Planetary Atmospheres
-
Molecular Spectroscopy

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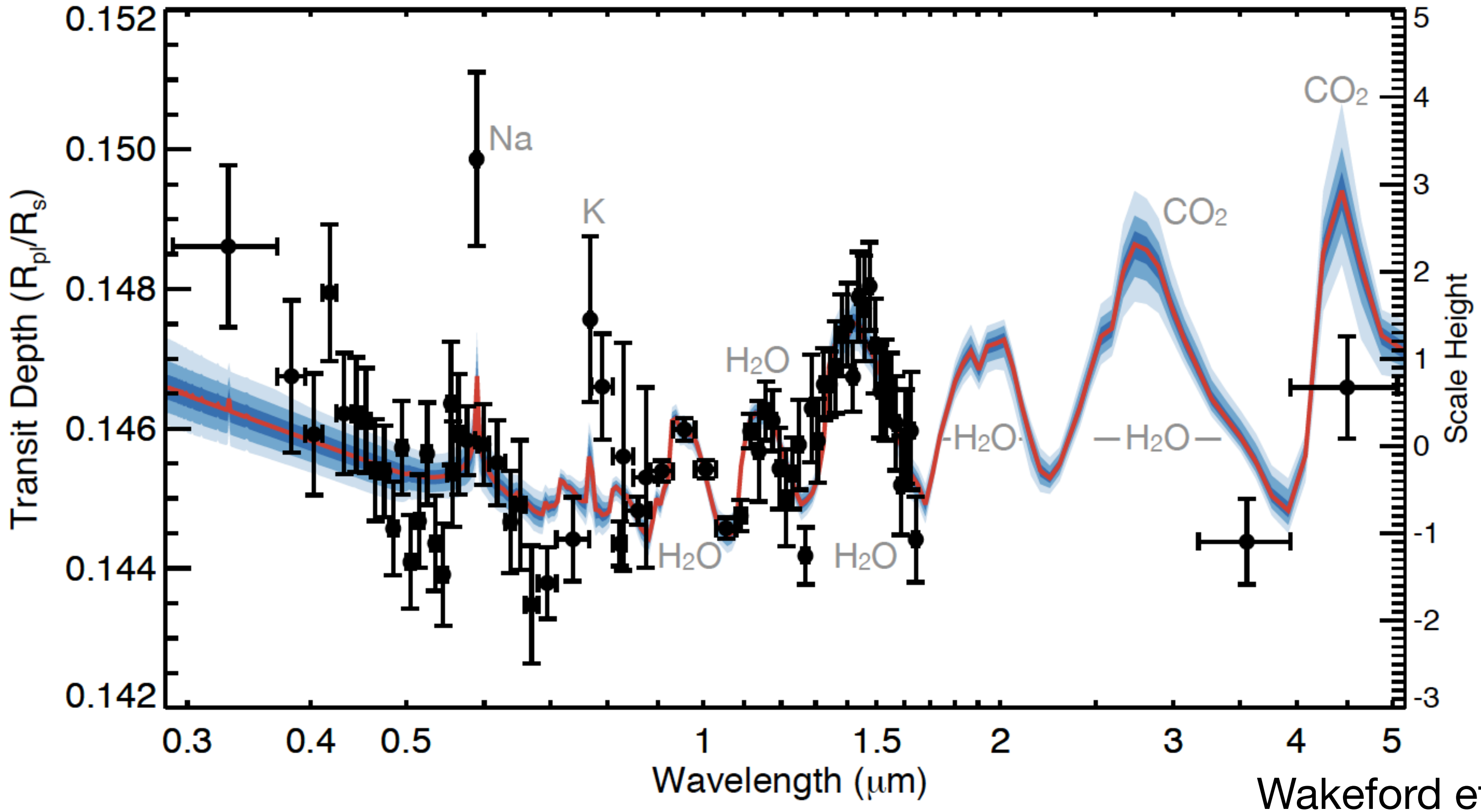
ARES 2, Biarritz, October, 5th 2021

Outline

- Introduction
- Energy levels, structure of molecules
- Electronic, vibrational, rotational transitions
- Collision-Induced Absorption
- Molecular and Planetary spectra

Spectroscopy



Wakeford et al. 2017

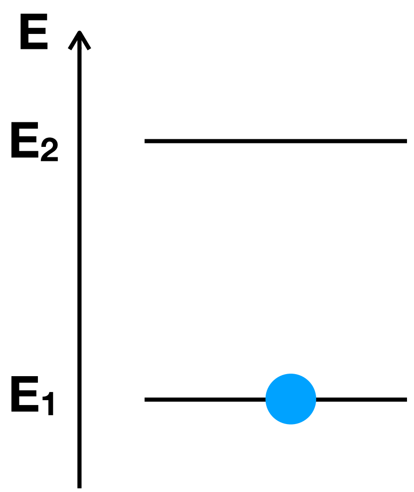
FIG. 6.— The complete transmission spectrum of WASP-39b (black points). This transmission spectrum incorporates data from HST STIS and WFC3, *Spitzer* IRAC, and VLT FORS2 completing the spectrum from 0.3–5.0 μm with currently available instruments. Using the ATMO retrieval code, which implements an isothermal profile and equilibrium chemistry, we determine the best fit atmospheric model (red) and show the 1, 2, and 3σ confidence regions (dark to light blue) based on the retrieved parameters.

Why are we able to say that H_2O, CO_2,… are in the atmosphere ?

➡ thanks to molecular spectroscopy !

Spectroscopy

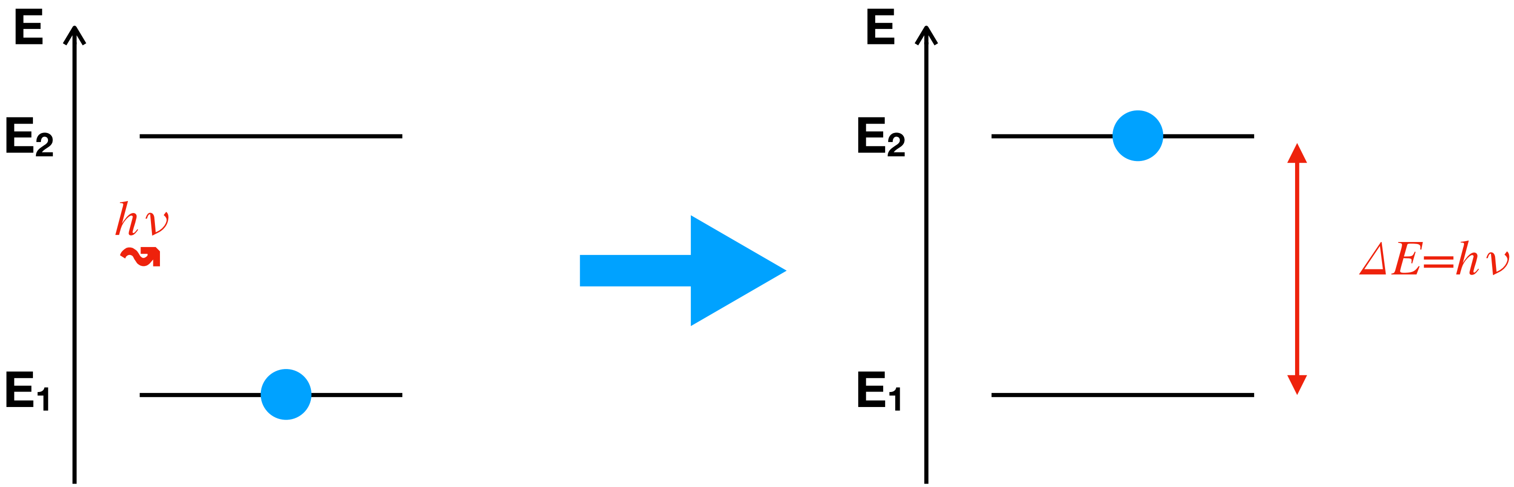
- Molecules have discrete energy states



- E1, the lowest energy level, is called ground state

Spectroscopy

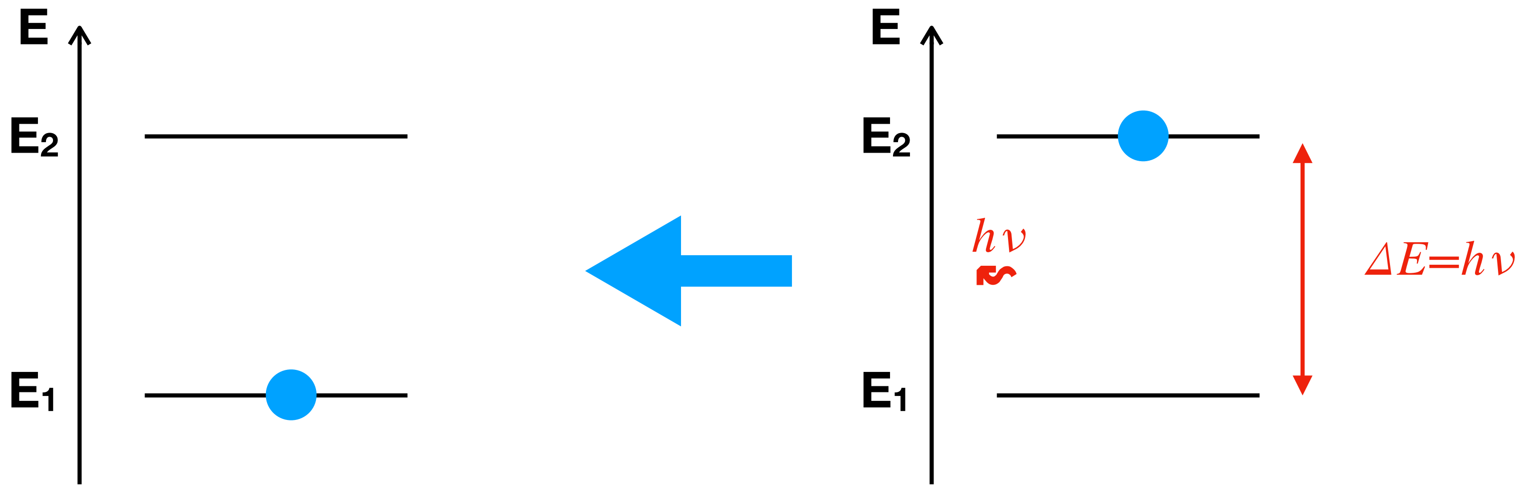
- Molecules have discrete energy states



- An electromagnetic wave (a photon) induces transition between energy levels of a molecule

