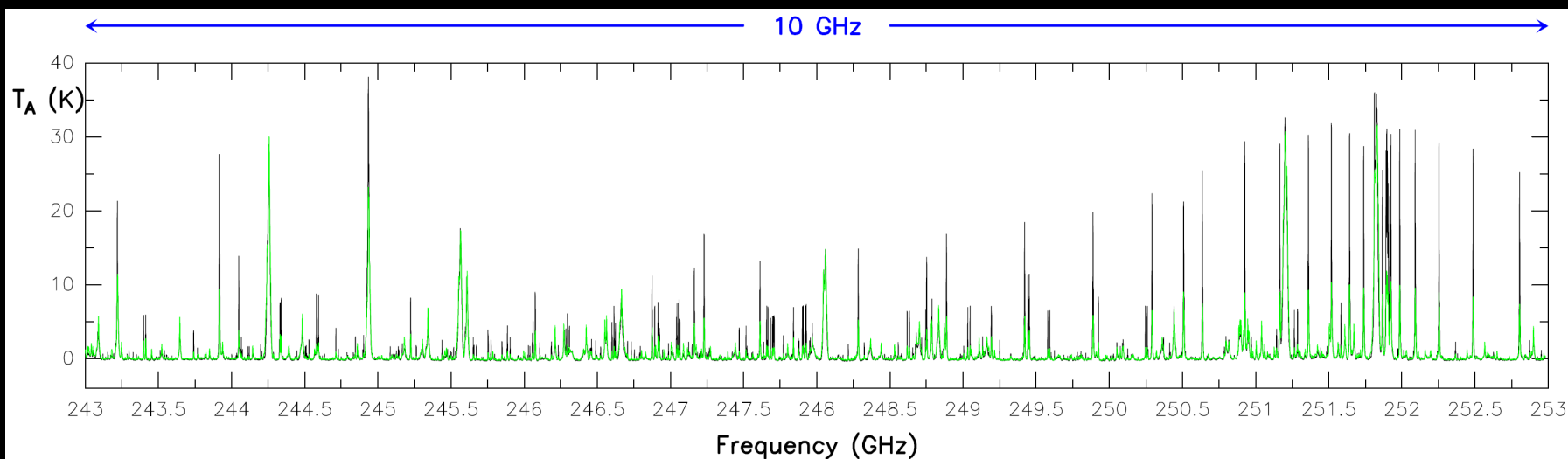


# An Introduction to Molecular Spectroscopy

**José Cernicharo**

**IFF-CSIC**

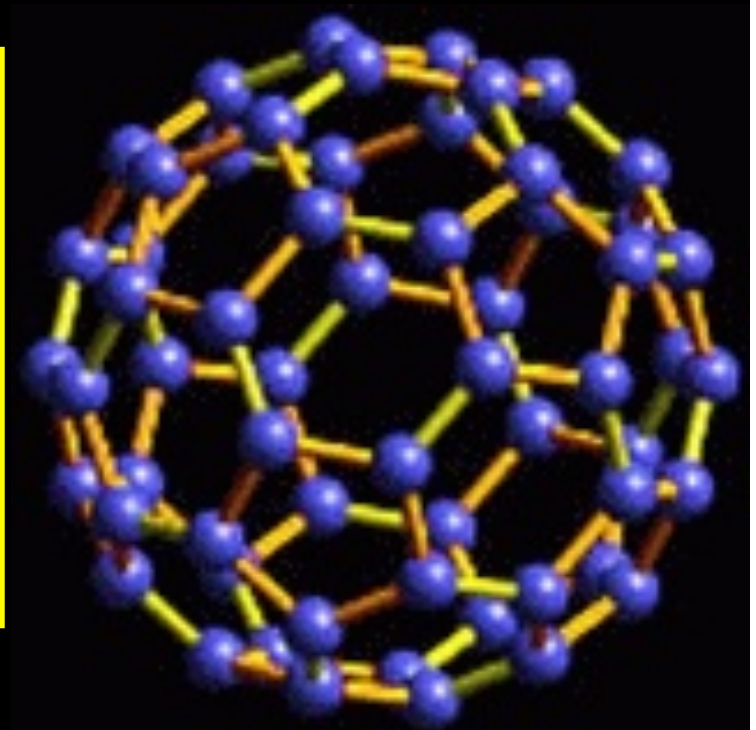
*jose.cernicharo@csic.es*



# INTRODUCTION TO MOLECULAR RADIO ASTRONOMY FROM MILLIMETER TO SUBMILLIMETER AND FAR INFRARED

## Molecular Spectroscopy

What are the mechanisms  
of emitting spectral lines  
for molecules? Which kind  
of transitions are allowed?



# Or how to shock our students

## Hot Molecular Cores



# Ground Based observations of high Mass star forming regions

A&A 517, A96 (2010)  
DOI: 10.1051/0004-6361/200913501  
©ESO 2010

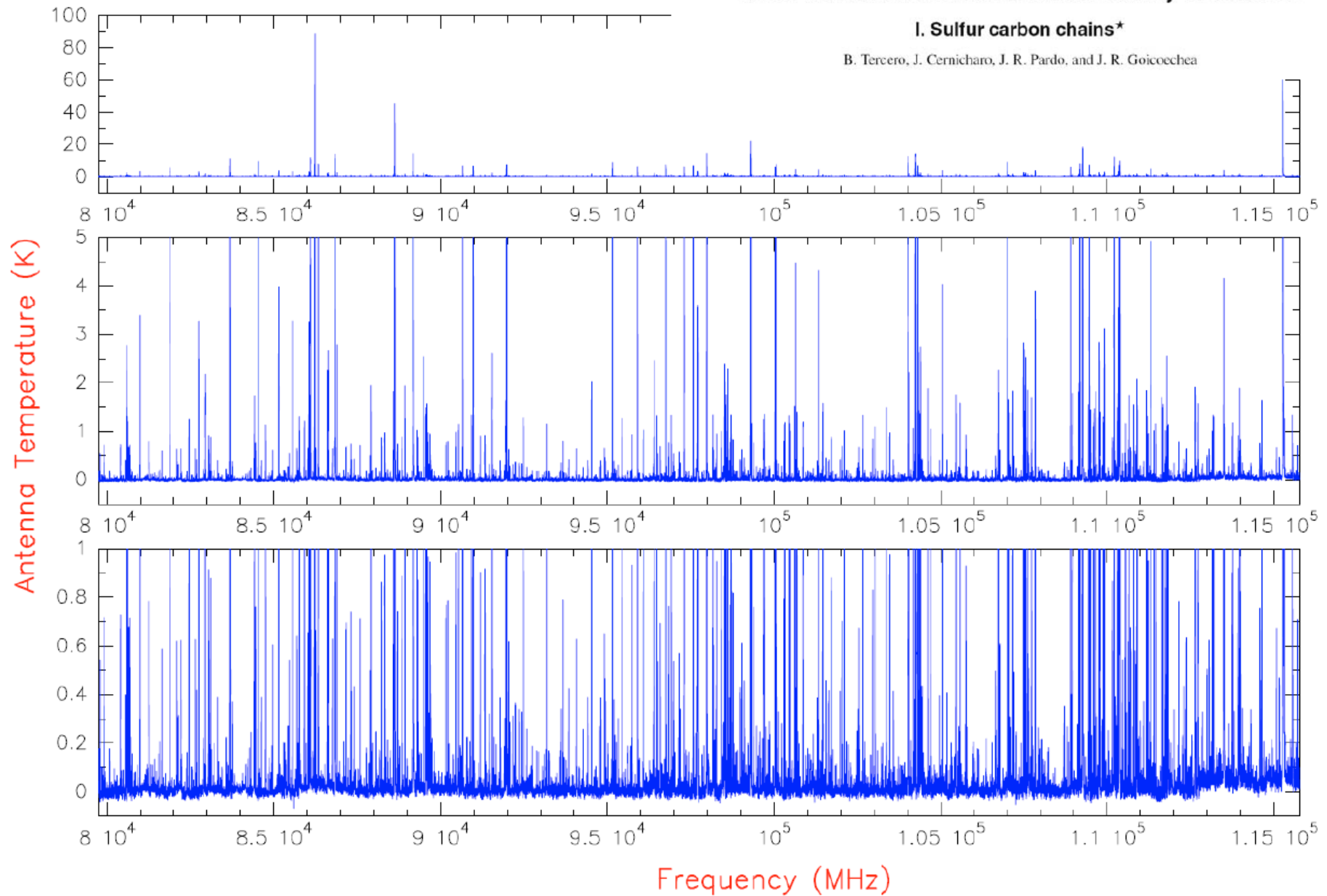
Astronomy  
& Astrophysics

A&A 517, A

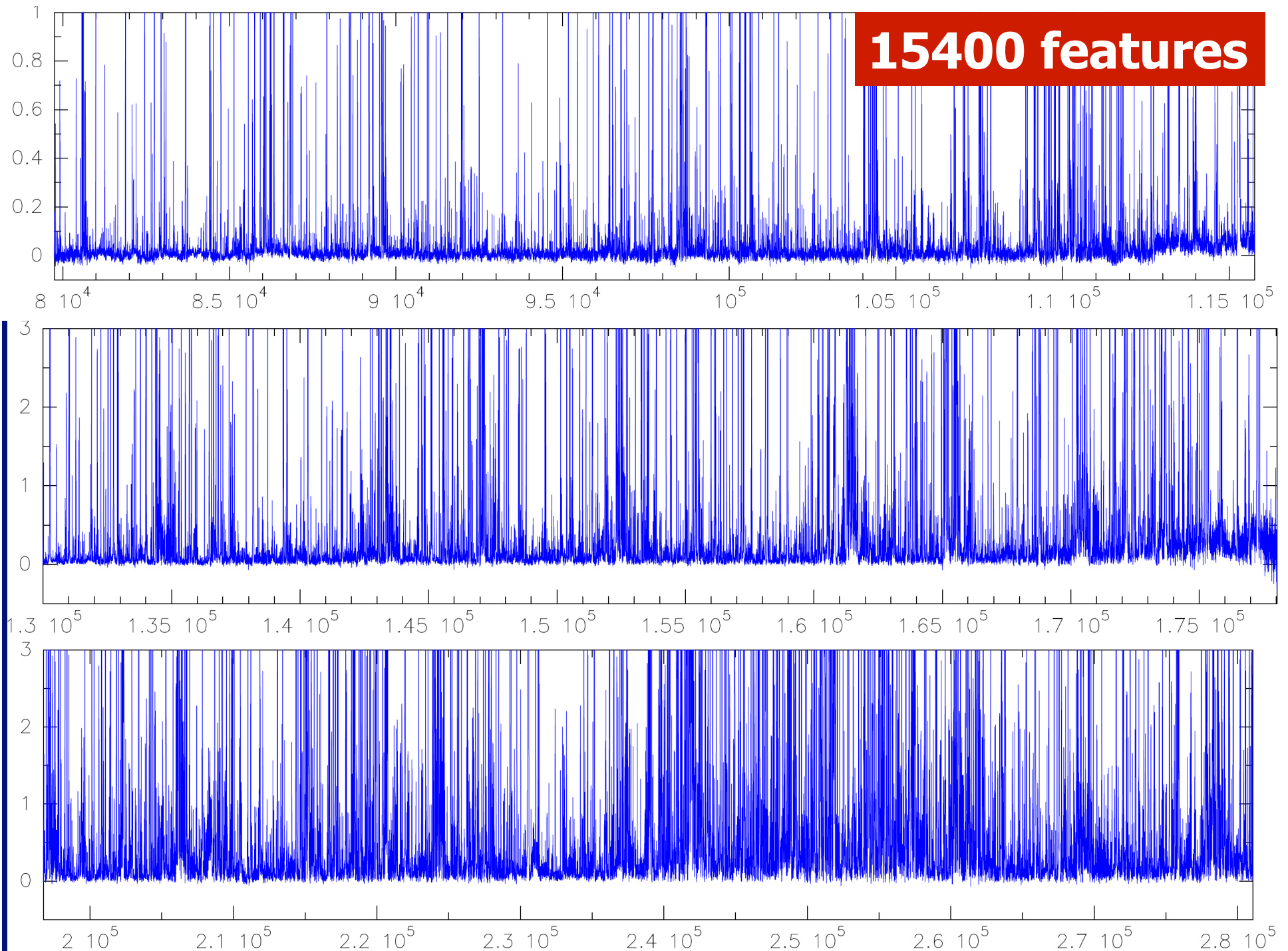
## A line confusion limited millimeter survey of Orion KL

### I. Sulfur carbon chains\*

B. Tercero, J. Cernicharo, J. R. Pardo, and J. R. Goicoechea

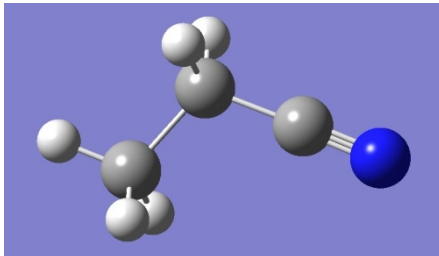
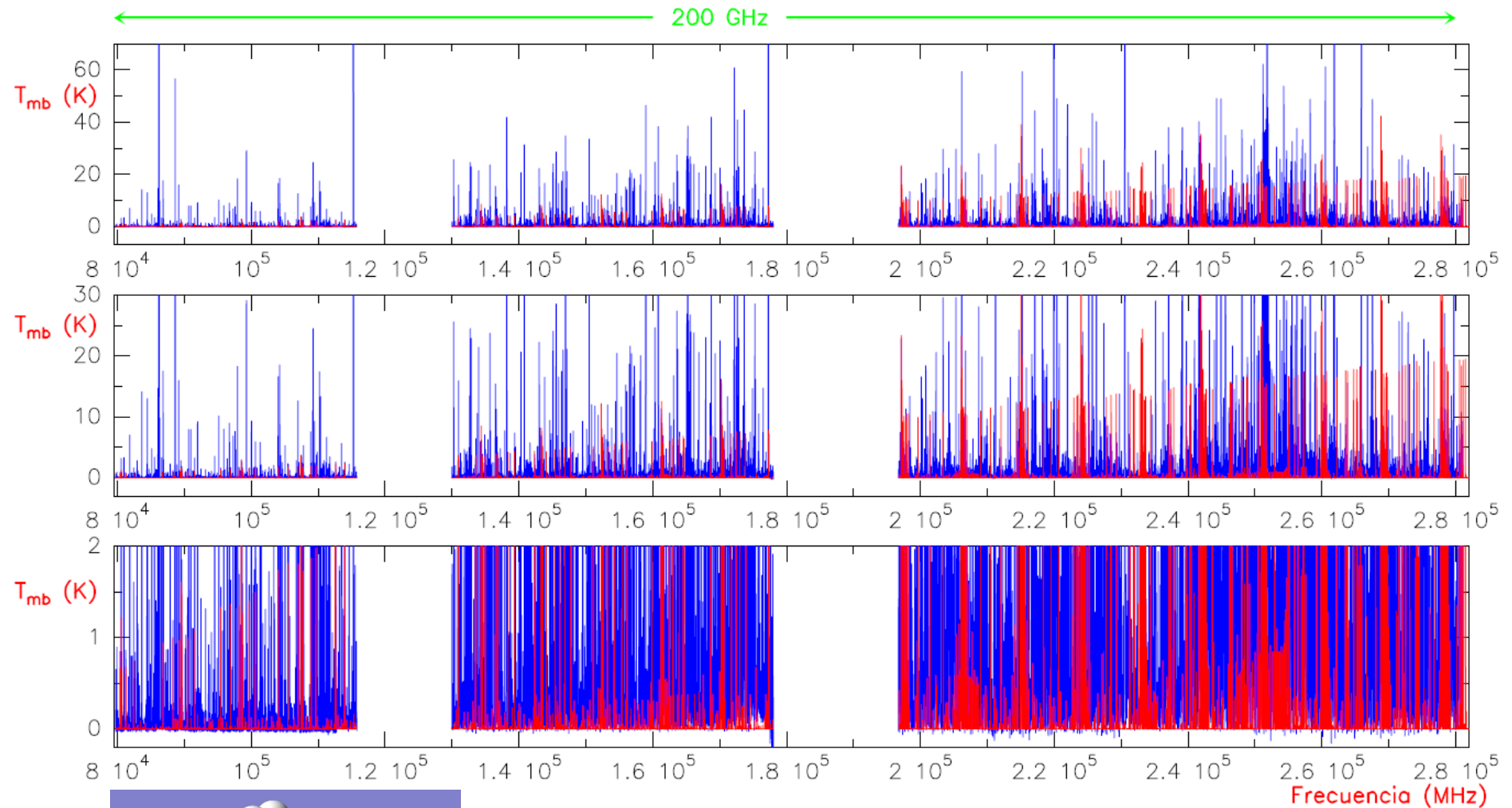


