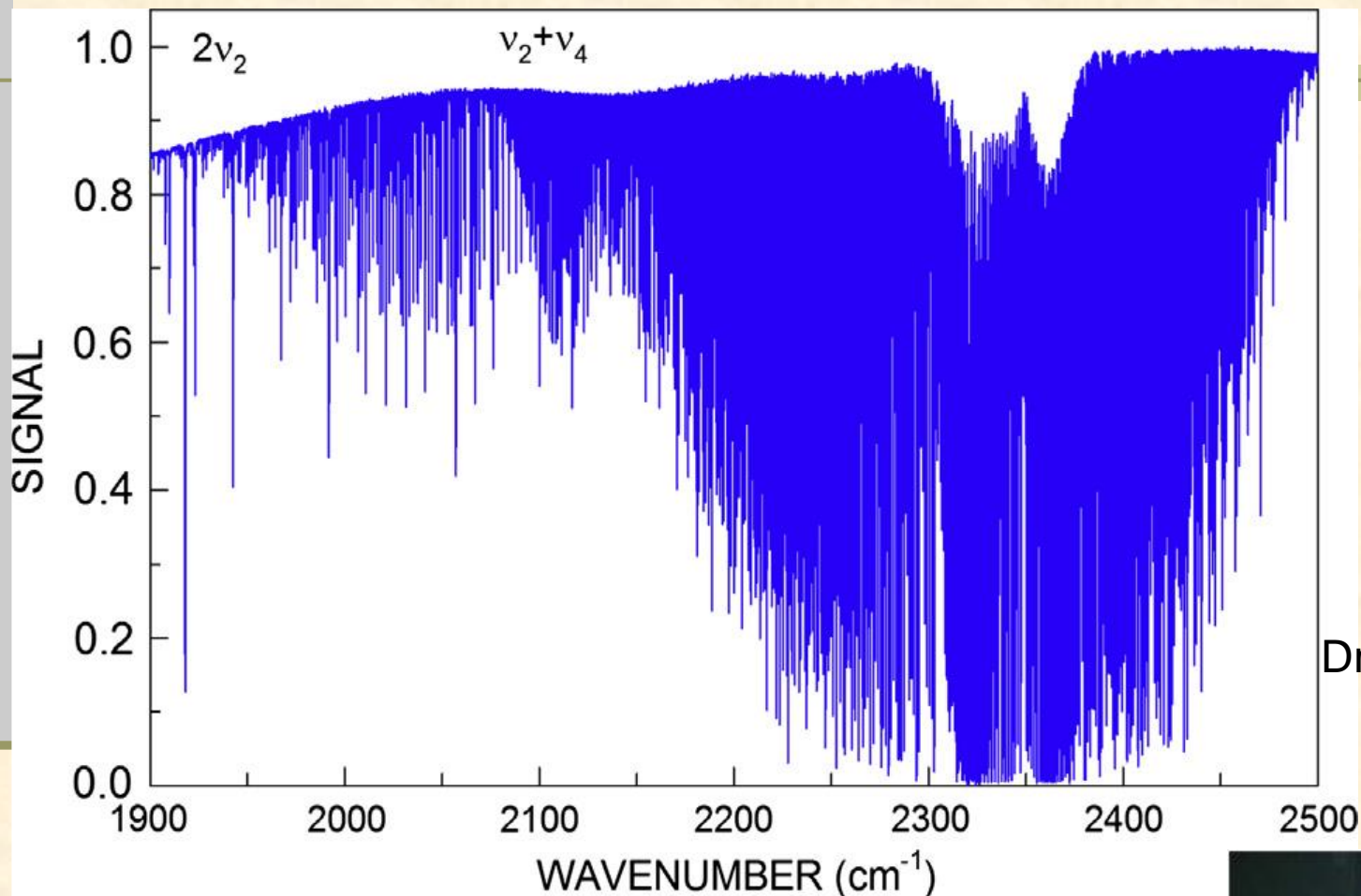
PH$_3$ spectrum at McMath-Pierce FTS (Kitt Peak),
res: 0.0115 cm^{-1}, 425 cm,
0.95 Torr at 294cK

Dr Keeyoon Sung

Dr Linda Brown

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 ???**

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

Observed-calculated in the pentad region
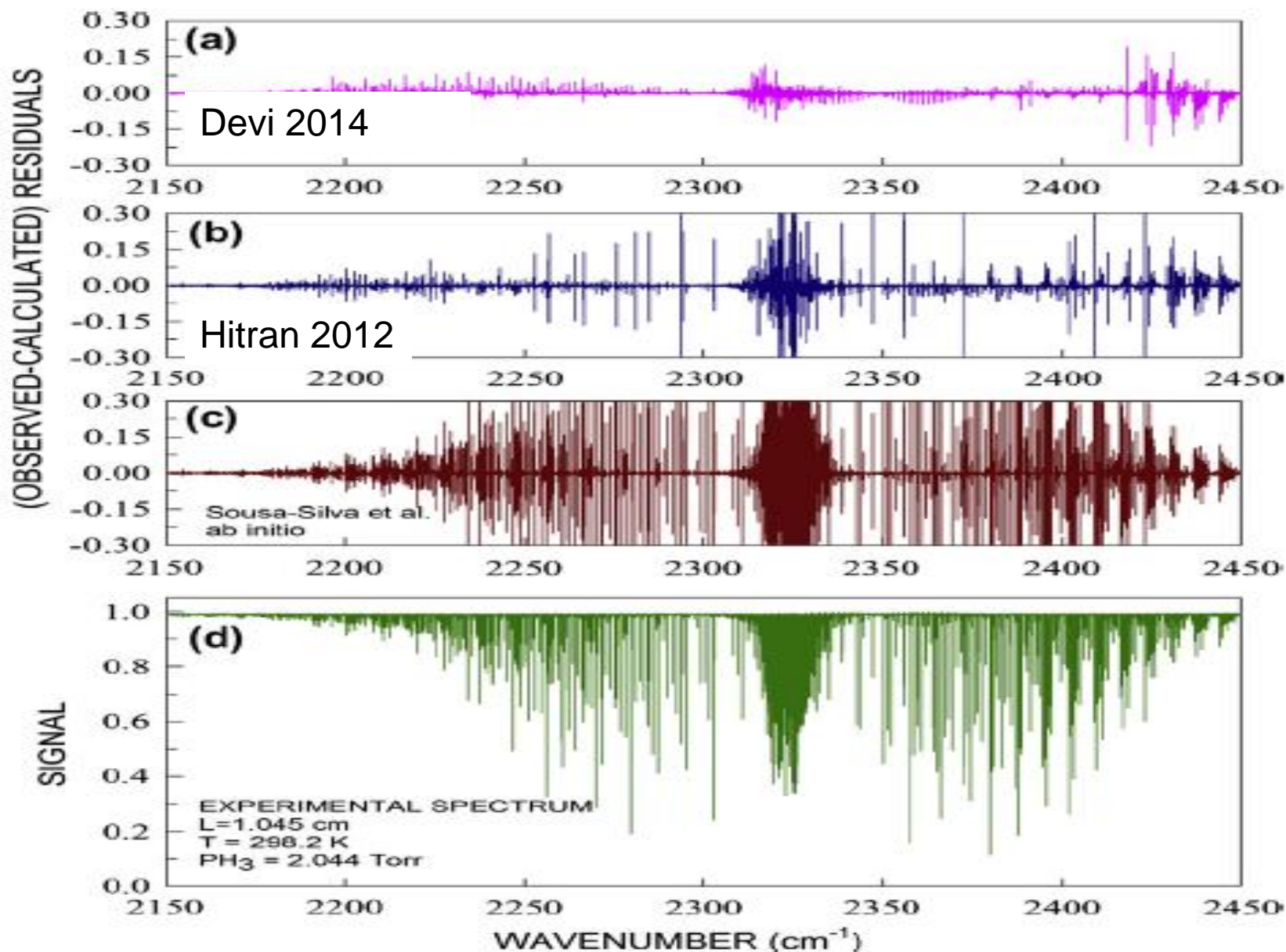
Michael Rey

