

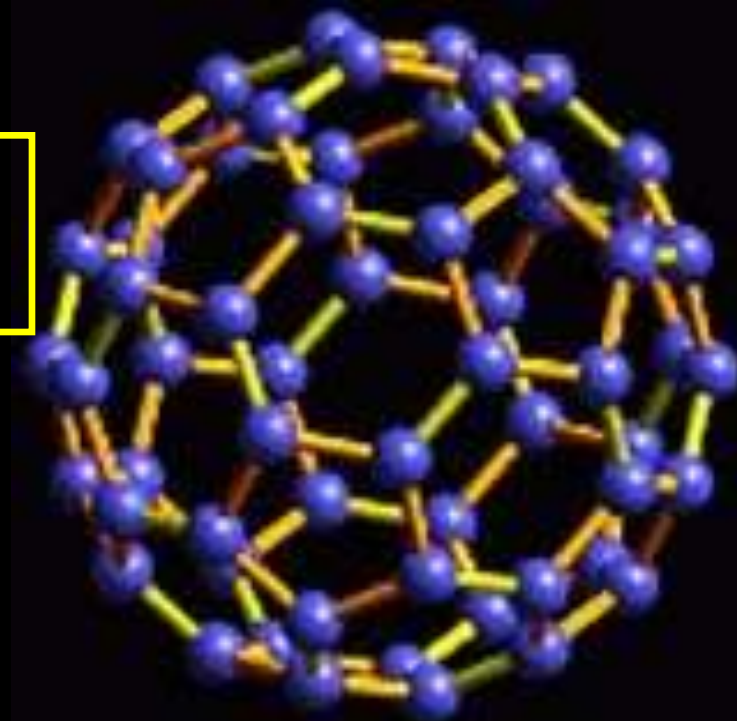
THE CHEMICAL COMPLEXITY OF THE UNIVERSE

Hunting for new molecular species

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Instituto de Estructura de la Materia - Consejo Superior de Investigaciones Científicas

- I. **Molecules in the Universe.** Why are them so important?
- II. **Molecular Spectroscopy.** How can we learn about the universe from molecular observations?
- III. **Astrochemistry.** What are the key mechanisms to form molecules in the Universe?
- IV. **AGB to PN transition.** Example of a research project based on molecular physics. To be continued with Herschel.



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.

SECOND EDITION

**Molecular spectroscopy
can lead to fundamental
knowledge of the
Universe**

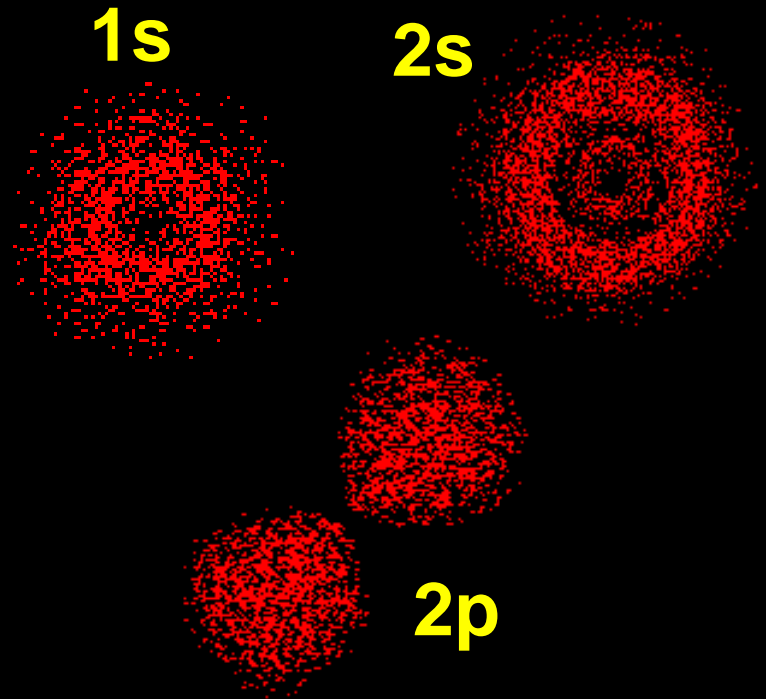
1950

The observation that in interstellar space only the very lowest rotational levels of CH, CH⁺, 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⁺ on account of the smaller dipole moment as well as the smaller frequency [due to the factor ν^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.

MOLECULAR ORBITALS AND THE STABILITY OF MOLECULES

The Molecular Bond

- The problem of molecular stability has to be addressed in a strict quantum-mechanical frame.
- In atoms the electrons are described by their atomic orbitals.
- Each atom has a number of configurations corresponding to the different ways the electrons fill the energy levels.
- All atomic properties are perfectly defined by the atomic orbitals describing the electronic density around the nucleus.



EVEN FOR A SINGLE ATOM, ORBITALS CAN GET VERY COMPLICATED

l: orbital quantum number **m**: angular momentum quantum number

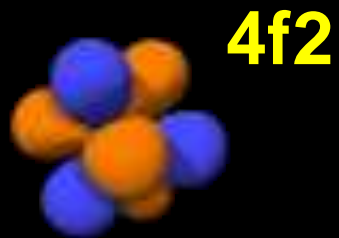
n: principal quantum number



l=2 m=0
n=3



l=3 m=0
n=4



l=3 m=2
n=4



l=3 m=1
n=5

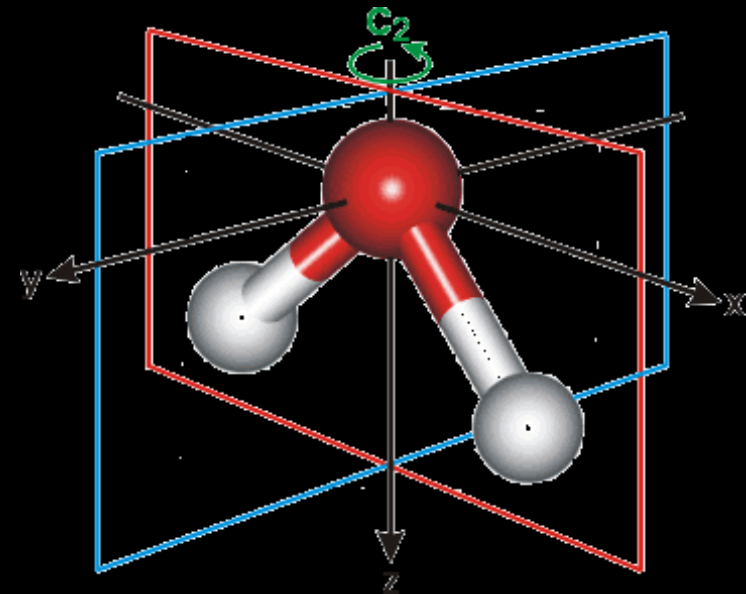
l=2 m=0
n=5

5d0



Molecular stability under the hypothesis of quantum physics

- 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.



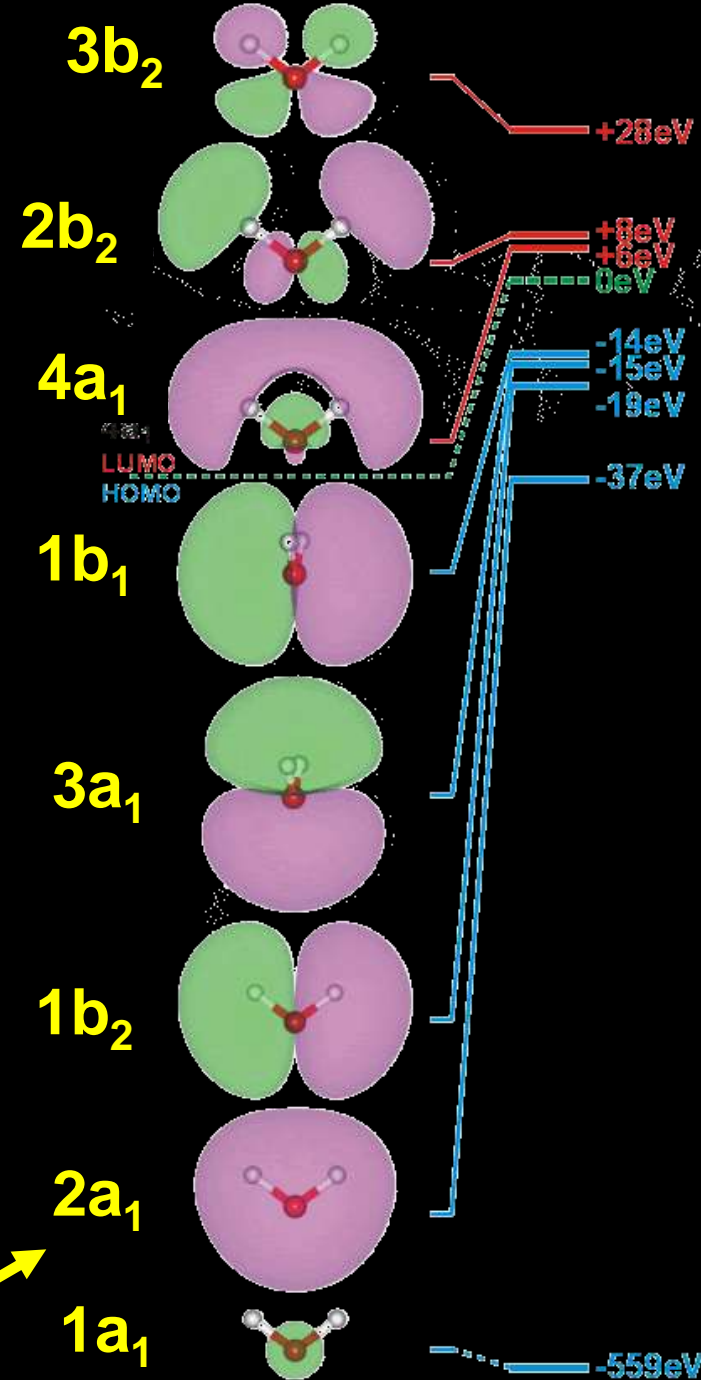
Geometry for nuclei in the water molecule

As molecules are not spherically symmetric, the positions of the nuclei in space are important for the total energy.

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

ψ^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)

Molecular orbitals for water



Assuming that a molecule can be described with an analogy to 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 assumptions let us consider molecular hydrogen (H_2), i.e., the simplest molecule, and the most abundant one in space.

Let H_A and H_B be two atoms of hydrogen and let ψ_A and ψ_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.