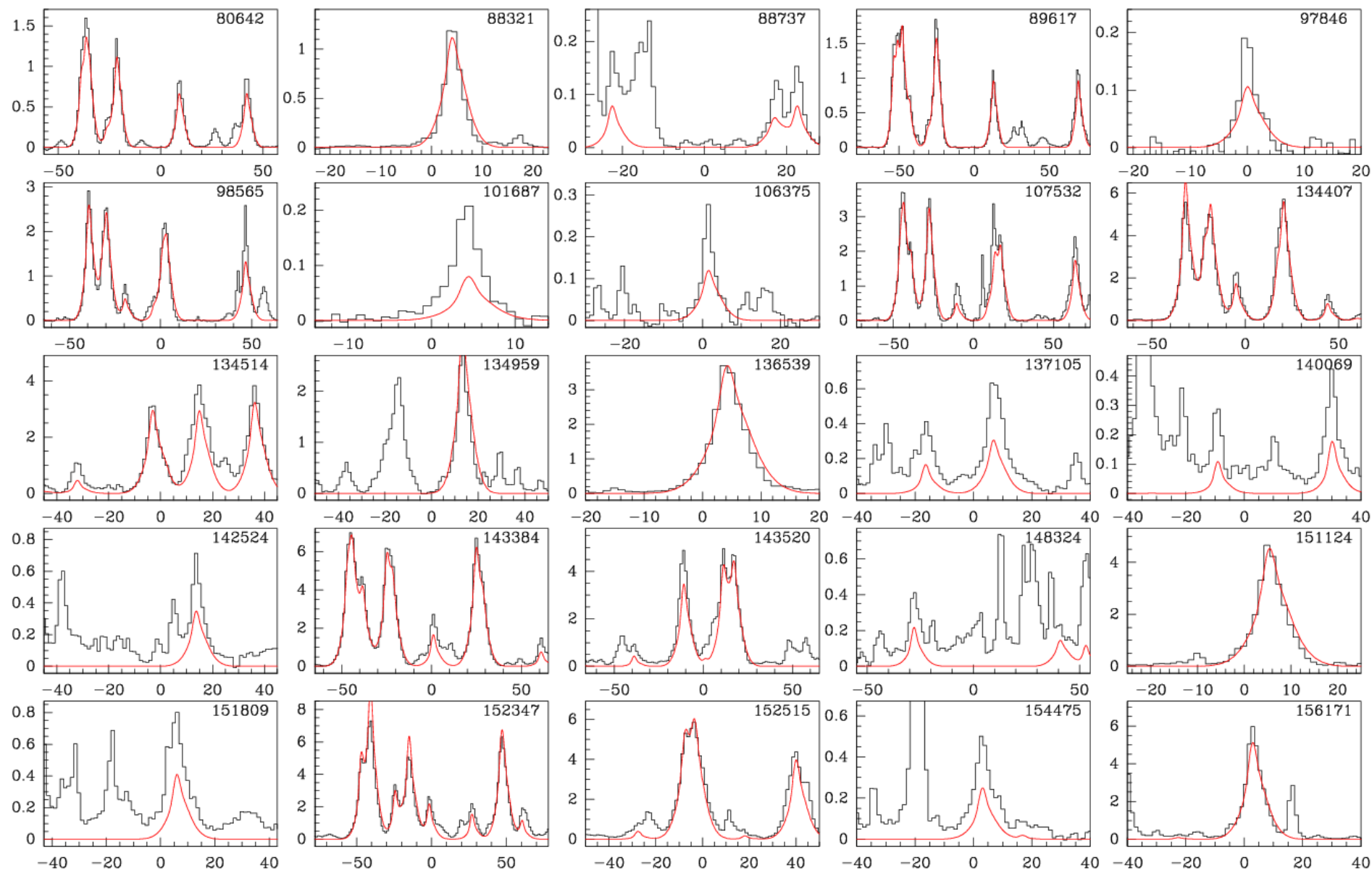
**15400 features**

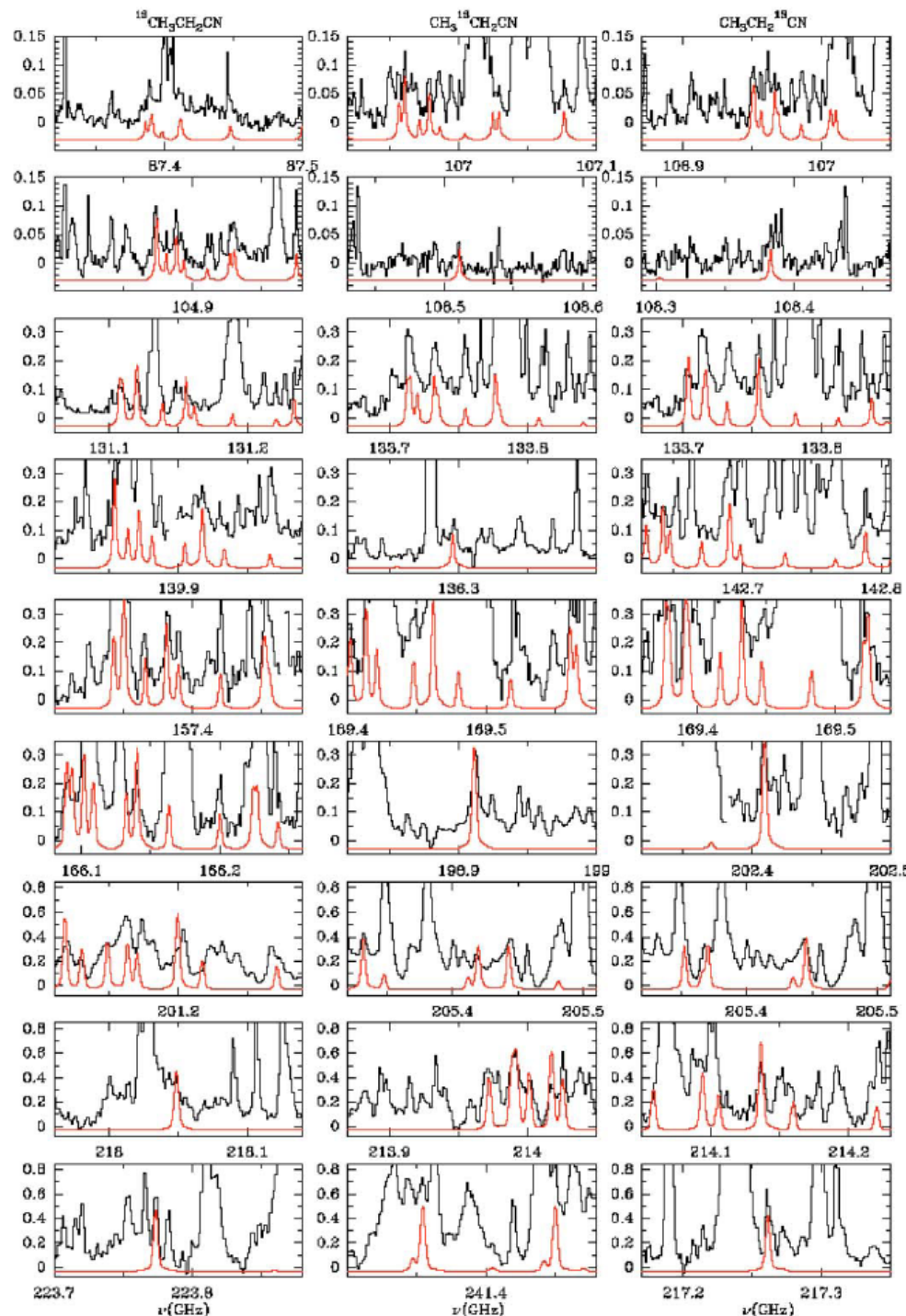




# Ethyl Cyanide (The Contaminator), $\text{CH}_3\text{CH}_2\text{CN}$







**Collaboration with L. Margules, I. Kleiner et al. →**

More than 800 lines from the isotopes of  $\text{CH}_3\text{CH}_2\text{CN}$

Around 600 lines from the vibrational excited states of ethyl cyanide

More than 400 lines from those of  $\text{CH}_3\text{OCOH}$

Around 800-1000 lines identified every 2 years in Orion. All lines above confusion limit could be identified around 2020 !!!

Belen started her PhD based on this line survey in 2006.

When combined with HEXOS data=> Work for a long period

ALMA ?

# Line frequencies: public and private catalogs

**WARNING: Frequency predictions can be very uncertain for frequency ranges outside the observed domains in the laboratories**

# **Formation of molecules and molecular stability**

# ¿ How to explain the molecular stability under the hypothesis of quantum physics?

**The first hypothesis has to be established from analogy with atoms :**

**Each electron in a molecule must be described by a wave function which provides the electronic density probability around the nuclei**

The main difference between atoms and molecules is that  
In atoms electrons are submitted to a central potential while  
In molecules the electrons are submitted to a potential  
arising from all nuclei, i.e., each electron moves under  
the action of all nuclei.

The goal of molecular physics is to find the wave function  
 $\psi(r, \theta, \varphi)$  for each electron in the molecule and obviously  
the different energy levels of the molecule (rotation,  
vibration, and electronic levels).

$\psi^2$  represents the density of electronic cloud in each point  
around the nuclei. Very sophisticated methods have to be  
used to obtain the energy levels with the accuracy required  
in molecular spectroscopy (Earth or Space)

**Assuming a molecule can be described from our experience in atomic physics :**

- 1) Each molecular orbital will contain two electrons with opposite spins.***
- 2) In the ground state electrons start to fill orbitals from the lowest energy to the highest levels***
- 3) In the ground state and in the simplest approximation the electronic energy is obtained by adding the energies of the individual electrons (no interaction at all between electrons).***
- 4) The wave function is the product of the mono-electronic wave functions.***

With these simple assumption let us consider molecular hydrogen ( $H_2$ ), i.e., the simplest molecule, and the most abundant one in the space.

Let  $H_A$  and  $H_B$  be two atoms of hydrogen and let  $\psi_A$  and  $\psi_B$  the wave functions of the electron in atoms  $H_A$  and  $H_B$  when both atoms are far away.

Obviously these wave functions do not represent the electrons when the two atoms are very close and forming, perhaps, molecular hydrogen.

However, the electron of atom  $H_A$  when  $H_A$  is far from  $H_B$  will be reasonably well represented by  $\psi_A$  and when the same electron is close to atom  $H_B$  by  $\psi_B$ .

It is reasonable to think that the wave function describing the electrons in the molecule of hydrogen can be given by

$$\Psi_{AB} = \psi_A + \lambda \psi_B$$

The square of  $\lambda$  represents the contribution of each atomic orbital to the molecular orbital. In the case of  $H_2$  it is obvious that  $\lambda^2 = 1$  and  $\lambda = \pm 1$

Hence, these very simple hypothesis let us to the following conclusions :

A) There are two possible states with different electronic energy. If the energy of the electrons 1s in the hydrogen atoms is  $E_0$ , then one of these two levels will have energy  $E_+ < E_0$  and the other will have an energy  $E_- > E_0$ .

## B) The molecular orbital

$$\Psi_+ = \psi_A + \psi_B$$

will have the energy  $E_+$  while the molecular orbital

$$\Psi_- = \psi_A - \psi_B$$

will have the energy  $E_-$ .

C) The ground state of the molecule is obtained when two electrons are placed in the orbital  $E_+$ . Obviously, both electrons should have opposite spins.

D) The orbital  $E_-$  may be partially or fully used by the electrons. The associated states correspond to the excited states of the molecule.

E) The electronic energy of the molecule, in this simple approximation, is the sum of the individual energies of the electrons. In the ground state is, hence,  $2E_+$ .

F) The wave function of the system,  $\Phi$ , is the product of the individual wave functions of the electrons (1 y 2)

$$\Phi = \Psi_+(1) \Psi_+(2) = [\psi_A(1) + \psi_B(1)] [\psi_A(2) + \psi_B(2)]$$

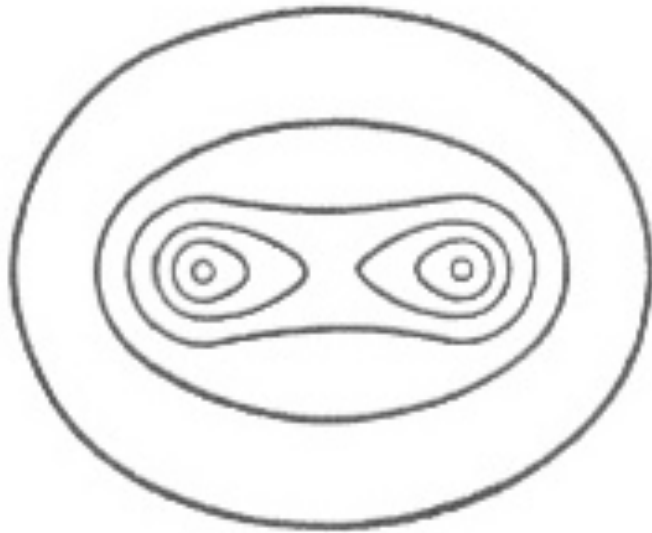
F) The dependency of the electronic energy of the system as a function of the internuclear distance will have the following shape

The function corresponding to the orbital  $\Psi_+$  has a very well defined minimum for  $r = 0.85 \text{ \AA}$  (experimental =  $0.74 \text{ \AA}$  !!!) and the binding energy is  $2.7 \text{ eV}$  (experimental  $4.7 \text{ eV}$  !!!, the interaction between electrons has not been considered; also the fact that two protons interact with each electron has to be included).

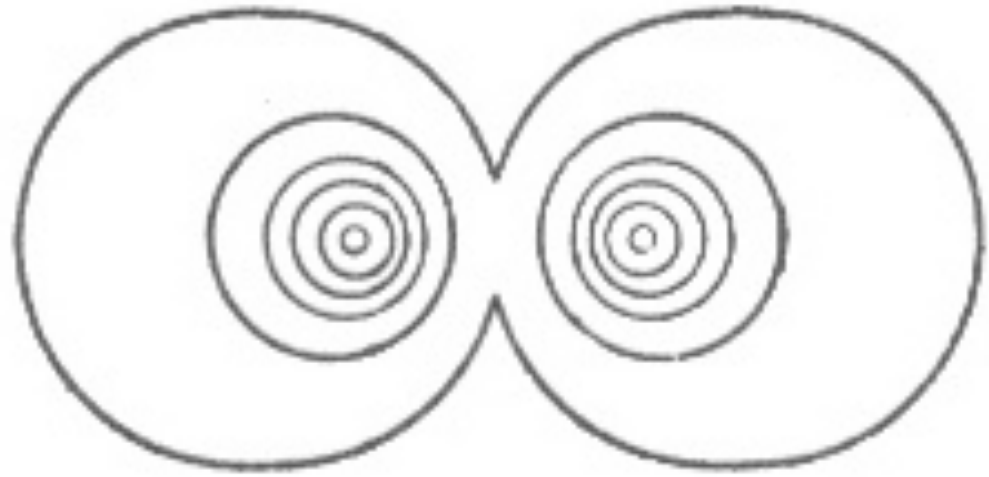
The orbital  $\Psi_-$  shows a continuum increase of energy when the distance between the atoms decreases. It is an unbound state. The electronic density probability in both orbitals  $\Psi_+$  and  $\Psi_-$  is given by

$$\begin{aligned}\Psi_+^2 &= \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B \\ \Psi_-^2 &= \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B\end{aligned}$$

The electronic isodensity contours have the following shape

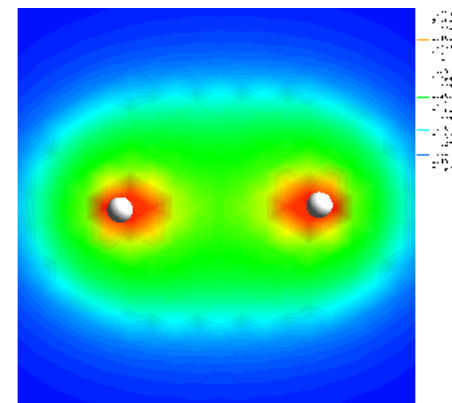
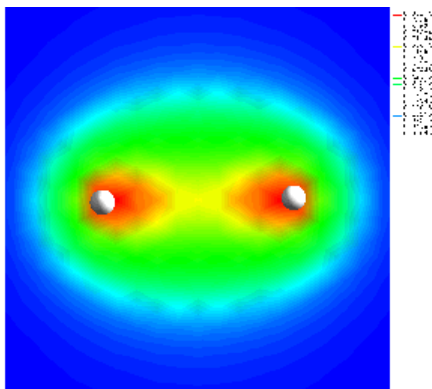


$\Psi_+$

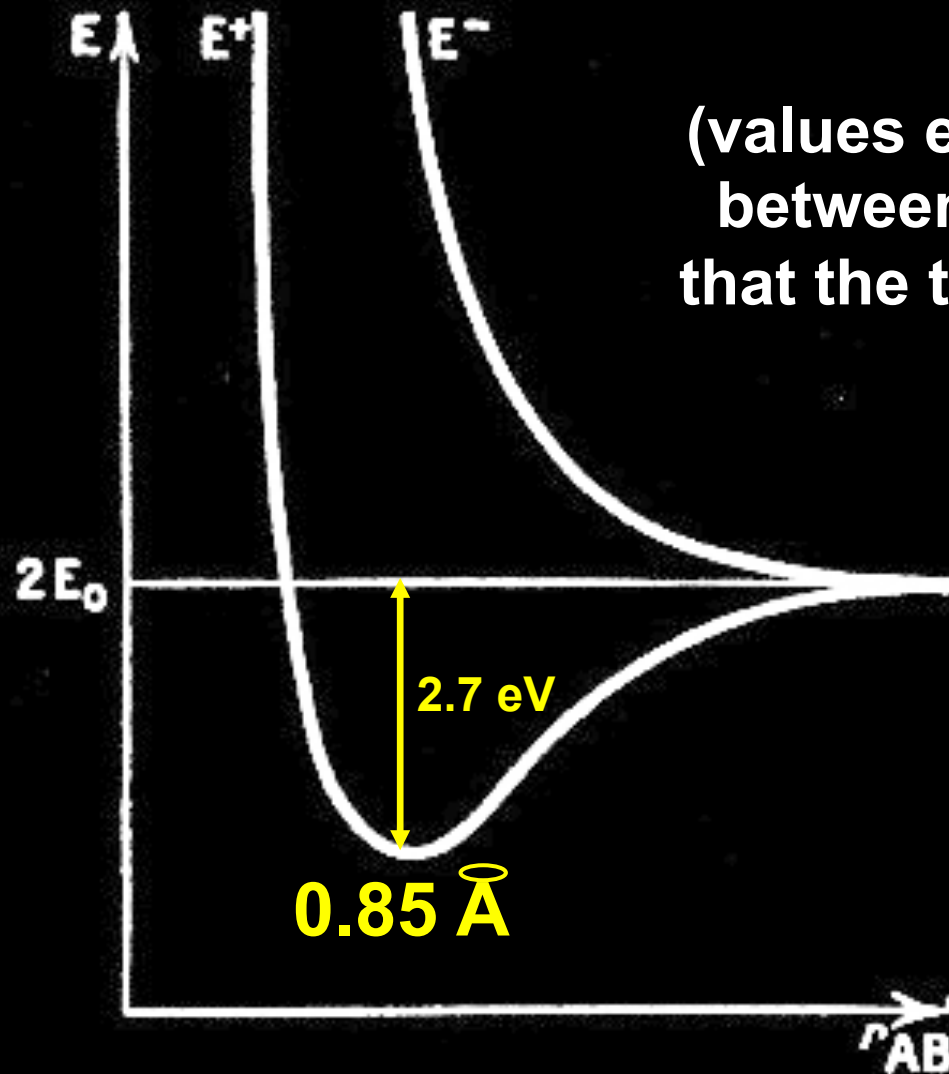


$\Psi_-$

In  $\Psi_+$  the electronic density has a maximum between the protons while in  $\Psi_-$  the electronic density is concentrated around each proton.



The dependency of the electronic energy of the system as a function of the internuclear distance has the following shape:



(values excluding the interaction between electrons and the fact that the two protons interact with the electrons)

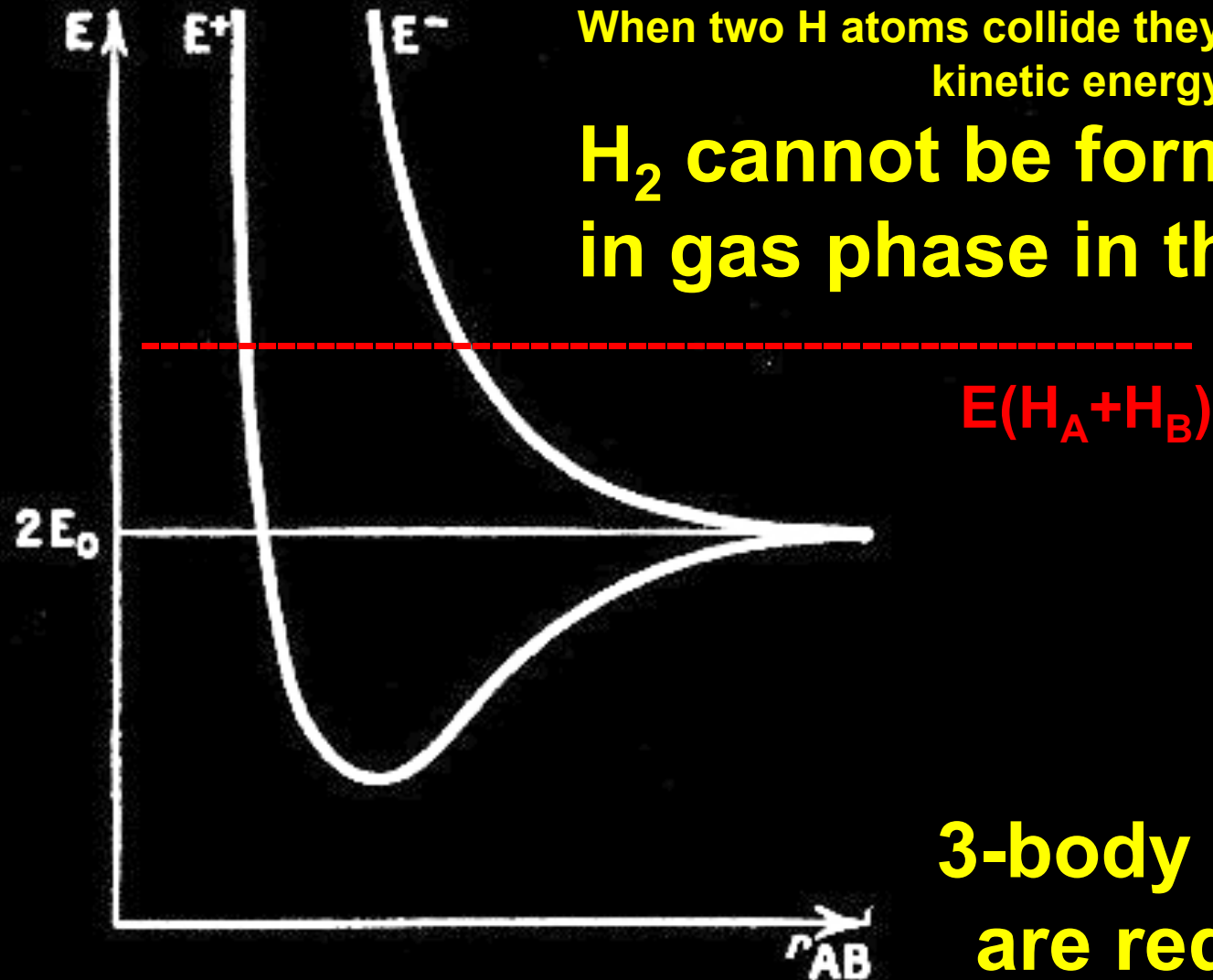
Experimental values:

$0.74 \text{ \AA}$  and  $4.7 \text{ eV}$

## IMPORTANT:

When two H atoms collide they have some extra kinetic energy

**H<sub>2</sub> cannot be formed  
in gas phase in the ISM !!!**



**3-body collisions  
are required  
(3rd body will carry out  
the excess of energy)**

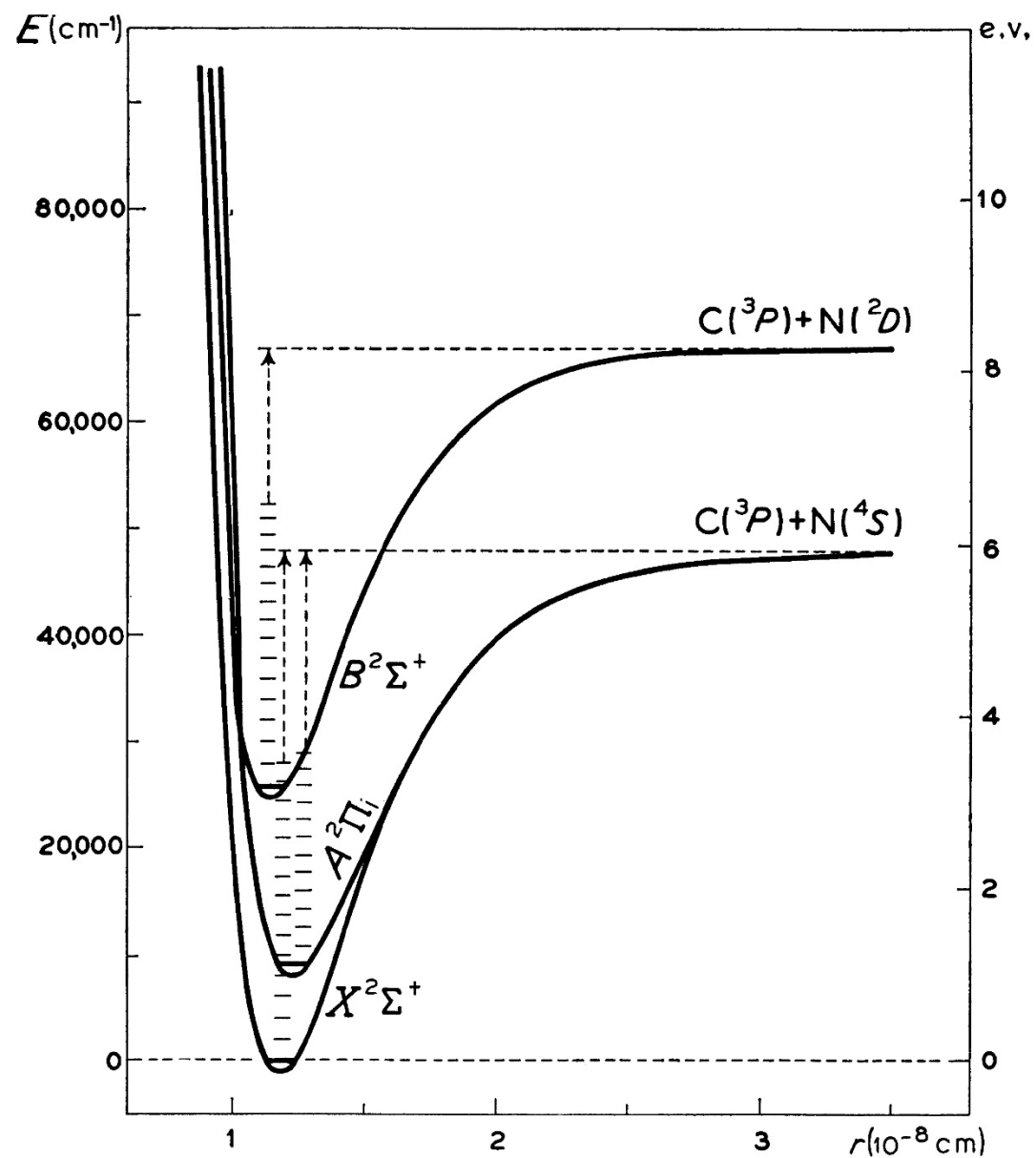
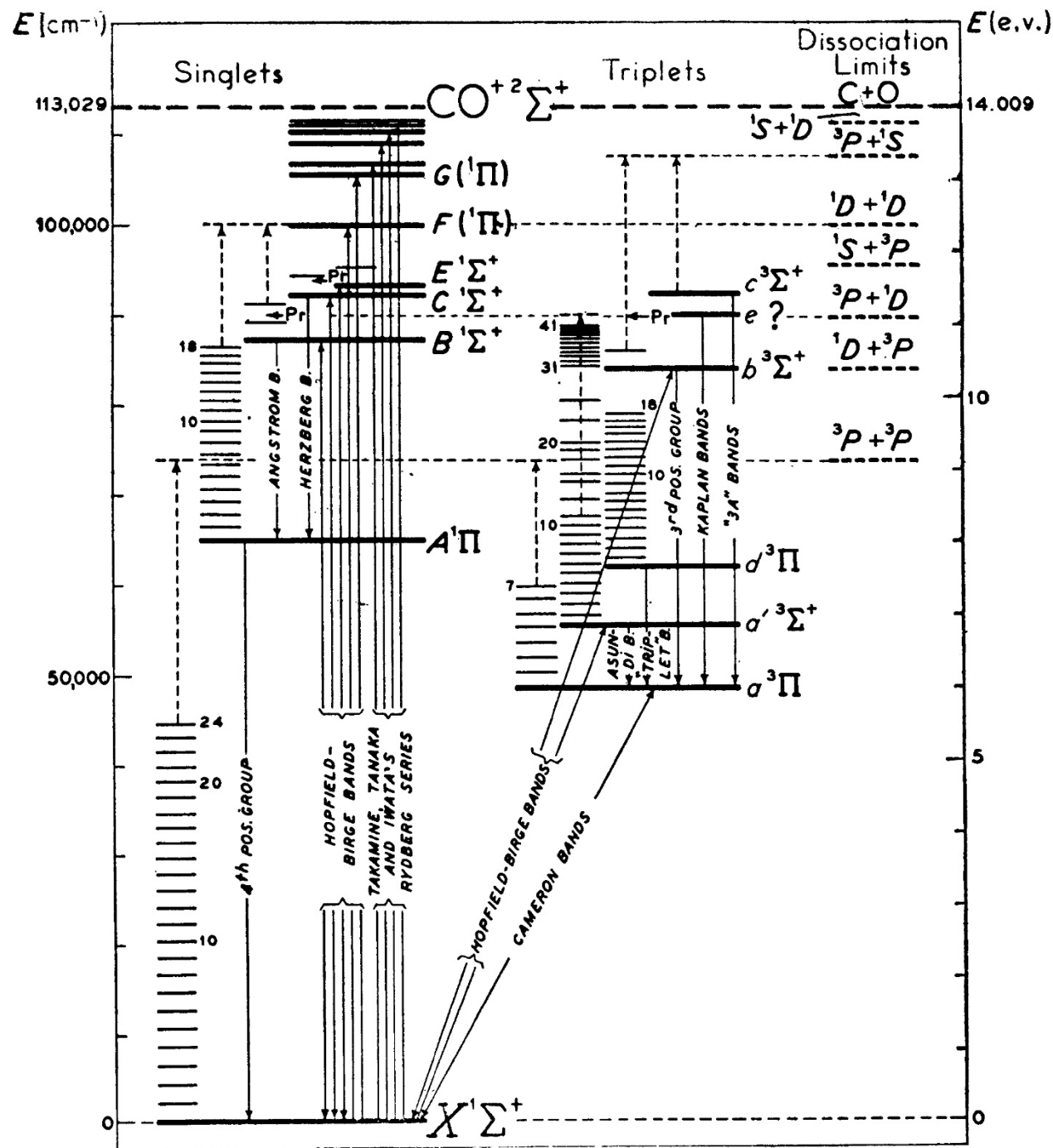


FIG. 200. Potential Curves of the Observed Electronic States of the CN Molecule. The magnitude of the heat of dissociation is not yet certain. If Gaydon's (34) high value for  $D_0^0(\text{CO})$  should turn out to be correct, a  $D_0^0(\text{CN})$  value of 7.6 e.v. would follow and the asymptotes in the figure would have to be altered correspondingly.



**Once a molecule is formed...**

# ONCE A MOLECULE IS FORMED THE INTERNAL ENERGY IS HIGHLY DIVERSIFIED

**Electronic:** Energy of the electronic orbitals

**Vibrational:** Energy of the vibrations of the nuclei around the equilibrium position

**Rotational:** Energy associated to the rotation of an electric dipole.

**Other:** unpaired **electron spins or nuclear spins** can couple with the angular momentum of the **electric dipole rotation**. Internal **magnetic dipoles** can couple with external magnetic fields, etc...

**MOST OF THESE EFFECTS ARE TREATED AS PERTURBATIONS OF THE ROTATIONAL ENERGY**

**There is a hierarchy in the  
energies needed for transitions**

**Energy, Frequency ( $E=h\nu$ )**



**Wavelength ( $\lambda=c/\nu$ )**



**Molecular Transitions**

**Rotational**

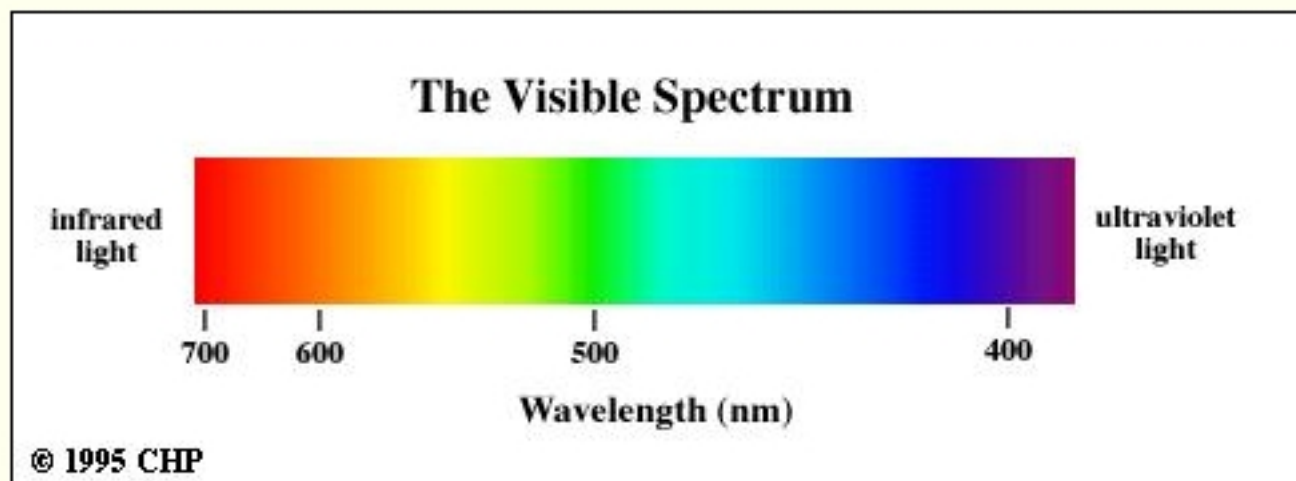
**Vibrational**

**Electronic**

**The quantum mechanical problem is relatively  
simple only for very small molecules.**

## Electromagnetic Spectrum

Type of Radiation	Frequency Range (Hz)	Wavelength Range	Type of Transition
gamma-rays	$10^{20}$ - $10^{24}$	<1 pm	nuclear
X-rays	$10^{17}$ - $10^{20}$	1 nm-1 pm	inner electron
ultraviolet	$10^{15}$ - $10^{17}$	400 nm-1 nm	outer electron
visible	$4$ - $7.5 \times 10^{14}$	750 nm-400 nm	outer electron
near-infrared	$1 \times 10^{14}$ - $4 \times 10^{14}$	2.5 $\mu$ m-750 nm	outer electron molecular vibrations
infrared	$10^{13}$ - $10^{14}$	25 $\mu$ m-2.5 $\mu$ m	molecular vibrations
microwaves	$3 \times 10^{11}$ - $10^{13}$	1 mm-25 $\mu$ m	molecular rotations, electron spin flips*
radio waves	$<3 \times 10^{11}$	>1 mm	nuclear spin flips*



**G. Herzberg, "Atomic Spectra and Atomic Structure"**

**G. Herzberg, "Spectra of Diatomic Molecules"**

**G. Herzberg, "Infrared and Raman Spectra"**

**G. Herzberg, "Electronic Spectra of Polyatomic Molecules"**

**G. Herzberg, "The Spectra and Structures of Simple Free Radicals  
An Introduction to Molecular Spectroscopy"**

**G. M. Barrow, "Introduction to Molecular Spectroscopy"**

**H. B. Dunford, "Elements of Diatomic Molecular Spectra"**

**R. N. Dixon, "Spectroscopy and Structure"**

**W G Richards and P R Scott "Structure and Spectra of Molecules",.**

**C N Banwell and E M McCash, "Fundamentals of Molecular  
Spectroscopy",.**

**J M Hollas, "Modern Spectroscopy", 3rd ed, Wiley, 1996.**

**J. M. Brown, "Molecular Spectroscopy", Oxford University Press,  
1998.**

**I.N. Levine "Molecular Spectroscopy", John Wiley, 1975**

**D. Emerson "Interpreting Astronomical Spectra"**

**Gordy and Cook, Microwave Molecular Spectra, Wiley**

**Townes and Schalow, Microwave Spectroscopy, Dover**

# How to characterize molecules spectroscopically from astronomical data?

- Looking for species difficult to be produced in the laboratory
- We proceed exactly in the same way than in the laboratory
- We identify the lines that we believe are produced by a molecular species (harmonic relations between the frequencies for linear molecules for example)
- We assign quantum numbers to these lines
- We check for hyperfine structure (N, H,  $^{17}\text{O}$ ,  $^{33}\text{S}$ ,...)
- We fit a Hamiltonian to the observed lines
- What accuracy can be obtained ?

# Frequency accuracy

- Normally lines are gaussians with linewidths in dark clouds  $<0.5$  km/s which means an accuracy in velocity determination of 0.05 km/s.
- This velocity accuracy corresponds to a relative frequency uncertainty of  $1.7 \cdot 10^{-7}$
- In some sources the linewidths can be as narrow as 0.15 km/s.
- Additional uncertainty due to precision on the velocity of the source (0.2 km/s or  $6.7 \cdot 10^{-7}$  relative frequency error)

# ROTATIONAL SPECTRUM OF LINEAR MOLECULES (basic concepts)

From a “classical” point of view of quantum theory a molecule has a rotational energy proportional to the square of the angular momentum,  $J^2$ . Hence the energy levels should have a dependency on  $J$  given by

$$E(J) \propto J(J+1)$$

The frequencies of the transitions (allowed transitions have  $\Delta J = \pm 1$ ) could be given by

$$\nu(J \rightarrow J-1) \propto J$$

From a classical point of view the angular momentum of the molecule is given by  $I\omega$ , where  $I$  is the momentum of inertia of the molecule,

$$I = \mu r^2$$

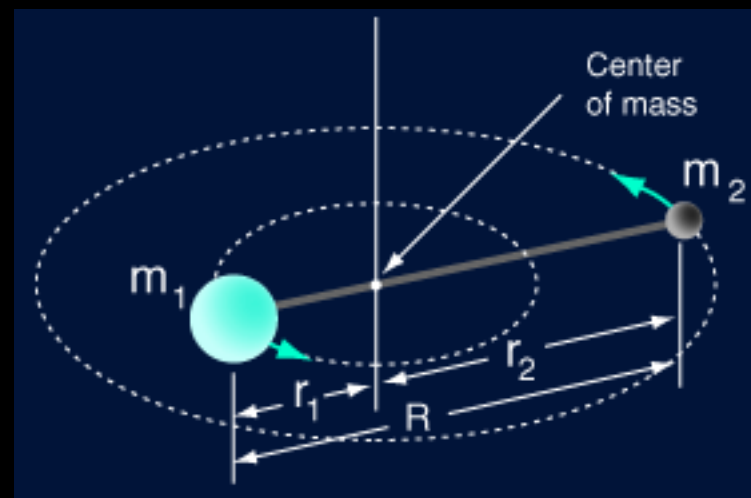
where  $\mu$  is the reduced mass,  $\mu = M_1 M_2 / (M_1 + M_2)$ , and  $r$  is the separation between the nuclei.

In this “classical” approximation for the energy of a rigid molecule the energies can be written as

$$E(J) = B J(J+1)$$

and the frequencies as

$$\nu = 2 B J_u$$



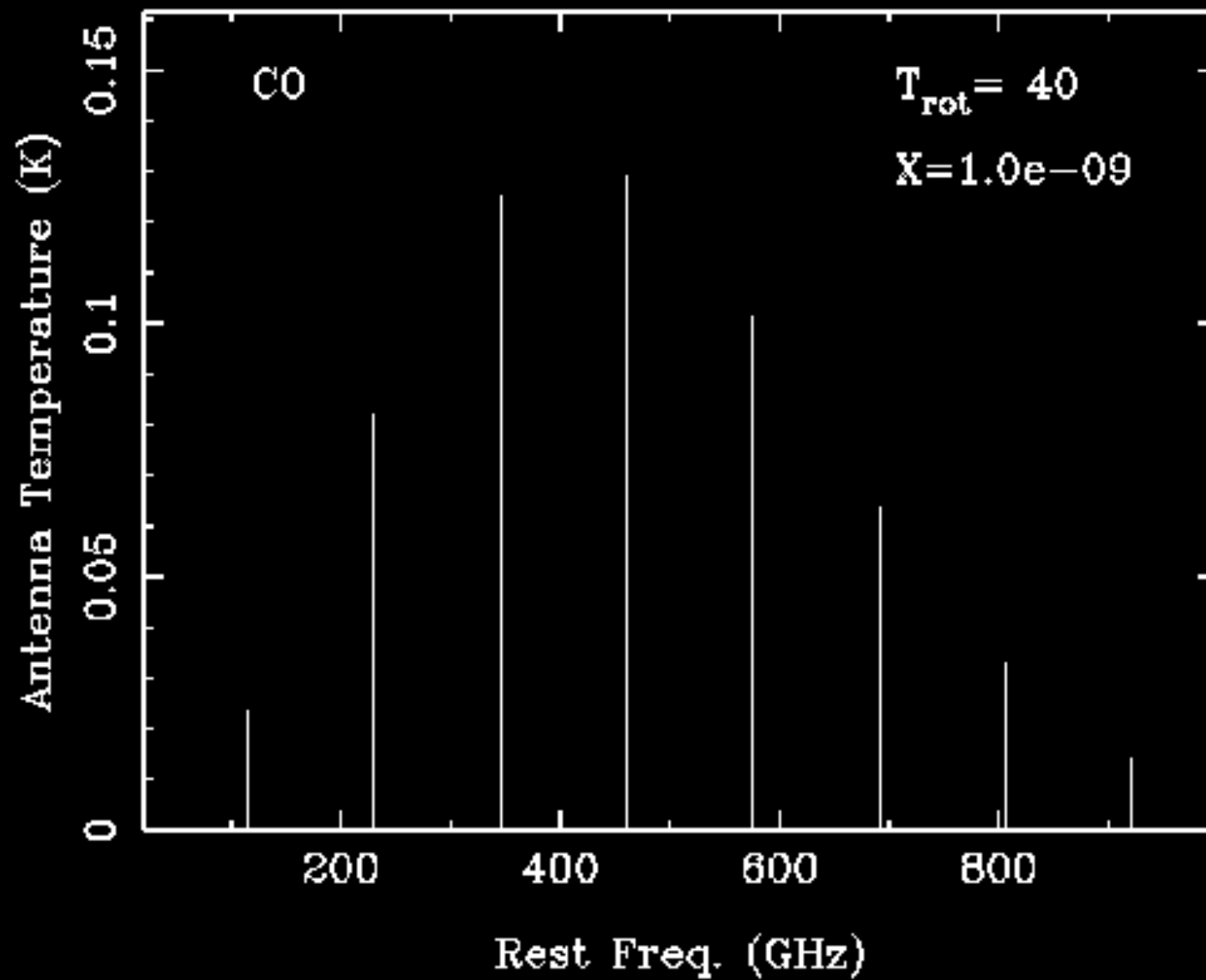
The constant  $B$ , the rotational constant, is given by