Global variational Reims calculations

Vladimir Tyuterev

- Potential energy surface by Nikitin et al. (2009) but refined for this work
  RMS (O-C) = 0.04 cm^{-1} (dyad), 0.05 cm^{-1} (pentad) and 0.066 cm^{-1} (octad) up to J=20

- Dipole moment surface by Nikitin et al. 2013
  ~1-4 % on strong lines

- Normal mode model and nuclear motion calculations by Rey et al. (2010, 2012, 2018)

  619 A1, 437 A2 and 1049 E vibrational functions used in the variational calculation
  Jmax = 55 (beyond if necessary) => possibility to compute hot line lists
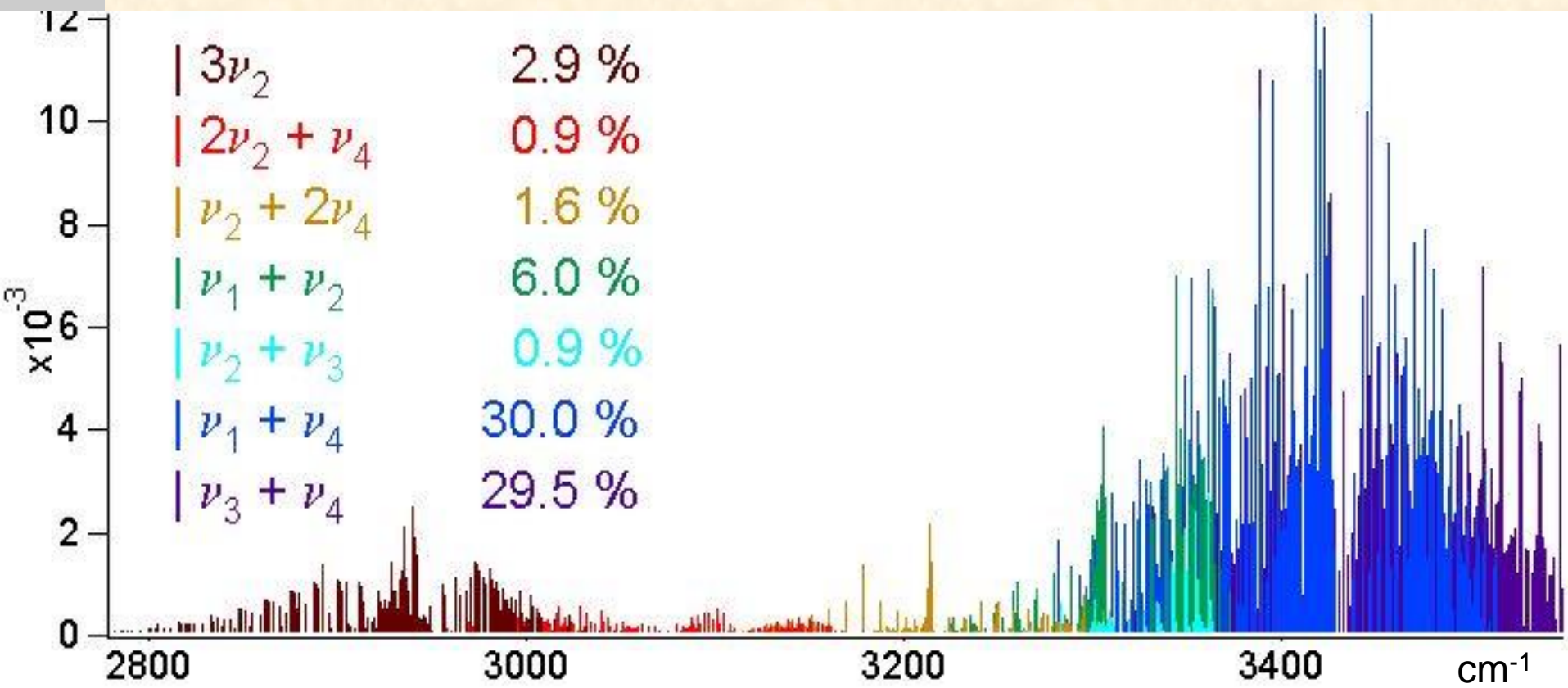
⇩

Refined room-T line list

⇩

Algorithm to (i) identify the rovibrational states and (ii) replace calculated energy levels
by OBS or Empirical levels (effective models), when available *(same strategy as for methane)*

Best of both worlds: refined line positions + accurate *ab initio* line intensities

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 3ν_4**

3ν_2	2.9 %
2$\nu_2 + \nu_4$	0.9 %
$\nu_2 + 2\nu_4$	1.6 %
$\nu_1 + \nu_2$	6.0 %
$\nu_2 + \nu_3$	0.9 %
$\nu_1 + \nu_4$	30.0 %
$\nu_3 + \nu_4$	29.5 %