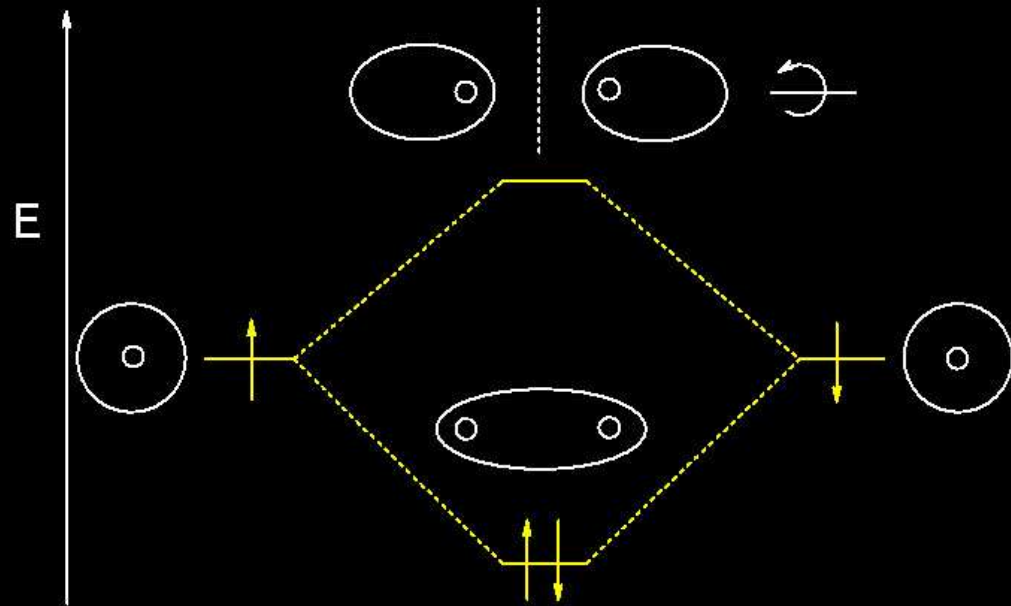
$1s_0$

However, the electron of atom H_A when H_A is far from H_B will be reasonably well represented by ψ_A and when the same electron is close to atom H_B by ψ_B .

The atomic orbitals can overlap in two ways depending on the phase when combining the eigenfunctions of electrons in the isolated atoms. When both atoms are still far away:

$$\Psi_{AB}(\text{for one of electrons}) = \psi_A + \lambda \psi_B$$

With $\lambda = \pm 1$. There are then two possible final 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 $E_- > E_0$. The former is called the σ bond and the latter is called the σ^* or anti-bonding. The reduction in energy towards the σ molecular state is the driving force for chemical bond formation.

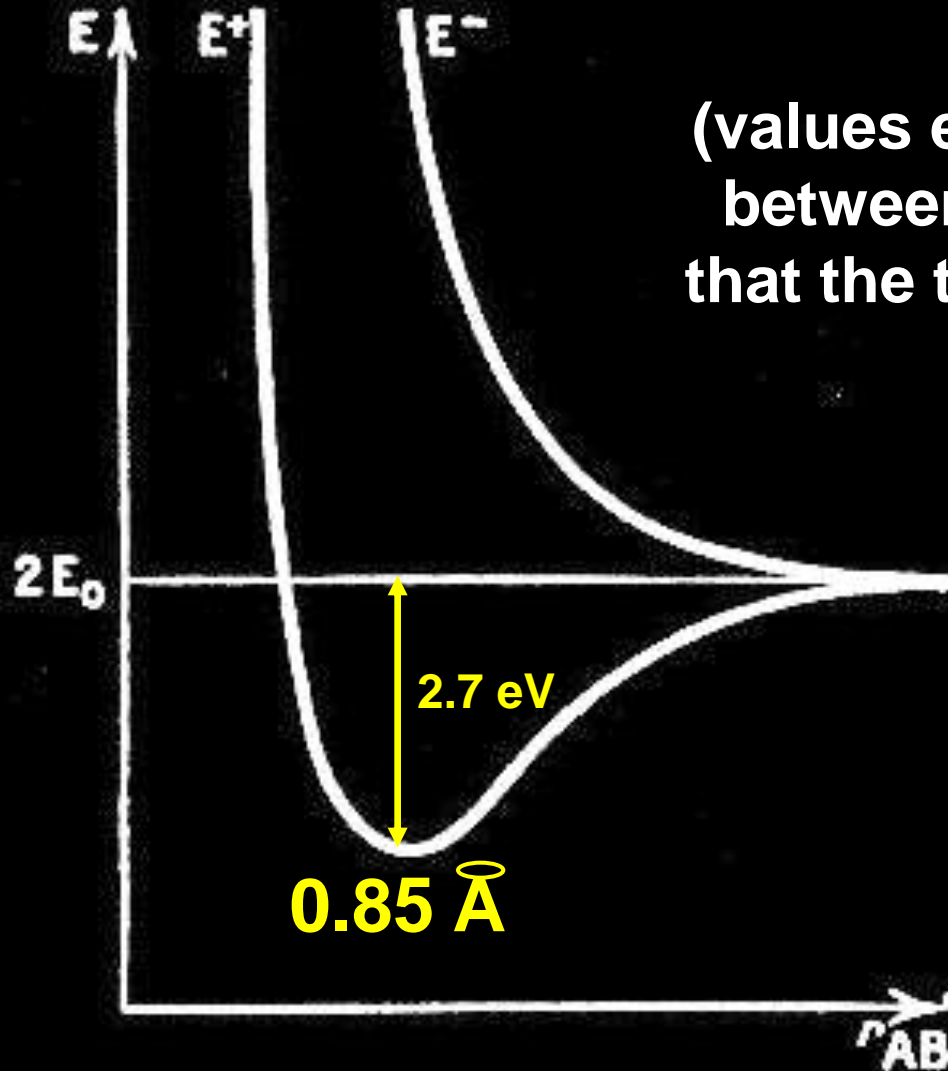


- The ground state of the molecule is obtained when two electrons are placed in the orbital σ . Obviously, both electrons should have opposite spins according to Pauli's principle.
- The electronic energy of the σ molecule in the simple approximation is the sum of the individual energies of the electrons (but that is true before the bond itself is built)
- The wave function of the system, Φ , also in the simple approximation is the product of the individual wave functions of the electrons.

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

...But the reality is more complex...

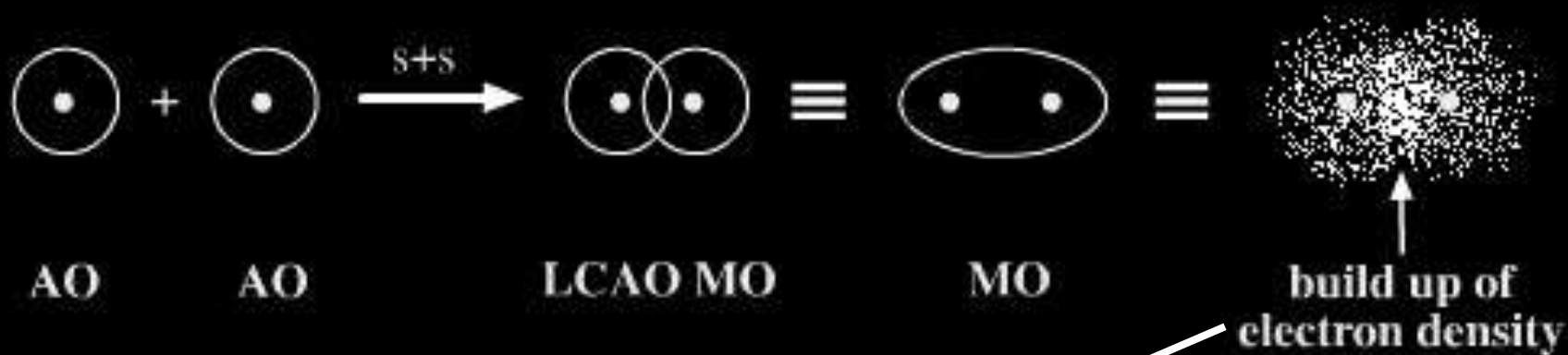
However, the dependency of the electronic energy of the system as a function of the internuclear distance has the following shape:



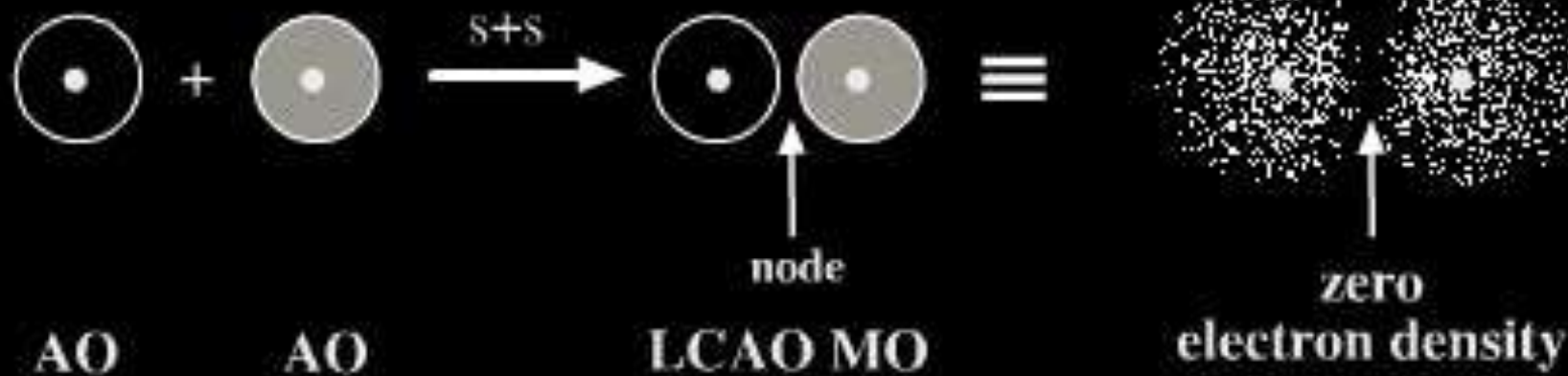
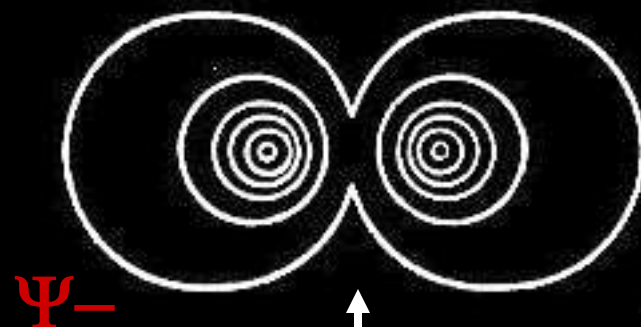
(values excluding the interaction between electrons and the fact that the two protons interact with the electrons)

Experimental values:

0.74 \AA and 4.7 eV



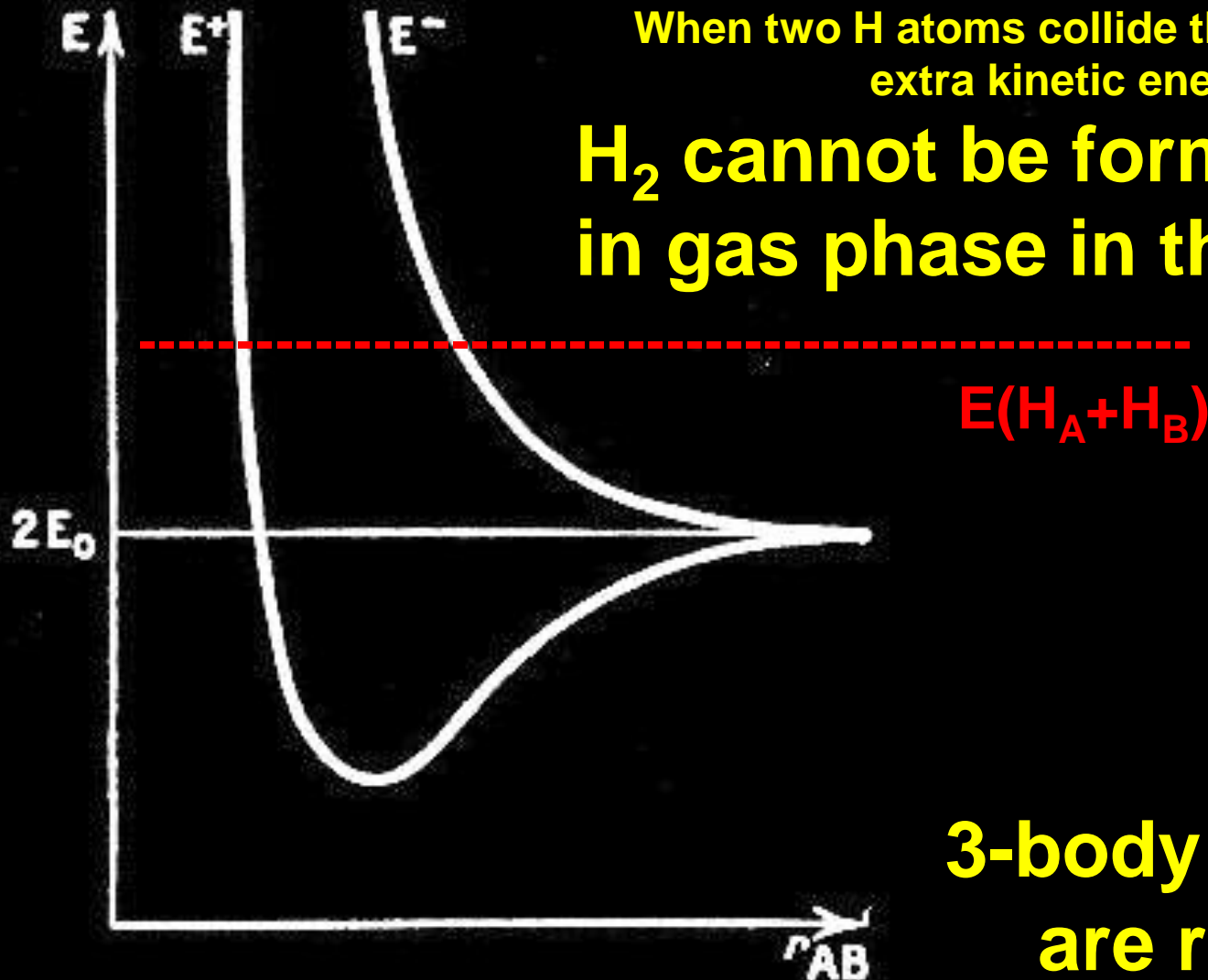
Electronic isodensity contours:



IMPORTANT:

When two H atoms collide they have some extra kinetic energy

**H₂ cannot be formed
in gas phase in the ISM !!!**



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

ONCE A MOLECULE IS FORMED THE INTERNAL ENERGY IS MUCH 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 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

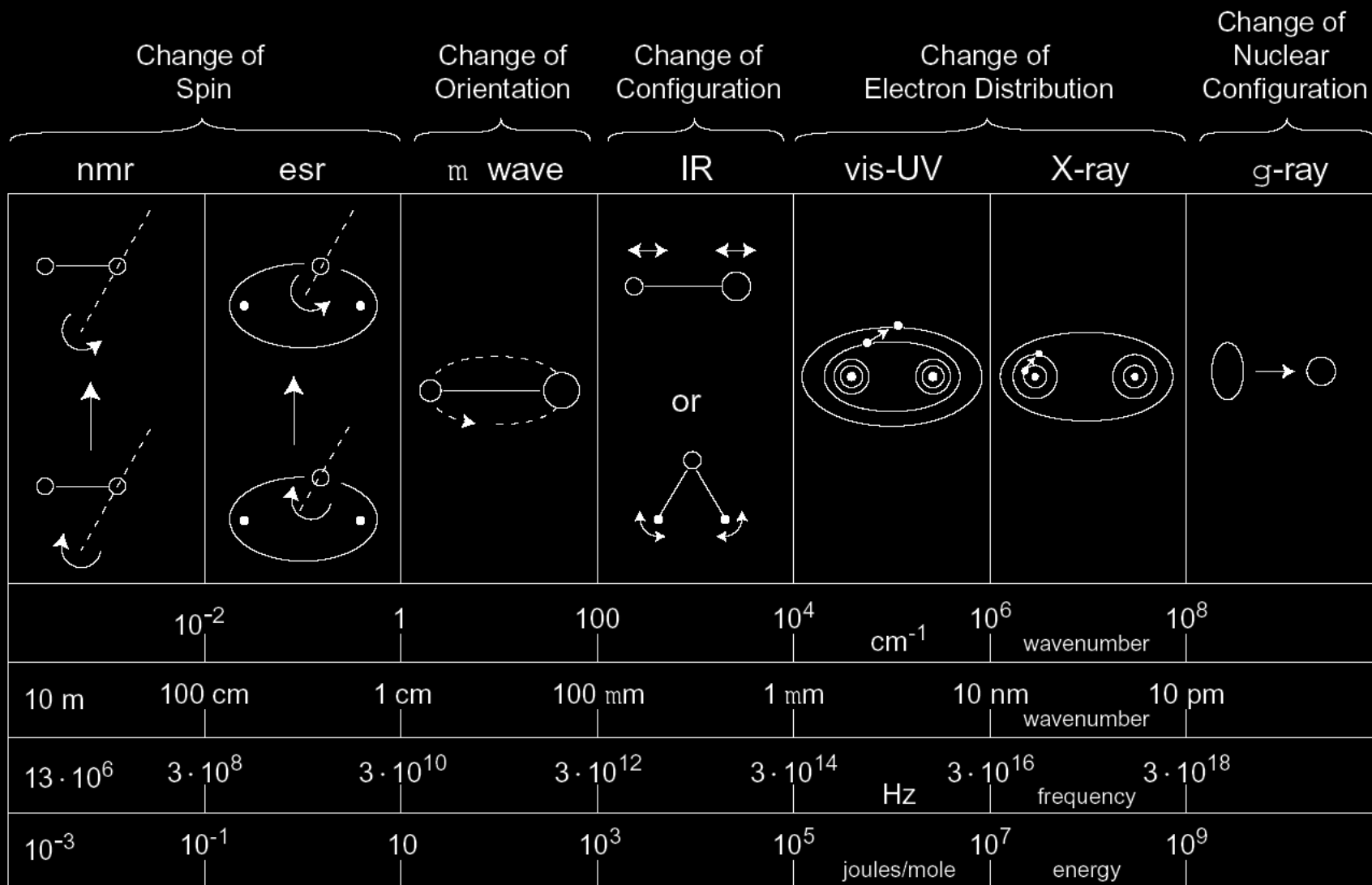
Rotational

Vibrational

Electronic

However, the quantum mechanical problem is relatively simple only for very small molecules.

Overview of the entire spectrum



SIMPLE CASE: ROTATIONAL SPECTRUM OF DIATOMIC OR LINEAR MOLECULES

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 could be given by

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

The angular momentum of the molecule is given by $I\omega$, where I is the momentum of inertia of the molecule,

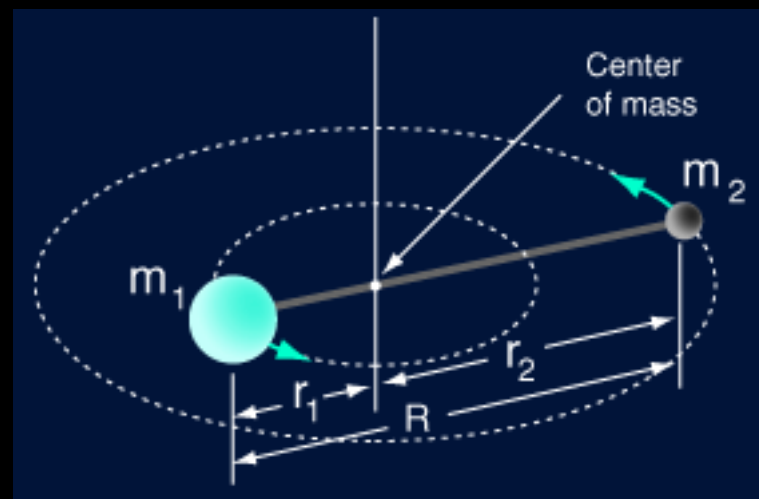
$I = \mu r^2$, μ : reduced mass, r : separation between the nuclei.