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

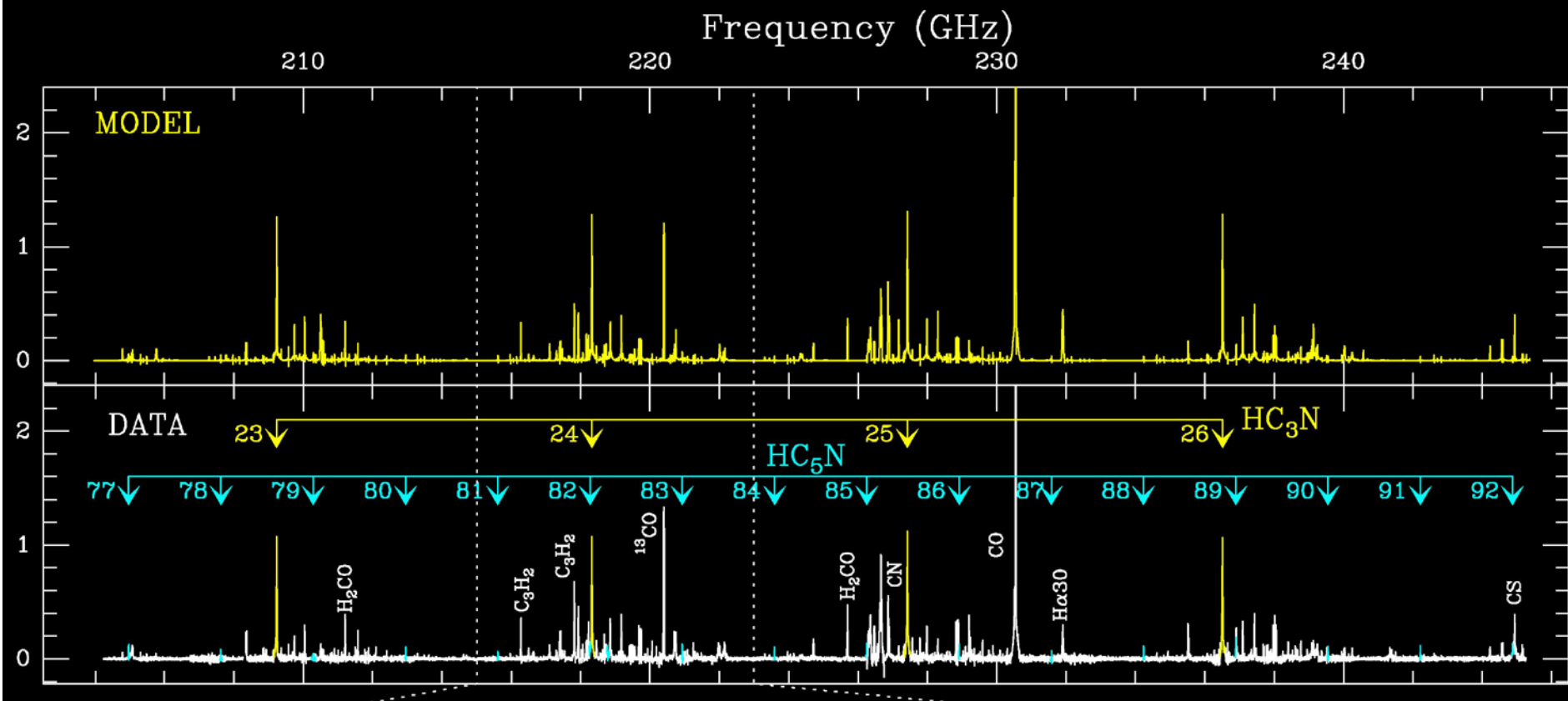
$$B = (h / 8 \pi^2 I) \quad [\text{frequency units}]$$

$$1 \text{ cm}^{-1} = 29979.2459 \text{ MHz} \approx 30 \text{ GHz} \approx 1.4388 \text{ K}$$

The heavier the molecule, the smaller  $B$ ; the rotational spectrum will be tighter.



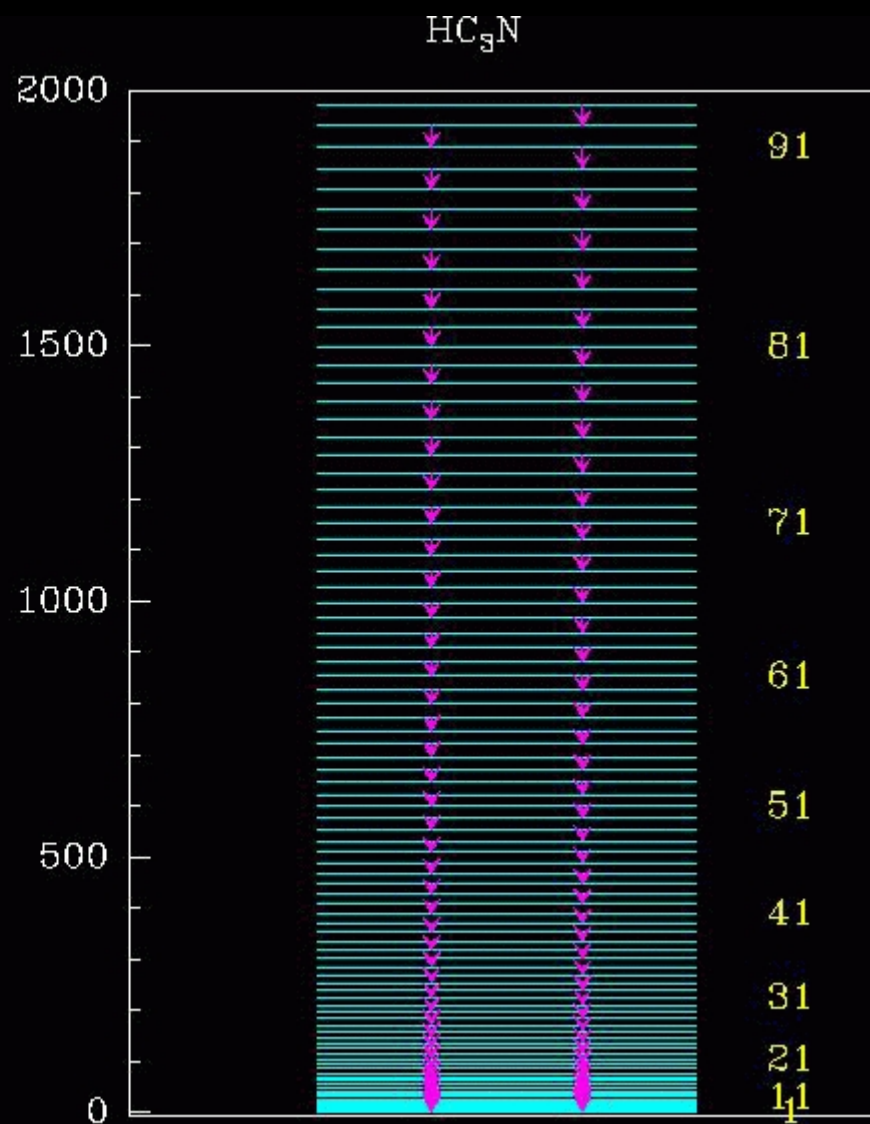
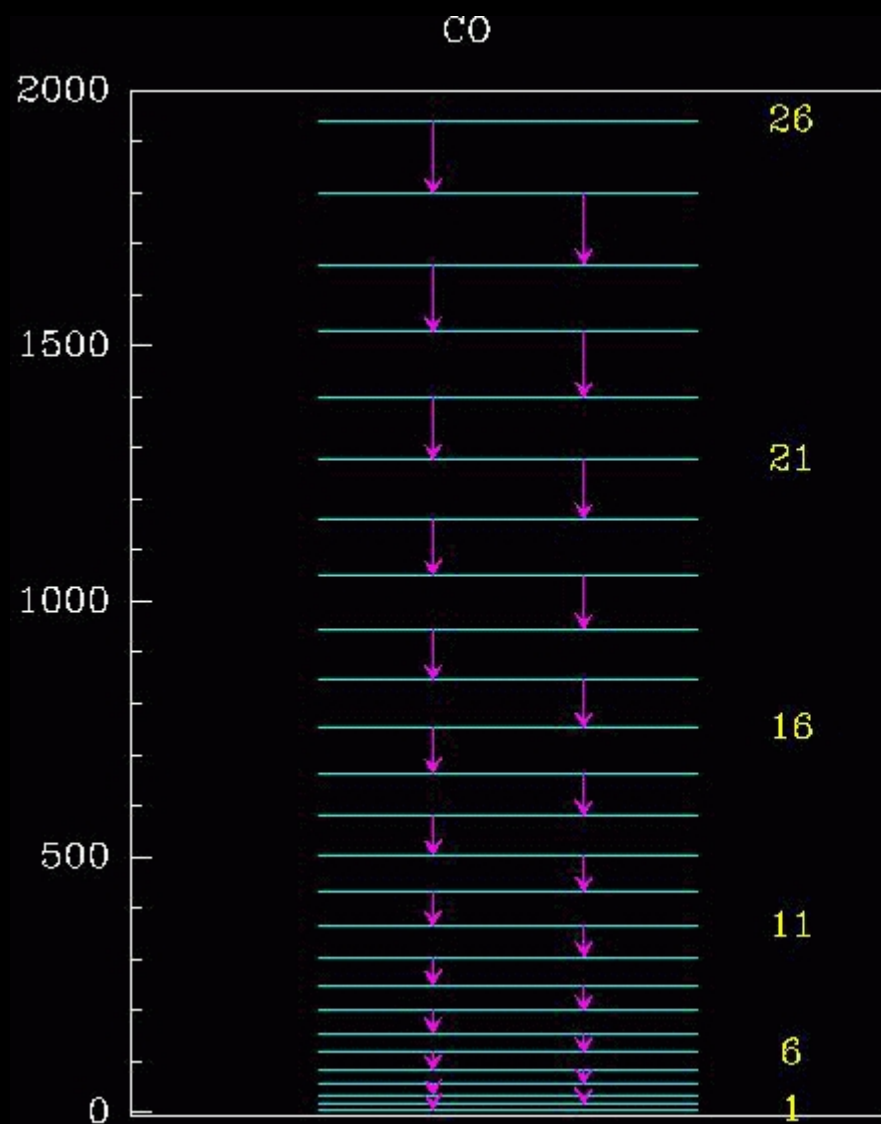
## ROTATIONAL SPECTRUM OF CARBON MONOXIDE



**ROTATIONAL SPECTRUM OF  $\text{HC}_3\text{N}$  (linear)**

**ROTATIONAL SPECTRUM OF  $\text{HC}_5\text{N}$  (linear)**

**Spectrum  
Getting  
tighter**



**Selection rules  $\Delta J = \pm 1$**

**This simple expression for the energy works fine for heavy molecules. However, when the accuracy of the observations is large it is observed that the frequencies of successive rotational transitions do not follow this simple approximation.**

**¿ WHY ?**

**Because when molecules are rotating the nuclei are submitted to centrifugal forces which increase the distance between them and increase the momentum of inertia.**

**The distance between the nuclei is defined by the molecular orbitals. We need a potential  $U(r)$  describing the energy of the system as a function of the internuclear distance.**

**As the movement of the nuclei is much slower than those of the electrons we could consider that the electronic energy of the molecule is independent of the vibration and of the rotation.**

**This approximation (Born-Oppenheimer) allows to separate the total energy into electronic, vibrational and rotational energies, i.e., the total energy of the molecule could be written as a sum of terms depending on  $(m_e/M_N)^{1/2}$ .**

**The problem is to find the potential energy of the molecules,  $U(r)$ , describing in a reasonable way the variation of energy as a function of the internuclear distance.**

**The empirical expression used in spectroscopy to fit the ro-vibrational spectra of diatomic molecules is**

$$F_{vJ} = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 \\ + B_v J(J + 1) - D_e J^2(J + 1)^2 + H_e J^3(J + 1)^3 + \dots$$

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 \dots$$

**From the spectroscopic constants it is possible to derive important information, through the Morse or Dunham expression for the potential energy, on the dissociation energy, equilibrium distance, etc.**

# The spectra of diatomic molecules

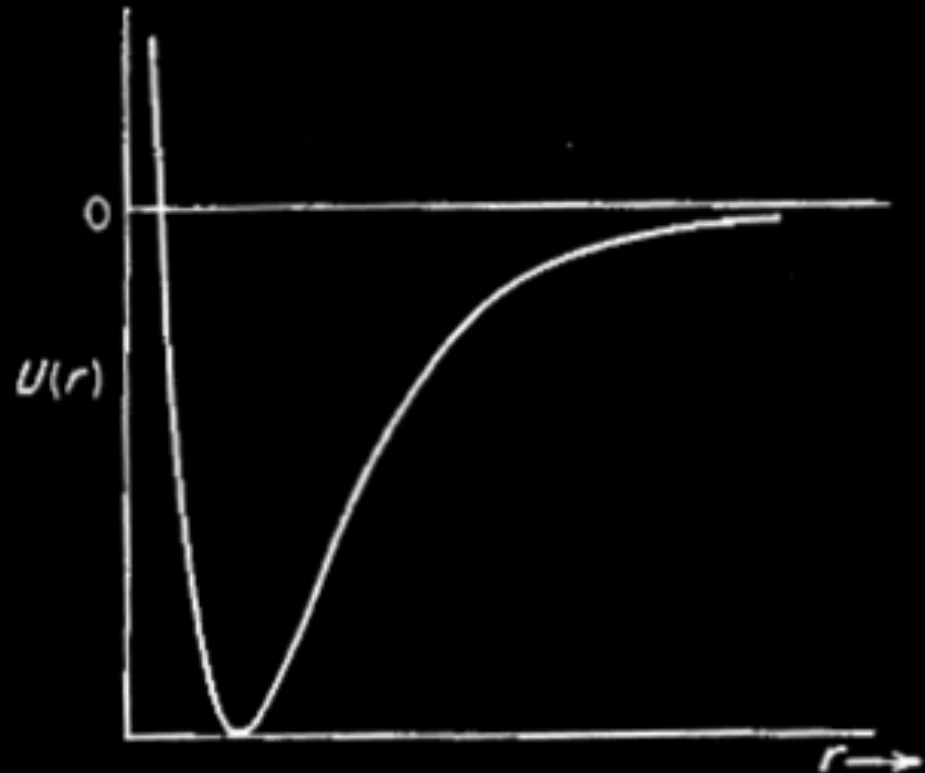
The quantum treatment of rotation,  
vibration and electronic movements

# Potential Surfaces

As the movement of the nuclei is much slower than those of the electrons we could consider that the electronic energy of the molecule is independent of the vibration and rotation.

(Born-Oppenheimer approximation)

**Problem:** finding the potential energy of the molecule,  $U(r)$ , describing in a reasonable way the variation of energy as a function of the internuclear distance for a given electronic state. The solution of the Schrödinger equation will depend on this potential.



**Morse Potential :**  $U(r) = D(1 - e^{-a(r-r_e)})^2$

$D$  = dissociation energy of the molecule

$r_e$  = equilibrium distance between nuclei

$a$  = a constant

**The wave equation is then :**

$$\frac{d^2S}{dr^2} + \left[ -\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2} (W - D - De^{-2a(r-r_e)} + 2De^{-a(r-r_e)}) \right] S = 0$$

**Making the following changes:**

$$y = e^{-a(r-r_e)} \quad \text{and} \quad A = J(J+1) \frac{h^2}{8\pi^2\mu r_e^2}$$

**We obtain :**

$$\frac{d^2S}{dy^2} + \frac{1}{y} \frac{dS}{dy} + \frac{8\pi^2\mu}{a^2h^2} \left( \frac{W - D}{y^2} + \frac{2D}{y} - D - \frac{Ar_e^2}{y^2r^2} \right) S = 0$$

**For A = 0, i.e., J=0 it is possible to find an analytical solution. In the general case the solution is given by:**

$$\frac{W_{Jv}}{h} = \underbrace{\omega_e(v + \frac{1}{2}) - x_e\omega_e(v + \frac{1}{2})^2}_{\text{Vibrational terms}} + \underbrace{J(J+1)B_e}_{\text{Undisturbed rotation}} - \underbrace{D_eJ^2(J+1)^2}_{\text{Centrifugal distortion}} - \underbrace{\alpha_e(v + \frac{1}{2})J(J+1)}_{\text{Higher order corrections}}$$

Harmonic oscillator
anharmonicity
Centrifugal distortion

**Where:**

$$\omega_e = \frac{a}{2\pi} \sqrt{\frac{2D}{\mu}} \quad x_e = \frac{h\omega_e}{4D} \quad B_e = \frac{h}{8\pi^2 I_e}$$

$$D_e = \frac{h^3}{128\pi^6 \mu^3 \omega_e^2 r_e^6} = \frac{4B_e^3}{\omega_e^2}$$

$$\alpha_e = \frac{3h^2\omega_e}{16\pi^2 \mu r_e^2 D} \left( \frac{1}{ar_e} - \frac{1}{a^2 r_e^2} \right) = 6 \sqrt{\frac{x_e B_e^3}{\omega_e}} - \frac{6B_e^2}{\omega_e}$$

**There is another potential proposed by Dunham. It is represented by a series in  $(r - r_e)$ , where  $r_e$  is the equilibrium distance**

$$U = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + \dots) + B_e J(J + 1) (1 - 2\xi + 3\xi^2 - 4\xi^3 + \dots)$$

**Where  $\xi = (r - r_e)/r_e$  and  $B_e = h^2/8\pi^2\mu r_e^2$**

**The solution can be given as**

$$F_{v,J} = \sum_{l,j} Y_{lj} (v + \frac{1}{2})^l J^j (J + 1)^j$$

**Where the terms  $Y_{lj}$  are the Dunham coefficients**

**IN SUMMARY:** The empirical expression used in spectroscopy to fit the ro-vibrational spectra of diatomic molecules is

$$F_{vJ} = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 \\ + B_v J(J + 1) - D_e J^2(J + 1)^2 + H_e J^3(J + 1)^3 + \dots$$

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 \dots$$

**INVERSE PROBLEM:** From spectroscopic measurements it is possible to fit spectroscopic constants and from them it is possible to derive important information, through the Morse or Dunham expression for the potential energy, on the dissociation energy, equilibrium distance, etc.

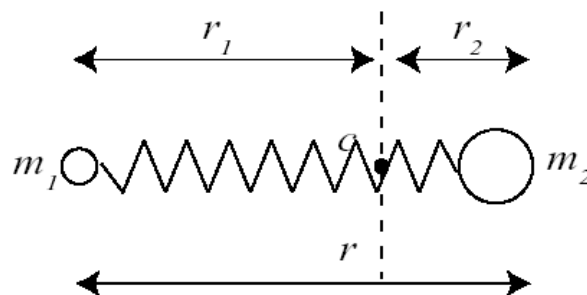
This is the main subject of papers in journals such as the *Journal of Molecular Spectroscopy* or the *Journal of Molecular Structure*

**For simple molecules we can separate the vibrational and rotational parts of the wave function as another Born-Oppenheimer approximation...**

# The Simple Harmonic Oscillator

## Lecture # 2

We next consider the vibrational modes of a diatomic molecule. There are a number of different models, which describe the vibrational motion of a diatomic molecule. We shall consider firstly the simplest model and later consider more sophisticated and more accurate models. The simplest is the Simple Harmonic Oscillator Model (S.H.O.), which assumes that the nuclei of the molecule can be represented by two masses connected by a massless spring obeying Hook's law, as illustrated in the following diagram.