Analysis of PH$_3$ spectra in the Octad range 2733–3660 cm^{-1}
Nikitin, Ivanova, Rey, Tashkun, Toon, Sung, Tyuterev, JQSRT 2017
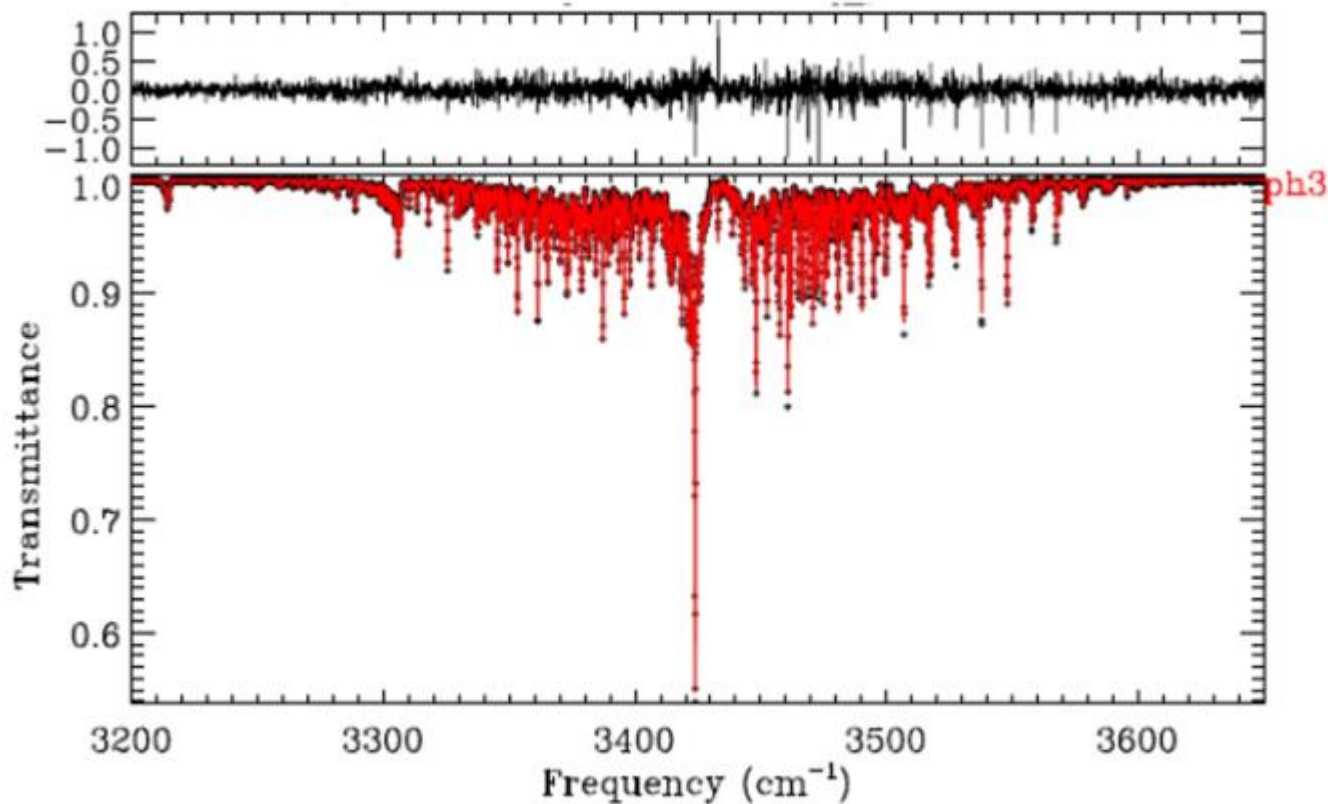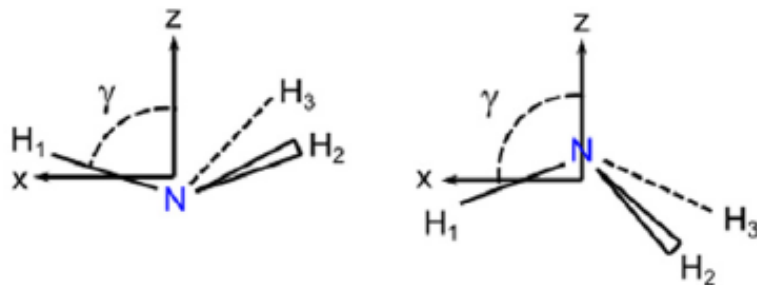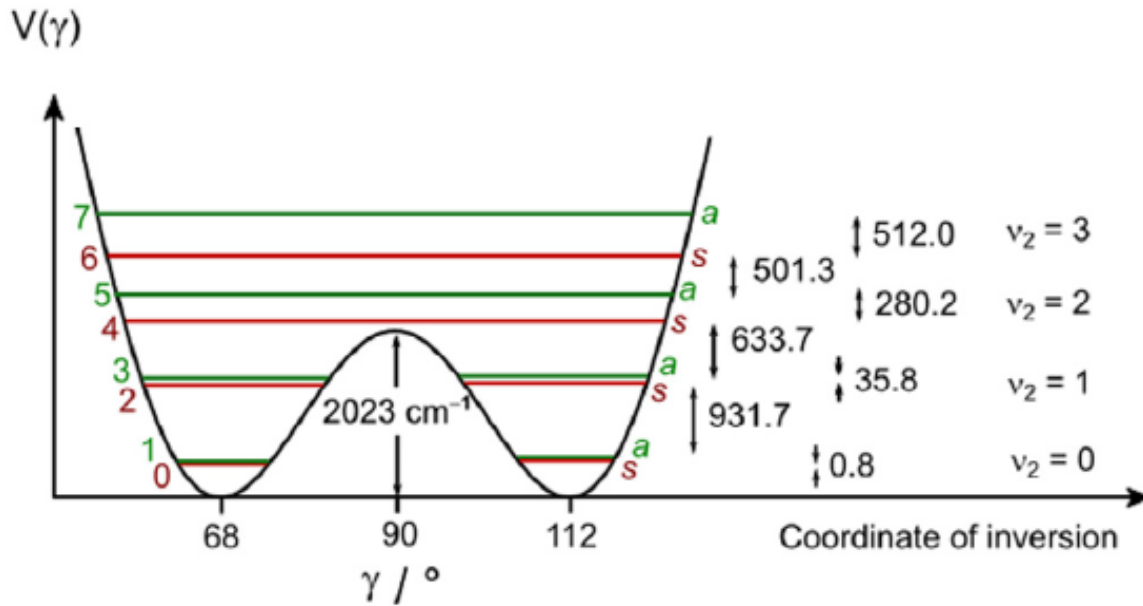

Global fit:

GS, dyad, pentad, octad
For the pentad:
374 fixed parameters
144 floated parameters

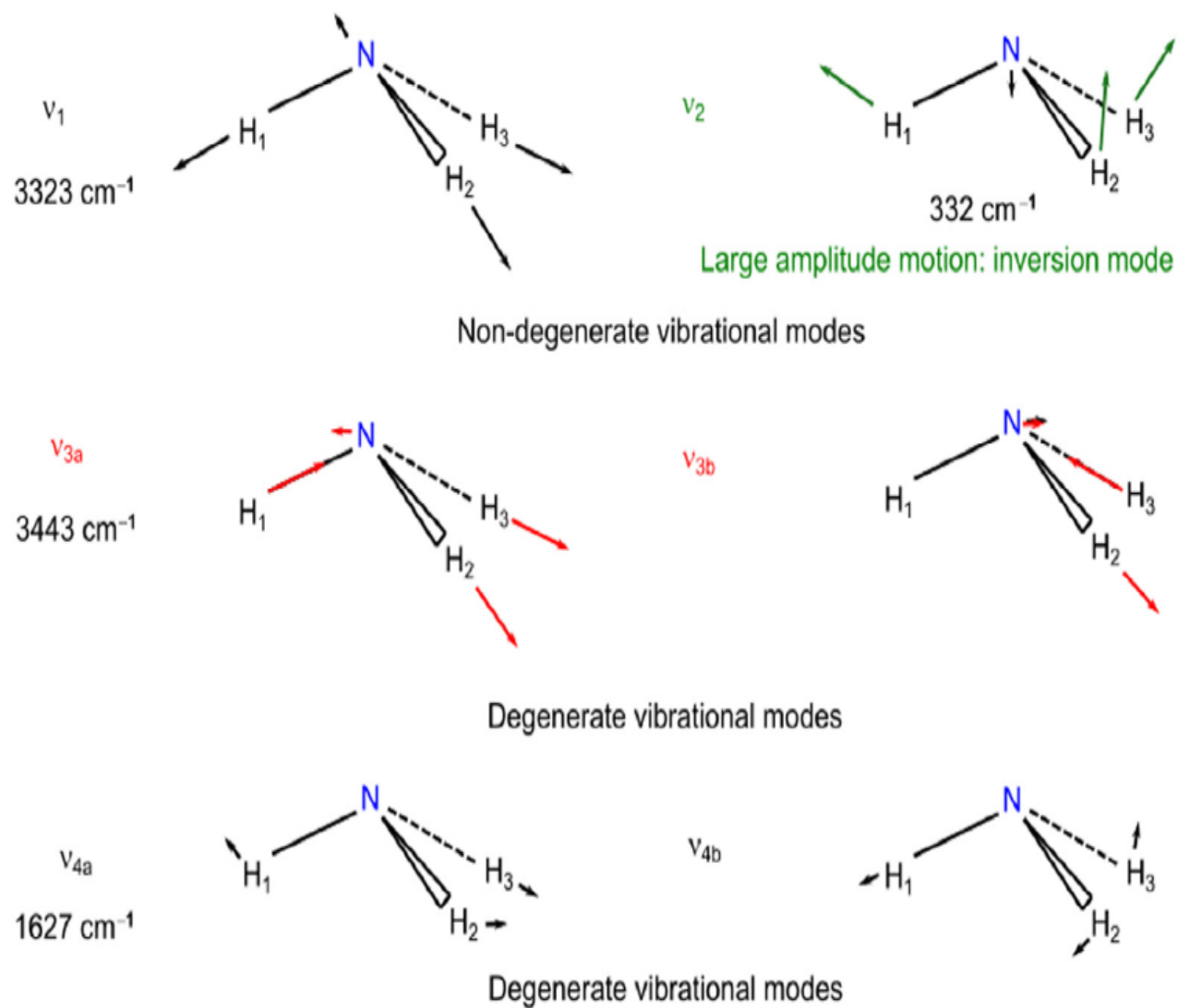What makes NH_3 so hard???