Spectroscopy

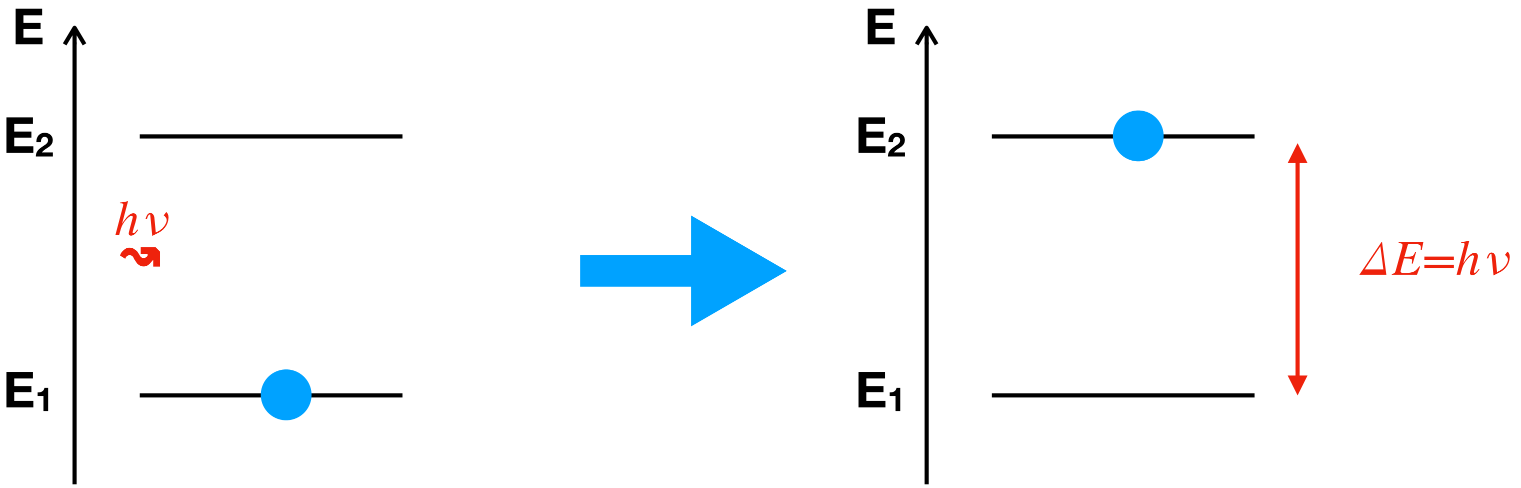
- Molecules have discrete energy states



- A downward transition can also happen and involves the emission of a photon

Spectroscopy

- Molecules have discrete energy states

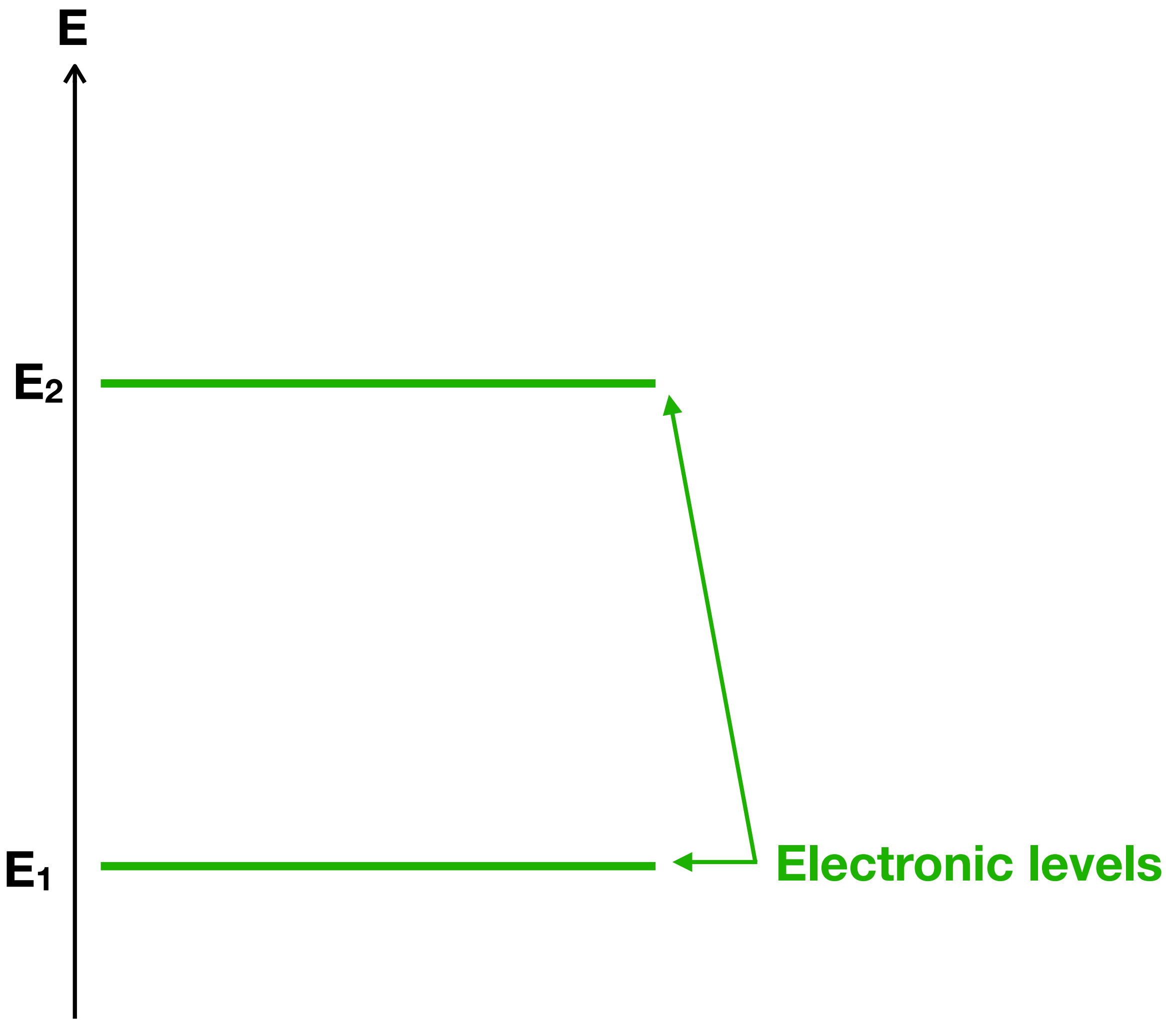


- An electromagnetic wave (a photon) induces transition between energy levels of a molecule

- The total energy of a molecule is the sum of its translation, vibration, rotation and electronic energies: $E_{tot} = E_{trans} + E_{rot} + E_{vib} + E_{elec}$

- Only E_{rot}, E_{vib}, and E_{elec} can be modified with a photon

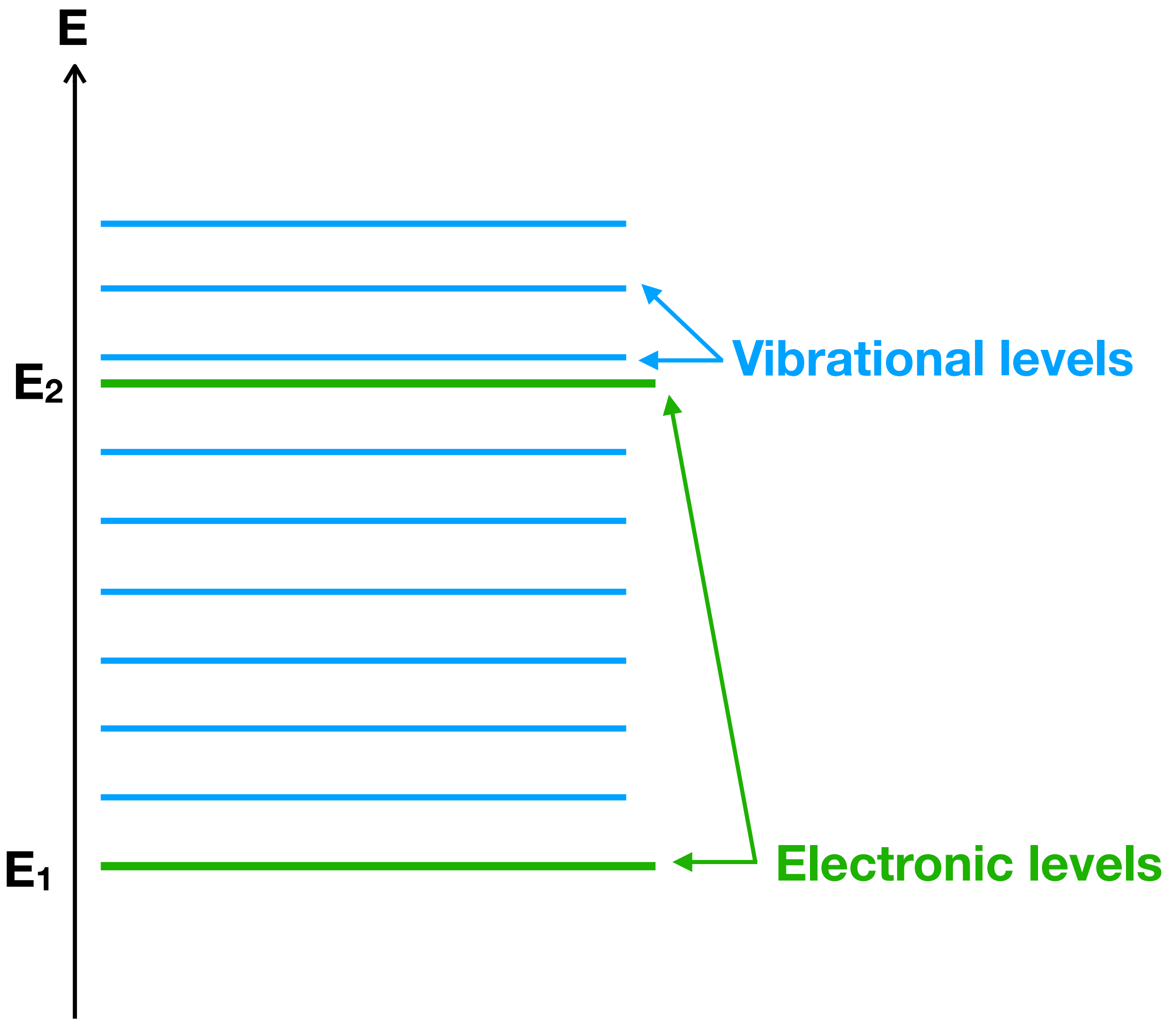
Energy levels



Transitions are induced by photons of different energies:

- V-UV (λ=1-700 nm): electronic
→ can break bonds in molecules (photodissociation)

Energy levels



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- V-UV (λ=1-700 nm): electronic
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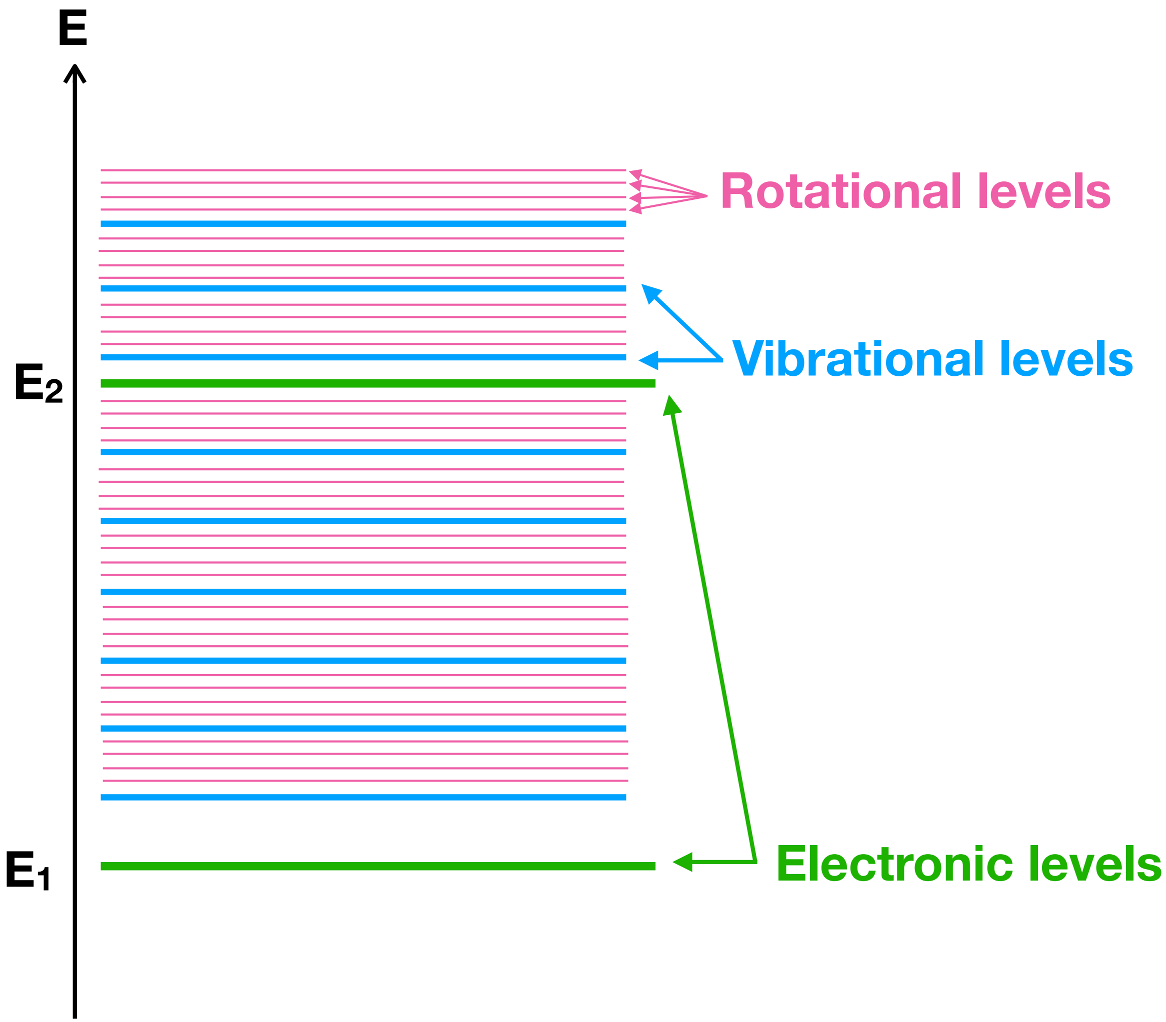
- IR (λ=0.7-1000 μm) : vibrational