Frank Houwing's Lecture Notes Web site!

[www.anu.edu.au/Physics/houwing/LectureNotes/Phys3034\\_MolSpec/MolSpec\\_L2\\_OH.pdf](http://www.anu.edu.au/Physics/houwing/LectureNotes/Phys3034_MolSpec/MolSpec_L2_OH.pdf)

To determine the spectrum we again adopt the convention that  $E' > E''$  which means that  $v' > v''$  for pure vibration.

Hence

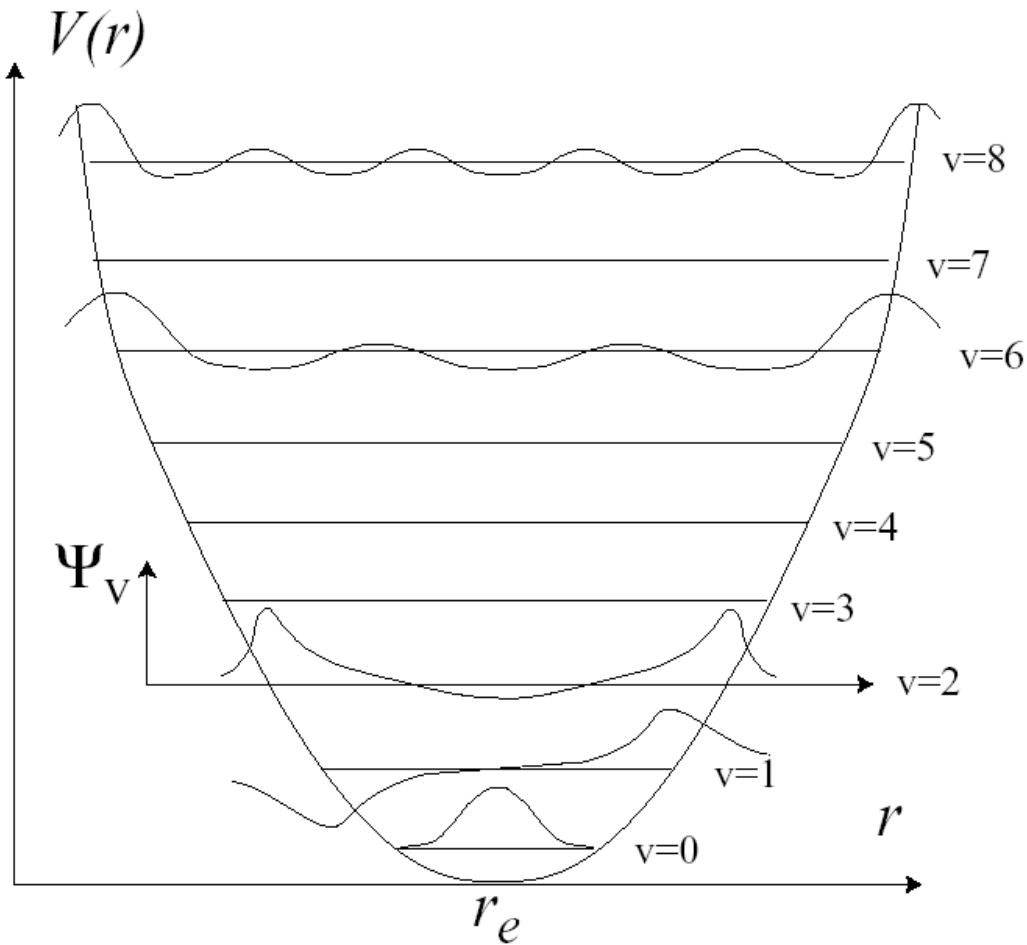
$$v' = v'' + 1 .$$

The spectral lines will therefore be given by

$$\begin{aligned} \nu &= \frac{E(v')}{hc} - \frac{E(v'')}{hc} = G(v') - G(v'') \\ &= G(v''+1) - G(v'') = \omega \left( v'' + \frac{3}{2} \right) - \omega \left( v'' + \frac{1}{2} \right) \\ &= \omega \quad \dots \text{ all lines are coincident.} \\ &\quad \dots\dots\dots \text{consequence of assuming S.H.O.} \end{aligned}$$

In reality, however, the system is not and the vibrational lines are not coincident.

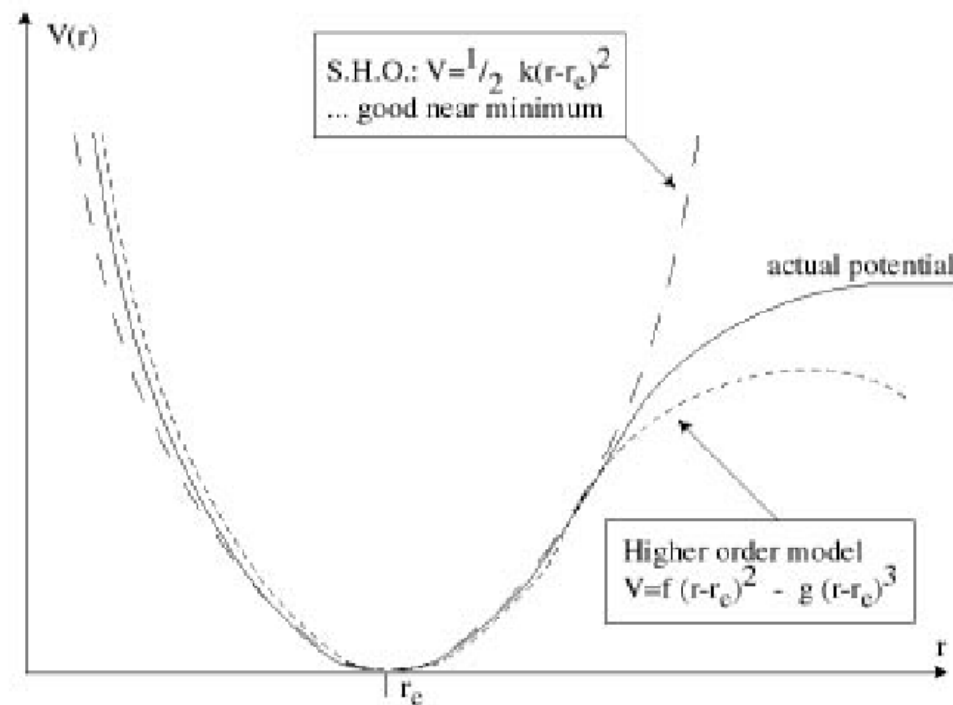
Continuing to discuss the S.H.O. we shall consider the form of the wavefunctions  $\Psi_v$ . Consider the following figure.



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

## The Anharmonic Oscillator

The simple harmonic oscillator (S.H.O.) that we have been using up to now to describe the vibrational motion of a molecule is an approximation, which gives a good representation of the potential energy curve near its minimum. However to give a better description, which more closely follows the actual potential for more energetic vibrations, it is necessary to add higher order terms. In fact, it is found that a cubic potential is very good.



If we substitute this higher order model into the wave equation (Schrödinger's equation) and solve for the eigenvalues, we find that the vibrational energy is given by a high order polynomial

$$E(v) = hc\omega_e\left(v + \frac{1}{2}\right) - hc\omega_e x_e\left(v + \frac{1}{2}\right)^2 + hc\omega_e y_e\left(v + \frac{1}{2}\right)^3 + \dots$$

In fact, because of this, a general polynomial is often simply assumed and the coefficients are found experimentally by fitting methods. More terms are included if higher accuracy is required. However, in most cases, it is sufficient to truncate the polynomial for  $E(v)$  at the cubic or even the quadratic terms. To express the energy in wave numbers, we simply divide by  $hc$  to produce the vibrational energy term:

$$G(v) = \frac{E(v)}{hc} = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + \omega_e y_e\left(v + \frac{1}{2}\right)^3 + \dots$$

where  $v = 0, 1, 2, \dots$  and  $\omega_e \gg \omega_e x_e \gg \omega_e y_e$ .

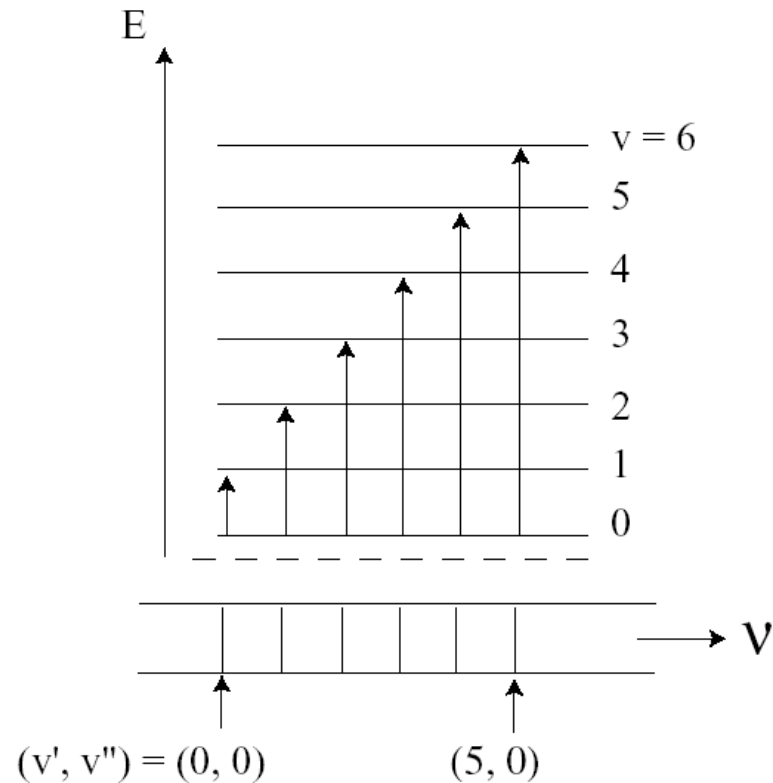
also, unlike the S.H.O.,  $\omega_e c \neq \nu'_{osc}$ .

## Selection Rules for Vibrational Transitions allowed by the Anharmonic Oscillator Model

We will not go into the analysis for deriving the selection rules. However, the derivation will proceed along the same lines as for the S.H.O. model except that the wavefunctions of the anharmonic model will be used. Such a derivation will show that all vibrational transitions are allowed, with

$$\Delta v = \pm 1, \pm 2, \pm 3, \text{ etc} \quad (\text{selection rules for A.O.})$$

However, examination of the transition probabilities shows that the  $\Delta v = \pm 1$  transition is most intense.



The values of the wavenumbers  $\nu$  for the transitions with  $\Delta v = 2, 3, 4, \dots$  are approximately  $2\times, 3\times, 4\times, \dots$  the value of  $\nu$  for the  $\Delta v = 1$  transition. Because of this, the transitions are often termed:

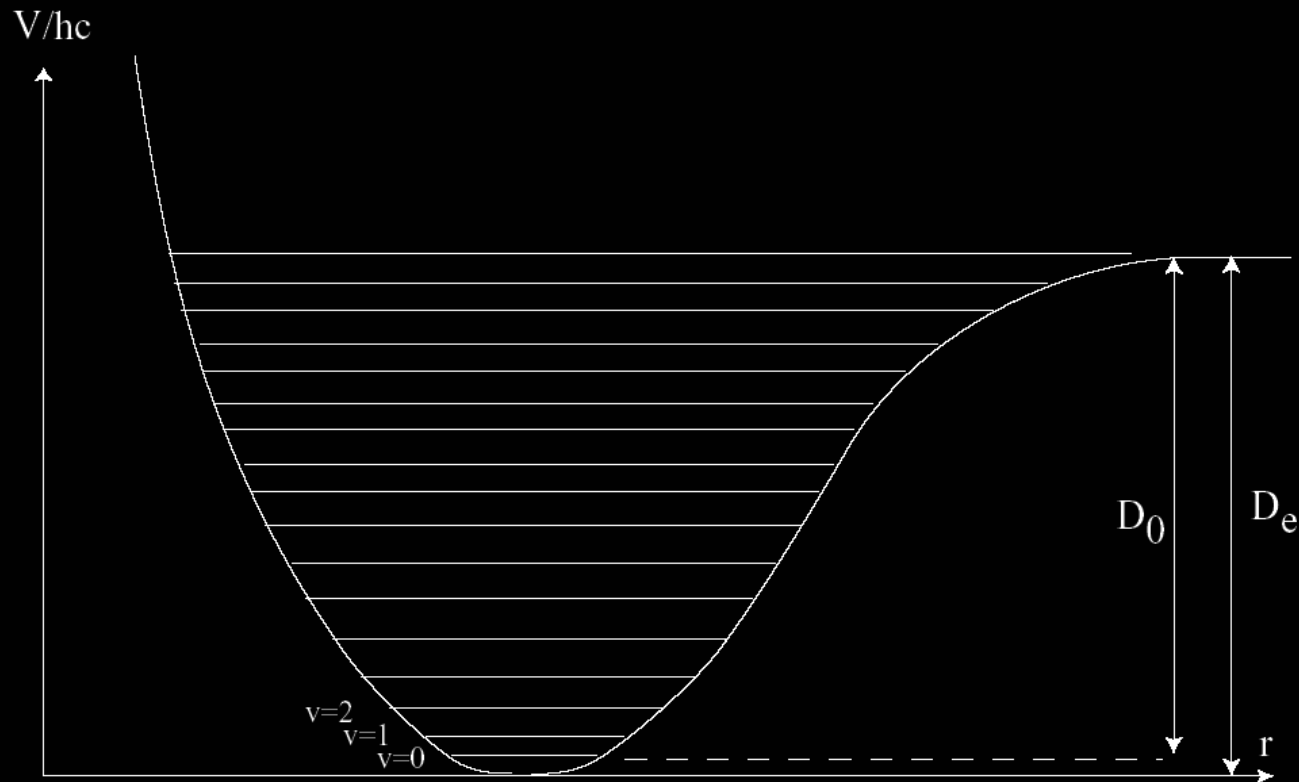
$(1, 0)$ : "fundamental";  $(2, 0)$ : "second harmonic";  $(3, 0)$ : "third harmonic".

However, they are not true harmonics.

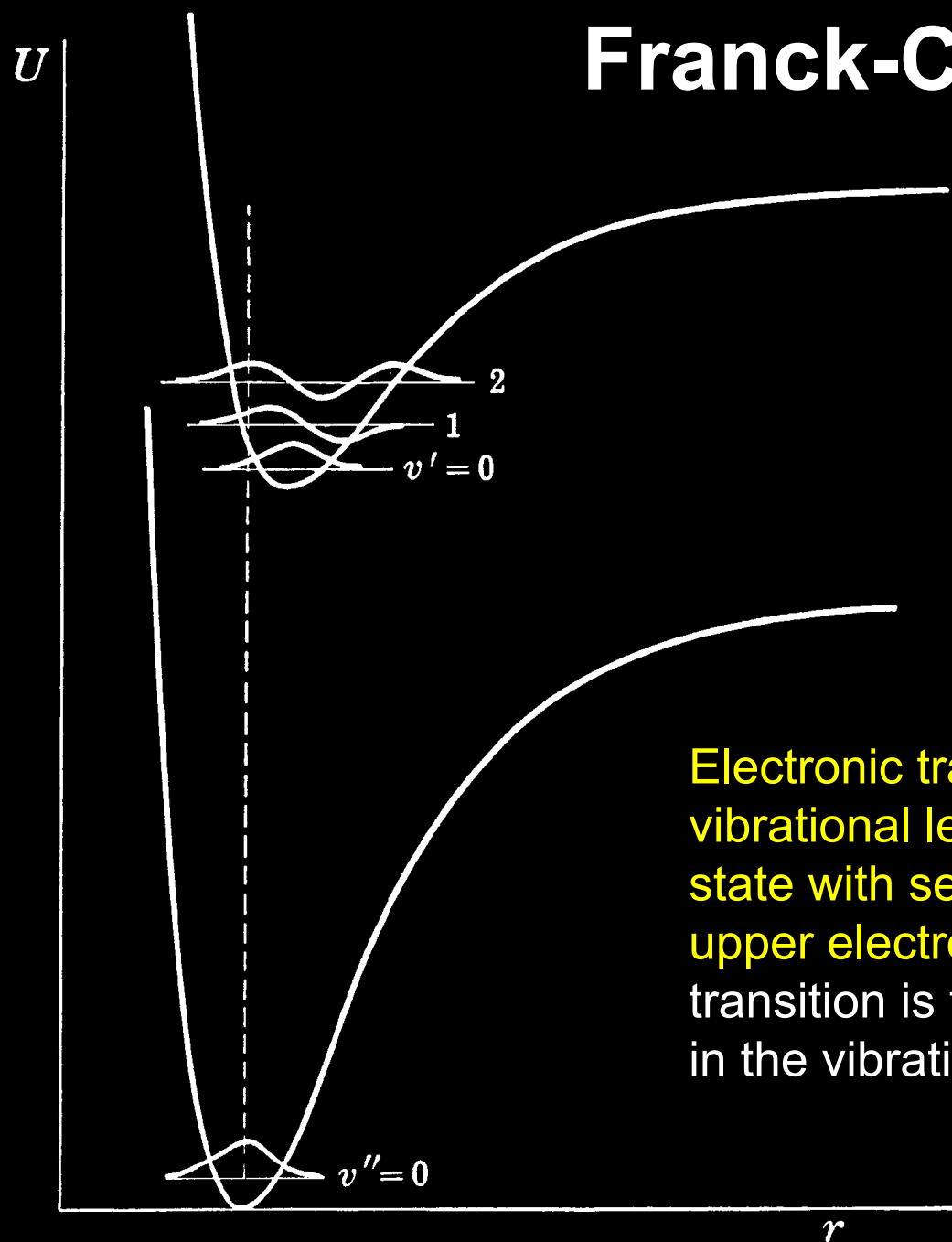
# A few facts...

## Continuous term spectra and dissociation

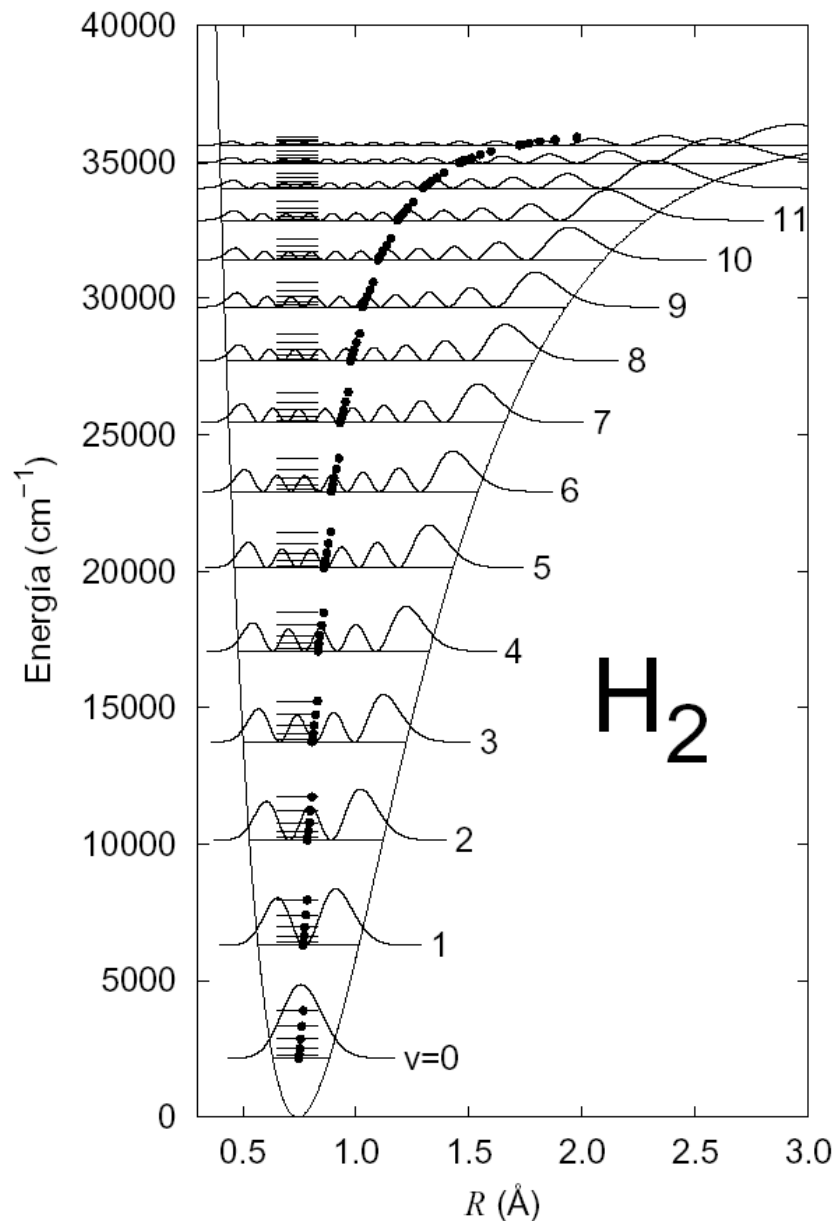
If oscillator has more energy  $E'$  than,  $hcD_e$ , then  $r \rightarrow \infty$  and molecule dissociates. For  $E' > hcD_e$ , system has excess energy (kinetic energy) after dissociation.  $\therefore (K.E)_{\text{atoms}} > 0$  and not quantized.



