Show EvZ nonresonant absorption and emission sections 8-4-3 and 8-4-4

Extinction coefficient and Optical thickness

   The attenuation of the intensity, I, (watts/steradian) of light changes as it passes through a slab of material, dz thick with an ***absorption extinction coefficient***, α_a, in units of inverse length.

$$dI = -\alpha_a I \, dz = -I \, d\tau$$

where $d\tau$ is the change in the **optical depth**. (EvZ notation uses $\alpha_\alpha = \rho\alpha$ where ρ is mass density and α is crossectional area per kg which they call the absorption coefficient). As a result, after passing through a length, L, through the slab, the intensity is

$$I(L) = I_0 \, e^{-\alpha_a L}$$

where the intensity of the light entering the slab is I_0.
   So the concept of **optical depth** is related to the extinction coefficient as follows

$$\tau(v, z_1, z_2) = \int_{z_1}^{z_2} \alpha(v, z) dz$$

This form indicates the dependence of extinction coefficient along the (vertical) path and the dependence on frequency as we've learned from the absorption lines and their spectral shapes. Optical depth is a crucial concept for radiative transfer and one should develop some intuition about it to understand radiative transfer in the atmosphere.
   Continuing with the example above, after passing through a length, L, through the slab, the intensity is

$$I(L = z_2 - z_1) = I_0 \exp\left[\int_{z_1}^{z_2} \alpha(v, z) dz\right] = I_0 \exp\left[-\tau(v, z_1, z_2)\right] = I_0 e^{-\tau}$$

Emission: Thermal Source
   An atmospheric layer of thickness, dz, and temperature, T, emits radiation following the Planck law:

$$dI = \psi_t \, dz = \alpha_a(z) \, B(v, T) \, dz$$

where $B(v, T)$ is the Planck function (in watts/m^2/steradian). Since temperature and constituent density are functions of altitude, the thermal source is written as

$$\psi_t(v, T, z) = \alpha_a(z) \, B(v, T)$$

Note that the source is proportional to the absorption coefficient. If a layer of the atmosphere has a temperature, T, but does not interact with electromagnetic radiation, then α_a is 0 and ψ_t is therefore 0. So there is no thermal electromagnetic radiation emitted from that layer. There is also no *absorption* by that layer since α_a is 0.

Combined attenuation and thermal source

$$dI = -\alpha_a \, I \, ds + \psi \, ds = -\alpha_a \, I \, ds + \alpha_a \, B(v,T) \, ds$$

More on the extinction coefficient and thermal source via Einstein Coefficients

Equilibrium following G&Y written in terms of number of photons including the lineshape:

$$n(u) \, A(u,l) f_s(v\text{-}v_0) - n(l) \, u_v \, C(l,u) \, f_a(v\text{-}v_0) + n(u) u_v C(u,l) f_i(v\text{-}v_0) = 0$$

$$\textit{spont emission} \qquad \textit{absorption} \qquad \textit{induced emission}$$

where u_v is photons per unit volume. In thermodynamic equilibrium, the relation between populations in the upper and lower levels is

$$n(u) = n(l) \, g_u/g_l \exp(-hv/kT)$$

and u and l refer to upper and lower energy levels. Rewriting the equilibrium equation

$$A_{ji} n_i \frac{g_j}{g_i} e^{-hv_{ij}/kT} f_s - C_{ij} n_i u_{v_{ij}} f_a + C_{ji} n_i \frac{g_j}{g_i} e^{-hv_{ij}/kT} u_{v_{ij}} f_i = 0$$

where i is the lower level, j is the upper level

Now we use the Planck function to determine u_v. The question is which form do we use. For u_v, the answer is we want the energy density form with the understanding that it alters the dimensions of the Einstein coefficients, B_{ij} and B_{ji}. To generalize we write the Planck function as

$$B(v,T) = F(v) \frac{1}{e^{hv/kT} - 1}$$

where $F(v) = \dfrac{2hv^3}{c^2}$ using the radiance form and $F(v) = \dfrac{8\pi h v^3}{c^3}$ using the radiant energy density form. Here, G&Y use u_v in the density form divided by hv to get the photon number density

$$u_{v,T} = \frac{8\pi v^2}{c^3} \frac{1}{e^{hv/kT} - 1}$$

Plugging this in to the equation above yields

$$A_{ji} n_i \frac{g_j}{g_i} e^{-hv_{ij}/kT} f_s - C_{ij} n_i \frac{8\pi v^2}{c^3} \frac{1}{e^{hv/kT}-1} f_a + C_{ji} n_i \frac{g_j}{g_i} e^{-hv_{ij}/kT} \frac{8\pi v^2}{c^3} \frac{1}{e^{hv/kT}-1} f_i = 0$$

