Quantitative Emission and Absorption

7

We are ready to begin discussion of quantitative emission and absorption spectroscopy, with the goal of being able to specify emission and absorption as a function of wavelength. Two steps are involved in this treatment. In the first step, a simple form of the equation of radiative transfer will be used to identify a new parameter, known as the spectral absorption coefficient, which will be seen as the governing quantity which characterizes emission and absorption of light, as a function of wavelength. In the second step, the Einstein theory of radiation is employed to show that the spectral absorption coefficient is given simply by the product of the line strength and a lineshape function; the relationship of the line strength to fundamental quantities known as Einstein coefficients is also shown. With these relationships in hand, it will become evident how spectrally resolved absorption (or emission) can be used as a nonintrusive means of measuring a variety of gasdynamic parameters, including: species concentration, pressure, temperature, density, and even flow velocity.

7.1 Spectral Absorption Coefficient

We begin with an overview of possibilities when collimated light at frequency ν enters a gas sample of differential length dx: there are four separate possibilities, with probabilities summing to 1 (100 %).

$$1 = \underbrace{\text{absorption}}_{\alpha_\nu} + \underbrace{\text{reflection}}_{=0} + \underbrace{\text{scattering}}_{=0} + \underbrace{\text{transmission}}_{T_\nu} \tag{7.1}$$

Therefore, in the common case where reflection and scattering are negligible,

$$\alpha_\nu + T_\nu = 1 \tag{7.2}$$

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where α_ν and T_ν are known as the spectral absorptivity and transmissivity, respectively. The result in Eq. (7.2) follows from conservation of energy.

We now express α_ν, the fraction of incident light I_ν for the frequency range $\nu \rightarrow \nu + d\nu$ that is absorbed, in terms of an absorption coefficient per unit length, k_ν, i.e.

$$\alpha_\nu \equiv k_\nu dx = \frac{-dI_\nu}{I_\nu} \text{ [no units]} \tag{7.3}$$

k_ν is the *spectral absorption coefficient* (the fraction of incident light I_ν over frequency range $\nu \rightarrow \nu + d\nu$ that is absorbed per unit length dx). Thus

$$\boxed{k_\nu \equiv -\frac{(dI_\nu/dx)}{I_\nu} \text{ [cm}^{-1}\text{]}} \tag{7.4}$$

where I_ν may have units of power per unit area per unit spectral interval at frequency ν (i.e., power per unit area over the spectral range $\nu \rightarrow \nu + d\nu$), or can be substituted with $I(\nu)$, which denotes power at frequency ν or power per unit area at frequency ν. In the former case, which is most common for our purposes, I_ν is known as the spectral intensity and has units

$$\left(\frac{\text{W/cm}^2}{\text{cm}^{-1}}\right) \text{ or } \left(\frac{\text{W/cm}^2}{\text{Hz}}\right).$$

The spectral intensity I_ν can be integrated over frequency to obtain the total radiant intensity, I:

$$I \text{ [W/cm}^2\text{]} = \int_\nu I_\nu d\nu \tag{7.5}$$

In general, the equations that relate spectral intensity, spectral radiancy, and total radiancy to other parameters can use I_ν or $I(\nu)$ interchangeably. The exceptions are integral relations such as Eqs. (7.5) and (7.13); they require the differential form of spectral intensity, I_ν. Thus, Eqs. (7.3) and (7.4) also define α_ν, the fraction of incident light absorbed, and k_ν, the fraction of incident light absorbed *per unit length*, each *at* frequency ν.

Hence, α_ν and k_ν are the spectral absorptivity and spectral absorption coefficient *at* frequency ν **or** *over the frequency range* $\nu \rightarrow \nu + d\nu$.

7.2 Equation of Radiative Transfer: Classical Approach

We wish to perform a simple one-dimensional radiation energy balance on a thin slab of gas. To do this, we must first introduce the spectral emissivity, which is the way that we account for the "emission" from the gas slab. (If a gas sample can absorb light, it follows that it must be allowed to emit, in order to satisfy detailed balance arguments for equilibrium.) The spectral emissivity is conventionally defined as the radiation emitted by the gas sample (I_ν^{em}) relative to that of a blackbody (an "equilibrium" radiator which sets the upper bound on the emission for a specified temperature):

$$\varepsilon_\nu = \frac{I_\nu^{\mathrm{em}}}{I_\nu^{\mathrm{bb}}} \text{ [no units]} \tag{7.6}$$

$$= \frac{I^{\mathrm{em}}(\nu)}{I^{\mathrm{bb}}(\nu)} \text{ [no units]} \tag{7.7}$$

where I_ν^{bb} is the blackbody spectral radiancy. At this point, we employ Kirchhoff's law, which states that "emissivity equals absorptivity," so that

$$\varepsilon_\nu = \alpha_\nu. \tag{7.8}$$

(This law also follows from equilibrium arguments.) Now consider the radiation energy balance at frequency ν for a gas slab of thickness dx; for simplicity, we consider only collimated light (Fig. 7.1).

$$\text{emission} = \varepsilon_\nu I_\nu^{\mathrm{bb}}$$

$$\text{absorption} = \alpha_\nu I_\nu$$

$$dI_\nu = \text{emission} - \text{absorption}$$

$$= \varepsilon_\nu I_\nu^{\mathrm{bb}} - \alpha_\nu I_\nu \tag{7.9}$$

$$= \alpha_\nu (I_\nu^{\mathrm{bb}} - I_\nu) \tag{7.10}$$

Therefore,

$$\boxed{dI_\nu = k_\nu dx (I_\nu^{\mathrm{bb}} - I_\nu).} \tag{7.11}$$

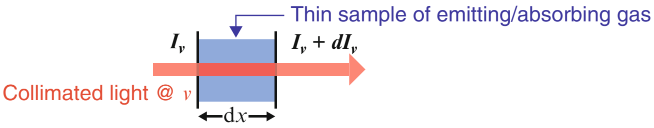

Fig. 7.1 Radiation energy balance across a slab of gas

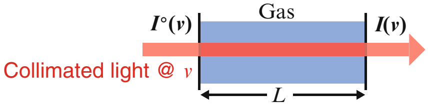

Fig. 7.2 Radiation energy across a slab of gas of width L

This is the *differential form* of the equation of radiative transfer. Integrating over a distance L, for a uniform sample (i.e., constant k_ν, see Fig. 7.2), with an incident intensity I_ν^0 at $x = 0$ (the boundary condition):

$$\boxed{I_\nu(L) = I_\nu^0 \exp(-k_\nu L) + I_\nu^{\text{bb}}[1 - \exp(-k_\nu L)]} \tag{7.12}$$

This important result is the *integrated form* of the equation of radiative transfer. The quantity $k_\nu L$ is known as the "optical depth" (and also as the absorbance at frequency ν). Note that the gas sample is not required to radiate as a blackbody, but we can relate the actual emission to the blackbody level.