Energy levels



Transitions are induced by photons of different energies:

- V-UV (λ=1-700 nm): electronic
→ can break bonds in molecules (photodissociation)

- IR (λ=0.7-1000 μm) : vibrational

- μwave (λ=1-300 mm): rotational

Structure of molecules

- Internal structure of molecules is very complex to describe because electrons behave <u>both like particles and waves</u>

- Classical physics is not sufficient and quantum mechanics must be used

- Impossible to know precisely where the electrons are: *Heisenberg Uncertainty Principle*

- Instead, only probabilities of finding an electron in a particular region around the atom can be calculated

- However, for simple molecules, classical physics can give correct results

- That is what will see in this course

Electronic energy levels

- For Hydrogen and hydrogen-like atoms, the Bohr model is accurate to determine the electronic energy levels:

$$E_n = -\frac{Z^2 m e^2}{8 n^2 h^2 \epsilon_0^2} = \frac{-13.6 Z^2}{n^2}\ eV$$

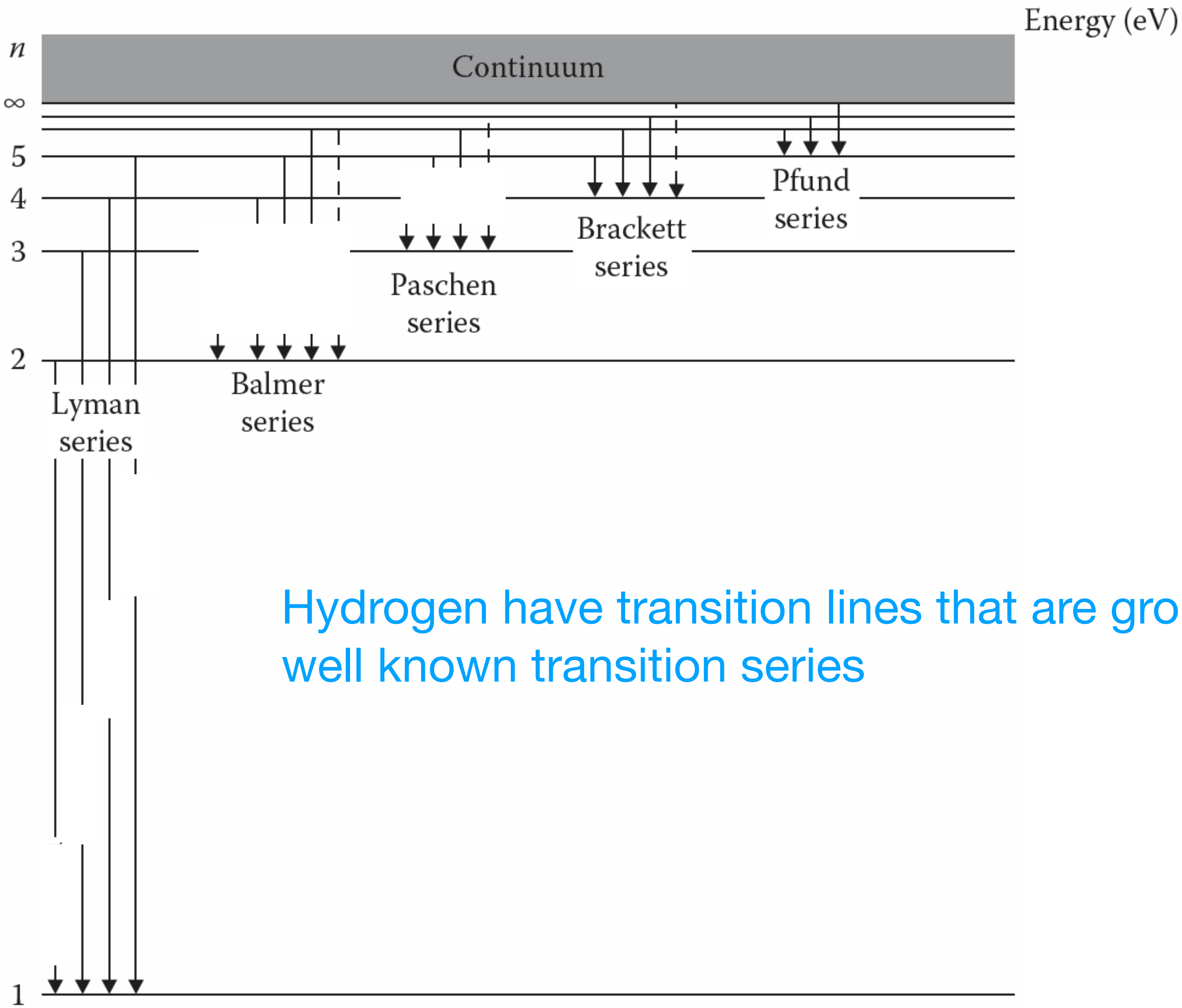
with n: energy level
ε_0: vacuum permittivity
h: Planck constant
m: atom mass
Z: nuclei charge
e: electron charge

- Transition between two electronic levels implies the absorption or emission of a photon with

$$\Delta E = -13.6 Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]\ eV \text{ with } n_1 > n_2$$

⇒ *Only photons with these energies can be absorbed or emitted*

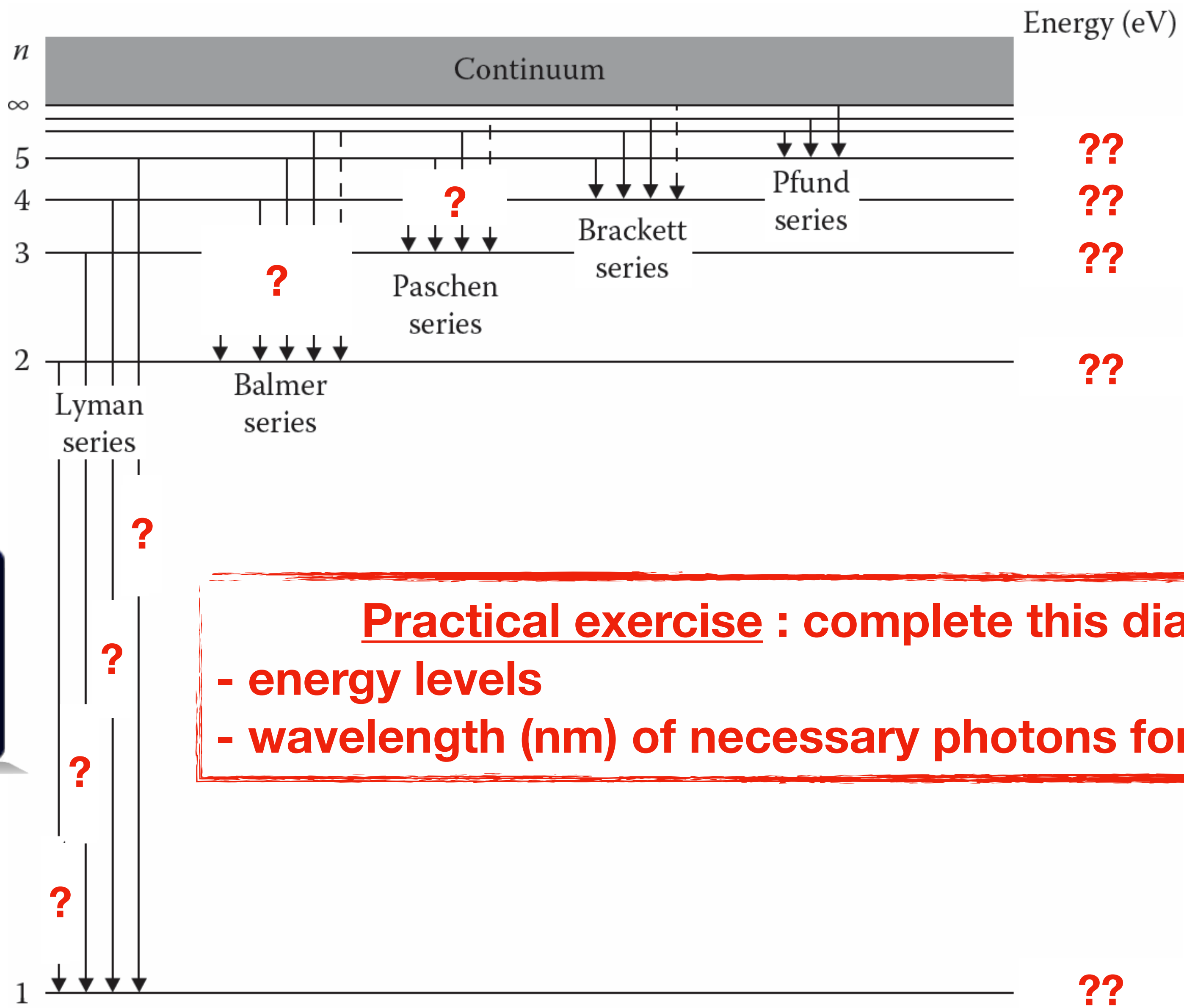
Electronic energy levels



Radiative transition series for the hydrogen atom H

Hydrogen have transition lines that are grouped in very well known transition series

