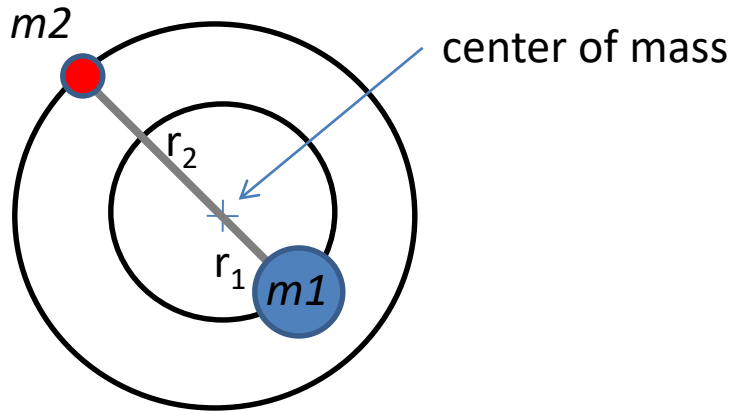
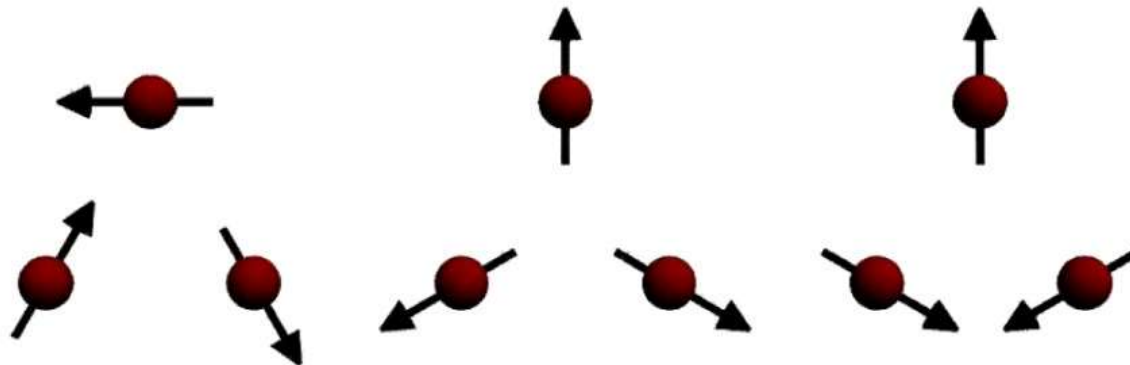
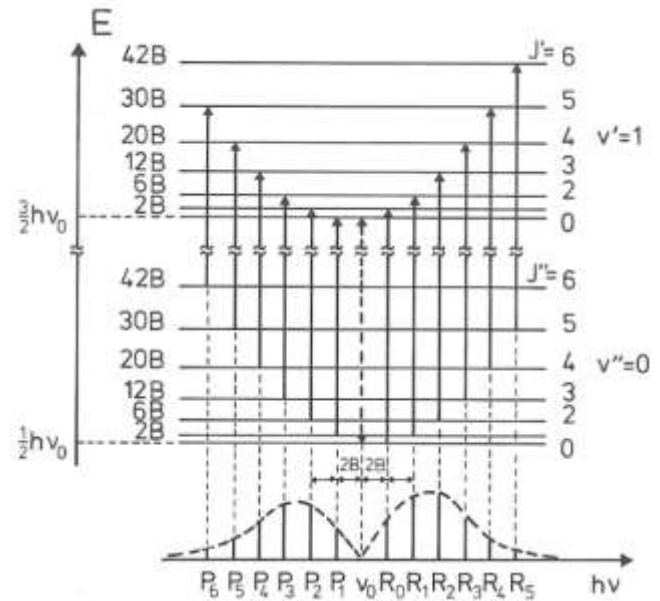


Lecture 2

Molecular Properties and Spectroscopy



Rotations



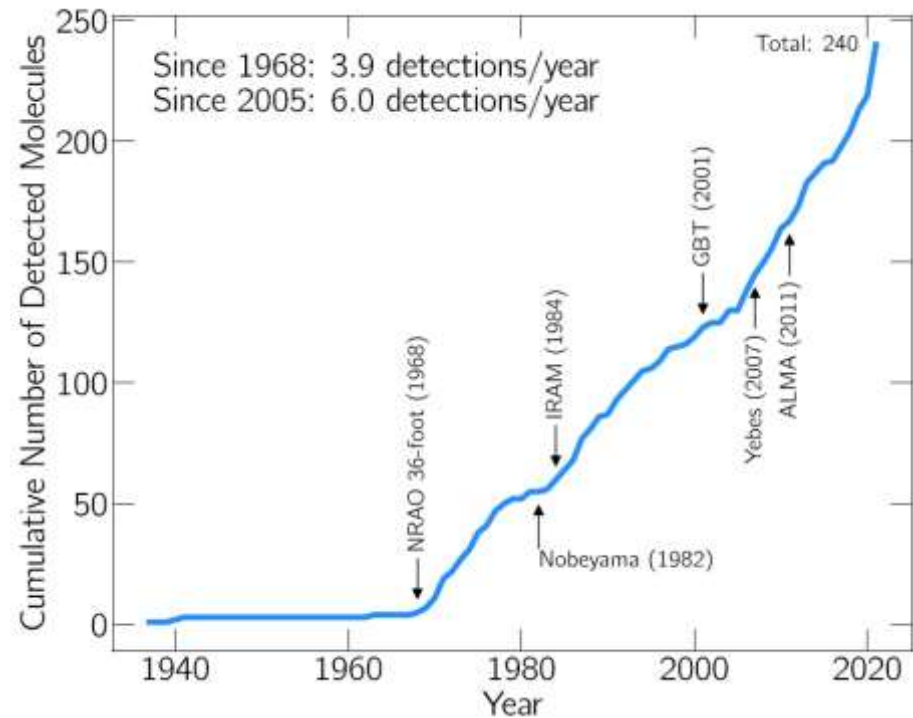
Vibrations

Today we know: Molecules Everywhere!



“It is difficult to admit the existence of molecules in interstellar space because when once a molecule becomes dissociated there seems no chance of the atoms joining up again.”

A. Eddington 1926

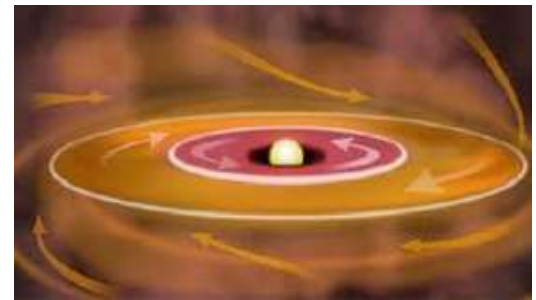
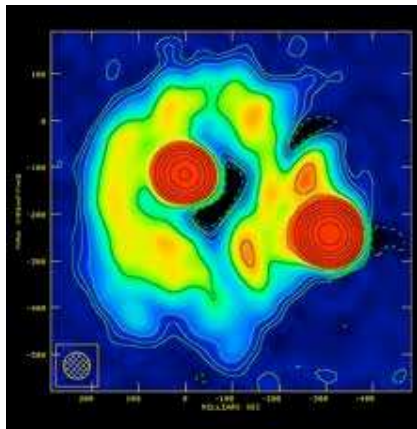


McGuire, ApJS 259, 30 (51pp), 2022

Molecules are everywhere!

Molecules are found everywhere in the Universe:

- Appeared in the Early Universe, a few min after Big Bang
- High-z quasars and galaxies
- Milky Way: interstellar and circumstellar medium
- Solar system: solar photosphere, planet. atmospheres, comets, meteorites



Importance of molecules

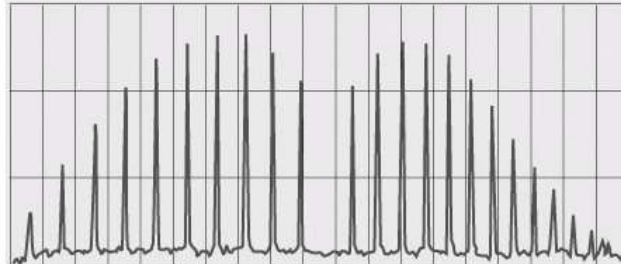
- Unique probes of physical conditions
 - Temperature
 - Density
 - Ionization balance
- Molecules may change the physical conditions
 - Coolants of gas
 - Electron recombination
- Chemical composition and evolution
 - Organic chemistry
 - Biology

Lecture 2

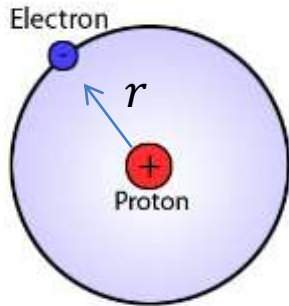
Molecular Properties and Spectroscopy

Outline

- 1) Atomic Hydrogen
- 2) Di-atomic Molecules
- 3) Born Oppenheimer Approximation
- 4) Molecular Vibrations (harmonic oscillator)
- 5) Molecular Rotations (rigid rotor)
- 6) Polyatomic molecules: adding complexity
- 7) Consequences for Astrophysics
- 8) Transitions strength: Einstein coefficients, selection rules, etc ...
- 9) Molecular and astronomical Spectroscopy



Basics: Atomic Hydrogen



Schrödinger Equation

$$H \Psi = E \Psi$$

with

Hamiltonian

$$H = \underbrace{\frac{-\hbar^2}{2\mu} \nabla^2}_{\text{kin. energy}} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r}}_{\text{pot. energy}}$$

Eigenvalue equation:

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} - E \right] \Psi(\vec{r}) = 0$$

Reduced mass

$$\mu = \frac{m_p m_e}{m_p + m_e}$$

Discrete solutions with quantum numbers:

n : principle (energy) quantum number

1, 2, 3 ...