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

$$\nu = 2 B J_u$$



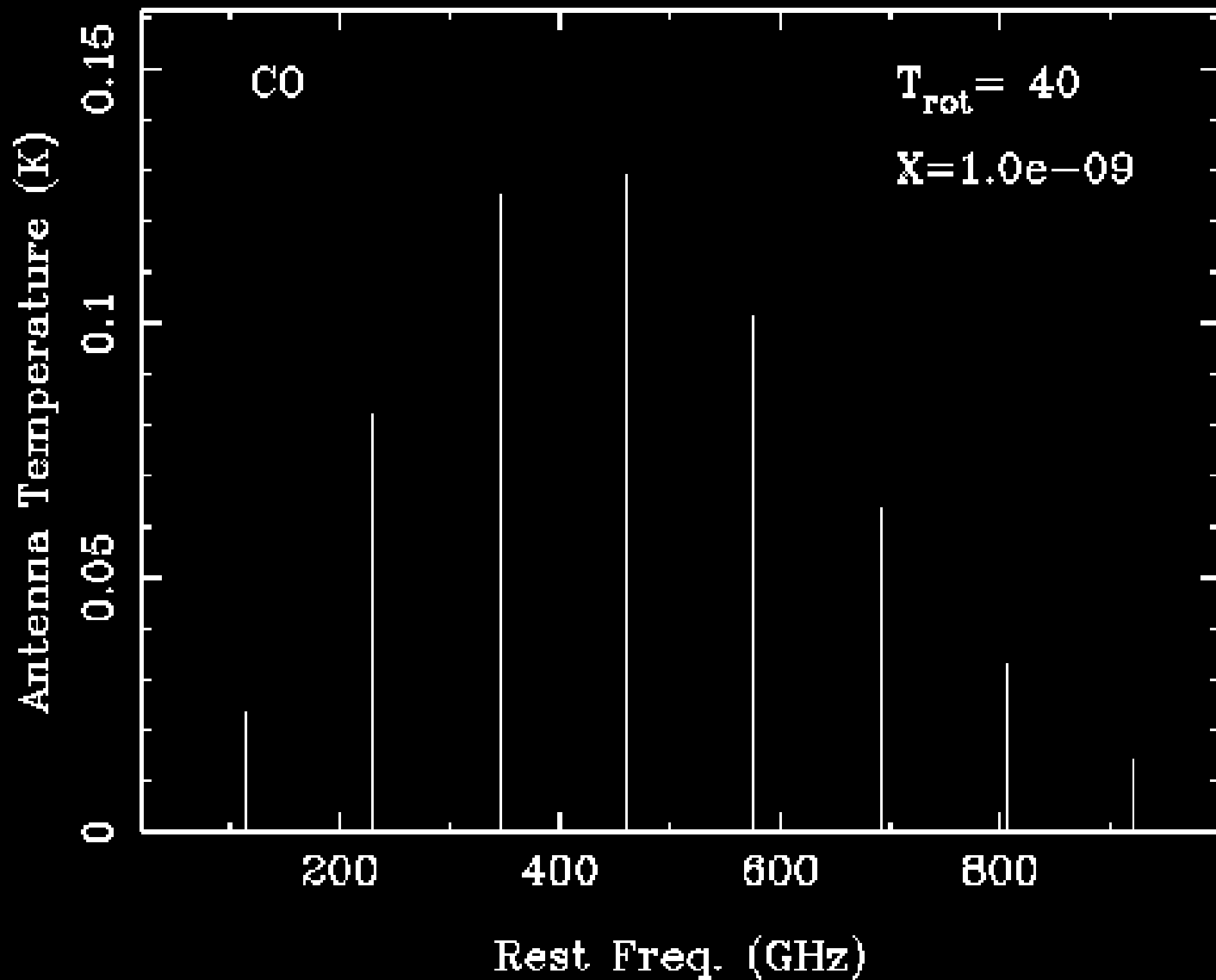
The constant B , the rotational constant, is given by

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

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

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

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



ROTATIONAL SPECTRUM OF CARBON MONOXIDE

Frequency (GHz)

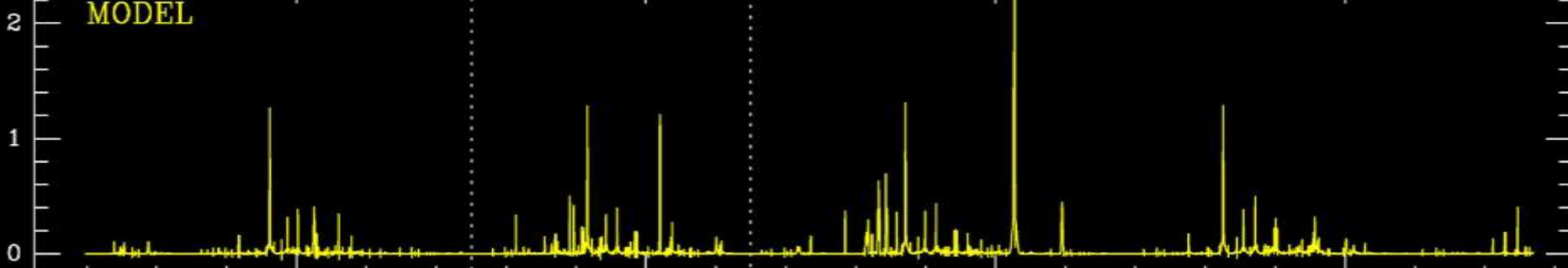
210

220

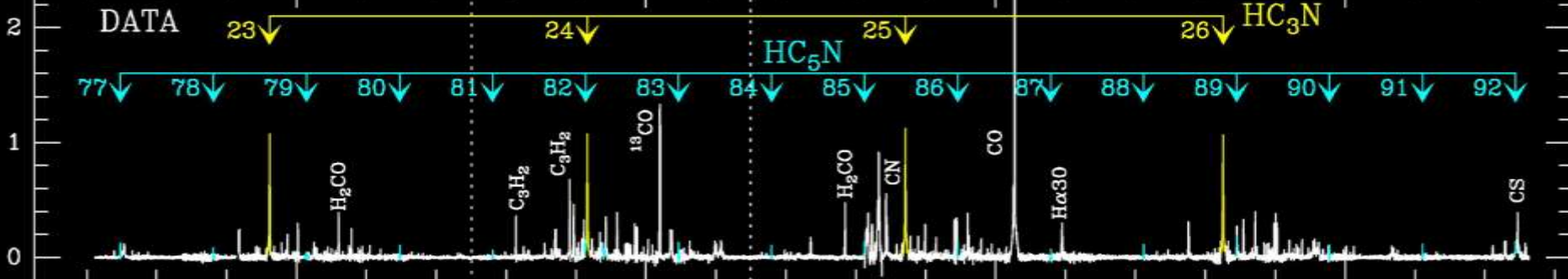
230

240

MODEL



DATA



ROTATIONAL SPECTRUM OF HC_3N (linear)

ROTATIONAL SPECTRUM OF HC_5N (linear)

**Spectrum
Getting
tighter**



However, when the spectral accuracy of the observations is large it is observed that the frequencies of successive rotational transitions depart from the last expression.

¿ 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.

Errors with respect to the simple approximation increase:

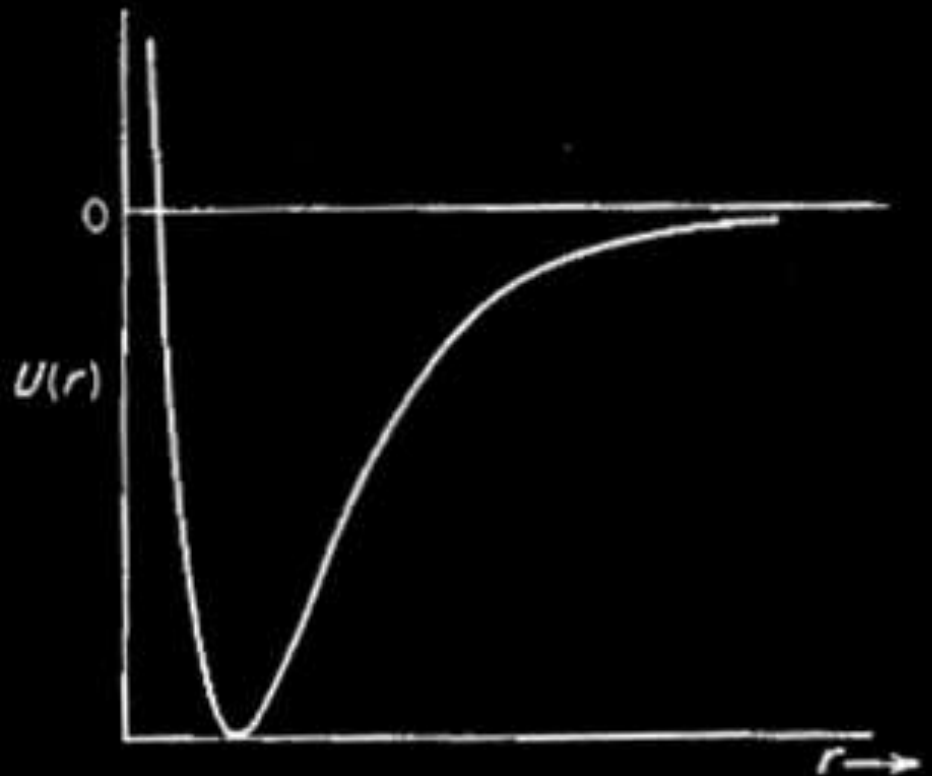
- For lighter molecules.
- For larger rotational numbers.

THIS IS JUST ONE OF MANY DISTORTION EFFECTS
THEY GET INCREASINGLY COMPLICATED AS THE NUMBER
OF ATOMS IN THE MOLECULE INCREASES

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:

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

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

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

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

...these terms can be calculated easily....

$$Y_{00} = B_e/8(3a_2 - 7a_1^2/4)$$

$$Y_{10} = \omega_e[1 + (B_e^2/4\omega_e^2)(25a_4 - 95a_1a_3/2 - 67a_2^2/4 + 459a_1^2a_2/8 - 1155a_1^4/64)]$$

$$Y_{20} = (B_e/2)[3(a_2 - 5a_1^2/4) + (B_e^2/2\omega_e^2)(245a_6 - 1365a_1a_5/2 - 885a_2a_4/2 - 1085a_3^2/4 + 8535a_1^2a_4/8 + 1707a_2^3/8 + 7335a_1a_2a_3/4 - 23,865a_1^3a_3/16 - 62,013a_1^2a_2^2/32 + 239,985a_1^4a_2/128 - 209,055a_1^6/512)]$$

$$Y_{30} = (B_e^2/2\omega_e)(10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 - 705a_1^4/32)$$

$$Y_{40} = (5B_e^3/\omega_e^2)(7a_6/2 - 63a_1a_5/4 - 33a_2a_4/4 - 63a_3^2/8 + 543a_1^2a_4/16 + 75a_2^3/16 + 483a_1a_2a_3/8 - 1953a_1^3a_3/32 - 4989a_1^2a_2^2/64 + 23,265a_1^4a_2/256 - 23,151a_1^6/1024)$$

and Obviously, there is a relation between the Dunham coefficients and those obtained with the Morse potential

$$\begin{array}{lll} Y_{10} \approx \omega_e & Y_{20} \approx -\omega_e x_e & Y_{30} \approx \omega_e^2 y_e \\ Y_{01} \approx B_e & Y_{11} \approx -\alpha_e & Y_{21} \approx \gamma_e \\ Y_{02} \approx -D_e & Y_{12} \approx -\beta_e & Y_{40} \approx \omega_e z_e \\ Y_{03} \approx H_e & & \end{array}$$