Electronic energy levels

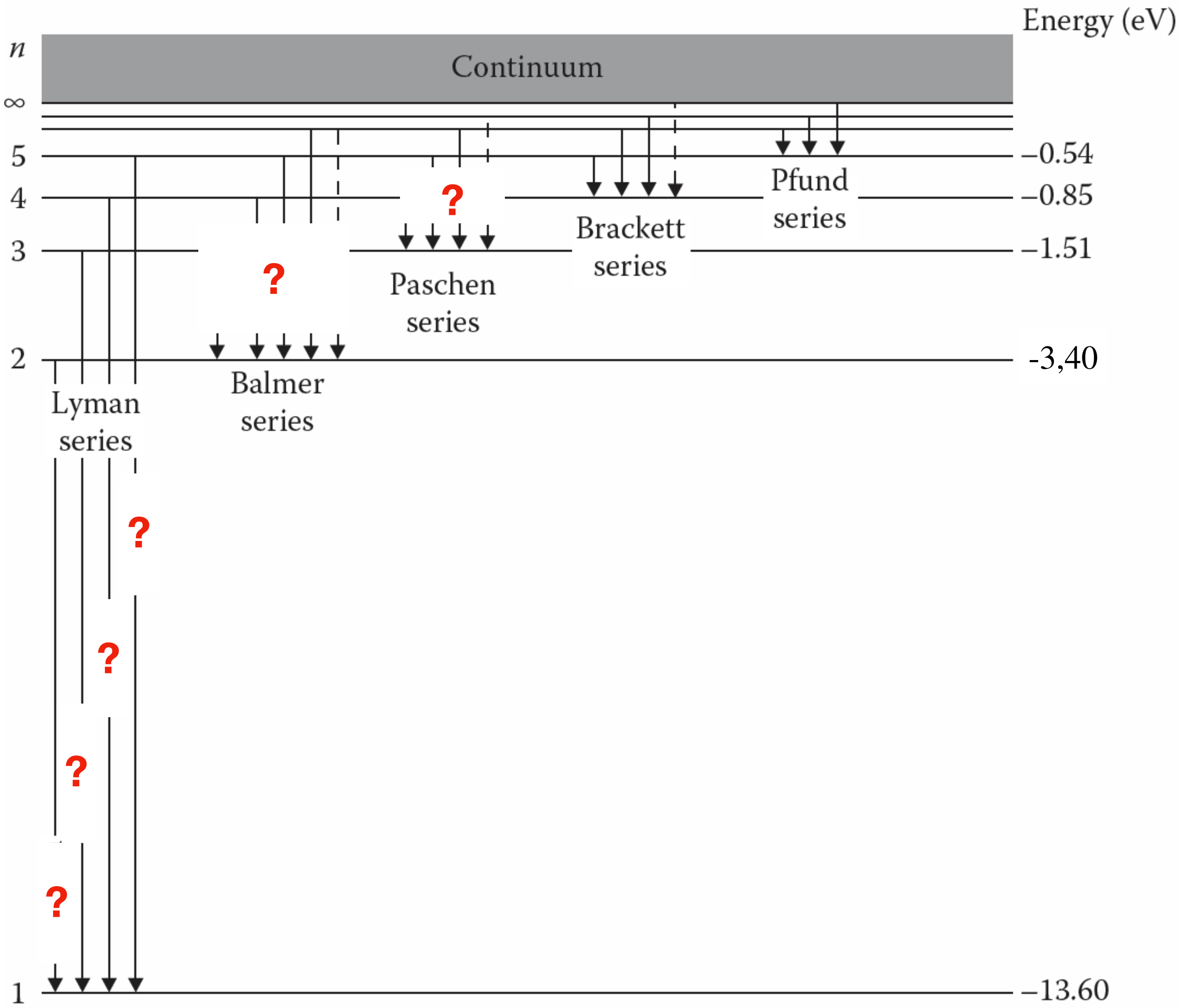


Radiative transition series for the hydrogen atom H

Practical exercise : complete this diagram

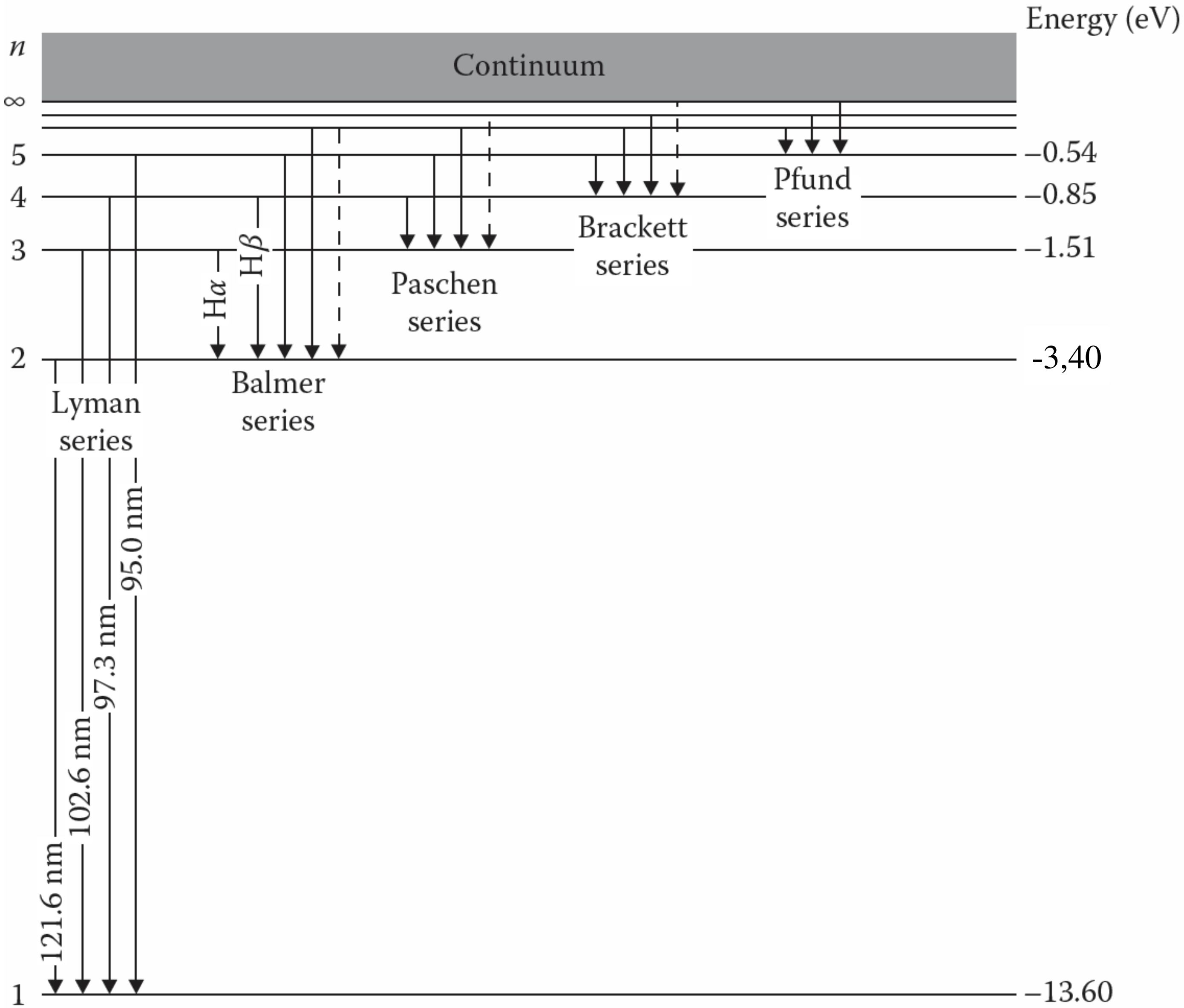
- **energy levels**
- **wavelength (nm) of necessary photons for transitions**

Electronic energy levels



Radiative transition series for the hydrogen atom H

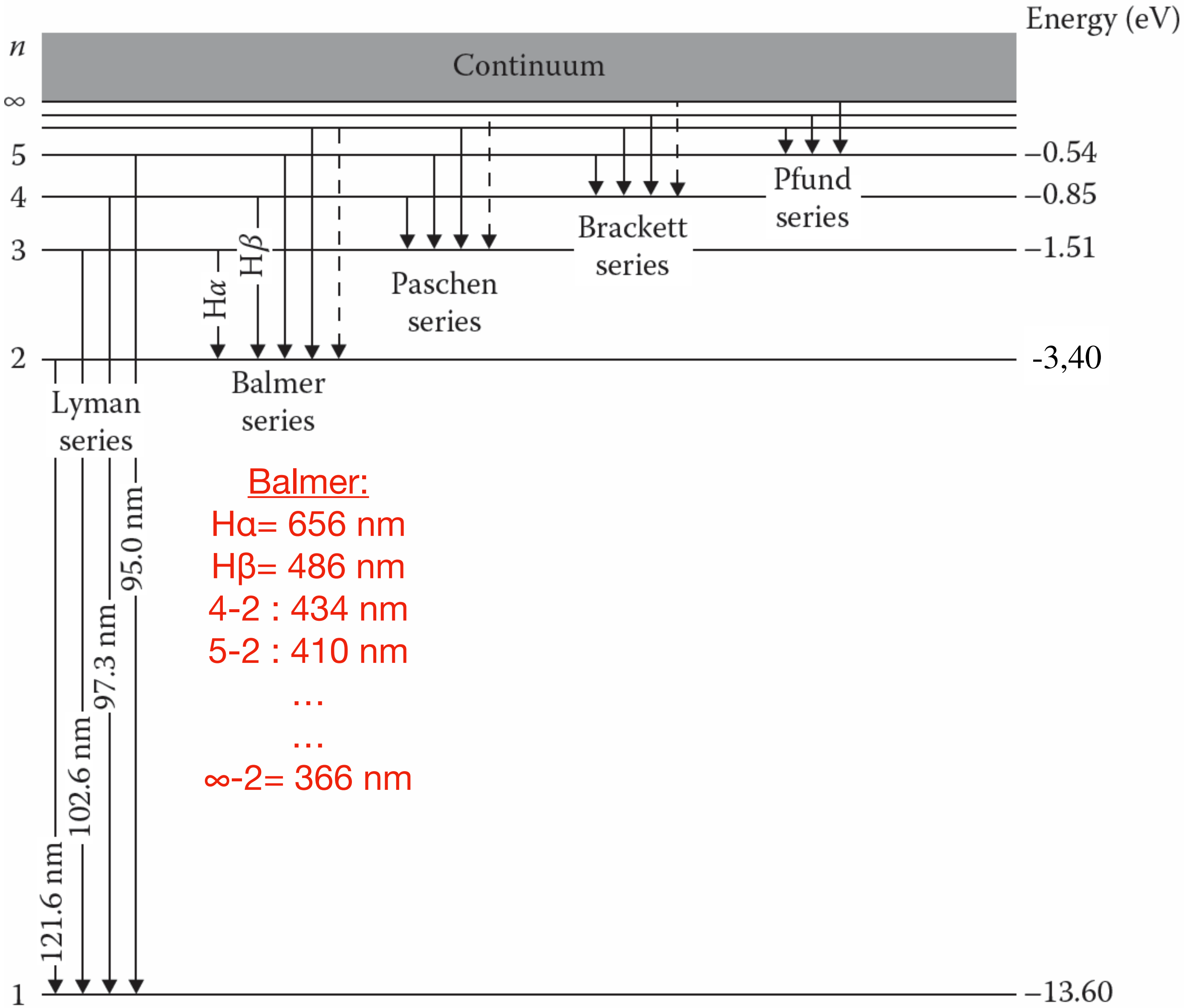
Electronic energy levels



Radiative transition series for the hydrogen atom H

Lyman:
Lyα= 121.6 nm
3-1= 102.6 nm
4-1 : 97.3 nm
5-1 : 95.0 nm
…
…
∞-1= 91.4 nm

Electronic energy levels



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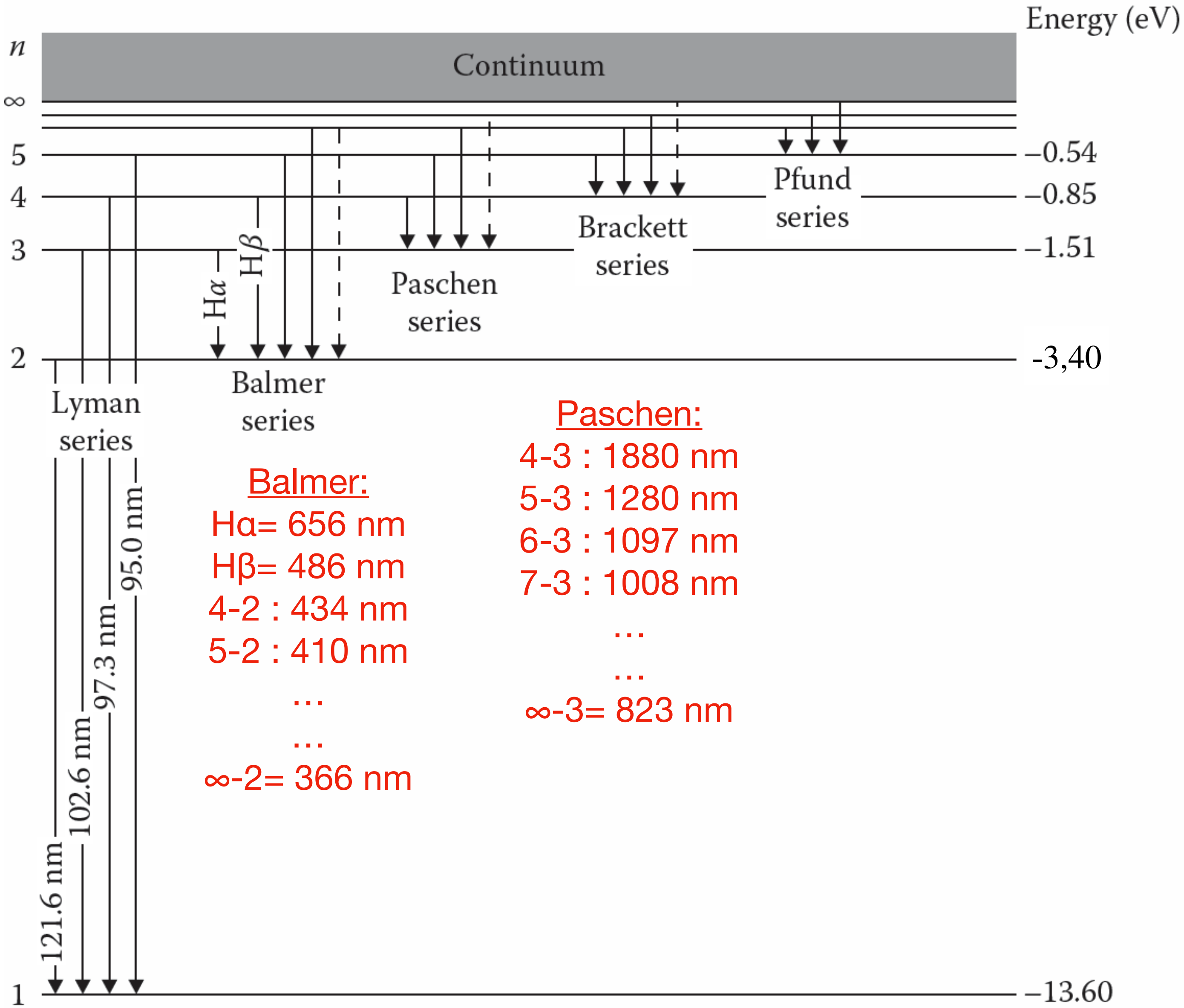
Balmer:
Hα= 656 nm
Hβ= 486 nm
4-2 : 434 nm
5-2 : 410 nm
…
…
∞-2= 366 nm

