

## Chemistry 21b – Spectroscopy

### Lecture # 3 – Spectroscopic Line Shapes

Now that we have established the strength and time-dependence of the interaction of light with matter, the last general set of trends we will need to think about before beginning a detailed examination of specific spectroscopic systems are that of the shapes of the spectroscopic lines that arise from the transitions between various eigenstates. We start with the transition rate between two levels in terms of the electric field strength, that is, Eq. (2.9), which may be rewritten

$$R_{fi}(\omega) = \frac{2\pi}{\hbar^2} | \langle f | \mathbf{E}_0 \cdot \boldsymbol{\mu} | i \rangle |^2 \rho_i \delta(\omega_{fi} \pm \omega) ,$$

where we have now included the population density of initial states  $\rho_i$  in the transition rate (since in real life we will be dealing with an ensemble of atoms or molecules in a sample).  $R_{fi}(\omega)$  is proportional to the field squared, and thus to the intensity  $I$  of the incident radiation field ( $I$  is the energy flux per unit area per unit time).

Energy should therefore be removed from a light beam at a constant rate, and phenomenologically this can be written in the form

$$-\frac{dI}{dt} = k_{abs}(\omega)I ,$$

where  $k_{abs}$  is the macroscopic, frequency dependent absorption coefficient (in the language of the Kramers-Kronig relationship,  $k_{abs}$  is the real part of the  $I$  and the imaginary part of the refractive index). In terms of the rate noted above,  $-(dI/dt) = \sum_f \hbar \omega_{fi} R_{fi}$ . From the Heisenberg form of the Schrödinger equation, the time evolution of an operator may be written as

$$\frac{dF}{dt} = \frac{i}{\hbar} [H, F] . \quad (3.1)$$

Equation (3.1) leads to a general solution like (provided  $H$  is independent of  $t$ )

$$F(t) = e^{iHt/\hbar} F(0) e^{-iHt/\hbar} .$$

Using this formalism and the integral form of the delta function it is possible to show that the frequency dependence of the intensity profile for a spectroscopic transition is given by

$$I(\omega) = \frac{3}{2\pi} \int_{-\infty}^{\infty} \sum_i \sum_f \rho_i \langle i | \vec{\varepsilon} \cdot \vec{\mu} | f \rangle \langle f | \vec{\varepsilon} \cdot \vec{\mu}(t) | i \rangle dt ,$$

where  $\vec{\mu}$  is the dipole moment of the system at  $t = 0$  and  $\vec{\varepsilon}$  is a dimensionless unit vector which indicates the direction, but not the magnitude, of the electric field. Using the completeness relation ( $\sum_f |f\rangle\langle f| = 1$ ) and by treating the sum over the populations of the initial states  $i$  as an ensemble, we have

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle_{avg} dt , \quad (3.2)$$

where the factor of one-third comes from averaging the electric field over an isotropic absorbing medium. The quantity  $\langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle_{avg}$  is very important in spectroscopy, and is called the *dipole correlation function*  $G(t)$ . Eq. (6.2) tells us the general result that the line shape or frequency response of a system interacting with light is just the Fourier transform of its dipole correlation function, or

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} G(t) dt .$$

### The Natural Lifetime and Homogeneous Line Shapes

Let's look at a specific example or two, and see what Eq. (3.2) means quantitatively. First, think about a rigid rotor or a harmonic oscillator which has a dipole of strength  $\mu_0$  and a characteristic frequency  $\omega_0$  (rotation for the rigid rotor, vibration for the harmonic oscillator). In this case we have

$$\mu(t) = \mu_0 \cos \omega_0 t = \mu_0 (e^{i\omega_0 t} + e^{-i\omega_0 t}) .$$

Equation (3.2) then yields

$$I(\omega) = \frac{\mu_0^2}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega \pm \omega_0)t} dt = \frac{\mu_0^2}{2\pi} \delta(\omega \pm \omega_0) .$$

Thus, as we expect the spectrum consists of absorption or emission at a frequency of  $\omega_0$ , which is just the classical analogue of the Bohr-Einstein frequency rule.

