Molecular spectroscopy for exoplanets

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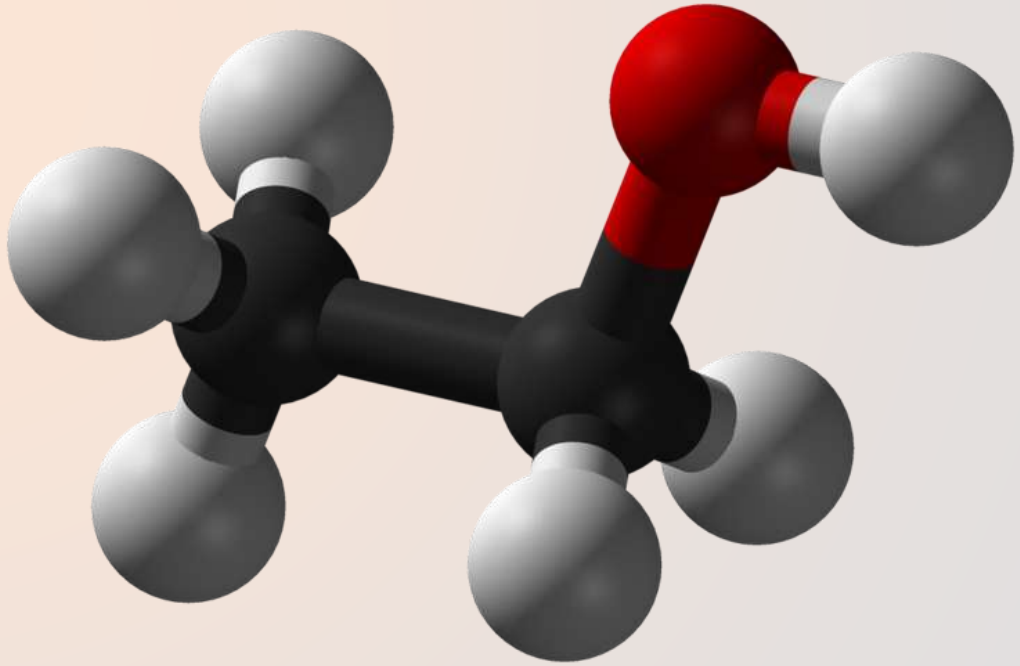
+ see credits at the end



INFRARED AND RAMAN SPECTRA
of
POLYATOMIC MOLECULES

By

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Forming the second volume of
MOLECULAR SPECTRA AND
MOLECULAR STRUCTURE