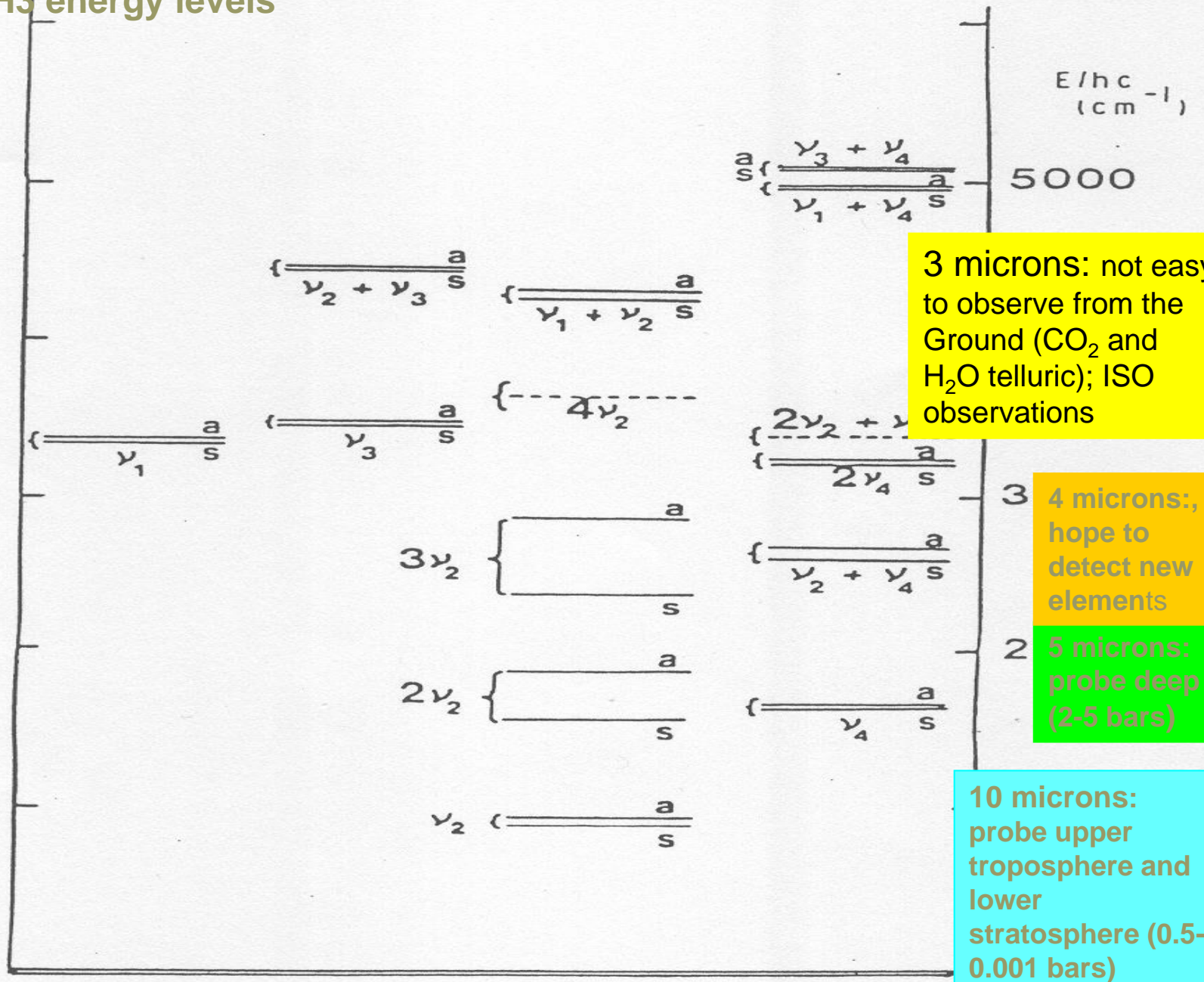Large amplitude motion : inversion

Fig. 4. The vibrational modes of ammonia. For the degenerate modes, two orthogonal components are depicted.

