

Molecular Spectroscopy

Data for Modelling Atomic and Molecular Processes in Plasmas

Joint IAEA-ICTP School

18 – 22 March 2024

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Uses of Molecular Spectroscopy

- Diagnostics, monitoring and classification:
 - Composition
 - Density
 - Temperature
- “Physical” structure
- Electronic structure
- Testing physical theories

This Lecture

Spectroscopy: **Rotational** **Vibrational** **(Electronic)**

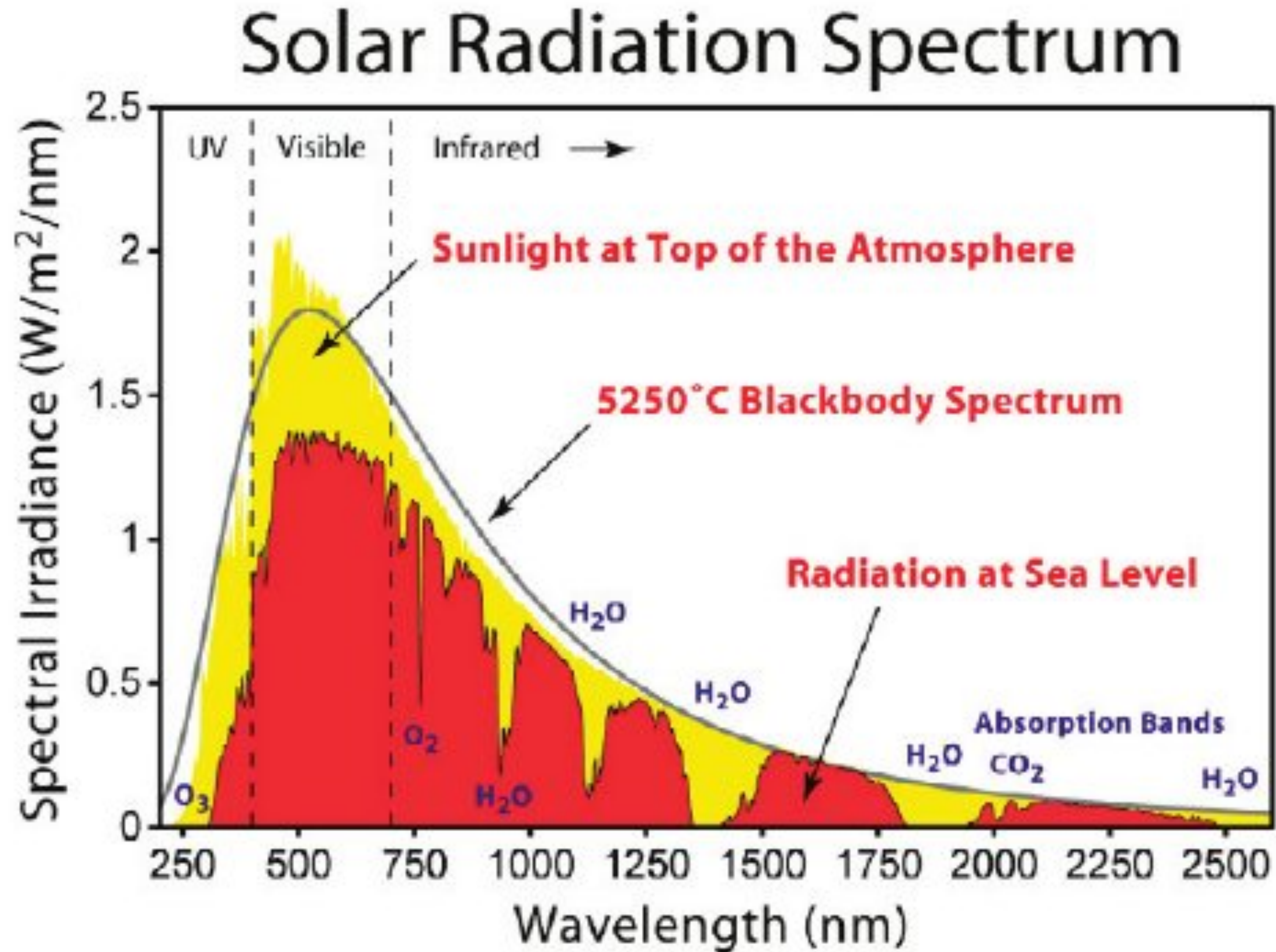
Focus on:

- Theory and meaning of molecular spectra
- Small molecules (esp. diatomics)
- Where the key formulae come from

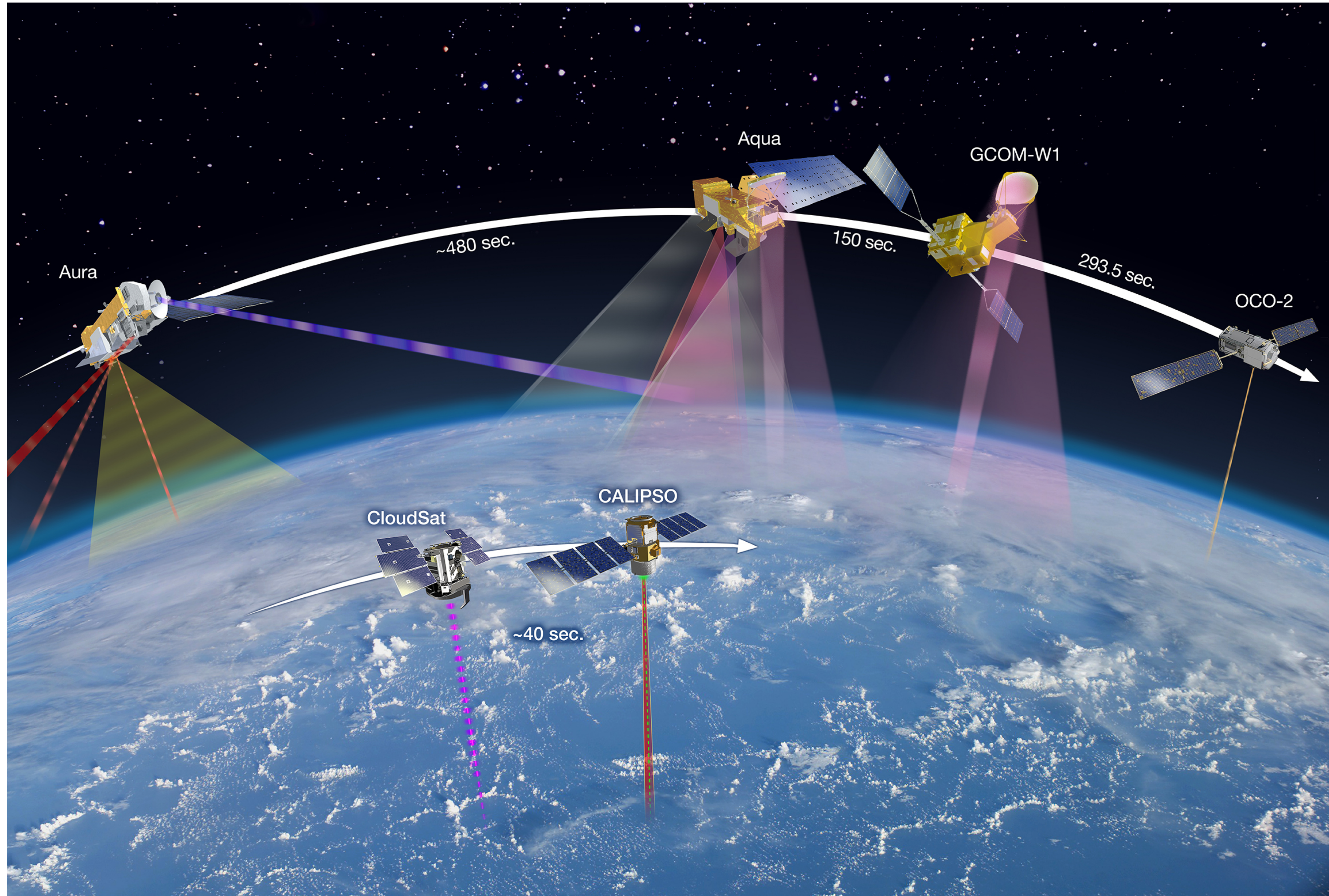
Not so much:

- Experimental techniques
- Modelling spectra, line shapes
- Condensed-matter spectroscopy