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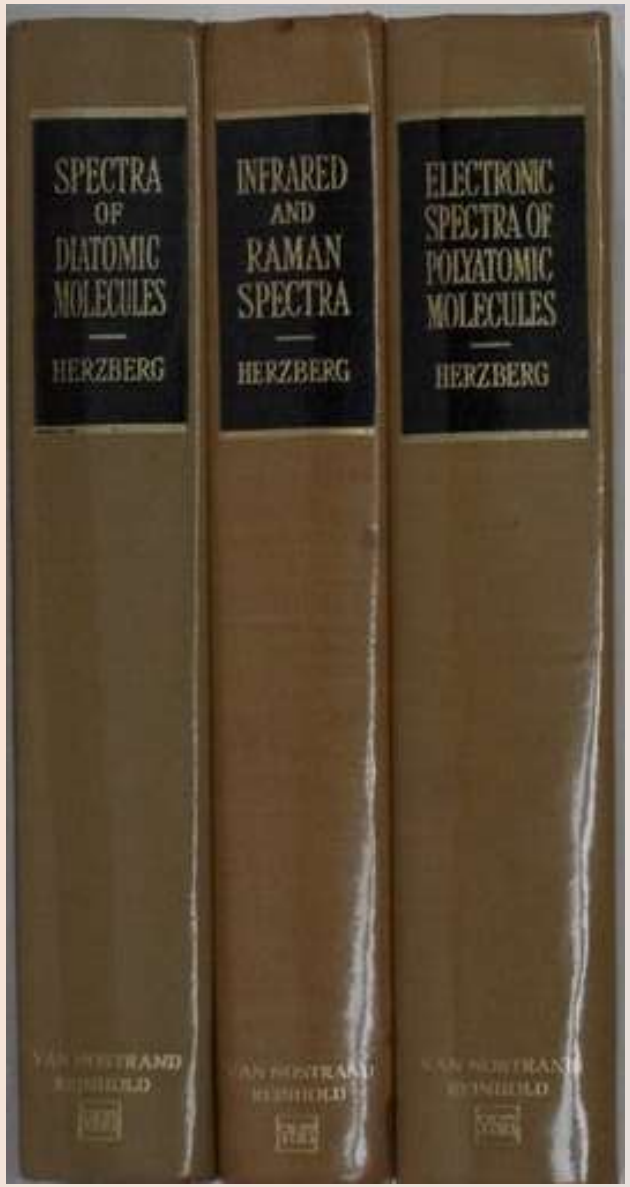
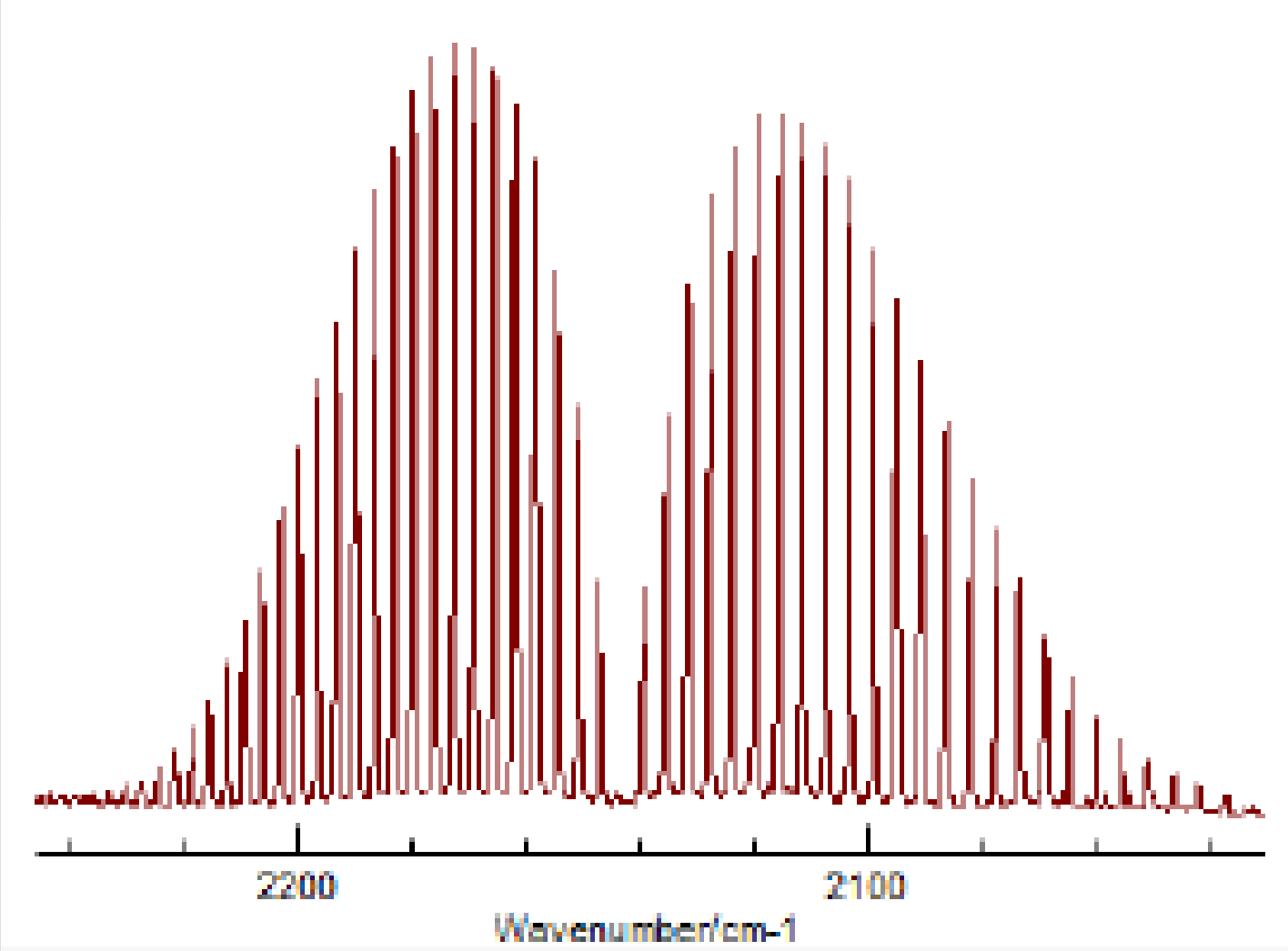