Life gets more interesting if, for some reason, relaxation processes result in a decay of the dipole. Let's suppose things decay exponentially in time, that is

$$\mu(t) = \mu_0 \cos(\omega_0 t) \times e^{-\gamma t/2} ,$$

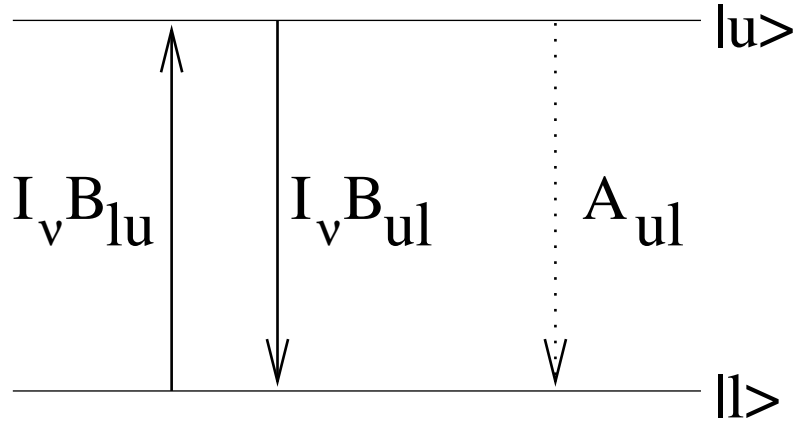
where  $\gamma$  is the temporal decay constant. We then have

$$\begin{aligned} I(\omega) &= \frac{\mu_0^2}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega \pm \omega_0)t} e^{-\gamma t/2} dt \\ &= \frac{\mu_0^2}{\sqrt{(2\pi)}} \frac{1}{i(\omega - \omega_0) + \gamma/2} = \frac{\mu_0^2}{\sqrt{(8\pi)}} \frac{\gamma/2 - i(\omega - \omega_0)}{(\omega - \omega_0)^2 + \gamma^2/4} . \end{aligned}$$

Since the real part of  $I(\omega)$  is the absorption coefficient, we see

$$k_{abs} = k_0 \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2/4} .$$

The functional form is called a *Lorentzian* line shape, and holds for any system whose dipole correlation function decays exponentially. These include natural radiative decay via spontaneous emission, collisional broadening, and power, or saturation, broadening, which are all referred to as *homogeneous* forms of line broadening. These ultimately reflect the



uncertainty principle. If some decay process limits the lifetime of a system in a given state to a time of approximately  $\Delta t$ , then the line width will be given by, on average,  $\gamma = 1/\Delta t$ . We'll look at lifetime and collisional broadening next, and then turn to a brief look at Doppler broadening.

### The Einstein Coefficients and Lifetime Broadening

Consider the two level energy diagram noted above, and embed it in a radiation field of intensity  $I_\nu d\nu$  [ $\text{erg cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$ ] in the frequency interval  $d\nu$  about  $\nu$ . Einstein introduced three parameters which describe this situation: a spontaneous transition probability  $A_{ul}$  and two other factors, stimulated absorption and emission, which describe the interaction of the electromagnetic field and transition. The absorption coefficient  $B_{lu}$  gives the rate at which upward transitions occur  $l \rightarrow u$  in this radiation field at  $\nu$ :

$$N(l)B_{lu}I_\nu \quad [\text{s}^{-1}]$$

where  $N(l)$  is the number of atoms initially in state  $l$ . The radiation field also produces induced downward transitions  $u \rightarrow l$  at the same frequency at a rate:

$$N(u)B_{ul}I_\nu \quad [\text{s}^{-1}].$$

The Einstein coefficients  $A_{ul}$ ,  $B_{ul}$  and  $B_{lu}$  are inherent properties of an atom independent of the radiation field. Thus we can arbitrarily choose a specific radiation field for the purpose of determining the relationships between these coefficients. It is most useful to consider the case of thermodynamic equilibrium (TE), in which the intensity of radiation is given by the Planck function:

$$I_\nu = B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

We can now apply the principle of “detailed balance” (also called “microscopic reversibility”), which states that in TE, the rate of upward transitions must exactly match the rate of the corresponding downward transition (Otherwise, the system is not in equilibrium!). In TE, the relative state populations are given by the Boltzmann formula:

$$N(u)/N(l) = \frac{g_u}{g_l} e^{-(E_u - E_l)/kT}$$

where  $g_n$  is the statistical weight factor (degeneracy) of state  $n$ . Thus,

$$N(l)B_{lu}I_\nu = N(u)[A_{ul} + B_{ul}I_\nu].$$

From these considerations, it is possible to derive explicit relations between  $B_{ul}$  and  $B_{lu}$ , and between  $A_{ul}$  and  $B_{lu}$ , that are independent of  $T$  (i.e., that are intrinsic properties of the atom only). In so doing, we recover Einstein's relations:

$$g_u B_{lu} = g_l B_{ul}$$

$$A_{ul} = \frac{2h\nu^3}{c^2} B_{ul}$$

The steep dependence of the spontaneous emission rate with frequency has important consequences. For a strong transition in the optical region, such as that of the sodium D line at 589 nm, the  $A$ -coefficient can be of order  $10^{7-8} \text{ s}^{-1}$ , which results in lifetimes of a few to a few tens of nanoseconds and natural line widths of several hundred MHz to 1 GHz (GHz =  $10^9$  Hz). As we'll see in a moment, this broadening is quite important, and can be the dominant effect. At longer wavelengths, however, say of order 589  $\mu\text{m}$  (so in the rotational transition range), the  $\nu^3$  factor results in lifetimes of order seconds, and so natural line widths of order a few Hz. If the radiation field is sufficiently intense, stimulated emission overwhelms spontaneous emission, and the line width becomes power dependent. The necessary power is related to the Rabi frequency, given by  $\mu_0 \mathbf{E}_0 t / \hbar$ . For numerical details, see Problem Set #1.

### Collisional Broadening

There is an additional kind of broadening that results from the perturbations of energy levels and lifetimes by "collisions" with other particles in a dense gas. This is usually called "pressure broadening" or "collision broadening". There are at least 3 categories of theories used to describe this: 2 of these are approximate theories for limiting cases, called "quasi-static" and "impact" theories, and the other is an attempt at a completely quantum theory of line broadening. Note that line broadening effects can often be measured directly.

One theory considers a collision while an atom is radiating to interrupt the wave train of the radiation. This produces a random phase shift, which manifests itself as a broadening of the frequency distribution of emitters when the random phase interruptions are averaged over an "ensemble" (a whole lot) of emitting atoms and collision partners. If these perturbing collisions are characterized by a collision frequency  $\Gamma_{coll}$ , then the Lorentzian part of the line broadening is given by a total width

$$\Gamma = \Gamma_{natural} + 2\Gamma_{coll}$$

where  $\Gamma_{natural} = \sum_l A_{ul} = 1/\tau_{rad}$  is the natural line width.

Clearly,  $\Gamma_{coll}$  must depend on (a) the cross section for "phase interruption"; (b) the gas density; (c) the gas temperature (that is, the speed of the colliding particles).

Alternatively, one can think of the ions, atoms and electrons in a dense gas as creating an average external electric field around a radiating atom. This quasi-static Stark effect then perturbs the energy levels of the radiating atom and gives rise to

Lorentzian line broadening. This is the reason why pressure broadening is sometimes called “Stark broadening”. In either case, the collisional broadening is typically characterized phenomenologically with pressure broadening coefficients  $\alpha(T)$ , which are temperature dependent and given in units of MHz/Torr. Typical values of  $\alpha$  at room temperature are 1-10 MHz/Torr. Thus, at long wavelength, pressure broadening becomes important with respect to lifetime broadening at nearly any reasonable pressure, but for strong transitions in the optical the pressure must be several hundred torr, or nearly an atmosphere, before pressure broadening becomes significant compared to lifetime broadening.

### Doppler Broadening

In real gases, there will usually be another important contribution to the line broadening due to the motions of the absorbing atoms or molecules, which, due to the distribution of “Doppler Shifts” allow them to absorb over some finite distribution of frequencies. Microscopically, this usually results from thermal Doppler broadening with a Maxwellian distribution of speeds characterized by a temperature T. The frequency and velocity shifts are related by the expression

$$\frac{\delta v}{v} = \frac{\delta \nu}{c} ,$$

while the 3D Maxwell-Boltzmann velocity distribution is given by

$$\rho_v dv = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-(mv^2/kT)} dv .$$

Combining these equations gives rise to a Gaussian line profile function, namely

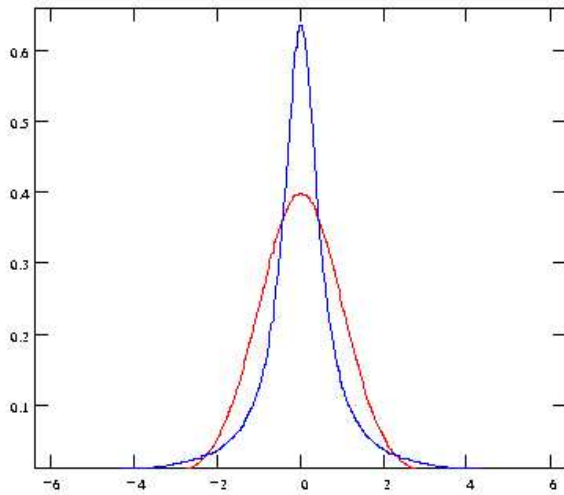
$$\phi_D(\nu - \nu_0) = \frac{1}{\sqrt{(\pi)\alpha_D}} e^{-\ln 2 [(\nu - \nu_0)/\alpha_D]^2} ,$$