Remote Sensing of the Atmosphere

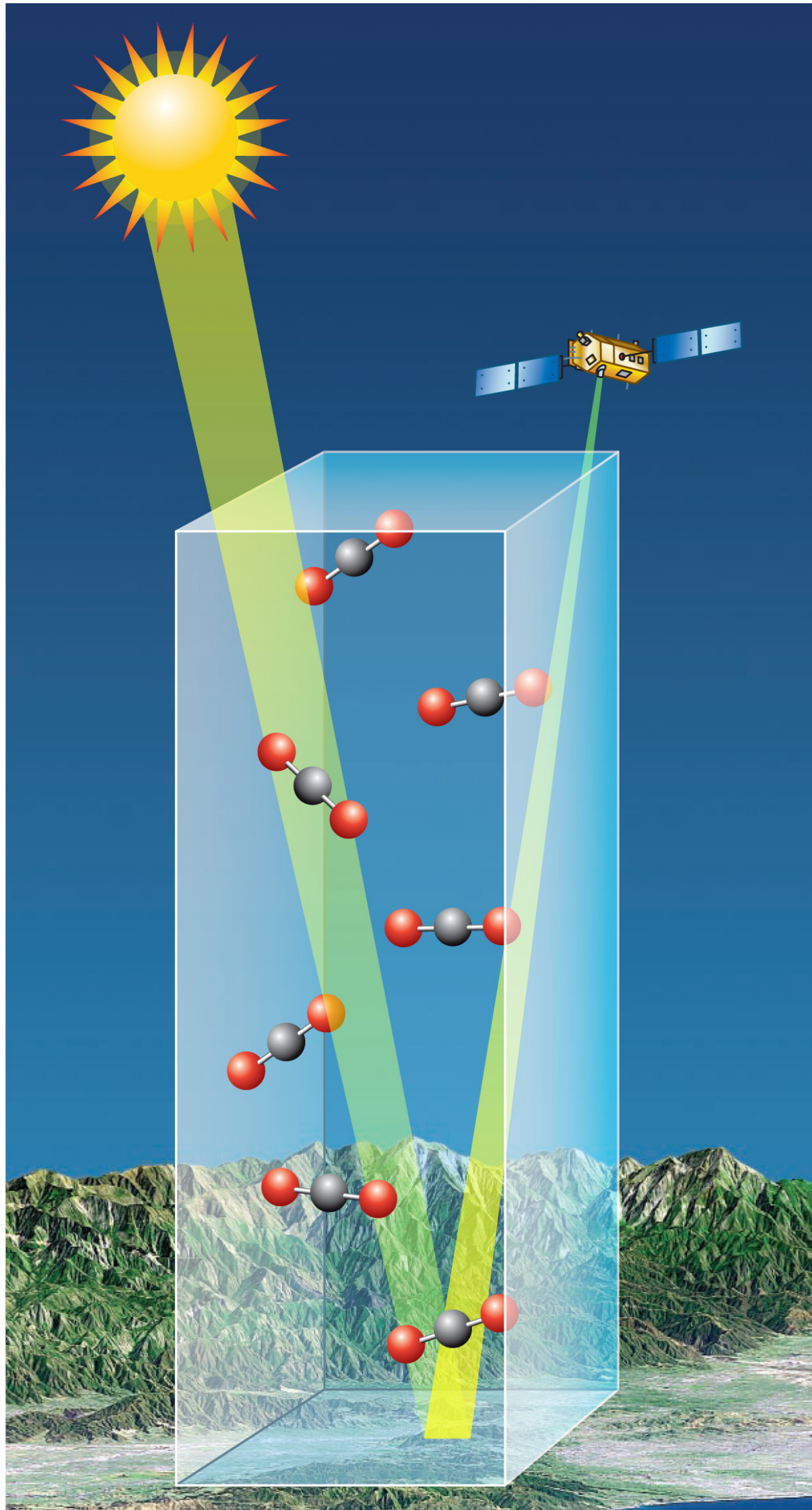


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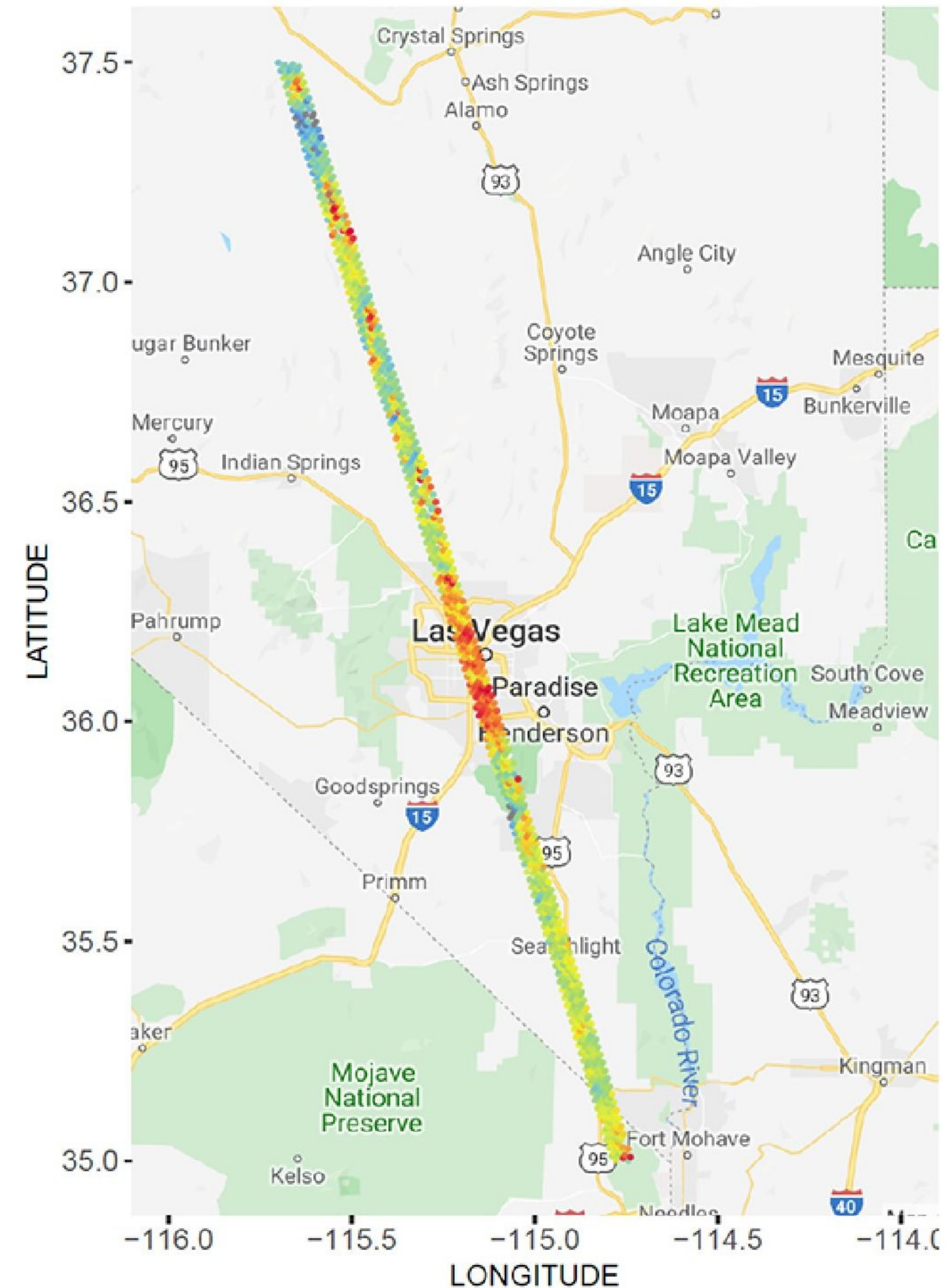
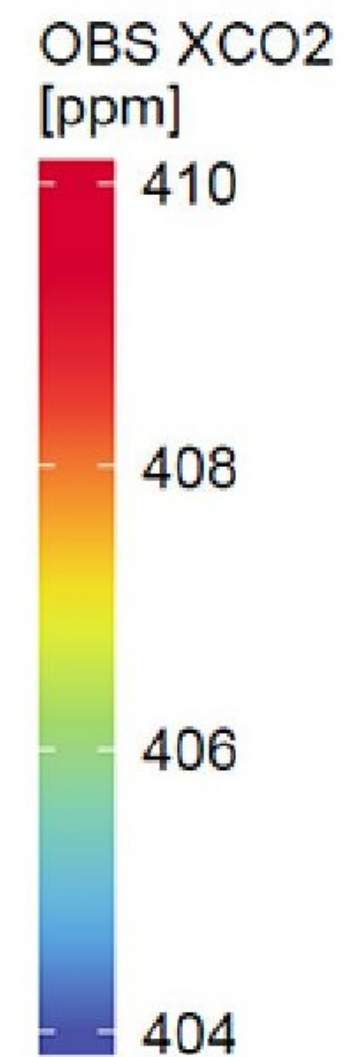
A-Train
(2013)

OCO-2: Orbiting Carbon Observatory

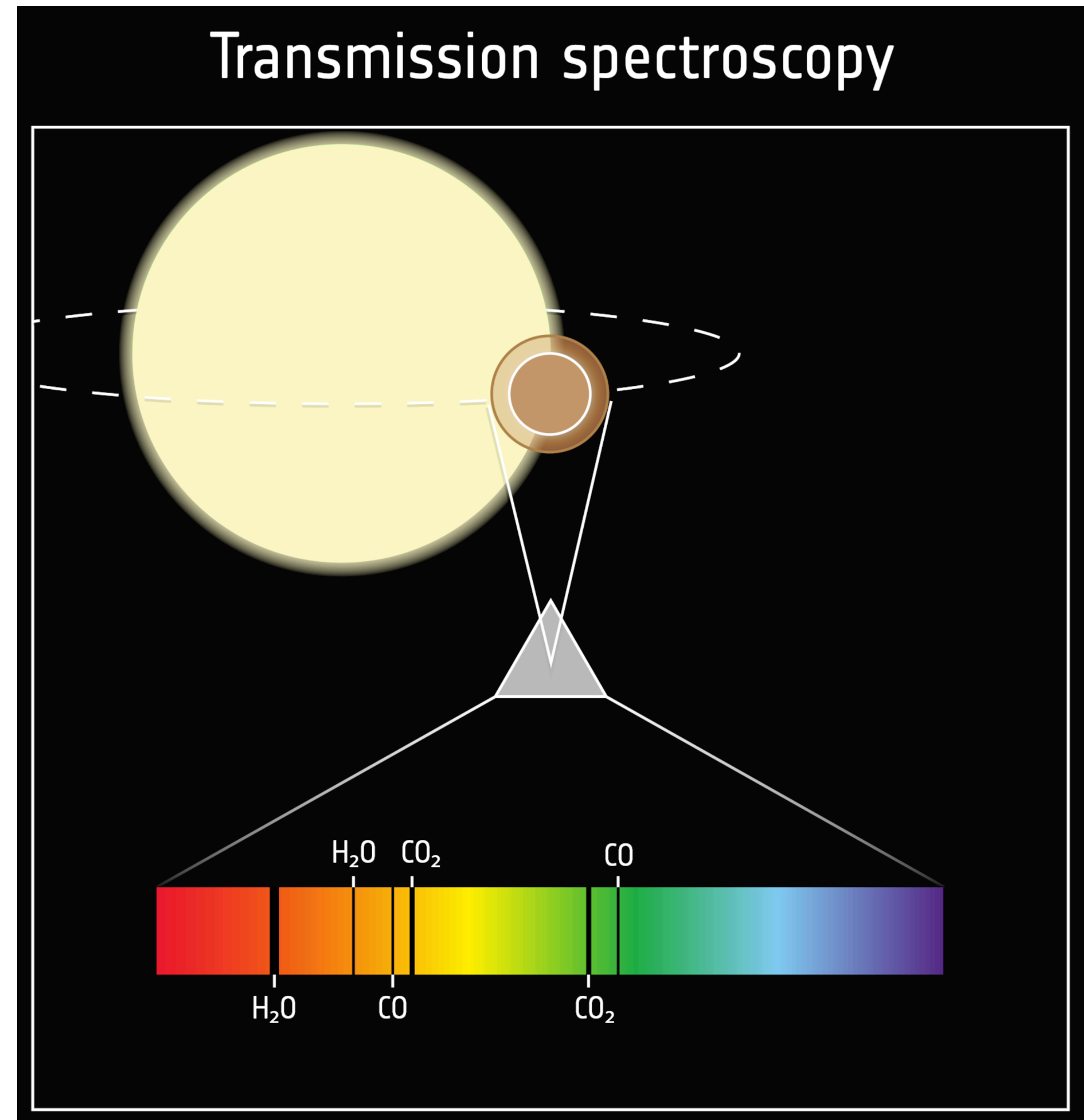
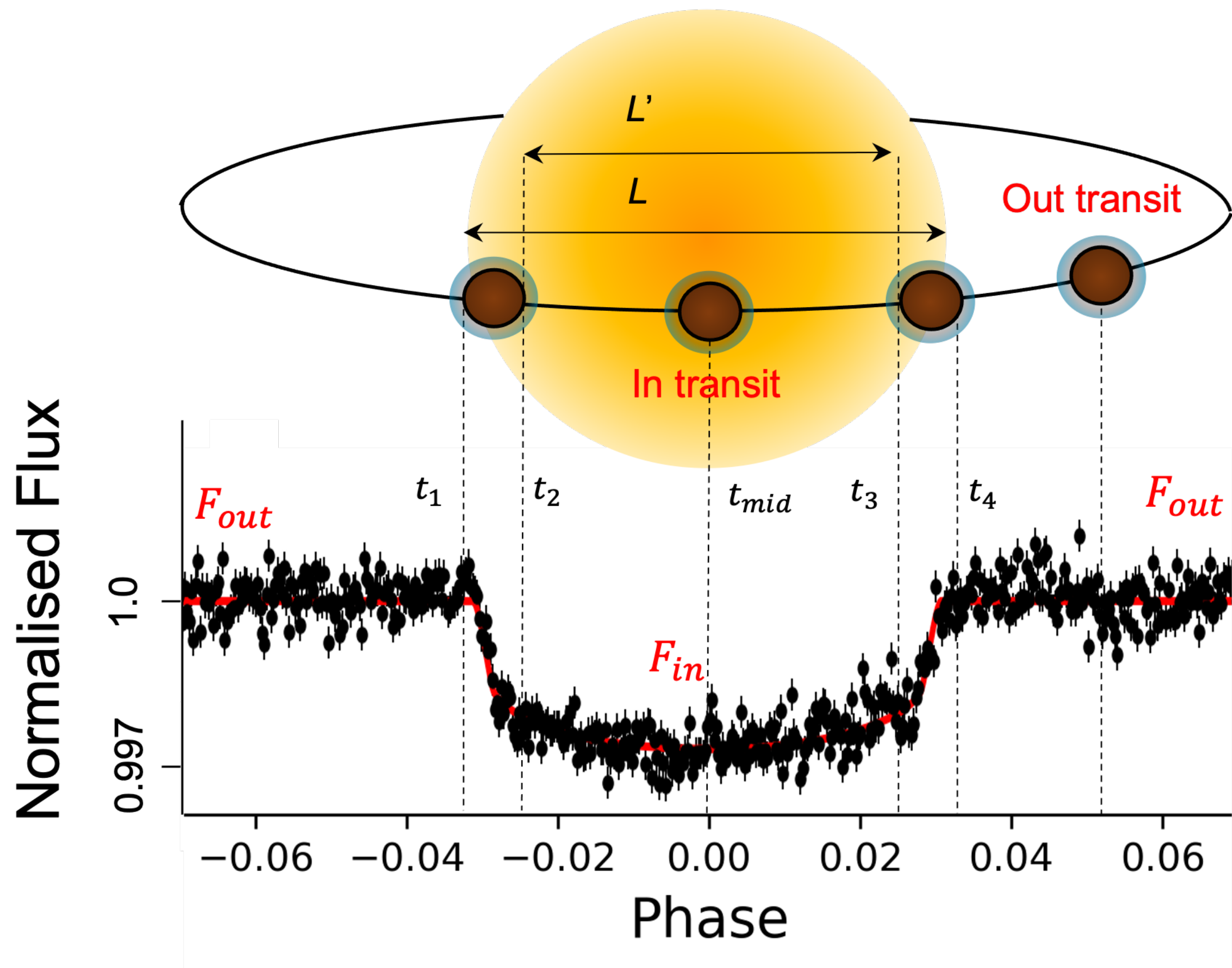


