MANFRED BRATH, WS 2022

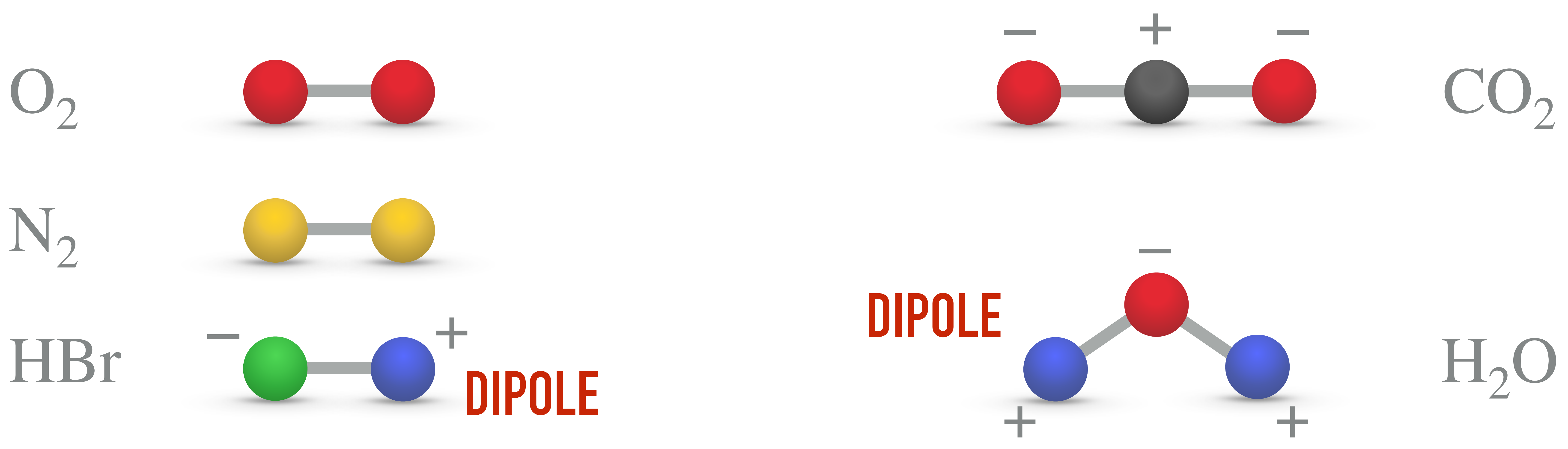
ADVANCED RADIATION AND REMOTE SENSING: ABSORPTION PROPERTIES OF THE ATMOSPHERE

MOLECULE SPECTRA

MOLECULE STRUCTURE

- This will be only a brief overview without going into any details.
- For those who interested in the details see
  - Haken, Hermann, und Hans Christoph Wolf. Molekülphysik Und Quantenchemie. Fünfte, völlig neubearbeitete und erweiterte Auflage. Springer-Verlag Berlin Heidelberg, 2006. https://dx.doi.org/10.1007/3-540-30315-4. (ebook/book, Stabi)
  - Demtröder, Wolfgang. Atoms, Molecules and Photons. Third edition. Springer, 2018. https://dx.doi.org/10.1007/978-3-662-55523-1. (ebook/book, Stabi)
  - or any other book about spectroscopy and molecular physics

MOLECULE STRUCTURE



- Quantum mechanics and electrodynamic and states that we need a dipole to interact with em radiation.
    - Where do we have dipoles?