# Franck-Condon Principle



Electronic transitions will connect the lowest vibrational level of the ground electronic state with several vibrational states of the upper electronic state. The most probable transition is the one having the best overlap in the vibrational eigen functions.



### Energía vibracional:

$$E_{vib}(v) = h\nu_e \left( v + \frac{1}{2} \right) - h\nu_e x_e \left( v + \frac{1}{2} \right)^2.$$

La separación entre estados vibracionales sucesivos,

$$\frac{\Delta E_v}{h} = \frac{E_{vib}(v+1) - E_{vib}(v)}{h} = \nu_e - \nu_e x_e 2(v+1),$$

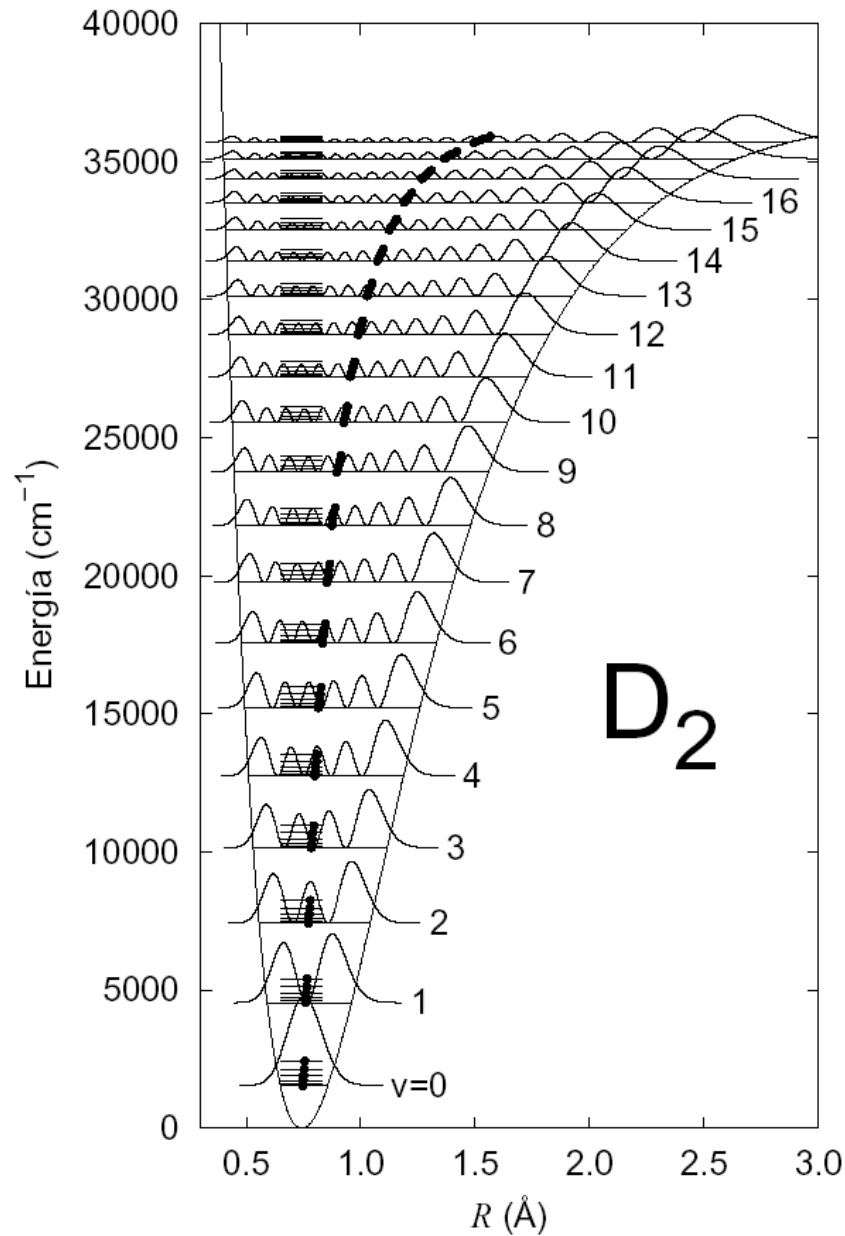
se reduce al aumentar  $v$  (Excepción: algunas moléculas con  $x_e < 0$ ).

### Separación nuclear efectiva:

$$\frac{1}{R_{vJ}^2} = \left\langle \frac{1}{R^2} \right\rangle = \left\langle \psi_v \left| \frac{1}{R^2} \right| \psi_v \right\rangle.$$

### Constante rotacional efectiva:

$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right) = \frac{h^2}{8\pi^2 \mu R_{vJ}^2}.$$



### Energía rotacional:

$$E_{rot} = hB_v J(J+1) - h\bar{D}_e [J(J+1)]^2$$

La separación entre estados rotacionales sucesivos,

$$\frac{\Delta E_J}{h} = \frac{E_{v,J+1} - E_{v,J}}{h} = B_v 2(J+1) - \bar{D}_e 4(J+1)^3$$

disminuye con  $J \uparrow$  y  $v \uparrow$ .

### Energía de punto cero:

$$\epsilon_0 = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e + hY_{00}.$$

**Importancia relativa:** Generalmente  $\nu_e \gg \nu_e x_e \approx B_e \gg \alpha_e \gg \bar{D}_e$ .

Constantes espectroscópicas en  $\text{cm}^{-1}$ .

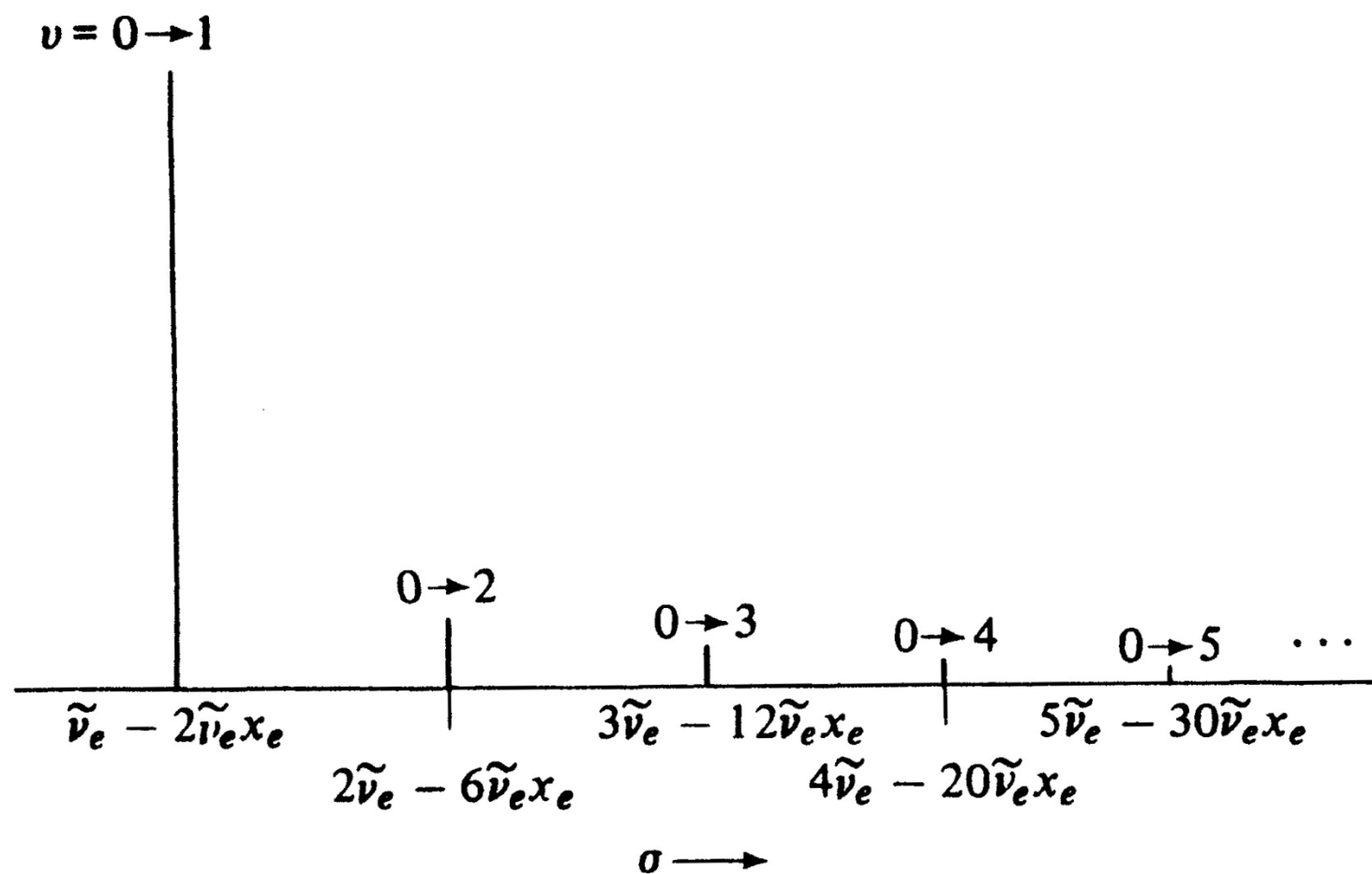
		$U_e$	$\nu_e$	$\nu_e x_e$	$B_e$	$\alpha_e$	$\bar{D}_e$	$R_e$
H <sub>2</sub>	$X -^1 \Sigma_g^+$	0	4401.213	121.336	60.8530	3.0622	$47.1 \times 10^{-3}$	0.74144
	$B -^1 \Sigma_u^+$	91700.0	1358.09	20.888	20.0154	1.1845	$16.25 \times 10^{-3}$	1.29282
D <sub>2</sub> †	$X -^1 \Sigma_g^+$	0	3115.50	61.82	30.4436	1.0786	$11.41 \times 10^{-3}$	0.74152
OH	$X -^2 \Pi$	0	3737.761	84.8813	18.9108	0.7242	$1.938 \times 10^{-3}$	0.96966
HF	$X -^1 \Sigma^+$	0	4138.32	89.88	20.9557	0.798	$2.151 \times 10^{-3}$	0.916808
N <sub>2</sub> †	$X -^1 \Sigma_g^+$	0	2358.57	14.324	1.998241	0.017318	$5.76 \times 10^{-6}$	1.097685
CO	$X -^1 \Sigma^+$	0	2169.81358	13.28831	1.93128087	0.01750441	$6.12147 \times 10^{-6}$	1.128323
NO	$X -^2 \Pi_{1/2}$	0	1904.204	14.075	1.67195	0.0171	$0.54 \times 10^{-6}$	1.15077
	$X -^2 \Pi_{3/2}$	119.82	1904.040	14.100	1.72016	0.0182	$10.23 \times 10^{-6}$	1.15077
	$A -^2 \Sigma^+$	43965.7	2374.31	10.106	1.9965	0.01915	$5.4 \times 10^{-6}$	1.06434
O <sub>2</sub> †	$X -^3 \Sigma_g^-$	0	1580.193	11.981	1.4376766	0.01593	$4.839 \times 10^{-6}$	1.20752
F <sub>2</sub> †	$X -^1 \Sigma_g^+$	0	916.64	11.236	0.89019	0.013847	$3.3 \times 10^{-6}$	1.41193
ICl	$X -^1 \Sigma^+$	0	384.293	1.501	0.1141587	0.0005354	$40.3 \times 10^{-9}$	2.320878
I <sub>2</sub>	$X -^1 \Sigma_g^+$	0	214.502	0.6147	0.037372	0.0001138	$4.25 \times 10^{-9}$	2.6663

†  $\nu_e y_e$  : 0.562 (D<sub>2</sub>), -0.00226 (N<sub>2</sub>), 0.04747 (O<sub>2</sub>), -0.113  $\text{cm}^{-1}$  (F<sub>2</sub>).

$$\omega' \approx \omega \sqrt{\frac{\mu}{\mu'}}$$

$$\text{Ejemplo: H}_2 \text{ y D}_2 \quad \omega' \approx \omega \sqrt{\frac{1}{2}} = 4401.213 / 1.414 = 3112.1 \text{ vs } 3115.5 \text{ cm}^{-1}$$

**Breakdown of the Bohr-Oppenheimer approximation**



**Fig. 4.7** Positions of the band origins of the infrared absorption spectrum of a diatomic molecule.

**Espectro roto-vibracional:**  $\Delta J \neq 0$ ,  $v \rightarrow v'$ : Para la transición fundamental  $v : 0 \rightarrow 1$  tenemos:

**Banda origen :**  $\nu_{or} = \nu_e - 2\nu_e x_e,$

**Rama P** ( $\Delta J = -1$ ) :  $\nu_P(J) = \nu_{or} - 2B_e(J+1) - \alpha_e(J-1)(J+1) + 4\bar{D}_e(J+1)^3,$

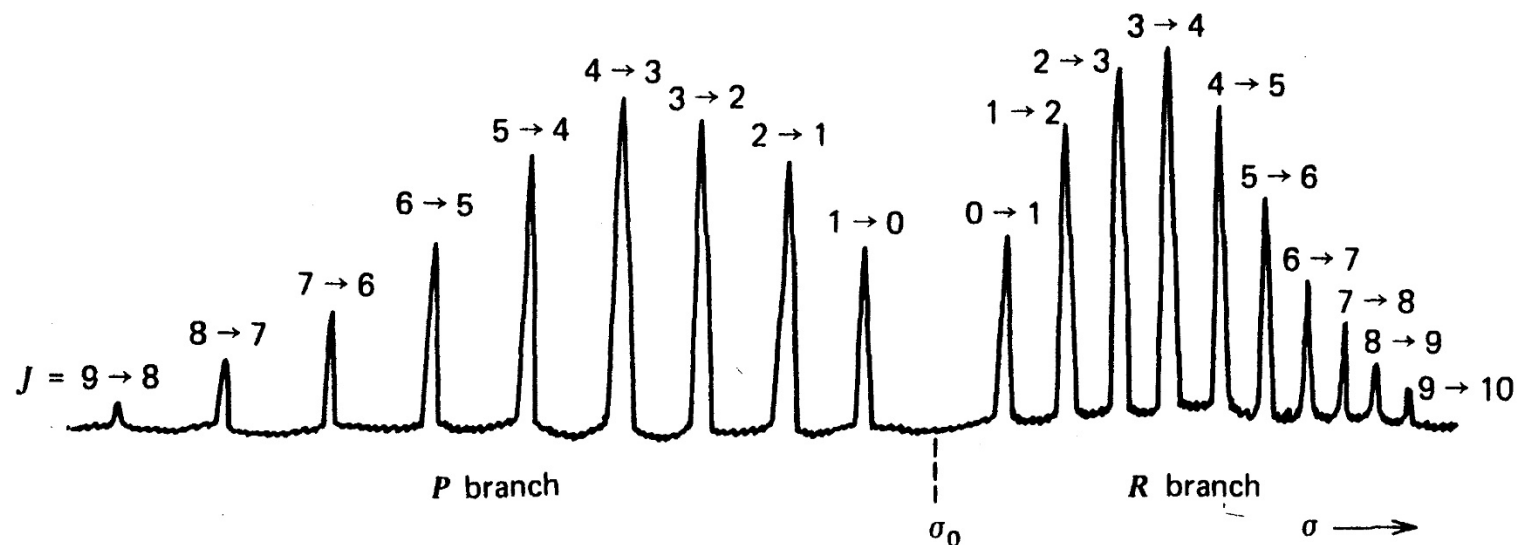
**Rama Q** ( $\Delta J = 0$ ) :  $\nu_Q(J) = \nu_{or} - \alpha_e J(J+1),$

**Rama R** ( $\Delta J = +1$ ) :  $\nu_R(J) = \nu_{or} + 2B_e(J+1) - \alpha_e(J+1)(J+3) - 4\bar{D}_e(J+1)^3,$

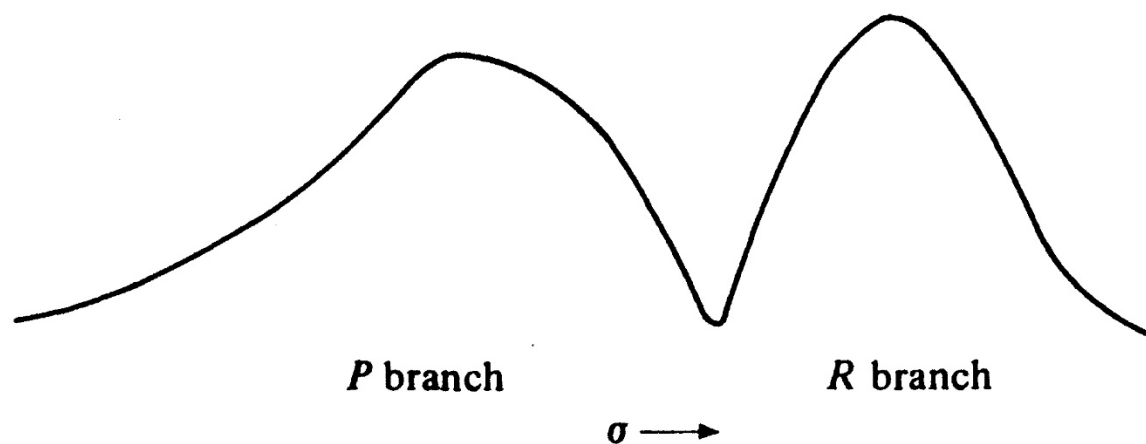
$$I_{v,J \rightarrow v',J'} = I_{or}(v \rightarrow v') N_J \propto I_{or}(v \rightarrow v') \frac{hB_e}{kT} (2J+1) e^{-J(J+1)hB_e/kT},$$

Separación entre líneas sucesivas:	<b>Rama P :</b> $\Delta\nu_P(J) = -2B_e - \alpha_e(2J-1) + 4\bar{D}_e(3J^2 - 9J + 7),$
	<b>Rama Q :</b> $\Delta\nu_Q(J) = -\alpha_e 2(J+1),$
	<b>Rama R :</b> $\Delta\nu_R(J) = +2B_e - \alpha_e(2J+5) - 4\bar{D}_e(3J^2 - 9J + 7).$

- $\nu_P < \nu_{or} < \nu_R$  ( $\nu_Q \approx \nu_{or}$  pero no es visible).
- $\Delta\nu_P(J) \approx \Delta\nu_R(J) \approx 2B_e.$
- $J \uparrow \implies \nu_P \downarrow, \nu_R \uparrow, \Delta\nu_P(J) \downarrow, \Delta\nu_R(J) \uparrow.$
- La rama P puede presentar **cabeza de banda** cuando  $\Delta\nu_R(J) = 0 \approx 2B_e - \alpha_e(2J_{CB} + 5).$  El fenómeno es más fácil en moléculas ligeras:  $J_{CB} = 24$  (HF y OH), 108 (CO) y 211 (ICl).