High temporal and spatial resolution of CO₂ column amounts

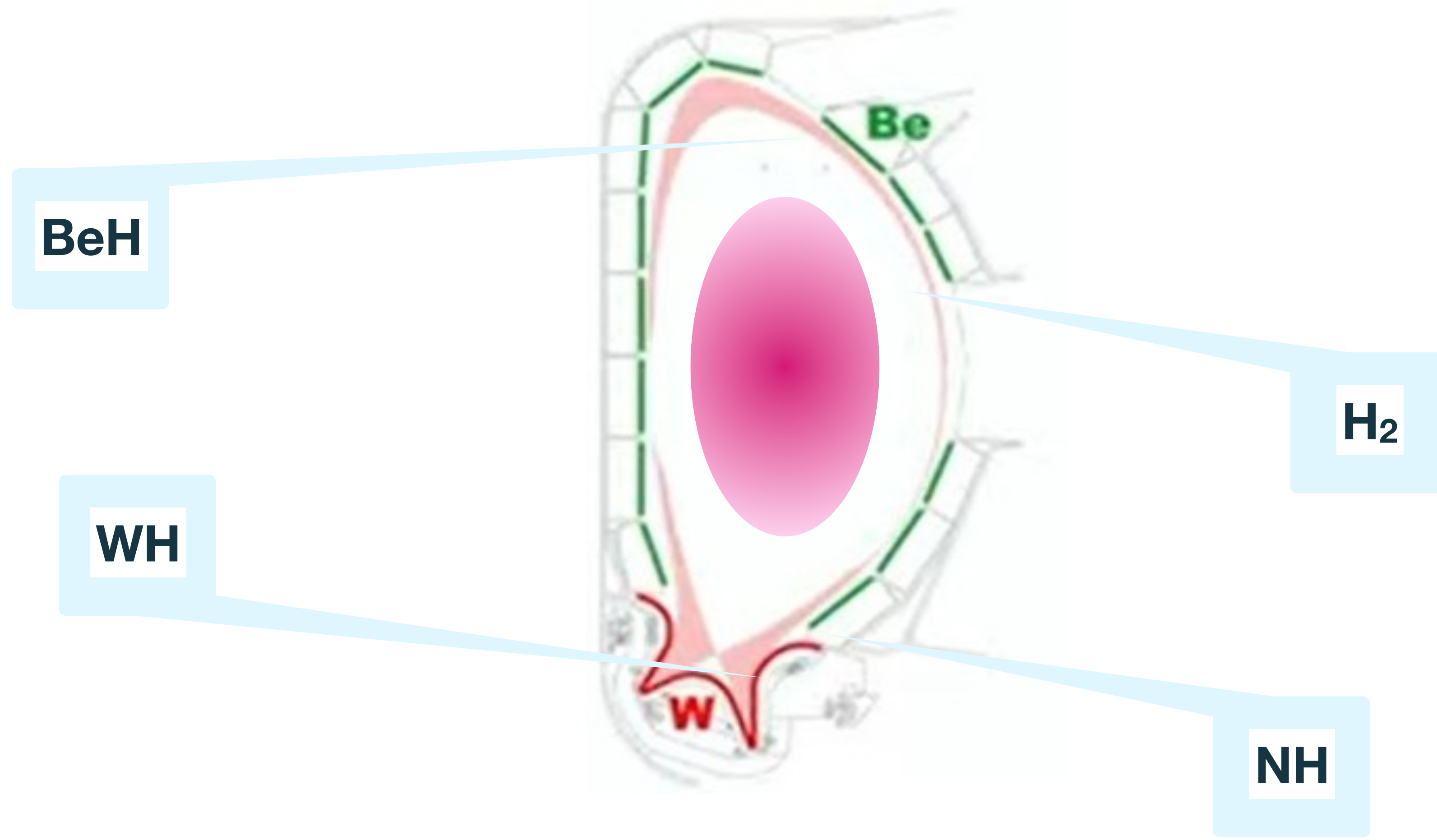
e.g. Las Vegas, 8 February 2018



Exoplanet Spectroscopy



Fusion Plasma Spectroscopy



The molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j<i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{iA}} + \frac{Z_B}{\rho_{iB}} \right) \right]$$

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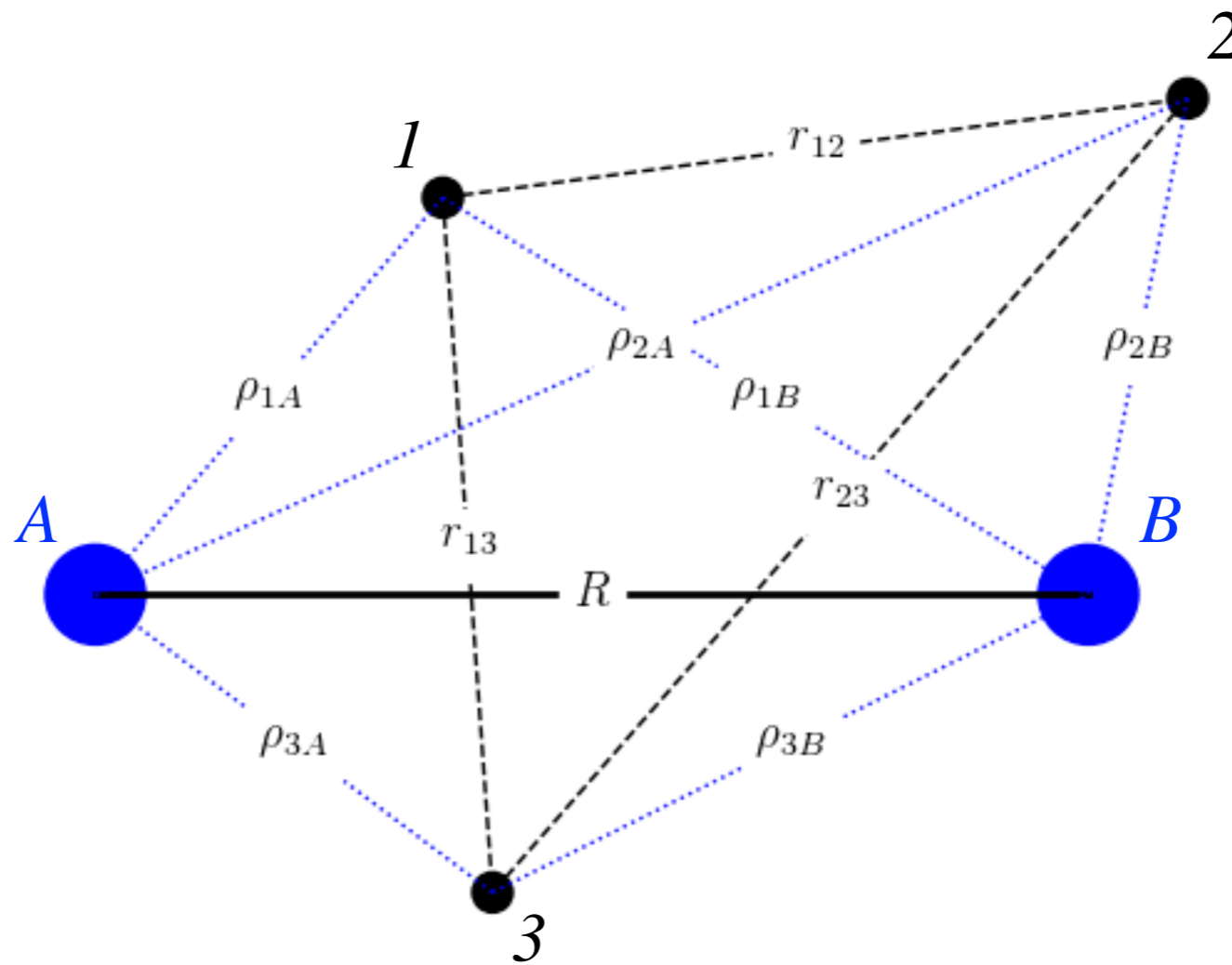
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is the potential energy of attraction between each electron and the two nuclei (separations ρ_{iA} and ρ_{iB}).