What is spectroscopy ?



CO vibration – rotation band at 4.3 micrpn

The Born-Oppenheimer approximation

Problem : solve the Heisenberg equation for a molecule : $H\,\Psi(q_i, Q_i) = E\,\Psi(q_i, Q_i)$

⇔ Find the eigenvalues E of the Hamiltonian operator H

Heisenberg, W. (1925) Über quantentheoretische Umdeutung kinematischer und mechanischer Beziehungen. Zeitschrift für Physik, 33, 879-893.

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

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

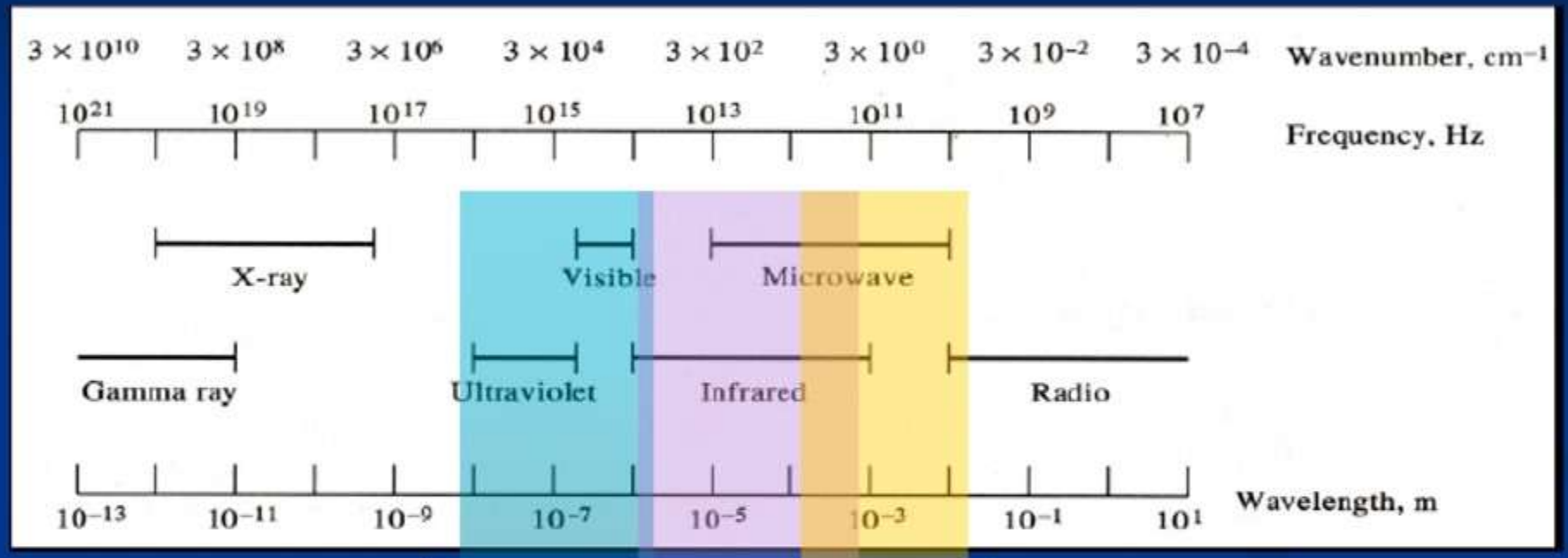
The total energy of the molecule is the sum of :