Consider the two important cases: Emission and Absorption.

7.2.1 Case 1: Emission Experiments ($I_\nu^0 = 0$)

For emission experiments, the incident radiation intensity $I_\nu^0 = 0$ (i.e., there is no radiation source such as a laser involved).

Spectral radiancy: $I_\nu(L) = I_\nu^{\text{bb}}[1 - \exp(-k_\nu L)]$

Spectral emissivity: $\varepsilon_\nu(k_\nu, L) = \frac{I_\nu(L)}{I_\nu^{\text{bb}}} = 1 - \exp(-k_\nu L)$

We can integrate these relations over frequency to obtain results for the total radiancy:

$$I(L) = \int_0^\infty I_\nu(L) d\nu = \int_0^\infty I_\nu^{\text{bb}}[1 - \exp(-k_\nu L)] d\nu \tag{7.13}$$

$$\varepsilon(L) = \frac{I(L)}{I^{\text{bb}}} = \frac{1}{\sigma T^4} \int_0^\infty I_\nu^{\text{bb}}[1 - \exp(-k_\nu L)] d\nu \tag{7.14}$$

Note:

$$I^{\text{bb}} = \int_0^\infty I_\nu^{\text{bb}} d\nu = \sigma T^4,$$

where

$$\sigma = 5.67 \times 10^{-5}\ [\mathrm{erg\,cm^{-2}\,s^{-1}\,K^{-4}}]$$

is the Stefan–Boltzmann constant.

Emission Types

The emission for the formulas above may be of any type, including single line, multiple line, single or multiple bands, or continuum.

Optical Depth

The optical depth, $k_\nu L$, is a key parameter. When $k_\nu L \gg 1$, the system is *optically thick* and the spectral radiance approaches that of a blackbody. When $k_\nu L \ll 1$, the system is *optically thin* and the spectral radiance approaches $(k_\nu L) I_\nu^{\mathrm{bb}}$.

$$\begin{aligned} \text{optically thick: } k_\nu L \gg 1, &\quad I_\nu(L) \to I_\nu^{\mathrm{bb}} \\ \text{optically thin: } k_\nu L \ll 1, &\quad I_\nu(L) \to (k_\nu L) I_\nu^{\mathrm{bb}} \end{aligned}$$

7.2.2 Case 2: Absorption Experiments ($I_\nu^0 \gg I_\nu^{\mathrm{bb}}$)

For absorption experiments, the incident radiant intensity is much greater than the blackbody radiation intensity.

$$\text{Absorption:} \quad I_\nu^0 \gg I_\nu^{\mathrm{bb}}$$

The equation of radiative transfer, Eq. (7.12), then becomes

$$\boxed{I_\nu(L) = I_\nu^0 \exp(-k_\nu L)} \tag{7.15}$$

This relation, known as Beer's Law or the Beer–Lambert Law, may be *the most important relation in absorption spectroscopy*. Alternate forms in terms of the fractional transmission or "transmissivity," T_ν, are

$$T_\nu = \left(\frac{I}{I^0}\right)_\nu \tag{7.16}$$

$$= \exp(-k_\nu L) \tag{7.17}$$

$$= \frac{I(\nu)}{I^0(\nu)} \tag{7.18}$$

We make two observations:

1. The same equation would apply to the transmission of a pulse of laser excitation, with energy E_ν [$\mathrm{J/cm^2/cm^{-1}}$], i.e. $T_\nu = E_\nu / E_\nu^0$.
2. The fundamental parameter controlling absorption over length L is the spectral absorption coefficient, k_ν.

Our next step is to establish a relationship between k_ν and the fundamental molecular parameters that govern the "strengths" and "shapes" of absorption lines, namely the *Einstein coefficients* and *line-broadening coefficients*.

7.3 Einstein Theory of Radiation

We begin with a simplified theory, without regard to lineshape or structure (sometimes termed the Milne Theory). Consider two states of an atom (or molecule) which are radiatively coupled (i.e., have radiative transitions that are "allowed"), with $E_2 - E_1 = h\nu$.

The total transition rates [molec/s] are N_2A_{21}, $N_1B_{12}\rho(\nu)$, and $N_2B_{21}\rho(\nu)$, where N_i is the total number of molecules in state i. Alternatively the transition rate per unit volume [molec/cm^3/s] can be expressed using the number density n_i.

7.3.1 Einstein Coefficients

A_{21}, B_{12}, and B_{21} in Fig. 7.3 are the Einstein coefficients of radiation.

$B_{12}\rho(\nu)$	the probability/s that a molecule in state 1 exposed to radiation of spectral density $\rho(\nu)$ [J/(cm^3 Hz)][1] will absorb a quantum $h\nu$ and pass to state 2. The Einstein B-coefficient thus carries units of cm^3 Hz/(J s).

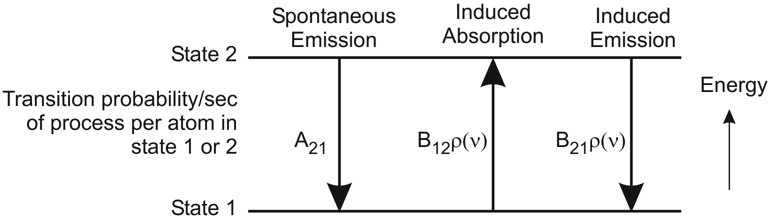

Fig. 7.3 Transition probabilities between states 1 and 2

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[1] The spectral density is the energy density per unit frequency contained in an electric field.