Electronic energy levels



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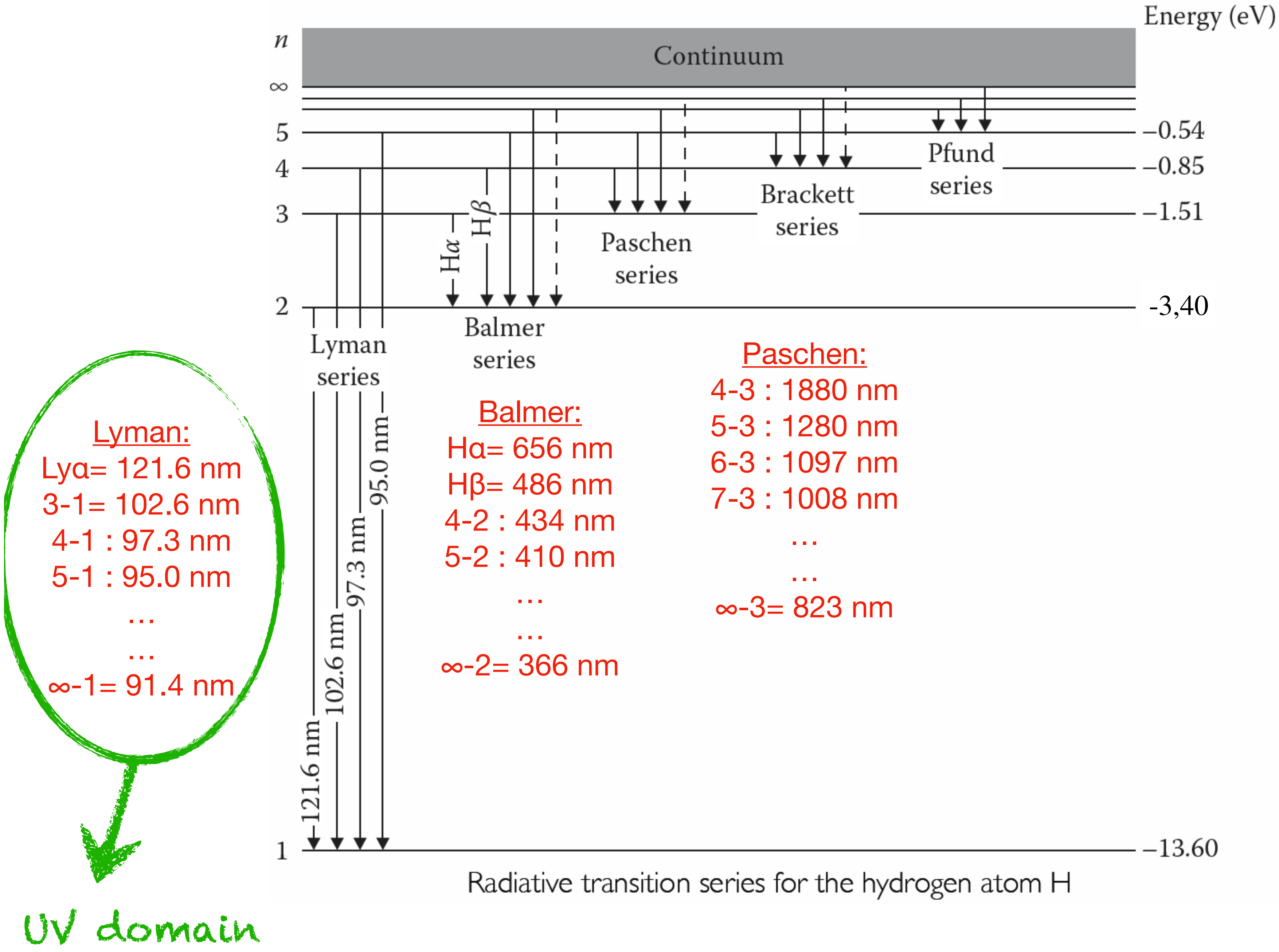
<u>Balmer:</u>
Hα= 656 nm
Hβ= 486 nm
4-2 : 434 nm
5-2 : 410 nm
…
…
∞-2= 366 nm

<u>Paschen:</u>
4-3 : 1880 nm
5-3 : 1280 nm
6-3 : 1097 nm
7-3 : 1008 nm
…
…
∞-3= 823 nm

Electronic energy levels



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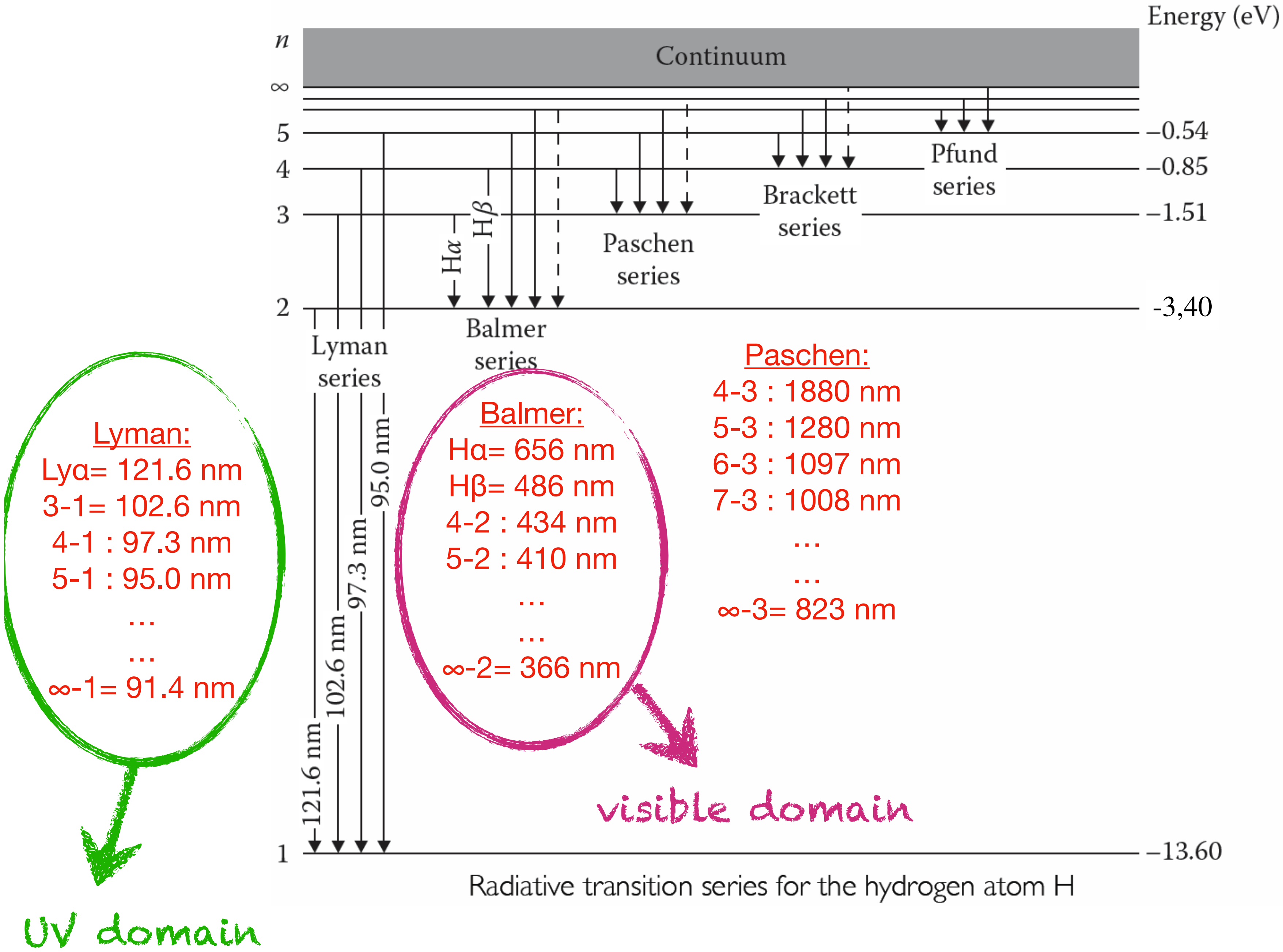

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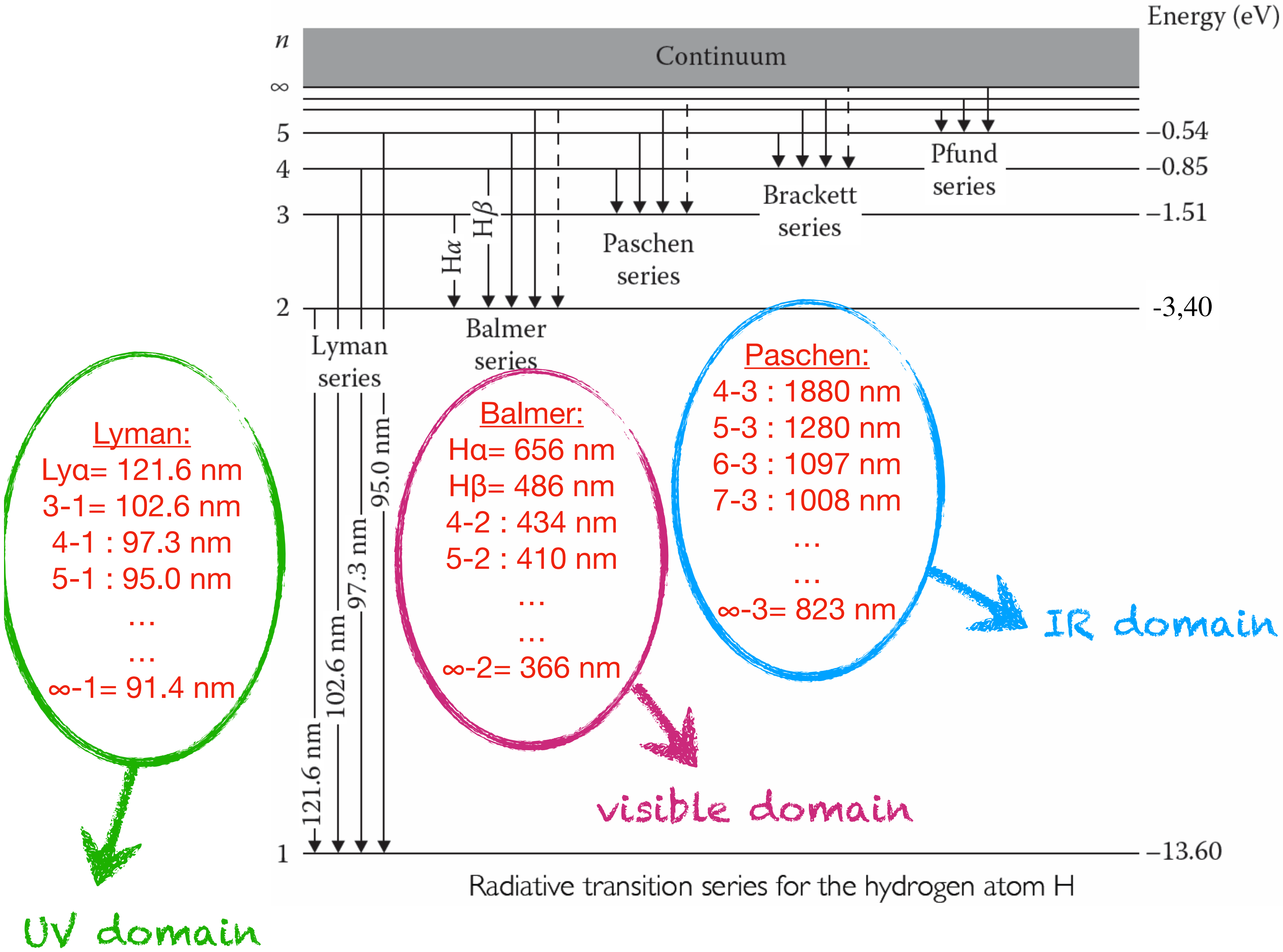