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

wich can be solved independently

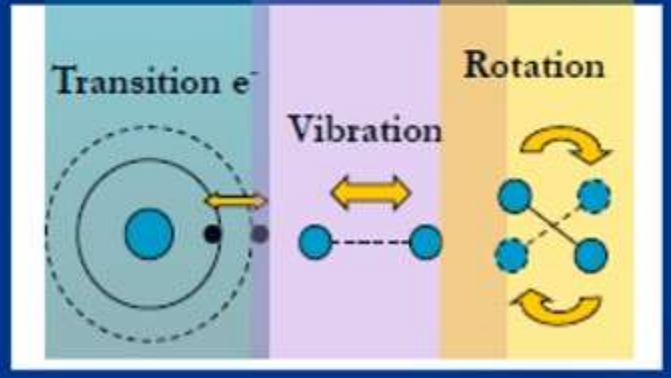
*Max Born; J. Robert Oppenheimer (1927). "Zur Quantentheorie der Molekeln". Annalen der Physik. **389** (20): 457–484.*

Spectral range and molecular motions



Interaction

Rayonnement-Matière



Electronic structure

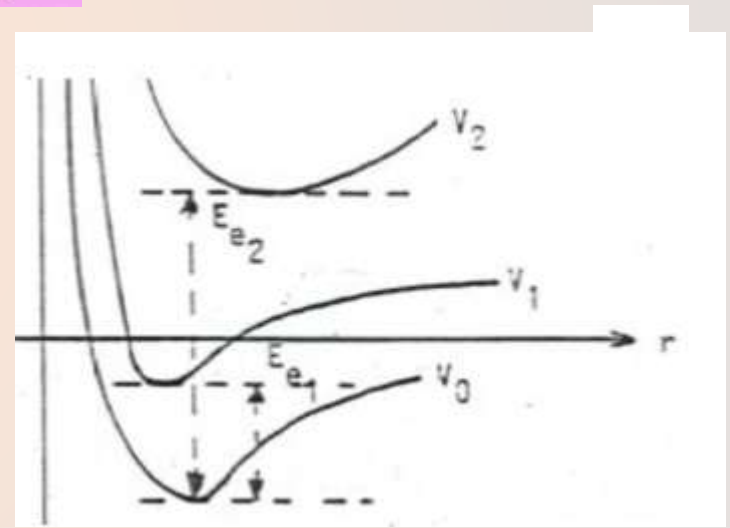
Recipe: freeze the nuclei at fixed position and solve the electronic Schrödinger equation :

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

Where $H_{el} = T_e + V_{ne} + V_{ee}$

is the potential energy of the electrons. The Term associated to the electric repulsion of the nuclei is simply an additional constant V_{nn}.