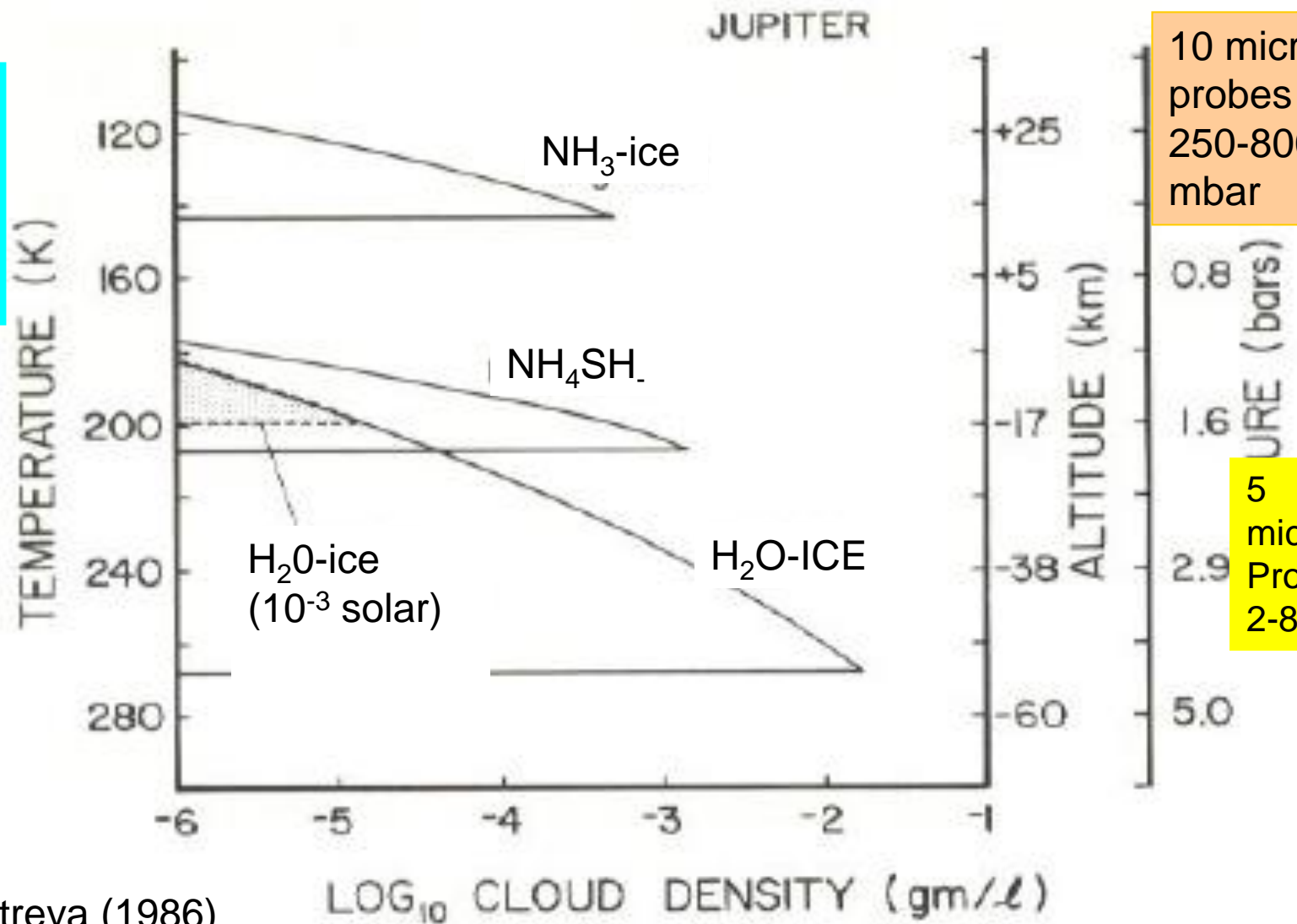# NH$_3$ ENERGY LEVELS

NH3 energy levels

E/hc (cm^{-1})

$\nu_3 + \nu_4$ a s

$\nu_1 + \nu_4$ a s

5000

$\nu_2 + \nu_3$ a s

$\nu_1 + \nu_2$ a s

$4\nu_2$

ν_1 a s

ν_3 a s

$2\nu_2 + \nu$

$2\nu_4$ a s

3

$3\nu_2$ a s

$\nu_2 + \nu_4$ a s

$2\nu_2$ a s

2

ν_4 a s

ν_2 a s

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 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
2200-3100	$3\nu_2/\nu_2+\nu_4$ +hot bands	1.	0.0069	6	Kleiner et al 1995 Cottaz et al 2001
1300-2000	$2\nu_2/\nu_4$ +hot bands	120.	0.003	5	Cottaz et al 2000 Cottaz et al 2001
700-1200	ν_2 +hot bands	568.	0.00005	2	Chen et al 1998, Belov et al 1980, 1998 Urban et al 1981, 2000
19-40	rotation	441.	0.000002	2	Sasada et al. 1992 and many others !

3 microns

4 microns

5 microns

10 microns

AMMONIA NH$_3$: INDICATOR OF THE JOVIAN DYNAMICS AND METEOROLOGY

JUPITER

3 microns: Broad signature NH$_3$-ice

10 microns: probes 250-800 mbar

5 microns: Probes 2-8 bars

NH$_3$-ice

NH$_4$SH

H$_2$0-ice (10^{-3} solar)

H$_2$O-ICE

TEMPERATURE (K)

ALTITUDE (km)

URE (bars)

LOG$_{10}$ CLOUD DENSITY (gm/ℓ)

From Atreya (1986)

In Saturn, troposphere colder -> condensation levels lower

Observed ISO-SWS spectrum of Jupiter and synthetic spectrum at 3 μm:
Spectral signature of the NH₃ ice cloud at 0.5 bar,
first spectroscopically identified!
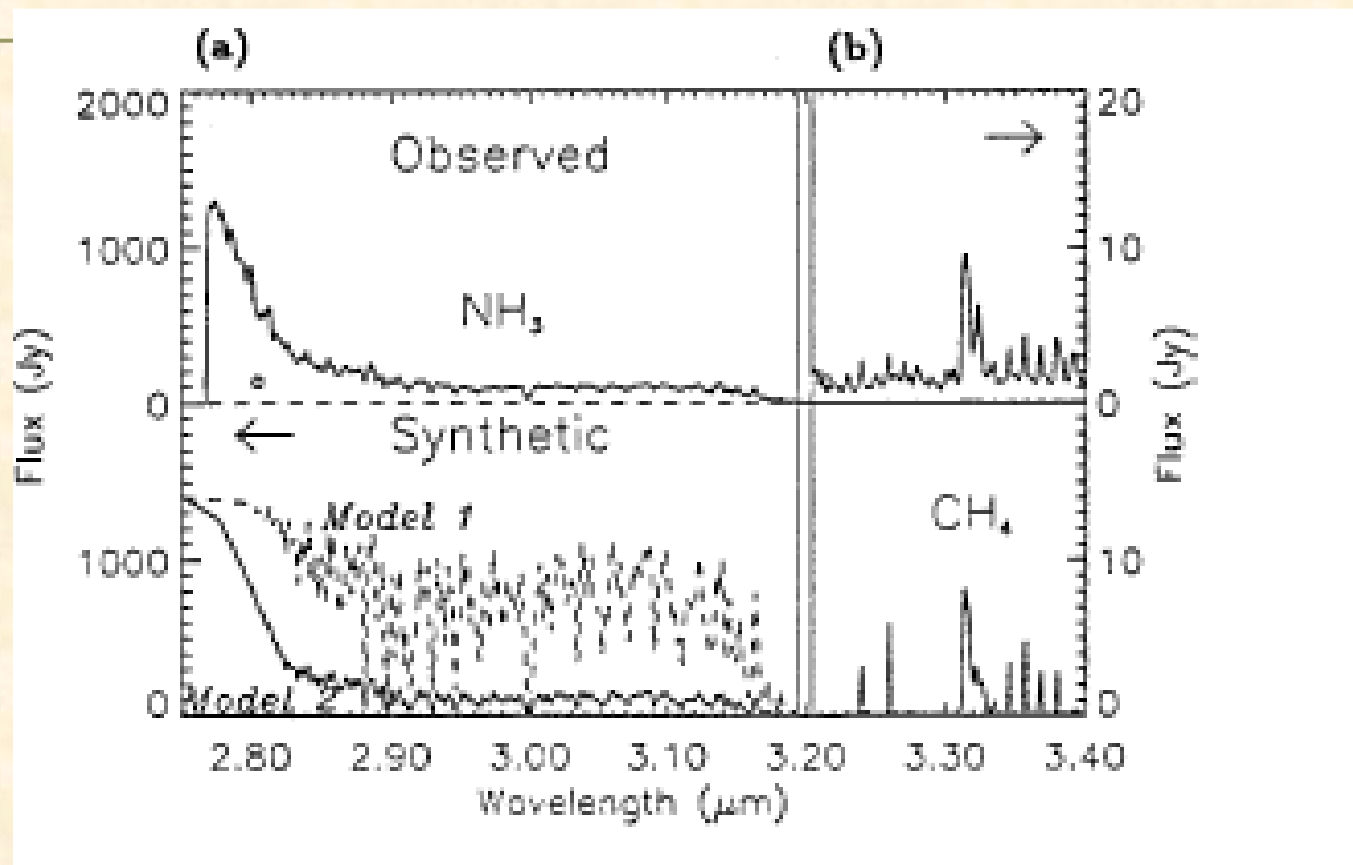
Molecular absorptions: NH₃, CH₄ and CH₃D.
Model 1: constant albedo cloud
Model 2: albedo-varying cloud

