12.815, Atmospheric Radiation Prof. Ronald Prinn Lecture:

Thermodynamic concepts of radiation

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



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

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

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

<u>Stefan's Law</u>: Kondratyev:

$$\int_{0}^{\infty} B_{\lambda} d\lambda = \frac{2 K^{4} T^{4}}{c^{2} h^{3}} \int_{0}^{\infty} \frac{x^{3} dx}{e^{x} - 1} \qquad \left(x = \frac{h c}{\lambda K T}\right)$$
$$= \left[\frac{2 \pi^{5} K^{4}}{15 c^{2} h^{3}}\right] \frac{T^{4}}{\pi} \qquad \left(\frac{erg}{cm^{2} \cdot sec \cdot steradian}\right)$$
Stefan's constant (σ)

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

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(b) <u>ideal black body</u>: one which is in equilibrium with the Planck distribution. It absorbs <u>all</u> the radiation incident upon it and emits the Planck distribution for its temperature.

Practical Examples:

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

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

- (iii) a multiple scattering cloud (see later)
- (c) <u>application to real gases</u> 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 <u>enclosed</u> gas at <u>constant</u> temperature (i.e. in <u>local thermodynamic equilibrium</u> (LTE)) consider 2 energy levels
 i (excited) ↔ 0 (ground state)

Rate of <u>induced</u> emission = $N_i b_{i0} I_{v_{i0}}$

Rate of <u>induced</u> absorption = $N_0 b_{i0} I_{v_{i0}}$

where $b_{i0} = \underline{\text{Einstein "b" coefficient}}$ (see later)

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



For vibrations N_i << N₀ (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} (sec⁻¹ ster⁻¹). Equivalently define the <u>radiative</u> relaxation time $\tau_{i0} = 1/4\pi a_{i0}$.

Therefore in LTE (in absence of collisions):

$$\begin{array}{rcl} & & & & & \\ & & & \\ & & & \\$$

$$\underline{i.~e.}~~\frac{N_{i}}{N_{o}}=\frac{b_{i0}~I_{\nu_{i0}}}{b_{i0}~I_{\nu_{i0}}~+~a_{i0}~h\nu_{i0}}=e^{-h\nu_{i0}/KT}$$

$$\underline{i.\ e.} \qquad I_{v_{i0}} = \frac{a_{i0}}{b_{i0}} \ \frac{hv_{i0}}{\left(e^{-hv_{i0}/KT} - 1\right)} \qquad \left(\equiv \ B_{v_{i0}}\right)$$

From time-dependent quantum theory $a_{i_0} = \frac{2 v_{i_0}^2}{c^2} b_{i_0}$ so that $I_{v_{i_0}} = B_{v_{i_0}}$. Hence total rate of emission given by

= $4 \pi \beta_{i0} B_{v_{in}}$ ($\beta_{i0} = N_0 b_{i0}$ = integrated absorption coefficient)

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 v_{10} to $v_{.}$

$$4 \pi N_0 \int_0^{\Delta v} k_v B_v dv \qquad (k_v = \underline{absorption \ cross-section})$$

$$(m^2)$$

$$= 4 \pi \int_0^{\Delta v} \beta_v B_v dv \qquad (\beta_v = \underline{absorption \ coefficient})$$

$$(m^{-1})$$

- (d) <u>Application to the real atmosphere</u> the atmosphere is a <u>non-enclosed</u> space and generally has <u>external</u> radiation (e.g. solar; thermal from ground or distant atmosphere). Clearly, $I_v \neq B_v$ (as defined by T_{local}).
 - If $4\pi \int_{0}^{\infty} \beta_{v} I_{v} dv > 4\pi \int_{0}^{\infty} \beta_{v} B_{v} dv$ get <u>radiative heating</u> (absorption) (emission) $4\pi \int_{0}^{\infty} \beta_{v} I_{v} dv < 4\pi \int_{0}^{\infty} \beta_{v} B_{v} dv$ get <u>radiative cooling</u> (absorption) (emission)

Energy Levels in molecules

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

For a linear molecule (e.g. CO_2 , N_2O , O_2 , CO, H_2 , etc.)

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

= B J (J+1)
and N_J/N₀ = (2J+1) exp(-BJ (J+1)/KT)
degeneracy

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) <u>Vibrational Energies</u> (quantum no. v=0, 1, 2,.....)

For a <u>diatomic</u> molecule:

$$\mathsf{E}_{\mathsf{vib}} = \left(\mathsf{v} + \frac{1}{2}\right)\mathsf{h}\left[\frac{1}{2\pi}\sqrt{\frac{\mathsf{C}}{\left(\frac{1}{\mathsf{m}_1} + \frac{1}{\mathsf{m}_2}\right)}}\right] = \left(\mathsf{v} + \frac{1}{2}\right)\mathsf{h}\mathsf{v}_{\mathsf{o}}$$

12.815, Atmospheric Radiation Prof. Ronald Prinn 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 $N_v/N_0 = \exp(-vhv_0/KT)$ (Boltzmann distribution). Note $N_1/N_0 \simeq \exp(-5) \simeq 0.01$ at room temperature so almost all molecules in ground state. For complex molecules:

Number of fundamental vibrations/frequencies

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

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

Examples :



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(c) Electronic Energies

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

<u>e.g.</u> for <u>linear molecules</u> electronic states are conveniently designated by informative symbols:



e.g. energy level diagram for O2



 $\label{eq:conversions: 1ev = 8067 cm^{-1} = 1.24 \ \mu\text{m} \ (near \ infrared) \\ 2ev = 16134 \ cm^{-1} = 0.62 \ \mu\text{m} \\ 3ev = 24201 \ cm^{-1} = 0.41 \ \mu\text{m} \\ 5ev = 40335 \ cm^{-1} = 0.248 \ \mu\text{m} \ (ultraviolet) \\ \end{tabular}$