$B_{21}\rho(\nu)$	the probability/s that a molecule in state 2 exposed to radiation of spectral density $\rho(\nu)$ will emit a quantum $h\nu$ and pass to state 1.[2]
A_{21}	the probability/s of spontaneous transfer from state 2 to 1 with release of photon of energy $h\nu$ (without regard to the presence of $\rho(\nu)$)

Similar expressions apply when isotropic radiation intensity or parallel beam intensity (e.g., a laser) are involved.

7.3.2 Equilibrium

At equilibrium, the net rate of change of molecules in any molecular state is zero. Consider a detailed balance of the optical processes at equilibrium for the population change in state 2:

$$\left(\dot{N}_2\right)_{\text{rad}} = \underbrace{N_1 B_{12}\rho(\nu)}_{\text{molec/s entering state 2}} - \underbrace{N_2(A_{21} + B_{21}\rho(\nu))}_{\text{molec/s leaving state 2}} = 0 \tag{7.19}$$

The molecule balance in Eq. (7.19) is simply the difference between the rate of molecules entering state 2 and the rate of molecules leaving state 2. Equilibrium requires that all transitions from state 1 to 2 (induced absorption) are balanced by transitions from state 2 to 1 (induced and spontaneous emission). Another way to express the equilibrium condition is with the Boltzmann fraction from statistical mechanics:

$$\frac{N_2}{N_1} = \underbrace{\frac{B_{12}\rho(\nu)_{\text{eq}}}{A_{21} + B_{21}\rho(\nu)_{\text{eq}}}}_{\text{rad. equil.}} = \underbrace{\frac{g_2}{g_1}\exp(-h\nu/kT)}_{\text{statistical equil.}} \tag{7.20}$$

Solving for $\rho(\nu)_{\text{eq}}$ in Eq. (7.20) and equating it to the known result for $\rho(\nu)_{\text{eq}}$, i.e. Planck's blackbody distribution,

$$\rho(\nu)_{\text{eq}} = \frac{(8\pi h\nu^3/c^3)}{\exp(+h\nu/kT) - 1} \tag{7.21}$$

gives

$$\rho(\nu)_{\text{eq}} = \frac{(A_{21}/B_{21})}{\frac{g_1}{g_2}\frac{B_{12}}{B_{21}}\exp(h\nu/kT) - 1} = \underbrace{\frac{(8\pi h\nu^3/c^3)}{\exp(h\nu/kT) - 1}}_{\text{Planck's distribution}} \tag{7.22}$$

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[2] This induced emission occurs in phase with and in the same direction as the incident beam. Hence, for collimated incident light (e.g., a collimated laser beam) the induced emission appears as gain in the exciting beam.

Equation (7.22) must hold for all ν and T, producing the two following important conclusions [1]:

$$g_1 B_{12} = g_2 B_{21} \tag{7.23}$$

$$A_{21} = \left(\frac{8\pi h\nu^3}{c^3}\right) B_{21} \tag{7.24}$$

$$\equiv 1/\tau_{21} \tag{7.25}$$

where τ_{21}, the inverse of A_{21}, is the "radiative lifetime" in state 2. We must note here that even though Eq. (7.24) was derived from thermodynamic equilibrium arguments and Planck's blackbody distribution, the relationship between A and B holds even for systems not in equilibrium, and it does not depend on $\rho(\nu)$. A_{21}, and hence B_{12} and B_{21} are theoretically calculable from quantum mechanics, but in practice, τ_{21} and/or B_{12} are often measured.

Note: For collimated light (as in the case for most absorption experiments):
$\rho(\nu)_{\text{eq}} = n_p \cdot h\nu$ [J/cm^3 s^{-1}] (n_p is the number of photons/cm^3 s^{-1})
$I_\nu = n_p \cdot h\nu \cdot c$ [W/cm^2 s^{-1}] (power per unit area per unit frequency)
Therefore,

$$\rho(\nu) = I_\nu / c \tag{7.26}$$

Where is the link to k_ν ? Find this next.

7.3.3 What is k_ν?

We proceed now to find the relationship between the spectral absorption coefficient, k_ν, and the Einstein coefficients, for the case of a structureless absorption line of width $\delta\nu$. Recall that Beer's Law is

$$T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L) \tag{7.27}$$

where I_ν may be either the spectral intensity [W/cm^2 s^{-1}] or intensity [W/cm^2] or power [W] at frequency ν, and that

$$k_\nu \equiv -\frac{dI_\nu}{I_\nu dx} \tag{7.28}$$

Figure 7.4 plots T_ν and k_ν versus frequency for this case. Note that $T_\nu = 1$ everywhere but in the region of the absorption line.

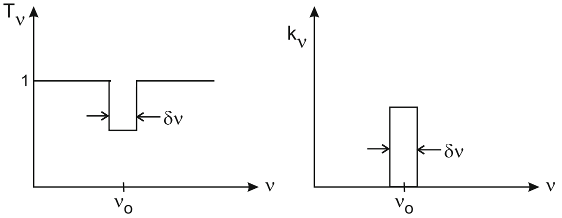

Fig. 7.4 T_ν and k_ν versus frequency for a structureless absorption line of width $\delta\nu$

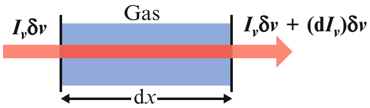

Fig. 7.5 Transmission of laser intensity across a gas slab of depth dx

Imagine that a spectrally broad light source of uniform spectral intensity I_ν^0 is used to illuminate a sample gas with the spectral absorption coefficient shown in Fig. 7.4; the length of the sample is L. What is the absorbed power in W/cm^2?

$$\begin{aligned} P_{\text{abs}} &= (\text{incident power over } \delta\nu) \times (\text{fraction absorbed}) \quad [\text{W/cm}^2] \\ &= (I_\nu^0\, \delta\nu) \times (1 - T_\nu) \qquad (7.29) \\ &= (I_\nu^0\, \delta\nu)(1 - \exp(-k_\nu L)) \qquad (7.30) \end{aligned}$$

where I_ν^0 has units of W/cm^2 s^{-1} and $\delta\nu$ has units of s^{-1}. The product $I_\nu^0\delta\nu$ represents the incident power per unit area (W/cm^2) contained in the spectral interval $\delta\nu$ over which absorption may occur.

