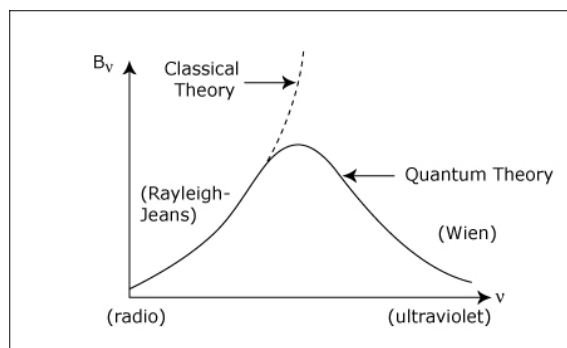


Thermodynamic concepts of radiation

(a) Black-body radiation – classical theory predicted (wrongly) increasing emission with increasing frequency (ν) from an amorphous black surface. Quantum theory introduced by Planck agreed with observations. The blackbody radiation is defined by the Planck function.

$$B_{\nu}(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/KT} - 1} \left(\frac{\begin{matrix} \text{(Joule)} \\ \text{erg} \end{matrix}}{\begin{matrix} \text{(cm}^2\text{)} \\ \text{(m}^2\text{)} \end{matrix} \text{sec. freq. ster.}} \right)$$

$$B_{\lambda}(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda KT} - 1} = \left(\frac{\nu^2}{c} \text{ or } \frac{\nu}{\lambda} \right) B_{\nu}$$



which agrees with observation and provided the first evidence for the quantum theory (h = Planck constant; K = Boltzmann constant).

Asymptotes: $\lambda \rightarrow 0, B_{\lambda} \rightarrow \frac{2hc^2}{\lambda^5} e^{-hc/\lambda KT}$; Wien wing (UV)

$\lambda \rightarrow \infty, B_{\lambda} \rightarrow \frac{2KTc}{\lambda^4}$; Rayleigh-Jeans wing (radio)

Stefan's Law:
 Kondratyev:

$$\int_0^{\infty} B_{\lambda} d\lambda = \frac{2K^4 T^4}{c^2 h^3} \overbrace{\int_0^{\infty} \frac{x^3 dx}{e^x - 1}}^{\pi^4/15} \quad \left(x = \frac{hc}{\lambda KT} \right)$$

$$= \left[\frac{2\pi^5 K^4}{15c^2 h^3} \right] \frac{T^4}{\pi} \quad \left(\frac{\text{erg}}{\text{cm}^2 \cdot \text{sec. steradian}} \right)$$

Stefan's constant (σ)

$$= \frac{\sigma T^4}{\pi}$$

Energy Levels in molecules

(a) Rotational Energies (quantum no. $J=0, 1, 2, \dots$)

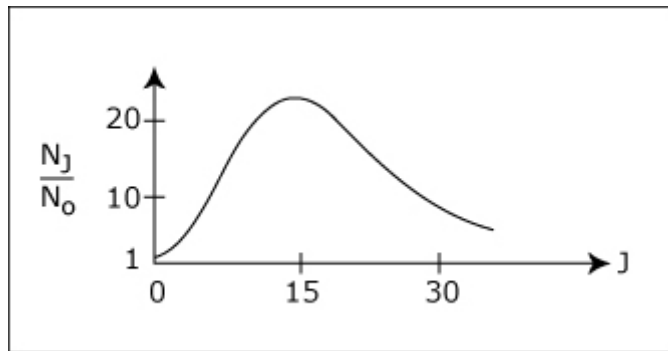
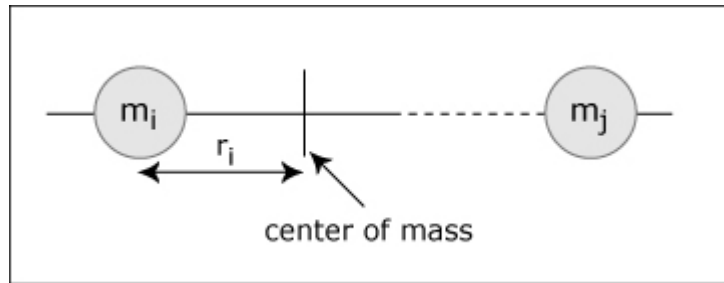
For a linear molecule (e.g. $\text{CO}_2, \text{N}_2\text{O}, \text{O}_2, \text{CO}, \text{H}_2$, etc.)