MOLECULE STRUCTURE

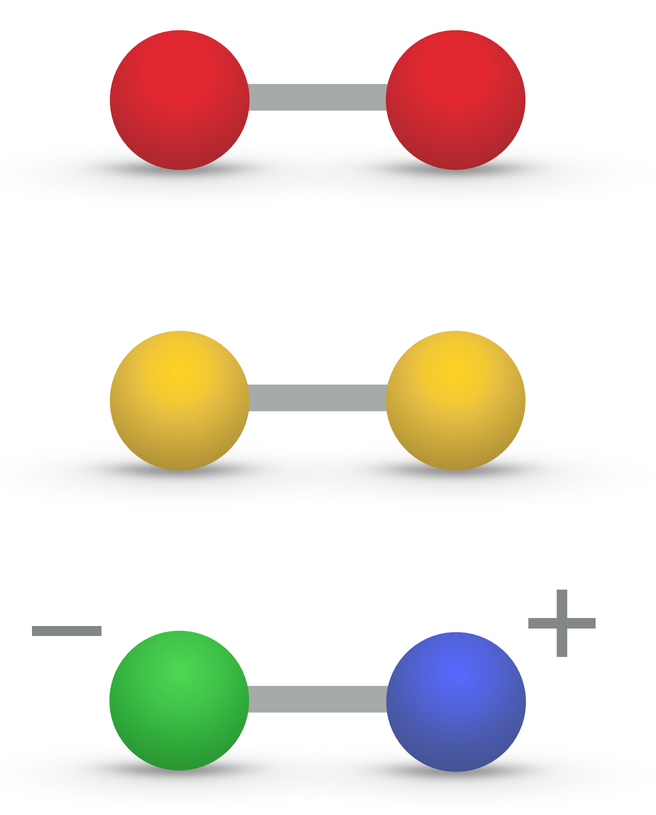
- A dipole is not enough. What else do we need?
- We need a periodically moving dipole.
- Two ways: Rotation and Vibration

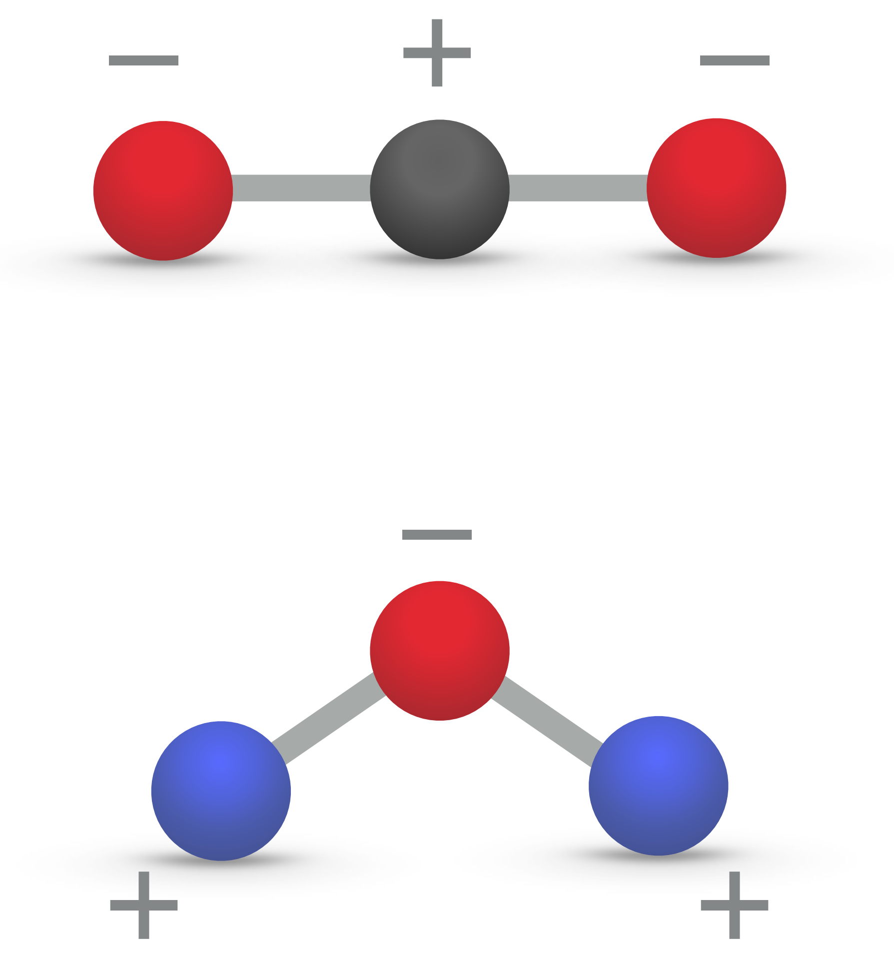
MOLECULE STRUCTURE

O_2

N_2

HBr





CO_2

H_2O

- What takes more energy into account rotation or vibration?

$$E_{rot} < E_{vib} < E_{el}$$

ENERGY-FREQUENCY RELATIONS

- Energy E and frequency ν differ only by the Planck constant h.

$$E = h\nu$$

- In quantum mechanics a different version is often used.

$$E = \hbar\omega = \frac{h}{2\pi}2\pi\nu$$

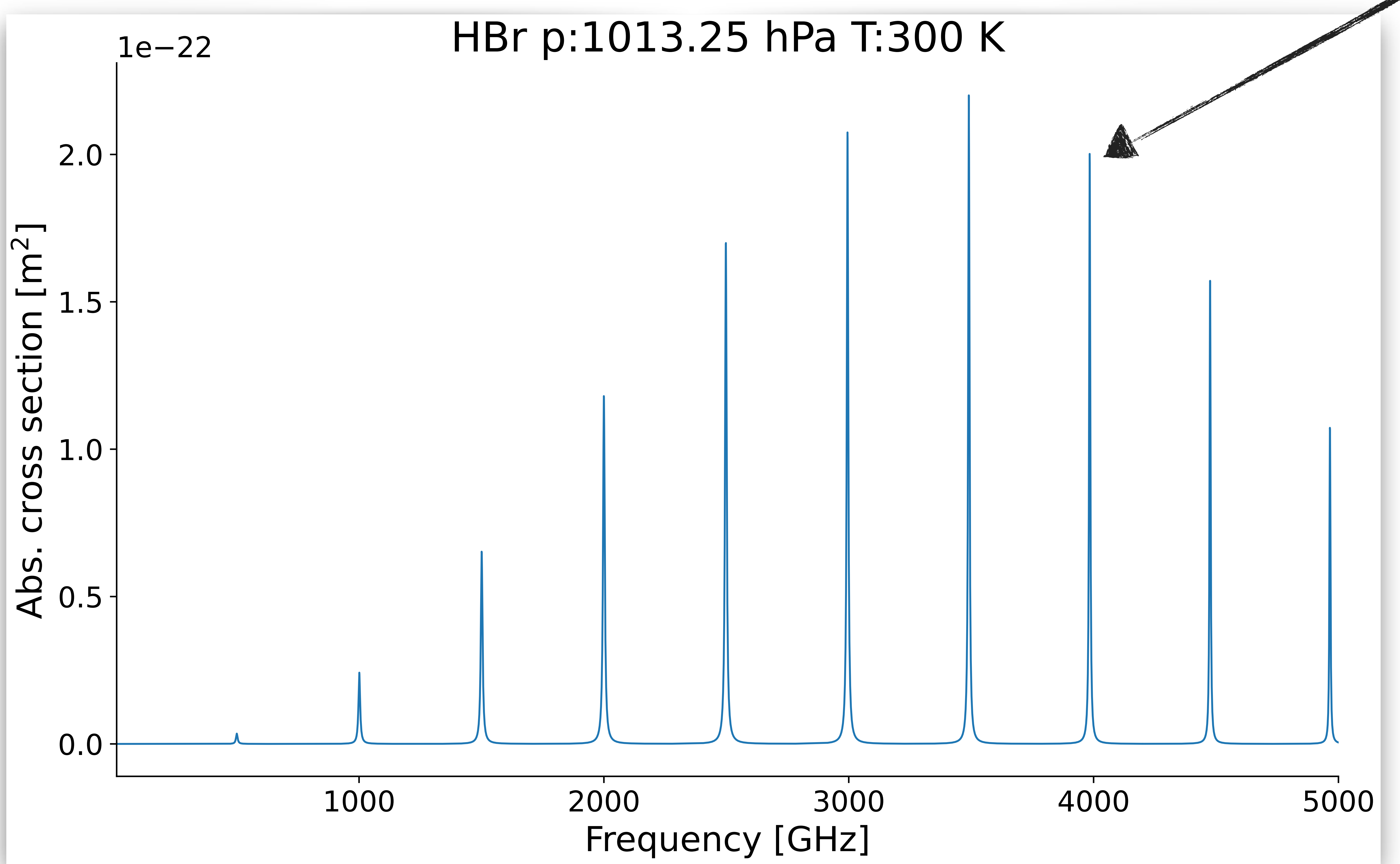
TYPICAL SPECTRAL QUANTITIES, UNITS AND ORDER OF MAGNITUDE

Microwave (MW)	Frequency	ν	$\mathcal{O}(100\,\mathrm{GHz})$
Infrared (IR)	Wavenumber	$\tilde{\nu}$	$\mathcal{O}(1000\,\mathrm{cm}^{-1})$
	Wavelength	λ	$\mathcal{O}(15\,\mu\mathrm{m})$
Visible	Wavelength	λ	$\mathcal{O}(500\,\mathrm{nm})$