What happens to Eq. (7.30) for a small (incremental) width dx, such that $k_\nu dx \ll 1$? For small optical thickness, the exponential term can be linearized, leading to the simple result

$$P_{\text{abs}} = (I_\nu^0\, \delta\nu)(k_\nu dx) \qquad (7.31)$$

or

$$\frac{P_{\text{abs}}}{I_\nu^0\, \delta\nu} = \text{fraction absorbed} = k_\nu dx. \qquad (7.32)$$

This is known as the optically thin limit.

We can use a simple energy balance on an incremental slab of gas to find k_ν (Fig. 7.5).

In this model, we recognize that the *change* in intensity, i.e. $(dI_\nu)\delta\nu$, is equal to the net combined effects of emission and absorption,

$$(dI_\nu)\delta\nu = (\text{induced emission} + \underbrace{\text{spontaneous emission}}_{=0}) - \text{induced absorption} \tag{7.33}$$

where the spontaneous emission is approximately zero for collimated light and

$$\text{induced emission} = \underbrace{(n_2 dx)}_{\substack{\text{molec/cm}^2\\ \text{in state 2}}} \times \underbrace{B_{21}\rho(\nu)}_{\substack{\text{prob/s of}\\ \text{emission}}} \times \underbrace{h\nu}_{\substack{\text{energy per}\\ \text{photon}}} \tag{7.34}$$

$$\text{induced absorption} = \underbrace{(n_1 dx)}_{\substack{\text{molec/cm}^2\\ \text{in state 1}}} \times \underbrace{B_{12}\rho(\nu)}_{\substack{\text{prob/s of}\\ \text{absorption}}} \times \underbrace{h\nu}_{\substack{\text{energy per}\\ \text{photon}}} \tag{7.35}$$

Recalling Eq. (7.26), Eq. (7.33) becomes

$$(dI_\nu)\delta\nu = [n_2 B_{21} - n_1 B_{12}]\frac{h\nu}{c} I_\nu dx \tag{7.36}$$

Therefore,

$$\frac{dI_\nu}{I_\nu dx} \equiv -k_\nu = \frac{h\nu}{c}\frac{1}{\delta\nu}[n_2 B_{21} - n_1 B_{12}] \tag{7.37}$$

which may be simplified further to give

$$\boxed{k_\nu\ [\text{cm}^{-1}] = \frac{h\nu}{c}\frac{1}{\delta\nu} n_1 B_{12}\,(1 - \exp(-h\nu/kT))} \tag{7.38}$$

While this result is immediately helpful in understanding the fundamental coupling between k_ν and B_{12}, n_1, ν, and T, we can see now that the shape and width of absorption lines (evident in Eq. (7.38) with the term $\delta\nu$) are also relevant. How would the use of a more realistic lineshape model affect Eq. (7.38)?

7.4 Revised Treatment of Einstein Theory (with Lineshape)

We now repeat the derivation for k_ν using an improved lineshape model that includes the structure of absorption and emission lines. Compared with the uniform and structureless feature in Fig. 7.4, real spectra have shapes. These realistic shapes for the spectral transmission, T_ν, spectral absorption, k_ν, and normalized lineshape function, ϕ, of a single absorption line are shown in Fig. 7.6.

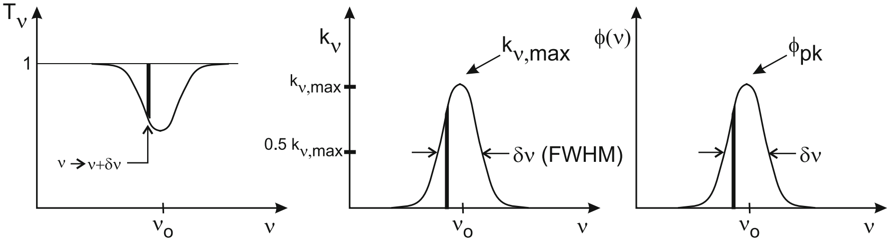

Fig. 7.6 T_ν, k_ν, and ϕ versus frequency for an absorption line with typical structure

Recall that the general form for Beer's Law is

$$T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L) \tag{7.39}$$

Solving for k_ν yields

$$k_\nu = -\frac{1}{L}\ln T_\nu \tag{7.40}$$

In addition, we define a new parameter, ϕ, as the *normalized* lineshape function

$$\phi \equiv \frac{k_\nu}{\int\limits_{\text{line}} k_\nu d\nu}\quad [\text{cm}]\text{ or }[\text{s}] \tag{7.41}$$

so that

$$\int\limits_{\text{line}} \phi d\nu = 1 \tag{7.42}$$

The units for ϕ are inverse frequency (and hence may have units of either centimeters or seconds). The lineshape function, whose integral over the line is 1, provides a useful way of characterizing the shape of a line.

Note: Since

$$\int k_\nu d\nu \approx k_{\nu,\text{max}}\delta\nu$$

where $\delta\nu$ is an average width, then

$$\phi_{pk} = \frac{k_{\nu,\text{max}}}{\int k_\nu d\nu} \approx \frac{1}{\delta\nu}$$

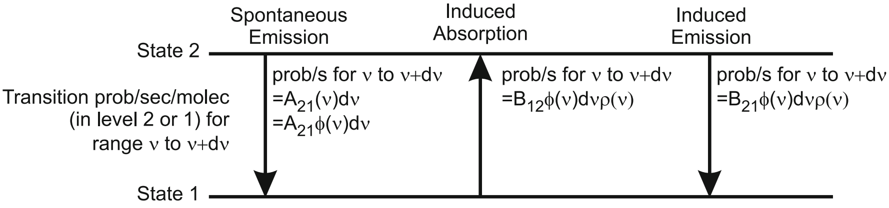

Fig. 7.7 Transition probabilities per second per molecule in level 2 or 1

> Thus we should not be surprised if we find that the term $1/\delta\nu$ in Eq. (7.38) is simply replaced by ϕ in the revised formulation, with ϕ varying smoothly from zero in the "wings" of an absorption line to a peak value proportional to $1/\delta\nu$ (see Fig. 7.6 above).