$$A_{ji} n_i \frac{g_j}{g_i} e^{-hv_{ij}/kT} \left[e^{hv/kT} - 1 \right] f_s - C_{ij} n_i \frac{8\pi v^2}{c^3} f_a + C_{ji} n_i \frac{g_j}{g_i} e^{-hv_{ij}/kT} \frac{8\pi v^2}{c^3} f_i = 0$$

$$A_{ji} n_i \frac{g_j}{g_i} \left[1 - e^{-hv_{ij}/kT} \right] f_s = \frac{8\pi v^2}{c^3} n_i \left[C_{ij} f_a - C_{ji} \frac{g_j}{g_i} e^{-hv_{ij}/kT} f_i \right]$$

These can only be equal if

$$C_{ji} \, g_j/g_i f_i = C_{ij} f_a.$$

and

$$A_{ji}\frac{g_j}{g_i}f_s = \frac{8\pi v^2}{c^3}C_{ij}f_a = \frac{8\pi v^2}{c^3}C_{ji}f_i\frac{g_j}{g_i}$$

so $A_{ji}f_s = \frac{8\pi v^2}{c^3}C_{ji}f_i$ which matches G&Y (2.52)

However, the first relation does *not* match G&Y (2.53): $\dfrac{g_l C(l,u)f_a}{g_u C(u,l)f_i} = \exp\left[\dfrac{h(v-v_0)}{kT}\right]$

G&Y is apparently wrong and the exp[ ] should be 1.

$hv\, u_v\, dv$ = energy density form of Planck function $= \dfrac{8\pi h v^3}{c^3}\dfrac{1}{e^{hv/kT}-1}$ which is $4\pi/c$ times the flux form. Now we write the equlibrium equation in terms of the change in the intensity of an incident EM beam.

$$\frac{dI_v}{ds}d\omega = hv\,A_{ji}n_j f_s\frac{d\omega}{4\pi} - \frac{I_v d\omega}{c}C_{ij}n_i f_a + \frac{I_v d\omega}{c}C_{ji}n_j f_i$$

$$\qquad\quad \textit{spontaneous emission}\qquad\quad \textit{absorption}\qquad \textit{induce emission}$$

$$\frac{dI_v}{ds}d\omega = n_j\frac{g_i}{g_j}\frac{8\pi h v^3}{c^3}C_{ij}f_a\frac{d\omega}{4\pi} - n_i\frac{I_v d\omega}{c}C_{ij}f_a + n_j\frac{g_i}{g_j}\frac{I_v d\omega}{c}C_{ij}f_a$$

Note how this last equation differs from (2.54) in G&Y. They missed an *hv* in the spontaneous emission term, they have an extra 1/c in the spontaneous emission term and their exp[ ] should be 1.

Extinction coefficient and thermal Source Function

$$\frac{dI_v}{ds}d\omega = n_i e^{-hv_{ij}/kT}\frac{8\pi h v^3}{c^3}C_{ij}f_a\frac{d\omega}{4\pi} - n_i\frac{I_v d\omega}{c}C_{ij}f_a + n_i e^{-hv_{ij}/kT}\frac{I_v d\omega}{c}C_{ij}f_a$$

$$\qquad\qquad \textit{spontaneous emission}\qquad\quad \textit{absorption}\qquad \textit{induced emission}$$

Do some algebra to obtain a form closely related to extinction coefficient….

$$\frac{dI_v}{ds}d\omega = -n_i C_{ij}f_a\left[1-e^{-hv_{ij}/kT}\right]\frac{I_v d\omega}{c} + n_i C_{ij}f_a e^{-hv_{ij}/kT}\frac{8\pi h v^3}{c^3}\frac{d\omega}{4\pi}$$

$$\frac{dI_v}{ds}d\omega = -n_i C_{ij}f_a\left[1-e^{-hv_{ij}/kT}\right]\frac{I_v d\omega}{c} + n_i C_{ij}f_a\left[1-e^{-hv_{ij}/kT}\right]\frac{e^{-hv_{ij}/kT}\frac{8\pi h v^3}{c^3}}{\left[1-e^{-hv_{ij}/kT}\right]}\frac{d\omega}{4\pi}$$

$$\frac{dI_v}{ds}d\omega = -\frac{n_i C_{ij}f_a}{c}\left[1-e^{-hv_{ij}/kT}\right]I_v d\omega + \frac{n_i C_{ij}f_a}{c}\left[1-e^{-hv_{ij}/kT}\right]\frac{\frac{2hv^3}{c^2}}{\left[e^{hv_{ij}/kT}-1\right]}d\omega$$

$$\frac{dI_v}{ds}d\omega = -k_v I_v d\omega + k_v B_v d\omega$$

where $k_v = \dfrac{N_i C_{ij} f_a}{c}\left[1 - e^{-hv_{ij}/kT}\right]$. This means

$$dI_v = -k_v I_v ds + k_v B_v ds$$

In comparing this to

$$dI = -\alpha_a I\, ds + \alpha_a \psi\, ds = -\alpha_a I\, ds + \alpha_a B(v,T)\, ds$$

we see that k_v is the absorption coefficient, α_a, in units of inverse length, and the thermal source function, ψ, is indeed B_v which is the Planck function in watts/steradian/m^2:

$$B(v,T) = \frac{2hv^3}{c^2}\frac{1}{e^{hv/kT}-1}$$

Line Strength

From the equation that relates extinction coefficient to line strength, $k_v = S_v f(v-v_0)$, we see that the line strength is

$$S_v = \frac{n_i C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right]$$

A word on Crosssections

The concept of a molecule or particle having a crosssection is a useful concept for developing physical insight into extinction. Crosssection is an area in this case that interacts with light, either absorbing or scattering the light. The electromagnetic cross section may be quite different from the *geometric* area crosssection of the molecule. The crossections of individual molecules can then be added to get the collective crossection of many molecules per unit volume.

Back to line Strengths

Before checking units and determining which form of the line strength we have in the equation above, we need to be a bit careful here about n_i. The following form is the crosssection per molecule that is in the energy state, E_i.

$$S_v = \frac{C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right]$$

We want the crosssection per molecule so that we can multiply it by the number density of molecules to get a crosssection per volume which gives us the inverse length units of an extinction coefficient. So we also need to know the fraction of molecules in energy level, E_i, which we can write simply as

$$S_{v,n} = \frac{n_i}{n_{tot}}\frac{C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right]$$

Assuming thermodynamic equilibrum,

$$\frac{n_i}{n_{tot}} = \frac{g_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)} = \frac{g_i \exp(-E_i/kT)}{Z}$$

where g_i is the degeneracy or the number of states with the same energy level.

$$S_{v,n} = \frac{g_i \exp(-E_i/kT)}{Z}\frac{C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right]$$

Check Units: sec m^{-1} s^{-1} m^3 s^{-3} s^2 = s^{-1} m^2 = m^2 Hz. This is the *molecular* line strength in Hz. Multiplying it by the number density of this molecule, n_m, yields the *volume* line strength in m^{-1} Hz (or some other inverse length unit).

$$S_{v,v} = n_m \frac{g_i \exp(-E_i/kT)}{Z}\frac{C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right] = n\frac{n_m}{n}\frac{g_i \exp(-E_i/kT)}{Z}\frac{C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right]$$

where n is the total number density of the gas $= P/kT$ and n_m/n is the volume mixing ratio of constituent m of the gas and the *volume* extinction coefficient is

$$k_{v,v} = S_{v,v} f(v - v_0)$$

Line strength and the electric dipole moment

To get the relation between the line strength and the **electric dipole,** we need a relation between an Einstein coefficient and the electric dipole moment

DO NOT USE G&Y: $A_{ij} = \dfrac{64\pi^4 v_{ij}^3}{3hc^3}\left|R_{ij}\right|^2$ units: m^{-3}J^{-1} s^{-1} m^2 = **WRONG**:

Robert Hilborn notes:

$$A_{ij} = \frac{2e^2 8\pi^3 v_{ij}^3}{3\varepsilon_0 hc^3}\left|R_{ij}\right|^2$$

units: C^2 m^{-3}J^{-1} s^{-1} m^2 C^{-2} N m^2 = s^{-1} m N/J = s^{-1} **OK**! So we can to make the connection to the electic dipole moment

$$S_v = \frac{N_i C_{ij}}{c}\left[1 - e^{-hv_{ij}/kT}\right] = N_i\left[1 - e^{-hv_{ij}/kT}\right]A_{ji}\frac{g_j}{g_i}\frac{f_s}{f_a}\frac{c^2}{8\pi v^2} = N_i\left[1 - e^{-hv_{ij}/kT}\right]\frac{g_j}{g_i}\frac{f_s}{f_a}\frac{2e^2\pi^2 v_{ij}}{3\varepsilon_0 hc}\left|R_{ij}\right|^2$$

Scattering crosssection
See mie scattering equations in EvZ
I find it physically intuitive to express the scattering crosssection in terms of the geometric crosssection, $\sigma_{geom} = \pi r^2$ where r is the particle radius. EvZ writes things in terms of the particle diameter, D. When the particle is small relative to the wavelength (the so-called *Rayleigh* scattering regime), then $\pi D/\lambda = 2\pi r/\lambda = q \ll 1$, (Note EvZ's $\gg$ is backwards). So the particle scattering and absorption crosssections become

$$\sigma_s = \frac{2}{3}\frac{\pi^5 D^6}{\lambda^4}\left|K\right|^2 = \frac{2^7}{3}\frac{\pi^5 r^6}{\lambda^4}\left|K\right|^2 = \pi r^2\frac{2^3}{3}\frac{2^4\pi^4 r^4}{\lambda^4}\left|K\right|^2 = \frac{8}{3}q^4\left|K\right|^2\sigma_{geom}$$

$$\sigma_a = \frac{\pi^2 D^3}{\lambda} \text{Im}(-K) = \frac{\pi^2 2^3 r^3}{\lambda} \text{Im}(-K) = \pi r^2 2^3 \frac{\pi r}{\lambda} \text{Im}(-K) = 4q \, \text{Im}(-K) \, \sigma_{geom}$$

where $K = (n_c^2-1)/(n_c^2+2)$ and n_c is the *complex* index of refraction. The real part of the index of refraction affects the speed of the light. The imaginary part affects the amplitude of the light, generally attenuating it although with stimulated emission it could amplify it. The *extinction* crosssection, σ_e, is the sum of the absorption and scattering crosssections: $\sigma_e = \sigma_a + \sigma_s$.

Notice that the electromagnetic scattering crosssection in particular can be ***MUCH*** smaller than the geometric crosssection.

To be clear, from p24 G&Y equation (2.22):

$$e_u = k_u + s_u$$

indicating e_v, the extinction coefficient is the sum of absorption coefficient, k_v, and the scattering coefficient, s_v.

Extinction coefficient: relation to the crosssection and its multiple forms

Now let's return to the extinction coefficient and see how it is related to the crosssection and the multiple ways of expressing extinction coefficients.

EvZ write the absorption coefficient as though it depends on mass, $\alpha_a = \rho\alpha$. This should be written as $\alpha_a = \rho\alpha_m$ to reflect the fact that α_m is the **mass** extinction coefficient. To understand the extinction coefficient and the several forms it can be written in and the relation to the crosssection, it is instructive to write the extinction coefficient as

$$\alpha_v = \sigma \, n \, f$$

where σ is the crosssection per molecule and n is the molecular number density. Notice this gives us the units of inverse length as required. So this is a physically simple and correct way to think of the extinction coefficient. This form is called the volume extinction coefficient.

Using the *e* notation of G&Y and Eric Weinstein's notation on the web page below where , *e* = α, the volume extinction coefficient, e_v, represents a crosssection per molecule times the molecular number density. The volume coefficient is in units of inverse length, usually cm^{-1}. The volume extinction coefficient at standard temperature and pressure (s.t.p.) is e_s .

The relationships are as follows (*see caveat for pure rotational transitions given below*).

$$e_v = e_s \, n_s/n \ = \rho \, e_m = n \, e_n.$$
$$e_s = e_v \, n/n_s = \rho_s \, e_m = n_s \, e_n.$$

Table: Extinction Coefficient Summary

symbol	e_v	e_m	e_n	e_s
name	volume	mass	molecular	e.c. per cm stp
cgs	cm^{-1}	$\text{g}^{-1} \, \text{cm}^2$	cm^2	cm^{-1}
mks	m^{-1}	$\text{kg}^{-1} \, \text{m}^2$	m^2	m^{-1}
	Crosssection per unit volume	Crosssection per unit density	Crosssection per molecule or mole	Crosssection per volume at s.t.p.

See also http://scienceworld.wolfram.com/physics/ExtinctionCoefficient.html for more explanation on extinction coefficients.

Connection between line strength, *S*, and extinction coefficients, *e*.

We need to make the connection between the line spectral quantities and the various forms of the extinction coefficients. We have the spectral line relation that $k(v) = S f(v)$ where $f(v)$ is the normalized line shape and S is the line strength. Although EvZ doesn't make the connection, the connection is simply $k(v) = e(v) = \alpha(v)$ but one must be very careful of units in doing so.

Example: if we want the volume extinction coefficient, e_v, which has units of cm^{-1}, and v is in units of cm^{-1} such that $f(v)$ is in units of $1/\text{cm}^{-1} = \text{cm}$, then S must be in units of cm^{-1} cm^{-1} = cm^{-2}. Many of the various combinations of line intensity units to achieve a particular extinction coefficient are given in Table A.2.4 of G&Y that has been reproduced to try and help with this issue

Spectral units	e_m (g^{-1} cm^2)	e_n (cm^2)	e_v (cm^{-1})
Wavelength, cm	g^{-1} cm^3	cm^3	1
Wavenumber, cm^{-1}	g^{-1} cm	cm	cm^{-2}
Frequency, Hz	g^{-1} cm^2 s^{-1}	cm^2 s^{-1}	cm^{-1} s^{-1}

Be careful of spectral quantities that are in per unit wavenumber. This will result in a unit of cm since wavenumber has units of inverse cm. Be careful of mixed units, for instance cm mixed with meters.

Dependence of linestrength and absorption coefficient on temperature and pressure

The *volume* linestrength depends on temperature in several ways

$$S_{v,v} = n \frac{n_m}{n} \frac{g_i \exp(-E_i/kT)}{Z} \frac{C_{ij}}{c} \left[1 - e^{-hv_{ij}/kT}\right] = \frac{P}{kT} \frac{n_m}{n} \frac{g_i \exp(-E_i/kT)}{Z} \frac{C_{ij}}{c} \left[1 - e^{-hv_{ij}/kT}\right]$$

the stimulated emission term defining the amount of absorption minus the amount of stimulated emission, the Boltzmann distribution term which determines the fraction of the n_m molecules that are in the lower energy state of the transition and the bulk number density of the gas, *n*.

The line strength is often given at some reference temperature (and pressure) level. If just the crosssection per molecule form is used, there is no pressure dependence. The terms standard temperature and pressure (stp) is used although care is required in understanding what stp means. The JPL catalog, see http://spec.jpl.nasa.gov, gives the crosssection form of the linestrength at T=300K.

Note that the absorption coefficient, $k_{v,v}$, has additional dependance on *T* and *P* through the Doppler and collisional line shapes, $f(v-v_0)$.

The importance of the stimulated emission term in natural radiation

Let's examine the $-\exp(-hv/kT)$ term for a moment. This is the stimulated emission term. For pure rotational transitions, let's use the very strong 557 GHz water line, $\lambda = 0.539$ mm $= 539$ microns. Let's assume a mid-tropospheric temperature of 250 K. $hv/kT \sim 0.1$ and $\exp(-hv/kT) \sim 0.9$ so $[1- \exp(-hv/kT)] \sim 0.1$. Clearly in this case the $\exp(-hv/kT)$ is quite important.

For a vibrational transition at say 6 microns, the frequency, v, of the transition is = 50 THz. Using T = 250K, hv/kT ~ 9.6 and exp(-*hv/kT*) ~ 0.00007 so 1- exp(-*hv/kT*) ~1. Clearly in this case the exp(-*hv/kT*) is quite *unimportant*.

So the exp(-*hv/kT*) term can be ignored for vibrational and higher energy transitions but not for pure rotational transitions.

So, in the extinction coefficient and line strength, the n_j/n depends on temperature as does the [1- exp(-*hv/kT*)] term. This is important because the scaling between different forms of the extinction coefficient given by G&Y,

$$e_v = e_s \, n_s/n \ = \rho \, e_m = n \, e_n.$$

is not true for pure rotational transitions because it ignores the [1- exp(-*hv/kT*)] term.

Miscellaneous

Careful, there are 2 definitions of *n*. One has to do with number of states or population and the other in EvZ is the index of refraction.

Line strength, extinction coefficient and Optical depth
Units: But there has to be per Hz because of the eventual integral across the line spectrum.

Switch to EvZ Radiative Transfer Equation
  • Discuss 4 general terms in the radiative transfer equation
  • Absorption coefficient as both absorption and emission
  • The emission source function
  • Scattering as both extinction and source
Note: The extinction coefficient refers to absorption *and* scattering coefficients.