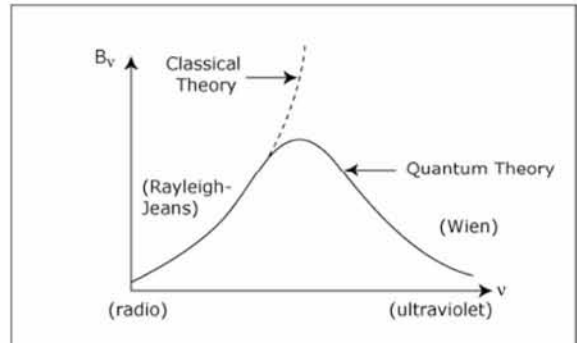


Thermodynamic concepts of radiation

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

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

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



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:

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

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

Stefan's constant ( $\sigma$ )

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

<u>Wien law:</u> (defines the maximum in B)	$\underbrace{\frac{dB_\nu(T)}{d\nu} = 0,}_{\frac{cT}{\nu} = 0.51 \text{ (cm. }^\circ\text{K)}}$ (peak in flux per unit frequency)	$\underbrace{\frac{dB_\lambda(T)}{d\lambda} = 0}_{\lambda T = 0.29 \text{ (cm. }^\circ\text{K)}}$ (peak in flux per unit wavelength)
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(b) ideal black body: one which is in equilibrium with the Planck distribution. It absorbs all the radiation incident upon it and emits the Planck distribution for its temperature.

Practical Examples:

(i) a hole in a blackened sphere (radiation entering the hole is totally absorbed and the hole radiates the Planck distribution).

(ii) an infinite crystal (oscillator energies are very closely spaced and possess a Boltzmann distribution of energy levels – solid and liquid particles, where dimensions  $\gg$  wavelength of radiation of interest are good black bodies in regions covered by their oscillator energies – that is, in regions where they absorb very strongly).

(iii) a multiple scattering cloud (see later)

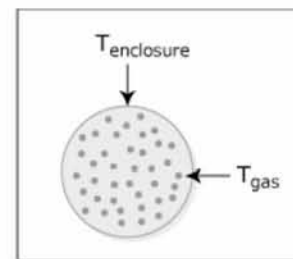
(c) application to real gases – providing the discrete energy levels in the molecule are populated according to Boltzmann’s distribution, we can show these levels will be in  $m$  with black body radiation. Consider an enclosed gas at constant temperature (i.e. in local thermodynamic equilibrium (LTE)) – consider 2 energy levels  $i$  (excited)  $\leftrightarrow$  0 (ground state)

Rate of induced emission =  $N_i b_{i0} I_{\nu_{i0}}$

Rate of induced absorption =  $N_0 b_{i0} I_{\nu_{i0}}$

where  $b_{i0}$  = Einstein “b” coefficient (see later)

and  $\frac{N_i}{N_0} = g_i e^{-h\nu_{i0}/kT}$  ( $g_i = 1$  for vibrations  
 $= 2J+1$  for rotations)



For vibrations  $N_i \ll N_0$  (room temp.) so induced absorption far exceeds induced emission. Einstein argued (from the fact that molecules do not fall apart at low pressures) that the statistical Boltzmann distribution for energy should be maintained even at very low pressures where collisions do not occur. He therefore proposed the existence of spontaneous emission with a rate =  $a_{i0}$  ( $\text{sec}^{-1} \text{ ster}^{-1}$ ). Equivalently define the radiative relaxation time  $\tau_{i0} = 1/4\pi a_{i0}$ .

Therefore in LTE (in absence of collisions):

$$\begin{array}{c} \text{Dominant} \\ \downarrow \\ 4\pi N_i (b_{i0} I_{\nu_{i0}} + a_{i0} h\nu_{i0}) = 4\pi N_0 (b_{i0} I_{\nu_{i0}}) \\ \text{(total rate of emission)} \quad \text{(total rate of absorption)} \end{array}$$

$$\text{i. e.} \quad \frac{N_i}{N_0} = \frac{b_{i0} I_{\nu_{i0}}}{b_{i0} I_{\nu_{i0}} + a_{i0} h\nu_{i0}} = e^{-h\nu_{i0}/KT}$$

$$\text{i. e.} \quad I_{\nu_{i0}} = \frac{a_{i0}}{b_{i0}} \frac{h\nu_{i0}}{(e^{h\nu_{i0}/KT} - 1)} \quad (= B_{\nu_{i0}})$$