Consider the small frequency interval, $\nu \rightarrow \nu + d\nu$, in Fig. 7.6. What are the relevant transition probabilities for this spectral interval? We recognize that these probabilities should have the same spectral dependence (shape) as k_ν and $\phi(\nu)$, i.e. having a peak value at line center and falling to zero away from the line. We achieve this shape with a simple modification to our previous model (with the constant probabilities A_{21}, B_{12}, B_{21}) by multiplying the Einstein coefficients by $\phi(\nu)d\nu$ (see Fig. 7.7).

$A_{21}\phi(\nu)d\nu$	the probability/s of a molecule undergoing spontaneous emission, in the range $\nu \rightarrow \nu + d\nu$ [Note that the integral of this quantity over the range of allowed ν is just A_{21} [s^{-1}], i.e. $\int A_{21}\phi(\nu)(d\nu) = A_{21}$.]
$B_{12}\phi(\nu)d\nu\rho(\nu)$	the probability/s of a molecule undergoing a transition from $1 \rightarrow 2$, in the range $\nu \rightarrow \nu + d\nu$
$B_{21}\phi(\nu)d\nu\rho(\nu)$	the probability/s of a molecule undergoing a transition from $2 \rightarrow 1$, in the range $\nu \rightarrow \nu + d\nu$

Recall: $\rho(\nu) = I_\nu/c$, where $\rho(\nu)$ is the spectral energy density [J/cm^3 s^{-1}] and I_ν is the spectral intensity [W/cm^2 s^{-1}] of collimated laser light.

We are now ready to do a simple energy/power balance on an incremental gas slab of width dx, for the frequency range $\nu \rightarrow \nu + d\nu$ (Fig. 7.8).

The energy balance for the slab requires that the incremental gain in intensity, $dI_\nu d\nu$, is equal to the difference between the emission and absorption over the frequency interval $d\nu$ in the gas slab:

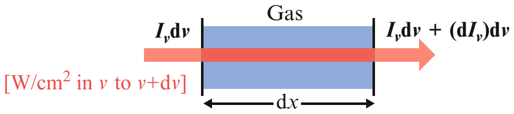

Fig. 7.8 Energy/power balance on an incremental gas slab

$$dI_\nu d\nu = \text{emission in } d\nu - \text{absorption in } d\nu$$

$$= \underbrace{\overbrace{n_2}^{\#/\text{cc}} dx}_{\text{molec/cm}^2} \times \overbrace{[B_{21}\phi(\nu)d\nu I_\nu/c]}^{\text{prob/s}\cdot\text{molec for } d\nu} \times \underbrace{h\,\nu_0}_{\substack{\text{energy/}\\ \text{photon}}} - \quad n_1 dx[B_{12}\phi(\nu)d\nu I_\nu/c]h\nu_0$$

Therefore,

$$-\frac{dI_\nu}{I_\nu dx} \equiv k_\nu = \frac{h\nu}{c}[n_1B_{12} - n_2B_{21}]\phi(\nu) \tag{7.43}$$

so

$$\boxed{k_\nu = \frac{h\nu}{c} n_1 B_{12}\,(1 - \exp(-h\nu/kT))\,\phi(\nu)} \tag{7.44}$$

which is, as suggested, equal to our earlier result for k_ν aside from the substitution of $\phi(\nu)$ for $1/\delta\nu$! Integrating k_ν over the absorption line yields

$$S_{12} \equiv \int_{\text{line}} k_\nu d\nu \quad [\text{cm}^{-1}\,\text{s}^{-1}] \tag{7.45}$$

$$\boxed{S_{12} = \frac{h\nu}{c} n_1 B_{12}(1 - \exp(-h\nu/kT))} \tag{7.46}$$

S_{12} is an important quantity known as the "integrated absorption" for the absorption transition 1 → 2[1]. It is also often called the "line strength." Note that the quantity does not depend on lineshape and is simply a function of n_1, T, and B_{12}. Changes in lineshape, e.g. owing to pressure-broadening, thus do not affect S_{12}. This quantity, like Einstein coefficients, is thus fundamental in nature. In view of the interrelationships of A_{21}, B_{12}, and B_{21}, we may also write

$$S_{12} = \frac{\lambda^2}{8\pi} n_1 A_{21} \frac{g_2}{g_1} (1 - \exp(-h\nu/kT)) \quad [\mathrm{cm}^{-1}\,\mathrm{s}^{-1}] \tag{7.47}$$

$$S_{12} = \left(\frac{\pi e^2}{m_e c}\right) n_1 f_{12} (1 - \exp(-h\nu/kT)) \quad [\mathrm{cm}^{-1}\,\mathrm{s}^{-1}] \tag{7.48}$$

(Note that the units of S_{12} shown here as $\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$ depend on the choice of units for frequency, typically either s^{-1} or cm^{-1}, so that S_{12} may have units of $\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$ or cm^{-2}. Other variations also appear in the literature.)

Equation (7.47) makes use of the relationship between A_{21} and B_{12}. Equation (7.48) utilizes the *oscillator strength*, f:

$$f_{12} = \frac{S_{12,\mathrm{actual}}}{S_{12,\mathrm{classical}} (1 - \exp(-h\nu/kT))} \tag{7.49}$$

The oscillator strength of a transition (or group of transitions like a vibrational band or electronic system) compares the integrated strength of the transition with the classical electromagnetic model of an oscillating electron in a magnetic field. $S_{\mathrm{classical}}$ is given by[2]:

$$S_{\mathrm{classical}} = \left(\frac{\pi e^2}{m_e c}\right) n_1 \tag{7.50}$$

where

$$\left(\frac{\pi e^2}{m_e c}\right) = 0.0265\,\mathrm{cm}^2\,\mathrm{Hz}.$$

so that

$$S_{12,\mathrm{actual}} = (0.0265\,\mathrm{cm}^2\,\mathrm{Hz}) n_1 f_{12} (1 - \exp(-h\nu/kT)) \tag{7.51}$$

