The Abdus Salam International Centre for Theoretical Physics

IAEA
International Atomic Energy Agency
Atoms for Peace

Molecular Spectroscopy 1

Christian Hill
Joint ICTP-IAEA School on Atomic and Molecular Spectroscopy in Plasmas
6 – 10 May 2019
Trieste, Italy

Uses of molecular spectroscopy

- Diagnostics, monitoring and classification:
  - Composition
  - Density
  - Temperature

- “Physical” structure
- Electronic structure
- Testing physical theories

These lectures

- Introduction and context } – Lecture 1
- Rotational Spectroscopy
- (Ro)vibrational Spectroscopy – Lecture 2
- Electronic Spectroscopy – Lecture 3

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Focus on

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

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- Electronic Spectroscopy – Lecture 3

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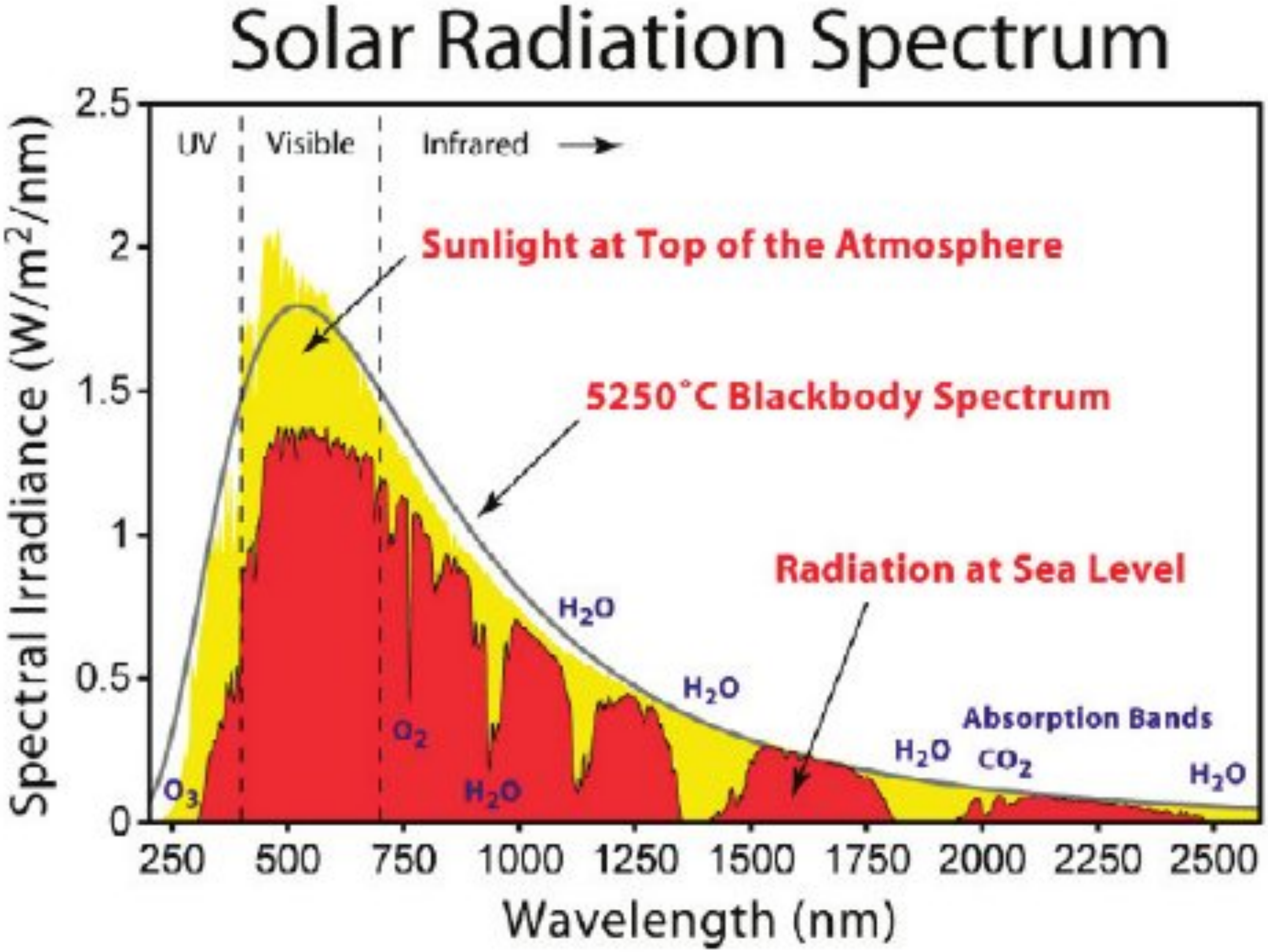
Not so much