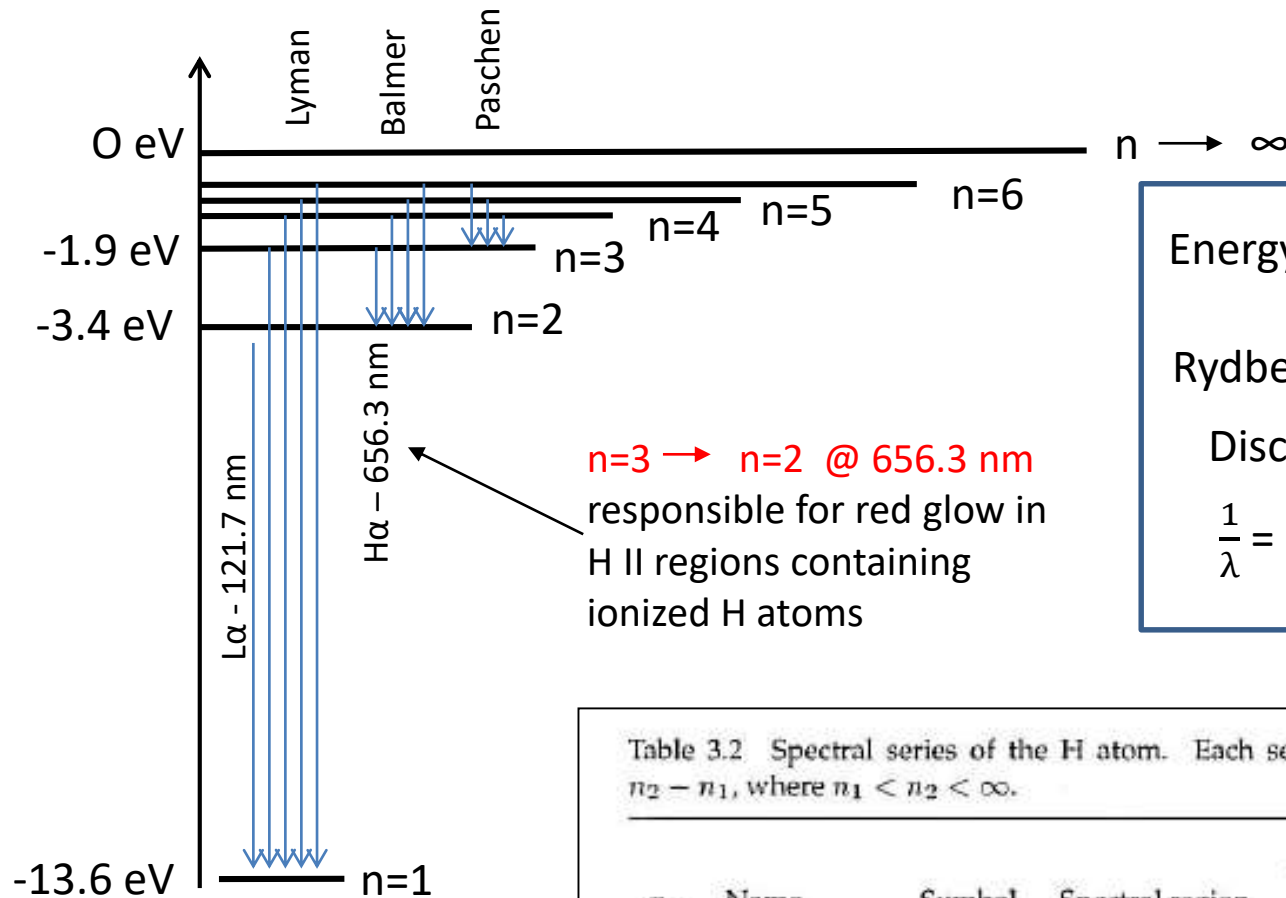
l : angular momentum

0, 1, 2, ... , (n-1)

m : magnetic quantum number

-l, (-l + 1), ..., l

Atomic Hydrogen: Transitions



Energy levels: $E_n = -R_H \frac{Z^2}{n^2}$

Rydberg $R_H = 13.6 \text{ eV}$

Discrete transitions:

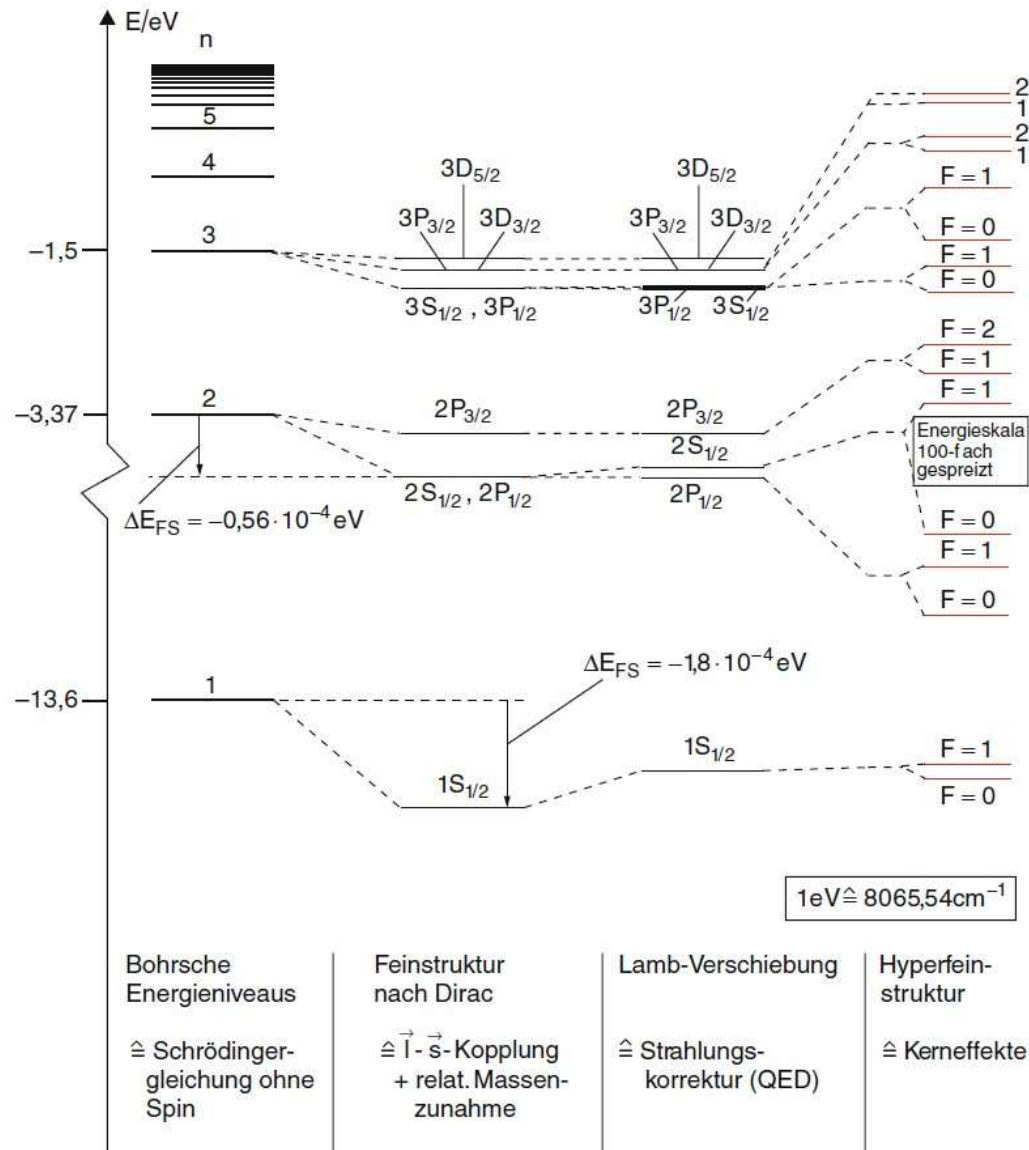
$$\frac{1}{\lambda} = \frac{1}{hc} (E_{n_1} - E_{n_2})$$

- $\Delta n = 1$ is α ,
- $\Delta n = 2$ is β ,
- $\Delta n = 3$ is γ ,
- $\Delta n = 4$ is δ ,
- $\Delta n = 5$ is ϵ .

Table 3.2 Spectral series of the H atom. Each series comprises the transitions $n_2 - n_1$, where $n_1 < n_2 < \infty$.

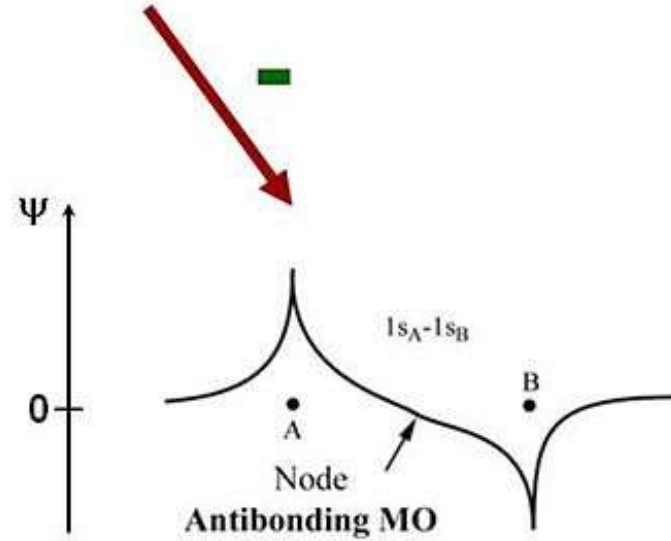
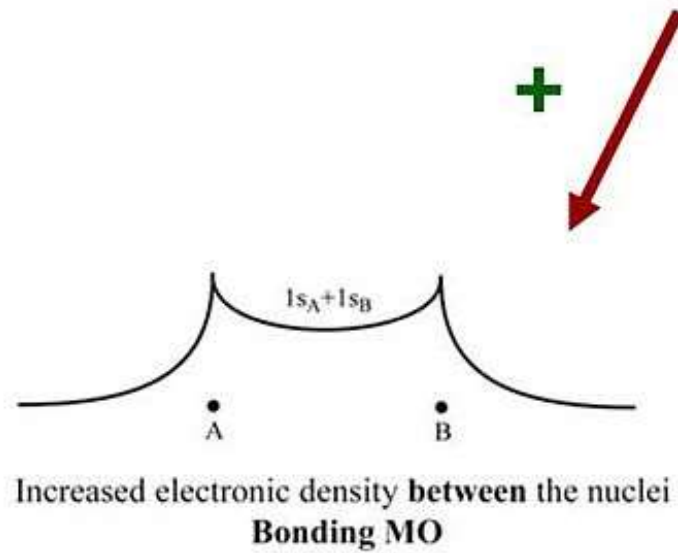
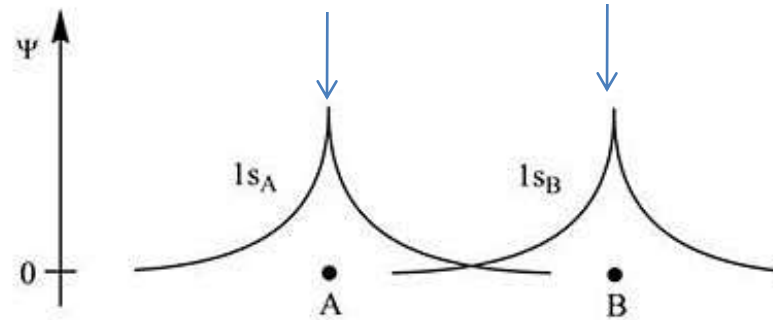
n_1	Name	Symbol	Spectral region	Range/ cm^{-1}	
				$n_2 = n_1 + 1$	$n_2 = \infty$
1	Lyman	Ly	ultraviolet	82257	- 109677
2	Balmer	H	visible	15237	- 27427
3	Paschen	P	infrared	5532	- 12186
4	Brackett	Br	infrared	2468	- 6855
5	Pfund	Pf	infrared	1340	- 4387
6	Humphreys	Hu	infrared	808	- 3047