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Separating electronic and nuclear motion



The adiabatic approximation

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- The electrons adjust their positions rapidly following a change in the internuclear separation
- The kinetic energy of the nuclear motion is small compared to that of the electrons
- Treat it as a perturbation to the Hamiltonian for the rigid molecule: $\hat{H} = \hat{H}_0 + \hat{T}_{\text{nuc}}$

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- The *adiabatic approximation*: factorize the total molecular wavefunction into the product of a nuclear part and an electronic part: $\psi(r_i, R_\alpha) = \chi(R_\alpha) \cdot \phi(r_i; R_\alpha)$

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- The electronic wavefunction, $\phi(r_i; R_\alpha)$, depends *parametrically* on the nuclear positions, R_α : the effect of the nuclear *velocities* is ignored

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This can only hold if each side is equal to some constant, $E_n^{(0)}$:

$$\hat{H}_0 \phi = E_n^{(0)} \phi \quad \text{and} \quad (\hat{T}_{\text{nuc}} + E_n^{(0)}) \chi = E_{n,m} \chi$$

The potential energy curve

- Solve the electronic Schrödinger equation,

$$\hat{H}_0 \phi_n(r_i; R_\alpha) = E_n^{(0)} \phi_n(r_i; R_\alpha)$$

for different nuclear geometries, R_α , to obtain the *potential energy curve* of the n th state.

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- Then solve for the nuclear motion:

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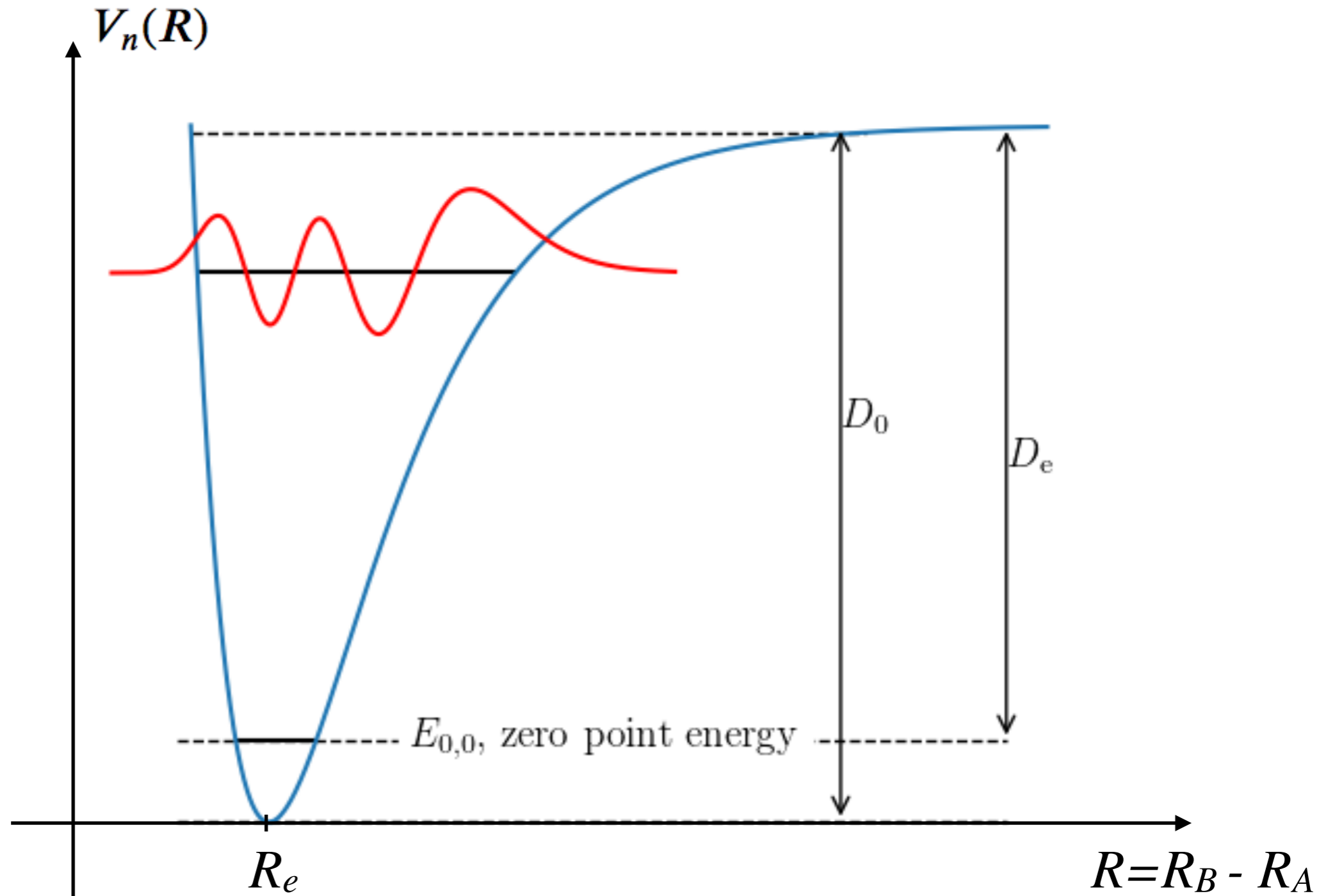
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From now on, we will relabel $E_n^{(0)}$ as $V_n(R)$.

The potential energy curve



Separating vibration and rotation

- The Schrödinger equation governing the nuclear motion is:

$$\left[-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V_n(R) \right] \chi_{n,m}(R_\alpha) = E_{n,m} \chi_{n,m}(R_\alpha).$$

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- In the centre-of-mass frame this becomes:

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- Note that the potential energy does not depend on the angular components of \mathbf{R} : it is *spherically symmetric*.
- So the nuclear Schrödinger equation is separable, as for the hydrogen atom:

$$\chi(\mathbf{R}) \equiv \chi(\mathbf{R}, \theta, \phi) = S(\mathbf{R}) \cdot Y(\theta, \phi)$$

Separating vibration and rotation

- We then have two equations:

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + J(J+1)Y = 0$$

for $J = 0, 1, 2, \dots$ describes the molecule's rotation and $Y(\theta, \phi)$ are the *spherical harmonic* functions.

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- and

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{dS}{dR} \right) + \frac{2\mu}{\hbar^2} \left(E - V_n(R) - \frac{J(J+1)\hbar^2}{2\mu R^2} \right) S = 0$$

describes the molecule's vibration.

Rotational spectroscopy

The rigid rotor

- A rigid rotor is one with a fixed internuclear separation (bond length), R_e :

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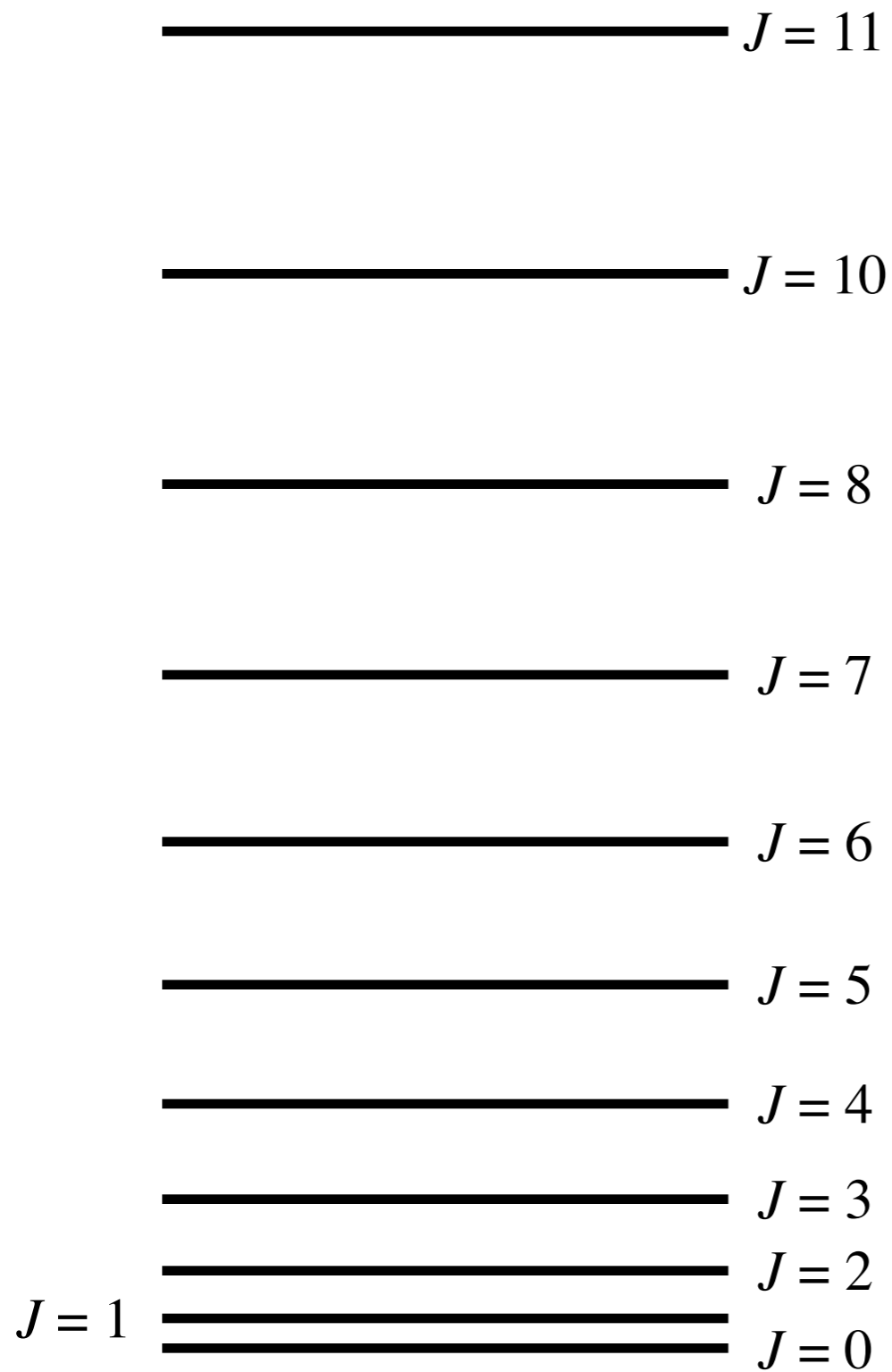
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- Spectroscopists like to use term values, $F(J) = E/hc$, in units of cm^{-1} :

$$F(J) = B_e J(J+1), \quad B_e = \frac{\hbar^2}{2hc\mu R_e^2} = \frac{h}{8\pi^2 cI},$$

where $I = \mu R_e^2$ is the moment of inertia.