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

Remote sensing of the atmosphere



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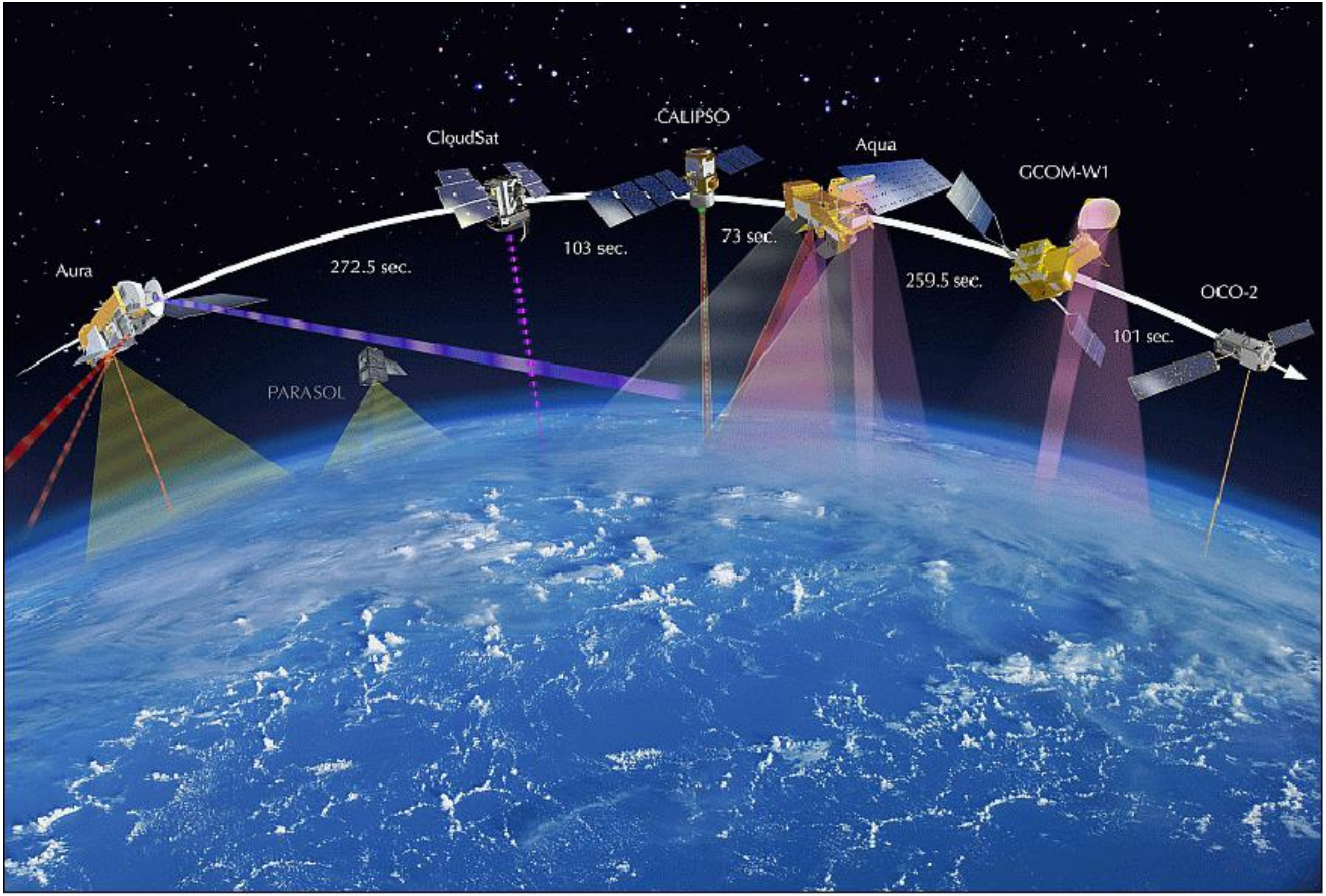
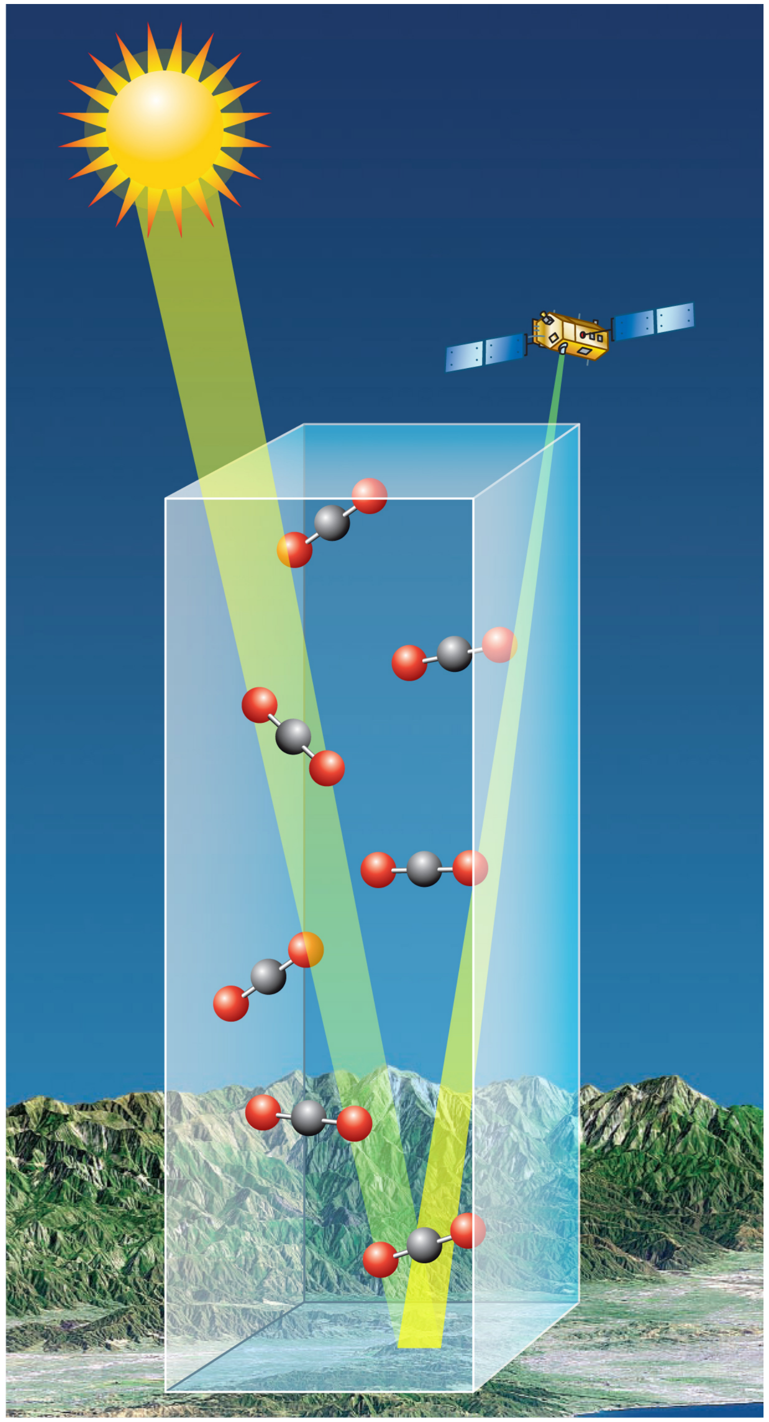
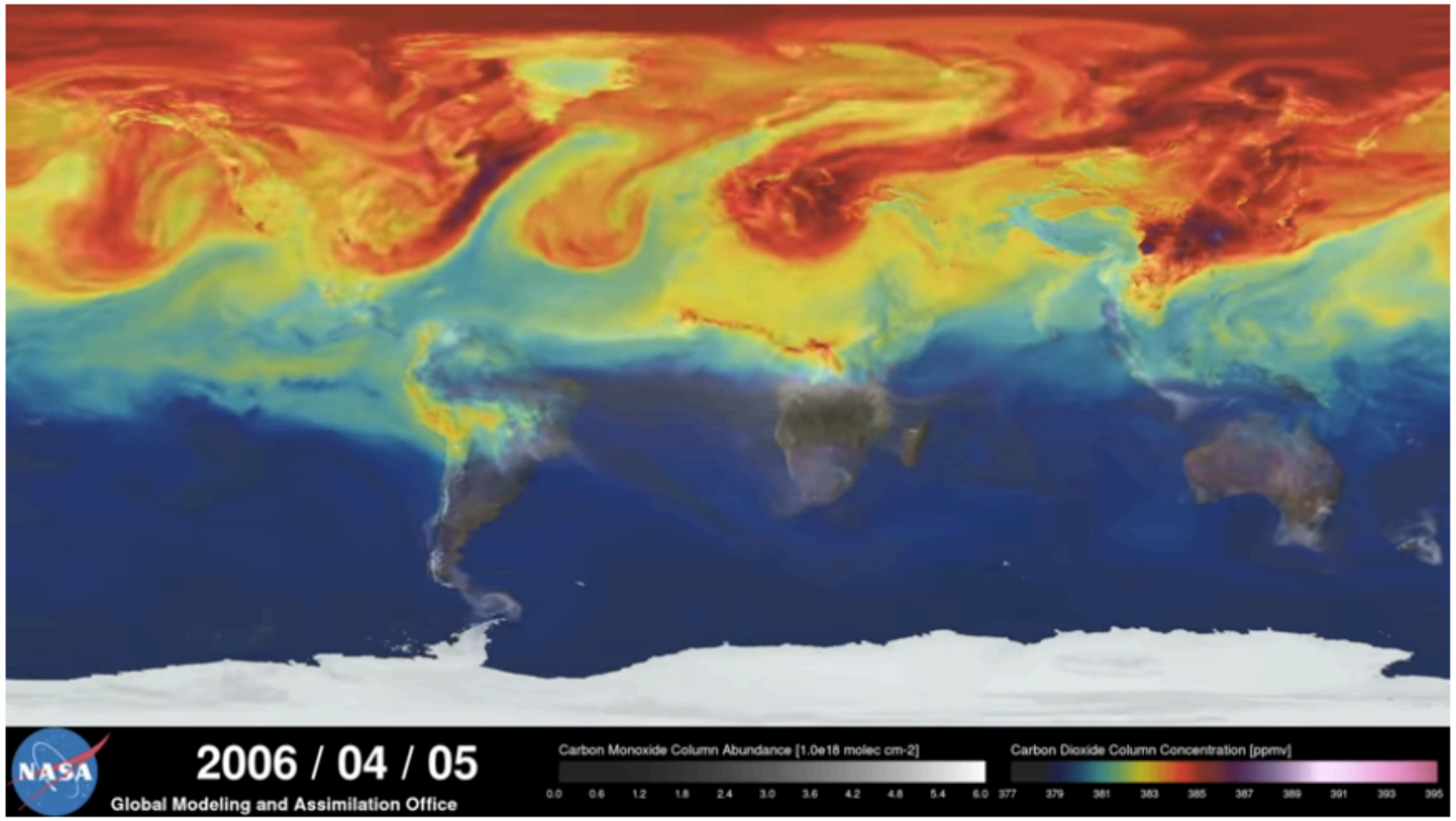


OCO-2: Orbiting Carbon Observatory

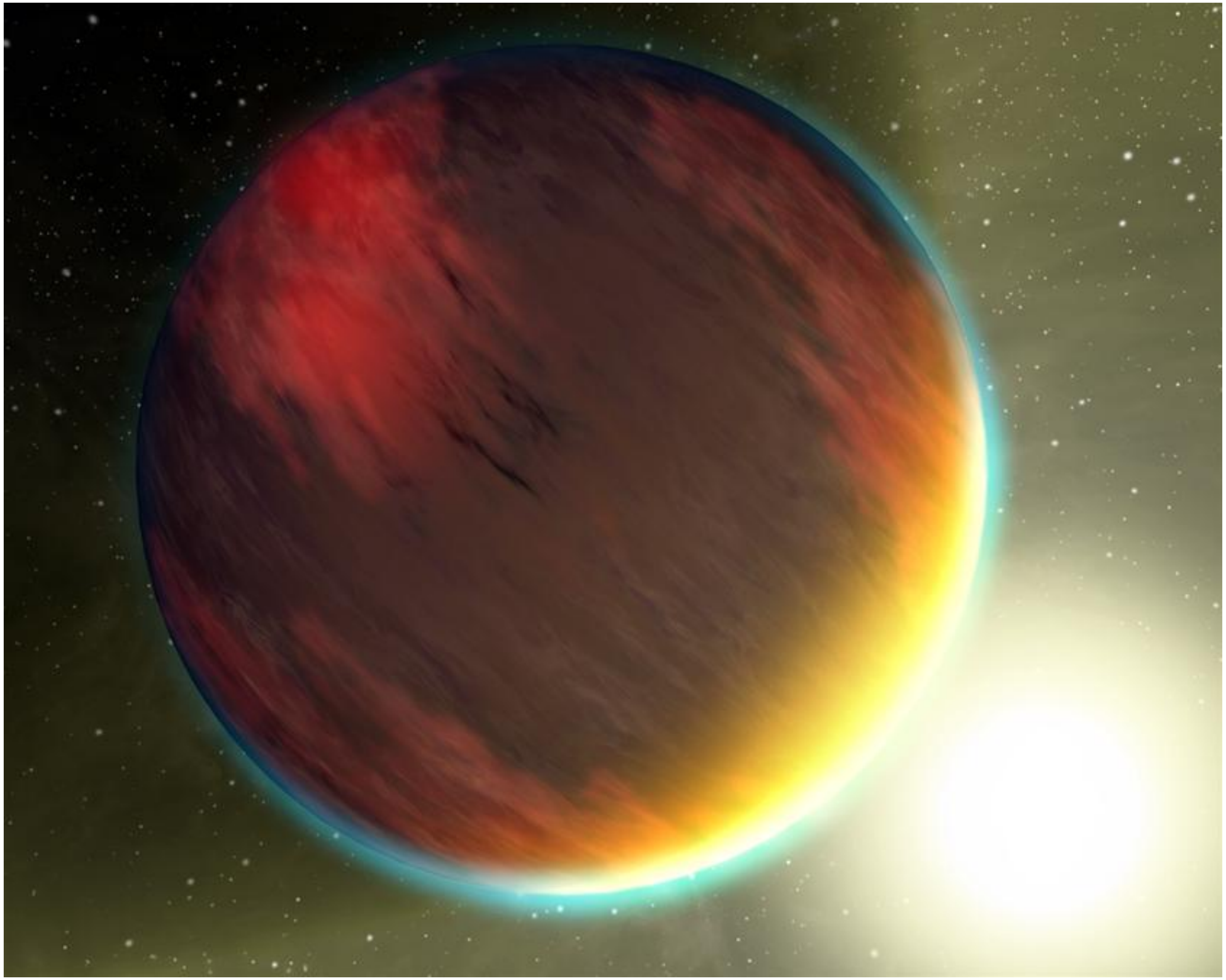


High temporal and spatial resolution CO_2 column amounts:

https://ocov2.jpl.nasa.gov/galleries/Videos/



Exoplanet spectroscopy



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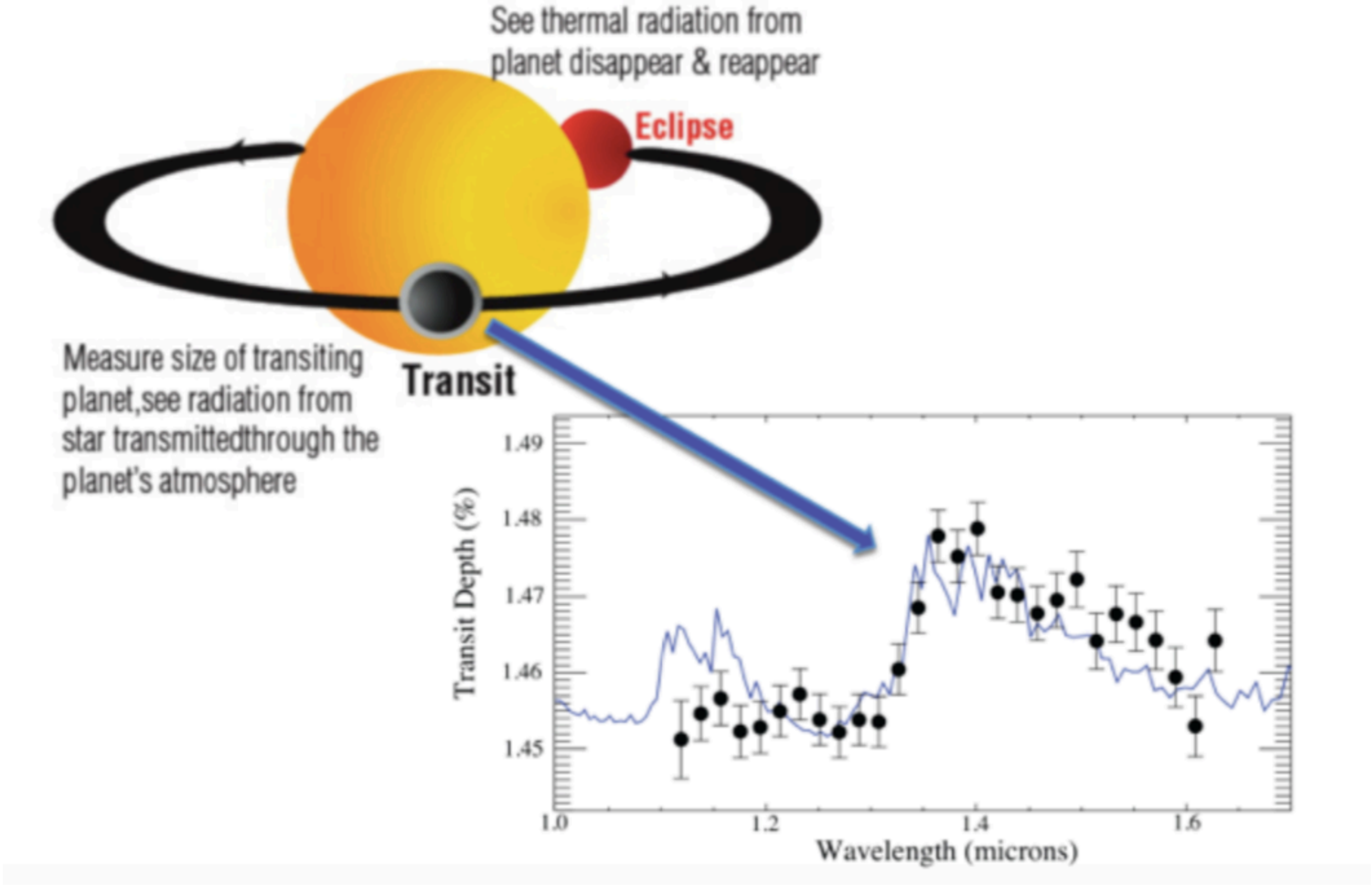

See thermal radiation from planet disappear & reappear

Measure size of transiting planet,see radiation from star transmittedthrough the planet's atmosphere

Separating electronic and nuclear motion

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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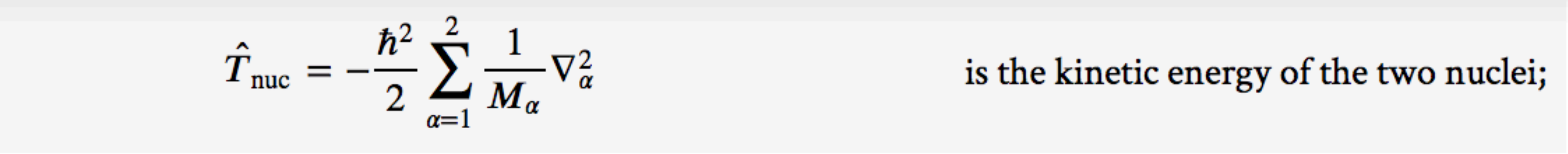

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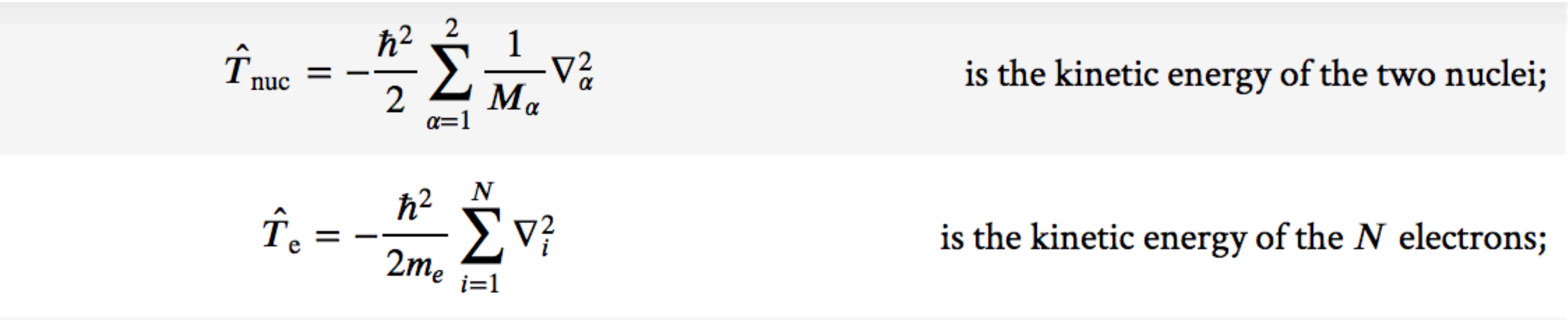

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$-\frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{N}\left(\frac{Z_A}{\rho_{iA}} + \frac{Z_B}{\rho_{iB}}\right)$	is the potential energy of attraction between each electron and the two nuclei (separations ρ_{iA} and ρ_{iB}).

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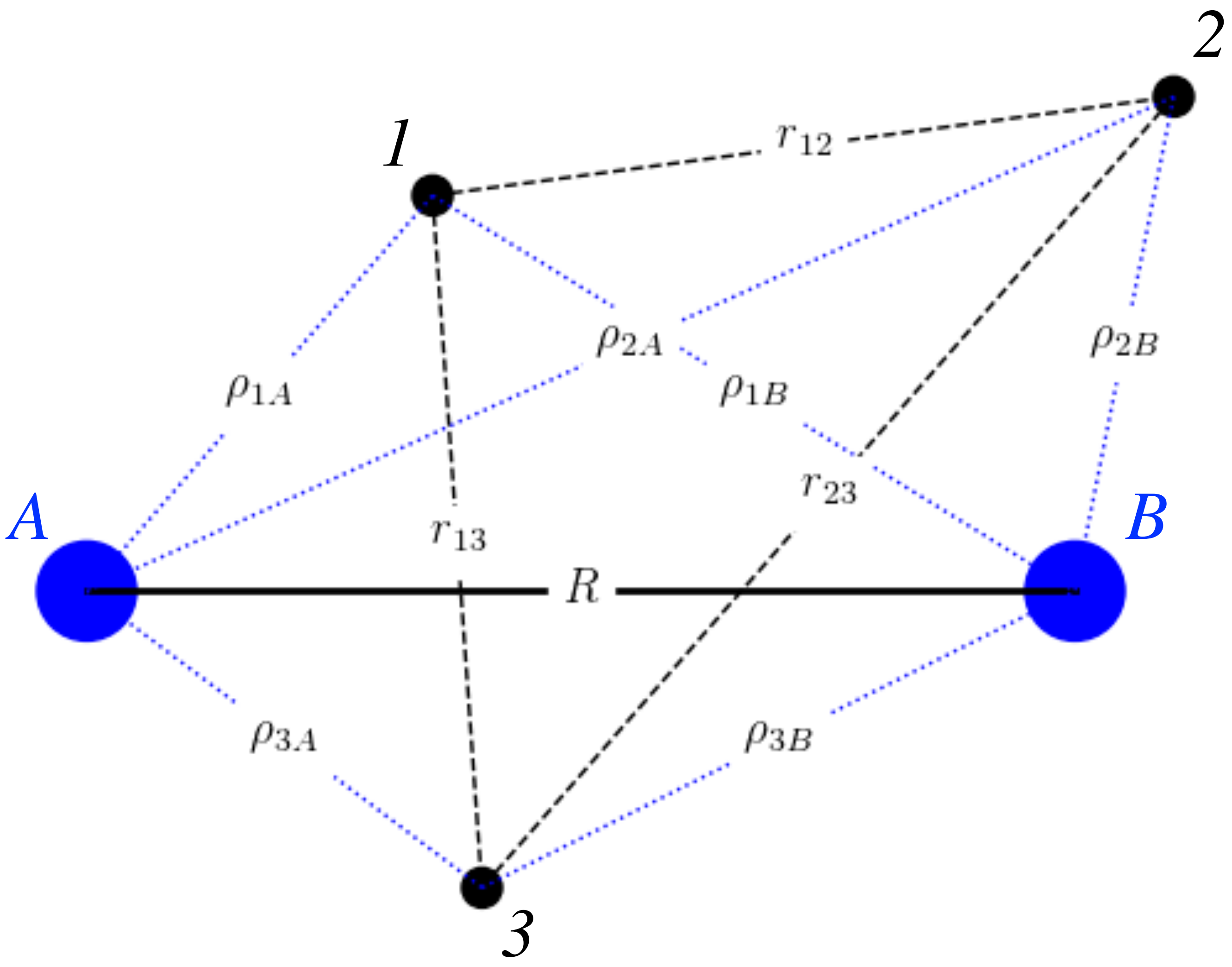