$$\tilde{\nu} = \frac{\nu}{c_0}$$

$$\lambda = \frac{c}{\nu}$$

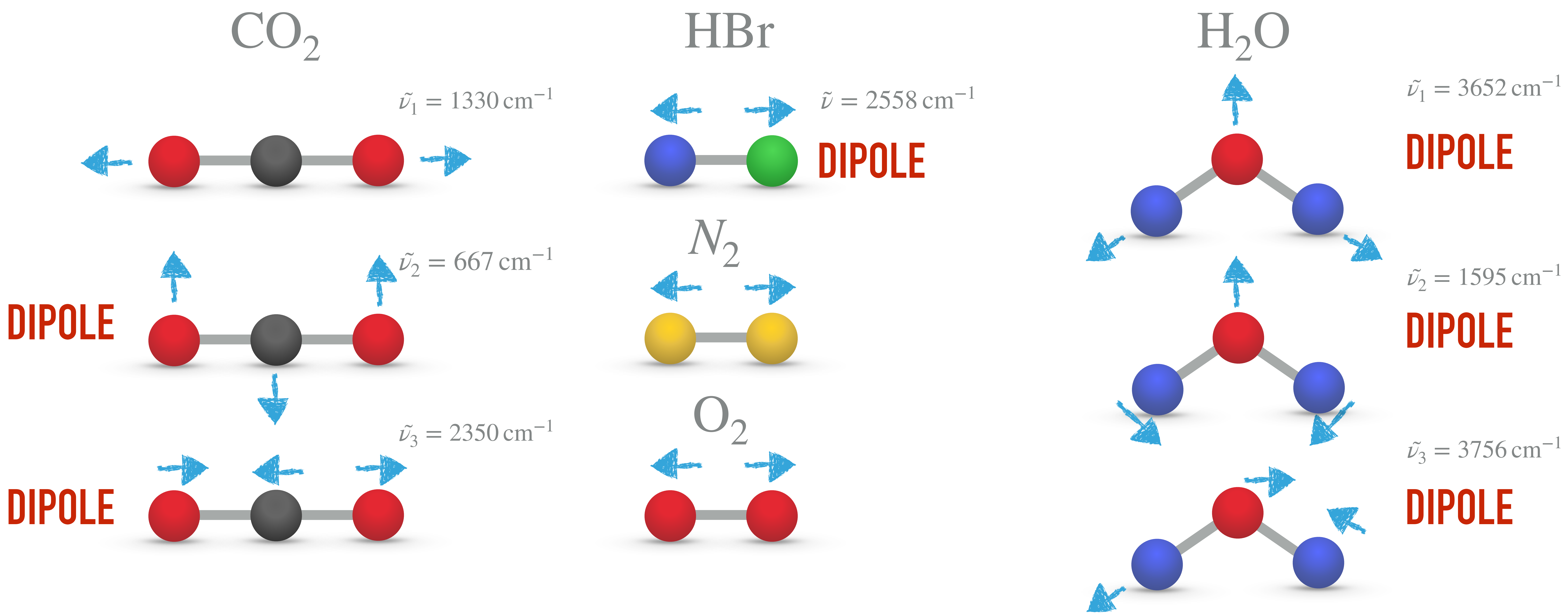
ROTATION SPECTRA



Transition from one state to another **not** the rotational state

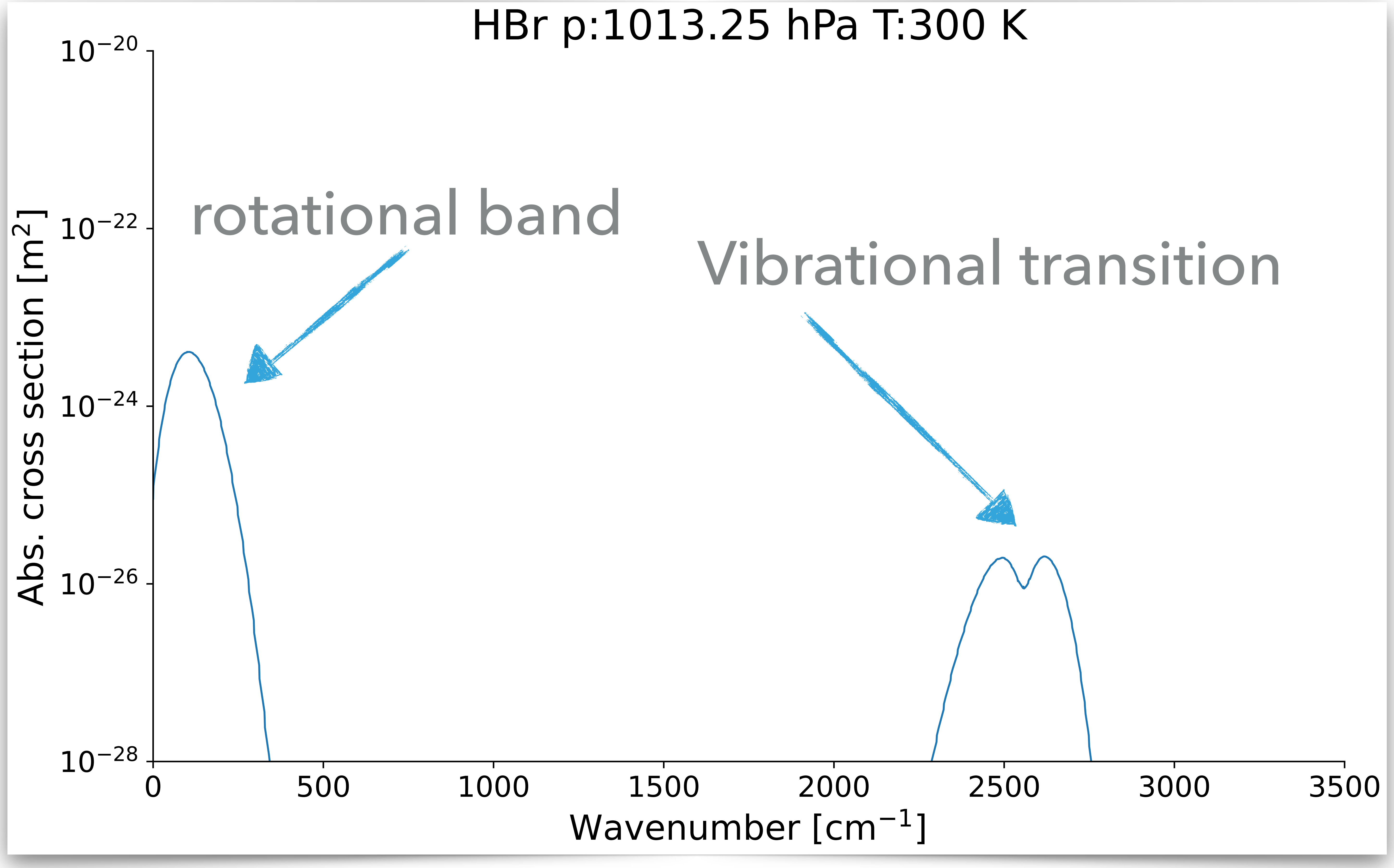
- Spectrum consists several discrete lines.
- Rotational states are discrete (quantised).