Encrenaz et al Astron. Astrophys. 315, L397 (1996); Brooke et al Icarus 136, 1 (1998)

Comparison between observed and predicted spectra of NH_3 at 5 microns
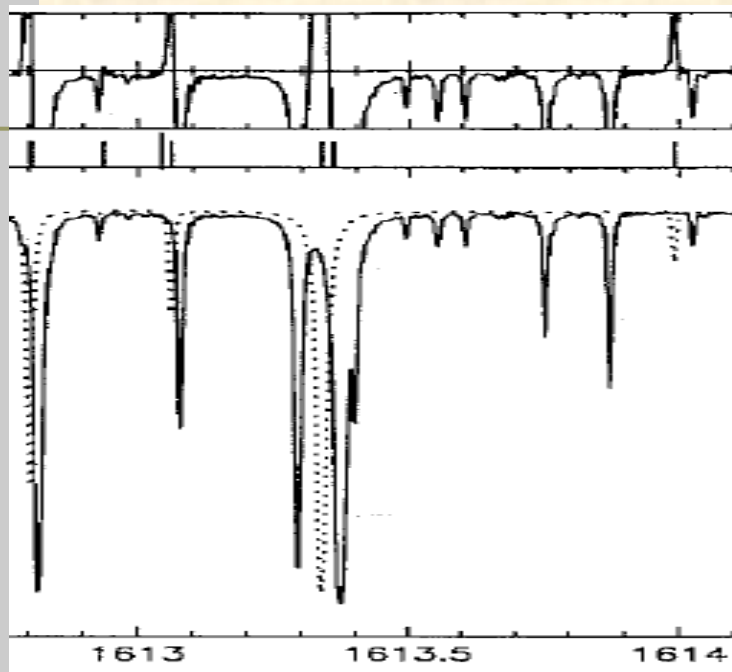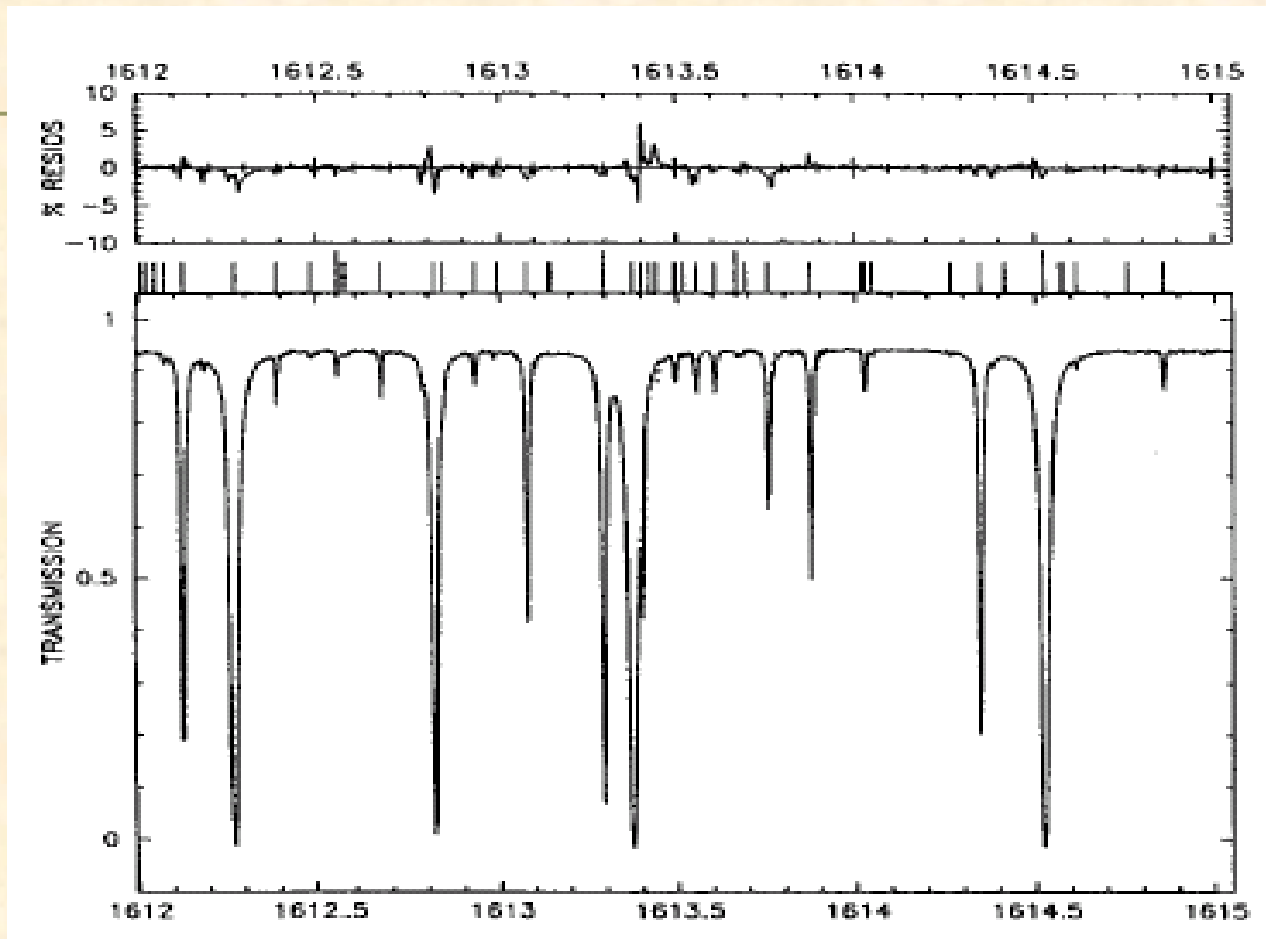
.... 1996 Hitran database
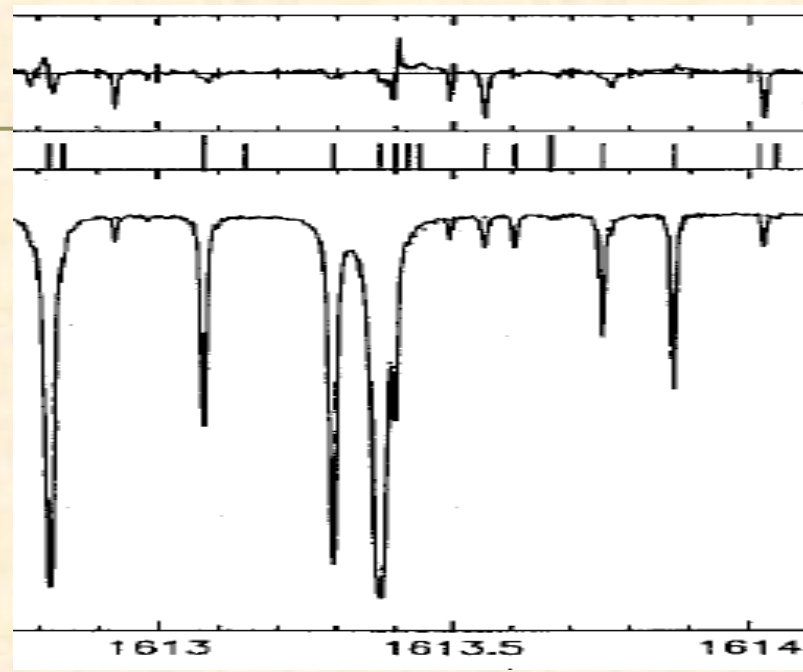
Cottaz et al, JMS 203, 285 (2000)