Since n_1 can be written in terms of pressure, i.e.,

$$n_1 = \frac{p_1}{kT} \tag{7.52}$$

then at STP, if all the absorbing atoms are in the ground state ($n_1 = n = 2.7 \times 10^{19}\,\mathrm{cm}^{-3}$) and $\exp(-h\nu_{12}/kT) \ll 1$, the line strength S_{12} is simply $7.17 \times 10^{17} f_{12}$ [cm^{-1} Hz/atm], or equivalently

$$S_{12}[\mathrm{cm}^{-2}/\mathrm{atm}] = 2.380 \times 10^7 f_{12} \tag{7.53}$$

From Eqs. (7.47) and (7.48), the reader may note that the oscillator strength is also directly related to the Einstein coefficients for a given transition, and like the coefficients for stimulated emission,

$$f_{21} = \left(\frac{g_1}{g_2}\right) f_{12} \tag{7.54}$$

We now make two important observations:

1. From the original definition of k_ν and S_{12} we have

$$\boxed{k_\nu = S_{12}\phi(\nu)}$$

2. When

$$h\nu/kT \gg 1,$$

as is common for electronic state transitions,

$$S_{12} \quad [\text{cm}^{-1}\,\text{Hz}] = \left(\frac{\pi e^2}{m_e c}\right) n_1 f_{12} \tag{7.55}$$

$$= (0.0265\,\text{cm}^2\,\text{Hz}) n_1 f_{12} \tag{7.56}$$

$$= \frac{\lambda^2}{8\pi} n_1 A_{21} \frac{g_2}{g_1} \tag{7.57}$$

and, by comparison of right-hand sides

$$f_{12}/A_{21} = f_{12}\tau_{21} = 1.51 \frac{g_2}{g_1} (\lambda\ [\text{cm}])^2 \tag{7.58}$$

where $\tau_{21} = 1/A_{21}$ is the *radiative lifetime* of the $2 \rightarrow 1$ transition.

Example: "Resonance Transition"

A resonance transition is one that couples the ground state to the first excited state. Let's look at a case for an electronic transition of a sodium atom:

$$\text{Na}\ (\overbrace{3^2S_{1/2}}^{\text{lower(L)}} - \overbrace{3^2P_{1/2}}^{\text{upper(U)}}),$$

$$\frac{g_2}{g_1} = 1,$$

$$\lambda = 589\,\text{nm} = 5.89 \times 10^{-5}\,\text{cm} \tag{7.59}$$

Table 7.1 Oscillator strengths of selected sodium transitions, abstracted from [1]

Transition	f_{21}	λ[nm]
$3^2S_{1/2} - 3^2P_{1/2}$	0.33	589.6
$3^2S_{1/2} - 3^2P_{3/2}$	0.67	589.0
$3^2S - 4^2P$	0.04	330.2

Conventions:

atoms: (L – U)
molecules: (U $\leftrightarrow$ L), arrow denotes absorption or emission
f_{ij}: i denotes initial state, j denotes final

From Eq. (7.58),

$$f_{12}\tau_{589\,\text{nm}} = 5.24 \times 10^{-9}\,\text{s},$$

where the radiative lifetime is

$$\tau = 16.1 \times 10^{-9}\,\text{s (measured, corresponds to } A = 0.62 \times 10^{8}\,\text{s}^{-1}\text{)}$$

Thus, $f \approx 0.325$ (strong atomic transition; single electron). Values of f for molecular transitions tend to be much smaller, $\sim 10^{-2}$–10^{-4}, owing to the relatively strong coupling between the multiple electrons and protons in a molecule and can be very much smaller for highly forbidden transitions. The "term symbols" for electronic states in atoms will be discussed in Chap. 9.

Table 7.1 lists the emission (f_{21}) oscillator strengths and spectral locations for a few transitions of the sodium atom.

These values can be compared with electronic and vibrational oscillator strengths in a few molecules (Table 7.2).

7.5 Radiative Lifetime

The concept of radiative lifetime merits further discussion. If we write a rate equation for radiative decay from an upper level u, accounting for all allowed spontaneous decay paths to lower states l, then

Table 7.2 Absorption oscillator strengths of selected vibrational and vibronic bands of a few molecules

Molecule	$v' \leftarrow v''$	Electronic transition	Band center [cm^{-1}]	f_{12}
CO	$1 \leftarrow 0$	–	2143	1.09×10^{-5}
	$2 \leftarrow 0$	–	4260	7.5×10^{-8}
OH	$1 \leftarrow 0$	–	3568	4.0×10^{-6}
	$0 \leftarrow 0$	$^2\Sigma \leftarrow {}^2\Pi$	32,600	1.2×10^{-3}
CN	$0 \leftarrow 0$	$^2\Pi \leftarrow {}^2\Sigma$	9117	2.0×10^{-2}

$$\frac{dn_u}{dt} = -n_u \sum_l A_{u \to l} \quad \text{(radiation only)} \tag{7.60}$$

Thus, for an initial number density $n_u(0)$, the time-dependent density, allowing for radiative decay only, is:

$$n_u(t) = n_u(0) \exp\left[-t \sum_l A_{u \to l}\right] \tag{7.61}$$

so

$$\boxed{\tau_r = \text{radiative lifetime} = \frac{1}{\sum_l A_{u \to l}}} \tag{7.62}$$

Of course, collisions and radiative excitation into the upper levels will also be present and will maintain a non-zero population in the upper level. τ_r is also sometimes described as the *zero-pressure lifetime*.

The decay $u \to l$ may also occur through non-radiative (i.e., collisional) processes; corresponding energy may be given to neighboring molecules as translational energy or, quite commonly, as internal energy. In the case of non-radiative decay, the rate of decays per unit volume can be written in terms of a rate parameter $k_{\mathrm{nr}}(s^{-1})$

$$\left(\frac{dn_u}{dt}\right)_{\mathrm{nr}} = -k_{\mathrm{nr}} n_u = -\frac{n_u}{\tau_{\mathrm{nr}}} \tag{7.63}$$

where τ_{nr} is the *non-radiative decay time*. This parameter depends on the transition considered and on the surrounding molecules.

With the simultaneous presence of both radiative and non-radiative transitions, the time variation of the upper level u population can be written as

$$\frac{dn_u}{dt} = -\frac{n_u}{\tau_r} - \frac{n_u}{\tau_{\text{nr}}} = -\frac{n_u}{\tau} \tag{7.64}$$

where $\tau^{-1} = \tau_r^{-1} + \tau_{\text{nr}}^{-1}$ is called the *lifetime* of level u.