The rigid rotor



$$F(J) = B_e J(J + 1)$$

The rigid rotor populations

- The equilibrium populations of the rotational energy levels are given by statistical mechanics:

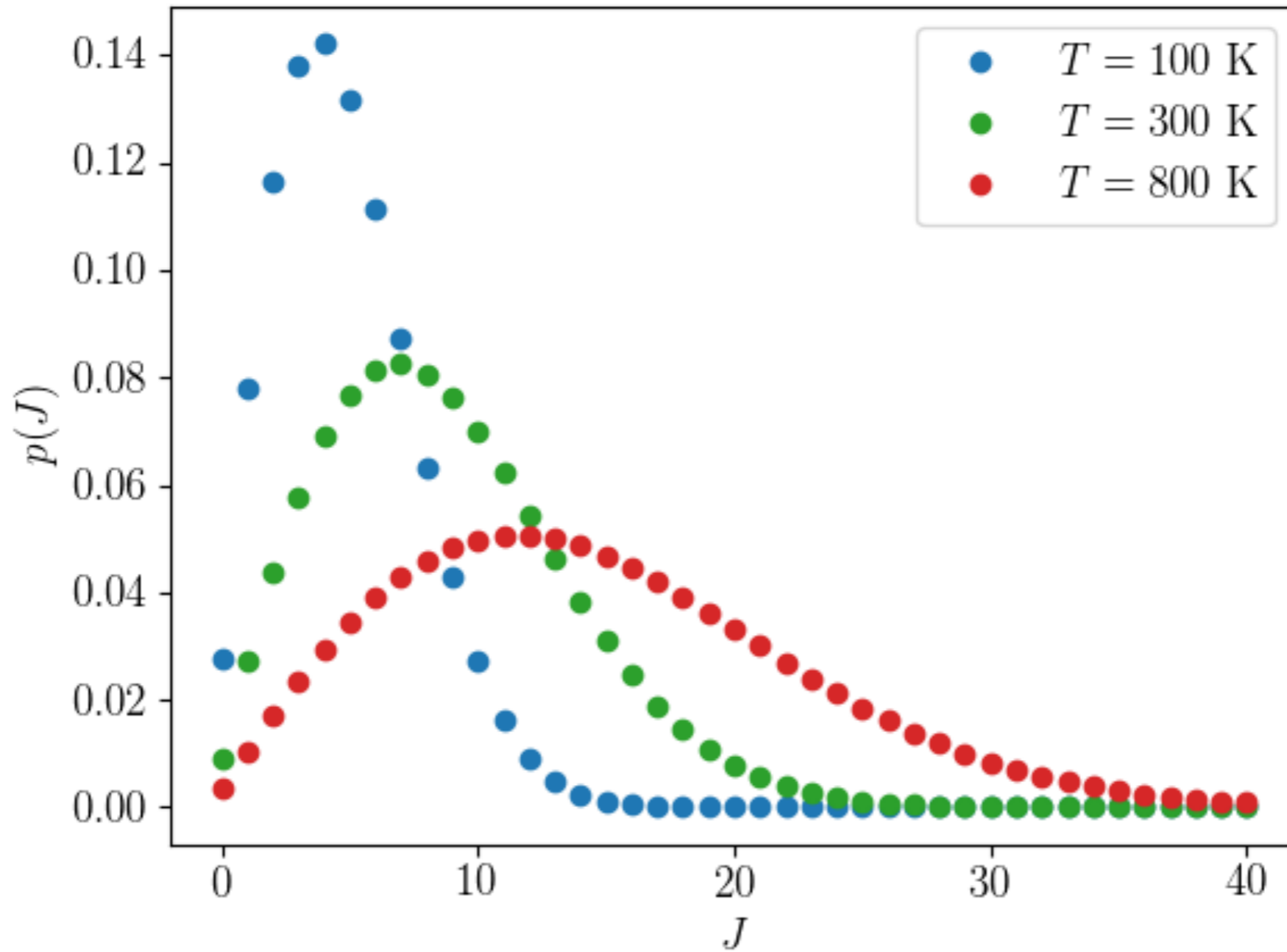
$$p(J) = \frac{g_J \exp\left(-\frac{E_J}{k_B T}\right)}{q(T)},$$

where $g_J = 2J+1$ is the degeneracy of the J^{th} energy level and

$$q(T) = \sum_{J=0}^{\infty} g_J \exp\left(-\frac{E_J}{k_B T}\right)$$

is the temperature-dependent *partition function*.

The rigid rotor populations



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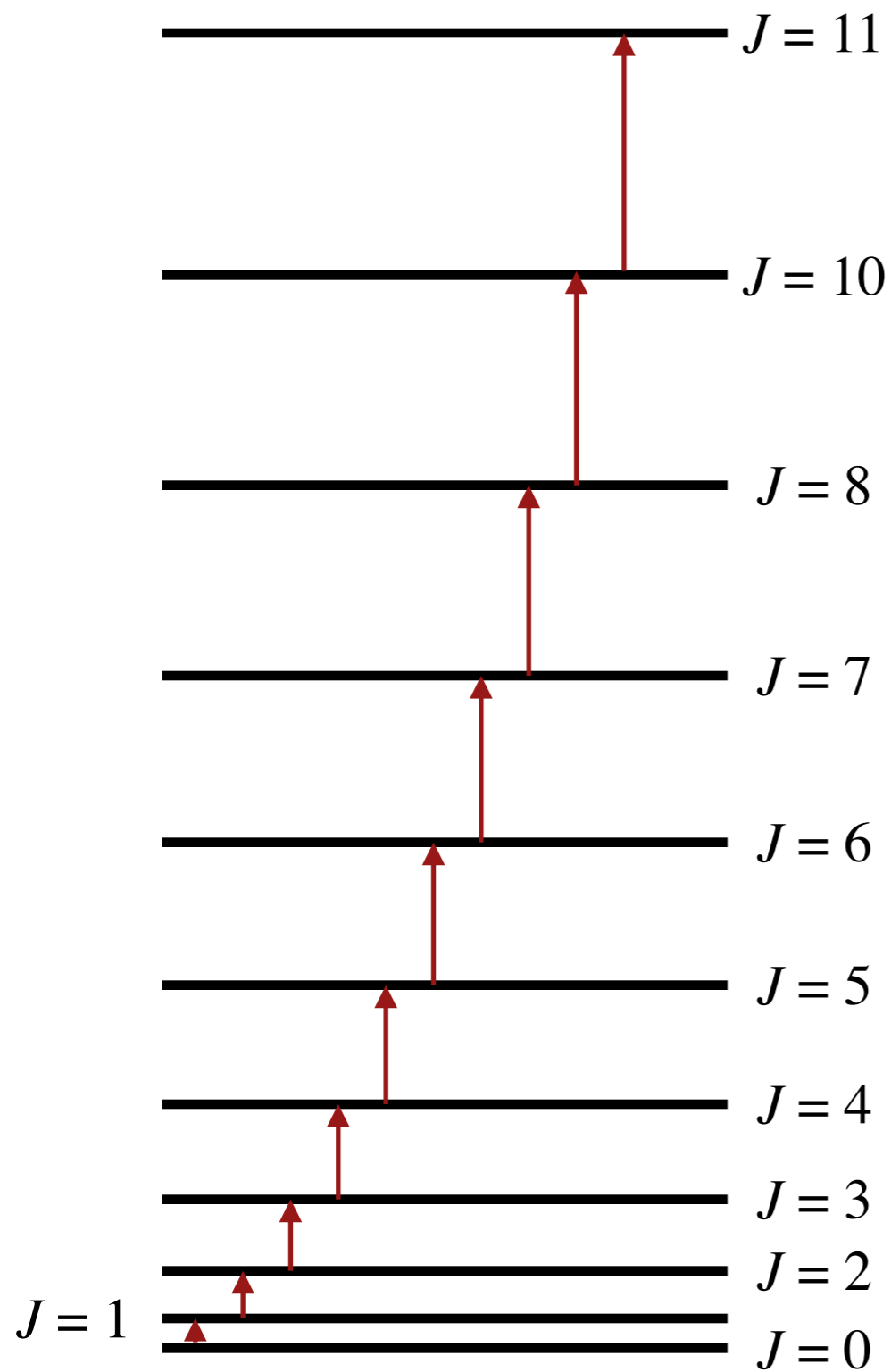
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- Lines, evenly spaced every $2B_e$
- Corresponds to:
 - Wavenumbers: $0.1 - 100 \text{ cm}^{-1}$;
 - Frequency: $10^9 - 10^{12} \text{ Hz}$ (“Gigahertz–Terahertz radiation”);
 - Wavelength: $1 \text{ }\mu\text{m} - 10 \text{ cm}$ (“microwaves”).

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- ◉ Transition intensities depend on:
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 - ◉ The population difference between the two states involved;
 - ◉ The permanent electric dipole moment of the molecule, μ_0 ;
 - ◉ A *Hönl-London factor*: for a linear molecule with no electronic angular momentum projection along the internuclear axis, this is J or $J + 1$ for $\Delta J = -1$ and $\Delta J = +1$ respectively.