VIBRATION



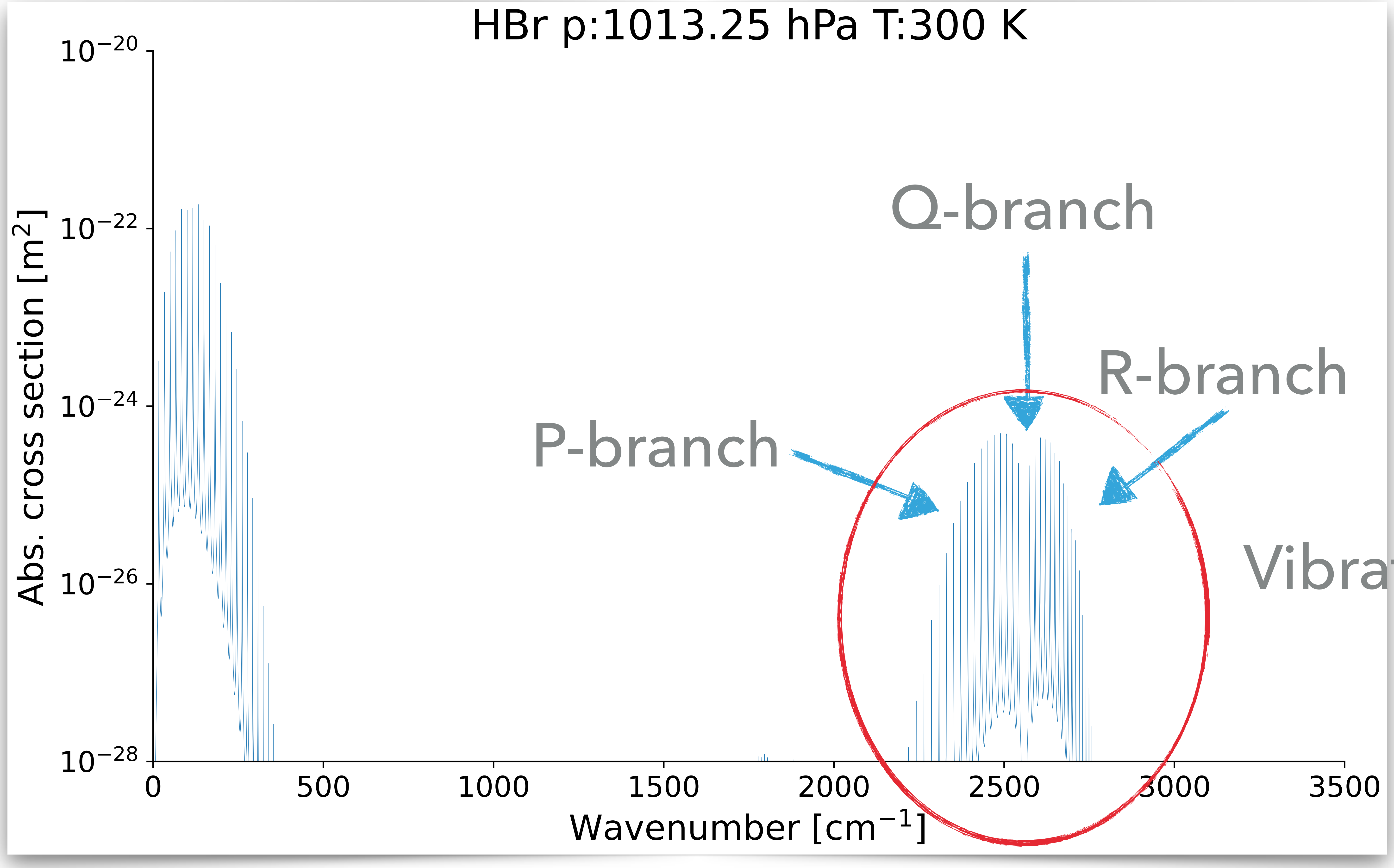
- Which of these vibrational modes induce a changing dipole?

VIBRATION (LOW-RES)



- Vibrational transitions occur at 10 to 100 times larger energy levels than rotational transitions.
- Vibrational transitions are also quantised.

VIBRATION (HI-RES)



Vibration-rotation spectrum

- Vibrational transitions in general never occur alone but are coupled with simultaneous rotational transitions.
- CO_2 is one of the exclusions.