Atomic Hydrogen: Complete level scheme

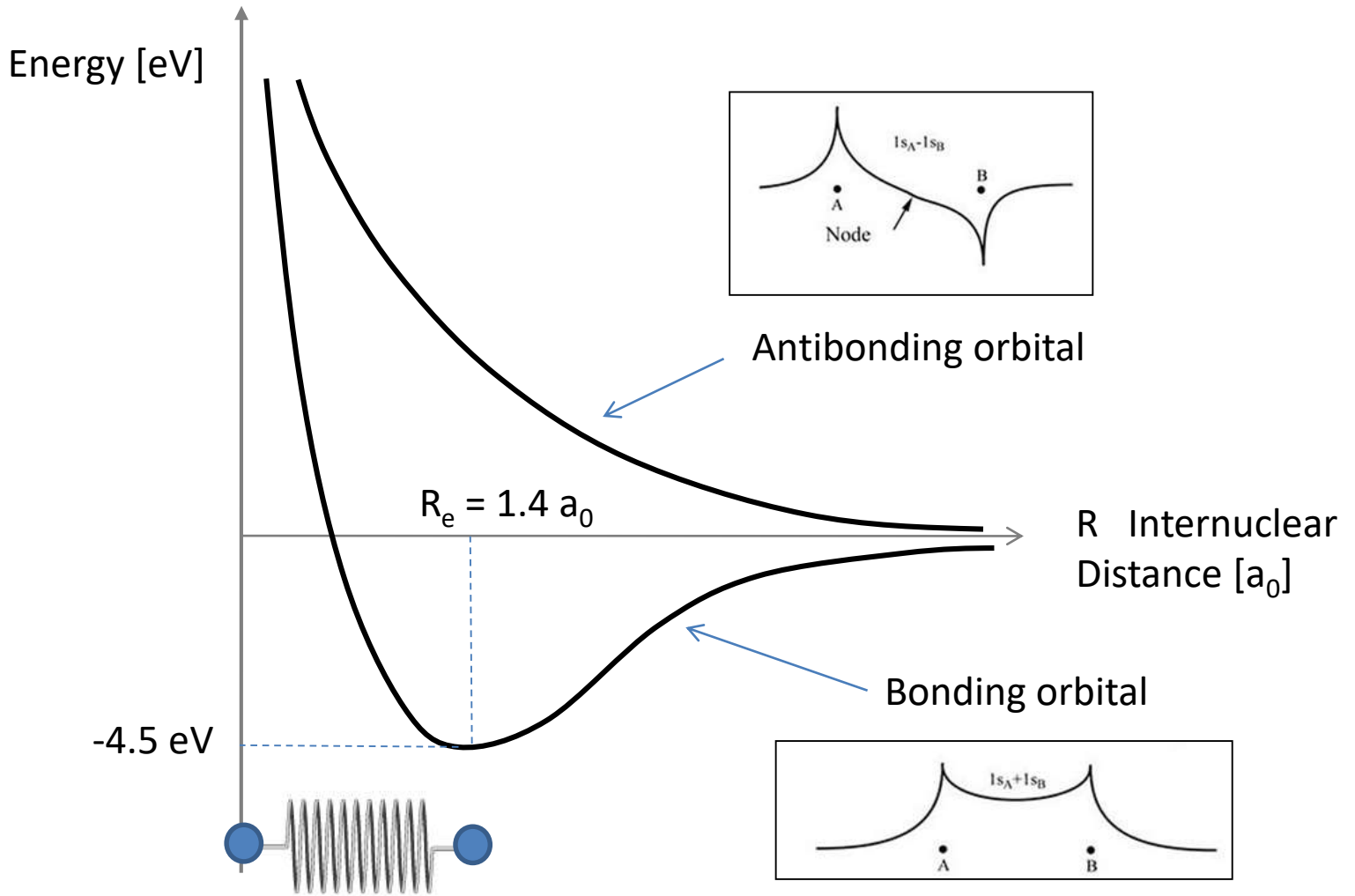


Molecular Orbitals

Electron orbitals of H atoms

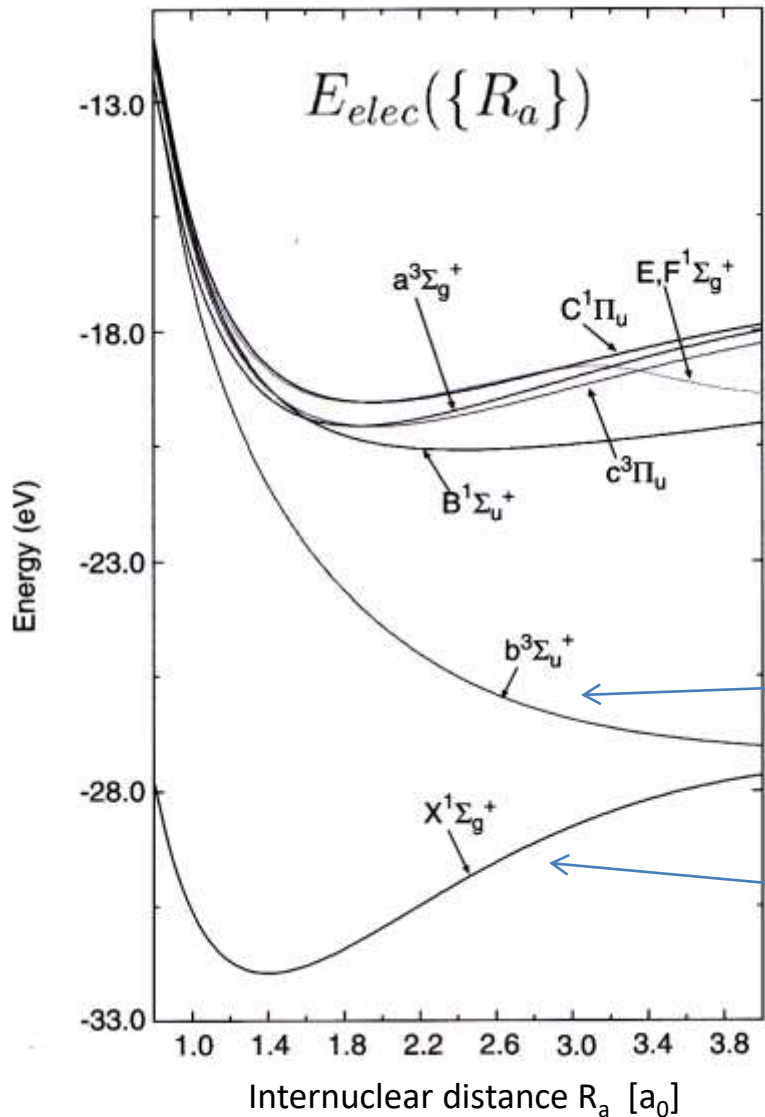


H₂ potential energy curves



$$V = \frac{1}{2} k (R - R_e)^2$$

H₂ electronic potential curves



Electronically excited states

Antibonding orbital

Bonding orbital

- X labels the electronic ground state
- A, B, C ... labels states with the same spin multiplicity as the ground state
- a, b, c ... labels states with different spin multiplicity compared to the ground state

Notation

$$2S+1 \Lambda^{(+/-)}_{(g/u)}$$

S: spin quantum number

Λ : projection of orbital angular momentum along internuclear axis

u/g: parity (inversion operation)

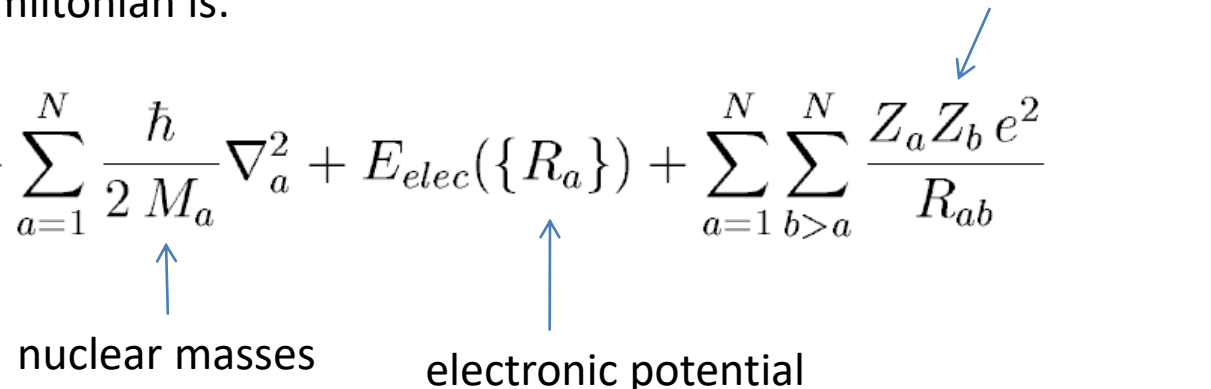
(+/-): reflection symmetry (through a plane containing the molecular axis)

The Born-Oppenheimer Approximation

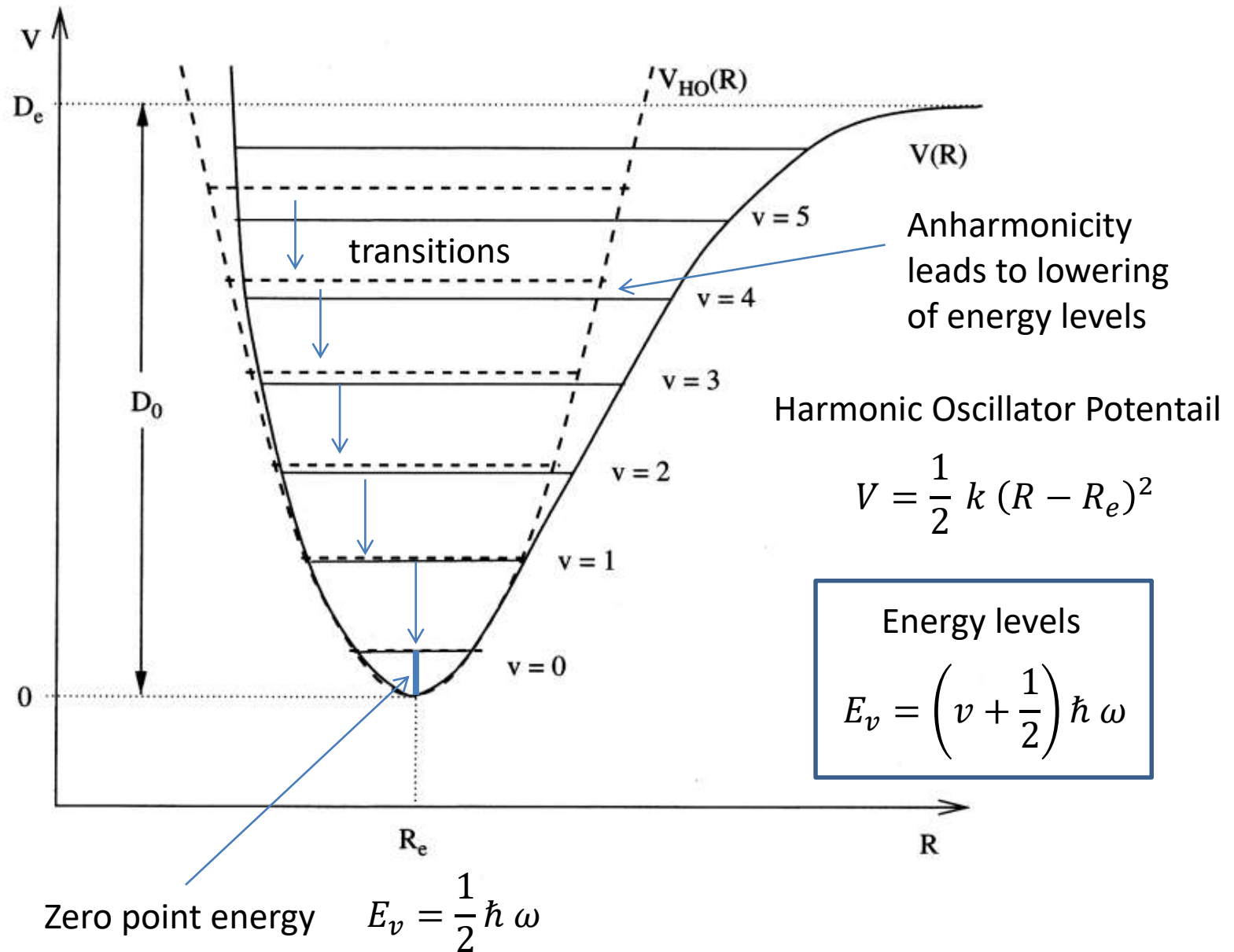
The Born Oppenheimer Approximation assumes that electrons in a molecule move much faster than the nuclei, and adapt instantaneously, finding the lowest potential energy for each nuclear configuration. Therefore, it is possible to calculate an electronic energy for each nuclear configuration, considering the nuclei frozen.