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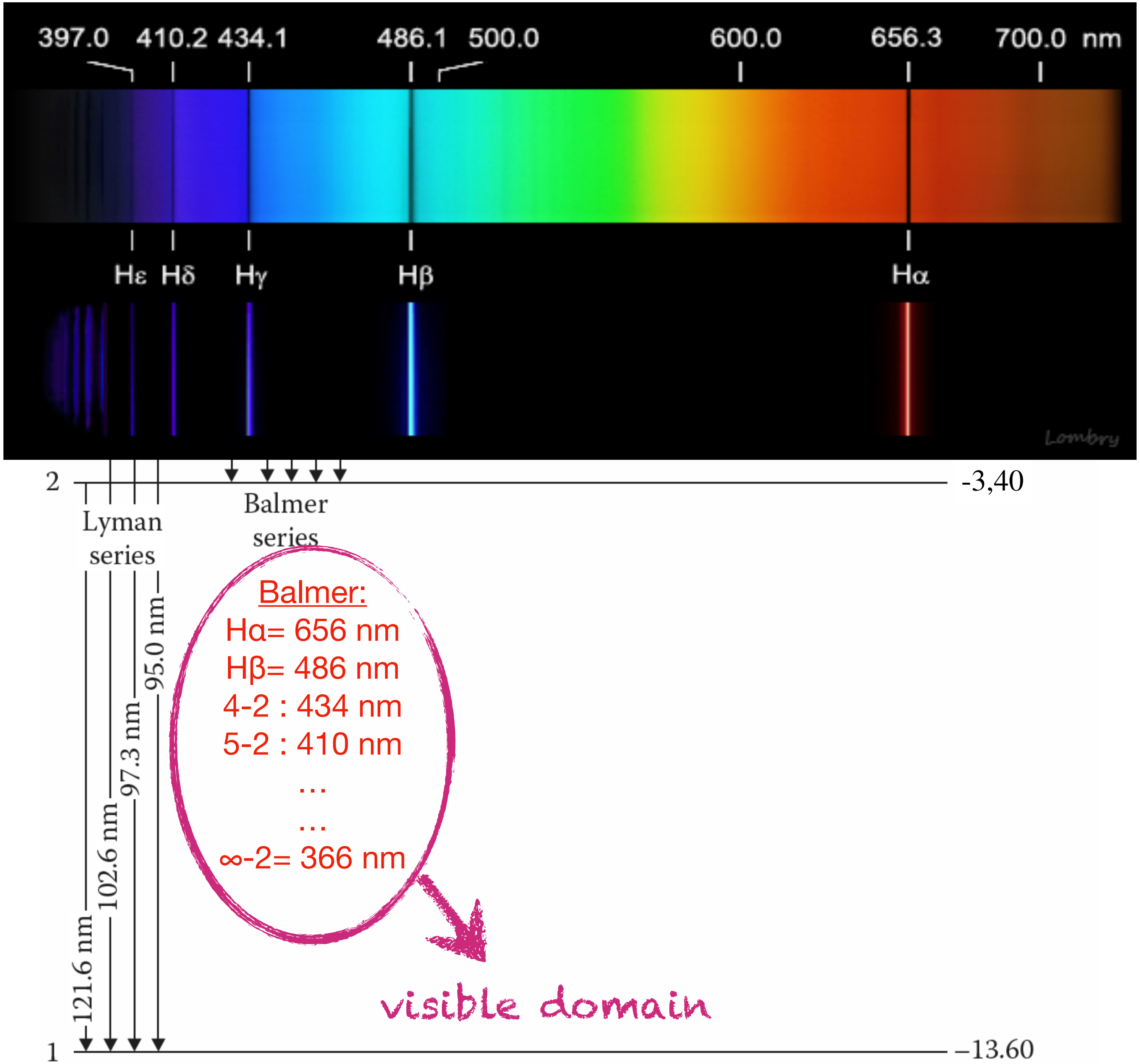
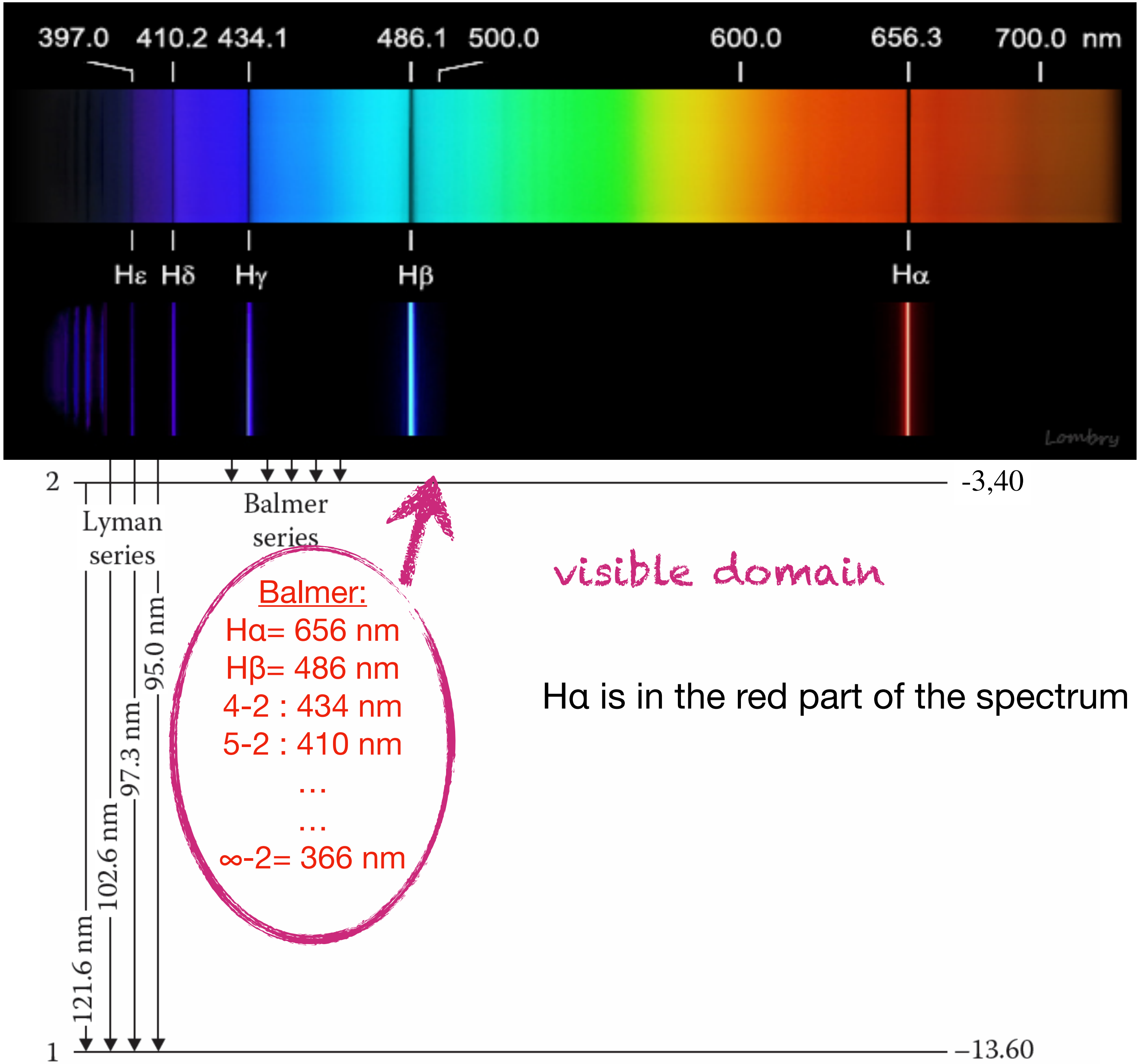
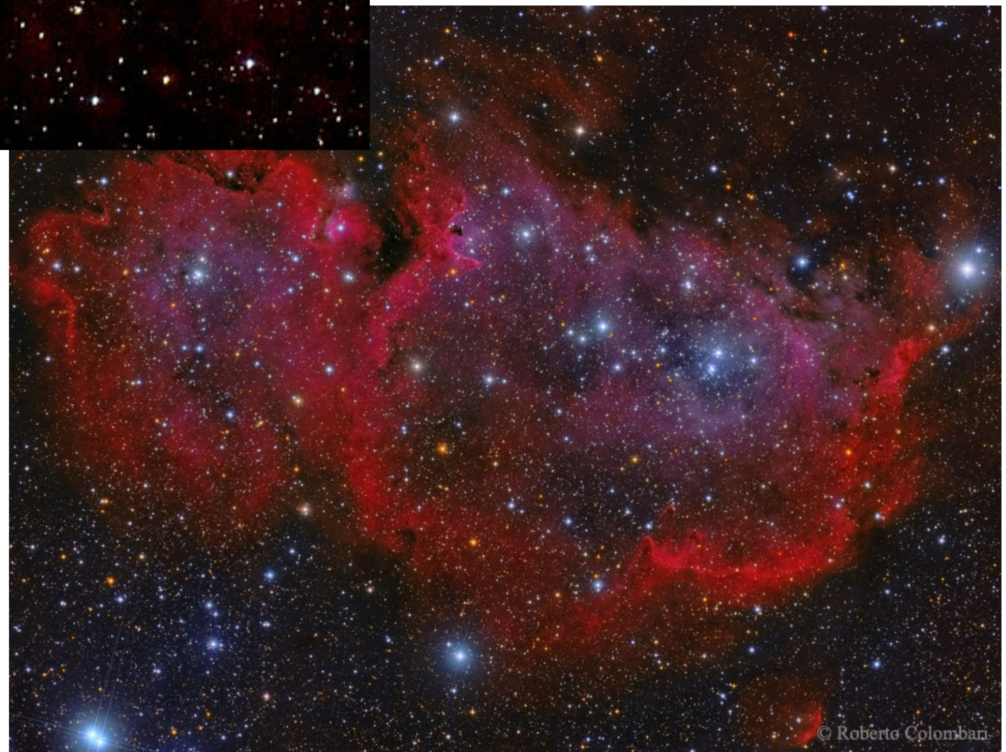


Radiative transition series for the hydrogen atom H



Radiative transition series for the hydrogen atom H

Hα is in the red part of the spectrum



Hα is used to observed nebula, which contain mainly hydrogen

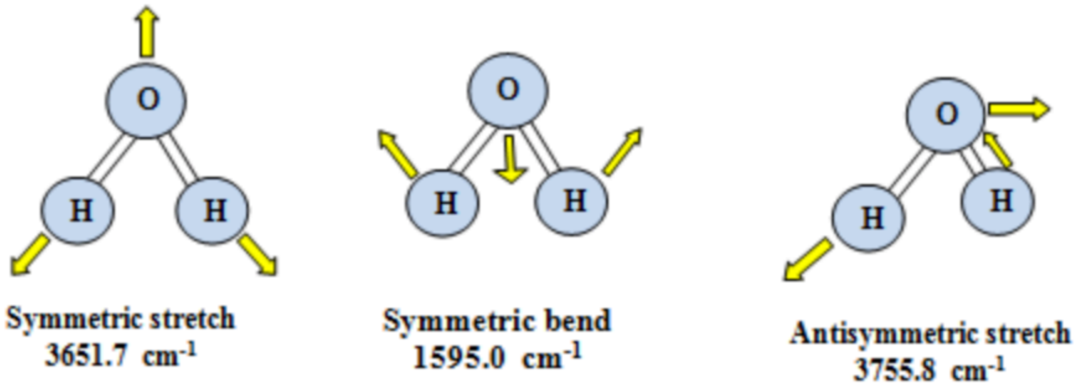
Not as simple to calculate the energy levels of more complex molecules, but they all have discrete electronic energy levels, with specific transition lines

Vibration energy levels

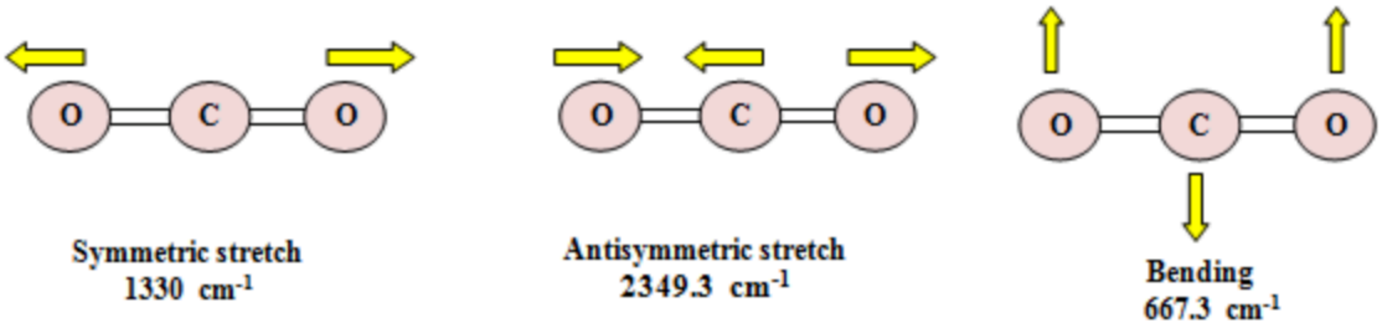
- In addition to electronic levels, a molecule with several atoms has vibrational energy levels.

- Each molecule has a defined number of vibration modes and each mode has its own frequency.

H_2O



CO_2



Vibration energy levels

- A diatomic molecule can be treated as a harmonic oscillator: 2 masses on a spring with a potential energy that depends upon the square of the displacement from equilibrium position: $E_p(x) = \frac{1}{2}K(x - x_0)^2$

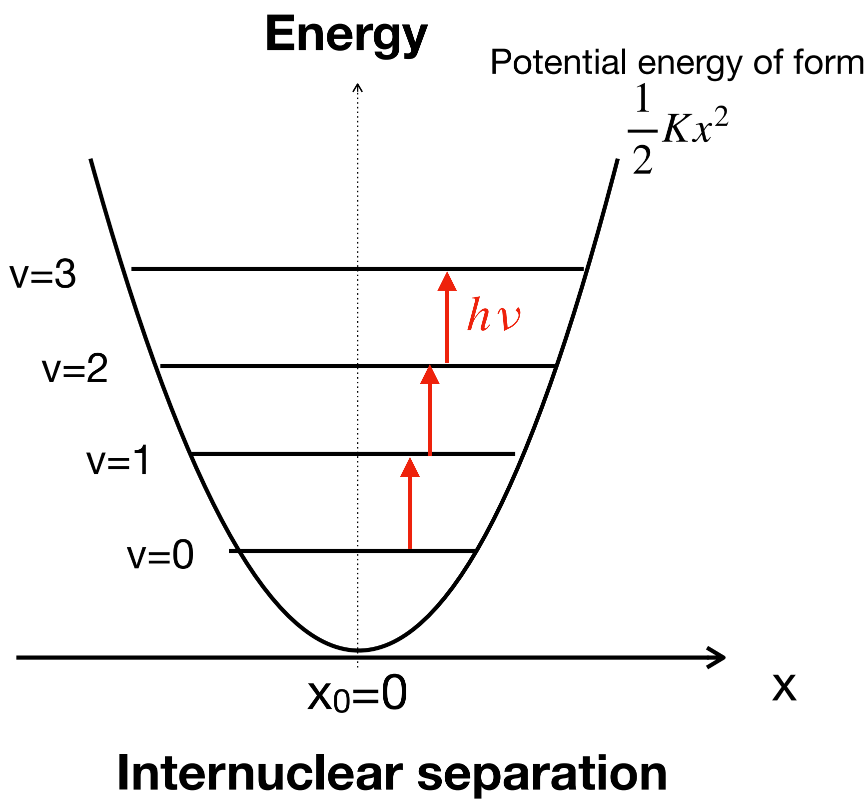
  The force constant: K

- The vibrational frequency is $\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu_r}}$

  where the reduced mass $\mu_r = \frac{m_1 m_2}{m_1 + m_2}$

- The energy levels are $E_\mathrm{v} = (\mathrm{v} + \frac{1}{2})h\nu_{osc}$ with v an integer value

- Only transitions with Δv = ±1 are allowed by quantum mechanics.



With a finer treatment (anharmonic oscillator), we find that transitions with Δv = ±2, ±3 exist but with a low intensity

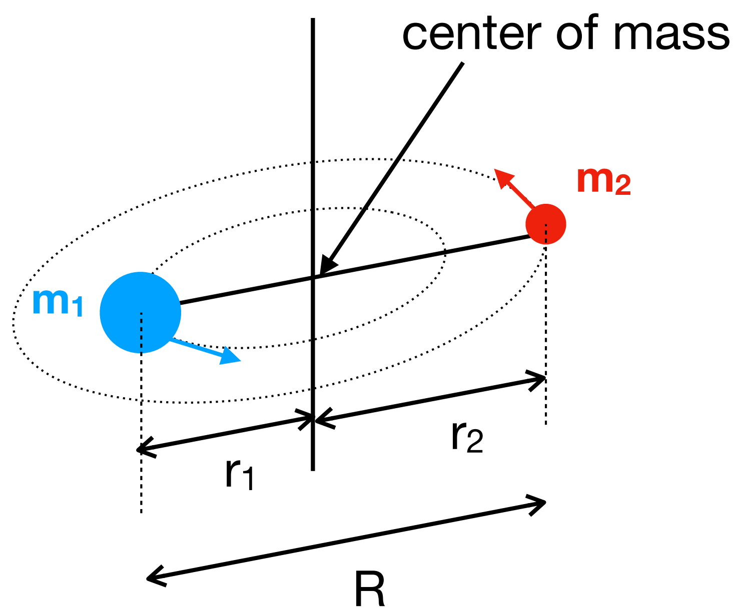
Rotation energy levels

- Finally, a diatomic molecule can rotate as a whole around an axis passing through the center of mass and perpendicular to the internuclear axis

- Treating the molecule as a rigid rotator and solving Schrödinger equation, we find that the possible energy levels are $E_{rot} = \frac{h^2 J(J+1)}{8\pi^2 I}$, with J an integer value, the moment of inertia $I = \mu_r R^2$, and the reduced mass $\mu_r = \frac{m_1 m_2}{m_1 + m_2}$

- The rotational frequency is $\nu_{rot} = \frac{h}{4\pi^2}\sqrt{J(J+1)}$

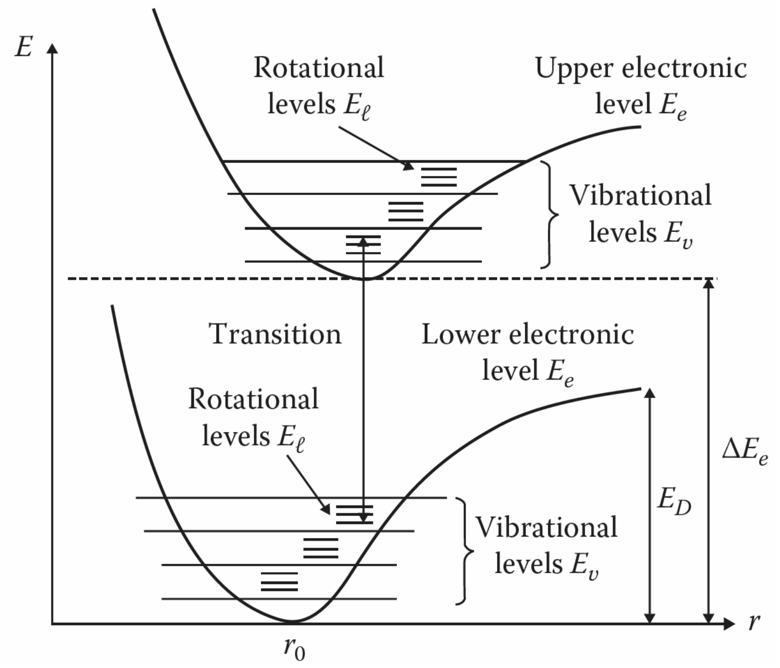
- Only transitions with ΔJ = ±1 are allowed by quantum mechanics.



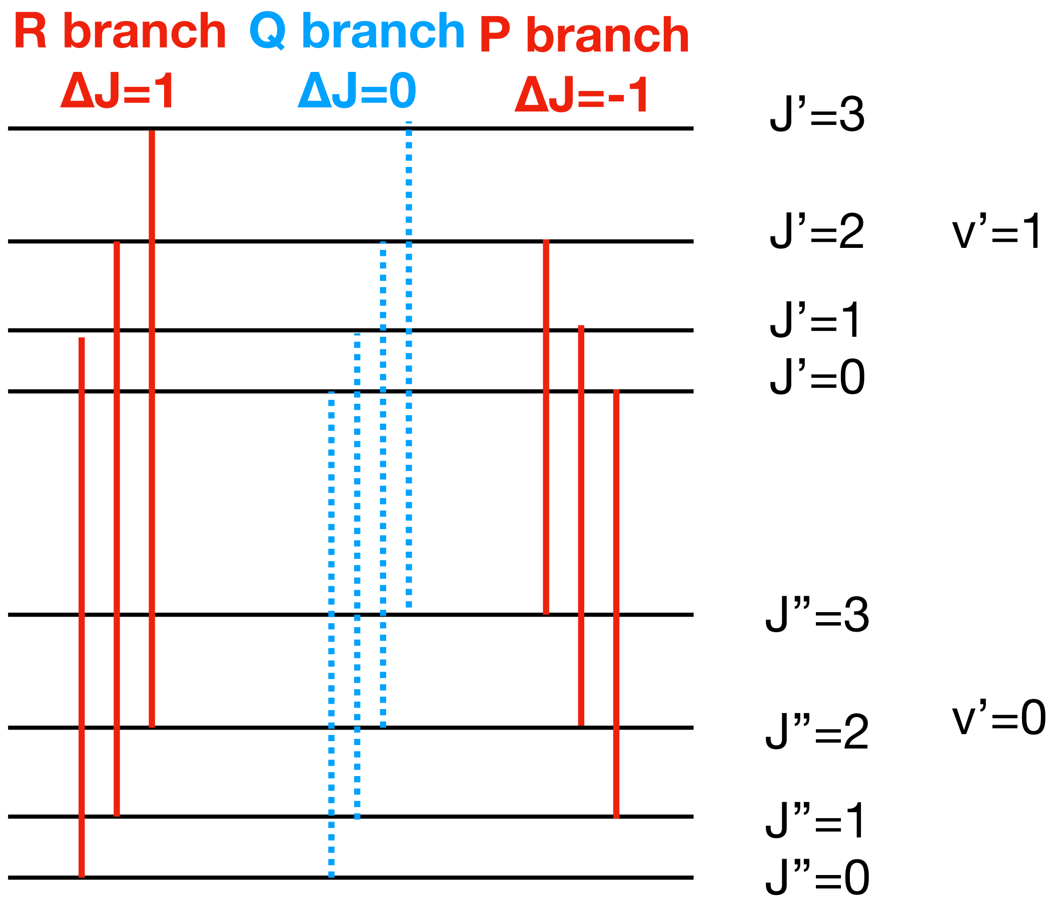
To rotate, the molecule must have a dipolar moment non-null (O_2, N_2 don't have)