---- observed spectra , Kitt Peak FTS
0.0056 cm^{-1} resolution,
P = 0.25m, P =5.5 Torr

Taking into account the hot bands …

Cottaz et al JMS, 209, 30 (2001)

HITRAN 2000: 29084 lines for $^{14}NH_3$ and $^{15}NH_3$ from 0.06 to 5294.5 cm^{-1}….

Atmospheres of other planets and exo-planets: CH_4

1) Solar system: many molecules studied during the Cassini mission In Titan (CH_4, CH_3CN, CH_3D, C_4H_2 HC_5N, C_3H_4…) or during Mars express and venus express (CO et CO_2).

Challenge: how to model the complex Vibration-rotation couplings?

2) exoplanets: very high temperatures Large pressure domain, large spectral Range. Atmospheres are unknown Observational constraints ?

Challenge: develop new approaches To extend at high temperature (ab initio, approximations in hamiltonian)
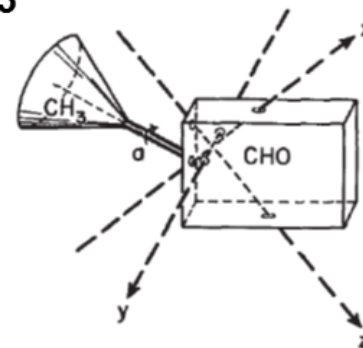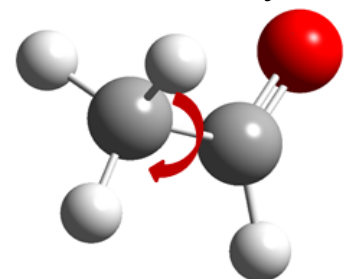
New missions to Jupiter JUNO (NASA) JUICE (ESA)