7.6 Alternate Forms

There are many alternate forms for the linestrength and Beer's Law, each with its own units and notation.

7.6.1 Line Strengths

Alternate forms for linestrength notation and units are as follows:

1.

$$k_\omega\ [\text{cm}^{-1}] = S_{12}\ [\text{cm}^{-2}]\ \phi_\omega\ [\text{cm}],\ \text{or}$$
$$k_\nu\ [\text{cm}^{-1}] = S_{12}\ [\text{cm}^{-2}]\ \phi_\nu\ [\text{cm}]$$

where

$$\nu\ [\text{cm}^{-1}] \text{ or } \omega\ [\text{cm}^{-1}] \equiv 1/\lambda\ [\text{cm}],$$
$$\phi_\nu\ [\text{cm}] \text{ or } \phi_\omega\ [\text{cm}] = c\ [\text{cm/s}]\ \phi_\nu\ [\text{s}]$$

and

$$d\nu\ [\text{cm}^{-1}] \text{ or } d\omega\ [\text{cm}^{-1}] = (1/c)d\nu\ [\text{s}^{-1}]$$

2.

$$S_{12}\ [\text{cm}^{-2}] = (1/c)S_{12}\ [\text{cm}^{-1}/\text{s}]$$

3.

$$\begin{aligned} S_{12}\ [\text{cm}^{-2}/\text{atm}] &= S_{12}\ [\text{cm}^{-2}]/P_i\ [\text{atm}] \\ &= \left(\frac{n_1}{P_i\ [\text{atm}]}\right)\left(\frac{c}{8\pi\nu^2}\right)A_{21}\frac{g_2}{g_1}\,(1-\exp(-h\nu/kT)) \end{aligned}$$

where n_1 is the number density of the absorbing species i in state 1.

4. The typical units for linestrengths include a per-unit-pressure version, S [$\text{cm}^{-2}\,\text{atm}^{-1}$], and a per-unit-number-density version used by HITRAN96, S^* [$\text{cm}^{-1}/(\text{molecule}\,\text{cm}^{-2})$]. The conversion between S and S^* is

$$S\,[\text{cm}^{-2}\,\text{atm}^{-1}] = \frac{S^*\;[\text{cm}^{-1}/(\text{molecule}\,\text{cm}^{-2})] \times n\;[\text{molecules/cc}]}{P\;[\text{atm}]}, \tag{7.65}$$

where n is the number density of the absorbing species in [molecules/cc] and P is the corresponding partial pressure in [atm]. Using the ideal gas law and converting pressure units from [dynes/cm^2] to [atm] yields the following relation

$$S\,[\text{cm}^{-2}\,\text{atm}^{-1}] = \frac{S^*\;[\text{cm}^{-1}/(\text{molecule}\,\text{cm}^{-2})] \times 1013250\;[\text{dynes}/(\text{cm}^2\,\text{atm})]}{kT}, \tag{7.66}$$

where $k = 1.38054 \times 10^{-16}$ erg/K is the Boltzmann constant and T [K] is the temperature at which the conversion is being performed and the linestrength is known. Equation (7.66) reduces to

$$S = \frac{S^* \times (7.34 \times 10^{21})}{T}\;[\text{cm}^{-2}\,\text{atm}^{-1}]. \tag{7.67}$$

For converting room-temperature linestrength ($T = 296$ K), the conversion is

$$S = S^* \times (2.4797 \times 10^{19})\;\;[\text{cm}^{-2}\,\text{atm}^{-1}]. \tag{7.68}$$

7.6.2 Beer's Law

It follows from the alternate forms for the linestrength that multiple expressions for Beer's Law also exist, e.g.

$$\left(\frac{I}{I^0}\right)_{\nu,\omega,\lambda} = \exp\left(-k_\nu L\right) \tag{7.69}$$

$$= \exp\left(-n\sigma_\nu L\right) \tag{7.70}$$

$$= \exp\left(-\beta_\omega P_i L\right) \tag{7.71}$$

$$= \exp(-S\phi_\nu P_i L) \tag{7.72}$$

where

n = number density of the absorbing species [molecules/cm^3]

σ_ν = absorption cross-section [cm^2/molecule]

$$\begin{aligned} S &= \text{“linestrength” } [\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}] \text{ or } [\mathrm{cm}^{-1}\,\mathrm{s}^{-1}/\mathrm{atm}] \\ \beta_\omega &= \text{frequency-dependent absorption coefficient } [\mathrm{cm}^{-1}/\mathrm{atm}] \\ P_i &= \text{partial pressure of species } i \text{ [atm]} \\ \phi_\nu &= \text{frequency-dependent lineshape function [cm] or [s]} \end{aligned} \tag{7.73}$$

In the IR, it is common to use atmosphere and wavenumber units, i.e. $\beta_\omega = k_\nu / P_i$ = absorption coefficient per atmosphere of pressure. Thus,

$$\begin{aligned} S_{12}\ [\mathrm{cm}^{-2}/\mathrm{atm}] &= \int \beta_\omega d\omega \\ &= \frac{S_{12}\ [\mathrm{cm}^{-1}\,\mathrm{s}^{-1}]}{cP_i\ [\mathrm{atm}]} \\ &= 8.82 \times 10^{-13} \frac{n_1}{P_i\ [\mathrm{atm}]} f_{12} \left(1 - \exp(-h\nu/kT)\right) \\ &= \frac{c}{8\pi\nu^2} \frac{n_1}{P_i} A_{21} \frac{g_2}{g_1} \left(1 - \exp(-h\nu/kT)\right) \end{aligned}$$

7.7 Temperature-Dependent Linestrengths

As Eq. (7.46) demonstrates, linestrengths are directly dependent on the number density, n_1, and exponentially dependent on the temperature, T. Using the Boltzmann fraction to relate n_1 at various temperatures and combining with Eq. (7.46) yields an expression for the linestrength as a function of temperature.