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- The nuclei in a molecule move much more slowly than the electrons: $(m_p/m_e \approx 1836)$
- The electrons adjust their positions rapidly following a change in the internuclear separation
- The kinetic energy of the nuclear motion is small compared to that of the electrons
- Treat it as a perturbation to the Hamiltonian for the rigid molecule: $\hat{H} = \hat{H}_0 + \hat{T}_{\mathrm{nuc}}$

The adiabatic approximation

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2}\sum_{\alpha=A,B}\frac{1}{M_\alpha}\nabla_\alpha^2}_{\hat{T}_{\text{nuc}}} \underbrace{- \frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left[\frac{Z_A Z_B}{R} + \sum_{i,j<i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\left(\frac{Z_A}{\rho_{iA}} + \frac{Z_B}{\rho_{iB}}\right)\right]}_{\hat{H}_0},$$

- 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, $\phi(\boldsymbol{r}_i; \boldsymbol{R}_\alpha)$, depends *parametrically* on the nuclear positions, $\boldsymbol{R}_\alpha$: the effect of the nuclear *velocities* is ignored

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

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

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

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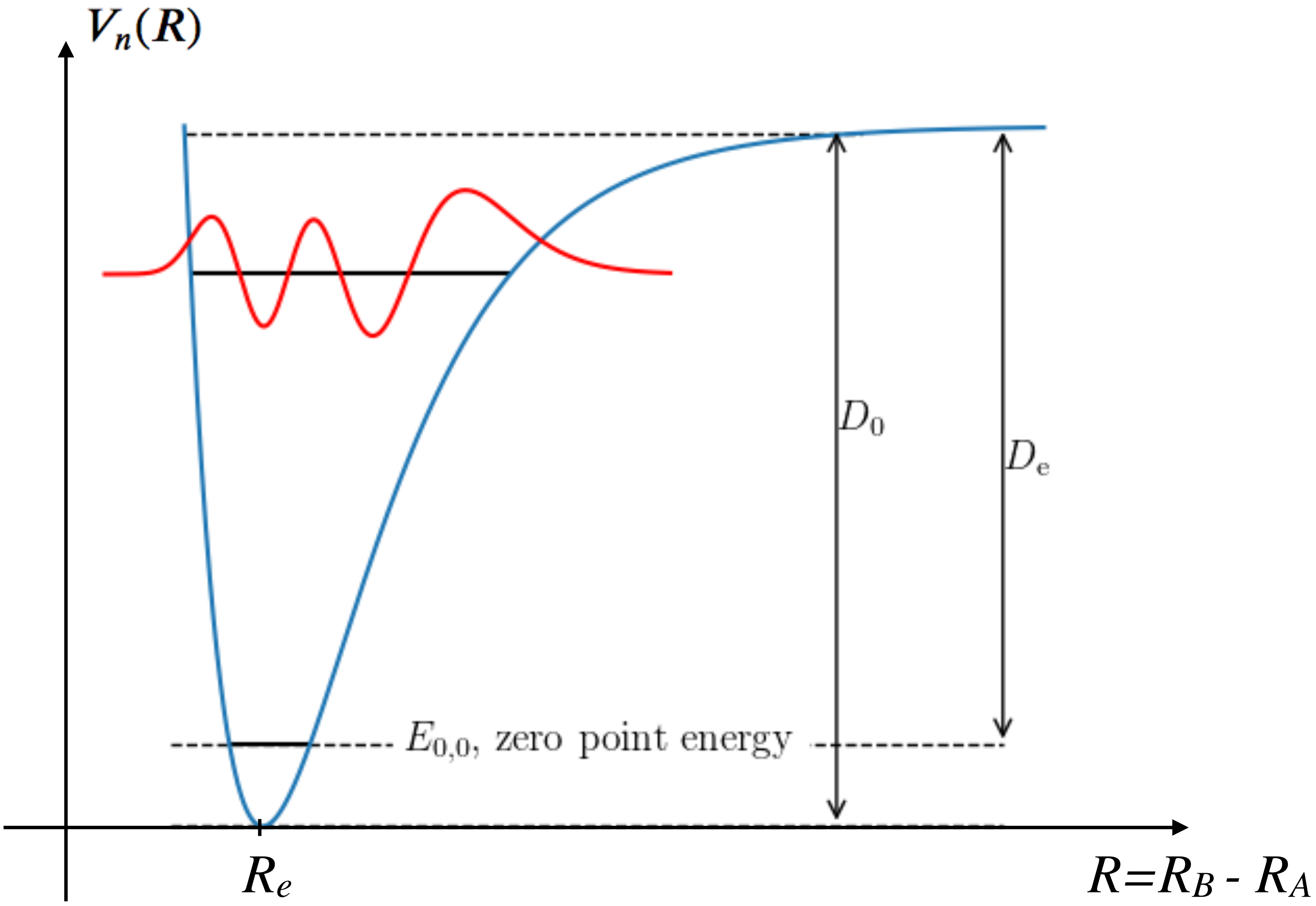

Separating vibration and rotation

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

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2+V_n(R)\right]\chi_{n,m}(R)=E_{n,m}\chi_{n,m}(R).$$

where $\mu=\frac{m_\mathrm{A}m_\mathrm{B}}{m_\mathrm{A}+m_\mathrm{B}}$ is the reduced mass.

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- Note that the potential energy does not depend on the angular components of $\boldsymbol{R}$: it is *spherically symmetric*.

- So the nuclear Schrödinger equation is separable, as for the hydrogen atom:

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

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

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- and

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

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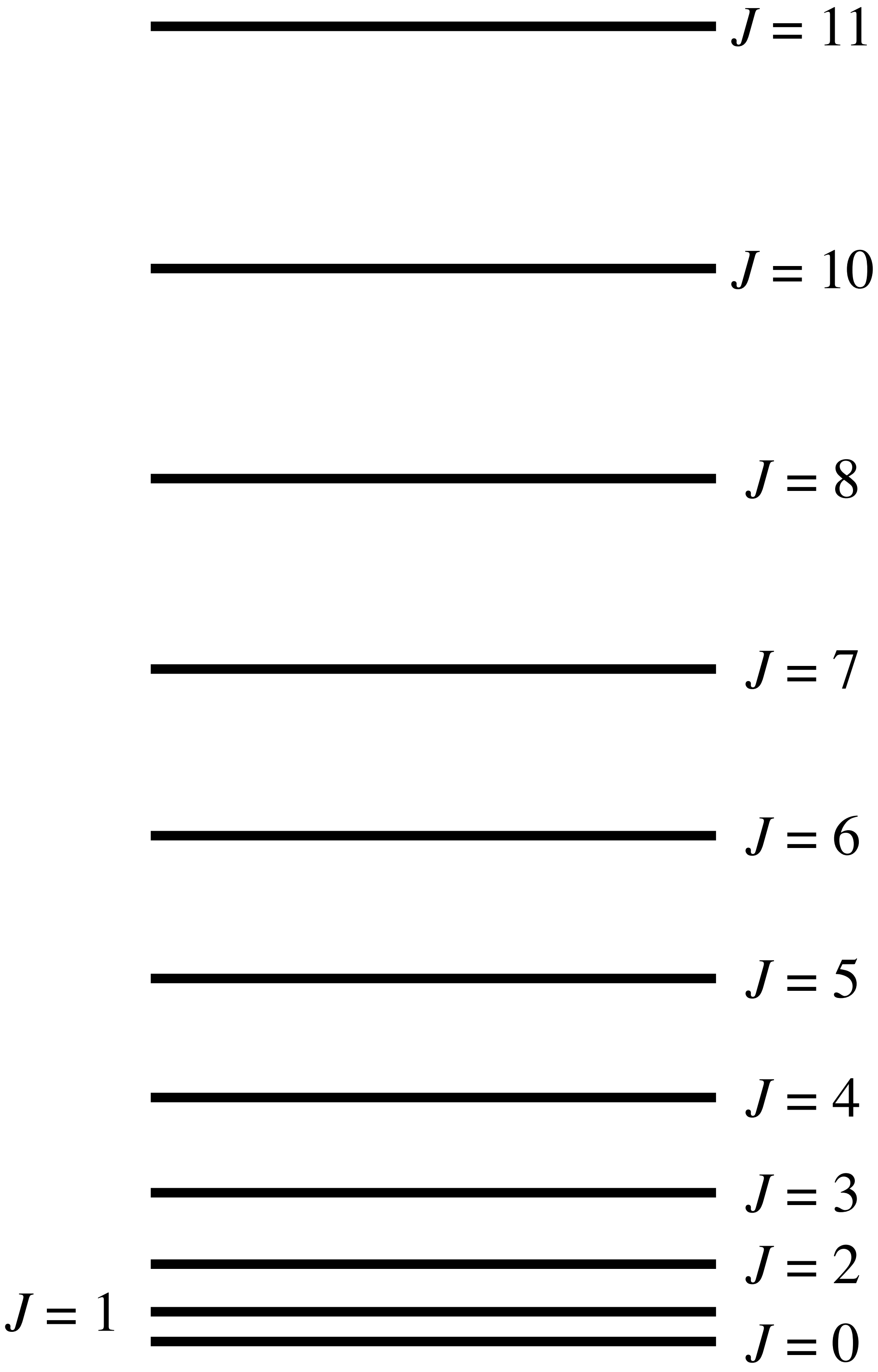
- Spectroscopists like to use term values, $F(J) = E/hc$, in units of cm^{-1}:

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

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:

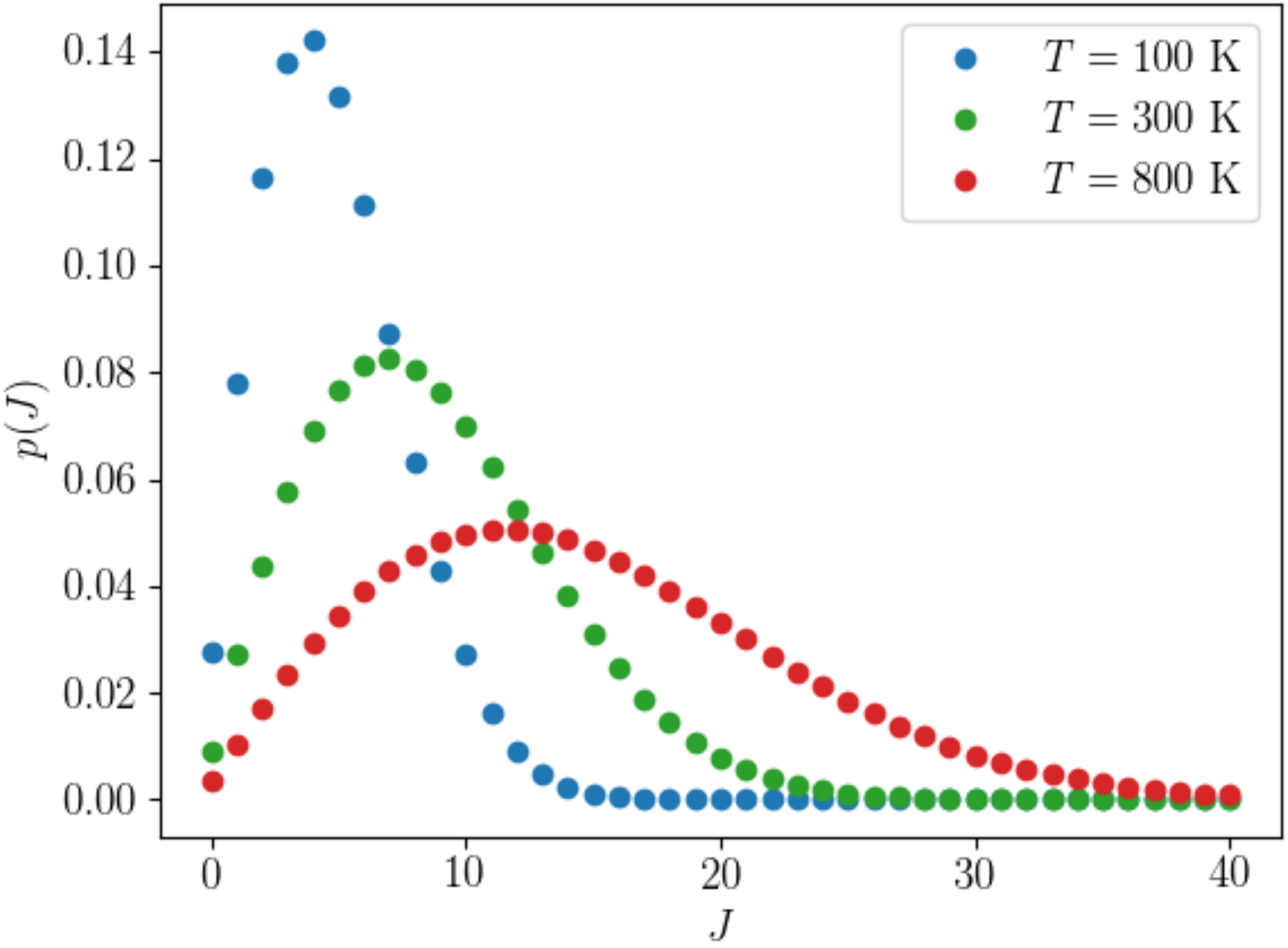
  $$p(J) = \frac{g_J \exp\left(-\frac{E_J}{k_B T}\right)}{q(T)},$$

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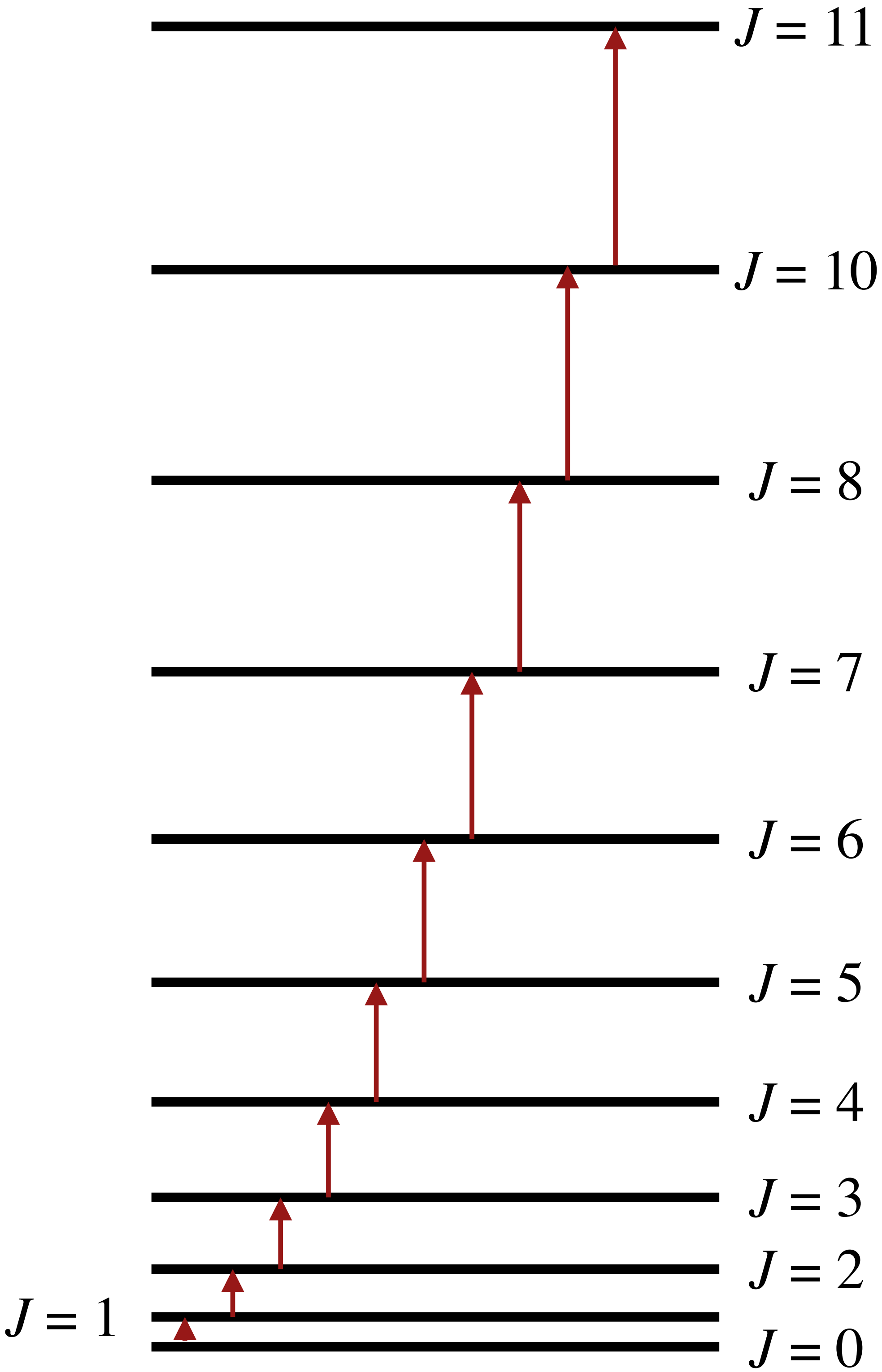
- Lines, evenly spaced every $2B_\mathrm{e}$
- Corresponds to:
    - Wavenumbers: 0.1 – 100 cm^{-1};
    - Frequency: 10^9 – 10^{12} Hz (“Gigahertz–Terahertz radiation”);
    - Wavelength: 1 μm – 10 cm (“microwaves”).

The rigid rotor



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  - The transition frequency;
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  - 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 $\Delta \mathrm{J} = -1$ and $\Delta \mathrm{J} = +1$ respectively.