The rigid rotor spectrum

- In absorption ($\Delta J = +1$), the absorption cross section is:

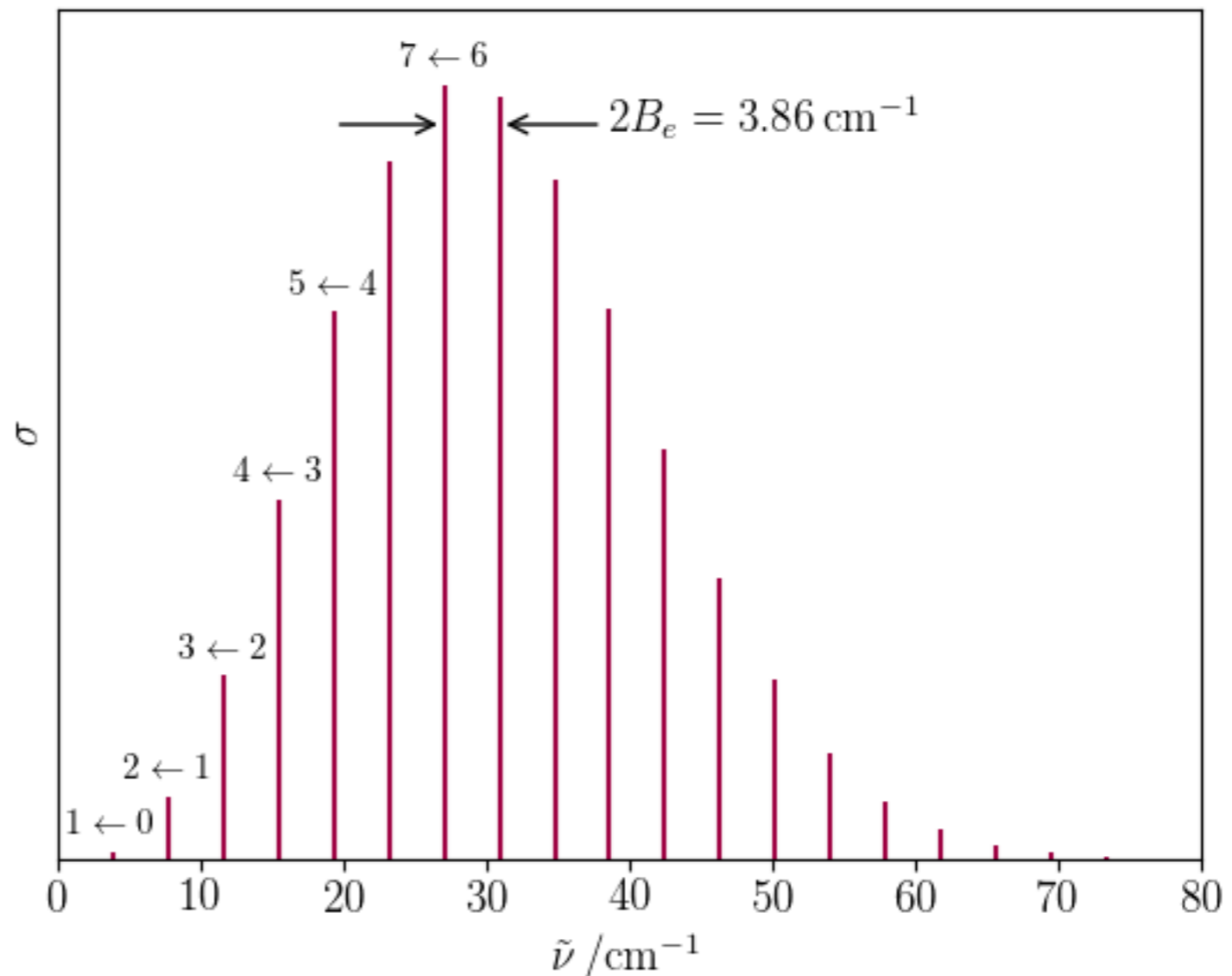
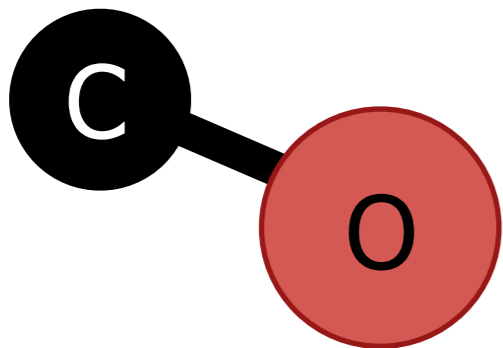
$$\sigma \propto \mu_0 \frac{2B_e(J+1)^2}{q(T)} \exp\left(-\frac{F(J)hc}{k_B T}\right) \left[1 - \exp\left(-\frac{\tilde{\nu}(J)hc}{k_B T}\right)\right]$$

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- In absorption ($\Delta J = +1$), the absorption cross section is:

$$\sigma \propto \mu_0 \frac{2B_e(J+1)^2}{q(T)} \exp\left(-\frac{F(J)hc}{k_B T}\right) \left[1 - \exp\left(-\frac{\tilde{\nu}(J)hc}{k_B T}\right)\right]$$

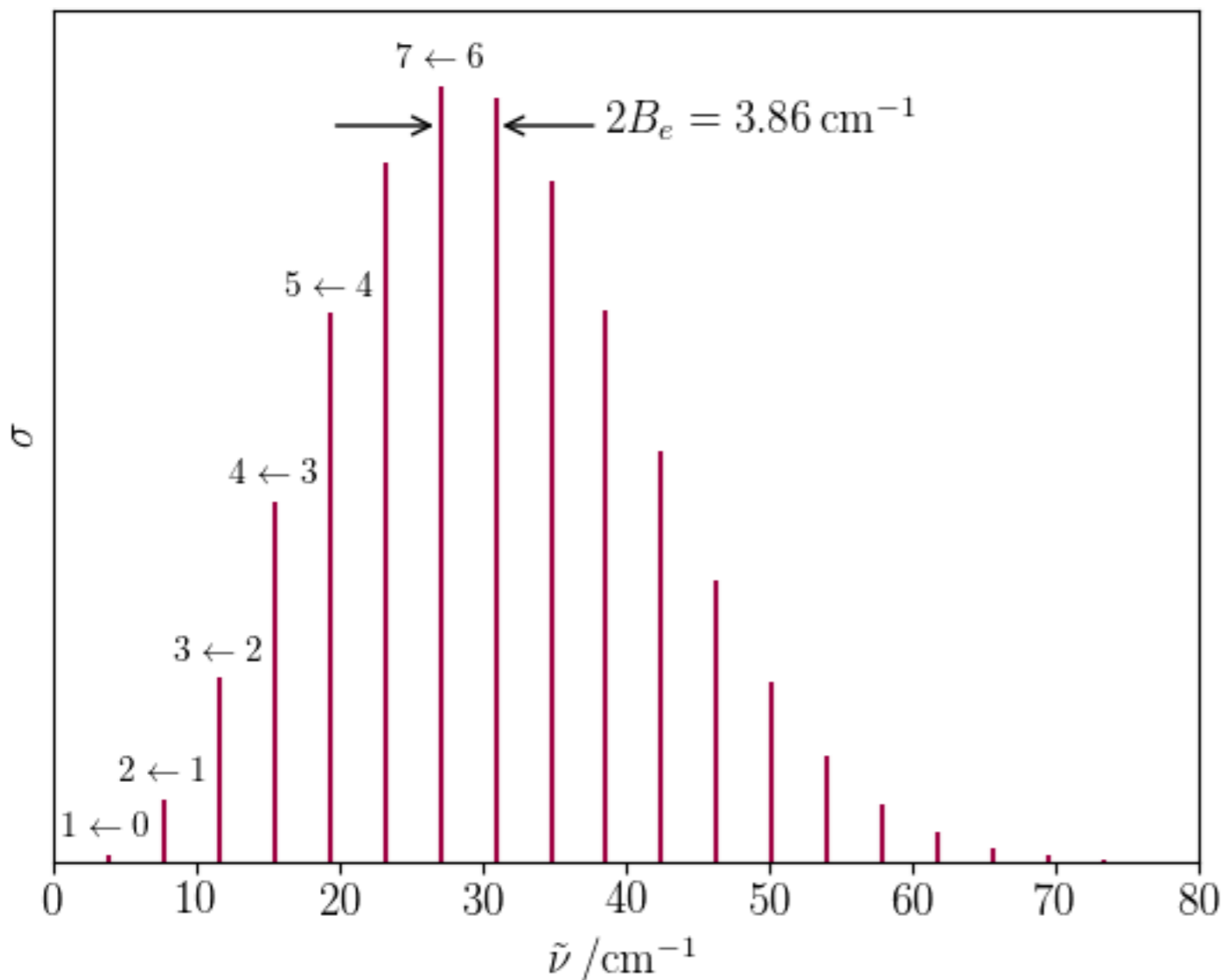
e.g. CO at 100 K:



The rigid rotor spectrum

- Estimating temperature: the most intense transition in absorption originates on the level

$$J_{\max} = \sqrt{\frac{3k_B T}{2B_e hc}} - \frac{\sqrt{3}}{2} \Rightarrow T \approx \frac{2B_e hc}{k_B} \left(\frac{J_{\max}}{\sqrt{3}} + \frac{1}{2} \right)^2$$



In this case, $J_{\max} = 6$
and estimate
 $T \approx 87 \text{ K}$

The rigid rotor spectrum

- In emission ($\Delta J = -1$), the emission intensity ($J' \rightarrow J' - 1$) in units of energy per unit time varies as

$$I_{\text{em}}(J') \propto 8B_e^4 J'^5 \exp\left(-\frac{B_v J'(J' + 1)}{k_B T}\right) \Rightarrow J_{\text{max}} \approx \sqrt{\frac{5k_B T}{2B_e hc}} - \frac{\sqrt{5}}{2}.$$

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- If the detector used to measure emission counts the number of emitted photons rather than their energy (e.g. a photoelectric detector):