The nuclear Hamiltonian is:

$$H_{nucl} = - \sum_{a=1}^N \frac{\hbar^2}{2 M_a} \nabla_a^2 + E_{elec}(\{R_a\}) + \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b e^2}{R_{ab}}$$



Molecular Vibration: Harmonic Oscillator Potential



Isotopic Fractionation

Consider energy balance of: $\text{H}_2 + \text{D} \leftrightarrow \text{HD} + \text{H}$

Harmonic approximation

Harmonic Oscillator Potential

$$V = \frac{1}{2} k (R - R_e)^2$$

Zero point energy:

$$\omega_0 = \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

← reduced mass

$$\frac{\omega(\text{HD})}{\omega(\text{H}_2)} = \left(\frac{\mu_{\text{H}_2}}{\mu_{\text{HD}}} \right)^{\frac{1}{2}}$$

with

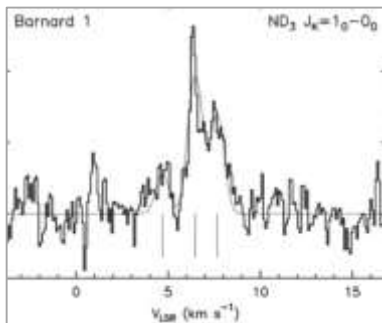
$$\mu_{\text{H}_2} = \frac{M_{\text{H}}}{2},$$

$$\mu_{\text{HD}} = \frac{M_{\text{H}} M_{\text{D}}}{M_{\text{H}} + M_{\text{D}}} = \frac{2}{3} M_{\text{H}}$$

→ $\text{zpe}(\text{H}_2) = 2198 \text{ cm}^{-1}$ while $\text{zpe}(\text{HD}) = 1903 \text{ cm}^{-1}$ →

$\Delta E = 289 \text{ cm}^{-1}$
(exothermic,
kT: 415K)

At low temperature chemical reactions favor heavier isotopes!



Detection of fully deuterated ammonia ND_3
Lis et al, *ApJ* 571, L55 (2002)

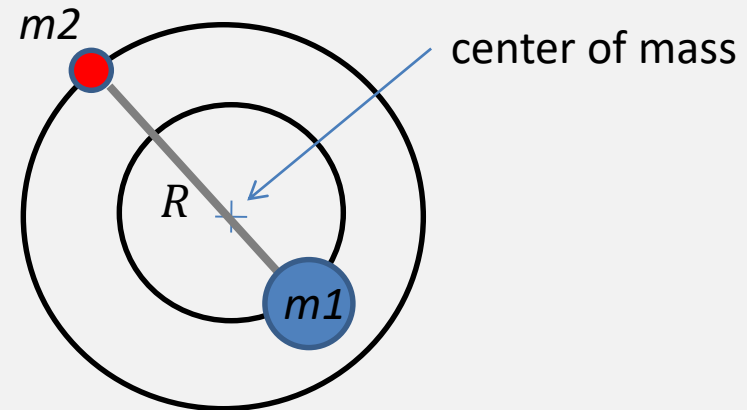
Rotations: the Rigid Rotor approximation

Example: Diatomic

$$\left[\frac{-\hbar^2}{2M_A} \nabla^2 + E_{elec}(R) - E \right] \psi_N(\mathbf{R}) = 0$$

Separate nuclear wavefunction into vibrational and rotational terms:

$$\psi_N(R, \vartheta, \varphi) = \psi_{vib}(R) \psi_{rot}(\vartheta, \varphi)$$



Laplace operator
in spherical coordinates:

$$\Delta f = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial f}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2 f}{\partial \phi^2}$$

Solution: $\psi_r(\vartheta, \varphi) = Y_{J, M_J}(\vartheta, \varphi) \leftarrow$ Spherical harmonics

Energy levels

$$E_r = \frac{\hbar^2}{2\mu R^2} J(J+1)$$

Rotational constant B

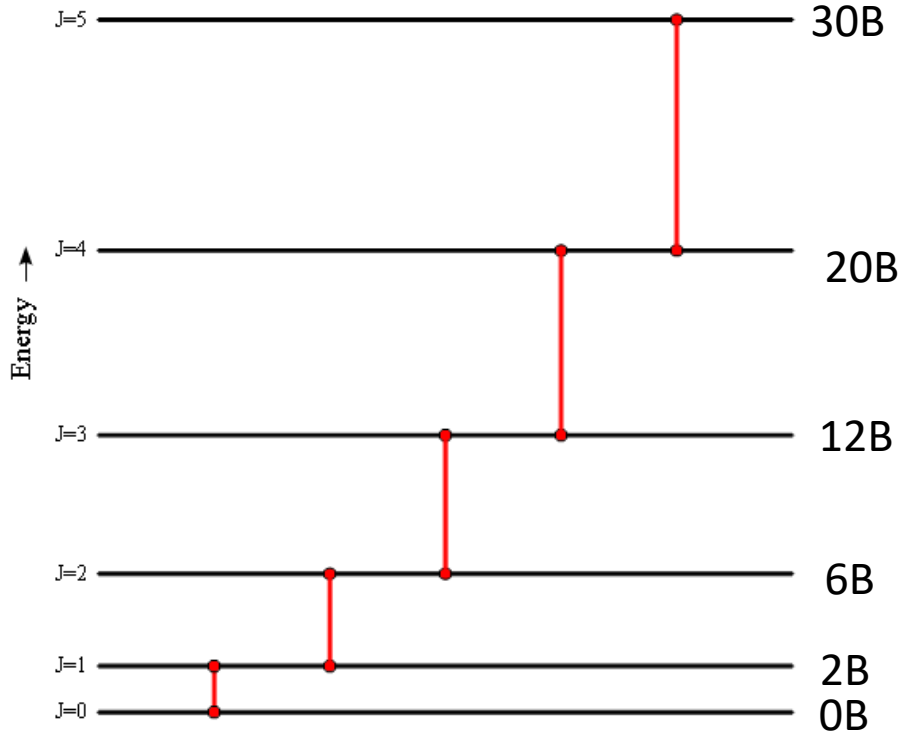
rotational
quantum
number

In the denominator:

Moment of inertia $I = \sum_i m_i r_i^2$

Large and heavy molecules have small rotational constants!

Rigid Rotor Levels and Transitions



Energy levels

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

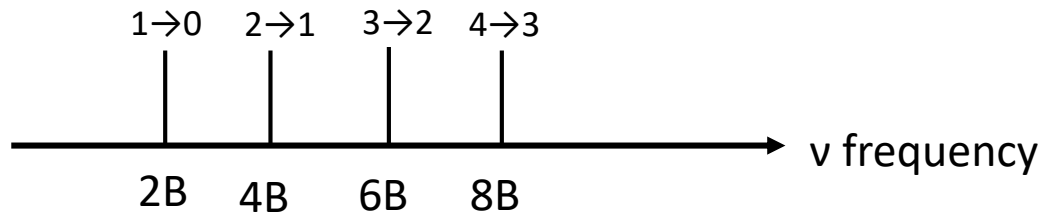
Selection rule:

$$\Delta J = \pm 1$$

Transitions:

$$E_r(J + 1) - E_r(J) \\ = B [(J + 1)(J + 2) - J(J + 1)]$$

$$\Delta E = 2B[J + 1]$$



Summary: Molecular Transitions

Electronic
Transitions:

$\Delta E = 1-15 \text{ eV}$

Visible-UV

Vibrational
Transitions:

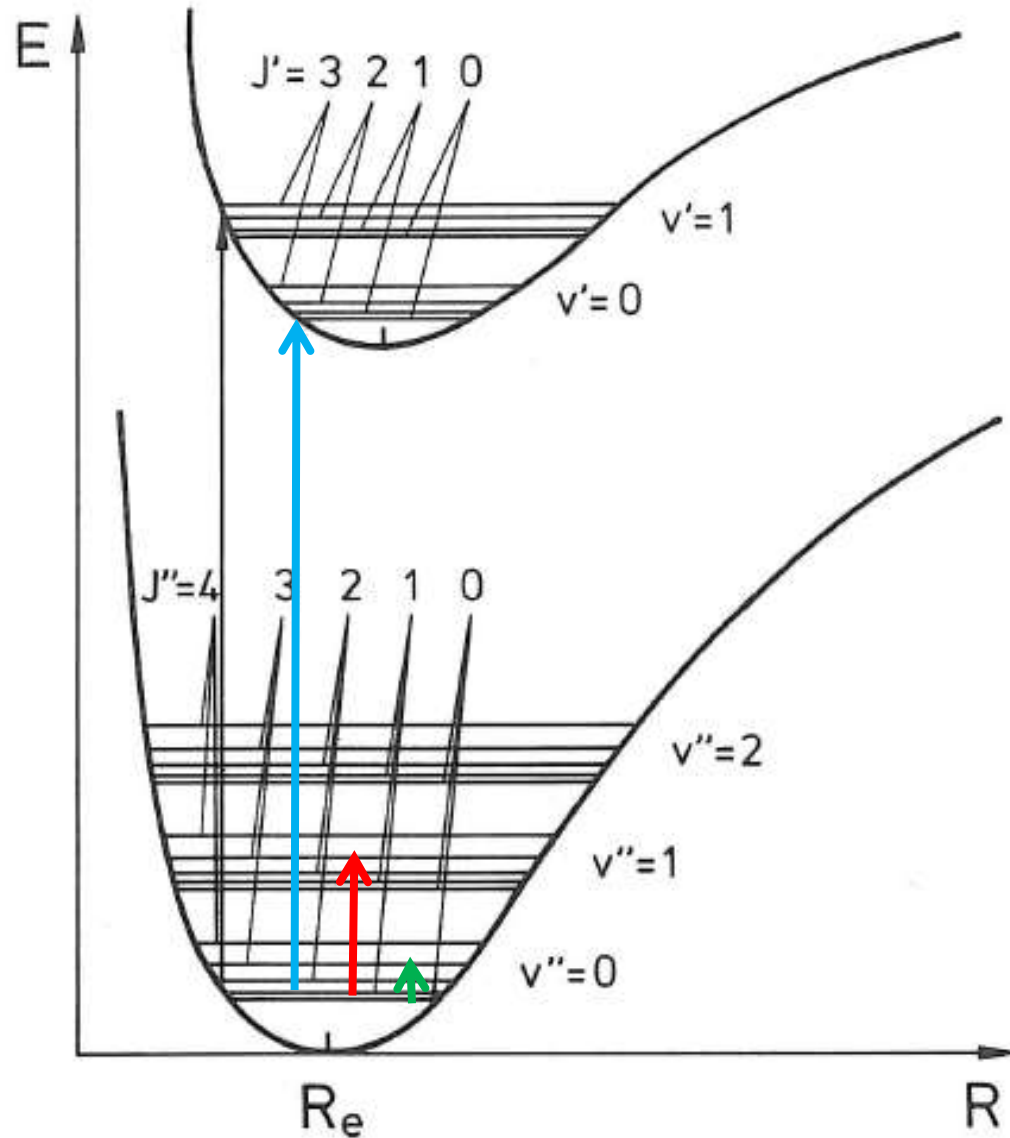
$\Delta E \approx 0.1 \text{ eV}$

Infrared

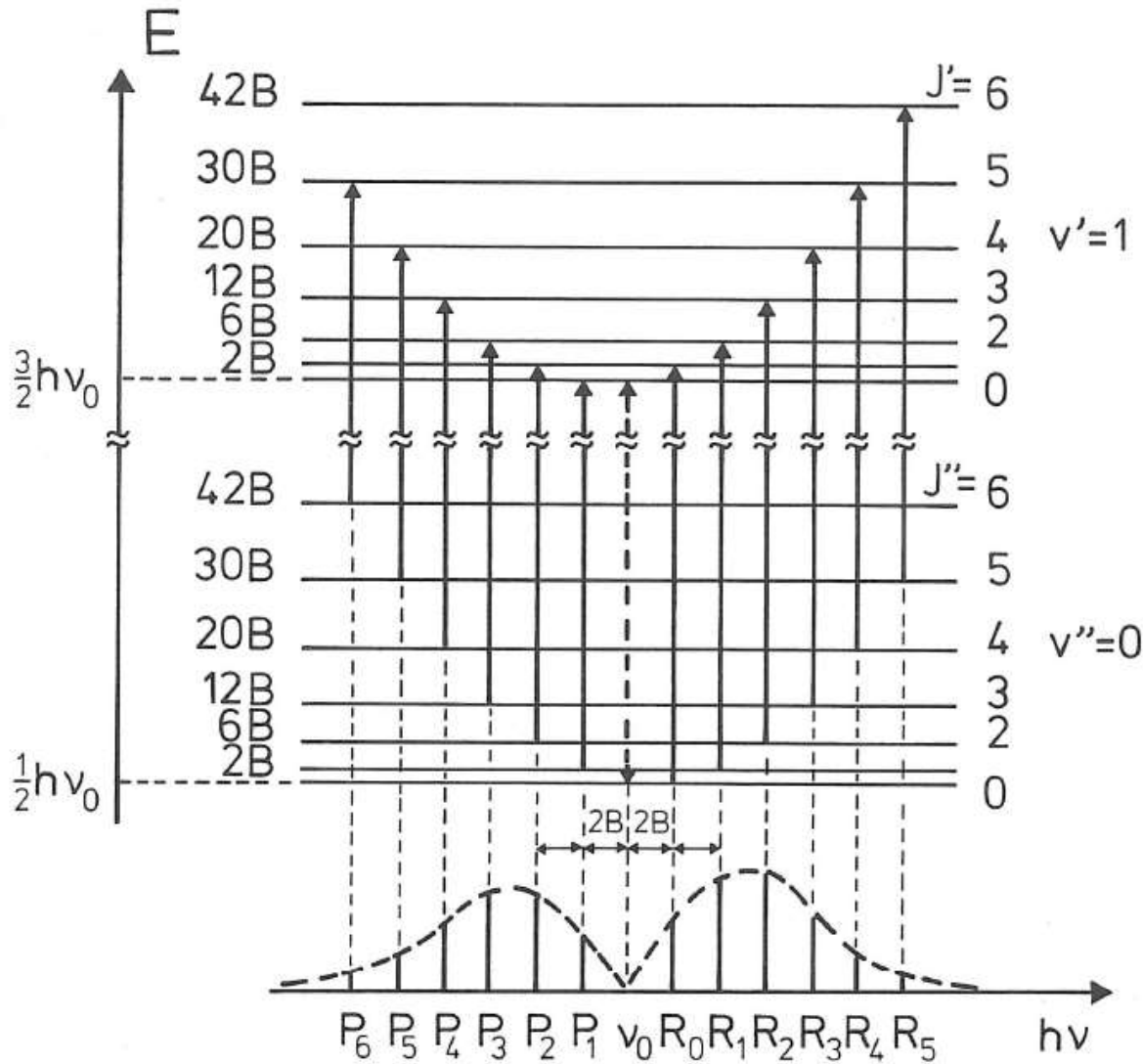
Rotational
Transitions:

$\Delta E \approx 0.001-0.01 \text{ eV}$

(sub)-Millimeter



Vibration-Rotation Spectra Diatomics



Rotational
state populations

Boltzmann distribution

$$\frac{P_J}{P_0} = \frac{g_J}{g_0} e^{-\left(\frac{E_J}{kT}\right)}$$

↑
rel. populations

↑
multiplicities

P-Branch $\Delta J=-1$

R-Branch $\Delta J=+1$

Vibration-Rotation Energy Diatomic Molecules

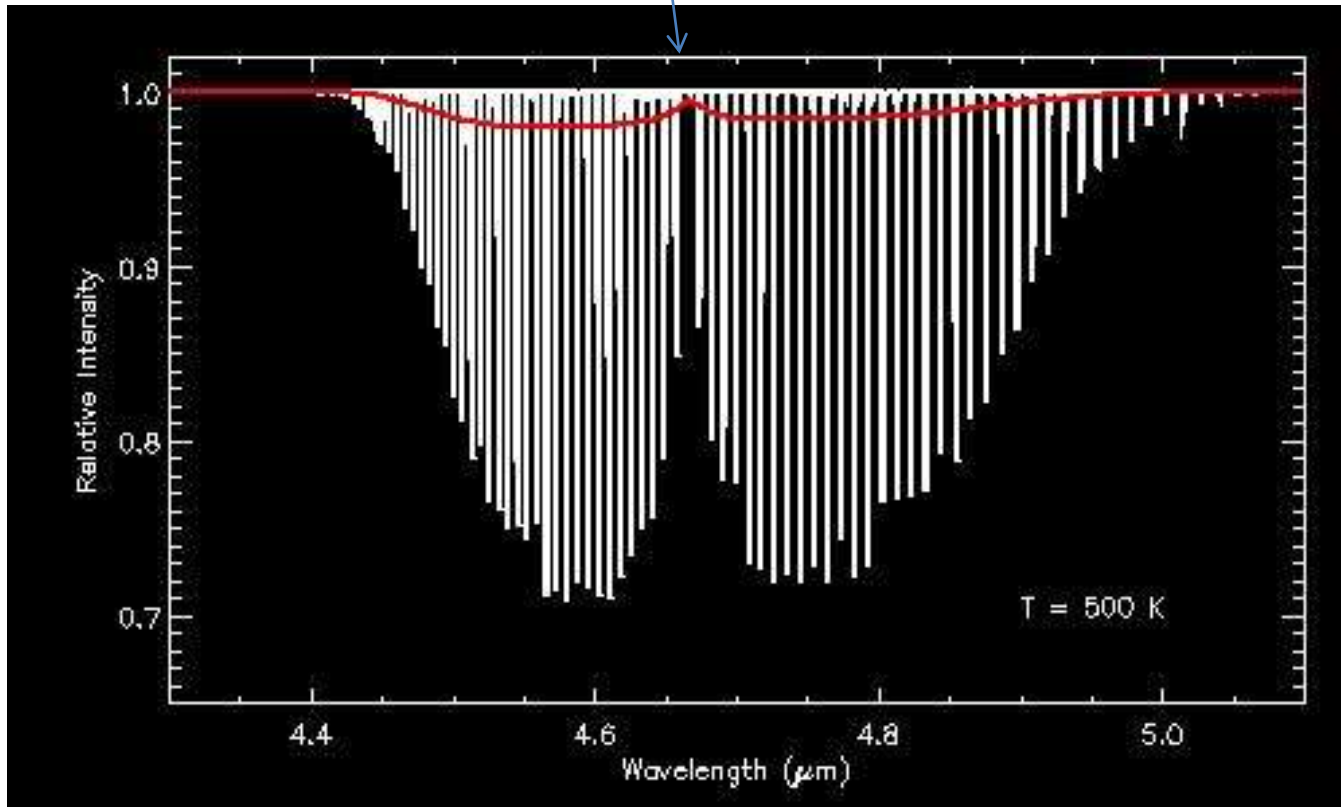
$$E_{vib-rot} = \omega_e \left(v + \frac{1}{2} \right) + B J(J + 1) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 - D_e J^2(J + 1)^2 - \alpha_e \left(v + \frac{1}{2} \right) J(J + 1) + \dots$$

- ω_e : harmonic (vibrational) frequency
- B : rotational constant
- $\omega_e x_e$: leading anharmonic correction
- D_e : centrifugal distortion
- α_e : variation of B with vibrational state

Example: which molecule is it

Vibrational band at 4.65 microns $\approx 2100 \text{ cm}^{-1}$

**Model with PGopher:
CO at 500K**



Interstellar CO (rotational lines)

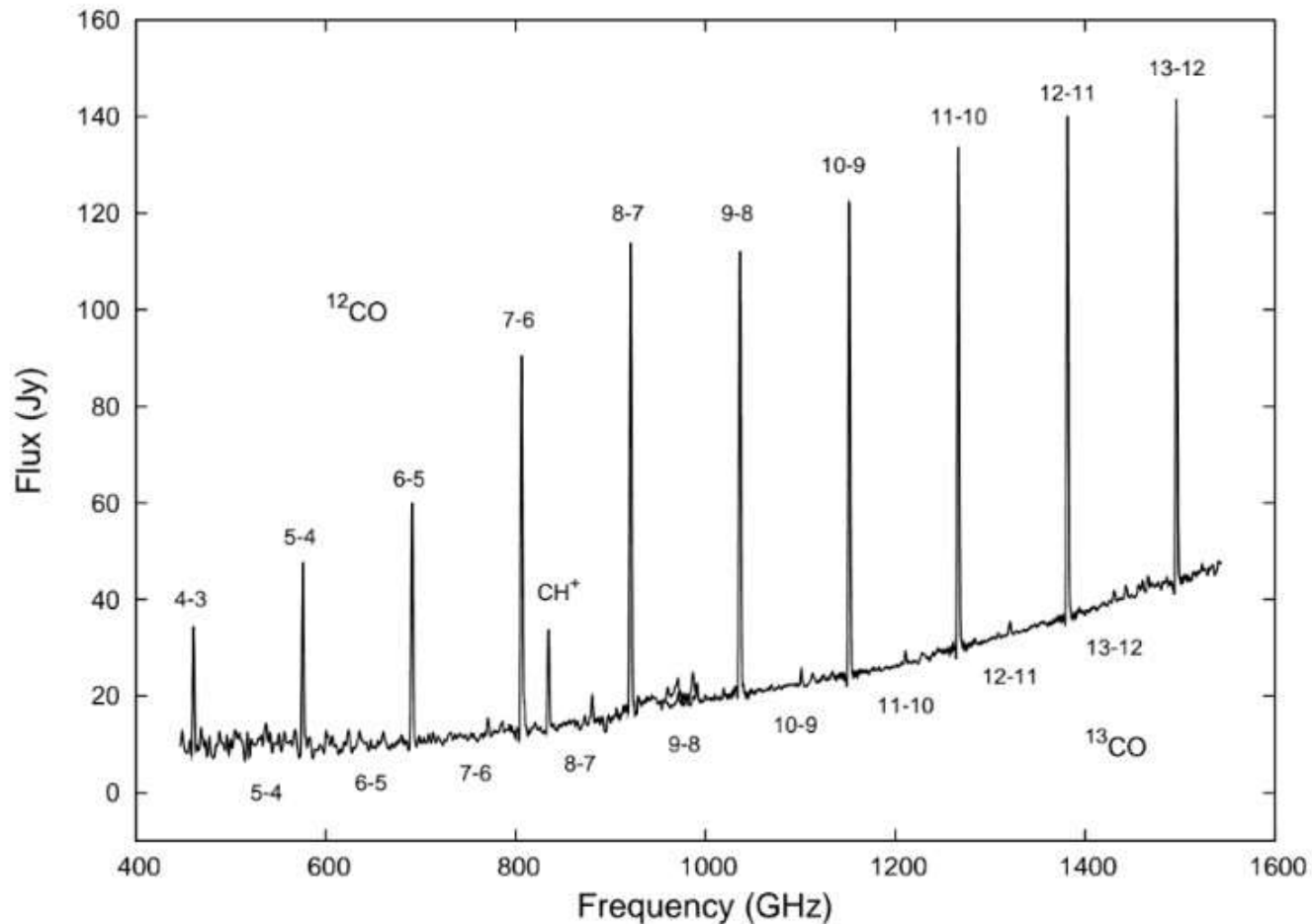
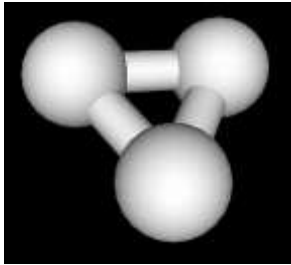
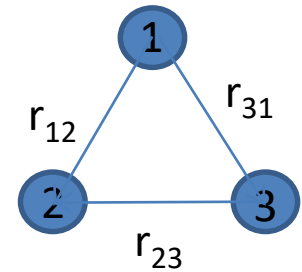