$$E_{\text{rot}} = \left(\frac{h^2}{8\pi^2 I} \right) J(J+1)$$

$$= B J (J+1)$$

and $N_J/N_0 = \underbrace{(2J+1)}_{\text{degeneracy}} \exp(-BJ (J+1)/KT)$

where $I =$ moment of inertia $= \sum_i m_i r_i^2$ and r_i is distance of atom i from center of mass:



(b) Vibrational Energies (quantum no. $v=0, 1, 2, \dots$)

For a diatomic molecule:

$$E_{\text{vib}} = \left(v + \frac{1}{2} \right) h \left[\frac{1}{2\pi} \sqrt{\frac{C}{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)}} \right] = \left(v + \frac{1}{2} \right) h\nu_0$$

Fundamental Frequency \swarrow

where potential energy = $\frac{1}{2}C(r - r_0)^2$ ("Hookes Law"), but note that a "spring" has a continuous set of energy states while a molecule does not. We can compare E_{vib} to the amplitude of the "spring" vibration.

Also $N_v/N_0 = \exp(-vh\nu_0/KT)$ (Boltzmann distribution). Note $N_1/N_0 \approx \exp(-5) \approx 0.01$ at room temperature so almost all molecules in ground state. For complex molecules:

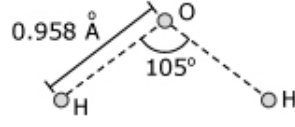
Number of fundamental vibrations/frequencies

$$= 3N_{(\text{atoms})} - 3_{(\text{translation})} - \begin{bmatrix} 3 \text{ (nonlinear)} \\ 2 \text{ (linear)} \end{bmatrix} (\text{rotation})$$

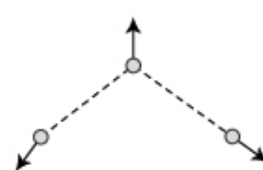
Each fundamental vibration has a fundamental frequency ν_i with its own set of quantum numbers ($\nu_i = 0, 1, 2, \text{ etc.}$). Choose fundamentals using group theory or simple geometry so vector sets representing vibrations linearly independent :

Examples :

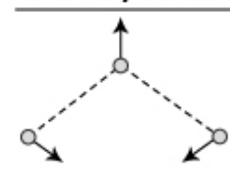
① **Water Vapor Molecule**


(3N-6 = 3)


Vibratory States



Symmetric band stretching
 $\nu_1 = 3657 \text{ cm}^{-1} = 2.73 \mu\text{m}$

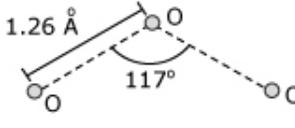


Bending
 $\nu_2 = 1595 \text{ cm}^{-1} = 6.25 \mu\text{m}$

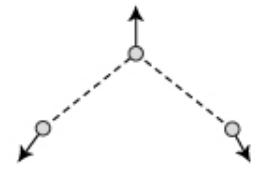


Asymmetric band stretching
 $\nu_3 = 3756 \text{ cm}^{-1} = 2.66 \mu\text{m}$

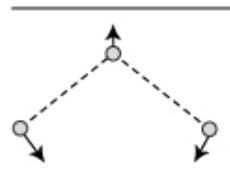
② **Ozone Molecule**


(3N-6 = 3)


Vibratory States



Symmetric band stretching
 $\nu_1 = 1110 \text{ cm}^{-1} = 9.0 \mu\text{m}$




Bending
 $\nu_2 = 701 \text{ cm}^{-1} = 14.3 \mu\text{m}$

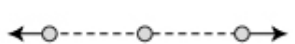


Asymmetric band stretching
 $\nu_3 = 1045 \text{ cm}^{-1} = 9.6 \mu\text{m}$

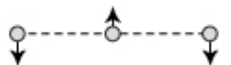
③ **Carbon Dioxide Molecule**


(3N-5 = 4)