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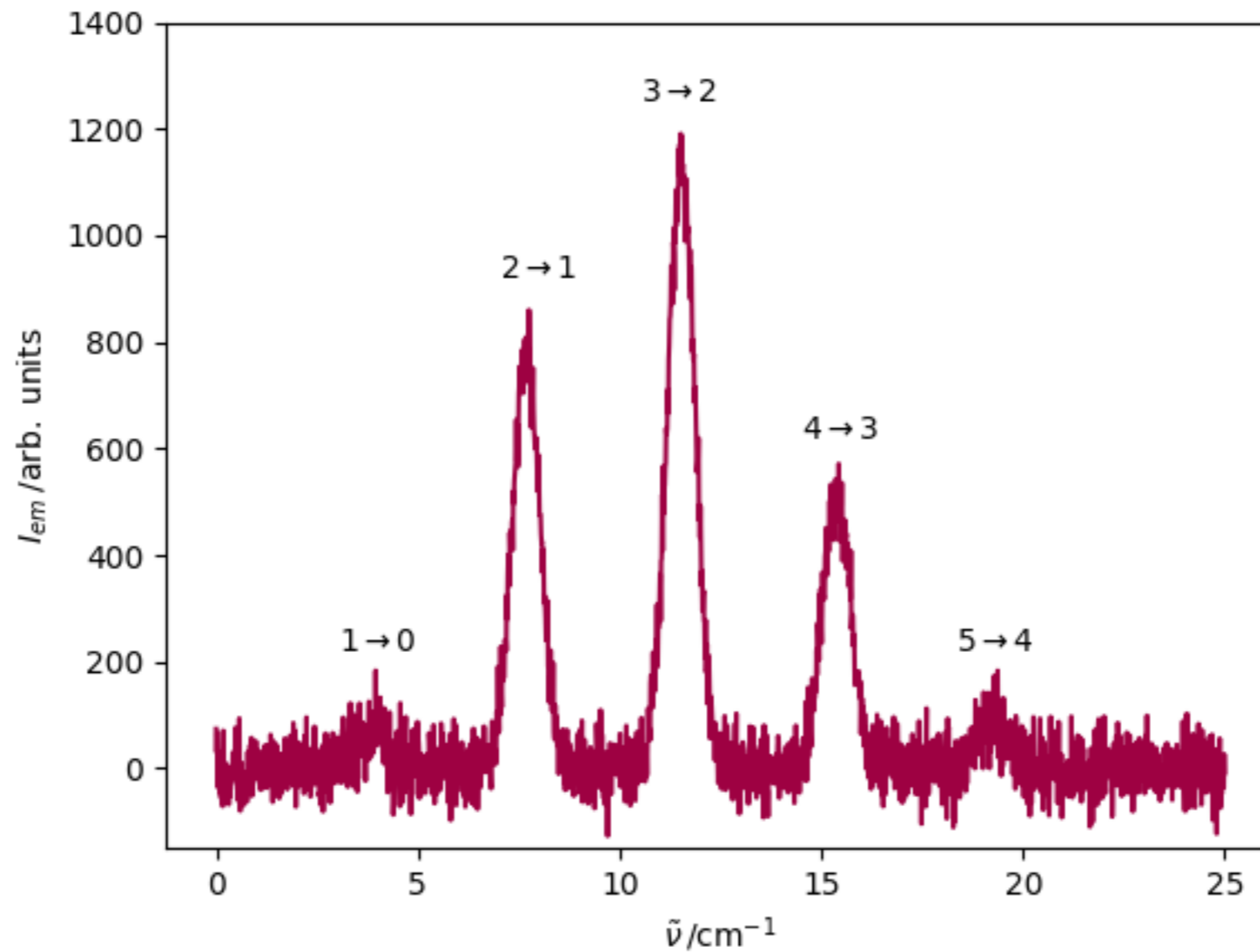
The rigid rotor spectrum

- Example: CO, excited by collisions with H_2 in molecular clouds in the ISM



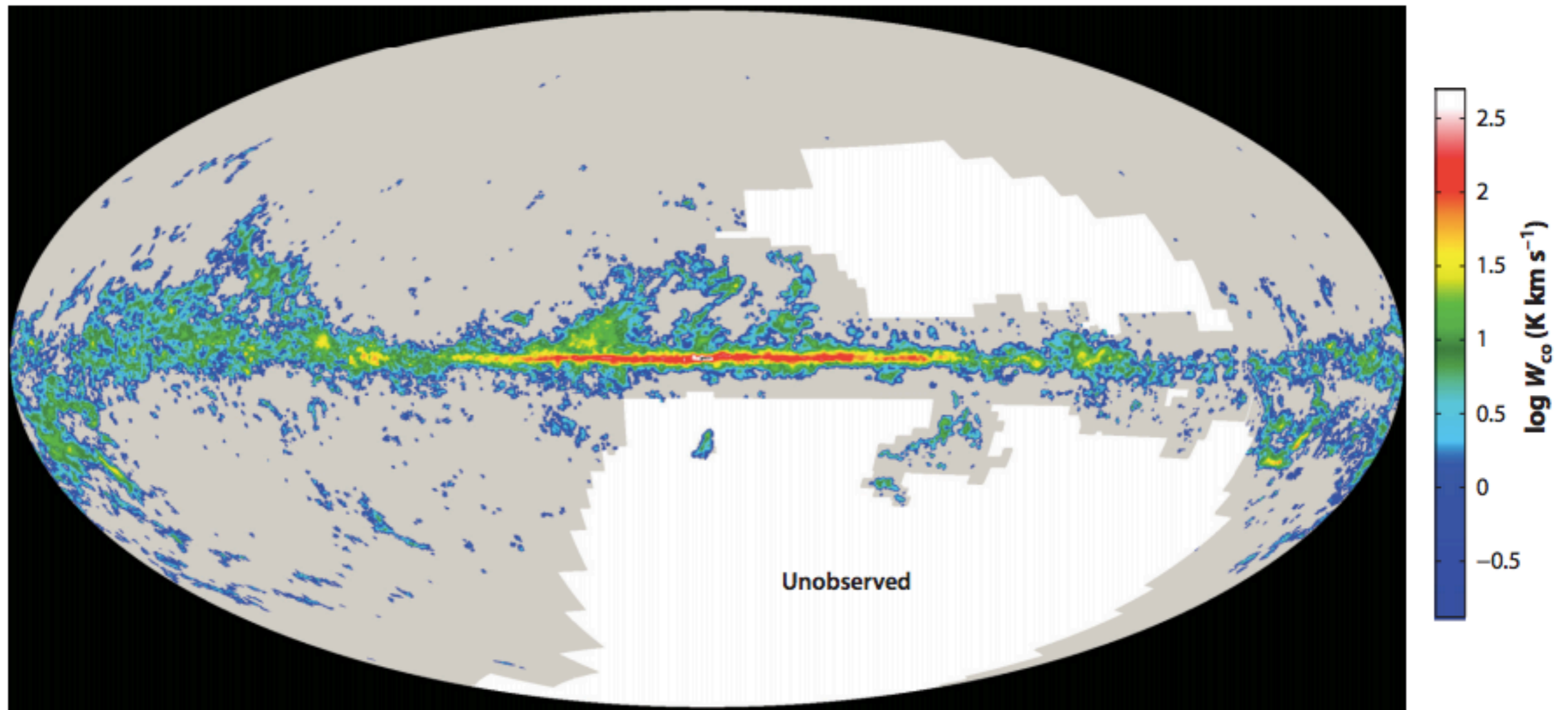
The rigid rotor spectrum

- Carbon monoxide (CO) emission spectrum



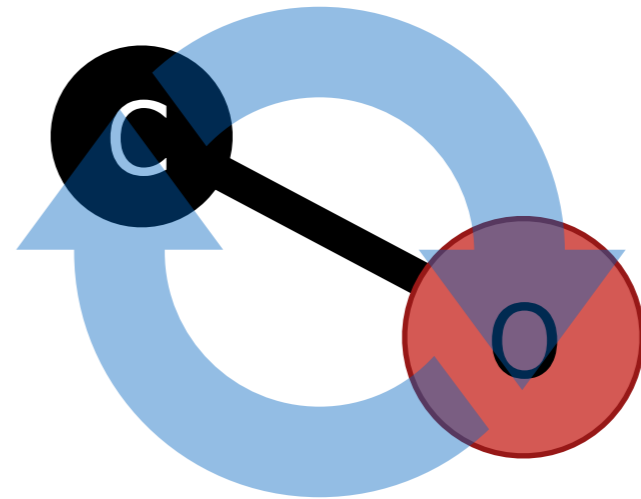
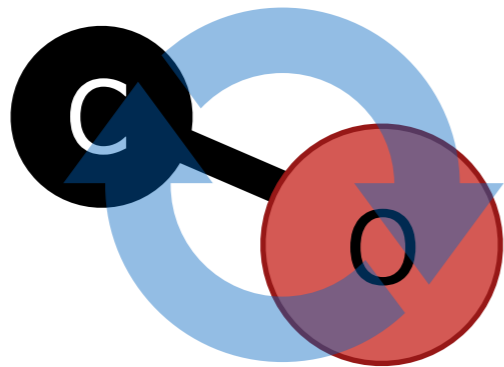
The rigid rotor spectrum

$J = 1 \rightarrow 0$ emission of CO in the Milky Way



Centrifugal distortion

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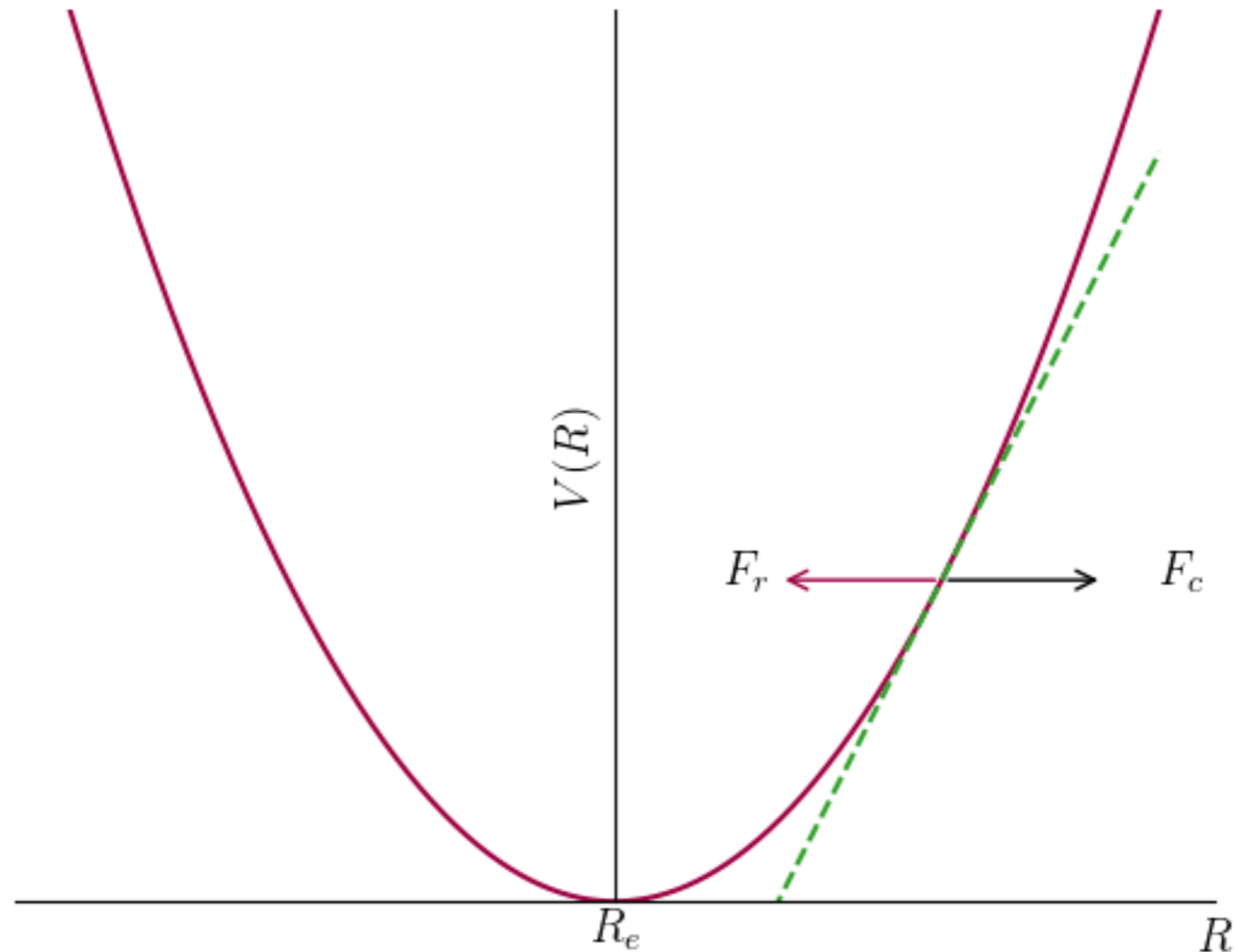
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This force is balanced by a restoring force due to the potential binding the atoms together:

$$F_r = -dV_n(R)/dR$$

Centrifugal distortion

- Near the bottom of the potential well, $V_n(R)$ may be approximated as a parabola: $V_n(R) \approx \frac{1}{2}k(R - R_e)^2$.



Centrifugal distortion

- For equilibrium in a given rotational state, J , we must have $F_c + F_r = 0$:

$$\frac{\hbar^2}{\mu R^3} J(J+1) = k(R - R_e)$$

$$\Rightarrow R = R_e + \frac{\hbar^2}{\mu k R^3} J(J+1)$$
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Now, since $\frac{\hbar^2}{\mu k R_e^4} \ll 1$, we may expand $R^{-2} = R_e^{-2}(1+x)^{-2} = R_e^{-2}(1 - 2x + 3x^2 - \dots)$:

$$\frac{1}{R^2} = \frac{1}{R_e^2} \left[1 - \frac{2\hbar^2}{\mu k R_e^4} J(J+1) + \frac{3\hbar^4}{\mu^2 k^2 R_e^8} J^2(J+1)^2 - \dots \right]$$

$$E = \frac{\hbar^2}{2\mu R_e^2} J(J+1) - \frac{\hbar^4}{2\mu^2 k R_e^6} J^2(J+1)^2 + \frac{3\hbar^6}{2\mu^3 k^2 R_e^{10}} J^3(J+1)^3 + \dots$$

Centrifugal distortion

- In terms of wavenumbers:

$$F(J) = B_e J(J + 1) - D_e J^2(J + 1)^2 + H_e J^3(J + 1)^3 + \dots$$

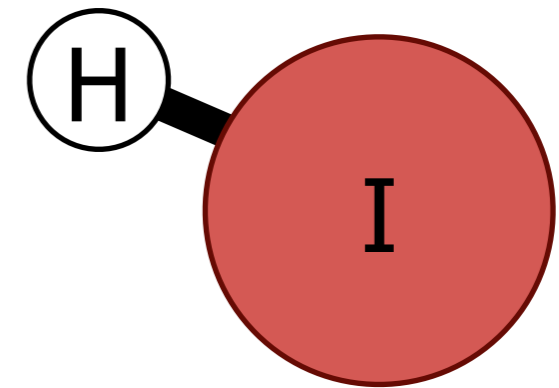
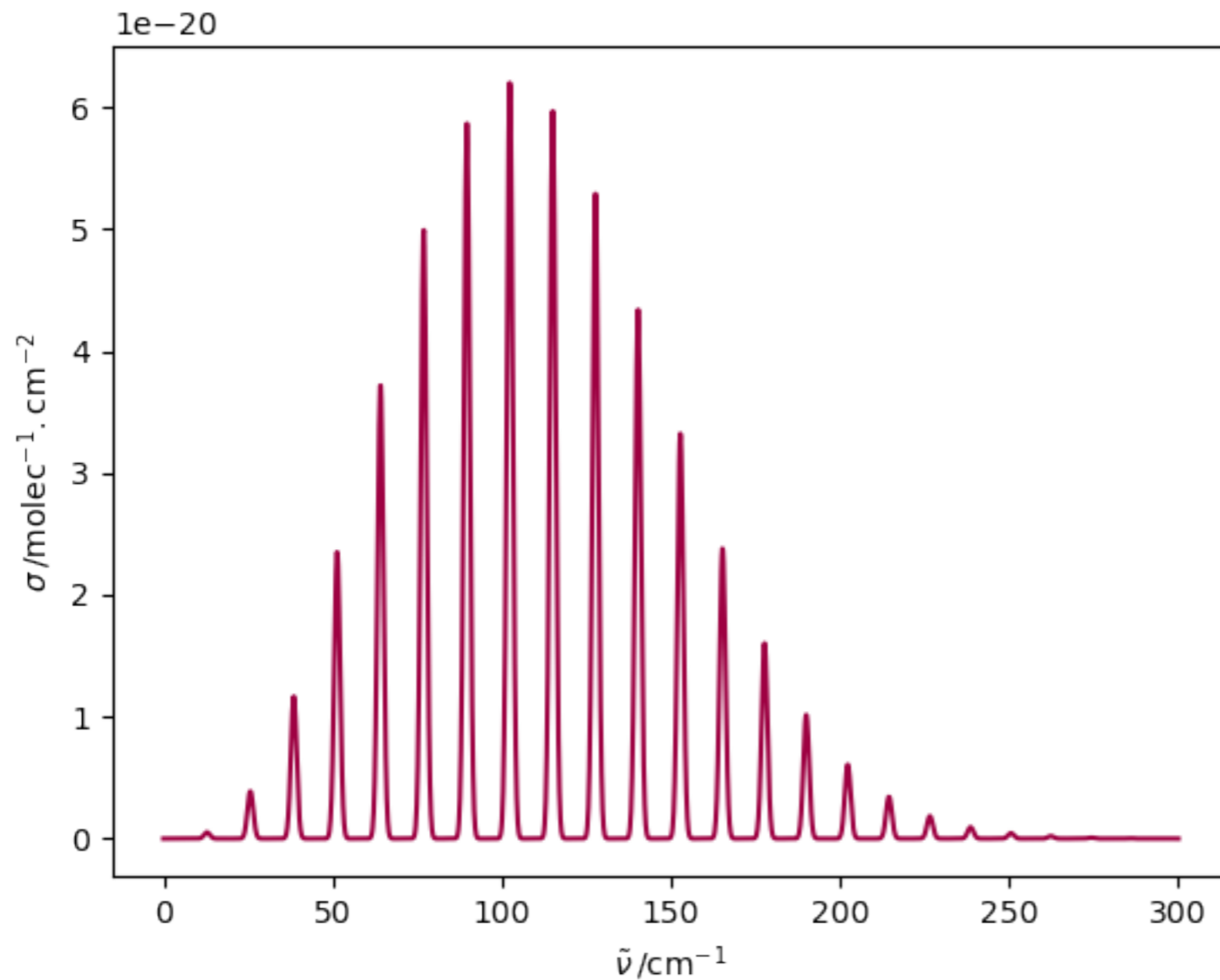
$$B_e = \frac{h}{8\pi^2 \mu c R_e^2}$$

$$D_e = \frac{h^3}{32\pi^4 k \mu c R_e^6}$$

$$H_e = \frac{3h^5}{128\pi^6 k^2 \mu^3 c R_e^{10}}$$

Centrifugal distortion

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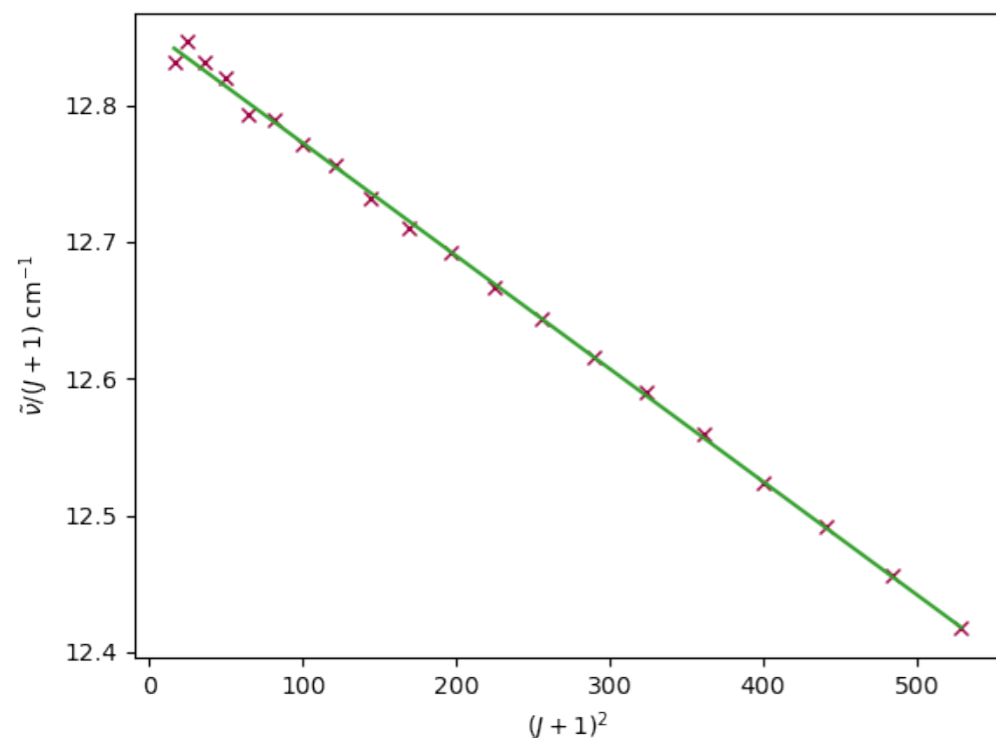
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In this case, we get

$$B_e = 6.42749 \text{ cm}^{-1}$$

$$D_e = 2.066 \times 10^{-4} \text{ cm}^{-1}$$