The rigid rotor spectrum

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

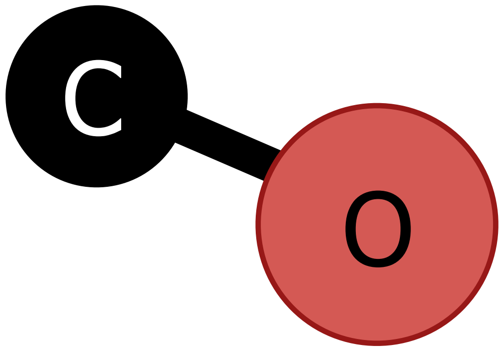
$$\sigma \propto \mu_0 \frac{2B_e(J+1)^2}{q(T)} \exp\left(-\frac{F(J)hc}{k_{\mathrm{B}}T}\right)\left[1-\exp\left(-\frac{\tilde{\nu}(J)hc}{k_{\mathrm{B}}T}\right)\right]$$

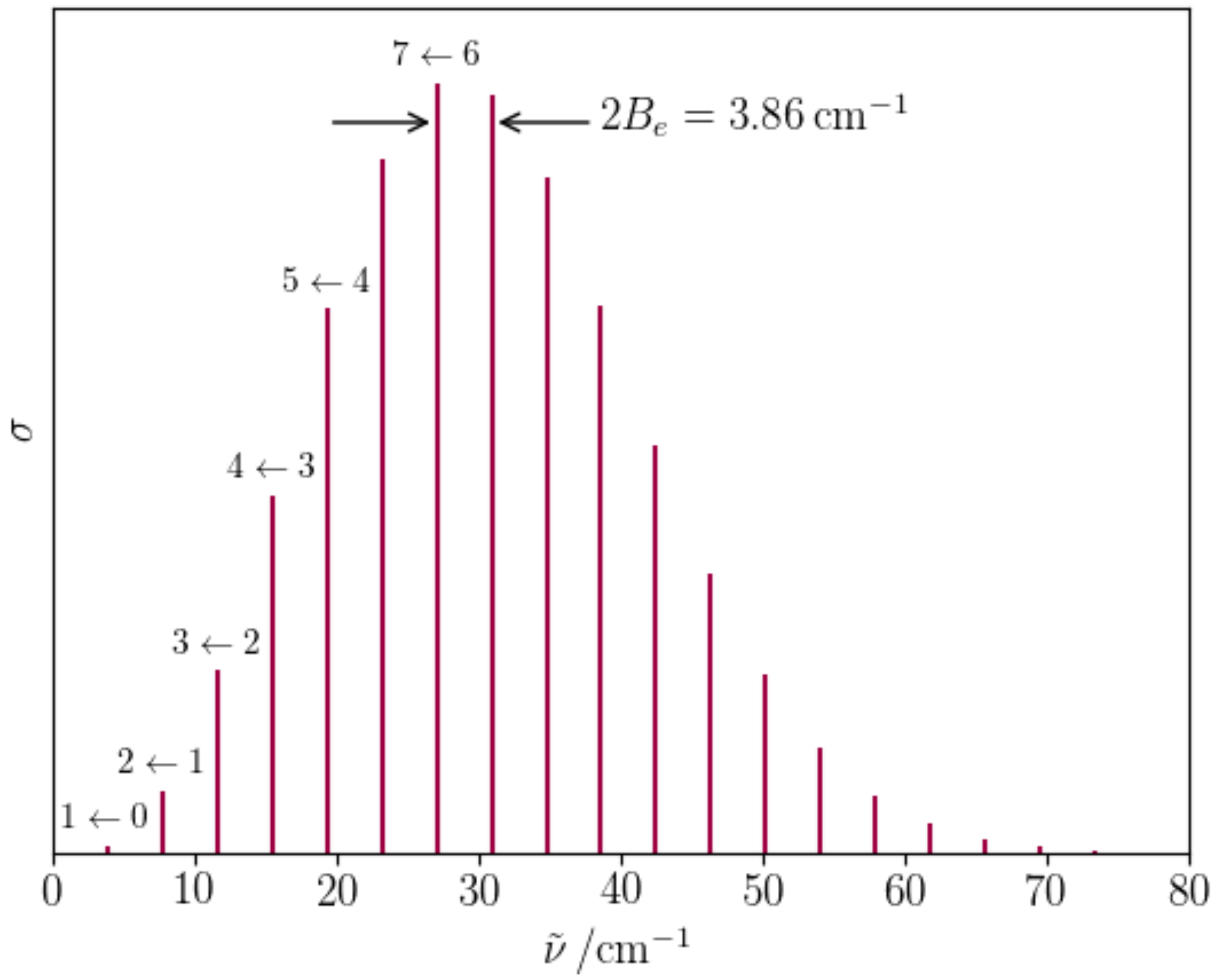
The rigid rotor spectrum

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

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

e.g. CO at 100 K:

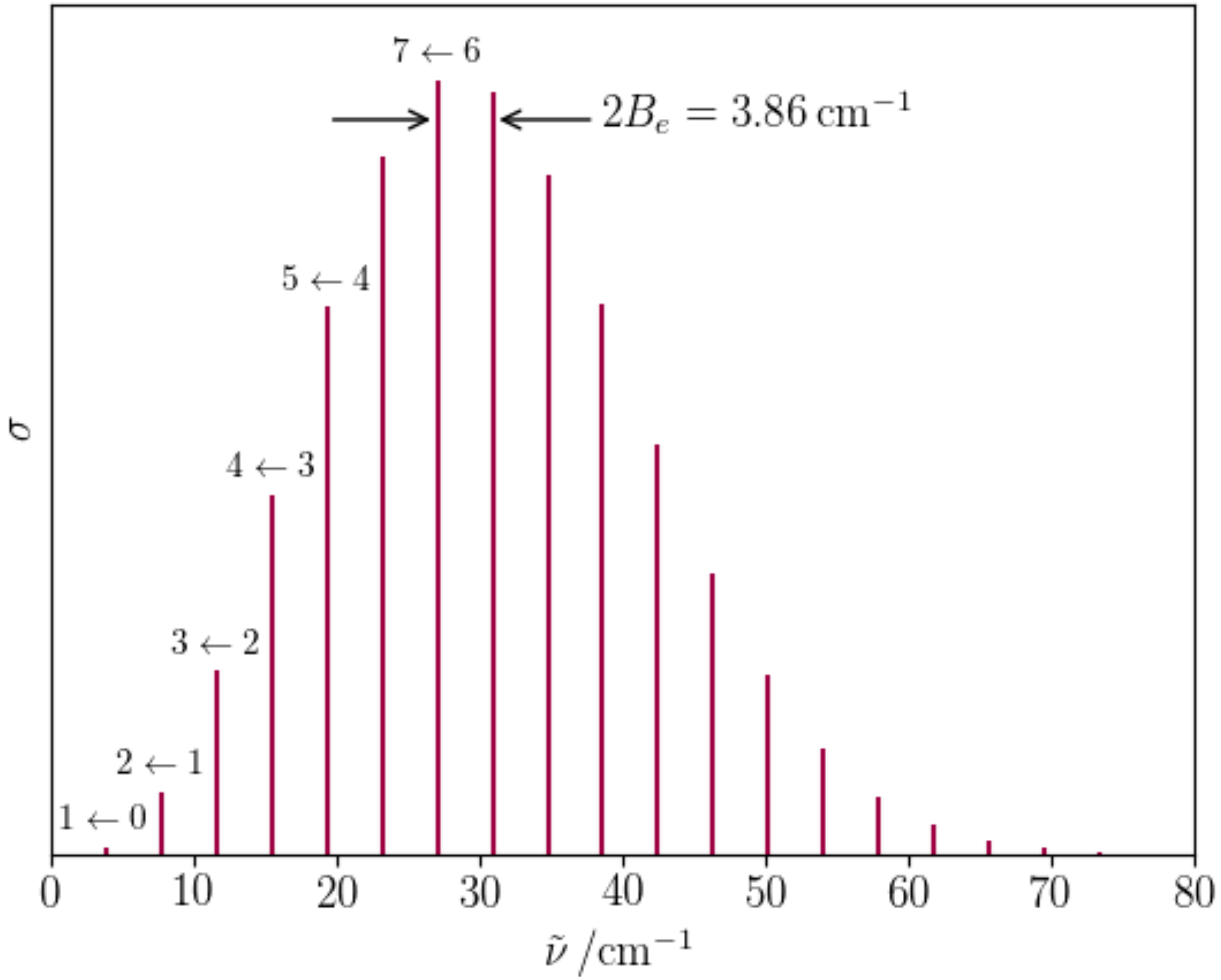




The rigid rotor spectrum

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

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



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

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

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

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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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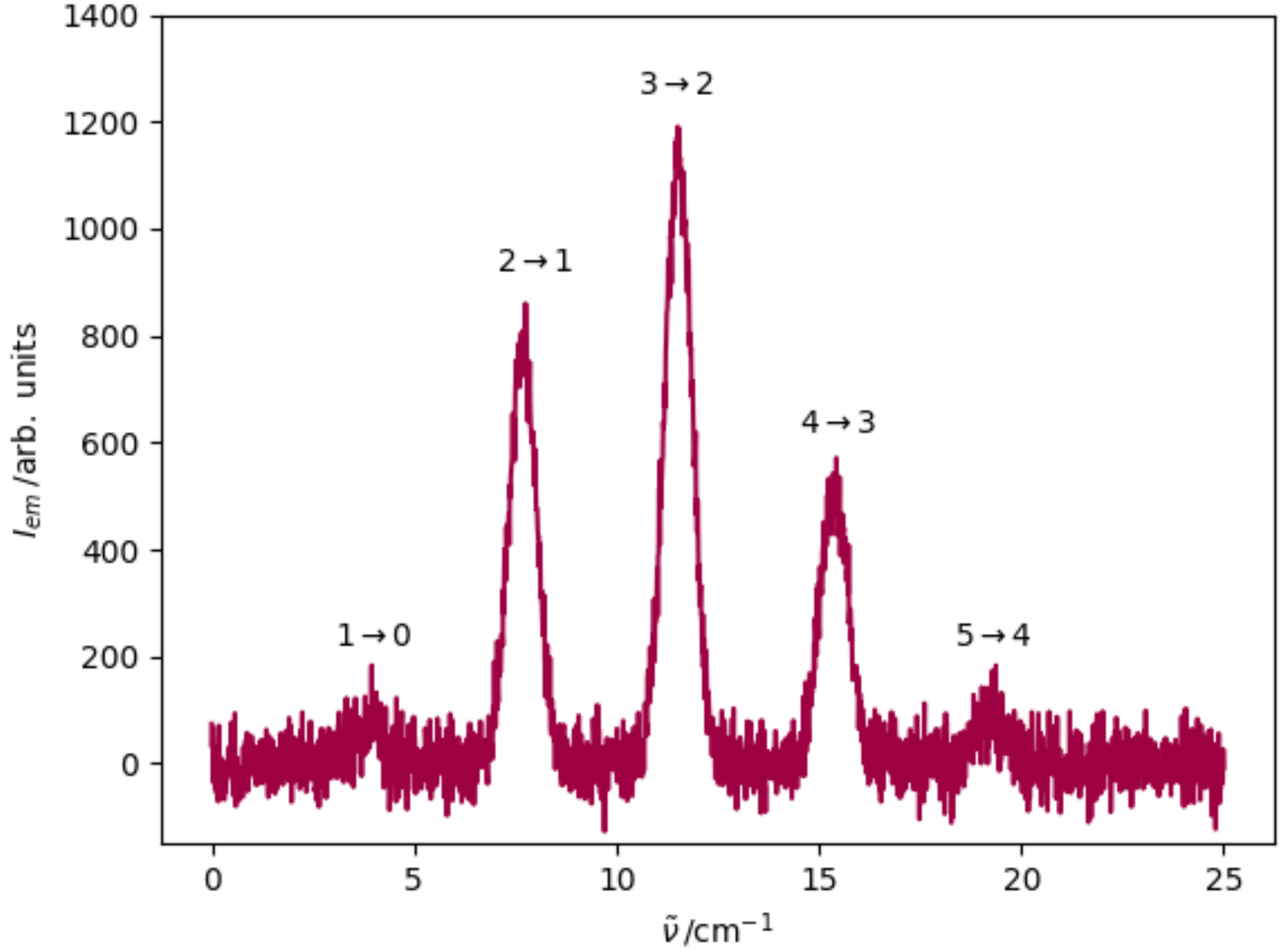
The rigid rotor spectrum