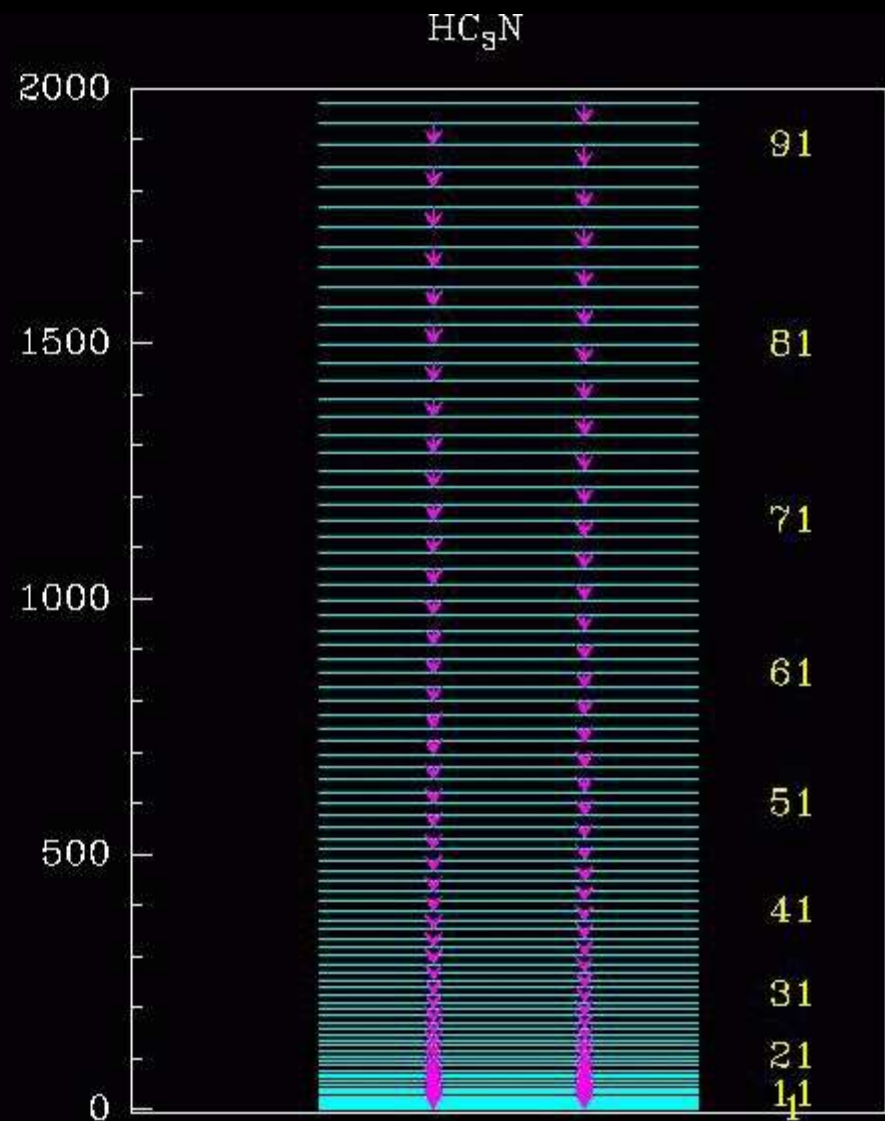
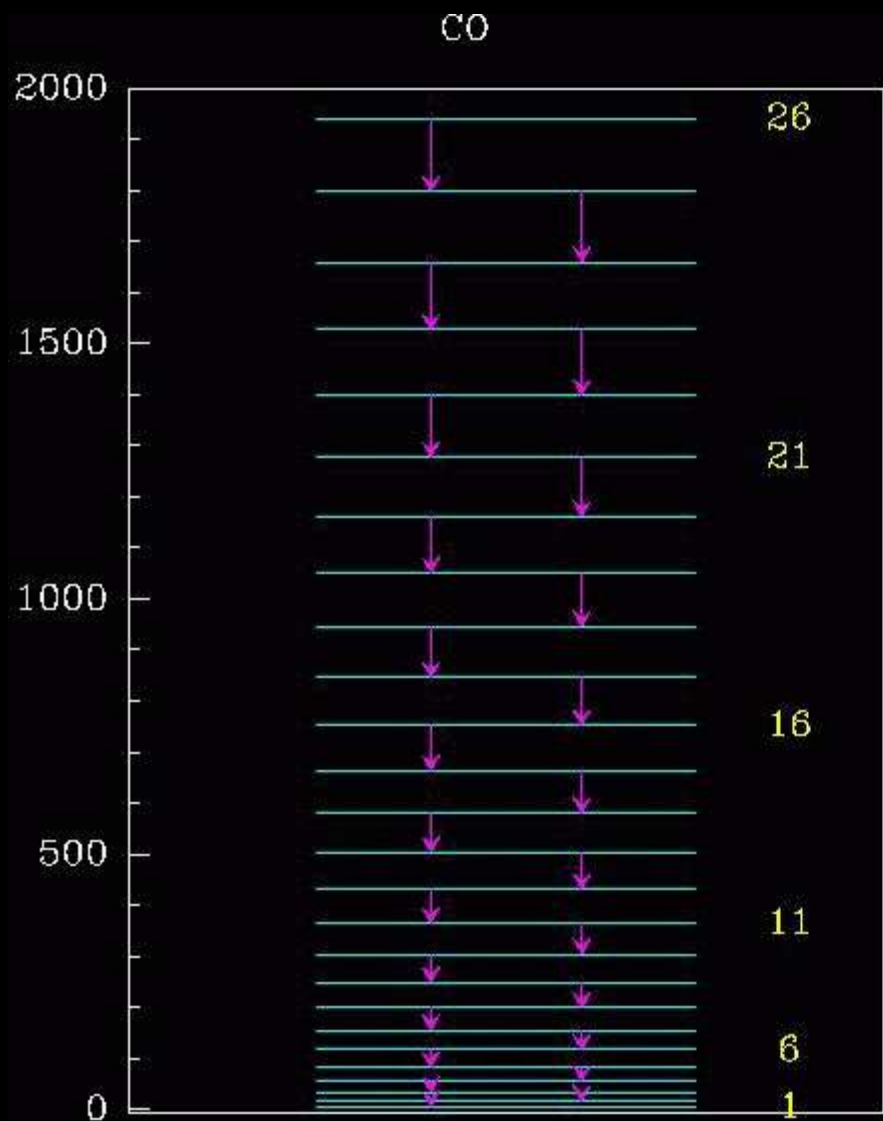
IN SUMMARY: The empirical expression used in spectroscopy to fit the ro-vibrational spectra of diatomic molecules is

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

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

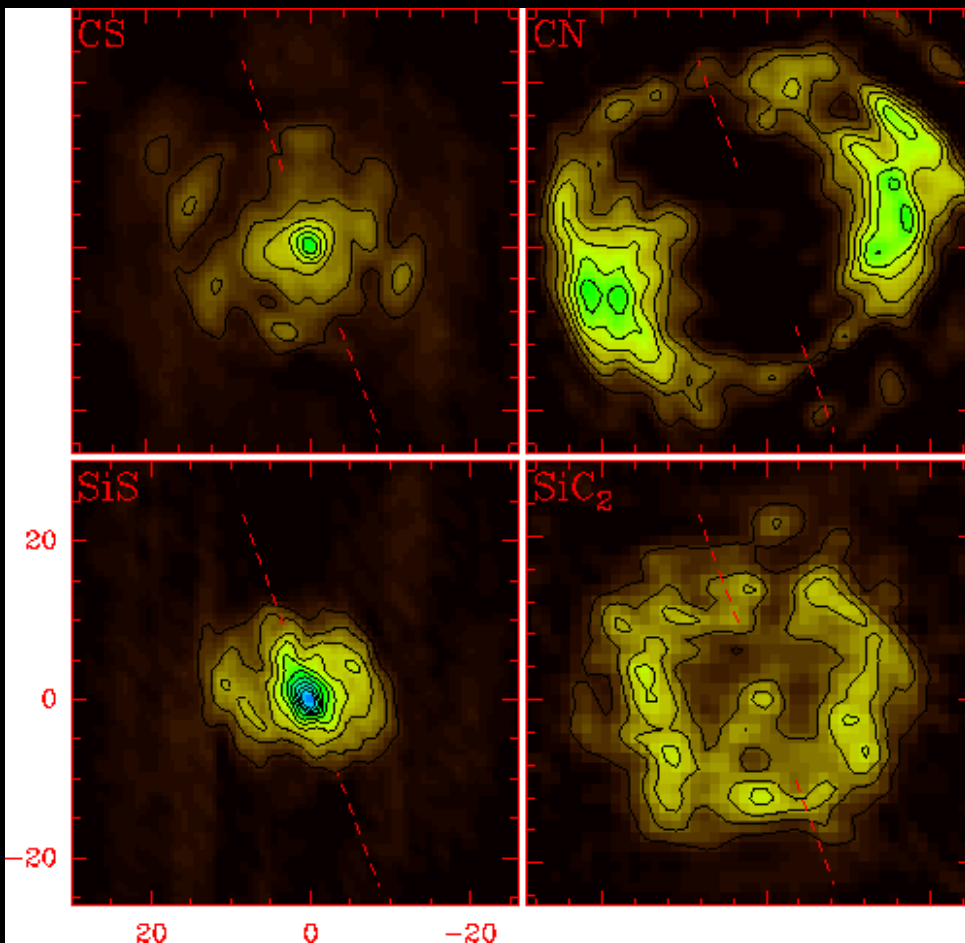
INVERSE PROBLEM: From spectroscopic measurements it is possible to fit spectroscopic constants and from them it is possible to derive important information, through the Morse or Dunham expression for the potential energy, on the dissociation energy, equilibrium distance, etc.

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



Selection rules $\Delta J = \pm 1$

IN ASTROPHYSICS: By selecting the appropriate molecule we can trace different physical parameters and/or gas submitted to different physical conditions.

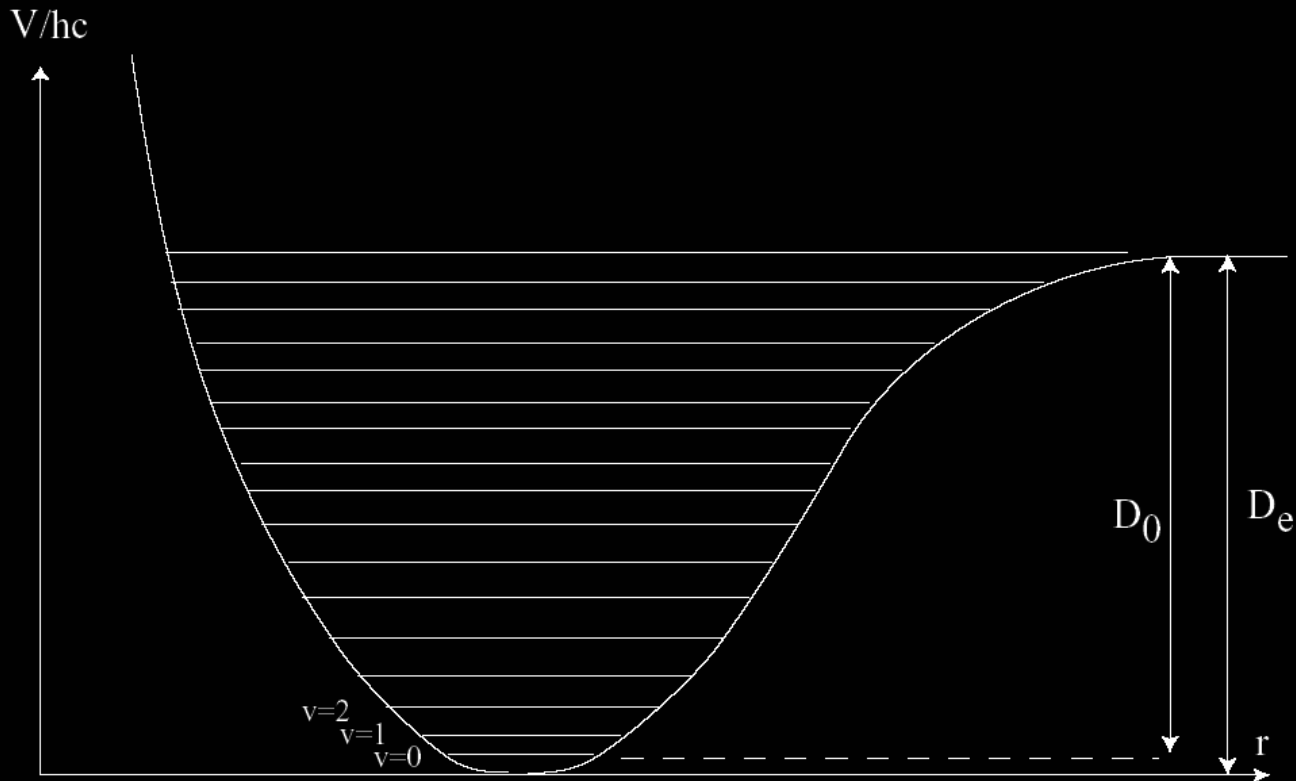


- Molecules with low dipole moment, as CO, are easily excited through collisions with H₂, even for low volume densities. Under some assumptions these molecules could trace the kinetic temperature of the gas.
- High dipole moment molecules could be used as tracers of the gas volume density $[n(\text{H}_2)]$.