where

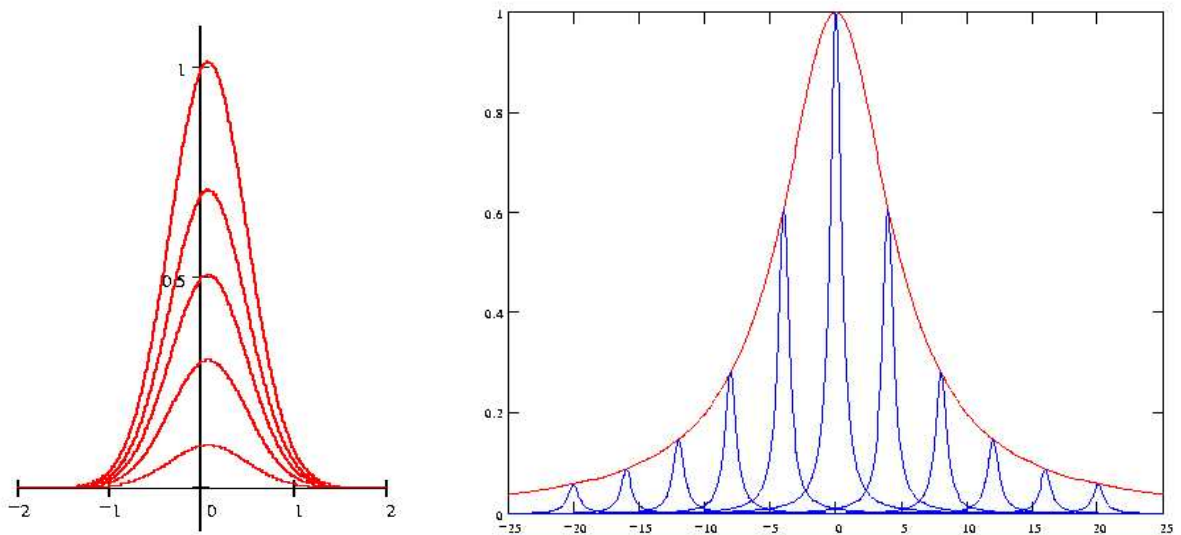
$$\alpha_D = \frac{\nu_0}{c} \left[ \frac{2kT}{M} \ln 2 \right]^{1/2}$$

is the ‘half-width’ at half-maximum and M is the mass of the absorber. With M in amu:  $\alpha_D = 3.5825 \times 10^{-7} \nu_0 (T_D/M_{\text{amu}})^{1/2}$  [Hz]. The full-width at half-maximum is  $2\alpha_D$ .

Again, the broadening due to the lifetime of the upper state and collisions is known as a homogeneous form of line broadening; which nearly always has a Lorentzian shape. Doppler broadening of the line is known as inhomogeneous broadening. At long wavelengths, the Doppler broadening is typically of order 1 MHz (at 500  $\mu\text{m}$ , say), and only dominates at very low pressures. As the frequency increases, the Doppler width also goes up, but less quickly than the natural line width. Thus, it is often the case that the various broadening terms are similar in size. The convolution of a Gaussian and Lorentzian line shape is called a *Voigt profile*, and it must be calculated numerically. On the next page, we present two figures which compare Gaussian and Lorentzian line shapes and which outline the physical differences between homogeneously and inhomogeneously broadened transitions.



**Figure 3.1** A comparison of normalized Lorentzian and Gaussian lines with the same integrated area, for which the Gaussian shape has a higher maximum intensity, but where the Lorentzian line shape has much more absorption (or emission) in the far line wings.



**Figure 3.2** Homogeneous (left) and inhomogeneous (right) lineshapes. For a homogeneous transition, excitation in any one part of the line profile results in an interaction with all of the atoms or molecules in the sample. For an inhomogeneous transition, the total line shape is composed of a number of sub-populations with their own intrinsic (homogeneous) line shape that are slightly displaced in frequency w.r.t. each other.