The linestrength $S_i(T)$ for a particular transition i at some temperature T can be determined from the molecule's reference temperature linestrength $S_i(T_0)$; the absorbing molecule's partition function $Q(T)$; the frequency of the transition, $\nu_{0,i}$; and the lower-state energy of the transition, E_i''. This relationship is given by

$$\begin{aligned} S_i(T) = S_i(T_0) &\frac{Q(T_0)}{Q(T)} \left(\frac{T_0}{T}\right) \exp\left[-\frac{hcE_i''}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \\ &\times \left[1 - \exp\left(\frac{-hc\nu_{0,i}}{kT}\right)\right]\left[1 - \exp\left(\frac{-hc\nu_{0,i}}{kT_0}\right)\right]^{-1}, \end{aligned} \tag{7.74}$$

where S is in units of $[\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}]$. For units of $[\mathrm{cm}^{-1}/(\mathrm{molecule\,cm}^{-2})]$, the following temperature scaling can be used

$$S_i^*(T) = S_i^*(T_0)\frac{Q(T_0)}{Q(T)}\exp\left[-\frac{hcE_i''}{k}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$
$$\times\left[1-\exp\left(\frac{-hc\nu_{0,i}}{kT}\right)\right]\left[1-\exp\left(\frac{-hc\nu_{0,i}}{kT_0}\right)\right]^{-1}. \tag{7.75}$$

Thus, a ratio of linestrengths with the different units can be calculated as follows:

$$\frac{S(T)}{S(T_0)} = \frac{S_i^*(T)}{S_i^*(T_0)}\times\frac{T_0}{T}. \tag{7.76}$$

7.8 Concept of Band Strength

The concept of band strength is common in the IR. Recall that a band is a group of lines for different upper and lower vibrational quantum numbers. The band strength is determined by the number and strength of individual lines, and is expressed as a sum of the linestrengths.

$$S_{\text{band}} = \sum_{\text{band}} S_{\text{lines}} \tag{7.77}$$

Example: Heteronuclear Diatomic Band Strength

For the 1 ← 0 band of a heteronuclear diatomic molecule, the band strength is

$$S^{1\leftarrow 0} = \sum_{J''}^{v'=1\leftarrow v''=0}\left[S_{J'\leftarrow J''}^{1\leftarrow 0}(P) + S_{J'\leftarrow J''}^{1\leftarrow 0}(R)\right]$$

where

$$S_{J'J''}^{10}(R) = \frac{c}{8\pi\nu^2}\overbrace{\frac{n_{J''}}{n_i kT/1.013\times 10^6}}^{\frac{n_{J''}}{P_i,\ \text{atm}}}\overbrace{\left[\frac{g_{J'}}{g_{J''}} = \frac{2J'+1}{2J''+1}\right]}^{\approx 1}\overbrace{\left[A_R^{10}\approx\frac{J''+1}{2J''+1}A^{10}\right]}^{A_P^{10}\approx\frac{J''}{2J''+1}A^{10}}$$
$$\times\,(1-\exp(-h\nu/kT)).$$

Note: The approximations shown for A_R^{10} and A_P^{10} are based on the normalized Hönl–London factors, to be discussed in Chap. 10.

Then

$$S^{10}(R) = \frac{(1.013\times 10^6)\,c}{8\pi\nu^2 kT}A^{10}\sum_{J''}\left[\frac{n_{J''}}{n_i}\frac{J''+1}{2J''+1}\right],$$

and similarly

$$S^{10}(P) = \frac{(1.013 \times 10^6)\,c}{8\pi \nu^2 kT} A^{10} \sum_{J''} \left[\frac{n_{J''}}{n_i} \frac{J''}{2J'' + 1} \right]$$

Therefore, since $\sum_{J''} (n_{J''}/n_i) = 1$,

$$\boxed{S^{10}(T) = \frac{(1.013 \times 10^6)\,c A^{10}}{8\pi \nu^2 kT}}$$

Example: Band Strength of CO

The measured band strength of CO at 273 K, as measured at Stanford, is

$$S^{10}_{\mathrm{CO}}(273\,\mathrm{K}) = \frac{3.2 \times 10^{28} A^{10}}{\nu^2} \approx 280\,\mathrm{cm}^{-2}/\mathrm{atm}$$

But,

$$\omega \approx 2150\,\mathrm{cm}^{-1}$$

and

$$\nu \approx 6.4 \times 10^{13}\,\mathrm{s}^{-1},$$

yielding

$$A^{10} = 36\,\mathrm{s}^{-1},$$

or, equivalently,

$$\tau^{10} = 0.028\,\mathrm{s}$$

Compare the value for τ^{10} with the previous example of $\tau_{\mathrm{Na}} \approx 16\,\mathrm{ns}$. CO requires 28 ms to decay by radiation! Thus, IR transitions, due to their smaller changes in dipole moment, have much lower values of A and longer radiative lifetime τ than UV/Visible transitions.

7.9 Exercises

1. Light is transmitted through an optically thin (but absorbing) medium. If the path length (L) is doubled, what happens to the fractional absorption?
2. The fractional transmission of monochromatic light through a uniform absorbing medium of length L is 0.75. What is the fractional transmission if the path length is doubled?
3. A discrete electronic transition of a monatomic gas at high temperature ($T = 5000\,\mathrm{K}$) and low pressure ($P = 0.01\,\mathrm{atm}$) has a measured linecenter spectral absorption coefficient k_{ν_o} of $0.1\,\mathrm{cm}^{-1}$ at a wavelength of 500 nm. Determine the linecenter spectral emissivity of the gas if the gas sample is 10 cm thick and $\phi(500\,\mathrm{nm}) = 6\,\mathrm{cm}$.
4. The Einstein-A coefficient for a particular rovibrational transition of CO_2 is $220\,\mathrm{s}^{-1}$. In the absence of collisions, what is the characteristic lifetime of the upper state? Compare this with the Na transition near 589.6 nm which has an Einstein-A coefficient of $6.14 \times 10^7\,\mathrm{s}^{-1}$.
5. The partial pressure of H_2O is 0.10 atm and an absorption transition with a linestrength of $7.58 \times 10^{-22}\,\mathrm{cm}^{-1}/\mathrm{molecule\,cm}^2$ is excited by a 10 mW laser near 1392 nm that is resonant with the transition linecenter. How much power is absorbed by the 10 cm gas sample if $\phi(1392\,\mathrm{nm}) = 5\,\mathrm{cm}$?
6. Given the Einstein-A coefficient of a transition, what additional information do you need to calculate the temperature-dependent linestrength of this transition?

References

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