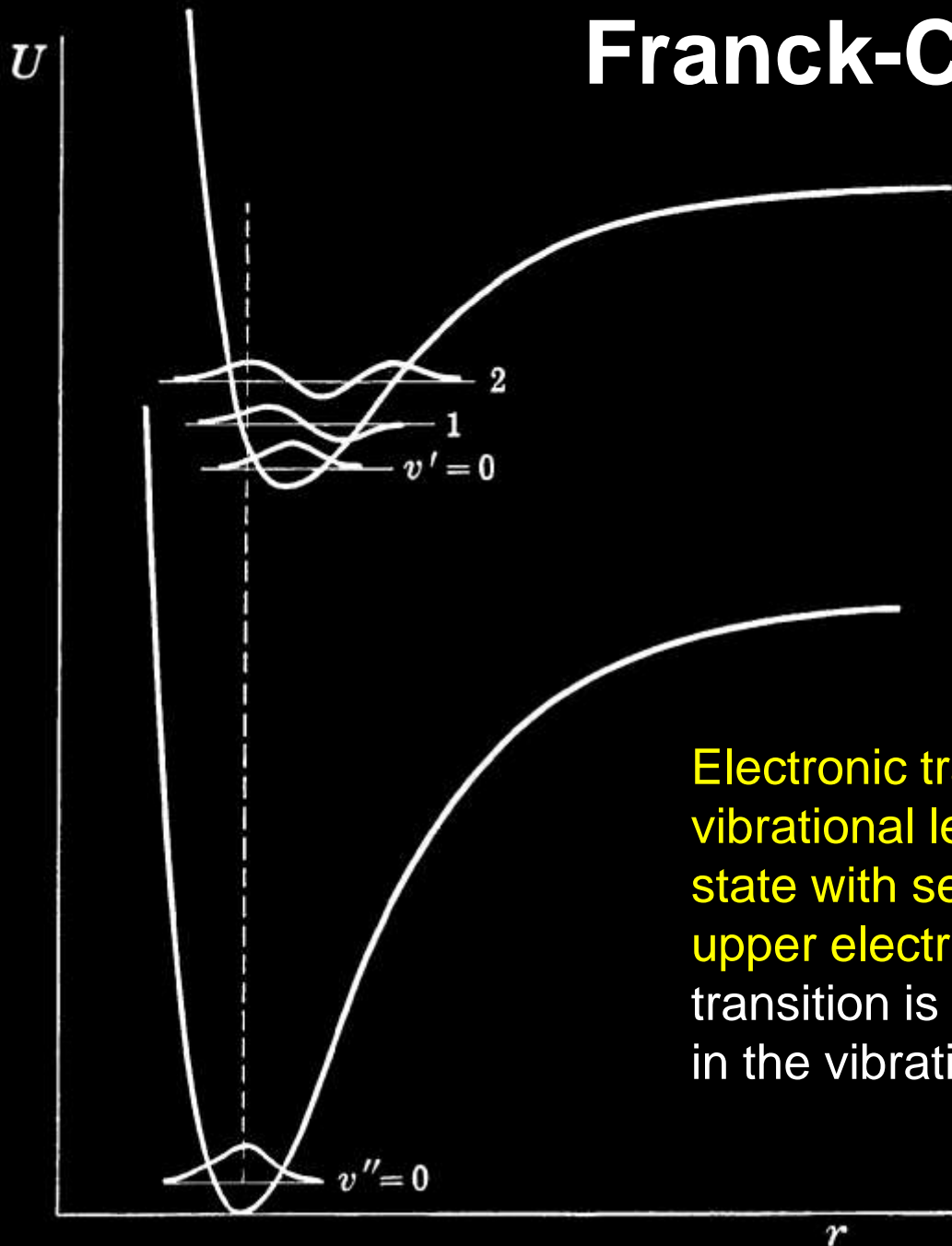
A few facts...

Continuous term spectra and dissociation

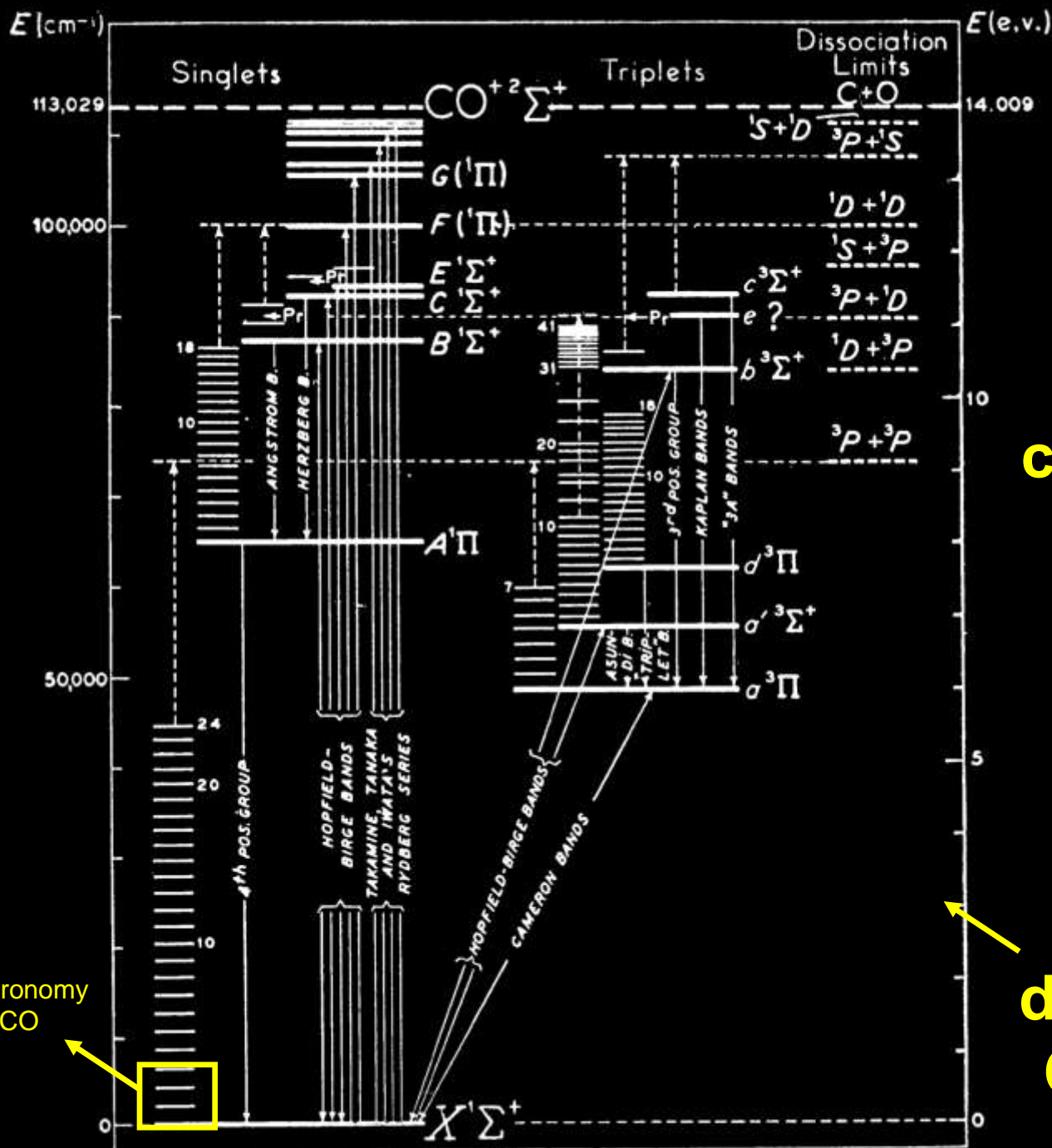
If oscillator has more energy E' than, hcD_e , then $r \rightarrow \infty$ and molecule dissociates. For $E' > hcD_e$, system has excess energy (kinetic energy) after dissociation. $\therefore (K.E)_{\text{atoms}} > 0$ and not quantized.



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.