Boudon et al
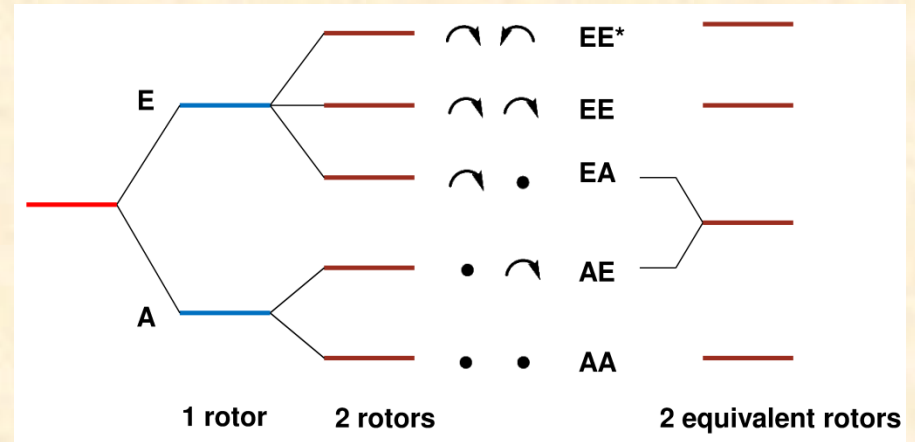*J. Quant. Spectrosc. Radiat. Transf., 190, 88-88 (2017)*
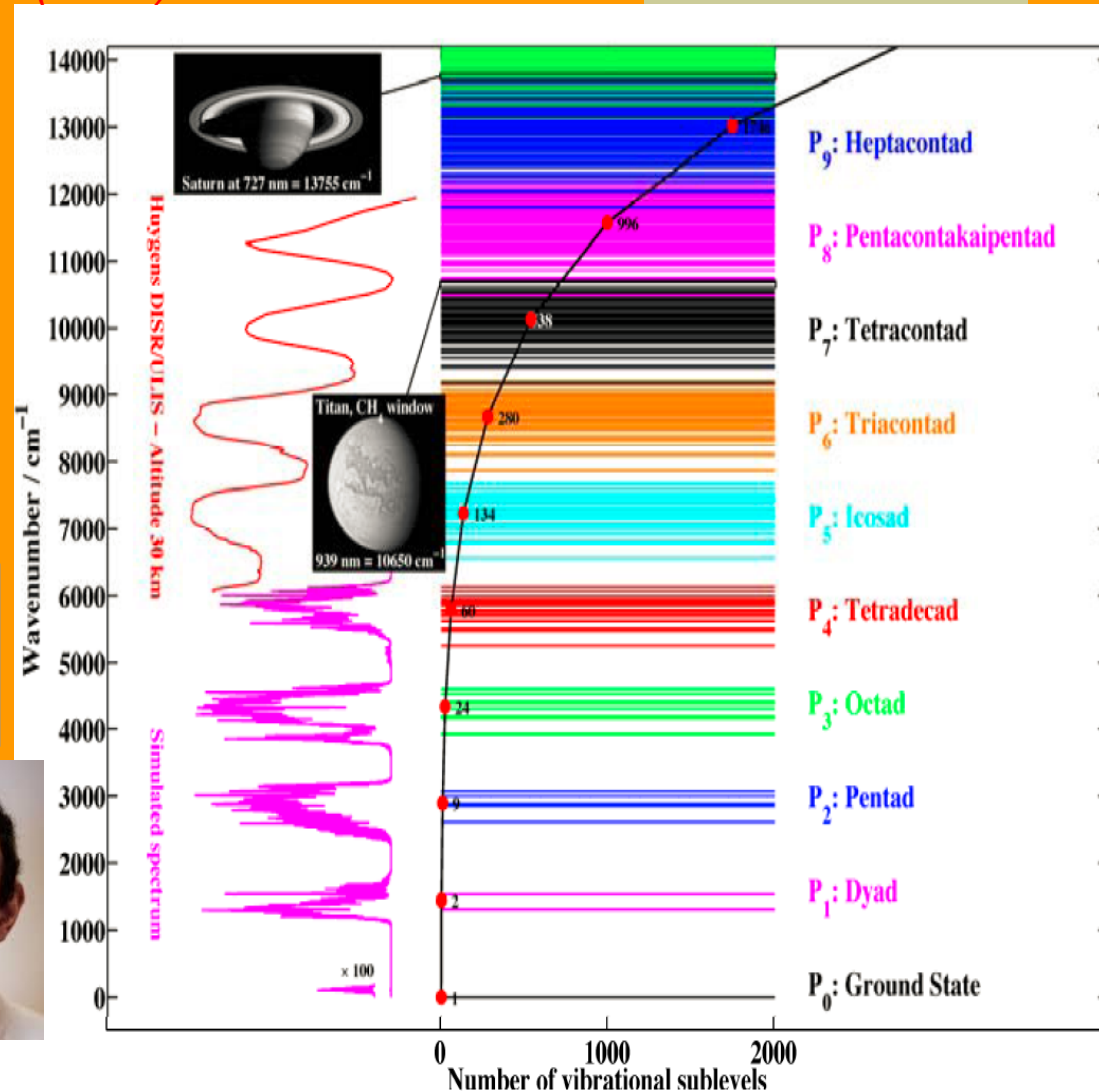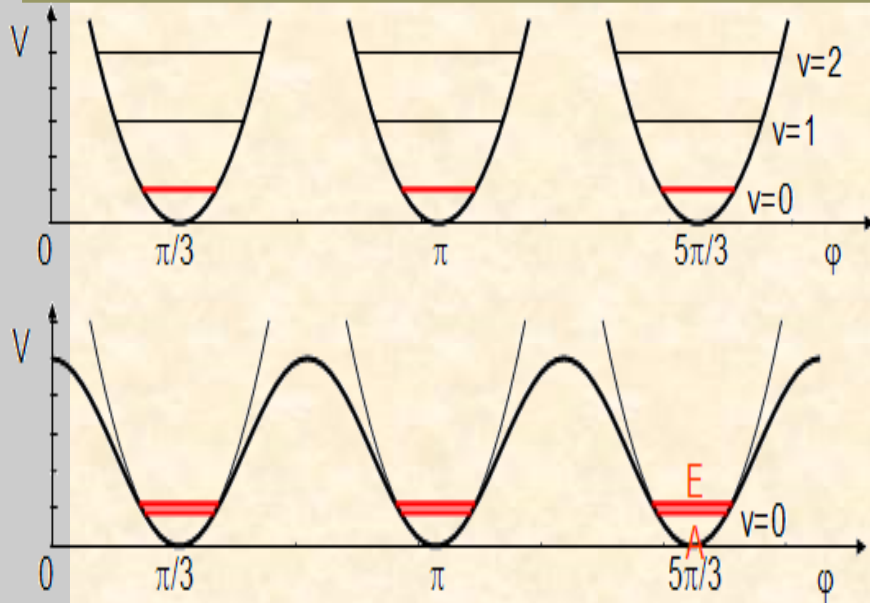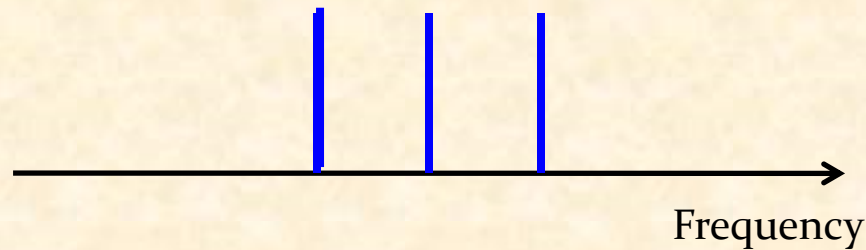
Internal rotation
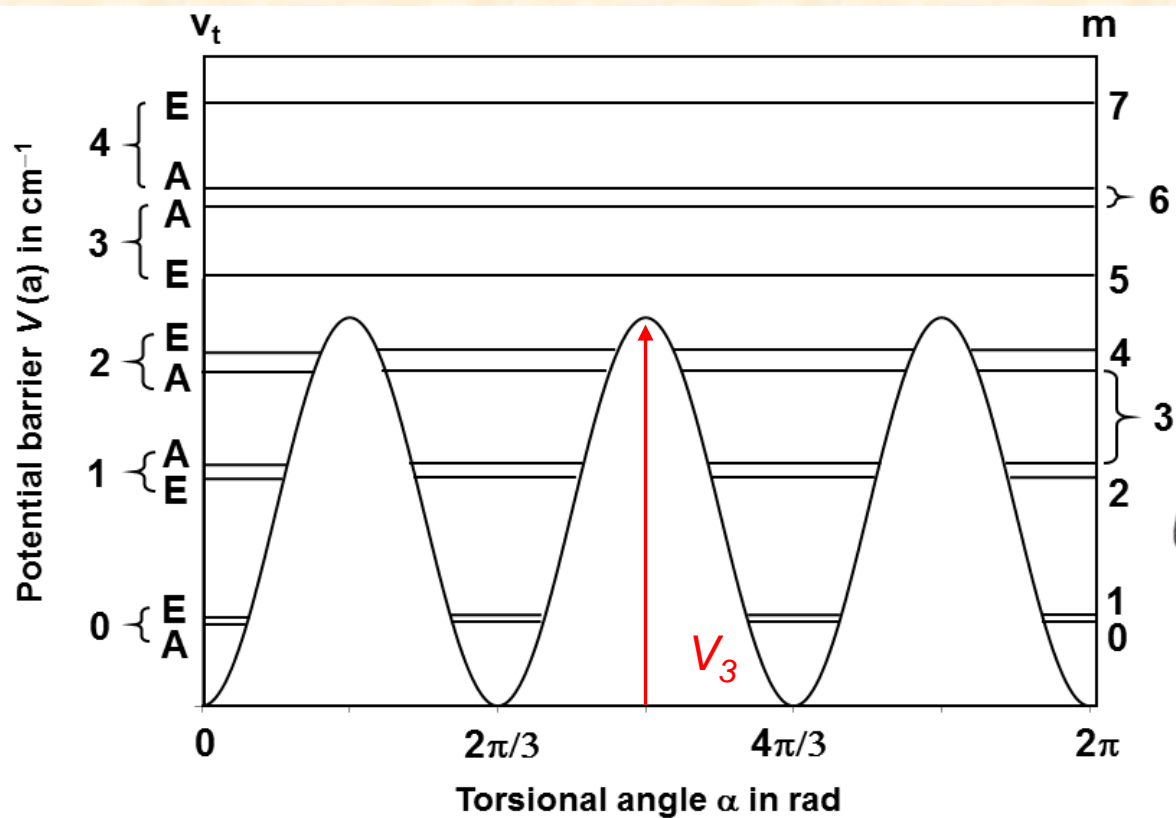
Acetaldehyde

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

Lin and Swalen Rev. Mod. Phys 1959

Internal rotation

Internal rotors are detected in the interstellar medium (ISM), comets, meteorites and asteroids

present in any of the different phases leading to stellar and planetary formation from the molecular clouds to the star and its planets

6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms
CH_3OH	CH_3CHO	$HC(O)OCH_3$	CH_3OCH_3	CH_3COCH_3	$CH_3C(O)OCH_3$	$C_2H_5OCH_3$
CH_3SH	CH_3NH_2	CH_3COOH	CH_3CONH_2	CH_3CHCH_2O		
	CH_3NCO	CH_3CHNH	CH_3NHCHO^b	CH_3OCH_2OH		