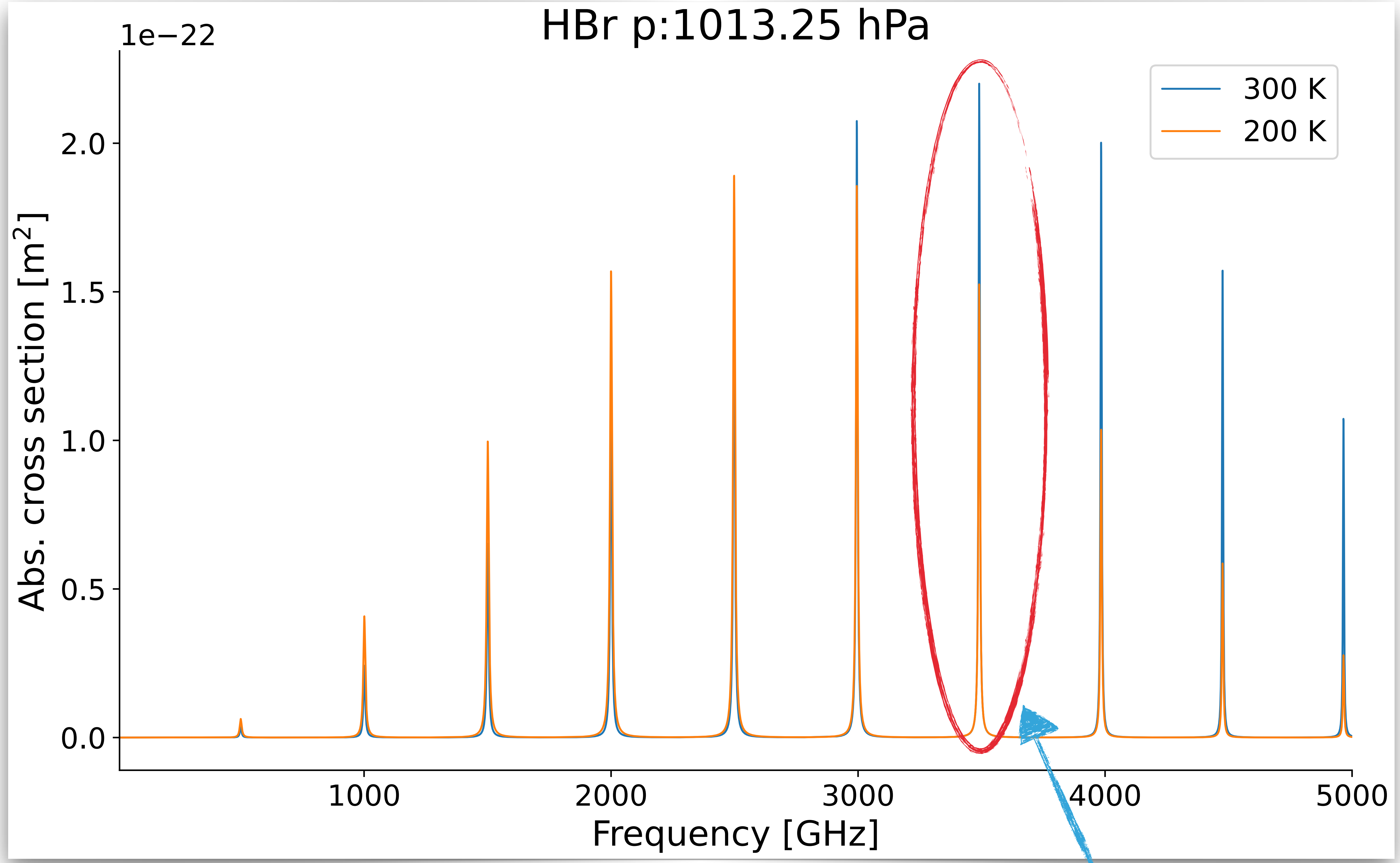
SWITCH TO EXERCISE 1

RECAP MOLECULE SPECTRA

- Permanent or induced dipole is needed for interaction with em radiation.
- Spectrum consists several discrete lines.
- Vibrational transitions occur at 10 to 100 times larger energy levels than rotational transitions.
- Vibrational transitions in general never occur alone but are coupled with simultaneous rotational transitions.
- Spectra change with temperature.

LINE STRENGTH

ABSORPTION LINE



- The absorption cross section of a given line

$$\hat{\sigma} = S_{fi}(T, \nu_{fi})\, \Phi(\nu_{fi} - \nu)$$

line strength

line shape

LINE STRENGTH

- The line strength S_{lu} is different for each transition.

$$S_{lu} = \boxed{\frac{8\pi^3}{3hc}}\boxed{\nu_{lu}|\mu_{lu}|^2 q_u}\boxed{\frac{e^{-\Delta E_{lu}/(k_B T)}}{Q(T)}}$$

fundamental constants

transition constants

temperature dependent

S_{lu} is the connection between radiative transfer and quantum mechanics

TRANSITION CONSTANTS

frequency (energy) of transition lu

$$\boxed{\nu_{lu}|\mu_{lu}|^2 q_u}$$

statistical weight of transition lu

probability of dipole transition lu derived from quantum mechanics

- Spectral line catalogues are collections of these transition parameters. There is one line in the catalogue for each spectral line (thousands for each molecule). The most well-known is the HITRAN catalogue.