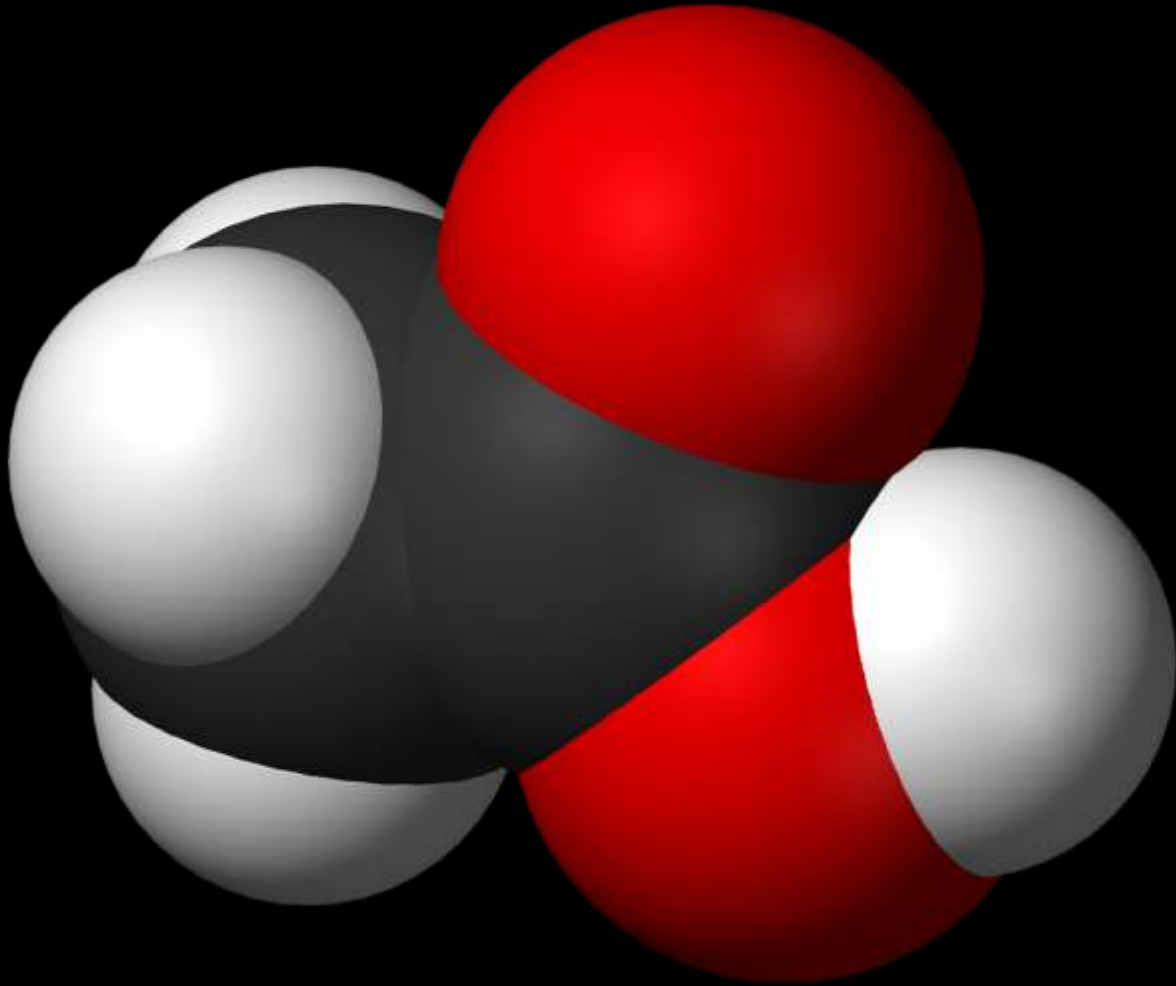
Well, the whole thing can get very complicated...

Energy level diagram of the CO molecule

Radioastronomy with CO



**Imaging the mess for just slightly
more complex molecules...**



**This is why hunting for new
molecules in space is so difficult.**

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 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: H_2O) (J, K_+, K_-)

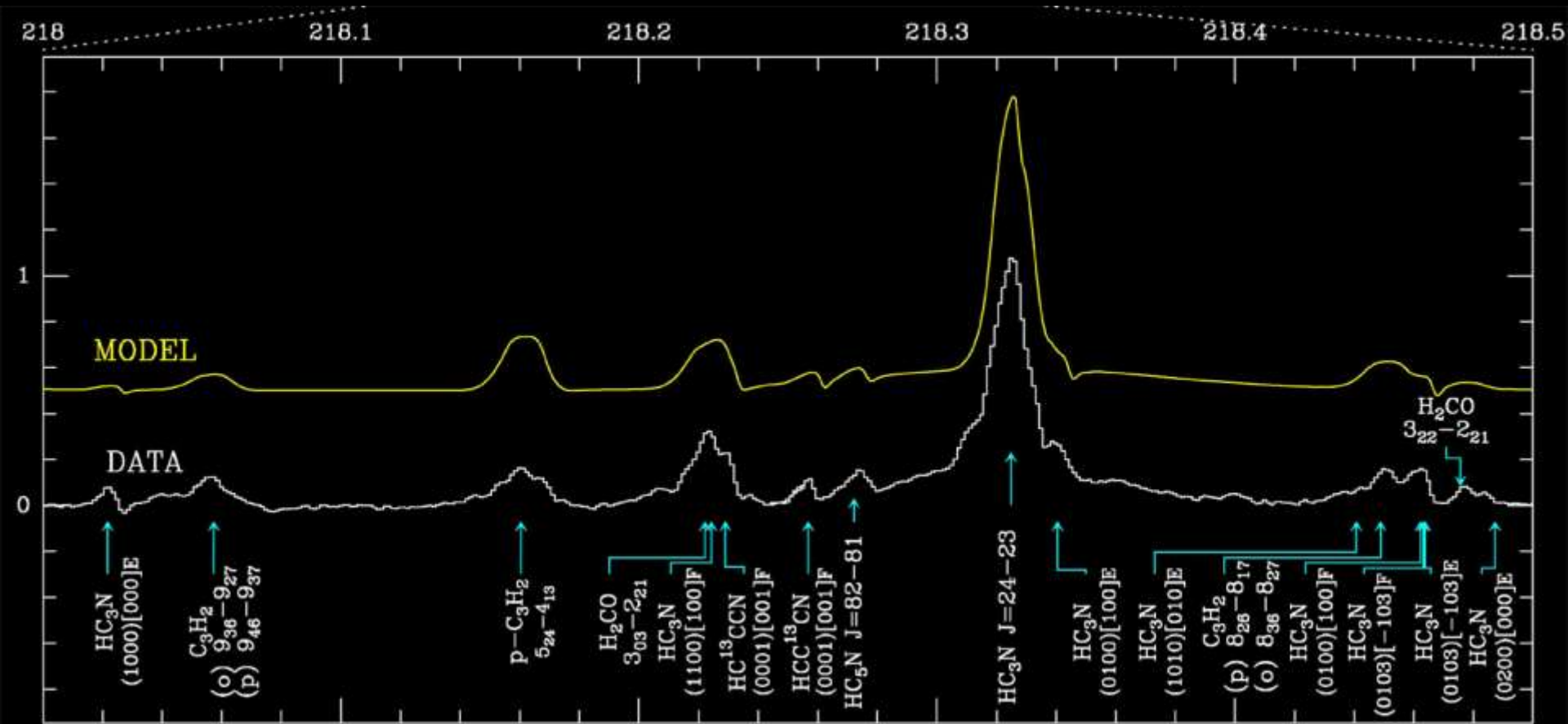
Unperturbed Hamiltonian	Centrifugal Distortion	
$A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2$	$-\Delta_J\hat{J}^4 - \Delta_{JK}\hat{J}^2\hat{J}_z^2 - \Delta_K\hat{J}_z^4$ $- \frac{1}{2}[\delta_J\hat{J}^2 + \delta_K\hat{J}_z^2, \hat{J}_+^2 + \hat{J}_-^2]$	$+H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_z^2 + H_{KJ}\hat{J}^2\hat{J}_z^4 + H_K\hat{J}_z^6$ $+ \frac{1}{2}[\phi_J\hat{J}^4 + \phi_{JK}\hat{J}^2\hat{J}_z^2 + \phi_K\hat{J}_z^4, \hat{J}_+^2 + \hat{J}_-^2]_+$
	Quartic	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).
- There is an internal specular symmetry (Ex: NH_3)
- There is an internal symmetry by rotation (CH_3CCH)
- 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)



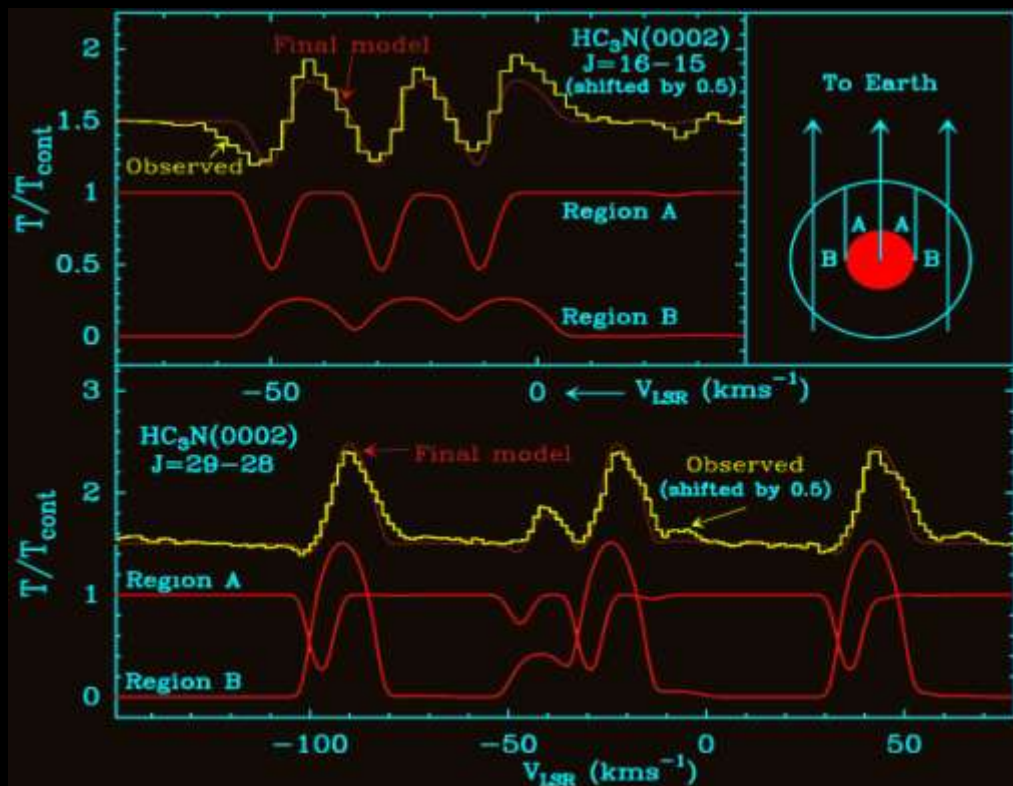
As a result, line identification can become a very difficult task...