Vibratory States




Symmetric band stretching
No band



Bending
 $\nu_2 = 667 \text{ cm}^{-1} = 15 \mu\text{m}$



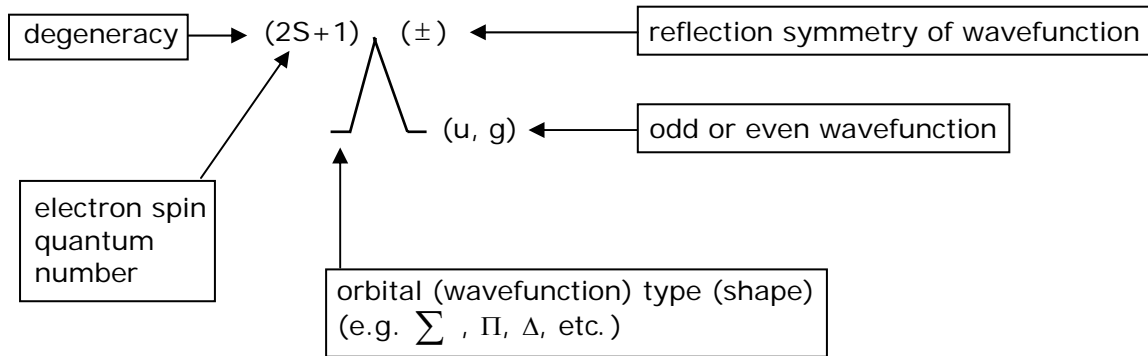
Asymmetric band stretching
 $\nu_3 = 2349 \text{ cm}^{-1} = 4.3 \mu\text{m}$



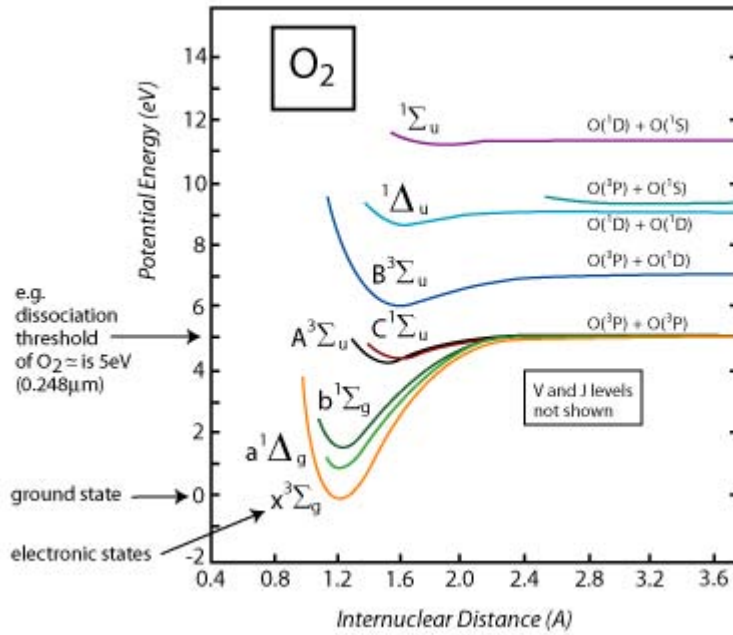
(c) Electronic Energies

These are also quantized but much more complex as we proceed from atoms, to diatomic molecules, to multiatomic molecules.

e.g. for linear molecules electronic states are conveniently designated by informative symbols:



e.g. energy level diagram for O₂



Conversions: 1eV = 8067 cm⁻¹ = 1.24 μm (near infrared)
 2eV = 16134 cm⁻¹ = 0.62 μm } (visible)
 3eV = 24201 cm⁻¹ = 0.41 μm }
 5eV = 40335 cm⁻¹ = 0.248 μm (ultraviolet)