From time-dependent quantum theory  $a_{i0} = \frac{2\nu_{i0}^2}{c^2} b_{i0}$  so that  $I_{\nu_{i0}} = B_{\nu_{i0}}$ . Hence total rate of emission given by

$$\begin{aligned} 4\pi N_0 b_{i0} B_{\nu_{i0}} \quad & \text{(Kirchoff's Law)} \\ = 4\pi \beta_{i0} B_{\nu_{i0}} \quad & (\beta_{i0} = N_0 b_{i0} = \text{integrated absorption coefficient}) \end{aligned}$$

in LTE (as well as non-LTE). Also due to "broadening" of absorption and emission lines (discussed later) we allow for absorption or emission over a range of frequencies by generalizing  $\nu_{i0}$  to  $\nu$ .

$$\begin{aligned} 4\pi N_0 \int_0^{\Delta\nu} k_\nu B_\nu d\nu \quad & (k_\nu = \text{absorption cross-section}) \\ & (m^2) \\ = 4\pi \int_0^{\Delta\nu} \beta_\nu B_\nu d\nu \quad & (\beta_\nu = \text{absorption coefficient}) \\ & (m^{-1}) \end{aligned}$$

(d) Application to the real atmosphere – the atmosphere is a non-enclosed space and generally has external radiation (e.g. solar; thermal from ground or distant atmosphere). Clearly,  $I_\nu \neq B_\nu$  (as defined by  $T_{local}$ ).

$$\begin{array}{ll} \text{If } 4\pi \int_0^\infty \beta_\nu I_\nu d\nu > 4\pi \int_0^\infty \beta_\nu B_\nu d\nu & \text{get radiative heating} \\ \text{(absorption)} \quad \text{(emission)} & \end{array}$$

$$\begin{array}{ll} 4\pi \int_0^\infty \beta_\nu I_\nu d\nu < 4\pi \int_0^\infty \beta_\nu B_\nu d\nu & \text{get radiative cooling} \\ \text{(absorption)} \quad \text{(emission)} & \end{array}$$

## Energy Levels in molecules

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

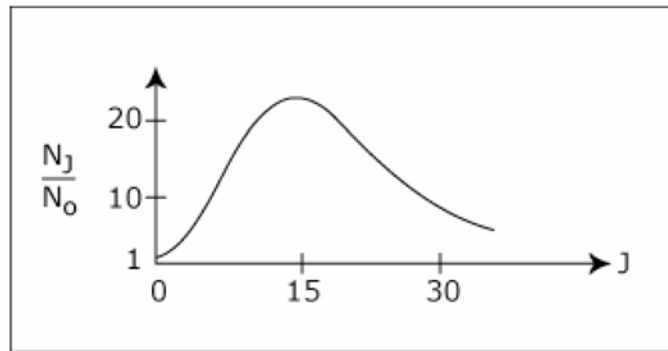
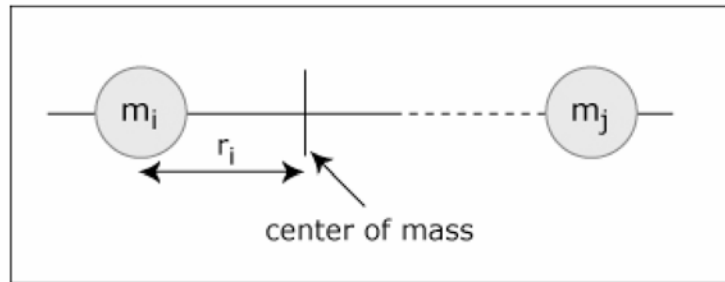
For a linear molecule (e.g.  $\text{CO}_2, \text{N}_2\text{O}, \text{O}_2, \text{CO}, \text{H}_2$ , etc.)

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

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

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

where  $I = \text{moment of inertia} = \sum_i m_i r_i^2$  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  $N_v/N_0 = \exp(-v h \nu_0 / KT)$  (Boltzmann distribution). Note  $N_1/N_0 = \exp(-5) \approx 0.01$  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  $\nu_i$  with its own set of quantum numbers ( $v_i = 0, 1, 2$ , etc.). Choose fundamentals using group theory or simple geometry so vector sets representing vibrations linearly independent :

Examples :

① **Water Vapor Molecule**

$0.958 \text{ \AA}$   $105^\circ$   $(3N-6 = 3)$

**Vibratory States**

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

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

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

② **Ozone Molecule**

$1.26 \text{ \AA}$   $117^\circ$   $(3N-6 = 3)$

**Vibratory States**

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

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

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

③ **Carbon Dioxide Molecule**

$1.16 \text{ \AA}$   $(3N-5 = 4)$

**Vibratory States**

Symmetric band stretching  
No band

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

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

(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:

