EPS 237 Lesson 9: Line broadening and line strengths

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This is probably the most mathematically intensive lecture in the course. For further reading, I recommend Bernath, *Spectra of Atoms and Molecules*.

1 Line broadening types and Lorentz lineshape

- Natural broadening (lorentz lineshape). From Heisenburg's uncertainty principle. Not significant in real atmospheres.
- Collision/pressure broadening (lorentz lineshape). Important in lower atmosphere.
- Doppler broadening (gaussian lineshape). Important in mesosphere and above.

The Lorentz lineshape is

$$f_L(\nu) = \frac{\gamma_L}{\pi[(\nu - \nu_0)^2 + \gamma_L^2]}. \tag{1}$$

where γ_L is line width, ν is frequency (or wavenumber if γ_L is expressed in cm^{-1} units), and ν is the line frequency. γ_L is a function of temperature and pressure in general. Simple theories for the value of γ_L for each line given collision broadening yield poor results. Self- and air-broadened values for γ_L for each line are therefore given in the HITRAN database. The air-broadened width may be used for greenhouse gases on Earth. Broadening data when the background gas is not Earth air is often hard to come by.

For fixed T, the collision frequency is proportional to pressure. Conversion of pressure broadening coefficients in HITRAN to other pressures and temperatures is given by

$$\gamma_L(p, T) = \gamma_L(p_0, T_0)\frac{p}{p_0}\left(\frac{T_0}{T}\right)^n. \tag{2}$$

where p_0 and T_0 are 1 atm and 296 K, and the value of n (for Earth air!) is given in the HITRAN database.

2 Doppler Lineshape

This is *inhomogenous broadening*, in sense that it affects different molecules differently. It arises from the Boltzmann distribution of molecule speeds in a gas. This leads to random shifting of photon frequencies for molecules.

The frequency shift for gas molecule speeds much less than c can be written as

$$\nu = \nu_0(1 - v/c), \tag{3}$$

implying

$$v^2 = c^2 \left(\frac{\nu_0 - \nu}{\nu_0} \right)^2. \tag{4}$$

The distribution for particle velocities follows Boltzmann statistics

$$f_D(v) \propto e^{-E/k_B T} \propto e^{-\frac{1}{2}v^2/RT} \tag{5}$$

where R is the specific gas constant. Hence with correct normalization to give an integral $\int f_D d\nu = 1$,

$$f_D(\nu) = \frac{1}{\gamma_D \sqrt{\pi}} e^{-\frac{(\nu-\nu_0)^2}{\gamma_D^2}} \tag{6}$$

with the Doppler broadening width $\gamma_D = \frac{\nu_0}{c}\sqrt{2RT}$.

3 Voigt profile

This is simply the convolution of Lorentz and Doppler profiles

$$f_V(\nu - \nu_0) = f_D(\nu - \nu_0) \otimes f_L(\nu - \nu_0) \tag{7}$$

$$f_V(\nu - \nu_0) = \int_{-\infty}^{+\infty} f_D(\nu' - \nu_0) f_L(\nu - \nu') d\nu'. \tag{8}$$

There are several ways to calculate Voigt profiles in practice.

4 Time-dependent quantum theory

As noted before, the key equation of quantum mechanics in the non-relativistic limit is the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{9}$$

where $\hat{H} = -(\hbar^2/2m)\nabla^2 + V(\mathbf{r}, t)$ is the hamiltonian operator that expresses the total energy of system. The simplest case is when $\hat{H}$ has no time-dependence $[V(\mathbf{r}, t) = V(\mathbf{r})]$. Then we can solve the equation by separation of variables: $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t) = \psi(\mathbf{r})e^{-iEt/\hbar}$. There are a number of possible stationary states ψ_m with separation constants E_m. So we can write Ψ as an expansion

$$\Psi(\mathbf{r}, t) = \sum_m a_m \psi_m(\mathbf{r}) e^{-iE_m t/\hbar} \tag{10}$$

The ψ_m are the eigenstates and the E_m are the eigenvalues (energy levels), but in a real system, the a_m are additional coefficients that have to be determined. Physically, it turns out that $|a_m|^2$ is the probability of finding a particle in state m. So in the classical limit, a_m can tell us how many molecules occupy state m. To understand quantum transitions, we therefore need to look at the evolution of $a_m(t)$.

First we separate the potential term in the hamiltonian into static and time-varying parts:

$$\hat{H} = -(\hbar^2/2m)\nabla^2 + V_0(\mathbf{r}) + V'(\mathbf{r},t) = \hat{H}_0 + \hat{H}' \tag{11}$$

For electromagnetic (EM) waves interacting with molecules, we can write the time-varying term as

$$\hat{H}' = V'(\mathbf{r},t) = -\mathbf{p}\cdot\mathbf{E} \tag{12}$$

where $\mathbf{p}$ is the molecule's dipole moment. In a classical context $\mathbf{p} = \sum_k q_k \mathbf{x}_k$, where q is charge and $\mathbf{x}$ is separation. If we want to be specific, we can think of a system with a charge oscillating in the z-axis in response to a sinusoidal EM wave $\mathbf{E} = E_{ext}cos(\omega t)\hat{z}$, so

$$V'(z,t) = -p_z E_{ext} cos(\omega t). \tag{13}$$

where p_z is the dipole moment in the z-direction. Then

$$i\hbar\frac{\partial\Psi}{\partial t} = (\hat{H}_0 + \hat{H}')\Psi \tag{14}$$

$$i\hbar\left(\sum_m \dot{a}_m(t)\psi_m(\mathbf{r})e^{-iE_m t/\hbar} - (i/\hbar)\sum_m E_m a_m(t)\psi_m(\mathbf{r})e^{-iE_m t/\hbar}\right) = (\hat{H}_0+\hat{H}')\sum_m a_m(t)\psi_m(\mathbf{r})e^{-iE_m t/\hbar} \tag{15}$$

The second term on the left and the first term on right hand side fall out, because $\hat{H}_0\Psi = E\Psi = \sum_m E_m a_m(t)\psi_m(\mathbf{r})e^{-iE_m t/\hbar}$. Hence

$$i\hbar\sum_m \dot{a}_m(t)\psi_m(\mathbf{r})e^{-iE_m t/\hbar} = \sum_m a_m(t)\psi_m(\mathbf{r})V'(\mathbf{r},t)e^{-iE_m t/\hbar}. \tag{16}$$

Now multiply everything by $\int \psi_n^* d^3\mathbf{r}$, and use $\int \psi_n^*\psi_m d^3\mathbf{r} = \delta_{nm}$. Remember, the integral is only over ψ terms and V' because nothing else depends on $\mathbf{r}$.

$$i\hbar\sum_m \dot{a}_m(t)e^{-iE_m t/\hbar}\int \psi_n^*\psi_m d^3\mathbf{r} = \sum_m a_m(t)e^{-iE_m t/\hbar}\int \psi_n^* V'(\mathbf{r},t)\psi_m d^3\mathbf{r}. \tag{17}$$

For simplicity, we now focus on just two states and write $m = 1$ and $n = 2$. We end up with

$$\dot{a}_2 = -\frac{i}{\hbar}a_1 e^{-i\omega_{12}t}\left(\int \psi_2^* V'(\mathbf{r},t)\psi_1 d^3\mathbf{r}\right) \tag{18}$$

Note $\omega_{12} = (E_1 - E_2)/\hbar$ is angular frequency difference between the 2 states. Using our definition of V' in terms of E_{ext} and p_z, we can write this as

$$\dot{a}_2 = +\frac{i}{2\hbar}E_{ext}|R_{12}|e^{-i\omega_{12}t}(e^{i\omega t} + e^{-i\omega t}) \tag{19}$$

where $|R_{21}|$ is the *transition dipole moment*:

$$|R_{21}| \equiv \int \psi_2^* p_z \psi_1 d^3\mathbf{r} \equiv \langle\psi_2|p_z|\psi_1\rangle. \tag{20}$$

Note that here $|R_{21}| = |R_{12}|$ also.

5 The Einstein coefficients

We imagine a transition between two energy levels. This could be an electron changing its occupancy level, or a molecule transitioning between vibrational levels.

- A_{21} is the probability per unit time that an atom in state 2 will spontaneously emit a photon and undergo a transition to state 1. If n_2 atoms in a unit volume are in state 2, the number of photons emitted per unit time is $n_2 A_{21}$.
- B_{12} is the probability that a photon will be absorbed and cause a transition from 1 to 2 for a given background radiant energy. If n_1 atoms are in state 1, the number of photons absorbed per unit time is $n_1 B_{12} \epsilon_\nu$, where ϵ_ν is the radiant energy density at wavenumber ν.
- B_{21} is the probability that photon emission will be *induced*. The number of photons emitted per unit time by this is $n_2 B_{21} \epsilon_\nu$.

In thermal equilibrium, ϵ_ν is given by the Planck relation, with $\epsilon_\nu = \frac{4\pi}{c} B_\nu$ and detailed energy balance must apply so

$$n_1 B_{12} \epsilon_\nu = n_2 A_{21} + n_2 B_{21} \epsilon_\nu. \tag{21}$$

Solve for ϵ_ν

$$\epsilon_\nu = \frac{n_2 A_{21}}{n_1 B_{12} - n_2 B_{21}} = \frac{A_{21}/B_{21}}{(n_1/n_2)(B_{12}/B_{21}) - 1} \tag{22}$$

But radiant energy density ϵ_ν is known vs. ν. Also Boltzmann law gives $n_1/n_2 = (g_1/g_2) e^{h\nu/k_B T}$. Hence

$$\frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} = \frac{(A_{21}/B_{21})}{\left(\frac{g_1 B_{12}}{g_2 B_{21}}\right) e^{h\nu/k_B T} - 1} \tag{23}$$

We can derive *Einstein relations*

$$A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21} \tag{24}$$

$$g_1 B_{12} = g_2 B_{21} \tag{25}$$

Because these are properties of atoms/molecules themselves, they must even hold out of equilibrium.

6 Linking the transition dipole moment to Einstein coefficients

Light is exciting atoms from state 1 to state 2. But (key assumption), we don't let state 1 get significantly depleted. $a_n(0) = \{a_1(0) \quad a_2(0)\}$, $a_1(0) = 1$ (probability of state 1 is 1). Also assume $a_2(0) = 0$. Integrating our equation for $\dot{a}_2(t)$, we get

$$a_2(t) = \frac{1}{2\hbar} E_{ext} |R_{12}| \left[\frac{e^{-i(\omega_{12} - \omega)t} - 1}{\omega_{12} - \omega} + \frac{e^{-i(\omega_{12} + \omega)t} - 1}{\omega_{12} + \omega} \right]. \tag{26}$$

We lose the antiresonant term (assume $\omega \approx \omega_{12}$) to get

$$a_2(t) = \frac{1}{2\hbar} E_{ext} |R_{12}| \frac{e^{-i(\omega_{12} - \omega)t} - 1}{\omega_{12} - \omega}, \tag{27}$$

and write $|a_2|^2 = a_2^* a_2$ to get the probability of a transition given radiation at a single frequency:

$$\mathcal{P}_{12} = |a_2|^2 = \frac{E_{ext}^2 |R_{12}|^2}{4\hbar^2} \frac{(e^{-i(\omega_{12}-\omega)t} - 1)(e^{+i(\omega_{12}-\omega)t} - 1)}{(\omega_{12} - \omega)^2}. \tag{28}$$

Assume radiation doesn't vary as strongly with ω as the line absorption (broadband), and integrate over all possible frequencies

$$\int_{-\infty}^{+\infty} \mathcal{P}_{12} d\nu \approx \frac{E_{ext}^2 |R_{12}|^2}{\hbar^2} \int_{-\infty}^{+\infty} \frac{\sin^2[(\omega_{12} - \omega)t/2]}{(\omega_{12} - \omega)^2} d\nu \tag{29}$$

Write $u = \frac{1}{2}(\omega - \omega_{12})t$, $d\nu = du/\pi t$

$$\int_{-\infty}^{+\infty} \mathcal{P}_{12} d\nu \approx \frac{E_{ext}^2 |R_{12}|^2}{4\pi\hbar^2} t \int_{-\infty}^{+\infty} \frac{\sin^2[u]}{u^2} du \tag{30}$$

Integral is just π, so transition *rate*

$$\frac{d}{dt} \int_{-\infty}^{+\infty} \mathcal{P}_{12} d\nu \approx \frac{E_{ext}^2 |R_{12}|^2}{4\hbar^2}. \tag{31}$$

Finally, use an expression from EM theory (and assume thermal equilibrium)

$$\epsilon_\nu = \frac{1}{4\pi} \frac{1}{2} E_{ext}^2 \rightarrow \frac{1}{4} E_{ext}^2 = 2\pi\epsilon_\nu \tag{32}$$

to get

$$\frac{d}{dt} \int_{-\infty}^{+\infty} \mathcal{P}_{12} d\nu \approx \frac{2\pi |R_{12}|^2}{\hbar^2} \epsilon_\nu = \frac{(2\pi)^3 |R_{12}|^2}{h^2} \epsilon_\nu \tag{33}$$

Now remember, by defn. the Einstein absorption coefficient tells us that rate of transitions is

$$\frac{d}{dt} \int_{-\infty}^{+\infty} \mathcal{P}_{12} d\nu = B_{12} \epsilon_\nu \tag{34}$$

in equilibrium. So

$$B_{12} = \frac{(2\pi)^3 |R_{12}|^2}{h^2} \tag{35}$$

But

$$A_{21} = \frac{8\pi h \nu_{12}^3}{c^3} B_{12} \tag{36}$$

ignoring degeneracy, so adding a factor of $\frac{1}{3}$ from the random molecular orientation we get

$$A_{21} = \frac{64\pi^4 \nu_{12}^3 |R_{12}|^2}{3hc^3}. \tag{37}$$

This expression linking Einstein coefficients to the transition dipole moment is stated (not derived) in classical radiative transfer textbooks like Goody & Yung.

7 Line Strength

Our final task is to link this analysis back to things that we can measure. We again use the Einstein coefficients. Note that

$$\left.\frac{dn_1}{dt}\right|_{abs} = -B_{12} n_1 \epsilon_\nu \tag{38}$$

where n_1 is number concentration [molecules/m^3] in the ground state. In general, the absorption coefficient for a single transition [m^{-1}] can be defined as

$$k_{12}(\nu) = \frac{h\nu}{c}(n_1 B_{12} - n_2 B_{21}) f(\nu - \nu_{12}) \tag{39}$$

where f is the lineshape [1/Hz in SI units] as defined previously.

In the absence of degeneracy $B_{12} = B_{21}$ and in equilibrium $n_2 = n_1 \mathrm{e}^{-h\nu_{12}/k_B T}$, so

$$k_{12} = \frac{h\nu}{c} n_1 B_{12}[1 - e^{-h\nu_{12}/k_B T}] f(\nu - \nu_{12}). \tag{40}$$

Line *strength* is defined as

$$S_{12} \equiv \frac{1}{n}\int_{-\infty}^{+\infty} k_{12}(\nu) d\nu \tag{41}$$

where $n = n_1 + n_2$ is the number of molecules per unit volume in the system. If the band is narrow then we can simply write

$$S_{12} \approx \frac{h\nu_{12}}{c}\frac{n_1}{n} B_{12}[1 - e^{-h\nu_{12}/k_B T}]. \tag{42}$$

Given the definition for B_{12} derived at end of last section,

$$S_{12} = \frac{8\pi^3 \nu_{12} |R_{12}|^2}{3hc}\frac{n_1}{n}[1 - e^{-h\nu_{12}/k_B T}]. \tag{43}$$

In general form (without accounting for isotopic abundance or degeneracy) we can write

$$S_{ij} = \frac{8\pi^3}{3hc}\nu_{ij}|R_{ij}|^2 \left[1 - e^{-h\nu_{ij}/k_B T}\right] \frac{e^{-h\nu_i/k_B T}}{Z(T)}. \tag{44}$$

Note difference in n_2/n_1 vs. n_1/n.

In HITRAN, values of S_{ij} at reference temperatures are given. To get the temperature scaling, we write

$$S_{ij}(T) = S_{ij}(T_0)\frac{Z(T_0)}{Z(T)}\frac{1 - e^{-h\nu_{ij}/k_B T}}{1 - e^{-h\nu_{ij}/k_B T_0}}\frac{e^{-h\nu_i/k_B T}}{e^{-h\nu_i/k_B T_0}}. \tag{45}$$

i denotes the ground state. Ground state 'energy' in cm^{-1} ν_i is given in the HITRAN table. ν_{ij} is the wavenumber of the transition (line center location), also in cm^{-1}.