Vibration-Rotation energy levels

- In reality, movements of rotation and vibration happen simultaneously.
- Rules of selection are the same Δv=±1, ΔJ=1 (*R branch*) and ΔJ=-1 (*P branch*)
- The transition with ΔJ=0 is called *Q branch* but is « forbidden » (in practise, happens but with a very low probability)



Courtesy of E. Hébrard , University of Exeter

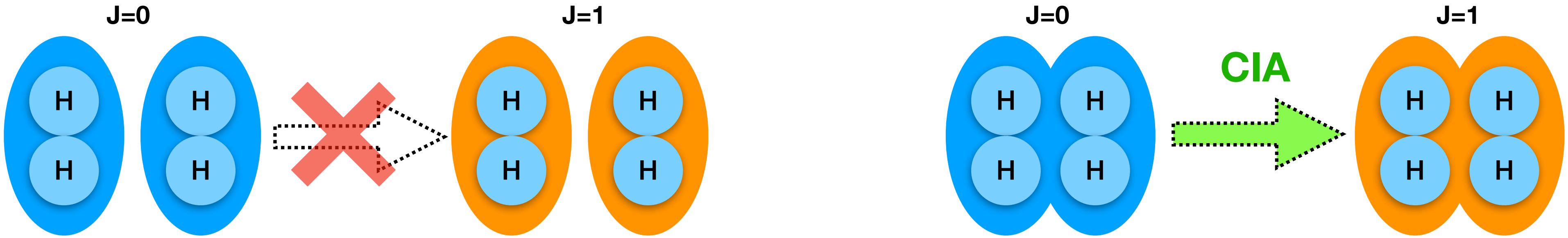


Collision-Induced Absorption

- We said previously: To rotate, the molecule must have a dipolar moment non-null, which is not the case for symmetric molecules (e.g. H_2, O_2, N_2 …)

- However, if densities and/or absorption path lengths are sufficiently high, even these infrared inactive gases can absorb infrared radiation

- These molecules can thus form a « complex of interacting molecules », in which a transient dipole is created, which causes collision-induced absorption (CIA).



- CIA phenomenon plays an important role in the total absorption of radiation in atmosphere and must be considered in radiative transfer models.

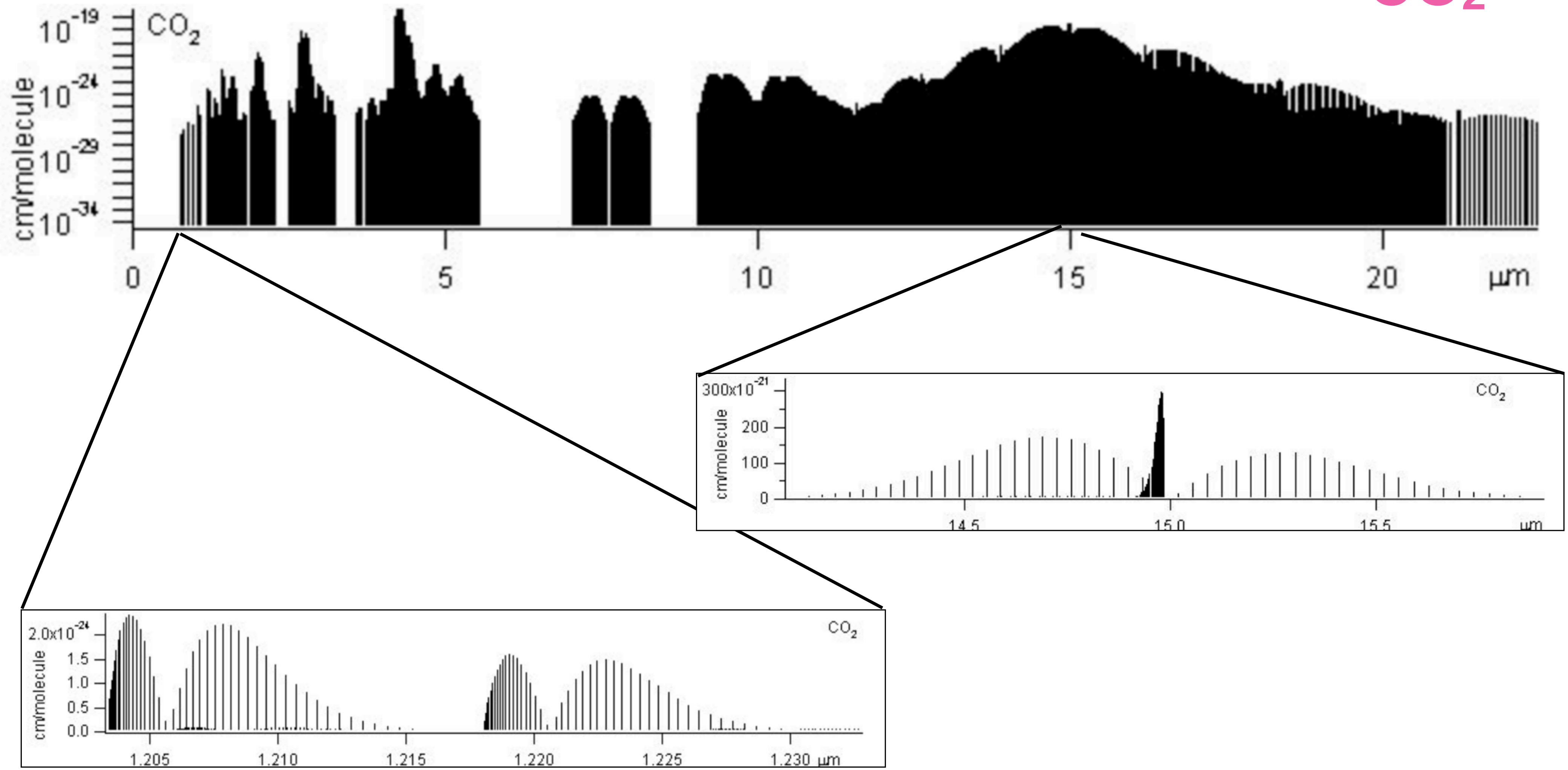
- In warm exoplanets, collision-induced dipole of H_2-H_2 and H_2-He are the main contributors to the opacity of the atmosphere in the far-infrared.

- CIA floor is the lowest possible depth we can probe in hot Jupiter atmospheres

Molecular spectra

- Each atom or molecule has its own unique set of energy transitions, with different intensities.

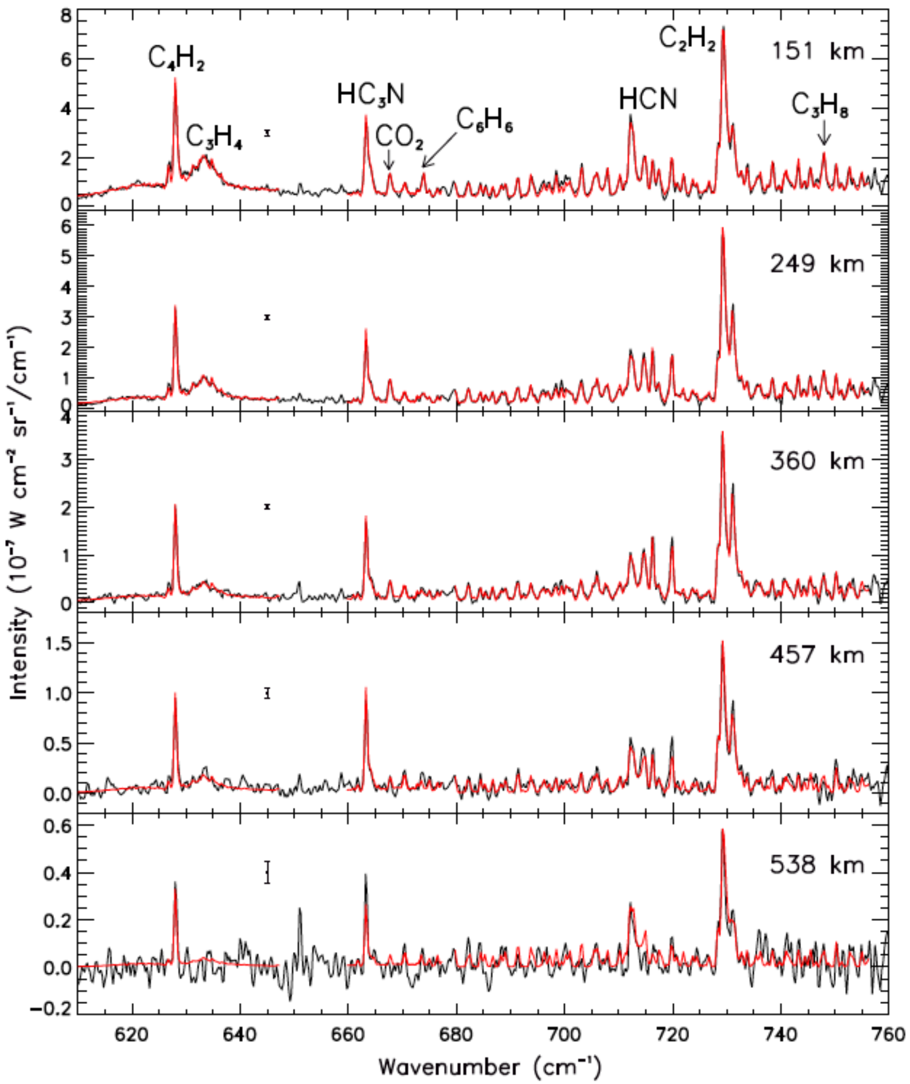
CO_2



Planetary Spectra

- Identification of individual molecular bands in planetary spectra permit to determine the composition of atmospheres.

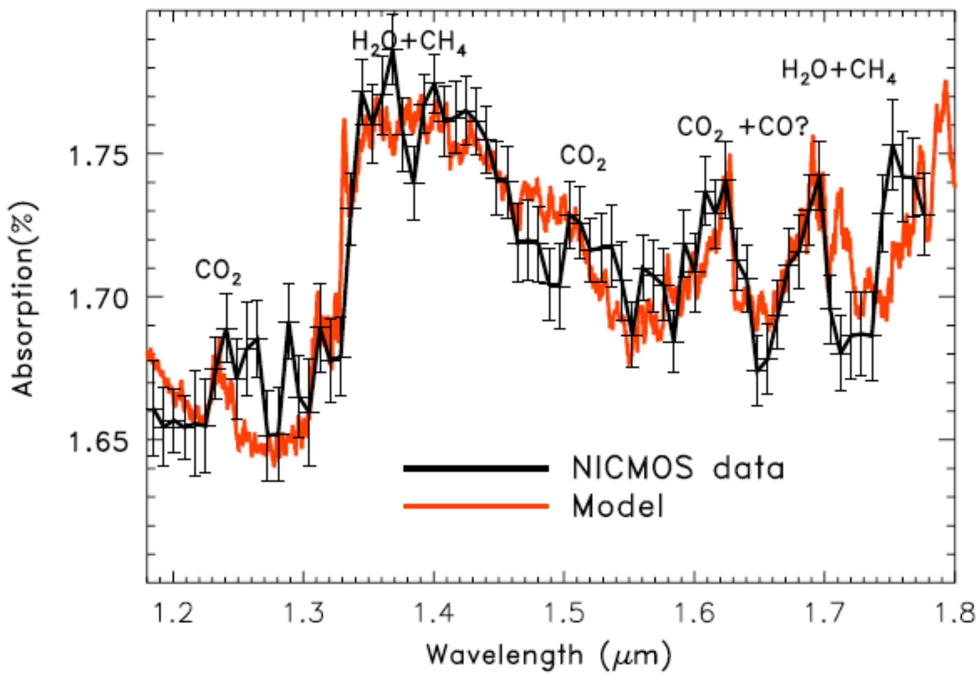
Titan atmosphere Vinatier et al. 2010



- Comparison between synthetic spectra and observations

- Much better resolution for Solar System bodies than for exoplanets…

XO-1b atmosphere Tinetti et al. 2010



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