Example for a diatomic molecules

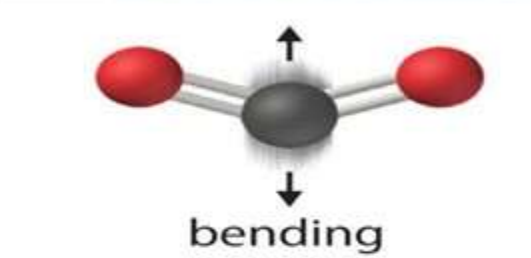


Lines, bands, systems : the components of spectra

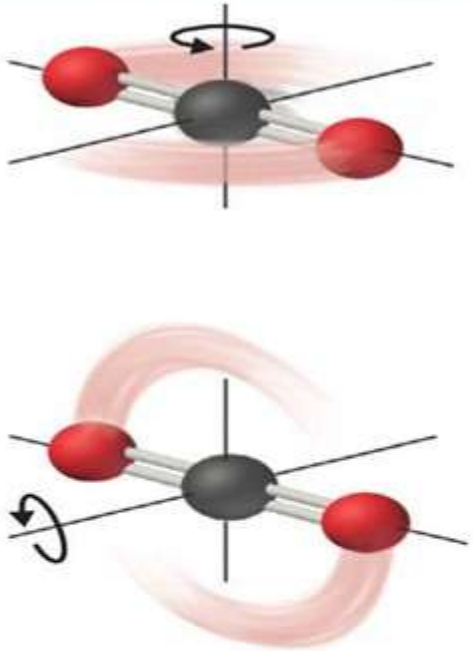
See
- Hanson, Summer School on Combustion and the Environment, June 19-24, 2022, Princeton, NJ, USA

https://cefrc.princeton.edu/sites/g/files/toruqf1071/files/documents/Lecture%20Notes%20-%20Hanson.pdf

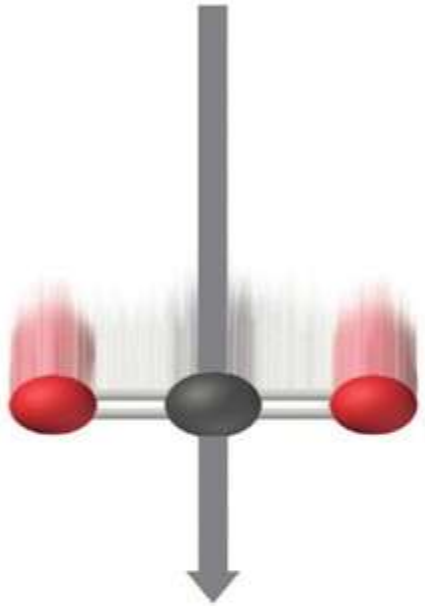
3 types of nuclear motions



vibrational motion



rotational motion



translational motion

Harmonic Oscillator model

Rigid rotor model

Can be separated
From the other motions
Energy = constante

Rigid rotor model of diatomic molecule

Vibration of diatomic molecules

Classification of polyatomic molecules

The rotation of polyatomic molecules

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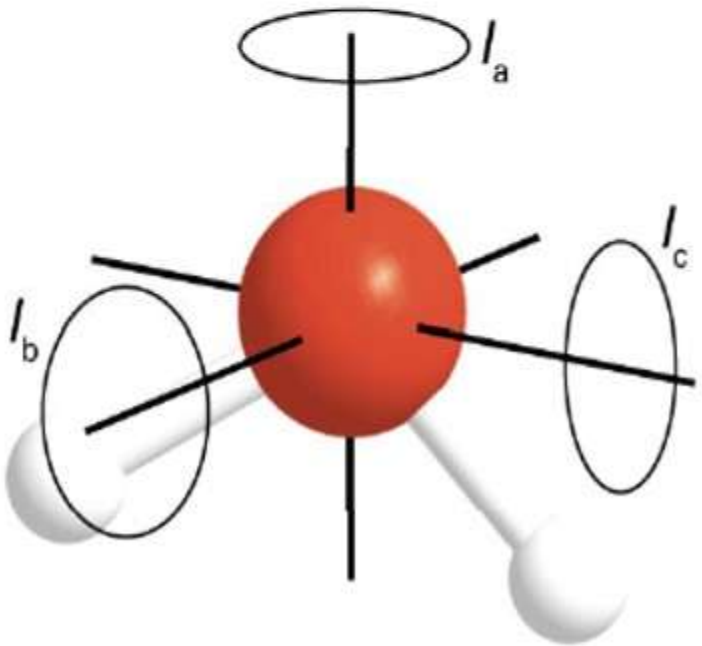
Rotational constants are related to molecular structure

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

In general we require three such rotational constants:

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

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



H_2O molecule

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

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

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

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

Symmetries

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

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

Concept of normal vibrations - fundamentals

Types of bands

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Additional complexities : internal motions

Molecules with internal motions have additional complexity in their spectroscopy

Examples :

- NH_3 : inversion motion
- CH_3-OH : methanol
- CH_3-SH : methylmercaptan
- CH_3-C=OH : acetaldehyde