TEMPERATURE DEPENDENCY

$$\boxed{\frac{e^{-\Delta E_{lu}/(k_B T)}}{Q(T)}}$$

Boltzmann factor

partition sum

$$\Delta E_{lu} = h\nu_{lu}$$

$$\Delta E_{lu} \gg k_b T \quad \Rightarrow e^{-\Delta E_{lu}/(k_B T)} \approx 0$$

$$\Delta E_{lu} \ll k_b T \quad \Rightarrow e^{-\Delta E_{lu}/(k_B T)} \approx 1$$

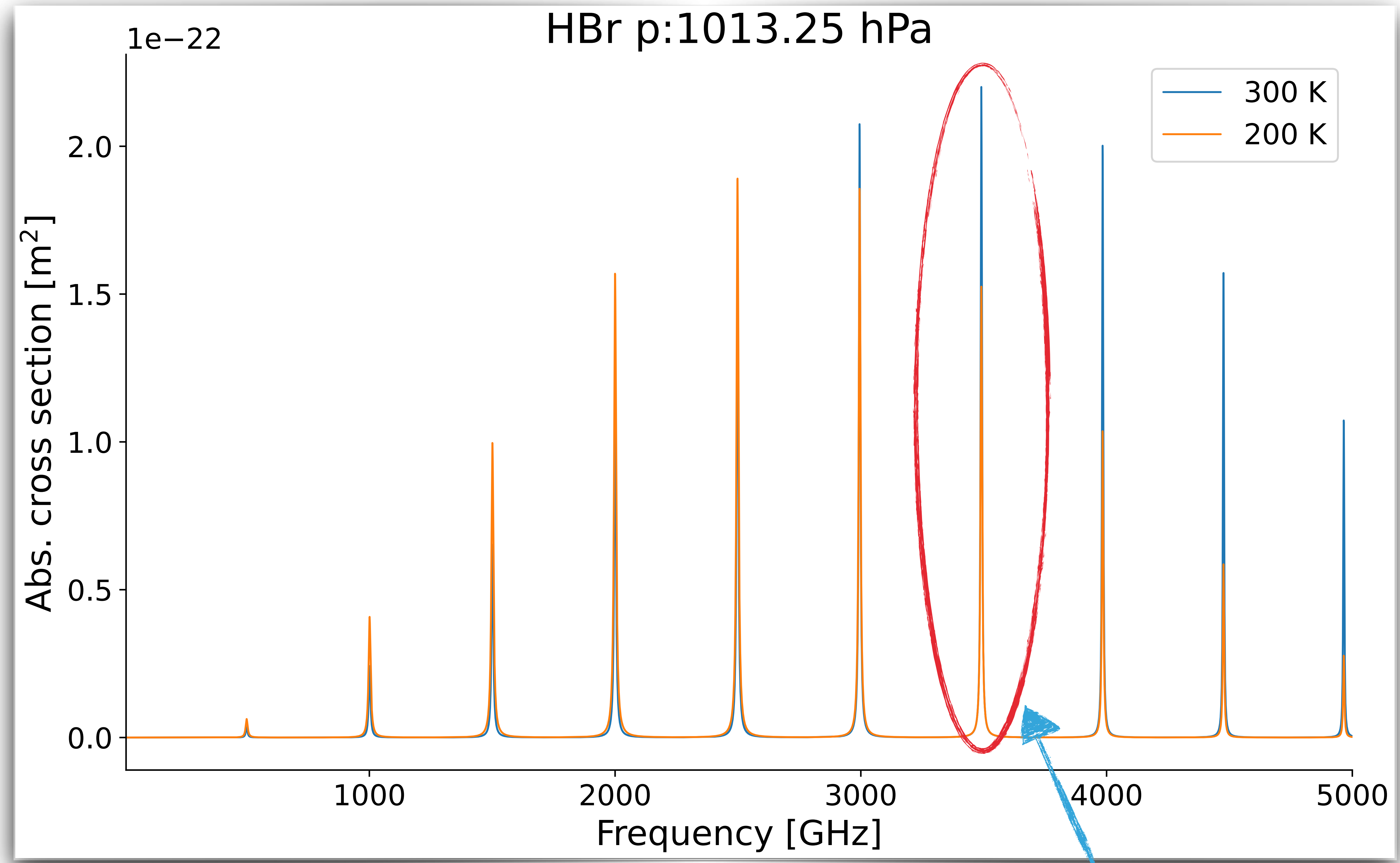
- Describes the probability of transition lu at given temperature T.
- $Q(T)$ is usually tabulated by the spectroscopic databases.

RECAP LINE STRENGTH

- Transition constants define basic strength of the absorption line and at which frequency the transition happens.
- Transition constants are derived from quantum mechanics.
- Temperature controls the resulting strength of the line.

LINE SHAPE

ABSORPTION LINE



absorption line

- The absorption cross section of a given line

$$\hat{\sigma} = S_{fi}(T, \nu_{fi})\, \Phi(\nu_{fi} - \nu)$$

line strength

line shape