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

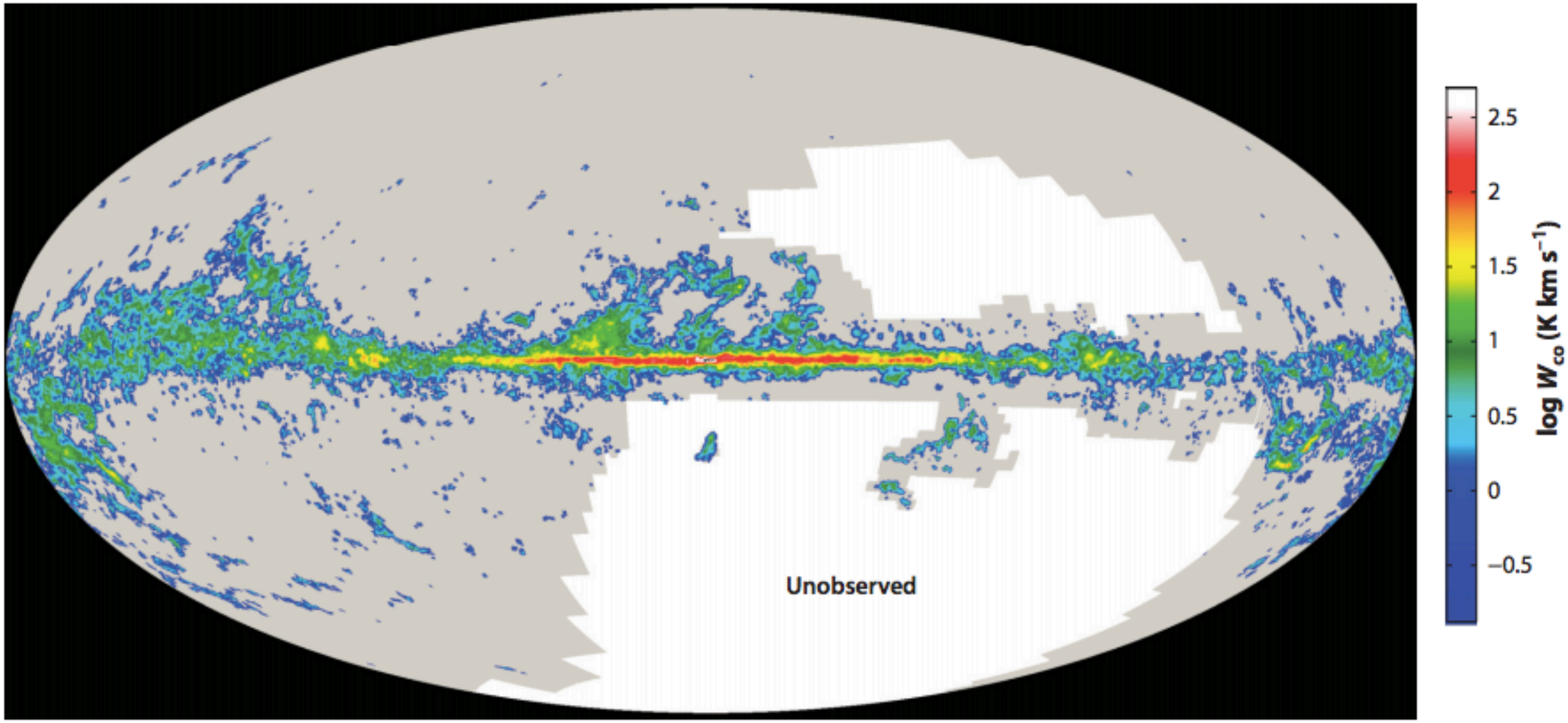
The rigid rotor spectrum

- Carbon monoxide (CO) emission spectrum



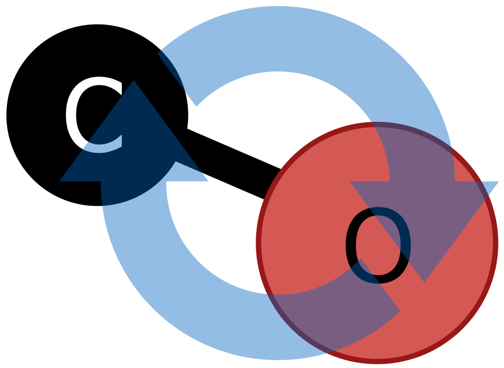
The rigid rotor spectrum

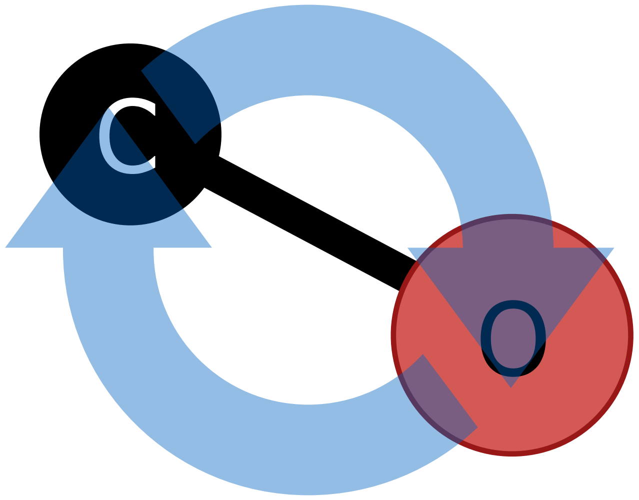
$J = 1 \rightarrow 0$ emission of CO in the Milky Way



Centrifugal distortion

- A real molecule is not rigid, but subject to a centrifugal force, $F_c = \mu\omega^2 R$ as it rotates:





Centrifugal distortion

- A real molecule is not rigid, but subject to a centrifugal force, $F_c = \mu\omega^2 R$ as it rotates, where the angular velocity, ω, satisfies:

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

hence:

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

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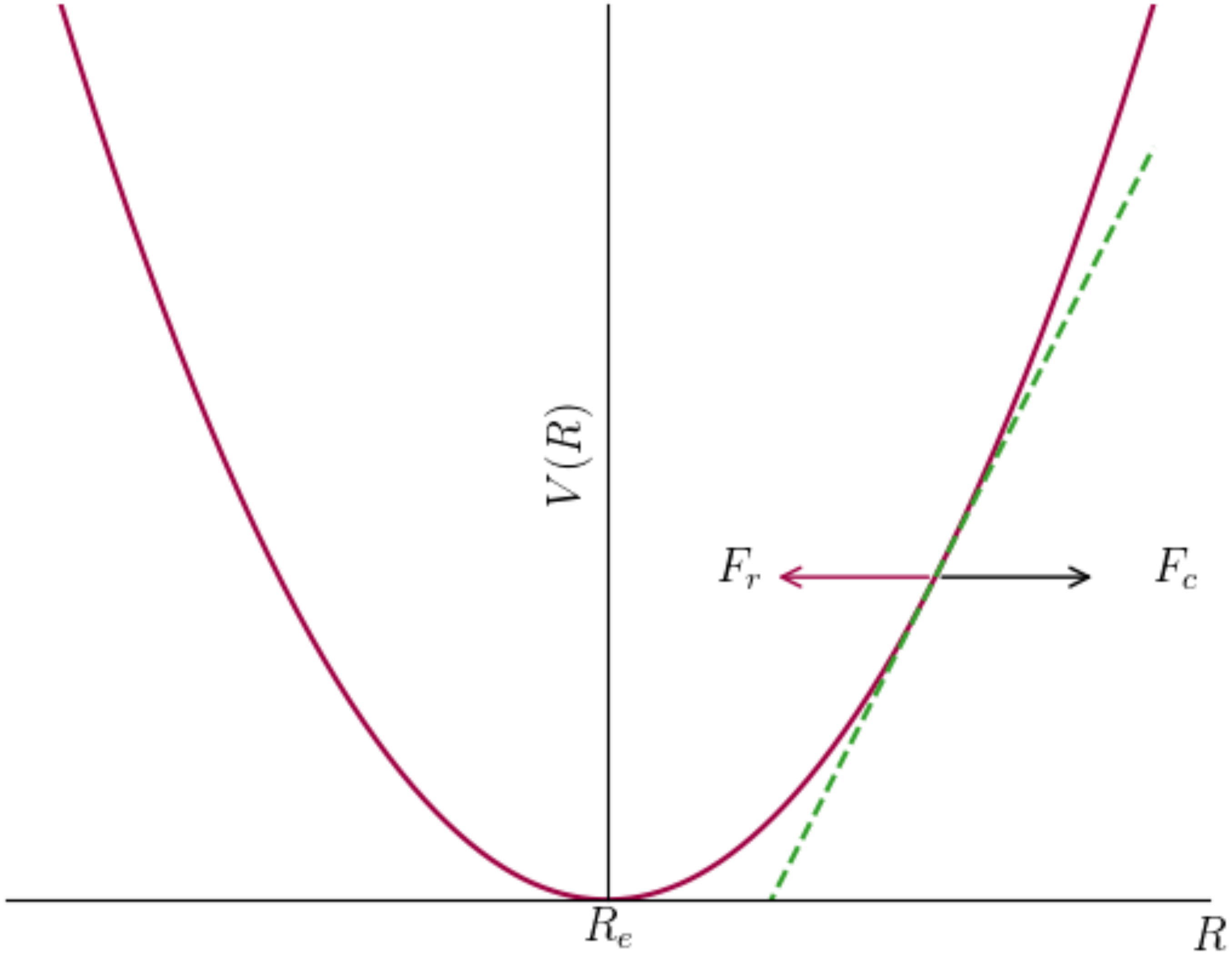
This force is balanced by a restoring force due to the potential binding the atoms together:

$$F_r = -\mathrm{d}V_n(R)/\mathrm{d}R$$

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 $F_\mathrm{c} + F_\mathrm{r} = 0$:

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

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

$$\approx R_e \left(1 + \frac{\hbar^2}{\mu k R_e^4} J(J+1)\right).$$

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

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

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

Centrifugal distortion

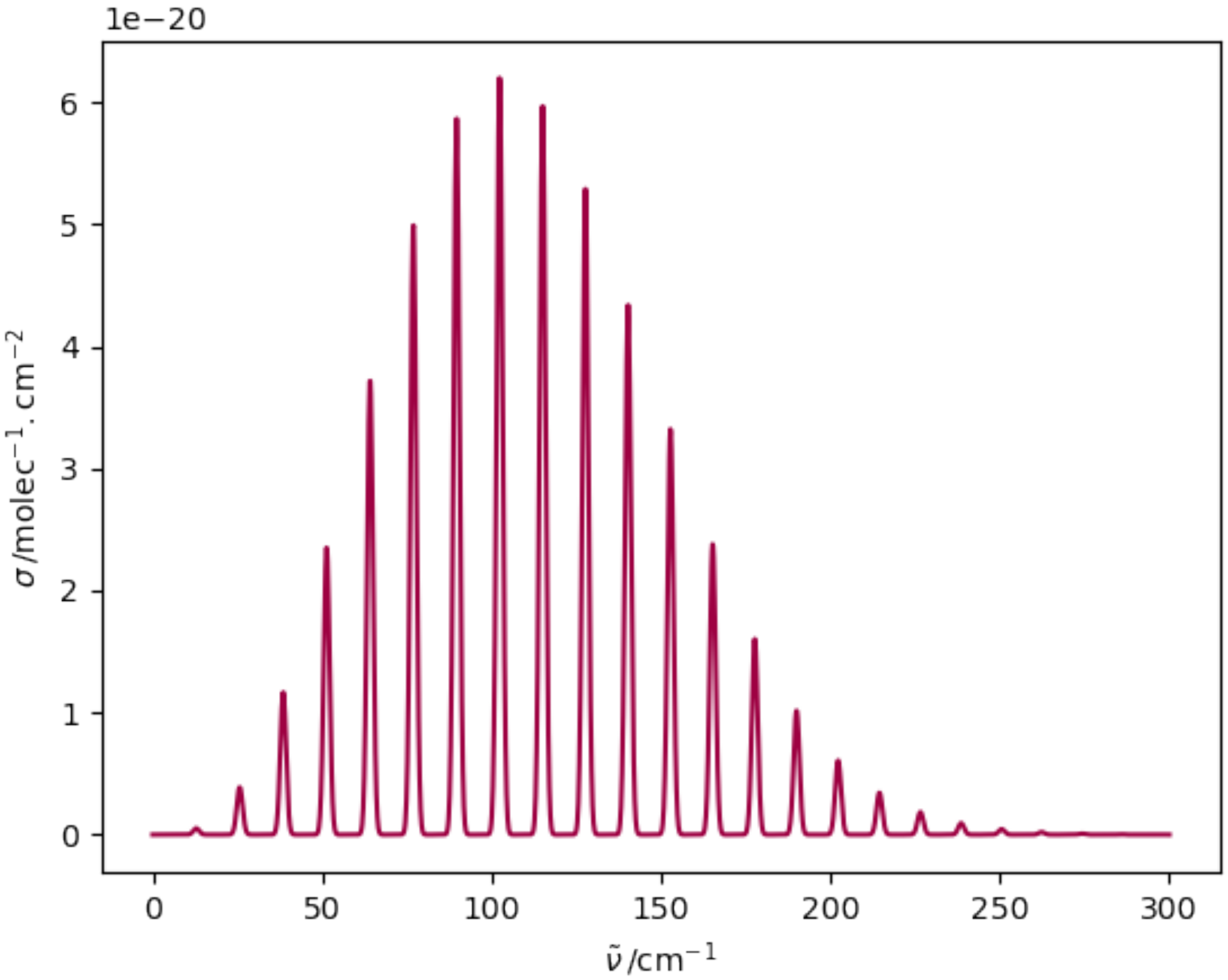
- In terms of wavenumbers:

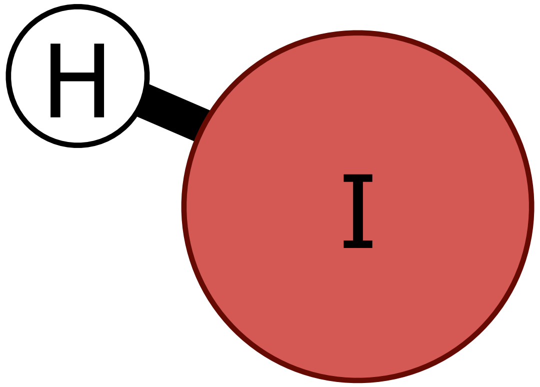
$$F(J) = B_e J(J+1) - D_e J^2 (J+1)^2 + H_e J^3 (J+1)^3 + \cdots$$

$$\begin{aligned} B_e &= \frac{h}{8\pi^2 \mu c R_e^2} \\ D_e &= \frac{h^3}{32\pi^4 k \mu c R_e^6} \\ H_e &= \frac{3h^5}{128\pi^6 k^2 \mu^3 c R_e^{10}} \end{aligned}$$

Centrifugal distortion

- Example: the microwave spectrum of hydrogen iodide (HI)





Centrifugal distortion

- Example: the microwave spectrum of hydrogen iodide (HI)
- Ignoring higher-order terms,

$$\tilde{\nu}(J) = F(J+1) - F(J) = 2B_e(J+1) - 4D_e(J+1)^3$$

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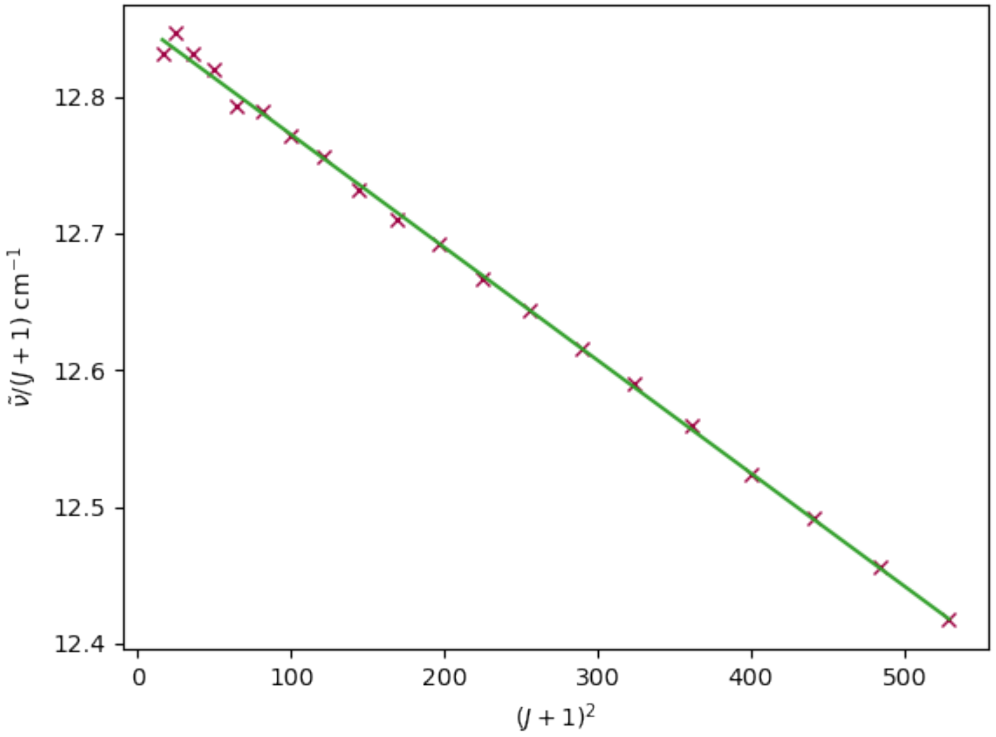

In this case, we get

$B_\mathrm{e} = 6.42749$ cm^{-1}

$D_\mathrm{e} = 2.066 \times 10^{-4}$ cm^{-1}