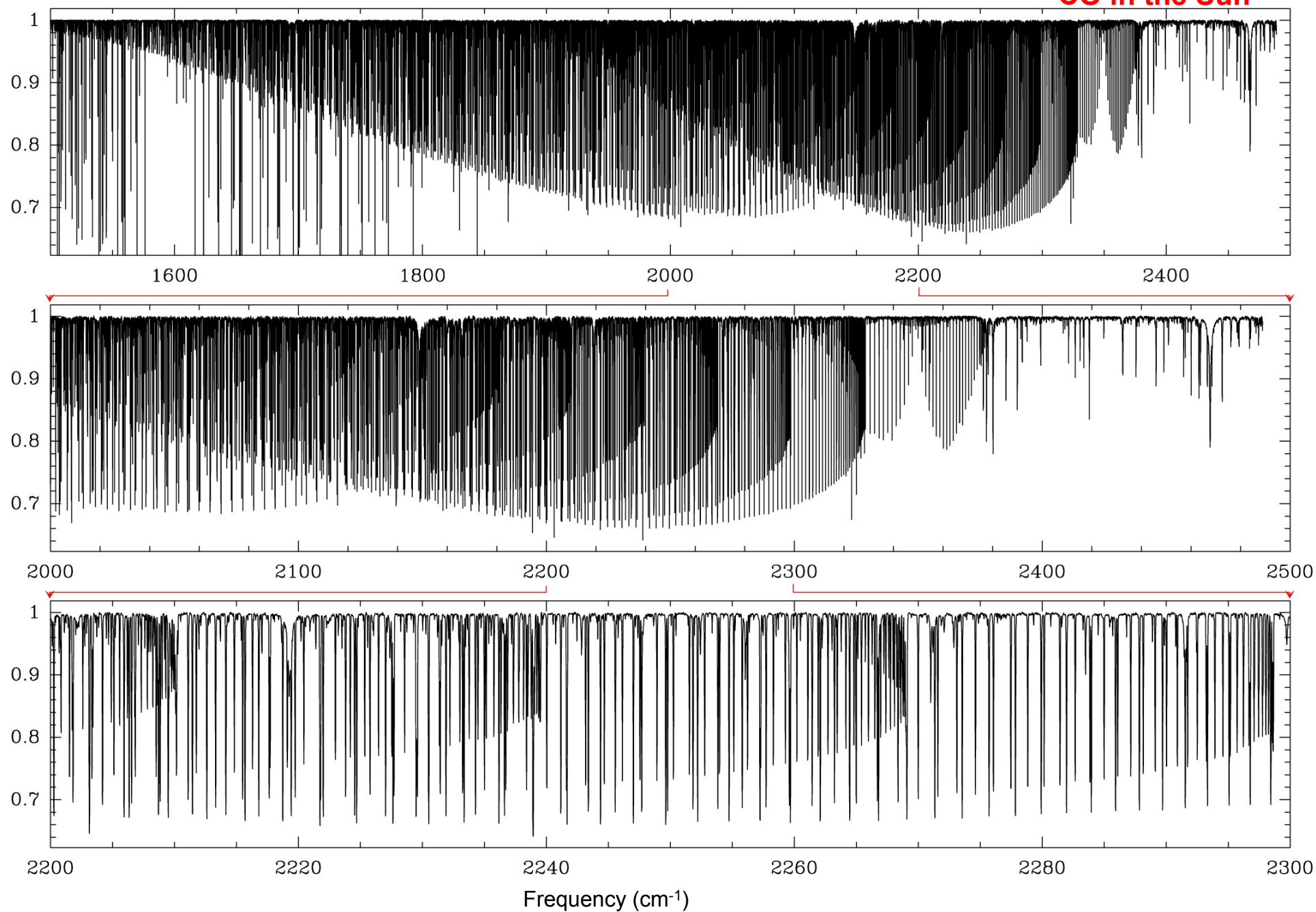
**Fig. 4.9** Rotational fine structure of a vibration-rotation band of a diatomic molecule. Note the decreasing spacing with increasing  $J$  in the  $R$  branch, and the increasing spacing with increasing  $J$  in the  $P$  branch.



**Fig. 4.10** Appearance of a vibration-rotation band of a diatomic molecule under low resolution.

# ATMOS (SKYLAB) SOLAR SPECTRUM

CO in the Sun



All frequencies can be computed with a few constants and with a relative accuracy between a few  $10^{-8}$  to  $4 \cdot 10^{-10}$

ROTATIONAL CONSTANTS (Yij) USED FOR FREQUENCY PREDICTIONS, LINE INTENSITIES AND ENERGIES IN MADEX

Y10 (cm-1) =	2169.81272147	ERROR (1sigma) =	.00000356
Y20 (cm-1) =	-13.28791503	ERROR (1sigma) =	.00000280
Y30 (cm-1) =	1.04230043E-02	ERROR (1sigma) =	8.71724663E-07
Y40 (cm-1) =	6.75125585E-05	ERROR (1sigma) =	1.20645180E-07
Y50 (cm-1) =	3.26953608E-07	ERROR (1sigma) =	8.56996098E-09
Y60 (cm-1) =	-5.79731191E-09	ERROR (1sigma) =	3.26608992E-10
Y70 (cm-1) =	-6.26610004E-10	ERROR (1sigma) =	6.34448969E-12
Y80 (cm-1) =	9.06043909E-12	ERROR (1sigma) =	4.92657662E-14
Y90 (cm-1) =	-6.17053672E-14	ERROR (1sigma) =	.00000000
Y01 (MHz) =	57898.34440307	ERROR (1sigma) =	.00015568
Y11 (MHz) =	-524.76175591	ERROR (1sigma) =	.00041569
Y21 (MHz) =	1.80115040E-02	ERROR (1sigma) =	2.45807930E-04
Y31 (MHz) =	-4.71867991E-05	ERROR (1sigma) =	4.77632641E-05
Y41 (MHz) =	8.66859871E-05	ERROR (1sigma) =	4.23503613E-06
Y51 (MHz) =	-2.30684772E-06	ERROR (1sigma) =	1.86487796E-07
Y61 (MHz) =	4.56008373E-09	ERROR (1sigma) =	3.96223816E-09
Y71 (MHz) =	-4.00605025E-10	ERROR (1sigma) =	3.23262843E-11
Y02 (MHz) =	-.18351892	ERROR (1sigma) =	2.05966918E-07
Y12 (MHz) =	3.06017813E-05	ERROR (1sigma) =	3.10233614E-07
Y22 (MHz) =	-5.00667407E-06	ERROR (1sigma) =	8.34577408E-08
Y32 (MHz) =	7.70219531E-09	ERROR (1sigma) =	5.33917091E-09
Y42 (MHz) =	-2.04206155E-09	ERROR (1sigma) =	.00000000
Y52 (MHz) =	7.95573653E-11	ERROR (1sigma) =	.00000000
Y03 (MHz) =	1.73912087E-07	ERROR (1sigma) =	2.10858800E-10
Y13 (MHz) =	-4.78671372E-09	ERROR (1sigma) =	5.46158704E-11
Y23 (MHz) =	-1.53877206E-11	ERROR (1sigma) =	9.29239351E-12
Y33 (MHz) =	5.23188498E-13	ERROR (1sigma) =	.00000000
Y43 (MHz) =	-4.28843372E-14	ERROR (1sigma) =	.00000000
Y04 (MHz) =	1.56388520E-13	ERROR (1sigma) =	8.32772613E-14
Y14 (MHz) =	-2.15397911E-14	ERROR (1sigma) =	.00000000
Y24 (MHz) =	-1.18564210E-16	ERROR (1sigma) =	.00000000
Y34 (MHz) =	-4.36681631E-17	ERROR (1sigma) =	.00000000
Y44 (MHz) =	2.08681608E-18	ERROR (1sigma) =	.00000000
Y05 (MHz) =	-1.38717863E-18	ERROR (1sigma) =	.00000000
Y15 (MHz) =	-1.62968088E-19	ERROR (1sigma) =	.00000000
Y25 (MHz) =	-2.75517128E-21	ERROR (1sigma) =	.00000000
Y35 (MHz) =	7.81937501E-23	ERROR (1sigma) =	.00000000
Y06 (MHz) =	-2.32787184E-23	ERROR (1sigma) =	.00000000
Y16 (MHz) =	-1.19013866E-24	ERROR (1sigma) =	.00000000
Y26 (MHz) =	-1.75689536E-25	ERROR (1sigma) =	.00000000
Y36 (MHz) =	7.59714424E-27	ERROR (1sigma) =	.00000000
Y07 (MHz) =	-1.24275243E-28	ERROR (1sigma) =	.00000000
Y17 (MHz) =	-1.19610126E-29	ERROR (1sigma) =	.00000000
Y27 (MHz) =	5.06551541E-31	ERROR (1sigma) =	.00000000

These constants allow to predict the rotational and rovibrational lines up to J=50, v=40 of:

CO

<sup>13</sup>CO

<sup>14</sup>CO

C<sup>17</sup>O

C<sup>18</sup>O

<sup>13</sup>C<sup>17</sup>O

<sup>13</sup>C<sup>18</sup>O

<sup>14</sup>C<sup>17</sup>O

<sup>14</sup>C<sup>18</sup>O

Accuracy better than 10<sup>-7</sup> and in most cases frequencies predicted with relative accuracies as high as 10<sup>-10</sup>-10<sup>-9</sup>

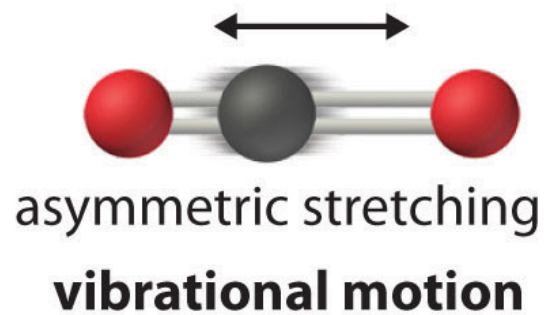
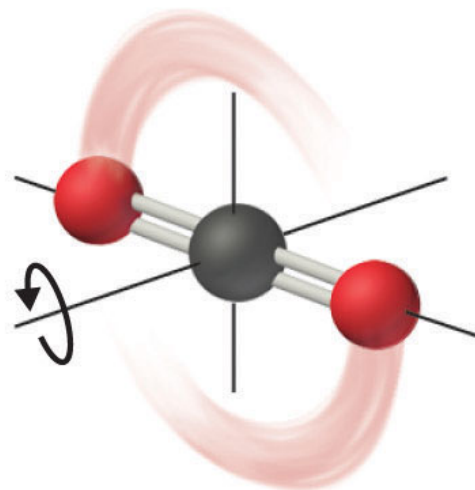
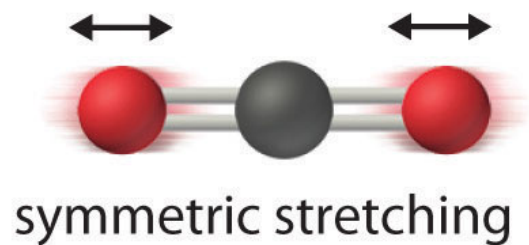
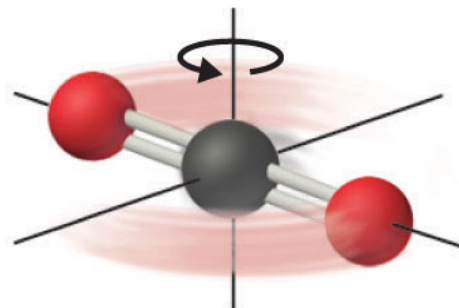
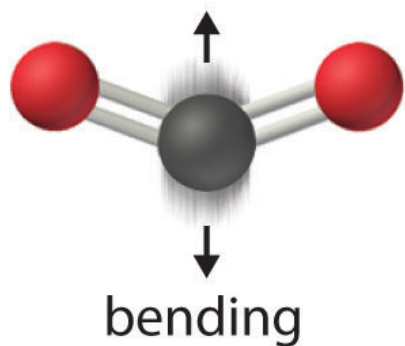
CO J=1-0

ν=115271.20204±0.000046 MHz

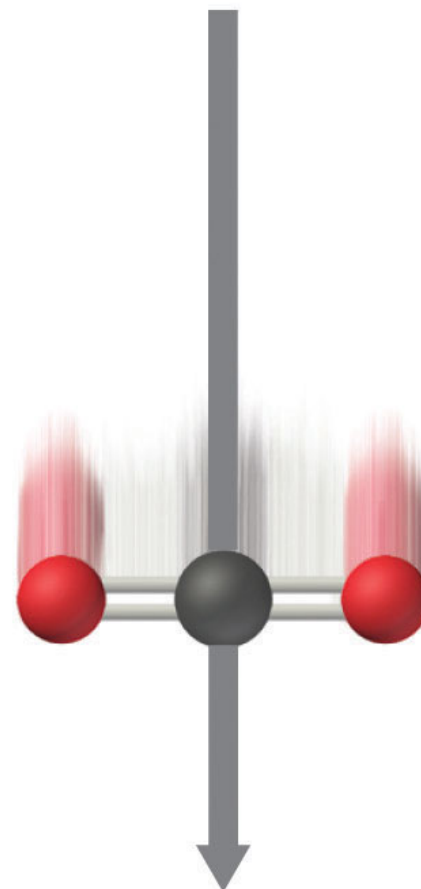
Δν/ν=4 10<sup>-10</sup>

In polyatomic molecules the number of vibrational modes can be large (HCN : three modes, antisymmetrical stretching, symmetrical stretching and bending)

The role of vibrational states  
in the pumping of the  
molecular energy levels

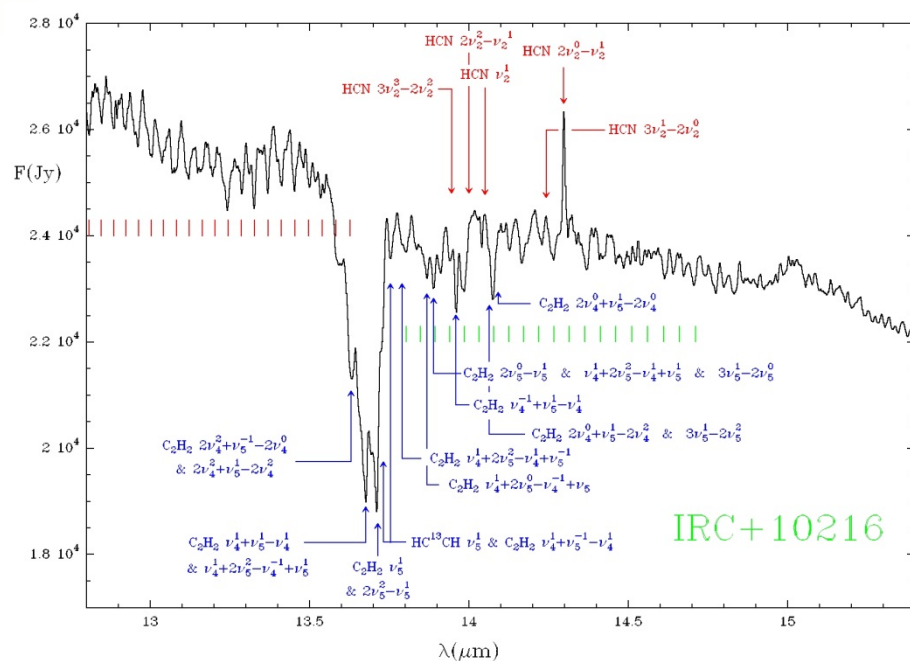
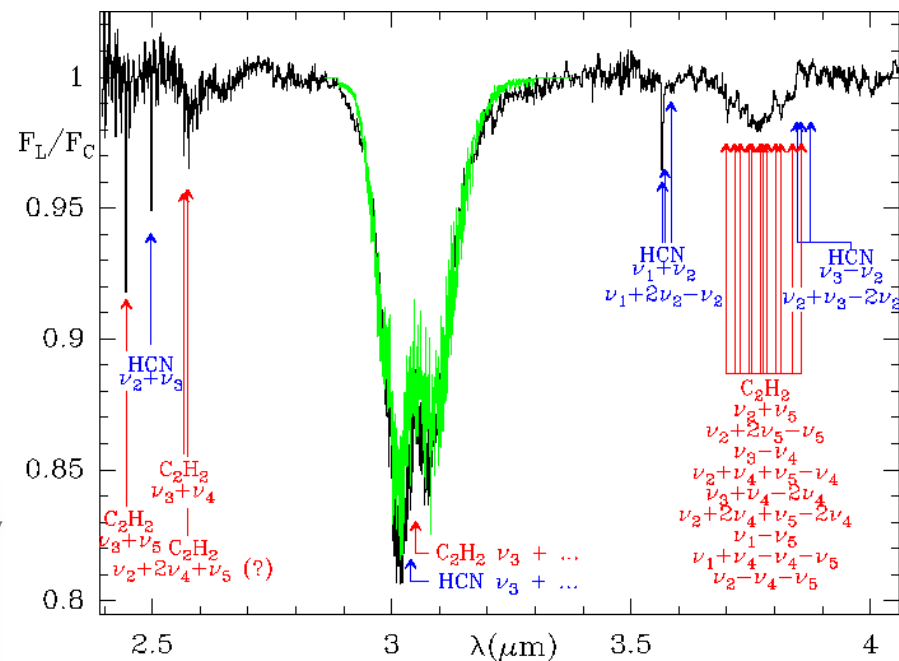
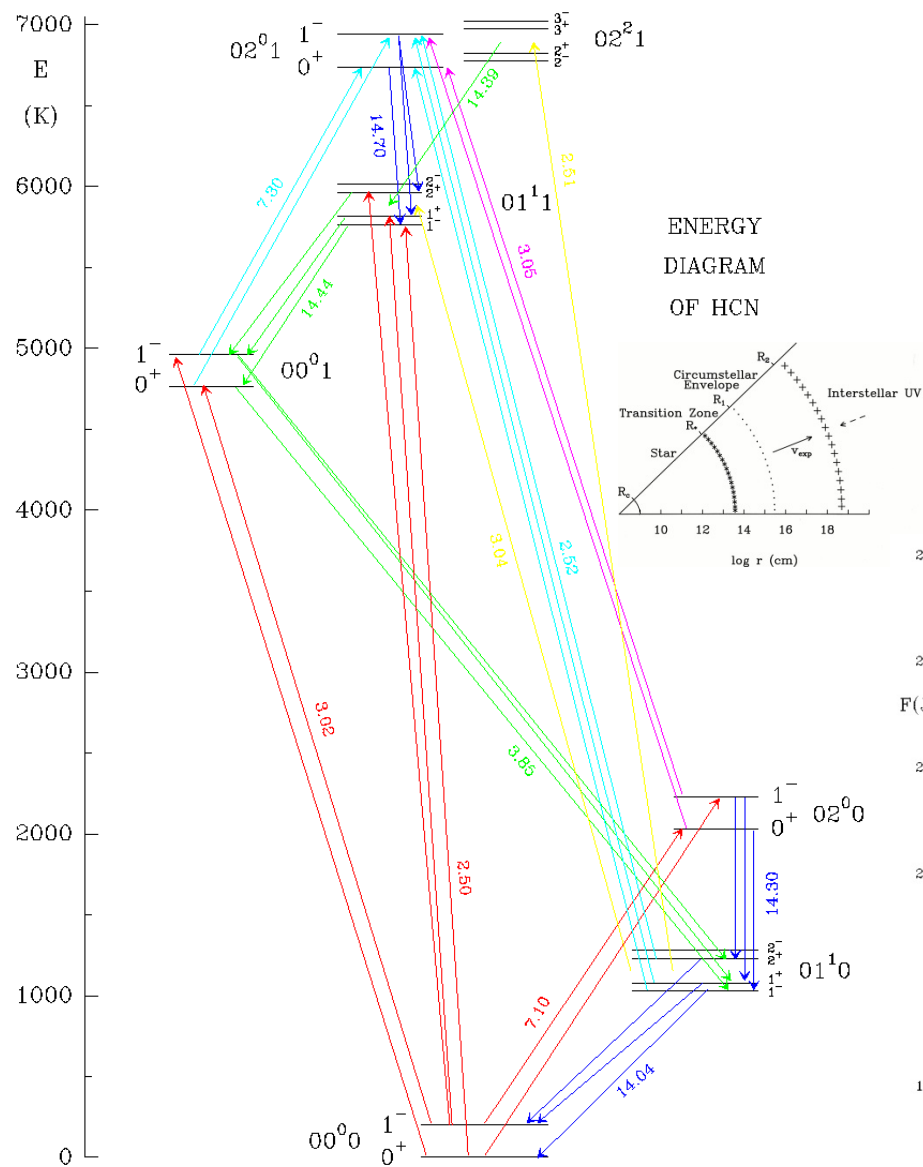