Physical parameters that can be extracted from molecular lines

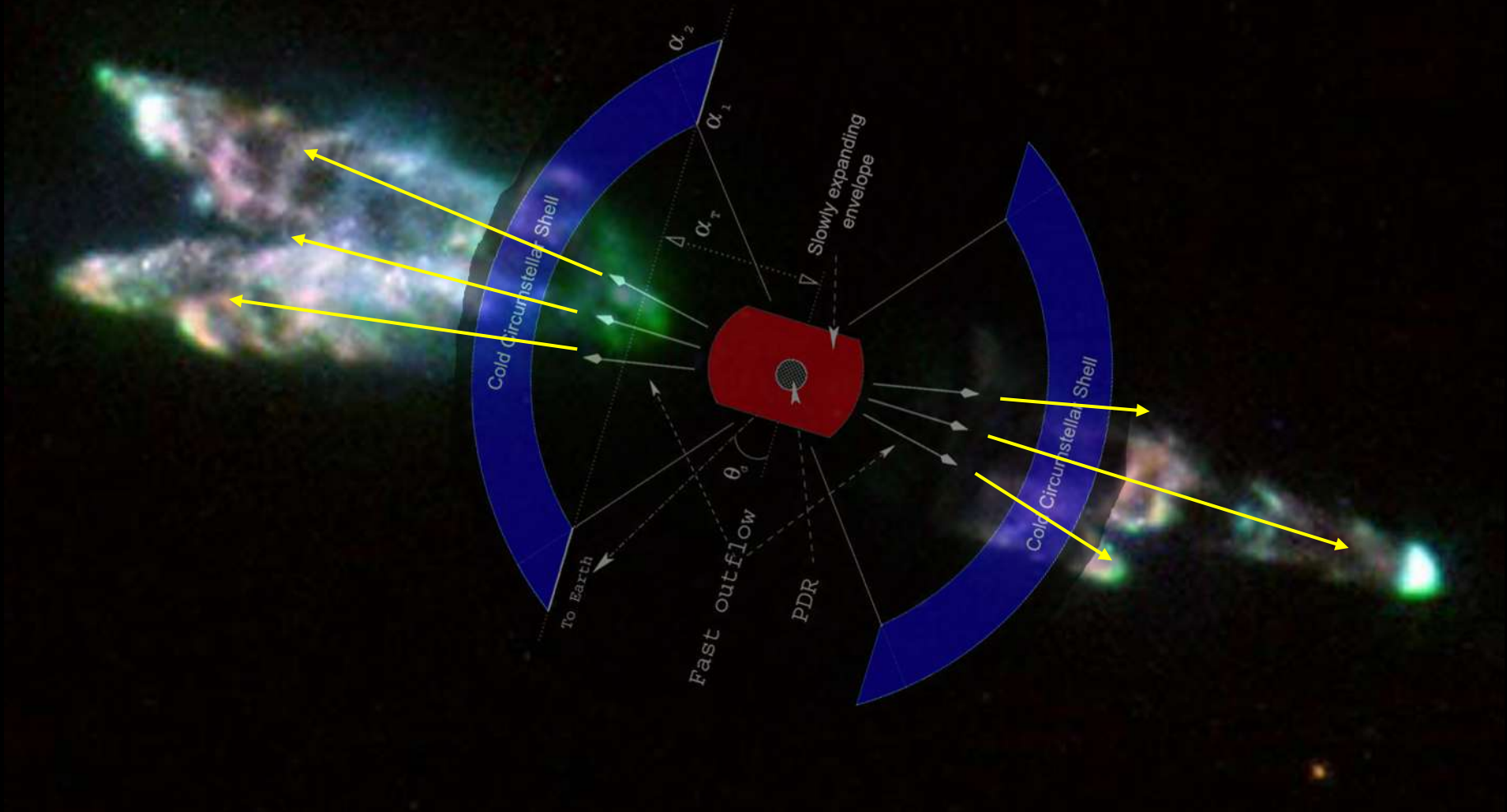
USUALLY MORE THAN ONE LINE IS REQUIRED TO GET PROPER VALUES OF PHYSICAL PARAMETERS

THE QUALITY OF THE INFORMATION DEPENDS ON THE ANGULAR RESOLUTION OF THE OBSERVATIONS.

- Dynamics (LSR Velocity, turbulence, internal motions).
- Temperature.
- Density.
- Chemical composition.
- Magnetic fields.
- External radiation field.

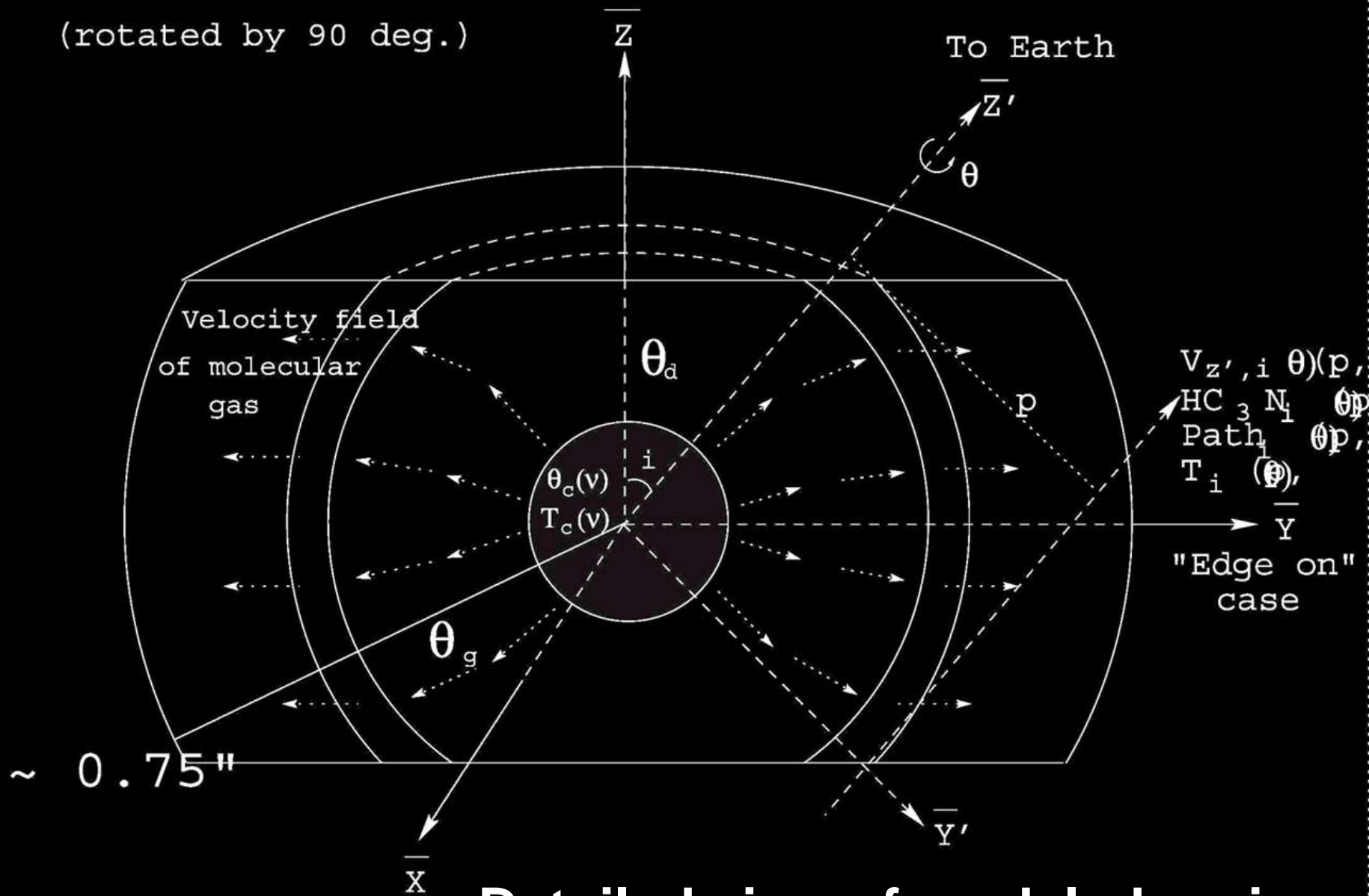


The spectra from the previous page allow to study the physical conditions in the dark region towards the center of this object



(The region in red in the model)

(rotated by 90 deg.)



Detailed view of modeled region

Inclination	
	SEE
parameter	value
Diameter	1.5''
Truncation	0.7
T_{rot}	263 K
v_r at 0.27''	5.0 kms ⁻¹
v_r at 1.5''	12.0 kms ⁻¹
v_{xy} at 0.27''	0.0 kms ⁻¹
v_{xy} at 1.5''	6.0 kms ⁻¹
v_{turb} at 0.27''	3.5 kms ⁻¹
v_{turb} at 1.5''	3.5 kms ⁻¹
[HC ₃ N] at 0.27''	154 cm ⁻³
[HC ₃ N] exponent	-1.8

Notes on molecular spectral analysis

The quality of the information obtained depends on:

- The number of lines used.
- How well their energy levels fit into the typical temperatures of the region under study
- The emission is well detected but not saturated (low opacities)
- The assumption on the molecular excitation is correct:
 - LTE: Valid when the collisions are extremely frequent.
 - Non-LTE: Appropriate collisional rates have to be introduced.
- The angular resolution (if it is high the conditions of the emitting gas are more uniform)

$$\frac{dI_\nu}{ds} = \epsilon_\nu - \kappa_\nu I_\nu + \iint \sigma_\nu(\Omega, \nu') I_\nu d\nu' d\Omega$$

RT EQUATION

LOCAL THERMODYNAMIC EQUILIBRIUM

$$\frac{\epsilon_\nu}{\kappa_\nu} = B_\nu(T)$$

When the gas is thermalized (collisions with a maxwellian gas dominate), the ratio between emission and absorption coefficient equals the Planck Function

$$I_\nu(s) = I_\nu(s_0)e^{-\tau(s_0,s)} + \int_{s_0}^s B_\nu(T(s'))\kappa_\nu(s')e^{-\tau(s',s)} ds'$$

The solution of the RT equation is then very simple and the forward and inverse problems are easy to treat. Non-local calculations can be easily performed. 3D models easy to build.

NON-LOCAL THERMODYNAMIC EQUILIBRIUM

$$\frac{\epsilon_\nu}{K_\nu} \neq B_\nu(T)$$

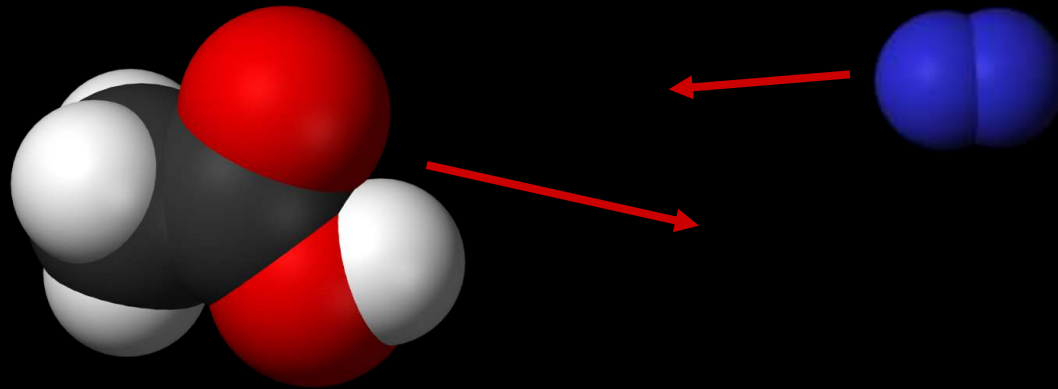
. The levels are not populated according to a Boltzmann law and therefore the output spectra are very difficult to compute.

One occurs

. This is the (LVG) approximation. The equilibrium status can be computed and line predictions can be made.

In more complicated situations, the radiative coupling of different parts of the emitting cloud can be simulated via .

PROBLEM: Collisional excitation of molecule X means studying the quantum-mechanical problem X-H₂



This is very difficult simply because the potential of the colliding species (H₂) is not spherically symmetric. For a long time collisional rates with He, extrapolated by the difference in reduced mass, have been used in RT models. Collisional rates with H₂ start to become available for a number of molecules of astrophysical interest.

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