Fig. 11.3 Rotational spectrum of carbon monoxide recorded in emission from planetary nebula **NGC 7027** using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory [Adapted from R **Wesson** *et al*, *Astron. Astrophys.*, **518**, L144 (2010)].

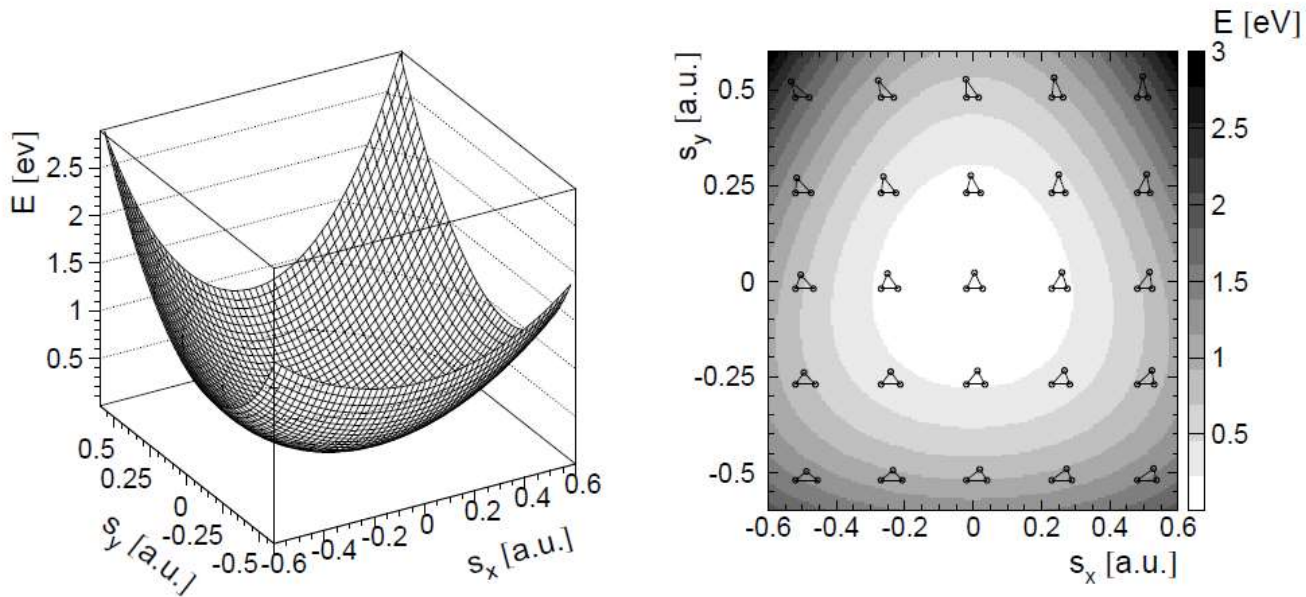
Polyatomic Molecules: Example H_3^+



- Simplest Polyatomic molecule
- Consists of 3 protons and 2 electrons
- 3 internuclear distances
- 3 vibrational degrees of freedom



Electronic Potential curve is a Hyper-Surface of 3 coordinates,
can not be plotted!



$$s_x = \frac{1}{\sqrt{6}}(2r_{12} - r_{23} - r_{31}),$$
$$s_y = \frac{1}{\sqrt{2}}(r_{23} - r_{31}).$$

Normal Modes of Vibration

Normal modes:

- independent modes of vibration
- diagonalize the Molecular Hamiltonian
- linear combinations of the internuclear distances

Finding Normal Modes: Use **Molecular Symmetry / Group Theory**

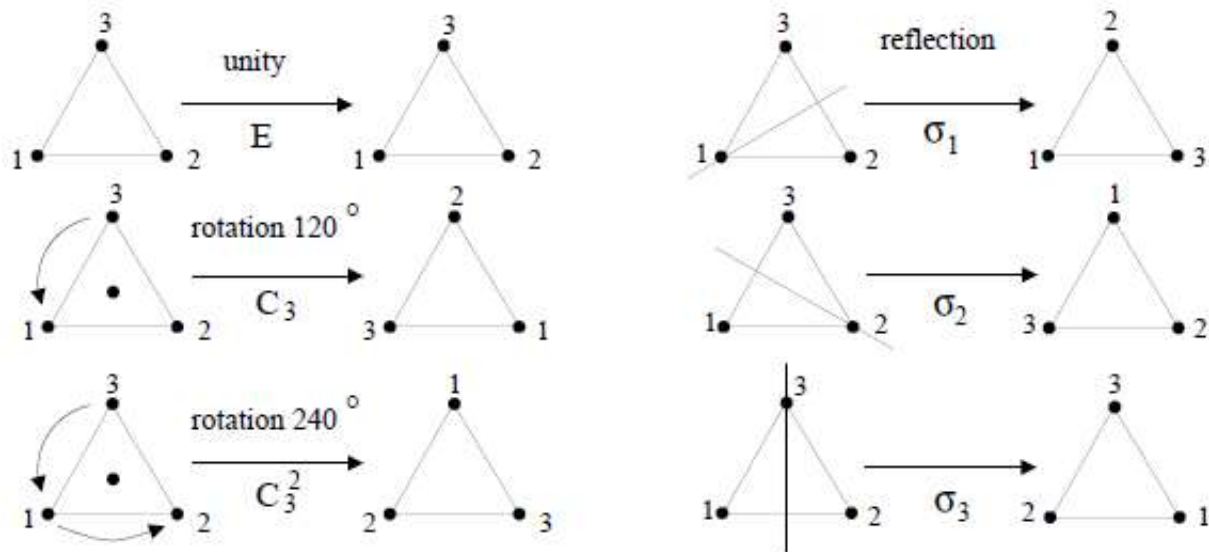


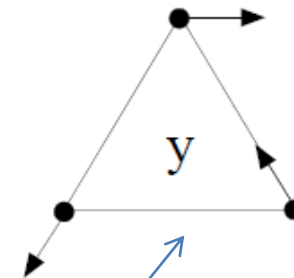
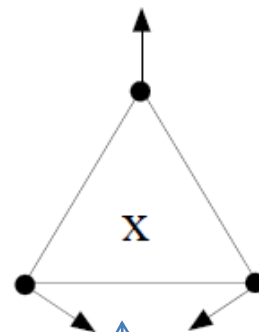
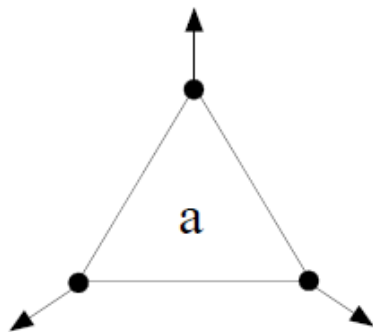
Figure 5.1: *The symmetry operations of the C_{3v} group*

The Normal Modes of H_3^+

$$s_a = \frac{1}{\sqrt{3}}(r_{12} + r_{23} + r_{31})$$

$$s_x = \frac{1}{\sqrt{6}}(2r_{12} - r_{23} - r_{31})$$

$$s_y = \frac{1}{\sqrt{2}}(r_{23} - r_{31})$$



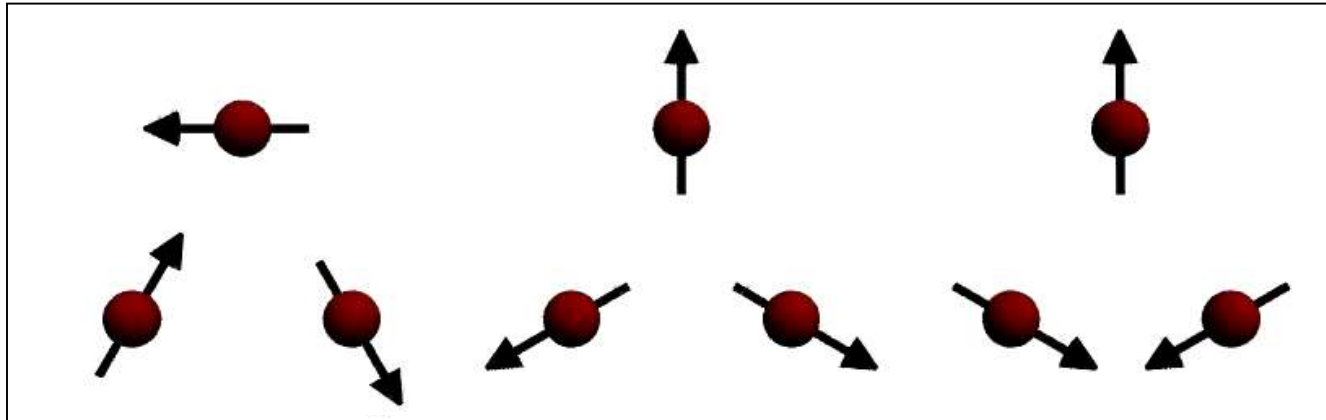
Degenerate (the same frequency)