**rotational motion**



**translational motion**

*González-Alfonso & Cernicharo 1998*



# More on rotational spectroscopy...

- Diatomic or linear molecules are just a simple case (J)

- In general a molecule will have three principal axis with moment of inertia  $I_A, I_B, I_C$ . Here we can distinguish:

Spherical tops:  $I_A = I_B = I_C$  Example: Ammonium ion  $\text{NH}_4^+$

Symmetric tops:  $I_A = I_B < I_C$  (prolate)  $I_A < I_B = I_C$  (oblate) (J, K)

Asymmetric tops:  $I_A, I_B, I_C$  all different (Ex:  $\text{H}_2\text{O}$ ) (J,  $K_+, K_-$ )

Unperturbed  
Hamiltonian

$$A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2$$

Centrifugal Distortion

$$-\Delta_J \hat{J}^4 - \Delta_{JK} \hat{J}^2 \hat{J}_z^2 - \Delta_K \hat{J}_z^4 \\ - \frac{1}{2} [\delta_J \hat{J}^2 + \delta_K \hat{J}_z^2, \hat{J}_+^2 + \hat{J}_-^2]$$

Quartic

$$+ H_J \hat{J}^6 + H_{JK} \hat{J}^4 \hat{J}_z^2 + H_{KJ} \hat{J}^2 \hat{J}_z^4 + H_K \hat{J}_z^6 \\ + \frac{1}{2} [\phi_J \hat{J}^4 + \phi_{JK} \hat{J}^2 \hat{J}_z^2 + \phi_K \hat{J}_z^4, \hat{J}_+^2 + \hat{J}_-^2]$$

Sextic

The description of energy levels needs 3 rotational quantum numbers: J (main rotation quantum number),  $K_+$  (projection of J on the symmetry axis of the limiting oblate symmetric top),  $K_-$  (same projection but for the limiting prolate symmetric top)

# More on rotational spectroscopy...

Additional quantum numbers are needed or levels can be missing if:

- Electric dipole moment does not follow a principal axis of inertia (example HDO,  $\mu_a=0.65$   $\mu_b=1.73$ ; for H<sub>2</sub>O  $\mu_b=1.85$ ).
- There is an internal specular symmetry (Ex: NH<sub>3</sub>)
- There is an internal symmetry by rotation (CH<sub>3</sub>CCH)
- There is a nuclear spin (small degeneracy breakdown)
- There is a magnetic dipole moment and an external magnetic field.
- There are degenerate vibrational modes (l-type doubling)

## Generalizing the moment of inertia from Rigid Rotator to Polyatomic Molecules

It is helpful to consider the molecular moment of inertia projected on each of the three Cartesian (xyz) axes. Written in this way, we see that the moment of inertia is actually a two-dimensional vector, called a *tensor*, or the ***inertia tensor***

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$

where the individual elements are defined as

$$\begin{aligned} I_{xx} &= \sum_{j=1}^N m_j [(y_j - y_{cm})^2 + (z_j - z_{cm})^2] \\ I_{yy} &= \sum_{j=1}^N m_j [(x_j - x_{cm})^2 + (z_j - z_{cm})^2] \\ I_{zz} &= \sum_{j=1}^N m_j [(y_j - y_{cm})^2 + (x_j - x_{cm})^2], \text{ and} \\ I_{xy} &= - \sum_{j=1}^N m_j [(x_j - x_{cm})(y_j - y_{cm})], \dots \text{ with} \\ &I_{xy} = I_{yx}, \dots \end{aligned}$$

with the subscript  $_{cm}$  representing the center of mass positions for the molecule.

The mathematics of classical rigid bodies tells us that the ***inertia tensor*** for molecules can always be diagonalized so that the off-diagonal elements (*e.g.*,  $I_{xy}$ ) are zero. The convention is that the resulting ***diagonalized inertia tensor*** has the diagonal elements relabeled as  $I_{xx} = I_A$ ,  $I_{yy} = I_B$ , and  $I_{zz} = I_C$ , or

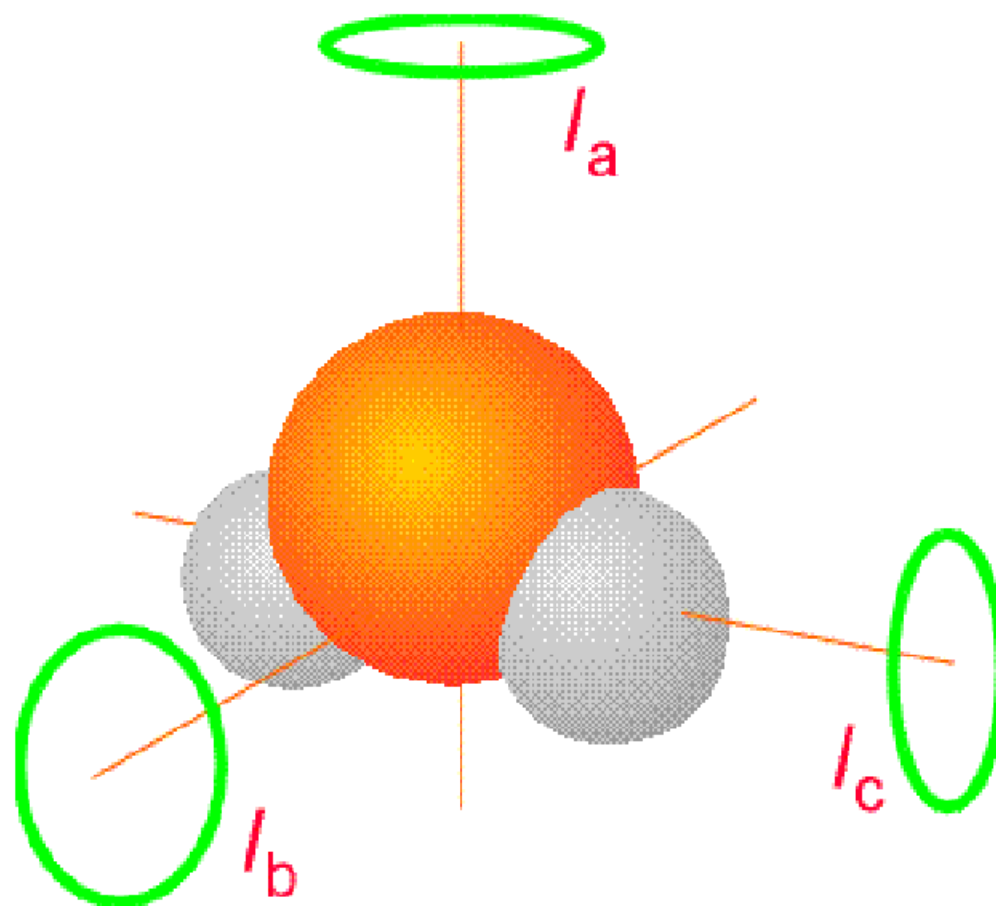
$$\mathbf{I} = \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix}$$

Thus, to represent molecular rotations for even the most asymmetric molecules, we need consider only the three axes  $A$ ,  $B$ , and  $C$  that are mutually orthogonal along the  $x$ ,  $y$ , and  $z$  directions. Another convention is that for molecules, we always define the  $A$  axis to have the smallest moment of inertia, and hence the highest rotation frequency, as  $I_A \leq I_B \leq I_C$ .

***Spherical rotors***, (or ***spherical tops***) are molecules for which  $I_A = I_B = I_C$ . Examples of ***spherical top*** molecules are methane ( $\text{CH}_4$ ), sulfur hexafluoride ( $\text{SF}_6$ ), and carbon tetrachloride ( $\text{CCl}_4$ ).

Linear molecules have  $I_A = I_B$ , and  $I_C = 0$ . Examples of linear rotors are all of the diatomic molecules, plus carbon dioxide ( $\text{CO}_2$ ).

As shown below, water is also an *asymmetric rotor*.



The generalization of the *rigid rotor* to the three-dimensional case for an *asymmetric rotor* requires that we consider the fact that the angular momentum squared operator  $\mathbf{J}$  is now represented as

$$J^2 = J_A^2 + J_B^2 + J_C^2$$

and consequently, the Hamiltonian operator for the *asymmetric rotor* is given by

$$\hat{H} = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

There are in general three rotational energies, one for rotation about each of the three orthogonal axes  $A$ ,  $B$ , and  $C$ . Because of orthogonality, the rotational axes have separable rigid rotor solutions, leading to energy eigenvalues

$$E_A(J) = h^2/(8\pi^2 I_A) \times J(J+1), E_B(J) = h^2/(8\pi^2 I_B) \times J(J+1), \text{ and } E_C(J) = h^2/(8\pi^2 I_C) \times J(J+1).$$

It is *very important* to keep track of units in spectroscopy. In rotational spectroscopy, the energies may be reported in GHz ( $10^9 \text{ s}^{-1}$ ), or  $\text{cm}^{-1}$  ( $1 \text{ cm}^{-1} = 30 \text{ GHz}$ ). It is quite common to find the rotational energies written in terms of the three *rotational constants*  $A$ ,  $B$ , and  $C$ , given by

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}; \tilde{B} = \frac{h}{8\pi^2 c I_B}; \text{ and } \tilde{C} = \frac{h}{8\pi^2 c I_C};$$

where the units are wavenumbers ( $\text{cm}^{-1}$ ).

## Centrifugal Distorsion

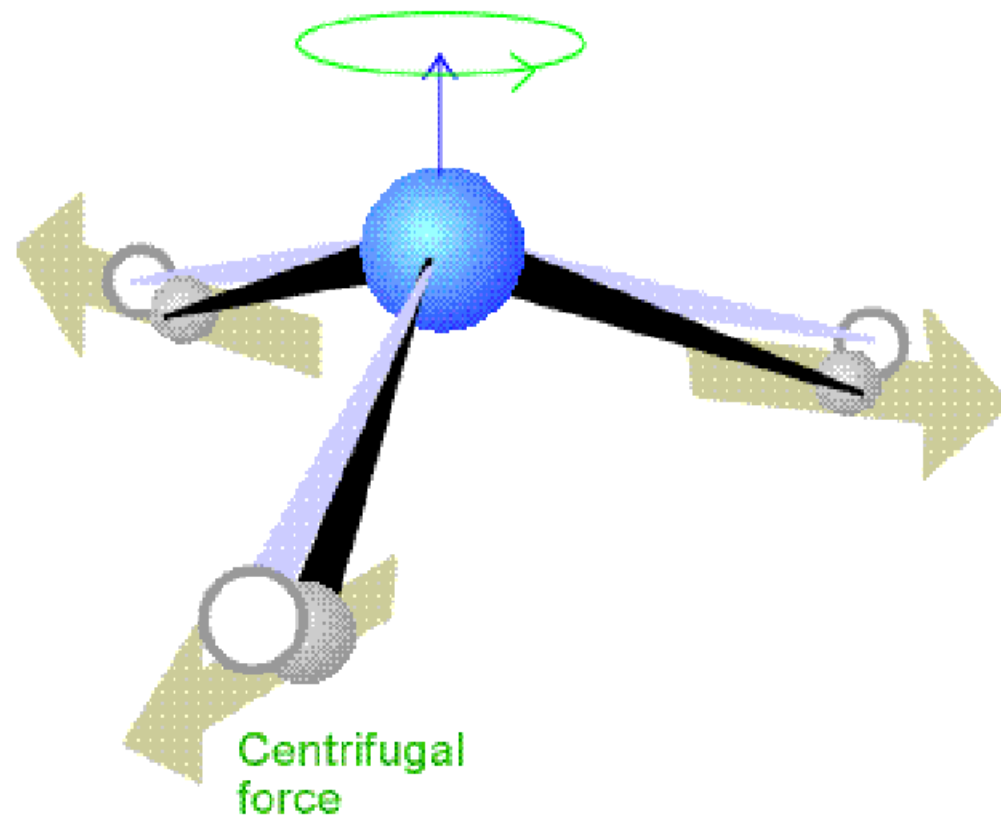
Centrifugal stretching is treated as a perturbation on the eigenstates of the rigid rotor. If  $\mathcal{H}_r$  represents the Hamiltonian of the rigid rotor and  $\mathcal{H}_d$  represents that of the distortional energy, the rotational Hamiltonian is

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d \quad (6.9)$$

In Chapter 8 it is shown that the centrifugal distortional Hamiltonian has the form

$$\mathcal{H}_d = \frac{\hbar^4}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta \quad (6.10)$$

where  $\alpha, \beta, \gamma, \delta$  represent the principal coordinate axes of the moments of inertia and where each must be summed over all three coordinate axes. However, in the first-order perturbation treatment, the terms with odd powers in any angular momentum which occur in the sum average to zero. Furthermore, by use of the angular momenta commutation rules and the fact that many of the  $\tau$ 's are equal, the Hamiltonian can be further simplified.



$$\begin{aligned}
 \mathcal{H}_d^{(1)} &= \frac{1}{4} \sum \tau'_{\alpha\alpha\beta\beta} P_\alpha^2 P_\beta^2 \\
 &= \frac{1}{4} [\tau'_{xxxx} P_x^4 + \tau'_{yyyy} P_y^4 + \tau'_{zzzz} P_z^4 + \tau'_{xxyy} \\
 &\quad \times (P_x^2 P_y^2 + P_y^2 P_x^2) + \tau'_{xxzz} (P_x^2 P_z^2 + P_z^2 P_x^2) \\
 &\quad + \tau'_{yyzz} (P_y^2 P_z^2 + P_z^2 P_y^2)]
 \end{aligned}$$

$$E_d^{(1)} = (J, K | \mathcal{H}_d^{(1)} | J, K)$$

---

Matrix Elements of  $P_\alpha^2 P_\beta^2$  in a Symmetric Rotor Representation<sup>a</sup>

---

$$(K | P_z^4 | K) = K^4$$

$$(K | P_y^4 | K) = \frac{1}{4}[(P^2 - K^2)^2 + \frac{1}{4}\{f_+(0)f_+(1) + f_-(0)f_-(1)\}]$$

$$(K | P_x^4 | K) = (K | P_y^4 | K)$$

$$(K | P_x^2 P_y^2 + P_y^2 P_x^2 | K) = \frac{1}{2}[(P^2 - K^2)^2 - \frac{1}{4}\{f_-(0)f_+(1) + f_-(0)f_-(1)\}]$$

$$(K | P_y^2 P_z^2 + P_z^2 P_y^2 | K) = K^2[P^2 - K^2]$$

$$(K | P_x^2 P_z^2 + P_z^2 P_x^2 | K) = (K | P_y^2 P_z^2 + P_z^2 P_y^2 | K)$$

$$(K | P_y^4 | K \pm 2) = \frac{1}{8}\{2P^2 - K^2 - (K \pm 2)^2\}\{f_\pm(0)f_\pm(1)\}^{1/2}$$

$$(K | P_x^4 | K \pm 2) = -(K | P_y^4 | K \pm 2)$$

$$(K | P_y^2 P_z^2 + P_z^2 P_y^2 | K \pm 2) = \frac{1}{4}\{K^2 + (K \pm 2)^2\}\{f_\pm(0)f_\pm(1)\}^{1/2}$$

$$(K | P_x^2 P_z^2 + P_z^2 P_x^2 | K \pm 2) = -(K | P_y^2 P_z^2 + P_z^2 P_y^2 | K \pm 2)$$

$$(K | P_y^4 | K \pm 4) = \frac{1}{16}\{f_\pm(0)f_\pm(1)f_\pm(2)f_\pm(3)\}^{1/2}$$

$$(K | P_x^4 | K \pm 4) = (K | P_y^4 | K \pm 4)$$

$$(K | P_x^2 P_y^2 + P_y^2 P_x^2 | K \pm 4) = -2(K | P_y^4 | K \pm 4)$$

$$P^2 = J(J + 1); \quad f_\pm(l) = \{P^2 - (K \pm l)(K \pm l \pm 1)\}$$


---

$$E_d^{(1)} = -h[D_J J^2(J + 1)^2 + D_{JK} J(J + 1)K^2 + D_K K^4]$$

The energies of symmetric rotor are :

$$E_{J,K} = h[BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4]$$

and the frequencies for a transition  $J \Rightarrow J+1$  :

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$$

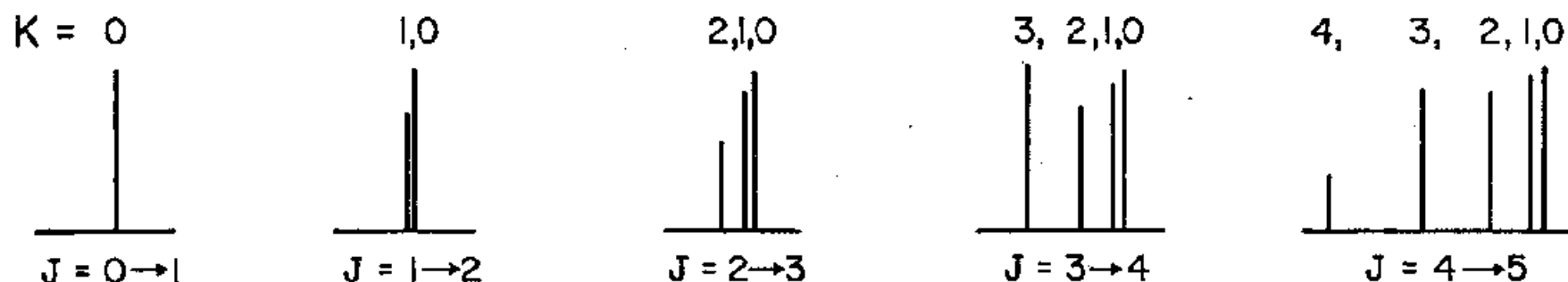


Fig. 6.2. Diagram indicating the general appearance of the rotational spectrum of a symmetric-top molecule. The lines of different  $K$  for the same  $J$  transition are separated by centrifugal distortion. This separation is extremely small compared with the separation of the different  $J$  transitions.

**Each molecule will have different excitation mechanisms depending on:**

**Its frequencies and rotational dipole(s) moment(s)**

**Its collisional rates with  $\text{H}_2$ , He, H,  $\text{e}^-$  (depending on the media)**

**Infrared pumping (depends on the media and the source structure and on the dust effect on the IR photons). It depends also on the vibrational dipole moments**

**Its molecular abundance (opacity effects, radiative trapping)**

**The spatial structure of the source**

**Chemical pumping ( $\text{NH}_3$ ,  $\text{CH}_3\text{CN}$ , ....)**

# MOLECULAR SPECTRA *and* MOLECULAR STRUCTURE

## I. SPECTRA OF DIATOMIC MOLECULES

BY

GERHARD HERZBERG, F.R.S.  
*National Research Council of Canada*

With the co-operation, in the first edition, of  
J. W. T. SPINKS, F.R.S.C.

1950

---

SECOND EDITION

---

That's all  
Thank you very much for your  
attention

The observation that in interstellar space only the very lowest rotational levels of CH, CH<sup>+</sup>, and CN are populated is readily explained by the depopulation of the higher levels by emission of the far infrared rotation spectrum (see p. 43) and by the lack of excitation to these levels by collisions or radiation. The intensity of the rotation spectrum of CN is much smaller than that of CH or CH<sup>+</sup> on account of the smaller dipole moment as well as the smaller frequency [due to the factor  $\nu^4$  in (I, 48)]. That is why lines from the second lowest level ( $K = 1$ ) have been observed for CN. From the intensity ratio of the lines with  $K = 0$  and  $K = 1$  a rotational temperature of 2.3° K follows, which has of course only a very restricted meaning.