The Normal Modes of H_3^+

bending mode 1

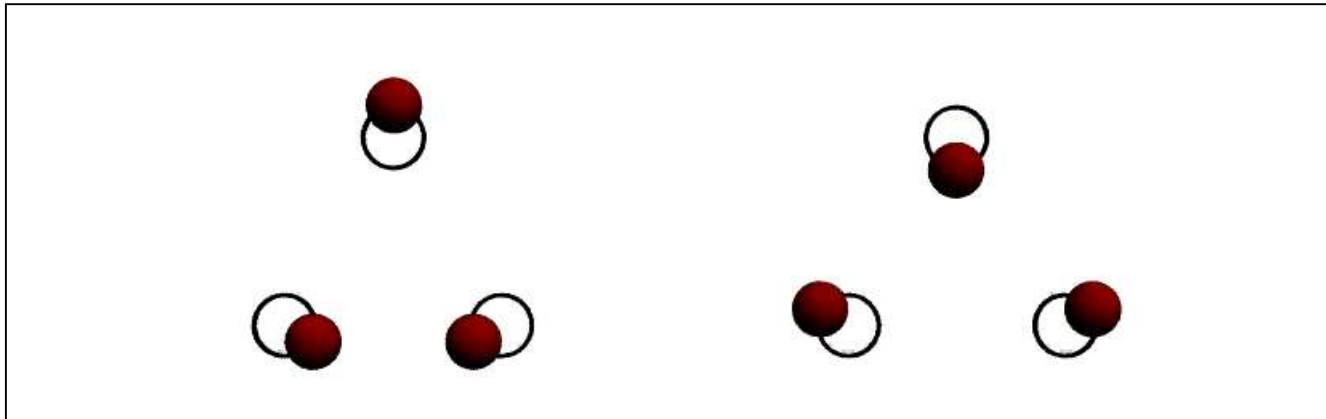
breathing mode

bending mode 2



+90° phase

-90° phase



Vibrational motion can induce angular momentum

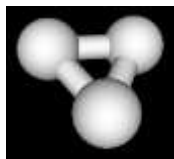
→ Vibrational and rotational quantum numbers mix

Vibrations bear a lot of Potential For Complexity

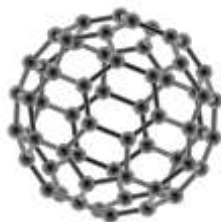
In general molecules have $3N$ degrees of freedom

	Linear	Non-linear
Translational degrees of freedom	3	3
Rotational degrees of freedom	2	3
Vibrational degrees of freedom	$3N - 5$	$3N - 6$

But: **Symmetry helps!**

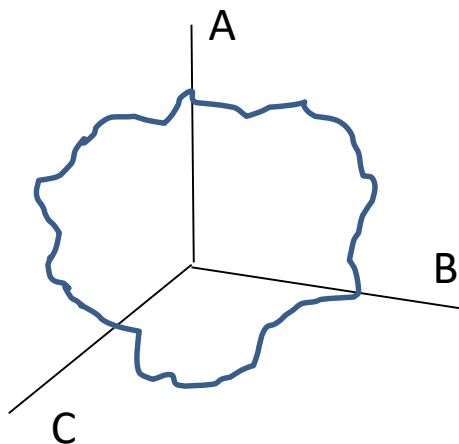


H_3^+ : 3 vibrational degrees of freedom \longrightarrow 2 distinct normal modes



C_{60} : 174 vibrational degrees of freedom \longrightarrow 46 normal modes

General Rotational Structure of Polyatomic Molecules



Any arbitrarily shaped solid body has three principal axes of rotation ($A < B < C$), the principle axes are orthogonal and they diagonalize the moment of inertia matrix

$$I_A \leq I_B \leq I_C$$

Rotational constants:

$$A = \frac{\hbar^2}{2I_C} \quad B = \frac{\hbar^2}{2I_B} \quad C = \frac{\hbar^2}{2I_A}$$

Class 1: linear molecules ($I_A=0, I_B=I_C$)

H₂, C₂, C₄, ...

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

Class 2: spherical molecules ($I_A=I_B=I_C$)

CH₄, C₆₀, ...

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

Class 3: symmetric top molecules ($I_B=I_C$ or $I_A=I_B$)

H₃⁺, NH₃, ...

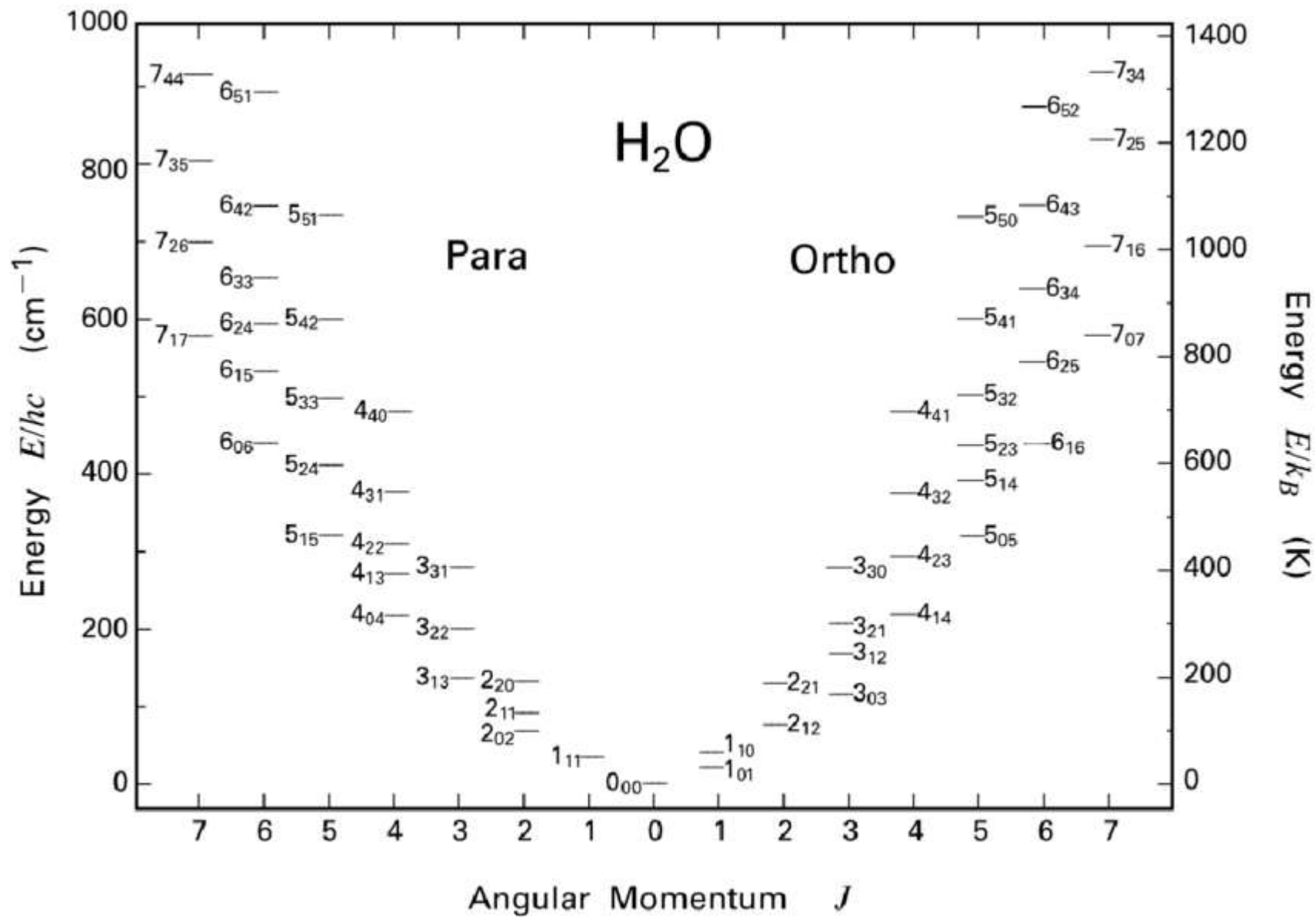
$$E_r = B J(J + 1) - (A - B)K^2$$

$$E_r = B J(J + 1) - (C - B)K^2$$

Class 4: asymmetric top molecules ($I_A \neq I_B \neq I_C$)

Water, H₂CO, etc ...

No simple general formula



Molecular Properties: more complexity

Diatomics (2 nuclei)



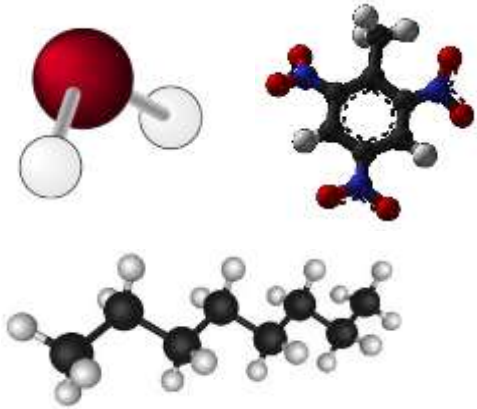
Homonuclear (e.g. H₂)



Heteronuclear (e.g. OH, CO)

Present in objects with $T < 8000$ K

Polyatomics (>2 nuclei)



Present in objects with $T < 4000$ K

Molecular binding energies are relatively small (1-5 eV),
smaller than ionization energies (>10 eV)



Molecules are easily destroyed and are found in cooler,
less ionized environments.

Typical bond energies

$\text{C}\equiv\text{O}$	Carbon Monoxide	11.16 eV
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	Acetylene	10.07 eV
$\text{N}\equiv\text{N}$	Nitrogen	9.71 eV
$\text{C}\equiv\text{N}$	Cyanogen	7.77 eV
$\text{O}=\text{C}=\text{O}$	Carbon dioxide	5.50 eV
$\text{O}=\text{O}$	Oxygen	5.11 eV
$\text{H}-\text{O}-\text{H}$	Water	5.11 eV
NH_3	Ammonia	4.58 eV
CH_4	Methane	4.49 eV
$\text{H}-\text{H}$	Hydrogen	4.478 eV
$\text{O}-\text{H}$	Hydroxyl	4.41 eV

**Molecules only survive at low to modest temperatures
 $T \approx 10 - 4000 \text{ K}$ (molecular clouds, protoplanetary disks, ...)**

Summary: Molecular Transitions

Electronic
Transitions:

$\Delta E = 1-15 \text{ eV}$

Visible-UV

Vibrational
Transitions:

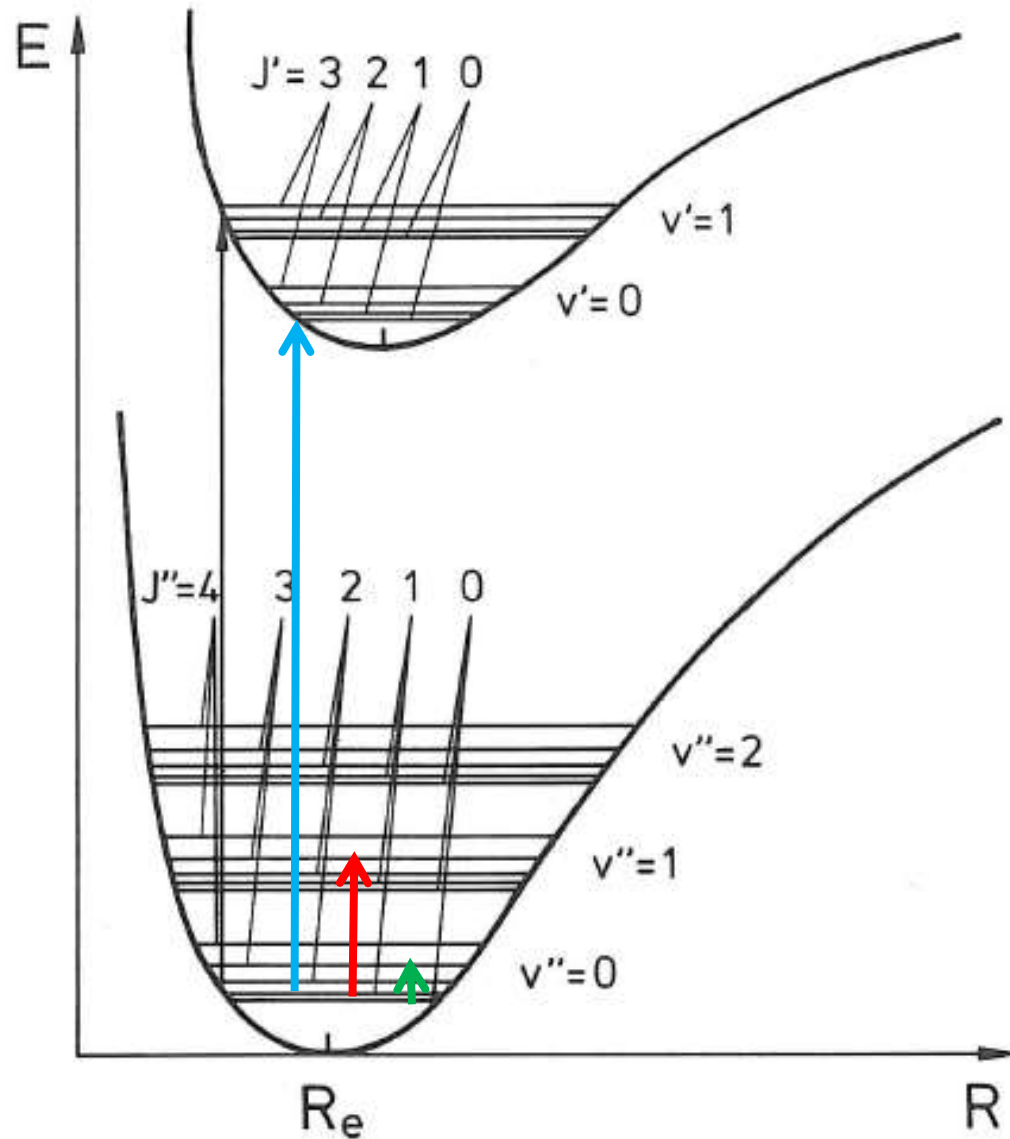
$\Delta E \approx 0.1 \text{ eV}$

Infrared

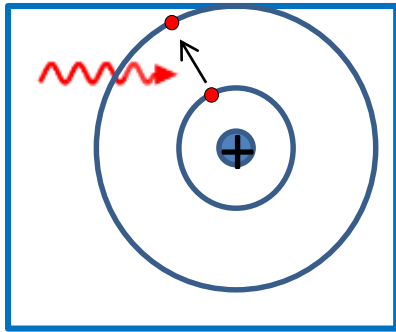
Rotational
Transitions:

$\Delta E \approx 0.001-0.01 \text{ eV}$

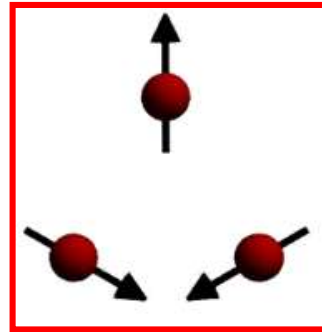
(sub)-Millimeter



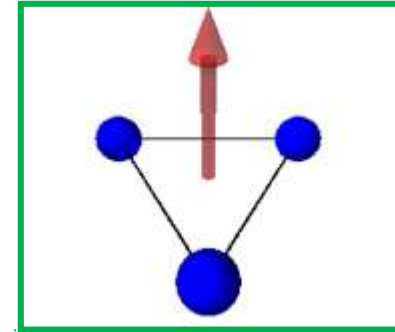
Transmission of Earth's atmosphere



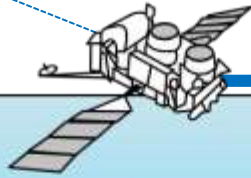
electronic



vibration



rotation



Gamma rays, X-rays and ultraviolet light blocked by the upper atmosphere (best observed from space).

Visible light observable from Earth, with some atmospheric distortion.

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

Radio waves observable from Earth.

Long-wavelength radio waves blocked.

Atmospheric opacity

100 %

50 %

0 %

0.1 nm

1 nm

10 nm

100 nm

1 μ m

10 μ m

100 μ m

1 mm

1 cm

10 cm

1 m

10 m

100 m

1 km

Wavelength



Resources: HITRAN database

The HITRAN Database



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. The database is a long-running project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 1960's in response to the need for detailed knowledge of the infrared properties of the atmosphere.

For additional background, see [Interview](#).

The HITRAN database and its associated HITRAN molecular spectroscopic parameters development (MolSpect) project at Harvard University for Astrophysics continues to be maintained by [Laurence](#)

HITRAN Facts

The HITRAN2012 Database contains 7,400,447 spectral lines for 47 different molecules, incorporating 120 isotopologues. Included in these 47 species are the oxygen atom (singlet) and the NO^+ ion. Files for three of the molecules (ClONO_2 , SF_6 , and CF_4) are stored separately in the `/HITRAN2012/Supplemental/` folder.

- See a [list](#) of molecules and their associated isotopologues that are currently included in the HITRAN database.
- You can see their allowable [vibrational modes](#).
- See a [list](#) of molecules represented by infrared absorption cross-sections that are currently included in the HITRAN compilation.
- The [uncertainty indices](#) used in HITRAN are defined in this table.
- Database [formats](#) are shown for the most recent HITRAN compilations.
- It is helpful to view the [tree structure](#) of the HITRAN compilation.

<http://www.cfa.harvard.edu/hitran/>

Resources: Cologne Database for Molecular Spectroscopy

The Cologne Database for Molecular Spectroscopy

CDMS

C. P. Endres, S. Schiemmer, P. Schilke, J. Stutzki, and H. S. P. Müller,
The Cologne Database for Molecular Spectroscopy, CDMS, in the Virtual Atomic and Molecular Data Centre, VAMDC
J. Mol. Spectrosc. **327**, 95–104 (2016)
Please visit also the VAMDC-compatible version of the CDMS

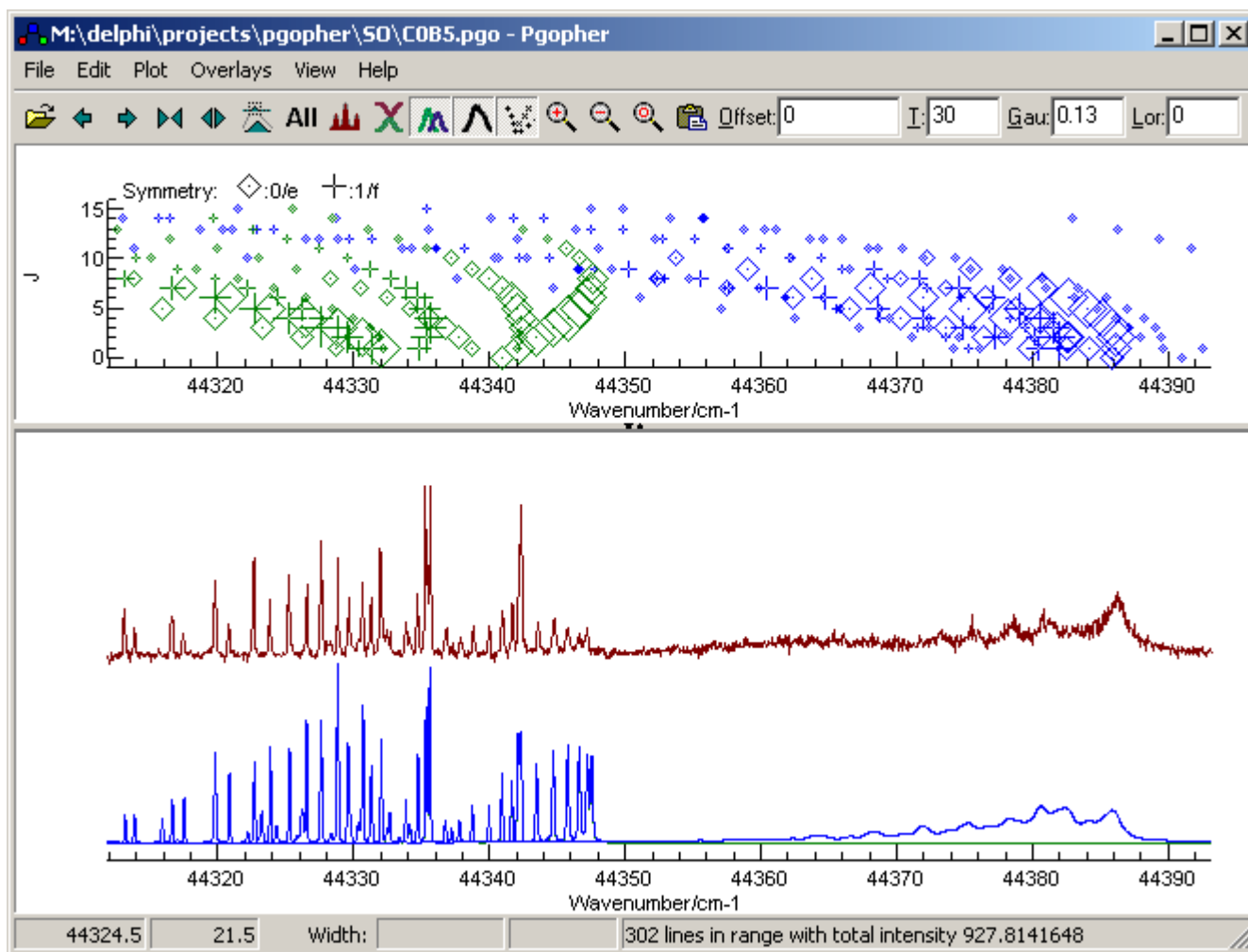
H. S. P. Müller, F. Schlöder, J. Stutzki, and G. Winnewisser,
The Cologne Database for Molecular Spectroscopy, CDMS: a Useful Tool for Astronomers and Spectroscopists
J. Mol. Struct. **742**, 215–227 (2005)

H. S. P. Müller, S. Thorwirth, D. A. Roth, and G. Winnewisser,
The Cologne Database for Molecular Spectroscopy
Astron. Astrophys. **370**, L49–L52 (2001)

<https://www.astro.uni-koeln.de/cdms>

Computational Resources:

PGOPHER: A program for simulating rotational, vibrational and electronic spectra



<http://pgopher.chm.bris.ac.uk/>

Literature

Molecules:

Haken/ Wolf

*“Molecular Physics and Elements of Quantum Chemistry:
Introduction to Experiments and Theory”*

Springer

Herzberg, Gerald

“Molecular Spectra and Molecular Structure: Spectra of Diatomic
Molecules”

Krieger

Khristenko, Maslov, Shevelko

“Molecules and their spectroscopic properties”

Springer

Astro-
Spectroscopy

Tennyson, Jonathan

“Astronomical spectroscopy”

World Scientific

Einstein
Coefficients,
linewidths, etc .

W. Demtröder

„Experimentalphysik III“

Springer